Accurate Excited-State Geometries: a CASPT2 and Coupled-Cluster Reference Database for Small Molecules: SI

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This SI contains GS and ES geometrical parameters for all considered levels of theory and provides comparison with previous theoretical and/or experimental works when possible. Note that we do not intend to list all previous theoretical works and generally limit ourselves to the most recent/highest level results published previously. For all molecules, we provide the Cartesian coordinates with the “best” level of theory that was accessible. We also give the EOM-CCSD/def²-TZVPP Cartesian coordinates as this stands as the highest level of theory for which frequency calculations were performed. For all (EOM-)CCSD/def²-TZVPP structures, we have reported the $T_1$ diagnostic computed on the GS CCSD wavefunction.
# Acetylene

Table S1: Selected geometrical parameters (bond lengths in Å, valence angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). ∆ gives the difference between the two states (in eV for the ∆ZPVE).

| Method         | State | PG     | ZPVE  | C≡C | C-H | C≡C-H | Ref.          |
|----------------|-------|--------|-------|-----|-----|-------|--------------|
| ADC(2)/def2-TZVPP | GS    | D∞h   | 0.026789 | 1.209 | 1.059 | 180.0 | This work    |
|               | ES (A_u) | C_2h  | 0.022922 | 1.373 | 1.090 | 122.0 |              |
|               | ∆      |        | -0.105  | 0.164 | 0.031 | -58.0 |              |
|               | ES (B_u) | C_2h  | 0.020753\(^a\) | 1.335 | 1.072 | 140.0 |              |
|               | ∆      |        | -0.164  | 0.126 | 0.013 | -31.0 |              |
|               | ES (A_2) | C_2v  | 0.022448 | 1.351 | 1.092 | 131.8 |              |
|               | ∆      |        | -0.118  | 0.142 | 0.033 | -48.2 |              |
| ADC(2)/aug-cc-pVTZ | GS    | D∞h   | 1.206  | 1.058 | 180.0 |              |
|               | ES (A_u) | C_2h  | 1.369  | 1.086 | 122.1 |              |
|               | ∆      |        | 0.022922 | 0.028 | -57.9 |       |              |
|               | ES (B_u) | C_2h  | 1.330  | 1.068 | 150.5 |              |
|               | ∆      |        | 0.124   | 0.010 | -29.5 |       |              |
|               | ES (A_2) | C_2v  | 1.345  | 1.087 | 132.1 |              |
|               | ∆      |        | 0.139   | 0.030 | -47.9 |       |              |
| CC2/def2-TZVPP | GS    | D∞h   | 0.026498 | 1.214 | 1.060 | 180.0 | This work    |
|               | ES (A_u) | C_2h  | 1.377  | 1.086 | 124.0 |              |
|               | ∆      |        | 0.022922 | 0.030 | -55.9 |       |              |
|               | ES (B_u) | C_2h  | 1.333  | 1.068 | 150.5 |              |
|               | ∆      |        | 0.120   | 0.012 | -29.5 |       |              |
|               | ES (A_2) | C_2v  | 1.349  | 1.088 | 135.0 |              |
|               | ∆      |        | 0.136   | 0.032 | -47.8 |       |              |
| CC2/aug-cc-pVTZ | GS    | D∞h   | 1.213  | 1.056 | 180.0 |              |
|               | ES (A_u) | C_2h  | 1.377  | 1.086 | 122.0 |              |
|               | ∆      |        | 0.022922 | 0.032 | -49.1 |       |              |
|               | ES (B_u) | C_2h  | 1.333  | 1.068 | 150.5 |              |
|               | ∆      |        | 0.120   | 0.012 | -29.5 |       |              |
|               | ES (A_2) | C_2v  | 1.349  | 1.088 | 135.0 |              |
|               | ∆      |        | 0.136   | 0.032 | -47.8 |       |              |
| CCSD/def2-TZVPP | GS    | D∞h   | 0.027114 | 1.201 | 1.060 | 180.0 | This work    |
|               | ES (A_u) | C_2h  | 1.372  | 1.094 | 122.2 |              |
|               | ∆      |        | 0.022922 | 0.032 | -49.1 |       |              |
|               | ES (B_u) | C_2h  | 1.333  | 1.076 | 148.3 |              |
|               | ∆      |        | 0.126   | 0.014 | -31.7 |       |              |
|               | ES (A_2) | C_2v  | 1.342  | 1.098 | 132.0 |              |
|               | ∆      |        | 0.135   | 0.036 | -48.0 |       |              |
| CCSD/aug-cc-pVTZ | GS    | D∞h   | 1.207  | 1.062 | 180.0 |              |
|               | ES (A_u) | C_2h  | 1.372  | 1.094 | 122.2 | This work    |
|               | ∆      |        | 0.022922 | 0.032 | -49.1 |       |              |
|               | ES (B_u) | C_2h  | 1.333  | 1.076 | 148.3 |              |
|               | ∆      |        | 0.126   | 0.014 | -31.7 |       |              |
|               | ES (A_2) | C_2v  | 1.342  | 1.098 | 132.0 |              |
|               | ∆      |        | 0.135   | 0.036 | -48.0 |       |              |

\(^a\)Gives an imaginary frequency.
Continuation of Table S1

| Method                          | State        | PG   | ZPVE | C=CC | C-H  | C=CC-H | Ref.   |
|---------------------------------|--------------|------|------|------|------|--------|--------|
| **CC3/def2-TZVPP**              | GS           | $D_{\infty}$ | 1.208 | 1.062 | 180.0 | This work |
|                                 | ES (Au) C$_{2h}$ |      | 1.376 | 1.095 | 122.1 |      |
|                                 | Δ             |      | 0.168 | 0.033 | -57.9 |      |
|                                 | ES (Bu) C$_{2h}$ |      | 1.337 | 1.076 | 148.1 |      |
|                                 | Δ             |      | 0.129 | 0.014 | -31.9 |      |
|                                 | ES (A$_2$) C$_{2v}$ |      | 1.345 | 1.097 | 132.5 |      |
|                                 | Δ             |      | 0.137 | 0.035 | -47.5 |      |
| **CC3/aug-cc-pVTZ**             | GS           | $D_{\infty}$ | 1.207 | 1.058 | 180.0 | This work |
|                                 | ES (Au) C$_{2h}$ |      | 1.371 | 1.090 | 122.2 |      |
|                                 | Δ             |      | 0.164 | 0.032 | -57.8 |      |
|                                 | ES (Bu) C$_{2h}$ |      | 1.331 | 1.071 | 149.7 |      |
|                                 | Δ             |      | 0.124 | 0.013 | -30.3 |      |
|                                 | ES (A$_2$) C$_{2v}$ |      | 1.342 | 1.093 | 132.9 |      |
|                                 | Δ             |      | 0.135 | 0.035 | -47.1 |      |
| **CASPT2(10e,10o)/ANO-L-VQZP**  | GS           | $D_{\infty}$ | 1.209 | 1.064 | 180.0 | This work |
|                                 | ES (Au) C$_{2h}$ |      | 1.374 | 1.096 | 122.0 |      |
|                                 | Δ             |      | 0.165 | 0.032 | -58.0 |      |
|                                 | ES (Bu) C$_{2h}$ |      | 1.325 | 1.068 | 163.0 |      |
|                                 | Δ             |      | 0.116 | 0.004 | -17.0 |      |
|                                 | ES (A$_2$) C$_{2v}$ |      | 1.345 | 1.099 | 132.2 |      |
|                                 | Δ             |      | 0.137 | 0.035 | -47.8 |      |
| **CASPT2(10e,10o)/aug-cc-pVTZ** | GS           | $D_{\infty}$ | 1.207 | 1.060 | 180.0 | This work |
|                                 | ES (Au) C$_{2h}$ |      | 1.370 | 1.092 | 122.2 |      |
|                                 | Δ             |      | 0.163 | 0.032 | -57.8 |      |
|                                 | ES (Bu) C$_{2h}$ |      | 1.324 | 1.071 | 151.7 | a    |
|                                 | Δ             |      | 0.117 | 0.011 | -28.3 |      |
|                                 | ES (A$_2$) C$_{2v}$ |      | 1.342 | 1.094 | 132.4 |      |
|                                 | Δ             |      | 0.135 | 0.034 | -47.6 |      |
| **EOM-CCSD/TZ2P**               | ES (Au) C$_{2h}$ |      | 1.358 | 1.091 | 123.6 | 1     |
| **CASPT2/ANO[14,9,4,3]**        | GS           | $D_{\infty}$ | 1.217 | 1.066 | 180.0 | 2     |
|                                 | ES (Au) C$_{2h}$ |      | 1.382 | 1.094 | 122.0 |      |
|                                 | Δ             |      | 0.165 | 0.028 | -58.0 |      |
|                                 | ES (A$_2$) C$_{2v}$ |      | 1.353 | 1.097 | 132.0 |      |
|                                 | Δ             |      | 0.136 | 0.031 | -48.0 |      |
| **MR-AQCC/Extrap.**             | GS           | $D_{\infty}$ | 1.205 | 1.067 | 180.0 | 3     |
|                                 | ES (Au) C$_{2h}$ |      | 1.369 | 1.091 | 123.2 |      |
|                                 | Δ             |      | 0.164 | 0.024 | -56.8 |      |
|                                 | ES (Bu) C$_{2h}$ |      | 1.327 | 1.071 | 149.9 |      |
|                                 | Δ             |      | 0.122 | 0.004 | -30.1 |      |
|                                 | ES (A$_2$) C$_{2v}$ |      | 1.339 | 1.093 | 132.9 |      |
|                                 | Δ             |      | 0.134 | 0.026 | -47.1 |      |
| **Mk-MRCCSD/cc-pVCTZ**          | GS           | $D_{\infty}$ | 1.200 | 1.062 | 180.0 | 4     |
|                                 | ES (Au) C$_{2h}$ |      | 1.368 | 1.093 | 123.3 |      |
|                                 | Δ             |      | 0.168 | 0.031 | -56.7 |      |
|                                 | ES (A$_2$) C$_{2v}$ |      | 1.347 | 1.095 | 132.5 |      |
|                                 | Δ             |      | 0.137 | 0.033 | -47.5 |      |
| **Experiment**                  | GS           | $D_{\infty}$ | 1.21  | 1.06  | 180.0 | 5     |
|                                 | ES (Au) C$_{2h}$ |      | 1.38  | 120.0 |      |
|                                 | Δ             |      | 0.17  | -60.0 |      |
|                                 | ES (Au) C$_{2h}$ |      | 1.375 | 1.097 | 122.5 | 6     |

*aNon-standard IPEA of 0.4.
**CASPT2 active space**

The full valence shell, i.e., the pairs of bonding/antibonding $\sigma$(C-H), $\sigma$(C≡C) and $\pi$(C≡C) orbitals were used as an active space.

**Cartesian coordinates**

**CC3**

$CC3/\text{aug-cc-pVTZ}$ total energies (au) and Cartesian coordinates (Å).

**Ground-state**

$E = -77.22863807$

|  |  |  |  |  |
|---|---|---|---|
| 6 | 0 | 0.000000 | 0.000000 | -0.603518 |
| 6 | 0 | 0.000000 | 0.000000 | 0.603518 |
| 1 | 0 | 0.000000 | 0.000000 | 1.661664 |
| 1 | 0 | 0.000000 | 0.000000 | -1.661664 |

**Excited-state ($A_u$)**

$E = -77.03393107$

|  |  |  |  |  |
|---|---|---|---|
| 6 | 0.685643 | 0.000000 | -0.009769 |
| 6 | -0.685643 | 0.000000 | 0.009769 |
| 1 | 1.280284 | 0.000000 | 0.904267 |
| 1 | -1.280284 | 0.000000 | -0.904267 |

**Excited-state ($A_2$)**

$E = -77.02012256$

|  |  |  |  |  |
|---|---|---|---|
| 6 | 0 | 0.000000 | 0.671179 | -0.062052 |
| 6 | 0 | 0.000000 | -0.671179 | 0.062052 |
| 1 | 0 | 0.000000 | 1.414397 | 0.738886 |
| 1 | 0 | 0.000000 | -1.414397 | 0.738886 |

**CASPT2**

$CASPT2(10e,10o)/\text{ANO-L-VQZP}$ total energies (au) and Cartesian coordinates (Å).

**Ground-state**

$E = -77.18133276$

|  |  |  |  |  |
|---|---|---|---|
| 6 | 0 | 0.000000 | 0.000000 | 0.604389 |
| 6 | 0 | 0.000000 | 0.000000 | -0.604389 |
| 1 | 0 | 0.000000 | 0.000000 | -1.668079 |
| 1 | 0 | 0.000000 | 0.000000 | 1.668079 |
Excited-state ($B_u$)
\[ E = -76.92673187 \]

|   | 6   | 6   | 1   | 1   |
|---|-----|-----|-----|-----|
| 6 | 0.338760 | -0.569152 | 0.000000 |
| 6 | -0.338760 | 0.569152 | 0.000000 |
| 1 | -0.593072 | 1.606750 | 0.000000 |
| 1 | 0.593072 | -1.606750 | 0.000000 |

EOM-CCSD

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

Ground-state
\[ E = -77.211018410 \quad (T_1^{\text{diag}} = 0.011) \]

|   | 6   | 6   | 1   | 1   |
|---|-----|-----|-----|-----|
| 6 | 0.000000 | 0.000000 | 0.600377 |
| 6 | 0.000000 | 0.000000 | -0.600377 |
| 1 | 0.000000 | 0.000000 | 1.660213 |
| 1 | 0.000000 | 0.000000 | -1.660213 |

Excited-state ($A_u$)
\[ E = -77.00621174 \quad (T_1^{\text{diag}} = 0.019) \]

|   | 6   | 6   | 1   | 1   |
|---|-----|-----|-----|-----|
| 6 | 0.000000 | 0.677795 | 0.000000 |
| 6 | 0.000000 | -0.677795 | 0.000000 |
| 1 | 0.903942 | 1.287328 | 0.000000 |
| 1 | -0.903942 | -1.287328 | 0.000000 |

Excited-state ($B_u$)
\[ E = -76.95200337 \quad (T_1^{\text{diag}} = 0.015) \]

|   | 6   | 6   | 1   | 1   |
|---|-----|-----|-----|-----|
| 6 | 0.000000 | 0.660237 | 0.000000 |
| 6 | 0.000000 | -0.660237 | 0.000000 |
| 1 | 0.519901 | 1.596886 | 0.000000 |
| 1 | -0.519901 | -1.596886 | 0.000000 |

Excited-state ($A_2$)
\[ E = -76.9924319374 \quad (T_1^{\text{diag}} = 0.016) \]

|   | 6   | 6   | 1   | 1   |
|---|-----|-----|-----|-----|
| 6 | 0.000000 | 0.661756 | -0.110394 |
| 6 | 0.000000 | -0.661756 | -0.110394 |
| 1 | 0.000000 | 1.434286 | 0.662366 |
| 1 | 0.000000 | -1.434286 | 0.662366 |
S2 Formaldehyde
Table S2: Selected geometrical parameters (bond lengths in Å, valence and dihedral angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). Δ gives the difference between the two states (in eV for the ΔZPVE). The considered ES is the lowest A\textsuperscript{\textprime} state of n → π\textsuperscript{\textstar} nature. η measures how the CO bond is out of the HCH plane.

| Method                  | State | PG     | ZPVE | C=O | C-H | H-C-H | η | Ref. |
|-------------------------|-------|--------|------|-----|-----|-------|----|------|
| ADC(2)/def2-TZVPP       | GS    | C\textsubscript{2v} | 0.026974 | 1.209 | 1.098 | 116.4 | 0.0 | This work |
|                         | ES    | C\textsubscript{s}  | 0.022530 | 1.380 | 1.082 | 123.4 | 19.8 |
|                         | Δ     |         | -0.121 | 0.171 | -0.016 | 7.0 | 19.8 |
| ADC(2)/aug-cc-pVTZ      | GS    | C\textsubscript{2v} | 0.026641 | 1.216 | 1.098 | 116.4 | 0.0 | This work |
|                         | ES    | C\textsubscript{s}  | 0.022982 | 1.354 | 1.086 | 120.9 | 30.8 |
|                         | Δ     |         | -0.110 | 0.138 | -0.013 | 4.6 | 30.8 |
| CC2/def2-TZVPP          | GS    | C\textsubscript{2v} | 0.027100 | 1.201 | 1.099 | 116.4 | 0.0 | This work |
|                         | ES    | C\textsubscript{s}  | 0.023645 | 1.305 | 1.088 | 119.0 | 31.8 |
|                         | Δ     |         | -0.094 | 0.104 | -0.011 | 2.6 | 31.8 |
| CC2/aug-cc-pVTZ         | GS    | C\textsubscript{2v} | 0.027100 | 1.201 | 1.099 | 116.4 | 0.0 | This work |
|                         | ES    | C\textsubscript{s}  | 0.023645 | 1.305 | 1.088 | 119.0 | 31.8 |
|                         | Δ     |         | -0.094 | 0.104 | -0.011 | 2.6 | 31.8 |
| CCSD/def2-TZVPP         | GS    | C\textsubscript{2v} | 0.027100 | 1.201 | 1.099 | 116.4 | 0.0 | This work |
|                         | ES    | C\textsubscript{s}  | 0.023645 | 1.305 | 1.088 | 119.0 | 31.8 |
|                         | Δ     |         | -0.094 | 0.104 | -0.011 | 2.6 | 31.8 |
| CCSD/aug-cc-pVTZ        | GS    | C\textsubscript{2v} | 0.027100 | 1.201 | 1.099 | 116.4 | 0.0 | This work |
|                         | ES    | C\textsubscript{s}  | 0.023645 | 1.305 | 1.088 | 119.0 | 31.8 |
|                         | Δ     |         | -0.094 | 0.104 | -0.011 | 2.6 | 31.8 |
| CCSDR(3)/def2-TZVPP     | GS    | C\textsubscript{2v} | 0.027100 | 1.201 | 1.099 | 116.4 | 0.0 | This work |
|                         | ES    | C\textsubscript{s}  | 0.023645 | 1.305 | 1.088 | 119.0 | 31.8 |
|                         | Δ     |         | -0.094 | 0.104 | -0.011 | 2.6 | 31.8 |
| CCSDR(3)/aug-cc-pVTZ    | GS    | C\textsubscript{2v} | 0.027100 | 1.201 | 1.099 | 116.4 | 0.0 | This work |
|                         | ES    | C\textsubscript{s}  | 0.023645 | 1.305 | 1.088 | 119.0 | 31.8 |
|                         | Δ     |         | -0.094 | 0.104 | -0.011 | 2.6 | 31.8 |
| CC3/def2-TZVPP          | GS    | C\textsubscript{2v} | 0.027100 | 1.201 | 1.099 | 116.4 | 0.0 | This work |
|                         | ES    | C\textsubscript{s}  | 0.023645 | 1.305 | 1.088 | 119.0 | 31.8 |
|                         | Δ     |         | -0.094 | 0.104 | -0.011 | 2.6 | 31.8 |
| CC3/aug-cc-pVTZ         | GS    | C\textsubscript{2v} | 0.027100 | 1.201 | 1.099 | 116.4 | 0.0 | This work |
|                         | ES    | C\textsubscript{s}  | 0.023645 | 1.305 | 1.088 | 119.0 | 31.8 |
|                         | Δ     |         | -0.094 | 0.104 | -0.011 | 2.6 | 31.8 |
| CASPT2(12e,10o)/ANO-L-VQZP | GS  | C\textsubscript{2v} | 0.027100 | 1.201 | 1.099 | 116.4 | 0.0 | This work |
|                         | ES    | C\textsubscript{s}  | 0.023645 | 1.305 | 1.088 | 119.0 | 31.8 |
|                         | Δ     |         | -0.094 | 0.104 | -0.011 | 2.6 | 31.8 |
| CASPT2(12e,10o)/aug-cc-pVTZ | GS  | C\textsubscript{2v} | 0.027100 | 1.201 | 1.099 | 116.4 | 0.0 | This work |
|                         | ES    | C\textsubscript{s}  | 0.023645 | 1.305 | 1.088 | 119.0 | 31.8 |
|                         | Δ     |         | -0.094 | 0.104 | -0.011 | 2.6 | 31.8 |
| CCSD/6-311++G(d,p)      | GS    | C\textsubscript{2v} | 0.027100 | 1.201 | 1.099 | 116.4 | 0.0 | This work |
|                         | ES    | C\textsubscript{s}  | 0.023645 | 1.305 | 1.088 | 119.0 | 31.8 |
|                         | Δ     |         | -0.094 | 0.104 | -0.011 | 2.6 | 31.8 |
| MR-AQCC/Extrapol.       | GS    | C\textsubscript{2v} | 0.027100 | 1.201 | 1.099 | 116.4 | 0.0 | This work |
|                         | ES    | C\textsubscript{s}  | 0.023645 | 1.305 | 1.088 | 119.0 | 31.8 |
|                         | Δ     |         | -0.094 | 0.104 | -0.011 | 2.6 | 31.8 |
| CR-EOM-CCSD(T)/cc-pVXZ\textsuperscript{a} | GS   | C\textsubscript{2v} | 0.027100 | 1.201 | 1.099 | 116.4 | 0.0 | This work |
|                         | ES    | C\textsubscript{s}  | 0.023645 | 1.305 | 1.088 | 119.0 | 31.8 |
|                         | Δ     |         | -0.094 | 0.104 | -0.011 | 2.6 | 31.8 |

\textsuperscript{a}cc-pVTZ for the ES, cc-pVQZ for the GS; \textsuperscript{b}Deduced by rotational analysis from the 0\textsuperscript{0} data; \textsuperscript{c}Deduced by rotational analysis from the 4\textsuperscript{1} data; \textsuperscript{d}Given the fact that Ref. 12 refers to Ref. 13 for the excited-state structure, the origin of the differences between the two is rather unclear; \textsuperscript{e}A 34\textsuperscript{o} value is also reported in the best fit of Ref. 14.

S7
**CASPT2 active space**

The full valence shell, i.e., the pairs of bonding/antibonding $\sigma$(C-H), $\sigma$(C=O) and $\pi$(C=O) orbitals and two oxygen lone pairs were used as an active space.

**Cartesian coordinates**

**CC3**

$CC3/aug$-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

| Ground-state | $E$= $-114.37705348$ |
|--------------|-----------------------|
| 6            | 0.000000 0.000000 $-0.602985$ |
| 8            | 0.000000 0.000000 $0.605394$  |
| 1            | 0.000000 0.934673 $-1.182175$ |
| 1            | 0.000000 $-0.934673$ $-1.182175$ |

| Excited-state | $E$= $-114.24549682$ |
|--------------|----------------------|
| 6            | $-0.052615$ 0.000000 $0.672431$ |
| 8            | 0.010516 0.000000 $-0.652373$ |
| 1            | 0.226376 0.935213 $1.156098$ |
| 1            | 0.226376 $-0.935213$ $1.156098$ |

**EOM-CCSD**

$EOM$-CCSD/$def2$-TZVPP total energies (au) and Cartesian coordinates (Å).

| Ground-state | $E$= $-114.34654983$ ($T_{1}^{\text{diag}}= 0.013$) |
|--------------|-----------------------------------------------|
| 6            | 0.000000 0.000000 $-0.528028$ |
| 8            | 0.000000 0.000000 $0.672819$  |
| 1            | 0.000000 0.933449 $-1.107191$ |
| 1            | 0.000000 $-0.933449$ $-1.107191$ |

| Excited-state | $E$= $-114.221824159$ ($T_{1}^{\text{diag}}= 0.017$) |
|--------------|---------------------------------------------|
| 6            | $-0.032577$ 0.591312 0.000000 |
| 8            | $-0.032577$ $-0.713140$ 0.000000 |
| 1            | 0.228037 1.078622 0.937247 |
| 1            | 0.228037 1.078622 $-0.937247$ |
Excited-state (constrained $C_{2v}$)

When constraining the ES in the $C_{2v}$ point group, the lowest ES belongs to the $A_2$ representation. It is a transition-state like minimum with an imaginary vibrational mode of 439 cm$^{-1}$ at the EOM-CCSD level (the same is obtained with CC2) corresponding to an out-of-plane deformation. The EOM-CCSD energy is only 0.017 eV (or 141 cm$^{-1}$) higher than in the true minimum. The corresponding CC2 barrier is 243 cm$^{-1}$.

$$E = -114.221182812 \quad (T_1^{\text{diag}} = 0.018)$$

|   |   |   |   |
|---|---|---|---|
| 6 | 0.000000 | 0.000000 | -0.588954 |
| 8 | 0.000000 | 0.000000 | 0.718074 |
| 1 | 0.000000 | 0.952269 | -1.105434 |
| 1 | 0.000000 | -0.952269 | -1.105434 |
Table S3: Selected geometrical parameters (bond lengths in Å, valence angles and dihedral angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). ∆ gives the difference between the two states (in eV for the $\Delta_{ZPVE}$). The considered ES is the lowest $A_2$ state of $n \rightarrow \pi^*$ nature.

| Method                  | State  | PG    | ZPVE   | C=S   | C-H   | H-C-H   | Ref. |
|-------------------------|--------|-------|--------|-------|-------|---------|------|
| ADC(2)/def2-TZVPP       | GS     | $C_{2v}$ | 0.025051 | 1.606 | 1.084 | 116.2   | This work |
|                         | ES     | $C_{2v}$ | 0.021979 | 1.719 | 1.080 | 121.0   | This work |
|                         | $\Delta$ |       | -0.084 | 0.113 | -0.004 | 4.8     |       |
| ADC(2)/aug-cc-pVTZ      | GS     | $C_{2v}$ | 1.610  | 1.082 | 116.1   | This work |
|                         | ES     | $C_{2v}$ | 1.725  | 1.079 | 121.0   | This work |
|                         | $\Delta$ |       | 0.115  | -0.003 | 4.9    |       |
| CC2/def2-TZVPP          | GS     | $C_{2v}$ | 0.024844 | 1.614 | 1.084 | 116.3   | This work |
|                         | ES     | $C_{2v}$ | 0.021964 | 1.706 | 1.080 | 120.9   | This work |
|                         | $\Delta$ |       | -0.078 | 0.091 | -0.004 | 4.6     |       |
| CC2/aug-cc-pVTZ         | GS     | $C_{2v}$ | 1.618  | 1.082 | 116.1   | This work |
|                         | ES     | $C_{2v}$ | 1.710  | 1.079 | 120.8   | This work |
|                         | $\Delta$ |       | 0.092  | -0.003 | 4.7    |       |
| CCSD/def2-TZVPP         | GS     | $C_{2v}$ | 1.605  | 1.083 | 116.0   | This work |
|                         | ES     | $C_{2v}$ | 1.679  | 1.079 | 119.5 | This work |
|                         | $\Delta$ |       | 0.074  | -0.004 | 3.5    |       |
| CCSD/aug-cc-pVTZ        | GS     | $C_{2v}$ | 1.690  | 1.081 | 115.9   | This work |
|                         | ES     | $C_{2v}$ | 1.682  | 1.077 | 119.4   | This work |
|                         | $\Delta$ |       | 0.073  | -0.004 | 3.5    |       |
| CCSDR(3)/def2-TZVPP     | GS     | $C_{2v}$ | 1.618  | 1.083 | 116.1   | This work |
|                         | ES     | $C_{2v}$ | 1.709  | 1.080 | 120.4   | This work |
|                         | $\Delta$ |       | 0.090  | -0.005 | 4.1    |       |
| CCSDR(3)/aug-cc-pVTZ    | GS     | $C_{2v}$ | 1.618  | 1.083 | 116.1   | This work |
|                         | ES     | $C_{2v}$ | 1.705  | 1.078 | 120.1   | This work |
|                         | $\Delta$ |       | 0.087  | -0.005 | 4.0    |       |
| CC3/def2-TZVPP          | GS     | $C_{2v}$ | 1.620  | 1.085 | 116.3   | This work |
|                         | ES     | $C_{2v}$ | 1.713  | 1.080 | 120.5   | This work |
|                         | $\Delta$ |       | 0.093  | -0.005 | 4.2    |       |
| CC3/aug-cc-pVTZ         | GS     | $C_{2v}$ | 1.619  | 1.083 | 116.1   | This work |
|                         | ES     | $C_{2v}$ | 1.709  | 1.078 | 120.2   | This work |
|                         | $\Delta$ |       | 0.090  | -0.005 | 4.2    |       |
| CASPT2(12e,15o)/ANO-L     | GS     | $C_{2v}$ | 1.618  | 1.087 | 116.4   | This work |
| a                        | ES     | $C_{2v}$ | 1.709  | 1.082 | 120.7   | This work |
|                         | $\Delta$ |       | 0.091  | -0.005 | 4.3    |       |
| CASPT2(12e,15o)/aug-cc-pVTZ | GS     | $C_{2v}$ | 1.620  | 1.084 | 116.1   | This work |
| a                        | ES     | $C_{2v}$ | 1.711  | 1.079 | 120.3   | This work |
|                         | $\Delta$ |       | 0.091  | -0.005 | 4.2    |       |
| CCSD/6-311++G(d,p)       | GS     | $C_{2v}$ | 1.615  | 1.096 | 116.2   | 7 |
|                          | ES     | $C_{2v}$ | 1.698  | 1.087 | 119.7   | 7   |
|                         | $\Delta$ |       | 0.083  | -0.009 | 3.5    |       |
| CC2/aug-cc-pVQZ          | ES     | $C_{2v}$ | 1.706  | 1.083 | 121.2   | 15  |
| Theor. Best Estimateb   | GS     | $C_{2v}$ | 1.609  | 1.085 | 121.8   | 16  |

\( ^a \) Maximum contraction of ANO-L basis set was used, i.e., H: 6s4p3d, C: 7s7p4d5f, S: 7s7p5d4f; \( ^b \) CCSD(T)-F12b with CBS and extra corrections, see Ref. 16; \( ^c \) In this earlier study, a slightly out-of-plane structure is deduced; \( ^d \) Considering the 0\(^0\) band, out-of-plane estimate: 8.9\(^o\); \( ^e \) Considering the 4\(^1\) band, out-of-plane estimate: 27.8\(^o\).
**CASPT2 active space**

The full valence shell, i.e., the pairs of bonding/antibonding $\sigma$(C-H), $\sigma$(C=S) and $\pi$(C=S) orbitals and two sulfur lone pairs were used as active space. This active space was further expanded by adding low lying $d$ orbitals on sulfur, their occupation numbers at optimized geometry are ca. 0.02 electron.

**Cartesian coordinates**

**CC3**

CC3/\textit{aug}-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

| Ground-state | $E= -436.99803030$ |
|--------------|---------------------|
| 6            | 0.000000 0.000000 -1.104273 |
| 16           | 0.000000 0.000000 0.514631 |
| 1            | 0.000000 0.918957 -1.677563 |
| 1            | 0.000000 -0.918957 -1.677563 |

| Excited-state | $E= -436.92084978$ |
|--------------|---------------------|
| 6            | 0.000000 0.000000 -1.165548 |
| 16           | 0.000000 0.000000 0.543556 |
| 1            | 0.000000 0.934708 -1.703471 |
| 1            | 0.000000 -0.934708 -1.703471 |

**EOM-CCSD**

(EOM)-CCSD/\textit{def2}-TZVPP total energies (au) and Cartesian coordinates (Å).

| Ground-state | $E= -437.08912015$ ($T_1^{\text{diag}} = 0.011$) |
|--------------|---------------------|
| 6            | 0.000000 0.000000 -1.022305 |
| 16           | 0.000000 0.000000 0.582884 |
| 1            | 0.000000 0.918395 -1.596159 |
| 1            | 0.000000 -0.918395 -1.596159 |

| Excited-state | $E= -437.007126729$ ($T_1^{\text{diag}} = 0.014$) |
|--------------|---------------------|
| 6            | 0.000000 0.000000 -1.074119 |
| 16           | 0.000000 0.000000 0.604983 |
| 1            | 0.000000 0.932493 -1.617506 |
| 1            | 0.000000 -0.932493 -1.617506 |

S11
### Table S4: Selected geometrical parameters (bond lengths in Å, valence angles and dihedral angle in degrees).

PG is the point group and ZPVE is the zero-point vibrational energy (in au). ∆ gives the difference between the two states (in eV for the $\Delta_{\text{ZPVE}}$). The considered ES is the lowest $A_2$ state of $n \rightarrow \pi^*$ nature.

| Method             | State | PG   | ZPVE  | C=Se  | C-H  | H-C-H | Ref. |
|--------------------|-------|------|-------|-------|------|-------|------|
| ADC(2)/def2-TZVPP  | GS    | $C_{2v}$ | 0.024412 | 1.744 | 1.081 | 117.2 | This work |
|                    | ES    | $C_{2v}$ | 0.021823 | 1.876 | 1.079 | 121.9 |       |
|                    | $\Delta$ | | -0.070 | 0.132 | -0.002 | 4.7 |       |
| ADC(2)/aug-cc-pVTZ | GS    | $C_{2v}$ | 1.737 | 1.079 | 116.6 | This work |
|                    | ES    | $C_{2v}$ | 1.863 | 1.078 | 121.3 |       |
|                    | $\Delta$ | | 0.126 | -0.001 | 4.7 |       |
| CC2/def2-TZVPP     | GS    | $C_{2v}$ | 0.024175 | 1.757 | 1.081 | 117.3 | This work |
|                    | ES    | $C_{2v}$ | 0.021740 | 1.855 | 1.079 | 121.8 |       |
|                    | $\Delta$ | | -0.066 | 0.098 | -0.002 | 4.5 |       |
| CC2/aug-cc-pVTZ    | GS    | $C_{2v}$ | 1.749 | 1.080 | 116.7 | This work |
|                    | ES    | $C_{2v}$ | 1.843 | 1.078 | 121.2 |       |
|                    | $\Delta$ | | 0.094 | -0.002 | 4.5 |       |
| CCSD/def2-TZVPP    | GS    | $C_{2v}$ | 0.024452 | 1.746 | 1.078 | 116.8 | This work |
|                    | ES    | $C_{2v}$ | 1.838 | 1.077 | 120.1 |       |
|                    | $\Delta$ | | 0.005 | 0.007 | 3.3 |       |
| CCSD/aug-cc-pVTZ   | GS    | $C_{2v}$ | 1.759 | 1.078 | 116.2 | This work |
|                    | ES    | $C_{2v}$ | 1.813 | 1.076 | 119.5 |       |
|                    | $\Delta$ | | 0.074 | -0.002 | 3.3 |       |
| CCSDR(3)/def2-TZVPP | GS  | $C_{2v}$ | 1.757 | 1.082 | 117.0 | This work |
|                    | ES    | $C_{2v}$ | 1.849 | 1.078 | 120.7 |       |
|                    | $\Delta$ | | 0.092 | -0.004 | 3.7 |       |
| CCSDR(3)/aug-cc-pVTZ | GS   | $C_{2v}$ | 1.750 | 1.080 | 116.5 | This work |
|                    | ES    | $C_{2v}$ | 1.838 | 1.077 | 120.1 |       |
|                    | $\Delta$ | | 0.088 | -0.003 | 3.6 |       |
| CC3/def2-TZVPP     | GS    | $C_{2v}$ | 1.759 | 1.082 | 117.0 | This work |
|                    | ES    | $C_{2v}$ | 1.854 | 1.079 | 120.8 |       |
|                    | $\Delta$ | | 0.095 | -0.003 | 3.8 |       |
| CC3/aug-cc-pVTZ    | GS    | $C_{2v}$ | 1.751 | 1.080 | 116.5 | This work |
|                    | ES    | $C_{2v}$ | 1.843 | 1.077 | 120.3 |       |
|                    | $\Delta$ | | 0.092 | -0.003 | 3.8 |       |
| CASPT2(12e,15o)/aug-cc-pVTZ | GS | $C_{2v}$ | 1.753 | 1.082 | 116.6 | This work |
|                    | ES    | $C_{2v}$ | 1.845 | 1.077 | 120.3 |       |
|                    | $\Delta$ | | 0.092 | -0.005 | 3.7 |       |
| Experiment         | GS    | $b$ | 1.759 | 1.082 | 117.0 | | 21$^a$ |
|                    | ES    | | 1.856 | 1.075$^c$ | 121.6$^c$ | | 22$^d$ |
|                    | $\Delta$ | | 0.097 | 1.2 | | |

$^a$Microwave results assuming a C-H bond length of 1.090 Å; $^b$Though the authors concluded that the ES was planar, the FC fit yields a slightly out-of-plane structure. The parameters reported are those deduced from the $0^0$ level which is thus considered of $C_s$ symmetry in this fit (out-of-plane angle: 12.2$^o$). An analysis of $^1$ yields a C-Se bond length of 1.858 Å and an out-of-plane angle of 29.2$^o$, using a C-H distance of 1.093 Å and a H-C-H angle of 116.8$^o$, fixed at their corresponding thioformaldehyde value. See the discussion in Ref. 22; $^c$Fixed at the thioformaldehyde value in the fit.
CASPT2 active space

The full valence shell, i.e., the pairs of bonding/antibonding $\sigma$(C-H), $\sigma$(C=Se) and $\pi$(C=Se) orbitals and two selenium lone pairs were used as active space. This active space was further expanded by adding low lying $d$ orbitals on selenium, their occupation numbers at optimized geometry are ca. 0.02 electron. As in this case we did not find the ANO-L basis set for selenium we applied the aug-cc-pVTZ basis set only.

Cartesian coordinates

CC3

$\text{CC3/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).}$

| Ground-state | $E$= -2439.390961 |
|-------------|-------------------|
| 6           | 0.000000 0.000000 -1.473191 |
| 34          | 0.000000 -0.000000 0.278162 |
| 1           | 0.000000 0.918606 -2.042081 |
| 1           | -0.000000 -0.918606 -2.042081 |

| Excited-state | $E$= -2439.32567795 |
|--------------|-------------------|
| 6           | 0.000000 0.000000 -1.560136 |
| 34          | 0.000000 -0.000000 0.282637 |
| 1           | 0.000000 0.934079 -2.096655 |
| 1           | -0.000000 -0.934079 -2.096655 |

EOM-CCSD

$(\text{EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).}$

| Ground-state | $E$= -2439.3794439 ($T_1^{\text{diag}}$ = 0.011) |
|--------------|-------------------|
| 6           | 0.000000 0.000000 -1.386422 |
| 34          | 0.000000 -0.000000 0.359512 |
| 1           | 0.000000 0.919714 -1.952431 |
| 1           | -0.000000 -0.919714 -1.952431 |

| Excited-state | $E$= -2439.31075471 ($T_1^{\text{diag}}$ = 0.014) |
|--------------|-------------------|
| 6           | 0.000000 -0.000000 -1.449744 |
| 34          | -0.000000 0.000000 0.372762 |
| 1           | -0.000000 0.933421 -1.987724 |
| 1           | -0.000000 -0.933421 -1.987724 |
Table S5: Selected geometrical parameters (bond lengths in Å, valence angles and dihedral angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). $\Delta$ gives the difference between the two states (in eV for the $\Delta Z$). The considered ES is the lowest $A^*$ state of $\pi \rightarrow \pi^*$ nature.

| Method                  | State | PG  | ZPVE | C=O  | C=C  | C-H  | C=H  | C=C=O | C=C-H | Ref.          |
|------------------------|-------|-----|------|------|------|------|------|-------|-------|--------------|
| ADC(2)/def2-TZVPP      | GS    | $C_{2v}$ | 0.031715 | 1.164 | 1.314 | 1.073 | 1.073 | 180.0 | 119.0 | This work    |
| ADC(2)/aug-cc-pVTZ     | ES    | $C_s$      | 0.031783 | 1.200 | 1.429 | 1.081 | 1.073 | 130.3 | 118.5 |              |
|                        | $\Delta$ | 0.001 | 0.036 | 0.115 | 0.008 | 0.000 | -49.7 | -0.5  |      |              |
| CC2/def2-TZVPP         | GS    | $C_{2v}$ | 0.031295 | 1.164 | 1.311 | 1.073 | 1.073 | 180.0 | 119.0 | This work    |
| CC2/aug-cc-pVTZ        | ES    | $C_s$      | 0.031417 | 1.200 | 1.428 | 1.081 | 1.073 | 130.6 | 118.5 |              |
|                        | $\Delta$ | 0.035 | 0.111 | 0.009 | -0.001 | -49.7 | -0.5  |      |      |              |
| CCSD/def2-TZVPP        | GS    | $C_{2v}$ | 0.032030 | 1.157 | 1.312 | 1.074 | 1.074 | 180.0 | 119.1 | This work    |
| CCSD/aug-cc-pVTZ       | ES    | $C_s$      | 0.031999 | 1.190 | 1.416 | 1.083 | 1.075 | 131.4 | 119.5 |              |
|                        | $\Delta$ | 0.003 | 0.036 | 0.119 | 0.008 | 0.000 | -50.7 | -0.2  |      |              |
| CASPT2(14e,13o)/ANO-L-VQZ | GS | $C_{2v}$ | 1.165 | 1.317 | 1.073 | 1.073 | 180.0 | 119.0 | This work    |
| CASPT2(16e,14o)/ANO-L-VQZP | ES | $C_s$      | 1.199 | 1.430 | 1.084 | 1.076 | 129.8 | 119.4 |              |
|                        | $\Delta$ | 0.035 | 0.113 | 0.008 | -0.004 | -50.2 | 0.3   |      |      |              |
| TD-CCSD/cc-pVTZ        | GS    | $C_{2v}$ | 1.166 | 1.317 | 1.073 | 1.073 | 180.0 | 119.0 | This work    |
| MS-CASPT2/6-31+G(d)    | ES    | $C_s$      | 1.199 | 1.430 | 1.084 | 1.076 | 129.9 | 119.5 |              |
|                        | $\Delta$ | 0.036 | 0.112 | 0.008 | 0.001 | -50.1 | 0.5   |      |      |              |

$^a$ Note that for the GS, using aug-cc-pVTZ and a larger active space yields shorter bonds, e.g., 1.166 and 1.319 Å for C-O and C-C, respectively. Both are closer to our CASPT2 (and CC) counterparts.
CASPT2 active space

All valence atomic orbitals were included in the active space, i.e. 16 electrons in 14 orbitals were used. We have tested the possibility of omitting the 2s lone pair on oxygen atom in the active space. This would be supported by its low energy compared to the rest of the active space and its high occupation numbers when included in CAS, around 1.99. For the aug-cc-pVTZ basis set we observed minimal change in geometries with respect to CAS size, nevertheless we report values obtain with full valence CAS as our best estimate on CASPT2 level of theory. For ANO-L basis set we observed larger difference especially for the CCO angle. We consider full valence CAS as our best estimate for given basis set.

Cartesian coordinates

CC3

CC3/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

**Ground-state**

\[ E = -152.42409065 \]

|   | 6   | 6   | 8   | 1   | 1   |
|---|-----|-----|-----|-----|-----|
|   | 0.000000 | -0.000000 | 1.295480 |
| 6 | 0.000000 | 0.000000 | 0.018514 |
| 8 | 0.000000 | 0.000000 | 1.183578 |
| 1 | 0.000000 | 0.938930 | -1.818814 |
| 1 | 0.000000 | -0.938930 | -1.818814 |

**Excited-state**

\[ E = -152.32635151 \]

|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 6 | 1.081142 | -0.492435 | 0.000000 |
| 6 | 0.002122 | 0.442029 | 0.000000 |
| 8 | -1.183824 | 0.248632 | 0.000000 |
| 1 | 0.865753 | -1.554127 | 0.000000 |
| 1 | 2.096668 | -0.141021 | 0.000000 |
EOM-CCSD

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

Ground-state
\[ E = -152.39461433 \ (T_1^{\text{diag}} = 0.014) \]

|   |   |   |   |
|---|---|---|---|
| 6 | 0.000000 | -0.000000 | -1.208085 |
| 6 | 0.000000 | 0.000000 | 0.104135 |
| 8 | 0.000000 | 0.000000 | 1.260597 |
| 1 | 0.000000 | 0.937929 | -1.730540 |
| 1 | -0.000000 | -0.937929 | -1.730540 |

Excited-state
\[ E = -152.288242805 \ (T_1^{\text{diag}} = 0.016) \]

|   |   |   |   |
|---|---|---|---|
| 6 | 1.077299 | -0.491655 | 0.000000 |
| 6 | -0.000000 | 0.427593 | -0.000000 |
| 8 | -1.178337 | 0.259605 | -0.000000 |
| 1 | 0.871207 | -1.555054 | 0.000000 |
| 1 | 2.091691 | -0.137411 | 0.000000 |

Excited-state (constrained \( C_{2v} \))
This structure (\( A_2 \) symmetry) presents an imaginary frequency of 761 cm\(^{-1}\) (789 cm\(^{-1}\) with CC2) and is 0.87 eV (0.99 eV with CC2) less stable than the actual minimum. The MS-CASPT2/6-31+G(d) value is 1.03 eV.\(^{24}\)

\[ E = -152.256162739 \ (T_1^{\text{diag}} = 0.016) \]

|   |   |   |   |
|---|---|---|---|
| 6 | 0.000000 | 0.000000 | -1.257107 |
| 6 | -0.000000 | -0.000000 | 0.117264 |
| 8 | -0.000000 | -0.000000 | 1.315494 |
| 1 | 0.000000 | 0.922150 | -1.842446 |
| 1 | -0.000000 | -0.922150 | -1.842446 |
S6  Thio ketene

Table S6: Selected geometrical parameters (bond lengths in Å, valence angles and dihedral angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). Δ gives the difference between the two states (in eV for the $\Delta ZPVE$). The considered ES is the lowest $\pi^* \rightarrow \pi$ state of nature.

| Method                     | State | PG | ZPVE  | C=C=S | C=C-H | C-H$_1$ | C-H$_2$ | C=C=H$_1$ | C=C=H$_2$ | Ref.   |
|---------------------------|-------|----|-------|-------|--------|---------|---------|------------|------------|--------|
| ADC(2)/def2-TZVPP        | GS    | $C_{2v}$ | 0.029067 | 1.551 | 1.314 | 1.078 | 1.078 | 180.0 | 120.1 | This work |
|                           | ES    | $C_{s}$ | 0.029258 | 1.615 | 1.363 | 1.085 | 1.079 | 139.2 | 120.2 | This work |
|                           | Δ     |       | -0.009 | 0.064 | 0.049 | 0.007 | 0.001 | -40.8 | 0.1  |         |
| ADC(2)/aug-cc-pVTZ       | GS    | $C_{2v}$ | 1.555 | 1.309 | 1.076 | 1.076 | 180.0 | 120.2 |         | This work |
|                           | ES    | $C_{s}$ | 1.622 | 1.355 | 1.084 | 1.077 | 139.7 | 121.1 |         | This work |
|                           | Δ     |       | 0.067 | 0.046 | 0.008 | 0.001 | -40.3 | 0.1  |       |         |
| CC2/def2-TZVPP           | GS    | $C_{2v}$ | 0.029343 | 1.560 | 1.317 | 1.078 | 1.078 | 139.8 | 121.1 | This work |
|                           | ES    | $C_{s}$ | 0.029141 | 1.612 | 1.373 | 1.086 | 1.079 | 137.8 | 120.2 | This work |
|                           | Δ     |       | -0.005 | 0.052 | 0.056 | 0.008 | 0.001 | -42.2 | 0.9  |         |
| CC2/aug-cc-pVTZ          | GS    | $C_{2v}$ | 1.564 | 1.312 | 1.077 | 1.077 | 180.0 | 120.2 |         | This work |
|                           | ES    | $C_{s}$ | 1.617 | 1.365 | 1.084 | 1.078 | 138.2 | 121.1 |         | This work |
|                           | Δ     |       | 0.067 | 0.046 | 0.008 | 0.001 | -40.3 | 0.2  |       |         |
| CCSD/def2-TZVPP          | GS    | $C_{2v}$ | 0.029875 | 1.555 | 1.309 | 1.078 | 1.078 | 139.8 | 121.1 | This work |
|                           | ES    | $C_{s}$ | 0.029574 | 1.603 | 1.358 | 1.086 | 1.080 | 140.1 | 121.1 | This work |
|                           | Δ     |       | -0.008 | 0.048 | 0.049 | 0.008 | 0.002 | -39.9 | 0.8  |         |
| CCSD/aug-cc-pVTZ         | GS    | $C_{2v}$ | 1.558 | 1.304 | 1.076 | 1.076 | 180.0 | 120.2 |         | This work |
|                           | ES    | $C_{s}$ | 1.607 | 1.350 | 1.084 | 1.078 | 140.7 | 121.0 |         | This work |
|                           | Δ     |       | 0.049 | 0.046 | 0.008 | 0.002 | -39.3 | 0.7  |       |         |
| CCSDR(3)/def2-TZVPP      | GS    | $C_{2v}$ | 1.565 | 1.315 | 1.080 | 1.080 | 180.0 | 120.2 |         | This work |
|                           | ES    | $C_{s}$ | 1.621 | 1.369 | 1.086 | 1.081 | 136.8 | 121.0 |         | This work |
|                           | Δ     |       | 0.056 | 0.054 | 0.006 | 0.001 | -42.2 | 0.8  |       |         |
| CCSDR(3)/aug-cc-pVTZ     | GS    | $C_{2v}$ | 1.565 | 1.311 | 1.078 | 1.078 | 180.0 | 120.3 |         | This work |
|                           | ES    | $C_{s}$ | 1.619 | 1.362 | 1.085 | 1.079 | 137.4 | 120.9 |         | This work |
|                           | Δ     |       | 0.054 | 0.051 | 0.007 | 0.001 | -41.6 | 0.6  |       |         |
| CC3/def2-TZVPP           | GS    | $C_{2v}$ | 1.567 | 1.316 | 1.080 | 1.080 | 180.0 | 120.3 |         | This work |
|                           | ES    | $C_{s}$ | 1.621 | 1.374 | 1.087 | 1.081 | 137.0 | 120.9 |         | This work |
|                           | Δ     |       | 0.054 | 0.058 | 0.007 | 0.001 | -43.0 | 0.6  |       |         |
| CC3/aug-cc-pVTZ          | GS    | $C_{2v}$ | 1.567 | 1.311 | 1.078 | 1.078 | 180.0 | 120.3 |         | This work |
|                           | ES    | $C_{s}$ | 1.619 | 1.367 | 1.086 | 1.080 | 137.6 | 120.8 |         | This work |
|                           | Δ     |       | 0.052 | 0.056 | 0.008 | 0.002 | -42.4 | 0.5  |       |         |
| CASPT2(16e,14o)/ANO-L-VQZP | GS   | $C_{2v}$ | 1.563 | 1.315 | 1.079 | 1.079 | 180.0 | 120.6 |         | This work |
|                           | ES    | $C_{s}$ | 1.616 | 1.375 | 1.090 | 1.083 | 136.8 | 120.9 |         | This work |
|                           | Δ     |       | 0.053 | 0.060 | 0.011 | 0.004 | -43.2 | 0.3  |       |         |
| CASPT2(16e,14o)/aug-cc-pVTZ | GS   | $C_{2v}$ | 1.562 | 1.310 | 1.076 | 1.076 | 180.0 | 120.6 |         | This work |
|                           | ES    | $C_{s}$ | 1.613 | 1.367 | 1.090 | 1.082 | 140.4 | 120.9 |         | This work |
|                           | Δ     |       | 0.051 | 0.057 | 0.014 | 0.006 | -39.6 | 0.3  |       |         |

Experiment GS $C_{2v}$ 1.554 1.314 1.080 1.080 180.0 120.1 25
CASPT2 active space

All valence atomic orbitals were taken into the active space, i.e., 16 electrons in 14 orbitals.

Cartesian coordinates

CC3

CC3/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

Ground-state
\[ E = -475.03688189 \]

|    |        |        |        |        |
|----|--------|--------|--------|--------|
| 6  | 0.000000 | 0.000000 | -1.692512 |        |
| 6  | 0.000000 | 0.000000 | -0.381149 |        |
| 16 | 0.000000 | 0.000000 |  1.185320 |        |
|  1 | 0.000000 | 0.931042 | -2.236042 |        |
|  1 | 0.000000 |-0.931042  |-2.236042  |        |

Excited-state
\[ E = -474.95903178 \]

|    |        |        |        |        |
|----|--------|--------|--------|--------|
| 6  | 1.142234 | -0.500790 |  0.000000 |        |
| 6  | 0.107610 | 0.392421  |  0.000000 |        |
| 16 |-1.510910 | 0.347552  |  0.000000 |        |
|  1 | 0.954334 | -1.570031 |  0.000000 |        |
|  1 | 2.168592 |-0.166075  |  0.000000 |        |

EOM-CCSD

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

Ground-state
\[ E = -475.11575237 \ (T_{\text{diag}} = 0.013) \]

|    |        |        |        |        |
|----|--------|--------|--------|--------|
| 6  | 0.000000 | 0.000000 | -1.752852 |        |
| 6  | 0.000000 | 0.000000 | -0.444055 |        |
| 16 | -0.000000 | -0.000000 |  1.110782 |        |
|  1 | -0.000000 | 0.930865  | -2.295538 |        |
|  1 | -0.000000 |-0.930865  |-2.295538  |        |
**Excited-state**

\[ E = -475.032961634 \left(T_1^{\text{diag}} = 0.015\right) \]

|   |       |       |       |
|---|-------|-------|-------|
| 6 | 1.229595 | 1.180833 | -0.000000 |
| 6 | -0.000000 | 0.605443 | -0.000000 |
| 16 | -0.678500 | -0.846700 | 0.000000 |
| 1 | 2.131052  | 0.575547  | -0.000000 |
| 1 | 1.347384  | 2.253998  | -0.000000 |

**Excited-state (constrained \(C_{2v}\))**

This structure (\(A_2\) symmetry) presents an imaginary frequency of 338\,\text{cm}^{-1} (359\,\text{cm}^{-1} with CC2) and is 0.24 eV (0.29 eV with CC2) less stable than the actual minimum. These values are significantly smaller than in ketene.

\[ E = -475.024213222 \left(T_1^{\text{diag}} = 0.014\right) \]

|   |       |       |       |
|---|-------|-------|-------|
| 6 | 0.000000 | -0.000000 | -1.794459 |
| 6 | 0.000000 | -0.000000 | -0.448337 |
| 16 | 0.000000 | 0.000000 | 1.137535 |
| 1 | 0.000000 | 0.921494 | -2.371896 |
| 1 | -0.000000 | -0.921494 | -2.371896 |
Table S7: Selected geometrical parameters (bond lengths in Å, valence angles and dihedral angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). ∆ gives the difference between the two states (in eV for the ∆ZPVE). The considered ES is the lowest A state of π → π* nature.

| Method                  | State | PG | ZPVE  | N=N  | C=N  | C-H1 | C-H2 | C=NN=N | N=C-H1 | Ref.          |
|------------------------|-------|----|-------|------|------|------|------|--------|--------|---------------|
| ADC(2)/def2-TZVPP      | GS    | C2v| 0.031639 | 1.135 | 1.307 | 1.070 | 1.070 | 180.0  | 116.9  | This work     |
|                        | ES    | Cs | 0.030581 | 1.161 | 1.447 | 1.077 | 1.070 | 128.1  | 116.8  |               |
|                        | ∆     |    | -0.029 | 0.026 | 0.140 | 0.007 | 0.000 | -51.9  | -0.1   |               |
| ADC(2)/aug-cc-pVTZ     | GS    | C2v| 1.134  | 1.305 | 1.070 | 1.070 | 180.0 | 116.9  |        | This work     |
|                        | ES    | Cs | 1.160  | 1.438 | 1.076 | 1.069 | 128.6 | 116.8  |        |               |
|                        | ∆     |    | 0.026  | 0.133 | 0.006 | -0.001| -51.4 | -0.1   |        |               |
| CC2/def2-TZVPP         | GS    | C2v| 0.031007 | 1.131 | 1.301 | 1.072 | 1.072 | 180.0  | 117.2  | This work     |
|                        | ES    | Cs | 0.030344 | 1.193 | 1.414 | 1.079 | 1.071 | 128.1  | 117.5  |               |
|                        | ∆     |    | -0.018 | 0.039 | 0.110 | 0.007 | 0.000 | -51.5  | 0.3    |               |
| CC2/aug-cc-pVTZ        | GS    | C2v| 1.152  | 1.301 | 1.071 | 1.071 | 128.5 | 117.5  |        | This work     |
|                        | ES    | Cs | 1.190  | 1.408 | 1.078 | 1.071 | 128.5 | 117.5  |        |               |
|                        | ∆     |    | 0.038  | 0.107 | 0.007 | 0.000 | -51.5  | 0.3    |        |               |
| CCSD/def2-TZVPP        | GS    | C2v| 0.032074 | 1.131 | 1.295 | 1.071 | 1.071 | 180.0  | 117.5  | This work     |
|                        | ES    | Cs | 0.031280 | 1.193 | 1.361 | 1.079 | 1.073 | 126.2  | 119.3  |               |
|                        | ∆     |    | -0.022 | 0.062 | 0.066 | 0.008 | 0.002 | -53.8  | 1.8    |               |
| CCSD/aug-cc-pVTZ       | GS    | C2v| 1.130  | 1.292 | 1.070 | 1.070 | 180.0 | 117.5  |        | This work     |
|                        | ES    | Cs | 1.189  | 1.357 | 1.079 | 1.072 | 126.7 | 119.3  |        |               |
|                        | ∆     |    | 0.059  | 0.065 | 0.009 | 0.002 | -53.3  | 1.8    |        |               |
| CCSDR(3)/def2-TZVPP    | GS    | C2v| 1.141  | 1.300 | 1.073 | 1.073 | 180.0 | 117.5  |        | This work     |
|                        | ES    | Cs | 1.197  | 1.382 | 1.080 | 1.074 | 125.6 | 119.0  |        |               |
|                        | ∆     |    | 0.056  | 0.082 | 0.007 | 0.001 | -54.4  | 1.5    |        |               |
| CCSDR(3)/aug-cc-pVTZ   | GS    | C2v| 1.139  | 1.297 | 1.072 | 1.072 | 180.0 | 117.4  |        | This work     |
|                        | ES    | Cs | 1.193  | 1.378 | 1.080 | 1.073 | 126.1 | 118.9  |        |               |
|                        | ∆     |    | 0.054  | 0.081 | 0.008 | 0.001 | -53.9  | 1.5    |        |               |
| CC3/def2-TZVPP         | GS    | C2v| 1.142  | 1.301 | 1.073 | 1.073 | 180.0 | 117.4  |        | This work     |
|                        | ES    | Cs | 1.197  | 1.390 | 1.080 | 1.074 | 125.7 | 118.9  |        |               |
|                        | ∆     |    | 0.055  | 0.089 | 0.007 | 0.001 | -54.3  | 1.5    |        |               |
| CC3/aug-cc-pVTZ        | GS    | C2v| 1.140  | 1.298 | 1.073 | 1.073 | 180.0 | 117.5  |        | This work     |
|                        | ES    | Cs | 1.194  | 1.385 | 1.080 | 1.073 | 126.2 | 118.8  |        |               |
|                        | ∆     |    | 0.054  | 0.087 | 0.007 | 0.000 | -53.8  | 1.3    |        |               |
| CASPT2(16e,14o)/ANO-L-VQZP | GS    | C2v| 1.142  | 1.301 | 1.075 | 1.075 | 180.0 | 117.4  |        | This work     |
|                        | ES    | Cs | 1.196  | 1.386 | 1.083 | 1.077 | 126.5 | 118.9  |        |               |
|                        | ∆     |    | 0.054  | 0.085 | 0.008 | 0.002 | -53.5  | 1.5    |        |               |
| CASPT2(16e,14o)/aug-cc-pVTZ | GS    | C2v| 1.141  | 1.297 | 1.074 | 1.074 | 180.0 | 117.5  |        | This work     |
|                        | ES    | Cs | 1.194  | 1.382 | 1.081 | 1.075 | 126.5 | 118.9  |        |               |
|                        | ∆     |    | 0.053  | 0.085 | 0.007 | 0.001 | -53.5  | 1.4    |        |               |
**CASPT2 active space**

All valence atomic orbitals were taken into the active space, i.e., 16 electrons in 14 orbitals.

**Cartesian coordinates**

**CASPT2**

CASPT2/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

| Ground-state | $E = -148.52633656$ |
|--------------|----------------------|
| 6            | 0.000000 0.000000 -1.141888 |
| 7            | 0.000000 0.000000 0.154691 |
| 7            | 0.000000 0.000000 1.295247 |
| 1            | 0.000000 -0.952848 -1.636982 |
| 1            | 0.000000 0.952848 -1.636982 |

| Excited-state | $E = -148.45268214$ |
|--------------|----------------------|
| 6            | 0.000000 0.952612 -0.546212 |
| 7            | 0.000000 -0.009376 0.446430 |
| 7            | 0.000000 -1.192590 0.287949 |
| 1            | 0.000000 0.636947 -1.579896 |
| 1            | 0.000000 1.981295 -0.234793 |

**CC3**

CC3/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

| Ground-state | $E = -152.42409065$ |
|--------------|----------------------|
| 6            | 0.000000 0.000000 -1.221500 |
| 7            | 0.000000 0.000000 0.076508 |
| 7            | 0.000000 0.000000 1.216701 |
| 1            | 0.000000 0.951859 -1.715975 |
| 1            | 0.000000 -0.951859 -1.715975 |

| Excited-state | $E = -148.48759639$ |
|--------------|----------------------|
| 6            | 0.000000 0.953610 -0.547113 |
| 7            | 0.000000 -0.009227 0.448437 |
| 7            | 0.000000 -1.191727 0.285941 |
| 1            | 0.000000 0.635624 -1.578960 |
| 1            | 0.000000 1.980608 -0.234827 |
EOM-CCSD

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

**Ground-state**

\[ E = -148.50621235 \ (T_1^{\text{diag}} = 0.017) \]

| 6  | 7  | 7  | 1  | 1  |
|----|----|----|----|----|
| 0.000000 | 0.000000 | 0.000000 | -1.138989 |
| 0.000000 | 0.000000 | 0.000000 | 0.155828 |
| 0.000000 | -0.950264 | 0.950264 | 1.286936 |
| 0.000000 | 0.000000 | 0.950264 | -1.632708 |

**Excited-state**

\[ E = -148.446441014 \ (T_1^{\text{diag}} = 0.029) \]

| 6  | 7  | 7  | 1  | 1  |
|----|----|----|----|----|
| 0.944286 | -0.539279 | 0.000000 |
| 0.000000 | 0.440227 | 0.000000 |
| -1.181720 | 0.280259 | 0.000000 |
| 0.633063 | -1.572695 | 0.000000 |
| 1.973258 | -0.235035 | 0.000000 |

**Excited-state (constrained \( C_{2v} \))**

This structure (\( A_2 \) symmetry) presents an imaginary frequency of 579 \( \text{cm}^{-1} \) (588 \( \text{cm}^{-1} \) with CC2) and is 0.78 eV (0.75 eV with CC2) less stable than the actual minimum.

\[ E = -148.417690646 \ (T_1^{\text{diag}} = 0.022) \]

| 6  | 7  | 7  | 1  | 1  |
|----|----|----|----|----|
| 0.000000 | 0.000000 | 0.000000 | -1.159185 |
| 0.000000 | 0.000000 | 0.000000 | 0.146294 |
| 0.000000 | 0.000000 | 0.000000 | 1.336137 |
| 0.000000 | -0.937310 | 0.937310 | -1.710955 |
| 0.000000 | 0.937310 | 0.937310 | -1.710955 |
Table S8: Selected geometrical parameters (bond lengths in Å, valence angles and dihedral angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). ∆ gives the difference between the two states (in eV for the ∆ZPVE). The considered ES is the lowest A" state of n → π* nature. The values in italics corresponding to the CC3/aug-cc-pVTZ ES geometry have been extrapolated (see the main text for details).

| Method                      | State | PG | ZPVE | N=O  | C-N  | C=O-C | C-N=O | H₃-C-N | Ref. |
|-----------------------------|-------|----|------|------|------|-------|-------|--------|------|
| ADC(2)/def2-TZVPP          | GS    | Cₛ | 0.043625 | 1.222 | 1.470 | 1.085 | 112.8 | 111.2  | This work |
| ADC(2)/aug-cc-pVTZ         | ES    | Cₛ | 0.042200 | 1.284 | 1.465 | 1.080 | 114.2 | 107.4  | This work |
| CC2 /def2-TZVPP            | GS    | Cₛ | 0.042996 | 1.232 | 1.476 | 1.086 | 113.1 | 111.3  | This work |
| CC2 /aug-cc-pVTZ           | ES    | Cₛ | 0.042277 | 1.278 | 1.460 | 1.080 | 115.0 | 107.5  | This work |
| CCSD/def2-TZVPP            | GS    | Cₛ | 0.043954 | 1.200 | 1.477 | 1.086 | 113.2 | 111.1  | This work |
| CCSD/aug-cc-pVTZ           | ES    | Cₛ | 0.043451 | 1.226 | 1.474 | 1.081 | 117.1 | 107.3  | This work |
| CCSDR(3)/def2-TZVPP        | GS    | Cₛ | 0.044354 | 1.209 | 1.477 | 1.087 | 113.1 | 111.0  | This work |
| CCSDR(3)/aug-cc-pVTZ       | ES    | Cₛ | 0.044351 | 1.235 | 1.475 | 1.083 | 118.4 | 107.1  | This work |
| CC3/def2-TZVPP             | GS    | Cₛ | 0.044354 | 1.209 | 1.477 | 1.087 | 113.1 | 111.0  | This work |
| CC3/aug-cc-pVTZ            | ES    | Cₛ | 0.044351 | 1.235 | 1.475 | 1.083 | 118.4 | 107.1  | This work |
| CASPT2(18e,15o)/ANO-L-VQZP<sup>a</sup> | GS    | Cₛ | 1.213 | 1.482 | 1.090 | 113.1 | 111.1  | This work |
| CASPT2(18e,15o)/aug-cc-pVTZ<sup>b</sup> | ES    | Cₛ | 1.219 | 1.480 | 1.085 | 118.7 | 107.2  | This work |
| MR-AQCC/cc-pVTZ            | GS    | Cₛ | 1.212 | 1.483 | 1.087 | 112.9 | 111.0  | This work |
| MR-AQCC/cc-pVTZ            | ES    | Cₛ | 1.212 | 1.483 | 1.087 | 112.9 | 111.0  | This work |

| Experiment | ∆ | Ref. |
|------------|----|------|
|           | 0.11<sup>c</sup> | ±0.02 |
|           | 0.08<sup>c</sup> | ±0.01 |
|           | 0.04<sup>c</sup> | ±1    |

<sup>a</sup>Frozen core option applied. <sup>b</sup>Note that the CASPT2 ES optimization fails to converge with this diffuse basis set. <sup>c</sup>No frozen core orbitals used in order be comparable with CC methods. <sup>d</sup>MR-CI/cc-pVDZ result. <sup>26</sup> <sup>e</sup>Obtained performing “simple” FC calculations. <sup>28</sup>
CASPT2 active space

The full valence active space was used in CAS calculation with the largest basis set, i.e., 18 electrons in 15 orbitals.

Cartesian coordinates

CCSDR(3)

CCSDR(3)/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

Ground-state

\[ E = -169.60836048 \]

|   |   |   |   |
|---|---|---|---|
| 6 | -0.943824 | -0.566993 | 0.000000 |
| 7 | -0.002789 | 0.571534  | 0.000000 |
| 8 | 1.156578  | 0.229465  | 0.000000 |
| 1 | -0.409277 | -1.515123 | 0.000000 |
| 1 | -1.573709 | -0.457421 | 0.882488 |
| 1 | -1.573709 | -0.457421 | -0.882488 |

Excited-state

\[ E = -169.54180119 \]

|   |   |   |   |
|---|---|---|---|
| 6 | 0.984824  | -0.560709 | 0.000000 |
| 7 | 0.002701  | 0.540074  | 0.000000 |
| 8 | -1.198875 | 0.254307  | 0.000000 |
| 1 | 1.970145  | -0.110800 | 0.000000 |
| 1 | 0.839381  | -1.169636 | 0.893724 |
| 1 | 0.839381  | -1.169636 | -0.893724 |

EOM-CCSD

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

Ground-state

\[ E = -169.57881354 \ (T^\text{diag}_1 = 0.013) \]

|   |   |   |   |
|---|---|---|---|
| 6 | -0.942382 | -0.567258 | 0.000000 |
| 7 | 0.000000  | 0.569955  | 0.000000 |
| 8 | 1.151234  | 0.230360  | 0.000000 |
| 1 | -0.411100 | -1.514121 | 0.000000 |
| 1 | -1.572241 | -0.457448 | 0.879243 |
| 1 | -1.572241 | -0.457448 | -0.879243 |
Excited-state
\[ E = -169.511088034 \ (T_1^{\text{diag}} = 0.014) \]

| 6  | 0.983749 | -0.560080 | 0.000000 |
| 7  | 0.000000 | 0.537091  | 0.000000 |
| 8  | -1.193758 | 0.256322  | 0.000000 |
| 1  | 1.966747 | -0.110843 | 0.000000 |
| 1  | 0.840410 | -1.169445 | 0.890579 |
| 1  | 0.840410 | -1.169445 | -0.890579 |

Ground-state (staggered)
In the GS, the staggered conformation yields an imaginary frequency mode of 185 \( \text{cm}^{-1} \) (190 \( \text{cm}^{-1} \) with CC2). This TS-like structure is 0.05 eV less stable than the eclipsed minimum. This corresponds to a rotational barrier of 419 \( \text{cm}^{-1} \) (429 \( \text{cm}^{-1} \) with CC2), in very good agreement with the experimental values of 400 \( \text{cm}^{-1} \),\(^{29}\) and 383 \( \text{cm}^{-1} \) (obtained for CD\(_3\)NO),\(^{29}\) as well as with the MR-AQCC/cc-pVTZ estimate of 397 \( \text{cm}^{-1} \).\(^{27}\)

\[ E = -169.57690266 \ (T_1^{\text{diag}} = 0.013) \]

| 6  | 0.946700 | -0.563813 | 0.000000 |
| 7  | 0.000000 | 0.584087  | 0.000000 |
| 8  | -1.144900 | 0.225270  | 0.000000 |
| 1  | 1.959785 | -0.180673 | 0.000000 |
| 1  | 0.759609 | -1.163608 | 0.886295 |
| 1  | 0.759609 | -1.163608 | -0.886295 |

Excited-state (eclipsed)
In the ES, the eclipsed conformation yields an imaginary frequency mode of 201 \( \text{cm}^{-1} \). This TS-like structure is only 0.07 eV less stable than the eclipsed minimum, which corresponds to a rotational barrier of 541 \( \text{cm}^{-1} \) (618 \( \text{cm}^{-1} \) with CC2). The MR-AQCC/cc-pVTZ value attains 522 \( \text{cm}^{-1} \).\(^{26}\) The available experimental data are 475 \( \pm \) 50 \( \text{cm}^{-1} \),\(^{30}\) and an a former rather broad estimate of 500 \( \pm \) 100 \( \text{cm}^{-1} \) (all values between 450 and 700 \( \text{cm}^{-1} \) were found compatible with the measurements in that work).\(^{28}\)

\[ E = -169.508623866 \ (T_1^{\text{diag}} = 0.014) \]

| 6  | -0.988841 | -0.572731 | 0.000000 |
| 7  | 0.000000 | 0.524759  | 0.000000 |
| 8  | 1.201977 | 0.280721  | 0.000000 |
| 1  | -0.464979 | -1.522919 | 0.000000 |
| 1  | -1.608896 | -0.479889 | 0.886355 |
| 1  | -1.608896 | -0.479889 | -0.886355 |
Table S9: Selected geometrical parameters (bond lengths in Å, valence angles and dihedral angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). Δ gives the difference between the two states (in eV for the $\Delta ZPVE$). The considered ES is the lowest $A^+$ state of $n \rightarrow \pi^*$ nature. The values in italics corresponding to the CC3/aug-cc-pVTZ ES geometry have been extrapolated (see the main text for details).

| Method          | State | PG | ZPVE | N=N-C | C-N | N=O | N=N-C-N | C=N-O | Ref.          |
|-----------------|-------|----|------|-------|-----|-----|---------|-------|---------------|
| ADC(2)def2-TZVPP| GS    | $C_s$ | 0.012766 | 1.171 | 1.412 | 1.222 | 172.1 | 113.0 | This work     |
|                 | ES    | $C_s$ | 0.012801 | 1.180 | 1.313 | 1.250 | 174.7 | 129.0 |               |
| $\Delta$        |       |     | 0.001   | 0.009 | -0.099 | 0.028 | 2.6 | 16.0 |               |
| ADC(2)aug-cc-pVTZ| GS    | $C_s$ | 1.170 | 1.404 | 1.221 | 171.2 | 113.3 |       | This work     |
|                 | ES    | $C_s$ | 1.179 | 1.306 | 1.245 | 174.2 | 130.4 |       |               |
| $\Delta$        |       |     | 0.009  | -0.098 | 0.024 |    | 3.0 | 17.1 |               |
| CC2/def2-TZVPP  | GS    | $C_s$ | 0.011909 | 1.181 | 1.419 | 1.234 | 171.7 | 113.3 | This work     |
|                 | ES    | $C_s$ | 0.011887 | 1.206 | 1.283 | 1.247 | 171.4 | 138.5 |               |
| $\Delta$        |       |     | -0.001 | 0.025 | -0.136 | 0.013 | -0.3 | 25.2 |               |
| CC2/aug-cc-pVTZ | GS    | $C_s$ | 1.180 | 1.408 | 1.232 | 170.6 | 113.6 |       | This work     |
|                 | ES    | $C_s$ | 1.207 | 1.272 | 1.240 | 170.3 | 141.9 |       |               |
| $\Delta$        |       |     | 0.027  | -0.136 | 0.008 | -0.3 | 28.4 |       |               |
| CCSD/def2-TZVPP | GS    | $C_s$ | 0.013714 | 1.153 | 1.429 | 1.198 | 172.8 | 113.1 | This work     |
|                 | ES    | $C_s$ | 0.013872 | 1.163 | 1.318 | 1.216 | 174.8 | 130.5 |               |
| $\Delta$        |       |     | 0.004  | 0.010 | -0.111 | 0.018 | 2.0 | 17.4 |               |
| CCSD/aug-cc-pVTZ| GS    | $C_s$ | 1.152 | 1.419 | 1.196 | 172.2 | 113.3 |       | This work     |
|                 | ES    | $C_s$ | 1.162 | 1.310 | 1.211 | 174.3 | 132.1 |       |               |
| $\Delta$        |       |     | 0.010  | -0.109 | 0.015 | 2.1 | 18.8 |       |               |
| CCSDR(3)/def2-TZVPP| GS    | $C_s$ | 1.163 | 1.431 | 1.210 | 172.0 | 113.1 |       | This work     |
|                 | ES    | $C_s$ | 1.176 | 1.313 | 1.228 | 174.1 | 131.2 |       |               |
| $\Delta$        |       |     | 0.013  | -0.118 | 0.018 | 2.1 | 18.1 |       |               |
| CCSDR(3)/aug-cc-pVTZ| GS    | $C_s$ | 1.161 | 1.420 | 1.209 | 171.1 | 113.4 |       | This work     |
|                 | ES    | $C_s$ | 1.175 | 1.304 | 1.223 | 173.5 | 133.2 |       |               |
| $\Delta$        |       |     | 0.014  | -0.116 | 0.014 | 2.4 | 19.8 |       |               |
| CC3/def2-TZVPP  | GS    | $C_s$ | 1.164 | 1.433 | 1.211 | 171.9 | 113.1 |       | This work     |
|                 | ES    | $C_s$ | 1.182 | 1.306 | 1.231 | 173.4 | 132.5 |       |               |
| $\Delta$        |       |     | 0.016  | -0.129 | 0.020 | 2.5 | 19.4 |       |               |
| CC3/aug-cc-pVTZ | GS    | $C_s$ | 1.163 | 1.422 | 1.210 | 171.0 | 113.5 |       | This work     |
|                 | ES    | $C_s$ | 1.181 | 1.297 | 1.226 | 172.8 | 134.5 |       |               |
| $\Delta$        |       |     | 0.018  | -0.125 | 0.016 | 1.8 | 21.0 |       |               |
| CASPT2(16e,14o)/ANO-L-VQZP | GS    | $C_s$ | 1.165 | 1.429 | 1.212 | 170.4 | 113.5 |       | This work     |
|                 | ES    | $C_s$ | 1.182 | 1.303 | 1.229 | 172.8 | 132.9 |       |               |
| $\Delta$        |       |     | 0.017  | -0.126 | 0.017 | 2.4 | 19.4 |       |               |
| CASPT2(16e,14o)/aug-cc-pVTZ | GS    | $C_s$ | 1.162 | 1.416 | 1.211 | 170.8 | 113.5 |       | This work     |
|                 | ES    | $C_s$ | 1.184 | 1.304 | 1.231 | 173.0 | 132.9 |       |               |
| $\Delta$        |       |     | 0.022  | -0.112 | 0.020 | 2.2 | 19.4 |       |               |
| Experiment      | GS    | $C_s$ | 1.163 | 1.418 | 1.217 | 170.0 | 113.6 |       | 31            |
|                 | ES    | $C_s$ | 1.198 | 1.316 | 1.221 | 162.0 | 126.9 |       |               |
| $\Delta$        |       |     | 0.035  | -0.102 | 0.004 | -8.0 | 13.3 |       |               |
CASPT2 active space

The active space used in our calculation included all valence orbitals on all atoms with exception of 2s orbitals on oxygen and cyano nitrogen which were kept inactive. In short CAS space was 16 electrons in 14 orbitals.

Cartesian coordinates

CCSDR(3)

CCSDR(3)/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

Ground-state
\[ E = -222.44352599 \]

7  0.588965  0.618875  0.000000
6  -0.010782 -0.668667  0.000000
8  -0.214129  1.522271  0.000000
7  -0.332911 -1.784506  0.000000

Excited-state
\[ E = -222.39048253 \]

7  0.434584  -0.542761  0.000000
6  -0.012162  0.682172  0.000000
8  -0.115239 -1.635341  0.000000
7  -0.287954  1.824178  0.000000

EOM-CCSD

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

Ground-state
\[ E = -222.40578077 \quad (T_{1}^{\text{diag}} = 0.013) \]

7  0.591217  0.627316  0.000000
8  -0.218005  1.510176  0.000000
6  0.000000 -0.674005  0.000000
7  -0.342069 -1.775513  0.000000

Excited-state
\[ E = -222.349626178 \quad (T_{1}^{\text{diag}} = 0.015) \]

7  0.457708  -0.551187  0.000000
8  -0.134603 -1.613034  0.000000
6  0.000000  0.684703  0.000000
7  -0.303877  1.807767  0.000000
Table S10: Selected geometrical parameters (bond lengths in Å, valence angles and dihedral angle in degrees) for methylenecyclopropene. The $C_{2v}$ point group was enforced for the excited-state in order to avoid reaching a conical intersection. This is why no ZPVE is provided here – all ES present imaginary frequencies. $\Delta$ gives the difference between the two states. The considered ES is the lowest $B_2$ state of $\pi \rightarrow \pi^\ast$ nature. The values in italics corresponding to the CC3/$aug$-cc-pVTZ ES geometry have been extrapolated (see the main text for details).

| Method            | State | PG     | $C_2-C_2$ | $C_1-C_3$ | $C_3-C_4$ | $C_2-C_3-C_4$ | Ref.        |
|-------------------|-------|--------|-----------|-----------|-----------|----------------|-------------|
| ADC(2)/def2-TZVPP | GS    | $C_{2v}$ | 1.328    | 1.439    | 1.323    | 152.6          | This work   |
|                   | ES    | $C_{2v}$ | 1.465    | 1.350    | 1.519    | 145.8          |             |
|                   | $\Delta$ |        | 0.137    | -0.089   | 0.196    | -6.8           |             |
| ADC(2)/$aug$-cc-pVTZ | GS    | $C_{2v}$ | 1.325    | 1.436    | 1.322    | 152.6          | This work   |
|                   | ES    | $C_{2v}$ | 1.458    | 1.348    | 1.515    | 145.8          |             |
|                   | $\Delta$ |        | 0.133    | -0.088   | 0.193    | -6.8           |             |
| CC2/def2-TZVPP    | GS    | $C_{2v}$ | 1.332    | 1.441    | 1.327    | 152.6          | This work   |
|                   | ES    | $C_{2v}$ | 1.461    | 1.353    | 1.512    | 146.0          |             |
|                   | $\Delta$ |        | 0.129    | -0.088   | 0.186    | -6.5           |             |
| CC2/$aug$-cc-pVTZ | GS    | $C_{2v}$ | 1.329    | 1.437    | 1.326    | 152.5          | This work   |
|                   | ES    | $C_{2v}$ | 1.454    | 1.351    | 1.508    | 146.1          |             |
|                   | $\Delta$ |        | 0.125    | -0.086   | 0.182    | -6.4           |             |
| CCSD/def2-TZVPP   | GS    | $C_{2v}$ | 1.327    | 1.439    | 1.316    | 152.8          | This work   |
|                   | ES    | $C_{2v}$ | 1.442    | 1.353    | 1.481    | 146.8          |             |
|                   | $\Delta$ |        | 0.115    | -0.086   | 0.164    | -6.0           |             |
| CCSD/$aug$-cc-pVTZ | GS    | $C_{2v}$ | 1.324    | 1.436    | 1.315    | 152.7          | This work   |
|                   | ES    | $C_{2v}$ | 1.455    | 1.351    | 1.476    | 146.9          |             |
|                   | $\Delta$ |        | 0.111    | -0.085   | 0.161    | -5.8           |             |
| CCSDR(3)/def2-TZVPP | GS    | $C_{2v}$ | 1.332    | 1.446    | 1.324    | 152.7          | This work   |
|                   | ES    | $C_{2v}$ | 1.456    | 1.361    | 1.501    | 146.5          |             |
|                   | $\Delta$ |        | 0.124    | -0.085   | 0.177    | -6.2           |             |
| CCSDR(3)/$aug$-cc-pVTZ | GS    | $C_{2v}$ | 1.329    | 1.442    | 1.323    | 152.7          | This work   |
|                   | ES    | $C_{2v}$ | 1.450    | 1.358    | 1.498    | 146.5          |             |
|                   | $\Delta$ |        | 0.121    | -0.084   | 0.175    | -6.2           |             |
| CC3/def2-TZVPP    | GS    | $C_{2v}$ | 1.333    | 1.446    | 1.325    | 152.7          | This work   |
|                   | ES    | $C_{2v}$ | 1.460    | 1.363    | 1.502    | 146.6          |             |
|                   | $\Delta$ |        | 0.127    | -0.083   | 0.177    | -6.1           |             |
| CC3/$aug$-cc-pVTZ | GS    | $C_{2v}$ | 1.329    | 1.442    | 1.323    | 152.7          | This work   |
|                   | ES    | $C_{2v}$ | 1.453    | 1.360    | 1.498    | 146.6          |             |
|                   | $\Delta$ |        | 0.124    | -0.082   | 0.175    | -6.1           |             |
| CASPT2(4,4)/cc-pVTZ | GS    | $C_{2v}$ | 1.331    | 1.442    | 1.324    | 152.7          | This work   |
|                   | ES    | $C_{2v}$ | 1.460    | 1.360    | 1.495    | 146.7          |             |
|                   | $\Delta$ |        | 0.129    | -0.082   | 0.171    | -6.0           |             |
| RASPT2(20,12)/cc-pVTZ | GS    | $C_{2v}$ | 1.331    | 1.444    | 1.323    | 152.7          | This work   |
|                   | ES    | $C_{2v}$ | 1.460    | 1.362    | 1.495    | 146.7          |             |
|                   | $\Delta$ |        | 0.129    | -0.082   | 0.172    | -6.0           |             |
| RASPT2(20,12)/ANO-L-VQZP | GS    | $C_{2v}$ | 1.331    | 1.440    | 1.321    | 152.7          | This work   |
|                   | ES    | $C_{2v}$ | 1.456    | 1.360    | 1.489    | 146.8          |             |
|                   | $\Delta$ |        | 0.125    | -0.080   | 0.168    | -5.9           |             |
| CASPT2(4,4)/$aug$-cc-pVTZ | GS    | $C_{2v}$ | 1.326    | 1.435    | 1.320    | 152.6          | This work   |
|                   | ES    | $C_{2v}$ | 1.451    | 1.360    | 1.488    | 146.7          |             |
|                   | $\Delta$ |        | 0.125    | -0.075   | 0.168    | -5.9           |             |
| CC2/cc-pVTZ       | GS    | $C_{2v}$ | 1.328    | 1.438    | 1.325    | 152.6          | 32          |
|                   | ES    | $C_{2v}$ | 1.456    | 1.349    | 1.512    | 145.7          |             |
|                   | $\Delta$ |        | 0.128    | -0.089   | 0.187    | -6.7           |             |
| CASPT2/cc-pVTZ    | GS    | $C_{2v}$ | 1.331    | 1.442    | 1.324    | 152.7          | 32          |
|                   | ES    | $C_{2v}$ | 1.461    | 1.360    | 1.496    | 146.6          |             |
|                   | $\Delta$ |        | 0.130    | -0.082   | 0.172    | -6.0           |             |
| VMC/$pVTZ^\ast$   | GS    | $C_{2v}$ | 1.324    | 1.434    | 1.316    | 153.0          | 32          |
|                   | ES    | $C_{2v}$ | 1.456    | 1.351    | 1.483    | 146.7          |             |
|                   | $\Delta$ |        | 0.132    | -0.083   | 0.167    | -6.3           |             |
**CASPT2 active space**

For the MCP geometry optimization we used two significantly different active spaces. First, a small active space encompassing the $\pi$ orbitals only was tested. Later we selected the full valence as active space, which means 20 electrons in 20 orbitals. Due to the size of this space we partitioned orbitals using three restricted active spaces. The RAS1 space included all $\sigma$ occupied orbitals while RAS3 included the respective $\sigma$ anti-bonding orbitals. Maximally two holes in RAS1 and two electrons in RAS3 space were allowed. The $\pi$ orbitals were included in RAS2 space and here all possible configurations were allowed. The geometry of both GS and ES were optimized using both spaces using the diffuse-less cc-pVTZ basis set. The differences between the obtained geometries are trifling (max 0.002 Å) and we therefore used only the smaller active space (4 electrons in 4 orbitals) for augmented basis set calculation.

**Cartesian coordinates**

**CCSDR(3)**

CCSDR(3)/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

**Ground-state**

\[ E = -154.49064214 \]

|   |   |   |   |
|---|---|---|---|
| 6 | 0.000000 | 0.000000 | 0.283701 |
| 6 | 0.000000 | 0.000000 | 1.612577 |
| 6 | 0.000000 | 0.661285 | -0.997221 |
| 6 | 0.000000 | -0.661285 | -0.997221 |
| 1 | 0.000000 | 1.570584 | -1.566882 |
| 1 | 0.000000 | -1.570584 | -1.566882 |
| 1 | 0.000000 | 0.927782 | 2.162128 |
| 1 | 0.000000 | -0.927782 | 2.162128 |
**Excited-state \((C\textsubscript{2v} \text{ constrained})\)**

\[ E = -154.37044439 \]

|   |   |   |   |   |
|---|---|---|---|---|
| 6 | 0.000000 | 0.000000 | 0.175905 |
| 6 | 0.000000 | 0.000000 | 1.625887 |
| 6 | 0.000000 | 0.748755 | -0.956917 |
| 6 | 0.000000 | -0.748755 | -0.956917 |
| 1 | 0.000000 | 1.689898 | -1.460290 |
| 1 | 0.000000 | -1.689898 | -1.460290 |
| 1 | 0.000000 | 0.933052 | 2.162753 |
| 1 | 0.000000 | -0.933052 | 2.162753 |

**EOM-CCSD**

(EOM)-CCSD/\textit{def2-TZVPP} total energies (au) and Cartesian coordinates (Å).

**Ground-state**

\[ E = -154.45302037 \ (T\textsubscript{1}^{\text{diag}} = 0.011) \]

|   |   |   |   |   |
|---|---|---|---|---|
| 6 | 0.000000 | 0.000000 | 0.262167 |
| 6 | 0.000000 | 0.000000 | 1.588970 |
| 6 | 0.000000 | 0.658200 | -1.017900 |
| 6 | 0.000000 | -0.658200 | -1.017900 |
| 1 | 0.000000 | 1.568274 | -1.584343 |
| 1 | 0.000000 | -1.568274 | -1.584343 |
| 1 | 0.000000 | 0.926321 | 2.138333 |
| 1 | 0.000000 | -0.926321 | 2.138333 |

**Excited-state \((C\textsubscript{2v} \text{ constrained})\)**

\[ E = -154.319237867 \ (T\textsubscript{1}^{\text{diag}} = 0.015) \]

|   |   |   |   |   |
|---|---|---|---|---|
| 6 | 0.000000 | 0.000000 | 0.151701 |
| 6 | 0.000000 | 0.000000 | 1.593173 |
| 6 | 0.000000 | 0.740260 | -0.981178 |
| 6 | 0.000000 | -0.740260 | -0.981178 |
| 1 | 0.000000 | 1.683282 | -1.478252 |
| 1 | 0.000000 | -1.683282 | -1.478252 |
| 1 | 0.000000 | 0.931740 | 2.130699 |
| 1 | 0.000000 | -0.931740 | 2.130699 |
## S11 Carbonyl Difluoride

Table S11: Selected geometrical parameters (bond lengths in Å, valence angles and dihedral angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). ∆ gives the difference between the two states (in eV for the ΔZPVE). The considered ES is the lowest $A^-$ state of $n \rightarrow \pi^*$ nature. $\eta$ is the angle between the CO bond and the F-C-F plane.

| Method                  | State  | PG   | ZPVE  | C=O   | C-F   | F-C-F | $\eta$ | Ref.        |
|-------------------------|--------|------|-------|-------|-------|-------|--------|-------------|
| ADC(2)/def2-TZVPP       | GS     | $C_2v$ | 0.014154 | 1.174 | 1.314 | 107.6 | 0.00   | This work   |
|                         | ES     | $C_s$  | 0.012071 | 1.359 | 1.317 | 115.8 | 50.2   |             |
|                         | $\Delta$ |        | -0.057 | 0.185 | 0.003 | 8.2   | 50.2   |             |
| ADC(2)/aug-cc-pVTZ      | GS     | $C_2v$ | 1.174  | 1.313 | 107.5 | 0.00   | This work |
|                         | ES     | $C_s$  | 1.357  | 1.315 | 115.9 | 50.5   |         |
|                         | $\Delta$ |        | 0.183  | 0.002 | 8.4   | 50.5   |         |
| CC2/def2-TZVPP          | GS     | $C_2v$ | 0.013748 | 1.181 | 1.321 | 107.4 | 0.00   | This work   |
|                         | ES     | $C_s$  | 1.369  | 1.325 | 115.2 | 52.0   |         |
|                         | $\Delta$ |        | 0.188  | 0.004 | 7.8   | 52.0   |         |
| CC2/aug-cc-pVTZ         | GS     | $C_2v$ | 1.180  | 1.320 | 107.2 | 0.00   | This work |
|                         | ES     | $C_s$  | 1.367  | 1.324 | 115.3 | 52.3   |         |
|                         | $\Delta$ |        | 0.183  | 0.002 | 8.4   | 52.3   |         |
| CCSD/def2-TZVPP         | GS     | $C_2v$ | 0.014551 | 1.168 | 1.306 | 107.9 | 0.00   | This work   |
|                         | ES     | $C_s$  | 1.328  | 1.316 | 113.0 | 53.9   |         |
|                         | $\Delta$ |        | 0.158  | 0.010 | 5.1   | 53.9   |         |
| CCSD/aug-cc-pVTZ        | GS     | $C_2v$ | 1.167  | 1.305 | 107.8 | 0.00   | This work |
|                         | ES     | $C_s$  | 1.324  | 1.314 | 112.9 | 54.0   |         |
|                         | $\Delta$ |        | 0.157  | 0.009 | 5.1   | 54.0   |         |
| CCSDR(3)/def2-TZVPP     | GS     | $C_2v$ | 1.173  | 1.313 | 107.8 | 0.00   | This work |
|                         | ES     | $C_s$  | 1.352  | 1.321 | 113.1 | 55.9   |         |
|                         | $\Delta$ |        | 0.179  | 0.008 | 5.3   | 55.9   |         |
| CCSDR(3)/aug-cc-pVTZ    | GS     | $C_2v$ | 1.172  | 1.312 | 107.6 | 0.00   | This work |
|                         | ES     | $C_s$  | 1.348  | 1.320 | 113.1 | 56.1   |         |
|                         | $\Delta$ |        | 0.176  | 0.008 | 5.5   | 56.1   |         |
| CC3/def2-TZVPP          | GS     | $C_2v$ | 1.175  | 1.315 | 107.7 | 0.00   | This work |
|                         | ES     | $C_s$  | 1.357  | 1.324 | 113.4 | 56.0   |         |
|                         | $\Delta$ |        | 0.182  | 0.009 | 5.7   | 56.0   |         |
| CC3/aug-cc-pVTZ         | GS     | $C_2v$ | 1.174  | 1.313 | 107.6 | 0.00   | This work |
|                         | ES     | $C_s$  | 1.353  | 1.323 | 113.2 | 56.2   |         |
|                         | $\Delta$ |        | 0.179  | 0.010 | 5.6   | 56.2   |         |
| CASPT2(18e,14o)/ANO-L-VQZP | GS     | $C_2v$ | 1.174  | 1.315 | 107.7 | 0.00   | This work |
|                         | ES     | $C_s$  | 1.360  | 1.325 | 113.1 | 56.9   |         |
|                         | $\Delta$ |        | 0.186  | 0.010 | 5.4   | 56.9   |         |
| CASPT2(18e,13o)/aug-cc-pVTZ | GS     | $C_2v$ | 1.172  | 1.313 | 107.7 | 0.00   | This work |
|                         | ES     | $C_s$  | 1.355  | 1.322 | 113.0 | 52.4   |         |
|                         | $\Delta$ |        | 0.183  | 0.009 | 5.5   | 52.4   |         |
| CASPT2(24e,16o)/ANO-L-VQZP | GS     | $C_2v$ | 1.175  | 1.320 | 107.6 | 0.00   | This work |
|                         | ES     | $C_s$  | 1.358  | 1.330 | 112.9 | 52.3   |         |
|                         | $\Delta$ |        | 0.183  | 0.010 | 5.3   | 52.3   |         |
| CASPT2(24e,16o)/aug-cc-pVTZ | GS     | $C_2v$ | 1.172  | 1.313 | 107.5 | 0.00   | This work |
|                         | ES     | $C_s$  | 1.353  | 1.322 | 113.0 | 52.3   |         |
|                         | $\Delta$ |        | 0.183  | 0.009 | 5.5   | 52.3   |         |
| QCISD/6-31G(d)          | GS     | $C_2v$ | 1.183  | 1.324 | 117.0 | 33     |         |
|                         | ES     | $C_s$  | 1.367  | 1.337 | 112.7 | 33     |         |
|                         | $\Delta$ |        | 0.184  | 0.013 | -4.3  | 33     |         |
| MR-AQCC/cc-pVTZ         | ES     | $C_s$  | 1.364  | 1.324 | 112.9 | 52.6   | 9       |
| Experiment              | $\Delta$ |        | 0.26   | 0.06  | 31.8  | 34     |         |
| Experiment              | $\Delta$ |        | 0.30   | 0.40  | 50.4  | 14     |         |
CASPT2 active space

All valence atomic orbitals were taken into the active space for all atoms this leads to an active space of 24 electrons in 16 orbitals. We tested also smaller space in which the 2s orbitals of both oxygen and fluorine atoms are set as inactive, i.e., 18 electrons in 13 orbitals. The main reason for this test is their low energy which usually prevents them from mixing with 2p orbitals in active space. For the aug-cc-pVTZ basis set the differences between geometries optimized by these two active spaces are negligible. The ANO-L basis set is more sensitive to the change of the active space although the occupation numbers of the lone pairs included in the larger active space are around 1.99. The difference in bond lengths and FCF angle are both minimal but the size of the active space influences the bending potential quite significantly. Indeed, $\eta$ varies from 56.9° to 52.3° in the larger active space. For the benchmark purposes we report aug-cc-pVTZ basis set results which are converged with respect to active space size. For the ANO-L basis set we consider larger active space results as more accurate.

Cartesian coordinates

CC3

CC3/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

|       |       |       |       |
|-------|-------|-------|-------|
| ground-state | $E= -312.73143551$ |       |       |
| 6     | 0.000000 | 0.000000 | -0.162207 |
| 8     | 0.000000 | 0.000000 | -1.336011 |
| 9     | 0.000000 | 1.059704 | 0.613862 |
| 9     | 0.000000 | -1.059704 | 0.613862 |

|       |       |       |       |
|-------|-------|-------|-------|
| excited-state | $E= -312.55693508$ |       |       |
| 6     | 0.025851 | 0.000000 | -0.316825 |
| 8     | 1.320526 | 0.000000 | 0.076566 |
| 9     | -0.574756 | 1.104601 | 0.094452 |
| 9     | -0.574756 | -1.104601 | 0.094452 |
EOM-CCSD

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

**Ground-state**
\[ E = -312.70030245 \ (T_{1}^{\text{diag}} = 0.012) \]

\[ \begin{array}{ccc}
6 & 0.000000 & 0.000000 & 0.140412 \\
8 & 0.000000 & 0.000000 & 1.307952 \\
9 & 0.000000 & 1.056464 & -0.628116 \\
9 & -0.000000 & -1.056464 & -0.628116 \\
\end{array} \]

**Excited-state**
\[ E = -312.511761805 \ (T_{1}^{\text{diag}} = 0.018) \]

\[ \begin{array}{ccc}
6 & -0.249775 & 0.189752 & -0.000000 \\
8 & 0.749325 & 1.064885 & -0.000000 \\
9 & -0.249775 & -0.536533 & 1.097338 \\
9 & -0.249775 & -0.536533 & -1.097338 \\
\end{array} \]

**Excited-state (constrained \( C_{2v} \))**

This structure (\( A_{2} \) symmetry) presents an imaginary frequency of 1184 cm\(^{-1}\) (1213 cm\(^{-1}\) with CC2). It is much less stable than the global minimum and corresponds to a barrier of 8614 cm\(^{-1}\) (8120 cm\(^{-1}\) with CC2).

\[ E = -312.472513000 \ (T_{1}^{\text{diag}} = 0.017) \]

\[ \begin{array}{ccc}
6 & 0.000000 & 0.000000 & 0.028598 \\
8 & 0.000000 & 0.000000 & 1.381145 \\
9 & 0.000000 & 1.136017 & -0.623375 \\
9 & -0.000000 & -1.136017 & -0.623375 \\
\end{array} \]
### Table S12: Selected geometrical parameters (bond lengths in Å, valence angles and dihedral angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). ∆ gives the difference between the two states (in eV for the $\Delta^{ZPVE}$). The considered ES is the lowest $A$ state of $n \rightarrow \pi^*$ nature. $\eta$ is the out-of-plane angle of the hydrogen. The values in italics corresponding to the CC3/\textit{aug}-cc-pVTZ ES geometry have been extrapolated (see the main text for details).

| Method                  | State | PG  | ZPVE | C=O  | C-F  | C-H  | F-C-H | F-C=O | $\eta$ | Ref. |
|-------------------------|-------|-----|------|------|------|------|-------|-------|-------|------|
| ADC(2)/\textit{def2}-TZVPP | GS    | $C_s$ | 0.021012 | 1.181 | 1.343 | 1.088 | 109.1 | 123.0 | 0.0   | This work |
|                         | ES    | $C_1$ | 0.018143 | 1.405 | 1.323 | 1.085 | 117.9 | 109.7 | 40.8  |       |
|                         | $\Delta$ |       | -0.078 | 0.224 | -0.020 | -0.003 | 8.8   | -13.2 | 40.8  |       |
| ADC(2)/\textit{aug}-cc-pVTZ | GS    | $C_s$ | 1.181 | 1.344 | 1.085 | 108.9 | 122.9 | 0.0   | This work |
|                         | ES    | $C_1$ | 1.405 | 1.321 | 1.083 | 116.4 | 109.3 | 40.4  |       |
|                         | $\Delta$ |       | 0.224 | -0.023 | -0.002 | 9.4   | -13.6 | 40.4  |       |
| CC2/\textit{def2}-TZVPP | GS    | $C_s$ | 0.020595 | 1.188 | 1.354 | 1.087 | 108.8 | 123.0 | 0.0   | This work |
|                         | ES    | $C_1$ | 1.187 | 1.356 | 1.086 | 116.7 | 108.8 | 44.8  |       |
|                         | $\Delta$ |       | -0.075 | 0.207 | -0.023 | 0.001 | 7.6   | -13.7 | 45.0  |       |
| CC2/\textit{aug}-cc-pVTZ | GS    | $C_s$ | 1.181 | 1.344 | 1.085 | 108.9 | 122.9 | 0.0   | This work |
|                         | ES    | $C_1$ | 1.405 | 1.321 | 1.083 | 116.4 | 109.3 | 40.4  |       |
|                         | $\Delta$ |       | 0.224 | -0.023 | -0.002 | 9.4   | -13.6 | 40.4  |       |
| CCSD/\textit{def2}-TZVPP | GS    | $C_s$ | 0.019009 | 1.332 | 1.336 | 1.085 | 115.0 | 110.1 | 45.8  |       |
|                         | ES    | $C_1$ | 1.355 | 1.339 | 1.087 | 114.7 | 109.3 | 45.8  |       |
|                         | $\Delta$ |       | 0.157 | 0.003 | -0.003 | 5.3   | -12.7 | 45.8  |       |
| CCSD/\textit{aug}-cc-pVTZ | GS    | $C_s$ | 1.174 | 1.333 | 1.085 | 109.5 | 122.8 | 0.0   | This work |
|                         | ES    | $C_1$ | 1.329 | 1.335 | 1.083 | 115.0 | 109.9 | 45.6  |       |
|                         | $\Delta$ |       | 0.155 | 0.002 | -0.002 | 5.5   | -12.9 | 45.6  |       |
| CCSDR(3)/\textit{def2}-TZVPP | GS    | $C_s$ | 1.180 | 1.341 | 1.090 | 109.5 | 122.8 | 0.0   | This work |
|                         | ES    | $C_1$ | 1.355 | 1.339 | 1.087 | 114.7 | 109.3 | 48.4  |       |
|                         | $\Delta$ |       | 0.172 | -0.003 | -0.002 | 5.4   | -13.7 | 48.3  |       |
| CC3/\textit{def2}-TZVPP | GS    | $C_s$ | 1.182 | 1.344 | 1.090 | 109.4 | 122.8 | 0.0   | This work |
|                         | ES    | $C_1$ | 1.364 | 1.340 | 1.088 | 114.7 | 109.3 | 48.6  |       |
|                         | $\Delta$ |       | 0.182 | -0.004 | -0.002 | 5.3   | -13.5 | 48.3  |       |
| CC3/\textit{aug}-cc-pVTZ | GS    | $C_s$ | 1.182 | 1.344 | 1.090 | 109.4 | 122.8 | 0.0   | This work |
|                         | ES    | $C_1$ | 1.364 | 1.340 | 1.088 | 114.7 | 109.3 | 48.6  |       |
|                         | $\Delta$ |       | 0.182 | -0.004 | -0.002 | 5.3   | -13.5 | 48.3  |       |
| CASPT2(4e,3o)/\textit{aug}-cc-pVTZ | GS    | $C_s$ | 1.177 | 1.340 | 1.084 | 109.0 | 123.1 | 0.0   | This work |
|                         | ES    | $C_1$ | 1.360 | 1.340 | 1.086 | 114.7 | 109.0 | 49.4  |       |
|                         | $\Delta$ |       | 0.179 | -0.004 | -0.001 | 5.5   | -13.8 | 48.5  |       |
| CASPT2(14e,11o)/\textit{aug}-cc-pVTZ | GS    | $C_s$ | 1.182 | 1.346 | 1.089 | 109.1 | 123.1 | 0.0   | This work |
|                         | ES    | $C_1$ | 1.362 | 1.338 | 1.085 | 114.7 | 109.3 | 49.4  |       |
|                         | $\Delta$ |       | 0.180 | -0.008 | -0.004 | 5.6   | -13.8 | 49.4  |       |
| CCSD/DZP | GS    | $C_s$ | 1.187 | 1.340 | 1.010 | 123.1 | 0.0   | 35    |       |
|                         | ES    | $C_1$ | 1.346 | 1.346 | 1.098 | 109.8 | 46.3  |       |
|                         | $\Delta$ |       | 0.159 | 0.006 | -0.002 | 3.9   | -13.6 | 46.3  |       |
| MR-CISD/\textit{cc-pVTZ} | GS    | $C_s$ | 1.374 | 1.324 | 1.081 | 114.9 | 109.5 | 45.8  |       |
|                         | ES    | $C_1$ | 1.344 | 1.346 | 1.098 | 109.7 | 36.0  |       |
|                         | $\Delta$ |       | 0.179 | 0.002 | 0.005 | -12.8 | 30–35 |       |
CASPT2 active space

Two types of active spaces were used. First, all valence atomic orbitals were taken into the active space for carbon and hydrogen atoms. The 2s orbitals of the oxygen and fluorine atoms were set as inactive. Next, we compared this with a much smaller active space compromising oxygen lone pair, and two π orbitals. The results are similar but we kept the one with the largest active space below.

Cartesian coordinates

CASPT2

CASPT2(14e,11o)/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

|       | Ground-state | Excited-state |       |
|-------|--------------|---------------|-------|
|       |  $E = -213.52527766$ |  $E = -213.32989208$ |       |
| 6     | 0.0033096  | 0.3980957  | 0.000000 |
| 8     | 1.1498469  | 0.1198249  | 0.000000 |
| 1     | -0.4431430 | 1.3854944  | 0.000000 |
| 9     | -0.9745585 | -0.5229190 | 0.000000 |

CCSDR(3)

CCSDR(3)/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

|       | Ground-state | Excited-state |       |
|-------|--------------|---------------|-------|
| 6     | $E = -213.56197208$ |  $E = -213.38680621$ |       |
| 8     | 0.397970  | 0.002169  | 0.000000 |
| 1     | 0.118022  | 1.148529  | 0.000000 |
| 9     | 1.389501  | -0.443103 | 0.000000 |

S35
EOM-CCSD

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

Ground-state
\[ E = -213.53898591 \ (T_{1}^{\text{diag}} = 0.014) \]

|   |   |   |   |
|---|---|---|---|
| 6 | 0.000000 | 0.395251 | 0.000000 |
| 8 | 1.142131 | 0.118718 | 0.000000 |
| 1 | -0.440380 | 1.390000 | 0.000000 |
| 9 | -0.966296 | -0.523473 | 0.000000 |

Excited-state
\[ E = -213.356381413 \ (T_{1}^{\text{diag}} = 0.018) \]

|   |   |   |   |
|---|---|---|---|
| 6 | -0.056444 | 0.487543 | -0.139747 |
| 8 | -1.133934 | -0.277104 | 0.029897 |
| 1 | -0.056351 | 1.446942 | 0.366810 |
| 9 | 1.051832 | -0.239486 | 0.025833 |

Excited-state (constrained \( C_s \))

As in formyl chloride, constraining the molecule in the planar conformation yields an imaginary frequency of 901 cm\(^{-1}\) (920 cm\(^{-1}\) with CC2) for the lowest excited-state of \( A'' \) symmetry. This geometry is a TS like structure that corresponds to a barrier of 1872 cm\(^{-1}\) (1822 cm\(^{-1}\) with CC2) compared to the true minimum.

\[ E = -213.347849130 \ (T_{1}^{\text{diag}} = 0.018) \]

|   |   |   |   |
|---|---|---|---|
| 6 | -0.000000 | 0.477122 | 0.000000 |
| 8 | 1.181303 | -0.152506 | 0.000000 |
| 1 | -0.124789 | 1.539744 | 0.000000 |
| 9 | -1.036182 | -0.353603 | 0.000000 |
### Table S13: Selected geometrical parameters (bond lengths in Å, valence angles and dihedral angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). Δ gives the difference between the two states (in eV for the $\Delta_{ZPVE}$). The considered ES is the lowest $A^\ast$ state of $n \rightarrow \pi^\ast$ nature. $\eta$ is defined as in formaldehyde.

| Method                | State | PG | ZPVE  | C=O  | C-Cl | Cl-C-Cl | $\eta$ | Ref.     |
|-----------------------|-------|----|-------|------|------|---------|--------|----------|
| ADC(2)/def2-TZVPP     | GS C$_2v$ | 0.010550 | 1.182 | 1.735 | 111.8 | 0.0 | This work |
|                       | ES C$_a$ | 0.007734 | 1.398 | 1.702 | 122.3 | 42.9 |          |
|                       | $\Delta$ | -0.077  | 0.216 | -0.033 | 10.5 | 42.9 | This work |
| ADC(2)/aug-cc-pVTZ    | GS C$_2v$ | 1.181 | 1.734 | 111.7 | 0.0 | This work |
|                       | ES C$_a$ | 1.394 | 1.701 | 122.6 | 43.3 |          |
|                       | $\Delta$ | 0.213  | -0.033 | 10.9 | 43.3 | This work |
| CC2/def2-TZVPP        | GS C$_2v$ | 0.010256 | 1.191 | 1.740 | 111.6 | 0.0 | This work |
|                       | ES C$_a$ | 0.007480 | 1.369 | 1.725 | 121.1 | 46.7 |          |
|                       | $\Delta$ | -0.076 | 0.178 | -0.014 | 9.5 | 46.7 | This work |
| CC2/aug-cc-pVTZ       | GS C$_2v$ | 1.180 | 1.739 | 111.5 | 0.0 | This work |
|                       | ES C$_a$ | 1.365 | 1.723 | 121.3 | 46.1 |          |
|                       | $\Delta$ | 0.176  | -0.016 | 9.8 | 46.1 | This work |
| CCSD/def2-TZVPP       | GS C$_2v$ | 0.010839 | 1.173 | 1.738 | 112.3 | 0.0 | This work |
|                       | ES C$_a$ | 0.008562 | 1.303 | 1.729 | 119.0 | 47.6 |          |
|                       | $\Delta$ | -0.062 | 0.130 | -0.009 | 6.7 | 47.6 | This work |
| CCSD/aug-cc-pVTZ      | GS C$_2v$ | 1.171 | 1.737 | 112.2 | 0.0 | This work |
|                       | ES C$_a$ | 1.297 | 1.729 | 119.0 | 48.0 |          |
|                       | $\Delta$ | 0.126  | -0.008 | 6.8 | 48.0 |          |
| CCSDR(3)/def2-TZVPP   | GS C$_2v$ | 1.179 | 1.748 | 112.1 | 0.0 | This work |
|                       | ES C$_a$ | 1.319 | 1.743 | 118.7 | 50.4 |          |
|                       | $\Delta$ | 0.140  | -0.005 | 6.6 | 50.4 |          |
| CCSDR(3)/aug-cc-pVTZ  | GS C$_2v$ | 1.178 | 1.743 | 111.9 | 0.0 | This work |
|                       | ES C$_a$ | 1.314 | 1.738 | 118.8 | 50.3 |          |
|                       | $\Delta$ | 0.136  | -0.005 | 6.9 | 50.3 |          |
| CC3/def2-TZVPP        | GS C$_2v$ | 1.180 | 1.745 | 111.8 | 0.0 | This work |
| CC3/aug-cc-pVTZ       | GS C$_2v$ | 1.181 | 1.746 | 111.7 | 0.0 | This work |
|                       | ES C$_a$ | 1.326 | 1.741 | 118.5 | 47.3 |          |
|                       | $\Delta$ | 0.145  | -0.005 | 6.8 | 47.3 |          |
| CASPT2(24e,16o)/ANO-L-VQZP | GS C$_2v$ | 1.178 | 1.742 | 111.7 | 0.0 | This work |
|                       | ES C$_a$ | 1.319 | 1.738 | 118.6 | 51.6 |          |
|                       | $\Delta$ | 0.141  | -0.004 | 6.9 | 51.6 |          |
| CCSD/cc-pVDZ          | GS C$_2v$ | 1.182 | 1.759 | 110.0 | 0.0 | This work |
|                       | ES C$_a$ | 1.311 | 1.759 | 119.3 | 49.3 |          |
|                       | $\Delta$ | 0.129  | 0.000 | 49.3 |          |
| CASPT2/cc-pVQZ        | ES C$_a$ | 1.340 | 1.713 | 119.4 | 44.5 | 9          |
| Experiment            | $\Delta$ | 0.17  | 32.5 | 39 |
|                       | ES C$_a$ | 0.42  | 14  |          |

$^a$This is the angle between the C=O and the bisector of the Cl-C-Cl angle, $\theta$, it is ca. 4 degrees smaller than $\eta$. 

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**S13 Phosgene**

Table S13: Selected geometrical parameters (bond lengths in Å, valence angles and dihedral angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). Δ gives the difference between the two states (in eV for the $\Delta_{ZPVE}$). The considered ES is the lowest $A^\ast$ state of $n \rightarrow \pi^\ast$ nature. $\eta$ is defined as in formaldehyde.
**CASPT2 active space**

Valence orbitals of all atoms were taken into the active space, i.e. 24 electrons in 16 orbitals.

**Cartesian coordinates**

**CASPT2**

CASPT2/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

| Ground-state | \(E = -1032.68277337\) |
|--------------|--------------------------|
| 6            | 0.0000000 0.0000000 0.4916078 |
| 8            | 0.0000000 0.0000000 1.6694510 |
| 17           | 0.0000000 1.4418188 -0.4856407 |
| 17           | 0.0000000 -1.4418188 -0.4856407 |

| Excited-state | \(E = -1032.52990680\) |
|---------------|--------------------------|
| 6             | 0.3654079 0.3600955 0.0000000 |
| 8             | 1.5992804 -0.1057674 0.0000000 |
| 17            | -0.4284562 -0.0375964 1.4944731 |
| 17            | -0.4284562 -0.0375964 -1.4944731 |

**CCSDR(3)**

CCSDR(3)/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

| Ground-state | \(E = -1032.74664055\) |
|--------------|--------------------------|
| 6            | 0.000000 0.000000 -0.504795 |
| 8            | 0.000000 0.000000 -1.682849 |
| 17           | 0.000000 1.444634 0.471093 |
| 17           | 0.000000 -1.444634 0.471093 |

| Excited-state | \(E = -1032.59089593\) |
|---------------|--------------------------|
| 6             | 0.121331 -0.324111 0.000000 |
| 8             | 1.378495 0.057387 0.000000 |
| 17            | -0.651481 0.107684 1.495777 |
| 17            | -0.651481 0.107684 -1.495777 |
EOM-CCSD

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

**Ground-state**

\[ E = -1032.9377709 \quad (T^\text{diag}_1 = 0.010) \]

|   |   |   |   |
|---|---|---|---|
| 6 | 0.000000 | 0.000000 | 0.490080 |
| 8 | 0.000000 | 0.000000 | 1.663153 |
| 17| 0.000000 | 1.443568 | -0.477815 |
| 17| 0.000000 | -1.443568| -0.477815 |

**Excited-state**

\[ E = -1032.77527880 \quad (T^\text{diag}_1 = 0.013) \]

|   |   |   |   |
|---|---|---|---|
| 6 | -0.149143 | 0.463354 | 0.000000 |
| 8 | 0.745717  | 1.410545 | 0.000000 |
| 17| -0.149143 | -0.413661| 1.490096 |
| 17| -0.149143 | -0.413661| -1.490096|

**Excited-state (constrained \(C_2\varepsilon\))**

This structure (\(A_2\) symmetry) presents an imaginary frequency of 501\(\tilde{\text{cm}}^{-1}\) (541\(\tilde{\text{cm}}^{-1}\) with CC2). It is significantly less stable than the global minimum and corresponds to a barrier of 2262 cm\(^{-1}\) (2502 cm\(^{-1}\) with CC2).

\[ E = -1032.76497277 \quad (T^\text{diag}_1 = 0.013) \]

|   |   |   |   |
|---|---|---|---|
| 6 | 0.000000 | 0.000000 | 0.322620 |
| 8 | 0.000000 | 0.000000 | 1.651653 |
| 17| 0.000000 | 1.500012 | -0.445557 |
| 17| 0.000000 | -1.500012| -0.445557 |
### Table S14: Selected geometrical parameters (bond lengths in Å, valence angles and dihedral angle in degrees).

PG is the point group and ZPVE is the zero-point vibrational energy (in au). ∆ gives the difference between the two states (in eV for the $\Delta^{ZPVE}$). The considered ES is the lowest $A$ state of $n \rightarrow \pi^*$ nature. $\eta$ is the out-of-plane angle of the hydrogen atom. The values in italics corresponding to the CC3/aug-cc-pVTZ structures have been extrapolated (see the main text for details).

| Method                  | State | PG | ZPVE | C=O  | C-Cl | C-H  | Cl-C-H | Cl-C=O | $\eta$ | Ref. |
|--------------------------|-------|----|------|------|------|------|--------|--------|-------|------|
| ADC(2)/def2-TZVPP        | GS    | Cs | 0.019249 | 1.187 | 1.759 | 1.090 | 110.1  | 123.7  | 0.0   | This work |
|                          | ES    | $C_1$ | 0.015919 | 1.410 | 1.688 | 1.083 | 120.4  | 112.4  | 33.7  | This work |
|                          | $\Delta$ | -0.091 | 0.223 | -0.071 | -0.007 | 10.3  | -11.3  | 33.7  |       |       |
| ADC(2)/aug-cc-pVTZ       | GS    | Cs | 1.186 | 1.760 | 1.086 | 110.0 | 123.7  | 0.0   | This work |
|                          | ES    | $C_1$ | 1.410 | 1.687 | 1.079 | 121.2 | 111.8  | 32.9  |       |       |
|                          | $\Delta$ | -0.080 | 0.224 | -0.073 | -0.007 | 11.2  | -11.9  | 32.9  |       |       |
| CC2/def2-TZVPP           | GS    | Cs | 0.018924 | 1.195 | 1.769 | 1.089 | 109.8  | 110.5  | 41.0  |       |
|                          | ES    | $C_1$ | 0.016991 | 1.310 | 1.733 | 1.086 | 116.2  | 110.8  | 41.8  |       |
|                          | $\Delta$ | -0.069 | 0.130 | -0.025 | -0.006 | 5.6   | -12.7  | 41.8  |       |       |
| CC2/aug-cc-pVTZ          | GS    | Cs | 1.184 | 1.767 | 1.086 | 110.4 | 123.6  | 0.0   | This work |
|                          | ES    | $C_1$ | 1.304 | 1.742 | 1.083 | 115.6 | 109.1  | 45.2  |       |       |
|                          | $\Delta$ | 0.139 | -0.025 | -0.005 | 5.5   | -14.5  | 45.2  |       |       |
| CCSD/def2-TZVPP          | GS    | Cs | 1.181 | 1.760 | 1.086 | 110.0 | 123.6  | 0.0   |       |
|                          | ES    | $C_1$ | 1.335 | 1.741 | 1.089 | 115.3 | 109.2  | 45.5  |       |       |
|                          | $\Delta$ | 0.154 | -0.019 | -0.007 | 5.2   | -14.3  | 46.6  |       |       |
| CCSD/aug-cc-pVTZ         | GS    | Cs | 1.184 | 1.769 | 1.089 | 109.9 | 123.7  | 0.0   |       |
|                          | ES    | $C_1$ | 1.331 | 1.739 | 1.085 | 115.3 | 109.2  | 50.0  |       |       |
|                          | $\Delta$ | 0.147 | -0.030 | -0.004 | 5.4   | -14.5  | 50.0  |       |       |
| CCSDR(3)/def2-TZVPP      | GS    | Cs | 1.185 | 1.770 | 1.091 | 110.3 | 123.6  | 0.0   |       |
|                          | ES    | $C_1$ | 1.324 | 1.742 | 1.083 | 115.6 | 109.1  | 45.2  |       |       |
|                          | $\Delta$ | 0.139 | -0.025 | -0.005 | 5.5   | -14.5  | 45.2  |       |       |
| CC3/def2-TZVPP           | GS    | Cs | 1.187 | 1.773 | 1.092 | 110.2 | 123.6  | 0.0   |       |
|                          | ES    | $C_1$ | 1.335 | 1.741 | 1.089 | 115.2 | 109.3  | 46.6  |       |       |
|                          | $\Delta$ | 0.154 | -0.026 | -0.005 | 5.1   | -14.2  | 45.9  |       |       |
| CC3/aug-cc-pVTZ          | GS    | Cs | 1.186 | 1.770 | 1.088 | 110.0 | 123.7  | 0.0   |       |
|                          | ES    | $C_1$ | 1.331 | 1.744 | 1.083 | 115.5 | 109.8  | 45.5  |       |       |
|                          | $\Delta$ | 0.145 | -0.026 | -0.005 | 5.5   | -13.9  | 45.5  |       |       |
| CASPT2(18e,13o)/ANO-L-VQZP | GS    | Cs | 1.181 | 1.760 | 1.082 | 110.0 | 123.6  | 0.0   |       |
|                          | ES    | $C_1$ | 1.335 | 1.741 | 1.089 | 115.2 | 109.3  | 46.6  |       |       |
|                          | $\Delta$ | 0.154 | -0.019 | -0.007 | 5.2   | -14.3  | 46.6  |       |       |
| CASPT2(18e,13o)/aug-cc-pVTZ | GS    | Cs | 1.184 | 1.769 | 1.089 | 109.9 | 123.7  | 0.0   |       |
|                          | ES    | $C_1$ | 1.331 | 1.739 | 1.085 | 115.3 | 109.2  | 50.0  |       |       |
|                          | $\Delta$ | 0.147 | -0.030 | -0.004 | 5.4   | -14.5  | 50.0  |       |       |
| MR-CISD/cc-pVTZ          | ES    | $C_1$ | 1.356 | 1.715 | 1.078 | 116.5 | 111.8  | 39.4  | 9     |       |
| Experiment               | ES    | $C_1$ | 1.308 | 1.76a | 1.10a | 119.7 | 109.0a | 39.4  | 40    |       |
|                          | ES    | $C_1$ | 1.345 | 1.725 | 1.084 | 116.4 | 110.2  | 39.4  | 41    |       |

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*Fixed during the fit; $^b$The experimental data of Ref. 41 were refitted in that work to account for the theoretical estimates. See Ref. 9 for details.*
CASPT2 active space

Valence orbitals of all atoms were taken into the active space, i.e., 18 electrons in 13 orbitals.

Cartesian coordinates

CASPT2

CASPT2/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

|       |       |       |       |
|-------|-------|-------|-------|
| Ground-state | $E = -573.52364786$ |       |       |
| 6     | 0.0022055 | 0.7928431 | 0.000000 |
| 8     | 1.1297643 | 1.1535152 | 0.000000 |
| 1     | -0.8807044 | 1.4308879 | 0.000000 |
| 17    | -0.4828923 | -0.9086042 | 0.000000 |

|       |       |       |       |
|-------|-------|-------|-------|
| Excited-state | $E = -573.37320101$ |       |       |
| 6     | -0.6224457 | 0.5615764 | -0.1553258 |
| 8     | -1.5174248 | -0.4041505 | 0.0385553 |
| 1     | -0.7979200 | 1.4952937 | 0.3680241 |
| 17    | 0.9777165 | -0.0972256 | 0.0163904 |

CCSDR(3)

CCSDR(3)/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

|       |       |       |       |
|-------|-------|-------|-------|
| Ground-state | $E = -573.56947713$ |       |       |
| 6     | 0.465838 | 0.073400 | 0.000000 |
| 8     | 0.202463 | 1.228377 | 0.000000 |
| 1     | 1.464065 | -0.358726 | 0.000000 |
| 17    | -0.751871 | -1.207596 | 0.000000 |

|       |       |       |       |
|-------|-------|-------|-------|
| Excited-state | $E = -573.41599904$ |       |       |
| 6     | -0.097711 | -0.604294 | -0.654480 |
| 8     | 0.016648 | 0.362025 | -1.552142 |
| 1     | 0.480375 | -1.505370 | -0.817690 |
| 17    | 0.016309 | 0.084730 | 0.941703 |
EOM-CCSD

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

Ground-state

\[ E = -573.65644799 \ (T_{1}^{\text{diag}} = 0.012) \]

\[
\begin{array}{cccc}
6 & 0.000000 & 0.788694 & 0.000000 \\
8 & 1.123121 & 1.148953 & 0.000000 \\
1 & -0.877859 & 1.434419 & 0.000000 \\
17 & -0.476889 & -0.903424 & -0.000000 \\
\end{array}
\]

Excited-state

\[ E = -573.497311881 \ (T_{1}^{\text{diag}} = 0.015) \]

\[
\begin{array}{cccc}
6 & -0.623197 & 0.546690 & -0.128486 \\
8 & -1.517288 & -0.397017 & 0.030166 \\
1 & -0.800655 & 1.500185 & 0.355737 \\
17 & 0.981067 & -0.094364 & 0.010226 \\
\end{array}
\]

Excited-state (constrained \(C_{s}\))

As expected, constraining the molecule in the planar conformation yields an imaginary
frequency of 627 \(\text{cm}^{-1}\) or 653 \(\text{cm}^{-1}\) with CCSD and CC2, respectively, for the lowest
excited-state of \(A^{+}\) symmetry. This geometry is a TS like structure that corresponds to an
inversion barrier of 847 \(\text{cm}^{-1}\) or 865 \(\text{cm}^{-1}\) with CCSD and CC2, respectively.

\[ E = -573.493452976 \ (T_{1}^{\text{diag}} = 0.015) \]

\[
\begin{array}{cccc}
6 & -0.000000 & 0.797486 & 0.000000 \\
8 & 1.316025 & 0.902143 & 0.000000 \\
1 & -0.646203 & 1.655822 & 0.000000 \\
17 & -0.581294 & -0.803405 & 0.000000 \\
\end{array}
\]
S15  Thiocarbonyl Difluoride

Table S15: Selected geometrical parameters (bond lengths in Å, valence angles and dihedral angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). ∆ gives the difference between the two states (in eV for the $\Delta_{ZPVE}$). The considered ES is the lowest $A^\ast$ state of $n \rightarrow \pi^\ast$ nature. $\theta$ is the angle between the CS bond and the bisector of the F-C-F angle. The values in italics corresponding to the CC3/aug-cc-pVTZ ES geometry have been extrapolated (see the main text for details).

| Method                  | State | PG   | ZPVE | C=S  | C-F  | F-C-F | $\theta$ | Ref.          |
|------------------------|-------|------|------|------|------|-------|----------|---------------|
| ADC(2)/def2-TZVPP      | GS    | $C_{2v}$ | 0.011534 | 1.588 | 1.313 | 107.1 | 0.0  | This work  |
|                        | ES    | $C_s$   | 0.010304 | 1.758 | 1.326 | 112.2 | 38.4 |              |
|                        | $\Delta$ |       | -0.033 | 0.170 | 0.013 | 5.1  | 38.4 |              |
| ADC(2)/aug-cc-pVTZ     | GS    | $C_{2v}$ | 1.591  | 1.311 | 107.1 | 0.0  | This work  |
|                        | ES    | $C_s$   | 1.759  | 1.323 | 112.2 | 38.6 |              |
|                        | $\Delta$ |       | 0.168  | 0.012 | 5.1  | 38.6 |              |
| CC2/def2-TZVPP         | GS    | $C_{2v}$ | 0.011203 | 1.595 | 1.320 | 106.9 | 0.0  | This work  |
|                        | ES    | $C_s$   | 1.739  | 1.322 | 110.8 | 40.1 |              |
|                        | $\Delta$ |       | -0.037 | 0.170 | 0.013 | 5.0  | 40.1 |              |
| CC2/aug-cc-pVTZ        | GS    | $C_{2v}$ | 1.598  | 1.318 | 106.9 | 0.0  | This work  |
|                        | ES    | $C_s$   | 1.765  | 1.331 | 111.7 | 40.4 |              |
|                        | $\Delta$ |       | 0.167  | 0.013 | 4.8  | 40.4 |              |
| CCSD/def2-TZVPP        | GS    | $C_{2v}$ | 0.011742 | 1.590 | 1.305 | 107.4 | 0.0  | This work  |
|                        | ES    | $C_s$   | 1.739  | 1.322 | 110.8 | 39.9 |              |
|                        | $\Delta$ |       | -0.0391 | 0.149 | 0.017 | 3.4  | 39.9 |              |
| CCSD/def2-TZVPP        | GS    | $C_{2v}$ | 1.592  | 1.302 | 107.4 | 0.0  | This work  |
|                        | ES    | $C_s$   | 1.740  | 1.319 | 110.7 | 40.1 |              |
|                        | $\Delta$ |       | 0.148  | 0.017 | 3.3  | 40.1 |              |
| CC3/def2-TZVPP         | GS    | $C_{2v}$ | 1.600  | 1.312 | 107.3 | 0.0  | This work  |
|                        | ES    | $C_s$   | 1.775  | 1.327 | 111.1 | 43.3 |              |
|                        | $\Delta$ |       | 0.175  | 0.015 | 3.8  | 43.3 |              |
| CC3/aug-cc-pVTZ        | GS    | $C_{2v}$ | 1.599  | 1.310 | 107.3 | 0.0  | This work  |
|                        | ES    | $C_s$   | 1.769  | 1.325 | 110.8 | 43.4 |              |
|                        | $\Delta$ |       | 0.170  | 0.015 | 3.5  | 43.4 |              |
| CCSDR(3)/def2-TZVPP    | GS    | $C_{2v}$ | 1.602  | 1.314 | 107.3 | 0.0  | This work  |
|                        | ES    | $C_s$   | 1.776  | 1.329 | 111.2 | 43.3 |              |
|                        | $\Delta$ |       | 0.174  | 0.015 | 3.9  | 43.3 |              |
| CCSDR(3)/aug-cc-pVTZ   | GS    | $C_{2v}$ | 1.600  | 1.312 | 107.2 | 0.0  | This work  |
|                        | ES    | $C_s$   | 1.769  | 1.328 | 110.9 | 43.4 |              |
|                        | $\Delta$ |       | 0.169  | 0.016 | 3.7  | 43.4 |              |
| CASPT2(24e,16o)/ANO-L-VQZP | GS   | $C_{2v}$ | 1.598  | 1.321 | 107.3 | 0.0  | This work  |
|                        | ES    | $C_s$   | 1.772  | 1.336 | 111.3 | 44.9 |              |
|                        | $\Delta$ |       | 0.174  | 0.015 | 4.0  | 44.9 |              |
| CASPT2(24e,16o)/aug-cc-pVTZ | GS  | $C_{2v}$ | 1.596  | 1.314 | 107.4 | 0.0  | This work  |
|                        | ES    | $C_s$   | 1.770  | 1.328 | 111.2 | 44.9 |              |
|                        | $\Delta$ |       | 0.174  | 0.014 | 3.8  | 44.9 |              |
| Experiment             | ES    | $C_s$   | ~ 0.1  | 0.12  | ca. 0.118 | 30.5 a, 34.1 | 42 |
|                        | $\Delta$ |       |        |        |        | 18     |        |
|                        | $\Delta$ |       |        |        |        | 43     |        |

a Assuming other parameters: C-S=1.63 Å and C-F=1.32 Å.
**CASPT2 active space**

All $s$ and $p$ valence orbitals were included in the active space, i.e., 24 electrons in 16 orbitals.

**Cartesian coordinates**

**CASPT2**

CASPT2$/aug$-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

| Ground-state                      | $E$ = -635.27663710 |
|----------------------------------|---------------------|
| 6                                | 0.000000 0.000000 -0.262543 |
| 16                               | 0.000000 0.000000 1.333227 |
| 9                                | 0.000000 1.059161 -1.040172 |
| 9                                | 0.000000 -1.059161 -1.040172 |

| Excited-state                    | $E$ = -635.17347077 |
|----------------------------------|---------------------|
| 6                                | -0.478688 -0.197374 0.000000 |
| 16                               | 0.682064 1.139703 0.000000 |
| 9                                | -0.426770 -0.946220 1.095850 |
| 9                                | -0.426770 -0.946220 -1.095850 |

**CCSDR(3)**

CCSDR(3)/$aug$-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

| Ground-state                      | $E$ = -635.32495455 |
|----------------------------------|---------------------|
| 6                                | 0.000000 0.000000 -0.263798 |
| 16                               | 0.000000 0.000000 1.334765 |
| 9                                | 0.000000 1.055044 -1.040455 |
| 9                                | 0.000000 -1.055044 -1.040455 |

| Excited-state                    | $E$ = -635.21752369 |
|----------------------------------|---------------------|
| 6                                | -0.473166 -0.196572 0.000000 |
| 16                               | 0.682496 1.142510 0.000000 |
| 9                                | -0.439757 -0.947890 1.091106 |
| 9                                | -0.439757 -0.947890 -1.091106 |
EOM-CCSD

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

**Ground-state**

\[
E = -635.40403000 \quad (T_1^{\text{diag}} = 0.012)
\]

| 6    | 16   | 9    | 9    |
|------|------|------|------|
| -0.000000 | 0.000000 | 0.288187 |
| 0.000000 | -0.000000 | 1.301536 |
| 0.000000 | 1.052164 | -1.060859 |
| -0.000000 | -1.052164 | -1.060859 |

**Excited-state**

\[
E = -635.287102778 \quad (T_1^{\text{diag}} = 0.017)
\]

| 6                  | 16                  | 9                  | 9                  |
|--------------------|--------------------|--------------------|--------------------|
| -0.446789          | -0.195418          | -0.000000          |                   |
| 0.670183           | 1.137477           | 0.000000           |                   |
| -0.446789          | -0.945951          | 1.087913           |                   |
| -0.446789          | -0.945951          | -1.087913          |                   |

**Excited-state (constrained \( C_{2v} \))**

This structure (\( A_2 \) symmetry) presents an imaginary frequency of 645\( \text{ cm}^{-1} \) (688\( \text{ cm}^{-1} \) with CC2). It is slightly less stable than the global minimum and corresponds to a barrier of 2981\( \text{ cm}^{-1} \) (3265\( \text{ cm}^{-1} \) with CC2).

\[
E = -635.273521129 \quad (T_1^{\text{diag}} = 0.015)
\]

| 6                  | 16                  | 9                  | 9                  |
|--------------------|--------------------|--------------------|--------------------|
| 0.000000           | -0.000000          | -0.361548          |                   |
| -0.000000          | 0.000000           | 1.348236           |                   |
| 0.000000           | 1.108493           | -1.077916          |                   |
| -0.000000          | -1.108493          | -1.077916          |                   |

S45
## Thiophosgene

Table S16: Selected geometrical parameters (bond lengths in Å, valence angles and dihedral angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). ∆ gives the difference between the two states (in eV for the \( \Delta_{\text{ZPVE}} \)). The considered ES is the lowest \( A^\ast \) state of \( n \rightarrow \pi^\ast \) nature. \( \eta \) is the angle between the CS bonds and CCl\(_2\) plane.

| Method                  | State | PG   | ZPVE | C=S | C-Cl | Cl-C-Cl | \( \eta \) | Ref. |
|-------------------------|-------|------|------|-----|------|---------|---------|------|
| ADC(2)/def2-TZVPP       | GS    | \( C_{2v} \) | 0.008236 | 1.599 | 1.723 | 111.1 | 0.0 | This work |
|                         | ES    | \( C_s \) | 0.006735 | 1.773 | 1.699 | 119.8 | 27.3 |
|                         | \( \Delta \) |       | -0.041 | 0.174 | -0.024 | 8.7 | 27.3 |
| ADC(2)/aug-cc-pVTZ      | GS    | \( C_{2v} \) | 1.602 | 1.722 | 111.1 | 0.0 | This work |
|                         | ES    | \( C_s \) | 1.774 | 1.698 | 119.9 | 27.6 |
|                         | \( \Delta \) |       | 0.172 | -0.024 | 8.8 | 27.6 |
| CC2/def2-TZVPP          | GS    | \( C_{2v} \) | 1.606 | 1.728 | 110.8 | 0.0 | This work |
|                         | ES    | \( C_s \) | 1.754 | 1.708 | 119.0 | 30.7 |
|                         | \( \Delta \) |       | 0.006671 | 0.148 | -0.020 | 8.2 | 30.7 |
| CC2/aug-cc-pVTZ         | GS    | \( C_{2v} \) | 1.609 | 1.727 | 110.8 | 0.0 | This work |
|                         | ES    | \( C_s \) | 1.755 | 1.706 | 119.1 | 31.0 |
|                         | \( \Delta \) |       | 0.146 | -0.021 | 8.3 | 31.0 |
| CCSD/def2-TZVPP         | GS    | \( C_{2v} \) | 1.606 | 1.729 | 111.4 | 0.0 | This work |
|                         | ES    | \( C_s \) | 1.739 | 1.723 | 117.9 | 33.7 |
|                         | \( \Delta \) |       | 0.007104 | 0.110 | -0.016 | 7.1 | 33.7 |
| CCSD/aug-cc-pVTZ        | GS    | \( C_{2v} \) | 1.606 | 1.730 | 111.3 | 0.0 | This work |
|                         | ES    | \( C_s \) | 1.732 | 1.715 | 118.0 | 32.9 |
|                         | \( \Delta \) |       | 0.131 | -0.012 | 6.5 | 32.9 |
| CCSDR(3)/def2-TZVPP     | GS    | \( C_{2v} \) | 1.607 | 1.731 | 111.2 | 0.0 | This work |
|                         | ES    | \( C_s \) | 1.734 | 1.715 | 117.8 | 32.1 |
|                         | \( \Delta \) |       | 0.126 | -0.015 | 6.7 | 32.1 |
| CCSDR(3)/aug-cc-pVTZ    | GS    | \( C_{2v} \) | 1.602 | 1.729 | 111.1 | 0.0 | This work |
|                         | ES    | \( C_s \) | 1.734 | 1.715 | 117.8 | 32.1 |
|                         | \( \Delta \) |       | 0.132 | -0.014 | 6.7 | 32.1 |
| CC3/def2-TZVPP          | GS    | \( C_{2v} \) | 1.607 | 1.731 | 111.2 | 0.0 | This work |
|                         | ES    | \( C_s \) | 1.734 | 1.715 | 117.8 | 32.1 |
|                         | \( \Delta \) |       | 0.126 | -0.015 | 6.7 | 32.1 |
| CC3/aug-cc-pVTZ         | GS    | \( C_{2v} \) | 1.603 | 1.728 | 111.1 | 0.0 | This work |
|                         | ES    | \( C_s \) | 1.736 | 1.714 | 117.8 | 36.1 |
|                         | \( \Delta \) |       | 0.133 | -0.014 | 6.7 | 36.1 |
| CASPT2(24e,16o)/ANO-L\(^a\) | GS    | \( C_{2v} \) | 1.615 | 1.772 | 0.0 |        |        | 44   |
|                         | ES    | \( C_s \) | 1.793 | 1.758 | 35.8 |        |        |      |
|                         | \( \Delta \) |       | 0.178 | -0.014 | 35.8 |        |        |      |
| Experiment              | \( \Delta \) |       | 0.103 | 0.022 | 8.0 | 32.0 |        | 45   |
|                         | \( \Delta \) |       | 0.114 | 0.013 | -3.5 | 32.0 |        |      |
|                         | ES\(^b\) | \( C_s \) | 1.73 | 1.745 | 112.3 | 27.2 |        | 46   |
|                         | ES\(^b\) | \( C_s \) | 1.69 | 1.756 | 111.8 | 26.0 |        |      |
|                         | GS    | \( C_{2v} \) | 1.600 | 1.727 | 111.2 | 0.0 |        | 47   |
|                         | ES    | \( C_s \) | 1.694 | 1.720 | 117.6 | 23.9 |        |      |
|                         | \( \Delta \) |       | 0.094 | -0.007 | 6.4 | 23.9 |        |      |

\(^a\) Maximum contraction of ANO-L basis set (C: 7s7p4d3f, Cl and S: 7s7p5d4f) instead of ANO-L-VQZP one due to convergence difficulties during the geometry optimization.

\(^b\) In these works, two different analysis of the experimental output are performed, so two sets of parameters are proposed.
**CASPT2 active space**

All valence atomic orbitals were included in the active space, i.e., 24 electrons in 16 orbitals.

**Cartesian coordinates**

**CASPT2**

CASPT2/\textit{aug}-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

|       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|
| Ground-state |       |       |       |       |       |       |
| $E$     | -1355.27816908 |       |       |       |       |       |
| 6      | 0.000000 | 0.000000 | 0.133586 |       |       |       |
| 16     | 0.000000 | 0.000000 | 1.737067 |       |       |       |
| 17     | 0.000000 | 1.424557 | -0.844232 |       |       |       |
| 17     | 0.000000 | -1.424557 | -0.844232 |       |       |       |

|       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|
| Excited-state |       |       |       |       |       |       |
| $E$     | -1355.19142999 |       |       |       |       |       |
| 6      | -0.250048 | 0.083517 | 0.000000 |       |       |       |
| 16     | 0.487013 | 1.655138 | 0.000000 |       |       |       |
| 17     | -0.143949 | -0.795480 | 1.468109 |       |       |       |
| 17     | -0.143949 | -0.795480 | -1.468109 |       |       |       |

**CCSDR(3)**

CCSDR(3)/\textit{aug}-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

|       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|
| Ground-state |       |       |       |       |       |       |
| $E$     | -1355.34955603 |       |       |       |       |       |
| 6      | 0.000000 | 0.000000 | -0.148617 |       |       |       |
| 16     | 0.000000 | 0.000000 | -1.754370 |       |       |       |
| 17     | 0.000000 | 1.427690 | 0.827852 |       |       |       |
| 17     | 0.000000 | -1.427690 | 0.827852 |       |       |       |

|       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|
| Excited-state |       |       |       |       |       |       |
| $E$     | -1355.26117558 |       |       |       |       |       |
| 6      | -0.237565 | 0.000000 | 0.083924 |       |       |       |
| 16     | 0.484262 | 0.000000 | 1.658621 |       |       |       |
| 17     | -0.169857 | 1.470608 | -0.796580 |       |       |       |
| 17     | -0.169857 | -1.470608 | -0.796580 |       |       |       |
EOM-CCSD

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

**Ground-state**

\[ E = -1355.6490637 \ (T_{1}^{\text{diag}} = 0.010) \]

|   | x   | y   | z   |
|---|-----|-----|-----|
| 6 | 0.000000 | 0.000000 | 0.134153 |
| 16 | 0.000000 | 0.000000 | 1.730113 |
| 17 | 0.000000 | 1.425544 | -0.837845 |
| 17 | 0.000000 | -1.425544 | -0.837845 |

**Excited-state**

\[ E = -1355.55550110 \ (T_{1}^{\text{diag}} = 0.011) \]

|   | x   | y   | z   |
|---|-----|-----|-----|
| 6 | -0.186033 | 0.080262 | 0.000000 |
| 16 | 0.465082 | 1.656702 | 0.000000 |
| 17 | -0.186033 | -0.793789 | 1.468861 |
| 17 | -0.186033 | -0.793789 | -1.468861 |

**Excited-state (constrained \( C_{2v} \))**

This structure (\( A_{2} \) symmetry) presents an imaginary frequency of 191 cm\(^{-1} \) (247 cm\(^{-1} \) with CC2). It is slightly less stable than the global minimum and corresponds to a barrier of 138 cm\(^{-1} \) (326 cm\(^{-1} \) with CC2).

\[ E = -1355.55487086 \ (T_{1}^{\text{diag}} = 0.012) \]

|   | x   | y   | z   |
|---|-----|-----|-----|
| 6 | 0.000000 | 0.000000 | 0.030411 |
| 16 | 0.000000 | 0.000000 | 1.733084 |
| 17 | 0.000000 | 1.471894 | -0.820935 |
| 17 | 0.000000 | -1.471894 | -0.820935 |

S48
Table S17: Selected geometrical parameters (bond lengths in Å, valence angles and dihedral angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). ∆ gives the difference between the two states (in eV for the $\Delta_{\text{ZPVE}}$). The considered ES is the lowest $A'/A$ state of $n \rightarrow \pi^*$ nature. $\eta$ is the out of plane angle of the hydrogen atom.

| Method          | State   | PG | ZPVE  | C=S  | C-Cl | C-H  | Cl-C-H | Cl-C=S | $\eta$ | Ref.   |
|-----------------|---------|----|-------|------|------|------|--------|--------|--------|--------|
| ADC(2)/def2-TZVPP | GS      | $C_s$ | 0.017156 | 1.597 | 1.725 | 1.082| 110.3  | 125.7  | 0.0   | This work |
|                 | ES      | $C_1$ | 0.014341 | 1.753 | 1.698 | 1.078| 119.1  | 117.9  | 9.5   |        |
| $\Delta$        | GS      | $C_s$ | -0.077 | 0.156 | -0.027| -0.004| 8.8    | -7.8   | 9.5   |        |
|                 | ES      | $C_1$ | 1.600  | 1.725 | 1.077 | 110.3 | 125.5  | 0.0    | This work |
| ADC(2)/aug-cc-pVTZ | GS      | $C_s$ | 1.757  | 1.699 | 1.073 | 119.3 | 117.2  | 8.9    |        |
|                 | ES      | $C_1$ | 0.157  | -0.026| -0.004| 9.0  | -8.3   | 8.9    |        |
| $\Delta$        | GS      | $C_s$ | 1.608  | 1.733 | 1.078 | 110.0 | 125.7  | 0.0    | This work |
|                 | ES      | $C_1$ | 1.737  | 1.708 | 1.074 | 118.4 | 116.6  | 18.6   |        |
| $\Delta$        | GS      | $C_s$ | -0.063 | 0.130 | -0.026| -0.005| 8.2    | -8.5   | 18.0  |        |
|                 | ES      | $C_1$ | 0.129  | -0.025| -0.004| 8.4  | -9.1   | 18.6   |        |
| CC2/def2-TZVPP   | GS      | $C_s$ | 1.598  | 1.727 | 1.075 | 110.5 | 125.6  | 0.0    | This work |
|                 | ES      | $C_1$ | 1.695  | 1.711 | 1.069 | 117.9 | 118.7  | 0.0    |        |
| $\Delta$        | GS      | $C_s$ | 1.608  | 1.737 | 1.082 | 110.4 | 125.7  | 0.0    | This work |
|                 | ES      | $C_1$ | 1.727  | 1.722 | 1.078 | 116.9 | 117.4  | 23.2   |        |
| $\Delta$        | GS      | $C_s$ | 0.119  | -0.015| -0.004| 6.5  | -8.3   | 23.2   |        |
|                 | ES      | $C_1$ | 0.097  | -0.016| -0.006| 7.4  | -6.9   | 0.0    |        |
| CC2/aug-cc-pVTZ  | GS      | $C_s$ | 1.608  | 1.734 | 1.077 | 110.3 | 125.5  | 0.0    | This work |
|                 | ES      | $C_1$ | 1.721  | 1.717 | 1.077 | 117.1 | 117.1  | 21.9   |        |
| $\Delta$        | GS      | $C_s$ | 1.607  | 1.739 | 1.082 | 110.3 | 125.7  | 0.0    | This work |
|                 | ES      | $C_1$ | 1.728  | 1.718 | 1.081 | 116.5 | 116.4  | 28.4   |        |
| $\Delta$        | GS      | $C_s$ | 1.606  | 1.734 | 1.077 | 110.3 | 125.5  | 0.0    | This work |
|                 | ES      | $C_1$ | 1.725  | 1.714 | 1.074 | 116.7 | 116.5  | 25.8   |        |
| $\Delta$        | GS      | $C_s$ | 1.605  | 1.735 | 1.079 | 110.1 | 125.5  | 0.0    | This work |
|                 | ES      | $C_1$ | 1.725  | 1.714 | 1.074 | 116.7 | 116.5  | 25.8   |        |
| CASPT2(18e,13o)/ANO-L-VQZP | GS      | $C_s$ | 1.609  | 1.739 | 1.082 | 110.3 | 125.7  | 0.0    | This work |
|                 | ES      | $C_1$ | 1.728  | 1.718 | 1.081 | 116.5 | 116.4  | 28.4   |        |
| $\Delta$        | GS      | $C_s$ | 1.607  | 1.739 | 1.082 | 110.3 | 125.7  | 0.0    | This work |
|                 | ES      | $C_1$ | 1.728  | 1.718 | 1.081 | 116.5 | 116.4  | 28.4   |        |
| $\Delta$        | GS      | $C_s$ | 1.606  | 1.740 | 1.085 | 110.1 | 125.3  | 0.0    | This work |
|                 | ES      | $C_1$ | 1.728  | 1.718 | 1.081 | 116.5 | 116.4  | 28.4   |        |
| $\Delta$        | GS      | $C_s$ | 1.605  | 1.735 | 1.079 | 110.1 | 125.5  | 0.0    | This work |
|                 | ES      | $C_1$ | 1.725  | 1.714 | 1.074 | 116.7 | 116.5  | 25.8   |        |
| $\Delta$        | GS      | $C_s$ | 1.605  | 1.735 | 1.079 | 110.1 | 125.5  | 0.0    | This work |
|                 | ES      | $C_1$ | 1.725  | 1.714 | 1.074 | 116.7 | 116.5  | 25.8   |        |

Experiment | ES | $C_1$ | 25.0 | 48 |
CASPT2 active space

All valence atomic $s$ and $p$ orbitals were included in the active space, i.e., 18 electrons in 13 orbitals.

**Cartesian coordinates**

**CASPT2**

CASPT2/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

|        | $x$   | $y$   | $z$    |
|--------|-------|-------|--------|
| Ground-state | $E$  |       |        |
| 6      | 0.001836 | 0.610051 | 0.000000 |
| 16     | 1.519483 | 0.087831 | 0.000000 |
| 1      | -0.285069 | 1.650468 | 0.000000 |
| 17     | -1.409766 | -0.398967 | 0.000000 |

|        | $x$   | $y$   | $z$    |
|--------|-------|-------|--------|
| Excited-state | $E$  |       |        |
| 6      | 0.056392 | -0.740935 | 0.056354 |
| 16     | -0.008838 | 0.167477 | 1.521737 |
| 1      | -0.268883 | -1.763878 | 0.010317 |
| 17     | -0.008637 | 0.155564 | -1.403240 |

**CCSDR(3)**

CCSDR(3)/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

|        | $x$   | $y$   | $z$    |
|--------|-------|-------|--------|
| Ground-state | $E$  |       |        |
| 6      | 0.000138 | 0.609671 | 0.000000 |
| 16     | 1.519806 | 0.089571 | 0.000000 |
| 1      | -0.282887 | 1.649013 | 0.000000 |
| 17     | -1.410573 | -0.398869 | 0.000000 |

|        | $x$   | $y$   | $z$    |
|--------|-------|-------|--------|
| Excited-state | $E$  |       |        |
| 6      | 0.040733 | -0.736862 | 0.057832 |
| 16     | -0.002681 | 0.166713 | 1.522354 |
| 1      | -0.265512 | -1.764010 | 0.015827 |
| 17     | -0.002506 | 0.152386 | -1.410844 |
EOM-CCSD

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

Ground-state
\[ E = -896.37372105 \ (T_1^{\text{diag}} = 0.011) \]

|   |      |          |          |          |
|---|---|---|---|---|
| 6 | -0.000000 | 0.605506 | -0.000000 |
| 16| 1.510857  | 0.092849 | 0.000000  |
| 1 | -0.278790 | 1.649134 | -0.000000 |
| 17| -1.405583 | -0.398103| -0.000000 |

Excited-state
\[ E = -896.281089126 \ (T_1^{\text{diag}} = 0.013) \]

|   |      |          |          |          |
|---|---|---|---|---|
| 6 | -0.000000 | 0.685346 | 0.000000  |
| 16| 1.512442  | -0.075332| 0.000000  |
| 1 | -0.118364 | 1.753574 | 0.000000  |
| 17| -1.416512 | -0.274138| 0.000000  |
## S18 Selenocarbonyl Difluoride

Table S18: Selected geometrical parameters (bond lengths in Å, valence angles and dihedral angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). ∆ gives the difference between the two states (in eV for the $\Delta ZPVE$). The considered ES is the lowest $A^*$ state of $n\rightarrow\pi^*$ nature. $\theta$ is the angle between the CSe bond and the bisector of the F-C-F angle.

| Method                  | State  | PG   | ZPVE  | C-Se  | C-F   | F-C-F | $\theta$ | Ref.     |
|-------------------------|--------|------|-------|-------|-------|-------|----------|----------|
| ADC(2)/def2-TZVPP       | GS     | $C_{2v}$ | 0.010722 | 1.734 | 1.311 | 107.5 | 0.0       | This work |
|                         | ES     | $C_{s}$  | 0.009852 | 1.894 | 1.327 | 112.2 | 36.1      |          |
|                         | $\Delta$ |       | -0.024 | 0.160 | 0.016 | 4.7   | 36.1      |          |
| ADC(2)/aug-cc-pVTZ      | GS     | $C_{2v}$ | 1.726  | 1.310 | 107.3 | 0.0   | This work |
|                         | ES     | $C_{s}$  | 1.884  | 1.325 | 112.0 | 36.7  |          |
|                         | $\Delta$ |       | 0.156  | 0.015 | 4.7   | 36.7  |          |
| CC2/def2-TZVPP          | GS     | $C_{2v}$ | 0.010369 | 1.745 | 1.318 | 107.4 | 0.0       | This work |
|                         | ES     | $C_{s}$  | 0.009393 | 1.908 | 1.333 | 111.7 | 38.5      |          |
|                         | $\Delta$ |       | -0.027 | 0.163 | 0.015 | 4.3   | 38.5      |          |
| CC2/aug-cc-pVTZ         | GS     | $C_{2v}$ | 1.736  | 1.317 | 107.2 | 0.0   | This work |
|                         | ES     | $C_{s}$  | 1.896  | 1.331 | 111.4 | 39.1  |          |
|                         | $\Delta$ |       | 0.160  | 0.014 | 4.2   | 39.1  |          |
| CCSD/def2-TZVPP         | GS     | $C_{2v}$ | 0.010869 | 1.741 | 1.303 | 107.8 | 0.0       | This work |
|                         | ES     | $C_{s}$  | 0.009810 | 1.891 | 1.321 | 110.4 | 39.5      |          |
|                         | $\Delta$ |       | -0.029 | 0.150 | 0.018 | 2.6   | 39.5      |          |
| CCSD/aug-cc-pVTZ        | GS     | $C_{2v}$ | 1.733  | 1.301 | 107.7 | 0.0   | This work |
|                         | ES     | $C_{s}$  | 1.879  | 1.318 | 110.2 | 39.7  |          |
|                         | $\Delta$ |       | 0.146  | 0.017 | 2.5   | 39.7  |          |
| CCSDR(3)/def2-TZVPP     | GS     | $C_{2v}$ | 1.749  | 1.310 | 107.8 | 0.0   | This work |
|                         | ES     | $C_{s}$  | 1.922  | 1.327 | 110.7 | 42.8  |          |
|                         | $\Delta$ |       | 0.173  | 0.017 | 2.9   | 42.8  |          |
| CCSDR(3)/aug-cc-pVTZ    | GS     | $C_{2v}$ | 1.740  | 1.309 | 107.6 | 0.0   | This work |
|                         | ES     | $C_{s}$  | 1.910  | 1.325 | 110.4 | 48.7  |          |
|                         | $\Delta$ |       | 0.170  | 0.016 | 2.8   | 48.7  |          |
| CC3/def2-TZVPP          | GS     | $C_{2v}$ | 1.750  | 1.312 | 107.7 | 0.0   | This work |
|                         | ES     | $C_{s}$  | 1.908  | 1.328 | 110.8 | 44.5  |          |
|                         | $\Delta$ |       | 0.172  | 0.017 | 3.2   | 44.5  |          |
| Experiment              | $\Delta$ |       | ca. 0.077 |   | 30.1  |   |          | 43       |
CASPT2 active space

All valence atomic $s$ and $p$ orbitals were included in the active space, i.e., 24 electrons in 16 orbitals.

Cartesian coordinates

CASPT2

CASPT2/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

Ground-state

$E = -2637.67194175$

|   | 6 | 34 | 9 | 9 |
|---|---|---|---|---|
|   | 0.000000 | 0.000000 | -0.777539 | 0.958647 |
| 34 | 0.000000 | 0.000000 | 1.058348 | -1.552076 |
| 9  | 0.000000 | -1.058348 | -1.552076 | 0.958647 |
| 9  | 0.000000 | -1.058348 | -1.552076 | 1.058348 |

Excited-state

$E = -2637.58676879$

|   | 6 | 34 | 9 | 9 |
|---|---|---|---|---|
|   | -0.738245 | 0.000000 | -0.618673 | 0.829713 |
| 34 | 0.504329 | 0.000000 | 0.829713 | -0.618673 |
| 9  | -0.687319 | 1.092930 | -1.371002 | 0.504329 |
| 9  | -0.687319 | -1.092930 | -1.371002 | 1.092930 |

CCSDR(3)

CCSDR(3)/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

Ground-state

$E = -2637.71309384$

|   | 6 | 34 | 9 | 9 |
|---|---|---|---|---|
|   | 0.000000 | 0.000000 | -0.779222 | 0.960594 |
| 34 | 0.000000 | 0.000000 | 1.055714 | -1.552340 |
| 9  | 0.000000 | -1.055714 | -1.552349 | 0.960594 |
| 9  | 0.000000 | -1.055714 | -1.552349 | 1.055714 |

Excited-state

$E = -2637.62363910$

|   | 6 | 34 | 9 | 9 |
|---|---|---|---|---|
|   | -0.731241 | 0.000000 | -0.620303 | 0.835637 |
| 34 | 0.505170 | 0.000000 | 0.835637 | -0.620303 |
| 9  | -0.695164 | 1.088258 | -1.375296 | 0.505170 |
| 9  | -0.695164 | -1.088258 | -1.375296 | 1.088258 |
EOM-CCSD

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

**Ground-state**

\[ E = -2637.6894391 \left( T_{1}^{\text{diag}} = 0.012 \right) \]

|  |  |  |  |
|---|---|---|---|
| 6 | -0.000000 | 0.000000 | -0.782405 |
| 34 | 0.000000 | -0.000000 | 0.958509 |
| 9 | 0.000000 | 1.052744 | -1.549715 |
| 9 | -0.000000 | -1.052744 | -1.549715 |

**Excited-state**

\[ E = -2637.59308945 \left( T_{1}^{\text{diag}} = 0.017 \right) \]

|  |  |  |  |
|---|---|---|---|
| 6 | -0.704584 | -0.621771 | 0.000000 |
| 34 | 0.497354 | 0.838081 | -0.000000 |
| 9 | -0.704584 | -1.375784 | 1.084040 |
| 9 | -0.704584 | -1.375784 | -1.084040 |

**Excited-state (constrained \(C_{2v}\))**

This ES of \(A_{2}\) symmetry presents an imaginary frequency of 602 cm\(^{-1}\) (620 cm\(^{-1}\) with CC2), which represents a barrier of 2703 cm\(^{-1}\) (2636 cm\(^{-1}\) with CC2) compared to the true minimum. The available experimental estimate for this barrier is 2483 cm\(^{-1}\).\(^{43}\)

\[ E = -2637.58077207 \left( T_{1}^{\text{diag}} = 0.015 \right) \]

|  |  |  |  |
|---|---|---|---|
| 6 | 0.000000 | 0.000000 | -0.863346 |
| 34 | 0.000000 | 0.000000 | 0.991763 |
| 9 | 0.000000 | 1.105233 | -1.585547 |
| 9 | -0.000000 | -1.105233 | -1.585547 |
Table S19: Selected geometrical parameters (bond lengths in Å, valence angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). $\Delta$ gives the difference between the two states (in eV for the $\Delta^{ZPVE}$). The considered ES is the lowest $A^*$ state of $n \rightarrow \pi^*$ nature. $\eta$ measures how the CO bond is out of the CCH$_{ald}$ plane.

| Method                  | State | PG | ZPVE  | C=O  | C-C  | C-C-H$_{ald}$ | C-C=O  | C-C-H$_{ald}$ | $\eta$ | Ref. |
|-------------------------|-------|----|-------|------|------|---------------|--------|---------------|-------|------|
| CCSD/def2-TZVPP         | GS    | $C_s$ | 0.056277 | 1.203 | 1.501 | 1.103 | 124.4 | 115.4 | 0.0 | This work |
|                         | ES    | $C_1$ | 0.053557 | 1.310 | 1.507 | 1.089 | 116.2 | 119.6 | 34.8 |          |
|                         | $\Delta$ |       | -0.074 | 0.107 | 0.006 | -0.014 | -8.2 | 4.2 | 34.8 |          |
| CCSDR(3)/def2-TZVPP     | GS    | $C_s$ | 1.209 | 1.503 | 1.105 | 124.3 | 115.4 | 0.0 | This work |
|                         | ES    | $C_1$ | 1.331 | 1.508 | 1.091 | 115.2 | 119.3 | 38.7 |          |
|                         | $\Delta$ |       | 0.122 | 0.005 | -0.014 | -9.1 | 3.9 | 38.7 |          |
| CASSCF/ANO              | GS    | $C_s$ | 1.222 | 1.501 | 1.092 | 124.2 | 116.3 | 0.0 | 49       |
|                         | ES    | $C_1$ | 1.383 | 1.501 | 1.080 | 114.5 | 120.3 | 37.5 |          |
|                         | $\Delta$ |       | 0.161 | 0.000 | -0.012 | -9.7 | 4.0 | 37.5 |          |
| P-EOM-MP2/6-31G(d)      | ES    | $C_1$ | 1.359 | 1.494 | 1.095 | 116.0 | 114.3 | 30.1 | 50       |
| Experiment              | GS    | $C_s$ | 1.21 |       |       |       |       |       | 0 | 51       |
|                         | ES    | $C_1$ | 1.32 |       |       |       |       | 26 |          |
|                         | $\Delta$ |       | 0.11 |       |       |       |       | 26 |          |
## Cartesian coordinates

### CCSDR(3)

CCSDR(3)/\textit{def2-TZVPP} total energies (au) and Cartesian coordinates (Å).

| Atom | \(E\) | \(x\)  | \(y\)  | \(z\)  |
|------|------|------|------|------|
| 6    | -0.090227 | -0.516399 | -0.085451 |
| 6    | 0.009961   | 0.187889  | 1.243954  |
| 8    | 0.011908   | 0.270656  | -1.153526 |
| 1    | 0.385206   | -1.489897 | -0.210548 |
| 1    | -0.138446  | -0.538363 | 2.038825  |
| 1    | 0.988598   | 0.662464  | 1.366700  |
| 1    | -0.754285  | 0.960043  | 1.319246  |

### Excited-state

| Atom | \(E\) | \(x\)  | \(y\)  | \(z\)  |
|------|------|------|------|------|
| 6    | -0.000030 | 0.000000 | 0.463393 |
| 6    | -0.932837 | 0.000000 | -0.715582 |
| 8    | 1.206546  | 0.000000 | 0.379488 |
| 1    | -0.488394 | 0.000000 | 1.454609 |
| 1    | -1.578770 | 0.877925 | -0.665947 |
| 1    | -1.578770 | -0.877925 | -0.665947 |
| 1    | -0.368995 | 0.000000 | -1.644059 |

### EOM-CCSD

(EOM)-CCSD/\textit{def2-TZVPP} total energies (au) and Cartesian coordinates (Å).

| Atom | \(E\) | \(x\)  | \(y\)  | \(z\)  |
|------|------|------|------|------|
| 6    | 0.000000 | 0.462302 | 0.000000 |
| 6    | -0.931747 | -0.714272 | 0.000000 |
| 1    | -0.486735 | 1.451506 | 0.000000 |
| 8    | 1.199998 | 0.379128 | 0.000000 |
| 1    | -1.576508 | -0.665421 | 0.876613 |
| 1    | -1.576508 | -0.665421 | -0.876613 |
| 1    | -0.369750 | -1.641868 | 0.000000 |

\[T_{1}^{\text{diag}} = 0.012\]
Excited-state
\[ E = -153.4806236 \ (T_1^{\text{diag}} = 0.016) \]

| 6   | -0.200205 | 0.484031 | -0.110265 |
|-----|-----------|----------|-----------|
| 6   | 1.156242  | -0.160146| 0.014279  |
| 1   | -0.352952 | 1.494842 | 0.264953  |
| 8   | -1.232978 | -0.310297| 0.023018  |
| 1   | 1.918679  | 0.589030 | -0.171928 |
| 1   | 1.301962  | -0.582701| 1.011387  |
| 1   | 1.259914  | -0.962108| -0.712638 |
### Table S20: Selected geometrical parameters (bond lengths in Å, valence angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). $\Delta$ gives the difference between the two states (in eV for the $\Delta_{ZPVE}$). The considered ES is the lowest $A^\pi$ state of $n \rightarrow \pi^*$ nature. $\eta$ measures how the CO bond is out of the CCC plane.

| Method                | State | PG    | ZPVE  | C=O  | C-C  | C-C-C | $\eta$ | Ref.      |
|-----------------------|-------|-------|-------|------|------|-------|--------|-----------|
| CCSD/def2-TZVPP       | GS    | $C_{2v}$ | 0.084568 | 1.207 | 1.510 | 116.3 | 0.0    | This work |
|                       | ES    | $C_{s}$  | 0.082538 | 1.314 | 1.506 | 119.7 | 39.7   | This work |
| $\Delta$              |       |        | -0.055 | 0.107 | -0.004 | 3.4   | 39.7   |           |
| CCSDR(3)/def2-TZVPP   | GS    | $C_{2v}$ | 1.213   | 1.513 | 116.3 | 0.0   |        | This work |
|                       | ES    | $C_{s}$  | 1.336   | 1.507 | 119.5 | 42.3  |        |           |
| $\Delta$              |       |        | 0.123   | -0.006 | 3.2   | 42.3  |        |           |
| CC2/cc-pVTZ           | GS    | $C_{2v}$ | 1.222   | 1.504 |      |       |        | 32        |
|                       | ES    | $C_{s}$  | 1.404   | 1.477 |      |       |        |           |
| $\Delta$              |       |        | 0.182   | -0.027 |      |       |        |           |
| CASPT2/cc-pVTZ        | GS    | $C_{2v}$ | 1.214   | 1.509 |      |       |        | 32        |
|                       | ES    | $C_{s}$  | 1.350   | 1.496 |      |       |        |           |
| $\Delta$              |       |        | 0.136   | -0.013 |      |       |        |           |
| VMC/pVTZ'             | GS    | $C_{2v}$ | 1.205   | 1.502 |      |       |        | 32        |
|                       | ES    | $C_{s}$  | 1.344   | 1.489 |      |       |        |           |
| $\Delta$              |       |        | 0.139   | -0.013 |      |       |        |           |
Cartesian coordinates

CCSDR(3)

CCSDR(3)/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

| Ground-state |
|---------------|
| $E = -192.92059411$ |
| 6  | 0.000000 | 1.285118 | 0.696325 |
| 6  | 0.000000 | -1.285118 | 0.696325 |
| 6  | 0.000000 | 0.000000 | -0.102525 |
| 8  | 0.000000 | 0.000000 | -1.316018 |
| 1  | 0.000000 | 2.137074 | 0.023350 |
| 1  | 0.000000 | -2.137074 | 0.023350 |
| 1  | 0.878002 | 1.320511 | 1.342576 |
| 1  | -0.878002 | 1.320511 | 1.342576 |
| 1  | 0.878002 | -1.320511 | 1.342576 |
| 1  | -0.878002 | -1.320511 | 1.342576 |

| Excited-state |
|---------------|
| $E = -192.77949130$ |
| 6  | -0.193014 | 1.301688 | -0.562654 |
| 6  | -0.193014 | -1.301688 | -0.562654 |
| 6  | -0.215816 | 0.000000 | 0.195682 |
| 8  | 0.578089 | 0.000000 | 1.270606 |
| 1  | -0.392928 | 2.139640 | 0.102285 |
| 1  | -0.392928 | -2.139640 | 0.102285 |
| 1  | 0.787287 | 1.459172 | -1.028900 |
| 1  | 0.787287 | -1.459172 | -1.028900 |
| 1  | -0.955011 | 1.271999 | -1.338699 |
| 1  | -0.955011 | -1.271999 | -1.338699 |
EOM-CCSD

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

**Ground-state**

\[ E = -192.88844078 \quad (T_{1}^{\text{diag}} = 0.012) \]

|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 6 | 0.000000 | 1.282877 | -0.611721 |
| 6 | 0.000000 | -1.282877 | -0.611721 |
| 6 | 0.000000 | 0.000000 | 0.185210  |
| 8 | 0.000000 | 0.000000 | 1.392088  |
| 1 | 0.000000 | 2.133711  | 0.059851  |
| 1 | -0.876575 | 1.319344  | -1.256757 |
| 1 | 0.876575  | 1.319344  | -1.256757 |
| 1 | 0.000000  | -2.133711 | 0.059851  |
| 1 | 0.876575  | -1.319344 | -1.256757 |
| 1 | -0.876575 | -1.319344 | -1.256757 |

**Excited-state**

\[ E = -192.740983075 \quad (T_{1}^{\text{diag}} = 0.015) \]

|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 6 | -0.191434 | -0.562180 | 1.301879 |
| 6 | -0.191434 | -0.562180 | -1.301879|
| 6 | -0.191434 | 0.194440  | 0.000000 |
| 8 | 0.573795  | 1.262750  | 0.000000 |
| 1 | -0.404809 | 0.102891  | 2.134137 |
| 1 | 0.784281  | -1.027604 | 1.477309 |
| 1 | -0.951748 | -1.336527 | 1.259750 |
| 1 | -0.404809 | 0.102891  | -2.134137|
| 1 | -0.951748 | -1.336527 | -1.259750|
| 1 | 0.784281  | -1.027604 | -1.477309|
## Table S21: Selected geometrical parameters (bond lengths in Å, valence angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). ∆ gives the difference between the two states (in eV for the ∆ZPVE). The considered ES is the lowest A* state of n→π* nature.

| Method                  | State | PG | ZPVE | C=O | C-C | C=C | O=C-C | C=C=C | Ref.         |
|-------------------------|-------|----|------|-----|-----|-----|-------|-------|--------------|
| CCSD/def2-TZVPP         | GS    | C_s | 0.062076 | 1.205 | 1.476 | 1.332 | 124.1 | 120.5 | This work    |
|                         | ES    | C_s | 0.058620 | 1.304 | 1.413 | 1.357 | 124.5 | 123.6 |              |
|                         | ∆     |     | -0.094 | 0.099 | -0.063 | 0.025 | 0.4   | 3.2   |              |
| CCSDR(3)/def2-TZVPP     | GS    | C_s | 1.213  | 1.476 | 1.340 | 124.2 | 120.3 |       | This work    |
|                         | ES    | C_s | 1.324  | 1.395 | 1.377 | 125.1 | 123.3 |       |              |
|                         | ∆     |     | 0.111  | -0.081 | 0.037 | 0.9   | 3.0   |       |              |
| CASPT2/6-31G(d)         | GS    | C_s | 1.226  | 1.469 | 1.345 | 123.6 | 121.1 |       | 52           |
|                         | ES    | C_s | 1.345  | 1.384 | 1.392 | 124.2 | 123.4 |       |              |
|                         | ∆     |     | 0.119  | -0.085 | 0.047 | 0.6   | 2.3   |       |              |
| SAC-CI/[4s2p1d/2s] + [2s2p] | GS    | C_s | 1.214  | 1.475 | 1.341 | 123.8 | 120.3 |       | 53           |
|                         | ES    | C_s | 1.288  | 1.435 | 1.350 | 124.4 | 125.0 |       |              |
|                         | ∆     |     | 0.074  | -0.040 | 0.009 | 0.6   | 4.7   |       |              |
| CC2/cc-pVTZ             | GS    | C_s | 1.220  | 1.462 | 1.335 | 124.4 | 120.0 |       | 32           |
|                         | ES    | C_s | 1.371  | 1.369 | 1.382 | 126.7 | 122.2 |       |              |
|                         | ∆     |     | 0.151  | -0.093 | 0.047 | 2.3   | 2.2   |       |              |
| CASPT2/cc-pVTZ          | GS    | C_s | 1.211  | 1.468 | 1.337 | 122.7 | 120.3 |       | 32           |
|                         | ES    | C_s | 1.332  | 1.375 | 1.389 | 124.4 | 123.3 |       |              |
|                         | ∆     |     | 0.121  | -0.093 | 0.052 | 1.7   | 3.0   |       |              |
| VMC/pVTZ'               | GS    | C_s | 1.205  | 1.464 | 1.328 | 123.7 | 120.9 |       | 32           |
|                         | ES    | C_s | 1.327  | 1.368 | 1.383 | 125.8 | 122.6 |       |              |
|                         | ∆     |     | 0.122  | -0.096 | 0.055 | 2.1   | 1.7   |       |              |
| Experiment              | GS    | C_s | 1.22   | 1.45  | 1.36  | 122   | 122   |       | 54           |
|                         | ES    | C_s | 1.32   | 1.35  | 1.46  | 125   | 125   |       |              |
|                         | ∆     |     | 0.10   | -0.10 | 0.10  | 3     | 3     |       |              |
**Cartesian coordinates**

**CCSDR(3)**

CCSDR(3)/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

**Ground-state**

\[ E = -191.67994137 \]

|   | x     | y     | z     |
|---|-------|-------|-------|
| 6 | 0.027067 | -0.015935 | 0.000000 |
| 6 | 1.366616  | -0.021406 | 0.000000 |
| 6 | 2.116417  | 1.249827  | 0.000000 |
| 8 | 3.326694  | 1.326746  | 0.000000 |
| 1 | -0.551364 | -0.927768 | 0.000000 |
| 1 | -0.518681 | 0.919209  | 0.000000 |
| 1 | 1.945760  | -0.934498 | 0.000000 |
| 1 | 1.486493  | 2.158283  | 0.000000 |

**Excited-state**

\[ E = -191.55445006 \]

|   | x     | y     | z     |
|---|-------|-------|-------|
| 6 | -0.017125 | -0.024704 | 0.000000 |
| 6 | 1.359319  | 0.028393  | 0.000000 |
| 6 | 2.079483  | 1.223667  | 0.000000 |
| 8 | 3.400641  | 1.315762  | 0.000000 |
| 1 | -0.529034 | -0.973240 | 0.000000 |
| 1 | -0.614542 | 0.875500  | 0.000000 |
| 1 | 1.932833  | -0.888737 | 0.000000 |
| 1 | 1.587428  | 2.197817  | 0.000000 |

**EOM-CCSD**

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

**Ground-state**

\[ E = -191.64571278 \ (T_{1}^{\text{diag}} = 0.013) \]

|   | x     | y     | z     |
|---|-------|-------|-------|
| 6 | 1.211427 | -1.277138 | 0.000000 |
| 6 | 0.000000 | -0.722546 | 0.000000 |
| 6 | -0.151326 | 0.745683  | 0.000000 |
| 8 | -1.212850 | 1.316281  | 0.000000 |
| 1 | 1.352755 | -2.345898 | 0.000000 |
| 1 | 2.099878 | -0.661755 | 0.000000 |
| 1 | -0.907198 | -1.307168 | 0.000000 |
| 1 | 0.796766  | 1.308582  | 0.000000 |
Excited-state

\[ E = -191.51182693 \ (T_1^{\text{diag}} = 0.016) \]

|   | 1.175646 | 1.364826 | 0.000000 |
|---|----------|----------|-----------|
| 6 | 0.000000 | 0.686615 | 0.000000 |
| 6 | -0.090665| -0.723242| 0.000000 |
| 8 | -1.210407| -1.391762| 0.000000 |
| 1 | 1.185431 | 2.441194 | 0.000000 |
| 1 | 2.124888 | 0.852502 | 0.000000 |
| 1 | -0.935888| 1.224908 | 0.000000 |
| 1 | 0.798943 | -1.353703| 0.000000 |
## Table S22: Selected geometrical parameters (bond lengths in Å, valence angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). ∆ gives the difference between the two states (in eV for the $\Delta_{\text{ZPVE}}$). The values in italics corresponding to the CC3/aug-cc-pVTZ ∆ ES geometry have been extrapolated (see the main text for details).

| Method                  | State | PG    | ZPVE  | N≡C | C-C | C≡C | C-H | N≡C-C | C-C≡C | C≡C-H | Ref. |
|-------------------------|-------|-------|-------|-----|-----|-----|-----|-------|-------|-------|------|
| CCSD/def2-TZVPP         | GS    | $C_{\text{occ}}$ | 0.027258 | 1.155 | 1.385 | 1.262 | 1.060 | 180.0 | 180.0 | 180.0 | This work |
|                         | ES ($A'$) | $C_{\text{s}}$ | 0.023023 | 1.179 | 1.350 | 1.336 | 1.088 | 173.0 | 141.8 | 123.6 |      |
|                         | ∆     |       | -0.115 | 0.024 | -0.035 | 0.134 | 0.028 | -7.1  | -39.2 | -56.4 |      |
|                         | ES ($\Delta$) | $C_{\text{occ}}$ | 0.023390 | 1.209 | 1.306 | 1.275 | 1.060 | 180.0 | 180.0 | 180.0 | This work |
| CCSD/aug-cc-pVTZ        | GS    | $C_{\text{occ}}$ | 1.153 | 1.377 | 1.199 | 1.059 | 180.0 | 180.0 | 180.0 | This work |
|                         | ES ($A'$) | $C_{\text{s}}$ | 1.179 | 1.335 | 1.328 | 1.085 | 173.8 | 145.7 | 124.1 |      |
|                         | ∆     |       | 0.026 | -0.042 | 0.129 | 0.026 | 6.2   | -34.3 | -55.9 |      |
|                         | ES ($\Delta$) | $C_{\text{occ}}$ | 1.207 | 1.301 | 1.272 | 1.060 | 180.0 | 180.0 | 180.0 |      |
| CCSDR(3)/def2-TZVPP     | GS    | $C_{\text{occ}}$ | 1.163 | 1.381 | 1.210 | 1.062 | 180.0 | 180.0 | 180.0 | This work |
|                         | ES ($A'$) | $C_{\text{s}}$ | 1.186 | 1.359 | 1.355 | 1.092 | 172.5 | 153.5 | 122.1 |      |
|                         | ∆     |       | 0.023 | -0.022 | 0.145 | 0.030 | -7.5  | -44.3 | -55.9 |      |
|                         | ES ($\Delta$) | $C_{\text{occ}}$ | 1.221 | 1.308 | 1.283 | 1.062 | 180.0 | 180.0 | 180.0 |      |
| CCSDR(3)/aug-cc-pVTZ    | GS    | $C_{\text{occ}}$ | 1.162 | 1.374 | 1.208 | 1.061 | 180.0 | 180.0 | 180.0 | This work |
|                         | ES ($A'$) | $C_{\text{s}}$ | 1.186 | 1.346 | 1.347 | 1.088 | 173.0 | 138.9 | 122.4 |      |
|                         | ∆     |       | 0.024 | -0.028 | 0.135 | 0.027 | -7.0  | -41.1 | -55.9 |      |
|                         | ES ($\Delta$) | $C_{\text{occ}}$ | 1.219 | 1.303 | 1.280 | 1.062 | 180.0 | 180.0 | 180.0 |      |
| CC3/def2-TZVPP          | GS    | $C_{\text{occ}}$ | 1.165 | 1.381 | 1.211 | 1.062 | 180.0 | 180.0 | 180.0 | This work |
|                         | ES ($A'$) | $C_{\text{s}}$ | 1.227 | 1.305 | 1.285 | 1.063 | 180.0 | 180.0 | 180.0 |      |
|                         | ∆     |       | 0.062 | -0.076 | 0.073 | 0.001 | 0.0   | 0.0   | 0.0   |      |
| CC3/aug-cc-pVTZ         | GS    | $C_{\text{occ}}$ | 1.163 | 1.374 | 1.209 | 1.061 | 180.0 | 180.0 | 180.0 | This work |
|                         | ES ($A'$) | $C_{\text{s}}$ | 1.225 | 1.300 | 1.282 | 1.062 | 180.0 | 180.0 | 180.0 |      |
|                         | ∆     |       | 0.062 | -0.074 | 0.073 | 0.001 | 0.0   | 0.0   | 0.0   |      |
| CASSCF/6-31G(d)         | GS    | $C_{\text{occ}}$ | 1.175 | 1.387 | 1.210 | 1.078 | 180.0 | 180.0 | 180.0 | 55 |
|                         | ES ($A'$) | $C_{\text{s}}$ | 1.191 | 1.377 | 1.388 | 1.081 | 173.0 | 129.7 | 121.0 |      |
|                         | ∆     |       | 0.016 | -0.010 | 0.178 | 0.003 | -7.0  | -50.3 | -59.0 |      |
| CIS/6-31G(d)            | GS    | $C_{\text{occ}}$ | 1.136 | 1.391 | 1.185 | 1.058 | 180.0 | 180.0 | 180.0 | 55 |
|                         | ES ($A'$) | $C_{\text{s}}$ | 1.187 | 1.311 | 1.273 | 1.056 | 180.0 | 180.0 | 180.0 |      |
|                         | ∆     |       | 0.051 | -0.080 | 0.088 | -0.002 | 0.0   | 0.0   | 0.0   |      |
| CASSCF/cc-pVTZ          | GS    | $C_{\text{occ}}$ | 1.167 | 1.333 | 1.203 | 1.074 | 180.0 | 180.0 | 180.0 | 56 |
|                         | ES ($A'$) | $C_{\text{1}}$ | 1.182 | 1.396 | 1.341 | 1.103 | 172.4 | 131.0 | 124.1 | a |
|                         | ∆     |       | 0.015 | 0.013 | 0.138 | 0.029 | -7.6  | -49.0 | -55.9 |      |
| Experiment              | GS    | $C_{\text{occ}}$ | 1.159 | 1.378 | 1.205 | 1.057 | 180.0 | 180.0 | 180.0 | 57 |
|                         | ES ($A'$) | $C_{\text{s}}$ | 1.159 b | 1.400 | 1.250 | 1.08 b | 180.0 b | 143.2 | 164 |      |
|                         | ∆     |       | 0.022 | 0.045 |       |       | -36.8 | -16 |      |      |
|                         | ES ($\Delta$) | $C_{\text{occ}}$ | 180.0 c | 180.0 c | 180.0 c |      |      |      |      |

a Very slight distortion from planarity with a NCCC dihedral angle of 179.4 degrees; b Assumed during the fit; c Found to be linear.
## Cartesian coordinates

### CCSDR(3)

CCSDR(3)/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

#### Ground-state

\[ E = -169.36101518 \]

| n | x   | y   | z    |
|---|-----|-----|------|
| 6 | 0.000000 | 0.000000 | -1.899799 |
| 6 | 0.000000 | 0.000000 | -0.692004 |
| 6 | 0.000000 | 0.000000 | 0.682146 |
| 7 | 0.000000 | 0.000000 | 1.844105 |
| 1 | 0.000000 | 0.000000 | -2.960608 |

#### Excited-state (\( \Delta \))

\[ E = -169.17922891 \]

| n | x   | y   | z    |
|---|-----|-----|------|
| 6 | 1.062025 | 1.490489 | 0.000000 |
| 6 | -0.030462 | 0.703250 | 0.000000 |
| 6 | -0.335929 | -0.607482 | 0.000000 |
| 7 | -0.744194 | -1.721298 | 0.000000 |
| 1 | 0.998278 | 2.577061 | 0.000000 |

### EOM-CCSD

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

#### Ground-state

\[ E = -169.32269797 (T^\text{diag}_1 = 0.012) \]

| n | x   | y   | z    |
|---|-----|-----|------|
| 6 | 0.000000 | 0.000000 | -1.867252 |
| 6 | 0.000000 | 0.000000 | -0.587260 |
| 6 | 0.000000 | 0.000000 | 0.715433 |
| 7 | 0.000000 | 0.000000 | 1.934143 |
| 1 | 0.000000 | 0.000000 | -2.929179 |

S65
**Excited-state \((A^-)\)**
\[ E = -169.13387713 \quad (T_1^{\text{diag}} = 0.020) \]

|    |       |       |       |
|----|-------|-------|-------|
| 6  | 1.060296 | 1.501250 | 0.000000 |
| 6  | 0.000000 | 0.688207 | 0.000000 |
| 6  | -0.333916 | -0.618662 | 0.000000 |
| 7  | -0.763604 | -1.715998 | 0.000000 |
| 1  | 0.986943  | 2.587222  | 0.000000 |

**Excited-state \((\Delta)\)**
\[ E = -169.10987713 \quad (T_1^{\text{diag}} = 0.014) \]

|    |       |       |       |
|----|-------|-------|-------|
| 6  | 0.000000 | 0.000000 | -1.869507 |
| 6  | 0.000000 | 0.000000 | -0.594693 |
| 6  | 0.000000 | 0.000000 | 0.711577  |
| 7  | 0.000000 | 0.000000 | 1.920796  |
| 1  | 0.000000 | 0.000000 | -2.929836 |
## S23 Cyanoformaldehyde

Table S23: Selected geometrical parameters (bond lengths in Å, valence angles and dihedral angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). ∆ gives the difference between the two states (in eV for the $\Delta^{ZPVE}$). The considered ES is the lowest $A^*$ state.

| Method               | State  | PG | ZPVE  | C=O   | C-C   | C-H   | C≡N   | H-C=O | C-C=O | Ref.       |
|----------------------|--------|----|-------|-------|-------|-------|-------|-------|-------|------------|
| ADC(2)/def2-TZVPP    | GS     | $C_s$ | 0.026125 | 1.208 | 1.467 | 1.094 | 1.169 | 123.1 | 122.1 | This work |
|                      | ES     | $C_s$ | 0.022621 | 1.399 | 1.383 | 1.083 | 1.180 | 114.9 | 121.0 | This work |
|                      | ∆      |      | -0.095 | 0.191 | -0.084 | -0.011 | 0.011 | -8.2 | -1.1 |            |
| ADC(2)/aug-cc-pVTZ   | GS     | $C_s$ | 1.208 | 1.459 | 1.092 | 1.168 | 122.9 | 122.3 |       |            |
|                      | ES     | $C_s$ | 1.399 | 1.377 | 1.080 | 1.179 | 114.7 | 121.0 |       |            |
|                      | ∆      |      | 0.191 | -0.082 | -0.008 | 0.011 | -8.2 | -1.3 |       |            |
| CC2/def2-TZVPP       | GS     | $C_s$ | 0.025535 | 1.215 | 1.468 | 1.095 | 1.177 | 123.2 | 122.1 | This work |
|                      | ES     | $C_s$ | 0.022480 | 1.371 | 1.381 | 1.084 | 1.191 | 114.7 | 121.4 |            |
|                      | ∆      |      | -0.083 | 0.156 | -0.087 | -0.011 | 0.014 | -8.5 | -0.7 |            |
| CC2/aug-cc-pVTZ      | GS     | $C_s$ | 1.215 | 1.459 | 1.093 | 1.176 | 123.0 | 122.2 |       |            |
|                      | ES     | $C_s$ | 1.370 | 1.375 | 1.082 | 1.189 | 114.5 | 121.4 |       |            |
|                      | ∆      |      | 0.155 | -0.084 | -0.011 | 0.013 | -8.5 | -0.8 |       |            |
| CCSD/def2-TZVPP      | GS     | $C_s$ | 0.026878 | 1.197 | 1.476 | 1.093 | 1.152 | 123.4 | 122.1 | This work |
|                      | ES     | $C_s$ | 0.024118 | 1.309 | 1.405 | 1.084 | 1.160 | 116.8 | 120.8 |            |
|                      | ∆      |      | -0.075 | 0.112 | -0.071 | -0.009 | 0.008 | -6.6 | -1.3 |            |
| CCSD/aug-cc-pVTZ     | GS     | $C_s$ | 1.196 | 1.467 | 1.091 | 1.150 | 123.1 | 122.3 |       | This work |
|                      | ES     | $C_s$ | 1.309 | 1.405 | 1.084 | 1.160 | 116.8 | 120.8 |       |            |
|                      | ∆      |      | 0.113 | -0.064 | -0.007 | 0.010 | -6.3 | -1.5 |       |            |
| CCSDR(3)/def2-TZVPP  | GS     | $C_s$ | 1.204 | 1.476 | 1.095 | 1.161 | 123.3 | 122.1 |       | This work |
|                      | ES     | $C_s$ | 1.330 | 1.398 | 1.084 | 1.171 | 116.2 | 121.0 |       |            |
|                      | ∆      |      | 0.126 | -0.078 | -0.011 | 0.010 | -7.1 | -1.1 |       |            |
| CCSDR(3)/aug-cc-pVTZ | GS     | $C_s$ | 1.204 | 1.466 | 1.093 | 1.159 | 123.1 | 122.3 |       | This work |
|                      | ES     | $C_s$ | 1.326 | 1.391 | 1.082 | 1.168 | 116.0 | 121.2 |       |            |
|                      | ∆      |      | 0.122 | -0.075 | -0.011 | 0.009 | -7.1 | -1.1 |       |            |
| ROHF/6-31G(d)        | GS     | $C_s$ | 1.179 | 1.479 | 1.085 | 1.134 | 123.6 | 122.0 |       | 59         |
|                      | ES     | $C_1$ | 1.351 | 1.421 | 1.072 | 1.137 | 115.5 | 117.6 |       |            |
|                      | ∆      |      | 0.172 | -0.058 | -0.013 | 0.003 | -8.1 | -4.4 |       |            |
| CASSCF/cc-pVTZ       | GS     | $C_s$ | 1.178 | 1.479 | 1.175 |       |       |       |       | 60         |
|                      | ES     | $C_1$ | 1.346 | 1.412 | 1.167 |       |       |       |       |            |
|                      | ∆      |      | 0.168 | -0.067 | -0.008 |       |       |       |       |            |

$^a$A out-of-plane structure is predicted with a H atom 25° out of the CCO plane, but a very low torsion potential (barrier for planarity: 113 cm$^{-1}$). $^b$A out-of-plane structure is predicted with a H atom 24.9° out of the CCO plane.
Cartesian coordinates

CCSDR(3)

CCSDR(3)/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

| Ground-state | $E$ = -206.50154953 |
|--------------|----------------------|
| 6            | -0.483865 -0.648215  0.000000 |
| 6            | -0.003961 0.737471   0.000000 |
| 8            | 0.267796 -1.589135  0.000000 |
| 7            | 0.337260 1.845148   0.000000 |
| 1            | -1.571684 -0.753175 0.000000 |

| Excited-state | $E$ = -206.37659806 |
|---------------|----------------------|
| 6             | 0.547721 -0.551779  0.000000 |
| 6             | 0.003933 0.728732   0.000000 |
| 8             | -0.226777 -1.627533 0.000000 |
| 7             | -0.442450 1.808448  0.000000 |
| 1             | 1.614513 -0.734467  0.000000 |

EOM-CCSD

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

| Ground-state | $E$ = -206.46641073 ($T_1^{\text{diag}} = 0.013$) |
|--------------|-----------------------------------------------|
| 6            | -0.483697 -0.652648  0.000000 |
| 6            | 0.000000 0.741850   0.000000 |
| 8            | 0.265053 -1.586080  0.000000 |
| 7            | 0.336261 1.844076   0.000000 |
| 1            | -1.572071 -0.755103 0.000000 |

| Excited-state | $E$ = -206.33463140 ($T_1^{\text{diag}} = 0.015$) |
|---------------|-----------------------------------------------|
| 6             | 0.548262 -0.560324  0.000000 |
| 6             | 0.000000 0.733278   0.000000 |
| 8             | -0.225090 -1.616442 0.000000 |
| 7             | -0.443770 1.804487  0.000000 |
| 1             | 1.617538 -0.737598  0.000000 |
Table S24: Selected geometrical parameters (bond lengths in Å, valence angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). ∆ gives the difference between the two states (in eV for the $\Delta ZPVE$). The considered state is the lowest ES ($\Sigma^{-}\text{u}$).

| Method          | State   | PG   | ZPVE  | C≡N   | C-C   | Ref.   |
|-----------------|---------|------|-------|-------|-------|--------|
| ADC(2)/def2-TZVPP | GS      | $D_{\infty h}$ | 0.015300 | 1.172 | 1.377 | This work |
|                 | ES      | $D_{\infty h}$ | 0.012656 | 1.254 | 1.293 |         |
|                 | $\Delta$ |       | -0.072 | 0.082 | -0.084 |        |
| ADC(2)/aug-cc-pVTZ | GS      | $D_{\infty h}$ | 1.170 | 1.370 |       | This work |
|                 | ES      | $D_{\infty h}$ | 1.251 | 1.288 |       |         |
|                 | $\Delta$ |       | 0.081 | -0.082 |     |        |
| CC2/def2-TZVPP  | GS      | $D_{\infty h}$ | 0.014817 | 1.180 | 1.377 | This work |
|                 | ES      | $D_{\infty h}$ | 0.012306 | 1.266 | 1.288 |         |
|                 | $\Delta$ |       | -0.068 | 0.086 | -0.089 |        |
| CC2/aug-cc-pVTZ | GS      | $D_{\infty h}$ | 1.178 | 1.369 |       | This work |
|                 | ES      | $D_{\infty h}$ | 1.263 | 1.283 |       |         |
|                 | $\Delta$ |       | 0.085 | -0.086 |     |        |
| CCSD/def2-TZVPP | GS      | $D_{\infty h}$ | 0.016327 | 1.153 | 1.392 | This work |
|                 | ES      | $D_{\infty h}$ | 0.013626 | 1.223 | 1.305 |         |
|                 | $\Delta$ |       | -0.073 | 0.070 | -0.087 |        |
| CCSD/aug-cc-pVTZ | GS      | $D_{\infty h}$ | 1.150 | 1.383 |       | This work |
|                 | ES      | $D_{\infty h}$ | 1.220 | 1.299 |       |         |
|                 | $\Delta$ |       | 0.070 | -0.084 |     |        |
| CCSDR(3)/def2-TZVPP | GS | $D_{\infty h}$ | 1.162 | 1.389 |       | This work |
|                 | ES      | $D_{\infty h}$ | 1.235 | 1.308 |       |         |
|                 | $\Delta$ |       | 0.073 | -0.081 |     |        |
| CCSDR(3)/aug-cc-pVTZ | GS | $D_{\infty h}$ | 1.160 | 1.381 |       | This work |
|                 | ES      | $D_{\infty h}$ | 1.232 | 1.302 |       |         |
|                 | $\Delta$ |       | 0.072 | -0.079 |     |        |
| CC3/def2-TZVPP  | GS      | $D_{\infty h}$ | 1.163 | 1.389 |       | This work |
|                 | ES      | $D_{\infty h}$ | 1.240 | 1.306 |       |         |
|                 | $\Delta$ |       | 0.077 | -0.083 |     |        |
| CC3/aug-cc-pVTZ | GS      | $D_{\infty h}$ | 1.161 | 1.380 |       | This work |
|                 | ES      | $D_{\infty h}$ | 1.237 | 1.299 |       |         |
|                 | $\Delta$ |       | 0.076 | -0.081 |     |        |
| CASSCF/6-31G(d) | GS      | $D_{\infty h}$ | 1.173 | 1.395 |       | 55      |
|                 | ES      | $D_{\infty h}$ | 1.255 | 1.296 |       |         |
|                 | $\Delta$ |       | 0.082 | -0.099 |     |        |
| CASSCF/10s6p    | GS      | $D_{\infty h}$ | 1.167 | 1.391 |       | 61      |
|                 | ES      | $D_{\infty h}$ | 1.254 | 1.292 |       |         |
|                 | $\Delta$ |       | 0.087 | -0.099 |     |        |

$^a$This work hints that the symmetry of the GS and ES are equivalent.
Cartesian coordinates

CC3

CC3/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

**Ground-state**
\[ E = -185.43636292  
\]

|  |  |  |  |
|---|---|---|---|
| 6 | 0.000000 | 0.000000 | 0.690057 |
| 6 | 0.000000 | 0.000000 | -0.690057 |
| 7 | 0.000000 | 0.000000 | 1.850978 |
| 7 | 0.000000 | 0.000000 | -1.850978 |

**Excited-state**
\[ E = -185.22623796  
\]

|  |  |  |  |
|---|---|---|---|
| 6 | 0.000000 | 0.000000 | 0.649746 |
| 6 | 0.000000 | 0.000000 | -0.649746 |
| 7 | 0.000000 | 0.000000 | 1.886319 |
| 7 | 0.000000 | 0.000000 | -1.886319 |

EOM-CCSD

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

**Ground-state**
\[ E = -185.39743709 \ (T_{1}^{\text{diag}} = 0.013)  
\]

|  |  |  |  |
|---|---|---|---|
| 6 | 0.000000 | 0.000000 | 0.695815 |
| 6 | 0.000000 | 0.000000 | -0.695815 |
| 7 | 0.000000 | 0.000000 | 1.848335 |
| 7 | 0.000000 | 0.000000 | -1.848335 |

**Excited-state**
\[ E = -185.176305575 \ (T_{1}^{\text{diag}} = 0.014)  
\]

|  |  |  |  |
|---|---|---|---|
| 6 | 0.000000 | 0.000000 | 0.652704 |
| 6 | 0.000000 | 0.000000 | -0.652704 |
| 7 | 0.000000 | 0.000000 | 1.876127 |
| 7 | 0.000000 | 0.000000 | -1.876127 |
Table S25: Selected geometrical parameters (bond lengths in Å, valence angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). Δ gives the difference between the two states (in eV for the ΔZPVE).

| Method                  | State | PG | ZPVE | C≡C | C-C | C-H | C≡C-C | C≡C-H | Ref.            |
|-------------------------|-------|----|------|-----|-----|-----|-------|-------|-----------------|
| CCSD/def2-TZVPP         | GS    | D_{och} | 0.037864 | 1.204 | 1.380 | 1.060 | 180.0 | 180.0 | This work       |
|                         | ES (A_u) | C_{2h} | 0.033103 | 1.287 | 1.298 | 1.078 | 167.3 | 133.1 |                 |
|                         | Δ      |       | -0.130 | 0.083 | -0.082 | 0.018 | -12.7 | -46.9 |                 |
|                         | ES (Δ_u) | D_{och} | 0.032376 | 1.266 | 1.301 | 1.059 | 180.0 | 180.0 |                 |
|                         | Δ      |       | -0.149 | 0.062 | -0.079 | -0.001 | 0.0 | 0.0 |                 |
| CCSD/aug-cc-pVTZ        | GS    | D_{och} | 1.292 | 1.374 | 1.059 | 180.0 | 180.0 |       | This work       |
|                         | ES (A_u) | C_{2h} | 1.283 | 1.294 | 1.075 | 167.0 | 133.9 |       |                 |
|                         | Δ      |       | 0.081 | -0.080 | 0.016 | -13.0 | -46.1 |       |                 |
|                         | ES (Δ_u) | D_{och} | 1.263 | 1.297 | 1.059 | 180.0 | 180.0 |       |                 |
|                         | Δ      |       | 0.061 | -0.077 | 0.000 | 0.0 | 0.0 |       |                 |
| CCSDR(3)/def2-TZVPP     | GS    | D_{och} | 1.213 | 1.377 | 1.062 | 180.0 | 180.0 |       | This work       |
|                         | ES (A_u) | C_{2h} | 1.301 | 1.301 | 1.082 | 165.5 | 130.5 |       |                 |
|                         | Δ      |       | 0.088 | -0.076 | 0.020 | -14.5 | -49.5 |       |                 |
|                         | ES (Δ_u) | D_{och} | 1.275 | 1.302 | 1.061 | 180.0 | 180.0 |       |                 |
|                         | Δ      |       | 0.062 | -0.075 | -0.001 | 0.0 | 0.0 |       |                 |
| CCSDR(3)/aug-cc-pVTZ    | GS    | D_{och} | 1.211 | 1.371 | 1.061 | 180.0 | 180.0 |       | This work       |
|                         | ES (A_u) | C_{2h} | 1.296 | 1.296 | 1.079 | 165.2 | 131.2 |       |                 |
|                         | Δ      |       | 0.085 | -0.075 | 0.018 | -14.8 | -48.8 |       |                 |
|                         | ES (Δ_u) | D_{och} | 1.272 | 1.298 | 1.061 | 180.0 | 180.0 |       |                 |
|                         | Δ      |       | 0.061 | -0.073 | 0.000 | 0.0 | 0.0 |       |                 |
| CC3/def2-TZVPP          | GS    | D_{och} | 1.214 | 1.376 | 1.062 | 180.0 | 180.0 |       | This work       |
|                         | ES (A_u) | C_{2h} | 1.277 | 1.301 | 1.062 | 168.0 | 180.0 |       |                 |
|                         | Δ      |       | 0.063 | -0.075 | 0.000 | 0.0 | 0.0 |       |                 |
| CC3/aug-cc-pVTZ         | GS    | D_{och} | 1.212 | 1.370 | 1.061 | 180.0 | 180.0 |       | This work       |
|                         | ES (Δ_u) | D_{och} | 1.275 | 1.297 | 1.062 | 180.0 | 180.0 |       |                 |
|                         | Δ      |       | 0.063 | -0.073 | 0.001 | 0.0 | 0.0 |       |                 |
| CI/TZ+d                 | GS    | D_{och} | 1.198 | 1.378 | 1.062 | 180.0 | 180.0 |       | 63^c           |
|                         | ES (A_u) | C_{2h} | 1.288 | 1.286 | 1.082 | 167.1 | 131.4 |       |                 |
|                         | Δ      |       | 0.090 | -0.092 | 0.020 | -12.9 | -48.6 |       |                 |
| CASSCF/6-31G(d)         | GS    | D_{och} | 1.212 | 1.383 | 1.077 | 180.0 | 180.0 |       | 55             |
|                         | ES (A_u) | C_{2h} | 1.303 | 1.295 | 1.097 | 163.9 | 129.9 |       |                 |
|                         | Δ      |       | 0.091 | -0.088 | 0.020 | -16.1 | -50.1 |       |                 |
| Experiment              | ES (A_u) | C_{2h} |       |       |       |       |       |       | 135^c          |
|                         | ES (Δ_u) | D_{och} |       |       |       | ~180^c | ~180^c |       | 64             |

*aIn this work, a B_u ES close to a ∆_u one (angles > 165°) is also reported, but it was obtained with a smaller basis set, namely, 4-31G; ^bAssuming 180° for the C≡C angle; ^cReported to be mostly linear with some cumulenic character.
Cartesian coordinates

CC3

CC3/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

|          |       |       |       |
|----------|-------|-------|-------|
| Ground-state | $E = -153.28161102$ |       |       |
| 6        | 0.000000 0.000000 0.685008 |
| 6        | 0.000000 0.000000 -0.685008 |
| 6        | 0.000000 0.000000 1.896827 |
| 6        | 0.000000 0.000000 -1.896827 |
| 1        | 0.000000 0.000000 2.957799 |
| 1        | 0.000000 0.000000 -2.957799 |

| Excited-state ($\Delta_u$) | $E = -153.09238859$ |       |       |
| 6        | 0.000000 0.000000 0.648263 |
| 6        | 0.000000 0.000000 -0.648263 |
| 6        | 0.000000 0.000000 1.923287 |
| 6        | 0.000000 0.000000 -1.923287 |
| 1        | 0.000000 0.000000 2.985066 |
| 1        | 0.000000 0.000000 -2.985066 |

CCSDR(3)

CCSDR(3)/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

|          |       |       |       |
|----------|-------|-------|-------|
| Ground-state | $E = -153.27946330$ |       |       |
| 6        | 0.000000 0.000000 0.685369 |
| 6        | 0.000000 0.000000 -0.685369 |
| 6        | 0.000000 0.000000 1.896260 |
| 6        | 0.000000 0.000000 -1.896260 |
| 1        | 0.000000 0.000000 2.957059 |
| 1        | 0.000000 0.000000 -2.957059 |

| Excited-state ($A_u$) | $E = -153.11459388$ |       |       |
| 6        | -0.081220 1.928309 0.000000 |
| 6        | 0.084627 0.642563 0.000000 |
| 6        | -0.084627 -0.642563 0.000000 |
| 6        | 0.081220 -1.928309 0.000000 |
| 1        | 0.632710 2.737929 0.000000 |
| 1        | -0.632710 -2.737929 0.000000 |
EOM-CCSD

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

**Ground-state**

\[ E = -153.24037940 \quad (T_1^{\text{diag}} = 0.012) \]

|  |  |  |  |
|---|---|---|---|
| 6 | 0.000000 | 0.000000 | 1.894407 |
| 6 | 0.000000 | 0.000000 | 0.689976 |
| 6 | 0.000000 | 0.000000 | -0.689976 |
| 6 | 0.000000 | 0.000000 | -1.894407 |
| 1 | 0.000000 | 0.000000 | 2.954086 |
| 1 | 0.000000 | 0.000000 | -2.954086 |

**Excited-state \((A_u)\)**

\[ E = -153.06770842 \quad (T_1^{\text{diag}} = 0.016) \]

|  |  |  |  |
|---|---|---|---|
| 6 | -0.071249 | 1.924696 | 0.000000 |
| 6 | 0.071249 | 0.645205 | 0.000000 |
| 6 | -0.071249 | -0.645205 | 0.000000 |
| 6 | 0.071249 | -1.924696 | 0.000000 |
| 1 | 0.630278 | 2.743402 | 0.000000 |
| 1 | -0.630278 | -2.743402 | 0.000000 |

**Excited-state \((\Delta_u)\)**

\[ E = -153.04365092 \quad (T_1^{\text{diag}} = 0.013) \]

|  |  |  |  |
|---|---|---|---|
| 6 | 0.000000 | 0.000000 | 1.915946 |
| 6 | 0.000000 | 0.000000 | 0.650270 |
| 6 | 0.000000 | 0.000000 | -0.650270 |
| 6 | 0.000000 | 0.000000 | -1.915946 |
| 1 | 0.000000 | 0.000000 | 2.975250 |
| 1 | 0.000000 | 0.000000 | -2.975250 |
Table S26: Selected geometrical parameters (bond lengths in Å, valence angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). ∆ gives the difference between the two states (in eV for the $\Delta ZPVE$). The considered ES is the lowest $A_u$ state of $n \rightarrow \pi^*$ nature.

| Method                | State | PG | ZPVE  | C=O   | C-C   | C-H   | C-C=O | C-C-H | Ref. |
|-----------------------|-------|----|-------|-------|-------|-------|-------|-------|------|
| CCSD/def2-TZVPP       | GS    | $C_{2h}$ | 0.037744 | 1.201 | 1.519 | 1.098 | 121.4 | 115.1 | This work |
|                       | ES    | $C_{2h}$ | 0.034916 | 1.226 | 1.491 | 1.092 | 123.7 | 113.8 | |
|                       | ∆     |       | -0.077 | 0.025 | -0.027 | -0.006 | 2.3 | -1.3 | |
| CCSDR(3)/def2-TZVPP   | GS    | $C_{2h}$ | 1.208 | 1.520 | 1.100 | 121.4 | 115.1 | This work |
|                       | ES    | $C_{2h}$ | 1.238 | 1.485 | 1.094 | 123.5 | 114.3 | |
|                       | ∆     |       | 0.030 | -0.035 | -0.006 | 2.1 | -0.8 | |
| CCSD/TZ2P             | GS    | $C_{2h}$ | 1.203 | 1.524 | 1.098 | 121.2 | 115.4 | 66 |
|                       | ES    | $C_{2h}$ | 1.229 | 1.496 | 1.098 | 123.5 | 114.0 | |
|                       | ∆     |       | 0.026 | -0.028 | 0.000 | 2.3 | -1.4 | |
| SAC-CI/[4s2p1d/2s] + [2s2p] | GS    | $C_{2h}$ | 1.208 | 1.527 | 121.1 | 114.9 | 53 |
|                       | ES    | $C_{2h}$ | 1.227 | 1.500 | 123.8 | 113.6 | |
|                       | ∆     |       | 0.019 | -0.027 | 2.7 | -1.3 | |
| Experiment            | GS    | $C_{2h}$ | 1.22 | 1.50 | 1.07 | 122 | 120 | 54 |
|                       | ES    | $C_{2h}$ | 1.32 | 1.40 | 1.07 | 125 | 120 | |
|                       | ∆     |       | 0.10 | -0.10 | 0.00 | 3 | 0 | |
| Experiment            | GS    | $C_{2h}$ | 1.202 | 1.527 | 1.109 | 121.2 | 115.5 | 67 |
|                       | ES    | $C_{2h}$ | 1.252 | 1.460 | 1.115 | 123.7 | 114.4 | |
|                       | ∆     |       | 0.050 | -0.067 | 0.006 | 2.5 | -1.1 | |
Cartesian coordinates

CCSDR(3)

CCSDR(3)/\textit{def2}-TZVPP total energies (au) and Cartesian coordinates (Å).

\begin{tabular}{cccc}
\textbf{Ground-state} & & \\
$E= -227.57233864$ & & \\
6 & 0.328117 & 0.000000 & 0.685413 \\
6 & 0.328117 & 0.000000 & -0.685413 \\
8 & 0.330606 & 0.000000 & 1.698437 \\
8 & -0.330606 & 0.000000 & -1.698437 \\
1 & -1.428958 & 0.000000 & 0.675442 \\
1 & 1.428958 & 0.000000 & -0.675442 \\
\end{tabular}

\begin{tabular}{cccc}
\textbf{Excited-state} & & \\
$E= -227.46768112$ & & \\
6 & 0.318173 & 0.000000 & 0.670611 \\
6 & 0.318173 & 0.000000 & -0.670611 \\
8 & 0.319770 & 0.000000 & 1.731629 \\
8 & -0.319770 & 0.000000 & -1.731629 \\
1 & -1.412063 & 0.000000 & 0.649357 \\
1 & 1.412063 & 0.000000 & -0.649357 \\
\end{tabular}

EOM-CCSD

(EOM)-CCSD/\textit{def2}-TZVPP total energies (au) and Cartesian coordinates (Å).

\begin{tabular}{cccc}
\textbf{Ground-state} & & \\
$E= -227.53681420$ ($T_1^{\text{diag}} = 0.014$) & & \\
6 & -0.327553 & 0.685066 & 0.000000 \\
6 & 0.327553 & -0.685066 & 0.000000 \\
8 & 0.327553 & 1.691471 & 0.000000 \\
8 & -0.327553 & -1.691471 & 0.000000 \\
1 & -1.425864 & 0.675808 & 0.000000 \\
1 & 1.425864 & -0.675808 & 0.000000 \\
\end{tabular}

\begin{tabular}{cccc}
\textbf{Excited-state} & & \\
$E= -227.42743418$ ($T_1^{\text{diag}} = 0.014$) & & \\
6 & -0.317190 & 0.674875 & 0.000000 \\
6 & 0.317190 & -0.674875 & 0.000000 \\
8 & 0.317190 & 1.724385 & 0.000000 \\
8 & -0.317190 & -1.724385 & 0.000000 \\
1 & -1.408993 & 0.647776 & 0.000000 \\
1 & 1.408993 & -0.647776 & 0.000000 \\
\end{tabular}
S27  Maleimide
Table S27: Selected geometrical parameters (bond lengths in Å, valence angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). ∆ gives the difference between the two states (in eV for the $\Delta^{ZPVE}$). The considered ES is the lowest $B_1$ state of $n \rightarrow \pi^*$ nature.

| Method           | State | PG  | ZPVE  | N-C  | C=O  | C-C  | C=C  | N-H  | C-H  | C-N-C | N-C=O | C-C=O | Ref. |
|------------------|-------|-----|-------|------|------|------|------|------|------|-------|-------|-------|------|
| CCSD/def2-TZVPP  | GS    | $C_{2v}$ | 0.069528 | 1.388 | 1.199 | 1.500 | 1.331 | 1.002 | 1.075 | 111.8 | 126.5 | 108.8 | This work |
|                  | ES    | $C_{2v}$ | 0.064739 | 1.400 | 1.237 | 1.436 | 1.371 | 1.003 | 1.072 | 110.0 | 119.6 | 108.7 | This work |
|                  | Δ     |       | -0.130 | 0.012 | 0.038 | -0.064 | 0.040 | 0.001 | -0.003 | -1.8 | -6.9 | -0.1 | |
| CCSDR(3)/def2-TZVPP | GS    | $C_{2v}$ | 1.393 | 1.207 | 1.502 | 1.339 | 1.005 | 1.077 | 111.8 | 126.4 | 108.8 | |
|                  | ES    | $C_{2v}$ | 1.404 | 1.248 | 1.432 | 1.386 | 1.006 | 1.074 | 109.8 | 119.3 | 108.5 | |
|                  | Δ     |       | 0.011 | 0.041 | -0.070 | 0.047 | 0.001 | -0.003 | -2.0 | -7.1 | -0.3 | |
| CASSCF/[4s3p1d/2s1p] | GS    | $C_{2v}$ | 1.383 | 1.193 | 1.492 | 1.339 | 0.994 | 1.071 | 111.8 | 126.2 | 108.6 | 69 |
|                  | ES    | $C_{2v}$ | 1.407 | 1.214 | 1.419 | 1.384 | 0.995 | 1.068 | 109.0 | 117.4 | 108.8 | |
|                  | Δ     |       | 0.024 | 0.021 | -0.073 | 0.045 | 0.001 | -0.003 | -2.8 | -8.8 | 0.2 | |
| CC2/TZVP         | ES    | $C_{2v}$ | 1.406 | 1.278 | 1.421 | 1.399 | 1.077 | 109.2 | 117.8 | 108.3 | |

This work

69

70
Cartesian coordinates

CCSDR(3)

CCSDR(3)/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

| Ground-state |  |  |  |
|--------------|--------------------------|--------------------------|
|              |  |  |  |
|              |  |  |  |
| 7            | 0.000000                | 0.000000                | -0.915399                |
| 6            | 0.000000                | 1.153337                | -0.135024                |
| 6            | 0.000000                | -1.153337               | -0.135024                |
| 6            | 0.000000                | 0.669606                | 1.286494                 |
| 6            | 0.000000                | -0.669606               | 1.286494                 |
| 8            | 0.000000                | 2.290933                | -0.537913                |
| 8            | 0.000000                | -2.290933               | -0.537913                |
| 1            | 0.000000                | 0.000000                | -1.920406                |
| 1            | 0.000000                | 1.351770                | 2.119378                 |
| 1            | 0.000000                | -1.351770               | 2.119378                 |

| Excited-state |  |  |  |
|---------------|--------------------------|--------------------------|
|  |  |  |  |
| 7            | 0.000000                | 0.000000                | -0.876795                |
| 6            | 0.000000                | 1.148083                | -0.069346                |
| 6            | 0.000000                | -1.148083               | -0.069346                |
| 6            | 0.000000                | 0.692977                | 1.288779                 |
| 6            | 0.000000                | -0.692977               | 1.288779                 |
| 8            | 0.000000                | 2.273538                | -0.609107                |
| 8            | 0.000000                | -2.273538               | -0.609107                |
| 1            | 0.000000                | 0.000000                | -1.882367                |
| 1            | 0.000000                | 1.364983                | 2.126662                 |
| 1            | 0.000000                | -1.364983               | 2.126662                 |
### EOM-CCSD

(EOM)-CCSD/\textit{def2}-TZVPP total energies (au) and Cartesian coordinates (Å).

#### Ground-state

\[ E = -358.95581207 \quad (T_{1}^{\text{diag}} = 0.014) \]

|  |  |  |  |
|---|---|---|---|
| 7 | 0.000000 | 0.000000 | 0.936101 |
| 6 | 0.000000 | 1.149288 | 0.158629 |
| 6 | 0.000000 | -1.149288 | 0.158629 |
| 6 | 0.000000 | 0.665674 | -1.261424 |
| 6 | 0.000000 | -0.665674 | -1.261424 |
| 8 | 0.000000 | 2.280263 | 0.557992 |
| 8 | 0.000000 | -2.280263 | 0.557992 |
| 1 | 0.000000 | 0.000000 | 1.938303 |
| 1 | 0.000000 | 1.346591 | -2.092673 |
| 1 | 0.000000 | -1.346591 | -2.092673 |

#### Excited-state

\[ E = -358.81511923 \quad (T_{1}^{\text{diag}} = 0.015) \]

|  |  |  |  |
|---|---|---|---|
| 7 | 0.000000 | 0.000000 | 0.899202 |
| 6 | 0.000000 | 1.146226 | 0.096031 |
| 6 | 0.000000 | -1.146226 | 0.096031 |
| 6 | 0.000000 | 0.685367 | -1.263469 |
| 6 | 0.000000 | -0.685367 | -1.263469 |
| 8 | 0.000000 | 2.263799 | 0.625681 |
| 8 | 0.000000 | -2.263799 | 0.625681 |
| 1 | 0.000000 | 0.000000 | 1.902141 |
| 1 | 0.000000 | 1.357294 | -2.099100 |
| 1 | 0.000000 | -1.357294 | -2.099100 |
## Table S28: Selected geometrical parameters (bond lengths in Å, valence angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). ∆ gives the difference between the two states (in eV for the $\Delta ZPVE$). The considered ES is the lowest $A^*$ state of $n \rightarrow \pi^*$ nature.

| Method                  | State | PG  | ZPVE  | C-O1 | C=O2 | C-C | C=C | C-C=O2 | C=C=O | O2=C-O1 | Ref.    |
|-------------------------|-------|-----|-------|------|------|-----|-----|-------|-------|---------|---------|
| CCSD/def2-TZVPP         | GS    | $C_s$ | 0.054448 | 1.249 | 1.246 | 1.534 | 1.332 | 116.4 | 123.7 | 129.7   | This work |
|                         | ES    | $C_s$ | 0.051258 | 1.292 | 1.296 | 1.398 | 1.393 | 126.3 | 124.8 | 105.8   |         |
|                         | Δ     |       | -0.087 | 0.043 | 0.050 | -0.136 | 0.061 | 9.9   | 1.1   | -23.9   |         |
| CCSDR(3)/def2-TZVPP     | GS    | $C_s$ | 1.256  | 1.253 | 1.536 | 1.339 | 116.3 | 123.5 | 129.7   | This work |
|                         | ES    | $C_s$ | 1.300  | 1.307 | 1.398 | 1.411 | 126.6 | 124.0 | 105.2   |         |
|                         | Δ     |       | 0.044  | 0.054 | -0.138 | 0.072 | 10.3  | 0.5   | -24.5   |         |
| CASPT2/6-31+G(d)        | GS    | $C_s$ | 1.272  | 1.266 | 1.526 | 1.343 | 116.8 | 124.0 | 129.0   | 52      |
|                         | ES    | $C_s$ | 1.272  | 1.394 | 1.401 | 1.409 | 117.3 | 126.7 | 111.8   |         |
|                         | Δ     |       | 0.000  | 0.128 | -0.125 | 0.066 | 0.5   | 2.7   | -17.2   |         |
| CC2/cc-pVTZ             | GS    | $C_s$ | 1.265  | 1.261 | 1.521 | 1.324 | 123.5 | 129.6 | 102.3   | 32      |
|                         | ES    | $C_s$ | 1.311  | 1.331 | 1.385 | 1.415 | 123.4 | 129.6 | 102.3   |         |
|                         | Δ     |       | 0.046  | 0.070 | -0.136 | 0.091 | 0.01  | -27.3 | -27.3   |         |
| CASPT2/cc-pVTZ          | GS    | $C_s$ | 1.260  | 1.253 | 1.531 | 1.338 | 123.7 | 129.7 | 104.0   | 32      |
|                         | ES    | $C_s$ | 1.309  | 1.299 | 1.387 | 1.412 | 124.7 | 104.0 |         |         |
|                         | Δ     |       | 0.049  | 0.046 | -0.144 | 0.074 | 1.0   | -25.7 | -25.7   |         |
| VMC/pVTZ'               | GS    | $C_s$ | 1.245  | 1.241 | 1.526 | 1.324 | 124.0 | 129.7 | 107.2   | 32      |
|                         | ES    | $C_s$ | 1.291  | 1.284 | 1.379 | 1.401 | 124.5 | 107.2 |         |         |
|                         | Δ     |       | 0.046  | 0.043 | -0.147 | 0.077 | 0.5   | -22.5 | -22.5   |         |
Cartesian coordinates

CCSDR(3)

CCSDR(3)/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

|   |   |   |   |
|---|---|---|---|
| 6 | -0.574782 | -0.797222 | 0.000000 |
| 6 | 0.000038 | 0.627351 | 0.000000 |
| 6 | 0.183068 | -1.900735 | 0.000000 |
| 8 | -0.873438 | 1.529975 | 0.000000 |
| 8 | 1.249103 | 0.722684 | 0.000000 |
| 1 | -1.657836 | -0.872473 | 0.000000 |
| 1 | -0.242896 | -2.898101 | 0.000000 |
| 1 | 1.259927 | -1.790885 | 0.000000 |

Excited-state
\(E= -266.17678301\)

|   |   |   |   |
|---|---|---|---|
| 6 | -0.716572 | -0.704457 | 0.000000 |
| 6 | -0.003516 | 0.497537 | 0.000000 |
| 6 | -0.113605 | -1.979663 | 0.000000 |
| 8 | -0.473032 | 1.710021 | 0.000000 |
| 8 | 1.296498 | 0.632527 | 0.000000 |
| 1 | -1.796073 | -0.606637 | 0.000000 |
| 1 | -0.711668 | -2.880100 | 0.000000 |
| 1 | 0.962249 | -2.083083 | 0.000000 |

EOM-CCSD

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

|   |   |   |   |
|---|---|---|---|
| 6 | -0.570722 | -0.798142 | 0.000000 |
| 6 | 0.000000 | 0.626077 | 0.000000 |
| 6 | 0.182196 | -1.896744 | 0.000000 |
| 8 | -0.870659 | 1.521563 | 0.000000 |
| 8 | 1.242008 | 0.724644 | 0.000000 |
| 1 | -1.651405 | -0.871775 | 0.000000 |
| 1 | -0.245695 | -2.891149 | 0.000000 |
| 1 | 1.257461 | -1.793879 | 0.000000 |
Excited-state

\[ E = -266.118696756 \ (T_{1}^{\text{diag}} = 0.017) \]

|   | \( -0.703577 \) | \(-0.709700\) | \(0.000000\) |
|---|-----------------|-------------|-------------|
| 6 | 0.000000        | 0.498416    | 0.000000    |
| 6 | \(-0.115357\)  | \(-1.972390\) | \(0.000000\) |
| 8 | \(-0.481791\)  | 1.697675    | \(0.000000\) |
| 8 | 1.288989        | 0.635500    | \(0.000000\) |
| 1 | \(-1.780808\)  | \(-0.609178\) | \(0.000000\) |
| 1 | \(-0.719783\)  | \(-2.865998\) | \(0.000000\) |
| 1 | 0.956608        | \(-2.088182\) | \(0.000000\) |
Table S29: Selected geometrical parameters (bond lengths in Å, valence angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). Δ gives the difference between the two states (in eV for the Δ_{ZPVE}). The considered ES is the lowest B_{3u} state of n → π* nature.

| Method         | State     | PG  | ZPVE         | C=C  | C=N  | C-H  | C=N=C  | Ref.       |
|----------------|-----------|-----|--------------|------|------|------|--------|-----------|
| CCSD/def2-TZVPP| GS        | D_{2h} | 0.077723     | 1.390| 1.331| 1.079| 115.7  | This work |
|                | ES (B_{3u})| D_{2h} | 0.069771     | 1.391| 1.338| 1.078| 119.7  |           |
|                | Δ         |       | -0.216       | 0.001| 0.007| -0.001| 4.0     |           |
| CCSDR(3)/def2-TZVPP| GS       | D_{2h} | 1.395        | 1.338| 1.081| 115.4 |         | This work |
|                | ES (B_{3u})| D_{2h} | 1.396        | 1.346| 1.080| 119.5 |         |           |
|                | Δ         |       | 0.001        | 0.008| -0.001| 4.1   |         |           |
Cartesian coordinates

CCSDR(3)

CCSDR(3)/\textit{def2}-TZVPP total energies (au) and Cartesian coordinates (Å).

**Ground-state**

\[E= -263.97826962\]

|   |   |   |   |
|---|---|---|---|
| 6 | 0.000000 | 0.697706 | 1.130422 |
| 6 | 0.000000 | -0.697706 | 1.130422 |
| 6 | 0.000000 | 0.697706 | -1.130422 |
| 6 | 0.000000 | -0.697706 | -1.130422 |
| 7 | 0.000000 | 1.412960 | 0.000000 |
| 7 | 0.000000 | -1.412960 | 0.000000 |
| 1 | 0.000000 | 1.249272 | 2.060689 |
| 1 | 0.000000 | -1.249272 | 2.060689 |
| 1 | 0.000000 | 1.249272 | -2.060689 |
| 1 | 0.000000 | -1.249272 | -2.060689 |

**Excited-state**

\[E= -263.82667276\]

|   |   |   |   |
|---|---|---|---|
| 6 | 0.000000 | 0.698005 | 1.162566 |
| 6 | 0.000000 | 0.698005 | -1.162566 |
| 6 | 0.000000 | -0.698005 | 1.162566 |
| 6 | 0.000000 | -0.698005 | -1.162566 |
| 7 | 0.000000 | 1.376506 | 0.000000 |
| 7 | 0.000000 | -1.376506 | 0.000000 |
| 1 | 0.000000 | 1.222433 | 2.106518 |
| 1 | 0.000000 | 1.222433 | -2.106518 |
| 1 | 0.000000 | -1.222433 | 2.106518 |
| 1 | 0.000000 | -1.222433 | -2.106518 |
**EOM-CCSD**

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

**Ground-state**

\[ E = -263.92104990 \ (T_{1}^{\text{diag}} = 0.010) \]

|   |   |   |   |
|---|---|---|---|
| 6 | 0.000000 | 1.126153 | 0.695167 |
| 6 | 0.000000 | 1.126153 | -0.695167 |
| 6 | 0.000000 | -1.126153 | -0.695167 |
| 6 | 0.000000 | -1.126153 | 0.695167 |
| 7 | 0.000000 | 0.000000 | -1.403646 |
| 7 | 0.000000 | 0.000000 | 1.403646 |
| 1 | 0.000000 | 2.054503 | 1.245639 |
| 1 | 0.000000 | 2.054503 | -1.245639 |
| 1 | 0.000000 | -2.054503 | -1.245639 |
| 1 | 0.000000 | -2.054503 | 1.245639 |

**Excited-state**

\[ E = -263.76516835 \ (T_{1}^{\text{diag}} = 0.010) \]

|   |   |   |   |
|---|---|---|---|
| 6 | 0.000000 | 1.157047 | 0.695354 |
| 6 | 0.000000 | 1.157047 | -0.695354 |
| 6 | 0.000000 | -1.157047 | -0.695354 |
| 6 | 0.000000 | -1.157047 | 0.695354 |
| 7 | 0.000000 | 0.000000 | -1.367960 |
| 7 | 0.000000 | 0.000000 | 1.367960 |
| 1 | 0.000000 | 2.099318 | 1.218231 |
| 1 | 0.000000 | 2.099318 | -1.218231 |
| 1 | 0.000000 | -2.099318 | -1.218231 |
| 1 | 0.000000 | -2.099318 | 1.218231 |
Table S30: Selected geometrical parameters (bond lengths in Å, valence angle in degrees). The $C_{2v}$ point group was enforced for the excited-state. This is why no ZPVE is provided here - all ES present imaginary frequencies. $\Delta$ gives the difference between the two states. The considered ES is the lowest $B_2$ state of $\pi \rightarrow \pi^*$ nature.

| Method                  | State | PG | C-N   | C-H   | N-H$_1$ | N-H$_2$ | N-C-N | Ref.       |
|-------------------------|-------|----|-------|-------|--------|--------|-------|------------|
| CCSD/def2-TZVPP         | GS    | $C_{2v}$ | 1.305 | 1.079 | 1.007 | 1.005 | 125.1 | This work |
|                         | ES    | $C_{2v}$ | 1.412 | 1.067 | 1.010 | 1.009 | 108.1 | This work |
|                         | $\Delta$ |       | 0.107 | -0.012 | 0.003 | 0.004 | -17.0 |            |
| CCSD/aug-cc-pVTZ        | GS    | $C_{2v}$ | 1.303 | 1.078 | 1.005 | 1.006 | 125.2 | This work |
|                         | ES    | $C_{2v}$ | 1.404 | 1.067 | 1.010 | 1.010 | 108.3 |            |
|                         | $\Delta$ |       | 0.101 | -0.011 | 0.005 | 0.004 | -16.9 |            |
| CCSDR(3)/def2-TZVPP     | GS    | $C_{2v}$ | 1.309 | 1.081 | 1.007 | 1.009 | 125.0 | This work |
|                         | ES    | $C_{2v}$ | 1.426 | 1.070 | 1.012 | 1.011 | 107.7 |            |
|                         | $\Delta$ |       | 0.115 | -0.011 | 0.005 | 0.002 | -17.3 |            |
| CCSDR(3)/aug-cc-pVTZ    | GS    | $C_{2v}$ | 1.308 | 1.079 | 1.007 | 1.008 | 125.1 | This work |
|                         | ES    | $C_{2v}$ | 1.418 | 1.068 | 1.012 | 1.012 | 107.8 |            |
|                         | $\Delta$ |       | 0.110 | -0.011 | 0.005 | 0.004 | -17.2 |            |
| CC3/def2-TZVPP          | GS    | $C_{2v}$ | 1.310 | 1.081 | 1.007 | 1.009 | 125.0 | This work |
|                         | ES    | $C_{2v}$ | 1.428 | 1.070 | 1.012 | 1.012 | 107.6 |            |
|                         | $\Delta$ |       | 0.118 | -0.011 | 0.005 | 0.003 | -17.4 |            |
| CC3/aug-cc-pVTZ         | GS    | $C_{2v}$ | 1.309 | 1.079 | 1.007 | 1.009 | 125.1 | This work |
|                         | ES    | $C_{2v}$ | 1.420 | 1.069 | 1.012 | 1.012 | 107.7 |            |
|                         | $\Delta$ |       | 0.111 | -0.010 | 0.005 | 0.003 | -17.4 |            |
Cartesian coordinates

CCSDR(3)
CCSDR(3)/\textit{aug}-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

**Ground-state**

\[ E = -150.2073345 \]

|   | x  | y  | z       |
|---|----|----|---------|
| 6 | 0.000000 | 0.000000 | 0.425509 |
| 7 | 0.000000 | 1.160622 | -0.425509 |
| 7 | 0.000000 | -1.160622 | -0.425509 |
| 1 | 0.000000 | 0.000000 | 1.504585 |
| 1 | 0.000000 | 1.160622 | -1.181715 |
| 1 | 0.000000 | -1.160622 | -1.181715 |
| 1 | 0.000000 | 2.007051 | 0.367411 |
| 1 | 0.000000 | -2.007051 | 0.367411 |

**Excited-state**

\[ E = -149.97641225 \]

|   | x  | y  | z       |
|---|----|----|---------|
| 6 | 0.000000 | 0.000000 | 0.599834 |
| 7 | 0.000000 | 1.145269 | -0.235591 |
| 7 | 0.000000 | -1.145269 | -0.235591 |
| 1 | 0.000000 | 0.000000 | 1.668191 |
| 1 | 0.000000 | 1.049253 | -1.242668 |
| 1 | 0.000000 | -1.049253 | -1.242668 |
| 1 | 0.000000 | 2.081660 | 0.147374 |
| 1 | 0.000000 | -2.081660 | 0.147374 |

EOM-CCSD

(EOM)-CCSD/\textit{def}2-TZVPP total energies (au) and Cartesian coordinates (Å).

**Ground-state**

\[ E = -150.18225360 \]

\[ T_{1}^{\text{diag}} = 0.012 \]

|   | x  | y  | z       |
|---|----|----|---------|
| 6 | 0.000000 | 0.000000 | 0.426290 |
| 7 | 0.000000 | 1.158150 | -0.174843 |
| 7 | 0.000000 | -1.158150 | -0.174843 |
| 1 | 0.000000 | 0.000000 | 1.505660 |
| 1 | 0.000000 | 1.252313 | -1.176928 |
| 1 | 0.000000 | -1.252313 | -1.176928 |
| 1 | 0.000000 | 2.002779 | 0.369129 |
| 1 | 0.000000 | -2.002779 | 0.369129 |
**Excited-state**

\[ E = -149.93960246 \ (T_{1}^{\text{diag}} = 0.016) \]

|   |       |       |       |
|---|-------|-------|-------|
| 6 | 0.000000 | 0.000000 | 0.603587 |
| 7 | 0.000000 | 1.143283 | -0.225486 |
| 7 | 0.000000 | -1.143283 | -0.225486 |
| 1 | 0.000000 | 0.000000 | 1.672170 |
| 1 | 0.000000 | 1.053101 | -1.230444 |
| 1 | 0.000000 | -1.053101 | -1.230444 |
| 1 | 0.000000 | 2.075699 | 0.162000 |
| 1 | 0.000000 | -2.075699 | 0.162000 |
Table S31: Selected geometrical parameters (bond lengths in Å, valence angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). ∆ gives the difference between the two states (in eV for the $\Delta^{ZPVE}$). The considered ES is the lowest $B_{3u}$ state of $n \rightarrow \pi^*$ nature. The values in italics corresponding to the CC3/aug-cc-pVTZ geometries have been extrapolated (see the main text for details).

| Method                     | State | PG    | ZPVE  | N=N  | C=N  | C-H  | N=C=N | Ref.     |
|----------------------------|-------|-------|-------|------|------|------|-------|----------|
| CCSD/def2-TZVPP            | GS    | $D_{2h}$ | 0.052185 | 1.314 | 1.330 | 1.077 | 126.4 | This work |
|                            | ES    | $D_{2h}$ | 0.049001 | 1.310 | 1.325 | 1.075 | 121.1 |          |
|                            | $\Delta$ |       | -0.087 | -0.004 | -0.005 | -0.002 | -5.3 |          |
| CCSDR(3)/def2-TZVPP        | GS    | $D_{2h}$ | 1.326 | 1.338 | 1.079 | 126.8 | This work |
|                            | ES    | $D_{2h}$ | 1.320 | 1.332 | 1.077 | 121.4 |          |
|                            | $\Delta$ |       | -0.006 | -0.006 | -0.002 | -5.4 |          |
| CCSDR(3)/aug-cc-pVTZ       | GS    | $D_{2h}$ | 1.321 | 1.335 | 1.077 | 126.7 | This work |
|                            | ES    | $D_{2h}$ | 1.316 | 1.330 | 1.075 | 121.2 |          |
|                            | $\Delta$ |       | -0.005 | -0.005 | -0.002 | -5.5 |          |
| CC3/def2-TZVPP             | GS    | $D_{2h}$ | 1.327 | 1.339 | 1.079 | 126.9 | This work |
|                            | ES    | $D_{2h}$ | 1.323 | 1.334 | 1.077 | 121.6 |          |
|                            | $\Delta$ |       | -0.004 | -0.005 | -0.002 | -5.3 |          |
| CC3/aug-cc-pVTZ            | GS    | $D_{2h}$ | 1.323 | 1.336 | 1.078 | 126.7 | This work |
|                            | ES    | $D_{2h}$ | 1.319 | 1.331 | 1.077 | 121.4 |          |
|                            | $\Delta$ |       | -0.004 | -0.005 | -0.001 | -5.3 |          |
| CASPT2/[14s9p4d/4s3p2d]    | GS    | $D_{2h}$ | 1.325 | 1.339 | 1.074 | 126.6 | 71 |
|                            | ES    | $D_{2h}$ | 1.321 | 1.333 | 1.073 | 121.5 |          |
|                            | $\Delta$ |       | -0.004 | -0.006 | -0.001 | -5.1 |          |
| CCSD/TZ2P                  | GS    | $D_{2h}$ | 1.320 | 1.334 | 1.077 | 126.6 | 72 |
|                            | ES    | $D_{2h}$ | 1.317 | 1.328 | 1.075 | 121.5 |          |
|                            | $\Delta$ |       | -0.003 | -0.006 | -0.002 | -5.1 |          |
| Mk-MRCCSD/cc-pVCTZ         | GS    | $D_{2h}$ | 1.313 | 1.330 | 1.078 | 126.5 | 4 |
|                            | ES    | $D_{2h}$ | 1.309 | 1.325 | 1.076 | 121.1 |          |
|                            | $\Delta$ |       | -0.004 | -0.005 | -0.002 | -5.4 |          |
| Experiment                 | $\Delta$ |       | -0.043 | 0.007 |         | 2.4 | 73 |
| Experiment                 | GS    | $D_{2h}$ | 1.334 | 1.338 |         | 126.5 | 74 |
|                            | ES    | $D_{2h}$ | 1.280 | 1.358 |         | 118 |          |
|                            | $\Delta$ |       | -0.054 | 0.020 |         | -8.5 |          |
| Experiment                 | GS    | $D_{2h}$ | 1.326 | 1.341 | 1.073 | 126.4 | 75 |
|                            | ES    | $D_{2h}$ | 1.349 | 1.324 | 1.063 | 123.2 |          |
|                            | $\Delta$ |       | 0.023 | -0.017 | -0.010 | -3.2 |          |
| Experiment                 | $\Delta$ |       | 0.045 | -0.008 | 0.003 | -2.8 | 76 |
**Cartesian coordinates**

**CCSDR(3)**

CCSDR(3)/aug-cc-pVTZ total energies (au) and Cartesian coordinates (Å).

| Ground-state | $E= -295.97040064$ |
|--------------|---------------------|
| 6            | 0.000000 0.000000 1.259862 |
| 6            | 0.000000 0.000000 -1.259862 |
| 7            | 0.000000 1.193213 0.660709 |
| 7            | 0.000000 -1.193213 0.660709 |
| 7            | 0.000000 1.193213 -0.660709 |
| 7            | 0.000000 -1.193213 -0.660709 |
| 1            | 0.000000 0.000000 2.337205 |
| 1            | 0.000000 0.000000 -2.337205 |

| Excited-state | $E= -295.88218833$ |
|---------------|---------------------|
| 6            | 0.000000 0.000000 1.310707 |
| 6            | 0.000000 0.000000 -1.310707 |
| 7            | 0.000000 1.158537 0.658138 |
| 7            | 0.000000 -1.158537 0.658138 |
| 7            | 0.000000 1.158537 -0.658138 |
| 7            | 0.000000 -1.158537 -0.658138 |
| 1            | 0.000000 0.000000 2.386001 |
| 1            | 0.000000 0.000000 -2.386001 |

**EOM-CCSD**

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

| Ground-state | $E= -295.86053114$ ($T_1^{\text{diag}} = 0.010$) |
|--------------|---------------------|
| 6            | 0.000000 0.000000 1.256607 |
| 6            | 0.000000 0.000000 -1.256607 |
| 7            | 0.000000 1.187551 0.656767 |
| 7            | 0.000000 -1.187551 0.656767 |
| 7            | 0.000000 1.187551 -0.656767 |
| 7            | 0.000000 -1.187551 -0.656767 |
| 1            | 0.000000 0.000000 -2.333237 |
| 1            | 0.000000 0.000000 2.333237 |
**Excited-state**

\[ E = -295.813263393 \quad (T_1^{\text{diag}} = 0.010) \]

|   |   |   |   |
|---|---|---|---|
| 6 | 0.000000 | 0.000000 | 1.306670 |
| 6 | 0.000000 | 0.000000 | -1.306670 |
| 7 | 0.000000 | 1.153407 | 0.654996 |
| 7 | 0.000000 | 1.153407 | -0.654996 |
| 7 | 0.000000 | -1.153407 | 0.654996 |
| 7 | 0.000000 | -1.153407 | -0.654996 |
| 1 | 0.000000 | 0.000000 | -2.381186 |
| 1 | 0.000000 | 0.000000 | 2.381186 |
S32   Thioacrolein

Table S32: Selected geometrical parameters (bond lengths in Å, valence angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). ∆ gives the difference between the two states (in eV for the $\Delta_{ZPVE}$). The considered ES is the lowest $A^*$ state of $n \rightarrow \pi^*$ nature.

| Method          | State | PG  | ZPVE  | C=S  | C-C  | C=C  | S=C-C | C-C=C | Ref. |
|-----------------|-------|-----|-------|------|------|------|-------|-------|------|
| CCSD/def2-TZVPP | GS    | $C_s$ | 0.060074 | 1.617 | 1.456 | 1.337 | 125.1  | 121.7  | This work |
|                 | ES    | $C_s$ | 0.058050 | 1.697 | 1.420 | 1.353 | 124.7  | 123.7  | This work |
|                 | ∆     |       | -0.055 | 0.080 | -0.036 | 0.016 | -0.4  | 2.0  |       |
| CCSR(3)/def2-TZVPP | GS    | $C_s$ | 1.632  | 1.453 | 1.345 | 124.9  | 121.6  | This work |
|                 | ES    | $C_s$ | 1.731  | 1.405 | 1.370 | 124.8  | 123.4  | This work |
|                 | ∆     |       | 0.099  | -0.048 | 0.035 | -0.1  | 1.8  |       |
Cartesian coordinates

CCSDR(3)

CCSDR(3)/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

Ground-state

\[ E = -514.28366209 \]

|   | X       | Y       | Z       |
|---|---------|---------|---------|
| 6 | 2.264785| -0.468333| 0.000000|
| 6 | 0.933384| -0.661462| 0.000000|
| 6 | 0.002311| 0.454598 | 0.000000|
| 16| -1.623780| 0.313592| 0.000000|
| 1 | 2.956986| -1.297316| 0.000000|
| 1 | 2.681320| 0.530276 | 0.000000|
| 1 | 0.509345| -1.656571| 0.000000|
| 1 | 0.461186| 1.441229 | 0.000000|

Excited-state

\[ E = -514.21041405 \]

|   | X       | Y       | Z       |
|---|---------|---------|---------|
| 6 | 2.339689| -0.279132| 0.000000|
| 6 | 0.995631| -0.543605| 0.000000|
| 6 | 0.009275| 0.457746 | 0.000000|
| 16| -1.696605| 0.163231| 0.000000|
| 1 | 3.062645| -1.079600| 0.000000|
| 1 | 2.709182| 0.736821 | 0.000000|
| 1 | 0.668904| -1.576125| 0.000000|
| 1 | 0.297936| 1.503138 | 0.000000|

EOM-CCSD

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

Ground-state

\[ E = -514.37424797 \] \( (T_{\text{diag}} = 0.013) \)

|   | X       | Y       | Z       |
|---|---------|---------|---------|
| 6 | 2.259081| -0.467821| 0.000000|
| 6 | 0.935969| -0.661123| 0.000000|
| 6 | 0.000000| 0.453966 | 0.000000|
| 16| -1.610719| 0.314591| 0.000000|
| 1 | 2.950764| -1.294917| 0.000000|
| 1 | 2.677187| 0.528018 | 0.000000|
| 1 | 0.513693| -1.654651| 0.000000|
| 1 | 0.459562| 1.437949 | 0.000000|
**Excited-state**

\[ E = -514.293960766 \ (T_{1}^{\text{diag}} = 0.015) \]

|     |     |     |     |
|-----|-----|-----|-----|
| 6   | 2.330005 | -0.280787 | 0.000000 |
| 6   | 1.003053 | -0.543926 | 0.000000 |
| 6   | 0.000000 | 0.461490  | 0.000000 |
| 16  | -1.670130 | 0.162243  | 0.000000 |
| 1   | 3.052991  | -1.079263 | 0.000000 |
| 1   | 2.701973  | 0.732431  | 0.000000 |
| 1   | 0.674862  | -1.573923 | 0.000000 |
| 1   | 0.293904  | 1.504210  | 0.000000 |
## S33  Thiocarbonyl Dibromide

Table S33: Selected geometrical parameters (bond lengths in Å, valence angles and dihedral angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). Δ gives the difference between the two states (in eV for the Δ_{ZPVE}). The considered ES is the lowest A' state of n → π* nature. θ is the angle between the CS bond and the bisector of the Br-C-Br angle.

| Method             | State | PG  | ZPVE   | C=S  | C-Br | Br-C-Br | θ   | Ref.       |
|--------------------|-------|-----|--------|------|------|---------|-----|-----------|
| CCSD/def2-TZVPP    | GS    | $C_2v$ | 0.007235 | 1.593 | 1.891 | 111.9   | 0.0 | This work |
|                    | ES    | $C_s$  | 0.006063 | 1.693 | 1.870 | 119.4   | 25.9|           |
|                    | Δ     |        | -0.032  | 0.100 | -0.021 | 7.5    | 25.9|           |
| CCSDR(3)/def2-TZVP | GS    | $C_2v$ | 1.606   | 1.898 | 111.7 | 0.0     |     | This work |
|                    | ES    | $C_s$  | 1.725   | 1.880 | 118.9 | 29.4    |     |           |
|                    | Δ     |        | 0.119   | -0.018| 7.2   | 29.4    |     |           |
| Experiment         | Δ     |        |         |       |       |         | 19 ± 1| 77        |
| Experiment         | Δ     |        |         |       |       |         | 0.12 | 17.5 ± 1  | 78    |
Cartesian coordinates

**CCSDR(3)**

CCSDR(3)/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

**Ground-state**

\[ E = -5581.33106703 \]

|   |        |        |        |          |
|---|--------|--------|--------|----------|
| 6 | 0.000000 | 0.000000 | -0.576306 |
| 16| 0.000000 | 0.000000 | -2.181927 |
| 35| 0.000000 | 1.570519 | 0.489762  |
| 35| 0.000000 | -1.570519| 0.489762  |

**Excited-state**

\[ E = -5581.24712967 \]

|   |        |        |        |          |
|---|--------|--------|--------|----------|
| 6 | -0.169247 | 0.450725 | -0.000000 |
| 16| 0.563263 | 2.012703 | -0.000000 |
| 35| -0.097418 | -0.501788| 1.618714 |
| 35| -0.097418 | -0.501788| -1.618714|

**EOM-CCSD**

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

**Ground-state**

\[ E = -5581.4110021 \]  \( (T^\text{diag}_1 = 0.008) \)

|   |        |        |        |          |
|---|--------|--------|--------|----------|
| 6 | 0.000000 | -0.000000 | 0.529014 |
| 16| 0.000000 | -0.000000| 2.121618 |
| 35| 0.000000 | 1.566952 | -0.530285|
| 35| -0.000000| -1.566952 | -0.530285|

**Excited-state**

\[ E = -5581.32254326 \]  \( (T^\text{diag}_1 = 0.009) \)

|   |        |        |        |          |
|---|--------|--------|--------|----------|
| 6 | -0.113817| 0.446456 | -0.000000 |
| 16| 0.540630 | 2.007768 | -0.000000|
| 35| -0.113817| -0.497186| 1.614232 |
| 35| -0.113817| -0.497186| -1.614232|
Excited-state (constrained \( C_{2v} \))

This ES of \( A_2 \) symmetry presents an imaginary frequency of 168i cm\(^{-1}\). At this level of theory, it represents a barrier of 125 cm\(^{-1}\) compared to the planar structure. The available experimental estimates for this barrier are 465 ± 30 cm\(^{-1}\),\(^{77}\) and 524 ± 10 cm\(^{-1}\).\(^{78}\)

\[
E = -5581.32197264 \quad (T_1^{\text{diag}} = 0.009)
\]

|   |       |       |       |
|---|-------|-------|-------|
| 6 | -0.000000 | 0.000000 | 0.404100 |
| 16 | -0.000000 | 0.000000 | 2.095581 |
| 35 | 0.000000 | 1.616799 | -0.513627 |
| 35 | -0.000000 | -1.616799 | -0.513627 |
## Table S34: Selected geometrical parameters (bond lengths in Å, valence angles and dihedral angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). ∆ gives the difference between the two states (in eV for the ∆ZPVE). The considered ES is the lowest A state of n → π* nature. η is the angle between CS and F-C-Cl plane.

| Method              | State | PG | ZPVE   | C=\(\text{S}\) | C-F | C-Cl | F-C-Cl | F-C=\(\text{S}\) | η  | Ref.     |
|---------------------|-------|----|--------|-------------|-----|------|--------|----------------|----|----------|
| CCSD/\(\text{def2-TZVPP}\) | GS    | \(C_s\) | 0.009971 | 1.592  | 1.318 | 1.715 | 109.1  | 123.8         | 0.0 | This work |
|                     | ES    | \(C_1\) | 0.008683 | 1.720 | 1.331 | 1.712 | 114.4 | 116.3         | 38.3|          |
|                     | ∆     |       | -0.035 | 0.128 | 0.013 | -0.003 | 5.3    | -7.3          | 38.3|          |
| CCSDR(3)/\(\text{def2-TZVPP}\) | GS    | \(C_s\) | 1.603   | 1.325 | 1.725 | 109.0 | 127.1  | 0.0           |    | This work |
|                     | ES    | \(C_1\) | 1.756   | 1.334 | 1.726 | 114.2 | 115.1  | 42.4          |    |          |
|                     | ∆     |       | 0.153   | 0.009 | 0.001 | 5.2   | -12.0  | 42.4          |    |          |
| CCSD/6-311++G(2d)  | GS    | \(C_s\) | 1.597   | 1.325 | 1.732 | 123.1 |       |               |    | 79       |
|                     | ES    | \(C_1\) | 1.735   | 1.336 | 1.731 | 115.9 |       |               |    |          |
|                     | ∆     |       | 0.138   | 0.011 | -0.001 | -7.2 |       |               |    |          |
| Experiment         | ES    | \(C_1\) |          |        |        |        |        | 37.0          |    | 80       |
|                     | ∆     |       |        | 0.20 or 0.15 |     |        |        |               |    | 18       |

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**S34  Thiocarbonyl Chlorofluoride**
Cartesian coordinates

CCSDR(3)

CCSDR(3)/\textit{def}2-TZVPP total energies (au) and Cartesian coordinates (Å).

**Ground-state**
\[
E = -995.30380766
\]

|   | 0.000368 | 0.281098 | 0.000000 |
|---|----------|----------|----------|
| 6 |          |          |          |
| 16| 1.596179 | 0.128271 | 0.000000 |
| 9 | -0.630584| 1.446267 | 0.000000 |
| 17| -1.167370| -0.988321| 0.000000 |

**Excited-state**
\[
E = -995.20432290
\]

|   | 0.301529 | -0.335088 | -0.044126 |
|---|----------|-----------|-----------|
| 6 |          |           |           |
| 16| -0.042391| 0.550642  | -1.520810 |
| 9 | -0.077920| -1.614034 | -0.050188 |
| 17| -0.037135| 0.497737  | 1.429288  |

EOM-CCSD

(EOM)-CCSD/\textit{def}2-TZVPP total energies (au) and Cartesian coordinates (Å).

**Ground-state**
\[
E = -995.52457786 \quad (T_{\text{diag}} = 0.011)
\]

|   | 0.000000 | 0.280746 | -0.000000 |
|---|----------|----------|-----------|
| 6 |          |          |           |
| 16| 1.584181 | 0.128461 | 0.000000  |
| 9 | -0.626013| 1.440963 | -0.000000 |
| 17| -1.159575| -0.982854| -0.000000 |

**Excited-state**
\[
E = -995.417716528 \quad (T_{\text{diag}} = 0.014)
\]

|   | -0.034688 | 0.335421 | 0.268764 |
|---|-----------|----------|----------|
| 6 |          |          |           |
| 16| -1.500347 | -0.514288| -0.030756 |
| 9 | -0.017875 | 1.621773 | -0.070737 |
| 17| 1.433798  | -0.492934| -0.028462 |
Excited-state (constrained $C_s$)

This structure ($A^+$ symmetry) presents an imaginary frequency of 390 cm$^{-1}$. It is slightly less stable than the global minimum and corresponds to a barrier of 1002 cm$^{-1}$. This value is quite similar to the 1154 cm$^{-1}$ reported in Ref. 79 at the EOM-CCSD/6-311++G(2d) level. The available experimental estimate for this barrier is 1556 ± 45 cm$^{-1}$.

\[ E = -995.413148906 \ (T^\text{diag}_{1} = 0.013) \]

|   |      |      |      |
|---|------|------|------|
| 6 | 0.000000 | 0.306243 | 0.000000 |
| 16 | -1.574384 | -0.356795 | 0.000000 |
| 9  | 0.154617 | 1.627954 | 0.000000 |
| 17 | 1.399917 | -0.634136 | -0.000000 |
S35  Trifluoronitrosomethane

Table S35: Selected geometrical parameters (bond lengths in Å, valence angles and dihedral angle in degrees). PG is the point group and ZPVE is the zero-point vibrational energy (in au). ∆ gives the difference between the two states (in eV for the ∆ZPVE). The considered ES is the lowest A” state of n → π* nature.

| Method               | State | PG | ZPVE  | N=O  | C-N  | F-F-C | C-N=O | F-F-C-N | Ref. |
|----------------------|-------|----|-------|------|------|-------|-------|---------|------|
| ADC(2)/def2-TZVPP    | GS    | C₄s | 0.021031 | 1.206 | 1.515 | 1.315 | 112.0 | 113.6   | This work |
|                      | ES    | C₄s | 0.020165 | 1.256 | 1.464 | 1.313 | 116.9 | 107.7   |       |
|                      | ∆     |     | -0.024 | 0.050 | -0.051 | -0.002 | 4.9   | -5.9   |       |
| ADC(2)/aug-cc-pVTZ   | GS    | C₄s | 1.204 | 1.509 | 1.314 | 112.0 | 113.7 |       | This work |
|                      | ES    | C₄s | 1.252 | 1.458 | 1.313 | 117.1 | 107.8 |       |       |
|                      | ∆     |     | 0.048 | -0.051 | -0.001 | 5.1   | -5.9 |       |       |
| CC2/def2-TZVPP       | GS    | C₄s | 0.020340 | 1.217 | 1.527 | 1.319 | 111.9 | 113.5   | This work |
|                      | ES    | C₄s | 0.019725 | 1.261 | 1.465 | 1.318 | 117.7 | 107.6   |       |
|                      | ∆     |     | -0.017 | 0.044 | -0.062 | -0.001 | 5.8   | -5.9   |       |
| CC2/aug-cc-pVTZ      | GS    | C₄s | 1.215 | 1.520 | 1.318 | 112.0 | 113.7 |       | This work |
|                      | ES    | C₄s | 1.257 | 1.459 | 1.318 | 117.9 | 107.7 |       |       |
|                      | ∆     |     | 0.043 | -0.061 | 0.000 | 5.9   | -6.0 |       |       |
| CCSD/def2-TZVPP      | GS    | C₄s | 0.021863 | 1.189 | 1.514 | 1.311 | 112.3 | 113.5   | This work |
|                      | ES    | C₄s | 0.021315 | 1.220 | 1.460 | 1.309 | 118.8 | 107.7   |       |
|                      | ∆     |     | -0.015 | 0.031 | -0.054 | 0.002 | 6.5   | -5.8   |       |
| CCSD/aug-cc-pVTZ     | GS    | C₄s | 1.187 | 1.507 | 1.309 | 112.3 | 113.6 |       | This work |
|                      | ES    | C₄s | 1.216 | 1.453 | 1.308 | 119.0 | 107.8 |       |       |
|                      | ∆     |     | 0.029 | -0.054 | -0.001 | 6.7   | -5.8 |       |       |
| CCSDR(3)/def2-TZVPP  | GS    | C₄s | 1.199 | 1.524 | 1.315 | 112.0 | 115.5 |       | This work |
|                      | ES    | C₄s | 1.233 | 1.467 | 1.314 | 118.0 | 107.7 |       |       |
|                      | ∆     |     | 0.034 | -0.057 | -0.001 | 6.0   | -7.8 |       |       |
| MR-AQCC/cc-pVTZ(-f)  | GS    | C₄s | 1.207 | 1.524 | 1.316 | 111.9 | 113.5 |       | 81    |
|                      | ES    | C₄s | 1.245 | 1.481 | 1.315 | 116.7 | 107.4 |       |       |
|                      | ∆     |     | 0.038 | -0.043 | -0.001 | 4.8   | -6.1 |       |       |

Experiment ∆ 0.05 6.5 82
Cartesian coordinates

CCSDR(3)

CCSDR(3)/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

Ground-state
$E = -467.09083587$

| 7  | 0.553712 | -1.093108 | 0.000000 |
| 8  | -0.349273 | -1.882229 | 0.000000 |
| 6  | 0.054293  | 0.346889  | 0.000000 |
| 9  | -1.257309 | 0.446369  | 0.000000 |
| 9  | 0.550077  | 0.923430  | 1.082651 |
| 9  | 0.550077  | 0.923430  | -1.082651 |

Excited-state
$E = -467.02645139$

| 7  | -1.153161 | 0.224067  | 0.000000 |
| 8  | -1.773850 | -0.841573 | 0.000000 |
| 6  | 0.312483  | 0.166560  | 0.000000 |
| 9  | 0.759618  | 1.401877  | 0.000000 |
| 9  | 0.753343  | -0.470174 | 1.075572 |
| 9  | 0.753343  | -0.470174 | -1.075572 |

EOM-CCSD

(EOM)-CCSD/def2-TZVPP total energies (au) and Cartesian coordinates (Å).

Ground-state
$E = -467.04010710 \ (T_{1}^{\text{diag}} = 0.012)$

| 7  | 0.548055  | -1.087389 | 0.000000 |
| 8  | -0.344384 | -1.873107 | 0.000000 |
| 6  | 0.054154  | 0.343641  | 0.000000 |
| 9  | -1.252359 | 0.445279  | 0.000000 |
| 9  | 0.548055  | 0.918179  | 1.078247 |
| 9  | 0.548055  | 0.918179  | -1.078247 |

Excited-state
$E = -466.974447277 \ (T_{1}^{\text{diag}} = 0.012)$

| 7  | -1.147655 | 0.216027  | 0.000000 |
| 8  | -1.772638 | -0.831836 | 0.000000 |
| 6  | 0.311312  | 0.165004  | 0.000000 |
| 9  | 0.753586  | 1.397067  | 0.000000 |
| 9  | 0.753586  | -0.467840 | 1.070849 |
| 9  | 0.753586  | -0.467840 | -1.070849 |
Ground-state (staggered)

In the GS, the staggered conformation yields an imaginary frequency mode of 69\textit{i} cm\textsuperscript{−1}. This TS-like structure is only 0.03 eV less stable than the eclipsed minimum. This corresponds to a barrier of 265 cm\textsuperscript{−1}, agreeing very well with both MR-AQCC results (251 cm\textsuperscript{−1}),\textsuperscript{81} and the available experimental values are 250 cm\textsuperscript{−1},\textsuperscript{83} and 238 cm\textsuperscript{−1}.\textsuperscript{84}

\[ E = -467.03890141 \ (T_{1}^{\text{diag}} = 0.012) \]

\[
\begin{array}{cccc}
7 & -1.211153 & 0.211771 & 0.000000 \\
8 & -1.649879 & -0.895641 & 0.000000 \\
6 & 0.303925 & 0.173224 & 0.000000 \\
9 & 0.735317 & 1.413756 & 0.000000 \\
9 & 0.735317 & -0.448912 & 1.077432 \\
9 & 0.735317 & -0.448912 & -1.077432 \\
\end{array}
\]

Excited-state (eclipsed)

In the ES, the eclipsed conformation yields an imaginary frequency mode of 122\textit{i} cm\textsuperscript{−1}. This TS-like structure is only 0.08 eV less stable than the eclipsed minimum. This corresponds to a barrier of 656 cm\textsuperscript{−1}, agreeing very well with the MR-AQCC result (628 cm\textsuperscript{−1}),\textsuperscript{81} and slightly overestimating the available experimental estimates of 550–575 cm\textsuperscript{−1},\textsuperscript{83} and 601.5 \pm 10 cm\textsuperscript{−1}.\textsuperscript{82,85}

\[ E = -466.971456673 \ (T_{1}^{\text{diag}} = 0.012) \]

\[
\begin{array}{cccc}
7 & 0.522203 & -1.037754 & 0.000000 \\
8 & -0.258935 & -1.973897 & 0.000000 \\
6 & 0.056554 & 0.349059 & 0.000000 \\
9 & -1.258102 & 0.405904 & 0.000000 \\
9 & 0.522203 & 0.961553 & 1.068964 \\
9 & 0.522203 & 0.961553 & -1.068964 \\
\end{array}
\]
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