Carbene Routes to Cyclopropatetrahedrane

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**Platonic Solids**

Tetrahedrane (2), hexahedrane (3; cubane), and dodecahedrane (4) are fused polycyclic hydrocarbons (Table S1). Their cage-like C-atom frameworks correspond to a regular (1) tetrahedron, (2) hexahedron (i.e., cube), and (3) dodecahedron, which are three of the five regular polyhedra that have been considered sacred since the time of the ancient Greeks. The syntheses of 3 and 4 are a remarkable achievement despite the structures’ high symmetries and total strain energies (E_s)s. However, 2 has never been prepared although polysubstituted derivatives are known. The six curved C–C “banana” bonds of 2 have high p orbital character and bow outside the C–C internuclear axes by 21 deg to relieve strain. The E_s per C–C bond value for 2 exceeds that of 3 and far exceeds that of 4.

### Table S1. Comparison of Platonic-Solid-Like Hydrocarbons

|                  | 2     | 3     | 4     |
|------------------|-------|-------|-------|
| symmetry         | T_d   | O_h   | I_h   |
| faces (f)        | 4     | 6     | 12    |
| C–H units (v)    | 4     | 8     | 20    |
| C–C bonds (e)    | 6     | 12    | 30    |
| SODAR^b          | 3     | 5     | 11    |
| φ (deg)          | 144.74| 125.26| 110.91|
| E_s (kcal/mol):  |
| (a) total^c      | 136.18| 159.99| 60.45 |
| (b) per C–C bond | 22.70 | 13.33 | 2.02  |

^a Euler’s formula: f + n – 2 = e. ^b Sum of double bonds and rings (SODAR) for (CH)_v is [((v/2) + 1] and is equivalent to (f – 1). ^c cf. Ref. S2.
**Computational Modeling**

**Computational Methods.** Quantum chemical calculations were performed on 1, carbenes 8–11, transition states TSa–TSd, and intrinsic reaction coordinate (IRC) paths a–d using the Spartan’20 (v. 1.1.4) computer program.\textsuperscript{54} Restricted SCF wave functions of molecular equilibrium geometries and transition states were computed using a (100,434) DFT integration grid, the RSH-GGA functional ωB97X-D,\textsuperscript{55} and Dunning’s cc-pVTZ basis set. Unrestricted SCF wave functions were computed for triplet-state carbenes. Normal-mode vibrational analyses were performed at the level of geometry optimization. The harmonic frequencies were used to obtain temperature-independent zero-point vibrational energy (\(E_{ZPVE}\))\textsuperscript{56} and temperature-dependent thermal vibrational energy (\(\Delta_{vib}H\)) values. Each reaction TS had one, and only one, imaginary frequency \(v_{TS}\). Its vibration was animated to verify that the motions conformed to the elementary step. An IRC was computed to ensure that the carbene followed a direct route to 1. Single-point energy (\(E\)) values were computed using the CCSD(T)(full) coupled-cluster theory method and Dunning’s cc-pVTZ basis set. All \(E_{ZPVE}\) values were scaled by \(z = 1.3686\)\textsuperscript{57} before being added to \(E\) (\(T = 0 \text{ K}; p = 0 \text{ atm}\)). Relative energy values (\(\Delta_{rel}E\))s are specified with regard to 1 (\((\Delta_{rel}E = [0])\). Conversion of \(E\) values to enthalpy (\(H_T\)) values was done according to eq S1 (computational standard-state: \(T = 298.15 \text{ K}; p = 1 \text{ atm}; \text{ cf. Table S2}\)). All \(\Delta_{vib}H\) values were scaled by \(H = 0.956\)\textsuperscript{57} before being added to the ZPVE-corrected \(E\) values. The increase in kinetic energy, due to translations (3(½)\(RT\)) and rotations (3(½)\(RT\)), for each nonlinear molecule was then added. Finally, \(RT\) (i.e., “\(pV\) work” needed to expand one mole of ideal gas to \(V = 24.465 \text{ L at } T = 298.15 \text{ K and } p = 1 \text{ atm}\)) was added to obtain \(H_T\) (eq S1). The experimental singlet–triplet energy gap (\(\Delta E_{S–T}\)) of \(\text{CH}_2\) (eq S2)\textsuperscript{58} was used to compute the corrected \(\Delta E_{S–T}\) of carbene 8 (eq S3).
Table S2. Values Used in Computations with Equation S1

| Parameter  | Value                                      |
|------------|--------------------------------------------|
| \( V \)    | \( nRT/p \)                                |
|            | \( = 24.465 \text{ L} \)                  |
| \( p \)    | \( = 1 \text{ atm} \)                      |
| \( n \)    | \( = 1 \text{ mol} \)                      |
| \( R \)    | \( = 1.9872 \times 10^{-3} \text{ (kcal/mol)/K} \) |
|            | \( = 8.2057 \times 10^{-2} \text{ (L·atm/mol)/K} \) |
| \( T \)    | \( = 298.15 \text{ K} \)                   |
|            | \( = 25 \text{ °C} \)                      |
| \( RT \)   | \( = 0.592 \text{ kcal/mol} \)             |
| \( 3(\frac{1}{2})RT \) | \( = 0.889 \text{ kcal/mol} \)         |
| 1 hartree  | \( = 627.5095 \text{ kcal/mol} \)         |

\[
H_T = [E + z(E_{ZPVE})] + H(\text{vib}) + (3(\frac{1}{2})RT)_{\text{translational}} + (3(\frac{1}{2})RT)_{\text{rotational}} + (RT)_{\text{ideal gas}} \tag{S1}
\]

\[
\Delta E_{S-T} = \Delta E_{S-T(\text{comp})} - [\Delta E_{S-T(\text{comp})} - \Delta E_{S-T(\text{exp't})}]_{\text{CH}_2} \tag{S2}
\]

\[
\Delta E_{S-T} = \Delta E_{S-T(\text{comp})} - 1.247 \text{ kcal/mol} \tag{S3}
\]
Molecular Energies and 3-D Cartesian Coordinates

All ORTEP structures are shown as 50% ellipsoids.

Methylene ($^1$CH$_2$);
CCSD(T)(full)/cc-pVTZ//ωB97X-D/cc-pVTZ + 1.3686($E_{ZPVE}$):

\[ E + z(E_{ZPVE}) = -24505.30 \text{ kcal/mol} \]

\[ T = 298.15 \text{ K} \]

\[ H_T = -24502.92 \text{ kcal/mol} \]

| Atom | x     | y     | z     |
|------|-------|-------|-------|
| C    | 0.0000000 | 0.0000000 | 0.1820529 |
| H    | 0.8612946 | 0.0000000 | -0.5174490 |
| H    | -0.8612946 | 0.0000000 | -0.5174490 |

Methanediyl ($^3$CH$_2$);
UCCSD(T)(full)/cc-pVTZ//ωB97X-D/cc-pVTZ + 1.3686($E_{ZPVE}$):

\[ E + z(E_{ZPVE}) = -24502.92 \text{ kcal/mol} \]

\[ T = 298.15 \text{ K} \]

\[ H_T = -24513.37 \text{ kcal/mol} \]

| Atom | x     | y     | z     |
|------|-------|-------|-------|
| C    | 0.0000000 | 0.0000000 | 0.1036352 |
| H    | 0.9943111 | 0.0000000 | -0.3150600 |
| H    | -0.9943111 | 0.0000000 | -0.3150600 |
Cyclopropatetrahedrane (1; tetracyclo[2.1.0.0^1,3.0^2,4]^pentane); CCSD(T)(full)/cc-pVTZ//ωB97X-D/cc-pVTZ + 1.3686(E_ZPVE):

\[ E + z(E_{ZPVE}) : -120693.23 \text{ kcal/mol} \]

\[ T = 298.15 \text{ K} \]

\[ H_T : -120690.22 \text{ kcal/mol} \]

| Atom | x     | y     | z         |
|------|-------|-------|-----------|
| C    | 0.0000000 | 0.0000000 | -1.3639010 |
| C    | 0.0000000 | 0.8222895 | -0.0944911 |
| C    | 0.0000000 | -0.8222895 | -0.0944911 |
| C    | 0.7530674 | 0.0000000 | 0.8583930  |
| C    | -0.7530674 | 0.0000000 | 0.8583930  |
| H    | 1.6266535 | 0.0000000 | 1.4771491  |
| H    | -1.6266535 | 0.0000000 | 1.4771491  |
| H    | 0.9145992 | 0.0000000 | -1.9456671 |
| H    | -0.9145992 | 0.0000000 | -1.9456671 |
(Tetrahedryl)carbene \((8; (\text{tricyclo}[1.1.0.0^{2,4}]\text{but-1-yl})\text{methylene})\);
CCSD(T)(full)/cc-pVTZ//\(\omega\)B97X-D/cc-pVTZ + 1.3686\(E_{\text{ZPVE}}\):

\[
E + z(E_{\text{ZPVE}}) = -120643.03 \text{ kcal/mol}
\]

\(T = 298.15 \text{ K}\)

\(H_T = -120639.55 \text{ kcal/mol}\)

| Atom | \(x\) | \(y\) | \(z\) |
|------|------|------|------|
| C    | 0.4406085 | 0.0534540 | 0.4349542 |
| C    | -0.7894082 | -0.7700605 | 0.3130382 |
| C    | -0.8286348 | 0.7593716 | 0.2357073 |
| C    | -0.4482145 | -0.0546304 | -0.8835848 |
| C    | 1.7616002 | 0.1706280 | 0.0309249 |
| H    | -1.3354576 | -1.6191480 | 0.6690817 |
| H    | -1.4240687 | 1.6089756 | 0.4977220 |
| H    | -0.2328387 | -0.0911725 | -1.9323936 |
| H    | 2.1754413 | -0.8521786 | -0.0208441 |

(Tetrahedryl)carbene triplet \((^38; (\text{tricyclo}[1.1.0.0^{2,4}]\text{but-1-yl})\text{methanediyl}))\);
UCCSD(T)(full)/cc-pVTZ//\(U\omega\)B97X-D/cc-pVTZ + 1.3686\(E_{\text{ZPVE}}\):

\[
E + z(E_{\text{ZPVE}}) = -120637.55 \text{ kcal/mol}
\]

\(T = 298.15 \text{ K}\)

\(H_T = -120633.81 \text{ kcal/mol}\)

| Atom | \(x\) | \(y\) | \(z\) |
|------|------|------|------|
| C    | 0.7644593 | -0.4614847 | 0.7362688 |
| C    | 0.7644593 | -0.4614847 | -0.7362688 |
| C    | 0.7829180 | 0.8017868 | 0.0000000 |
| C    | -0.4659120 | -0.0176167 | 0.0000000 |
| C    | -1.8368338 | 0.0951632 | 0.0000000 |
| H    | 1.1310111 | 1.8123758 | 0.0000000 |
| H    | -2.6616046 | -0.5976657 | 0.0000000 |
| H    | 1.1198584 | -0.9706518 | 1.6063754 |
| H    | 1.1198584 | -0.9706518 | -1.6063754 |
Tricyclo[1.1.1.0^{1,3}]pent-2-ylidene (9); CCSD(T)(full)/cc-pVTZ//ωB97X-D/cc-pVTZ + 1.3686(E_{ZPVE}):

\[ E + z(E_{ZPVE}): -120668.71 \text{ kcal/mol} \]

\[ T = 298.15 \text{ K} \]

\[ H_T: -120665.41 \text{ kcal/mol} \]

| Atom | x     | y     | z          |
|------|-------|-------|------------|
| C    | 0.00000000 | 0.00000000 | -1.3697075 |
| C    | 1.1249653   | 0.00000000 | 0.5209824  |
| C    | -1.1249653  | 0.00000000 | 0.5209824  |
| C    | 0.00000000  | 0.7983562  | -0.1004006 |
| C    | 0.00000000  | -0.7983562 | -0.1004006 |
| H    | 1.1642895   | 0.00000000 | 1.6035277  |
| H    | -1.1642895  | 0.00000000 | 1.6035277  |
| H    | 2.0836611   | 0.00000000 | 0.0194302  |
| H    | -2.0836611  | 0.00000000 | 0.0194302  |

trans-Tricyclo[2.1.0^{1,3}]pent-2-ylidene (10); CCSD(T)(full)/cc-pVTZ//ωB97X-D/cc-pVTZ + 1.3686(E_{ZPVE}):

\[ E + z(E_{ZPVE}): -120664.05 \text{ kcal/mol} \]

\[ T = 298.15 \text{ K} \]

\[ H_T: -120660.90 \text{ kcal/mol} \]

| Atom | x     | y     | z         |
|------|-------|-------|-----------|
| C    | -0.0081795 | -0.4345073 | 0.5950044 |
| C    | 0.8744954  | 0.6582343  | 0.2245362 |
| C    | 1.1400068  | -0.8247856 | -0.1336219|
| C    | -0.2158522 | 0.4282309  | -0.7497125|
| C    | -1.3596092 | -0.0553002 | 0.1534798 |
| H    | 1.3233488  | 1.5021016  | 0.7145638 |
| H    | -0.0419469 | -0.0906870 | -1.6957574|
| H    | -2.0194039 | -0.8153141 | -0.2542960|
| H    | -1.8474828 | 0.7116628  | 0.7430040 |
4-methylenebicyclo[1.1.0]but-2-ylidene (11); 
CCSD(T)(full)/cc-pVTZ//ωB97X-D/cc-pVTZ + 1.3686(E_{ZPVE}): 

\[ E + Z(E_{ZPVE}) = -120703.26 \text{ kcal/mol} \]

\[ T = 298.15 \text{ K} \]

\[ H_T = -120699.94 \text{ kcal/mol} \]

| Atom | x    | y    | z    |
|------|------|------|------|
| C    | 0.6417445 | 0.1610869 | 0.8283118 |
| C    | 0.6417445 | 0.1610869 | -0.8283118 |
| C    | 1.6208845 | -0.4673074 | 0.0000000 |
| C    | -0.5478140 | 0.0504135 | 0.0000000 |
| C    | -1.8565107 | -0.1059036 | 0.0000000 |
| H    | 0.8305334 | 0.8519009 | 1.6415358 |
| H    | 0.8305334 | 0.8519009 | -1.6415358 |
| H    | -2.4032176 | -0.1820810 | 0.9276798 |
| H    | -2.4032176 | -0.1820810 | -0.9276798 |

TSa; 
CCSD(T)(full)/cc-pVTZ//ωB97X-D/cc-pVTZ + 1.3686(E_{ZPVE}): 

\[ E + Z(E_{ZPVE}) = -120627.19 \text{ kcal/mol} \]

\[ T = 298.15 \text{ K} \]

\[ H_T = -120623.84 \text{ kcal/mol} \]

| Atom | x    | y    | z    |
|------|------|------|------|
| C    | -0.2272812 | 0.0206392 | 0.7878857 |
| C    | 0.8303660 | 0.7593271 | 0.0778881 |
| C    | 0.8690167 | -0.7568780 | 0.2652301 |
| C    | 0.0844535 | -0.1404997 | -0.8077560 |
| C    | -1.5153744 | -0.1410754 | 0.2032869 |
| H    | 1.4372237 | 1.6433148 | 0.0843197 |
| H    | 1.5204804 | -1.5928724 | 0.4202580 |
| H    | -1.0428854 | -0.6298454 | -1.0178656 |
| H    | -1.9559995 | 0.8378898 | -0.0132471 |
SUPPORTING INFORMATION

TSb;
CCSD(T)(full)/cc-pVTZ//ωB97X-D/cc-pVTZ + 1.3686(E_{ZPVE}):

\[ E + z(E_{ZPVE}) = -120654.53 \text{ kcal/mol} \]

\[ T = 298.15 \text{ K} \]

\[ H_T = -120651.29 \text{ kcal/mol} \]

| Atom | x     | y     | z     |
|------|-------|-------|-------|
| C    | -0.2098599 | 0.8088502 | 0.0114610 |
| C    | -0.2098599 | -0.8088502 | 0.0114610 |
| C    | -1.2373062 | 0.0000000 | -0.7721676 |
| C    | -0.0573475 | 0.0000000 | 1.2688401 |
| C    | 0.5456639 | 0.0000000 | -0.9478803 |
| H    | 1.5147359 | 0.0000000 | -1.4153330 |
| H    | -0.3621737 | 0.0000000 | -1.8522700 |
| H    | 0.9152113 | 0.0000000 | 1.7444079 |
| H    | -0.8990640 | 0.0000000 | 1.9514810 |

TSc;
CCSD(T)(full)/cc-pVTZ//ωB97X-D/cc-pVTZ + 1.3686(E_{ZPVE}):

\[ E + z(E_{ZPVE}) = -120660.59 \text{ kcal/mol} \]

\[ T = 298.15 \text{ K} \]

\[ H_T = -120657.34 \text{ kcal/mol} \]

| Atom | x     | y     | z     |
|------|-------|-------|-------|
| C    | -0.0722746 | -0.1214417 | 0.7605083 |
| C    | 0.9097646 | 0.6776172 | 0.0553228 |
| C    | 0.9431212 | -0.8846241 | 0.0713048 |
| C    | -0.1190331 | 0.1966518 | -0.8479002 |
| C    | -1.3549160 | 0.0449137 | 0.0761435 |
| H    | 1.5715340 | 1.5120681 | 0.1769667 |
| H    | 0.3800498 | -1.0266014 | -1.0821693 |
| H    | -1.9119569 | 0.9582075 | 0.2520532 |
| H    | -1.9603343 | -0.8389315 | -0.0975726 |
SUPPORTING INFORMATION

\[ E + z(E_{ZPVE}) = -120675.45 \text{ kcal/mol} \]

\[ T = 298.15 \text{ K} \]

\[ H_T = -120672.11 \text{ kcal/mol} \]

| Atom |  \( x \) |  \( y \) |  \( z \) |
|------|--------|--------|--------|
| C    | 0.1495165 | 0.7571575 | -0.9634904 |
| C    | 0.1495165 | -0.7571575 | -0.9634904 |
| C    | 0.5058738 | 0.0000000 | 0.2100193 |
| C    | -0.1057233 | 0.0000000 | 1.4264178 |
| C    | -1.0685679 | 0.0000000 | -0.6051027 |
| H    | 0.4378255 | 1.6270523 | -1.5188101 |
| H    | 0.4378255 | -1.6270523 | -1.5188101 |
| H    | -0.2531333 | 0.9266041 | 1.9666334 |
| H    | -0.2531333 | -0.9266041 | 1.9666334 |
**Molecular Orbitals of Select Molecules**

(a) Cyclopropane
{HOMO} \( e'_{\text{sym}} \)

(b) Cyclopropane
{HOMO} \( e'_{\text{sym}} \)

(c) Tetrahedrane (2)
{HOMO} \( e_{\text{sym}} \)

(d) Tetrahedrane (2)
{HOMO} \( e_{\text{sym}} \)

(e) (Tetrahedryl)carbene (8)
{HOMO–1}

(f) (Tetrahedryl)carbene (8)
{HOMO–1}

(g) Tetrahedrane (2)
{HOMO} \( e_{\text{asym}} \)

(h) (Tetrahedryl)carbene triplet (\( ^3g \))
{HOMO}_{\alpha\text{-spin}}

**Figure S1.** Molecular orbitals (MOs) from select molecules are displayed above. (a, b) Cyclopropane has a high-lying C–C “banana” bond. The outwardly curved \( \sigma/\pi \) bond is a hybrid between a C–C \( \sigma \) bond and a C–C \( \pi \) bond. (c, d) Tetrahedrane (2) also has high-lying C–C “banana” bonds. (e, f) In (tetrahedryl)carbene (8), the vacant p orbital of the :CH-group attracts electron density from the vicinal C–C “banana” bond. This elongates and weakens the C1′–C4′ bond of the tetrahedryl group. (g, h) The :CH-group’s p orbital is not vacant in triplet (tetrahedryl)carbene (\( ^3g \)). Its :CH-group does not bend toward the C1′–C4′ bond because a nodal plane exists between the tetrahedryl group and the singly occupied p orbital. All structures and MOs were computed using the (U)\( \omega \)B97X-D/cc-pVTZ // (U)\( \omega \)B97X-D/cc-pVTZ theoretical model. All computer-generated MOs are shown with an isosurface value of 0.110 to emphasize the cores of the electron-clouds.
**GEOMETRIC ANALYSIS OF INVERTED CARBON ATOMS**

Below is a straightforward procedure for determining whether the four bonds emanating from a tetracoordinate carbon atom are monohemispherical. Carbene 8 is used as an example (see the original spreadsheet file for the detailed formulas).

**Example 1:**

(1) Map von Baeyer atom labels to those of computed Cartesian coordinates: C1' → C1, etc.

Translate atom of interest (e.g., C1) to the origin (0, 0, 0) by subtracting its (x, y, z) coordinates from all other atoms.

(2) Calculate cross product \( \mathbf{u} \times \mathbf{v} \) (in that order) to find \( \mathbf{t} \), which is perpendicular to both \( \mathbf{u} \) and \( \mathbf{v} \).

(3) Compute \( \phi_{st} \) and \( \phi_{rt} \) from the dot products \( \mathbf{s} \cdot \mathbf{t} \) and \( \mathbf{r} \cdot \mathbf{t} \), respectively.

(4) Tetracoordinate C1 is an inverted carbon atom if \( \pi/2 < \phi_{st} < 3\pi/2 \) and \( \pi/2 < \phi_{rt} < 3\pi/2 \).

(Tetrahedryl)carbene (8; (tricyclo[1.1.0.0\textsuperscript{2,4}]but-1-yl)methylene);
\( \omega \text{B97X-D/cc-pVTZ}/\omega \text{B97X-D/cc-pVTZ}: \)

| Atom\textsubscript{von Baeyer} | Atom\textsubscript{Cartesian} | \( x \)     | \( y \)     | \( z \)     |
|-------------------------------|------------------------------|------------|------------|------------|
| C1'   \( \rightarrow \) C1    | 0.4406085                    | 0.0534540 | 0.4349542 |
| C2'   \( \rightarrow \) C2    | -0.7894082                   | -0.7700605| 0.3130382 |
| C3'   \( \rightarrow \) C3    | -0.8286348                   | 0.7593716 | 0.2357073 |
| C4'   \( \rightarrow \) C4    | -0.4482145                   | -0.0546304| -0.8835848|
| C1    \( \rightarrow \) C5    | 1.7616002                    | 0.1706280 | 0.0309249 |
| H2'   \( \rightarrow \) H2    | -1.3354576                   | -1.6191480| 0.6690817 |
| H3'   \( \rightarrow \) H3    | -1.4240687                   | 1.6089756 | 0.4977220 |
| H4'   \( \rightarrow \) H5    | -0.2328387                   | -0.0911725| -1.9323936|
| H1    \( \rightarrow \) H5'   | 2.1754413                    | -0.8521786| -0.0208441|

**CARBENE ROUTES TO CYCLOPROPATETRAHEDRANE**

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Figure S2. The C1' atom of (tetrahedral)carbene (8) is an inverted carbon atom.
Example 2:

(1) Map von Baeyer atom labels to those of computed Cartesian coordinates: $C4' \rightarrow C4$, etc.

   Translate atom of interest (e.g., $C4$) to the origin $(0, 0, 0)$ by subtracting its $(x, y, z)$ coordinates from all other atoms.

(2) Calculate cross product $u \times v$ (in that order) to find $t$, which is perpendicular to both $u$ and $v$.

(3) Compute $\phi_{st}$ and $\phi_{rt}$ from the dot products $s \cdot t$ and $r \cdot t$, respectively.

(4) Tetracoordinate $C4$ is an inverted carbon atom if $\pi/2 < \phi_{st} < 3\pi/2$ and $\pi/2 < \phi_{rt} < 3\pi/2$.

(Tetrahedryl)carbene ($8$; (tricyclo[1.1.0.0\textsuperscript{2,4}]but-1-yl)methylene);

\[ \omega B97X-D/cc-pVTZ///\omega B97X-D/cc-pVTZ: \]

| Atom\textsuperscript{von Baeyer} | Atom\textsuperscript{Cartesian} | $x$    | $y$    | $z$    |
|---------------------------------|---------------------------------|--------|--------|--------|
| $C1'$                           | $C1$                            | 0.4406085 | 0.0534540 | 0.4349542 |
| $C2'$                           | $C2$                            | -0.7894082 | -0.7700605 | 0.3130382 |
| $C3'$                           | $C3$                            | -0.8286348 | 0.7593716  | 0.2357073 |
| $C4'$                           | $C4$                            | -0.4482145 | -0.0546304 | -0.8835848 |
| $C1$                            | $C5$                            | 1.7616002  | 0.1706280  | 0.0309249  |
| $H2'$                           | $H2$                            | -1.3354576 | -1.6191480 | 0.6690817  |
| $H3'$                           | $H3$                            | -1.4240687 | 1.6089756  | 0.4977220  |
| $H4'$                           | $H5$                            | -0.2328387 | -0.0911725 | -1.9323936 |
| $H1$                            | $H5'$                           | 2.1754413  | -0.8521786 | -0.0208441 |
Figure S3. The C4' atom of (tetrahedryl)carbene (8) is not an inverted carbon atom.

| Atom | x     | y     | z     | vector | norm (Å) |
|------|-------|-------|-------|--------|----------|
| C1   | 0.4406085 | 0.0534540 | 0.4349542 | r     | 1.594 Å  |
| C2   | -0.7894082 | -0.7700605 | 0.3130382 | t     | 1.594 Å  |
| C3   | -0.8286348 | 0.7593716 | 0.2357073 | s     | 1.435 Å  |
| C4   | -0.4482149 | 0.0546304 | -0.8835848 | u     | 1.435 Å  |
| C5   | 1.7616002 | 0.1706280 | 0.0309249 | v     | 1.435 Å  |
| H2   | -1.3354576 | -1.6191480 | 0.6690817 | s     | 1.071 Å  |
| H3   | -1.4240697 | 1.6089756 | 0.4977220 | t     | 1.594 Å  |
| H5   | -0.2328387 | -0.0911725 | -1.9323936 | r     | 1.594 Å  |
| H5'  | 2.1754134 | -0.8521786 | -0.0208441 | s     | 1.071 Å  |

**Bond length check**

| Vector | x     | y     | z     | norm (Å) | dot product |
|--------|-------|-------|-------|----------|-------------|
| u      | -0.3411937 | -0.7154301 | 1.1966230 | 1.435 | 0.000000000 u • t |
| v      | -0.3804203 | 0.8140020 | 1.1192921 | 1.435 | 0.000000000 v • t |
| t = u × v | -1.7748288 | -0.0733243 | -0.5498965 | 1.860 | —          |

**Perpendicularity check**

| Vector  | x     | y     | z     | norm (Å) | dot product |
|---------|-------|-------|-------|----------|-------------|
| s       | 0.2153758 | -0.0365421 | -1.0488088 | 1.071 | 0.0999699 s • t |
| r       | 0.8888230 | 0.1080844 | 1.3185390 | 1.594 | -0.7795952 r • t |
|        | -0.7001050 | -0.7001050 | -0.7001050 | —      | —          |

**Angle check**

| Angle | deg | 90 < Φ < 270 | Inverted C atom | by | 5.7 deg |
|-------|-----|--------------|-----------------|----|---------|
| Φ_h   | 84.3 | FALSE | — | — | — |
| Φ_r   | 141.2 | TRUE | — | — | — |
| Φ_w   | 134.6 | FALSE | — | — | by |
| sum   | 360.0 | — | — | — | — |
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(S9) According to the (U)CCSD(T)(full)/cc-pVTZ//(U)ωB97X-D/cc-pVTZ + 1.3686($E_{ZPVE}$) theoretical model.