Supporting Information

for

Tuning the solid-state emission of liquid crystalline nitro-cyanostilbene by halogen bonding

Subrata Nath, Alexander Kappelt, Matthias Spengler, Bibhisan Roy, Jens Voskuhl and Michael Giese

*Beilstein J. Org. Chem.* 2021, 17, 124–131. doi:10.3762/bjoc.17.13

Detailed descriptions of the experimental procedures and comprehensive analytical data
1. Materials and methods

Compounds and solvents were used as obtained from suppliers without further purification. \(^1\)H and \(^{13}\)C NMR spectra of the intermediates and products were recorded in deuterated solvents (CDCl\(_3\), DMSO-d\(_6\) or MeOD) with a Bruker DRX 300. Mass spectra were obtained with a Bruker amaZon (MS) and IR spectra were recorded with a Varian 3100 FT-IR, Excalibur Series, ATR IR spectrometer. Polarized optical microscopy (POM) images/videos were taken on a Nikon Eclipse Ni equipped with an OptixCam Summit K2 OCS-D3K4-14-52X microscope camera and an LTS420 hotstage from Linkam Scientific Instruments Ltd. The images were recorded by an Imaging Source camera OptixCam K2. DSC thermograms were recorded using a Mettler Toledo DCS3+/700/866/Argon with a heating/cooling speed of 10 °C/min (sample weight ≈5 mg). UV–visible spectroscopy was performed using a Thermo Fisher Evolution 201 spectrophotometer.

Experimental procedures

Scheme S1: The synthetic route for the synthesis of XB-acceptors, XB-donors and supramolecular assemblies.

**Synthesis of compound NO\(_2\)-C\(_n\) (n = 1, 8, 9, 10, 11):**

The desired compounds were synthesised based on a reported procedure\(^5\) with a small modification. 4-Alkoxybenzaldehyde (1 equiv), CH\(_3\)ONa (1 equiv) and 20 ml ethanol were placed into a 250 ml boiling flask. When the 4-alkoxybenzaldehyde and CH\(_3\)ONa had completely dissolved in ethanol, 4-nitrophenylacetonitrile (1 equiv) was added and the
mixture was stirred at 25 °C for 8 h. The final reaction mixture was filtered, the solid products were collected and washed several times with ethanol to obtain the yellow green solid products with a yield of 60–65%.

**NO₂-C₅:** ¹H NMR (CDCl₃, 300 MHz, ppm): δ 8.30-8.26 (m, 2H), 7.96 (d, J = 9Hz, 2H), 7.83-7.80 (m, 2H), 7.61 (s, 1H), 7.02 (d, J = 9Hz, 2H), 3.89 (s, 3H, 1×CH₃); ¹³C (CDCl₃, 75 MHz, ppm): δ 162.6, 147.7, 145.2, 141.3, 132.1, 126.5, 125.9, 124.5, 117.9, 114.8, 106.4, 55.7.

FT-IR (ATR): n (cm⁻¹) = 2978, 2843, 2212, 1597, 1579, 1508, 1381, 1334, 1311, 1261, 1180, 1034, 922, 848, 825, 752, 686, 621.

HRMS m/z (%): positive: calc. (M+Na⁺): C₁₆H₁₂N₂NaO₃⁺ = 303.0740, found: 303.0749.

**NO₂-C₆:** ¹H NMR (CDCl₃, 300 MHz, ppm): δ 8.31-8.28 (m, 2H), 7.94 (d, J = 9Hz, 2H), 7.83-7.80 (m, 2H), 7.60 (s, 1H), 7.0 (d, J = 9Hz, 2H), 4.04 (t, J = 6 Hz, 2H, OCH₂), 1.84-1.77 (m, 2H, 1×CH₂), 1.54-1.30 (m, 10H, 5×CH₂), 0.89 (t, J = 6Hz, 3H, 1×CH₃); ¹³C NMR (CDCl₃, 75 MHz, ppm): δ 161.5, 146.7, 140.2, 132.0, 130.3, 126.6, 125.1, 124.6, 115.4, 115.1, 109.3, 68.5, 32.0, 29.5, 29.4, 29.3, 26.2, 22.9, 14.3.

FT-IR (ATR): n (cm⁻¹) = 2962, 2920, 2854, 2212, 1578, 1508, 1333, 1311, 1259, 1198, 1180, 1110, 1039, 997, 914, 850, 825, 752, 688, 629.

HRMS m/z (%): positive: calc. (M+Na⁺): C₂₃H₂₆N₂NaO₃⁺ = 401.1836, found: 401.1844.

**NO₂-C₇:** ¹H NMR (CDCl₃, 300 MHz, ppm): δ 8.30-8.27 (m, 2H), 7.94 (d, J = 9Hz, 2H), 7.84-7.80 (m, 2H), 7.60 (s, 1H), 7.01-6.98 (m, 2H), 4.04 (t, J = 6 Hz, 2H, OCH₂), 1.86-1.77 (m, 2H, 1×CH₂), 1.52-1.29 (m, 12H, 6×CH₂), 0.89 (t, J = 6Hz, 3H, 1×CH₃); ¹³C NMR (CDCl₃, 75 MHz, ppm): δ 162.3, 147.7, 145.3, 141.4, 132.2, 126.6, 125.7, 124.6, 118.0, 115.4, 106.2, 68.6, 32.1, 29.7, 29.6, 29.5, 29.3, 26.2, 22.9, 14.3.

FT-IR (ATR): n (cm⁻¹) = 2920, 2852, 2214, 1575, 1508, 1472, 1375, 1335, 1311, 1263, 1197, 1177, 1108, 1015, 917, 880, 849, 832, 751, 687, 623.

HRMS m/z (%): positive: calc. (M+Na⁺): C₂₄H₂₈N₂NaO₃⁺ = 415.1992, found: 415.2003.

**NO₂-C₈:** ¹H NMR (CDCl₃, 300 MHz, ppm): δ 8.29 (d, J = 9Hz, 2H), 7.94 (d, J = 9Hz, 2H), 7.94-7.79 (m, 2H), 7.60 (s, 1H), 6.99 (d, 2H), 4.04 (t, J = 6 Hz, 2H, OCH₂), 1.86-1.77 (m, 2H, 1×CH₂), 1.47-1.29 (m, 14H, 7×CH₂), 0.89 (t, J = 6Hz, 3H, 1×CH₃); ¹³C NMR (CDCl₃, 75 MHz, ppm): δ 162.3, 147.7, 145.3, 141.4, 132.2, 126.5, 125.7, 124.5, 118.0, 115.3, 106.1, 68.6, 32.1, 29.8, 29.6, 29.5, 29.3, 26.2, 22.9, 14.3.

FT-IR (ATR): n (cm⁻¹) = 2960, 2918, 2850, 2210, 1599, 1578, 1506, 1469, 1333, 1309, 1255, 1179, 1107, 1047, 1020, 993, 914, 850, 823, 796, 752, 717, 688, 607.

HRMS m/z (%): positive: calc. (M+Na⁺): C₂₅H₃₀N₂NaO₃⁺ = 429.2149, found: 429.2157.

**NO₂-C₉:** ¹H NMR (CDCl₃, 300 MHz, ppm): δ 8.30-8.27 (m, 2H), 7.94 (d, J = 9Hz, 2H), 7.84-7.80 (m, 2H), 7.60 (s, 1H), 7.02-6.98 (m, 2H), 4.04 (t, J = 6 Hz, 2H, OCH₂), 1.84-1.79 (m, 2H, 1×CH₂), 1.47-1.29 (m, 16H, 8×CH₂), 0.91-0.86 (m, 3H, 1×CH₃); ¹³C NMR (CDCl₃, 75 MHz, ppm): δ 162.3,
147.5, 145.3, 141.4, 132.2, 126.5, 125.7, 124.5, 118.0, 115.4, 106.2, 68.6, 32.1, 29.8, 29.7, 29.6, 29.5, 29.3, 26.2, 22.9, 14.3.

FT-IR (ATR): \( n \ (\text{cm}^{-1}) = 2916, 2850, 2216, 1604, 1585, 1516, 1433, 1379, 1309, 1271, 1178, 1115, 1066, 989, 945, 918, 881, 847, 825, 750, 719, 684, 627. \)

HRMS m/z (%): positive: calc. (M+Na\(^+\)): C\(_{26}\)H\(_{32}\)N\(_2\)O\(_3\)+: 443.2305, found: 443.2316.

**Synthesis of the complexes NO\(_2\)-C\(_n\)···F\(_4\)St & NO\(_2\)-C\(_n\)···F\(_4\)Az:**

CH\(_2\)Cl\(_2\) solutions of compound NO\(_2\)-C\(_n\) and compound F\(_4\)St/F\(_4\)Az\(^{52,53}\) were mixed in a 1:1 molar ratio. The solvent was allowed to evaporate overnight followed by subsequent drying under vacuum to give an orange solid.

![Diagram](image)

**Figure S1:** \(^1\)H NMR (300 MHz) spectrum of NO\(_2\)-C\(_4\) in CDC\(_3\).
Figure S2: $^{13}$C NMR (75 MHz) spectrum of NO$_2$-C$_1$ in CDCl$_3$. 

Figure S3: $^1$H NMR (300 MHz) spectrum of NO$_2$-C$_8$ in CDCl$_3$. 

C$_{8}$H$_{12}$O
$\text{N}C$ $\text{NO}_2$
Figure S4: $^{13}$C NMR (75 MHz) spectrum of NO₂-C₈ in CDCl₃.

Figure S5: $^1$H NMR (300 MHz) spectrum of NO₂-C₈ in CDCl₃.
Figure S6: $^{13}$C NMR (75 MHz) spectrum of NO$_2$-C$_9$ in CDCl$_3$.

Figure S7: $^1$H NMR (300 MHz) spectrum of NO$_2$-C$_{10}$ in CDCl$_3$. 
Figure S8: $^{13}$C NMR (75 MHz) spectrum of NO$_2$-C$_{10}$ in CDCl$_3$.

Figure S9: $^1$H NMR (300 MHz) spectrum of NO$_2$-C$_{11}$ in CDCl$_3$. 
Figure S10: $^{13}$C NMR (75 MHz) spectrum of NO$_2$-C$_{11}$ in CDCl$_3$. 

![Figure S10: $^{13}$C NMR (75 MHz) spectrum of NO$_2$-C$_{11}$ in CDCl$_3$.](image)
POM images:

Figure S11: POM images of (a, b) NO$_2$-C$_{11}$ (in heating and cooling, respectively); (c) NO$_2$-C$_8$-F$_3$St (cooling); (d) NO$_2$-C$_9$-F$_4$St (cooling); (e) NO$_2$-C$_9$-F$_3$St (cooling); (f, g) NO$_2$-C$_{11}$-F$_4$St (in heating and cooling, respectively); (h) NO$_2$-C$_9$-F$_4$Az (cooling) and (i) NO$_2$-C$_{11}$-F$_4$Az (cooling), at the different mentioned temperatures.
DSC thermograms:

**Figure S12**: DSC traces obtained from the 2nd heating and 2nd cooling cycle at a rate of 5 °C min$^{-1}$ for compound NO$_2$-Cs.

**Figure S13**: DSC traces obtained from the 2nd heating and 2nd cooling cycle at a rate of 10 °C min$^{-1}$ for compound NO$_2$-Cs.
Figure S14: DSC traces obtained from the 2\textsuperscript{nd} heating and 2\textsuperscript{nd} cooling cycle at a rate of 10 °C min\(^{-1}\) for compound NO\textsubscript{2}-C\textsubscript{10}.

Figure S15: DSC traces obtained from the 2\textsuperscript{nd} heating and 2\textsuperscript{nd} cooling cycle at a rate of 10 °C min\(^{-1}\) for compound NO\textsubscript{2}-C\textsubscript{11}.
Figure S16: DSC traces obtained from the 2nd heating and 2nd cooling cycle at a rate of 10 °C min⁻¹ for compound NO₂-C₆–FeSt.

Figure S17: DSC traces obtained from the 2nd heating and 2nd cooling cycle at a rate of 10 °C min⁻¹ for compound NO₂-C₆–FeSt.
Figure S18: DSC traces obtained from the 2nd heating and 2nd cooling cycle at a rate of 10 °C min⁻¹ for compound NO₂-C₁₀₋₄St.

Figure S19: DSC traces obtained from the 2nd heating and 2nd cooling cycle at a rate of 10 °C min⁻¹ for compound NO₂-C₁₁₋₄₅St.
Figure S20: DSC traces obtained from the 2nd heating and 2nd cooling cycle at a rate of 10 °C min⁻¹ for compound NO₂-C₉-F₆Az.

Figure S21: DSC traces obtained from the 2nd heating and 2nd cooling cycle at a rate of 10 °C min⁻¹ for compound NO₂-C₉-F₆Az.
Figure S22: DSC traces obtained from the 2nd heating and 2nd cooling cycle at a rate of 10 °C min⁻¹ for compound NO$_2$-C$_{10}$-F$_4$Az.

Figure S23: DSC traces obtained from the 2nd heating and 2nd cooling cycle at a rate of 10 °C min⁻¹ for compound NO$_2$-C$_{11}$-F$_4$Az.
Figure S24: DSC traces obtained from the 2nd heating and 2nd cooling cycle at a rate of 10 °C min⁻¹ for compound NO₂-C₁₀⁻F₂Az.

Figure S25: DSC traces obtained from the 2nd heating and 2nd cooling cycle at a rate of 10 °C min⁻¹ for compound NO₂-C₁₀⁻F₂Az.
Figure S26: DSC traces obtained from the 2nd heating and 2nd cooling cycle at a rate of 10 °C min⁻¹ for compound NO₂-C₁₀-²F₂Az.

Computational studies:

Theoretical specifications:

Structures of all complexes were optimised with the Gaussian 09 packages. The interaction energies were obtained as the energy differences counterpoise correction on the mp2/LanL2DZ. The basis set super position error (BSSE) has been undertaken for achieving errorless data of the supramolecule. Imaginary modes were minimised using the screwing method. In this method, the optimised geometry is resubmitted upon manual displacement of the second frequency. During the second job submission, the command Opt = tight was used.

Theoretical specifications: p opt freq mp2/LanL2DZ counterpoise = 2

Table S1: Calculated interaction energies of the different complexes.

| Complex       | EAB (BSSE corrected) (Hartree) | (Eₐ+E) BSSE Corrected (Hartree) | Eint. (BSSE corrected) (Hartree) | Eint. (BSSE corrected) (kJ/Mol) |
|---------------|--------------------------------|---------------------------------|---------------------------------|--------------------------------|
| NO₂-C₁₀-²F₂St | -2006.44759                    | -2006.446575                    | -0.007692308                    | -20.19                         |
| NO₂-C₁₀-²F₂Az | -2038.42375                    | -2038.421206                    | -0.006620833                    | -17.38                         |
| NO₂-C₁₀-²F₂Az | -1939.4923                     | -1939.4893                      | -0.006201607                    | -16.28                         |
| NO₂-C₁₀-²F₂Az | -1840.77384                    | -1840.766828                    | -0.00466                        | -12.23                         |
| NO₂-C₁₀-²F₂Az | -1840.75995                    | -1840.753543                    | -0.004406667                    | -11.57                         |
Coordinates for the optimised geometry of NO$_2$-C$_1$⋯F$_4$St

Charge = 0; multiplicity = 1 in supermolecule

Charge = 0; multiplicity = 1 in fragment 1.

Charge = 0; multiplicity = 1 in fragment 2.

| C(Fragment=1)  | -3.19669 | 2.82106 | -0.01305 |
| C(Fragment=1)  | -2.01506 | 3.05855 | -0.74136 |
| C(Fragment=1)  | -2.07746 | 3.71164 | -1.9783  |
| C(Fragment=1)  | -3.27913 | 4.27811 | -2.39692 |
| C(Fragment=1)  | -4.44271 | 4.09723 | -1.65057 |
| C(Fragment=1)  | -4.43183 | 3.31767 | -0.4797  |
| C(Fragment=1)  | -5.73348 | 4.8551  | -2.10671 |
| C(Fragment=1)  | -6.97153 | 4.30557 | -2.07845 |
| C(Fragment=1)  | -7.20384 | 2.78492 | -2.00605 |
| C(Fragment=1)  | -8.51771 | 2.29513 | -2.00811 |
| C(Fragment=1)  | -8.77283 | 0.96244 | -1.99046 |
| C(Fragment=1)  | -7.72319 | 0.03958 | -1.99219 |
| C(Fragment=1)  | -6.39266 | 0.49332 | -1.95863 |
| C(Fragment=1)  | -6.12726 | 1.87575 | -1.96418 |
| O(Fragment=1)  | -8.01634 | -1.36333 | -1.99212 |
| C(Fragment=1)  | -7.04931 | -2.07107 | -2.76881 |
| N(Fragment=1)  | -0.70201 | 2.6152  | -0.2268  |
| O(Fragment=1)  | 0.09121  | 2.24427 | -1.28062 |
| O(Fragment=1)  | -0.86202 | 1.52863 | 0.59341  |
| C(Fragment=1)  | -5.59433 | 6.17493 | -2.56603 |
| N(Fragment=1)  | -5.48096 | 7.25055 | -2.94036 |
| H(Fragment=1)  | -3.16005 | 2.26053 | 0.89747  |
| H(Fragment=1)  | -1.20741 | 3.76955 | -2.59102 |
| H(Fragment=1)  | -3.30912 | 4.83921 | -3.31117 |
| H(Fragment=1)  | -5.3301  | 3.11964 | 0.04324  |
| H(Fragment=1)  | -7.82429 | 4.95178 | -2.14103 |
| H(Fragment=1)  | -9.33952 | 2.98562 | -2.03564 |
| Fragment          | X1     | X2     | X3     |
|-------------------|--------|--------|--------|
| H(Fragment=1)     | -9.78573 | 0.61186 | -2.00139 |
| H(Fragment=1)     | -5.58454 | -0.20747 | -1.95066 |
| H(Fragment=1)     | -5.12654 | 2.23119 | -1.95047 |
| H(Fragment=1)     | -7.27933 | -3.11507 | -2.75878 |
| H(Fragment=1)     | -7.07286 | -1.71207 | -3.77689 |
| H(Fragment=1)     | -6.07585 | -1.91522 | -2.35891 |
| C(Fragment=2)     | 3.80177  | -1.27299 | -0.15156 |
| C(Fragment=2)     | 4.8818   | -2.01535 | -0.55633 |
| C(Fragment=2)     | 6.2027   | -1.67651 | -0.24661 |
| C(Fragment=2)     | 6.4315   | -0.69378 | 0.70576 |
| C(Fragment=2)     | 5.34386 | 0.0864  | 1.11574  |
| C(Fragment=2)     | 4.03758 | -0.1759 | 0.64339 |
| I(Fragment=2)     | 2.42311 | 1.12594 | 0.99253 |
| C(Fragment=2)     | 7.01357 | -2.59036 | -1.19547 |
| C(Fragment=2)     | 8.25538 | -2.93373 | -1.6438 |
| C(Fragment=2)     | 9.71183 | -3.40721 | -1.37683 |
| C(Fragment=2)     | 10.33985 | -4.22114 | -0.46279 |
| C(Fragment=2)     | 10.41594 | -2.89012 | -2.4531 |
| C(Fragment=2)     | 11.45244 | -4.9086 | -0.95121 |
| H(Fragment=2)     | 9.98568  | -4.34845 | 0.53436 |
| C(Fragment=2)     | 11.51918 | -3.51942 | -2.93473 |
| H(Fragment=2)     | 10.06049 | -1.97599 | -2.93365 |
| C(Fragment=2)     | 11.96645 | -4.61389 | -2.25208 |
| H(Fragment=2)     | 11.9095  | -5.67928 | -0.38287 |
| H(Fragment=2)     | 11.98588 | -3.17872 | -3.84044 |
| O(Fragment=2)     | 12.95868 | -5.44201 | -2.87316 |
| C(Fragment=2)     | 14.23006 | -4.97903 | -2.48865 |
| H(Fragment=2)     | 14.31843 | -5.06351 | -1.42861 |
| H(Fragment=2)     | 14.9875  | -5.56136 | -2.96254 |
| H(Fragment=2)     | 14.33937 | -3.95245 | -2.77583 |
| H(Fragment=2)     | 6.30267  | -3.16599 | -1.74952 |
| H(Fragment=2)     | 8.19552  | -2.81419 | -2.66155 |
### Coordinates for the optimised geometry of NO$_2$-C$_1\cdots$F$_4$Az

Charge = 0; multiplicity = 1 in supermolecule

Charge = 0; multiplicity = 1 in fragment 1.

Charge = 0; multiplicity = 1 in fragment 2.

| Atom (Fragment=1) | X         | Y         | Z       |
|-------------------|-----------|-----------|---------|
| C                 | -0.55763  | 1.44208   | -0.00476|
| C                 | 0.624     | 1.67957   | -0.73307|
| C                 | 0.5616    | 2.33266   | -1.97001|
| C                 | -0.64007  | 2.89913   | -2.38863|
| C                 | -1.80365  | 2.71825   | -1.64228|
| C                 | -1.79277  | 1.93869   | -0.47141|
| C                 | -3.09442  | 3.47612   | -2.09842|
| C                 | -4.33247  | 2.92659   | -2.07016|
| C                 | -4.56478  | 1.40594   | -1.99776|
| C                 | -5.87865  | 0.91615   | -1.99982|
| C                 | -6.13377  | -0.41654  | -1.98217|
| C                 | -5.08413  | -1.3394   | -1.9839 |
| C                 | -3.7536   | -0.88566  | -1.95034|
| C                 | -3.4882   | 0.49677   | -1.95589|
| O                 | -5.37728  | -2.74231  | -1.98383|
| C                 | -4.41025  | -3.45006  | -2.76052|
| N                 | 1.93705   | 1.23622   | -0.21851|
| O                 | 2.73027   | 0.86528   | -1.27233|
| O                 | 1.77704   | 0.14965   | 0.6017  |
| C                 | -2.95527  | 4.79595   | -2.55774|
| N                 | -2.8419   | 5.87157   | -2.93207|
| H                 | -0.52099  | 0.88155   | 0.90576 |
| Atom (Fragment=1) | X  | Y  | Z  |
|------------------|----|----|----|
| H                | 1.43165 | 2.39057 | -2.58273 |
| H                | -0.67006 | 3.46023 | -3.30288 |
| H                | -2.69104 | 1.74066 | 0.05153 |
| H                | -5.18523 | 3.5728 | -2.13274 |
| H                | -6.70046 | 1.60664 | -2.02735 |
| H                | -7.14667 | -0.76712 | -1.9931 |
| H                | -2.94548 | -1.58646 | -1.94237 |
| H                | -2.48748 | 0.85221 | -1.94218 |
| H                | -4.64027 | -4.49406 | -2.75049 |
| H                | -4.4338 | -3.09105 | -3.7686 |
| H                | -3.43679 | -3.2942 | -2.35062 |
| C                | 6.43959 | -2.65586 | -0.13375 |
| C                | 7.51962 | -3.39822 | -0.53852 |
| C                | 8.84052 | -3.05938 | -0.2288 |
| C                | 9.06932 | -2.07665 | 0.72357 |
| C                | 7.98168 | -1.29647 | 1.13355 |
| C                | 6.6754 | -1.55877 | 0.66119 |
| I                | 5.06093 | -0.25693 | 1.01034 |
| C                | 12.34965 | -4.79008 | -1.35902 |
| C                | 12.97766 | -5.60401 | -0.44499 |
| C                | 13.05376 | -4.273 | -2.43529 |
| C                | 14.09026 | -6.29148 | -0.9334 |
| H                | 12.62349 | -5.73133 | 0.55217 |
| C                | 14.15699 | -4.90229 | -2.91692 |
| H                | 12.69831 | -3.35886 | -2.91585 |
| C                | 14.60426 | -5.99677 | -2.23427 |
| H                | 14.54732 | -7.06216 | -0.36507 |
| H                | 14.6237 | -4.56159 | -3.82263 |
| O                | 15.5965 | -6.82488 | -2.85535 |
| C                | 16.86788 | -6.3619 | -2.47084 |
| H                | 16.95625 | -6.44638 | -1.4108 |
| H                | 17.62532 | -6.94423 | -2.94473 |
Coordinates for the optimised geometry of NO₂-C₁⋯F₂Az

Charge = 0 multiplicity = 1 in supermolecule
Charge = 0 multiplicity = 1 in Fragment 1.
Charge = 0 multiplicity = 1 in Fragment 2.
| Fragment  | O       | C       | N       | H       | I       | C       | H       |
|-----------|---------|---------|---------|---------|---------|---------|---------|
| 1         | 1.79803 | -0.05694| 0.62444 |         |         |         |         |
| 1         | -2.81747| 4.68054 | -2.55719|         |         |         |         |
| 1         | -2.69442| 5.72909 | -3.00254|         |         |         |         |
| 1         | -0.46633| 0.68321 | 0.93219 |         |         |         |         |
| 1         | 1.61914 | 2.53372 | -2.31355|         |         |         |         |
| 1         | -0.48505| 3.57222 | -3.07142|         |         |         |         |
| 1         | -2.61554| 1.54716 | 0.04036 |         |         |         |         |
| 1         | -5.05941| 3.51275 | -1.97943|         |         |         |         |
| 1         | -6.57816| 1.54711 | -1.80416|         |         |         |         |
| 1         | -7.02366| -0.8278 | -1.80332|         |         |         |         |
| 1         | -2.82214| -1.64421| -1.78118|         |         |         |         |
| 1         | -2.36343| 0.79539 | -1.76904|         |         |         |         |
| 1         | -4.49525| -4.54789| -2.61292|         |         |         |         |
| 1         | -4.2768 | -3.13435| -3.61704|         |         |         |         |
| 1         | -3.30081| -3.34708| -2.1836  |         |         |         |         |
| 2         | 6.31469 | -2.71096| -0.18594|         |         |         |         |
| 2         | 7.36024 | -3.46518| -0.7745  |         |         |         |         |
| 2         | 8.68048 | -2.99534| -0.67015 |         |         |         |         |
| 2         | 8.94284 | -1.93932| 0.22155  |         |         |         |         |
| 2         | 7.89787 | -1.27981| 0.85826  |         |         |         |         |
| 2         | 6.58225 | -1.59835| 0.56662  |         |         |         |         |
| 2         | 5.02142 | -0.37204| 1.25321  |         |         |         |         |
| 2         | 11.96547| -4.89113| -1.67692 |         |         |         |         |
| 2         | 12.62212| -5.72401| -0.80925 |         |         |         |         |
| 2         | 12.70901| -4.31639| -2.71691 |         |         |         |         |
| 2         | 13.90558| -6.21466| -1.12412 |         |         |         |         |
| 2         | 12.18255| -6.0033 | 0.11621  |         |         |         |         |
| 2         | 13.96383| -4.83149| -3.04631 |         |         |         |         |
| 2         | 12.32902| -3.50498| -3.29893 |         |         |         |         |
| 2         | 14.47805| -5.88109| -2.3501  |         |         |         |         |
| 2         | 14.44239| -6.83859| -0.42802 |         |         |         |         |
| 2         | 14.52674| -4.42003| -3.86057 |         |         |         |         |

S23
Coordinates for the optimised geometry of NO$_2$-C$_1$⋯F$_2$Az

Charge = 0; multiplicity = 1 in supermolecule
Charge = 0; multiplicity = 1 in fragment 1.
Charge = 0; multiplicity = 1 in fragment 2.
| Atoms     | Fragment=1 | X    | Y    | Z   |
|-----------|------------|------|------|-----|
| C         | -8.56856   | 0.97556 | 1.02835 |
| O         | -9.7245    | 4.29113 | -0.43483 |
| C         | -8.64697   | 5.10323 | 0.02677  |
| N         | -3.12655   | 0.03255 | 0.22356  |
| O         | -2.21571   | -0.69932 | 0.87507  |
| O         | -2.81477   | 0.04311 | -1.08089 |
| C         | -8.61613   | -3.54433 | 1.7508  |
| N         | -8.75091   | -4.71177 | 2.32913 |
| H         | -5.21847   | 0.11367 | -1.48023 |
| H         | -3.96197   | -1.50916 | 2.26349 |
| H         | -6.17554   | -2.57651 | 2.56333 |
| H         | -7.52111   | -0.68392 | -1.06164 |
| H         | -10.43765  | -1.98509 | 0.41503  |
| H         | -11.18792  | -0.00178 | -0.8874  |
| H         | -11.13257  | 2.36952 | -1.51553 |
| H         | -7.97508   | 3.05746 | 1.28927  |
| H         | -7.82971   | 0.59788 | 1.71275  |
| H         | -8.74995   | 6.09967 | -0.35003 |
| H         | -8.66258   | 5.12873 | 1.08606  |
| H         | -7.72235   | 4.70966 | -0.30013 |
| C         | 3.35835    | 0.44447 | -0.17558 |
| C         | 4.6878     | 0.43683 | 0.25178  |
| C         | 5.55128    | -0.5693 | -0.13462 |
| C         | 5.13495    | -1.51313 | -1.12197 |
| C         | 3.76395    | -1.54026 | -1.50463 |
| C         | 2.88379    | -0.56643 | -1.01988 |
| I         | 0.85809    | -0.60028 | -1.54861 |
| C         | 9.13417    | 0.5791  | 0.76236  |
| C         | 9.80842    | 1.80448 | 0.49722  |
| C         | 9.85812    | -0.58071 | 0.93904  |
| C         | 11.20275   | 1.86218 | 0.74889  |
| H         | 9.28003    | 2.67907 | 0.14937  |
|          | X (Å)  | Y (Å)  | Z (Å)  |
|----------|--------|--------|--------|
| C(Fragment=2) | 11.23375 | -0.53295 | 1.11519 |
| H(Fragment=2)  | 9.33831  | -1.50948 | 0.94727 |
| C(Fragment=2) | 11.89651 | 0.69796  | 1.11841 |
| H(Fragment=2)  | 11.73107 | 2.78579  | 0.66492 |
| H(Fragment=2)  | 11.77507 | -1.43775 | 1.25222 |
| O(Fragment=2)  | 13.26862 | 0.76214  | 1.50345 |
| C(Fragment=2) | 14.11241 | 0.63992  | 0.38679 |
| H(Fragment=2)  | 13.90284 | 1.42521  | -0.29234 |
| H(Fragment=2)  | 15.13715 | 0.69882  | 0.68437 |
| H(Fragment=2)  | 13.94227 | -0.29523 | -0.08313 |
| F(Fragment=2)  | 3.28929  | -2.50697 | -2.32626 |
| F(Fragment=2)  | 2.5401   | 1.4386   | 0.22586 |
| H(Fragment=2)  | 5.8229   | -2.22004 | -1.56911 |
| N(Fragment=2)  | 6.84582  | -0.63144 | 0.55519 |
| N(Fragment=2)  | 7.66436  | 0.45968  | 0.93155 |
| H(Fragment=2)  | 5.0503   | 1.20267  | 0.88315 |

**Coordinates for the optimised geometry of complex NO₂-C₁⋯F₂∙Az**

**Charge = 0; multiplicity = 1 in supermolecule**

**Charge = 0; multiplicity = 1 in fragment 1.**

**Charge = 0; multiplicity = 1 in fragment 2.**

|          | X (Å)  | Y (Å)  | Z (Å)  |
|----------|--------|--------|--------|
| C(Fragment=1) | -5.46415 | -0.32047 | -0.52736 |
| C(Fragment=1) | -4.45539 | -0.55024 | 0.41093 |
| C(Fragment=1) | -4.71367 | -1.3403  | 1.55958 |
| C(Fragment=1) | -5.99021 | -1.90431 | 1.73667 |
| C(Fragment=1) | -7.01268 | -1.58027 | 0.86999 |
| C(Fragment=1) | -6.76428 | -0.80746 | -0.29232 |
| C(Fragment=1) | -8.43977 | -2.11293 | 1.08363 |
| C(Fragment=1) | -9.50835 | -1.44809 | 0.58495 |
| C(Fragment=1) | -9.49705 | 0.08421  | 0.36378 |
| Atom (Fragment=1) | X   | Y   | Z   |
|-------------------|-----|-----|-----|
| C                 | -10.4559 | 0.6218 | -0.48378 |
| C                 | -10.48031 | 1.99665 | -0.76552 |
| C                 | -9.5972 | 2.87248 | -0.13307 |
| C                 | -8.64597 | 2.36163 | 0.76425 |
| C                 | -8.55513 | 0.95984 | 0.98668 |
| O                 | -9.76287 | 4.29733 | -0.38887 |
| C                 | -8.62681 | 5.07815 | 0.03967 |
| N                 | -3.11342 | 0.02395 | 0.2268 |
| O                 | -2.21186 | -0.75399 | 0.84232 |
| O                 | -2.81953 | 0.03821 | -1.08582 |
| C                 | -8.62017 | -3.49448 | 1.79749 |
| N                 | -8.77195 | -4.65678 | 2.39805 |
| H                 | -5.25486 | 0.19486 | -1.44391 |
| H                 | -3.9518 | -1.5376 | 2.26833 |
| H                 | -6.16437 | -2.59577 | 2.52037 |
| H                 | -7.54173 | -0.63269 | -1.02008 |
| H                 | -10.37186 | -2.02994 | 0.31435 |
| H                 | -11.18911 | -0.01056 | -0.9403 |
| H                 | -11.18389 | 2.38747 | -1.46766 |
| H                 | -7.98206 | 3.04373 | 1.28349 |
| H                 | -7.7868 | 0.58523 | 1.62604 |
| H                 | -8.74123 | 6.07211 | -0.33161 |
| H                 | -8.60742 | 5.07453 | 1.09487 |
| H                 | -7.71676 | 4.66633 | -0.34325 |
| C                 | 3.35559 | 0.46284 | -0.1801 |
| C                 | 4.66273 | 0.43351 | 0.27319 |
| C                 | 5.53413 | -0.57737 | -0.10166 |
| C                 | 5.13703 | -1.49952 | -1.10447 |
| C                 | 3.79521 | -1.51382 | -1.53434 |
| C                 | 2.91145 | -0.54444 | -1.03294 |
| I                 | 0.89406 | -0.58874 | -1.56111 |
| C                 | 9.14203 | 0.56205 | 0.77881 |
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