Electronic Supplementary Material (ESI) for RSC Advances.

Supramolecular control of liquid crystals by doping with halogen-bonding dyes

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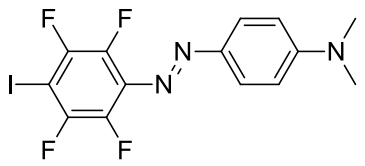
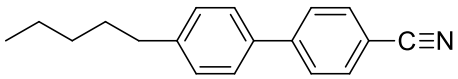
Electronic Supplementary Information (ESI)

1. Structural characterization



1



5CB

The structure of 5CB:**1** co-crystal, obtained by slow crystallization from a 5:1 chloroform solution, is shown in Figure S1. The asymmetric unit of the cocrystal is composed of one molecule of **1** and one molecule of 5CB. The complex assembles through halogen bonding occurring between nitrogen atom of the 5CB cyano group and iodine atom of **1**. The N···I distance in such halogen-bonded adduct is 3.033(3) Å (about 86 % of the sum of van der Waals radii), and the C-I···N angle is 177.1(5)° or 177.4(7)° depending on the conformer.

The structure is highly disordered, the only ordered atoms being the C-I and the cyano group. Disorder of compound **1** was modelled considering two *N*,*N*-dimethylamino-phenyldiazo groups rotated about 70° one towards one another, and two tetrafluorobenzene rings lying almost in the same plane. For 5CB, the degree of disorder was even higher. The two phenyl rings were rotated one towards the other of 85° and 38°, respectively, whereas the C_5 alkyl chain was split into two conformations, one nearly *all-trans* and the other in a *tgt* conformation. A population factor of 0.5 was assigned to all the disordered atoms. Since the space group is centrosymmetric, couples of XB-adducts in the cocrystal are related by an inversion center. Detailed crystal data for **1**:5CB complex are given in Table S1.

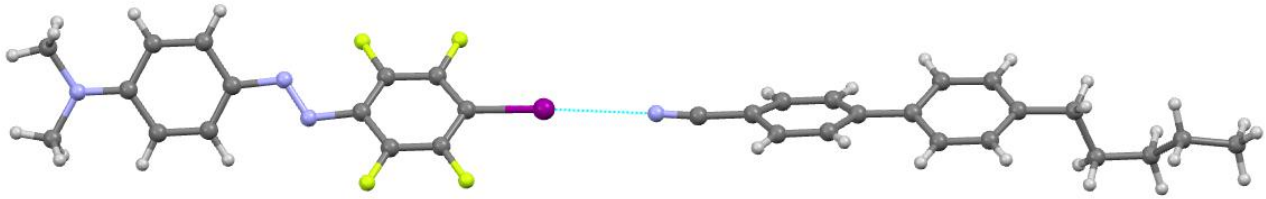


Figure S1. Crystal structure of the halogen bonded complex between 1 and 5CB. For clarity, only the most populated conformer of each molecule is shown.

Table S1. Crystallographic data for **1:5CB** cocrystal.

	1:5CB
Chemical Formula	$C_{32}H_{29}F_4IN_4$
Molecular Formula	$C_{14}H_{10}F_4IN_3$, $C_{18}H_{19}N$
M_r	672.49
Crystal system, space group	triclinic, P -1
Temperature (K)	103(2)
***a* (Å)**	9.1034(12)
***b* (Å)**	10.3247(15)
***c* (Å)**	15.994(2)
α (°)	77.627(10)
β (°)	89.947(12)
γ (°)	79.950(10)
***V* (Å^3)**	1444.8(3)
Z	2
Crystal size (mm^3)	0.02, 0.09, 0.12
P_{calc} **(g.cm^{-3})**	1.546
μ **(mm^{-1})**	1.163
Absorption correction	multi-scan
Tmin, Tmax	0.8313, 0.9011
Data collection	
Diffractometer	Bruker *APEX*-II CCD area detector diffractometer
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	42909, 7120, 5749
R_{int}	0.047
θ_{max} (°)	28.3
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.118
No. of parameters	604
No. of restraints	1241
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.34, -1.16

2. Infrared characterization

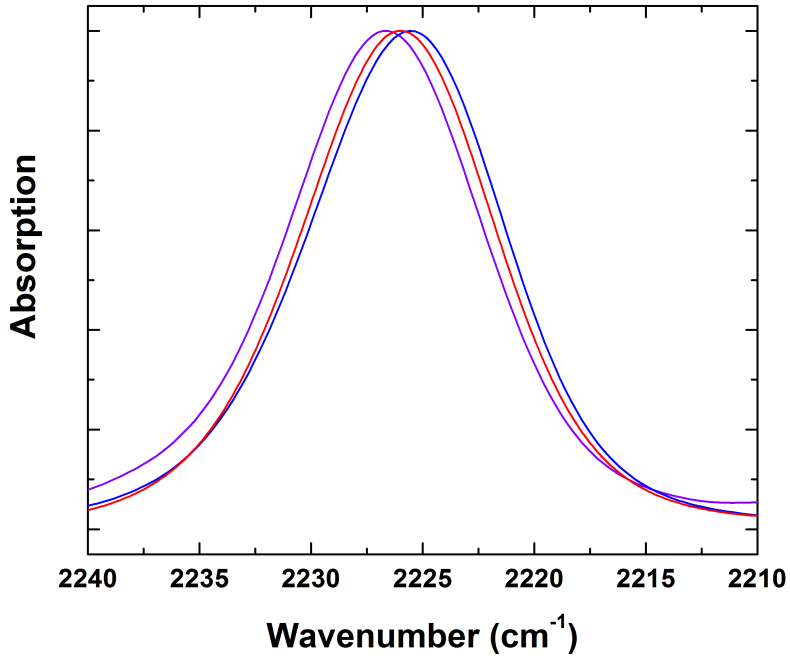


Figure S2. ATR-IR spectra of cyano stretching vibration of pure 5CB (blue), 5CB doped with 1-mol% of **1** (red), and 5CB:**1** cocrystal solution (violet; 5:1 molar ratio). The doped 5CB shows a shift of 0.5 cm^{-1} and the cocrystal a shift of 1.1 cm^{-1} towards higher wavenumbers as compared to pure 5CB. According to DFT calculations this stretching vibration should shift 5 cm^{-1} towards higher wavenumbers upon halogen-bonding, and the resulting shift is convolution of non-affected and affected cyano stretching vibrations, taking into account that nominally only 1% and 20% of 5CB are bonded to **1** in the cases of doped LC and the cocrystal solution, respectively.

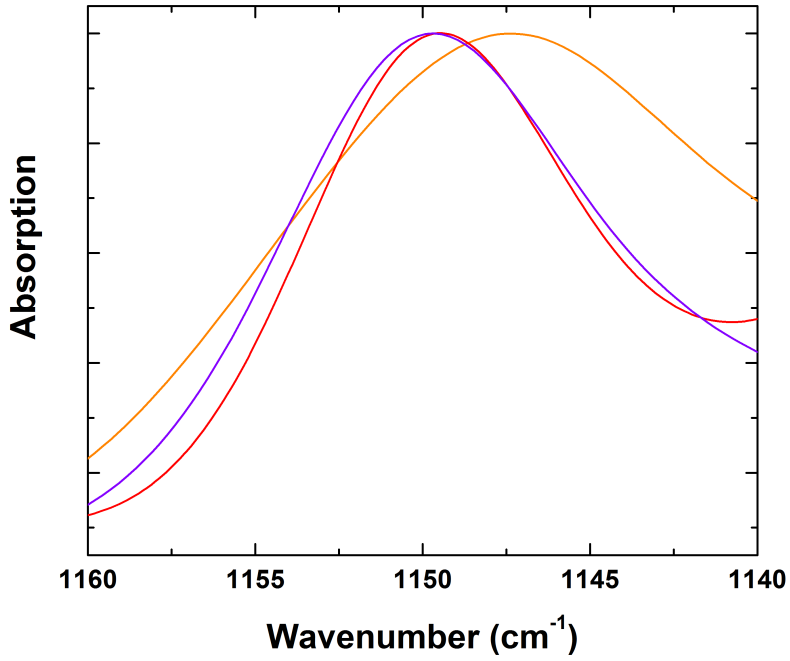


Figure S3. ATR-IR spectra of pure **1** (orange), 5CB doped with 1-mol% of **1** (red), and **1**:5CB cocrystal solution (violet) in the region of 1160-1140 cm^{-1} showing that **1** is not phase-separated into domains of pure **1** neither in the doped LC nor in the cocrystal.

3. Differential scanning calorimetry

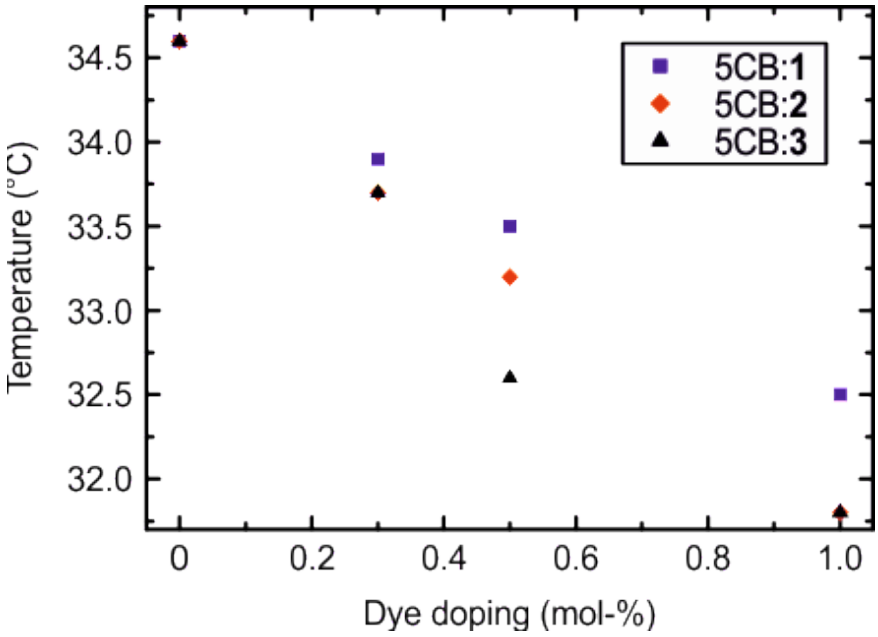


Figure S4. The clearing points of the 5CB:**x** systems as a function of dye doping, measured with Seiko Instruments EXSTAR 6000 differential scanning calorimeter.

4. *Cis*-lifetimes of 1-3 in 5CB

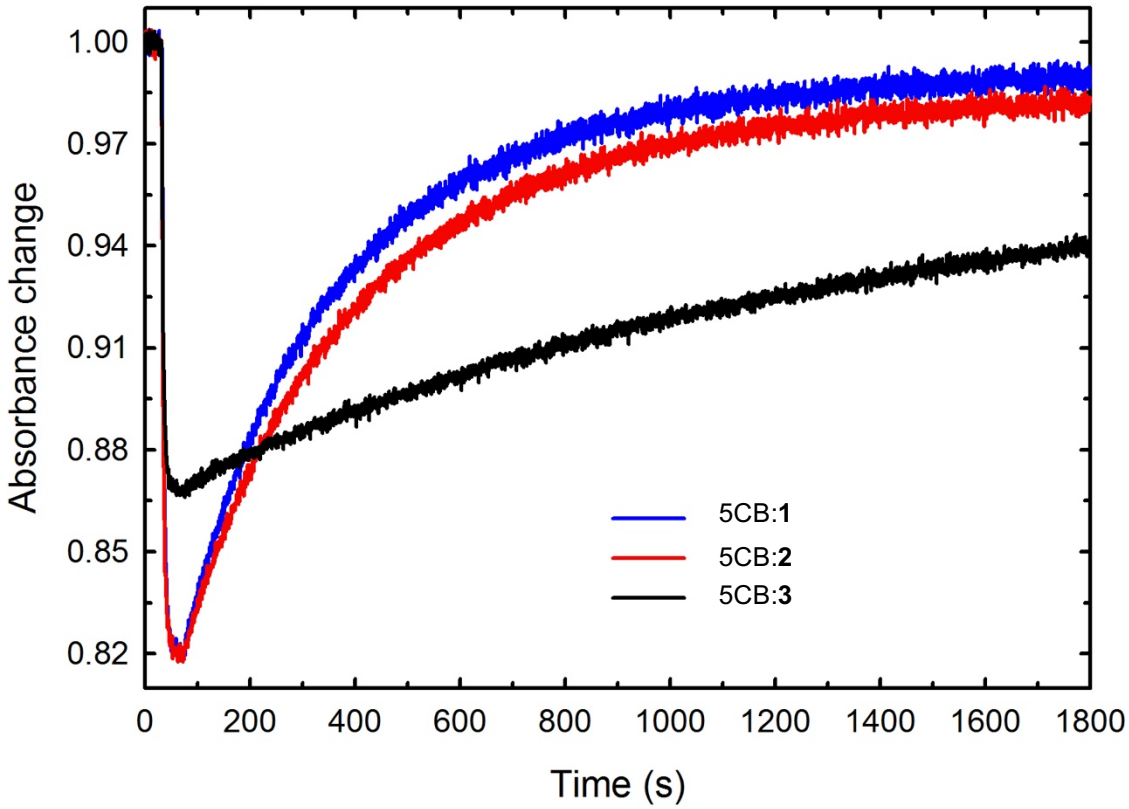


Figure S5. Pump-probe experiment pointing out that the thermal relaxation of **3** in 5CB is significantly slower that the thermal relaxation of **1** or **2**. Based on the absorbance changes, we estimate the cis half-lives of **1** and **2** to be approximately similar, while the half life of **3** is at least by a factor of 5 longer.

5. QTAIM Topological Analysis of Electron Density Distribution

A Quantum Atoms in Molecules (QTAIM)[S1] analysis was performed on the electron density distribution of all complexes. Figures S5-S8 show the resulting molecular graphs, consisting in bond paths and associated bond critical points, which are indicative of the existence of intra- and intermolecular noncovalent interactions. An Interacting Quantum Atoms (IQA)[S2] analysis performed on noncovalent interactions confirmed halogen and hydrogen bonds as stabilizing interactions ($E_{IQA} < 0$, blue lines in Figures S4-S7). On the other hand, there are also destabilizing interactions ($E_{IQA} > 0$, red lines in Figures S4-S7) between an ortho-fluorine and the azo group, and between an *ortho*-fluorine and the cyano group in the non-linear **3-1CB** complex.

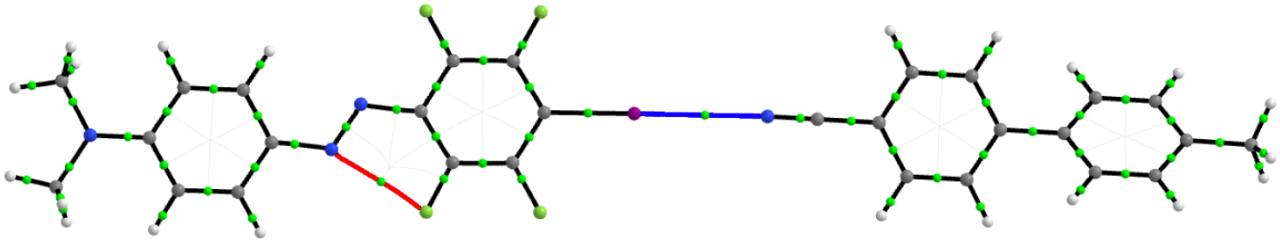


Figure S6. Bond Critical Points (green dots) and bond paths for the **1-1CB** complex. The destabilizing non-covalent interaction is shown in red and the stabilizing one in blue.

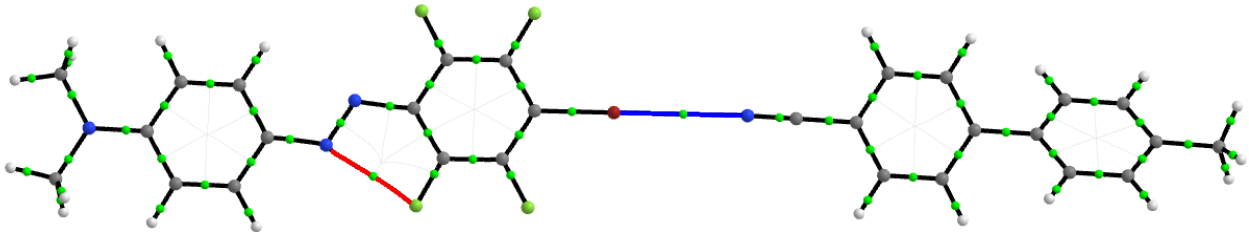


Figure S7. Bond Critical Points (green dots) and bond paths for the **2-1CB** complex. The destabilizing non-covalent interaction is shown in red and the stabilizing one in blue.

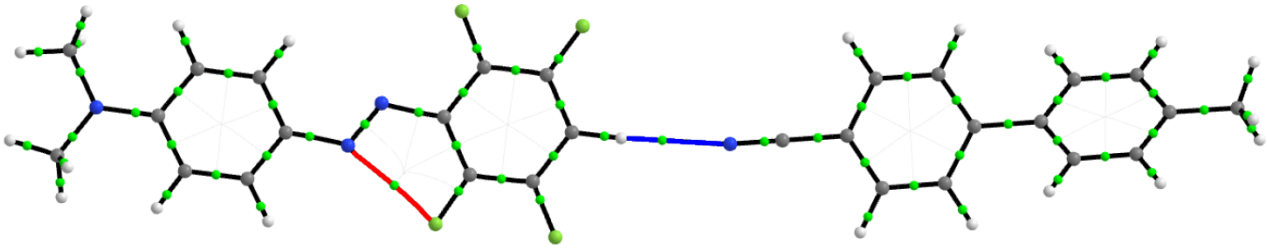


Figure S8. Bond Critical Points (green dots) and bond paths for the linear **3-1CB** complex. The destabilizing non-covalent interaction is shown in red and the stabilizing one in blue.

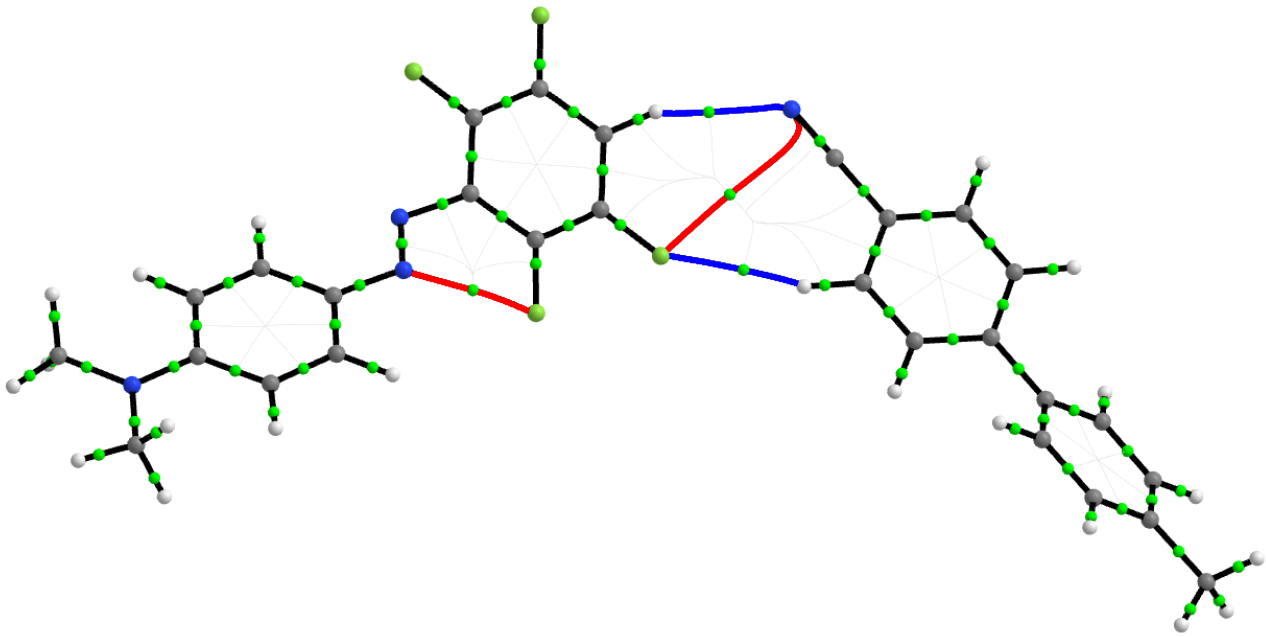


Figure S9. Bond Critical Points (green dots) and bond paths for the non-linear **3-1CB** complex. The destabilizing non-covalent interactions are shown in red and the stabilizing ones in blue.

Table S2. Optimized halogen and hydrogen bond lengths (R) and angles (θ), and interaction energies for the complexes of **1**, **2** and **3** with 1CB.

Complex	R(X···N) (Å)	θ(C-X···N) (°)	θ(X···NC) (°)	R(H···F) (Å)	θ(C-H···F) (°)	Interaction energy (kcal/mol)
1-1CB	3.069	179.2	175.4	-	-	3.09
2-1CB	3.137	179.1	175.4	-	-	1.53
linear-3-1CB	2.391	175.0	171.4	-	-	2.17
non-linear-3-1CB	2.452	156.7	124.3	2.552	153.2	2.45

Table S3. Electron density (ρ_{BCP}) and Laplacian of the electron density ($\nabla^2\rho_{BCP}$) at the Bond Critical Points, and Interacting Quantum Atoms interaction energies (E_{IQA}) for the noncovalent halogen and hydrogen bond interactions in the complexes of **1**, **2** and **3** with 1CB.

Complex	$\rho_{BCP(X\cdots N)}$ e bohr^{-3}	$\nabla^2\rho_{BCP(X\cdots N)}$ e bohr^{-5}	$E_{IQA}(X\cdots N)$ (Hartree)	$\rho_{BCP(H\cdots F)}$ e bohr^{-3}	$\nabla^2\rho_{BCP(H\cdots F)}$ e bohr^{-5}	$E_{IQA}(H\cdots F)$ (Hartree)
1-1CB	0.0139	0.0503	-0.0878	-	-	-
2-1CB	0.0097	0.0383	-0.0370	-	-	-
linear-3-1CB	0.0104	0.0379	-0.0456	-	-	-
non-linear-3-1CB	0.0089	0.0315	-0.0420	0.0050	0.0224	-0.0125

(S1) R. F. W. Bader, Chem. Rev. **91**, 893-928 (1991).

(S2) (a) M. A. Blanco, A. Martin Pendas and E. Francisco, J. Chem. Theory Comput. **1**, 1096-1109 (2005). (b) E. Francisco, A. Martin Pendas and M. A. Blanco, J. Chem. Theory Comput. **2**, 90-102 (2006).

Coordinates for the **1-1CB** complex:

C -4.90623 -0.70087 -0.22957
N -4.06490 -1.78097 0.22000
H -4.79785 0.19105 0.39825
H -5.94650 -1.01676 -0.18483
H -4.68581 -0.41562 -1.26449
C -4.66524 -3.01778 0.64987
H -5.74589 -2.94650 0.54502
H -4.44167 -3.23718 1.70052
H -4.32331 -3.86701 0.04713
C -2.10119 -0.42411 -0.16159
C -0.73757 -0.27086 -0.13361
C 0.08830 -1.31085 0.30828
C -0.50354 -2.50430 0.71900
C -1.87017 -2.67121 0.69579
C -2.71069 -1.63161 0.25202
H -2.29005 -3.61226 1.02277
H 0.14399 -3.30442 1.05923
H -2.71169 0.39877 -0.50787
H -0.28248 0.65893 -0.45187
N 1.47801 -1.25778 0.37650
N 1.99010 -0.17349 0.02125
C 3.38734 -0.13804 0.05185
C 3.97453 1.11781 0.23658
C 5.34763 1.27932 0.22639
C 6.19010 0.20815 0.00872
C 5.61804 -1.03010 -0.19878
C 4.24755 -1.22020 -0.17334
F 3.78067 -2.43480 -0.42545
F 3.20473 2.17679 0.44899
F 5.85295 2.49312 0.43150
H 7.26724 0.33192 -0.00226
F 6.39860 -2.08871 -0.43633
N 9.61543 -0.37169 0.04559
C 9.96475 -1.46948 0.06270
C 10.38429 -2.83154 0.08515
C 11.74215 -3.15123 0.07611
C 12.13645 -4.47418 0.09953
C 11.19777 -5.50880 0.13206
C 9.84228 -5.17015 0.13948
C 9.43285 -3.85165 0.11667
H 12.47959 -2.35806 0.06026
H 13.19347 -4.71194 0.11891
H 9.09566 -5.95538 0.13677
H 8.37931 -3.60097 0.11382
C 11.62713 -6.91789 0.15947
C 12.74761 -7.34357 -0.55400
C 13.14605 -8.66875 -0.53005
C 12.44939 -9.61897 0.21147
C 11.33046 -9.19324 0.92222

C 10.92405 -7.87072 0.89682
H 13.29673 -6.63375 -1.16270
H 14.01247 -8.97421 -1.10798
H 10.76844 -9.91112 1.51108
H 10.06066 -7.56801 1.47886
C 12.90175 -11.04591 0.26359
H 13.59369 -11.20522 1.09675
H 13.42241 -11.33263 -0.65179
H 12.05964 -11.72572 0.40562

Coordinates for the **2-1CB** complex:

C -6.14003 0.47267 -0.21481
N -5.48612 -0.78328 0.05247
H -5.92470 1.21765 0.55960
H -7.21658 0.31649 -0.23802
H -5.83948 0.89228 -1.18172
C -6.27765 -1.97399 0.22765
H -7.33091 -1.72257 0.12107
H -6.13504 -2.41631 1.22048
H -6.03528 -2.73757 -0.52052
C -3.33156 0.30791 -0.04390
C -1.96282 0.24674 0.03454
C -1.31625 -0.96739 0.29425
C -2.09265 -2.11209 0.47065
C -3.46661 -2.06454 0.39384
C -4.12731 -0.84809 0.13317
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C 2.86725 0.87406 0.64615
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F 4.88977 1.96441 1.03865
Br 6.81530 -0.32660 0.43626
F 4.86082 -2.54882 -0.29221
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C 12.52088 -0.51071 0.32389
C 13.27524 0.64152 0.10156
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C 15.31176 -0.66543 0.15722
C 14.54114 -1.80958 0.37928

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H 12.77577 1.59749 0.00266
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H 12.57828 -2.63630 0.62592
C 16.78003 -0.74730 0.06956
C 17.49594 0.06328 -0.81144
C 18.87515 -0.01664 -0.89194
C 19.59525 -0.90319 -0.09588
C 18.88033 -1.70662 0.78827
C 17.50066 -1.63525 0.86843
H 16.96452 0.74929 -1.46181
H 19.40444 0.62128 -1.59259
H 19.41525 -2.39558 1.43416
H 16.97719 -2.25666 1.58666
C 21.08550 -1.00629 -0.20413
H 21.52986 -0.05641 -0.50660
H 21.37099 -1.75334 -0.95159
H 21.53367 -1.30716 0.74450

Coordinates for the linear **3**-**1CB** complex:

C -6.14003 0.47267 -0.21481
N -5.48612 -0.78328 0.05247
H -5.92470 1.21765 0.55960
H -7.21658 0.31649 -0.23802
H -5.83948 0.89228 -1.18172
C -6.27765 -1.97399 0.22765
H -7.33091 -1.72257 0.12107
H -6.13504 -2.41631 1.22048
H -6.03528 -2.73757 -0.52052
C -3.33156 0.30791 -0.04390
C -1.96282 0.24674 0.03454
C -1.31625 -0.96739 0.29425
C -2.09265 -2.11209 0.47065
C -3.46661 -2.06454 0.39384
C -4.12731 -0.84809 0.13317
H -4.03238 -2.97477 0.53580
H -1.58371 -3.04822 0.67040
H -3.80063 1.26140 -0.24566
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C 4.22896 -1.42841 0.03136
C 2.84520 -1.41964 -0.00024
F 2.23837 -2.52944 -0.39021
F 2.24240 2.00342 0.94867

F 4.88977 1.96441 1.03865
Br 6.81530 -0.32660 0.43626
F 4.86082 -2.54882 -0.29221
N 9.95206 -0.37224 0.47410
C 11.10012 -0.43323 0.40730
C 12.52088 -0.51071 0.32389
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C 15.31176 -0.66543 0.15722
C 14.54114 -1.80958 0.37928
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C 17.49594 0.06328 -0.81144
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C 18.88033 -1.70662 0.78827
C 17.50066 -1.63525 0.86843
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H 19.41525 -2.39558 1.43416
H 16.97719 -2.25666 1.58666
C 21.08550 -1.00629 -0.20413
H 21.52986 -0.05641 -0.50660
H 21.37099 -1.75334 -0.95159
H 21.53367 -1.30716 0.74450

Coordinates for the non-linear **3-1CB** complex:

C -5.34198 0.80780 0.02008
N -4.75733 -0.43823 0.44575
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H -6.42294 0.75079 0.13112
H -5.12324 1.02359 -1.03202
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