

EFFECT OF METHOXY SUBSTITUENTS ON THE STRUCTURAL AND ELECTRONIC PROPERTIES OF FLUORINATED CYCLOBUTENES: A STUDY OF HEXAFLUOROCYCLOBUTENE AND ITS VINYL METHOXY DERIVATIVES BY XRD AND PERIODIC DFT CALCULATIONS

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SUPPORTING INFORMATION

2. Experimental

Crystallization details. A capillary of 0.5 mm diameter was filled with the substance under analysis (i.e. HFCB, PMCB or TDCB) to a maximum linear extent of about 5 mm. Then the capillary was sealed and mounted on the precooled goniometer head of a Bruker SMART CCD 1000 TM diffractometer. The fast cooling of the sample to the temperature selected for the data collection led to “snow-like” solids. Then, the temperature was increased with a 0.2 deg/min gradient till a tiny leftover of solid survived in equilibrium with surrounding liquid. Each sample was left overnight at this temperature (with small oscillations of 0.2 - 0.5 deg.) to get the suitable single-crystalline seed. The temperature was subsequently decreased with an approximate 3 deg/hour gradient, with the capillary slowly rotating around the ϕ goniometer axis. The crystal growth was monitored by rotational x-ray exposures. Unfortunately, many attempts with various temperature gradients gave polycrystalline patterns or showed co-existence of many single-crystals. As an example, even the most satisfactory HFCB sample contained approximately 10 crystalline individuals. The

fraction of reflections belonged to one single crystal was carefully separated in reciprocal space by means of a visual procedure using the RLATT software.¹

Refinement results. An empirical absorption correction was applied with SADABS^{2,3} by fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. As regards HFCB, 728 unique reflections with an internal agreement factor $R_{int}=0.0511$ were used in the refinement, giving as final R -factors for all the data $R(F)=0.0578$ and $wR(F^2)=0.2029$, with $GOF=0.991$. The most relevant density features $\Delta\rho$ in the residual map were as large as $+0.47 / -0.41 \text{ e } \text{\AA}^{-3}$. For PMCB, the internal agreement factor was $R_{int}=0.0123$ for 1004 independent reflections covering slightly more than an half-sphere. The least square refinement on this set resulted in final agreement indices as low as $R(F) = 0.0610$ and $wR(F^2) = 0.1698$, with a GOF of 1.122 (all the data, independent atom model) and with $\Delta\rho = +0.36 / -0.28 \text{ e } \text{\AA}^{-3}$. For TDCB, 880 independent reflections were obtained within an entire sphere and gave $R_{int}=0.0551$, $R(F) = 0.1021$, $wR(F^2) = 0.2435$, $GOF=1.316$ and $\Delta\rho = +0.40(11) / -0.59(11) \text{ e } \text{\AA}^{-3}$. The hydrogen atoms were refined in an isotropic approximation using the “riding model”.⁴

3. Computational Details

3.1. Geometry optimizations. In the periodic geometry optimizations performed with CRYSTAL03⁵ the minima on the potential energy surface were located by means of a modified form conjugate gradient algorithm proposed by Schlegel.⁶ All the gradients were computed analytically. Four thresholds define the minimum force, the rms force, the minimum atomic displacement and the rms atomic displacement to be reached in order to achieve convergence. A stationary point on the potential energy surface was considered to be found when all the four condition were simultaneously satisfied. In the present work, the thresholds were set to 0.00045, 0.0003, 0.0018 and 0.0012 au, respectively. The level of accuracy in evaluating coulomb and exchange series is controlled by five tolerances,⁵ which were set to 10^{-10} , 10^{-10} , 10^{-10} , 10^{-10} and 10^{-15} (4 to 5 order of magnitude smaller than the standard values reported in the CRYSTAL03 manual⁵). To increase the precision of calculation, the thresholds on eigenvalues and total energy changes between successive cycles in the SCF iteration were reduced to 10^{-9} and 10^{-7} , respectively. A 40 % mixing of the Fock matrices and an eigenvalue level shift of 0.8 au were applied to accelerate convergence.⁵ The reciprocal space was sampled according to a regular sublattice defined by 4 points on each axis in the irreducible Brillouin zone.

¹ Bruker AXS Inc. *SMART1000 User Manual*, Madison, Wisconsin, USA 2001.

² Bruker AXS Inc. *SADABS User Manual*, version 2.03, Madison, Wisconsin, USA 2004.

³ Blessing, R. H. *Acta Cryst.* **1995**, *A51*, 33–38.

⁴ G. M. Sheldrick, *Acta Cryst.* **2008**, *A64* 112-122.

⁵ V. R. Saunders, R. Dovesi, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, N. M. Harrison, K. Doll, Civalieri, B.; I. J. Bush, Ph. D'Arco, M. Llunell, *CRYSTAL2003 User's Manual*, University of Torino, Torino, 2003.

⁶ H. B. Schlegel, *J. Comput Chem.*, **1982**, *3*, 214–218.

Acceptable convergence was achieved by imposing as a starting point the ideal C–H geometrical distances (1.066 Å) around the methyl groups according to Allen *et al.*,⁴ and then performing the following three-step refinement strategy: (1) the hydrogen coordinates were optimized, while all the other non-H positions were kept fixed; (2) all the atoms that had been kept fixed during the first step were allowed to relax, this time keeping fixed the hydrogen coordinates; (3) eventually, all the atom coordinates in the asymmetric unit were allowed to relax until convergence criteria were satisfied. For the two low-symmetry derivatives this procedure was quite slow. As an example, for TDCB the calculations took about 67 days on a machine with 999 MHz CPU (RAM 1003 MB) with Linux 2.4.9-34smp (x86) as operating system before a satisfactory stationary point could be found.

3.2. Topological analysis of the electron density. As regards the CRYSTAL98 single-point calculation at the optimized periodic geometry, we used the default pruned (55,434) grid for the integration of the exchange-correlation potential. At convergence, the same energies as at the end of the CRYSTAL03 optimization routine were obtained within 1.0 kcal mol⁻¹. The integral properties of the atomic basins were evaluated using 120 radial points inside the β -sphere while the $\vartheta \times \phi$ angular grids outside the β -sphere ranged from 64x48 to 96x64 points.

3.3. Cohesive energies. In the E_{cryst} approach the total crystal energy is defined according to

$$E_{cryst} = \frac{1}{2} \sum_B E_{AB} \quad (\text{S-A})$$

with E_{AB} being the interaction energy between each pair made up by an unique molecule A and the surrounding molecules B within a cluster built around the reference cell.⁷ In turn, E_{AB} can be partitioned as:

$$E_{AB} = E_{rep} + E_{dis} + E_{el} \quad (\text{S-B})$$

where E_{rep} and E_{dis} take into account short-range repulsions and long-range dispersion contributions, respectively; they are defined by means of approximated atom-atom potentials of $\exp[-\alpha R]$ and R^{-6} form. In particular, the dispersion energy E_{dis} was approximated by the following atom-atom potential, which was dampened according to Grimme⁸ with an inverse exponential function in order to avoid singularities at small R .

$$E_{dis} \propto - \sum_{i=1}^{N_{at}-1} \sum_{j=i+1}^{N_{at}} \frac{\sqrt{C_6^i \cdot C_6^j}}{R_{ij}^6} \cdot \frac{1}{1 + e^{-d(R_{ij}/R_r-1)}} \quad (\text{S-C})$$

In the above formula N_{at} is the number of atoms, C_6^i and C_6^j are semiempirical constants⁸ associated to atoms i and j , R_{ij} is the corresponding interatomic distance, d is a dimensionless parameter taken equal to that used in the Grimme's work,⁸ and R_r is the sum of the Van der Waals radii of atoms i and j .

The latter term in the E_{cryst} expression, E_{el} , refers to the electrostatic energy and can be decomposed into the following contributions:

⁷ M. Barzaghi: *PAMoC (Version 2002.0), Online User's Manual*, CNR-ISTM, Institute of Molecular Science and Technologies, Milano, Italy, 2002. URL: www.istm.cnr.it/~barz/pamoc/

⁸ S. Grimme, *J. Comput. Chem.* 27 (2006) 1787–1799.

$$E_{el} = E_{pro-pro} + E_{pro-def} + E_{def-def} \quad (\text{S-D})$$

where $E_{pro-pro}$ involves a sum over coulomb interactions between pairs of spherical (promolecule) atomic charge densities and can be determined as a function of the separation, $E_{def-def}$ arises from the deformation (multipole) terms of the molecular charge distribution, and $E_{pro-def}$ is the interaction of the spherical charge distribution of one molecule with the deformation charge density of its interacting counterpart.

4. Results and discussion

4.1 Comparison of geometry optimization results for HFCB. Although the geometries calculated with different hamiltonians and basis sets are not strictly comparable, it is worth noting that our computed, solid-state bond lengths of the cyclobutene ring are all four longer (on average, by a modest 0.48 %) than the CCSD(T) / cc-pVTZ results⁹Error! Bookmark not defined. for the isolated HFCB molecule, while the C–F bonds are, on average, much longer (1.3 %) in the periodic optimization (see Table 2, columns P opt and GP opt). Similar or even large overestimates are evident for all the covalent bond lengths in the cyclobutene plane when the optimized periodic geometry is compared with the MW results. For instance, the vinylic C–F bond lengths are longer by roughly 3 experimental esd's in the present solid-state calculation, whereas the periodic C–C bond lengths in the cyclobutene ring are, on average, greater by about 7 esd's with respect to the MW values. By contrast, the four out-of-plane C–F bonds are virtually identical, within experimental error, in the two sets of values.

While small differences between the periodic and the gas-phase estimates may arise because of the crystal packing, the observed discrepancies are likely too high to be rationalized in terms of crystal field effects, and their true origin should be found elsewhere. A possible explanation for the overestimate of the bond lengths in the periodic calculation relies in the completeness of the basis set employed (6-31G(d)). It is well known that in solid state simulations smaller basis sets perform better than they would if employed in gas-phase optimizations.¹⁰ Actually, in isolated systems a consistent part of the variational freedom provided by diffuse functions is employed to describe the tails of the wavefunction, which are poorly represented by gaussian basis functions. On the contrary, in crystalline solids (particularly in non-metallic systems) there is a large overlap between neighbouring atom-centered basis functions in all directions, so diffuse functions do not contribute greatly to the wavefunction but enlarge dramatically the computational cost by increasing the number of bielectronic integrals in the coulomb and exchange series. Granted that it is probably possible to get results closer to both the triple zeta and the experimental ones by adopting a larger basis set, we believe that the current choice is a reasonable compromise between the accuracy of the calculation and its computational cost. Anyhow, the adoption of the same hamiltonian and basis set both for HFCB and its less symmetric derivatives permits the comparison of the three substances on identical theoretical grounds.

⁹ Császár, A. G. *J. Phys. Chem. A*, **2004**, *108*, 2002

¹⁰ Saunders, V. R.; Dovesi, R.; Roetti, C.; Orlando, R.; Zicovich-Wilson, C. M.; Harrison, N. M.; Doll, K.; Civalleri, B.; Bush, I. J.; D'Arco, Ph.; Llunell, M. *CRYSTAL2003 User's Manual*, University of Torino, Torino, 2003

Table S1.

Critical points (cps) of HFCB (C₄F₆) in the crystal. Optimized geometry DFT-B3LYP 6-31Gd (CRYSTAL98). Topological analysis performed with TOPOND98 on the theoretical electron density. Different colours refer to different dimmers (see Figure SF1).

Interaction	bcp	Symmetry op	$\rho(\mathbf{r})$	$\nabla^2[\rho(\mathbf{r})]$	G	V	ε	λ_1	λ_2	λ_3	xf	yf	zf	xc	yc	zc	Pairs
C(1)-C(4)	bcp_a	x y z	1.614	-12.63	133.72	-611.51	0.06	-11.52	-10.92	9.81	0.35279	0.48220	0.19784	1.62991	5.32098	1.47152	
C(1)-F(2)	bcp_b	x y z	1.802	-3.36	938.27	-1968.18	0.18	-13.54	-11.5	21.68	0.45369	0.56205	0.21721	2.18938	6.20211	1.61559	
C(1)-F(3)	bcp_c	x y z	1.788	-3.61	921.50	-1941.32	0.18	-13.36	-11.36	21.11	0.36050	0.56437	0.13129	1.84324	6.22771	0.97652	
C(1)-C(2)	bcp_d	x y z	1.768	-14.72	175.17	-751.23	0.06	-12.42	-11.67	9.38	0.29174	0.57007	0.23657	1.16489	6.29061	1.75959	
C(2)-F(1)	bcp_e	x y z	1.904	8.02	1283.37	-2348.43	0.02	-13.97	-13.75	35.74	0.18068	0.61381	0.29852	0.34028	6.77327	2.22037	
C(2)-C(3)	bcp_f	x y z	2.298	-23.03	364.47	-1356.15	0.50	-17.92	-11.93	6.82	0.17189	0.52278	0.29718	0.29067	5.76877	2.21040	
C(3)-F(6)	bcp_g	x y z	1.899	7.86	1276.91	-2339.87	0.02	-13.95	-13.66	35.46	0.10749	0.44392	0.32606	-0.16983	4.89857	2.42521	
C(3)-C(4)	bcp_h	x y z	1.768	-14.72	175.28	-751.60	0.06	-12.41	-11.69	9.37	0.23344	0.43476	0.25839	0.75885	4.79749	1.92188	
C(4)-F(4)	bcp_i	x y z	1.807	-3.17	947.15	-1980.55	0.18	-13.63	-11.59	22.05	0.28722	0.39428	0.15919	1.33168	4.35080	1.18404	
C(4)-F(5)	bcp_l	x y z	1.793	-3.53	927.17	-1950.40	0.18	-13.42	-11.42	21.31	0.38064	0.39236	0.24480	1.67998	4.32961	1.82080	
ring cp	rcp_l	x, y, z	0.622	11.43	346.43	-381.59	//	-2.6	6.93	7.09	0.26735	-0.49866	0.24473	0.99739	5.53202	1.82032	
F(6)-X_F(2)	bcp_1	1-x, 1-y, 1-z	0.029	0.68	14.65	-10.87	0.89	-0.11	-0.06	0.85	0.22356	0.41879	0.54145	-0.01045	4.62126	4.02726	A
F(5)-X_F(1)	bcp_2	1-x, 1-y, 1-z	0.030	0.68	14.65	-10.85	1.21	-0.11	-0.05	0.84	0.67411	0.34740	0.49781	2.81408	3.83349	3.70267	
F(4)-X_F(3)	bcp_3	-x, 1-y, -z	0.017	0.48	9.43	-5.90	4.86	-0.06	-0.01	0.54	-0.04964	0.39032	0.00613	-0.31451	4.30710	0.04559	B
F(4)-X_C(2)	bcp_4	-x, 1-y, -z	0.032	0.51	10.75	-7.63	0.18	-0.09	-0.08	0.68	0.01660	0.39578	-0.10321	0.35883	4.36735	-0.76767	
F(3)-X_C(3)	bcp_5	-x, 1-y, -z	0.026	0.46	9.51	-6.40	0.64	-0.08	-0.05	0.59	-0.08924	0.43950	0.13305	-0.87140	4.84979	0.98961	
F(4)-X_F(3)	bcp_6	1-x, 1-y, -z	0.030	0.69	14.77	-10.75	0.42	-0.11	-0.08	0.87	0.45367	0.38820	0.02790	2.66395	4.28371	0.20752	C
F(3)-X_F(3)	bcp_7	1-x, 1-y, -z	0.038	0.80	17.73	-13.61	0.50	-0.14	-0.09	1.03	0.50000	0.50000	0.00000	3.01310	5.51740	0.00000	
F(4)-X_F(2)	bcp_8	1-x, 1-y, -z	0.017	0.50	10.08	-6.41	0.59	-0.07	-0.04	0.62	0.32782	0.38906	-0.09851	2.22252	4.29320	-0.73271	
F(6)-X_F(5)	bcp_9	-1+x, y, z	0.022	0.60	12.82	-9.26	0.04	-0.09	-0.09	0.79	-0.24228	0.38084	0.33899	-2.31003	4.20249	2.52138	D
F(6)-X_F(2)	bcp_10	-1+x, y, z	0.024	0.62	13.24	-9.49	0.07	-0.1	-0.09	0.81	-0.19155	0.49513	0.32108	-1.95942	5.46366	2.38816	
F(1)-X_F(2)	bcp_11	-1+x, y, z	0.011	0.34	6.57	-3.92	0.65	-0.04	-0.02	0.4	-0.13085	0.62182	0.29538	-1.52918	6.86166	2.19701	
F(2)-X_F(5)	bcp_12	1-x, 1/2+y, 1/2-z	0.028	0.66	14.17	-10.26	0.20	-0.11	-0.09	0.87	0.54440	0.71538	0.22893	2.70663	7.89407	1.70276	E
F(6)-X_F(6)	bcp_13	-x, 1-y, 1-z	0.039	0.83	18.90	-15.14	0.14	-0.16	-0.14	1.13	0.00000	0.50000	0.50000	-1.25373	5.51740	3.71896	F
F(1)-X_F(6)	bcp_14	-x, 1-y, 1-z	0.033	0.74	16.53	-12.97	0.12	-0.13	-0.12	0.99	-0.05701	0.36683	0.52333	-1.65579	4.04790	3.89248	
F(1)-X_F(6)	bcp_15	-x, 1/2+y, 1/2-z	0.036	0.78	17.82	-14.27	0.03	-0.15	-0.14	1.08	0.05791	0.79330	0.22754	-0.22157	8.75391	1.69242	G
F(1)-X_F(4)	bcp_16	-x, 1/2+y, 1/2-z	0.013	0.41	8.24	-5.20	0.17	-0.05	-0.05	0.51	-0.04762	0.76839	0.37784	-1.23439	8.47903	2.81034	
F(6)-X_F(4)	bcp_17	x, 1/2-y, 1/2+z	0.010	0.34	6.54	-3.86	0.01	-0.04	-0.04	0.42	0.12347	0.27572	0.46607	-0.42460	3.04252	3.46659	H
F(1)-X_F(3)	bcp_18	x, 3/2-y, 1/2+z	0.028	0.68	14.95	-11.45	0.01	-0.12	-0.12	0.91	0.23152	0.79484	0.42551	0.32823	8.77090	3.16491	I

The electron density and its laplacian at the cp are expressed in e/Å³ and e/Å⁵, respectively.

G is the kinetic energy density; V is the virial density, all evaluated at the cps. Their units are kJ/mol per atomic unit volume.

$\varepsilon = \lambda_1/\lambda_2 - 1$, bond ellipticity (dimensionless).

λ_1, λ_2 and λ_3 are the Hessian eigenvalues at the cp (e/Å⁵).

xf, yf, and zf: fractional coordinates of the cp in the reference unit cell (dimensionless).

xc, yc and zc are the corresponding Cartesian coordinates (Å).

TABLE S2.

Critical points (cps) of PMCB (C₄F₅OCH₃) in the crystal. Optimized geometry DFT-B3LYP 6-31Gd (CRYSTAL98). Topological analysis performed with TOPOND98 on the theoretical electron density. Different colours refer to different dimmers (see figure SF2).

Interaction	bcp	Symmetry op	$\rho(\mathbf{r})$	$\nabla^2[\rho(\mathbf{r})]$	G	V	ε	λ_1	λ_2	λ_3	xf	yf	zf	xc	yc	zc	Pair
C(1)-C(4)	bcp_a	x y z	1.635	-12.93	135.85	-623.79	0.05	-11.65	-11.11	9.84	0.62734	0.35185	0.74693	6.36173	3.64894	5.75840	
C(1)-F(2)	bcp_b	x y z	1.779	-3.52	914.23	-1924.41	0.19	-13.23	-11.13	20.83	0.48042	0.29499	0.74913	5.37843	3.26776	5.77536	
C(1)-F(3)	bcp_c	x y z	1.765	-4.10	888.55	-1888.73	0.19	-12.97	-10.90	19.77	0.48519	0.28793	0.83705	5.62115	3.36912	6.45317	
C(1)-C(2)	bcp_d	x y z	1.765	-14.70	173.19	-746.77	0.05	-12.30	-11.72	9.32	0.43747	0.43945	0.77603	5.46378	4.29130	5.98274	
C(2)-O(1)	bcp_e	x y z	2.193	-2.19	1298.13	-2655.96	0.05	-17.59	-16.81	32.21	0.32099	0.58165	0.77707	5.03683	5.25568	5.99076	
C(2)-C(3)	bcp_f	x y z	2.234	-21.65	347.75	-1285.16	0.46	-17.08	-11.72	7.16	0.49988	0.58265	0.73674	6.00754	5.19403	5.67984	
C(3)-F(6)	bcp_g	x y z	1.827	6.86	1200.64	-2214.35	0.03	-12.74	-12.31	31.91	0.63895	0.65527	0.69323	6.86670	5.61181	5.34440	
C(3)-C(4)	bcp_h	x y z	1.805	-15.23	185.63	-786.05	0.10	-12.80	-11.67	9.24	0.68883	0.49731	0.70740	6.90364	4.56655	5.45364	
C(4)-F(4)	bcp_i	x y z	1.765	-4.20	885.84	-1886.11	0.17	-12.99	-11.13	19.92	0.79989	0.35973	0.74724	7.41257	3.70281	5.76079	
C(4)-F(5)	bcp_l	x y z	1.771	-4.44	883.98	-1888.86	0.17	-12.99	-11.11	19.66	0.79280	0.36958	0.65937	7.16135	3.62042	5.08336	
C(5)-O(1)	bcp_m	x y z	1.551	-7.11	625.03	-1443.68	0.01	-8.94	-8.85	10.69	0.14145	0.78450	0.78164	4.35551	6.63660	6.02599	
C(5)-H(5A)	bcp_n	x y z	1.894	-23.96	85.47	-823.41	0.04	-18.76	-18.04	12.85	0.17916	0.88624	0.82356	4.88273	7.39644	6.34917	
C(5)-H(5B)	bcp_o	x y z	1.908	-24.38	84.83	-833.65	0.04	-18.98	-18.24	12.84	-0.00199	0.88835	0.79950	3.73776	7.36991	6.16368	
C(5)-H(5C)	bcp_p	x y z	1.875	-23.36	86.23	-808.76	0.04	-18.46	-17.72	12.83	0.16650	0.89969	0.68377	4.47059	7.25034	5.27147	
Ring cp	rcp_1	x y z	0.627	11.49	350.19	-387.34	//	-2.57	6.92	7.14	0.56666	0.46146	0.74205	3.19253	4.38265	5.72077	
H(5C)-F(2)	bcp_1	1-x, 1-y, 1-z	0.011	0.21	3.95	-2.14	0.47	-0.03	-0.02	0.26	0.64125	0.16275	0.50040	5.44948	1.95062	3.85779	A
O(1)-F(5)	bcp_2	1-x, 1-y, 1-z	0.036	0.66	15.39	-12.91	0.08	-0.12	-0.11	0.89	0.84509	0.35156	0.38605	6.73382	3.03476	2.97622	
F(2)-C(3)	bcp_3	1-x, 1-y, 1-z	0.028	0.45	9.40	-6.49	0.26	-0.08	-0.07	0.60	0.43510	0.32742	0.49225	4.50335	3.05151	3.79496	
F(3)-F(6)	bcp_4	1-x, 1-y, 2-z	0.020	0.51	10.42	-6.95	1.63	-0.07	-0.03	0.60	0.39706	0.24488	1.13334	5.77752	3.58033	8.73739	B
F(3)-H(5A)	bcp_5	1-x, 1-y, 2-z	0.022	0.39	7.67	-4.75	0.05	-0.07	-0.07	0.53	0.35134	0.84623	0.94142	6.14484	7.32554	7.2578	
F(4)-H(5A)	bcp_6	1-x, 1-y, 2-z	0.034	0.61	12.87	-9.18	0.32	-0.12	-0.09	0.82	0.15194	0.79978	0.99383	4.99632	7.10001	7.66185	
F(3)-C(3)	bcp_7	1-x, 1-y, 2-z	0.019	0.39	7.64	-4.78	5.32	-0.05	-0.01	0.45	0.43093	0.30199	1.10936	6.02675	3.92625	8.55252	
F(5)-F(5)	bcp_8	2-x, 1-y, 1-z	0.048	0.96	22.34	-18.65	0.15	-0.19	-0.16	1.30	1.00000	0.50000	0.50000	8.23886	4.23292	3.85471	C
F(5)-F(6)	bcp_9	2-x, 1-y, 1-z	0.058	1.08	26.38	-23.47	0.07	-0.24	-0.22	1.53	1.09321	0.28778	0.44981	8.26654	2.71117	3.46777	
H(5B)-F(6)	bcp_10	-1+x, y, z	0.034	0.60	12.83	-9.20	0.30	-0.13	-0.10	0.83	-0.15802	0.83552	0.74001	2.54784	6.91136	5.70505	D
F(2)-F(4)	bcp_11	-1+x, y, z	0.022	0.58	12.17	-8.41	0.07	-0.09	-0.08	0.75	0.17009	0.27310	0.75199	3.48273	3.12443	5.79741	
O(1)-F(4)	bcp_12	-1+x, y, z	0.027	0.55	12.00	-9.12	0.02	-0.09	-0.09	0.73	0.02647	0.47226	0.80695	3.14028	4.56586	6.22111	
H(5B)-F(3)	bcp_13	-x, 1-y, 2-z	0.027	0.47	9.73	-6.59	0.01	-0.10	-0.10	0.67	0.23378	0.15061	1.07812	4.47673	2.8485	8.31168	E
O(1)-O(1)	bcp_14	-x, 1-y, 2-z	0.010	0.23	4.65	-2.94	0.05	-0.03	-0.03	0.30	0.00000	0.50000	1.00000	3.53343	5.08114	7.70942	
F(3)-F(3)	bcp_15	1-x, -y, 2-z	0.047	0.95	22.42	-19.04	0.05	-0.19	-0.18	1.32	0.50000	0.00000	1.00000	4.92357	3.13791	7.71011	F
H(5A)-F(2)	bcp_16	x, -1+y, z	0.022	0.41	8.27	-5.27	0.32	-0.08	-0.06	0.55	0.31164	0.04964	0.76573	3.94452	1.63505	5.90333	G
F(2)-F(6)	bcp_17	x, -1+y, z	0.013	0.43	8.43	-5.26	0.08	-0.05	-0.05	0.53	0.56447	-0.00102	0.67630	5.13400	1.14040	5.21388	
H(5C)-F(6)	bcp_18	1-x, 2-y, 1-z	0.019	0.34	6.76	-4.20	0.03	-0.07	-0.07	0.48	0.75664	0.94008	0.49283	7.59329	7.19984	3.79943	H
H(5B)-F(4)	bcp_19	-1+x, 1+y, z	0.033	0.60	12.25	-8.19	0.75	-0.10	-0.06	0.76	-0.03805	1.08411	0.80642	3.90984	8.70683	6.21703	I
F(5)-C(5)	bcp_20	-1+x, 1+y, z	0.017	0.32	6.19	-3.68	3.28	-0.04	-0.01	0.37	0.00332	1.10650	0.64541	3.78384	8.58525	4.97574	

The electron density and its laplacian at the cp are expressed in $e/\text{\AA}^3$ and $e/\text{\AA}^5$, respectively.
G is the kinetic energy density; V is the virial density, all evaluated at the cps. Their units are kJ/mol per atomic unit volume.
 $\varepsilon = \lambda_1/\lambda_2 - 1$, bond ellipticity (dimensionless).
 λ_1 , λ_2 and λ_3 are the Hessian eigenvalues at the cp ($e/\text{\AA}^5$).
xf, yf, and zf: fractional coordinates of the cp in the reference unit cell (dimensionless).
xc, yc and zc are the corresponding Cartesian coordinates ($\text{\AA}$).

TABLE S3.

Topology of the hydrogen bonds (PMCB). D is the hydrogen bond "donor", A is the "acceptor". All the H...A contacts within 3.2 Å are reported, leaving a '/' mark in the topological entries when the bcp was not found. Units are the same as in Table S1, S2 and S4.

Interaction	bcp	Symmetry op	D-H (Å)	D-A (Å)	H-A (Å)	DHA (deg)	$\rho(r)$	$\nabla^2[\rho(r)]$	G	V	Pair
C(5)-H(5C)···F(2)	bcp_1	1-x, 1-y, 1-z	1.0935	3.9617	3.0999	136.158	0.011	0.21	3.95	-2.14	A
C(5)-H(5C)···F(5)	//	1-x, 1-y, 1-z	1.0935	3.3810	2.9001	106.720	//	//	//	//	
C(5)-H(5A)···F(3)	bcp_5	1-x, 1-y, 2-z	1.0911	3.7789	2.8071	148.256	0.022	0.39	7.67	-4.75	B
C(5)-H(5A)···F(4)	bcp_6	1-x, 1-y, 2-z	1.0911	3.2277	2.6811	110.398	0.034	0.61	12.87	-9.18	
C(5)-H(5B)···F(6)	bcp_10	-1+x, y, z	1.0869	3.2612	2.6587	114.371	0.034	0.60	12.83	-9.20	D
C(5)-H(5B)···F(3)	bcp_13	-x, 1-y, 2-z	1.0869	3.6249	2.7062	141.986	0.027	0.47	9.73	-6.59	E
C(5)-H(5A)···F(2)	bcp_16	x, -1+y, z	1.0911	3.4523	2.8402	115.427	0.022	0.41	8.27	-5.27	G
C(5)-H(5C)···F(2)	//	x, -1+y, z	1.0935	3.4523	3.1379	97.334	//	//	//	//	
C(5)-H(5C)···F(6)	bcp_18	1-x, 2-y, 1-z	1.0935	3.8500	2.8200	156.934	0.019	0.34	6.76	-4.20	H
C(5)-H(5B)···F(4)	bcp_19	-1+x, 1+y, z	1.0869	3.1565	2.7869	99.648	0.033	0.60	12.25	-8.19	I
C(5)-H(5A)···F(4)	//	-1+x, 1+y, z	1.0911	3.1565	2.9444	90.921	//	//	//	//	
C(5)-H(5B)···F(3)	//	-1+x, 1+y, z	1.0869	4.1359	3.1395	152.763	//	//	//	//	
C(5)-H(5B)···F(5)	//	-1+x, 1+y, z	1.0869	3.5039	3.1812	98.113	//	//	//	//	
C(5)-H(5C)···F(5)	//	-1+x, 1+y, z	1.0935	3.5039	3.0246	106.992	//	//	//	//	

Interaction	bcp	Symmetry op	ε	λ_1	λ_2	λ_3	xf	yf	zf	xc	yc	zc	Pair
C(5)-H(5C)···F(2)	bcp_1	1-x, 1-y, 1-z	0.47	-0.03	-0.02	0.26	0.64125	0.16275	0.50040	5.44948	1.95062	3.85779	A
C(5)-H(5C)···F(5)	//	1-x, 1-y, 1-z	//	//	//	//	//	//	//	//	//	//	
C(5)-H(5A)···F(3)	bcp_5	1-x, 1-y, 2-z	0.05	-0.07	-0.07	0.53	0.35134	0.84623	0.94142	6.14484	7.32554	7.2578	B
C(5)-H(5A)···F(4)	bcp_6	1-x, 1-y, 2-z	0.32	-0.12	-0.09	0.82	0.15194	0.79978	0.99383	4.99632	7.10001	7.66185	
C(5)-H(5B)···F(6)	bcp_10	-1+x, y, z	0.30	-0.13	-0.10	0.83	-0.15802	0.83552	0.74001	2.54784	6.91136	5.70505	D
C(5)-H(5B)···F(3)	bcp_13	-x, 1-y, 2-z	0.01	-0.10	-0.10	0.67	0.23378	0.15061	1.07812	4.47673	2.8485	8.31168	E
C(5)-H(5A)···F(2)	bcp_16	x, -1+y, z	0.32	-0.08	-0.06	0.55	0.31164	0.04964	0.76573	3.94452	1.63505	5.90333	G
C(5)-H(5C)···F(2)	//	x, -1+y, z	//	//	//	//	//	//	//	//	//	//	
C(5)-H(5C)···F(6)	bcp_18	1-x, 2-y, 1-z	0.03	-0.07	-0.07	0.48	0.75664	0.94008	0.49283	7.59329	7.19984	3.79943	H
C(5)-H(5B)···F(4)	bcp_19	-1+x, 1+y, z	0.75	-0.10	-0.06	0.76	-0.03805	1.08411	0.80642	3.90984	8.70683	6.21703	I
C(5)-H(5A)···F(4)	//	-1+x, 1+y, z	//	//	//	//	//	//	//	//	//	//	
C(5)-H(5B)···F(3)	//	-1+x, 1+y, z	//	//	//	//	//	//	//	//	//	//	
C(5)-H(5B)···F(5)	//	-1+x, 1+y, z	//	//	//	//	//	//	//	//	//	//	
C(5)-H(5C)···F(5)	//	-1+x, 1+y, z	//	//	//	//	//	//	//	//	//	//	

Table S4. Critical points (cps) of TDCB (C₄F₄(OCH₃)₂) in the crystal. Optimized geometry DFT-B3LYP 6-31Gd (CRYSTAL98). Topological analysis performed with TOPOND98 on the theoretical electron density. Different colours refer to different pairs (see Figure SF3).

Interaction	bcp	Symmetry op	$\rho(\mathbf{r})$	$\nabla^2[\rho(\mathbf{r})]$	G	V	ε	λ_1	λ_2	λ_3	xf	yf	zf	xc	yc	zc	Pair
C(1)-C(4)	bcp_a	x, y, z	1.660	-13.35	137.55	-638.73	0.04	-11.84	-11.37	9.86	0.90057	0.15297	0.20134	5.99558	0.55402	1.45806	
C(1)-F(2)	bcp_b	x, y, z	1.773	-4.16	893.09	-1899.55	0.18	-13.15	-11.15	20.14	0.94683	0.22879	0.10726	6.18405	1.33679	0.77675	
C(1)-F(3)	bcp_c	x, y, z	1.737	-4.78	848.06	-1826.30	0.17	-12.58	-10.72	18.51	0.86107	0.13275	0.06067	5.85553	0.77975	0.43936	
C(1)-C(2)	bcp_d	x, y, z	1.817	-15.56	182.86	-789.51	0.08	-12.87	-11.95	9.27	0.81693	0.23324	0.15224	5.19804	1.25036	1.10249	
C(2)-O(1)	bcp_e	x, y, z	2.112	-3.12	1206.78	-2498.64	0.07	-16.44	-15.42	28.74	0.71862	0.30503	0.17477	4.27066	1.69899	1.26564	
C(2)-C(3)	bcp_f	x, y, z	2.194	-20.87	334.67	-1237.77	0.42	-16.54	-11.64	7.32	0.75559	0.25612	0.27857	4.60686	1.08103	2.01734	
C(3)-O(2)	bcp_g	x, y, z	2.086	-4.27	1158.19	-2432.55	0.08	-16.17	-14.99	26.89	0.74713	0.23898	0.40515	4.51034	0.62804	2.93400	
C(3)-C(4)	bcp_h	x, y, z	1.763	-14.40	181.95	-755.99	0.08	-12.27	-11.39	9.27	0.83711	0.17725	0.32933	5.38405	0.39024	2.38493	
C(4)-F(4)	bcp_i	x, y, z	1.763	-4.53	874.53	-1872.45	0.18	-12.94	-11.01	19.41	0.88117	0.05751	0.28031	6.06637	-0.32804	2.02994	
C(4)-F(5)	bcp_l	x, y, z	1.728	-4.83	837.06	-1805.63	0.17	-12.44	-10.63	18.24	0.97024	0.15146	0.32610	6.42525	0.21632	2.36154	
C(5)-O(1)	bcp_m	x, y, z	1.557	-7.03	631.22	-1453.92	0.01	-8.94	-8.84	10.74	0.57307	0.41381	0.19472	2.89950	2.41596	1.41012	
C(5)-H(5A)	bcp_n	x, y, z	1.897	-24.00	86.09	-825.77	0.04	-18.79	-18.08	12.88	0.45670	0.36151	0.24892	2.16232	1.90404	1.80262	
C(5)-H(5B)	bcp_o	x, y, z	1.904	-24.21	85.07	-829.55	0.04	-18.89	-18.17	12.85	0.48178	0.47521	0.17169	2.08141	2.91053	1.24334	
C(5)-H(5C)	_bcp_p	x, y, z	1.886	-23.57	88.02	-817.92	0.04	-18.57	-17.84	12.85	0.58995	0.51902	0.31000	2.65727	2.85781	2.24495	
C(6)-O(2)	bcp_q	x, y, z	1.565	-7.00	641.23	-1473.22	0.00	-9.03	-9.00	11.02	0.73654	0.21374	0.59755	4.37790	-0.05477	4.32732	
C(6)-H(6A)	bcp_r	x, y, z	1.886	-23.61	86.83	-816.71	0.04	-18.60	-17.87	12.87	0.73475	0.08776	0.60841	4.70514	-0.97413	4.40596	
C(6)-H(6B)	bcp_s	x, y, z	1.899	-24.06	85.74	-826.82	0.04	-18.81	-18.06	12.82	0.69826	0.20743	0.71307	4.04189	-0.40218	5.16388	
C(6)-H(6C)	bcp_t	x, y, z	1.878	-23.43	86.25	-810.70	0.04	-18.52	-17.77	12.85	0.85980	0.24655	0.68649	5.12589	-0.05587	4.97140	
Ring cp	rcp_l	x, y, z	0.629	11.60	353.84	-391.65	//	-2.53	7.00	7.14	0.83143	0.20181	0.23875	5.33390	0.80134	1.72897	
C(3)-C(3)	bcp_1	2-x, 1-y, 1-z	0.009	0.11	2.28	-1.51	0.51	-0.02	-0.01	0.14	1.00000	0.50000	0.50000	5.56775	2.22528	3.62088	A
H(6C)-C(2)	bcp_2	2-x, 1-y, 1-z	0.017	0.21	4.34	-2.85	2.10	-0.04	-0.01	0.27	1.05622	0.46402	0.74991	5.91333	1.31579	5.43067	
H(6C)-F(2)	bcp_3	2-x, 1-y, 1-z	0.020	0.37	7.38	-4.67	0.97	-0.06	-0.03	0.46	0.88585	0.45514	0.79149	4.67201	1.14400	5.73178	
H(5C)-F(5)	bcp_4	2-x, 1-y, 1-z	0.054	0.82	19.42	-16.39	0.01	-0.22	-0.21	1.25	0.74419	0.65954	0.45951	3.29421	3.45964	3.32766	
H(5A)-F(3)	bcp_5	1-x, -y, -z	0.045	0.74	16.72	-13.17	0.07	-0.17	-0.16	1.07	0.32384	0.17086	0.15949	1.77999	0.79023	1.15499	B
F(3)-F(3)	bcp_6	2-x, -y, -z	0.033	0.7	15	-10.94	0.84	-0.11	-0.06	0.87	1.00000	0.00000	0.00000	7.27110	0.00000	0.00000	C
F(3)-F(2)	bcp_7	2-x, -y, -z	0.031	0.7	15.13	-11.11	0.51	-0.11	-0.07	0.89	0.88968	-0.13080	-0.06865	6.87416	-0.74504	-0.49715	
F(3)-F(5)	bcp_8	2-x, -y, -z	0.027	0.62	13.16	-9.31	0.61	-0.09	-0.05	0.76	0.87358	-0.07939	-0.20983	6.70711	-0.01143	-1.51954	
F(2)-F(4)	bcp_9	2-x, -y, -z	0.020	0.56	11.34	-7.55	0.07	-0.07	-0.07	0.7	1.10575	0.18507	-0.08467	7.58483	1.53070	-0.61316	
H(6A)-F(5)	bcp_10	2-x, -y, 1-z	0.039	0.65	13.96	-10.34	0.04	-0.15	-0.14	0.93	1.19289	0.06241	0.39994	8.24167	-0.60696	2.89627	D
F(4)-F(5)	bcp_11	2-x, -y, 1-z	0.017	0.5	10	-6.39	0.14	-0.06	-0.05	0.61	1.13029	0.13287	0.56382	7.48576	-0.53824	4.08305	
H(6C)-F(4)	bcp_12	2-x, -y, 1-z	0.024	0.44	8.82	-5.7	0.26	-0.08	-0.06	0.58	1.01322	0.17079	0.71495	6.43178	-0.66622	5.17750	
H(6A)-O(2)	bcp_13	1-x, -y, 1-z	0.027	0.39	8.46	-6.17	0.19	-0.08	-0.07	0.55	0.45956	0.08077	0.44583	2.82912	-0.59741	3.22859	E
F(2)-O(1)	bcp_14	2-x, 1-y, -z	0.009	0.27	5.1	-2.97	0.78	-0.03	-0.02	0.31	1.20428	0.46863	-0.00424	7.46725	3.32514	-0.03071	F
H(5B)-F(2)	bcp_15	-1+x, y, z	0.039	0.7	15.04	-10.9	1.09	-0.14	-0.07	0.91	0.28230	0.39303	0.13600	0.88072	2.42292	0.98488	G
H(5A)-F(5)	bcp_16	-1+x, y, z	0.038	0.62	13.46	-9.94	0.01	-0.14	-0.14	0.91	0.27921	0.27167	0.31515	1.07641	1.09512	2.28224	
H(5C)-F(4)	bcp_17	x, -1+y, z	0.018	0.33	6.65	-4.28	0.69	-0.06	-0.03	0.42	0.70345	-0.28235	0.28405	5.70867	-2.74124	2.05702	H

Interaction	bcp	Symmetry op	rho	lap	G	V	ε	λ_1	λ_2	λ_3	xf	yf	zf	xc	yc	zc	Pair
F(3)-C(6)	bcp_18	x, y, -1+z	0.041	0.74	15.63	-11.22	0.76	-0.11	-0.06	0.91	0.76716	0.11485	-0.18976	5.38478	1.30958	-1.37420	I
H(6C)-F(2)	bcp_19	x, y, -1+z	0.018	0.33	6.42	-3.77	0.99	-0.05	-0.03	0.41	0.95464	0.27475	-0.12024	6.26197	2.25813	-0.87075	
H(6B)-O(1)	bcp_20	x, y, -1+z	0.031	0.43	9.27	-6.82	0.04	-0.1	-0.1	0.63	0.66353	0.27951	-0.09565	4.11618	2.22733	-0.69267	
H(6B)-H(5B)	bcp_21	1-x, 1-y, 1-z	0.020	0.25	4.99	-3.06	0.17	-0.06	-0.05	0.36	0.39311	0.63705	0.20721	0.96743	3.96191	1.50057	L
H(5C)-O(2)	bcp_22	1-x, 1-y, 1-z	0.016	0.27	5.46	-3.63	0.82	-0.04	-0.02	0.33	0.44999	0.61506	0.38848	1.32384	3.33127	2.81328	
H(5B)-H(5B)	bcp_23	1-x, 1-y, -z	0.035	0.52	10.48	-6.85	0.42	-0.12	-0.08	0.72	0.50000	0.50000	0.00000	2.25712	3.53586	0.00000	M
H(5B)-O(1)	bcp_24	1-x, 1-y, -z	0.032	0.46	10.16	-7.7	0.44	-0.1	-0.07	0.64	0.58987	0.44597	-0.03051	3.07935	3.23375	-0.22095	

The electron density and its laplacian at the cp are expressed in $e/\text{\AA}^3$ and $e/\text{\AA}^5$, respectively.

G is the kinetic energy density; V is the virial density, all evaluated at the cps. Their units are kJ/mol per atomic unit volume.

$\varepsilon = \lambda_1/\lambda_2 - 1$, bond ellipticity (dimensionless).

λ_1, λ_2 and λ_3 are the Hessian eigenvalues at the cp ($e/\text{\AA}^5$).

xf, yf, and zf: fractional coordinates of the cp in the reference unit cell (dimensionless).

xc, yc and zc are the corresponding Cartesian coordinates ($\text{\AA}$).

Table S5.

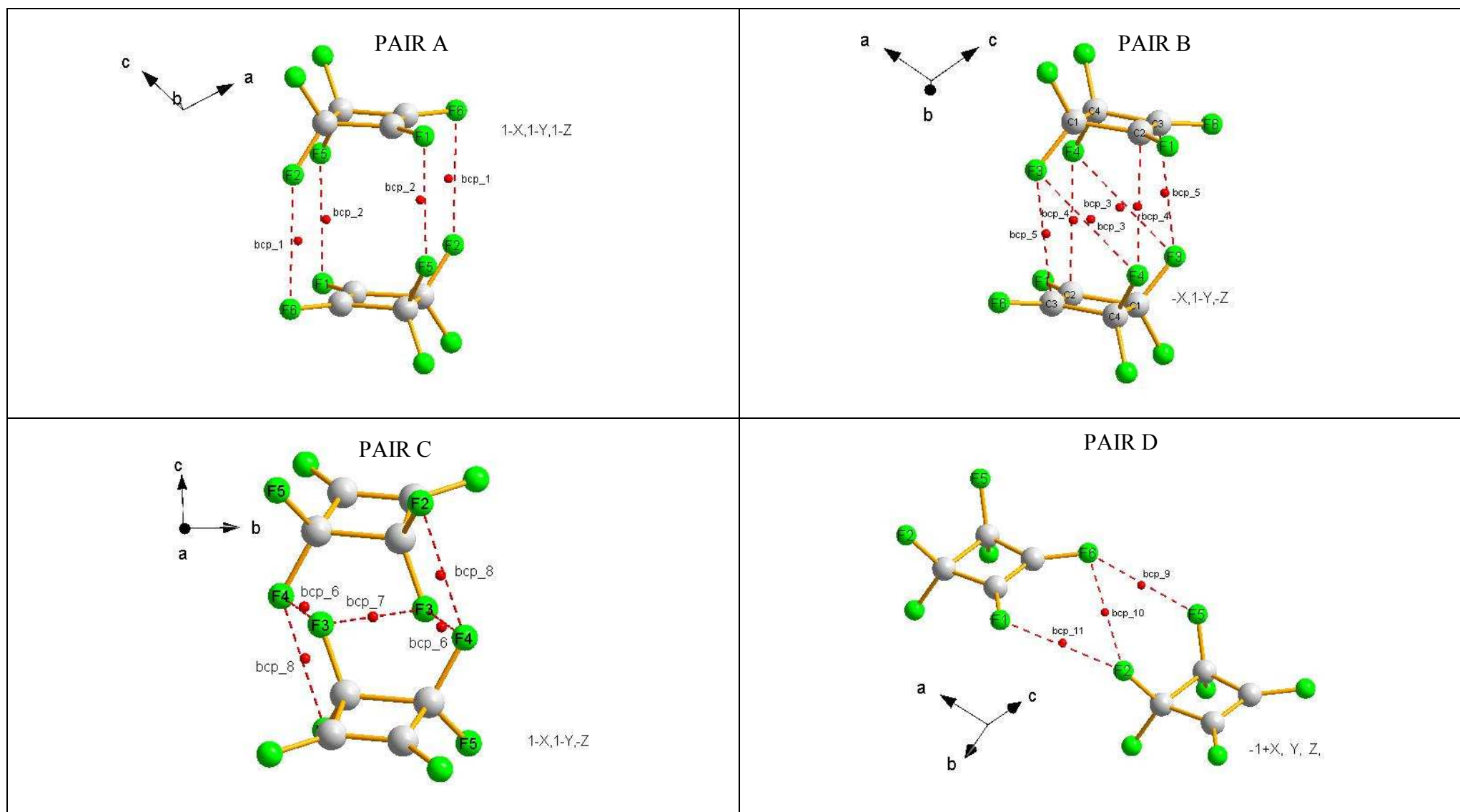
Topology of the hydrogen bonds (TDCB). D is the hydrogen bond "donor", A is the "acceptor". All the H...A contacts within 3.2 $\text{\AA}$ are reported, leaving a '/' mark in the topological entries when the bcp was not found. Units are the same as in Table S1, S2 and S4.

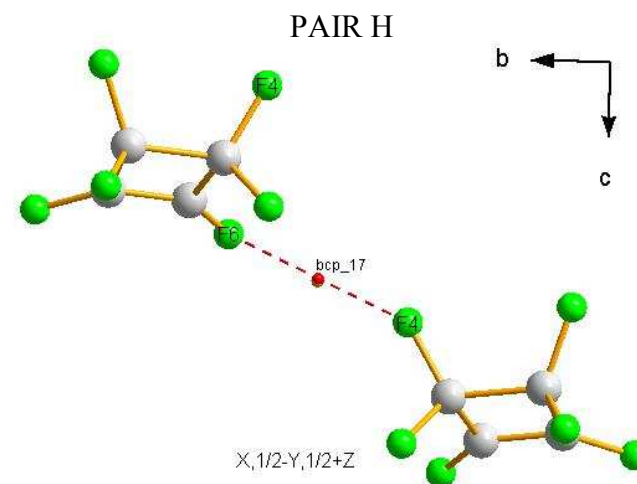
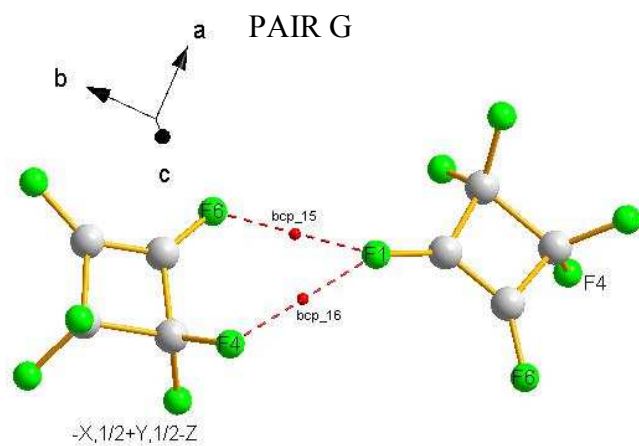
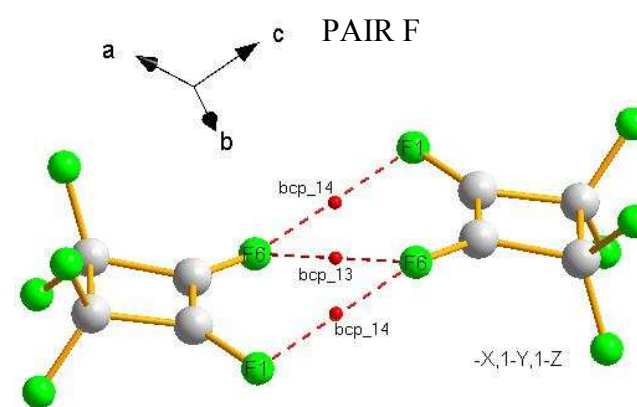
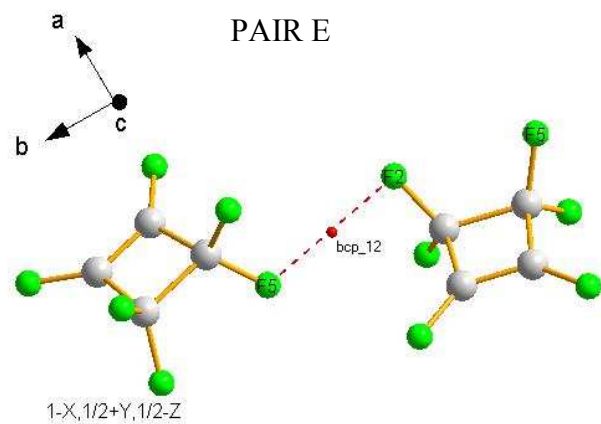
Interaction	bcp	Symmetry op	D-H ($\text{\AA}$)	D-A ($\text{\AA}$)	H-A ($\text{\AA}$)	DHA (deg)	$\rho(\mathbf{r})$	$\nabla^2[\rho(\mathbf{r})]$	G	V	Pair
C(6)-H(6C)...F(2)	bcp_3	2-x, 1-y, 1-z	1.0937	3.3958	2.9881	102.427	0.020	0.37	7.38	-4.67	A
C(6)-H(6B)...F(2)	//	2-x, 1-y, 1-z	1.0886	3.3958	3.1713	92.401	//	//	//	//	
C(5)-H(5C)...F(5)	bcp_4	2-x, 1-y, 1-z	1.0914	3.4617	2.4038	162.882	0.054	0.82	19.42	-16.39	
C(5)-H(5A)...F(3)	bcp_5	1-x, -y, -z	1.0899	3.2883	2.4976	128.473	0.045	0.74	16.72	-13.17	B
C(6)-H(6A)...F(5)	bcp_10	2-x, -y, 1-z	1.0922	3.4731	2.5862	137.739	0.039	0.65	13.96	-10.34	D
C(6)-H(6C)...F(4)	bcp_12	2-x, -y, 1-z	1.0937	3.4883	2.8041	120.455	0.024	0.44	8.82	-5.7	
C(6)-H(6A)...O(2)	bcp_13	1-x, -y, 1-z	1.0922	3.5728	2.9139	118.953	0.027	0.39	8.46	-6.17	E
C(5)-H(5B)...F(2)	bcp_15	-1+x, y, z	1.0878	3.1572	2.6089	110.400	0.039	0.7	15.04	-10.9	G
C(5)-H(5A)...F(2)	//	-1+x, y, z	1.0899	3.1572	2.7608	101.095	//	//	//	//	
C(5)-H(5A)...F(5)	bcp_16	-1+x, y, z	1.0899	3.5520	2.5841	147.503	0.038	0.62	13.46	-9.94	
C(5)-H(5C)...F(4)	bcp_17	x, -1+y, z	1.0914	3.4517	2.9484	108.390	0.018	0.33	6.65	-4.28	H
C(6)-H(6C)...F(2)	bcp_19	x, y, -1+z	1.0937	3.6143	2.9531	119.141	0.018	0.33	6.42	-3.77	I
C(6)-H(6C)...F(3)	//	x, y, -1+z	1.0937	3.0222	2.9887	81.245	//	//	//	//	
C(6)-H(6B)...F(3)	//	x, y, -1+z	1.0886	3.0222	2.7561	93.365	//	//	//	//	
C(6)-H(6A)...F(3)	//	x, y, -1+z	1.0922	3.0222	2.8381	88.941	//	//	//	//	
C(6)-H(6B)...O(1)	bcp_20	x, y, -1+z	1.0886	3.7657	2.7956	148.329	0.031	0.43	9.27	-6.82	
C(5)-H(5C)...O(2)	bcp_22	1-x, 1-y, 1-z	1.0914	3.5439	3.1747	100.725	0.016	0.27	5.46	-3.63	L
C(5)-H(5B)...O(1)	bcp_24	1-x, 1-y, -z	1.0878	3.8082	2.7432	166.140	0.032	0.46	10.16	-7.7	M

Interaction	bcp	Symmetry op	ϵ	λ_1	λ_2	λ_3	xf	yf	zf	xc	yc	zc	Pair
C(6)-H(6C)⋯F(2)	bcp_3	2-x, 1-y, 1-z	0.97	-0.06	-0.03	0.46	-0.11415	0.45514	-0.20851	-0.44857	4.21606	-1.50995	A
C(6)-H(6B)⋯F(2)	//	2-x, 1-y, 1-z	//	//	//	//	//	//	//	//	//	//	
C(5)-H(5C)⋯F(5)	bcp_4	2-x, 1-y, 1-z	0.01	-0.22	-0.21	1.25	-0.25581	-0.34046	0.45951	-2.44871	-2.92228	3.32768	
C(5)-H(5A)⋯F(3)	bcp_5	1-x, -y, -z	0.07	-0.17	-0.16	1.07	0.32384	0.17086	0.15949	1.94541	0.08970	1.15498	B
C(6)-H(6A)⋯F(5)	bcp_10	2-x, -y, 1-z	0.04	-0.15	-0.14	0.93	-0.19289	-0.06241	-0.39994	-0.68380	0.91807	-2.89624	D
C(6)-H(6C)⋯F(4)	bcp_12	2-x, -y, 1-z	0.26	-0.08	-0.06	0.58	-0.01322	-0.17079	0.28505	-0.53352	-1.89022	2.06427	
C(6)-H(6A)⋯O(2)	bcp_13	1-x, -y, 1-z	0.19	-0.08	-0.07	0.55	0.45956	0.08077	0.44583	2.41892	-1.58420	3.22862	E
C(5)-H(5B)⋯F(2)	bcp_15	-1+x, y, z	1.09	-0.14	-0.07	0.91	0.28230	0.39303	0.13600	1.70062	1.93753	0.98490	G
C(5)-H(5A)⋯F(2)	//	-1+x, y, z	//	//	//	//	//	//	//	//	//	//	
C(5)-H(5A)⋯F(5)	bcp_16	-1+x, y, z	0.01	-0.14	-0.14	0.91	0.27921	0.27167	0.31515	1.40068	0.62935	2.28218	
C(5)-H(5C)⋯F(4)	bcp_17	x, -1+y, z	0.69	-0.06	-0.03	0.42	-0.29655	-0.28235	0.28405	-2.45141	-1.98658	2.05702	H
C(6)-H(6C)⋯F(2)	bcp_19	x, y, -1+z	0.99	-0.05	-0.03	0.41	-0.04536	0.27475	-0.12024	-0.12000	2.47046	-0.87076	I
C(6)-H(6C)⋯F(3)	//	x, y, -1+z	//	//	//	//	//	//	//	//	//	//	
C(6)-H(6B)⋯F(3)	//	x, y, -1+z	//	//	//	//	//	//	//	//	//	//	
C(6)-H(6A)⋯F(3)	//	x, y, -1+z	//	//	//	//	//	//	//	//	//	//	
C(6)-H(6B)⋯O(1)	bcp_20	x, y, -1+z	0.04	-0.1	-0.1	0.63	-0.33647	0.27951	-0.09565	-2.13041	3.22115	-0.69269	
C(5)-H(5C)⋯O(2)	bcp_22	1-x, 1-y, 1-z	0.82	-0.04	-0.02	0.33	0.44999	-0.38494	0.38848	2.44337	-4.96717	2.81326	L
C(5)-H(5B)⋯O(1)	bcp_24	1-x, 1-y, -z	0.44	-0.1	-0.07	0.64	0.41013	-0.44597	0.03051	2.73087	-4.53547	0.22097	M

Figure SF1

Ball-and-stick representation of the HFCB pairs in the crystal at increasing centre-of-mass distances. The bcp's position are indicated as red dots. Blue dashed lines mark the H...A (A=F,O) interactions, whereas dashed red lines mark all the other interactions.





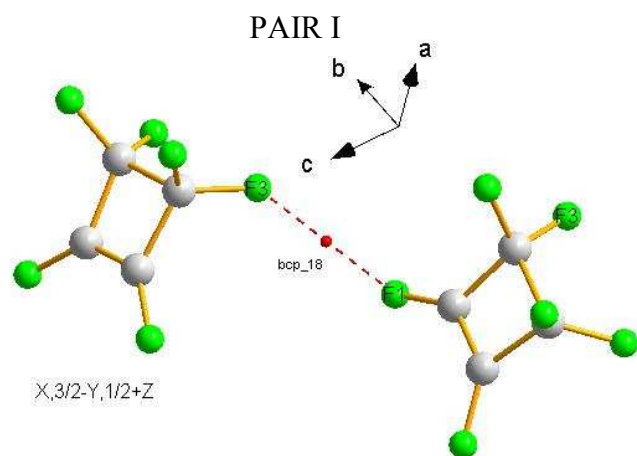
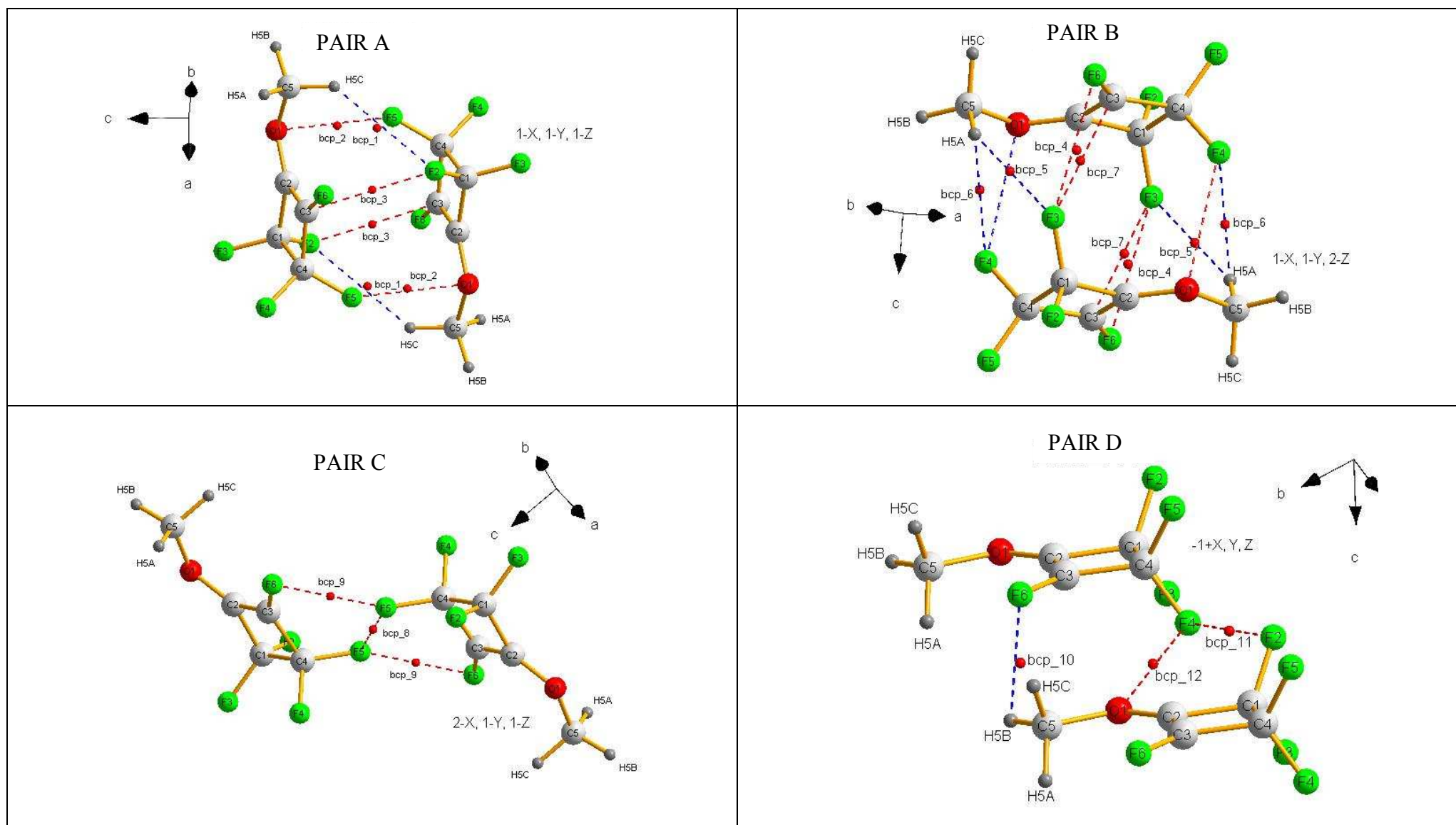
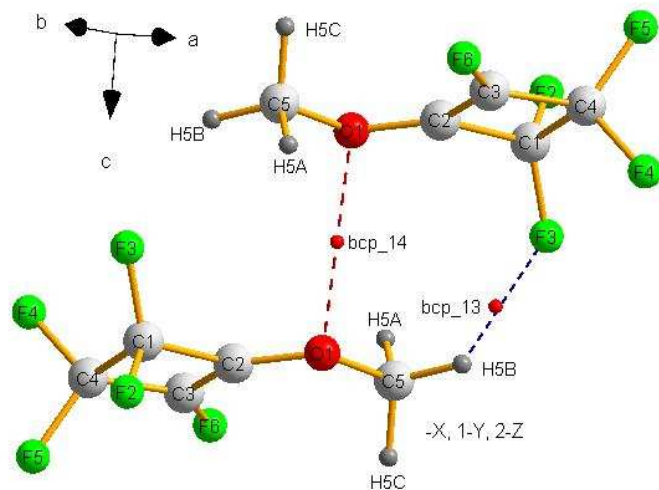


Figure SF2

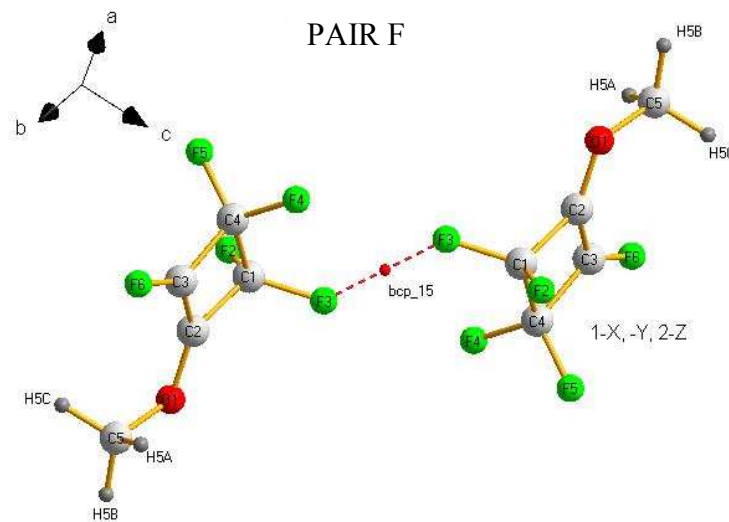
Ball-and-stick representation of the PMCB pairs in the crystal at increasing centre-of-mass distances. The bcp's position are indicated as red dots. Blue dashed lines mark the H...A (A=F,O) interactions, whereas dashed red lines mark all the other interactions.



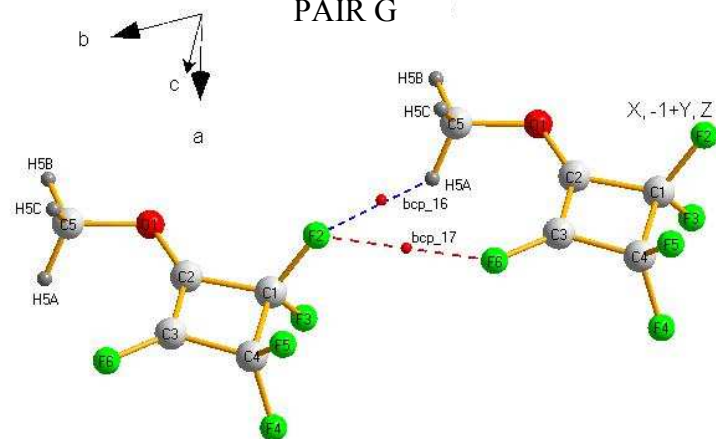
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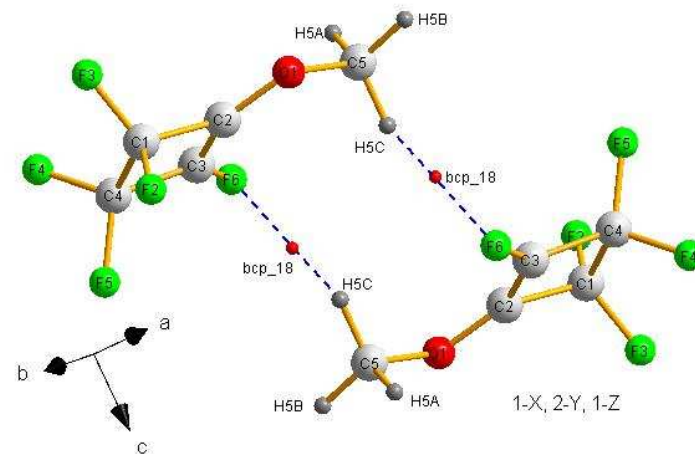
PAIR F



PAIR G



PAIR H



PAIR I

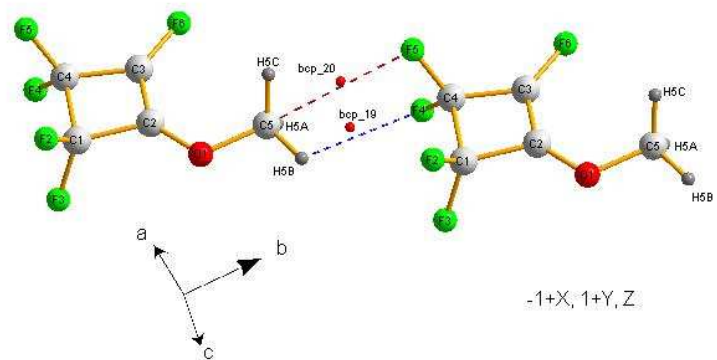
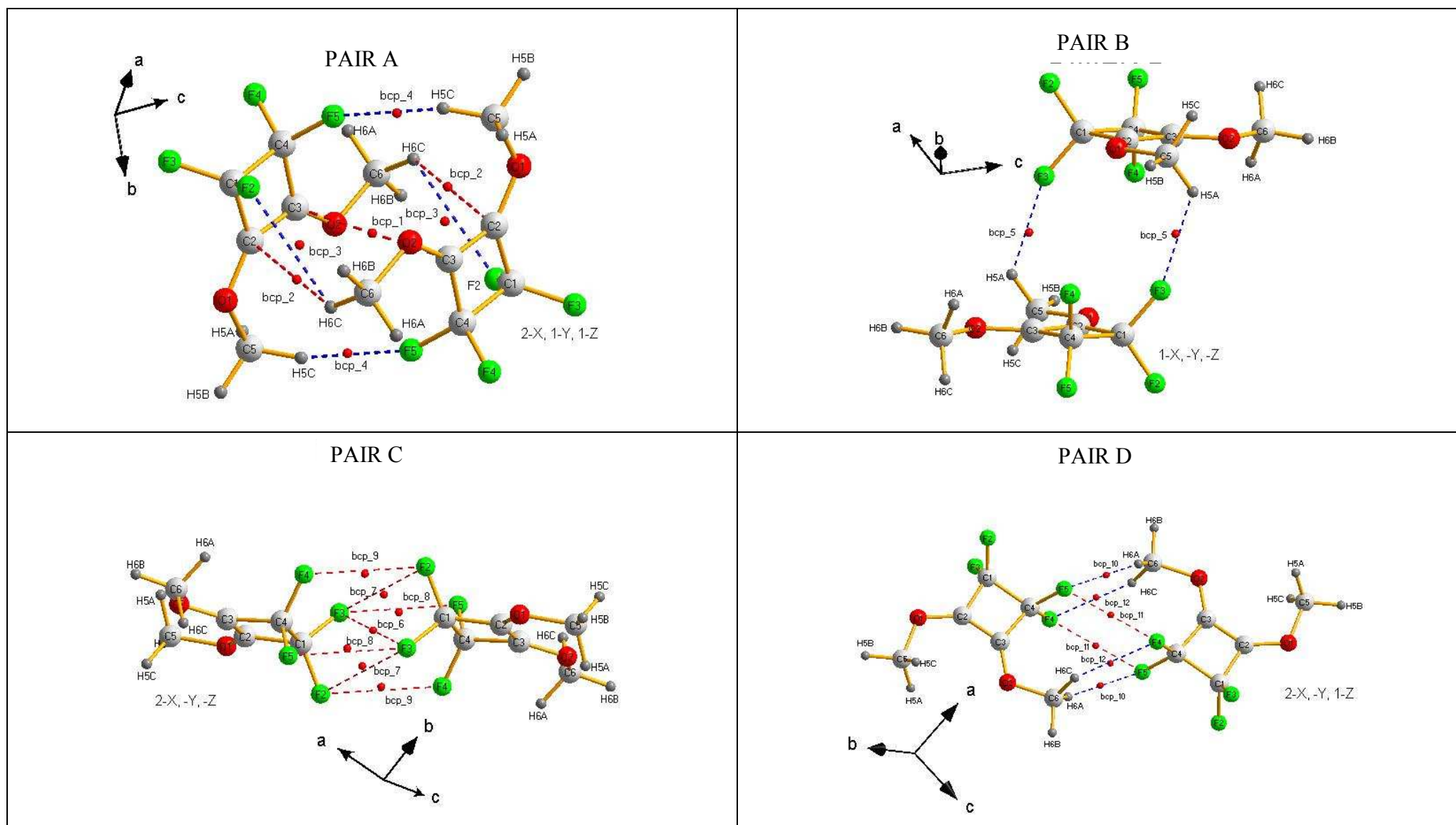
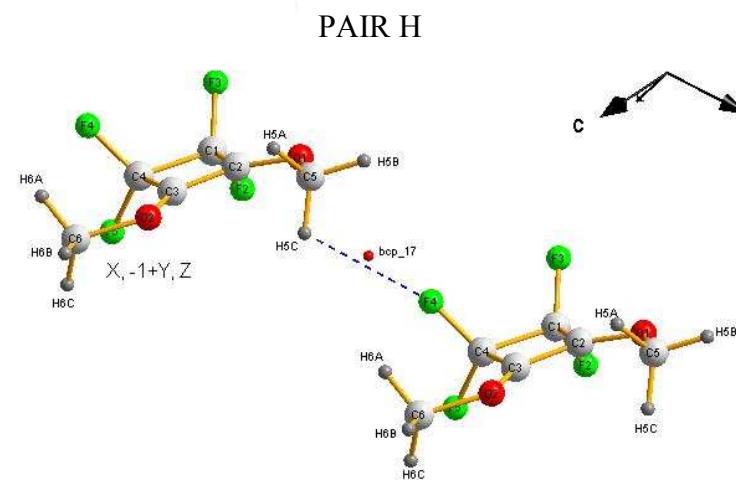
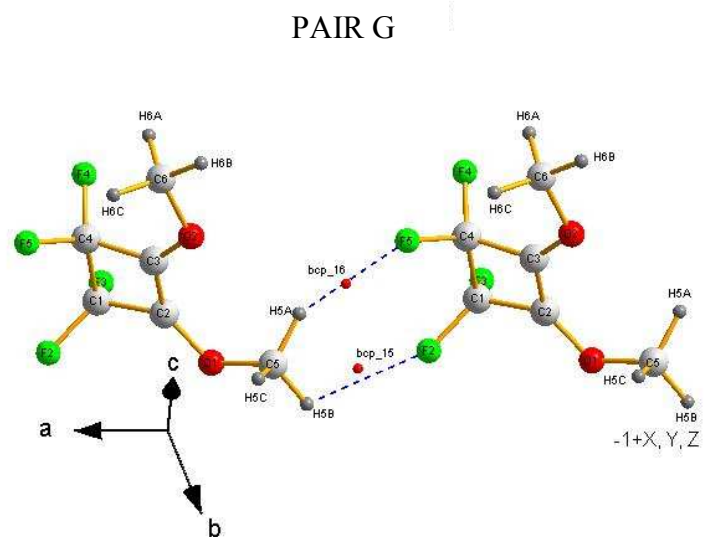
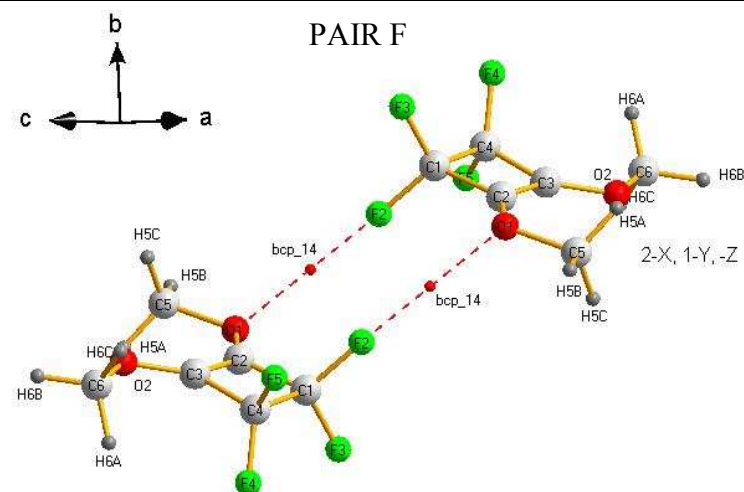
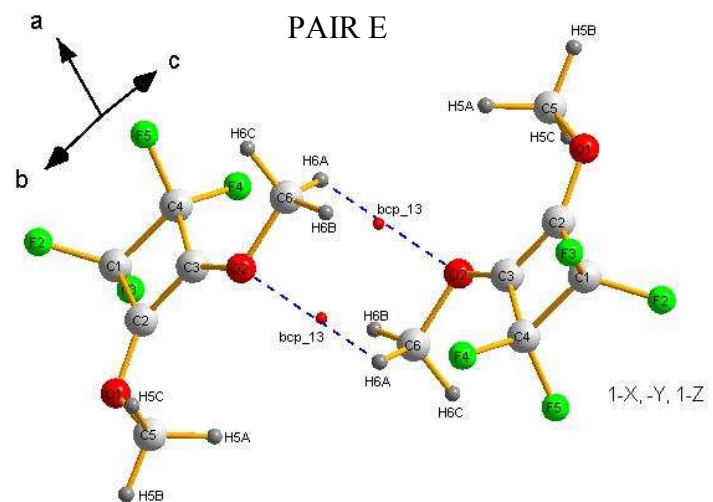
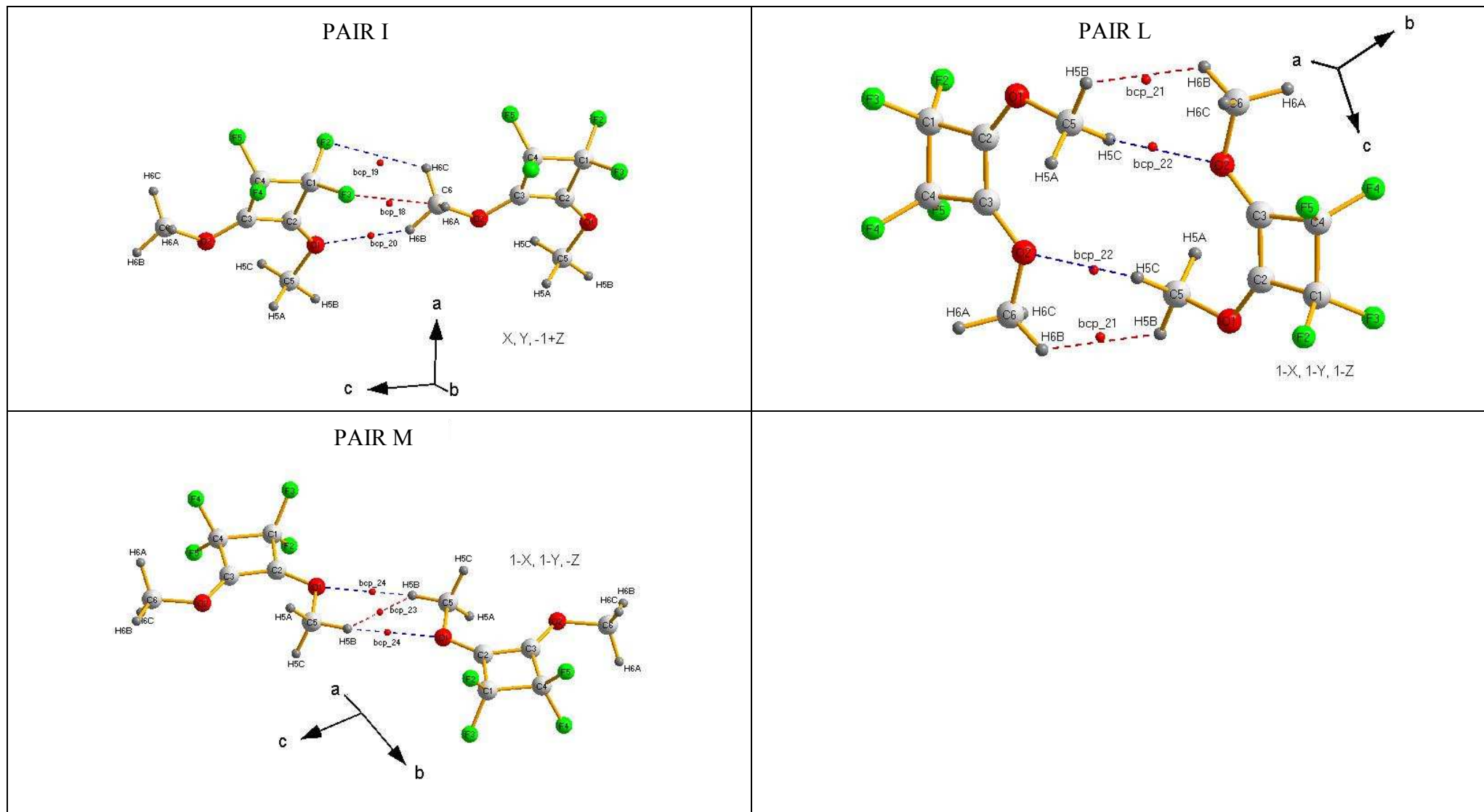


Figure SF3

Ball-and-stick representation of the TDCB pairs in the crystal at increasing centre-of-mass distances. The bcp's position are indicated as red dots. Blue dashed lines mark the H...A (A=F,O) interactions, whereas dashed red lines mark all the other interactions.







All the figures were realized with the software Diamond v3.1f, K. Brandenburg, *Diamond - Crystal and Molecular Structure Visualization*, Crystal Impact GbR: Bonn, Germany, 2008. See also <http://www.crystalimpact.com/diamond>