

Theoretical study on σ - and π -hole carbon $\cdots$ carbon bonding interactions:
Implications in CFC chemistry.

A. Bauzá and A. Frontera*

Department of Chemistry Universitat de les Illes Balears, Crta. de Valldemossa km 7.5,
07122 Palma (Balears), Spain. E-mail: toni.frontera@uib.es;

Fax: +34 971 173426

Electronic Supplementary Information

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Cartesian coordinates

6.

C	0.0000000	0.0000000	-1.0940769
F	0.0000000	0.0000000	-2.4835024
C	-0.0000000	0.0000000	2.3346213
O	0.0000000	0.0000000	3.4717312
H	-0.5153113	0.8925453	-0.7429244
H	-0.5153113	-0.8925453	-0.7429244
H	1.0306226	0.0000000	-0.7429244

7.

C	1.8538899	0.0060988	0.0000000
F	3.2436684	0.0056881	0.0000000
H	1.5025734	1.0367551	0.0000000
H	1.5012712	-0.5094001	-0.8921462
H	1.5012712	-0.5094001	0.8921462
C	-1.5982298	-0.0050278	-0.6666037
H	-1.6408257	-0.9290205	-1.2309646
H	-1.5622816	0.9191775	-1.2311374
C	-1.5982298	-0.0050278	0.6666037
H	-1.5622816	0.9191775	1.2311374
H	-1.6408257	-0.9290205	1.2309646

8.

C	0.0038802	-1.4954550	0.0000000
F	0.0505802	-2.8844116	0.0000000
H	-1.0382945	-1.1790444	0.0000000
H	0.5048252	-1.1263230	0.8934316
H	0.5048252	-1.1263230	-0.8934316
C	-0.6126798	1.9641430	0.0000000
H	-1.6768963	1.9996269	0.0000000
C	0.5995488	1.9335614	0.0000000
H	1.6642110	1.9142257	0.0000000

9.

C	0.0000000	0.0000000	-1.3268429
Cl	0.8352353	1.4466700	-0.7765791
Cl	0.8352353	-1.4466700	-0.7765791
Cl	-1.6704706	0.0000000	-0.7765791
F	0.0000000	0.0000000	-2.6725228
C	0.0000000	0.0000000	2.5956549
O	0.0000000	0.0000000	3.7334481

10.

C	2.1743470	-0.0435976	0.0000000
Cl	1.6452757	-0.8907504	1.4464324
Cl	1.6452757	-0.8907504	-1.4464324
Cl	1.5832077	1.6154573	0.0000000
F	3.5194691	-0.0072726	0.0000000
C	-1.7616315	0.0362935	-0.6665155

H	-2.1946669	-0.7810843	-1.2309243
H	-1.3274893	0.8532476	-1.2304642
C	-1.7616315	0.0362935	0.6665155
H	-1.3274893	0.8532476	1.2304642
H	-2.1946669	-0.7810843	1.2309243

11.

C	1.7961249	0.1204643	0.0000000
Cl	1.2870790	-0.7398012	1.4470331
Cl	1.2870790	-0.7398012	-1.4470331
Cl	1.1651634	1.7623356	0.0000000
F	3.1402207	0.1864894	0.0000000
C	-2.2996821	0.4447089	0.0000000
H	-2.5307375	1.4838038	0.0000000
C	-2.0370765	-0.7392904	0.0000000
H	-1.8081708	-1.7789091	0.0000000

12.

C	-0.0934078	1.2392055	0.0000000
C	0.0485443	-2.5063641	0.0000000
O	0.0592514	-3.6438837	0.0000000
F	-0.6507710	0.7042891	-1.0778579
F	-0.3457612	2.5436586	0.0000000
F	-0.6507710	0.7042891	1.0778579
Cl	1.6329153	0.9588054	0.0000000

13.

C	2.0680342	0.0318003	0.0000000
F	1.5756190	0.6262412	1.0779771
F	1.5756190	0.6262412	-1.0779771
F	3.3877305	0.1876297	0.0000000
Cl	1.6636184	-1.6704848	0.0000000
C	-1.7126882	0.0331047	0.6663865
H	-1.6140151	-0.8866559	1.2306162
H	-1.8086072	0.9528374	1.2308979
C	-1.7126882	0.0331047	-0.6663865
H	-1.8086072	0.9528374	-1.2308979
H	-1.6140151	-0.8866559	-1.2306162

14.

C	1.6625906	-0.3367742	0.0000000
Cl	0.9635736	-1.9396565	0.0000000
F	2.9890128	-0.4156996	0.0000000
C	-1.8119811	1.0643989	0.0000000
H	-1.3995825	2.0458356	0.0000000
C	-2.2778759	-0.0549965	0.0000000
H	-2.6909843	-1.0359784	0.0000000
F	1.2826234	0.3364353	-1.0776482
F	1.2826234	0.3364353	1.0776482

15.

C	1.2780785	0.0468637	0.0000000
C	-2.5414747	0.0998232	0.0000000
O	-3.6761413	0.0168348	0.0000000
F	0.7057755	1.2507557	0.0000000
F	2.6017163	0.2278545	0.0000000
Cl	0.8160229	-0.8210660	-1.4528176
Cl	0.8160229	-0.8210660	1.4528176

16.

C	2.0978894	0.1357444	0.0000000
F	1.3695091	1.2545302	0.0000000
F	3.3848994	0.4938081	0.0000000
Cl	1.7553110	-0.7847735	-1.4524937
Cl	1.7553110	-0.7847735	1.4524937
C	-1.7274877	-0.0524926	-0.6664753
H	-1.3519851	0.7932914	-1.2299384
H	-2.1019873	-0.8980666	-1.2311446
C	-1.7274877	-0.0524926	0.6664753
H	-2.1019873	-0.8980666	1.2311446
H	-1.3519851	0.7932914	1.2299384

17.

C	1.7230893	0.1123627	0.0000000
F	1.0875943	1.2856399	0.0000000
F	3.0351989	0.3650811	0.0000000
Cl	1.3078592	-0.7772673	-1.4529172

Cl	1.3078592	-0.7772673	1.4529172
C	-2.1356430	0.5538239	0.0000000
C	-2.0969079	-0.6581762	0.0000000
H	-2.0642934	-1.7222126	0.0000000
H	-2.1647566	1.6180158	0.0000000

18.

C	0.0000000	0.0000000	-1.5211242
O	-1.1689573	0.0000000	-1.5268222
O	1.1689573	0.0000000	-1.5268222
C	0.0000000	0.0000000	1.7188355
O	0.0000000	0.0000000	2.8559331

19a.

C	0.0000000	0.0000000	2.1763814
O	0.0000000	1.1690433	2.1818256
O	0.0000000	-1.1690433	2.1818256
C	0.0000000	-0.6667689	-1.0898001
H	-0.9243697	-1.2319606	-1.0901081
H	0.9243697	-1.2319606	-1.0901081
C	0.0000000	0.6667689	-1.0898001
H	0.9243697	1.2319606	-1.0901081
H	-0.9243697	1.2319606	-1.0901081

19b.

C	0.0000000	0.0000000	2.1669333
O	0.0000000	1.1690685	2.1741121

O	0.0000000	-1.1690685	2.1741121
C	0.6667456	0.0000000	-1.0852159
H	1.2299568	-0.9257282	-1.0861814
H	1.2299568	0.9257282	-1.0861814
C	-0.6667456	0.0000000	-1.0852159
H	-1.2299568	0.9257282	-1.0861814
H	-1.2299568	-0.9257282	-1.0861814

20a.

C	0.0000000	0.0000000	-1.8320426
O	-1.1688862	0.0000000	-1.8375696
O	1.1688862	0.0000000	-1.8375696
C	-0.6064509	0.0000000	1.3778245
H	-1.6712852	0.0000000	1.3757664
C	0.6064509	0.0000000	1.3778245
H	1.6712852	0.0000000	1.3757664

20b.

C	0.0000000	0.0000000	1.9027685
O	0.0000000	1.1690899	1.9085695
O	0.0000000	-1.1690899	1.9085695
C	0.6062896	0.0000000	-1.4267568
H	1.6710461	0.0000000	-1.4331969
C	-0.6062896	0.0000000	-1.4267568
H	-1.6710461	0.0000000	-1.4331969

21.

C	-0.0023332	-0.6068798	0.0000000
H	-0.0045447	-1.6730458	0.0000000
C	0.0004839	0.6065483	0.0000000
H	0.0032399	1.6726320	0.0000000
C	-0.0212270	5.3115488	0.0000000
H	1.0076994	5.6670769	0.0000000
H	-0.5403672	5.6526028	0.8940219
H	-0.5403672	5.6526028	-0.8940219
C	0.0218889	-5.3114808	0.0000000
H	-0.4903675	-5.6626678	-0.8940582
H	1.0577728	-5.6463385	0.0000000
H	-0.4903675	-5.6626678	0.8940582
F	0.0069553	-3.9202907	0.0000000
F	-0.0084658	3.9203596	0.0000000

22.

C	-0.0201079	0.6062004	0.0000000
H	-0.0571735	1.6707735	0.0000000
C	0.0201079	-0.6062004	0.0000000
H	0.0571735	-1.6707735	0.0000000
C	-3.4515833	-0.0027619	0.0000000
H	-3.0834648	0.4989661	-0.8935799
H	-3.1331865	-1.0444702	0.0000000
H	-3.0834648	0.4989661	0.8935799
F	-4.8399176	0.0413444	0.0000000
C	3.4515833	0.0027619	0.0000000

H	3.1331865	1.0444702	0.0000000
H	3.0834648	-0.4989661	0.8935799
H	3.0834648	-0.4989661	-0.8935799
F	4.8399176	-0.0413444	0.0000000

23.

C	0.0000000	0.6072129	-0.0546186
H	0.0000000	1.6741867	-0.0536019
C	0.0000000	-0.6072129	-0.0546186
H	0.0000000	-1.6741867	-0.0536019
C	0.0000000	-5.2481425	0.0511679
H	0.0000000	-5.5589586	1.0941935
H	0.8941953	-5.6087351	-0.4536941
H	-0.8941953	-5.6087351	-0.4536941
C	0.0000000	5.2481425	0.0511679
H	-0.8941953	5.6087351	-0.4536941
H	0.0000000	5.5589586	1.0941935
H	0.8941953	5.6087351	-0.4536941
F	0.0000000	3.8552108	0.0064040
F	0.0000000	-3.8552108	0.0064040
C	-3.3806599	0.0000000	-0.0280424
H	-3.0278018	0.8915879	0.4878539
H	-3.0307331	0.0000000	-1.0586954
H	-3.0278018	-0.8915879	0.4878539
F	-4.7724054	0.0000000	-0.0251268
C	3.3806599	0.0000000	-0.0280424
H	3.0278018	0.8915879	0.4878539

H	3.0278018	-0.8915879	0.4878539
H	3.0307331	0.0000000	-1.0586954
F	4.7724054	0.0000000	-0.0251268

Additional AIM analyses

In **Fig. S1** the distribution of critical points (CPs) and bond paths for some additional complexes is shown. As it can be observed, for complexes **9** and **16** where a CO molecule acts as electron donor three symmetrically distributed bond CPs (red spheres) connect the halogen and carbon atoms. In addition, a cage CP emerges and further characterizes the interaction. On the other hand, in complexes **11** and **13** it can be noticed three bond CPs that connect the halogen atoms with the carbon atoms of the π -system. These results are in good agreement with the NBO analysis, which showed orbital contributions involving the halogen atoms of the CFC molecules.

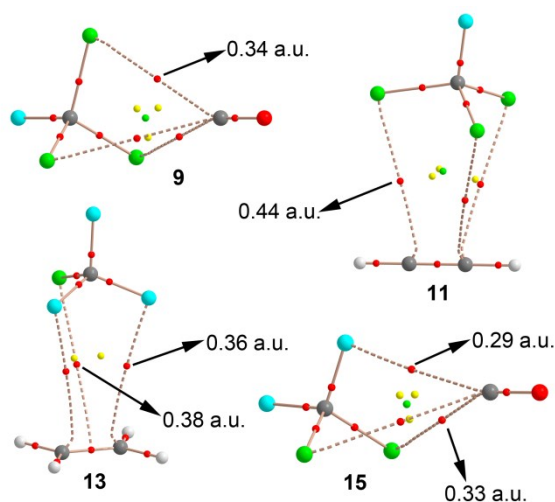


Fig. S1 Distribution of critical points and bond paths in complexes **9**, **11**, **13** and **15**. Bond, ring and cage critical points are represented by red, yellow and green spheres, respectively. The bond paths connecting bond critical points are also represented. The value of the density at the bond critical point ($\rho \cdot 10^2$) is also indicated.