



Analysis of the interactions between difluoroacetylene and one or two hydrogen fluoride molecules based on calculated spin–spin coupling constants

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ABSTRACT

A theoretical study of FCCF:(HF)_n complexes, with *n* = 1 and 2, has been carried out by means of ab initio computational methods. Two types of complexes are formed: those with FH...π interactions and those with FH...FC hydrogen bonds. The indirect spin–spin coupling constants have been calculated at the CCSD/aug-cc-pVTZ-*J* computational level. Special attention has been paid to the dependence of the different intramolecular coupling constants in FCCF on the distance between the coupled nuclei and the presence or absence of the hydrogen fluoride molecule. The sensitivity shown by these coupling constants to the presence of hydrogen fluoride is quite notorious.

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1. Introduction

Since the experimental observation of measurable indirect spin–spin coupling constants, *J*, through hydrogen bonds (HBs) in bis-iminophosphoranes [1], these couplings have been employed for the elucidation of molecular, conformational and structural characteristics of chemical compounds and their complexes [2,3]. Significant progress has e.g. been made in understanding the vibrational effects on NMR properties of hydrogen-bonded complexes [4]. It was also demonstrated that the environment influences these couplings which, at the same time, provides important information about the structure of the hydrogen bond [5–7].

In general, a given molecule can act with different moieties as hydrogen bond donor and/or hydrogen bond acceptor [8]. The location of the interaction affects the electron density and most of the properties of the molecule of interest in a specific way. Thus, theoretical knowledge of the effect of the interaction can help to identify which complex is formed experimentally. In the present article the FCCF molecule and its complexes with one and two hydrogen fluoride (HF) molecules have been studied.

The indirect spin–spin coupling constants in difluoroethyne (difluoroacetylene), FCCF, have been a challenging test for computational methods. The experimental values, described by Bürger

and Sommer [8], were 2.1 Hz for ³*J*(¹⁹F–¹⁹F) and a –287.3 Hz for ¹*J*(¹⁹F–¹³C). Recently, Del Bene et al. [9] were able to compute values similar to the experimental ones using the EOM-CCSD/Ahlrichs qzp computational level and the experimental geometry reported by Bürger et al. [10]. The computed values were 1.4 Hz for ³*J*(¹⁹F–¹⁹F), –277.7 Hz for ¹*J*(¹⁹F–¹³C) and 40.2 Hz for ²*J*(¹⁹F–¹³C). This last value was also estimated by Del Bene et al. from the experimental spectrum to be 28.7 Hz for ²*J*(¹⁹F–¹³C).

As seen above difluoroethyne has large intramolecular spin spin coupling constants, which added to the well-known sensitivity of the spin spin coupling constants to electronic induced changes like those caused by hydrogen bonding, makes hydrogen bonded complexes of difluoroethyne an interesting system to study. Two types of hydrogen bonds have been considered: one, where the fluorine atoms act as HB acceptors and one, where the π-cloud of the acetylene moiety is the HB acceptor.

2. Theoretical methods

The geometry of all the systems has been optimized at the MP2 [11] computational level with the 6-311++G(d,p) [12] basis set and the frozen core approximation using the Gaussian-03 program [13]. Frequency calculations have been performed on the minimized geometries in order to confirm that the obtained structures correspond to energetic minima [14].

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The theory of indirect nuclear spin–spin coupling constants (SSCCs) [15] and the different computational methods used for calculating them have extensively been described in the literature [16–20]. However, it is important to keep in mind that there are four contributions to the SSCC: the Fermi contact (FC) and the spin–dipolar (SD) terms, which come from the interaction of the nuclear magnetic moments with the spin of the electrons; the diamagnetic spin orbital (DSO) and the paramagnetic spin orbital (PSO) terms, which are due to the interaction of the nuclear spins with the orbital angular momentum of the electrons.

All coupling constants were calculated at the coupled cluster with single and double excitations (CCSD) level [21–24] using the aug-cc-pVTZ-*J* basis set [25,26]. This basis set ensures the cusp behavior of the wave function at the nuclear sites and consequently a very good description of the FC term [25] (and references therein). The CCSD formalism explicitly includes electron correlation effects, which are important for coupling constants involving the more electronegative atoms. In the present work the calculation were performed using the CFOUR program package [27].

3. Results and discussions

Fig. 1 shows the different systems considered in this work. Geometries **1** and **2** correspond to the isolated difluoroethyne (FCCF) and HF molecules and **3** to the HF dimer.

The complexes with even number (**4**, **6**, and **8**) are those that have HF groups facing the triple C≡C bond, i.e. that present FH·· π interactions while the odd-numbered complexes (**5**, **7**, and **9**) presents HB's between the HF molecule and one or two fluorine atoms of FCCF.

Attempts to obtain other complexes representing energy minima have been unsuccessful. For instance, starting structures with

a complex with two HF molecules bound to the same F atom of FCCF or with one HF bound to a F and the other HF interacting with the π (C≡C) bond lead in the optimization to the structures already included in Fig. 1. Finally, the analog complex to **7** but with symmetry C_{2v} , i.e. the two HF molecules in *cis* position, shows imaginary frequencies.

Table 1 shows the detailed geometry for all the complexes. The complexes where the interaction is between a HF molecule and the π -cloud of FCCF (**4**, **6** and **8**) show an elongation of the C≡C distance with respect to the isolated monomer. In contrast, the complexes with FH··F hydrogen bonds, show a shortening of the C≡C bond.

The carbon–fluorine distances show the opposite behavior to the carbon–carbon distances. Thus, the C–F intramolecular distance decreases with respect to that in the isolated FCCF molecule in complexes **4**, **6** and **8** and increases in complexes **5**, **7** and **9**, except for the C–F bond of **5** and **9** not involved in the HB interaction.

The cooperative and diminutive effects [28] associated with the donor/acceptor pattern of the hydrogen bonds are observed in the 1:2 complexes (**6–9**). Thus, if the 1:1 complexes, **4** and **5**, are used as reference, the complexes where the FCCF acts as double HB acceptor, **6** and **7**, show longer intermolecular distances while in those where a FCCF:HF:HF chain is formed, **8** and **9**, the intermolecular distances are shorter than in the corresponding 1:1 complexes. In the same way, the intermolecular distances between the HF molecules in the complexes **8** and **9** are shorter than the one found in the HF dimer (**3**), as confirmation of the cooperative effect observed in these clusters.

3.1. Electronic energies

The stabilization energies of the complexes have been calculated as the difference between the energy of the complexes and

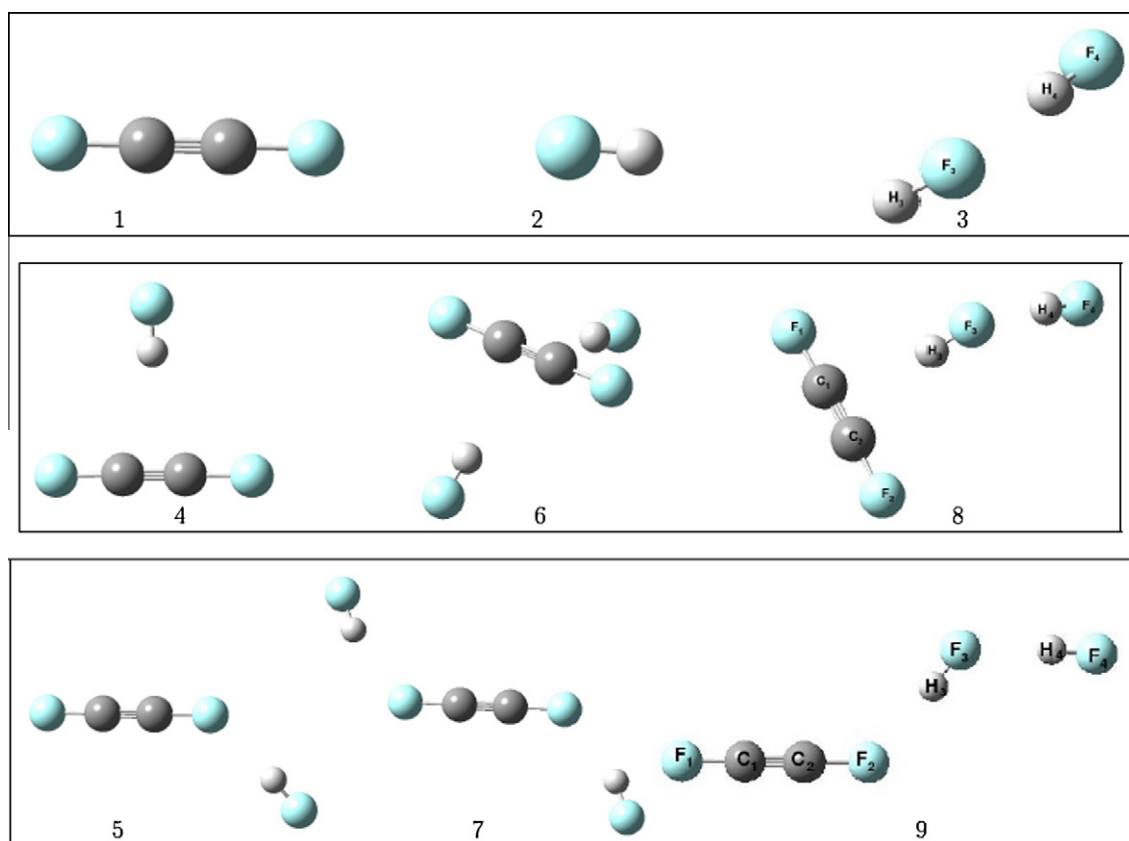


Fig. 1. Optimized geometries of the systems obtained at the MP2/6-311++G(d,p) computational level.

Table 1
Geometry (in Å and angles) of the systems considered in this article optimized at the MP2/6-311++G(d,p) level.

h	Intramolecular distances					Intermolecular distances		
	r(C,C)	r(F ₁ ,C ₁)	r(F ₂ ,C ₂)	r(F ₃ -H ₃)	r(F ₄ -H ₄)	r(H ₃ -,π _{C=C})	r _{HB} (H ₃ ,F ₂)	r _{HB} (H ₄ ,F ₃)
1	1.1973	1.2867						
2				0.9166				
3				0.9195	0.9212			1.8737 ^e
4	1.1996	1.2837	1.2837	0.9195		2.3493 ^a		
5	1.1966	1.2833	1.2930	0.9177			2.0978 ^b	
6	1.2013	1.2820	1.2820	0.9179		2.4703 ^c		
7	1.1959	1.2894	1.2894	0.9174			2.1651 ^d	
8	1.2006	1.2826	1.2826	0.9259	0.9221	2.1718 ^g	1.8363 ^g	
9	1.1964	1.2820	1.2952	0.9214	0.9219		1.9968 ^f	1.8495 ^f

^a Ang(H₃,π_{C=C},C₁) = 90.0.

^b Ang(C₁,F₁,H₃) = 129.86 and ang(F₁,H₃,F₃) = 175.29.

^c Ang(H₃,π_{C=C},C₁) = 90.0, ang(H₄,π_{C=C},C₁) = 90.0 and ang(H₃,π_{C=C},H₄) = 126.02.

^d Ang(C₁,F₁,H₃) = 128.40 and ang(F₁,H₃,F₃) = 161.68.

^e Ang(H₃,F₃,H₄) = 124.46 and ang(F₃,H₃,F₄) = 171.06.

^f Ang(C₁,F₁,H₃) = 130.08, ang(F₁,H₃,F₃) = 175.83, ang(H₃,F₃,H₄) = -126.26 and ang(F₃,H₄,F₄) = 174.83.

^g Ang(H₃,π_{C=C},C₁) = 90.0 and ang(H₃,F₃,H₄) = 124.45, ang(F₃,H₄,F₄) = 173.32.

^h All complex but **6** and **8** are planar.

Table 2
Total energy (in Hartree), stabilization energy, E_S , and cooperativity (in kJ mol⁻¹) of the complexes calculated at the MP2/6-311++G(d,p) level.

Complex	E_{tot}	E_S	Cooperativity
1	-275.20808		
2	-100.27889		
3	-200.56535	-4.75	
4	-375.48939	-1.52	
5	-375.48930	-1.47	
6	-475.76908	-2.02	4.20
7	-475.76979	-2.47	1.84
8	-475.77688	-6.92	-2.89
9	-475.77651	-6.68	-2.10

the sum of the energies of the isolated monomers in their minima configuration. No counterpoise corrections for basis-set superposition errors have been made since it has assumed that the effect of the BSSE should be small for the given basis sets like in previous studies on HCN complexes [29]. The total and the interaction energies of the studied complexes are gathered in Table 2.

$$E_S = E_{tot}^{(ABC\dots)} - [E_{tot}^{(A)} + E_{tot}^{(B)} + E_{tot}^{(C)} + \dots]$$

The cooperativity in the FCCF:(HF)₂ complexes has been evaluated by comparing its stabilization energy with those obtained in the corresponding 1:1 complexes with similar interactions. Thus, **6** and **7** have been compared to twice the stabilization energies of **4** and **5**, respectively.

Complexes **6** and **7** show diminutive effects (positive values of cooperativity) as indication that their E_S is smaller than the sum of the isolated interactions. The opposite is observed for the complexes **8** and **9** where cooperative effects are observed. These re-

Table 3
The ¹J(C-C) coupling in FCCF for the studied complexes. Also shown are the results corresponding to the isolated FCCF molecule with the same geometry than in the corresponding complex.

Complex	DSO	PSO	SD	FC	Total	Isolated
1	0.3	14.8	9.8	385.4	410.4	410.4
4	0.3	14.3	9.6	376.5	400.7	410.9
5	0.3	15.1	10.0	391.0	416.4	410.6
6	0.3	14.0	9.4	370.1	393.8	409.7
7	0.3	15.4	10.1	396.2	422.0	410.8
8	0.3	14.1	9.5	372.7	396.5	409.9
9	0.3	15.2	10.0	392.7	418.3	410.7

sults are in agreement with the intermolecular distances discussed for the 2:1 complexes previously.

3.2. Indirect nuclear spin coupling constants

The analysis of the J -coupling constants is divided into two parts: (i) the intramolecular couplings, Tables 3–7, and (ii) the intermolecular couplings, Tables 8–11. For intramolecular calculations we treat one-bond, two-bond and three-bond couplings separately. For intermolecular calculations we treat only one-bond and two-bond couplings constants.

The effect of the geometrical distortion of the FCCF molecule due to the complexation on the J 's values has been analyzed by calculating the coupling constant values on the isolated FCCF molecule while maintaining the geometry of the complex.

We could not perform a similar comparison for isolated FCCF with the geometry of the **4–6–8** complexes because the calculations did not converge, when using aug-cc-pVTZ- J basis set. In order to have an idea how these distorted FCCF molecules behave, we have calculated and plotted, when appropriate, for these three compounds, the coupling constants using the smaller: cc-pVTZ- J , basis set again at the CCSD level of approximation.

3.3. Intramolecular couplings

The major contribution to the ¹J(C-C) and ¹J(F-C) constants of FCCF arises from the Fermi contact term (FC), see Tables 3–7. For the ²J(F-C) case, the FC and spin-dipolar (SD) terms prevail but the paramagnetic spin orbital contribution (PSO), although third in absolute size, also plays a relevant role in the dependence of the coupling constant on the position of the HF molecules. Finally, for ³J(F-F) the PSO and SD components dominate, but the geometry dependence is governed basically by the SD term alone. In all three cases the diamagnetic spin orbital contribution is negligible.

In addition to the distortion of the molecular geometry due to the complexation, the presence of nearby HF molecules modifies the coupling constants.

3.3.1. ¹J(C-C)

The ¹J(C-C) couplings for each of the studied compounds (Fig. 1) are summarized in Table 3. The values range between 394 and 422 Hz, and are completely dominated by the Fermi contact term.

Fig. 2 illustrates the ¹J(C-C) couplings as a function of the length of the C≡C bond between the FCCF carbon atoms. The straight, so-

Table 4

The $^1J(\text{F}-\text{C})$ coupling in FCCF for the studied complexes. Also shown are the results corresponding to the isolated FCCF molecule with the same geometry than in the corresponding complex.

Complex	$^1J(\text{F}_1-\text{C}_1)$					$^1J(\text{F}_2-\text{C}_2)$			
	DSO	PSO	SD	FC	Total	Isolated	Total	Isolated	$d(\text{F}_2-\text{C}_2)$
1	0.6	-9.0	-8.4	-262.6	-279.5	-279.5			
4	0.6	-11.7	-9.1	-272.9	-293.0	-278.1			
5	0.6	-12.3	-9.2	-266.0	-286.9	-276.8	-249.6	-283.8	1.2930
6	0.7	-13.4	-9.5	-281.5	-303.8	-277.5			
7	0.7	-7.1	-7.7	-243.5	-257.6	-281.2			
8	0.6	-13.0	-9.4	-277.5	-299.2	-277.7			
9	0.6	-13.6	-9.6	-267.5	-290.1	-275.8	-239.9	-285.3	1.2952

Table 5

The $^2J(\text{F}-\text{C})$ coupling in FCCF for the studied complexes. Also shown are the results corresponding to the isolated FCCF molecule with the same geometry than in the corresponding complex.

Complex	$^2J(\text{F}_1-\text{C}_2)$						$^2J(\text{F}_2-\text{C}_1)$	
	DSO	PSO	SD	FC	Total	Isolated	Total	Isolated
1	-0.7	6.6	17.8	18.4	42.1	42.1		
4	-0.6	6.6	18.0	14.1	38.0	43.6		
5	-0.7	8.3	18.6	17.8	44.0	43.8	45.1	39.1
6	-0.6	6.6	18.1	11.0	35.1	44.5		
7	-0.6	6.3	17.3	23.9	46.8	40.8		
8	-0.6	6.7	18.1	12.0	36.2	44.3		
9	-0.7	8.9	18.9	17.5	44.6	44.5	46.1	38.0

Table 6

The $^3J(\text{F}-\text{F})$ coupling in FCCF for the studied complexes. Also shown are the results corresponding to the isolated FCCF molecule with the same geometry than in the corresponding complex.

Complex	DSO	PSO	SD	FC	Total	Isolated
1	-1.8	-39.4	29.8	7.4	-4.0	-4.0
4	-1.8	-39.1	31.7	8.1	-1.0	-1.4
5	-1.7	-39.9	28.1	6.4	-7.1	-5.4
6	-1.7	-39.1	33.1	8.7	0.9	0.0
7	-1.7	-40.0	26.6	5.6	-9.4	-6.5
8	-1.7	-39.0	32.4	8.4	-0.1	0.3
9	-1.7	-40.0	27.5	6.1	-8.1	-5.8

Table 7

$^1J(\text{H}-\text{F})$ Intramolecular spin-spin coupling constant in hydrogen fluoride (Hz).

Complex	$^1J(\text{F}_3-\text{H}_3)$	$d(\text{F}_3-\text{H}_3)$	$^1J(\text{F}_4-\text{H}_4)$	$d(\text{F}_4-\text{H}_4)$
2	529.5	0.9166		
3	555.8	0.9195	533.9	0.9212
4	524.0	0.9195		
5	530.0	0.9177		
6	524.3	0.9179		
7	528.9	0.9174		
8	542.0	0.9259	534.5	0.9221
9	557.6	0.9214	534.2	0.9219

Table 8

The intermolecular $^{11}\text{J}(\text{H}-\text{F})$ between H_{HF} and F_{FCF} .

Complex	$^{11}\text{J}(\text{F}_2-\text{H}_3)$				Total
	DSO	PSO	SD	FC	
4	1.3	-0.7	-0.3	0.2	0.5
5	4.1	-4.4	0.7	-13.2	-12.8
6	1.3	-0.7	-0.3	0.1	0.4
7	3.8	-4.2	0.7	-10.5	-9.6
8	1.3	-0.6	-0.5	0.4	0.6
9	4.5	-4.9	0.8	-18.2	-17.8

lid line corresponds to the best trend-line. We observe that $^1J(\text{C}-\text{C})$ depends inversely on the $\text{C}\equiv\text{C}$ distance. Larger values of $^1J(\text{C}-\text{C})$ are associated to the shorter $\text{C}\equiv\text{C}$ distances while smaller values are present in the longer $\text{C}\equiv\text{C}$ distances.

In order to reveal if this behavior is just a consequence of the change in geometry due to the complexation with the HF molecules, we computed also $^1J(\text{C}-\text{C})$ in the FCCF molecule with the geometry of complexes. The results of the $^1J(\text{C}-\text{C})$ are essentially constant, independently of the different geometries involved (Table 3 and the dashed line in Fig. 2).

A previous study [8] has reported a similar linear dependence of the $^1J(\text{C}-\text{C})$ with the $\text{C}-\text{C}$ distance in difluoroethyne. In that case, a 1% change in $d(\text{C}\equiv\text{C})$ produced a 1% variation in $^1J(\text{C}-\text{C})$. However, the effect in the presence of HF molecules is thirty times larger, as a 0.1% change in $d(\text{C}\equiv\text{C})$ brings about a 3% difference in $^1J(\text{C}-\text{C})$. This indicates that the environment strongly influences the value of this indirect coupling constant. Moreover, it is shown that for this case an exponential curve correlates a bit better than the linear one, in agreement with previous reports [30].

3.3.2. $^1J(\text{F}-\text{C})$

In Table 4 the results for $^1J(\text{F}-\text{C})$ are presented. In this case, all the values are large and negative in contradiction of the Dirac vector model that predicts positive values for 1J in agreement with previous reports that have indicated similar discrepancies with such a model [31]. As in the $^1J(\text{C}-\text{C})$ case, the Fermi contact term is the dominant contribution. In complexes **5** and **9**, where two different $\text{C}-\text{F}$ bonds are present, the one involved in the HB interaction has the longer bond distance (Table 1) and the smaller coupling constant.

The representation of the $^1J(\text{F}-\text{C})$ vs. the corresponding $\text{F}-\text{C}$ distances (Fig. 3) shows a linear relationship with increasing absolute

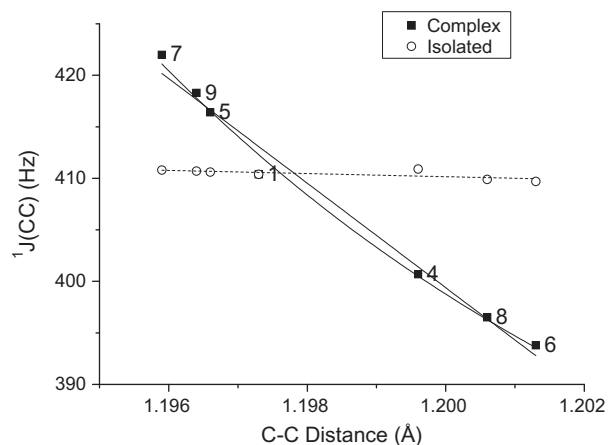


Fig. 2. The $^1J(\text{C}-\text{C})$ indirect coupling constant vs. the $\text{C}-\text{C}$ bond distance in the studied complexes. A linear and exponential relationship are shown.

values of the coupling constant as the interatomic distance becomes smaller. However, this behavior cannot be attributed to a mere dependence on the geometry since the values of $^1J(\text{F-C})$ in the isolated FCCF molecule with the geometry of the complexes indicates that the coupling slightly decreases in absolute value as the C-F distance becomes smaller. It is interesting to note that the three C-F moieties involved in HB interactions show smaller $^1J(\text{F-C})$ than those expected for the interatomic distance found in the complex, while in all the C-F moieties not involved in HB interaction the values obtained are larger in absolute value than the one calculated in the isolated FCCF molecule with the same geometry.

Noteworthy is the fact that $^1J(\text{F-C})$ shows negative PSO and SD contributions and both of the same order. This sign contrast with the analysis done by Anizelli et al. [37] in 4-t-butyl-2-fluorocyclohexanones and their alcohols derivatives, however the C-F moieties treated are different. Furthermore our results are in accordance with the predicted sign by Watson et al. [36b] for small separations.

3.3.3. $^2J(\text{F-C})$

The $^2J(\text{F-C})$ couplings are gathered in Table 5. Positive values of $^2J(\text{F-C})$ are obtained, again in disagreement with the Dirac vector model but in agreement with previous reports [31]. The dominant contributions to the $^2J(\text{F-C})$ arise from the spin-orbital (SD) and Fermi-contact (FC) terms, and this last one drives the variation between compounds. Also here it is worth mentioning that PSO as well as the FC and SD terms are all positive in contrast with the analysis done by Anizelli et al. [37] where the corresponding PSO contributions are negatives. Again our results are in agreement with the predicted sign by Watson et al. [36b] for large separation. For the asymmetric complexes **5** and **9** two results are given: $^2J(\text{F}_2-\text{C}_1)$, for the fluorine atom next to the interacting HF molecule, and $^2J(\text{F}_1-\text{C}_2)$, for the fluorine atom not involved in the HB interaction. Slightly larger values are obtained in the first case than in the later. The results are plotted as a function of the corresponding F_2-C_1 and F_1-C_2 distance in Fig 4a, both for the difluoroethyne-hydrogen fluoride complexes and for the isolated FCCF molecule in the geometry of the respective complex. While for the isolated molecules the coupling decreases linearly with distance, no such pattern appears for the complexes.

In the case of complexes **5** and **9** the $^2J(\text{F}_1-\text{C}_2)$ couplings, which correspond to the F-C moiety not involved in the HB interaction, are similar to those in the corresponding isolated molecule with the geometry in the complex, suggesting that the observed effect is of geometric origin. In contrast, the $^2J(\text{F}_2-\text{C}_1)$ coupling in these complexes is higher than for the isolated molecule, an indication

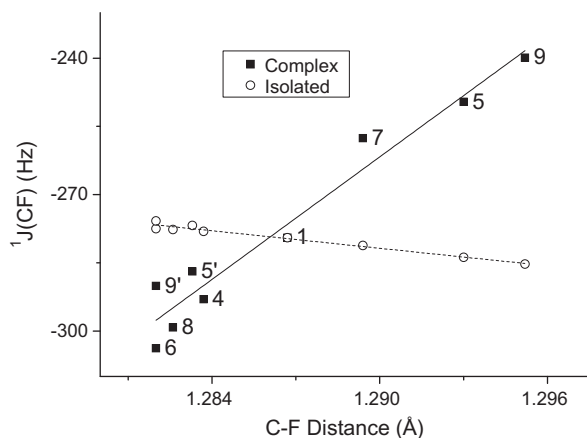


Fig. 3. $^1J(\text{F-C})$ coupling constant vs. F-C bond distance. The C-F moieties not involved in a HB interaction in **5** and **9** are indicated with a prime.

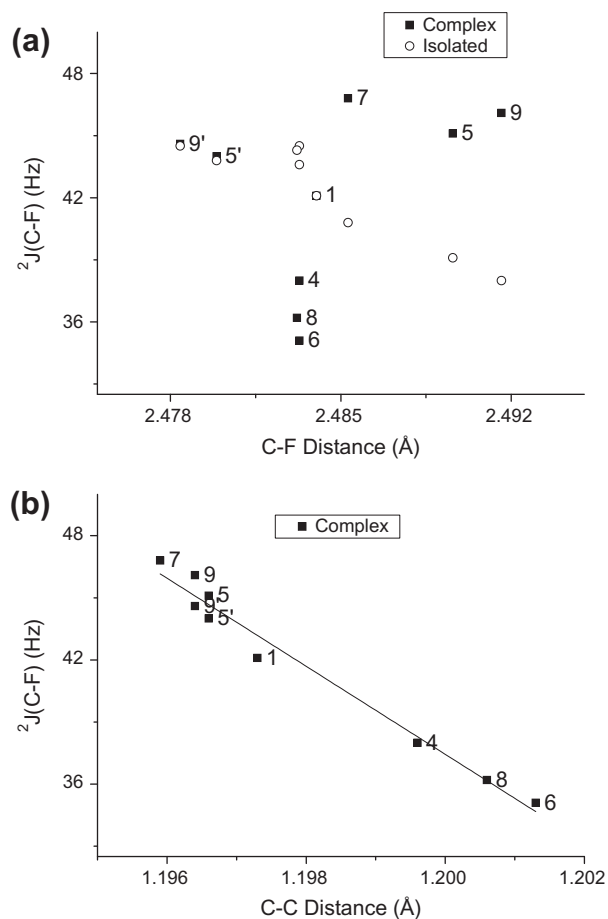


Fig. 4. The $^2J(\text{F-C})$ indirect coupling constant vs. (a) the F...C distance and (b) C-C distance in FCCF.

that the presence of the HF molecule and the hydrogen bond increase the 2J coupling. A similar result is obtained for **7** where both fluorine atoms of FCCF are involved in HB interactions.

Although there is no systematic relation between 2J and $d(\text{F-C})$, it is interesting to note that 2J presents a clear linear dependence with the $\text{C}\equiv\text{C}$ distance, as shown in Fig. 4b.

3.3.4. $^3J(\text{F-F})$

The $^3J(\text{F-F})$ results are given in Table 6 and plotted in Fig. 5 as a function of the F-F distance. The total values $^3J(\text{F-F})$ are small and negative, except for complex **6** where it is 0.9 Hz. Close inspection of the four contributions to $^3J(\text{F-F})$ reveals that this behavior is the consequence of a basically constant negative spin-orbital component and the partial cancelation by a positive spin-dipolar term, which decrease with the F-F distance as expected. There is a clear linear relation between $^3J(\text{F-F})$ and the F...F interatomic distance, but with the absolute value of 3J increasing with distance, which is opposite to the trend observed previously for the 1J and the 2J couplings.

The couplings of the isolated FCCF molecule with the geometry of the complex show a similar trend as the studied complexes which indicates that to a large extent the observed pattern has a geometric origin.

3.3.5. $^1J(\text{F-H})$ in hydrogen fluoride

The $^1J(\text{F-H})$ couplings for the whole set of complexes studied here are gathered in Table 7. The $^1J(\text{F-H})$ coupling constant has been studied a number of times in the literature [2,32]. The

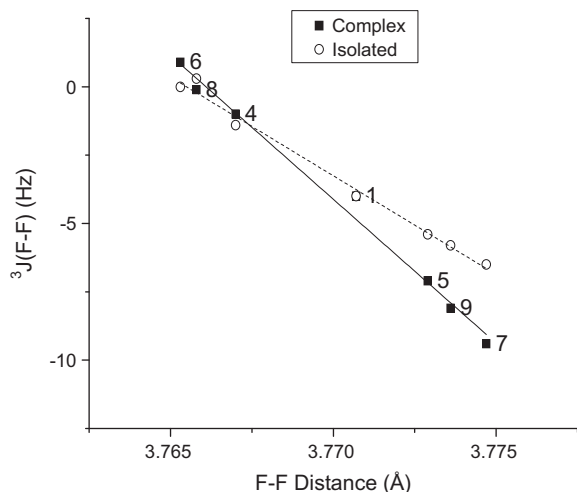


Fig. 5. $^3J(\text{F}-\text{F})$ indirect coupling constant vs. the F-F distance in the FCCF molecule.

measured experimental values for the isolated monomers are 521 Hz, 529 ± 23 Hz and 540 Hz [33]. The theoretical values lie within a wider range which goes from 476.09 Hz to 553.0 Hz [34]. The vibrational corrections were estimated between 26 and 37 Hz [35]. Therefore the approximations reported in the literature are quite good. The value obtained in the present article (529.5 Hz) nicely reproduces the experimental value.

The largest $^1J(\text{F}-\text{H})$ in the complexes studied corresponds to the HF interacting simultaneously with another HF molecule and with the fluorine atom of FCCF in complex **9**. In contrast, the smaller values of $^1J(\text{F}-\text{H})$ are associated to $\text{FH}\cdots\pi$ interactions in complexes **4** and **6**.

3.4. Intermolecular couplings

3.4.1. $^1J(\text{H}-\text{F})$

The intermolecular $^1J(\text{H}-\text{F})$ coupling between the H nucleus of HF and the fluorine nucleus in FCCF, and between the HF molecules in complexes **3**, **8** and **9** are summarized in Tables 8 and 9. They are plotted as a function of the corresponding H-F distance in Fig. 6.

The $^1J(\text{H}-\text{F})$ coupling is small and positive for the $\text{FH}\cdots\pi$ bonded complexes (**4**, **6**, and **8**). This is expected given the large H-F distance. In the rest of the complexes, where a direct interaction is observed between the fluorine atom and the hydrogen, negative values of $^1J(\text{H}-\text{F})$ are obtained, ranging from -9.6 to -30.2 Hz. An exponential relationship can be obtained between all the $^1J(\text{H}-\text{F})$ values and the corresponding H...F interatomic distance (Fig. 6 and Ref. [30]).

3.4.2. $^2J(\text{F}-\text{F})$

The intermolecular $^2J(\text{F}-\text{F})$ couplings between fluorine nuclei in FCCF and HF are given in Table 10. Negative values are obtained in all cases, being smaller for the complexes with $\text{FH}\cdots\pi$ interactions while larger, between -21.6 and -27.7 Hz, in those complexes with $\text{FH}\cdots\text{F}$ contacts. The two most important

Table 9
The intermolecular $^1J(\text{H}-\text{F})$ coupling between HF molecules.

Complex	$^1J(\text{F}_3-\text{H}_4)$				Total
	DSO	PSO	SD	FC	
3	4.1	-4.6	1.6	-28.1	-27.1
8	4.4	-4.9	1.7	-31.4	-30.2
9	4.3	-4.7	1.5	-30.7	-29.6

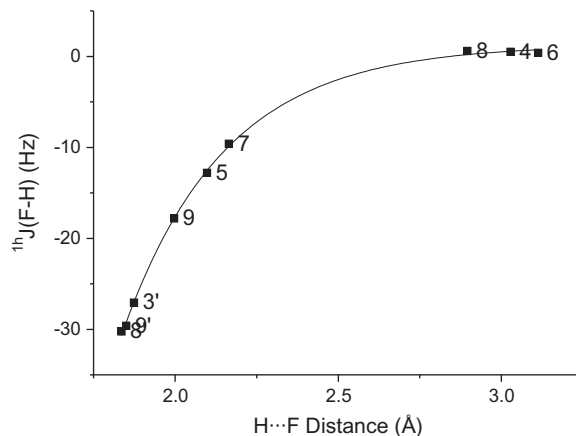


Fig. 6. The intermolecular couplings $^1J(\text{F}-\text{H})$ vs. the F...H distance. The coupling between HF molecules is indicated with a prime.

Table 10
The four contributions of the intermolecular $^2J(\text{F}_{\text{FCCF}}-\text{F}_{\text{HF}})$ couplings.

Complex	$^2J(\text{F}_2-\text{F}_3)$				Total	$d(\text{F}_2, \text{F}_3)$
	DSO	PSO	SD	FC		
4	-0.3	-2.1	-0.3	0.4	-2.2	3.79
5	0.2	-11.8	2.7	-18.9	-27.7	3.01
6	-0.2	-1.3	-0.2	0.3	-1.5	3.88
7	0.2	-10.5	2.6	-15.7	-23.5	3.05
8	-0.2	-3.6	-0.4	0.5	-3.7	3.65
9	0.3	-15.0	3.5	-10.5	-21.6	2.92

Table 11
The four contributions of the intermolecular $^2J(\text{F}_{\text{HF}}-\text{F}_{\text{HF}})$ couplings.

Complex	$^2J(\text{F}_3-\text{F}_4)$				Total	$d(\text{F}_3, \text{F}_4)$
	DSO	PSO	SD	FC		
3	-0.2	-28.6	6.3	-11.1	-33.6	2.79
8	-0.1	-32.7	7.1	-6.6	-32.3	2.75
9	-0.1	-30.1	6.3	-8.5	-32.3	2.49

components of the coupling constants are the paramagnetic spin-orbital (PSO) and the Fermi contact (FC) terms. The PSO term values show a linear dependence on the distance in the **5**, **7**, **9** series and in the **4**, **6**, **8** one.

Finally, Table 11 gives the $^2J(\text{F}-\text{F})$ couplings between the two HF fluorine nuclei. The values obtained for the three complexes with these interactions show very similar values of $^2J(\text{F}-\text{F})$, between -32.3 and -33.6 Hz. No simple relationship has been found between 2J and the F...F distances.

4. Conclusions

A theoretical study of the complexes formed between FCCF and one or two HF molecules has been carried out by means of ab initio methods. Two types of complexes have been found, those where the interaction is with the π cloud of FCCF ($\text{FH}\cdots\pi$) and those where there is a $\text{FH}\cdots\text{F}$ hydrogen bond. Both types of complexes show similar stabilization energies.

In the intramolecular spin-spin coupling interactions the FC contribution dominates the one-bond coupling constants, the two-bonds interactions have equal contributions from the SD and FC terms and finally the three-bond interactions are dominated by the PSO and SD terms. The intermolecular interactions show a

more complex pattern except for ${}^2J(\text{F}_{\text{HF}}-\text{F}_{\text{HF}})$ which is markedly dominated by the PSO contribution.

The intramolecular one-bond couplings in FCCF correlate linearly with their respective distance, though the ${}^1J(\text{C}-\text{C})$ exhibit an exponential dependence in accordance with earlier findings by Dobrowolskia et al. in β -alanine [30]. The ${}^2J(\text{F}-\text{C})$ does not correlate with its corresponding distance but with the $\text{C}\equiv\text{C}$ bond length. Remarkable is the fact that this last coupling constant seems to increase in absolute value with the distance as well as the ${}^3J(\text{F}-\text{F})$ coupling constant which has a clear linear dependence on the F–F distance.

The exponential behavior of ${}^1J(\text{H}-\text{F})$ respect to $\text{H}\cdots\text{F}$ interatomic distance is in complete accordance with the observed dependence of J on the distance between nuclei [36]. Surprisingly we did not find any relation between ${}^2J(\text{F}-\text{F})$ and its F...F distance.

For all the intramolecular couplings in FCCF we observe a significant effect of the presence of the hydrogen fluoride.

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