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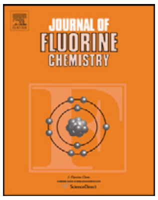

Density functional study of the one-bond C–F coupling constant in α-fluorocarbonyl and α-fluorosulfonyl compounds

Matheus P. Freitas [a,*], Michael Bühl [b,*]

[a] Department of Chemistry, Federal University of Lavras, CP 3037, 37200-000 Lavras, MG, Brazil
[b] EastChem School of Chemistry, University of St Andrews, North Haugh, St Andrews, Fife KY16 9ST, UK

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ABSTRACT

$^1J_{CF}$ coupling constants of α-fluorocarbonyl and α-fluorosulfonyl model compounds are analyzed at the BHandH/EPR-III level of density functional theory. For fluoroethanal, $^1J_{CF}$ follows the electrostatic-based behavior exhibited by 1,2-difluoroethane, whereas for (fluoromethyl)sulfone, hyperconjugation is indicated to be important as well. The variation of $^1J_{CF}$ during rotation about the C–S bond parallels that of the $n_F \rightarrow \sigma^*_{CS}$ donor–acceptor interaction, which is a result of the better electron acceptor ability of the $\sigma^*_{CS(O2)}$ orbital when compared to the corresponding $\sigma^*_{CC(O)}$ orbital of α-fluorocarbonyl compounds. Because the rotational profile of $^1J_{CF}$ is non-monotonic in (fluoromethyl)sulfone, this coupling constant is indicated to be of limited diagnostic value to probe the conformations of α-fluorosulfones.

1. Introduction

The C–F bond is an important functional group in organic and pharmaceutical chemistry [1,2] and ^{19}F NMR an ideal analytical probe for its stereoelectronic properties. While ^3J couplings are widely used to infer molecular conformations, $^1J_{CF}$ values can also be quite instructive. It has been shown computationally that $^1J_{CF}$ is dependent on the dipolar interaction involving the coupled fluorine [3,4]. Similar conclusions have been obtained for $^1J_{CH}$ and $^1J_{CC}$ [5,6], but since C–F bonds are more polar than C–H and C–C ones, they can give better and deeper insights about the effects governing J. While $|^1J_{CF}|$ increases with the molecular dipole moment in 1,2-difluoroethane (dictated by the mutual orientation of the C–F bonds) [3], the corresponding value in fluoro(methoxy)methane decreases linearly with the molecular dipole moment (dictated by the orientation of the C–F bond and of the oxygen lone pairs) [4]. Clearly, interaction of F with bonding and non-bonding orbitals can play opposite roles for $^1J_{CF}$. In order to better explore this behavior, we now extend our computational studies to other compounds where a fluoromethyl group in 1,2-difluoroethane is replaced by other polar groups, namely carbonyl and sulfonyl groups.

Fluoroacetone was found to exhibit two stable conformers, *cis* and *anti*, with the latter about 2.3 kcal mol^{-1} more stable than *cis* due to the strong electrostatic repulsion between the polar C–F and C=O bonds in the *cis* form [7]. This energy difference can be unequivocally attributed to electrostatic repulsion rather than steric repulsion because the energy differences for the other (bulkier) halogens are lower (from 1.5 to 1.8 kcal mol^{-1}). On the other hand, only few reports are concerned with the relative stability of conformers, as well as on the $^1J_{CF}$ coupling constant, in compounds containing the fluoro(methyl)sulfonyl motif, although their importance in synthetic and biological chemistry is widely recognized [8–16].

The experimental $^1J_{C,F}$ coupling constants for *cis* (**1**) and *trans* (**2**) 4-*tert*-butyl-2-fluorocyclohexanones are 191.9 and 177.2 Hz, respectively [17], i.e. the most polar isomer shows the highest (more negative) coupling constant (Fig. 1). This is well reproduced by calculations at the BHandH/EPR-III level (−209.4 and −190.8 Hz for **1** and **2**, respectively, and −220.3 and −196.4 Hz for *equatorial* (**3**) and *axial* (**4**) 2-fluorocyclohexanone, respectively), and is in agreement with the behavior based on dipolar repulsion obtained earlier for 1,2-difluoroethane [3]. The difference in the calculated J between *equatorial* (**5**) and *axial* (**6**) 2-fluoro-thiane-1,1-dioxide is significantly smaller (7.2 Hz)[1] than for the corresponding cyclohexanone (23.9 Hz), although the S=O bond is more polar than the C=O one. However, in absolute terms, the coupling constants in

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* Corresponding authors.
E-mail addresses: matheus@dqi.ufla.br (M.P. Freitas), buehl@st-andrews.ac.uk (M. Bühl).

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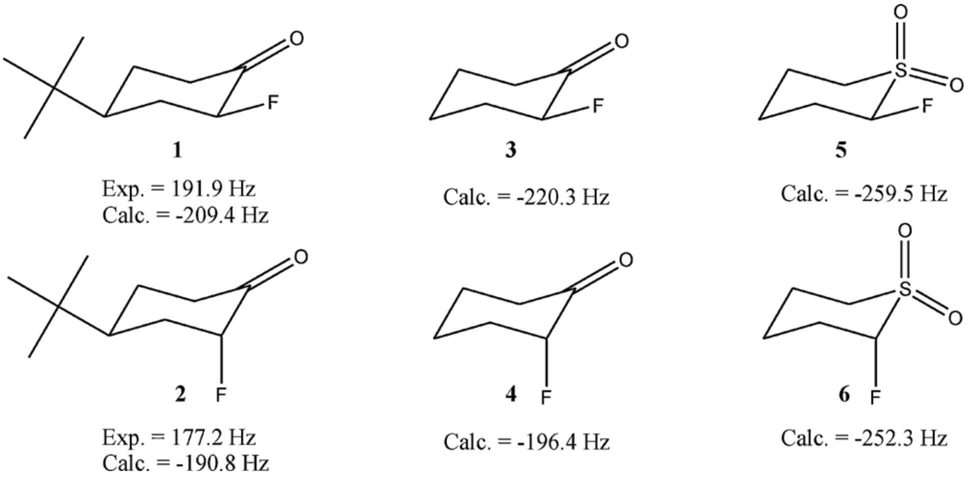


Fig. 1. Selected α-fluorocarbonyl and α-fluorosulfonyl compounds and the respective experimental [17] and/or calculated $^1J_{CF}$ coupling constants (BHandH level).

the sulfone are larger than in the ketone, consistent with the large $^1J_{CF}$ coupling constants observed in fluoro(methyl)sulfonyl compounds, which range from 220 Hz to more than 300 Hz [18,19]. In order to better understand the nature of $^1J_{CF}$ in different systems and to extend earlier studies carried out for simple fluoroalkanes and fluoroethers, we now present a computational study of two prototypical α-fluorinated carbonyl and sulfonyl model compounds.

2. Calculation

The angular dependence of energies and hyperconjugative interactions (through natural bond orbital (NBO) analysis [20a]) in fluoroethanal (**7**) and (dioxido-λ^6-sulfanyl)(fluoro)methane (**8**) were calculated at the B3LYP/aug-cc-pVDZ level [21]. Geometries were fully optimized, except for the F–C–C═O and F–C–S–H dihedral angles in **7** and **8**, respectively, which were fixed at 30° intervals between 0° and 180°. For better comparison of the two sets of rotational profiles, that for **8** is reported as F–C–S–X, where X denotes a point on the axis bisecting the O═S═O moiety.

$^1J_{CF}$ coupling constants were computed (as sum of the Fermi contact (FC), spin dipolar (SD), paramagnetic (PSO) and diamagnetic spin orbit (DSO) terms) at the BHandH/EPR-III level [22,23] (employing cc-pVTZ basis on sulfur), which has been found to perform well in estimating ^{19}F-based couplings [24]. These calculations were performed using the Gaussian09 program [25a]. In addition, the FC term was analyzed using natural *J*-coupling (NJC) analysis [26]. To minimize numerical noise, the most diffuse s and p functions were deleted in the EPR-III basis (which leaves the total FC term unchanged) and a field strength of 0.035 a.u. was employed in the finite-field perturbative method. This analysis was carried out using the NBO program [20b] in conjunction with Gaussian 03 [25b].

3. Results and discussion

Fluoroethanal (**7**, Fig. 2) was used as carbonyl model rather than fluoro-acetone in order to minimize steric repulsion between the F atom and the methyl group during rotation. For the same reason, (dioxo-λ^6-sulfanyl)(fluoro)methane (**8**) was used as a sulfone model.

As in 1,2-difluoroethane, the $|^1J_{CF}|$ in **7** increases exponentially with the molecular dipole moment, which is governed by the mutual orientation of the C–F and C═O bonds (Fig. 2). On the other hand, $|^1J_{CF}|$ does not relate to any donor-acceptor interaction involving CF, n_F (i.e. lone pair), or CF* NBOs: while $|^1J_{CF}|$ decreases monotonally between 0° and 180°, the most important donor–acceptor interactions have clear inflexions around 90° (Fig. 3), indicating that $|^1J_{CF}|$ is independent of hyperconjugation. Actually, the behavior of $^1J_{CF}$ in **7** fits very well with the behavior exhibited by a point charge model presented previously by Freitas et al. [3], suggesting that dipolar interaction is the dominating reason for the $^1J_{CF}$ coupling constant in the carbonyl compound.

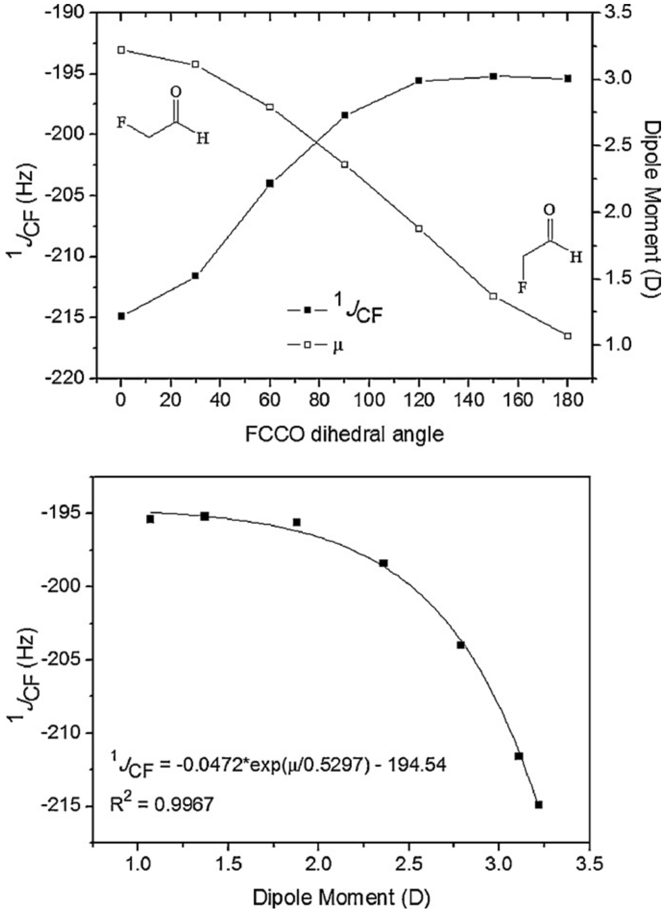


Fig. 2. (Top) Rotational dependence of $^1J_{C,F}$ (BHandH/EPR-III) and the molecular dipole moment μ in 2-fluoroethanal (7). (Bottom) Correlation between $^1J_{C,F}$ and μ.

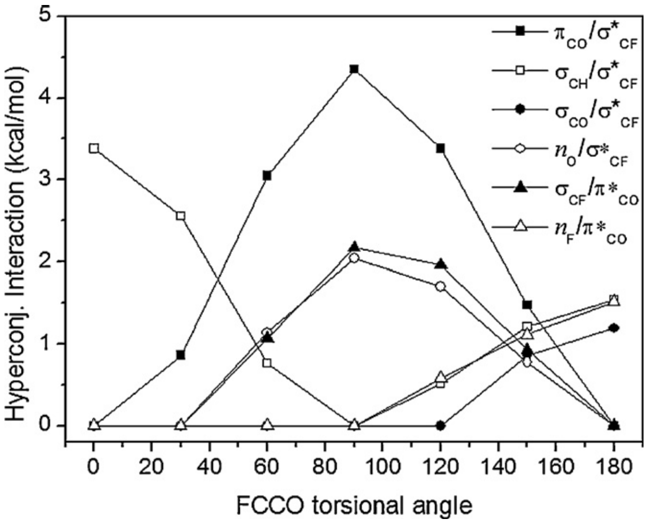


Fig. 3. Angular dependence of selected hyperconjugative interactions in 2-fluoroethanal (7) (from second-order perturbation analysis of donor-acceptor interactions between NBOs at the B3LYP/aug-cc-pVDZ level). Only interactions exceeding 1 kcal mol^{-1} are included; for a color version of this figure containing additional, weaker interactions, see Fig. S1 in the Supplementary data.

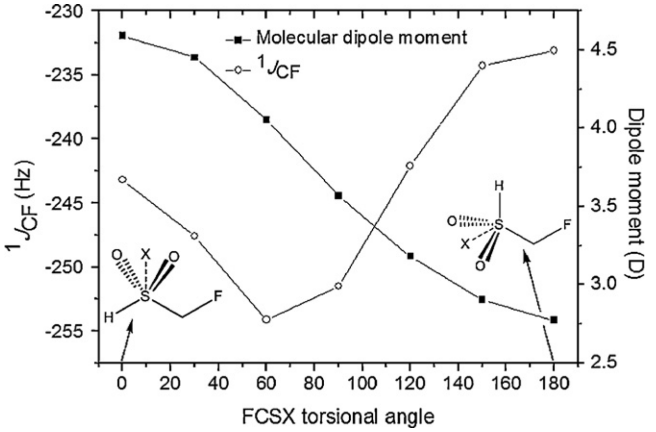


Fig. 4. Angular dependence of the molecular dipole moment in 8, relative to the behavior in $^1J_{CF}$. X denotes a point on the axis bisecting the two SO bonds.

The picture changes for the sulfone model **8**, where no apparent relationship exists between $|^1J_{CF}|$ and the molecular dipole moment (Fig. 4). The preferred conformer for **8** has the CF bond antiperiplanar to an SO bond (Fig. S2 in the Supplementary data), which is consistent with the structures of several compounds containing the (fluoromethyl)sulfone motif, as obtained from X-ray crystallography [27–29], as well as for the related 2-chlorothiane-1,1-dioxide determined via NMR [30]. This preference is indicative of stereoelectronic control, in keeping with the fact that the conformer with the smallest overall dipole moment (with an FCSX torsional angle of 180°) is a strongly disfavored eclipsed conformer. In order to confirm that $^1J_{CF}$ is independent on dipolar interaction in **8**, a point charge model on CH_3F was built to mimic **8**, similar to our approach for 1,2-difluoroethane [3]. A + 2 charge was placed at the position of the S atom and two −1 charges at distances of 0.85 Å along the putative S═O axes such that a dipole moment of 4D is obtained (the approximate value of a S═O bond).[2]

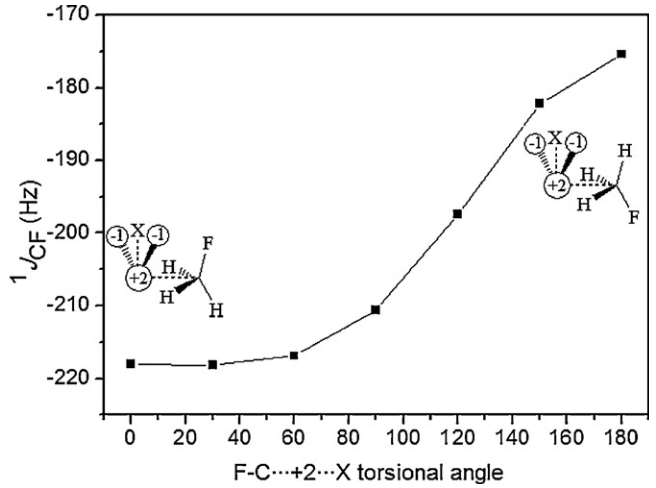
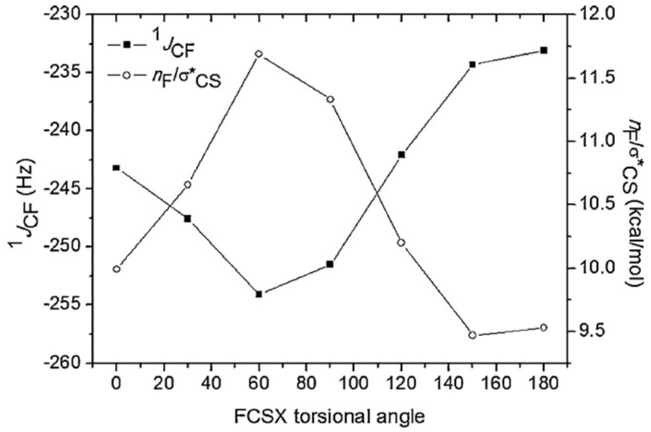


Fig. 5. Changes in the computed $^1J_{CF}$ in fluoromethane (Hz) in the presence of elementary charges (+2*e* and −1*e* charges separated by 0.85 Å, corresponding to μ = 4D), mimicking 8. X corresponds to a dummy atom along the resultant dipole from both +2 . . . −1 vectors.



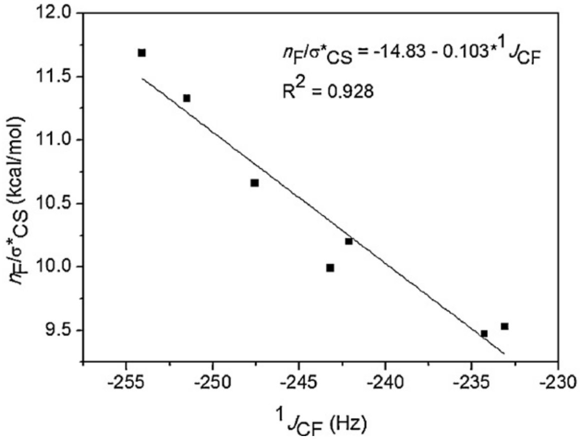


Fig. 6. Angular dependence of calculated $^1J_{CF}$ and $n_F \rightarrow \sigma^*_{CS}$ hyperconjugation in 8.

The $^1J_{CF}$ angular dependence in the point charge model (Fig. 5) is consistent with the angular dependence of the dipole moment in **8** (Fig. 4). Consequently, the point charge model does not explain the real behavior of $^1J_{CF}$ in **8** and, therefore, the dipole moment does not appear to be the dominant factor that governs this coupling constant in sulfonyl compounds.

In the second-order perturbation analysis, there is a large number of donor–acceptor (hyperconjugative) interactions.

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[2] A C_{2v}-symmetric model H_2SO_2 has an overall dipole moment of 3.6*D* at B3LYP/aug-cc-pVDZ, and an O═S═O angle of 123.3°; neglecting the S–H bonds (which carry only a very small positive charge on H according to natural population analysis), this corresponds to an S═O bond dipole of 3.8*D*.

Summed up together, they do not reflect the overall trend in $^1J_{CF}$ (Fig. S3 in the Supplementary data). The single most important interaction operating in **8** stems from the $n_F \rightarrow \sigma^*_{CS}$ pair (see Fig. S4 in the Supplementary data). Somewhat unexpectedly, this interaction correlates very well with $^1J_{CF}$ ($R^2 = 0.928$, Fig. 6). The corresponding interaction in **7** is less pronounced, since the σ^*_{CS} orbital is a better electron acceptor than $\sigma^*_{CC(O)}$. Thus, **7** and carbonyl compounds like 2-fluorocyclohexanone resemble other saturated organofluorine compounds (e.g. 1,2-difluoroethane and fluoro(methoxy)methane) in the factors that govern $^1J_{CF}$, whereas this property in fluoro(methyl)sulfonyl compounds is dependent on hyperconjugation ($n_F \rightarrow \sigma^*_{CS}$) rather than on dipolar interaction. In fact, the different trend in $^1J_{CF}$ between **7** and **8** is reflected in the different behavior of the Ramsey terms: while $^1J_{CF}$ in **7** is dictated mainly by SD and PSO terms, the FC term also contributes importantly for $^1J_{CF}$ in **8** (Fig. 7).

This term has subsequently been analyzed in the NJC framework [26]. For **8**, NJC analysis is plagued by problems with numerical stability (a rather high field strength had to be used, cf. Computational Details, which results in systematic deviations of the total FC term from the analytical values in Fig. 7); however, the qualitative trends should be informative. NJC analysis provides a breakdown of the total FC term into Lewis, delocalization and repolarization contributions, the rotational dependence of which is illustrated in Fig. 8. The overall trend in $^1J_{CF}$ (FC) appears to be dominated by the Lewis-type interactions (steric and electrostatic), modified by delocalization and repolarization contributions, which cancel to a large extent. Both are substantially enhanced at

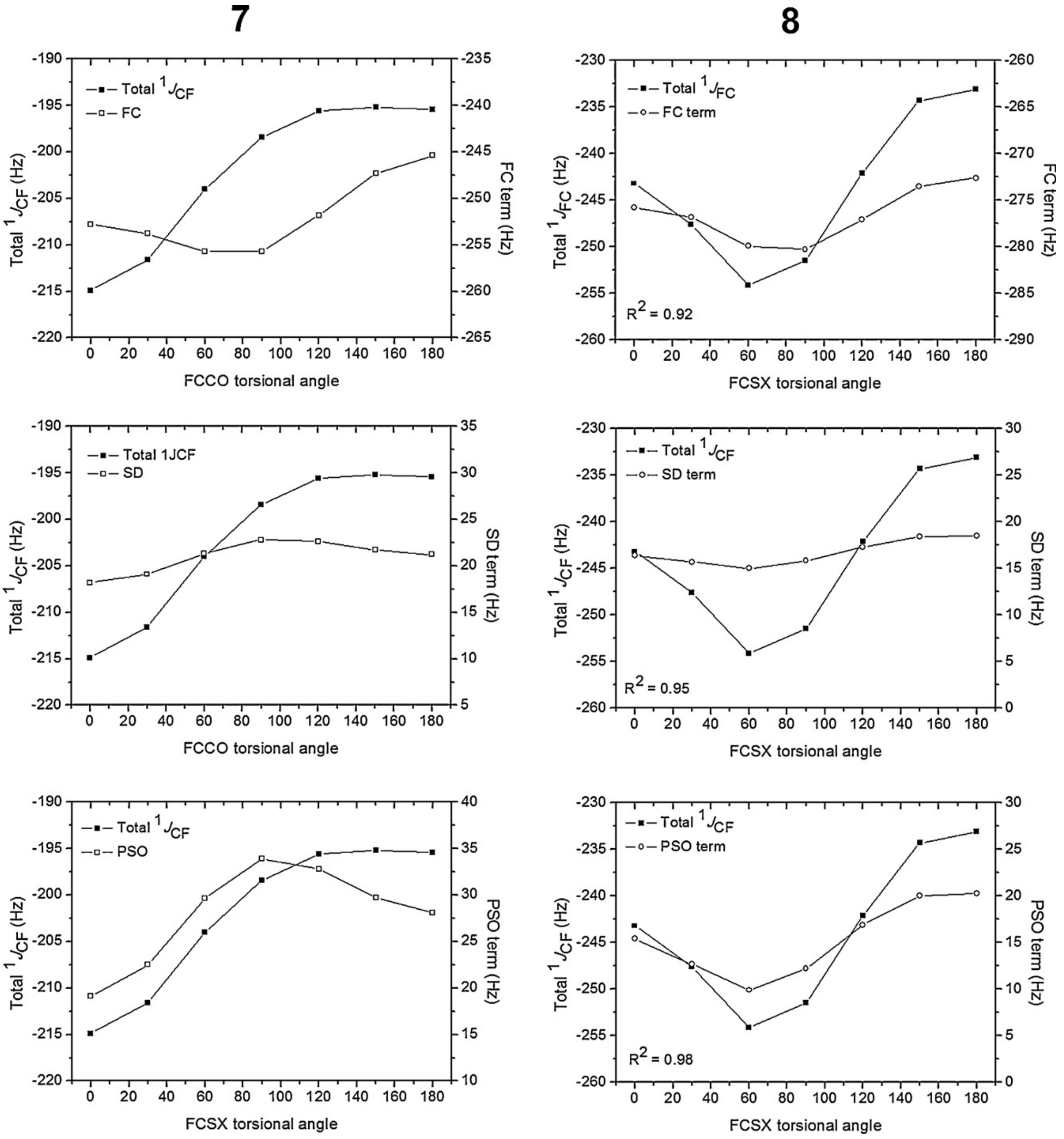

Fig. 7. Contribution of the FC, SD and PSO terms for total $^1J_{CF}$ in 7 and 8 (BHandH/EPR-III level).

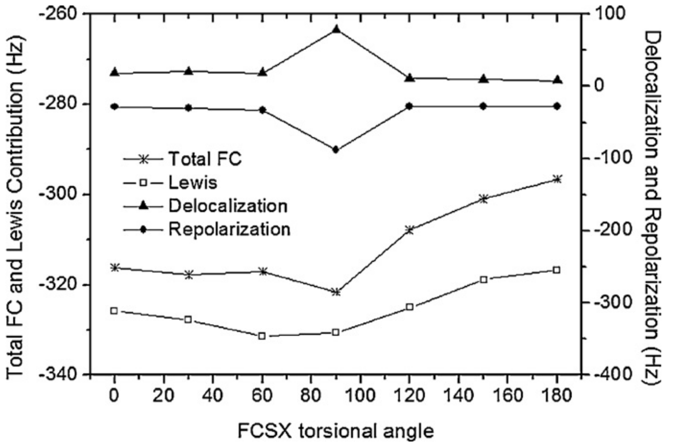

Fig. 8. Angular dependence of principal contributions to the FC term of $^1J_{CF}$ in 8 (from NJC analysis at a modified BHandH/EPR-III level, see text).

an FCSX angle of 90°. The Lewis contributions from the lone pairs at F decreases dramatically at this point (90°), and the $n_F \rightarrow \sigma^*_{CS}$ delocalizations, which typically contribute ca. 14 Hz, suddenly change sign to -15 Hz. Although there is no clear correlation between energetic and NJC contributions of the $n_F \rightarrow \sigma^*_{CS}$ interaction, it seems that the angular dependence of $^1J_{CF}$ (FC) in **8** is governed mostly by Lewis-type interactions and partially by hyperconjugation.

Whether or not $n_F \rightarrow \sigma^*_{CS}$ hyperconjugation dominates $^1J_{CF}$ in **8**, its presence has structural consequences: this interaction contributes to a [F–C–SO$_2$ ↔ F$^+$=C ··· $^-$SO$_2$] resonance, which should result in a lengthening of the C–S bond when compared to the non-fluorinated compound HSO$_2$CH$_3$. Indeed, rotation around the FCSX torsional angle in **8** gives calculated C–S bond lengths varying from 1.845 to 1.874 Å, while the corresponding value for the optimized HSO$_2$CH$_3$ compound is 1.809 Å. It is worth mentioning that the calculated C–C bond length for ethanal itself is 1.512 Å, and that it is much less affected by F substitution: the corresponding C–C distance as a function of the FCCO rotation in **7** varies between 1.512 and 1.531 Å. Also, as a consequence of the above mentioned resonance, as well as of the better electron donation $n_F \rightarrow \sigma^*_{CS}$ in **8** than the corresponding $n_F \rightarrow \sigma^*_{CC(O)}$ in **7**, the C–F bond in **8** should be shorter than in **7**; this expectation is borne out by the calculations, since rotation around the FCSX dihedral angle in **8** gives calculated C–F bond lengths varying from 1.367 to 1.382 Å, while the corresponding variations in **7** are from 1.382 to 1.406 Å. Thus placing a sulfonyl group in α-position to a C–F bond results in a contraction of that bond by ca. 0.02 Å.

Evidence for this type of resonance is also found in the solid state: a search of the Cambridge Structural Database [31,32] affords a mean C–S distance of 1.78 Å in PhSO$_2$CH$_2$R fragments (62 hits, R = alkyl or aryl), which is increased to 1.81 Å in PhSO$_2$CH(F)R fragments (5 hits). Likewise, the C–F distances decrease from a mean of 1.39 Å in RCH(F)–C(O)R′ fragments (86 hits) to 1.37 Å in RCH(F)–SO$_2$R′ fragments (6 hits).

As the σ^*_{CS} bond is essentially rotationally symmetric, one may wonder about the origin of the rotational dependence of the $n_F \rightarrow \sigma^*_{CS}$ interaction (Fig. 6). Closer inspection of the partially optimized structures along the rotational profile reveals that as the C–F and an S=O bond become eclipsed (at an FCSX torsion around 60°), the S–C–F bond angle increases noticeably (to ca. 111°), compared to staggered conformations or the transition state with eclipsed C–F and S–H bonds (where the S–C–F angle is ca. 107°). In fact, the variation of the S–C–F angle during rotation about the CS bond in **8** closely follows the changes in the $n_F \rightarrow \sigma^*_{CS}$ interaction and the explicit sensitivity of $^1J_{CF}$ in **8** toward the S–C–F angle is consistent with the changes during rotation about the C–S bond (see Figs. S5 and S6 in the Supplementary data).

The difference in $^1J_{CF}$ between the fluoroketone conformers **3** and **4** (or **1** and **2**) is sizeable, on the order of 20 Hz (Fig. 1). In conjunction with its rotational dependence in the model compound **7** (Fig. 2), this coupling can thus be a valuable indicator for conformations of α-fluorocarbonyl compounds. In contrast, there is only a small change in $^1J_{CF}$ between the fluorosulfone conformers **5** and **6**, ca. 7 Hz (Fig. 1), even though the S=O bonds are more polar than a C=O bond. The angular dependence of $^1J_{CF}$ in model compound **8** shows a pronounced minimum at an FCSX dihedral angle around 60° (Fig. 6), i.e. halfway between the conformations corresponding to those of **5** and **6** (i.e. with dihedral angles of ca. 0 and 120°, respectively), for which indeed very similar $^1J_{CF}$ values are obtained. Thus, this coupling constant should only be of limited use for conformational assignments of 2-fluoro-thiane-1,1-dioxides, and α-fluorosulfones in general.

4. Conclusion

Like in saturated organofluorine compounds containing two vicinal fluorines, dipolar repulsion has been shown to be the key effect determining the conformational dependence of $^1J_{CF}$ coupling constants in α-fluorocarbonyl compounds. However, it appears that the $^1J_{CF}$ transmission mechanism can be quite sensitive to the substituent in α-position to the C-F bond. For derivatives with strong σ-acceptors such as 2-fluorosulfonyl compounds, it appears that hyperconjugation, notably the $n_F \rightarrow \sigma^*_{CS}$ interaction, can modulate the angular dependence of $^1J_{CF}$ in addition to Lewis-type interactions, since the $\sigma^*_{CS(O2)}$ orbital is a better electron acceptor than the $\sigma^*_{CC(O)}$ orbital of carbonyl compounds. Because these specific orbital interactions induce a non-monotonic behavior of the $^1J_{CF}$ rotational profile, this coupling constant appears to be of little diagnostic value for probing the conformations of α-fluorosulfones.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2012.05.007.

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