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# ELECTRON COUPLING OF NUCLEAR SPINS.
## VII. $J_{FF}$ FOR 2-FLUOROBENZOTRIFLUORIDES.

by

H. S. Gutowsky and V. D. Mochel

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University of Illinois
Department of Chemistry and Chemical Engineering
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# ELECTRON COUPLING OF NUCLEAR SPINS.

## VII. $J_{FF}$ FOR 2-FLUOROBENZOTRIFLUORIDES.*

H. S. Gutowsky and V. D. Mochel†

Noyes Chemical Laboratory, University of Illinois,
Urbana, Illinois

The nmr spectra of several 2-F,6-X-benzotrifluorides yield values for $J_{FF}$ between the 2-fluorine and the fluorines in the $CF_3$ group of 13 to 34 cps, depending upon the 6-substituent. Furthermore, the magnitude of this $J_{FF}$ is proportional to the chemical shift of the $CF_3$ group and to the size of the 6-substituent. Two related factors appear to be involved: (a) The rotational configuration of the $CF_3$ group with respect to the plane of the benzene ring, and (b) Electrostatic deformation of the electron distribution about the fluorines in the $CF_3$ group. Our results for the benzotrifluorides and values reported earlier for the cis F-$CF_3$ coupling in $CF_3CX{=}CFY$ compounds are consistent with little or no hindrance to $CF_3$ group rotation in the latter.

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The indirect, H-H, H-F, and F-F coupling constants of nuclei in atoms bonded directly to a benzene ring are characteristic of their relative locations but quite insensitive to substituents.[1] On the other hand, the chemical shifts of the ring nuclei are governed largely by the substituents[2,3] which have, however, much smaller effects upon the chemical shifts of the fluorines in the $CF_3$ groups of benzotrifluorides.[2] In contrast, we have found that the F-F coupling between the fluorines in the $CF_3$ group of benzotrifluoride and a fluorine ortho to it depends very markedly upon the other substituent ortho to the $CF_3$ group. This dependence is the subject of the present report.

## EXPERIMENTAL PROCEDURE AND RESULTS

The high resolution $F^{19}$ nmr spectra were observed with two spectrometers; one a home-made Model-$T^{4,5}$ operating at a fixed frequency of 16.685 Mc/sec, the other a Varian Associates "Model-A" operating at 40 Mc/sec. Resolution was between about 0.5 and 1.2 cps for both spectrometers, and sometimes somewhat better for the lower frequency unit. The spectra were calibrated by means of the usual audiofrequency sideband technique.

The compounds studied were obtained from various sources. In all cases the purity was sufficiently high that there was no ambiguity as to the identity of the main resonances. The *m*-trifluoromethylbenzotrifluoride was obtained from Dr. O. R. Pierce, then at Purdue University. 2-Iodotetrafluorobenzotrifluoride and 2-chloro-tetrafluorobenzotrifluoride were obtained from Dr. L. Wall of the National Bureau of Standards. The remainder of the samples were supplied by Dr. G. C. Finger of the Illinois State Geological Survey.

The compounds are liquids at room temperature and the chemical shift of the $CF_3$ group was measured in all of them except *o*-fluorobenzotrifluoride and 2,4,6-trifluoro,3-nitrobenzotrifluoride, with respect to benzotrifluoride as an internal reference. Benzotrifluoride was employed as an external reference for the two exceptions. Because volume susceptibility data are lacking for these two compounds, it was assumed that the bulk diamagnetic susceptibility corrections to their apparent chemical shifts are $-0.02 \times 10^{-6}$, the correction for fluorobenzene. It is certain that any errors from this source are insufficient to alter the trends of the shifts.

Because of the large chemical shift ( $\sim 50 \times 10^{-6}$) between the $CF_3$ group in benzotrifluoride and the ring F in fluorobenzene,[2] $J_{FF}$(F-$CF_3$) in 2-fluorobenzotrifluorides produces first-order type splittings in the $CF_3$ group resonance, the center of which marks, therefore, the chemical shift of the group.

Moreover, the chemical shifts between the various $F^{19}$ nuclei in atoms bonded directly to the benzene ring are large enough compared to the coupling constants among them that the latter do not contribute to the apparent value of $J_{FF}(F\text{-}CF_3)$ *via* pseudo-equivalence[6] with the F's *ortho* to the $CF_3$ group. Therefore, the fluorine shifts and values for $J_{FF}(F\text{-}CF_3)$ could be measured directly and it does not seem necessary to reproduce any of the spectra here. Instead, the numerical results are summarized in Table I. The chemical shift $\delta$ is defined as $10^6(H_{ref}-H_c)/H_{ref}$, where $H_{ref}$ is the applied magnetic field for the fluorine resonance in the benzotrifluoride reference and $H_c$ is that for the $CF_3$ group in the substituted benzotrifluorides. Thus, a positive $\delta$ corresponds to a downfield or paramagnetic shift.

In our initial experiments at 40 Mc/sec on these compounds, the large ($\sim$33 cps) splitting of the $CF_3$ group resonance into a symmetrical doublet for 2-iodo- and 2-chloro-tetrafluorobenzotrifluoride was unexpected. Also, the resonance of the fluorine nucleus *ortho* to the $CF_3$ group in each compound was greatly broadened with much fine structure. So, in order to verify that the $CF_3$ group splitting was the result of an indirect, spin-spin coupling and not a chemical shift, the spectra were also obtained at 16.685 Mc/sec. The splittings at the two fields remained the same within the experimental error, thus confirming that it is due to the indirect coupling. Also, an effort was made to measure the coupling between the $CF_3$ group and ring fluorines *meta* and *para* to it. Splittings attributable to such coupling were not resolved. However, broadening of some of the lines was used to establish upper limits to the magnitude of the coupling, namely $J_m^{FF}(F\text{-}CF_3) < 1.5$ cps and $J_p^{FF}(F\text{-}CF_3) < 2$ cps, where the subscript on J defines the relative location of the F and $CF_3$ on the benzene ring.

After these measurements were completed, Richards and Schaeffer[7] reported some comparable results. From the fluorine spectrum of 2,4-difluorotrichlorobenzotrifluoride they found $J_o^{FF}(F\text{-}CF_3) = 34$ cps and $J_p^{FF}(F\text{-}CF_3) \approx 1$ cps, while from *m*-fluorobenzotrifluoride $J_m^{FF}(F\text{-}CF_3) < 0.5$ cps.

Table I. Chemical shifts of the $CF_3$ group and coupling constants $J_{\circ}^{FF}(F\text{-}CF_3)$ between the $CF_3$ and fluorines <u>ortho</u> to it in some substituted benzotrifluorides.

| Substituents | δ[a] | $CF_3$ Spectrum | $J_{\circ}^{FF}(F\text{-}CF_3)$ |
|---|---|---|---|
| 3-$CF_3$ | -0.423 ppm | Singlet | - - cps |
| 2-F | +1.23[b] | Doublet | 13.0 ± 0.2 |
| 2,3,5-F | +1.29 | Doublet | 13.4 ± 0.2 |
| 2,4,6-F-3-$NO_2$ | +5.48[b] | Triplet | 24.0 ± 1.0 |
| 2,3,4,5-F-6-Cl | +6.94 | Doublet | 32.7 ± 0.1 |
| 2,4-F-3,5,6-Cl[c] | - - | Doublet | 34 |
| 2,3,4,5-F-6-I | +7.11 | Doublet | 34.1 ± 0.2 |
| 3,5-F-2,6-Cl | +7.14 | Singlet | - - |

[a] $\delta = 10^6(H_{ref}-H_c)/H_{ref}$ with the $CF_3$ group of $C_6H_5CF_3$ as an internal reference. The probable error of the values given is about ±0.01.

[b] These shifts were measured with respect to an external reference and corrected for bulk susceptibility differences as described in the text.

[c] Taken from reference 7.

## DISCUSSION

### Comparison of $CF_3$ Shifts and $J_{FF}$

The data presented in Table I have several interesting features. The most striking is that the magnitude[8] of $J_o^{FF}(F\text{-}CF_3)$ increases by a 3-fold factor as the other substituent ortho to the $CF_3$ group increases in size from hydrogen to iodine. This change in the coupling constant is proportional to the chemical shift of the $CF_3$ group, as shown graphically in Fig. 1. Also, it is of interest to compare the dependence of $J_{FF}(F\text{-}CF_3)$ upon the relative locations of the F and $CF_3$ on the ring with the coupling between two F's on the ring. In the latter case,[1] $J_o^{FF} \approx 20$ cps $> J_p^{FF} \approx 13$ cps $> J_m^{FF} \approx 3$ cps. The same trend is preserved for $J_{FF}(F\text{-}CF_3)$, that is $J_o \approx 20$ cps $> J_p \approx 1$ cps $> J_m \approx 0$ cps, but the ortho coupling is an order of magnitude larger than one might have expected from the other values. These facts, as well as the relative insensitivity to substituents of the coupling constants other than $J_o^{FF}(F\text{-}CF_3)$, and the insensitivity of $\delta_{CF_3}$ to other than ortho substituents,[2] imply that "steric" interactions determine the changes in the latter and in $\delta_o(CF_3)$.

In the case of $\delta_o(CF_3)$, it is likely that the downfield substituent effects result from electrostatic deformations of the electron distribution about the fluorines in the $CF_3$ group.[9,10] The changes in $\delta_o(CF_3)$ are of the order of 5, that is the fluorine nuclear magnetic shielding changes by $\sim 5 \times 10^{-6}$. This is quite small compared to the total shielding which is $\sim 500 \times 10^{-6}$, and indeed it is of the size and direction predicted for electric field interactions between the $CF_3$ group and the ortho substituents.[9]

The situation with respect to $J_o^{FF}(F\text{-}CF_3)$ differs considerably. First, the effects of ortho substituents are comparable to the total coupling. Secondly, the ortho $F\text{-}CF_3$ coupling constant in 2-fluorobenzotrifluoride itself is

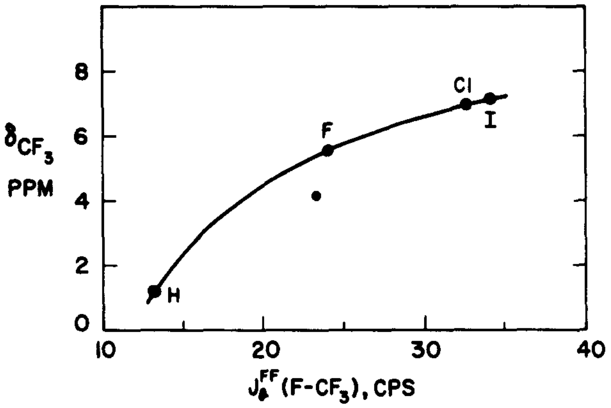


Fig. 1. The relationship between the F-$CF_3$ coupling constant in 2-F-benzotrifluorides and the chemical (downfield) shift of the $CF_3$ group with respect to benzotrifluoride. The symbols designate the substituent in the 6-position of the compound.

relatively large compared to the meta and para values of 0.5 and ~1 cps, respectively. Although it is clear that steric-type interactions between the $CF_3$ group and its ortho substituent are involved in these effects, the nature of the interaction mechanism is less certain. One possibility is that $J_o^{FF}(F\text{-}CF_3)$ is sensitive to the rotational conformation of the $CF_3$ group with respect to the ortho fluorine, and that the size of the other ortho group determines the coupling constant by changing the average, rotational conformation of the $CF_3$ group. Another type of model is one in which the distortion of the electron distribution indicated by $\delta_o(CF_3)$ accounts directly for the magnitude of and the changes in coupling constant, without any significant contributions due to changes in the rotational conformation. It seems to us that while both elements may be present to some degree, the first is the better approximation.

### $CF_3$ Group Rotation and $J_o^{FF}(F\text{-}CF_3)$

When there are two different monatomic substituents ortho to the $CF_3$ group, there are two distinguishable, preferred orientations of the $CF_3$ group with respect to the plane of the benzene ring, as shown in Fig. 2. In one such rotamer, an F from the $CF_3$ group is cis to the ortho substituent X and in the other it is trans. Internuclear distances $R_p^q(X\text{-}F)$ between the ortho substituent and the two structural types of F in the $CF_3$ group for each rotamer have been calculated for X = H, F, Cl, and I. The subscript of R designates the rotamers and the superscript, the two sets of F's in the $CF_3$ group. The results are summarized in Table II. Included in Table II are the quantities $(r_F+r_X) - R_c^c$ and $(r_F+r_X) - R_c^t$ where $r_F$ and $r_X$ are the covalent radii[11] of F and X. The first quantity and twice the second are a measure of the overlap and steric repulsion between the substituent X and the $CF_3$ group in the cis and trans rotamers, respectively.

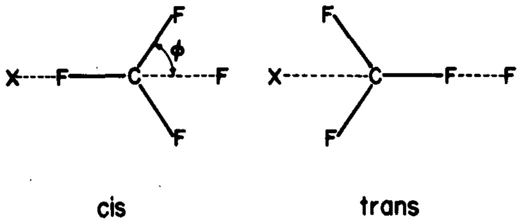


Fig. 2. Projection of a 2-F, 6-X-benzotrifluoride in the plane perpendicular to the $C_3$ axis of the $CF_3$ group, for the two rotamers. The dashed line represents the plane of the benzene ring.

Table II. Internuclear distances[a] in Angstroms for the F's in a $CF_3$ group and an ortho substituent X in the two rotational forms of 2-X-benzotrifluoride shown in Fig. 2.

| X | $R_c^c$ | $R_c^t$ | $(r_F+r_X) - R_c^c$ | $R_t^c$ | $R_t^t$ | $(r_F+r_X) - R_t^c$ |
|---|---|---|---|---|---|---|
| H | 2.33 | 3.70 | +0.22 | 2.86 | 4.06 | -0.31 |
| F | 2.31 | 3.80 | +0.39 | 2.90 | 4.19 | -0.20 |
| Cl | 2.33 | 3.96 | +0.82 | 2.97 | 4.37 | +0.18 |
| I | 2.42 | 4.20 | +1.02 | 3.13 | 4.64 | +0.32 |

[a] Bond distances and van der Waals' radii ($r_F$ and $r_X$) given in reference 11 were used in the calculations. Tetrahedral bond angles were assumed for the $CF_3$ group and 120° for angles involving a planar benzene ring and the substituents attached directly to it.

It is seen that in the *cis* rotamer, overlap of 0.22 A is present even for X = H and increases to 1.02 A for X = I. But for the *trans* rotamer it is much less, there being no overlap for X = H or F and a maximum of 2 x 0.32 A for X = I. Accordingly, with the rotamer now defined always with respect to the 2-F, the *trans* rotamer should be stabler than the *cis* for 2-fluorobenzotrifluoride, but the two forms are equivalent for the 2,6-difluorobenzotrifluoride and thus of equal energy. And for the 6-chloro- and 6-iodo-2-fluorobenzotrifluoride, the *cis* should be stabler than the *trans* form. In all cases, there was no evidence in the nmr spectra that the fluorines in the $CF_3$ group are non-equivalent, so any differences in coupling constants and chemical shifts with conformation are averaged out, which implies that the barriers to rotation must be no more than a few kcal. Nonetheless, if the coupling constant is a sensitive function of the rotational angle $\phi$ (see Fig. 2) of the $CF_3$ group, the change of $J_o^{FF}(F\text{-}CF_3)$ with substituents could result from changes in the relative populations of the *cis* and *trans* rotamers, with free internal rotation as a possible intermediate case.

Some evidence bearing upon such an angular dependence model can be found by assuming that the 2-F,6-H-benzotrifluorides exist solely as the *trans* rotamer and the 6-Cl and 6-I,2-F-benzotrifluorides as the *cis*. For the *trans* rotamer, we then have

$$J_o^{FF}(F\text{-}CF_3) \equiv \left\langle J_a^{FF}(F\text{-}CF_3)\right\rangle_{trans} = \frac{2}{3}J_t{}^{c} + \frac{1}{3}J_t{}^{t} \approx 13.2 \text{ cps} \quad , \qquad (1)$$

and for the *cis* rotamer

$$\left\langle J_o^{FF}(F\text{-}CF_3)\right\rangle_{cis} = \frac{1}{3}J_c{}^{c} + \frac{2}{3}J_c{}^{t} \approx 33.6 \text{ cps} \quad , \qquad (2)$$

where $J_p{}^{q}$ is the coupling between fluorines with the internuclear distance $R_p{}^{q}$. Unfortunately, Eqs. (1) and (2) involve four unknown J's so the latter cannot be evaluated without further assumptions or information. But an internal consistency check can be made by introducing the fact that 2,6-difluorobenzotrifluoride should exist half in the *cis* and half in the *trans* form, probably with little or no barrier to internal rotation. Thus, for it we have

$$J_{\odot}^{FF}(F\text{-}CF_3) = \frac{1}{2}\left\langle J_{\circ}^{FF}(F\text{-}CF_3)\right\rangle_{cis} + \frac{1}{2}\left\langle J_{\bullet}^{FF}(F\text{-}CF_3)\right\rangle_{trans} \quad , \qquad (3)$$

which upon introducing the observed, numerical values from Eqs. (1) and (2) becomes

$$J_{\odot}^{FF}(F\text{-}CF_3) = \frac{1}{2}(33.6+13.2) = 23.4 \text{ cps} \quad . \qquad (4)$$

This is virtually identical with the value of 24 cps observed in 2,4,6-F-3-$NO_2$-benzotrifluoride, as it would be if the angular dependence model were correct.

## Orbital versus Contact Contributions to $J_{FF}$

Our results alone do not indicate what the relative magnitudes of the four $J_p^q$ may be. Petrakis and Sederholm[12] have observed F-F coupling constants in a number of fluorine substituted, saturated organic compounds and proposed that $J_{FF}$ increases with decreasing F-F distance, particularly for distances less than about 2.5 A. If this is indeed the case, then as the shortest F-F distance $R_c^c$ is only 2.3 A, the largest $J_{FF}$ is $J_c^c$, which would be ~120 cps. In fact, the "empirical" curve of $J_{FF}$ versus $d_{FF}$ presented in their Fig. 2 agrees semi-quantitatively with our results. Still, it would be helpful in establishing the nature of the structural dependences of $J_{FF}$ to have experimental values in compounds similar to those studied here, but with a $CF_2X$ group (X = H and say Cl) instead of the symmetric $CF_3$ group.

The possible origin of any such distance (or angular) dependence of $J_{FF}$, in the 2-F,6-X-benzotrifluorides, might best be ignored in view of the difficulties which have become apparent in the valence-bond treatment of the geminal H-H coupling constant in methane.[13,14] However, even though the theory for $J_{FF}$ is much more difficult than that for $J_{HH}$, two pertinent comments appear to be reasonably safe.

First, the approximate, theoretical expression developed by Pople[10,15] for the orbital contribution to $J_{FF}$ leads to angular dependent values which are too small by at least an order of magnitude to account for the changes we observed. His treatment relates the anisotropy of the chemical shift and the molecular geometry to the orbital contribution. For our case, the relevant equation is

$$J^{FF}_{orb} = 35.4R^{-3}[(3\cos^2\theta-1) + (3\cos^2\theta'-1)] \text{ cps} \quad , \tag{5}$$

where R is the F-F internuclear distance, and $\theta$ (and $\theta'$) is the angle between the principal axis of the chemical shift tensor, which lies along the C-F bond, and the F-F vector. Using the values of $R_p^q$ given in Table II, and the appropriate angles, we obtain from Eq. (5) the following orbital contributions, in cps, to the four J's in Eqs. (1) and (2):

|  | $J_c^{\,c}$ | $J_c^{\,t}$ | $J_t^{\,c}$ | $J_t^{\,t}$ |
|---|---|---|---|---|
| $J^{FF}_{orb}$ | -5.5 | +0.3 | -2.5 | +0.8 |

(6)

In turn, upon substituting these values in Eqs. (1) and (2), we obtain

$$\left\langle J^{FF}_{orb} \right\rangle_{cis} = -1.6 \text{ cps} \quad \text{and} \quad \left\langle J^{FF}_{orb} \right\rangle_{trans} = -1.4 \text{ cps} \quad , \tag{7}$$

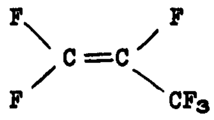
which are virtually identical whereas the observed substituent effects are ~20 cps.

The second point is that Karplus' valence-bond estimate of the contact contribution to $J_{FF}$ differs by a two-fold factor for cis and trans fluorines in fluoroethylenes,[16] which factor is similar to that found here. Moreover, the magnitude of the contribution is ~50 cps which is compatible with the range of values observed for $J^{FF}_{\theta}(F\text{-}CF_3)$, considering the presence of an added

C-C bond for the latter. It would seem, therefore, that the theoretical explanation of our results should be sought first in the contact term and its dependence upon molecular geometry and substituents.

## Concluding Comments

Some further experimental results bearing on our discussion have been obtained from the three fluorinated propenes[17] listed below.



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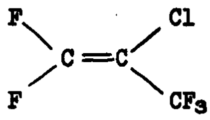

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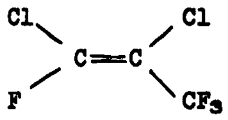

III

In these compounds the cis F-F coupling with the $CF_3$ group, $J_c^{FF}$($F$-$CF_3$), is the counterpart of the ortho coupling in the 2-F-benzotrifluorides, the difference being that the intervening bond is double instead of aromatic. Thus, it is noteworthy that $J_c^{FF}$($F$-$CF_3$) is quite insensitive to chlorine substitution, the values being 22.0, 23.8, and 24.3 cps, respectively, for I, II, and III. Moreover, these values bracket the 24 cps coupling found for the 2,6-difluorobenzotrifluoride listed in Table I. This agreement could be accidental. But, again, it is consistent with the angular dependence model for $J_{FF}$($F$-$CF_3$) and if indeed the latter is the case, then there is little or no internal barrier to $CF_3$ group rotation in compounds I to III.

A final comment should be made on the correlation between $\delta_{CF_3}$ and $J_o^{FF}$($F$-$CF_3$) given in Fig. 1. If the angular dependence model is the correct explanation for the effects of substituents upon $J_o^{FF}$($F$-$CF_3$), this correlation is indirect. That is, it results from the fact that both the rotational state and the chemical shift depend in much the same way upon the electrostatic, steric repulsions between the $CF_3$ fluorines and the ortho substituents. We have already discussed at length how the quantities $(r_F+r_X) - R_p^c$, in Table II, describing the overlap could affect the $CF_3$ rotational state and certainly one would expect $\delta_{CF_3}$ to have a similar dependence.

## ACKNOWLEDGMENT

We wish to acknowledge several discussions with Dr. M. Karplus of our experimental results and to thank him particularly for the suggestion that the orbital contribution to $J_{FF}$ be estimated by means of Pople's approximate treatment.

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[/] Now at Corning Glass Works, Corning, New York.

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