in this plant material, the dominant, if not exclusive, mode of ring fusion is *para*.[6]

(6) Subsequent to the submission of our manuscript we received a communication from Dr. Warnhoff that upon his later discovery of *para*-substituted benzene rings in two related *Ceanothus* alkaloids, he became suspicious that ceanothine-B might be similarly *para* fused and that his original assigned structure was incorrect.

(7) Woodrow Wilson Honorary Fellow; National Institutes of Health Predoctoral Fellow.

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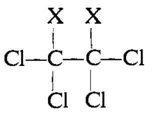
*Received April 19, 1968*

## Nuclear Magnetic Resonance Spectroscopy. Conformations and Conformational Equilibration of Bis(trifluoromethyl)tetrachloroethane[1]

*Sir:*

The factors which influence conformational populations and barriers to rotation in halogenated ethanes do not yet seem well understood. While the favored form for 1,1,2,2-tetrachloroethane (**1a**) has the hydrogens *gauche*,[2] 1,2-difluorotetrachloroethane (**1b**) has a slight preference for fluorines *trans*[3] and 1,2-dimethyltetrachloroethane (**1c**) has a strong preference for methyls *trans*.[4] The effect of trifluoromethyl groups has now been determined by investigating the temperature variation of the $^{19}F$ nmr spectrum of bis(trifluoromethyl)-tetrachloroethane (**1d**) (obtained from the Pierce Chemical Co.) with the aid of a Varian A-56/60A spectrometer and a V-6040 variable-temperature accessory.



$\mathrm{Cl{-}C(X)(Cl){-}C(X)(Cl){-}Cl}$

**1a**, X = H
**b**, X = F
**c**, X = $CH_3$
**d**, X = $CF_3$

A set of spectra of **1d** taken between −73 and −150° is shown in Figure 1. The complexity of these spectra below −150° shows that, under these conditions, rotation about *all* of the carbon–carbon bonds must be slow on the nmr time scale. At −112° rotation about the carbon–trifluoromethyl bond is slow in the *gauche* isomer but rapid in the *trans* isomer. Integration of the spectral peaks at this temperature indicates that **1d** is comprised of 8% of the *trans* and 92% of the *gauche* conformations. The spectrum at −150° could be matched by trial-and-error calculations with LAOCOON II.[5] The resulting shift and coupling parameters which fit the spectrum (see Figure 1) are given in Table I. In the analysis, advantage was taken of the fact that the *trans* isomer **2** is expected to give an $(XY_2)(XY_2)'$ spectrum while the *gauche* isomer **3** is expected to give an (ABC)(ABC)′ spectrum. The fluorine resonances of the *trans* isomer were inferred as deviations from the calculated spectrum of the *gauche* isomer.[6] The magnetic environment of $F_x$ in **2** is expected to be similar to that of $F_c$ in **3**, and the same should be true of $F_b$ and $F_y$. This was therefore taken as a basis for assigning the resonances in the *gauche* isomer to specific fluorines. The proximity of the trifluoromethyl group thus shifts the resonance of $F_a$ downfield relative to $F_b$.

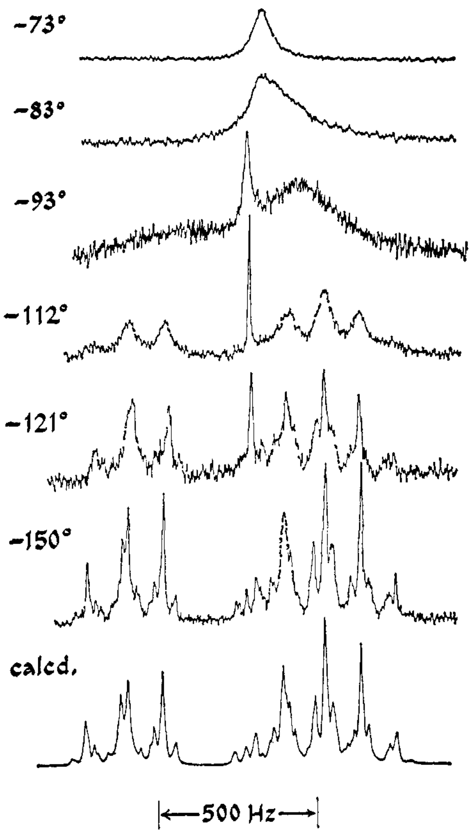


Figure 1. Experimental $^{19}F$ nmr spectra of bis(trifluoromethyl)-tetrachloroethane in difluorodichloromethane at 56.4 MHz as a function of temperature. Bottom curve is a theoretical spectrum calculated for the *gauche* isomer using the shift and coupling parameters in Table I.

**Table I.** Chmeical Shifts and Coupling Constants of Bis(trifluoromethyl)tetrachloroethane

| Fluorine | Chemical shift[a] | Fluorine couplings[b] | *J*, Hz |
|---|---|---|---|
| a | 69.8 | a,b | 105 |
| b | 73.5 | a,c | 124 |
| c | 61.1 | b,c | 116 |
| | | a,a′ | 75 |
| x | 61 ± 2 | | |
| y | 73 ± 2 | | |

[a] In parts per million upfield from trichlorofluoromethane. [b] The average value of $J_{FCCCCF}$ as determined from the $^{13}C$ satellites ($J_{CF}$ = 285.6 Hz and $^{13}C$ isotope effect on the fluorine chemical shift = 0.13 ppm) of the spectrum of **1d** at room temperature was 8.6 Hz.

The presence of *one* and *only one* large, five-bond, fluorine–fluorine coupling (a,a′ which is between the

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(1) Supported by the National Science Foundation.

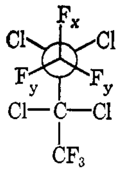
(2) H. S. Gutowsky, G. C. Belford, and P. E. McMahon, *J. Chem. Phys.*, 36, 3353 (1962).

(3) R. A. Newmark and C. H. Sederholm, *ibid.*, 43, 602 (1965). This assignment has been confirmed by investigation of the F–F couplings in the $^{13}C$ satellite spectra for each isomer (11 Hz for the *trans* and 21 Hz for the *gauche*) at −100° by Mr. Vernon Cormier in unpublished work in this laboratory.

(4) S. Borčić and J. D. Roberts, unpublished results.

(5) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).

(6) At −150°, rotation of the *trans* isomer is probably not completely stopped on the nmr time scale. The chemical-shift difference is taken from studies of other trifluoromethyl groups.



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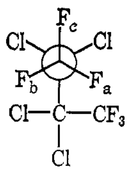

3

two fluorines in closest proximity to one another) suggests that the dominant effect may be one exerted through space rather than through the bonds.[7] The average long-range fluorine–fluorine coupling (8.6 Hz) measured in the $^{13}$C satellites on the fluorine spectrum at room temperature suggests that all the other five-bond coupling constants are either small or cancel each other.

The present system seems to afford the first direct measurements of geminal fluorine–fluorine couplings in a trifluoromethyl group and also the first instance of nmr observation of slow rotation about a carbon–trifluoromethyl bond in a saturated compound. With respect to the geminal F–F coupling, Dyer[8] has been able to correlate such couplings in derivatives of the type $QCF_2C\equiv$ with the electronegativity ($E_Q$) of Q by the expression $J_{FF} \approx 5.4 \times 10^2/E_Q$. The small value of the geminal fluorine–fluorine couplings observed here supports this correlation.

Although a complete analysis of the changes in line shapes with temperature of the complex six-spin system afforded by **1d** is not within our present capability, if we neglect *all* couplings, $E_a$ for the barrier to the rotation of the trifluoromethyl group seems to be about 8 kcal/mol for the *gauche* isomer and 6 kcal/mol for the *trans* isomer.[9] The barrier to rotation about the central carbon–carbon bond must be greater than 8 kcal/mol but cannot be accurately determined because of the small proportion of the *trans* conformation in the mixture and because of the similar coalescence temperatures associated with spectral changes arising from rotation about the central and exterior C–C bonds in the *gauche* isomer.

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(7) S. Ng and C. H. Sederholm, *J. Chem. Phys.*, 40, 2090 (1964). The calculated F–F internuclear distance between $F_a$ and the nearest fluorine in the remote $CF_3$ group in 3 for the all-staggered conformation with tetrahedral angles and normal C–C and C–F bond distances is 1.69 Å, which is substantially less than the 2.9-Å fluorine–fluorine distance expected at the van der Waals minimum.

(8) J. Dyer, *Proc. Chem. Soc.*, 275 (1963).

(9) These values for the barrier to rotation about a $CF_3$–$CCl_2C$ bond agree reasonably well with the 6-kcal barrier obtained for $CF_3CCl_3$ by E. Catalano and K. S. Pitzer, *J. Phys. Chem.*, 62, 838, 873 (1958); but much less well with the (10.7–)13.2-kcal value reported for $CF_3$–$CCl_3$ (and similar very high figures for other chlorofluoroethanes) by N. W. Luft, *ibid.*, **59**, 92 (1955).

(10) National Science Foundation Predoctoral Fellow, 1965–1968.

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## New Sulfur Chelate Chemistry

*Sir:*

Characterization of derivatives of the recently described difluorodithiophosphate anion,[1] $PS_2F_2^-$, has revealed a large class of metal chelates whose distinguishing features are relatively high volatility and unusual reactivity. Established examples of this class include the mono chelates of Cu(I), Ag(I), and $Cu[P(C_6H_5)_3]_2^+$, the bis chelates of divalent Mn, Fe, Co, Ni, Pd, Zn, Cd, and Hg, and the tris chelates of trivalent Cr and Co.

Preparation was effected under water- and oxygen-free conditions through reaction of the metals or metal halides with the anhydrous acid $HSPSF_2$ and by reaction of $(S_2PF_2)_2$ with the metals, *e.g.*, mercury, as well as oxidation of bis chelates with the disulfide to give the tris chelates. All of these compounds have been compositionally identified by complete elemental analyses. A representative analysis follows. *Anal.* Calcd for $Fe(S_2PF_2)_2$: Fe, 17.3; S, 39.8; P, 19.2; F, 23.6. Found: Fe, 17.7; S, 39.9; P, 19.3; F, 23.6. Of the compounds carefully examined to date with respect to molecularity, all were found to be monomeric in such solvents as heptane, toluene, and 1,2-dichloroethane (vapor tension technique[2]). Such a definition of molecularity is consistent with the high solubility of the complexes in nonpolar solvents such as heptane. Furthermore, facile vaporization implies that no significant intermolecular association occurs in the solid state for most of the bis and tris transition metal chelates. Illustrative vapor tension data are $Co(PS_2F_2)_2$, 20 mm (95°), and $Ni(PS_2F_2)_2$, 13.5 mm (95°). The Mn(II) and post-transition derivatives appear to be much less covalent, a point consistent with their lower volatilities, *e.g.*, $<1$ mm (95°) for the cadmium chelate and the absence of strong charge-transfer bands so pronounced in the chromium, cobalt, and nickel derivatives.

The reactivity of these new chelates varies with the metal electronic configuration and coordination number. Least reactive are the six-coordinate complexes exemplified by the relatively inert chromium(III) derivative. The cobalt(II) chelate is readily oxidized in air to the tris derivative. The generally high reactivity of the tetrahedral chelates required all manipulations to be effected in either a high-vacuum system or an efficient drybox.

Nuclear magnetic resonance studies show the nickel and palladium compounds to be diamagnetic and accordingly square planar. Susceptibility measurements by nmr technique revealed moments at 30° of 3.8, 5.9, 5.2, and 6.2 BM for Cr(III), Mn(II), Fe(II), and Co(II), respectively. These values were reproduced within 0.1 to 0.2 BM in solvents ranging from heptane to dichloromethane. The moments are consonant with octahedral chromium and tetrahedral manganese and iron. On the other hand, the value of 6.2 BM for a tetrahedral[3] cobalt complex is inexplicable. Solution Gouy measurements yielded a value of 5.1 BM which is still high but consistent with a very weak ligand field.

$F^{19}$ nmr data for the diamagnetic species show that the PF spin-spin coupling varies significantly from values of 1189 cps for the Cu(I) derivative to 1316 cps for the square-planar palladium species.[4] Similarly,

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(1) H. W. Roesky, F. N. Tebbe, and E. L. Muetterties, *J. Am. Chem. Soc.*, **89**, 1272 (1967).

(2) With the more reactive bis chelates, considerable difficulty was encountered in obtaining reproducible data because of oxidation and hydrolysis reactions; apparent molecular weights increased with time.

(3) There is no indication of association of this chelate, and the interaction of such a complex with heptane is implausible. Hence, we do not suspect a six-coordinate cobalt in such solutions of $Co(S_2PF_2)_2$.

(4) Variations in the PF coupling constants may reflect changes in the FPF angle. The $J_{PF}$ values of the apparently more ionic derivatives approach that of $HSPSF_2$ (1214 cps).