

III (m.p. 284–285°)³. Three types of hydrogen absorption in an abundance of 4, 6, and 8 are present (*cf.* Fig. 2). The two tertiary hydrogen absorptions centered at 230.5 and 185.5 cps. are still a doublet of doublets ($J = 10.5$ cps.) but have additional splitting of each line into symmetrical triplets ($J = 3$ cps.) by the new methylene groups. This confirms that these tertiary hydrogen atoms were α to the double bond in the photodimer and further identifies this coupling in Fig. 1.

The N-methyl line has shifted to lower field because of the removal of the double bond with its diamagnetic anisotropy. The new ring methylenes show an absorption at 116 cps. which lacked the usual distinction between hydrogens in the axial and equatorial conformations. The formation of symmetrical triplets ($J = 3$ cps.) is of interest because it indicates that the coupling to both methylene hydrogens which have different conformations is identical and that the dihedral angles are about 45°.

The situation was clarified when a Dreiding Stereomodel was constructed and *the molecule was observed to undergo very facile ring interconversion between two boat forms of the two six-membered rings.* The third form, with the ring fusions in the flagstaff positions, is highly strained and is the transition state between the other two. It is of interest to observe that the two forms (*cf.* Structure III) are mirror images after rotation of one through 180°. During this process, the equatorial hydrogens become axial and *vice versa* (see III), the net effect averaging the methylene hydrogens (only one absorption frequency) and the dihedral angle to about 45° as required.

This reaction has proved to be general. The products present interesting problems in magnetic anisotropy effects, rates of conformation mobility, and chemical synthesis which are presently under active investigation.

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THE RELATIVE SIGNS OF PROTON-FLUORINE COUPLING CONSTANTS IN ETHYL FLUORIDE

Sir:

There has been considerable interest recently in the relative signs and magnitudes of $\text{CH}_3\text{-X}$ and $\text{CH}_2\text{-X}$ coupling constants in compounds of the type $(\text{CH}_3\text{CH}_2)_n\text{X}$, where X is a nucleus of spin $1/2$.¹⁻⁴ We wish to report the analysis of the

(1) P. T. Narasimhan and M. T. Rogers, *J. Chem. Phys.*, **34**, 1049 (1961).

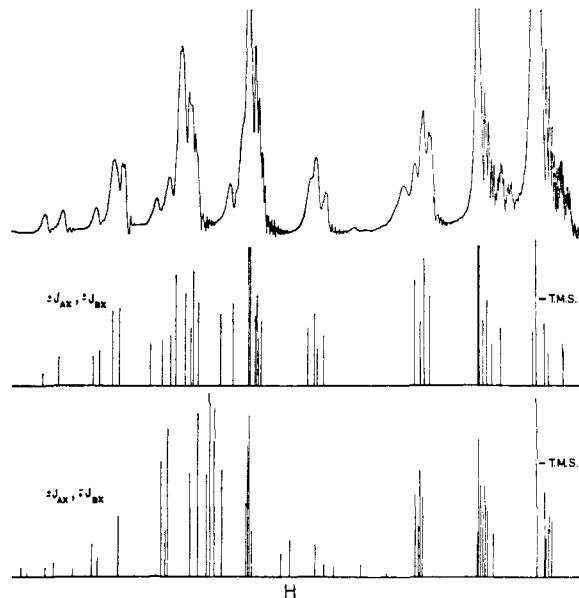


Fig. 1.—High field portion of proton n.m.r. spectrum of $\text{CH}_3\text{CH}_2\text{F}$ at 15.08 Mcps., with spectra calculated for like and opposite signs of $J_{\text{CH}_3\text{-F}}$ and $J_{\text{CH}_2\text{-F}}$.

spectrum of $\text{CH}_3\text{CH}_2\text{F}$, an additional compound of this type. The relative signs and magnitudes of the proton-fluorine coupling constants in ethyl fluoride apparently are inconsistent with the trends suggested from previous measurements.

TABLE I
COUPLING CONSTANTS IN SOME $(\text{CH}_3\text{CH}_2)_n\text{X}$ COMPOUNDS

Compound	Atomic number	$J_{\text{CH}_3\text{-X}}$ cps.	$J_{\text{CH}_2\text{-X}}$ cps.	$J_{\text{CH}_3\text{-X}}$ cps.	Rel. signs of $J_{\text{CH}_3\text{-X}}$ and $J_{\text{CH}_2\text{-X}}$ Ref.
$(\text{CH}_3\text{CH}_2)_2\text{F}^{19}$	9	6.9	25.2	46.7	Same ...
$(\text{CH}_3\text{CH}_2)_3\text{P}^{31}$	15	7.6	13.7	0.5	Opp. 1
$(\text{CH}_3\text{CH}_2)_4\text{Sn}^{117}$	50	~8.2	~68.1	~30.8	Opp. 1
$(\text{CH}_3\text{CH}_2)_4\text{Sn}^{119}$	50	8.2	71.2	32.2	Opp. 1
$(\text{CH}_3\text{CH}_2)_2\text{Hg}^{199}$	80	7.0	115.2	87.6	Opp. 1
$(\text{CH}_3\text{CH}_2)_3\text{Tl}^{205}$	81	~7.7	396	198	Opp. 4
$(\text{CH}_3\text{CH}_2)_4\text{Pb}^{207}$	82	8.2	125.0	41.0	Opp. 1

The n.m.r. spectrum of ethyl fluoride at 60 Mcps. is readily assigned from first order considerations. The coupling constants determined from this spectrum are given in the table. (Approximate coupling constants of $J_{\text{CH}_3\text{-F}} \sim 20$ cps. and $J_{\text{CH}_2\text{-F}} \sim 60$ cps. have been reported.⁵) The chemical shifts of the CH_3 and CH_2 protons are -1.24 and -4.36 ppm., respectively, relative to tetramethylsilane (these shifts have been reported previously⁶ as 6.07 and 2.89 ppm. relative to benzene). The F^{19} chemical shift relative to CCl_3F is 214 ppm.

(2) P. T. Narasimhan and M. T. Rogers, *ibid.*, **31**, 1430 (1959).

(3) P. R. Narasimhan and M. T. Rogers, *J. Am. Chem. Soc.*, **82**, 34 (1960).

(4) J. P. Maher and D. F. Evans, *Proc. Chem. Soc.*, 208 (1961).

(5) H. S. Gutowsky, L. H. Meyer and D. W. McCall, *J. Chem. Phys.*, **23**, 982 (1955).

(6) B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955).

The relative signs of the proton-fluorine coupling constants can be found from the analysis of the proton spectrum at 15.08 Mcps. at which the spectrum is a typical A_3B_2X spectrum. The observed spectrum of CH_3CH_2F at 15.08 Mcps., and the spectra calculated for like and opposite signs of J_{CH_3-F} and J_{CH_2-F} are shown in the figure. The spectrum calculated for like signs of J_{CH_3-F} and J_{CH_2-F} is in good agreement with that observed.

The coupling constants for other molecules of the type $(CH_3CH_2)_nX$ that have been reported previously are listed with those for ethyl fluoride in the table. For the molecules other than CH_3CH_2F , $|J_{CH_3-X}|$ will be seen to be larger than $|J_{CH_2-X}|$ and opposite in sign. Furthermore, the values of J_{CH_3-X} seem to increase regularly with the atomic number of X. The coupling constants of ethyl fluoride are quite inconsistent with these trends.

From theoretical and experimental considerations, both J_{CH_3-X} and J_{CH_2-X} would be expected to be positive, with $J_{CH_2-X} > J_{CH_3-X}$, when X is a proton.⁷ The coupling constants observed for ethyl fluoride are consistent with the results of valence bond theory, if it is assumed that when X is F¹⁹ contributions to the coupling constants from terms other than the contact electron-spin interaction can be neglected.

It has been suggested that the unusual relative signs and magnitudes of J_{CH_3-X} and J_{CH_2-X} in compounds other than CH_3CH_2F might arise from contributions to the coupling constants from terms other than the contact electron-spin interaction.¹ However, calculations have indicated that contributions from electron-orbital⁸ and dipolar electron-spin terms⁹ are not often very important.

Only s-type wave functions provide non-zero contributions to the Fermi contact term at the nucleus. It has been shown that the contributions of spin-polarized 1s, 2s, and 3s orbitals to the Fermi contact term can differ in sign.¹⁰⁻¹² Because of the competition between terms of differing sign, the value of the Fermi contact term is quite sensitive to the behavior of the d-electrons, for example, when the X atom is involved in chemical bonding.¹¹ Thus the results for molecules other than CH_3CH_2F in the table indicate that the 5d electrons in Pb, Tl, and Hg; the 4d electrons in Sn; and even the lone pair in $P(CH_2CH_3)_3$ may be involved in the chemical bonding of the ethyl group to atom X. The involvement of these additional electrons in the chemical bonding not only could give rise to changes in magnitude and sign of the Fermi contact term, but also could provide an additional contribution to the coupling, which of course could be opposite in sign to the contribution arising through the usual σ -bond.

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(7) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(8) J. A. Pople, *Molec. Phys.*, **1**, 216 (1958).

(9) G. A. Williams and H. S. Gutowsky, *J. Chem. Phys.*, **30**, 717 (1959).

(10) V. Heine, *Phys. Rev.*, **107**, 1002 (1957).

(11) R. E. Watson and A. J. Freeman, *ibid.*, **120**, 1125 (1960).

(12) R. E. Watson and A. J. Freeman, *ibid.*, **120**, 1134 (1960).

for the A_3B_2X spectra were performed on the IBM 709 computer of the M.I.T. Computation Center.

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A CYCLOPENTADIENYL DERIVATIVE OF TECHNETIUM

Sir:

It was of interest to obtain a cyclopentadienyl derivative of technetium for comparison with the known derivatives of manganese and rhenium. These two differ from each other both in their composition and nature of ring-to-metal bonding; while $(C_5H_5)_2Mn^1$ is ionic and possesses unpaired electrons, rhenium forms covalent, diamagnetic $(C_5H_5)_2ReH$.² We now wish to report the synthesis and properties of a corresponding derivative of technetium.

In a typical preparation, ammonium pertechnetate³ (1.50 g., 8.27 mmoles) was converted to the heptoxide⁴ in a Vycor tube (15 mm. diameter, 30 ml. capacity). After addition of carbon tetrachloride (9.2 ml.), the tube was sealed and heated to 400° in an autoclave for five hours, to form technetium tetrachloride after the method of K. Knox, S. Y. Tyree, Jr., *et al.*⁵ The moisture sensitive, blood-red tetrachloride was filtered in a dry atmosphere, washed with dry, redistilled pentane, and added at room temperature to a completely colorless⁶ solution of sodium cyclopentadienide (from sodium, 1.15 g., 50.0 mmole and monocyclopentadiene, 3.64 g., 55.0 mmole) in 30 ml. of tetrahydrofuran. The reaction mixture, now purple-red, was stirred for four hours at 50° as in the preparation of $(C_5H_5)_2ReH$.² Sodium borohydride (0.38 g., 10 mmole) was added, and after stirring for four more hours at 50°, solvent was removed by vacuum distillation. Sublimation of the dry reaction mixture at 55-60° (0.1 mm.), yielded 60-80 mg. of extremely air sensitive golden yellow crystals (I), m.p. 155° (corr.). More product could be obtained from the reaction mixture only by redissolving the salts in a quantity of dried tetrahydrofuran, stirring for a few hours at 50°, followed by solvent removal and a new sublimation. It was possible to obtain from three to five more crops of crystals each of about 30 mg., making total yield for a typical reaction from 150-200 mg. of I.

The infrared spectrum for carbon disulfide and tetrachloroethylene solutions of I consisted mainly

(1) G. Wilkinson, F. A. Cotton and J. M. Birmingham, *J. Inorg. & Nuclear Chem.*, **2**, 95 (1956).

(2) G. Wilkinson and J. M. Birmingham, *J. Am. Chem. Soc.*, **77**, 3421 (1955).

(3) Consisting mainly of isotope ⁹⁹Tc, obtained from Oak Ridge National Laboratories, Oak Ridge, Tennessee.

(4) Cf. J. C. Hileman, D. K. Huggins and H. D. Kaesz, *J. Am. Chem. Soc.*, **83**, 2953 (1961).

(5) K. Knox, *et al.*, *ibid.*, **79**, 3358 (1957); pentane (337 g.) was used as pressure equalizing liquid in the autoclave (1300 ml. capacity) rather than carbon tetrachloride which proved unsuitable for this purpose as it reacted to completion with steel at 400° causing the Vycor reaction tube to burst.

(6) For this stage of the preparation, as well as for handling extremely air sensitive product described below, rigorously oxygen-free nitrogen, (obtained by scrubbing with a solution of tri-isobutylaluminum in decane) is required.