

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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(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.

DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS

S. L. STAFFORD
J. D. BALDESCHWIELER

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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.

of these bands (cm.^{-1}): ν C-H (LiF prism) 3100 m; δ C-H, (NaCl prism) 1915-1940 w, broad, 1410 s, 1342 w, 1257 m, 1188 w, 1100 s, 1050 w, 1003 s, 996 s, 803 w, 775s. These closely parallel the bands reported for $(\text{C}_5\text{H}_5)_2\text{ReH}^7$ except for the noteworthy absence in our spectrum of a sharp band in the region where $\nu\text{Tc-H}$ would be expected ($\nu\text{Re-H cm.}^{-1}$, LiF prism, 2020 m).

Magnetic susceptibility for I was determined by nuclear magnetic resonance as already described in a previous work.⁴ For a solution of 66.1 mg. of I and 224 mg. (0.26 ml.) of toluene in an inner coaxial tube, the separation between the resonance of methyl protons of toluene and of protons of cyclohexane in the outer tube was found to be 18.4 cps., demonstrating diamagnetic character for I. Proton n.m.r. for I was obtained for solutions both in toluene and tetrahydrofuran, the latter permitting higher concentration of solute. A resonance at 5.61 τ ⁸ was observed (width, 0.8 δ cps.) whose ringing pattern displayed the exponential decay attributable to a single line. Scrutiny of the high field region up to 30 τ revealed no additional resonances. The n.m.r. of a sample of $(\text{C}_5\text{H}_5)_2\text{ReH}$ was investigated for comparison in our laboratory under similar conditions of measurement. A doublet centered at 5.69 τ ($A = 1.17$ cps., multiplet width, 1.8 δ cps.) and a peak at 23.4 τ (relative intensity 1/10, width 9 cps.) was found, in reasonable agreement with the previously reported data.⁷

The absence of a technetium bonded hydrogen atom, as ascertained by spectroscopic methods, demanded some explanation for the diamagnetic character of I. A molecular weight was obtained for the compound using the micro-tensimetric method.⁹ We observed a vapor pressure lowering of 3.75 mm. for a solution of 36.1 mg. of I in 852.7 mg. of diethyl ether ($P_0 = 535.6$ mm. at bath temperature during determination, 25.2 $^\circ$); found, 445 \pm 20. These results, taken together with the spectroscopic data above which attest to the presence solely of the (C_5H_5) group, strongly indicate the composition and molecular constitution for I to be $[(\text{C}_5\text{H}_5)_2\text{Tc}]_2$; mol. wt., 458. Analysis¹⁰ for carbon and hydrogen was carried out, using great care to exclude oxygen during the weighing: found: C, 52.87; H, 4.71; required for $(\text{C}_{10}\text{H}_{10}\text{Tc})_2$: C, 52.17; H, 4.82. The yield of I was of the order of 8%, based on ammonium pertechnetate.

The cyclopentadienyl derivative of technetium is not decomposed by water at room temperature; it dissolves in 10% aqueous tetrahydrofuran to give a pale yellow solution whose n.m.r. spectrum shows the resonance reported above, essentially un-

changed. Solution of I in tetrahydrofuran reacts with gaseous hydrogen chloride to yield an off-white precipitate. This redissolves upon addition of water, giving an air-sensitive, pale yellow solution for which a resonance appearing to be a singlet is observed at 4.60 τ .¹¹ Again, no resonances at high field in the region of absorptions of transition-metal bonded protons could be observed. Similar acid treatment of $(\text{C}_5\text{H}_5)_2\text{ReH}$ yielded a colorless aqueous tetrahydrofuran solution of $(\text{C}_5\text{H}_5)_2\text{ReH}_2^+\text{Cl}^-$ which in agreement with previous workers⁷ displays a barely resolvable triplet centered at 4.54 τ and broader resonance at 23.9 τ (1/5 relative intensity). The behavior under hydrolytic conditions thus indicates nature of ring-to-metal bonding in $[(\text{C}_5\text{H}_5)_2\text{Tc}]_2$ must be similar to that in $(\text{C}_5\text{H}_5)_2\text{ReH}$ rather than to that in $(\text{C}_5\text{H}_5)_2\text{Mn}$.

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(11) For aqueous solutions, central peak of $\beta\text{-CH}_2$ (high field) resonance of tetrahydrofuran was used as internal standard. Measurements were converted to τ -values using separation of tetramethylsilane given in ref. 8.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
LOS ANGELES 24, CALIFORNIA

D. K. HUGGINS
H. D. KAESZ

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THE STRUCTURE OF 1,2,5-THIADIAZOLE¹

Sir:

The detailed molecular structure of a new five-membered ring compound, containing sulfur-nitrogen bonds, first synthesized by Carmack and co-workers,² has been determined by electron diffraction. The preliminary results of this investigation are presented in this note.

The molecule 1,2,5-thiadiazole is isoelectronic with pyrazine, if of course the $1s^2$ electrons of the sulfur are not considered, so that the comparison of the chemistry and the structure of the two molecules provides a comparison of the effects of ethylene and sulfur as constituent groups. The available chemical evidence supports a planar ring structure with aromatic properties. Thiadiazole is isoelectronic with thiophene and electron diffraction data for thiophene also were obtained for comparison purposes. Structurally thiadiazole is also of interest since it provides a chance to obtain accurate bond length measurements of S-N and C-N bonds in what may be an aromatic system.

The electron diffraction data were obtained on the Iowa State University sector electron diffraction apparatus in Professor Bartell's laboratory and the photographic plates were microphotometered on the University of Michigan microphotometer in Professor Brockway's laboratory. The data analysis was carried out in a manner described elsewhere.³ The preliminary structural parameters

(1) Contribution number 994 from the Chemical Laboratories of Indiana University. The authors wish to thank the National Science Foundation and the Atomic Energy Commission for their financial support of this work.

(2) M. Carmack, L. M. Weinstock and D. Shew, Abstracts of Papers, 136th Meeting of the ACS, Atlantic City, N. J., September, 1959, page 37-P.

(3) R. A. Bonham and L. S. Bartell, *J. Chem. Phys.*, **31**, 702 (1959).

(7) M. L. H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 3916 (1958).

(8) Proton resonances observed at 40 Mc. (Varian V-43104 spectrometer) were measured for solutions in tetrahydrofuran with 1-2% internal toluene standard. Tetramethylsilane (1-2% internal standard) under these conditions appeared at 91.5 \pm 0.8 cps., on the high field side of the methyl protons of toluene, and also 69.3 cps. on the high field side of the center peak of the $\beta\text{-CH}_2$ (high field) resonance of tetrahydrofuran. Frequency measurements were made by the side-band method, using a calibrated Hewlett Packard Model 200 D audio-frequency oscillator.

(9) To be fully described in a forthcoming paper; for preliminary account, see ref. 4.

(10) We gratefully acknowledge the help of Miss Heather King, Microanalytical Laboratory, U.C.L.A.