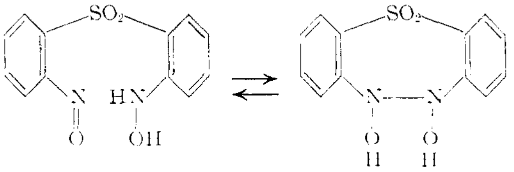
diazacyclohepta-2,4,6-triene. The purpose of this communication is to correct the erroneous conclusions which were published.

There exist two rather than three isomers of the cyclic azo and azoxy sulfones and they are the compounds which are referred to as IA, IB and IIA, IIC, respectively. The proposed conformational assignment of the isomers was shown correctly in the published Fig. 1.

The compound referred to as IC and later renamed III is the cyclic hydrazo sulfone and its ultraviolet spectrum was shown correctly in the published Fig. 2. The infrared spectrum of III shows strong absorption at 3430 cm.$^{-1}$ (N–H) and the published analytical data agree more satisfactorily when compared with those calculated for $C_{12}H_{10}O_2N_2S$ (C, 58.60; H, 4.09; N, 11.38; S, 13.00). The facile oxidation of the hydrazo compound III to IA under a variety of conditions explains the misunderstood "isomerizations" caused by perbenzoic acid and potassium permanganate (see footnote 9[1]).

The compound referred to as IIb and later renamed IV was obtained together with IIA by treating di-(*o*-aminophenyl) sulfone with peracetic acid. Compound IV is believed to be *o*-nitrosophenyl *o'*-hydroxylaminophenyl sulfone on the basis of its infrared spectrum (KBr disc) which showed a broad absorption band at 3500 cm.$^{-1}$ (O–H or N–H) and a sharp band at 1375 cm.$^{-1}$ (nitroso group). Also the analytical results agree more closely with those calculated for $C_{12}H_{10}O_4N_2S$ (S, 11.51; N, 10.07), found: S, 11.24; N, 10.07. The spatial proximity of the two nitrogen functions in IV suggests that this compound may partially exist in a cyclic state in analogy with cyclic dinitroso compounds.[2] In favor of this suggestion are the reported easy conversions of IV to IIA under dehydrating conditions and the reported reduction of IV to the cyclic hydrazo sulfone III by means of lithium aluminum hydride or zinc in acetic acid.



IV

In the published paper[1] there is described the reduction of di-(*o*-nitrophenyl) sulfide to what was thought to be the cyclic hydrazo sulfide (or dibenzo-1-thia-4,5-diazacyclohepta-2,6-diene) but which was later shown to be di-(*o*-hydroxylaminophenyl) sulfide. This compound can be crystallized from ethanol to give white plates, m.p. 119° dec., if care is taken to avoid excessive contact with air, and the material thus obtained gives the expected analytical results.

Calcd. for $C_{12}H_{12}O_2N_2S$: C, 58.00; H, 4.86; N, 11.28; S, 12.9. Found: C, 57.70; H, 4.65; N, 11.10; S, 13.0.

In this connection we wish to point out that it is now apparent that the reduction of di-(*o*-nitrophenyl) sulfone described in paper II of this series[3] also gave the corresponding hydroxylamino compound V[3] which upon oxidation in the presence of base gave the cyclic azoxy sulfone in accord with the observations of Jackson.[4]

Concerning the isomerizations of the two cyclic azoxy sulfones (II) it may be added that heating of either isomer in polar media (concd. sulfuric acid, acetic anhydride containing a few drops of concd. sulfuric acid) gave an apparent equilibrium mixture consisting predominantly of IIA, while prolonged heating in non-polar media (toluene) gives mixtures in which the other isomer predominates.

Also, it was possible to reduce IIA to IA by means of phosphorus tribromide according to the method of Ochiai.[5]

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(2) S. D. Ross and I. Kuntz, THIS JOURNAL, **74**, 1297 (1952).

(3) H. H. Szmant and R. L. Lapinski, *ibid.*, **78**, 458 (1956).

(4) E. L. Jackson, *ibid.*, **68**, 1438 (1946).

(5) E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).

(6) Present address where inquiries should be sent is Universidad de Oriente, Santiago de Cuba, Cuba.

DEPARTMENT OF CHEMISTRY
DUQUESNE UNIVERSITY H. HARRY SZMANT[6]
PITTSBURGH 19, PA. Y. L. CHOW

RECEIVED SEPTEMBER 19, 1957

THE SPIN RELAXATION TIME OF TRIPHENYLMETHYL AT LOW TEMPERATURES[1]

Sir:

Recently Aston, Fritz and Seki[2] have reported that the paramagnetism of solid solutions of triphenylmethyl in several organic crystals disappears at temperatures of a few degrees Kelvin. This result is puzzling since the optical fluorescence and absorption spectra of the crystals clearly indicate the presence of monomeric triphenylmethyl molecules.[3] The purpose of this note is to report on the long relaxation times encountered in the crystals. Our results can account for the observations of Aston, Fritz and Seki without the necessity of postulating a decrease in static susceptibility. These authors used an inductance method (frequency not reported) for the measurements at low temperatures. At frequencies rapid compared with the reciprocal of spin-lattice relaxation time T_1 the susceptibility measured by this method is smaller than the static susceptibility (approximately by the square of the ratio of $1/T_1$ to frequency).[4]

We obtained the relaxation time T_1 from observation of the magnetic resonance behavior of a solution of triphenylmethyl in triphenylamine. At 300 and 77°K. we observed the saturation of the electron resonance with increasing microwave power under slow passage conditions. At 4.2 and 1.2°K. we observed directly the increase in magnetization with time subsequent to turning on

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(1) This work has been supported in part by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command. Reproduction in whole or in part for any purpose of the United States Government is permitted.

(2) J. G. Aston, J. J. Fritz and S. Seki, THIS JOURNAL, **79**, 1000 (1957).

(3) S. I. Weissman, *J. Chem. Phys.*, **22**, 155 (1954).

(4) This result may be obtained from the Bloch equations. A similar result was demonstrated by Debye for electric susceptibilities of polar molecules.

the field under adiabatic fast passage conditions. At 300°K. $T_1 \simeq 10^{-3}$ sec., at 77°K. $T_1 \simeq 5 \times 10^{-3}$ sec., at 4.2°K. $T_1 \simeq 4$ min., at 1.2°K. $T_1 \simeq 20$ min. The magnetization was observed in each case at a field of 3200 oersteds; at 4.2 and 1.2°K. the field to which the magnetization was being equilibrated was 8000 oersteds. The concentration of triphenylmethyl was approximately 0.1 mole %.

In view of the remarkably long relaxation times at low temperature estimation of the static susceptibility from measurements of the inductance at a single frequency is not possible unless the frequency is lower than $\sim 10^{-3}$ cycle per second.

WASHINGTON UNIVERSITY
SAINT LOUIS, MISSOURI S. I. WEISSMAN
BELL TELEPHONE LABORATORIES, INC. G. FEHER
MURRAY HILL, NEW JERSEY E. A. GERE

RECEIVED SEPTEMBER 6, 1957

A NOVEL DEUTERIUM ISOTOPE EFFECT IN NUCLEAR RESONANCE SPECTROSCOPY

Sir:

I have observed a relatively large and hitherto unreported deuterium isotope effect in nuclear spin resonance (NSR) spectroscopy. By comparison of the fluorine NSR spectrum of n-C_3F_7D with that of n-C_3F_7H I have found that the fluorine nuclei in the $-CF_2D$ group are 0.60 ± 0.05 p.p.m. more shielded than those in the $-CF_2H$ group. This difference in shielding value ("chemical shift") should be of theoretical interest, inasmuch as the molecular wave function is not substantially altered. Qualitatively it may be seen that the direction of the shift indicates a *greater electron-donating power for deuterium than for hydrogen.* The atomic volume of deuterium in covalent compounds is well known to be smaller than that of hydrogen,[1,2] a fact which, by elementary particle-in-a-box considerations, requires a greater escaping tendency for the electrons.

The samples of n-C_3F_7H and n-C_3F_7D were prepared by decarboxylation of n-$C_3F_7CO_2Na$ (dried at 110°) in the presence of a slight excess of, respectively, H_2O and D_2O. The reactions were carried out at 200° for 2.5 hours in a stainless steel rocking autoclave; decarboxylation was quantitative, and the trace of C_3F_6 formed was readily removed by low-temperature distillation. The n-C_3F_7D was shown by infrared spectroscopy to contain less than 1% of n-C_3F_7H; however, one sample upon mere passage through a small P_2O_5–"Ascarite" (NaOH-on-asbestos) tube was found to contain 4 to 5% of the hydride.

The NSR spectra were determined with a Varian Associates V-4300 High Resolution spectrometer operating at 40 megacycles per second. The n-C_3F_7H and n-C_3F_7D were examined separately and also in mixture, by which means it was shown that the peaks due to the CF_3CF_2– group suffered no displacement larger than 3–5 c.p.s. upon isotopic substitution. Shielding S-values in parts-per-million, defined[3] by the equation $S = 10^6 (H_{\text{obs.}} - H_{CFBr_3})/H_{CFBr_3}$, are: for the CF_3 group, 94.6 p.p.m.; for the central CF_2 group, 145.4 p.p.m.; for the CF_2H group 150.2 p.p.m.; and for the CF_2D group, 150.8 p.p.m. The positions of the multiplet centers of the latter two groups were measured relative to the central CF_2 group in order that relative errors might be no greater than ± 0.05 p.p.m.; errors in the S-values are ± 0.1 to 0.2 p.p.m.

The CF_2H fluorine resonance is a doublet, with $J(CF_2H)$ being 51.5 ± 1 c.p.s., in good agreement with the value 50.2 ± 1 c.p.s. found for the triplet proton resonance. The doublet proton line in n-$C_6H_{13}F$ has $J(CH_2F) = 47.4 \pm 1$ c.p.s., and in $CHFBrCH_2Br$ has $J(CHFBr) = 49 \pm 2$ c.p.s.[4] The CF_2D fluorine resonance is an equal triplet, the extreme peaks being separated by 14.5 ± 2 c.p.s. The ratio $J(CF_2H)/2J(CF_2D)$ is thus 3.5 ± 0.5, the expected value being 3.26, the ratio of the nuclear moments of H and D. Both the CF_2H and CF_2D fluorine peaks show further splitting into triplets having J-values of 4.0–4.5 c.p.s. For the internal CF_2 group a quadruplet with splitting about 4.7 ± 1 c.p.s. is observed in n-C_3F_7H but *only a triplet* with splitting approximately 4.9 c.p.s. in n-C_3F_7D; this indicates that $J(HC{-}CF_2)$ is about the same as $J(F_2C{-}CF_2)$ in n-C_3F_7H, the smaller $J(DC{-}CF_2)$ not being observed.

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CONTRIBUTION NO. 127
CENTRAL RESEARCH DEPARTMENT
MINNESOTA MINING AND MANUFACTURING COMPANY
ST. PAUL 6, MINNESOTA GEORGE VAN DYKE TIERS

RECEIVED AUGUST 22, 1957

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[1] J. A. Dixon and R. W. Schiessler, THIS JOURNAL, **76**, 2197 (1954).

[2] C. K. Ingold, *et al.*, *J. Chem. Soc.*, 920 (1936); 235 (1946).

[3] G. V. D. Tiers, presented at the Nuclear Resonance Symposium at the 132nd A.C.S. Meeting, New York, 1957, and shortly to be submitted for publication. Virtually all carbon-bonded fluorine atoms yield positive S-values (*i.e.*, greater shielding of the fluorine nucleus) by the above equation, and accordingly $CFBr_3$ (b.p. 107°, f.p. below −80°) is suggested as a desirable and convenient primary standard for fluorine NSR spectroscopy.

[4] L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953), find $J = 48$ and 53 c.p.s. for H and F in CH_2F_2.