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Long-Range Proton Spin-Spin Coupling in Dimethyl Sulfone^{1a}

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A wide variety of chemical and spectral data suggest that a sulfone group is capable of interaction with an adjacent unsaturated center; however, it seems possible that the mode of this interaction may be significantly different from that of conjugation between first-row elements.² Moffit's molecular orbital treatment of sulfone groups indicates that two distinct types of conjugation are possible: "direct" conjugation utilizing the filled sulfur-oxygen molecular orbitals for overlap with an adjacent center, and "charge-transfer" conjugation, involving donation of electrons from

the adjacent center into unfilled sulfone molecular orbitals having predominantly d-orbital character.³ It is difficult to distinguish experimentally between these alternatives, but analysis of the e.p.r. spectrum of thioxanthone S,S-dioxide mononegative ion led Vincow to conclude that a charge-transfer mechanism was responsible for the observed conjugation through the sulfone group.⁴

To provide further evidence pertinent to the problem of conjugation in sulfones, we have compared the ability of several oxygen- and sulfur-containing groups to transmit proton spin-spin couplings (Table I).⁵

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- (1) (a) Supported in part by the Office of Naval Research and the National Science Foundation. (b) Contribution No. 3040.
(2) For reviews of this subject, see G. Cilento, *Chem. Rev.*, **60**, 147 (1960); C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Co., New York, N. Y., 1962.
(3) W. Moffit, *Proc. Roy. Soc. (London)*, **A200**, 409 (1950); H. P. Koch and W. E. Moffit, *Trans. Faraday Soc.*, **47**, 7 (1951).
(4) G. Vincow, *J. Chem. Phys.*, **37**, 2484 (1962).
(5) Somewhat similar results which are in agreement with those reported here have been published by N. van Meurs, *Spectrochim. Acta.* **19**, 1695 (1963).

Table I: Magnitudes of ^1H - ^1H and ^{13}C - ^1H Coupling Constants for CH_3XCH_3

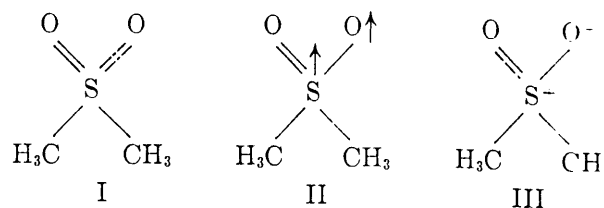
Compound	Sample	$J_{^{13}\text{C}\text{H}}$, c.p.s. ^a	J_{HH} , c.p.s. ^a	$\angle\text{C-X-C}$, deg.
CH_3SSCH_3	Pure liquid	...	0.0	...
CH_3OCH_3	Pure liquid	139	0.25	111 ± 4^c
CH_3SCH_3	Pure liquid	138	0.3	98.6 ± 10^d
CH_3SOCH_3	Pure liquid	138	0.4	100 ± 5^e
CH_3COCH_3	Pure liquid	127^h	0.54^h	119.6 ± 3^f
CH_3SCH_3	50% in water	138	0.9	115 ± 15^g
$(\text{CH}_3)_3\text{S}^+\text{I}^-$	50% in water	145	$(0.4)^b$...

^a Measurements were made using ^{13}C of natural abundance, as described by A. D. Cohen, N. Sheppard, and J. J. Turner, *Proc. Chem. Soc.*, 118 (1958), and for J_{HH} are ± 0.05 c.p.s. The signs of the coupling are unknown. ^b The accuracy of this value is low due to viscous broadening of the spectrum. ^c Private communication from V. Schomaker quoted by P. W. Allen and L. E. Sutton in *Acta Cryst.*, **3**, 46 (1950). ^d L. Pierce and M. Hayashi, *J. Chem. Phys.*, **35**, 479 (1961). ^e O. Bastiansen and H. Viervoll, *Acta Chem. Scand.*, **2**, 702 (1948). ^f P. W. Allen, H. J. M. Bowen, L. E. Sutton, and O. Bastiansen, *Trans. Faraday Soc.*, **48**, 991 (1952). ^g Private communication from R. E. Rundle, quoted by Allen and Sutton. ^h J. R. Holmes and D. Kivelson, *J. Am. Chem. Soc.*, **83**, 2959 (1961).

The relative magnitudes of the four-bond coupling constant J_{HH} in dimethyl sulfone, dimethyl sulfoxide, and dimethyl sulfide suggest that coupling through the sulfone group involves important contributions from some mechanism other than the usual σ -bond interactions.⁶ However, the unexceptional value observed for J_{HH} in trimethylsulfonium iodide makes it seem unlikely that charge transfer resulting from movement of the electrons of the methyl group orbitals to the empty sulfur d-orbitals is important in transmitting the coupling. Delocalization of the methyl group electrons into the d-orbitals is likely to be more important in the positively charged sulfonium salt than in

the sulfone⁷; however, the observed coupling constant in the sulfonium compound is significantly the smaller of the two.

Alternately, coupling through the sulfone group might well involve contributions of structures such as



II, similar to the type invoked by Kivelson to account for the long-range proton coupling in acetone.⁸

It is interesting that $J_{^{13}\text{C}\text{H}}$ is the same for dimethyl sulfide, sulfoxide, and sulfone, but significantly larger for trimethylsulfonium iodide. If the dipolar structures of type III make an important contribution to the resonance hybrid of dimethyl sulfone, the resultant partial positive charge on sulfur would be expected to increase the orbital electronegativity of the sulfur bonding orbital directed toward the methyl group, relative to the corresponding orbital in dimethyl sulfide, and hence to increase $J_{^{13}\text{C}\text{H}}$.⁹ The similarity of the ^{13}C -H coupling constants for dimethyl sulfide and dimethyl sulfone thus provides evidence that the sulfone is probably well represented by a structure of type I with predominantly covalent sulfur-oxygen bonds.

(6) The observed order is opposite to that which would be expected on the basis of variation in coupling through σ -bonds with changes in the C-X-C bond angle. See H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1958), and the C-X-C bond angles listed in Table I.

(7) For discussions of the effect of charge on d-orbital contraction, see H. H. Jaffe, *J. Phys. Chem.*, **58**, 185 (1954); D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sullivan, *J. Chem. Soc.*, 332 (1954); D. P. Craig and E. A. Magnusson, *ibid.*, 4895 (1956).

(8) J. R. Holmes and D. Kivelson, *J. Am. Chem. Soc.*, **83**, 2959 (1961); see also M. Barfield and D. M. Grant, *ibid.*, **85**, 1899 (1963).

(9) See, for example, N. A. Matwiyoff and R. S. Drago, *J. Chem. Phys.*, **38**, 2582 (1963); C. Juan and H. S. Gutowsky, *ibid.*, **37**, 2198 (1962), and references therein.