

Table I. Proton Nmr Parameters for Methylcyclopentadienes

Molecule	Nmr parameters				
	Chemical shifts ^a				
	1	2	3	4	5
	1.978	5.996	6.246	6.066	2.695
	Methyl proton coupling constants ^b				
	J_{12}	J_{13}	J_{14}	J_{15}	J_{15}
	-1.6	+0.4	-0.4	-0.2	-0.2
	Other coupling constants ^b				
	J_{23}	J_{24}	J_{25}	J_{34}	J_{35}
	+1.9	+1.4	-1.3	+5.4	-1.5
	J_{45}				+1.4
	Chemical shifts ^a				
	1	2	3	4	5
	5.834	1.911	6.230	6.230	2.788
	Methyl proton coupling constants ^b				
	J_{12}	J_{23}	J_{24}	J_{25}	J_{25}
	-1.5	-0.4	+0.4	+2.0	+2.0
	Other coupling constants ^b				
	J_{13}	J_{14}	J_{15}	J_{34}	J_{35}
	+1.4	+1.8	+1.8	+5.4	-1.4
	J_{45}				+1.4
	Chemical shifts ^a				
	Olefinic protons				
	~6.35				
	Chemical shifts ^a				
	5				
	3.03				
	(CH ₃) ₅				
	1.08				
	Coupling constants ^b				
	$J_{CH_3, H_5} \approx 7.8$				
	Chemical shifts ^a				
	1	2	3	4	5
	6.27	6.43	6.43	6.27	2.80
	Coupling constants ^b				
	J_{12}	J_{13}	J_{14}	J_{15}	J_{25}
	5.05	1.09	1.98	1.93	1.33
					-1.51

^a Chemical shifts in ppm downfield from TMS. ^b Coupling constants in Hz. ^c Data from ref 5 for nonequilibrated conditions. ^d Data from ref 9.

The results of the complete analysis are given in Table I. In accordance with the previously reported data no A₁ isomer has been detected. The ratio of vinylic isomers is equal to almost 1:1 (accuracy $\pm 1\%$). For the sake of comparison, the values are given in Table I for C₅H₆ and the A₁ isomer of C₅H₅CH₃ calculated through the full⁹ and partial⁵ analyses, respectively.

We can now make the following conclusions: (a) introduction of methyl in each of the isomers results in a displacement of all signals to the higher fields (compare with the cyclopentadiene's data, Table I); the displacement is especially pronounced for the ortho-positioned protons (proton 2 in isomer A₂, proton 1 in isomer A₃), where it is ~ 0.4 ppm for both of the isomers; (b) olefinic proton couplings are very close to the values previously reported^{6,9} in both their moduli and their relative signs; (c) allylic proton couplings, $^4J_{trans}$, are all negative (ca. -1.5 Hz); (d) the coupling constants of methyl protons with protons H₃ and H₄ for both the isomers are equal to 0.4 Hz, while their signs are alternating (see Table I); (e) finally, it is interesting to note that the coupling constant J_{CH_3, CH_2} across four bonds in isomer A₂ is equal to -0.2 Hz, while the respective coupling constant J_{CH_3, CH_2} across five bonds in isomer A₃ is equal to +2.0 Hz. The latter constant may serve as a good criterion for identifying methyl position in the cyclopentadienyl ring.

It is also noteworthy that the signs of coupling constants of methyl protons with olefinic ones strongly support the idea that π -electron contribution is almost

completely responsible for the spin coupling in such conjugated systems as *cis*-dienes.¹⁰

(10) (a) R. A. Hoffman, *Mol. Phys.*, **1**, 326 (1958); (b) P. Albritton, A. V. Cunliffe, and R. K. Harris, *J. Magn. Resonance*, **2**, 150 (1970).

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An Unusually Strong Intramolecular Interaction between the Sulfone or Sulfoxide and the Alkoxide Functions

Sir:

In further pursuit of the study¹ of conformational equilibria in 1,3-dioxanes bearing polar substituents at C-5 we have examined the equilibria of the 5-methylthio- (1a \rightleftharpoons 1b), 5-methylsulfinyl- (2a \rightleftharpoons 2b) and 5-methylsulfonyl-2-isopropyl-1,3-dioxanes (3a \rightleftharpoons 3b) (eq 1), the 2-isopropyl group acting as an effective holding group for the 1,3-dioxane ring.² The results for the 5-methylthio series 1 in several solvents are summarized in Table I; in parentheses, for comparison, are given the corresponding³ values for the 5-methoxy compounds. The results are on the whole unexceptional in that the equatorial (trans) isomer is favored throughout and in that there is a marked solvent effect such

- (1) E. L. Eliel and M. K. Kaloustian, *Chem. Commun.*, 290 (1970).
(2) F. W. Nader and E. L. Eliel, *J. Amer. Chem. Soc.*, **92**, 3050 (1970).
(3) R. J. Abraham, H. D. Banks, E. L. Eliel, O. Hofer, and M. K. Kaloustian, *J. Amer. Chem. Soc.*, **94**, 1913 (1972); E. L. Eliel and O. Hofer, submitted to *J. Amer. Chem. Soc.*

(9) M. A. Cooper, D. D. Elleman, C. D. Pearce, and S. L. Manatt, *J. Chem. Phys.*, **53**, 2343 (1970).

Table I. Configurational Equilibria for 2-Isopropyl-5-methylthio-1,3-dioxanes (1)^a

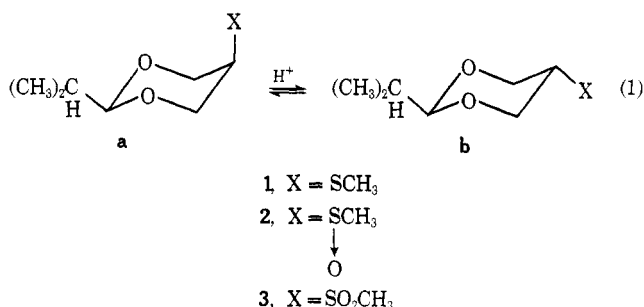
	Solvent Cyclohexane	CCl ₄	Ether ^b	Benzene ^c	Acetonitrile
$\Delta G^\circ_{\text{SMe}}$	-1.82 ± 0.01	-1.74 ± 0.02	-1.73 ± 0.02	-1.55 ± 0.01	-1.13 ± 0.02
$\Delta G^\circ_{\text{OMe}}$	(-1.06)	(-0.90)	(-0.83)	(-0.58)	(+0.01)

^a In parentheses, 2-isopropyl-5-methoxy-1,3-dioxanes. ΔG° in kcal/mol for the equilibrium shown in eq 1 at 26.5° for -SMe compounds, at 25.0° for -OMe compounds. Analysis by glpc. ^b Diethyl ether. ^c The anomalous solvent behavior of benzene has been recorded previously.³

Table II. Configurational Equilibria for 2-Isopropyl-5-methylsulfinyl- (2) and -5-methylsulfonyl-1,3-dioxanes (3)^a

	Solvent Cyclohexane	CCl ₄	Chloroform	Benzene	Acetonitrile
$\Delta G^\circ_{\text{SOMe}}$	N.d. ^b	Ca. 0.60	0.82 ± 0.11	0.74 ± 0.07	0.86 ± 0.09
$\Delta G^\circ_{\text{SO}_2\text{Me}}$	1.16 ± 0.10	N.d. ^b	1.19 ± 0.10	1.07 ± 0.09	Ca. 0.90

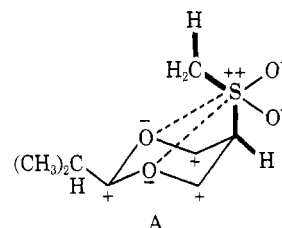
^a ΔG° in kcal/mol at 54.0° for the sulfoxides (2), at 50.0° for the sulfones (3). Analysis by nmr, using EuDPM as shift reagent for the sulfoxides; integration of (CH₃)₂CH peaks. ^b Not determined.



that more polar solvents shift the equilibrium toward the axial isomer with its higher dipole moment. However, we note that in the most polar solvent acetonitrile (in which dipolar interactions are minimized) ΔG° for methoxyl is nearly 0, in contrast to the value for methoxycyclohexane, which is -0.55 kcal/mol.⁴ In contrast, the ΔG° value for thiomethyl remains more negative than the corresponding value for methylthiocyclohexane (-1.07 kcal/mol⁴) even in acetonitrile. This is despite the fact that the sulfur-oxygen distance in axial 5-methylthio-1,3-dioxane, even without any deformation, is 3.2 Å, i.e., not less than the sum of the van der Waals radii of sulfur and oxygen. It appears that the M-shell electrons of sulfur, in contrast to the L-shell electrons of oxygen in axial methoxyl, extend far enough to engender a repulsive interaction with the p electrons of the ring oxygens.⁵ A parallel situation exists in the comparison of 5-fluoro- and 5-chloro- or 5-bromo-1,3-dioxane.³

A very different situation is found in the sulfoxides (2) and sulfones (3) as shown in Table II. The positive values of ΔG° for both sulfoxides and sulfones indicate that the axial group is more stable than the equatorial. Moreover, the solvent effect is very small for both series, possibly "reversed" for the sulfone. A further remarkable feature was found in the long-range coupling constants (⁴J) for sulfones 3a and 3b. In 3b the SO₂CH₃ group coupled with H-5 with $J = 0.39 \pm 0.02$ Hz which is probably an average coupling constant for the various rotamers of the group.⁶ In contrast, ⁴J for 3a was 1.14 ± 0.02 Hz which strongly suggests that the methyl

group is turned inward (structure A) since only in that



conformation is there the W arrangement of the long-range coupled hydrogens required for maximum J .^{7,8}

Our interpretation of the findings is shown in structure A; we hypothesize a dominant interaction of the positive end of the S⁺-O⁻ dipole with the negative end of the C⁺-O⁻ dipole of the ring. A similar interaction has been postulated by Lemieux and Chü to account for the anomeric effect in glycosides.⁹ The lack of solvent effect is probably due to the fact that the sulfur in sulfoxides and sulfones is relatively inaccessible to solvation whereas the outward-turned oxygen is equally accessible in the equatorial and axial conformations. The remarkable point is that, if as a minimum one takes the attractive dipolar force for the sulfone as being the difference¹⁰ in ΔG° (acetonitrile) between SCH₃ and SO₂CH₃, the electrostatic attraction between the ether functions of the dioxane and the SO₂CH₃ function of the sulfone amounts to about 2.3 kcal; i.e., it is of the same order of magnitude as an intramolecular hydrogen bond.¹ This finding has interesting implications concerning the chemistry of bifunctional compounds containing the SOR and SO₂R functions; we are presently exploring these implications.

Synthesis. Reaction of ClCH(COOEt)₂ with CH₃SK gave CH₃SCH(COOEt)₂ in 85% yield when the stoichiometric amount of CH₃SK was added slowly. The reaction undoubtedly proceeds *via* CH₃SCl and KCH-

(7) That coupling is indeed with H-5 was proved by preparing the 5-d compound which showed no coupling.

(8) A ⁴J of 1.14 Hz must be near the maximum; cf. M. Barfield, *J. Chem. Phys.*, **41**, 3825 (1964). We realize that the intervention of a sulfone group in the five-atom chain introduces an element of uncertainty.

(9) N. J. Chü, Ph.D. Dissertation, University of Ottawa, Ottawa, Ontario, Canada, 1959; cf. R. U. Lemieux and N. J. Chü, Abstracts of Papers, 133th National Meeting of the American Chemical Society, San Francisco, Calif., 1958, p 31N.

(10) This assumption is probably conservative, since it assumes the repulsion of the inward-turned methyl in axial SO₂CH₃ to be no greater than that of the unshared pairs in SCH₃, disregarding minor differences in the equatorial conformers.

(4) F. R. Jensen, C. M. Bushweller and B. H. Beck, *J. Amer. Chem. Soc.*, **91**, 344 (1969).

(5) Called the "hockey-sticks effect" by N. S. Zefirov, V. S. Blagoveshchensky, I. V. Kazimirchik, and N. S. Surova, *Tetrahedron*, **27**, 3111 (1971); cf. N. S. Zefirov and N. M. Shekhtman, *Russ. Chem. Rev.*, **40**, 315 (1971).

(6) Only the "methyl down" rotamer has the required W arrangement of the coupling protons.

(COOEt)₂, for excess CH₃SK gives much CH₃SSCH₃; however, reaction of CH₃SCl with NaCH(COOEt)₂ gives a product highly contaminated with (CH₃S)₂C(COOEt)₂ through a disproportionation of anions. Reduction of the ester by LiAlH₄ gives CH₃SCH(CH₂OH)₂ which, when condensed with isobutyraldehyde,³ gives a mixture of **1a** and **1b** separated by glpc; configuration is readily assigned by nmr (*J*_{4,5}). Oxidation of **1a** and **1b** with the stoichiometric amount of *m*-chloroperbenzoic acid at 0–5° gave **2a** and **2b** whose configurations were unequivocally assigned by dipole measurement: **2a**, 3.50 D, **2b**, 2.46 D. The stereoisomers differ appreciably in their uv absorption: **2a**, λ_{max} 202.5 nm (ε 1490); **2b**, λ_{max} 208 nm (ε 3400) (both in cyclohexane); the latter absorption is typical of compounds such as cyclohexyl methyl sulfoxides. The ir stretching frequency for S–O differed trivially for **2a** (1060 cm⁻¹) and **2b** (1065 cm⁻¹) (CCl₄). Oxidation of **1a** and **1b** with 2 mol of *m*-chloroperbenzoic acid at room temperature gave **3a** and **3b**. All compounds had carbon and hydrogen analyses within 0.3% of the calculated.

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Hyperconjugation and p–d Homoconjugation in Radicals Containing β Heavy Atom Substituents

Sir:

Following the discovery¹ that certain radicals of type R₂CCR₂(MR₃) have a preferred conformation in which the MR₃ group is held out of the radical plane such that the C_β–M bond has maximum overlap with the p orbital on the radical center, we showed² that for such radicals, there was an unusually large isotropic hyperfine coupling to the M nucleus and suggested that this could best be understood in terms of a hyperconjugative delocalization mechanism.

Recently, Kawamura and Kochi³ have reported some liquid-phase results for ²⁹Si and ^{117,119}Sn which strongly support our solid-state data and agree that the large "metal" hyperfine interactions indicate hyperconjugation interaction. Such an interaction is clearly sufficient to explain the hyperfine data and the preferred orientations, but Kawamura and Kochi maintain that in order to explain the *g*_{av} values a considerable amount of delocalization of the unpaired electron into the outer d orbitals of the metal atom is required. We feel that arguments based upon very small differences in *g*_{av} values are unsafe, but that, for these radicals, the deviations from the free-spin value are so small that they constitute evidence against significant d-orbital involvement.

The argument rests upon the *g*_{av} values, some of which are summarized in Table I. Of those used by Kawamura¹ and Kochi,³ only that for the tin compound need be considered seriously since the differences between the other three values must be close to experimental error. The value of 2.00205 for the tin compound deviates from the free-spin value by *ca.* –0.00025, which is a shift of *ca.* 0.4 G at the X band. This must also be quite close to the experimental error involved in its estimate. The issue is, can this really be utilized to prove a 12% delocalization into the tin d-orbital manifold?

The computation given³ utilizes the *g*_{av} values for the radicals MR₃ in order to estimate the *g* shift induced by hyperconjugation. For the tin compound, the shift is probably overestimated because no allowance seems to have been made for a spin-polarization contribution to the isotropic coupling to ^{117,119}Sn.² Also, the *g*_{av} value of 2.018 used is that given by Gordy and co-workers⁴ for SnH₃. Our value for Bu₃Sn radicals is *g*_{av} = 2.007,⁵ which would lead to a considerably reduced value for ρ_d (the d-orbital population).

The equation used to relate the Δ*g* values to ρ_d, namely³

$$\Delta g_d = 4\xi_a \rho_d (E_0 - E_d)$$

depends strongly upon the magnitude of *E*₀ – *E*_d, the energy gap between the carbon 2p orbital and the outer metal d orbital. (The d orbitals were assumed to be nearly degenerate.³) This gap was estimated to be about 6.9 eV,³ and it is this very large value that enables the authors to reconcile a very small *g* shift with a large d-orbital population. It seems to me that this energy gap is so large that no appreciable delocalization of the type envisaged could possibly occur. If, then, the gap is reduced (as a result, say, of d-orbital contraction) to a value that would accord with a 12% delocalization, then the equation would predict a negligible ρ_d value.

One has only to recall the known situation for first-row transition metal complexes⁶ to appreciate that, for systems involving nearly degenerate, magnetically coupled d orbitals, *g* shifts are very large indeed, and, even if the spin population is reduced to 10%, by delocalization onto ligands, *g* shifts of the order of 0.1 or more are to be expected. In other words, one would need to postulate a very large splitting of the d levels in order to accommodate the very small change in *g*_{av} with even a 1% delocalization into the d manifold.

The main point of this note, however, is to show that results for several other radicals in this class, all of which exhibit the required preferred conformation and, where measured, a large isotropic coupling to the metal nucleus, have *g* values which, when analyzed by the method of Kawamura and Kochi,³ give quite different results.

(i) The best documented radical of this class is MeCHCH₂AsO₃H, which has *g*-tensor components (corrected using the full Breit–Rabi equation) of 2.008, 2.002, and 2.012, giving *g*_{av} = 2.0073.² In order to

(1) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **91**, 6161 (1969).

(2) A. R. Lyons and M. C. R. Symons, *Chem. Commun.*, 1068 (1971); *J. Chem. Soc., Faraday Trans. 2*, 622 (1972).

(3) T. Kawamura and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 648 (1972).

(4) R. L. Morehouse, J. J. Christiansen, and W. Gordy, *J. Chem. Phys.*, **45**, 1751 (1966).

(5) Unpublished result.

(6) This comparison is valid, since the spin-orbit coupling constants are of similar magnitude to that for tin.