a Dry Ice–acetone bath and freshly distilled propionic acid (0.5 ml) was added cautiously. After warming to room temperature, most of the tetrahydrofuran was evaporated under reduced pressure. Propionic acid (10 ml) was added, the reaction mixture was heated under reflux for 17 hr and then poured onto ice. The residue from extraction with ether, washing with sodium bicarbonate solution, drying, and evaporation of the ether was chromatographed on alumina (activity 1). The crude product (68 mg) upon elution with petroleum ether was further purified by tlc on 10% silver nitrate containing silica gel H in hexane, yielding 49 mg (49%) of olefin free **5α-cholestane-14α-d_1** (XLVI), mp 74–76°. (For isotopic purity see Table II).

Cholestane-15ζ-d_1 (XLVII). 5α-Cholest-14-ene[28] (XLV, 95 mg) was hydroborated and then hydrolyzed in the same manner as described above (see XLVI) except that lithium aluminum hydride and propionic acid-0-*d* were used in place of lithium aluminum deuteride and propionic acid. Analogous work-up and purification gave 23 mg (24%) of olefin-free **5α-cholestane-15α-d_1** (XLVII), mp 79–80.5° (MeOH).

5α-Cholest-7-en-3β-ol-6-one (XLIX).[52] 5α-Cholest-7-ene-3β,6α-diol[31] (XLVIII, 1 g) in chloroform (100 ml) was treated with manganese dioxide (14 g). After stirring at room temperature for 22 hr the excess reagent was removed by filtration and the chloroform was evaporated. The residue was chromatographed on an alumina column (activity 2). Elution with chloroform gave some 3,6-dione, followed by the desired **5α-cholest-7-en-3β-ol-6-one** (XLIX): yield 400 mg (40%); mp 196–197° (petroleum ether–$CHCl_3$); λ_{max} 246.5 mμ (log ϵ 4.10); ν_{max} 3570 (OH), 1650, and 1605 cm^{-1} (CO–C=C); $[\alpha]_D$ $-3.63°$ (*c* 1.1).

Anal. Calcd for $C_{27}H_{44}O_2$: C, 80.94; H, 11.07. Found: C, 80.99; H, 10.96.

5α-Cholestane-3,6-dione-8β-d_1 (LI).[53] Approximately 5 ml of deuterioammonia was generated by the addition of 14 ml of deuterium oxide to a stirred suspension of magnesium nitride (20 g) in mineral oil (30 ml). The deuterioammonia was collected directly in the reaction flask (equipped with a Dry Ice trap) at $-79°$ after passing through a trap at 0°. While keeping it at Dry Ice–isopropyl alcohol bath temperature, lithium wire (10 mg) was added, followed by a solution of 5α-cholest-7-en-3β-ol-6-one (XLIX, 50 mg) in 4 ml of anhydrous tetrahydrofuran. The reaction mixture was stirred for 20 min, the bath was then removed and the ammonia was allowed to boil under reflux for 40 min. A saturated solution of ammonium chloride in tetrahydrofuran was then added until the deep blue color disappeared and the ammonia was allowed to evaporate. Ether was added and the organic layer was washed with dilute hydrochloric acid and sodium bicarbonate solutions and finally with water. Drying and evaporation of the solvent gave a semicrystalline residue (47 mg) which was dissolved in acetone and oxidized with chromic acid. After the usual work-up, the product was dissolved in methanol (20 ml) containing 0.2 g of sodium hydroxide and heated under reflux for 15 min to exchange any deuterium introduced at C-7. According to tlc spot test, the product was contaminated with some hydroxy ketone and, therefore, the oxidation step was repeated. The resulting product was purified by tlc in methylene chloride giving 45 mg (90%) of diketone. Recrystallization from methanol gave 13 mg of **5α-cholestane-3,6-dione-8β-d_1** (LI): mp 160–164° (lit.[31] mp 169–171°); ν_{max} 1700 cm^{-1} (C=O).

5α-Cholestane-8β-d_1 (LII).[53] The 5α-cholestane-3,6-dione-8β-d_1 (LI, 40 mg) was reduced under modified Huang-Minlon conditions (see above) and purified by filtration through a small alumina column (0.5 g, activity 2) using petroleum ether as eluent. The crude product (16 mg, 44%) upon recrystallization from methanol–ether gave **5α-cholestane-8β-d_1** (LII, mp 72–75°).

5α-Cholestane-7,7-d_2 (LIX).[54] A solution of 5α-cholestan-7-one (LVII, 0.5 g) and *p*-toluenesulfonyl hydrazide (0.5 g) in methanol (100 ml) containing five drops of hydrochloric acid was heated under reflux for 1 hr. The hydrazone began to precipitate immediately. After cooling, dilute hydrochloric acid was added and the suspension was extracted with ether. Washing, drying, and evaporation of the ether gave 0.65 g (91%) of the tosylhydrazone derivative LVIII, mp 212–212.5° dec.

Anal. Calcd for $C_{34}H_{54}N_2O_2S$: N, 5.05; S, 5.72. Found: N, 5.37; S, 5.91.

The tosylhydrazone LVIII (100 mg) was dissolved in deuteriomethanol (10 ml) and sodium borodeuteride (100 mg) was added. After heating under reflux for 4 hr, the reaction mixture was cooled, dilute hydrochloric acid was added, and the product was extracted with ether. Washing, drying, and evaporation of the solvent gave 59 mg (88%) crude product which was contaminated with some olefin. Purification by tlc on 10% silver nitrate containing silica gel H in hexane, followed by recrystallization from methanol, gave pure **5α-cholestane-7,7-d_2** (LIX), mp 80–81°. (For isotopic composition see Table II.)

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(52) This experiment was performed by Dr. R. H. Shapiro of this laboratory.

(53) This reaction was carried out by Dr. Erich Blossey in this laboratory.

(54) This reaction was carried out by Dr. Zvi Pelah in this laboratory

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Electron Spin Resonance Spectra of Sulfone-Containing Aromatic Anion Radicals. Inductive Effects of the Sulfone Residue

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Contribution from the Department of Chemistry, Hope College,
Holland, Michigan 49423. *Received April 25, 1968*

Abstract: The effect of the sulfone dipole on esr spectra of aromatic anion radicals containing a sulfone residue is examined. This effect is approximated by increasing the electronegativity of the α-carbon atom of the aromatic ring, *i.e.*, setting $\alpha = \alpha_C + K\beta_{CC}$. For $K = 1.05$, modified Hückel calculations predict spin distributions in good agreement with esr results for diphenyl sulfone, dibenzothiophene sulfone, and thianthrene tetroxide anion radicals without postulating "d orbital" conjugation.

In the last few years several papers have appeared discussing d orbital effects on the esr spectra of sulfone-containing aromatic anion radicals.[1–3] Using the basic d orbital sulfone model proposed by Moffitt[4] and Koch and Moffitt,[5] Vincow[1] was able to calculate a theoretical spin density distribution for thioxanthone sulfone anion radical (I) which agreed well with experi-

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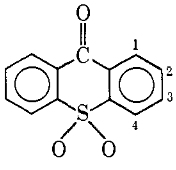
(1) G. Vincow, *J. Chem. Phys.*, 37, 2484 (1962).

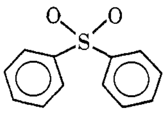
(2) E. T. Kaiser, M. M. Urberg, and D. H. Eargle, Jr., *J. Am. Chem. Soc.*, **88**, 1037 (1966).

(3) R. Gerdil and E. A. C. Lucken, *Mol. Phys.*, 9, 529 (1965).

(4) W. E. Moffitt, *Proc. Roy. Soc.* (London), **A200**, 409 (1950).

(5) H. P. Koch and W. E. Moffitt, *Tran. Faraday Soc.*, 47 (1951).


I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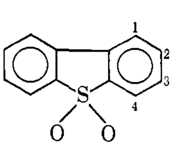
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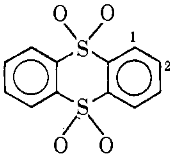

IV

ment.[6] Vincow described the $3d_{yz}$ orbital of the sulfone residue with the Hückel parameters $\alpha_S = \alpha_C - 3.0\beta_{CC}$, $\beta_{C,S} = 0.4\beta_{CC}$.

Kaiser, Urberg, and Eargle[2] described the $3d_{z^2}$ orbital of the sulfone residue with the parameters $\alpha_S = \alpha_C - 2.6\beta_{CC}$, $\beta_{CS} = 0.99\beta_{CC}$, which gave good results for the diphenyl sulfone anion radical II.

Gerdil and Lucken[3] described these two orbitals by the parameters $\alpha_S = \alpha_C - 2\beta$, $\beta_{CS} = 0.8\beta_{CC}$. These parameters gave good results for the anion radicals of diphenyl sulfone and reasonable results for dibenzothiophene sulfone (III). They found that better agreement with experiment is found for thianthrene tetroxide (IV) anion radical if β_{CS} is lowered to $0.6\beta_{CC}$. Some of these results are summarized in Table I.

Table I. Calculated and Experimental Spin Densities. d Orbital Model

Anion radical	Posn	Exptl	Calcd	K^a	δ^a	Ref
Thioxanthane	1	0.102	0.105	−3.0	0.4	1
sulfone	2	0.023	−0.025			
(Q = 23 G)	3	0.135	0.135			
	4	0.036	−0.037			
Dibenzothiophene	1	10.0044	0.0006			3
sulfone	2	0.104	0.0659	−2.0	0.8	
(Q = 25 G)	3	0.086	0.0844			
	4	0.0096	0.0060			
Diphenyl	*o*	0.095	0.0951	−2.6	0.99	2
sulfone	*m*	0.028	−0.0246			
(Q = 25 G)	*p*	0.190	0.1887			
	o	0.096	0.087	−2.0	0.8	3
	m	0.026	−0.022			
	p	0.185	0.178			
Thianthrene	1	0.0026	−0.0119	−2.0	0.8	3
tetroxide	2	0.0844	0.0717			
	1	0.0026	−0.0257	−2.0	0.6	3
	2	0.0844	0.0807			

[a] $\alpha_S = \alpha_C + K\beta_{CC}$, $\beta_{CS} = \delta\beta_{CC}$.

It is curious that similar parameters give calculated spin densities in good agreement with experiment for different d orbitals in diphenyl sulfone and dibenzothiophene sulfone while widely different parameters are needed for the same orbital in dibenzothiophene sulfone and thioxanthone sulfone.

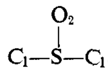
Strong conjugative interactions are proposed for these systems. It is found, however, that in bis(p-nitrophenyl) sulfone anion radical, the electron is strongly localized in one ring.[7,8] In bis(p-nitrophenyl)methane anion radical,[7] however, the spin is completely delocalized. This is hardly consistent with a strongly conjugating sulfone residue.

The purpose of this paper is to suggest that the dominant effect of the sulfone residue in these radicals is possibly inductive in nature. It is not argued that d orbital conjugation does not exist, but rather that its effect has been overestimated and that the inductive effects of the highly polar sulfone residue would affect esr spectra in the same way as does conjugation.

Discussion

It has been previously suggested[8] that inductive electron-withdrawing residues affect the esr spectra of many aromatic anion radicals in much the same way as does conjugation between aromatic rings.

Consider the two fragments A and B.


$$C_1\overset{O_2}{\overset{|}{-S-}}C_{1'}$$
A

$C_1—C_{1'}$

B

It is often found that the first unfilled molecular π orbital in an aromatic system is symmetrical on reflection through a plane perpendicular to the molecular plane. Assuming positions 1 and 1′ are equivalent in the molecule (as they are in the cases that follow) the orbital of proper symmetry to represent positions 1 and 1′ in the first unfilled MO is given by

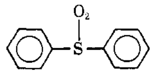
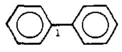
$$\psi_1 = (1/\sqrt{2})(\phi_1 + \phi_{1'})$$

For fragment A let us represent the electron-withdrawing effect of the sulfone residue on carbons 1 and 1′ by $\alpha_1 = \alpha + K\beta$, neglecting any possibility of conjugation. Then $\int\psi_1 H\psi_{1'} = \alpha + K\beta$.

For fragment B, if $\int\phi_1 H\phi_{1'} = \delta\beta$, $\int\psi_1 H\psi_1 = \alpha + \delta\beta$. To a first approximation, then, the effect of an electron-withdrawing group becomes mathematically equivalent to a partial π bond between positions 1 and 1′, this bond being represented by $K = \delta$.

McLachlan[9] has shown that the spin distribution in the biphenyl anion radical can be reproduced quite well if $\beta_{1,1'} = \beta$. The striking similarity between the coupling constants of the biphenyl anion radical and those of diphenyl sulfone anion radical (Table II) suggests that in a purely indictive model of the sulfone group $K \simeq 1$. Thus one predicts that the esr spectra

Table II. Coupling Constants for the Anion Radicals of Diphenyl Sulfone and Biphenyl (in Gauss)

Position	 Diphenyl sulfone[2]	 Biphenyl[9]
ortho	2.37	2.75
meta	0.70	0.45
para	4.74	5.50

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[6] Since the publication of Vincow's paper[1] the coupling constants have been rigorously assigned to positions in this radical. The experimental assignments agree with Vincow's calculation: (a) M. M. Urberg and E. T. Kaiser, *J. Am. Chem. Soc.*, **89**, 5179 (1967); (b) J. P. Keller and R. G. Hayes, *J. Chem. Phys.*, **46**, 816 (1967).

[7] J. E. Harriman and A. H. Maki, *ibid.*, **39**, 778 (1963).

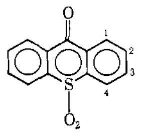
[8] M. M. Urberg, Ph.D. Thesis, The University of Chicago, Sept 1967.

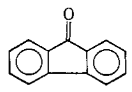
[9] A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

of aromatic sulfone anion radicals should be similar to the esr spectra of the anion radicals of analogous hydrocarbons in which the sulfone group has been replaced by a 1,1′ σ bond. Further, one does not expect this effect to depend strongly on geometry.

Some of these analogous compounds have been studied, and their spectra are compared in Tables III and IV.

Table III. Coupling Constants for the Anion Radicals of Thioxanthone Sulfone and Fluorenone (in Gauss)

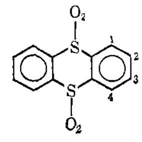


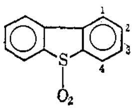


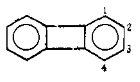
Position	Thioxanthone sulfone		Fluorenone		
	DME[6a]	Ethanol[1,6a]	DMF[a]	DME[b]	Ethanol[b]
1	2.04	2.35	1.96	2.01	2.67
2	0.36	0.52	0.03	0.17	0.38
3	3.07	3.10	3.07	3.01	3.34
4	0.84	0.82	0.65	0.67	0.73

[a] R. Dehl and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 1793 (1963). These numbers have been included here because they have been experimentally assigned to positions. The assignment of coupling constants in each of the other solvents is based on this assignment. [b] P. B. Asynscough and R. Wilson, *J. Chem. Soc.*, 5412 (1963).

Table IV. Coupling Constants for the Anion Radicals of Thianthrene Tetroxide, Dibenzothiophene Sulfone, and *o*-Biphenylene (in Gauss)







Position	Thianthrene[b,c] tetroxide	Dibenzothiophene[3,b] sulfone	*o*-Biphenylene[a]
1	0.07	0.11	0.21
2	2.11	2.61	2.86
3	2.11	2.15	2.86
4	0.07	0.24	0.21

[a] A. Carrington and J. dos Santos Veiga, *Mol. Phys.*, **5**, 285 (1962), found that they could calculate the spin distribution in *o*-biphenylene if they used $\beta_{\mathrm{OO}'} = {}^2/_3\beta$. If $\beta_{\mathrm{O.O}'}$ is increased to β the spin density at position 1 is increased and that at position 2 is decreased. Since ρ_1 is predicted to be negative, increasing $\beta_{\mathrm{O.O}}$, brings the predicted spin distribution into better agreement with that found for the thianthrene tetroxide anion radical. Unfortunately, they did not do a McLachlan calculation using $\beta_{\mathrm{O.O}'} = \beta$. [b] M. Urberg and E. T. Kaiser, unpublished results. For the hydrogens in the 1 position of thianthrene tetroxide a coupling constant of 0.069 G was measured. [c] E. T. Kaiser and D. H. Eargle, Jr., *J. Chem. Phy.*, **39**, 1353 (1963).

In each set of analogous radicals the order of the magnitudes of the coupling constants is essentially the same, and the coupling constants are strikingly similar. This confirms the expectation that a purely inductive model of sulfone π intereactions would yield theoretical spin distributions which are in good agreement with the experiment, and the range of inductive parameters necessary for different compounds should not be great.

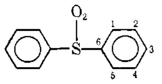
The purpose of this paper is to quantitatively examine this inductive model to see if a consistent inductive parameter K can describe the contribution of the sulfone residue in several systems. The compounds under study are diphenyl sulfone, thianthrene tetroxide, and dibenzothiophene sulfone anion radicals. No calculation has been done for thioxanthone sulfone since there are two extra parameters involved in the ketone description and it is desirable to limit our discussion to one parameter only. The qualitative discussion above shows that the model is adequate for this system also.

Calculations

The calculations were done on the IBM 1130 computer at Hope College. The usual Hückel approximations were used.[10] All α and all β integrals were assumed to be equal except for those involving the carbon atom α to the sulfone residue. That carbon atom was represented by $\alpha_1 = \alpha_C + K\beta$. The value of

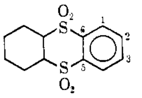
Table V. Calculated and Experimental Spin Densities (Q = 25 G)

Diphenyl Sulfone (II)



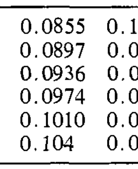
K	1	2	3	6
0.90	0.0919	−0.0011	0.1858	0.1326
0.95	0.0948	−0.0023	0.1860	0.1291
1.00	0.0977	−0.00354	0.1862	0.1256
1.05	0.1005	−0.0047	0.1864	0.1221
1.10	0.1032	−0.0058	0.1866	0.1187
Expt[3]	0.095	0.028	0.190	...

Thianthrene Tetroxide (IV)



K	1	2	5
0.90	0.0029	0.0908	0.1563
0.95	0.0057	0.0898	0.1545
1.00	0.0086	0.0888	0.1525
1.05	0.0117	0.0880	0.1503
1.10	0.0149	0.0873	0.1479
Expt[a]	0.0028	0.0844	...

Dibenzothiophene Sulfone (III)



K	6	1	2	3	4	5
0.90	0.15913	−0.0008	0.0855	0.1039	−0.01513	0.1674
0.95	0.1603	−0.0028	0.0897	0.0986	−0.0098	0.1670
1.00	0.1614	−0.0046	0.0936	0.0936	−0.0045	0.1604
1.05	0.1625	−0.0062	0.0974	0.0888	−0.0008	0.1566
1.10	0.1635	−0.0076	0.1010	0.0843	−0.0062	0.1526
Expt[a]	...	0.0044	0.104	0.086	0.0096	...

[a] See Table IV, footnote *b*.

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(10) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

K was varied systematically from 0.7 to 1.2. The method of McLachlan[9] was used to correct for spin polarization of the paired π electrons.

Results

Table V lists some of the spin densities calculated by this procedure along with "experimental" spin densities ($Q = 25$ G/electron).

Values of K between 1.00 and 1.10 give predicted spin densities in close agreement with experiment for all compounds studied. The value $K = 1.05$ predicts spin densities whose average deviation from the experimental results is 0.0074, corresponding to 0.19 G for all positions of these three compounds. The largest deviation, 0.0247 (0.62 G), is for the *meta* position of the diphenyl sulfone anion radical.

Conclusions

The spin density distributions in sulfone-containing aromatic anion radicals can be adequately explained by an inductive model for the sulfone residue. The inductive effect of the sulfone group was represented by assigning the Hückel coulomb integral of the α carbon atom the value $\alpha = \alpha_C + (1.05 \pm 0.05)\beta_{CC}$ in this work.

While it is not necessary to postulate d orbital interactions to explain the esr spectra of these systems, these calculations do not demonstrate that d orbital conjugation is not important in sulfone-containing aromatic systems. Since d orbital conjugation does affect calculated spin distributions in much the same way as do inductive effects, it is impossible to separate these two effects on the basis of simple calculations.

These results are similar to results obtained for systems containing divalent sulfur. It is not necessary to postulate any sulfur d orbital participation to explain the esr spectra of thioxanthone,[8] dibenzothiophene,[11] and 2,1,3-benzothiodiazole.[12]

Acknowledgment. The authors wish to thank Dr. Richard Brockmeier, Department of Physics, Hope College, for assistance in operating the IBM 1130 computer.

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(11) R. Gerdil and E. A. C. Lucken, *J. Am. Chem. Soc.*, **87**, 213 (1965).

(12) E. T. Strom and G. A. Russel, *ibid.*, **87**, 3326 (1965).

Pyridine-Induced Solvent Shifts in the Nuclear Magnetic Resonance Spectra of Hydroxylic Compounds[1]

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Contribution from the Lilly Research Laboratories, Indianapolis, Indiana 46206, and the Department of Chemistry, Indiana University, Bloomington, Indiana 47401. *Received April 8, 1968*

Abstract: Proton chemical shifts for a wide variety of structurally different compounds containing the hydroxyl function have been measured in deuteriochloroform and pyridine-d_5. The solvent shifts ($\Delta = \delta_{CDCl_3} - \delta_{C_5D_5N}$) observed are rationalized in terms of specific solute–solvent complexes between pyridine molecules and the polar hydroxyl function in the solute molecules. It is found that in saturated cyclic systems, protons occupying positions 1,3-diaxial, vicinal, or geminal to a hydroxyl function are deshielded. In phenolic systems, protons *ortho* to a hydroxyl function experience much larger deshielding effects than protons in the *meta* or *para* positions. Pyridine-induced solvent shifts can therefore be extremely useful in establishing both the location and stereochemical nature of protons situated in the vicinity of hydroxyl functions.

Pyridine has for some time now been recognized as a useful solvent for the nmr analysis of molecules containing polar functional groups for solubility reasons as well as for increased spectral simplification relative to chloroform or carbon tetrachloride.[3–5] Because of the ability of aromatic systems like pyridine to coordinate at electron-deficient sites within a solute molecule, protons situated in the vicinity of a polar functional group invariably experience large screening effects as a result of the large anisotropy in the magnetic susceptibility of the aromatic system.[6] The correlation of chemical shifts induced in benzene and pyridine (relative to chloroform) with specific structural features in a variety of carbonyl-containing compounds is well known, and the potential of this technique for use in structural analysis has been amply demonstrated.[7]

We wish to report a further extension of the use of pyridine to the study of polar molecules containing the

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(1) D. D., B. L. M., and E. W. gratefully acknowledge the support of Eli Lilly and Co. for that portion of this work carried out at Indiana University.

(2) (a) Lilly Research Laboratories; (b) Department of Chemistry, Indiana University.

(3) G. Slomp and F. MacKellar, *J. Amer. Chem. Soc.*, **82**, 999 (1960).

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