Determination of pK_a of V. pH measurements were made at 26° using a glass electrode with a Beckmann G Model pH meter in 90% ethanol (standardized against aqueous buffer). The titration curve gave a sharp break at 1 equiv of base. The pH at half-neutralization was 4.2 on titration with either sodium hydroxide or potassium ethoxide.

D_2O Exchange Experiment. A saturated solution of compound IV in perdeuteriodimethyl sulfoxide was prepared in a 4-mm nmr tube. A few microliters of D_2O was added to this solution and the spectrum was recorded at intervals using a HR-60 nmr spectrometer. The doublet at τ 3.0 started disappearing and completely disappeared after 2 hr. No change in any other aliphatic hydrogen peaks was noted.

Spin Decoupling.[20] A Howlett-Packard audio frequency oscillator (200J) and counter (5512A) were used with a Varian integrator utilizing the field-sweep technique. The spectra were recorded for 5% solution of IV in trifluoroacetic acid, and the chemical shift of each proton was measured by the usual side-band technique. The integrator operated in conjunction with a 2-kc field modulator using a modulation index of 1989 cps. The chemical shift between the doublet at τ 5.8 and 6.8 was approximately 105 cps. The triplet at τ 6.8 completely collapsed to form a doublet at the irradiation frequency 1877 cps. The doublet at τ 5.8 collapsed to form a single peak at the irradiation frequency 2088 cps. The modulation frequency differences were 110 and 100 cps for the first and second irradiations, respectively, in agreement with the measured chemical shifts.

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(20) We are grateful to Dr. Kermit C. Ramey, Research and Development Department, Atlantic Refining Co., for these data.

Diaryl Sulfone Anion Radicals[1,2]

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Abstract: The anion radicals of diphenyl sulfone and *p,p′*-ditolyl sulfone possess epr spectra which are closely related to those of the corresponding hydrocarbons, biphenyl and *p,p′*-bitolyl. This indicates that a strong conjugation mechanism is operating between the two aromatic rings of the sulfone radicals. Gas chromatographic analysis shows that the spectra of the reduced diaryl sulfones are not due to the presence of biphenyl or *p,p′*-bitolyl impurities. The spin densities observed at the ring positions of the diphenyl sulfone anion radical have been accounted for by means of a Hückel calculation assigning $\alpha_{SO_2} = \alpha_C - 2.60\beta_{C-C}$ and $\beta_{C-SO_2} = 0.99\beta_{C-C}$ as Hückel parameters for the sulfone $d_{(3z^2-r^2)}$ orbital which has the correct symmetry to combine with the two aromatic rings. The spin density on the sulfone group is not large.

Previous work on anion radicals produced by the alkali metal reduction of a variety of aromatic sulfones has demonstrated that these species tend to possess considerably narrower epr (electron paramagnetic resonance) spectra than those formed from the corresponding sulfides as illustrated in Table I.[2a–c] These observations have been interpreted to indicate that the total spin density located on the aromatic rings of the sulfone anion radicals is lowered by the concentration of spin density on the sulfonyl groups. In this paper we report that the anion radicals of diphenyl sulfone and *p,p′*-ditolyl sulfone provide a contrasting situation; relatively little spin density appears to be withdrawn from their aromatic rings by the sulfonyl groups.

Table I

Compound	Spectral width of anion radical, gauss
Thiaxanthone	17.3
Thiaxanthone sulfone	14.5
Dibenzothiophene	25.4
Dibenzothiophene sulfone	10.7

Experimental Section

Commercial samples of the sulfones were recrystallized before use. Formation of the anion radicals of the sulfones was accomplished by reduction of the parent compounds over potassium mirrors in 1,2-dimethoxyethane at −70°.[4–6] Spectra were taken at that temperature since at higher temperatures the resolution attained was inferior, and the anion radicals were unstable. Measurements of the epr spectra were carried out on Varian spectrometers.[7]

Since the epr spectrum observed when diphenyl sulfone was reduced by potassium was found to have some resemblance to that of the well-known biphenyl anion radical, it was felt important to exclude the possibility that biphenyl might be formed during the reduction of the sulfone. Accordingly, after the metallic reduction of a sample of the sulfone was complete, the solution was opened to air and analyzed by vapor phase chromatography by the procedure previously described by Britt and Kaiser.[8,9] This analysis showed that biphenyl was not formed in a detectable amount.

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(1) Grateful acknowledgment is made to the Donors of the Petroleum Research Fund for support of this research. M. M. U. thanks the National Science Foundation for a Predoctoral Fellowship.

(2) Previous publications in the series on Conjugative Effects of Sulfur in Aromatic Anion-Radicals include (a) E. T. Kaiser and D. H. Eargle, Jr., *J. Am. Chem. Soc.*, **85**, 1821 (1963); (b) E. T. Kaiser and D. H. Eargle, Jr., *J. Chem. Phys.*, **39**, 1353 (1963); (c) D. H. Eargle, Jr., and E. T. Kaiser, *Proc. Chem. Soc.*, 22 (1964); (d) E. T. Kaiser and D. H. Eargle, Jr., *J. Phys. Chem.*, **69**, 2108 (1965).

(3) To whom inquiries regarding this paper should be addressed at the University of Chicago.

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(7) A spectrometer at the U. S. Naval Research Laboratory was used with the kind consent of Dr. William B. Moniz of that laboratory.

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(9) The authors wish to thank Mr. P. L. Hall for performing the vapor phase chromatographic analysis.

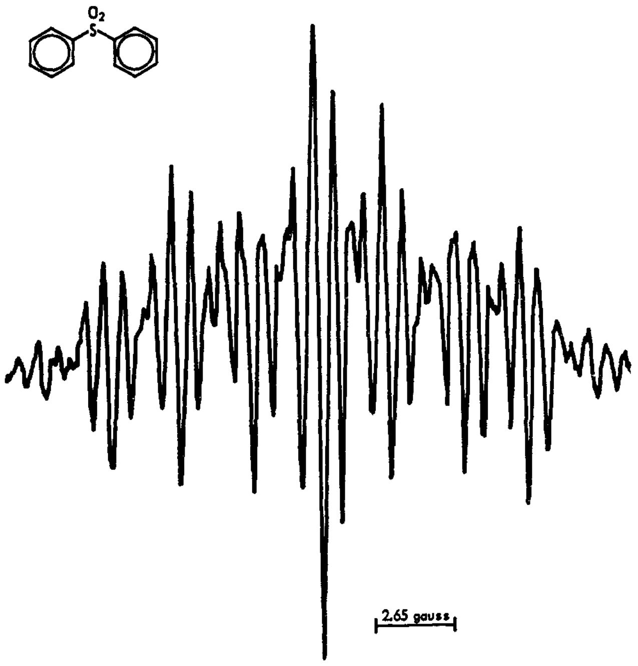

Figure 1.

Results

The epr spectrum of the diphenyl sulfone anion radical is shown in Figure 1. It is immediately seen to be similar to that of the biphenyl anion radical.[10,11] The total spectral widths are essentially the same (biphenyl 22.7 g, diphenyl sulfone 22.0 g) and each of the spectra exhibits nine principal groups of lines. Also, in both spectra these nine groups appear to be further split into five components although in the case of the diphenyl sulfone anion radical the hyperfine lines tend to overlap slightly into the neighboring groups.

The reduction of *p,p'*-ditolyl sulfone gave rise to a very complex epr spectrum. The spectrum was incompletely resolved, but it was seen to be similar to that of the *p,p'*-bitolyl anion radical.[12]

Table II

Anion radical of compound	No. of major lines/ splitting, gauss	Total width, gauss
Biphenyl	9/2.65	22.7
Diphenyl sulfone	9/2.37	22.0
p,p'-Bitolyl	17/2.65	39.1
p,p'-Ditolyl sulfone	15/2.32[a]	34.8 (39.4)[a]
Dibenzothiophene sulfone	5/2.4	10.7
Thianthrene disulfone	5/2.1	8.9

[a] Due to incomplete resolution of the epr spectrum only 15 of the expected 17 major lines were seen. A total width of 39.4 gauss would be expected had 17 lines been observed.

The principal features of the spectra of the sulfone anion radicals are summarized in Tables II and III. The assignments of the splittings observed for the epr spectra of the reduced diaryl sulfones given in Table III are based on the analogy between these spectra and those of the corresponding reduced hydrocarbons. The spectrum of the *p,p'*-dideuteriodiphenyl sulfone anion radical was found to be consistent with these splitting assignments.

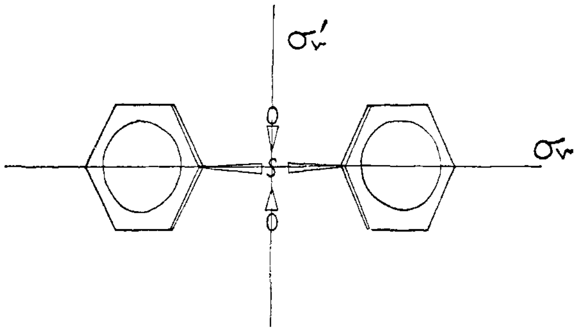

Figure 2.

Table III

Anion radical of compound	Splitting assignments, gauss: *ortho* position	*meta* position	*para* position
Diphenyl sulfone	2.37	0.70	4.74
p,p'-Ditolyl sulfone	2.32	0.77	5.01

Discussion

In 1951 Koch and Moffitt showed that empty d orbitals of symmetry A_1, A_1', A_2, B_1, and B_2 in the C_{2v} symmetry system described in Figure 2 are available in the sulfone group.[13] Their theoretical treatment was used to explain the physical properties of sulfones which seemed to require some participation of the sulfone group, *e.g.*, dipole moments.

Vincow was able to demonstrate that the epr spectrum of the thiaxanthone anion radical could be explained by proposing a small but real interaction of the B_2 orbital of the sulfone group with the π electron system.[14]

In the present work we have reached the conclusion that the postulation of participation by an orbital of A_1 symmetry in conjugation with the π electrons of the aromatic rings can explain the epr spectrum of the diphenyl sulfone anion radical.

Calculations

The B_1 orbital described by Koch and Moffitt is intimately tied up with the bonding structure between the sulfur and the oxygens of the sulfone group in diphenyl sulfone. Thus, it is expected to be of high energy and unavailable for significant overlap with the aromatic rings. Its presence will therefore be neglected. The A_2 and B_2 orbitals cannot combine with

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Table IV[a]

Position	Spin density
2	0.095
3	0.028
4	0.190

[a] The signs are of course not known.

Table V. Spin Densities

K	δ[a]	1	2	3	4	SO_2
−2.40	0.883	0.1185	0.0878	−0.0214	0.1862	0.1253
	0.919	0.1128	0.0917	−0.0233	0.1860	0.1290
	→0.933	0.1105	0.0933	−0.0241	0.1860	0.1303
	0.956	0.1071	0.0956	−0.0252	0.1859	0.1322
	0.990	0.1014	0.0998	−0.0270	0.1860	0.1350
−2.50	0.919	0.1178	0.0895	−0.0221	0.1876	0.1196
	0.941	0.1144	0.0918	−0.0232	0.1875	0.1217
	→0.956	0.1122	0.0934	−0.0239	0.1874	0.1230
	0.969	0.1099	0.0950	−0.0247	0.1874	0.1242
	0.990	0.1066	0.0973	−0.0258	0.1874	0.1258
−2.60	0.956	0.1170	0.0912	−0.0228	0.1888	0.1145
	0.977	0.1137	0.0936	−0.0238	0.1887	0.1164
	→0.990	0.1115	0.0951	−0.0246	0.1887	0.1176
	1.005	0.1092	0.0966	−0.0253	0.1887	0.1187
	1.025	0.1060	0.0989	−0.0263	0.1887	0.1203
−2.70	0.919	0.1269	0.0853	−0.0197	0.1902	0.1034
	0.956	0.1215	0.0891	−0.0216	0.1900	0.1068
	→0.990	0.1160	0.0930	−0.0234	0.1899	0.1099
	→1.025	0.1106	0.0968	−0.0252	0.1899	0.1127
	1.061	0.1052	0.1006	−0.0269	0.1899	0.1152
−2.80	0.956	0.1257	0.0871	−0.0205	0.1912	0.0998
	0.990	0.1203	0.0909	−0.0223	0.1910	0.1029
	→1.025	0.1150	0.0947	−0.0241	0.1910	0.1057
	1.061	0.1096	0.0985	−0.0258	0.1910	0.1083
	1.097	0.1043	0.1022	−0.0275	0.1911	0.1106

[a] Arrows indicate the values of δ which give approximately the right ratio of splitting constants.

those of the aromatic rings since orbitals on the phenyl groups with A_2 and B_2 symmetry have 0 coefficients at the 1,1′ positions of the rings. Thus, only A_1 orbitals are effective in conjugation. The two orbitals available are designated A_1 and A_1' by Koch and Moffitt.[13] They can be described as $3d_{(3z^2-r^2)}$ and $3d_{(x^2-y^2)}$, respectively. (The coordinates are shown in Figure 3.) They are formed by using linear combinations of the usual d orbitals to take the sulfur–oxygen bonds into account. The large lobe of the A_1 orbital between the phenyl rings makes very effective overlap possible. The A_1' orbital on the other hand has much less electron density where it counts. Thus, the former orbital is probably much more important to conjugation than the latter. In any event, participation by both orbitals can be considered if we assume that the orbital used in the calculation is some linear combination of the two which will still be of A_1 symmetry. That is, we can solve a secular equation for the A_1 and A_1' orbitals to get a high and a low energy orbital. The above interpretation is valid since the form of the functions used does not enter explicitly into the calculation.

The calculation was done using the simple Hückel approximations. All α and β integrals were taken to be equal except for those specifically involving the sulfone group.

$$\alpha_{SO_2} = \alpha_C + K\beta_{C\text{-}C}$$

$$\beta_{C\text{-}SO_2} = \delta\beta_{C\text{-}C}$$

The 13 × 13 secular determinant resulting from the 12-carbon 2p orbitals and the sulfone orbital can be factored by symmetry into A_1, A_2, B_1, and B_2 determinants of order 5, 2, 4, and 2, respectively. The sulfone integrals enter only into the A_1 determinant.

The similarity of the diphenyl sulfone anion radical spectrum with that of biphenyl and the small spin densities at the *meta* positions found experimentally and in preliminary calculations led us to suspect that the spin densities at the *meta* positions are negative. Thus the IBM 1074 computer was programmed to do McLachlan's approximate SCF treatment to account for the perturbation of the unpaired electron on the system.[15] We took $\lambda = 1.20$ which is a typical value used by McLachlan and others.

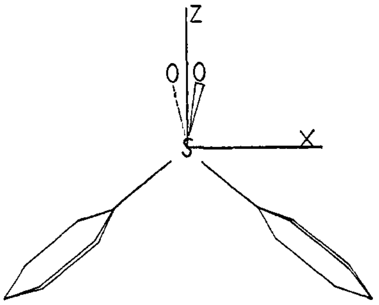

Figure 3.

If we assume that $Q = 25$ gauss/electron, we can get the "experimental" spin densities for the diphenyl sulfone anion radical (Table IV).

Table V lists results of the calculation. Theoretical spin densities are given along with the values of K

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and δ used. Values of δ are indicated which give approximately the right ratios of splitting constants. The values at $K = -2.60$ and $\delta = 0.990$ are in excellent agreement with experiment if we assume $Q = 25$. Unfortunately we have no way to determine the spin densities on the sulfone group and on the 1 positions. Little is known about the interactions of a free spin with a sulfur–carbon bond, nor with a sulfur nucleus in a sulfone linkage. Therefore even if we had ^{13}C coupling constants and those for ^{33}S, interpretation would be difficult.

In order to exclude the possibility that direct 1,1′ interactions were responsible for the conjugation between the two rings, we calculated a theoretical spectrum assuming only this interaction, *i.e.*, in direct analogy to biphenyl. Using the same procedure as described above and varying $\beta_{1,1'}$ from 0 to $0.40\beta_{C-C}$, we found that we could not approach the observed spectrum. This was also noted by McLachlan[15] who pointed out that $\beta_{1,1'}$ had to be larger than $0.5\beta_{C-C}$ to approach the observed spectrum for the biphenyl radical. Overlap of that extent was considered unlikely.

Conclusions

The calculations we have done demonstrate that the spin densities observed for the diphenyl sulfone anion radical can be adequately accounted for by proposing that an orbital of A_1 symmetry on the sulfone group is available for effective conjugation with the two phenyl rings. The exact nature of the orbital is not implied in a simple Hückel calculation, but if we wish to use LCAO language, it would seem that the orbital is mainly the sulfur $3d_{(3z^2-r^2)}$ orbital.

Nucleophilic Dequaternization of Condensed Azetidinium Salts

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Abstract: Complete reversal of quaternization by nucleophilic C substitution occurs with [1.5]methylenequinolizidinium tosylate and brosylate on reaction with nucleophiles, *e.g.*, sodium iodide, lithium bromide, sodium cyanide, and sodium methoxide in aprotic solvents (methylene chloride, or chloroform, and acetone). The homolog [1.5]ethylenequinolizidinium ion is not susceptible to this reaction, hence (1) steric compression in the condensed nonplanar azetidinium system, (2) the relative nucleophilicity of the reactants, and (3) the relative nucleophilicity of the solvents seem to determine whether internal quaternization or dequaternization takes place.

The quaternary salt[1] obtained from tosyllupinine[2] (IIa) has been shown[3] to have the condensed azetidinium ring structure I, as opposed to a diazaoctane ring (1) by osmometric molecular weight determination, (2) by infrared and nmr spectra, and (3) by X-ray crystallography[4] (this latter revealed noncoplanarity of the four-membered ring). It was also found that *quantitative ring opening* occurred when the tosylate Ia was dissolved in dichloromethane and treated with lithium bromide in acetone. "Bromolupinane,"[5,6] *i.e.*, (−)-1-bromomethylquinolizidine (IIc), was formed as the only product according to vpc; an authentic sample was prepared from lupinine with phosphorus tribromide.

Similarly, sodium iodide in acetone gave (−)-1-iodomethylquinolizidine (IId), while sodium cyanide in methanol, when added to the solution of the quaternary tosylate in dichloromethane, led to homolupinic nitrile (IIf).

Brosyllupinine was prepared. This is crystalline (mp 107°) but when heated to 85° for 3 hr is quantitatively isomerized during the operation to I brosylate (mp 155°) without melting. The brosylate has the same nmr signals as the tosylate (except for methyl protons) and undergoes the same substitution reactions in methylene chloride.

The brosylate gave, with sodium methoxide, lupinine methyl ether (IIg) and no trace of an olefinic Hofmann degradation product. In view of these facts, the alkali hydrolysis of I tosylate into lupinine (IIh) might also be considered as a nucleophilic substitution on the ring methylene carbon 11.

The conversion of I brosylate into II iodide was followed by nmr; it proved to be a very fast reaction as was the cleavage by lithium bromide to IIc.

Curiously enough, I picrate gave with aqueous hydrobromic acid a crystallized bromide, obviously Ic. The tetraphenylborate Ie is stable as well. In alcohol the iodide Id was formed from the tosylate along with iodomethylquinolizidine (IId). The ratio salt:covalent compound is much smaller in an acetone–alcohol mixture than in pure alcohol, but larger than in dichloromethane. It seems that the weak nucleophilicity of the tosylate, brosylate, and tetraphenylborate ion stabilizes those salts while bromide, iodide, and methoxide ions as stronger nucleophiles afford ring opening to the halogenomethyl and methoxy compounds (II), respectively.

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