

**815.** *The Electron Spin Resonance Spectra of Aryl- and Benzylthio-1,4-benzosemiquinones.*

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The electron spin resonance spectra of various phenylthio- and benzylthio-1,4-semiquinones have been measured in ethanolic solution. The observed hyperfine splitting constants indicate that, contrary to the conclusions based on chemical reactivity, the sulphur atom is essentially electron-releasing in its behaviour towards an aromatic ring. There does not, therefore, appear to be any need to invoke the use of acceptor  $3d$ -orbitals by the sulphur atom.

THE influence of the divalent sulphur atom on the physical and chemical properties of molecules containing it has been the subject of extensive investigations, which have been recently reviewed.<sup>1,2</sup> The majority of chemical investigations indicate that the net effect of the sulphur atom on a conjugated or potentially conjugated system is to accept electrons, while measurements of physical properties indicate the opposite behaviour. Thus the most recent values of the Hammett sigma constant of the methylthio-group<sup>3</sup> are  $\sigma_p = 0.220$ ,  $\sigma_m = 0.225$ , while the dipole moments of 4-thiopyrones indicate considerable contributions from resonance structures having a positive charge on the sulphur atom.<sup>4</sup>

The valence-state electronegativity of divalent sulphur appears to be similar to that of the tetrahedral carbon atom,<sup>5</sup> the pure inductive effect of the methylthio-group should, therefore, be small and probably essentially electron-releasing. By virtue of its lone pairs of electrons the sulphur atom should, however, also exercise an appreciable electron-releasing mesomeric effect, although owing to the longer carbon-sulphur bond and the diffuseness of  $3p$ -orbitals, this should be less marked than for the corresponding oxygen compounds. On balance therefore if these are the only considerations which govern its behaviour, the methylthio-group would be expected to be markedly electron releasing, for the weaker mesomeric effect—compared with the methoxy-group—would be to a great extent offset by the lower electronegativity of the sulphur atom. If, however,

<sup>1</sup> Cilento, *Chem. Rev.*, 1960, **60**, 147.

<sup>2</sup> Price and Oae, "Sulphur Bonding," Ronald Press, New York, 1962.

<sup>3</sup> Wells, *Chem. Rev.*, 1963, **63**, 171.

<sup>4</sup> Price and Oae, *Chem. Rev.*, **63**, 21.

<sup>5</sup> Hinze and Jaffé, *J. Amer. Chem. Soc.*, 1962, **84**, 540.

in addition to the two phenomena already discussed the sulphur atom can use its vacant  $3d$ -orbitals as acceptors then it is possible that in some circumstances the overall behaviour of the methylthio-group would be electron-withdrawing.

The discrepancy between the chemical and physical investigations makes it difficult to decide what in fact is the real behaviour of the sulphur atom. Conclusions based on chemical behaviour are open to a number of serious objections; even if two essentially similar reactions are being compared the substituent often influences the energy and entropy of activation in different and certainly not understood ways. As far as physical methods are concerned the measurement of electronic absorption spectra involves both the ground state and the excited states of the molecule with the consequent need of hypotheses about one or the other before the results can be interpreted, while the dipole moments must be resolved into often arbitrary components before a mesomeric effect can be deduced.

Provided that an appropriate free-radical can be prepared the technique of electron spin resonance offers an excellent means of determining the electron-distribution in molecular ground-states. The electron spin resonance spectra of 1,4-semiquinones are well understood<sup>6,7</sup> and a simple theory of the effect of substituents on the ring-proton splitting constants of 1,4-benzosemiquinones has been presented.<sup>8</sup> It is an essential feature of this simple theory that no distinction is or can be made between inductive and conjugative effects, and the behaviour of a substituent is expressed in terms of a parameter measuring the change in electronegativity it produces in the carbon atom to which it is

TABLE I.

Proton hyperfine splitting constants (in oersted  $\pm 0.05$ ) for arylthio-1,4-benzosemiquinones.

	Coupling constants		
	$a_3$	$a_5$	$a_6$
Phenylthio-1,4-benzosemiquinone .....	1.52	2.72	2.12
<i>p</i> -Tolylthio-1,4-benzosemiquinone .....	1.44	2.75	2.07
<i>p</i> -Fluorophenylthio-1,4-benzosemiquinone .....	1.53	2.78	2.15
<i>p</i> -Chloro " " " .....	1.67	2.68	2.14
<i>p</i> -Bromo " " " .....	1.70	2.70	2.19
<i>p</i> -Acetyl " " " .....	2.24 *	2.33	2.24 *
<i>p</i> -Nitro " " " .....	2.23 *	2.59	2.23 *
<i>p</i> -Amino " " " .....	1.26	2.96	2.10
$\alpha$ -Naphthylthio-1,4-benzosemiquinone .....	1.51	2.77	2.21
$\beta$ - " " " .....	1.51	2.73	2.04
2,5-Diphenylthio-1,4-benzosemiquinone .....	1.25	—	1.25
2,6- " " " .....	1.91	1.91	—
2-Phenylthio-1,4-naphthosemiquinone † .....	2.36	—	—

\* Uncertainly  $\pm 0.1$  oersted owing to overlapping lines. † Uninterpreted pattern from inequivalent protons in the benzeneoid ring. Line separation  $\sim 0.4$  gauss.

attached. These facts combined with the relative ease with which a variety of alkyl- and arylthio-substituted quinones can be prepared offer a simple means of measuring the overall electronic behaviour of these substituents and the results of such an investigation are presented here.

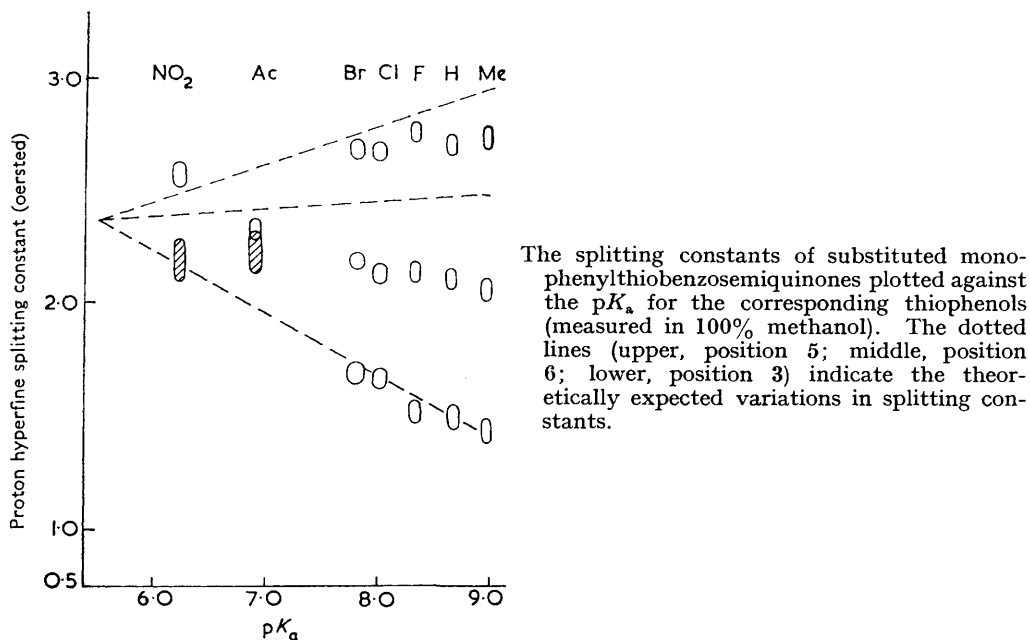
*The Arylthio-group.*—In Table I are shown the hyperfine splitting constants of various arylthio-1,4-semiquinones. The results for 2-phenylthio-1,4-naphthosemiquinone show that the proton *ortho* to the substituent in the monosubstituted free radical has one of the two smaller and probably the smallest splitting constant. The splitting constant of the 2,5-diphenylthio-derivative shows that the largest splitting constant is *para* to the substituent while the results for the 2,6-disubstituted derivative are consistent with an assignment of the intermediate splitting constant to the *meta*-proton.

<sup>6</sup> Vincow and Fraenkel, *J. Chem. Phys.*, 1961, **34**, 1333.

<sup>7</sup> Brandon and Lucken, *J.*, 1961, 4273.

<sup>8</sup> Fairbourn and Lucken, *J.*, 1963, 258.

The electronic properties of the phenylthio-group are modified by annular substituents and these modifications are reflected by the acid dissociation constants of the corresponding thiophenols. The three splitting constants of a variety of *para*-substituted phenylthio-semiquinones are plotted in the Figure against  $pK_a$  of the thiophenol.<sup>9</sup> If it is assumed that the splitting constants behave in an orderly manner, three straight lines may be drawn through these three sets of points which converge in an area around 2.3–2.5 gauss. A similar correlation obtains between the splitting constants and the Hammett *sigma* value of the substituent. The Figure implies that the phenylthio-group is electron-releasing since an electron-releasing group such as methyl increases the spread of the three splitting



constants and thus is reinforcing the behaviour of the phenylthio-group while electron-withdrawing groups have the opposite effect.

The Figure may now be directly compared with the predictions of the simple theory of substituent effects in semiquinones.<sup>8</sup> The splitting constants of the phenylthio-derivatives with the exception of that of the *meta*-proton in the monoderivative are in reasonable accord with a value for a change in coulomb integral of the substituted carbon atom of  $-0.3\beta$  where  $\beta$  is the carbon-carbon resonance integral. The comparison of theory and experiment in this case is shown in Table 2. If it is further assumed that the three splitting

TABLE 2.

Theoretical splitting constants of phenylthiobenzosemiquinones with  $\Delta\alpha = -0.3\beta$ .

1,4-Benzosemiquinone		Theory	Expt.	1,4-Benzosemiquinone		Theory	Expt.
Phenylthio	$a_3$	1.50	1.52	2,5-Diphenylthio	$a_3, a_6$	1.58	1.25
"	$a_5$	2.89	2.72	2,6-Diphenylthio	$a_3, a_5$	1.99	1.91
"	$a_6$	2.50	2.12				

constants of the monosubstituted derivatives will all be equal at a  $pK_a$  of the corresponding thiophenol of 5.5, then the three straight lines, shown broken in the Figure, are the predicted variations of the splitting constant with the acidity of the thiophenol. It can be seen

<sup>9</sup> Hudson and Klopman, *J.*, 1962, 1062. The value for *p*-nitrothiophenol is interpolated from the values of Schwartzbach, *Helv. Chim. Acta*, 1939, 22, 360.

TABLE 3.

Proton hyperfine splitting constants (in oersted  $\pm 0.05$ ) of arylthiobenzosemiquinones.

1,4-Benzosemiquinol	$a_3$	$a_5$	$a_6$	Alkyl protons
Benzylthio .....	1.28	2.77	2.10	0.61
2,5-Dibenzyl .....	0.91	—	0.91	0.79
2,6-Dibenzyl .....	1.77	1.77	—	0.57

that there is good agreement with experiment except for the protons *meta* to the substituent, where the splitting constant is smaller than 2.37 rather than greater as the theory requires. This is probably a consequence of the simplicity of the theory, which is based on the calculation of odd-electron densities by the Hückel molecular-orbital method. However, the order of the three splitting constants is given correctly and the quantitative agreement with experiment for the two extreme values is quite good.

It seems well established, therefore, that the phenylthio-group in these circumstances is behaving as an electron-releasing substituent. Moreover, since the odd electron in semiquinone radical anions is approximately non-bonding any tendency for the sulphur atom to act as an acceptor should have been noticeable.

*The Alkylthio-group.*—In Table 3 are given the splitting constants of mono- and 2,5- and 2,6-dibenzylthio-1,4-benzosemiquinone. The benzyl group was chosen for ease of preparation of the semiquinones and to simplify the interpretation of their spectra. In terms of the simple theory mentioned above, it is evident that the benzylthio-group must be considered to be even more electron-releasing than the phenylthio-group, and in Table 4 are given the theoretical results for a substituent parameter  $\Delta\alpha = -0.4\beta$ . The discrepancy for the *meta*-proton in the monoderivative is similar to that observed in the arylthio-compound.

The splitting from the alkyl protons demonstrates that the sulphur atom does in fact effectively conjugate with the aromatic ring. These splitting constants should be compared with those observed for 2,5-dimethoxy- and 2,5-diethoxy-benzosemiquinone<sup>10</sup> where the alkyl proton splitting constants are 1.05 and 1.17 oersteds, respectively, and the ring

TABLE 4.

Theoretical splitting constants of benzylthiobenzosemiquinones with  $\Delta\alpha = -0.4\beta$ .

Mono .....	$a_3$	Theory		Experiment			
		1.27	1.28	2,5-Di .....	$a_3, a_6$	1.33	0.91
„ .....	$a_5$	3.05	2.77	2,6-Di .....	$a_3, a_5$	1.77	1.77
„ .....	$a_6$	2.56	2.10				

proton splitting constant is 0.3 oersted. As expected the oxygen atom is both more electron-releasing and conjugates more effectively with the aromatic system.

Therefore, the measurements described here imply that both the aryl and alkylthio-groups are electron-releasing. The overall electron-releasing ability is comparable with, and slightly greater than, that observed for the methyl group.<sup>8</sup> It is unlikely that there is a significant contribution from the 3*d*-orbitals to the conjugation of divalent sulphur with an aromatic system.

## EXPERIMENTAL

Electron spin resonance spectra were measured at room temperature at a frequency of 9300 Mc./sec. on a modified "Microspin" spectrometer. The field sweep was calibrated at intervals against the spectrum of benzosemiquinone in aqueous ethanol ( $a_H = 2.37$  oersted).

Monophenylthio,<sup>11</sup> monobenzylthio,<sup>12</sup> 2,5- and 2,6-diphenylthio,<sup>11</sup> and 2,5-dibenzylthio-benzosemiquinone were prepared by standard methods. 2,6-Dibenzylthiobenzoquinone (m. p.

<sup>10</sup> Matsunaga and McDowell, *Canad. J. Chem.*, 1960, **38**, 1158.

<sup>11</sup> Snell and Weissberger, *J. Amer. Chem. Soc.*, 1939, **65**, 450.

<sup>12</sup> Posner and Lipski, *Annalen*, 1904, **336**, 117.

176—177°) (Found: C, 68.4; H, 4.5; S, 18.3.  $C_{20}H_{16}O_2S_2$  requires C, 68.1; H, 4.6; S, 18.2%) was isolated as a by-product in the preparation of the 2,5-dibenzylthio-derivative. The corresponding semiquinones were prepared from these quinones by either reducing them to the quinol with stannous chloride in an alcoholic solution containing a little concentrated hydrochloric acid and subsequently air-oxidising an alkaline alcoholic solution of the quinol, or by the direct action of sodium ethoxide on an alcoholic solution of the quinone. Identical spectra were obtained in each case although the solutions derived from the quinol were more stable. The other monoarylthio-semiquinones were prepared as follows: To an ethanolic solution of the thiol (0.1M) was added dropwise during 10 min. with vigorous stirring an equal volume of an ethanolic solution of benzoquinone (0.09M). To the resulting solution was added a drop of aqueous iodine solution to destroy the excess of thiol. A portion of the resulting solution was then rendered alkaline in an e.s.r. cell which was then stoppered and shaken to produce air oxidation of the substituted quinol. Spectra produced in this way for the phenylthio-derivative were identical with those produced from the separately prepared and isolated quinone or quinol.

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