# The Electron Spin Resonance Spectra of the Dibenzothiophene Radical Anion and Its Isologs and the Electronic Structure of Conjugated Sulfur-Containing Heterocycles

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*The electron spin resonance spectra of the radical anions of dibenzothiophene, dibenzofuran, and dibenzoselenophene have been measured and the hyperfine splitting constants assigned to the various protons by measurements of the splitting constants of various methylated and deuterated derivatives. The experimental hyperfine splitting constants in dibenzothiophene are compared with those calculated using two models for conjugation by the sulfur atom, with and without the participation of the sulfur 3d orbitals. It is concluded that the 3d orbitals play no significant part in either the bonding levels or the first unoccupied level of dibenzothiophene. A number of new syntheses of dimethyldibenzofurans and dibenzothiophenes are given.*

The suggestion by Longuet-Higgins[1] in 1949 that the vacant 3d orbitals of the sulfur atom in thiophene were as important in the $\pi$-bonding as the occupied 3p orbitals initiated a succession of theoretical and experimental investigations of the chemistry of organosulfur and -phosphorus derivatives in which this suggestion was developed with almost universal enthusiasm. This idea was implicit in several of the earlier theoretical discussions, but the arguments of Longuet-Higgins seemed to explain in a simple manner the similarity between thiophene and benzene and, in general, the resemblance between a sulfur atom and an ethylene molecule. This treatment of the sulfur atom has, however, been criticized on a number of occasions, and, in particular, it has been maintained that the energy of the sulfur 3d orbitals is too high for them to participate appreciably in the $\pi$-bonding in thiophene.[2]

Insofar as it yields the unpaired spin density at their proton-bearing carbon atoms, the hyperfine structure in the electron spin resonance spectra of planar conjugated free radicals affords a test of their molecular wave functions.[3] The considerations which will be discussed below suggested that the odd-electron distribution in the dibenzothiophene radical anion would be very sensitive to d-orbital participation in the $\pi$-bonding of the sulfur atom and would certainly be able to distinguish between a molecular wave function in which the sulfur atom only made use of its 3p electrons and one in which the 3d orbitals were involved to the extent suggested by Longuet-Higgins.[1]

We have, therefore, prepared the radical anions of dibenzofuran, dibenzothiophene, and dibenzoselenophene; measured their electron spin resonance spectra; and by the measurement of the spectra of deuterated and methylated derivatives, assigned the observed splitting constants to the four different protons in the first two compounds. The spin-density distributions in dibenzofuran and dibenzothiophene have been calculated by the method of McLachlan,[4] and the results for the first compound (in which the oxygen atom has essentially only its $2p_z$ electrons available for conjugation) serve as a check on the method. For dibenzothiophene, calculations were carried out using two models for the sulfur atom: one in which only the $3p_z$ orbitals were taken into consideration, and the other using in addition the $3d_{xz}$ and $3d_{yz}$ orbitals in the manner suggested by Longuet-Higgins. In the subsequent discussion, these are referred to as the p-orbital model and the d-orbital model, respectively. A distinction is also made between the term "odd-electron distribution" given by the square of the coefficients of the ring carbon atomic orbitals in the Hückel molecular orbital containing the unpaired electron and the term "spin-density distribution" given by McLachlan's equation and for which the odd-electron distribution serves as a starting point.

## Experimental

*Electron Spin Resonance Spectra.* The measurements were carried out at $-70°$ on a modified Microspin spectrometer at a frequency of 9600 Mc./sec. using magnetic field modulation at 100 kc./sec. The field sweep was calibrated at intervals against the spectrum of the naphthalene negative ion in dimethoxyethane.

*Preparation of the Radical Anions.* The following general method was employed. Into a standard electron spin resonance tube (consisting of a lower portion of 4 mm. diameter, 5 cm. long, and an upper portion of 10 mm. diameter and 5 cm. long) cooled in liquid nitrogen and containing the compound whose radical anion was to be prepared, a mirror of potassium on the upper portion of the tube and 1–2 ml. of dimethoxyethane were successively distilled under vacuum. The dimethoxyethane had previously been purified by refluxing over and distilling from sodium and was stored over sodium wire. Fluorenone was also added to the stock solution which thus contained fluorene ketyl whose continued dark color served as an indicator of the purity of the solvent. The tube was then sealed off under vacuum and allowed to warm up to the melting point of dimethoxyethane in a mixture of acetone and solid carbon dioxide, the tube being held vertically so that the solution did not come in

(1) H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **45**, 173 (1949).
(2) A. Mangini and C. Zauli, *J. Chem. Soc.*, 2210 (1960).
(3) A. Carrington, *Quart Rev.* (London), **17**, 67 (1963).
(4) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

contact with the potassium; this was also the position in which electron spin resonance spectra were measured. When melting was completed, the tube was reversed so that the solution could react with the metal and the spectrum looked at at intervals until it was judged to be satisfactory from the point of view of intensity and resolution.

*Preparation of Parent Heterocycles.* Dibenzothiophene (B. Newton Maine Ltd.) and dibenzofuran (Fluka "purum") were recrystallized in ethanol and sublimed before use. Dibenzoselenophene was prepared by a method described by McCullough, *et al.*[5] Large, colorless crystals, m.p. 75°, were obtained after crystallization from methanol–carbon tetrachloride. *Anal.* Calcd. for $C_{12}H_8Se$: C, 62.18; H, 3.49. Found: C, 62.18; H, 3.66.

Methylated and deuterated derivatives of dibenzofuran and dibenzothiophene were obtained by treatment of the corresponding dilithium compounds with dimethyl sulfate and deuterium oxide, respectively. All metalation reactions were carried out in an atmosphere of dry nitrogen.

*2,8-Dimethyldibenzofuran.* Metalation of 2,8-dibromodibenzofuran[6] was carried out according to the procedure of Gilman, *et al.*[7] Methylation with dimethyl sulfate in ether afforded 2,8-dimethyldibenzofuran in low yields, m.p. 68–69° from ethanol. *Anal.* Calcd. for $C_{14}H_{12}O$: C, 85.69; H, 6.16. Found: C, 85.84; H, 6.11.

*4,6-Dimethyldibenzofuran.* To a solution of dibenzofuran (16.8 g., 0.1 mole) in tetrahydrofuran (150 ml.) was added a solution of *n*-butyllithium (0.3 mole) in heptane (110 ml.); the temperature was maintained below −40° throughout the addition. Then the mixture was stirred for 30 min. at 0°, for 1 hr. at 20°, and finally refluxed for 3 hr. After cooling of the mixture in an ice bath, a solution or dimethyl sulfate (0.2 mole) in tetrahydrofuran (55 ml.) was added dropwise. The final mixture was treated with water, and the reaction products were removed by the usual ether extraction. After evaporation of the solvents, 4,6-dimethyldibenzofuran (6 g.) was isolated from the residue (19.9 g.) by fractional crystallization from ethanol. Sublimation afforded the pure product, m.p. 87–88°. *Anal.* Calcd. for $C_{14}H_{12}O$: C, 85.69; H, 6.16. Found: C, 85.94; H, 6.14.

*2,8-Dimethyldibenzothiophene.* A solution of *n*-butyllithium (0.012 mole) in ether (10 ml.) was added within 20 min. to a stirred suspension of 2,8-dibromodibenzothiophene[8] (0.006 mole) in ether (20 ml.) at 0°. The mixture was further stirred for 30 min. at 5°, whereby a yellow solution was obtained. Further stirring for 30 min. at 18° was accompanied by the formation of a colorless precipitate. The suspension was cooled at 0° in an ice bath and dimethyl sulfate (0.012 mole) was added dropwise. After treatment with water, ether extraction, and evaporation of the solvent, a crude crystalline product (1.2 g.) was obtained, m.p. 115–118°. Recrystallizations from ethanol and sublimation afforded the pure colorless product (0.65 g., 52%), m.p. 121–122°. *Anal.* Calcd. for $C_{14}H_{12}S$: C, 79.20; H, 5.70. Found: C, 79.32; H, 5.64.

*2,8-Dimethyldibenzothiophene Sulfone.* 2,8-Dimethyldibenzothiophene (230 mg.) was dissolved in glacial acetic acid (1.5 ml.), and hydrogen peroxide (30%, 1.5 ml.) was added. The solution was heated on a water bath for 1 hr.; after 15 hr. at room temperature the crystalline product (300 mg.) was filtered off. Recrystallization from ethanol afforded colorless needles, m.p. 295–298°.

*3,7-Dibromodibenzothiophene.* $LiAlH_4$ (2.83 g.) was added portionwise to a stirred suspension of 3,7-dibromodibenzothiophene sulfone[9] (15.5 g.) in ether (230 ml.), so as to maintain a gentle reflux. Then the reaction mixture was further refluxed for 1 hr. on a water bath. The excess of $LiAlH_4$ was carefully decomposed with water and enough hydrochloric acid was added to dissolve the thick precipitate formed. The reaction mixture was extracted, washed with water until neutral, and dried; the solvent was evaporated to dryness. The residue was triturated in a small amount of ether and then filtered off. This afforded pure 3,7-dibromodibenzothiophene (7.2 g., 51%), m.p. 180°. Recrystallization from chloroform yielded colorless needles, m.p. 180°.

*3,7-Dimethyldibenzothiophene.* A solution of *n*-butyllithium (0.036 mole) in ether (30 ml.) was added within 10 min. to a suspension of 3,7-dibromodibenzothiophene (0.0175 mole) in ether (60 ml.) in an atmosphere of dry nitrogen. The temperature of the mixture was kept below 0° during the addition. Thereupon dimethyl sulfate (0.036 mole) was added in the cold and the final mixture was worked up in the customary manner. Sublimation, then recrystallization of the crude product (3 g.) from ethanol, yielded colorless 3,7-dimethyldibenzothiophene (2.25 g., 60%), m.p. 151° (lit.[10] m.p. 151–152°).

The oxidation of the product with hydrogen peroxide, by the same procedure as described above for the 2,8- derivative, yielded 3,7-dimethyldibenzothiophene sulfone, m.p. 222–223° from ethanol. *Anal.* Calcd. for $C_{14}H_{12}SO_2$: C, 68.82; H, 4.95; S, 13.12. Found: C, 66.87; H, 5.07; S, 13.01.

*4,6-Dimethyldibenzothiophene.* Dibenzothiophene (0.081 mole) was dissolved in *n*-butyl ether (120 ml.) at 40°, and a solution of *n*-butyllithium (0.32 mole) in ether (240 ml.) was added at such a rate that the temperature did not rise above 50°. Thereafter the temperature was raised and kept at 60° for 21 hr. by means of a thermostated water bath, so as to maintain a gentle reflux of the reaction mixture. The methylation was carried out in the usual manner with a solution of dimethyl sulfate (0.16 mole) in ether (25 ml.). Fractional crystallization of the final residue from methanol–benzene yielded 4,6-dimethyldibenzothiophene (2.65 g.), m.p. 154–155° (lit.[11] m.p. 152–153°) (*Anal.* Calcd. for $C_{14}H_{12}S$: C, 79.20; H, 5.70. Found: C, 79.39; H, 5.72), and 4-methyldibenzothiophene (0.78 g.), m.p. 98° (lit.[12] m.p. 65°) (*Anal.* Calcd.

(5) J. D. McCullough, T. W. Campbell, and E. S. Gould, *J. Am. Chem. Soc.*, 72, 5753 (1950).
(6) W. Hoffmeister, *Ann.*, **159**, 215 (1871).
(7) H. Gilman, H. B. Willis, and J. Swislowsky, *J. Am. Chem. Soc.*, **61**, 1371 (1939).
(8) Prepared in 67% yield according to a procedure of C. R. Neumoyer and E. D. Amschutz, *ibid.*, **69**, 1920 (1947).
(9) Obtained in 60% yield by a procedure described by N. M. Cullinane, C. G. Davies, and G. I. Davies, *J. Chem. Soc.*, 1435 (1936).
(10) W. L. F. Armarego and E. E. Turner, *ibid.*, 1665 (1956).
(11) O. Kruber and A. Raeithel, *Chem. Ber.*, **87**, 1469 (1954).

for $C_{13}H_{10}S$: C, 78.75; H, 5.08. Found: C, 79.01; H, 4.96).

Oxidation of the dimethyl derivative with hydrogen peroxide in the manner described above afforded pure 4,6-dimethyldibenzothiophene sulfone as colorless needles from ethanol, m.p. 294°.

### Calculations of Odd-Electron and Spin-Density Distributions

All calculations were carried out on an IBM 1620 computer, and we wish to thank Professor E. Heilbronner of the Swiss Federal Technical High School, Zürich, who most kindly programmed and performed these calculations for us.

*1. Odd-Electron Distributions.* The Hückel molecular orbitals for dibenzothiophene and dibenzofuran were calculated in the usual manner with neglect of overlap using the following parameters for the oxygen atom and the sulfur atom (p-orbital model)

$$\alpha_O = \alpha + 2.0\beta \qquad \beta_{CO} = 1.0\beta$$
$$\alpha_S = \alpha + 1.0\beta \qquad \beta_{CS} = 1.566\beta$$

where $\alpha$ and $\beta$ are the coulomb integral of the carbon atom and the resonance integral of the carbon–carbon bond, respectively. The apparently odd choice for the carbon–sulfur resonance integral arises from the fact that this, together with the assumed value of $\alpha_S$, gives the same symmetric orbitals as the Longuet-Higgins d-orbital model. The results for dibenzothiophene using the d-orbital model were taken from the paper by Koutecky, Zahradnik, and Paldus.[13]

*2. Spin-Density Distributions.* These were calculated according to McLachlan's method[4] from the equation

$$\rho_r = (C_{or})^2 + \lambda \sum_{rs} \pi_{rs}(C_{os})^2$$

The atom–atom polarizabilities were calculated in the usual way from the Hückel molecular orbitals. The value of $\lambda$ in the above equation was taken as 1.2, a rounded-off value typical of those used by McLachlan.[4]

*3. Hyperfine Splitting Constants.* Proton hyperfine splitting constants attributed to the proton bonded to an $sp^2$-hybridized carbon atom having a spin density $\rho_r$ were calculated according to the relationship

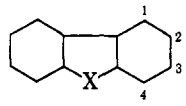
$$a_r = Q\rho_r$$

where $Q$ has been given the value 25 gauss which is again a rounded-off value typical of those used by McLachlan. As will be seen from the text, the conclusions drawn from the results presented here do not depend on the exact values of either $Q$ or $\lambda$. For the d-orbital model of dibenzothiophene hyperfine splitting constants were also calculated from the odd-electron densities $(C_{or})^2$ by an exactly similar equation in which the value of $Q$ was also taken to be 25 gauss (Table III) although a higher value would probably be more appropriate.

### Results

The splitting constants of the radical anions of dibenzofuran, dibenzothiophene, and dibenzoselenophene are shown in Table I. The signs of the splitting constants are, as usual, unknown. For the first two compounds the assignment of the splitting constants has been determined as described below. The splitting constants of dibenzoselenophene are assigned by analogy. Also shown are the splitting constants for the biphenyl[4] and phenanthrene[14] radical anions. For the former compound the splitting constant of the *para* proton is determined directly from the spectrum and there is no real doubt that the splitting constant of intermediate value should be assigned to the *ortho* protons. The protons at the 4,5-positions of phenanthrene (1 in the numbering employed here) have been shown to have one of the two smaller and probably the smallest of the experimental splitting constants; this is in agreement with theory, and the remainder of the assignments have been made on the basis of McLachlan's spin density calculations.[4]

**Table I.** Proton Hyperfine Splitting Constants of the Radical Anions of Dibenzofuran and Its Analogs




| X | $a_1$ | $a_2$ | $a_3$ | $a_4$ |
|---|---|---|---|---|
| O | 4.87 | 0.98 | 4·87 | 1·96 |
| S | 4.48 | 0.86 | 5.16 | 1.46 |
| Se | 4.27 | 1.02 | 5.27 | 1.02 |
| –CH=CH– | 0.32 | 2.88 | 0.72 | 3.60 |
| | Biphenyl | | | |
| | 2.75 | 0.45 | 5.50 | 0.45 |

*Assignment of Hyperfine Splitting Constants.* In Table II are shown the hyperfine coupling constants of 2,8-, 3,7-, and 4,6-dimethyldibenzothiophene and of 2,8- and 4,6-dimethyldibenzofuran. Of these the methyl group splitting constants are determined unambiguously from the form of the spectrum, and the remainder of the splitting constants are assigned on the basis of the splitting constants of the parent compounds. For both of the parent compounds the splitting constants fall into two groups, one in the neighborhood of 5.0 gauss and the other 1–2 gauss. The splitting constants of the methylated compounds show that in both compounds the 2,8- and 4,6-positions have small coupling constants and the 1,9- and 3,7-positions have large coupling constants. Moreover, for dibenzofuran it would seem likely that the splitting constant of 1.96 gauss belongs to the 4,6-positions. This conclusion was confirmed by the spectrum of 2,8-dideuteriodibenzofuran and completes the coupling constant as-

**Table II.** Hyperfine Splitting Constants of Dimethyldibenzofurans and -dibenzothiophenes

| | $a_{methyl}$ | $a_1$ | $a_2$ | $a_3$ | $a_4$ |
|---|---|---|---|---|---|
| 2,8-Dimethyldibenzothiophene | 1.08 | 4.6 | ... | 5.1 | 1.55 |
| 3,7-Dimethyldibenzothiophene | 5.0 | 5.0 | 0.83 | ... | 1.67 |
| 4,6-Dimethyldibenzothiophene | 0.80 | 4.10 | <0.10 | 5.19 | ... |
| 2,8-Dimethyldibenzofuran | 1.04 | 4.96 | ... | 4.96 | 2.08 |
| 4,6-Dimethyldibenzofuran | 1.84 | 4.60 | 0.92 | 4.60 | ... |

(12) H. Gilman and A. L. Jacoby, *J. Org. Chem.*, 3, 108 (1938).
(13) J. Koutecky, R. Zahradnik, and J. Paldus, *J. chim. phys.*, **56**, 455 (1959).
(14) S. H. Glarum and I. C. Snyder, *J. Chem. Phys.*, **36**, 2989 (1962).

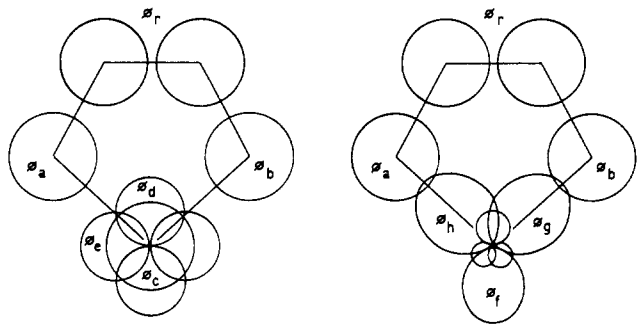



Figure 1. Hybridization of the sulfur atom $3p_z$, $3d_{yz}$, and $3d_{xz}$ orbitals in thiophene according to Longuet-Higgins.

signment of this compound. The spectra of 2,8- and 3,7-dideuteriodibenzothiophene showed that the splitting constants of 5.16 and 0.86 gauss are due to the protons at the 3,7- and 2,8-positions, respectively. These results yield the splitting constant assignments given in Table I.

## Discussion

It is convenient to recapitulate here the procedure used by Longuet-Higgins in his discussion of thiophene.[1] From the three orbitals on the sulfur atom suitable for $\pi$-bonding [$3p_z$, $3d_{yz}$, $3d_{xz}$], he formed three hybrid orbitals (h, g, and f) of the form

$$\left.\begin{matrix}\phi_h\\ \phi_g\end{matrix}\right\} \quad a_1 3p_z + a_2 3d_{yz} \pm a_3 3d_{xz}$$

$$\phi_f \quad a_4 3p_z - a_5 3d_{yz}; \quad a_1 a_4 = a_2 a_5$$

two of which (h and g) were directed toward one of the two neighboring carbon atoms and one of which (f) was directed away from both of them (Figure 1). By a particular choice of the mixing coefficients in terms of the various overlap integrals, the hybrid orbitals h and g were made mutually nonorthogonal, although both were orthogonal to f. Longuet-Higgins then assumed that the resonance integrals were proportional to the overlap integrals so that $\beta_{hf} = \beta_{gf} = 0$ and estimated that $\beta_{hg}$ was equal to the carbon–carbon resonance integral, $\beta$. He also estimated that the integral between the orbitals h and g and the neighboring carbon $p_z$ orbitals was a little less than $\beta$ and suggested the value $0.8\beta$. The coulomb integral of h and g was taken to be equal to $\alpha$, the carbon $2p_z$ coulomb integral.

This hybridization procedure has the great virtue of simplicity and brings out in a very attractive manner a strong resemblance between the sulfur atom and the ethylene molecule. This simplicity, however, disarms criticism and obscures the real nature of the phenomena which may or may not be occurring. In the first place, it is doubtful whether it is legitimate to construct formally nonorthogonal hybrid orbitals. This step was taken in order to eliminate the interaction between the orbital f and the orbitals h and g while retaining the interaction between h and g. Moreover, in the second place, the integral $\beta_{hg}$ is not a true resonance integral but is proportional to the 3p-3d promotional energy. Thus

$$\beta_{hg} = a_1^2\alpha_p + (a_2^2 - a_3^2)\alpha_d$$

where $\alpha_p$ and $\alpha_d$ are the coulomb integrals of the sulfur 3p and 3d orbitals, respectively. Similarly

$$\beta_{fh} = \beta_{fg} = a_1 a_4(\alpha_p - \alpha_d)$$

so that its neglect is quite unjustified, and the device of constructing the nonorthogonal orbitals h and g unnecessary.

Before any recourse is made to the results of molecular orbital calculations, the resemblance between the results for the three compounds measured here and their dissimilarity to phenanthrene is striking. Even if the remaining splitting constants in phenanthrene are incorrectly assigned, the considerable difference in splitting constant between dibenzothiophene and phenanthrene at position 1 is inescapable. This already militates against a large contribution from the sulfur 3d orbitals. Despite our criticisms of the method, Table III shows the odd-electron distribution

**Table III.** Hyperfine Splitting Constants in Dibenzothiophene Derived from the Odd-Electron Densities Calculated According to the d-Orbital Model

| $a_1$ | $a_2$ | $a_3$ | $a_4$ |
|---|---|---|---|
| 1.36 | 2.30 | 0.02 | 2.63 |

in dibenzothiophene calculated according to the Longuet-Higgins d-orbital model. It will be seen that they are in complete disagreement with experiment, and the calculation of the spin-density distribution would only worsen matters.

In Table IV are shown the results of the calculations of odd-electron and spin-density distributions for dibenzofuran—where there is no question of d-orbitals—

**Table IV.** Hyperfine Splitting Constants in Dibenzofuran and Dibenzothiophene Calculated by McLachlan's Method Using the p-Orbital Model for Dibenzothiophene

| | $a_1$ | $a_2$ | $a_3$ | $a_4$ |
|---|---|---|---|---|
| Dibenzofuran | 4.78 | −1.41 | 4.80 | 1.86 |
| Dibenzothiophene | 3.99 | −1.23 | 5.03 | 0.75 |

and dibenzothiophene in the p-orbital model, using the parameter values given in the Experimental section. No attempt has been made to achieve exact agreement with experiment; this could almost certainly be achieved with the three parameters which are available for adjustment, but it is unlikely that such manipulation has any real value. It is only intended to show that the main features of the spectra are explained by a p-orbital model and that the difference between the spectra is in accordance with the known electronegativities of oxygen and sulfur.

At this point it is illuminating to look at the behavior of the models used in a more qualitative way. Dibenzothiophene can be considered to be derived from biphenyl, and the sulfur atom can be introduced as conjugating with the $\pi$-electron system either with only its $3p_\pi$ electrons or by using in addition the two $3d_\pi$ orbitals as suggested by Longuet-Higgins. Dibenzothiophene retains the plane of symmetry of biphenyl which bisects the bond joining the two benzene rings and it is, therefore, convenient to classify the

Hückel molecular orbitals of biphenyl according to this symmetry with respect to this plane. The energies and symmetries of these orbitals are given in Table V,

**Table V.** Energies and Symmetries in the Plane Bisecting the Bond Joining the Two Benzene Rings of the $\pi$-Electron Hückel Molecular Orbitals of Biphenyl

| Energy (units of $\beta$) | Symmetry | Energy (units of $\beta$) | Symmetry |
|---|---|---|---|
| 2.280 | S | −0.705 | S |
| 1.891 | A | −1.000 | A |
| 1.318 | S | −1.000 | S |
| 1.000 | A | −1.318 | A |
| 1.000 | S | −1.891 | S |
| 0.705 | A | −2.280 | A |

and the effect on them of the perturbing sulfur atom orbitals in the two models is shown in Figure 2. Note that in the p-orbital model only the symmetric orbitals interact, while in the d-orbital model the orbitals h and g have been expressed in their symmetric and antisymmetric combinations, respectively. The energies

$$\frac{1}{\sqrt{2}}(\mathrm{h} + \mathrm{g}) = \sqrt{2}\,(a_1\mathrm{p}_z + a_2\mathrm{3d}_{yz})$$

$$\frac{1}{\sqrt{2}}(\mathrm{h} - \mathrm{g}) = a_3\sqrt{2}(\mathrm{3d}_{xz})$$

and resonance integrals for the sulfur atom orbitals are those used by Longuet-Higgins for the d-orbital model and those used below in this paper for the p-orbital model.

It can be at once seen that the sensitivity of the dibenzothiophene to d-orbital participation lies in the fact that for the values of the energies and resonance integrals employed by Longuet-Higgins, the unpaired electron moves in an antisymmetric orbital containing a large contribution from the sulfur $3d_{xz}$ orbital, while for the p-orbital model the electron moves in a symmetric orbital which is not too far different from the unperturbed orbital of biphenyl. Experimentally it has been shown that the coupling constant pattern resembles that of biphenyl (Table I) so that even apart from the criticisms given above the d-orbital model must be rejected.

It is, however, apparent from Figure 2 that at some combination of the values of the coulomb integral of the $3d_{xz}$ orbital and its resonance integral with the adjacent carbon $2p_z$ orbitals the energy of the 9A′ orbital will become greater than that of 7S′. The latter then becomes the acceptor orbital, as in the p-electron model, and for a particular choice of parameter values the odd-electron distribution in the two models is identical. It is fairly obvious that if $\alpha_d$ is much greater than $\alpha_c + 1.2\beta$, no reasonable value of $\beta_{CS}$ can depress 9A′ sufficiently, while for $\alpha_d = \alpha_c + \beta$ the transition occurs at about $\beta_{CS} = 0.5\beta_{CC}$.

Another point brought out clearly by Figure 2 is the fact that the properties of the bound $\pi$-electrons in dibenzothiophene are essentially governed by the symmetric combination $1/\sqrt{2}(\mathrm{h} + \mathrm{g})$, and we have only pure guesswork to tell us what amount of the $3d_{yz}$ orbital this contains. If the energy of the 3d

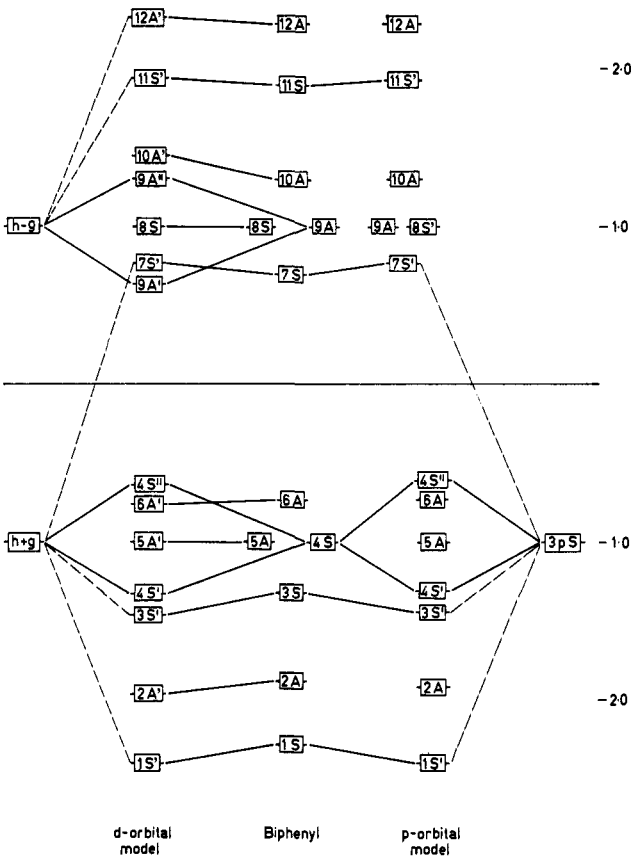



Figure 2.

orbitals is indeed of the order of $\alpha + 1.2\beta$ then it cannot be very much. The present work has shown that the 3d orbitals play little part in the first unoccupied orbital.

As indicated above, we consider, on purely theoretical grounds, that Longuet-Higgins' presentation of the problem of 3d orbital participation in thiophene, and hence in any of its homologs, is not rigorous. His assumptions virtually amount to the neglect of the $3d_{yz}$ orbital and since the CSC bond angle is not far removed from 90° (92.2° in thiophene),[15] it seems unlikely that either its coulomb integral or resonance integral with the neighboring carbon atom $2p_z$ orbital will be very different from those of $3d_{xz}$. In dibenzothiophene this orbital can interact both with 7S and 8S so that if the interaction is at all significant the lowest unoccupied orbital will be a mixture of $3d_{yz}$, 7S, and 8S. However, our results show that the lowest unoccupied orbital in dibenzothiophene is not very different from the lowest unoccupied orbital in dibenzofuran so that the contribution of $3d_{yz}$ to it cannot be very significant.

To sum up, therefore, our results show that the d-orbital model for the sulfur atom in dibenzothiophene predicts a completely incorrect odd-electron distribution in the radical anion. Good agreement with experiment is afforded by a p-orbital model for both dibenzofuran and dibenzothiophene and it seems likely that the d-orbitals of neither sulfur nor selenium play a great part in the lowest unoccupied orbitals of dibenzothiophene or dibenzoselenophene, respectively.

(15) R. A. Bonham and F. A. Momany, *J. Phys. Chem.*, **67**, 2474 (1963).