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Calculation of Proton Coupling Constants for Dibenzothiophene Radical Anion

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The calculation of proton hyperfine coupling constants for dibenzothiophene radical anion is reported.

Several experimental studies [1–3] on this topic have been performed in recent years, but a reliable assignment of splitting constants has been performed only recently by Gerdil and Lucken [3], who examined the EPR spectra of a number of dimethylbenzothiophenes and the deuterated dibenzothiothene radical anions. These authors also performed spin density calculations [2, 3], within the framework of the Hückel molecular orbital method, using both the *p*- and *d*-models [4, 5], with appropriate choice of parameters for the sulphur atom.

We feel that it would be interesting to compare the results of these crude calculations with the results of more sophisticated ones, and so we have calculated the spin density distribution for the dibenzothiophene radical anion using the SCF MO method with CI [6, 7].

The molecule was assumed to be planar. No *d*-orbital participation to the π-system, by sulphur was considered since several authors have pointed out that, should any such participation occurs, its influence on molecular properties (for example, dipole moments [8], polarographic reduction [9] or electronic spectra [10]) is negligible.

The following parameters, in standard notation, were used in the calculation: $\beta_{CC} = -2.395$ eV [11], $\beta_{CS} = -2.0$ eV [12] and $\delta W_S = -8.84$ eV [13]. The Coulomb integrals were approximated using a Mataga-Nishimoto [14] approximation, with $I_C = 11.42$ eV, $I_S = 22.3$ eV, $A_C = 0.58$ eV, $A_S = 11.0$ eV, $a_{CC} = 1.328$ Å, $a_{CS} = 1.300$ Å, $a_{SS} = 1.274$ Å, $r_{CC} = 1.4$ Å, $r_{CS} = 1.74$ Å [15–18].

The calculated SCF charge and spin densities are given in Table 1. Spin densities were converted to coupling constants using the following relationships [19, 20]:

$$a_r = -27\,\varrho_r \tag{I}$$

$$a_r = -27\,\varrho_r - 12.8\,(1 - q_r)\,\varrho_r \tag{II}$$

in standard notation. Calculated and experimental proton coupling constants are given in Tables 2 and 3.

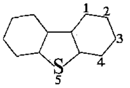

Fig. 1

The results obtained using relation (II) show a better overall agreement with experiment, than do those obtained using relation (I). Both sets of results give better agreement with experiment than the earlier Hückel calculations, although Gerdil and Lucken admittedly did not try to obtain better agreement with experiment by varying the parameters, but merely pointed out that the main features of the EPR spectrum could be explained by the p-model.

Table 1. *Charge and Spin Densities*

Dibenzo-thiophene Anion	Ring Position	Charge Density	Spin Density
	1	1.1135	0.1747
	2	1.0473	−0.0554
	3	1.1605	0.2044
	4	1.1067	0.0281
	5	1.8487	0.0160

Table 2. *Calculated proton hyperfine splitting constants of the radical anion of dibenzothiophene*

Molecule	Method of calculation of spin densities	a_1	a_2	a_3	a_4	Reference
Dibenzothiophene Anion	A $\beta_{CS}/\beta_{CC}=0.6$	2.54	0.135	2.28	1.49	1
	$\beta_{CS}/\beta_{CC}=0.8$	2.84	0.27	2.48	1.47	
	$\beta_{CS}/\beta_{CC}=1.0$	3.16	0.49	2.67	1.46	
	B a)	1.36	2.30	0.02	2.63	3
	b)	3.99	−1.23	5.03	0.75	
	C (I)	4.72	−1.50	5.51	0.76	
	(II)	4.47	−1.47	5.09	0.72	

A. HMO calculation of odd-electron density by using the d-orbital model of the sulphur atom and various values for the ratios β_{CS}/β_{CC}.

B. HMO calculation of odd-electron density for two models: a) the d-orbital model and b) the p-orbital model.

C. Our SCF calculations of odd-electron density for the p-orbital model using expressions (I) and (II) for converting the spin densities to coupling constants.

Table 3. *Proton hyperfine splitting constants of the radical anion of dibenzothiophene*

Molecule	a_1	a_2	a_3	a_4	Reference
Dibenzothio-phene anion	4.48	0.86	5.16	1.46	1
	4.48	0.86	5.16	1.46	3
	4.60	1.05	5.04	1.45	2

An examination of our results shows that the theory fails to reproduce accurately a_2 and a_4, but suggest that the experimental assignment has been made uncorrectly. However, this is probably not the case, and the difficulty no doubt arises from the fact that the "constants" in (I) and (II) vary quite considerably, even for a neutral alternant hydrocarbon radical. Thus, for example, if one uses

$a_r = (-27 \pm 2)\,\varrho_r$ then the a_1, a_2 and a_3 coupling constants reproduce exactly the experimental values. If the influence of sulphur on its nearest and next nearest neighbours is very significant then one should use a very different value of Q to reproduce a_4 correctly.

However, it is clear from the results presented here that the *p*-model, using SCF theory is as useful a model for the calculation of the spin density distribution in ions of sulphur containing molecules, as it is for the calculation of bond lengths [21, 22] and excited state properties [17, 18, 23] of neutral molecules.

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