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The Electron-Spin Resonance Spectra of 1,4-dithiin Radical-Cations and the Nature of the Carbon-Sulphur π-Bond

By

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The radical cations of 1,4-dithiin, 1,4-benzodithiin and thianthrene have been prepared and their electron-spin resonance spectra measured at room temperature in concentrated sulphuric acid solution. Spin densities for these radicals have been calculated using McLachlan's extension of the Hückel molecular orbital method with neglect of overlap and using two models for the sulphur atom, one with and the other without the participation of the $3d$-orbitals. It is concluded that the $3d$-model gives significantly better results although qualitatively a similar distribution is predicted by both models. Appropriate values for the sulphur atom parameters are those used by Longuet-Higgins in his discussion of thiophene. Owing to the probable non-planarity of these radicals the improvement arising from the inclusion of d-orbitals may in fact be due, at least in part, to interaction of the carbon $2p_z$ orbitals with the antibonding carbon-sulphur σ orbitals.

Die Radikal-Kationen von 1,4-Dithiin, Benzo-1,4-dithiin und Thianthren wurden dargestellt und ihre Elektronenspin-Resonanz-Spektren bei Raumtemperatur in konzentrierter Schwefelsäure gemessen. Die Spindichten für diese drei Radikale wurden nach der Methode von McLachlan unter Verwendung von zwei Modellen für das Schwefelatom berechnet; das eine Modell mit und das andere ohne Beteiligung von $3d$-Orbitalen. Es ergab sich, daß durch das $3d$-Modell eine bessere quantitative Übereinstimmung erzielt werden kann, obwohl beide Modelle eine ähnliche qualitative Verteilung ergeben. Die geeigneten Werte für die Parameter des Schwefelatoms sind die von Longuet-Higgins in seiner Diskussion über Thiophen benutzten. Da diese Radikale wahrscheinlich nicht planar gebaut sind, können, jedenfalls teilweise, die durch die Einbeziehung der d-Orbitale erzielten Verbesserungen von einer Wechselwirkung der Kohlenstoff $2p_z$-Bahnen mit den nichtbindenden Kohlenstoff-Schwefel-σ-Orbitalen herrühren.

Les radicaux cationiques de 1,4-dithiin, 1,4-benzodithiin et de thianthrène ont été préparés et leurs spectres de résonance électroniques mesurés à température ambiante en solution d'acide sulphurique concentré. Les densités de spin pour ces trois radicaux ont été calculées selon la méthode de McLachlan en utilisant deux modèles pour l'atome de soufre; l'un avec et l'autre sans la participation des orbitales $3d$. Il en résulte que le modèle $3d$ donne un meilleur accord quantitatif, quoique les deux donnent une distribution qualitativement semblable. Les valeurs appropriées des paramètres de l'atome de soufre sont celles utilisées par Longuet-Higgins dans sa discussion du thiophène. A cause de la non-planarité de ces radicaux, l'amélioration apportée par les orbitales d pourrait être due, du moins en partie, à l'interaction des orbitales $2p_z$ du carbone avec les orbitales antiliantes σ carbone-soufre.

I. Introduction

The study of the hyperfine structure in electron-spin resonance spectra as a means of determining the unpaired spin distribution in free radicals and the correlation of these results with those predicted by quantum-mechanical calculations has been the subject of a number of recent papers and of two reviews [*3*, *20*]. For homonuclear systems excellent agreement between theory and experiment has been obtained [*15*], so a method is afforded for the determination of the best description of heteroatoms in conjugated systems. An example of a successful application of this kind is a recent investigation of the electron-spin resonance spectra of various nitrogen-containing heterocycles [*4*].

Simple molecules containing a sulphur atom in the conjugated system have not so far been extensively studied, although the sulphur atom is particularly interesting in view of its often-invoked possibility of making use of its vacant $3d$-orbitals [*18*]. It has recently been shown, however, that the radicals produced when thianthrene is dissolved in concentrated sulphuric acid are the corresponding radical-cations [*19*, *12*] and that this property is a general one for the 1,4-dithiins.

Following the method previously employed for the determination of the best parameters for the oxygen atom in the *p*-benzosemiquinones [*21*, *2*], the radicals of 1,4-dithiin, 1,4-benzodithiin and thianthrene have been prepared and their electron-spin resonance spectra measured. Parallel experiments on substituted molecules have made possible the assignment of the observed coupling constants to the particular protons in the parent radicals.

Molecular orbital calculations of initially the odd-electron distribution by the Hückel method, neglecting overlap, and finally the spin-density distribution by MCLACHLAN's extension of this technique [*15*] were carried out using two models for the sulphur atom, i. e. with and without $3d$-orbital participation, and a variety of values for the various parameters describing the sulphur atom and the sulphur-carbon bond. In this way it was hoped that it would be possible to determine the best description of the sulphur atom in these systems.

II. Experimental Results

a) Experimental Techniques

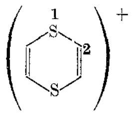
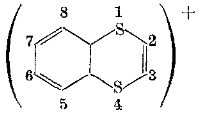
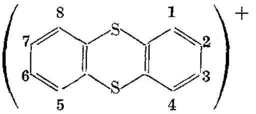
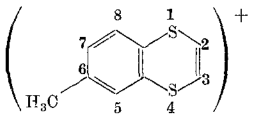
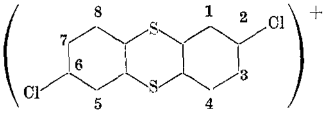
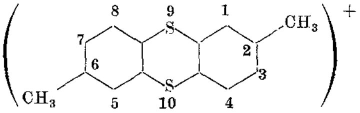
1,4-dithiin and 1,4-benzodithiin were prepared according to the methods of PARHAM et al. [*17*]; 6-methyl-1,4-benzodithiin was prepared as in reference [*12*]. 2,6-dimethyl-thianthrene [*5*] and 2,6-dichloro-thianthrene [*1*] were prepared by standard methods. Thianthrene was a purified commercial product.

The spectra were measured on a modified „Microspin" spectrometer in a field of 3.300 gauss. The field was calibrated at regular intervals against potassium naphthalenide in dimethoxyethane.

b) Experimental Results

The radicals were produced either by dissolving the parent compound in concentrated sulphuric acid or by adding a slight excess of antimony pentachloride to a solution of the parent compound in a 2:1 mixture of benzene and nitromethane. Both solutions were deoxygenated by bubbling nitrogen through them. At room temperature the spectra in sulphuric acid were much sharper than those in the benzene-nitromethane mixture which, however, become noticeably sharper on cooling. This is presumably a further example of the increased resolution often afforded by more viscous solvents, observed by HAUSSER [*6*], and which is thought to be due to exchange effects [*16*, *8*]. The splitting constants reported in Tab. 1 were those measured in sulphuric acid at room temperature, but they did not noticeably differ from those measured in benzene-nitromethane. In neither 1,4-benzodithiin and thianthrene was it possible to resolve the splitting due to the smallest coupling constant and the figure given is an upper limit indicated by the line-width. The spectrum of 1,4-benzodithiin is shown in Fig. 1.

Table 1. *Hyperfine splitting constants (in gauss) of 1,4-dithiinium radical-cations. The assignment to particular protons is discussed in the text*

	$[a_2^H]^{\mathrm{a}} = 2.80 \pm 0.05$
	$[a_2^H]^{\mathrm{b}} = 3.20 \pm 0.05$ $[a_5^H]^{\mathrm{b}} < 0.5$ $[a_6^H]^{\mathrm{b}} = 1.05 \pm 0.05$
	$[a_1^H]^{\mathrm{a}} < 0.5$ $[a_2^H]^{\mathrm{a}} = 1.30 \pm 0.05$
	$a_2^H \approx a_3^H \approx 1.5$ $a_7^H \approx a_{Me}^H \approx 3.0$ $a_5^H\,,\ a_8^H < 0.5$
	$[a_1^H]^{\mathrm{b}}, [a_4^H]^{\mathrm{b}} < 0.5$ $[a_3^H]^{\mathrm{b}} = 1.3$
	$[a_1^H]^{\mathrm{b}}, [a_4^H]^{\mathrm{b}} < 0.5$ $[a_3^H]^{\mathrm{b}} \approx [a_{Me}^H]^{\mathrm{b}} \approx 1.4$

[a] Coupling constant due to 4 equivalent protons;
[b] Coupling constant due to 2 equivalent protons.

c) *Assignment of Splitting Constants*

The reasonable assumption is made that the largest splitting constant in 1,4-benzodithiin is due to the protons in the 2,3 positions and the observed spectrum of nine bands for 6-methyl-1,4-benzodithiin indicates that the splitting of 1.05 gauss must be assigned to the protons in the 6,7 positions. Had this splitting been due to the 5,8 protons, then the spectrum would probably have only consisted of three bands and the overall width would have remained at about 8.5 gauss, in stead of the 12.0 gauss observed. The three-line spectrum of 2,6-dichlorothianthrene and the nine-line spectrum of the 2,6-dimethyl derivative leave no doubt that the splitting constant of 1.30 gauss in thianthrene is due to the protons at the 2, 3, 6, 7 positions.

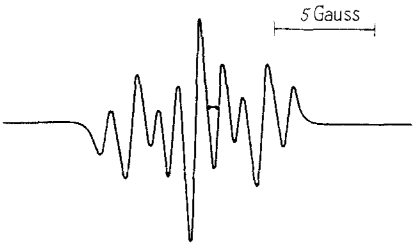


Fig. 1. ESR spectrum of 1,4-benzodithiin

III. The Shape of the Dithiin Radical Cations

The crystal structure of 1,4-dithiin [*7*] and of thianthrene [*13*] reveals that these molecules are bent about the line joining the two sulphur atoms, the dihedral angles being 137° and 128° respectively. The molecular orbital calculations to be discussed in the following section indicate that in the cation the formal charge is of the order of 0.25 on each sulphur atom, so that reduced electron repulsion might be expected to favour a larger dihedral angle. The principal components of the g-tensor of the thianthreneantimony pentachloride adduct, measured on the polycrystalline solid according to the method of KNEUBÜHL [9], are 2.0048, 2.0086 and 2.0142, which certainly do not favour a completely planar structure, although large deviations from spherical symmetry would be expected for a radical in which there is such a high spin density on the sulphur atom [14]. In the absence of more definite information, it must be assumed, therefore, that the radical-cations are non-planar.

IV. Molecular Orbital Calculations

In the absence of a plane of symmetry through the conjugated system a classification of the orbitals into σ- and π-types is no longer strictly possible. The molecules can, however, be considered to be built up from ethylene and or benzene units, so it is assumed initially that in the carbon framework the usual σ-π separation is justified. Orbitals on the sulphur atom are then sought which can interact with the π-system. In both 1,4-dithiin [7] and thianthrene [13] the $C\,S\,C$ angle is approximately 100°. The sulphur orbitals bonded to the carbon σ bonds are thus given by

$$\psi_{\pm} = p_y \frac{(2a-1)}{\sqrt{2}} \pm \frac{p_x}{\sqrt{2}} + s\sqrt{2a(1-a)}$$

where $\dfrac{1-a}{a} = \tan 5°$

and can be seen to be almost pure orbitals. Of the remaining two lone pairs, one is in an almost pure s-orbital and the other is in a p_z orbital perpendicular to the $C\,S\,C$ plane, and thus at an angle to the π-orbitals of the carbon system. The coordinate system is shown in Fig. 2.

For a planar molecule there are two d-orbitals of the appropriate π-symmetry, d_{xz} and d_{yz}. Bending of the molecule permits the other d-orbitals to interact with the π-system, but it will always be possible to construct just two d-orbitals suitably oriented for maximum overlap. In his treatment of thiophen LONGUET-HIGGINS [11] hybridised these two with the 3 p_z orbital and thus obtained two hybrids suitably oriented to interact with the carbon $2p_z$ orbitals. For the present purpose, at least, this obscures at this stage the way in which these two orbitals interact with the π-system for they are respectively symmetric and antisymmetric with respect to reflection in the molecular symmetry plane through the sulphur atoms in 1,4-dithiin and thianthrene.

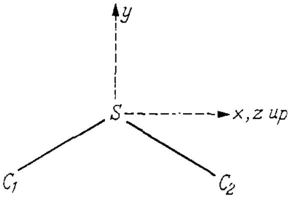


Fig. 2. Co-ordinate system

The object of this study was to see if it was possible on the basis of the electron-spin resonance results to choose between the two models for the conjugation of the sulphur atom, i. e. with and without the participation of the $3d$-orbitals. This object will only have been achieved if it is possible to show that for one of the models it is either impossible to achieve agreement with experiment or that very unlikely values of the sulphur atom parameters are required. A preliminary survey of the energy levels of these molecules showed that in all three cases the odd-electron was in a totally symmetric orbital. For 1,4-dithiin and thianthrene this can contain no contribution from the $3d_{yz}$ orbital so that, by calculation of the odd-electron density, no distinction can be made between the two models as the contribution of the $3d_{xz}$ orbital is absorbed into that of the $3p_z$ orbital. For 1,4-benzodithiin there is no plane of symmetry through the sulphur atoms and different odd-electron densities are predicted by the two models.

In the calculation of spin densities by McLachlan's method [*15*] a correction is applied to the odd-electron distributions which in general has the effect of increasing the spin densities at positions of high odd-electron density and decreasing and even making negative the spin densities at positions of low odd-electron density. Because these corrections involve contributions from all the occupied orbitals the two models for 1,4-dithiin and thianthrene now no longer give identical results.

The following approach was therefore adopted. For 1,4-dithiin and thianthrene odd-electron distributions were calculated in the p-orbital model for various values of the sulphur Coulomb integral, $\alpha_S = \alpha + \delta\beta$, and the sulphur-carbon resonance integral, $\beta_{CS} = \gamma\beta$, where α and β are the Coulomb and resonance integral of the carbon atom and carbon-carbon bond respectively. Bearing in mind the effect of the correction to be applied for a calculation of spin density an appropriate region of parameter space was thus chosen to give agreement with experiment for these two molecules.

Table 2. *Theoretical splitting constants for 1,4-dithiins*
For the p-model $\alpha_S = \alpha_C + 1.0\,\beta$, $\beta_{CS} = 0.566\,\beta$
d-model $\alpha_S = \alpha_C$, $\beta_{SS'} = \beta$, $\beta_{CS} = 0.8\,\beta$
For the calculations according to McLachlan's method $\lambda = 1.0$, $Q = 24.0$ for both methods.

Molecule	Splitting constant	Hückel		McLachlan		Experiment
		p	d	p	d	
1,4-dithiin ···················	a_2^H	3.00	3.00	2.42	3.00	2.90
1,4-benzodithiin ··············	a_2^H	3.80	3.16	3.92	3.59	3.20
	a_5^H	0.39	0.47	0.21	0.20	< 0.5
	a_6^H	0.78	0.98	0.34	0.74	1.05
thianthrene ··················	a_1^H	0.37	0.37	0.14	0.08	< 0.5
	a_2^H	1.06	1.06	0.75	0.98	1.30

Odd-electron densities for 1,4-benzodithiin were then calculated using both the p-orbital model and the Longuet-Higgins $3d$ orbital model for the sulphur atom [11] in order to limit the area of parameter space even further. In the latter case three parameters are required to describe the sulphur atom, $\alpha'_S = \alpha + \mu\beta$, $\beta'_{CS} = \nu\beta$ and $\beta'_{SS} = \varrho\beta$. For the two symmetrical molecules these parameters give identical results to the p-orbital model if $\delta = \mu + \varrho$ and $\gamma\sqrt{2} = \nu$. As here μ and ϱ cannot be separated, ϱ was assigned the value of 1.0 used by Longuet-Higgins and the calculations for 1,4-benzodithiin were performed for variations of only μ and ν. Finally spin densities were calculated in this region, using a value of the parameter λ in the McLachlan procedure [*15*] of $\lambda = 1.0$.

As a result of the odd-electron density calculations, it became apparent that appropriate values of the parameters were

$$0.4 \leqslant \gamma \leqslant 0.7 \text{ and } 0.7 \leqslant \delta \leqslant 1.2$$

In Tab. 2 are shown the results of both the odd-electron distributions and the spin densities for all three molecules in both models for a representative set of values of the parameters. It can be seen that the d-orbital model gives a somewhat better agreement with experiment than that using p-orbitals alone.

The most important defects of the p-orbital model arise in 1,4-dithiin and 1,4-benzodithiin. Here it does not seem possible to simultaneously obtain agreement with experiment for these two molecules for the errors are in opposite senses while, at least for the 2,3 position in 1,4-benzodithiin, the spin densities vary in similar ways as a function of the sulphur atom parameters. Moreover, a consideration of 1,4-benzodithiin alone shows that while it is possible to reduce the spin density at the 2,3 position, it is not possible to increase the density at the 6,7 position for reasonable values of the parameters.

It must be concluded, therefore, that the d-orbital model gives a significantly better agreement with experiment than that using only p-orbitals.

Discussion

The values of the parameters used for the results given in Tab. 2 are very similar to those used in previous calculations. Thus the parameters in the d-orbital model ($\mu = 0.0$, $\nu = 0.8$, $\varrho = 1.0$) are those used by LONGUET-HIGGINS in his discussion of thiophen [*11*] while the equivalent values in the p-orbital model ($\delta = 1.0, \gamma = 0.566$) are similar to those used by KREEVOY [*10*] ($\sigma = 0.82, \gamma = 0.42$) in a treatment of 1,4-dithiin by the method of PARISER and PARR. It is noteworthy that with these parameters the coefficient of the unexcited Hückel configuration in the ground-state wave function is 0.998.

Although it would appear that the d-orbital model is a significantly better one for the sulphur atom in these molecules, it must not immediately be concluded that the $3d$-orbitals are in fact employed. All that has been shown is that the inclusion of a vacant antisymmetric orbital of energy approximately β greater than that of the carbon $2p_z$ orbital improves agreement with experiment. The probable non-planarity of these radicals prevents, however, an unambiguous identification of this orbital with $3d_{yz}$ orbital of sulphur for the $3p_z$ orbitals of the carbon atom can now interact with the antibonding carbon-sulphur σ orbitals [*22*] which have approximately the appropriate energy. If these are written as symmetric and antisymmetric combinations of the two σ orbitals the antisymmetric one which interests us here becomes, in the numbering and co-ordinate system of Fig. 2:

$$\frac{1}{\sqrt{2}} p_y = \frac{1}{2} (\sigma_1 - \sigma_2).$$

This neglects the slight s-hybridisation of the sulphur σ orbitals and assumes the equal electronegativity of the carbon and sulphur atoms. If direct overlap with σ_1 and σ_2 is neglected and a dihedral angle of 130°, a carbon-sulphur bond length of 1.77 Å and a $C\,C\,S$ angle of 120° are assumed, then the overlap integral interpolated from the tables of MULLIKEN et al. has the value 0.087 to be compared with that of 0.145 for the $2p_z - 3p_z$ overlap with the same molecular geometry. Thus the overlap is by no means negligeable and at least a part of the orbital we require may arise from this source.

Conclusion

It is concluded that the $3d$-orbital model of the sulphur atom gives a quantitatively better description of the 1,4-dithiin radical-cations, although qualitatively a similar electron distribution is predicted by both this model and that using the $3p_z$ orbital. The sulphur atoms' use of $3d$-orbitals may in fact only be apparent as the probable non-planarity of these radicals allows the carbon π-system to interact with the carbon-sulphur antibonding σ-orbitals which qualitatively would have the same effect as a $3d$-orbital while their energy and overlap with the carbon $2p_z$ orbitals make it quite possible that this interaction plays a significant part in the electron structure of the 1,4-dithiins.

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