Dibenz[b.f]oxepin and Thiepin Radical Anions.
Conjugative Properties of Sulfur in its Different Oxidation States.

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The radical anion of dibenz[b,f]oxepin has been investigated by esr spectroscopy and the relative coupling constants compared with dibenzo[b,f]thiepin. In both cases assignments were obtained using a theoretical method (INDO). In addition radicals from dibenzo[b,f]thiepin sulfoxide and sulfone could be detected and, unusually, the free electron density on carbon atoms of the radical anion containing a sulfonyl group is larger than that on carbons of radical anions containing a sulfide or a sulfoxide group.

The conjugative properties of oxygen and sulfur in aromatic radical anions, as studied by esr, have received some attention during the last few years (1,2). From these investigations it was inferred that the spin density ρ_X^π; on the heteroatom is smaller in the sulfur with respect to the oxygen derivative as observed for related neutral and cation radicals (3).

In order to check whether this behaviour is shared by other sulfur and oxygen containing radicals, we examined the radical anions from molecules I and II which were found to be stable at low temperature.
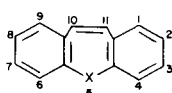
I   X = O
II   = S
III   = SO
IV   = SO₂

Moreover, since the possibility that groups containing oxidized sulfur delocalize odd electrons in aromatic systems has been relatively unexplored, we have also analyzed the esr spectra of the radicals made from III and IV. To our knowledge, only dibenzothiophen radical anion (4,5), showed noticeable internal differences when the three possible oxidation states of the sulfur atom were changed, whereas in the other few cases examined no appreciable differences exist among S, SO, SO₂ (6,7). Therefore this new example could contribute to the elucidation of the conjugative properties of sulfur.

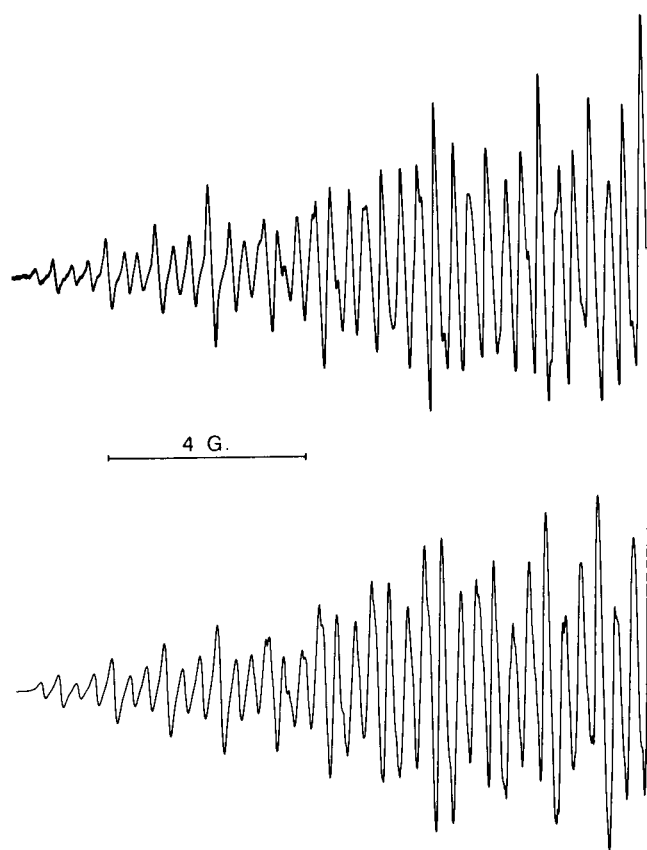The esr spectrum of the radical anion from I has been

4 G.

Figure   Experimental (upper) and simulated half esr
spectrum of dibenz[b,f]oxepin radical anion

Table

Experimental hyperfine splitting constants (gauss) of the radical anions I . . . IV;
the values in parenthesis are the theoretical coupling constants computed by INDO calculations.

Positions	I X = O	II X = S	III X = SO	IV X = SO$_2$
1,9	2.130 (-3.63)	1.475 (-3.49)	0.950 (-3.28)	1.850 (-3.05)
2,8	0.360 (1.99)	<0.120 (1.85)	0.140 (1.71)	0 200 (1.51)
3,7	4.220 (-4.12)	3.650 (-3.99)	3.520 (-3.84)	4.150 (-3.65)
4,6	1.080 (2.03)	1.325 (2.17)	0.710 (2.24)	1.500 (2.21)
10,11	4.500 (-4.42)	3.775 (-4.54)	3.520 (-4.59)	4.150 (-4.63)
Total widths (gauss)	24.58 (32.38)	20.45 (32.08)	17.68 (31.32)	23.70 (30.10)

interpreted (Figure) in terms of the hyperfine splittings reported in the Table. The coupling constants of the radical anion from II have been previously reported (8), however since we have been able to obtain a resolved spectrum we report in the Table our values where distinct hyperfine splittings from the pair of protons 1,9; 4,6 and 3.7; 10, 11 could be observed.

By comparing the proton coupling constants of the radical anions from I and II, it appears that the sulfur atom is better able to attract the electron spin density than is oxygen, thus reflecting the fact that the spin distribution in dibenz[b,f]oxepin radical anion is more like that of the stilbene anion (9).

In both cases the small spin density on the position para to the heteroatom indicates that conjugation through the sulfur or oxygen bridge is much weaker than conjugation through the vinyl residue, accordingly the radical structure approximates a cyclic-cis-stilbene more than a cyclic biphenyl sulfide or oxide.

Particular attention in this paper has been paid to the interpretation of the data obtained from the spectra of the radical anions containing the sulfoxide (III) and the sulfone (IV) moiety. Very few studies concerning the three possible oxidation states of the sulfur in aromatic radical anions have been made; nevertheless the observation that the total width of the esr spectra of SO and SO$_2$ derivatives is smaller than that of sulfur analogs (5), indicates a localizing ability of SO and SO$_2$ larger than sulfur.

The analysis of the spectrum of dibenzo[b,f]thiepin sulfoxide (7) (III), showed that this behaviour is also verified in the series of radicals here reported. On the contrary unexpected results were obtained from the corresponding sulfone radical anion (IV), in that the total width of its esr spectrum is larger than that measured for II and III, even though they are characterised by lower oxidation states.

To verify our results, INDO molecular orbital calculations were performed assuming for all the radicals examined a planar geometry. In fact it has been suggested that

cyclooctatetraene, although not planar in the neutral molecule, assumes a planar configuration in the corresponding radical anion (10). It is also known that dibenzo-[b,f]thiepin and oxepin are not planar in their ground states (11): the addition of a free electron in the π system of these molecules can remove the antiaromaticity of the 8π electrons in the same way as it happens in the cyclooctatetraene radical anion making the molecule planar.

The theoretical coupling constants for each radical are reported in parenthesis in the Table; the assignment of experimental hyperfine splittings to the various positions, is based on the computed values. The increased overall width of the esr spectrum of IV with respect to that of III is not in agreement with INDO calculations, which predict a further decreasing of the total width for the sulfur containing radicals with the highest oxidation state if a planar geometry is assumed.

This trend might indicate that the sulfonyl group is removed from conjugation in the system: in this case the molecule might not be planar in either the ground or the radical state, with the unpaired electron delocalized only on the stilbene-like fragment of the molecule. This particular configuration could make the sulfonyl moiety less electronegative than the other groups, thus explaining the anomalous increasing of the electron spin density.

EXPERIMENTAL

Dibenz[b,f]oxepin (1).

This compound was prepared (13) from 10,11-dihydrodibenz-[b,f]oxepin-10(11H)one. Reduction of the ketone to the corresponding carbinol was readily achieved by heating with aluminum isopropoxide in isopropyl alcohol and the carbinol was quantitatively dehydrated to 1 when warmed with p-toluenesulfonic acid.

Dibenzo[b,f]thiepin (II).

This compound was prepared (14) from thioxanthene which was metalated by means of butyllithium and condensed with formaldehyde to give 9-hydroxymethylthioxanthene. The p-toluenesulfonate of this alcohol, on treatment with boiling 95% formic acid, lost p-toluenesulfonic acid and rearranged to II.

Dibenzo[b,f]thiepinsulfone (IV).

This compound was prepared (14) from the corresponding dibenzothiepin with formic acid and hydrogen peroxide as described in the literature.

Acknowledgment.

The authors gratefully thank Professor L. Lunazzi, University of Bologna, for helpfull comments and discussions.

REFERENCES AND NOTES

(1) L. J. Aarons and F. C. Adam, Can. J. Chem., 50, 1390 (1972).

(2) E. T. Strom and G. A. Russel, J. Am. Chem. Soc., 87, 3326 (1965).

(3) M. F. Chiu, B. C. Gilbert and P. Hanson, J. Chem. Soc., (B), 1700 (1970); I. Degani, L. Lunazzi and G. F. Pedulli. Mol. Phys., 14, 217 (1968); I. Degani, L. Lunazzi, A. Mangini, G. F. Pedulli and C. Vincenzi, ibid., 18, 613 (1970); I. Degani, L. Lunazzi, A. Mangini, and G. Placucci and C. Vincenzi, ibid., 19, 543 (1970);

L. Lunazzi, A. Mangini, G. Placucci and C. Vincenzi, J. Chem. Soc., Perkin I, 2418 (1972).

(4) R. Gerdil and E. A. C. Lucken, Proc. Chem. Soc., 144 (1963).

(5) D. H. Eargle, Jr. and E. T. Kaiser, ibid., 22 (1964).

(6) M. M. Urberg and E. T. Kaiser. J. Am. Chem. Soc., 89, 5179 (1967).

(7) A. Trifunac and E. T. Kaiser. J. Phys. Chem., 74, 2236 (1970).

(8) M. M. Urberg and E. T. Kaiser, J. Am. Chem. Soc., 89, 5931 (1967).

(9) C. S. Jhonson, Jr. and R. Chang, J. Chem. Phys., 43, 3183 (1965).

(10) T. J. Katz, J. Am. Chem. Soc., 82, 3784 (1960); ibid., 82, 3785 (1960).

(11) M. Nógrádi, W. D. Ollis and I. O. Sutherland, Chem. Commun., 158 (1970).

(12) The freezing point of pure DME is $-58°$. but it is possible to cool the solutions to $-80°$ without freezing them, as confirmed by the other authors. 1. T. E. Gough and P. R. Hindle, Can. J. Chem., 49, 2412 (1971). 2. B. G. Segal, A. Reymond and G. K. Fraenkel, J. Chem. Phys., 51, 1336 (1969). 3. R. L. Kugel, W. G. Hodgson and H. R. Allcock, Chem. Ind. (London), 1649 (1962).

(13) R. H. F. Manske and A. E. Ledingham. J. Am Chem. Soc., 72, 4797 (1950).

(14) E. D. Bergmann and M. Rabinovitz, J. Org. Chem., 25, 828 (1960).