Tetrahedron Letters No.16, pp. 1079-1082, 1971. Pergamon Press. Printed in Great Britain.

ELECTRONIC AND ESR SPECTRA OF NAPHTHYLENE-1.8-DISULFIDE, BIPHENYLENE-2.2'-DISULFIDE AND RELATED COMPOUNDS

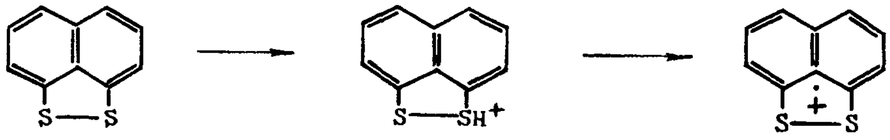
By B.I.STEPANOV, W.Ya.RODIONOV, A.Ya.ZHELTOV and V.V.ORLOV
(D.I.Mendeleyev's Institute of Chemical Technology, Moscow, A-47,USSR)

(Received in UK 10 March 1971; accepted for publication 19 March 1971)

Dissolving aromatic compounds of sulfur (bicovalent) in concentrated sulfuric acid leads to formation of the corresponding cation-radicals [1-5]. The stability of the disulfide-ring in the aromatic cyclodisulfides and the anomalous deep colour of the latter led us to investigate the electronic and ESR spectra of solutions in sulfuric acid of naphthylene-1.8- (I) and biphenylene-2.2'-disulfides (II) as the most typical representatives of this class of compounds, and also of some of their related derivatives which do not contain a S-S-bond.

A paramagnetic solution of golden-yellow colour, which gradually changes to reddish-brown, is formed when I is dissolved in 94% H_2SO_4. This is in an accordance (if spectra are measured as a function of time) with an increase of the absorption band intensity at 596, 520, 422 and 273 nm, decrease of intensity at 456, 335, 303, 266 and 244 nm (fig.1) and with a parallel increase of the ESR spectrum signal intensity during 2.5 hours after the preparation of the solution.

The disulfide I probably changes gradually into the cation-radical (Ib) via the intermediate sulfonium salt (Ia).



(I) (Ia) (Ib)

Assignment of the absorption bands of the electronic spectrum of the cation-radical Ib was based on the fact that the relation between the change of the extintion coefficients of the electronic spectrum and the increase of the signal ESR-spectrum intensity is linear.

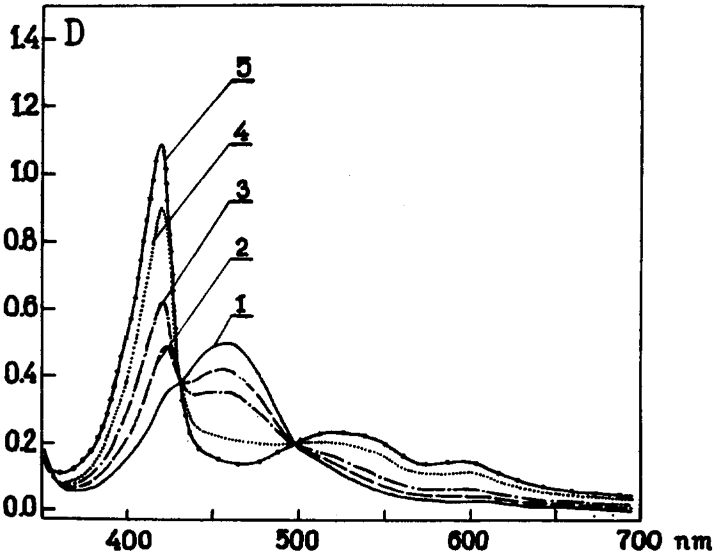


Fig.1. Electronic spectra of the solution I in concentrated H_2SO_4, recorded using a Perkin-Elmer-402 spectrophotometer for: 1 - 4 min., 2 - 15 min., 3 - 34 min., 4 - 75 min. and 5 - 225 min. after the preparation of the solution. $C = 0.77 \cdot 10^{-4}$ M/l; l = 1 cm.

The solution of I in H_2SO_4 retains its paramagnetic properties for ~72 hours, that is related to the stability of the pseudoaromatic system formed - a six electron condensed heterocycle [6].

In contrast to Zweig [6], we observed no paramagnetic properties in the solution of the S.S'-dimethyl derivative of I (and also of II) in H_2SO_4 probably because these cation-radicals have a negligible stability. However, S.S'-isopropylidene-derivatives of I and II (III and IV) unexpectedly gave stable paramagnetic solutions, giving ESR-signals even up to one day after the preparation of the solution.

ESR-spectra of cation-radicals of I (fig.2) and III are well defined quintets of triplets with the coupling constants in case I: a_p = 5.20 gs, a_o = 3.85 gs and a_m = 0.70 gs, that corresponds to a naphthalene spin density of 0.849. Easy delocalization of the unpaired electron is a result of the coplanarity of I. In the case of the cation-radical from III coupling constants are

a_p = 4.00 gs, a_o = 3.10 gs and a_m = 1.40 gs, and the naphthalene spin density decreases to 0.740. This difference may be result of deformation of the carbon skeleton of naphthalene because of the introduction of the rigid isopropylidene group and, consequently, of some decrease in the role of the 3p-π-interaction.

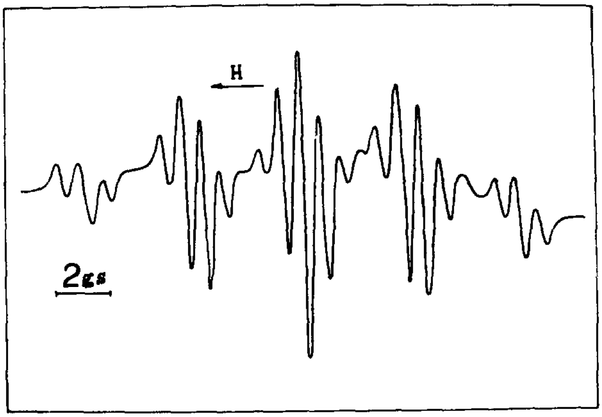
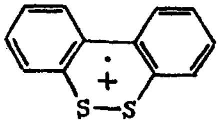


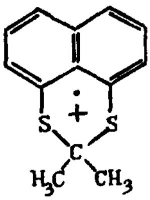
Fig.2. ESR-spectrum of cation-radical Ib in 94% H_2SO_4, recorded using radiospectrometer RE-1301 (10 000 MHz)

II and its isopropylidene-derivative IV slowly dissolve in 94% H_2SO_4 with the formation of green coloured paramagnetic solutions whose electronic spectra are closely similar (essentially in the visible region) whereas the spectra of their alcoholic solutions differ sharply (fig.3). The ESR-spectrum of II consists of seven equidistant lines of equal intensity with the coupling constants a_p = 1.40 gs, a_o = 0.70 gs and a_m = 0.00 gs that is in an accordance with the localization of unpaired electron on the S-S-bond (0.814). A similar ESR-spectrum was obtained for the solution of IV: a_p = 1.10 gs, a_o = 0.55 gs and a_m = 0.00 gs, that is also in an accordance with the localization of the unpaired electron on the dithio-fragment (0.856).

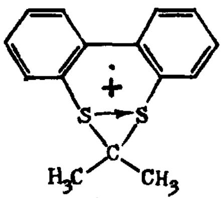
The similarity of electronic and ESR-spectra of II and IV leads to the conclusion that in concentrated sulfuric acid these cation-radicals have analogous structures.



(II)



(III)



(IV)

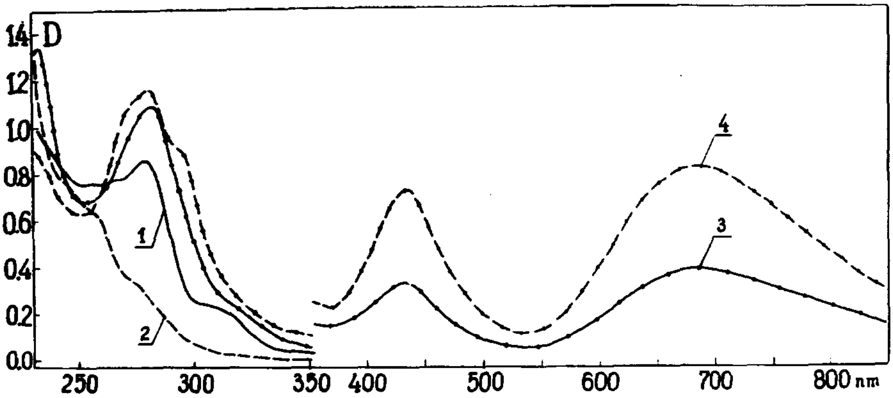


Fig.3. Electronic spectra of II: 1 - in 96% ethanol, 3 - in 94% H_2SO_4; and of IV: 2 - in 96% ethanol, 4 - in 94% H_2SO_4. C = $0.74 \cdot 10^{-4}$ M/l; l = 1 cm.

Further S-S-bonding in the cation-radical from IV may result from interaction of a 3p-(lone) pair of one atom sulfur with a vacant 3d-orbital of the other sulfur atom of the dithio-fragment [7].

REFERENCES

1. E.A.Lucken, J.Chem.Soc., 1962, 4963;
2. A.Zweig, W.G.Hodgson, W.H.Jura, D.L.Maricle, Tetrahedron Letters, 1963, 1821;
3. A.Zweig, W.G.Hodgson, Proc.Chem.Soc., 1964, 417;
4. J.S.Brinen, A.Zweig, B.Roberts, Chem.Phys.Letters, 1969, 3, 305;
5. H.J.Shine, L.Piette, J.Am.Chem.Soc., 1962, 84, 4799;
6. A.Zweig, A.K.Hoffman, J.Org.Chem., 1965, 30, 3997;
7. D.R.Williams, D.L.Coffen, P.E.Garrett, P.N.Schwarth, J.Chem.Soc., 1968 B, 1132.