

ROTAMERS OF 2,2'-DITHIENYL AND 2-PHENYLTHIOPHEN RADICAL ANIONS

P. Cavalieri d'Oro, A. Mangini, G.F. Pedulli, P. Spagnolo and M. Tiecco

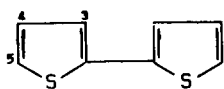
Istituto di Chimica Organica e di Chimica Industriale dell' Università

Viale Risorgimento, 4 - 40136 Bologna - Italy

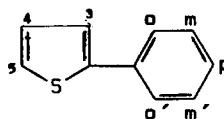
Laboratorio del C.N.R. per lo Studio di Composti Organici Contenenti Eteroatomi

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In connection with our recent studies on the chemical (1) and spectroscopic (2) behaviour of radicals containing the thiophen nucleus, we became interested in the electron spin resonance spectra of dithienyls and phenylthiophenes. In this communication we wish to report the results concerning the radical anions of 2,2'-dithienyl (I) and 2-phenylthiophen (II).



(I)



(II)

When an oxygen-free solution of (I) in DME (about  $10^{-3}$  M) was left to react at  $-80^\circ$  with potassium, a green colour developed and a well resolved e.s.r. spectrum could be recorded (Fig. 1). The spectrum was more complicated than that theoretically expected for the radical anion of 2,2'-dithienyl (I): in effect it is the result of the superimposition of the spectra of two very similar radicals, labeled A and B, with an intensity ratio of 4:1 and having their centers 0,29 gauss apart.

Both spectra can be analysed as the result of the coupling of the unpaired electron with three series of two equivalent protons; the spectral reconstruction of the radical present in lower concentration (B), reported in Fig. 1, was based on the hyperfine splitting constants listed in Table 1. In the same table are also reported the coupling constants of the other radical (A); the reconstruction of the spectrum of this radical is not indicated but its interpretation can be easily carried out. The relative hfs constants have been assigned by means of M.O.

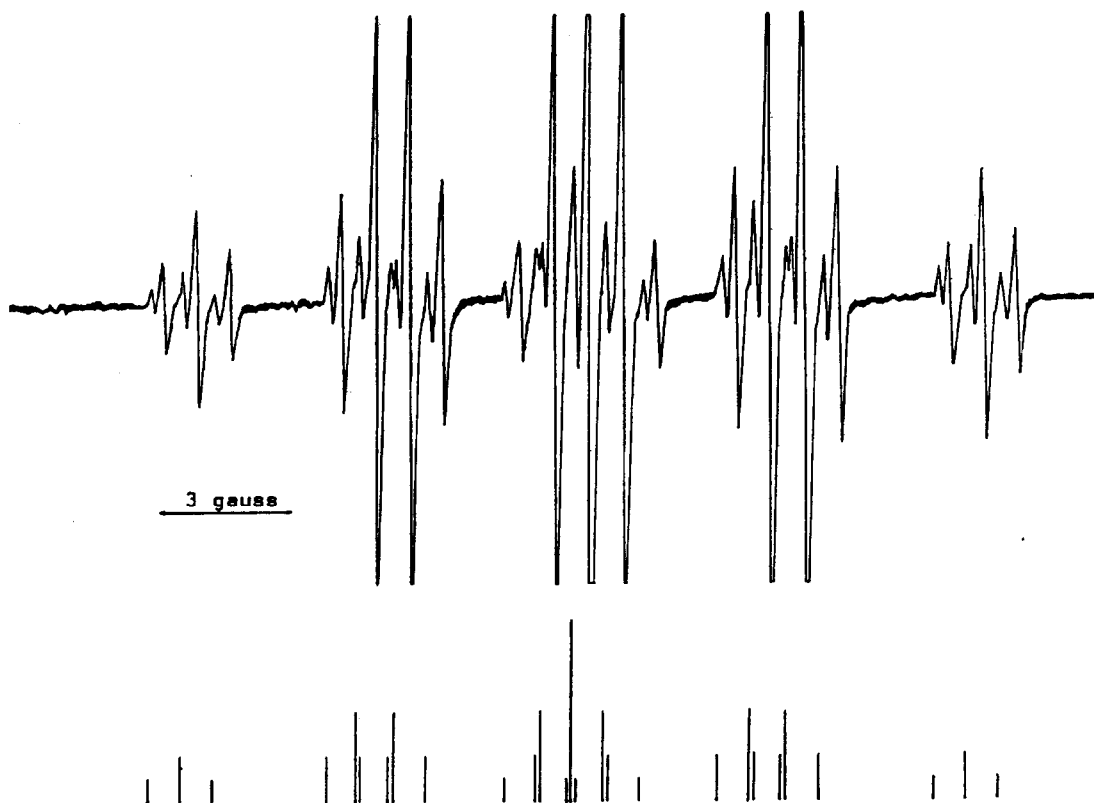


Fig. 1 - Experimental e.s.r. spectrum of the 2,2'-dithienyl radical anion (upper) and spectral reconstruction of the radical present in lower concentration (lower).

calculations and by comparison with the spectrum of 5,5'-dideutero 2,2'-dithienyl (3).

TABLE 1

	$a_3$	$a_4$	$a_5$	$a_o$	$a_{o'}$	$a_m$	$a_{m'}$	$a_p$
IA	4.01	0.75	4.76					
IB	3.97	0.70	4.80					
II	4.21	0.77	4.88	2.41	2.64	0.31	0.46	5.21

The similarity of the two e.s.r. spectra, the equal number of interacting protons

as well as the similarity of the hyperfine coupling constants in the two spectra seem to indicate that they are due to two very similar radical species which could be rotamers of the radical anion of (I). This means that the two aromatic rings are held in a planar or nearly planar conformation, where the sulphur atoms are in a cis or trans position, for a sufficient time for each rotamer to give an individual spectrum. The  $g$  factor difference in two isomeric radicals, although unusual, has already been pointed out in semidione radical anions (4). The experimental data so far accumulated, however, do not allow the assignment of the geometrical structure to the two species A and B.

Behaviour similar to that observed for the 2,2'-dithienyl should be expected for analogous systems. In this connection we have investigated the radical anion of the 2-phenylthiophen (II). In this case, if the molecule is locked in a rigid conformation, different values of the hfs constants relative to the protons in the  $q$ -,  $q'$ -, as well as  $m$ -,  $m'$ -positions, should be expected. This has been verified experimentally; the e.s.r. spectrum of the radical anion of (II), generated under the same experimental conditions reported above for the radicals of (I), can be interpreted on the basis of eight non-equivalent protons, as expected. The hfs constants reported in table 1 were assigned to the hydrogen atoms of the thiophen and benzene rings by analogy with those of the radicals of (I). The assignments of the constants to the  $q$ -,  $q'$ -, and  $m$ -,  $m'$ -hydrogens of the phenyl ring required a molecular orbital calculation, in which asymmetry has been introduced using the so-called  $\beta$  effect (5).

#### REFERENCES

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- 3) Prepared by reduction of 5,5'-diiodo-2,2'-dithienyl with Zn, acetic anhydride and deuterium oxide; the n.m.r. spectrum (in CDCl<sub>3</sub>) showed two doublets at 7.00 (J = 3.4 cps) and 6.80 (J = 3.4 cps) attributed to the hydrogens in 4,4'- and 3,3'-positions respectively.
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