

CATION AND ANION RADICALS OF THIENO[3,2-b]THIOPHEN

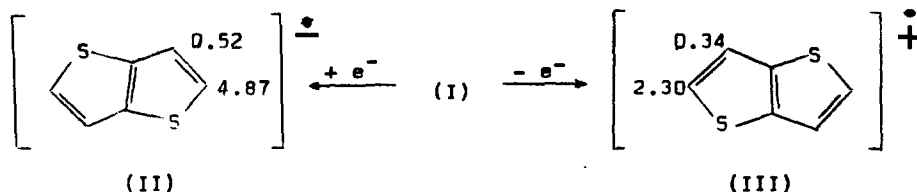
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It is quite unusual to obtain from the same heterocyclic compound both the positive and negative radical; to the best of our knowledge the only example so far reported is that of 1,3,6,8-tetraazapyrene¹. We wish to report that another heteroaromatic compound, the thieno[3,2-b]thiophen (I), can be either reduced to the radical anion (II)², or oxidized to the corresponding cation (III).

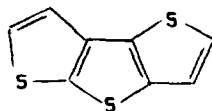
This seems to be the first example of the generation of a pair of radical ions from the same sulphur-containing molecule and also the first positive radical in the thiophen series unambiguously³ detected by E.S.R. spectroscopy.



The spectrum of the radical anion (II) has been reported²; the radical cation (III) has been obtained by reaction of (I) with $AlCl_3$ in nitromethane, or $SbCl_5$ in methylene chloride at $-20^\circ C$ and $-60^\circ C$ respectively. The E.S.R. spectra display nine lines with the expected intensity ratio; the hyperfine splittings (gauss) are reported on the formulae and have been assigned with the help of the spectrum of 2-methylthieno[3,2-b]thiophen. Although the pairing theorem only holds for alternant hydrocarbons⁴, nevertheless there is a fairly good correspondence between the splittings of the positive and negative radical even in the case of an alternant molecule containing heteroatoms^{1,5}. In the present case however not only are heteroatoms present but the molecule is not alternant, accordingly differences have to be expected between the splittings of the cation and anion: this is particularly evident at position 2. The h.f.s. constants are smaller in the cation than in the anion and this can be rationalized in terms of molecular orbital calculations^{2,6,7}. This kind of calculation actually predicts smaller values in the positive than in the negative radical (see Table). This molecule is particularly suitable^{2,8} to test the results given by the use of a model⁹ which takes into account the participation of the sulphur d-orbitals to the conjugative system: as it can be seen in the table this model is unsatisfactory since it predicts for the cation greater spin densities than for the anion,

whilst an opposite trend of the hyperfine splittings is observed.

Attempts to generate positive and negative radicals of other condensed thiophens under similar experimental conditions failed, although the cation of di-thieno/[2,3-b : 2',3'-d]thiophen (IV) could be obtained, its h.f.s. constants being 0.42 (2 H), 2.36 (1 H), 2.98 (1 H) gauss.



(IV)

Table

Calculated spin densities (McLachlan method⁶, $\lambda = 1.2$) for the radical anion (II) and the radical cation (III) of Thieno/[3,2-b]thiophen.

	Anion		Cation	
	H ₂	H ₃	H ₂	H ₃
p-model ²	0.368	-0.019	0.330	0.017
d-model ⁹	0.172	0.148	0.182	0.161

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