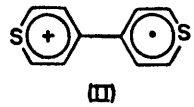
Characterisation of the 4,4'-Bithiopyrylium Radical Cation by Electron Spin Resonance Spectroscopy

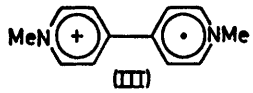
By Z. YOSHIDA,* T. SUGIMOTO, and S. YONEDA
(*Department of Synthetic Chemistry, Kyoto University, Yoshida, Kyoto, Japan*)

Summary The radical cation, formed by one-electron reduction of the 4,4'-bithiopyrylium dication, has been characterized by its e.s.r. spectrum.

RECENTLY we reported the synthesis of the 4,4'-bithiopyrylium dication (I),[1] a new heteroaromatic system. We now describe the characterisation of the 4,4'-bithiopyrylium



(II)



(III)

radical cation (II), generated by one-electron reduction of (I) with Zn–MeCN at room temperature. (II) had a hyperfine e.s.r. spectrum consisting of five overlapping pentuplets (Figure). The pentuplet splitting was 0·60 G resulting from coupling with four equivalent H_β protons. The five pentuplets were spaced at intervals of 2·37 G due to the splitting by four equivalent H_α protons. These assignments for the α- and β-protons are in good agreement with the result theoretically obtained from McConnel's equation,[2] $a_{CH}{}^{H}=Q_{CH}{}^{H}\rho_C$. The spin density distribution in the planar model ($\rho_\alpha = 0{\cdot}104$, $\rho_\beta = 0{\cdot}031$, $\rho_\beta = 0{\cdot}059$)† was calculated by the HMO method involving the sulphur

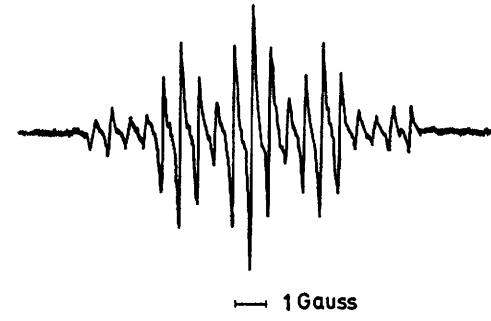


FIGURE. *The first-derivative e.s.r. spectrum of* (II).

3*d* orbitals,[3] and Q_{CH} was taken to be 24·2 G, according to McLachlan.[4] The e.s.r. spectrum pattern can be interpreted as that of the symmetrical 4,4'-radical cation system, where the odd electron is distributed equally in both the rings of (II). It is also noteworthy that the e.s.r. spectrum of (II) is quite different from that of the methyl viologen radical (III; *NN'*-dimethyl-4,4'-bipyridinium radical cation), iso-π-electronic with (II). The splitting constants in (III) are 1·33 G for the α-protons and 1·57 G for the β-protons,[5] indicating that both the splitting constants in (II) are in the reverse order and much more separated from each other compared with those in (III).

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† The spin density distribution calculated in the nonplanar model showed a similar tendency, *e.g.*, $\rho_\alpha = 0{\cdot}116$, $\rho_\beta = 0{\cdot}015$, $\rho_\beta = 0{\cdot}053$ at the twisted angle $\theta = 45°$.

[1] Z. Yoshida, S. Yoneda, T. Sugimoto, and O. Kikukawa, *Tetrahedron Letters*, 1971, 3999.
[2] H. M. McConnel, *J. Chem. Phys.*, 1956, **24**, 632.
[3] H. C. Longuet-Higgins, *Trans. Faraday Soc.*, 1949, **45**, 173.
[4] A. D. McLachlan, *Mol. Phys.*, 1960, **3**, 233.
[5] C. S. Johnson, jun., and H. S. Gutowsky, *J. Chem. Phys.*, 1963, **39**, 58.