

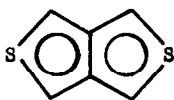
THE π ELECTRONIC STRUCTURE OF THIENO[3,4-c]THIOPHENE

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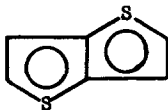
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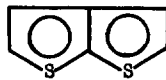
The recent communication¹ concerning the transitory existence of a dimethyl derivative of I thieno[3,4c]thiophene, prompts us to record the results of a self consistent field Pariser-Parr-Pople,^{2,3} calculation of the π electronic structure of this compound. For some time now we have been investigating theoretically the electronic spectra⁴ and reactivity of the isomeric thienothiophenes (II - IV) and the recent report of the synthesis of thieno[3,4b]thiophene (VI)⁵ led us to consider possible synthetic routes for the synthesis of I the remaining unsynthesized thienothiophene.



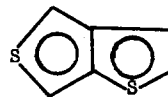
I



II



III



IV

This compound is of considerable interest since resonance structures which may be drawn for it either involve charge separation or a double bond to a sulphur atom, however a priori this does not mean that the bonding involved in this compound is any different in nature than that in compounds (II - IV).⁶

As a preliminary to attempts to synthesize I we thought it worthwhile to investigate theoretically the π electronic structure, in the hope that this would provide us with information relevant to the synthesis of this compound. In the event this proved to be the case and the information derived from these calculations led us to abandon attempts to synthesize it.

The calculations were carried out using the PPP SCF MO method. Full details of the parameters used and the method of calculation will be published elsewhere but it may be

mentioned that the method gives a good account of the heat of formation and reactivity of thiophene and the isomeric thienothiophenes.⁷ Only the $3p_z$ orbitals were considered for the sulphur atoms, since detailed Pople-Segal^{8,9,10} type SCF calculations which we have carried out on thiophene¹¹ including all valence electrons and 3s, 3p, 3d, 4s and 4p orbitals on sulphur, indicate that as far as the total energy of the molecule is concerned the 3d, 4s and 4p orbitals have a negligible effect. For the calculation, the C-S bond lengths and C-S-C bond angles were taken to be those on thiophene.¹² (1.714\AA , 92°). All C-C bond lengths were taken to be the same (1.39\AA) the average of the bond lengths in thiophene and II.^{12,13}

Table I shows the calculated eigenvalues for thieno[3.4c]thiophene.

Table I

<u>Orbital Number</u>	<u>Energy (in ev)</u>
8	2.109
7	0.5075
6	-2.098
5	-7.756
4	-10.463
3	-10.525
2	-12.021
1	-13.145

The interesting feature here is the small energy gap between orbitals 5 and 6. The lowest energy singlet state corresponds to $\begin{matrix} 2 & 2 & 2 & 2 & 2 \\ 1 & 2 & 3 & 4 & 5 \end{matrix}$. The lowest energy triplet state corresponds to $\begin{matrix} 2 & 2 & 2 & 2 \\ 1 & 2 & 3 & 4 & 5 & 6 \end{matrix}$ and the lower electron repulsion energy for this state more than offsets the excitation energy of an electron from 5 to 6 and the ground state of the molecule is therefore predicted to be a triplet 0.11 ev below the lowest singlet state. Even more revealing of the chemical nature of this compound is its relative heat of formation with respect to the other isomers (II - IV). This is shown in Table 2.

Table 2

Calculated differences in E_w Bonding in ev for the isomeric thienothiophenes

Compound	Difference in E_w Bonding in ev
II Thieno[3.2b]thiophene	0
III Thieno[2.3b]thiophene	0.054
IV Thieno[3.4b]thiophene	0.313
I Thieno[3.4c]thiophene	2.000

Thieno[3.4c]thiophene is predicted to be 46 Kcals less stable in a thermodynamic sense than II thieno[3.2b]thiophene. The prediction of a triplet ground state, together with the large difference in thermodynamic stability with respect to the "classical" thienothiophenes (II - IV) is entirely consistent with the evidence presented by Cava and Pollack,¹ and accounts for the transitory existence and facile addition reactions of the dimethyl derivative of I.

References

1. M. P. Cava and N. M. Pollack. J. Amer. Chem. Soc. 89, 3639, (1967).
2. R. Pariser and R.G. Parr, J. Chem. Phys. 21, 466 (1953).
3. J. A. Pople, Trans. Faraday Soc. 49, 1375 (1953).
4. D. T. Clark, submitted for publication.
5. H. Wynberg and D. J. Zwanenburg, Tetrahedron Letters, 2, 761 (1967).
6. Compare the case of meta benzoquinone. M.J.S. Dewar and G.J. Gleicher, J. Chem. Phys., 44, 759, (1966).
7. D. T. Clark, submitted for publication.
8. J. A. Pople, D. P. Santry and G. A. Segal, J. Chem. Phys. 43, S129 (1965).
9. J. A. Pople and G. A. Segal, J. Chem. Phys., 43, S136 (1965).
10. J. A. Pople and G. A. Segal, J. Chem. Phys., 44, 3289 (1966).
11. D. T. Clark, submitted for publication.
12. B. Bak, D. Christensen, L. Hansen-Nygaard and J. Rastrup-Aderson. J.Mol.Spectry, 7, 58 (1961).
13. E. G. Cox, R.J.T.H. Gillot and G.A. Jeffrey, Acta Cryst., 2, 356 (1949).