

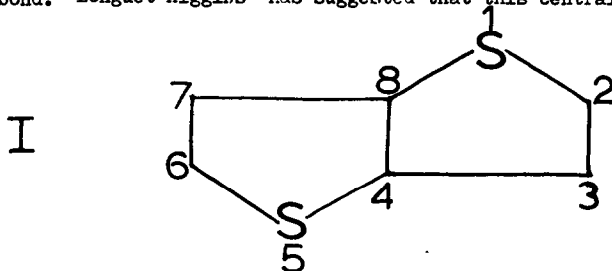
THE LENGTH OF THE CENTRAL BOND IN THIENO[3-2,b]THIOPHENE

D.T. Clark

Department of Chemistry, The University, Durham, England

(Received 13 April 1967)

The crystal structure of thieno[3-2,b]thiophene I has been investigated by Cox and his co-workers,¹ who found the central carbon-carbon bond distance to be quite short (1.36 Å), corresponding to a high π bond order for this bond. Evans and de Heer² calculated the π bond orders for this molecule, using the Longuet-Higgins³ pd^2 hybrid model for the sulphur atom, and the bond-bond polarizabilities of naphthalene. Their results are shown in Table I, together with their predicted bond lengths. The striking feature is the large discrepancy (0.05 Å) between the calculated and observed bond lengths for the central C-C bond. Longuet-Higgins⁴ has suggested that this central bond is compressed



by bond angle stresses, and by a consideration of the cumulative strains around C_4-C_8 has calculated that the amount of compression is ≈ 0.06 Å in agreement with the 0.05 Å discrepancy. However Schomaker⁵ has presented convincing arguments that the latter calculation is unrealistic and that any shortening due to distortion of this type would be of the order of 0.03 Å with concomitant contraction of the C_2-C_3 bond of 0.01 Å.

It is the purpose of this communication to show that this discrepancy in bond length disappears when electron interactions are included in a SCF Pariser - Parr - Pople treatment of the molecule.

Table I shows the results of calculations of bond orders and bond lengths, using the Coulson-Golebiewski⁸ relationship. For the PPF treatment, only the $3p_z$ orbitals were considered for the sulphur atoms, and core integrals and electron repulsion integrals were

estimated in the usual fashion^{6,9,10,11} from spectroscopic data and the uniformly charged sphere approximation, and were essentially the same as those reported by Bielefeld and Fitts.¹² For the calculation of the repulsion integrals the C-S bond lengths and C-S-C bond angles were taken to be those in thiophene¹³ (1.714 Å, 92°). All C-C bond lengths were taken to be the same (1.39 Å) the average of the bond lengths in thiophene.¹³

Table I

Bond	Bond Order	Calculated Bond Length (Å)	Experimental Bond Length (Å)	Δ (Experimental - Calculated) Bond Lengths	Ref.
C ₂ -C ₃	0.76	1.37	1.36	-0.01	2
"	"	1.38	"	-0.02	14
"	0.84	1.36	"	0	This work
Bond Length corrected for distortion ⁵		1.35			
C ₃ -C ₄	0.56	1.41	1.41	0	2
"	"	1.42	"	-0.01	14
"	0.47	1.43	"	-0.02	This work
Bond Length corrected for distortion ⁵		1.41			
C ₄ -C ₈	0.56	1.41	1.36	-0.05	2
"	"	1.41	"	-0.05	14
"	0.72	1.39	"	-0.03	This work
Bond Length corrected for distortion ⁵		1.38			

The calculated C-C bond lengths are in good agreement with those determined experimentally, and within experimental error are the same as those predicted by Schomaker.⁵ A similar situation obtains for naphthalene,¹⁵ where again Hückel theory tends to overestimate the length of the central C-C bond and the SCF treatment is in much better agreement with experiment.¹⁵

A detailed account of the electronic spectra and reactivity of the isomeric thiophenes will appear at a later date.

REFERENCES

- (1) E.G. Cox, R.J.J.H. Gillot, and G.A. Jeffrey, Acta Cryst., 2, 356 (1949).
- (2) M.G. Evans and J. de Heer, Acta Cryst., 2, 363 (1949).
- (3) H.C. Longuet-Higgins, Trans. Faraday Soc., 45, 173 (1949).
- (4) H.C. Longuet-Higgins, Acta Cryst., 3, 76 (1950).
- (5) V. Schomaker, Acta Cryst., 4, 158 (1951).
- (6) R. Pariser and R.G. Parr, J. Chem. Phys., 21, 466, 767 (1963).
- (7) J.A. Pople, Trans. Faraday Soc., 49, 1375 (1953).
- (8) C.A. Coulson and A. Golebiewski, Proc. Phys. Soc. (London), 78, 1310 (1961).
- (9) R. Pariser, J. Chem. Phys., 21, 568 (1953).
- (10) R.G. Parr, J. Chem. Phys., 20, 1499 (1952).
- (11) J. Hinze and H.H. Jaffe, J. Amer. Chem. Soc., 84, 540 (1962).
- (12) M.J. Bielefeld and D.D. Fitts, J. Amer. Chem. Soc., 88, 4804 (1966).
- (13) B. Bak, D. Christensen, L. Hansen Nygaard, and J. Rastrup Andersen, J. Mol. Spectry., 7, 58 (1961).
- (14) Bond orders taken from (2) bond lengths recalculated according to (8).
- (15) L. Salem, Molecular Orbital Theory of Conjugated Systems, 1966. W.A. Benjamin Inc. New York, page 140.