Tetrahedron, 1963, Vol. 19, pp. 471 to 477. Pergamon Press Ltd. Printed in Northern Ireland

THE LCAO–MO STUDY OF THIANTHRENE

A. K. CHANDRA
Department of Chemistry, University College of Science & Technology
Calcutta-9, India

(*Received* 20 *May*, *revised* 31 *October* 1962)

Abstract—The structure of thianthrene has been examined by the LCAO–MO method neglecting overlap, σ-π interaction and the contribution of sulphur d orbitals. Aromaticity has been predicted with 80·33 Kcal/mole of resonance energy. That the molecule is folded about S–S axis is correctly predicted with 6 $\sim$ 7 Kcal/mole of the energy for turning the molecule inside out. It is seen that the variation in σ bond energy is much smaller than the corresponding variation in π electron energy with dihedral angles and hence not important. Other properties are also discussed.

THE chemistry of thianthrene and its derivatives are well known.[1] The dipole moment[2] of the molecule indicates that it is non-planar and folded about the S–S axis. This is further substantiated by the recent X-ray analysis by Lynton and Cox.[3] Thianthrene has high thermal stability and exhibits the reactions of an aromatic system.

In the present paper the LCAO–MO method has been applied to thianthrene and the results compared with those obtained for thiophene which has been the subject of both experimental[4] and theoretical investigations.[5] In both molecules the C—S—C bond angles are distorted from their preferred values resulting in strain. The strain energy by which the energy of the molecule is raised or the apparent resonance energy is lowered is assumed proportional to the square of the distortion.[6] In the present LCAO–MO calculation, the sulphur 3*d* orbitals, the overlap integrals and the σ-π interaction have been neglected although for non-planar molecule the classification of orbitals into σ and π is not strictly legitimate.

Method of calculation

Pauling[7] regards the electronegativity of sulphur the same as that of carbon. The ionization potential for sulphur 3*p* orbital (10·98 eV)[8] is not very different from that for a carbon 2*p* orbital (11·54 eV).[8] Consequently, we have taken the coulomb integral for sulphur equal to that for carbon. The resonance integrals for the C—S and the C—C bonds have been estimated on the assumption that this resonance integral

---

[1] [a] H. Gilman and D. R. Swayampati, *J. Amer. Chem. Soc.* **79**, 991 (1957); [b] S. Krishna, *J. Chem. Soc.* 2786 (1923).

[2] R. J. W. Le Fevre, *Dipole Moment* p. 113. Methuen, London (1953).

[3] H. Lynton and E. G. Cox, *J. Chem. Soc.* 4886 (1956).

[4] H. D. Hartough, *Thiophene and its derivatives* Interscience, New York, N.Y. (1952).

[5] [a] H. C. Longuet Higgins, *Trans Farad. Soc.* **45**, 173 (1949); [b] J. De Heer, *J. Amer. Chem. Soc.* **76**, 4802 (1954).

[6] F. H. Westheimer, *Steric Effects in Organic Chemistry* (Edited by M. S. Newman), p. 523. John Wiley, New York, N.Y. (1956).

[7] L. Pauling, *Nature of the Chemical Bond* Cornell University Press, N.Y. (1948).

[8] H. A. Skinner and H. U. Pritchard, *Trans. Farad. Soc.* **49**, 1254 (1953).

is a constant fraction of bond energy. It follows from Mulliken's expression[9] for the bond energy that

$$\beta_{ab} = \beta \cdot \frac{A_{ab} I_{ab} S_{ab}/(1 + S_{ab})}{AIS/(1 + S)} \tag{1}$$

where the quantities marked with subscript *ab* refer to the interactions between the atomic orbitals ϕ_a and ϕ_b and others refer to an aromatic C—C π-bond. The parameters A are those of Mulliken and I_{ab} is assumed to be the mean ionization potentials of the two atoms in their appropriate valence states. The values of overlap integrals S, were taken from the Tables of Mulliken *et al.*[10]

Thiophene. With the bond lengths of thiophene as given in the literature[11] the resonance integral for the sulphur $3p_\pi$ orbitals with C_2 (Fig. 1) $2p_\pi$ orbital is $0{\cdot}744\beta$, that for C_2—C_3 is $1{\cdot}06\beta$ and that for C_3—C_4 is $0{\cdot}92\beta$ according to the Eq. (1) where β is the resonance integral for an aromatic C—C π-bond. The energy levels of the five molecular π-orbitals and the coefficients of the atomic orbitals in the filled molecular orbitals have been evaluated in the usual way.

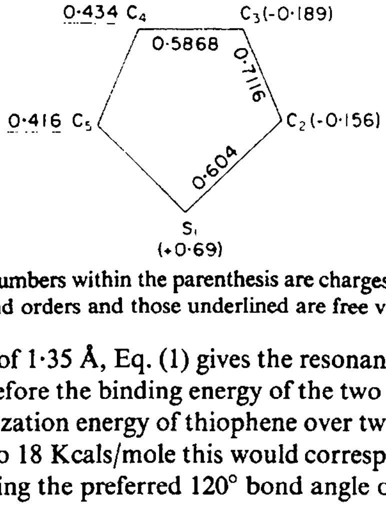

FIG. 1. Thiophene: The numbers within the parenthesis are charges, numbers along the bonds are bond orders and those underlined are free valences.

With C—C bond length of 1·35 Å, Eq. (1) gives the resonance integral of $1{\cdot}06\beta$ for π-bond in ethylene and therefore the binding energy of the two π-electrons in ethylene is $2{\cdot}12\beta$. The excess delocalization energy of thiophene over two ethylene molecules is $1{\cdot}658\beta$. Assuming β equal to 18 Kcals/mole this would correspond to 29·9 Kcal/mole. The strain caused by distorting the preferred 120° bond angle of ethylene to 112–113° must be evaluated. This was done by Westheimer's method using the appropriate bending force constant of ethylene given by Herzberg.[12] The total strain obtained in this way is about 3 Kcal/mole so that calculated resonance energy is 27 Kcal/mole. This is in fairly good agreement with empirical value 28–29 Kcal/mole given by Wheland.[13]

Thianthrene. As the thianthrene molecule is folded about S–S axis, the resonance integral for the C—S π-bond will depend on the dihedral angle α. For maximum overlap $3p_\pi$ orbital of sulphur atom and $2p_\pi$ orbital of carbon atom should have the

[9] R. S. Mulliken, *J. Phys. Chem.* **56,** 295 (1952).

[10] R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.* **17,** 1248 (1949).

[11] V. Schomaker and L. Pauling, *J. Amer. Chem. Soc.* **61,** 1769 (1939).

[12] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* p. 184. Van Nostrand, New York (1945).

[13] G. W. Wheland, *Resonance in Organic Chemistry* p. 99. John Wiley, New York, N.Y. (1955).

common nodal plane. This will be the case when α is 180° but under this condition the C—S—C bond angle (hereafter it will be denoted by γ) will be enlarged from its preferred value around 90° [14] to that around 120°. This results in appreciable strain in the molecule. As α is reduced, because of the decreased overlap between $3p_\pi$ orbital of sulphur atom and $2p_\pi$ orbital of the adjacent carbon atom, the binding energy of the π-electrons is decreased assuming that all other C—C bond lengths and C—C—S bond angles are fixed. At the same time γ will change, so the strain energy will be different. If it is assumed that σ bond energy is given by a constant quantity E_σ then total energy E of the molecule will be

$$E = E_\sigma + E_\pi + E_s \tag{2}$$

where E_s and E_π are the strain energy and π-electron binding energy respectively. Since both E_s and E_π are functions of α, the angle α can be found by minimizing the energy E.

The bond lengths were assumed to be 1·77 Å [3] for C—S bond and 1·39 Å for all other C—C bonds. Since it is not known which value of γ would be for planar thianthrene we have reported the results of two series of calculations.

In one series of calculations, for the planar molecule (i.e. $\alpha = 180°$) we assumed γ to have the value 110°. The C—C—S angle was assumed then to have a fixed value of 125°. In order to calculate the resonance integral for the C—S π-bond from Eq. (1) the overlap integral must be multiplied by the cosine of the angle θ, where θ is the angle of inclination of the $2p_\pi$ orbital of carbon with the $3p_\pi$ orbital of the sulphur atom. The Eq. (3) gives θ in terms of α

$$\theta = 90° - \alpha/2 \tag{3}$$

For calculating strain the angle γ is needed as a function of α and it is given by

$$\sin \gamma/2 = \sin 55° \sin \alpha/2 \tag{4}$$

E_π was calculated for different values of α by the usual method and E_s was calculated for different values of γ by Westheimer's method[6] using the force constant that for H_2S.[14] The unstrained bond angle was assumed to be 92° [15] as in H_2S. Since C—C—S angle was assumed to have a fixed value of 125°, strain due to this source is not a function of α and represents a constant factor 1·3 Kcal/mole[13] in E_s. The strain energies and the π-electron binding energies are shown in Table 1 for various values of α where energies are given in Kcal/mole assuming β to have the value 18 Kcal/mole.

In Table 2 are reported the results of the second series of calculations where, for the planar molecule, the γ was assumed to have the value 120° and the C—C—S angle to have the fixed value of 120°.

It is seen from Tables 1 and 2 that the rate at which the calculated energy changes with dihedral angle is small, so that it is certain that some of the neglected terms may not influence the final result. So it will be necessary to consider the energy of σ-bonds. This energy will vary through (a) possible changes of bond length when two halves of the molecule are bent relative to each other and (b) possible changes of hybridization at the S atoms when the two halves bend. Concerning (a) the problem is essentially

[14] Ref. 7. Chapter III.

[15] Ref. 12, p. 161.

one of geometry. If the S—C—C angles be fixed, the C—S—C angles (as functions of dihedral angle α which is varying) will be automatically fixed, and so there will be energy terms due to C—S—C angle change and also due to C—S bond length dependence. Concerning (b) if the hybridization at the *S* atom is altered, there will be changes in overlap and so in bond energy. In fact the equilibrium bond length will depend on this hybridization effect as well as on the geometry of the molecule.

TABLE 1. ENERGY AS A FUNCTION OF α

α	β_{C-S}	E_π (Kcal/mole)	$E_\pi + E_s$ (Kcal/mole)	γ
180°	0·774β	−315·00	−302·40	110°
140°	0·7058β	−312·30	−308·44	100° 41′
130°	0·6842β	−311·00	−309·15	95° 52′
128°	0·6792β	−310·86	−309·29	94° 50′
125°	0·6720β	−310·48	−309·13	93° 12′
120°	0·6579β	−309·82	−308·43	90° 22′
115°	0·6391β	−308·50	−306·47	87° 24′
110°	0·6273β	−307·80	−304·45	84° 18′

TABLE 2*. ENERGY AS A FUNCTION OF α

α	$E_\pi + E_s$ (Kcal/mole)	γ
180°	−287·90	120°
140°	−302·31	108° 56′
130°	−306·50	103° 24′
125°	−308·04	100° 22′
120°	−308·88	97° 10′
115°	−308·41	93° 48′
110°	−307·60	90° 22′

* For calculating E_s, γ is given in terms of α as $\sin \gamma/2 = \sin 60° \sin \alpha/2$.

The effect (b)[16] is not important, and, by comparison with similar changes in carbon atoms, it could be neglected. But the effect (a) may be important. If the molecule thianthrene is planar, then there will be considerable delocalization into C—S bonds and so there will be distinct π-bonds order for this bond. But when the planes of the two halves of the molecule are bent at right angles, this π-bond order must have effectively disappeared. So there will be changes of energy in the C—S σ-bonds as well as in the C—S π-bonds.

We first calculated the π-bond orders of all the bonds in thianthrene by the usual method at different dihedral angles. They are presented in Table 3. Using the bond orders of C—S single bond and C—S double bond as 1 and 2 respectively and bond length of C—S single and double bond as 1·81 Å and 1·64 Å (as in mercaptans and thiocarbonyls) respectively, an order-length curve was drawn and from this, change in bond order and hence the C—S bond length was read off at different dihedral angles. The changes in the other C—C bond length were evaluated from Coulson's bond

---

[16] Private communication from Prof. C. A. Coulson, Oxford.

TABLE 3. VARIOUS π-BOND ORDERS* IN THIANTHRNE AT DIFFERENT DIHEDRAL ANGLES (α)

α	1–2	2–3	1–11	11–12	9–11
180°	0·6302	0·6700	0·6220	0·5440	0·4400
140°	0·6311	0·6660	0·6262	0·5551	0·4274
130°	0·6350	0·6668	0·6282	0·5581	0·4160
128°	0·6370	0·6675	0·6288	0·5589	0·4122
120°	0·6394	0·6718	0·6306	0·5631	0·4040
110°	0·6406	0·6624	0·6336	0·5704	0·3941

* The bond assignment is same as in Fig. 2.

order-length curve.[17] The changes in bond length were then converted into energy by using the following simple parabolic function.

$$E\sigma = W + \tfrac{1}{2}\sum_i K\sigma i\chi i^2 \qquad (5)$$

where W is the sum of σ-bond energies at equilibrium bond lengths, $K\sigma i$ is the appropriate force constant of ith bond and χ_i is the difference from the equilibrium bond length. Using for C—S bond $K\sigma \sim 3{\cdot}05 \times 10^5$ dynes/cm and for C—C bond $K\sigma \sim 4{\cdot}5 \times 10^5$ dynes/cm and the equilibrium bond length for C—S bond and C—C bond as 1·81 Å and 1·54 Å respectively, the variation in energy of σ-bonds were evaluated. The results are reported in Table 4 along with the variation in calculated total energy of the molecule corresponding to the results of Table 1.

TABLE 4. VARIATION IN σ BOND ENERGY AND HENCE THE TOTAL ENERGY AS FUNCTION OF α

α	$E\sigma$ (Kcal/mole)	$E_\sigma + E_\pi + E_s$ (Kcal/mole)
180°	66·80	−235·60
140°	67·32	−241·12
128°	67·67	−241·63
120°	68·22	−240·21
110°	68·98	−235·47

Results and discussion

From the Tables 1 and 4 the predicted angle α is 128° and the γ is 94° 50′ in excellent agreement with the experimental values of 128° and 100° respectively.[3] It can also be predicted from the results in Tables 1 and 4 that the energy of the barrier for turning the molecule inside out should be 6 $\sim$ 7 Kcal/mole. This remains to be verified spectroscopically or calorimetrically. By subtracting the calculated total π-electron binding energy of seven ethylene molecules from 309·29, in Table 1 resonance energy of 80·33 Kcal/mole can be predicted for thianthrene. If the delocalization energy per electron be the index of aromaticity then thianthrene is expected to be more aromatic than thiophene but less than anthracene. This is in agreement with the experimental facts.[1]

---

[17] C. A. Coulson, *The Kekulé Symposium on Theoretical Organic Chemistry* p. 49. Butterworth's, London (1959).

From the results of the Table 2, predicted α is 120° and γ is 97° 10′. This conclusion will not change when the variation in the energy of σ-bonds is allowed. The energy of the barrier for turning the molecule inside out is about 21 $\sim$ 19 Kcal/mole. This result may not be very reliable in view of larger error involved in calculated strain energy for large distortion. The assumption of proportionality relationship of the strain energy with the square of distortion[6] is valid for small distortion. But both series of results lead to almost the same resonance energy, and a comparison of the results with the experimental values point to the fact that for planar thianthrene γ should lie somewhere between 110° and 120°. It is seen from Table 4 that the variation in the energy of σ-bonds with α is still smaller than the corresponding variation of π electron energy and this is due to very small change in π-bond orders. So the conclusions of the Tables 1 and 2 are not significantly changed by the additional terms in Table 4.

The atomic charges, bond order and free valences of the thianthrene molecule corresponding to $\alpha = 128°$ are shown in Fig. 2. It is interesting to note that two electrons in thianthrene are in an anti-bonding orbital. This indicates that ionization potential of the molecule should be considerably less than that of the related compound like anthracene and phenazine. This also suggests that the molecules should be quite susceptible to oxidation, which is in agreement with the facts.[1]

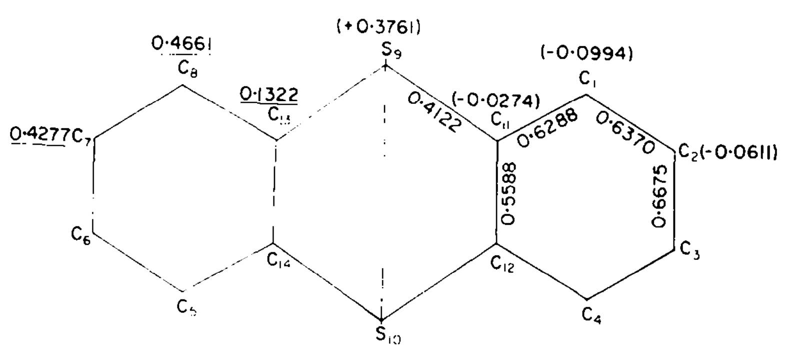

FIG. 2. Thianthrene: The numbers within the parentheses are charges, those along the bonds are bond orders and those underlined are free valences.

The bond orders, free valences and the partial charges of thiophene, anthracene and thianthrene are given in Table 5. The C—S bond has less double bond character in thianthrene than that in thiophene, which is also consistent with its length. One interesting difference emerges from the simple molecular orbital calculations of the π-bond orders in anthracene and thianthrene (Table 5). In anthracene the α—β bond is much more double bond than β—β' bond and the experimental evidence in favour of this conclusion is well known to any organic chemist. But in thianthrene such difference in the degree of double bond fixation in these two bonds is much reduced and even the β—β' bond has become slightly more double bond than α—β bond. This conclusion will not be changed even when the self-consistent calculation including some sort of dependence of β on bond length is undertaken. The effect of various iterations in this type of self-consistent calculations[18] is to increase the bond order of

---

[18] J. A. Pople, *Trans. Farad. Soc.* **49**, 1375 (1953).

TABLE 5*. PARTIAL CHARGES, FREE VALENCES AND BOND ORDERS

Compound	Partial charges in electronic units	Free valences	Bond orders
Benzene	0	0·40	0·67
Ethylene	0	0·73	1·00
Anthracene	0	0·459 (1), 0·408 (2)	0·7376 (1–2)
		0·520 (9), 0·106 (11)	0·5858 (2–3)
			0·5352 (1–11)
			0·4848 (11–12)
			0·6060 (9–11)
Thiophene	+0·69 (1), −0·156 (2)	0·416 (2)	0·604 (1–2)
	−0·189 (3)	0·434 (3)	0·7116 (2–3)
			0·5868 (3–4)
Thianthrene	−0·0994 (1), −0·0611 (2)	0·4661 (1)	0·6370 (1–2)
	−0·0274 (11), +0·3761 (9)	0·4274 (2)	0·6675 (2–3)
		0·1322 (11)	0·6288 (1–11)
			0·4122 (9–11)
			0·5588 (11–12)

* The figures within the parenthesis indicate the atoms or bonds (Figs. 1 and 2).

those bonds which are already fairly high and to decrease considerably those which are low. So it might be also expected that the bond order of the C—S bond in thianthrene will be much less than that reported in Table 3 when self-consistency will be obtained. In this way the observed 25% double bond character[19] of the C—S bond in thianthrene might be explained.

The partial negative charges on the various carbon atoms in thianthrene are less than that calculated for thiophene which suggests that thianthrene is less susceptible to attack by electrophilic reagents. The free valence of the carbon atoms are greater than that for benzene but less than that for ethylene or butadiene. This suggests the susceptibility to attack by free radicals. Both the electron density and the free valence calculations indicate that the α-position in thianthrene is more susceptible to electrophilic and radical attack than the β-position as in anthracene. This same conclusion may be drawn from the frontier orbital theory of Fukui[20] and, therefore, reinforces the suggestion.

Acknowledgement—Author's sincere thanks are due to Prof. C. A. Coulson F.R.S., Mathematical Institute, Oxford, for helpful suggestions and criticism through correspondence.

[19] I. Rowe and B. Post, *Acta Cryst.* **9**, 827 (1956).

[20] K. Fukui, T. Yonezawa, C. Nagata and H. Shingu, *J. Chem. Phys.* **22**, 1433 (1954).