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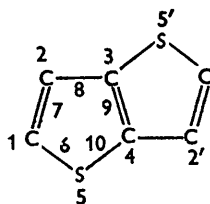
## Length of Central Bond in Thiophthen\*

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Longuet-Higgins (1950) has suggested that the central bond, 9, in the thiophthen molecule



is compressed by bond angle stresses, and, by a consideration of the cumulative strains around  $C_3=C_4$ , has calculated that the amount of this compression is 0.06 Å., in agreement with the 0.05 Å. discrepancy between the observed bond length (Cox, Gillot & Jeffrey, 1949) and Evans & de Heer's (1949) semi-theoretical estimate. If the suggested effect were so large in thiophthen, it might be important also in many other cyclic molecules for which it has likewise hitherto been neglected (presumably because the force constants of bond-bending are ordinarily regarded as much smaller than those of bond-stretching), and, indeed, Longuet-Higgins's method of calculation, which in effect neglects the angle strains at 2, 5, 2' and 5', would indicate a bond compression whenever the adjacent interior bond angles are constrained below their normal values. However, consideration of such a simple case as the symmetrical four-membered ring of cyclobutane, for which the tensile stress due to the opposite-angle strains obviously balances the compressive stress due to the adjacent angle strains, shows this method of calculation to be quite wrong as well as incomplete, and implies that Longuet-Higgins's interesting suggestion cannot ac-

count for the distance anomaly in thiophthen and will not prove fruitful except for rings which are *suitably* unsymmetrical as well as highly strained.

Consider a planar  $n$ -ring with potential function  $V(q_1, \dots, q_{2n})$ , in which the first  $n$  co-ordinates are the interior bond angles and the last  $n$  the bond lengths. The equations of static equilibrium may be written as

$$\frac{\partial V}{\partial q_i} + \lambda \xi_i + \mu \eta_i + \nu \zeta_i = 0,$$

and the auxiliary equations of ring closure, in first approximation, as

$$\Sigma \xi_i (q_i - q_i^0) = 0 \quad (x \text{ component}),$$

$$\Sigma \eta_i (q_i - q_i^0) = 0 \quad (y \text{ component}),$$

and

$$\Sigma \zeta_i (q_i - q_i^0) = 0 \quad (\text{angle sum}),$$

the three redundancies being handled by means of the Lagrangean multipliers  $\lambda$ ,  $\mu$ , and  $\nu$ . If the positive direction of a bond is counter-clockwise and the Cartesian co-ordinates of the atom at a bond angle  $q_i$  are  $x_i, y_i$  ( $i=1, \dots, n$ ) relative to an arbitrary origin, the quantities  $\xi_i$ ,  $\eta_i$  and  $\zeta_i$  may be written as  $\xi_i = -y_i$ ,  $\eta_i = x_i$ , and  $\zeta_i = 1$  for  $i=1, \dots, n$  and  $\xi_i = \cos(\vec{r}_i, \vec{OX})$ ,  $\eta_i = \sin(\vec{r}_i, \vec{OX})$ , and  $\zeta_i = 0$  for  $i=n+1, \dots, 2n$ .

If the Cartesian co-ordinate axes are rotated by the angle

$$\theta_0 = \cos^{-1}[\lambda/\sqrt{(\mu^2 + \nu^2)}] = \sin^{-1}[\mu/\sqrt{(\lambda^2 + \mu^2)}]$$

to give transformed Cartesian atomic co-ordinates  $x'_i, y'_i$ , the equations of equilibrium reduce to

$$\frac{\partial V}{\partial q_i} - \sqrt{(\lambda^2 + \mu^2)} y'_i + \nu = 0, \quad i=1, \dots, n,$$

and

$$\frac{\partial V}{\partial q_i} + \sqrt{(\lambda^2 + \mu^2)} \cos(\vec{r}_i, \vec{OX}') = 0, \quad i=n+1, \dots, 2n,$$

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with the interpretation, at least for the case of a simple valence force potential function, that a bond whose positive direction makes an angle  $\theta_i$  with the original  $x$  axis sustains a compressive force

$$\sqrt{(\lambda^2 + \mu^2)} \cos(\theta_i - \theta_0),$$

while a bond angle whose pivot atom has the co-ordinates  $x'_i, y'_i$  sustains a compressive moment  $\nu - \sqrt{(\lambda^2 + \mu^2)} y'_i$ ; the constants  $\lambda$  and  $\mu$ , it will be noted, alone determine the bond stresses. If, then, the origin of co-ordinates is shifted to give  $\Sigma y'_i = 0$ ,  $\lambda$  and  $\mu$  are invariant while  $\nu$  becomes  $\nu'$ , equal to the average moment of bond-angle compression. Consequently, only the deviations of the moments of bond bending from their average make any contribution to the resultant forces of bond tension or compression.

The treatment may readily be extended to fused rings, and for the centrosymmetric thiophthen no essential complication is added thereby; furthermore, the equations of constraint can be satisfied automatically (and exactly) by taking the equilibrium configuration as the reference configuration. Only the general equations of equilibrium for a simple ring need then be considered, and on the assumption of the simple quadratic valence force potential function as used by Longuet-Higgins most of the terms  $\partial V/\partial q_i$  in these equations become simply  $k_i S_i$ , with  $S_i$  the positive strain from the equilibrium value of the bond angle or bond length. The exceptions are

$$\frac{1}{2} k_9 S_9, k_3 S_3 + k_{34} (S_3 + S_4), \quad \text{and} \quad k_4 S_4 + k_{34} (S_3 + S_4),$$

$k_{34}$  being the force constant for the exterior angles at atoms 3 and 4. The values of  $k_2$  and  $k_3$  must be suitably chosen to allow for the exterior angle strains at atoms 2 and 3.

If now it is assumed with Longuet-Higgins that the bond lengths  $q_8, q_9$  and  $q_{10}$ , the bond angles  $q_3$  and  $q_4$ , the force constants  $k_3$  and  $k_4$ , and the angle strains  $S_3$  and  $S_4$  are respectively equal, it seems reasonable to assume further that the ring is a regular pentagon and that the angle force constants and strains are the same

at atom 1 as at atom 2. The angle strains around the central bond are then even greater than those indicated by the actual configuration of the molecule, but  $\lambda$  and  $\mu$ , and hence all bond-length strains, are readily found to vanish. On the other hand, the moment of bond bending is determined by  $\nu$  to be the same at each of the atoms ( $\lambda$  and  $\mu$  being zero), so that in view of the terms  $k_{34}(S_3 + S_4)$  and the appropriate values of  $k_1, k_2$  and  $k_3$  the corresponding strains  $S_1, S_2$  and  $S_3$  would have quite unreasonable values in the range of about two to three times the  $-12^\circ$  assumed for  $S_4$  and  $S_5$ .

When the actual configuration of the ring is retained the situation remains delicate, and with our very limited knowledge of the appropriate force constants (especially for bond bending), possible interaction and anharmonicity constants, and even of normal bond-angle values, it is impossible to make a reliable determination of  $\lambda, \mu, \nu$ , and the bond-length compressions. The results of a fairly plausible adjustment to the simple potential function, with values of the force constants that seem reasonable as well as generally consistent with those used by Longuet-Higgins, are, however, shown in Table 1. The indication is that only about a third of the apparent shortening of bond 9 can be accounted for as a compression. Moreover, any adjustment of  $\lambda$  and  $\mu$  whose principal effect was to decrease  $q_9$  by the desired amount would increase  $q_6$  by about the same amount, bonds 6 and 9 being so nearly antiparallel and  $k_6$  being approximately one-half  $k_9$ , and would decrease  $q_{10}$  somewhat; this would be equally unsatisfactory since Evans & de Heer's calculations do not even account for the full amount of the uncorrected difference  $q_{10} - q_6 = 0.023$  A. of the observed values.

Molecules probably exist, nevertheless, which have significant anomalies in bond length that may be properly ascribed primarily to bond-angle stress, once the other pertinent items just mentioned have been satisfactorily evaluated, and in any case the bond-angle strains in ring systems obviously must be significantly interrelated; yet it seems fair to conclude that at present the equations of static equilibrium can serve for any one

Table 1. Possible force constants, strains, and normal values of the bond angles and bond lengths in the thiophthen molecule

		$k^*$	$S$	$q_{\text{obs.}}^\dagger$	$q_{\text{obs.}} - S$	$q_{\text{calc.}}^\ddagger$
1	$\angle \text{C}=\text{C}-\text{S}$	0.75	$-10.8^\circ$	$112.5^\circ$	$123.3^\circ$	$(112.5^\circ)$
2	$\angle \text{C}-\text{C}=\text{C}$	1.05	$-11.2^\circ$	$111.7^\circ$	$122.9^\circ$	$(111.7^\circ)$
3	$\angle \text{C}=\text{C}-\text{C}$	0.7	$-7.4^\circ$	$114.3^\circ$	$121.7^\circ$	$(114.3^\circ)$
4	$\angle \text{S}-\text{C}=\text{C}$	0.5	$-10.8^\circ$	$110.2^\circ$	$121.0^\circ$	$(110.2^\circ)$
5	$\angle \text{C}-\text{S}-\text{C}$	0.7	$-16.4^\circ$	$91.2^\circ$	$107.6^\circ$	$(91.2^\circ)$
6	C-S	4.5	+0.015 A.	1.718 A.	1.703 A.	1.69 A.
7	C=C	8.5	+0.007 A.	1.359 A.	1.352 A.	1.37 A.
8	C-C	5.0	-0.005 A.	1.409 A.	1.414 A.	1.41 A.
9	C=C	8.0	-0.017 A.	1.362 A.	1.379 A.	1.41 A.
10	S-C	4.5	-0.008 A.	1.741 A.	1.749 A.	1.70 A.

$$(\lambda = \frac{1}{2}\mu = 0.34 \times 10^{-4} \text{ dyne}, \quad \nu = 2.0 \times 10^{-12} \text{ dyne cm.}, \text{ with } x_3 = y_3 = y_4 = 0.)$$

\* Units:  $10^{-11}$  dyne cm./radian for bending;  $10^6$  dyne/cm. for stretching.  $k_{34} = 0.7 \times 10^{-11}$  dyne cm./radian. Force constants  $k_1$  and  $k_2$  are respectively 50% greater than  $k_4$  and  $k_3$  to allow approximately for external angle strain; see text.

† Cox *et al.* (1949);  $q_1$  recalculated from parameters  $D$  of this reference.

‡ Evans & de Heer (1949).

molecule only to provide a certain number of important but insufficient relations among the values which may be ascribed to all these interesting quantities. Joint consideration of series of related molecules should prove more productive.

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## A Comparison of X-ray Measurements on Air-Dried Tobacco Necrosis Protein Crystals with Electron-Microscope Data

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From X-ray and goniometric measurements on large air-dried crystals of the Rothamsted tobacco necrosis protein, lattice constants for the triclinic unit cell have been determined and compared with observations made by Wyckoff using the electron microscope.

In examining crystals of the Rothamsted and other strains of tobacco necrosis protein, Wyckoff (1948) showed that it was possible to observe in the electron microscope the arrangement of the molecules in the different crystal faces, and so to make deductions about the probable crystal symmetry. The electron micrograms show that the particles are roughly spherical, although more space-filling than true spheres, and Wyckoff suggested that the faces shown were the cube and octahedral faces of a crystal having an essentially cubic close-packed structure. We have now carried out X-ray measurements on large air-dried crystals of the Rothamsted strain of tobacco necrosis protein and these provide an interesting comparison with Wyckoff's deductions. While the X-ray data give little exact evidence of the molecular shape, the shorter wave-lengths used do enable a more precise picture of the orientation and inter-particle distances to be obtained. These are found to be essentially similar to those suggested by Wyckoff, although the crystal symmetry is actually triclinic and not cubic.

The crystals of the tobacco necrosis protein were prepared by Dr N. W. Pirie at Rothamsted (Bawden & Pirie, 1945). They had separated from aqueous solution and had been allowed to dry very slowly over a period of months. In form they were weakly birefringent triclinic blocks, bounded by {100}, {010} and {001}, 0.15–0.5 mm. across. Direct observation under the microscope of the interfacial angles gave  $\alpha=99\text{--}102^\circ$ ,  $\beta=108\text{--}112^\circ$ ,  $\gamma=118\text{--}121^\circ$ . The faces developed were sufficiently clear for goniometric measurements to be attempted, though they showed some distortion and

gave blurred signal images. The angles measured by Miss M. W. Porter are

	Observed	Calculated from $\alpha, \beta, \gamma$ below
(010) : (001)	$64^\circ 47' \text{--} 66^\circ 1'$	$64^\circ 58' \alpha^*$
(100) : (001)	$59^\circ 4'$	$59^\circ 49' \beta^*$
(010) : (100)	$52^\circ 38'$	$52^\circ 49' \gamma^*$

A series of X-ray photographs was taken of single crystals using chromium radiation and plate-to-crystal distances of 10 and 20 cm. These were all  $2^\circ$  or  $4^\circ$  oscillation photographs taken with each axis in turn as rotation axis, the beam direction being initially parallel to a crystal face. The photographs showed at most only two orders of the main-face reflexions, and on the *c*-axis photographs the layer lines were practically invisible. No reflexions were observed with spacings smaller than 58 Å. From the photographs, in conjunction with the microscope measurements, the following lattice constants were derived:

$$\begin{aligned}
 a &= 157, & b &= 154, & c &= 147 \text{ \AA.}, \\
 d_{100} &= 116, & d_{010} &= 119, & d_{001} &= 123 \text{ \AA.}, \\
 \alpha &= 100, & \beta &= 110, & \gamma &= 120^\circ.
 \end{aligned}$$

The unit-cell volume calculated from these figures is  $2,572,000 \text{ \AA.}^3$ , and the crystal density measured by flotation in toluene/*o*-dichlorobenzene mixture was  $1.317 \text{ g.cm.}^{-3}$ . On drying in vacuo at  $100^\circ \text{C}$ . Weiler & Strauss found that the loss of solvent was 21.4% by weight of the air-dried crystals. The molecular weight of the protein present, calculated from these figures, is 1,600,000, in good agreement with earlier estimates derived from the wet crystals (Crowfoot & Schmidt,