tetragonal transition of NH_4NO_3, where maxima of about 2° C. occurred. It was noted that the transition toward the high-energy form provides a more reliable temperature point than does the transition in the opposite direction. The transition points of these crystals as determined by other investigators are listed in Table 2.

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Length of central bond in thiophthen.

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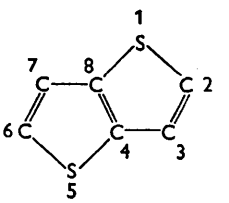
Calculations by Evans & de Heer (1949) on the bond lengths in thiophthen, assuming that the σ-bond system is free from strain, lead to a length for the bond 4–8 which is greater than the experimental value (Cox, Gillot & Jeffrey, 1949) by $\sim 0{\cdot}05$ A. The experimental X-ray study of thiophthen, carried out by Cox *et al.* (1949), shows, however, that the angles 1–8–7 and 3–4–5 are about 135°; and this means that it cannot be correct to neglect strain in the σ skeleton when calculating the equilibrium bond lengths. We shall here calculate the effect of this strain on the length of bond 4–8, assuming that the natural values of angles 1–8–7 and 3–4–5 are 120°.



To a first approximation the bond 4–8 bisects externally both the angles 1–8–7 and 3–4–5, and the bond lengths 4–8, 1–8, 8–7, 3–4 and 4–5 may be assigned the common value l_0.

Consider the system of bonds at atom 8. Then if g denotes the mean force constant for distortion of the angles at this atom, and if ϕ denotes the angle 1–8–7, the potential energy due to angular strain at atom 8 is given by

$$V_{\text{strain}} = \tfrac{1}{2}g\{(\phi-\tfrac{2}{3}\pi)^2+(\tfrac{1}{3}\pi-\tfrac{1}{2}\phi)^2+(\tfrac{1}{3}\pi-\tfrac{1}{2}\phi)^2\} = \tfrac{3}{4}g(\phi-\tfrac{2}{3}\pi)^2.$$

Denote by $2G$ the force in the central bond required to keep the angle 1–8–7 at its value ϕ. Then the work done by this force when 1–8–7 increases by $\delta\phi$ is

$$2G\delta(l_0\cos\tfrac{1}{2}\phi) = -Gl_0\sin\tfrac{1}{2}\phi\,\delta\phi.$$

Therefore in equilibrium

$$Gl_0\sin\tfrac{1}{2}\phi\,\delta\phi = \delta V_{\text{strain}} = \tfrac{3}{2}g(\phi-\tfrac{2}{3}\pi)\,\delta\phi,$$

so that

$$G = \frac{3g(\phi-\tfrac{2}{3}\pi)}{2l_0\sin\tfrac{1}{2}\phi}.$$

Now denote by f the force constant of the bond 4–8. Then, if l is the equilibrium length of this bond, we have

$$f(l-l_0) = -2G.$$

Therefore, eliminating G, we obtain

$$(l-l_0) = -\frac{3g(\phi-\tfrac{2}{3}\pi)}{fl_0\sin\tfrac{1}{2}\phi}.$$

A reasonable choice of values for f and g is

$$g = 0{\cdot}7\times10^{-11}\text{ dyne/radian},\quad f = 7{\cdot}0\times10^{5}\text{ dynes/cm.};$$

and from the X-ray study $\phi \doteqdot \frac{3}{4}\pi$, $l_0 \doteqdot 1{\cdot}4\times10^{-8}$ cm. Therefore

$$l-l_0 = -\frac{3\times0{\cdot}7\times10^{-11}\times\frac{1}{12}\pi}{7{\cdot}0\times10^{5}\times1{\cdot}4\times10^{-8}\times\sin\frac{3}{8}\pi} = -0{\cdot}06\times10^{-8}\text{ cm.}$$

We conclude that the effect of strain in the angles 1–8–7 and 3–4–5 is to shorten the central bond 4–8 by about 0·06 A.; and this brings the calculated bond lengths into line with those determined experimentally by Cox *et al.*

The author is much indebted to Professor M. G. Evans and Dr Jeffrey for drawing his attention to the present problem.

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A note on the diffraction patterns of crystalline proteins.

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Certain structures, C_n, have been proposed as models for the skeletons of native protein molecules (Wrinch, 1937). Before this hypothesis can be tested against X-ray diffraction data, the transforms of such structures into reciprocal space S^* must be investigated. In this note we take a preliminary step in this direction and demonstrate