used in this study were chosen because of their perfection as judged by the eye and also by the narrowness of the Bragg reflexion peak.

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References

Garrido, J. (1948). *Acta Cryst.* **1**, 3.
Jahn, H. A. (1942). *Proc. Roy. Soc.* A, **179**, 320.
Mason, W. P. (1946). *Phys. Rev.* **70**, 529.
Sen, R. K. (1949). *Acta Cryst.* **2**, 127.
Wooster, W. A., Ramachandran, G. N. & Lang, A. (1948). *J. Sci. Instrum.* **25**, 405.
Wooster, W. A., Ramachandran, G. N. & Lang, A. (1949). *J. Sci. Instrum.* **26**, 156.

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Hysteresis ranges of polymorphic transitions of some crystals.

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The polymorphic transitions which many substances undergo upon change of temperature are of considerable theoretical interest in the study of crystal chemistry and have been used experimentally to provide fixed points for temperature calibration (Buerger, Buerger & Chesley, 1943). The transition usually involves a change in the vibrational or rotational energy state of one of the ionic or molecular constituents, and generally occurs at an appreciably lower temperature when the high-temperature form is cooled than when the low-temperature form is heated. The separation of these two temperatures may be called a hysteresis range for the transition; its extent is found to vary widely among different crystals. Superheating or supercooling is to be expected in most transitions. It is also expected that the transitions will be somewhat sensitive to changes in pressure.

In an attempt to obtain a number of transition temperatures which might be used as 'fixed' points for calibration by the Buerger method of an electrically heated furnace for an X-ray powder camera, a survey of the literature was made. Considerable disagreement as to the value of each transition temperature was found, and information concerning the hysteresis range was meager. In order to correlate and evaluate these data it was necessary to study each transition experimentally. Measurements were made using reagent-grade samples placed inside carefully insulated containers which could be immersed in a constant-temperature oil bath or placed inside a controlled-temperature oven so as to provide slow, uniform heating or cooling toward a fixed temperature about 30° C. beyond the transition range. Temperatures of the samples were measured with fine-wire thermocouples calibrated against standardized Anschutz thermometers and read by means of a potentiometer circuit at intervals of $\frac{1}{2}$ min. or 1 min. Plateaus or inflections in the heating- or cooling-rate curves gave the transition temperatures.

Transition ranges have been studied carefully for potassium perchlorate, cesium perchlorate, and for two of the four known transitions of ammonium nitrate. It was found that the transitions for increasing temperature occurred at the same temperature (t_H) on each successive trial for a particular compound, but that the amount of superheating varied with the heating rate and with the history of the sample. Similarly, the transition toward the lower-energy form occurred at a sensibly constant temperature (t_C) on successive trials following a variable amount of supercooling. In cases of extreme superheating or supercooling the amount of energy involved in some transitions may be insufficient to return the sample to the transition point. The values of t_H and t_C determined for the substances named are given in Table 1.

The amounts of superheating and supercooling observed were small (less than 1° C.) except for the orthorhombic–

Table 1. *Results of this investigation*

Substance	Transition	t_H (° C.)	t_C (° C.)	Hysteresis ($t_H - t_C$) (° C.)
NH_4NO_3	orth.–tet.	84·4	83·7	0·7
	tet.–cubic	125·6	125·3	0·3
$CsClO_4$	orth.–cubic	218·6	203·8	14·8
$KClO_4$	orth.–cubic	299·6	294·0	5·6

Table 2. *Results of other investigators*

Investigator	$KClO_4$ (° C.)	$CsClO_4$ (° C.)	NH_4NO_3 tet.–cubic (° C.)	NH_4NO_3 orth.–tet. (° C.)
Buerger *et al.* (1943)	295·7	—	126·2	85·4
Early & Lowry (1919)	—	—	125·2	84·2
Zawidsky (1904)	—	—	125·0	85·4
Herman & Ilge (1930)	299·5	219	—	—
Vorlander & Kaascht (1923):				
(Heating)	299·5	219–221	—	—
(Cooling)	293·0	197–204	—	—
International Critical Tables (1927)	300 ± < 5	219 ± > 5	125·3 ± 0·2	83·9 ± < 1

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.

References

Buerger, M. J., Buerger, N. W. & Chesley, F. G. (1943). *Amer. Miner.* **28**, 285.

Early, R. G. & Lowry, T. M. (1919). *J. Chem. Soc.* **115**, 1387.

Herman, K. & Ilge, W. (1930). *Z. Krystallogr.* **75**, 41.

International Critical Tables (1927). New York and London: McGraw-Hill.

Vorlander, D. & Kaascht, E. (1923). *Ber. dtsch. chem. Ges.* **56**, 1157.

Zawidsky, J. (1904). *Z. phys. Chem.* **47**, 721.

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Length of central bond in thiophthen.

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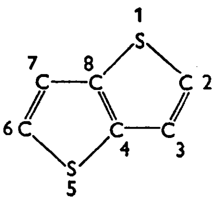
Calculations by Evans & de Heer (1949) on the bond lengths in thiophthen, assuming that the σ-bond system is free from strain, lead to a length for the bond 4–8 which is greater than the experimental value (Cox, Gillot & Jeffrey, 1949) by ~ 0·05 A. The experimental X-ray study of thiophthen, carried 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

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

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

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

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

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

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.

References

Cox, E. G., Gillot, R. J. J. H. & Jeffrey, G. A. (1949). *Acta Cryst.* **2**, 356.

Evans, M. G. & de Heer, J. (1949). *Acta Cryst.* **2**, 363.

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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