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On the structure of cyclo-octane at 0 °C.

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Cyclo-octane freezes at 14·4 °C and undergoes crystalline transformations at −89·4 °C and at −106·7 °C (Finke, Scott, Gross, Messerly & Waddington, 1956). An X-ray study has been carried out on the crystalline form stable between −89·4 °C and 14·4 °C.

Single crystals were grown at 0 °C and were photographed with a precession camera. Photographs taken with Mo $K\alpha$ radiation showed no reflections with d spacings less than 2·17 Å, so Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å) was used for subsequent pictures. Powder patterns were taken at 0 °C and at −64 °C. The photographs were indexed as primitive cubic with $a = 11{\cdot}90 \pm 0{\cdot}05$ Å at 0 °C and $a = 11{\cdot}82$ Å at −64 °C. The powder patterns showed three strong lines (200, 210, 211) and four weak lines (320, 321, 400, 410). Sixteen independent reflections were observed on the precession films, and their intensities were estimated visually. Seven additional reflections with $d > 2{\cdot}17$ Å are possible, but their intensities were below the minimum observable value. The systematic absence of hkl reflections with l odd suggests space group $P\bar{4}3n$ or $Pm3n$.

The density of liquid cyclo-octane, measured in calibrated pycnometers at 24·5 °C, is 0·8322 g.cm^{-3}. The density of the solid at the freezing point is greater than the density of the liquid. The calculated crystal density at 0 °C, based on eight molecules per unit cell, is 0·884 g.cm^{-3}.

The limitation on the number of data rules out direct determination of the parameters involved in this structure. However, of the molecular configurations which have been suggested for cyclo-octane (Bellis & Slowinski, 1959), only the crown or stretched crown has reasonable intramolecular H–H distances (minimum 2·0 Å) without extreme distortions of bond lengths and angles. This model is also supported by infrared spectra (Chiurdoglu, Doehaerd & Tursch, 1960), by dipole moment data (Allinger, Jindal & DaRooge, 1962), by nuclear magnetic resonance spectra (Anet & Hartman, 1963), by electron diffraction patterns (Danford, 1954), and by X-ray studies of azacyclo-octane hydrobromide (Dunitz & Prelog, 1960). The puckered ring of carbon atoms in the ideal crown has a thickness of 0·72 Å and a diameter of 3·54 Å. The corresponding dimensions for the hydrogen atoms are 0·69 Å and 5·70 Å for the peripheral atoms, and 2·03 Å and 3·88 Å for the vicinal atoms.

A suggested molecular arrangement (Fig. 1) has six molecules in positions 6(c) of space group $Pm3n$ ($\frac{1}{4}, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{4}, 0; 0, \frac{1}{2}, \frac{1}{4}; \frac{3}{4}, 0, \frac{1}{2}; \frac{1}{2}, \frac{3}{4}, 0; 0, \frac{1}{2}, \frac{3}{4}$) and two molecules in positions 2(a) ($0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$). The axis of the molecule at $\frac{1}{4}, 0, \frac{1}{2}$ is parallel to a, *etc.* The cubic symmetry implies disordering of the twofold molecules. Disordering of the sixfold molecules is also required if the crown configuration (symmetry D_{4d}) is assumed. This arrangement of molecules has been reported for β-F_2 and for γ-O_2 (Jordan, Streib, Smith & Lipscomb, 1964) with disordering similar to that suggested here. Alternative arrangements using positions 8(e) or using positions 6(b) plus 2(a) are not consistent with the data.

Structure factor calculations were based on twofold molecules with completely random orientations (spherical disorder) and on sixfold molecules undergoing free rotation about their molecular axes (Zachariasen, 1945). Agreement with the observed magnitudes could be attained only by assigning a large anisotropic temperature factor to the sixfold molecules. The contribution of the twofold molecules is given by

$$[1 + (-1)^{h+k+l}] \exp(-B_1 \sin^2\theta/\lambda^2)\, \Sigma f_j \sin sR_j/sR_j\,,$$

where B_1 is an isotropic temperature factor, $s = 4\pi \sin\theta/\lambda$, and R_j is the radius of the sphere generated by atom j ($R_j = 1{\cdot}80$ Å for carbon, for example). The contribution of the two molecules of the sixfold set whose axes are parallel to x is

$$2(-1)^l \cos 2\pi\, \frac{h}{4} \exp\{-[B_2h^2 + B_3(k^2+l^2)]/4a^2\}$$
$$\Sigma\{f_jJ_0[2\pi r_j(k^2+l^2)^{\frac{1}{2}}/a] \cos 2\pi h t_j\}\,,$$

where B_2 and B_3 are temperature factor components parallel and perpendicular, respectively, to the molecular axes, J_0 is a zero-order Bessel function, r_j is the radius of the ring generated by atom j ($r_j = 1{\cdot}77$ Å for carbon), and $t_j = x_j - \frac{1}{4}$ where x_j is the fractional x coordinate of atom j ($t_j = 0{\cdot}030$ for carbon). The summations are over all atoms in one molecule. Similar expressions give the contributions of the molecules whose axes are parallel to y and z. Least-squares methods were applied to determine the three temperature factors and to obtain a scale factor. The refinements gave $B_1 = 15{\cdot}5$ Å^2, $B_2 = 81$ Å^2 (corresponding to a root mean square displacement of 1·0 Å), and $B_3 = 8{\cdot}8$ Å^2.

The large anisotropic temperature factor component formally ascribed to the sixfold molecules may perhaps be attributed to steric effects. The intermolecular H–H distances involving the sixfold molecules are adequate, and these van der Waals contacts determine the unit cell size. However, the cavities occupied by the twofold molecules have radii of 4·0 Å, and a spherically disordered crown requires a radius of 4·9 Å. The crowding may be alleviated by displacing the sixfold molecules, and the instantaneous position of a sixfold molecule would depend upon the in-

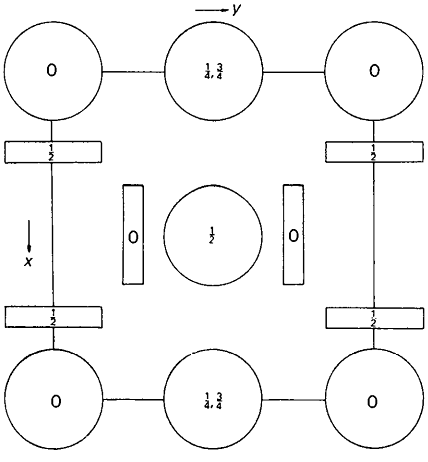

Fig. 1. Molecular arrangement in cyclo-octane.
The z coordinates of the molecular centers are indicated.

stantaneous orientations of the four twofold molecules which touch it. The phenomenon of molecular over-crowding has been observed in several disordered organic crystals (Dunning, 1961).

Table 1. *Observed and calculated structure factors for cyclo-octane*

hkl	F_o	F_c	*hkl*	F_o	F_c
110	5·8	10·7	330	14·6	10·9
200	49·2	45·0	420	15·4	−14·5
210	54·0	−52·2	421	17·1	8·8
211	47·3	47·1	332	—	−15·5
220	21·3	−22·1	422	4·7	7·9
310	<16·4	18·6	430	—	9·9
222	12·7	12·9	431	—	−4·4
320	25·8	−29·3	510	—	4·3
321	21·7	−17·1	520	—	−10·9
400	38·2	−46·2	432	15·0	−5·7
410	26·2	23·6	521	13·3	−7·9
411	<19·4	−10·6			

The discrepancy index for this structure is 0·16 (Table 1). The agreement is poorer at higher angles where the calculations are more sensitive to such details as partial ordering, molecular distortions, and the nature of the displacements. These details cannot be deduced from the limited data. Preliminary computations using the tub and the butterfly molecular configurations (Bellis & Slowinski, 1959) did not fit the data.

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References

Allinger, N. L., Jindal, S. P. & DaRooge, M. A. (1962). *J. Org. Chem.* **27**, 4290.
Anet, F. A. L. & Hartman, J. S. (1963). *J. Amer. Chem. Soc.* **85**, 1204.
Bellis, H. E. & Slowinski, E. J., Jr. (1959). *Spectrochim. Acta*, **15**, 1103.
Chiurdoglu, G., Doehaerd, T. & Tursch, B. (1960). *Bull. Soc. Chim. Fr.* p. 1322.
Danford, M. D. (1954). *Dissert. Abst.* **14**, 1936.
Dunitz, J. D. & Prelog, V. (1960). *Angew. Chem.* **72**, 896.
Dunning, W. J. (1961). *Phys. Chem. Solids*, **18**, 21.
Finke, H. L., Scott, D. W., Gross, M. E., Messerly, J. F. & Waddington, G. (1956). *J. Amer. Chem. Soc.* **78**, 5469.
Jordan, T. H., Streib, W. E., Smith, H. W. & Lipscomb, W. N. (1964). *Acta Cryst.* **17**, 777.
Zachariasen, W. H. (1945). *Theory of X-ray Diffraction in Crystals*, pp. 223–224. New York: Wiley.

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The unit-cell dimensions of potassium myristate and 1:1 acid potassium myristate.

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Piper (1929) investigated a series of neutral and 1:1 acid potassium soaps and reported the long-spacings of these compounds. Since that time a number of papers have been published on the structure and nature of neutral potassium soaps and it has been established that the neutral soaps studied by Piper were of the *B* form discussed by Lomer (1952). The same interest does not appear to have been shown in the 1:1 acid potassium soaps although studies of other acid salts have been undertaken to investigate the nature of the hydrogen bonding in these substances (Mills & Speakman, 1960). The study of the crystal structures of soaps has been hindered by the difficulty in obtaining single crystals and it was decided to try to grow single crystals of a *B* form potassium soap as a preliminary to a structure determination and potassium myristate was chosen. At the same time the growth of 1:1 acid potassium soap crystals was attempted.

Crystals of potassium myristate were grown from ethanol solution, the soap being first formed in solution by the reaction of potassium hydroxide and myristic acid. Phenolpthalein was used as indicator and the neutral solution was evaporated to dryness over calcium chloride *in vacuo* at room temperature. The crystals which formed were mostly needle-like with the *b* axis of the unit cell along the needle axis, but one or two twinned platelets were found, the large faces being (001). The twin components were found to have a common axis and this effect has been reported by Müller (1927). The crystal plates were very thin and malformed; no interedge angles could be measured. Although the crystals were not suitable for structure determination it was possible to obtain the unit-cell dimensions. The unit cell was triclinic with:

$$\begin{array}{ll} a = 4\cdot13 \pm 0\cdot02\ \text{Å} & \alpha = 91°6' \pm 20' \\ b = 5\cdot65 \pm 0\cdot02 & \beta = 91°25' \pm 20' \\ c = 34\cdot28 \pm 0\cdot08 & \gamma = 92°21' \pm 20' \\ d_{001} = 34\cdot26 \pm 0\cdot08 & \end{array}$$

These dimensions are in good agreement with those obtained by Lomer (1952) from powder photographs. The calculated density assuming 2 molecules of $CH_3(CH_2)_{12}COOK$ per unit cell was 1·105 g.cm^{-3} whilst the density

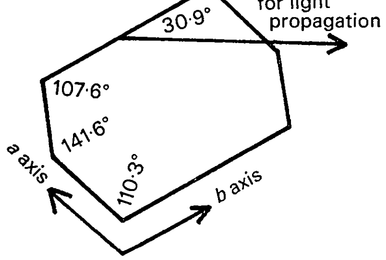

Fig. 1. Crystal of 1:1 acid potassium myristate on the (001) face.

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