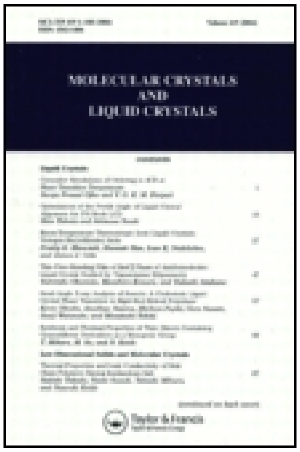

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X-ray Investigation of Some Plastic Crystals
I. Structure and Rotation: Cyclopentanol and dl-Camphene‡

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Abstract—X-ray photographs have been made of the two rotational forms of solid cyclopentanol and of the rotational form of dl-camphene. At -30 °C, cyclopentanol in rotational form I has a hexagonal structure with $a = 5.877$ Å and $c = 1.607$ Å and with two molecules per cell. Agreement with the observed intensities can be obtained by assuming that the molecules are located at (1/3, 2/3, 1/4) and (2/3, 1/3, 3/4) and that they are rotating with spherical symmetry about their centers of mass. At -56 °C, cyclopentanol in rotational form II also has a hexagonal structure but with $a = 10.1$ Å and $c = 9.49$ Å and with six molecules per cell. Intensity ratios are used to find the ratios of molecular scattering factors for camphene at six temperatures between $-83.1°$ and $+24.0°$. A model in which the camphene molecules rotate about their centers of mass with spherical symmetry does not produce agreement with the observed results. A model in which the camphene molecules fluctuate randomly among the twelve positions that result from applying the minimum symmetry operations for the point group in cubic lattice (class 23 or T) can be used to obtain agreement with the observed ratios.

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1. Introduction

Plastic crystals are characterized by having one or more solid forms for which unusual physical properties have led to the supposition of a hindered rotation of the individual molecules about their positions of equilibrium in the crystal. In these " rotational " forms, the plastic crystal lattice exhibits cubic symmetry except for a few cases of hexagonal symmetry.[1] In most cases the molecule does not have enough point symmetry to permit it to exist in such a highly symmetric lattice; but as Pauling[2] pointed out, rotational freedom of the molecule would result in increasing its effective symmetry.

At lower temperatures, all plastic solids undergo highly reconstructive transformations into one or more forms in which the rotational freedom is lost. Such low-temperature, non-rotational forms are much less symmetric than the high-temperature, rotational forms, but exceedingly little is known about the exact crystal structures. It was our original intention to determine crystal structures of some of the plastic solids in both the rotational and non-rotational forms, but we have been unable so far to obtain conclusive results in the case of the non-rotational forms. The reconstructive transformation into the non-rotational form makes it practically impossible to obtain sufficiently large single crystals for Laue diffraction work; consequently, we have had recourse to powder methods. We have been successful in obtaining good powder diffraction patterns in both forms, but the low scattering power of the organic substances involved makes it impossible to see more than a few lines. Furthermore, the large thermal motion of the molecules increases the background scattering and decreases the Bragg intensities. For the two rotational forms of cyclopentanol, we successfully indexed the lines and are therefore able to deduce the unit cell for each of these forms. The non-rotational form on the other hand is not sufficiently symmetrical to allow all of the necessary parameters to be deduced from the limited number of powder lines. Also, from a comparison of the intensities of the different Bragg diffraction lines, we are able to draw some conclusions about the type of orientational disorder in camphene as well as the two rotational forms of cyclopentanol.

2. Experimental

The cyclopentanol used had a melting point of −18 °C and was obtained by refluxing Eastman cyclopentanol over slaked lime and finally distilling over sodium metal. The dl-camphene from Eastman was distilled once and then recrystallized from alcohol; the melting point was 48.5 °C. Dielectric measurements on cyclopentanol by White and Bishop,[3] by Corfield and Davies,[4] and in this laboratory[5] indicate the existence of a rotational form I from the melting point down to about −37 °C, an additional rotational form II stable from −37° to −72°, and a non-rotational form III stable below −72°. The transformation at −37° is not reconstructive and involves little discontinuity in density. The transformation to form III occurs at reasonable speed below about −75° and involves a large change in density and crystal structure. Camphene is unusual in having a rotational form I stable all the way from the melting point near 50 °C down to the neighborhood of −120°, below which it transforms into a non-rotational form.[3]

X-ray powder photographs were made in a modified Norelco powder camera 114.6 mm in diameter. The temperature of the sample was controlled by having cold nitrogen gas flow continuously over the sample. The gas was first cooled by passing it through liquid nitrogen and then warmed to the proper temperature by means of an electric heater. The heater current and the rate of flow of the gas were controlled by thermistors located in the sample chamber itself. The temperature of the sample was monitored with a copper-constantan thermocouple and varied less than 0.2° during the longest exposures.

The quality of the powder diffraction lines was improved by a modification of the camera that permitted moving the sample back and forth in a direction parallel to the axis of rotation. This was accomplished by backing off the pulley that drives the sample spindle and attaching a coupling that permitted an externally imposed translation of about 1 mm without interfering with the normal rotation of the sample.

Samples of many small crystals produce the best powder diffraction lines; unfortunately the nature of the plastic crystals is such that upon freezing in the 0.2 mm diameter cellophane tubes used as sample holders only a few large crystals result. In the case of cyclopentanol, there is, however, the reconstructive transformation at −75°. As a result of passing back and forth through this transformation a few times, the aggregate would come to consist of many small crystals that would produce smooth diffraction lines. In the case of camphene, the transformation was beyond our easily accessible range of controlled temperatures, so fine crystals were obtained by simply sieving the camphene under liquid nitrogen before introducing it into the sample tubes. The diffraction lines produced by samples prepared in this way were quite sharp; consequently, we conclude that there were no extensive structural defects resulting from the method of preparation.

Film shrinkage and radius errors were eliminated by mounting the film in the Wilson configuration. Since absorption is negligible in these organic materials, the major remaining source of systematic error is the camera eccentricity. This was evaluated by mixing NaCl as a standard with cyclohexanol, one of the substances investigated and reported on in the following paper. It was found that in all cases the error in the measured lattice constant lay between zero and −0.1%; consequently a mean correction of +0.05% was made in all lattice parameters. Error in reading the line positions on the films was minimized.[6] The final accuracy of the lattice constants is estimated to be about 0.1%.

The intensities of the powder lines were measured from the films using a scanning densitometer. The readings were calibrated with films having known exposures that were developed at the same time as the films from the diffraction experiments. The wide range of intensities involved made it necessary to use a double film technique at times. This together with the large thermal background limited the accuracy of the intensity measurements.

3. Cyclopentanol: Structure and Rotation

Table 1 contains the observed inverse squared interplanar spacings $1/d^2$ together with the relative intensities corrected by the Lorentz-polarization factor for the two rotational crystal forms of cyclopentanol, form I at $-30°$ and form II at $-56\,°C$. The Bragg angles are included to indicate the very close similarity of the diffraction patterns produced by the two different forms. Because of the fact that cyclopentane was known to have a hexagonal structure in its rotational form,[1] it was suspected that cyclopentanol might behave the same way. This was found to be the case for both forms. The lines were indexed as shown in

TABLE 1 Powder Data for Cyclopentanol

Measured Bragg angle θ(°)	Assumed Indexing *hkl*	$1/d^2$(Å)$^{-2}$ calculated	$1/d^2$(Å)$^{-2}$ observed	Corrected relative intensity
1. Rotational Form I at $-30\,°C$:				
13.01	100	0.03865	0.03864	175 ± 10
14.01	002	0.04482	0.04470	148 ± 12
14.81	101	0.04986	0.04981	592 ± 30
19.31	102	0.08347	0.08334	30 ± 3
27.34	112	0.16079	0.16075	
27.81	201	0.16581	0.16591	
29.02	004	0.17936	0.17932	
2. Rotational Form II at $-56\,°C$:				
7.50	100	0.01302	0.01298	148 ± 12
13.08	110	0.03906	0.03906	1130 ± 120
13.95	002	0.04437	0.04431	1240 ± 150
14.87	111	0.05015	0.05019	4360 ± 84
19.32	112	0.08343	0.08347	152 ± 15
27.95	221	0.16733	0.16747	
28.86	004	0.17749	0.17755	

Table 1, and the calculated values of $1/d^2$ were obtained with the parameters given in Table 2.

The characteristic absences together with the c/a ratio for form I suggests a close-packed structure. The cyclopentanol molecule does not have sufficient symmetry to form such a structure; however, it can acquire the necessary symmetry if it is free to rotate. The most likely structure is one having the molecules located at (1/3, 2/3, 1/4) and (2/3, 1/3, 3/4). We investigated the effects of three different kinds of rotational motion. In Model 1 each molecule rotates freely about an axis through the center of the pentane ring and parallel to the c-axis; in Model 2 each molecule rotates with spherical symmetry about the center of the pentane ring; and in Model 3 each molecule rotates with spherical symmetry about its center of mass. Methods of calculating the effects of such motions of the molecules on the relative intensities have been worked out.[7,8] Atomic scattering factors were taken from tabulated values[9]; and the ordinary carbon-oxygen bond length[10] was used together with the known molecular structure of cyclopentane[11] to obtain the molecular structure of cyclopentanol. A sufficiently accurate Debye-Waller factor to correct for temperature was estimated from the known Debye temperature for cyclohexanol.[12] The results of the calculations are shown in Table 3; they are normalized by making the sum of the intensities the same for each model. That gross features of the motion can be distinguished is clearly indicated by the unsuitability of Model 1. The essentially equally good agreement for Models 2 and 3 shows that fine details of the motion cannot be

TABLE 2 Crystal Structures of the Two Rotational Forms of Cyclopentanol

Form	Temp.	Structure	a(Å)	c(Å)	c/a	Calculated number of molecules per cell
I	− 30 °C	hexagonal	5.877	9.445	1.607	1.98
II	− 56 °C	hexagonal	10.1	9.49	0.94	5.98

TABLE 3 Observed and Calculated Relative Intensities for Cyclopentanol in Form I for Three Different Models of Rotational Freedom

hkl	Observed	Model 1	Model 2	Model 3
100	175 ± 10	23	159	164
002	148 ± 12	327	171	173
101	592 ± 30	328	573	575
102	30 ± 3	268	44	34

distinguished. The motion of Model 3 is more likely on general physical grounds, however, and also we note that the diameter of the rotating molecules is only 4.9 Å for Model 3 compared to 6.1 Å for Model 2. For Model 3 the reliability factor calculated from

$$R = [\sum \big|\, |F_{\mathrm{obs}}| - |F_{\mathrm{calc}}| \,\big|]/\sum |F_{\mathrm{obs}}|$$

is only 0.01, and the largest difference between the calculated and observed intensities is 15%. It seems likely then that in form I the cyclopentanol molecules are rotating with near spherical symmetry about their centers of mass.

As can be seen in Table 1, form II has the same systematic absences as form I, and the interplanar distances are in some cases very close. These facts together with the knowledge that the transformation between the two forms at −37° is non-reconstructive led us to try to find a hexagonal structure for form II that is closely related to that for form I. The hexagonal cell having six molecules at (1/3, 0, 1/4; 0, 1/3, 1/4; $\overline{1/3}$, $\overline{1/3}$, 1/4; $\overline{1/3}$, 0, 3/4; 0, $\overline{1/3}$, 3/4; 1/3, 1/3, 3/4) involves no shift in relative position of any of the molecules; furthermore if all molecules stayed fixed, the new cell constant a_{II} would be given by $\sqrt{3}$ times a_{I}, or 10.2 Å. The necessary point symmetry for the new lattice is less than that needed in form I, and it is clear that rotation of the molecules with spherical symmetry is out of the question since this would lead to a structure completely identical with that of form I. The rotation in form II is therefore probably restricted to rotation of the molecules about some fixed axis.

We have tried a number of models involving such forms of rotation but were unable to find a model that gave satisfactory agreement with the observed intensities.

4. Camphene: Rotation

In the case of camphene, many of the lines were so weak that film grain and high background introduced large errors into the measurements. An occasional line would show 30% discrepancy between the readings taken to either side of 0°. Since it is the line ratios that will be of interest, errors of such a size could completely obscure important features; therefore, it was decided to discard measurements showing discrepancies greater than 20%. Camphene is known to be body-centered cubic[1] in the rotational form; consequently the multiplicity factors for the lines can be calculated and the data presented directly in terms of the structure factors. Table 4 gives values of $k_n \mid F \mid^2$ for three of the camphene lines for six different temperatures; k_n is a constant that will be different for each film number n. The 110 line in K_α radiation was too dark to measure, so the K_β line was used instead. The values of $K_n \mid F \mid^2$ obtained for these lines were multiplied by 147, the ratio of the K_α to K_β intensities, in order to obtain values that could be compared to the remaining two lines which were measured in K_α.

Table 4 Structure Factors of the (110), (200), and (211) Lines of dl-Camphene at Different Temperatures. (The errors indicated were obtained from the differences in the intensities measured to either side of $2\theta = 0°$. In the case of the (211) lines it was possible to measure only to one side. The missing values were either because the lines were not readable or because the two values showed discrepancies greater than 20%.)

Film	Temp (°C)	$k_n \mid F(110) \mid^2$	$k_n \mid F(200) \mid^2$	$k_n \mid F(211) \mid^2$
161	+ 24.0	13.3 ± 1.0	1.92 ± 0.02	0.141
172	0.0	14.0 ± 1.5	2.60 ± 0.21	—
167	- 23.7	9.55 ± 0.31	—	0.160
164	- 47.2	12.2 ± 2.2	2.83 ± 0.15	0.214
174	- 65.0	12.9 ± 0.65	3.06 ± 0.02	0.144
152	- 83.1	—	1.53 ± 0.06	0.176

In order to eliminate the unknown change in sensitivity from film to film, we now take the ratios of intensities for the different lines at each temperature. In addition we have corrected the intensities for the effects of thermal vibration following Debye[13] and using Debye temperatures obtained from ultrasonic work.[12] The resulting ratios of molecular scattering factors are shown in Table 5. If there were no thermal effects other than vibration, the ratios for each pair of lines would be the same for different temperatures. The fact that the ratios for the (110) : (200) lines increases with increasing temperature is of interest and will be discussed in the following paper.[14] The erratic behavior of the ratios involving the (211) line is due to the fact that this is a very weak line that falls in a region of high background.

TABLE 5 Ratios of Molecular Scattering Factors for Camphene Corrected for Thermal Vibration

Temp. (°C)	$[f_m^{\circ}(110)/f_m^{\circ}(200)]^2$	$[f_m^{\circ}(110)/f_m^{\circ}(211)]^2$	$[f_m^{\circ}(200)/f_m^{\circ}(211)]^2$
+ 24.0	5.5 ± 0.4	60	11
0.0	4.5 ± 0.6	—	—
− 23.7	—	43	—
− 47.2	3.6 ± 0.7	42	11
− 65.0	3.8 ± 0.2	71	19
− 83.1	—	—	8
Means	4.4 ± 0.8	54 ± 12	12 ± 4
Values predicted by models of molecular motion:			
1. Spherical symmetry	12	2.3×10^4	2.0×10^3
2. 23, minimum symmetry	4.0	43	11

Camphene does not possess the point symmetry necessary for it to form the body-centered cubic lattice that it does. In fact the minimum point symmetry required for a cubic lattice is 23, that is, a two-fold axis of symmetry in the [001] direction and a three-fold axis in the [111] direction. We tried two different models for the orientation of the camphene molecules to obtain ratios of intensities to compare to the experimental ones. The first model is one of spherically symmetric rotation about the center of mass. This would clearly provide the necessary point symmetry. Relations for this form of motion have already been worked out.[8] The exact dimensions of camphene are not known; however, a sufficiently good approximation can be made starting from the boat form of cyclohexane. If the prow and stern carbon atoms are bridged by a carbon atom placed at the usual distance of 1.54 Å from each, the bonds turn out to fall at an angle of 115°. The very small shift in position of the ring carbons needed to bring this angle down to 110° would not affect the results that follow. Two $-CH_3$ groups are placed on one of the remaining ring carbon atoms at the proper tetrahedral angles and at 1.54 Å. A $=CH_2$ group is placed on the adjacent ring carbon atom at a distance of 1.34 Å and in the plane formed by the remaining two tetrahedral bonds of the ring carbon atom. The hydrogen atoms were disregarded because of their small scattering cross-sections. Table V contains the predicted ratios for this model in spherical symmetry. Pinching the ring together at the bridge reduces the ratios somewhat, but not enough to come close to agreement with the experimental values.

The second model tried involves taking the camphene molecule and placing it in the twelve positions generated by the symmetry operations corresponding to the minimum 23 symmetry. The calculated ratios vary tremendously depending on the orientation from which one starts. There is a small cone of initial orientations, however, that results in ratios of which the values listed in Table 5 are typical. Increasing the cell parameter from 7.7 to 7.9 Å results in a decrease in value for the (110) : (200) ratio of about 5%. These results must not be taken too seriously because we were working with dl-camphene rather than a single isomer. The presence of the two isomers in the unit cell, one at (000) and the other at $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, would have consequences difficult to calculate exactly. These considerations would, however, have no effect on the model with spherical symmetry, so that we can still draw the interesting conclusion that the molecules of dl-camphene cannot rotate about their positions in the lattice with spherical symmetry but must be restricted to a more limited degree of reorientational freedom.

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