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Disordered Crystal Structure of the γ Form and Reversible Solid-Phase Transformations of *p*-Chlorobenzamide

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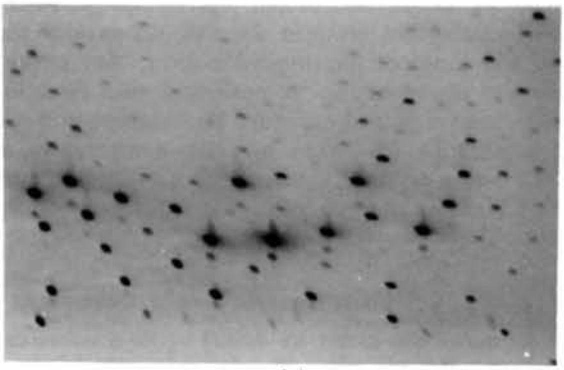
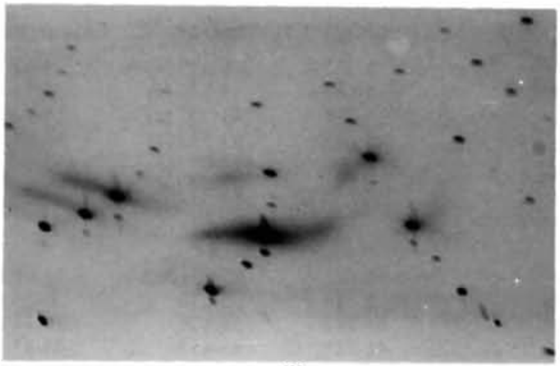
The crystal structure of a high-temperature disordered form, γ form, of *p*-chlorobenzamide (C_7H_6ClNO), and a reversible solid-phase transformation occurring between α and γ forms at about 44 °C were investigated by X-rays. Crystal data at 50°C are: $a = 5.015$ (4), $b = 5.530$ (4), $c = 14.707$ (7) Å, $\alpha = 97.53$ (6), $\beta = 113.03$ (6), $\gamma = 95.67$ (6)°, $Z = 2$, triclinic with space group $P\bar{1}$. Intensity data were collected by the equi-inclination Weissenberg technique. The photographs showed a marked diffuse scattering associated with reciprocal lattice points with $h = n \pm \frac{1}{3}$ (n integer). The 'averaged structure' was described in terms of four structural units; three of them, P, Q and R, with equal proportions are deduced from the structure of the α form by taking their unit-cell origins at 0, $\frac{1}{3}\mathbf{a}$ and $\frac{2}{3}\mathbf{a}$ along $\mathbf{a}$, and the remaining unit, V, has positional parameters very close to the mean values of those for the above three units. The final R value was 0.113 with the probability 0.75 of finding V in the crystal. The diffuse scattering patterns were well interpreted in terms of a random distribution of four kinds of 'domains', each consisting of any one of the above four structures. The domain containing 216 molecules has dimensions 15, 66 and 58 Å along $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}'$ respectively, where $\mathbf{c}' = 6\mathbf{a} + 9\mathbf{b} + 3\mathbf{c}$. A plausible process for the phase transformation occurring between the α and γ forms consists of two types of molecular movements: one is reorientation and repositioning of molecules in a molecular chain along $\mathbf{a}$, and the other is cooperative displacements of the chains along $\mathbf{a}$. It was found that the γ form undergoes a reversible solid-phase transformation at about 70°C to another disordered form, δ form.

Introduction

Crystals of the α form of *p*-chlorobenzamide (C_7H_6ClNO) undergo a reversible solid-phase transformation at about 44°C to a high-temperature disordered form, γ form (Harada, Taniguchi, Takaki & Sakurai, 1969). The unit cell of the γ form resembles that of the α form except that the a-axial length of the γ form is one third that of the α form. The main change in diffraction patterns on the transformation from the α to γ forms was that the Bragg reflexions with $h = 3n \pm 1$* (n integer) from the α form had disappeared and a strong diffuse scattering was found to occur as seen in Fig. 1. The structures of the α form at room temperature and −120°C have been investigated by Taniguchi, Nakata, Takaki & Sakurai (1978). The structure of the γ form given by Harada, Taniguchi, Takaki & Sakurai was, however, only an 'averaged structure' since their structure determination was made by means of sharp reflexions only. The main purpose of this paper is therefore to give a detailed description of the disordered structure of the γ form on the basis of an analysis of the diffuse scattering using a simple disorder model. A mechanism of the phase transformation occurring between the α and γ forms is also discussed.



(*a*)



(*b*)

Fig. 1. Equi-inclination *h2l* Weissenberg photographs (*a*) at room temperature and (*b*) at 50°C.

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* To avoid confusion, all crystallographic indices used in this paper will be referred to the unit cell corresponding to that of the α form (*i.e.* the *a*-axial length of the γ form should be multiplied by three).

In the course of this experiment we found that some of the sharp reflexions from the γ form changed remarkably in intensity at about 70 °C, suggesting that there exists another phase transformation from the γ to a new form, δ form, but no further study was made to obtain a disordered structure of the δ form.

Experimental

Crystals of the γ form were obtained from those of the α form by heating through the transition point (*ca* 44 °C). The specimen was immersed in a stream of hot air the temperature of which was held reasonably constant (±0·5 °C) for the period of X-ray exposure. By use of a heating (or cooling) rate less than 1° min^{-1} in the region of the transition, most of the crystals examined underwent the reversible solid-phase transformation without splitting. Occasionally some crystals were split into two or more slices on cooling through the transition point. The boundaries of these slices were found to be parallel to $(01\bar{3})$ which is, as seen later, in accord with the plane parallel to a molecular sheet in the α (or γ) form.

Cell dimensions

The cell dimensions of the γ form and the orientational relationship between the unit-cell axes of the γ form and those of the original α form, were obtained from the discrepancies in positional and directional parameters on double-exposure Weissenberg and oscillation photographs taken at room temperature and 50 °C, with a crystal rotating about **a** and **b** (Herbstein, 1965). Here we used the condition that the direction of **a** and that normal to $(01\bar{3})$ remain unchanged on the transition, which was deduced from the examination of an *a*-axis double-exposure Weissenberg photograph. Five crystals examined showed that their cell dimensions were slightly different from crystal to crystal, a large discrepancy in the *c*-axial length (about 0·4% smaller than the value in Table 1) being found when the largest crystal was used. The unit-cell dimensions of the crystal used for intensity measurement are given in Table 1, where those of the α form are also listed for comparison.

Table 1. *Cell dimensions for p-chlorobenzamide*

Cell dimensions with primes are derived by the transformations $\mathbf{a}' = 3\mathbf{a}$, $\mathbf{b}' = \mathbf{b}$ and $\mathbf{c}' = 6\mathbf{a} + 9\mathbf{b} + 3\mathbf{c}$ for the γ and δ forms and $\mathbf{a}' = \mathbf{a}$, $\mathbf{b}' = \mathbf{b}$ and $\mathbf{c}' = 2\mathbf{a} + 9\mathbf{b} + 3\mathbf{c}$ for the α form.

	α Form* (27 °C)	γ Form (50 °C)	δ Form (80 °C)
a	15·027 Å	5·015 (4) Å	5·02 Å
b	5·481	5·530 (4)	5·55
c	14·486	14·707 (7)	14·80
α	97·84°	97·53 (6)°	98·0°
β	111·99	113·03 (6)	112·9
γ	95·17	95·67 (6)	95·7
Space group	$P\bar{1}$	$P\bar{1}$	
Z	6	2	2
a'	15·027 Å	15·044 Å	15·06 Å
b'	5·481	5·530	5·55
c'	58·263	58·476	58·45
α'	45·71°	45·45°	45·8°
β'	80·78	82·22	82·3
γ'	95·17	95·67	95·7

* Taniguchi, Nakata, Takaki & Sakurai (1978).

As seen in a later section, the characteristic distribution of the diffuse scattering found in the γ form was very closely related to the arrangement of molecules. Therefore we transformed the axes a, b and c to new axes a', b' and c' (see Table 1), where the directions of $\mathbf{a}'$ and $\mathbf{b}'$ are the same as those of **a** and **b** and the direction of $\mathbf{c}'$ almost agrees with that of the long axis of a dimer (Fig. 4). The directions of the a', b' and c' axes for the γ form relative to the corresponding axes for the α form are given as follows:

	$\mathbf{a}'_\alpha$	$\mathbf{b}'_\alpha$	$\mathbf{c}'_\alpha$
$\mathbf{a}'_\gamma$:	0·00°	95·17°	80·78°
$\mathbf{b}'_\gamma$:	95·67	0·50	45·80
$\mathbf{c}'_\gamma$:	82·22	45·37	1·44.

From this result and the fact that photographs of crystals returned to room temperature after the transformation to the γ form were the same as those before the heating cycle, it may be said that the changes in the directions of the b' and c' axes on the α/γ phase transformation occur almost in the $a'b'$ and $a'c'$ planes respectively. The directions of $\mathbf{a}'$ and $\mathbf{b}'^*$ remain unchanged within experimental error, the direction of $\mathbf{b}'^*$ being normal to $(01\bar{3})$.

A series of oscillation photographs taken over the temperatures 50 to 95 °C showed that no significant change in the positions of sharp spots occurred at the 70 °C transition. A small but abrupt change at the transition could only be detected with certainty from the stationary-crystal strip photographs taken with a Weissenberg camera (Flack, 1970*b*). The unit-cell dimensions for the δ form are given in Table 1.

Sharp reflexions

Intensity data for sharp reflexions from the γ form at 50 °C were collected with Ni-filtered Cu $K\alpha$ radiation for $k = 0$ to 3 by the equi-inclination Weissenberg technique. Intensities of 818 independent non-zero reflexions were estimated visually and corrected for Lorentz and polarization factors. No absorption correction was applied. The intensity data were adjusted to an absolute scale from double-exposure multiple-film Weissenberg photographs taken at room temperature and 50 °C by comparing the intensities of sharp reflexions from the γ form with those of the corresponding reflexions from the α form of which the crystal structure is known. Note that the intensity distributions of the above two sets of reflexions were very similar to each other, but the reflexions from the γ form were on average 20% stronger than those from the α form; in particular the intensities of some particularly strong reflexions were twice as large as those of the α form.

The transformation from the γ to δ forms could be clearly detected by the behaviour of the particularly strong reflexions. Fig. 2 shows the variations of intensities for three reflexions with increasing temperature from room temperature to 95 °C. Marked changes in intensity can be seen for the $\bar{6}2\bar{2}$ and $\bar{3}2\bar{4}$ reflexions in the regions of the 44 and 70 °C transitions, whereas no significant change can be found for the $\bar{3}29$ reflexion at the two transition points. In general, the strong enhancement of the intensities in the region of the 70 °C transition could be found for the reflexions whose intensities strongly increased in the region of the 44 °C transition. This might suggest that the feature of the phase transformation occurring between the γ and δ forms is very closely related to that of the α/γ phase transformation.

Diffuse scattering

On Weissenberg photographs, especially on the second-layer photograph about **b**, a remarkable diffuse scattering was observed [Fig. 1(*b*)]. The features of the diffuse scattering patterns associated with $h = 3n \pm 1$ were:

1. Intensities of diffuse maxima were closely related to those of the corresponding Bragg reflexions from the α form.

2. Diffuse scattering was strongly elongated in the direction normal to $(30\bar{2})$. In some cases, it was extended to the neighbouring intense reflexion with $h = 3n$.

Intensities at 50 °C were estimated with a microdensitometer (MD-II, Mitaka-Koki Co.) on the $h1l$, $h2l$ and $4kl$ equi-inclination Weissenberg photographs. The estimation was made on one side of the film which gives a better resolution than the other, *i.e.* we used one side of the film showing contracted sharp spots.

As significant thermal diffuse scattering has been observed in the case of the α form [Fig. 1(*a*)], we examined the effect of thermal diffuse scattering on the total diffuse scattering arising above the 44 °C transition by taking a series of stationary-crystal strip photographs, raising the temperature from room temperature to 85 °C and then lowering to room temperature. Above 44 °C intensities of diffuse maxima associated with the reciprocal lattice points with $h = 3n \pm 1$ rapidly decreased with increasing temperature [Fig. 3(*a*)], while those near to the particularly strong reflexions with $h = 3n$ gradually decreased up to 70 °C [Fig. 3(*b*)]. At the mid-point between the above two reciprocal lattice points, the intensity of diffuse scattering rapidly increased in the region of the transition and then decreased as the temperature was further increased.

These observations may suggest that the diffuse scattering associated with the lattice points with $h = 3n$

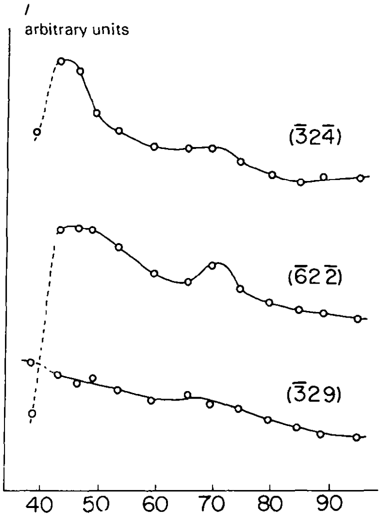
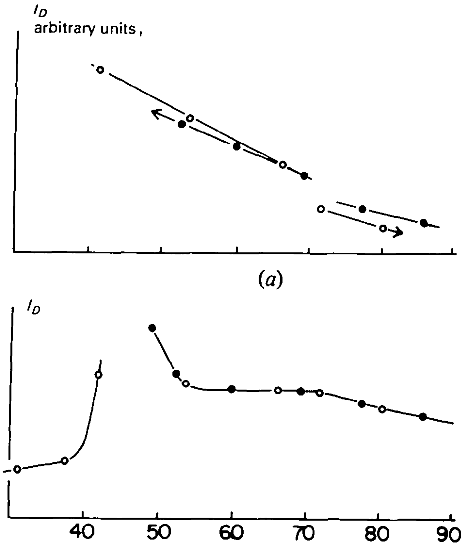


Fig. 2. Variations of the intensities of sharp reflexions with indices $\bar{3}2\bar{4}$, $\bar{6}2\bar{2}$ and $\bar{3}29$ as a function of temperature. The curves have been drawn empirically through the points. Note that the intensities were estimated with a microdensitometer.



(*a*)

(*b*)

Fig. 3. Variations of the intensities of diffuse scattering, (*a*) associated with $\bar{4}2\bar{5}$ and (*b*) near to the $\bar{3}2\bar{4}$ reflexion. The curves have been drawn empirically through the points. ○ temperature rising; ● temperature falling.

± 1 is mainly due to structural disorder, but the effect of the thermal scattering on the total diffuse scattering is pronounced near to the particularly strong reflexions. An examination of photographs of the α form revealed that the thermal diffuse scattering associated with the particularly strong reflexions is due to elastic thermal waves as expected from some molecular crystals (Amorós & Amorós, 1968). The significant changes in intensity of the diffuse scattering occurring in the region of the 70 °C transition can be clearly seen in Fig. 3.

Changes in spot shape during the α/γ transition

A series of Weissenberg photographs taken at temperatures increasing from 41 to 46 °C showed that reflexions with $h = 3n$ from the α and γ forms co-exist over the temperature range and are clearly separated in Bragg angle, suggesting an abrupt change of the cell parameters at the transition. Further, we took another series of photographs lowering the temperature from 46 to 41 °C and found that the two sets of photographs are very similar to each other, indicating that the thermal hysteresis is very small.

Closer inspection of the above photographs and other related ones revealed that there is a boundary plane between both the forms and the α/γ phase transformation successively propagates along the direction normal to this plane. This boundary plane was found to be parallel to $(01\bar{3})$ which is identical with the plane already found in the crystal splitting during the transition.

Solution of the averaged structure

Using three-dimensional diffraction data, refinements of the structure given by Harada, Taniguchi, Takaki & Sakurai (1969) (hereinafter referred to as 'positional averaged structure' of the γ form) were carried out by least-squares calculations. Non-hydrogen atom parameters were used for refinements. Contributions of H atoms located in the calculated positions were included in the structure factors. A weighting scheme of the type $w = 1 - \exp(-20s^2)$ with $s = \sin\theta/\lambda$ was used. The final R value was 0·114. Positional and thermal parameters for non-hydrogen atoms are listed in Table 2. For comparison the mean values of the positional parameters for molecules A, B and C in an asymmetric unit of the α form and thermal parameters for molecule B, whose orientation is fairly close to that for the 'positional averaged structure' of the γ form, are also listed in Table 2.

By comparing the above two sets of positional parameters in Table 2, one finds that they agree surprisingly well with each other. On the other hand, the observation of diffuse scattering in the *Experimental* (observation 1) indicates that there remains some aspect of the α form in the arrangement of the molecules. Referring to the above facts we first considered that the structure of the γ form would be described in terms of a disordered arrangement of three structural units, P, Q and R, which are deduced from the structure of the α form by taking their unit-cell origins at 0, $\frac{1}{3}\mathbf{a}$ and $\frac{2}{3}\mathbf{a}$ along $\mathbf{a}$. Since Bragg reflexions with $h = 3n \pm 1$ were not observed in the γ form, P, Q and R should have equal proportions. This model well explained the existence of the diffuse scattering associated with the reciprocal lattice points with $h = 3n \pm 1$, but did not explain the fact that many of the sharp reflexions from the γ form were remarkably more intense in comparison with the corresponding reflexions from the α form (*Experimental*).

Table 2. *Fractional coordinates and $\bar{U}$ values of the non-hydrogen atoms for the 'positional averaged structure' of the γ form at* 50 °C

The values are referred to the unit-cell axes of the γ form. The coordinates in parentheses are the mean values for those of molecules A, B and C in the α form. $\bar{U}$ are the mean values of the principal values of the $\mathbf{U}$ tensors for molecule B.

	x	y	z	$\bar{U}$ ($\times 10^3$)
Cl	0·807	1·234	0·426	113
	(0·810)	(1·233)	(0·427)	(97)
N	0·322	0·238	0·052	59
	(0·318)	(0·236)	(0·052)	(53)
O	−0·064	0·240	0·093	62
	(−0·063)	(0·240)	(0·093)	(54)
C(1)	0·186	0·335	0·108	50
	(0·186)	(0·334)	(0·107)	(42)
C(2)	0·340	0·557	0·185	40
	(0·340)	(0·558)	(0·186)	(42)
C(3)	0·545	0·726	0·177	71
	(0·545)	(0·724)	(0·179)	(56)
C(4)	0·687	0·929	0·250	90
	(0·686)	(0·929)	(0·252)	(68)
C(5)	0·627	0·971	0·333	71
	(0·627)	(0·971)	(0·333)	(63)
C(6)	0·426	0·807	0·343	96
	(0·424)	(0·807)	(0·342)	(74)
C(7)	0·282	0·602	0·269	81
	(0·282)	(0·607)	(0·269)	(63)

The second model was then obtained from the following considerations: since the bond lengths and angles and the hydrogen-bonding scheme found in the 'positional averaged structure' of the γ form are very reasonable as compared with those for the α form, and in addition the orientations of molecules A, B and C in the α form are not so different from those of the molecule in the 'positional averaged structure' of the γ form, there is a possibility that the γ form consists of a new arrangement of molecules, which is produced from movements of molecules, A, B and C, during the transformation from the α to γ forms. On the other hand, as has been described above, the γ form retains a nature of the α form in the arrangement of the molecules. Therefore we assumed that the structure of the γ form can be described to a first approximation in terms of the arrangement of the three structural units, P, Q and R, with equal proportions and the structure, V, having positional parameters very close to those of the 'positional averaged structure' of the γ form.

Taking the cell of the γ form with $3a_\gamma$ (a_γ; a-axial length of the γ form) as the unit cell of the four structural units, V, P, Q and R, we give the structure factors of the averaged structure of the γ form in the form

$$F = w_1 V + \tfrac{1}{3} w_2 (P + Q + R) \qquad (1)$$

where w_1 and $w_2/3$ ($w_1 + w_2 = 1$) are probabilities of finding V and each of the other three units in the crystal, respectively; V, P, Q and R are the structure factors for the corresponding units, the fractional coordinates and thermal parameters for the α form being used for the calculation of P, Q and R.

Since the positional parameters of V are considered to be very close to the mean values of those for P, Q and R and therefore phase angles of V and ($P + Q + R$) for $h = 3n$ ($F = 0$ for $h = 3n \pm 1$) are almost the same except the case where the values of ($P + Q + R$) are very small, structure V may be solved from (1) if a proper value of w_1 has been given. Initial atomic parameters for V used were those based on the 'positional averaged structure' of the γ form. Least-squares calculations were carried out for values of $0{\cdot}5 \le w_1 \le 0{\cdot}9$. It was found that the R value changed monotonically from 0·117 to 0·113 as w_1 increased, and changes in positional parameters were very small whereas marked changes were found in thermal parameters; the thermal parameters for $w_1 = 0{\cdot}5$ were generally small while those for $w_1 = 0{\cdot}9$ were large as compared with those for molecule B.

Table 3. *Fractional coordinates and $\bar{U}$ values for structure V at* 50°C

The values are referred to the unit-cell axes of the γ form.

	x	y	z	$\bar{U}$
Cl	0·8072	1·2332	0·4259	110
N	0·3226	0·2401	0·0515	51
O	−0·0645	0·2391	0·0932	56
C(1)	0·1854	0·3353	0·1079	48
C(2)	0·3405	0·5569	0·1842	37
C(3)	0·5453	0·7276	0·1765	62
C(4)	0·6870	0·9304	0·2498	84
C(5)	0·6275	0·9708	0·3331	67
C(6)	0·4248	0·8096	0·3424	83
C(7)	0·2811	0·6016	0·2686	71
H(3)	0·589	0·697	0·117	
H(4)	0·836	1·050	0·243	
H(6)	0·382	0·835	0·403	
H(7)	0·133	0·480	0·276	
H(N1)	0·533	0·238	0·066	
H(N2)	0·238	0·080	0·004	

Standard deviations for coordinates

	x	y	z
Cl	0·0007	0·0006	0·0002
N	0·0010	0·0013	0·0004
O	0·0008	0·0011	0·0003
C	0·0011–0·0022	0·0014–0·0022	0·0004–0·0006

Table 4. *Interatomic distances* (Å) *and angles* (°) *for structure V*

Cl–C(5)	1·74 (1)	N–C(1)–O	121 (1)
N–C(1)	1·36 (1)	N–C(1)–C(2)	118 (1)
O–C(1)	1·24 (1)	O–C(1)–C(2)	122 (1)
C(1)–C(2)	1·46 (1)	C(1)–C(2)–C(3)	123 (1)
C(2)–C(3)	1·37 (1)	C(1)–C(2)–C(7)	120 (1)
C(2)–C(7)	1·38 (1)	C(3)–C(2)–C(7)	117 (1)
C(3)–C(4)	1·36 (2)	C(2)–C(3)–C(4)	121 (1)
C(4)–C(5)	1·37 (2)	C(3)–C(4)–C(5)	121 (1)
C(5)–C(6)	1·34 (2)	C(4)–C(5)–C(6)	120 (1)
C(6)–C(7)	1·38 (2)	Cl–C(5)–C(4)	120 (1)
		Cl–C(5)–C(6)	120 (1)
		C(5)–C(6)–C(7)	120 (1)
		C(2)–C(7)–C(6)	121 (1)

Plane of amide group and least-squares plane of benzene ring referred to unit-cell axes of the γ form:

Amide group $-1{\cdot}024x + 4{\cdot}095y - 9{\cdot}405z = 0{\cdot}1687$
Benzene ring $-3{\cdot}192x + 3{\cdot}703y - 4{\cdot}146z = 0{\cdot}2170$

Angle between planes of amide group and benzene ring: 28·1°

The value of w_1 was then obtained as follows: since the packing schemes of molecules for the α and γ forms were very similar and the difference in density at room temperature and at 50°C was very small, it was expected that the temperature factors for the two forms would not deviate very much, and the mean value of the principal values of the U tensor, $\bar{U}$, for each atom at 50°C would not deviate much from the value at room temperature, especially for the atoms in the amide group linked by hydrogen bonds. On the basis of this assumption a proposed value of $w_1 = 0{\cdot}75$ was obtained. On the other hand, another attempt was made to obtain the value of w_1 more directly by comparing observed and calculated structure amplitudes which are sensitive to the change in w_1.

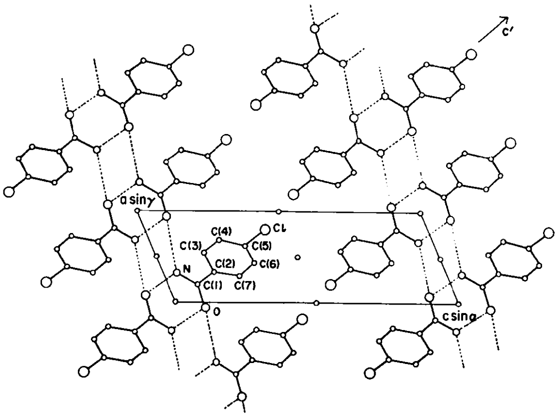


Fig. 4. Structure V viewed along **b**.

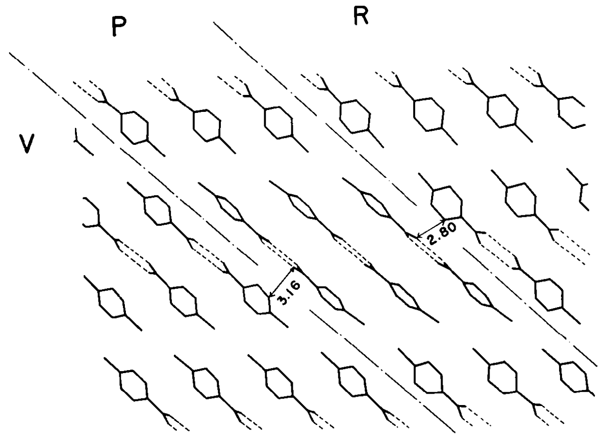


Fig. 5. Hypothetical packing of structural units *V*, *P* and *R* viewed along **a**. Half of the molecules have been omitted for clarity. The chain lines show the boundaries between the neighbouring units.

Although we failed in obtaining the most probable value owing to inaccuracy of the observed intensities, many of the values obtained fell in the region $0{\cdot}65 < w_1 < 0{\cdot}8$. By comparing the above results we used $w_1 = 0{\cdot}75 \pm 0{\cdot}1$ for the following calculations.

The final *R* value was 0·113. The atomic parameters for structure *V* are given in Table 3,* together with the $\bar{U}$ values of the non-hydrogen atoms. Bond lengths and angles are given in Table 4. Structure *V* viewed along **b** is illustrated in Fig. 4. It consists of stacking of molecular sheets parallel to (01$\bar{3}$) with interlayer spacing of 3·79 Å. Within a sheet, the dimers each formed by NH···O hydrogen bonds of 2·99 Å are held together by other NH···O hydrogen bonds of 2·89 Å to form an endless chain along **a**. The Cl—Cl distance of 3·33 Å is the shortest contact between the neighbouring chains. The structural relationship between *V* and the α form has been discussed in the preceding paper (Taniguchi, Nakata, Takaki & Sakurai, 1978).

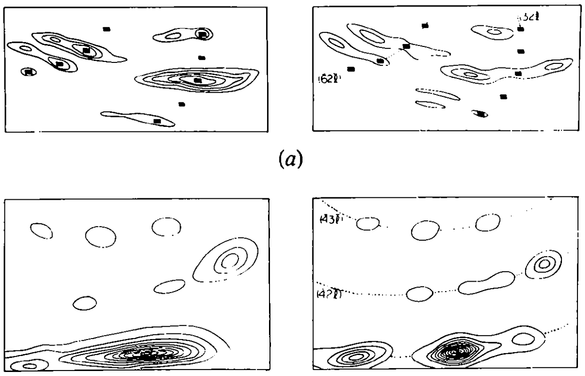
Although the 'averaged structure' of the γ form is well explained in terms of the four structural units, there still remains a problem in the arrangement of the four units. Fig. 5 shows a hypothetical packing of units *V*, *P* and *R* viewed along **a**. Very short intermolecular distances can be seen at the boundaries between the different neighbouring units. This would certainly suggest that the molecules on both sides of the boundaries deviate from each other (or rotate) to make van der Waals contacts, giving some statistical disorder. According to the above consideration, the significant differences found in the values of $\bar{U}$ for C(3), C(4), C(6) and C(7) between *V* and molecule *B* would be attributed to the existence of an orientational disorder mainly caused by the rotation of the benzene ring about C(2)–C(5). Note that a similar orientational disorder would be expected to occur also in *P*, *Q* and *R*.

Interpretation of the diffuse scattering

Flack (1970*a*,*b*) has interpreted the diffuse scattering from the crystal of anthrone by postulating that the disorder is caused by mistakes of molecular orientations arising independently along the unit-cell axes. The following analysis of the diffuse scattering of the γ form is essentially based on his idea, but a certain simplified treatment was employed because of complexity of the disordered structure.

By assuming a diffuse scattering pattern associated with a reciprocal lattice point to be ellipsoidal, we examined the characteristics of the patterns and found that the directions of the maximum and minimum diameters were closely related to the arrangement of the molecules; the latter direction coincides with that normal to the molecular sheet parallel to (01$\bar{3}$) and the former normal to the molecular layer parallel to (30$\bar{2}$). These observations suggest that there remains a strong tendency for ordering along **b** while a strong disorder exists along **a**. Referring to the above results we took a new unit cell having $\mathbf{a}' = 3\mathbf{a}_\gamma$, $\mathbf{b}' = \mathbf{b}$ and $\mathbf{c}' = 6\mathbf{a}_\gamma + 9\mathbf{b} + 3\mathbf{c}$, where the direction of the *c*′ axis almost coincides with that of the long axis of a dimer. The directions of the maximum and minimum diameters are then along $\mathbf{a}'^*$ and $\mathbf{b}'^*$ respectively. The unit-cell dimensions referred to the new axes are given in Table 1.

Let *V*′, *P*′, *Q*′ and *R*′ with the unit cell given above



(*a*)

(*b*)

Fig. 6. Observed (left) and calculated (right) diffuse scattering patterns. (*a*) *h*2*l*; (*b*) 4*kl*.

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* Lists of structure amplitudes and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33482 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

be the new structural units having the same structure as those of V, P, Q and R respectively. Then we assume that the disordered structure of the γ form can be described approximately in terms of a disordered arrangement of the four units, V', P', Q' and R', occurring independently along $\mathbf{a}'$, $\mathbf{b}'$ and $\mathbf{c}'$. The actual calculation of the intensity was carried out by assuming a random distribution of four units, each consisting of any one of the structures, V', P', Q' and R', and having dimensions of an integral multiple of each of the unit-cell axes. This unit (hereinafter referred to as 'domain') may be compared with the 'averaged short-range-order domain' given by Flack (1970*b*).

The intensity of diffuse scattering in electrons is then given by

$$I_D(\xi',\eta',\zeta')=\frac{N_1N_2N_3}{n_1n_2n_3}\times\frac{\sin^2 n_1\pi\xi'}{\sin^2\pi\xi'}\times\frac{\sin^2 n_2\pi\eta'}{\sin^2\pi\eta'}\times\frac{\sin^2 n_3\pi\zeta'}{\sin^2\pi\zeta'}\,[\tfrac{1}{3}w_1w_2(|V'-P'|^2+|V'-Q'|^2+|V'-R'|^2)+\tfrac{1}{9}w_2^2(|P'-Q'|^2+|Q'-R'|^2+|R'-P'|^2)] \qquad (2)$$

where ξ', η', ζ' are coordinates in the reciprocal space referred to $\mathbf{a}'$, $\mathbf{b}'$, $\mathbf{c}'$; N_1, N_2, N_3 are numbers of unit cells along $\mathbf{a}'$, $\mathbf{b}'$, $\mathbf{c}'$; n_1, n_2, n_3 are integers, n_1a', n_2b', n_3c' being dimensions of the domain along $\mathbf{a}'$, $\mathbf{b}'$, $\mathbf{c}'$; V', P', Q', R' are structure factors. It should be noted that, in the calculation of the intensities by (2), no account was taken of the effect due to the orientational disorder described in the previous section.

With the value of $w_1=0\cdot75$, the calculation was carried out for $h1l$, $h2l$ and $4kl$. Since the diffuse scattering is strongly elongated along the rows parallel to $\mathbf{a}'^*$, the diffuse scattering patterns on the $4kl$ photograph may be regarded as a superposition of the diffuse reflexions with ξ' ranging from $4-\Delta\xi'$ to $4+\Delta\xi'$, where the value of $\Delta\xi'$ ($\simeq 0\cdot4$) can be estimated from the width of the layer-line screen (2·0 mm). This effect was taken into account in the calculation of the intensities for $4kl$ although some approximation was made. Corrections for polarization factor and for broadening due to the shape of the crystal were applied to the calculated intensities. A satisfactory agreement was obtained between observed and calculated diffuse scattering patterns with the values $n_1=1$, $n_2=12$ and $n_3=1$ as shown in Fig. 6. In the vicinity of the reciprocal lattice points with $h=3n$, however, an agreement is seemingly not so good due to the strong thermal diffuse scattering. The dimensions of the domain are a', $12b'$ and c' (or 15, 66 and 58 Å) along $\mathbf{a}'$, $\mathbf{b}'$ and $\mathbf{c}'$ respectively and 216 molecules are contained in one domain.

Mechanism of the phase transformation

Here we summarize several important conclusions concerning the α/γ phase transformation:

1. The major change of the crystal structure on the transformation from the α to γ forms is repositioning (reorientation and shifting) of molecules to produce a new arrangement of molecules in a chain along $\mathbf{a}'$.

2. These molecular movements are the cause of the drastic decrease in the length of the a axis from 15·027 to 5·015 Å during the transition. The other changes in the unit-cell parameters on the transformation to the γ form can be expressed approximately in terms of the increases in the distance between the neighbouring chains in a molecular sheet by 0·7% and in the spacing of the sheets by 0·8%, and the increases in β' and γ' angles by 1·4 and 0·5° respectively.

3. The direction of the a' axis remains unchanged on the α/γ transformation, and the changes in the directions of the b' and c' axes occur almost in the $a'b'$ and $a'c'$ planes respectively.

4. The α/γ phase transformation successively propagates along the direction normal to the molecular sheets (or along $\mathbf{b}'^*$).

5. Diffuse scattering patterns are well interpreted in terms of a random distribution of four domains, each consisting of any one of the four structural units, V', P', Q' and R'. Dimensions of the domain are a', $12b'$ and c' along $\mathbf{a}'$, $\mathbf{b}'$ and $\mathbf{c}'$ respectively.

A plausible process for the phase transformation to the γ form might consist of two types of molecular movements: one is the rearrangement of molecules in a chain along $\mathbf{a}'$ as shown in conclusion 1 and repositioning of molecules, for example, from P' to Q'. The existence of very strong disorder along $\mathbf{a}'$ may be explained by these movements. The other is cooperative displacements of the molecular chains along $\mathbf{a}'$. Conclusions 2, 3 and 4 would support the occurrence of these movements, which would be very closely related to the formation of the averaged domain size along $\mathbf{b}'$ and $\mathbf{c}'$. Further, the occurrence of the displacements may well explain the fact that the phase transformation from the α to γ forms occurs without splitting of the crystal even when extraordinarily high heating rates are employed; a mechanical strain built up within the crystal during the rearrangement of molecules along $\mathbf{a}'$ would be released by these displacements.

Very short intermolecular distances between molecules A and B *etc.*, shown in Fig. 5, would indicate that, on the transformation from the α to γ forms, there exists a considerable energy barrier which prevents the occurrence of cooperative displacements of molecules if molecules on both sides of a gliding plane have the same orientations as in the α form. Presumably, the displacement would occur when the rearrangement of molecules along $\mathbf{a}'$ proceeds to a considerable degree.

Unfortunately, the experimental data are not sufficient to allow a definite comment on the process of the phase transformation from the γ to α forms. Nevertheless, it may be said that the major process might consist of ordering in a chain along **a**′ to produce the molecular arrangement for the α form. Cooperative displacements, however, would not easily occur during this transformation since a high energy barrier to the displacement of molecules may be rapidly built up as the ordering proceeds. The difficulties of the occurrence of cooperative displacements would certainly explain the occurrence of crystal splitting when high rates of temperature change were employed.

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24-Methylenecholest-5-ene-3β,7β,19-triol. A Case of Pseudotranslation. Calculation of Structure Invariants from Partial Structure Information

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The title compound, the sterol $C_{28}H_{46}O_3$, was isolated from the soft coral *Litophyton viridis*. The structure crystallizes in space group $P2_1$ with $a = 17{\cdot}00\ (1)$, $b = 12{\cdot}40\ (1)$, $c = 12{\cdot}67\ (1)$ Å, $\beta = 98{\cdot}07\ (5)°$, $Z = 4$, $D_x = 1{\cdot}074$ and $D_m = 1{\cdot}09$ g cm^{-3}. The two independent molecules are related by a pseudotranslation $(0,\frac{1}{2},\frac{1}{2})$; they differ in the conformation of the side chain and in the hydrogen bonding. The well known convergence procedure has been applied to discriminate between several structure invariants calculated from origin-displaced partial-structure information and to extract those invariants with phases most probably 0°.

Introduction

Chemical and spectroscopic investigations of the title compound (Fig. 1) were carried out by Bortolotto, Daloze, Braekman, Losman & Tursch (1976). The compound is, as far as we know, the first example of a naturally occurring 19-OH sterol.

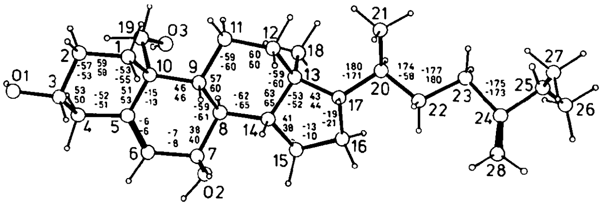

Fig. 1. 24-Methylenecholest-5-ene-3β,7β,19-triol, relative conformation. The thick bonds indicate double bonds.

The space group, refined cell parameters and structure factors were obtained from data collected on a Philips PW 1100 diffractometer with graphite-monochromatized Cu $K\alpha$ radiation. The measurement of half the reciprocal sphere up to a Bragg angle of 79° using an ω–2θ scan technique yielded 5025 unique F's after reduction and correction for the Lp factor.

A characteristic feature of the diffraction record is the relative weakness of all reflexions with $k + l$ odd, a consequence of a $(0,\frac{1}{2},\frac{1}{2})$ pseudotranslation affecting about 75% of the structure as evidenced in the Patterson function. In view of this, the solution of the structure was first attempted in space group $A2$, using the program *MULTAN* (Germain, Main & Woolfson, 1971). The *MULTAN* procedure did not solve the structure, but several recognizable steroid fragments, displaced from the correct origin, appeared in the E maps. The introduction of those *MULTAN* starting phases which gave the best fragment into the *MAGIC*

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