

Hydrogen Bond Studies

62.* The Crystal Structure of a High Temperature Modification of Dimethylammonium Chloride $(\text{CH}_3)_2\text{NH}_2\text{Cl}$: an X-Ray and Infrared Study

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The crystal structure of a high temperature modification of dimethylammonium chloride, $(\text{CH}_3)_2\text{NH}_2\text{Cl}$, has been determined from three-dimensional single-crystal X-ray data obtained at $+48^\circ\text{C}$. The crystals are tetragonal, space group $I4/mmm$, with two formula units in the cell of dimensions $a = 5.146$ (2) and $c = 9.959$ (2) Å. The structure is disordered containing planar domains which are internally ordered consisting of dimethylammonium and chloride ions linked together by hydrogen bonds. The choice among several models, possible from the X-ray data, was made from a study of the infrared spectra of N-H stretching vibrations of isotopically isolated $(\text{CH}_3)_2\text{NHD}^+$ ions.

Since the submission of our paper dealing with the crystal structure determination of dimethylammonium chloride¹ (DMAC) at $+20^\circ\text{C}$, an article² containing DTA studies of this compound has appeared. In this paper DMAC is reported to have two phase transitions between -150°C and its melting point (167°C); one at -13°C and one at $+40^\circ\text{C}$. The phase stable above $+40^\circ\text{C}$ will be referred to as α -DMAC and that between -13°C and $+40^\circ\text{C}$ as β -DMAC. In the present investigation the crystal structure of α -DMAC has been determined from single-crystal X-ray diffraction data obtained at $+48^\circ\text{C}$. Infrared spectra, between 2000 and 4000 cm^{-1} , of $(\text{CH}_3)_2\text{NHD}^+$ ions have been studied at several temperatures between $+22^\circ\text{C}$ and $+186^\circ\text{C}$.

EXPERIMENTAL

X-Ray analysis. An approximately cylindrical single-crystal obtained as described previously¹ (diameter 0.10 mm, length 1.3 mm) was used for the collection of intensity data. The crystal was sealed in a thin-walled glass capillary with the a -axis of β -DMAC

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parallel to the capillary axis. On increasing the temperature this a -axis in β -DMAC became the [110] direction in α -DMAC. Six layers were recorded employing the multiple film technique (5 films) and using unfiltered CuK radiation. The films were taken using a Weissenberg camera modified originally for operation at low temperature.⁴ In the present case, however, a heated air stream was used to maintain the crystal at $+48^\circ\text{C}$. The number of reflexions measured was 164. In this way symmetry related reflexions were measured, so reducing to two the number of scale factors used in the subsequent treatment of the data containing 111 independent reflexions. This interlayer scaling was performed using the program INTERSCALE.* The relative intensities were estimated visually by comparison with an intensity scale. The data were corrected for the Lorentz and polarization effects. No absorption or extinction corrections were applied. The linear absorption coefficients for $\text{CuK}\alpha$ radiation is 50.0 cm^{-1} ; for a crystal of radius 0.005 cm , $\mu R = 0.25$.

A crystal mounted with its tetragonal axis c as rotation axis was used to confirm the diffraction symmetry. The quality of this crystal was poor, however, so none of the intensity data obtained from this crystal could be used for the structure determination and subsequent refinement.

Infrared spectra. $(\text{CH}_3)_2\text{ND}_2\text{Cl}$ was prepared by repeated recrystallization from heavy water (99.9% D). The samples were studied either as hexachlorobutadiene mulls or as solid films using windows of CaF_2 . The solid films were prepared by melting a carefully ground powder between CaF_2 windows. The melt then crystallized as a polycrystalline film. The crystallization and melting were viewed through crossed optical polarizers. To make sure that no decomposition occurred on melting, the spectra were checked against spectra of hexachlorobutadiene mulls obtained at $+22^\circ\text{C}$. No difference was observed. The sample cell was mounted in a VLT-2 variable temperature cell (Research and Industrial Instruments Company, London). The VLT-2 cell was flushed with nitrogen gas to prevent contamination with atmospheric water. Samples (solid films) studied at high temperatures were allowed to cool afterwards and a spectrum was taken to check that no sample had sublimed or decomposed.

Spectra between $2.5\ \mu$ (4000 cm^{-1}) and $5\ \mu$ (2000 cm^{-1}) were recorded on a Leitz IR III G double-beam grating spectrometer.

UNIT CELL AND SPACE GROUP

The diffraction symmetry $4/mmm$ together with the general conditions on hkl that $h+k+l=2n$ give as possible space groups $I422$, $I4mm$, $I\bar{4}2m$, $I\bar{4}m2$ and $I4/mmm$. The structure is described in terms of the centrosymmetric space group $I4/mmm$.

The cell dimensions were obtained from quartz-calibrated Weissenberg photographs using the following constants: $a = 4.9128\ \text{\AA}$ for α -quartz at 18°C ; $\lambda(\text{CuK}\alpha_1) = 1.54051$ and $\lambda(\text{CuK}\alpha_2) = 1.54433\ \text{\AA}$. The cell dimensions were obtained from a least-squares fit to the observed θ -values using the program CELSIUS. The cell dimensions were $a = 5.146(2)**$ and $c = 9.959(2)\ \text{\AA}$.

DETERMINATION OF THE ATOMIC COORDINATES

A three-dimensional Patterson synthesis was calculated using the program DRF. From this the chlorine atoms could be located at or near $(0,0,0)$ and the dimethylammonium ion near $(0.5,0.5,0)$. Since a 4-fold axis would then pass through the dimethylammonium ion, the structure must be disordered.

* This and other programs mentioned in the following are described briefly by Nahrngbauer.³

** Numbers in parenthesis here and throughout this paper are the estimated standard deviations in the least significant digits.

To restrict the number of different structural models investigated in the subsequent least-squares refinements the centrosymmetric space group $I4/mmm$ was chosen. This would seem justified in view of the close relationship to the β -phase structure as required by the infrared spectra, see below. A description in any of the non-centrosymmetric space groups would give atomic positions only slightly different from the ones obtained below.

The least-squares refinements were carried out using three different models. A series of refinements was performed for each model in which successively more parameters were allowed to vary. This was done using the program LALS and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights were calculated according to the expression $w = 1/(a + |F_o| + c|F_o|^2)$, where the final values of a and c were 0.06 and 0.04. The atomic scattering factors used were those of Cl^- , N^0 and C^0 given in the *International Tables*.⁵ The hydrogen atoms were not included in the refinements. When anisotropic temperature factors were included, their high correlation with the atomic coordinates prevented a proper convergence in the refinements for model III A below. The resulting R -values of the different refinements are shown in Table 1. Observed and calculated structure factors from the anisotropic refinement using model III B are shown in Table 3.

Table 1. R -Values ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) obtained in the different refinements. Number of parameters varied are given within parenthesis.

	Model I	Model II	Model III A	Model III B
Isotropic	11.7 (8)	12.7 (5)	11.3 (9)	18.5 (5)
Anisotropic	9.3 (14)	10.4 (8)	—	9.4 (12)

Table 2. Atomic parameters in Model III B.

	Cl	N	C
x	0.0	0.5	0.5
y	0.0668	0.6028	0.5538
z	0.0	0.0	0.1222
β_{11}	0.0133 (20)	0.0310 (58)	0.0704 (100)
β_{22}	0.0163 (24)	0.0381 (56)	0.0598 (169)
β_{33}	0.0154 (6)	0.0120 (16)	0.0131 (13)
β_{12}	0.0	0.0	0.0
β_{13}	0.0	0.0	0.0
β_{23}	0.0	0.0	-0.0030 (62)

In model I, a 4-fold disorder was assumed with $1/4\text{N}$ in an 8-fold special position and $1/4\text{C}$ in a 16-fold one. The chlorine occupied a 2-fold special position and was assumed to be ordered. The orientation of the dimethylammonium ion was then chosen so that it could form two linear (or almost

Table 3. Observed and calculated X-ray structure factors for α -DMAC, using Model III B.

$h,k,l, F_o , F_c $					$h,k,l, F_o , F_c $				
0	0	2	34.3	42.6	1	3	10	1.7	1.8
0	0	4	14.1	15.0	1	4	1	4.1	4.0
0	0	6	15.8	14.3	1	4	3	5.1	5.2
0	0	8	11.7	11.5	1	4	5	3.7	3.9
0	0	10	4.6	4.6	1	4	7	1.7	1.7
0	0	12	1.1	1.1	1	4	9	0.7	0.9
0	1	1	2.7	5.8	1	5	0	3.2	2.7
0	1	3	25.2	22.0	1	5	2	2.3	2.1
0	1	5	14.1	13.9	1	5	4	1.5	1.4
0	1	7	2.3	2.4	1	5	6	1.1	1.2
0	1	9	1.3	0.9	1	5	8	0.6	0.9
0	1	11	1.8	1.9	1	6	1	0.6	0.6
0	2	0	38.1	34.8	1	6	3	0.6	0.6
0	2	2	23.8	22.0	1	6	5	0.3	0.4
0	2	4	10.5	9.4	2	2	0	18.2	18.4
0	2	6	10.2	9.3	2	2	2	11.4	12.1
0	2	8	8.1	7.8	2	2	4	6.0	5.7
0	2	10	3.1	3.2	2	2	6	6.1	5.9
0	2	12	0.7	0.8	2	2	8	5.3	5.0
0	3	1	7.6	6.1	2	2	10	2.3	2.0
0	3	3	10.4	10.0	2	3	1	5.2	5.2
0	3	5	6.9	7.3	2	3	3	7.1	7.3
0	3	7	2.6	2.5	2	3	5	5.6	5.5
0	3	9	1.0	1.2	2	3	7	2.2	2.2
0	3	11	0.6	1.3	2	3	9	1.1	1.1
0	4	0	6.9	7.9	2	4	0	4.2	3.7
0	4	2	6.3	5.8	2	4	2	3.2	2.5
0	4	4	3.5	3.4	2	4	4	1.6	1.3
0	4	6	3.4	3.2	2	4	6	1.3	1.4
0	4	8	2.5	2.5	2	4	8	1.1	1.2
0	4	10	0.8	1.1	2	5	1	1.8	1.2
0	5	1	2.3	2.3	2	5	3	2.1	1.4
0	5	3	2.3	2.6	2	5	5	1.5	1.0
0	5	5	1.8	1.9	2	5	7	0.6	0.5
0	5	7	0.6	0.9	2	6	0	0.6	0.4
0	6	0	1.8	1.5	2	6	2	0.6	0.4
0	6	2	1.3	1.3	2	6	4	0.3	0.3
0	6	4	0.5	1.0	3	3	0	5.7	4.1
1	1	0	48.5	49.2	3	3	2	2.9	2.6
1	1	2	29.9	29.8	3	3	4	1.8	1.2
1	1	4	12.1	11.6	3	3	6	1.6	1.4
1	1	6	12.4	11.4	3	3	8	1.3	1.3
1	1	8	10.2	9.4	3	4	1	3.1	1.7
1	1	10	3.7	3.8	3	4	3	3.2	2.1
1	1	12	0.9	0.9	3	4	5	2.4	1.6
1	2	1	8.6	7.0	3	4	7	0.9	0.7
1	2	3	16.1	14.3	3	5	0	1.1	1.3
1	2	5	10.6	10.0	3	5	2	1.1	1.4
1	2	7	3.1	2.7	3	5	4	0.9	1.2
1	2	9	1.3	1.2	3	5	6	0.5	0.8
1	2	11	1.7	1.6	4	4	0	1.4	1.8
1	3	0	14.2	14.6	4	4	2	1.3	1.8
1	3	2	10.2	10.0	4	4	4	1.2	1.6
1	3	4	4.9	5.1	4	4	6	0.8	1.1
1	3	6	5.4	5.1	4	5	1	0.7	1.4
1	3	8	4.2	4.3					

so) hydrogen bonds with the chlorine atoms in four different ways (*cf.* Fig. 5, where the situation for Model III is shown). The N...Cl distance obtained was 3.29 (3) Å.

In model II, the centre of the electron distribution for N and C obtained using the ordinary (isotropic or anisotropic) temperature factor model was distributed around a circle centred on the 4-fold axis. This model thus represents a free rotation or an approximation to some static disorder of the dimethylammonium ion. Such a model is expressed mathematically by replacing the normal contribution to the structure factors from the atoms N and C by the expression:⁶ $T_j f_j \exp[2\pi i(hx_j + ky_j + lz_j)] J_0(2\pi r_j \sqrt{h^2 + k^2}/a)$, where T_j is the temperature factor, f_j the atomic scattering factor, (x_j, y_j, z_j) the centre and r_j the radius of the circle on which the atoms move (or are disordered), a is the length of the a -axis and J_0 is a zero-order Bessel function. Since an impossible geometry was obtained when the z -coordinate for the carbon atom was allowed to vary, it was fixed to $z=0.1222$ (the value in the β -phase). The radii for the motion of N and C, which could not be refined using our version of the program LALS, were 0.53 and 0.28 Å. With this choice of radii the 4-fold axis passes through the centre of gravity of the ion.

In model III A, the chlorine atoms were allowed to occupy 8-fold special positions with 1/4Cl in each position. This model is otherwise identical with model I. In model III B the atomic coordinates were fixed to values deduced from the β -phase structure as discussed below. Model III B is the one chosen to give the best description of the structure when both X-ray and infrared data are considered (see Discussion). On comparing the results of the refinements of the two variants of model III, it is found that the chlorine coordinates differ significantly. Since, in this case, large correlations exist between the coordinates and the temperature factors, these differences can be a result of the systematic error introduced by being unable to use anisotropic temperature factors in the first variant.

INFRARED SPECTRA

Since our spectrometer did not cover the far-infrared region only intramolecular vibrations could be studied. Of these the N-H stretching vibrations are the most sensitive to changes in environment (*e.g.* hydrogen bond strength). Especially useful then is the method of isotopic solid solution in which correlation field effects are eliminated.^{7,8} In particular this method has found recent application in studying hydrates where it has been possible to detect differences in the environments of the hydrogen atoms within the same water molecule.^{9,10}

The same method can be employed in this case to study the N-H stretching bands of $(\text{CH}_3)_2\text{NHD}^+$ ions. In Fig. 1 spectra are shown of the N-H and N-D stretching bands for samples at +22°C containing decreasing percentages of hydrogen. In the non-deuterated case, two N-H stretching bands are found at 2985 and 2793 cm^{-1} (the corresponding N-D bands are at 2212 and 2121 cm^{-1}). In the spectrum of a sample containing only a few percent hydrogen, two N-H bands are still found but at slightly different

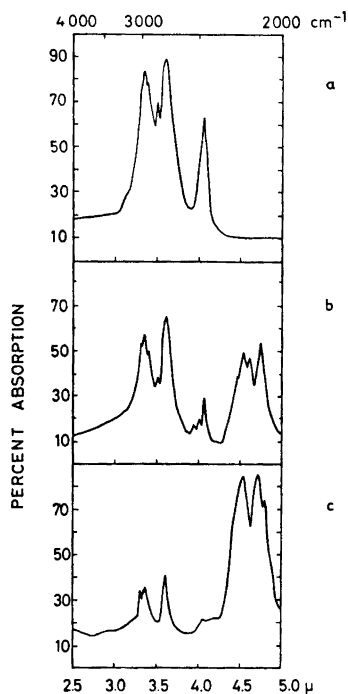


Fig. 1. Infrared spectra (hexachlorobutadiene mulls) of, (a) $(\text{CH}_3)_2\text{NH}_2\text{Cl}$, (b) $(\text{CH}_3)_2\text{NH}_2\text{Cl}$ recrystallized from D_2O (50%), (c) $(\text{CH}_3)_2\text{ND}_2\text{Cl}$ after several recrystallizations from D_2O (99.9%), obtained at $+22^\circ\text{C}$.

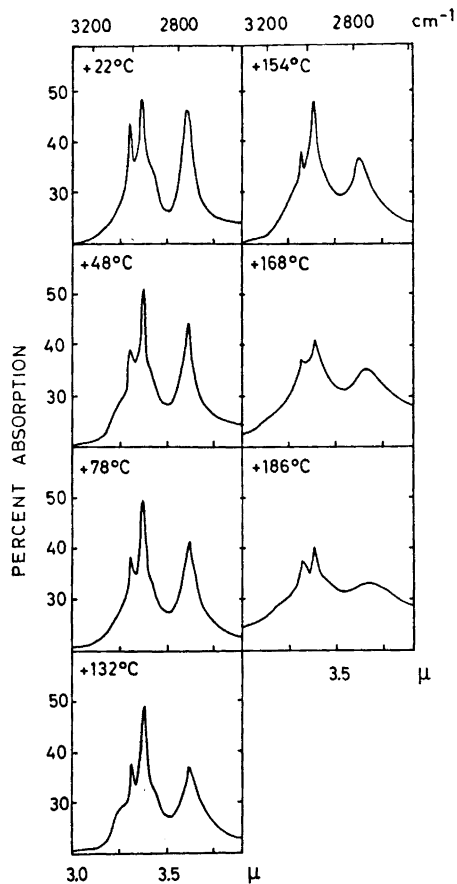


Fig. 2. Infrared spectra (solid film) of uncoupled N-H vibrations in dimethylammonium chloride at temperatures indicated in the figure. The N-H stretching region of Fig. 1 is shown.

frequencies (2967 and 2778 cm^{-1}). These bands thus show the existence of two nonequivalent ammonium hydrogens in the dimethylammonium ion of the β -phase in agreement with the result obtained in the crystal structure determination. Superposed on the higher wavenumber N-H band are two C-H stretching bands (3012 and 2963 cm^{-1}). Some other bands are also visible in the N-H stretching region in the non-deuterated case (2849 and 2457 cm^{-1}). These are probably combination bands having enhanced intensities caused by Fermi resonance with the fundamental N-H stretching bands.¹¹ They seem to disappear on increasing the deuteration. A $(\text{CH}_3)_2\text{NHD}^+$ ion does not give combination bands at the same wavenumbers as a $(\text{CH}_3)_2\text{NH}_2^+$ ion.

As can be seen in Fig. 2 the two N–H bands persist into the α -phase with no change in position and only gradual broadening as the temperature increases.

DISCUSSION

As mentioned above, three models were considered in the least-squares refinement. It does not seem possible to make a definite choice among the different models solely on the basis of the results of the refinements made. That the detailed arrangement of the atoms should be difficult to obtain in this case is perhaps not surprising in view of the high degree of disorder in the structure.

The conclusion which can be drawn from the infrared spectra of $(\text{CH}_3)_2\text{NHD}^+$ ions in the α -phase is that each of the two ammonium hydrogens in a dimethylammonium ion must have very nearly the same environment as in the β -phase. This is certainly not the case in models I and II since the shortest $\text{N}\cdots\text{Cl}$ distance is about 3.29 Å as compared to 3.13 and 3.09 Å in the β -phase. Furthermore the N–H bonds will have many possible environ-

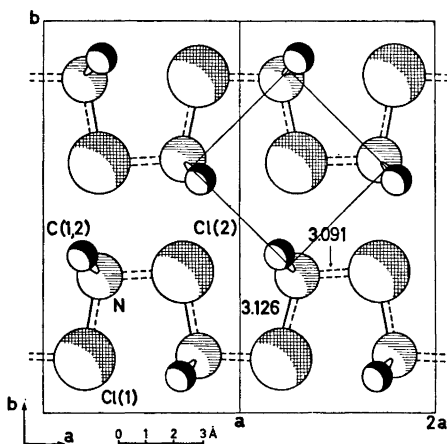


Fig. 3. $(\text{CH}_3)_2\text{NH}_2\text{Cl}$ (β -phase). A projection on the mirror plane $z=0$ of atoms in and close to this plane. The centres of gravity of four dimethylammonium ions have been connected to show the orientation of the unit cell of the α -phase. The atomic coordinates of the α -phase are, however, referred to a cell with the origin close to the chloride ion positions (see Figs. 4 and 5).

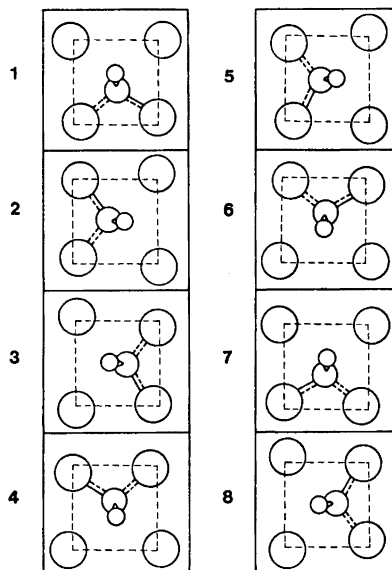


Fig. 4. Eight possible situations for the dimethylammonium ion, four of which are obtained from Fig. 3 and four by a rotation 90° . The unit cell of the α -phase is indicated with dashed lines.

ments instead of only two as required. This would result in one rather broad N–H band shifted to higher wavenumbers in contrast to the two unshifted bands observed.

An attempt will now be made to arrive at a structural description based on model III which fulfils the dual requirements imposed by the X-ray and IR data. Let us first consider some features of the β -phase structure. It consists of layers, perpendicular to [001], containing hydrogen bonded chains as shown in Fig. 3. Consecutive layers, separated by $c/2$, are translated $(a+b)/2$ relative to one another according to the space group symmetry $Ibam$. Within a layer each dimethylammonium ion is surrounded by four chloride ions at the corners of a distorted square. There are four symmetry related ions within each layer of the unit cell.

These four situations for the dimethylammonium ion together with those obtained from a rotation through 90° are illustrated in Fig. 4. All eight possible situations can occur for one particular dimethylammonium ion by rotating about an axis parallel to [001] and passing through the centre of gravity of the ion. At the same time, the chloride ions have to shift slightly. Starting from each of these possible situations for an individual dimethylammonium ion, a total of eight arrangements of chains can be created, each internally identical to the β -structure arrangement but related to one another by rotations and translations.

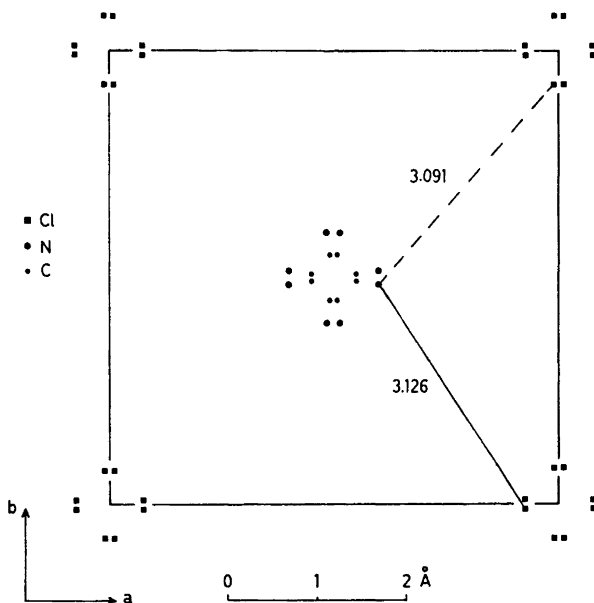


Fig. 5. Possible atomic positions in the plane $z=0$ of the unit cell of the α -phase, obtained from a superposition of the eight situations shown in Fig. 4. The hydrogen bonds for one orientation of the dimethylammonium ion are indicated.

It is possible that stacking faults can exist in the sequence of layers of the α -phase. All that is required, however, is that planar domains occur within which an arrangement of chains exists corresponding to one of the eight possibilities discussed above. There must be an equal probability for the occurrence of each of the eight different domain types. The actual size and shape of these domains and whether they are static or dynamical in nature cannot be ascertained from the present IR and X-ray investigation. The dynamical behaviour of the dimethylammonium ion and its implications are discussed in a subsequent paper¹² describing an NMR-investigation of the compound.

This structural model is consistent with the infrared data provided that the positions of the N-H bands do not depend on the situation in neighbouring layers or on long range effects within the same layer. That the model is consistent with the X-ray data can be seen from Fig. 5 in which a superposition of all atomic positions for the situations shown in Fig. 4 has been made. The space group symmetry is clearly seen to be fulfilled. It can also be seen that the eight atomic positions for each type of atom are grouped together in pairs. The separation within such pairs is greatest for the nitrogen atom positions and is there only ~ 0.1 Å. Such a small separation is impossible to detect by X-ray methods. Only the four mean positions for each type of atom were therefore refined in Model III above.

With the structural model chosen, the 4-fold rotation axis will pass through the centre of gravity of the dimethylammonium ion. By connecting the centres of gravity in the β -phase we obtain the unit cell for the α -phase as indicated in Fig. 4*. The length of the a -axis in the α -phase would then be obtained from the a - and b -axes of the β -structure by the relation $(b/4 + a/2)/\sqrt{2}$ ($= 5.148(2)$ Å). This value is in excellent agreement with the measured value, $5.146(2)$ Å.

Finally it can be noted that two N-H stretching bands were found even after the crystal had melted, indicating that some form of chain structure apparently persists even in the melt.

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* Actually the centres of gravity have to be displaced ~ 0.005 Å to exactly coincide with the unit cell of the α -phase.

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