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The Crystal Structure and Polymorphism of N-Methyl Acetamide*

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N-methyl acetamide ($CH_3CONHCH_3$) melts at 28 °C. and undergoes a solid phase transition at approximately 10 °C. An X-ray diffraction investigation at -35 °C. indicates that the unit cell is orthorhombic below the transition temperature, with $a = 9{\cdot}61$, $b = 6{\cdot}52$, $c = 7{\cdot}24$ Å. The space group is *Pnma*; there are four molecules per unit cell. The crystal structure determination was based on two and three-dimensional electron-density syntheses and least-squares refinement. The five 'heavy' atoms making up the amide residue of the molecule are coplanar to within 0·015 Å and are arranged in layers perpendicular to the *b* axis; the layer separation is 3·26 Å. Within each layer, molecules are linked by N–N · · · O bonds to form chains oriented approximately parallel to *a*; these hydrogen bonds are $2{\cdot}82_5$ Å long. Intramolecular bond lengths are:

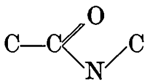
$$C_1\text{–}C_2 = 1{\cdot}53_6,\ C_2\text{–}O = 1{\cdot}23_6,\ C_2\text{–}N = 1{\cdot}290,\ N\text{–}C_3 = 1{\cdot}46_5\ \text{Å}\ .$$

Bond angles are:

$$C_1\text{–}C_2\text{–}O = 120{\cdot}5°,\ C_1\text{–}C_2\text{–}N = 116{\cdot}5°,\ O\text{–}C_2\text{–}N = 123°,\ C_2\text{–}N\text{–}C_3 = 120{\cdot}5°.$$

The high temperature modification (stable between 10 °C. and 28 °C.) is also orthorhombic, with only two molecules per unit cell; $a = 4{\cdot}85$, $b = 6{\cdot}59$, and $c = 7{\cdot}30$ Å. The space group is *Pnmm*. The reduction in unit-cell size is brought about by the existence of molecular orientational disorder in the high temperature phase.

Introduction

The  skeleton of N-methyl acetamide is the amide 'residue' so important in protein structure analysis. The work described in this paper was undertaken to determine the dimensions and configuration of this molecule and to compare the dimensions of the amide residue in N-methyl acetamide with results which have been reported for similar molecules (Corey & Donohue, 1950).

Experimental

N-methyl acetamide is colorless and hygroscopic; it melts at 28 °C. Samples were vacuum distilled and recrystallized several times to remove impurities and traces of water, and were then sealed into thin-walled glass capillary tubes, 0·3 mm. in diameter. The experimental procedures used to grow and maintain single crystals at low temperature have been described (Post, Schwartz & Fankuchen, 1951). The crystals always grew along what was later designated as the *a* axis of the unit cell. Weissenberg and precession cameras were used to accumulate data in three dimensions at -35 ± 5 °C. Filtered Cu *K* radiation was used with the Weissenberg and Mo *K* with the precession cameras. At -35 °C. the unit cell is orthorhombic with $a = 9{\cdot}61 \pm 0{\cdot}02$, $b = 6{\cdot}52 \pm 0{\cdot}01$, $c = 7{\cdot}24 \pm 0{\cdot}015$ Å.

Relative intensities of reflections were determined by visual comparison with calibrated intensity strips. Lorentz and polarization corrections were applied graphically. No absorption corrections were applied. 238 independent reflections were measured.

The density of N-methyl acetamide, determined by flotation in carbon tetrachloride–toluene mixtures, is 1·02 g.cm.$^{-3}$ at 10 °C. The calculated density, assuming four molecules per unit cell, is 1·07 g.cm.$^{-3}$ at -35 °C.

Reflections of the following types were not observed: ($hk0$) with h odd, ($0kl$) with k plus l odd. The space group is therefore either $Pn2_1a$ or *Pnma*.‡ If the space group is *Pnma*, all the atoms must be in planes at $y = \frac{1}{4}, \frac{3}{4}$; i.e., the only suitable four-fold positions would be:

$$(x, \tfrac{1}{4}, z),\ (\bar{x}, \tfrac{3}{4}, \bar{z}),\ (\tfrac{1}{2}-x, \tfrac{3}{4}, \tfrac{1}{2}+z),\ (\tfrac{1}{2}+x, \tfrac{1}{4}, \tfrac{1}{2}-z)\ .$$

The trigonometric portion of the structure factor expression for ($0k0$) in *Pnma* is '$\cos 2\pi ky$' and these reflections should show a 'normal' decrease in intensity

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‡ The 'true' space group can be *Pnma* only if the three hydrogen atoms in each methyl group are arranged so that they either have intrinsic mirror symmetry perpendicular to the *b* axis, (e.g. one hydrogen atom in the plane at $y = \frac{1}{4}, \frac{3}{4}$, and the other two hydrogens equally spaced above and below the planes), or are freely rotating or oscillating so as to have the necessary *m* symmetry on the average. If the hydrogen atoms are ordered and are not arranged as above, the 'true' space group is $Pn2_1a$. Both arrangements should yield essentially identical diffraction data.

with increasing Bragg angle. This was found to be the case. In addition, in *Pnma* the structure factor expression contains a term 'cos $2\pi ky$' for reflections with k even, and $\sin 2\pi ky$ for k odd. It is clear that with all atoms at $y=\frac{1}{4}$ and $\frac{3}{4}$, the trigonometric parts of the structure factors of all reflections with the same h and l indices and with k even, will be identical; the same will be true of reflections with the same h and l indices and k odd. Decreases in intensity will accompany increases of the k index in a given $(h-l)$ set of reflections but these should reflect only decreasing atomic scattering factors, and increasing temperature factors, at the larger Bragg angles. We should observe in each of these $(h-l)$ 'sets' the same 'normal' intensity decrease we observed in the $0k0$ reflections. Examination of Table 2 shows that such is indeed the case; in only two instances out of a total of about 50 sets do we observe exceptions to the 'normal' decrease rule. It is evident that this would not be true if the molecule were significantly tilted with respect to planes normal to b and *Pnma* was therefore taken to be the space group.

Determination of the crystal structure

A Patterson (U, O, W) section was computed and from this an approximate orientation of the molecule was derived. An (010) electron-density projection was then computed using only 11 reflections whose signs appeared to be unambiguously determined; this projection showed the five 'heavy' atoms clearly. The signs of all $(h0l)$ reflections were calculated on the basis of these positions and the usual iterative Fourier refinement process was then carried out. Atomic scattering factors computed by McWeeny were used (McWeeny, 1951). At this stage $R_{(h0l)}$ was 0·205. After corrections based on difference syntheses, $R_{(h0l)}$ dropped to 0·146; hydrogen atoms were included in these calculations.

An effort was then made to refine the structure by least-squares procedures; the IBM NYXRI program was used. Considerable difficulty was experienced in carrying out these calculations. The program broke down whenever the individual isotropic temperature factors were permitted to vary; refinement of the coordinate parameters was finally carried out with B fixed at 5 Å^{-2} for each 'heavy' atom. After four refinement cycles, $R_{(hkl)}$ had decreased from 24% to 16·9%. The program also broke down whenever efforts were made to make calculations without assuming that all atoms were at $y=\frac{1}{4}$ or $\frac{3}{4}$ (i.e., without assuming that the space group was *Pnma*), and efforts along these lines had to be abandoned.

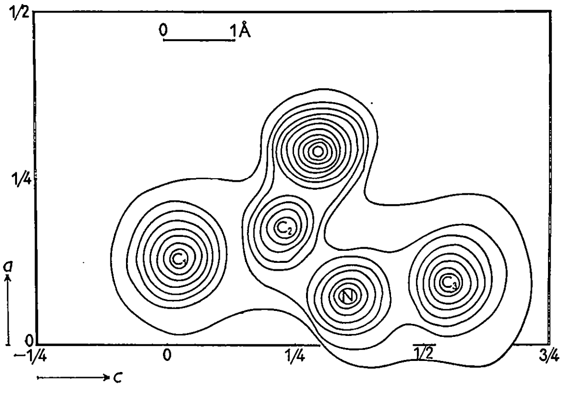


Fig. 1. Electron-density section through molecule, $y=\frac{1}{4}$. Contours at 1 e.Å^{-3}.

An electron-density section at $y=\frac{1}{4}$ was then computed (Fig. 1). The signs of the structure factors were those obtained from the least-squares calculation. Scale and temperature factors were computed using difference maps. Temperature factors applicable to the molecule as a whole were used; the expression is

$$\exp-(B_{11}h^2a^{*2}/4+B_{22}k^2b^{*2}/4+B_{33}^2c^{*2}/4)$$
$$(B_{11}=4{\cdot}42\ \text{Å}^{-2},\ B_{22}=6{\cdot}28\ \text{Å}^{-2},\ B_{33}=5{\cdot}43\ \text{Å}^{-2}).$$

The atomic positional parameters, determined in this way, are listed in Table 1 together with the least-squares results. Calculated and 'observed' structure factors are listed in Table 2; the former were computed on the basis of the electron-density section positions. At this stage, $R_{(hkl)}$ was 0·134.

Table 1. *Atomic positional parameters in* N-*methyl acetamide*

Refinement method		Least-squares	Section at $y=\frac{1}{4}$
C_1	x	0·1343	0·1316
	z	0·0306	0·0317
C_2	x	0·1697	0·1695
	z	0·2394	0·2378
C	x	0·0877	0·0894
	z	0·5520	0·5503
N	x	0·0660	0·0656
	z	0·3529	0·3504
O	x	0·2917	0·2919
	z	0·2906	0·2897
$R(hkl)$		0·169	0·134

Estimation of errors

Standard deviations of atomic positions were computed (Cruickshank & Rollett, 1953); $\sigma=0{\cdot}011$ Å for the three carbon atoms, 0·007 Å for the nitrogen atoms, and 0·005 Å for the oxygen atom.

Standard deviations of bond lengths are:

$$(\text{C–C})=0{\cdot}016\ \text{Å};\quad (\text{C–N})=0{\cdot}013\ \text{Å};\quad (\text{C–O})=0{\cdot}012\ \text{Å}.$$

The root mean square value of $\sigma(y)$ for the five heavy atoms is 0·005 Å. This was computed by hand from a least-squares calculation in which the atoms were not constrained to remain at $y=\frac{1}{4}$ and $\frac{3}{4}$. A scale factor and a molecular temperature factor, B_{22}, were computed in the course of this calculation. The latter, 6·28 Å^{-2}, agreed well with a value of 6·4 computed from measurements of the variations of the $(0k0)$ intensities with temperature between −40 °C. and −150 °C.

Table 2. *Observed and calculated structure factors*

$h\,k\,l$	F_o	F_c
k even		
0 2 0	90	−90
4	32	34
6	11	−13
8	5	5
2 0 0	10	−10
2	5	7
4 0 0	17	−16
2	9	10
4	5	−5
6	3	3
6 0 0	2	−5
2	1	3
8 0 0	9	−8
2	8	6
4	5	−4
6	3	2
10 0 0	3	2
1 0 1	17	15
2	10	−9
4	6	4
6	2	−2
2 0 1	11	−12
2	8	6
4	5	−3
6	2	2
3 0 1	20	21
2	13	−12
4	5	5
6	2	−2
4 0 1	18	−15
2	12	10
5 0 1	11	−10
2	7	7
6 0 1	8	8
2	5	−5
7 0 1	7	−11
2	5	8
8 0 1	9	−10
2	7	7
9 0 1	3	−3
2	2	2
10 0 1	6	6
2	5	−4
0 0 2	6	−9
2	9	7
4	4	−4
1 0 2	6	6
2	5	−4
4	2	2
2 0 2	25	24
2	17	−15
4	6	7
3 0 2	7	−4
2	4	3
4 0 2	17	−17
2	11	11
4	4	−5
5 0 2	11	12
2	8	−8
4	4	4
6 0 2	6	−8
2	5	5
7 0 2	5	5
2	4	−3
8 0 2	8	10
2	6	−7
4	3	4
9 0 2	4	−3
2	2	2
10 2 2	2	1
1 0 3	14	−14
2	8	9
2 0 3	5	3
2	1	−2
3 0 3	8	−9
2	5	6
4	2	−3
4 0 3	3	3
2	1	−2
5 0 3	8	10
2	6	−7
4	4	4
6 0 3	7	−5
2	4	3
7 0 3	5	−4
2	2	3
8 0 3	3	2
2	2	−2
9 0 3	4	3
2	2	−2
10 0 3	5	−5
2	2	3
0 0 4	14	14
2	9	−9
4	5	5
6	4	−3
1 0 4	19	−18
2	12	12
4	5	−6
6	2	3
2 0 4	13	−14
2	8	9
4	5	−5
6	2	2
3 0 4	6	−7
2	5	5
4	2	−3
4 0 4	5	−4
2	4	3
4	2	−2
5 0 4	3	−4
4	2	−2
6 0 4	5	6
2	4	−5
4	2	3
7 0 4	2	3
10 0 4	2	1
1 0 5	7	−6
2	5	4
4	3	−2
2 0 5	3	3
2	2	−2
3 0 5	8	8
2	5	−6
4	3	3
4 0 5	7	9
2	7	−7
4	5	4
5 0 5	5	−4
2	2	3
6 0 5	5	5
2	3	−4
4	2	2
7 0 5	3	2
8 0 5	4	−5
2	2	4
1 0 6	3	−1
2 0 6	3	3
2	2	−2
3 0 6	11	−9
2	8	6
4	5	−4
6 0 6	2	−3
k odd		
2 1 0	59	−58
3	26	25
5	12	−10
7	5	4
4 1 0	27	−26
3	15	14
5	5	−6
6 1 0	12	12
3	7	−7
5	2	3
8 1 0	6	−4
3	4	3
10 1 0	8	6
3	5	−4
5	3	2
0 1 1	54	−59
3	36	29
5	13	−11
7	4	4
1 1 1	6	5
3	3	−3
2 1 1	20	18
3	11	−10
5	3	4
3 1 1	8	10
3	5	
4 1 1	3	−3
5 1 1	14	15
3	8	−9
6 1 1	2	−3
8 1 1	9	8
3	8	−5
9 1 1	5	−8
1 1 2	4	−2
2 1 2	20	−20
3	7	10
5	3	−4
3 1 2	16	15
3	8	−8
5	5	3
4 1 2	3	2
5 1 2	3	−5
8 1 2	8	9
3	5	−6
9 1 2	5	−5
3	2	3
10 1 2	5	−5
3	2	3
0 1 3	24	25
3	12	−13
5	4	5
7	2	−2
1 1 3	18	−18
3	8	10
5	3	−4
2 1 3	11	−13
3	6	7
5	3	−3
4 1 3	2	2
5 1 3	3	−3
3	2	2
8 1 3	4	−4
3	3	3
1 1 4	11	−11
3	7	6
5	3	−3
2 1 4	5	−4
3	2	2
3 1 4	5	−5
3	2	3
4 1 4	5	5
3	3	−3
5	2	2
5 1 4	11	12
3	7	−8
5	4	4
6 1 4	7	7
3	3	−5
8 1 4	3	−4
3	2	2
2 1 5	8	8
3	5	−5
5	2	3
3 1 5	8	−6
3	3	3
5 1 5	5	3
6 1 5	8	−8
3	4	5
5	3	−3
1 1 6	8	−7
3	5	5
5	3	−3
3 1 6	5	5
3	3	−3
4 1 6	2	−3

Discussion

The molecules of N-methyl acetamide are arranged in layers perpendicular to the *b* axis. The separation between layers is 3·26 Å. Molecules within layers are linked by hydrogen bonds to form chains which zig-zag along *a*. These hydrogen bonds (N–H · · · O) are 2·825 Å long.

Bond lengths and angles are compared in Table 3 with corresponding values for two similar molecular crystals, *n*-acetylglycine (Shoemaker, Donohue, Schomaker & Corey, 1950) and *β*-glycylglycine (Carpenter & Donohue, 1950), and for the model of the amide residue proposed by Corey & Donohue (1950).

Among other effects, the N–H–O bonds appear to

Table 3. *Bond lengths and angles in some molecules containing amide groups*

Bond lengths	N-methyl acet-amide	N-acetyl-glycine	β-Glycyl-glycine	Corey & Donohue 'amide residue'
C_1–C_2	$1{\cdot}53_6$ Å	1·53 Å	1·50 Å	1·53 Å
C_2–O	$1{\cdot}23_6$	1·23	1·24	1·23
C_2–N	$1{\cdot}29_0$	1·29	1·32	1·32
N–C_3	$1{\cdot}46_5$	1·48	1·45	1·47
Bond Angles				
C_1–C_2–O	120·5°	121°	121°	121°
C_1–C_2–N	116·5	114	118	117
O–C_2–N	123	125	121	122
C_2–N–C_3	120·5	122	120	120

determine the direction of crystal growth in N-methyl acetamide. The crystals always grew most rapidly along the *a* direction, forming needle-like crystals with the long edge parallel to the averaged hydrogen bond directions.

The molecular arrangement is shown in Fig. 2. Molecules drawn with solid lines are at $y=\frac{1}{4}$; those drawn with dashed lines are at $y=\frac{3}{4}$. Intermolecular distances less than 4 Å are listed in Table 4.

Table 4. *Short intermolecular contacts*

Molecule (1)	Molecule (2)	Length
$C_{(3)}$	C_1 (translation along *c*)	3·51 Å
C_3	O (*n* glide)	3·86
O	C_1 (*n* glide)	3·77
O	C_1 (*a* glide)	3·50
O	C_3 (*a* glide)	3·77

The terms in brackets next to the atoms of 'molecule 2' refer to the symmetry operation which generates the latter from 'molecule 1'.

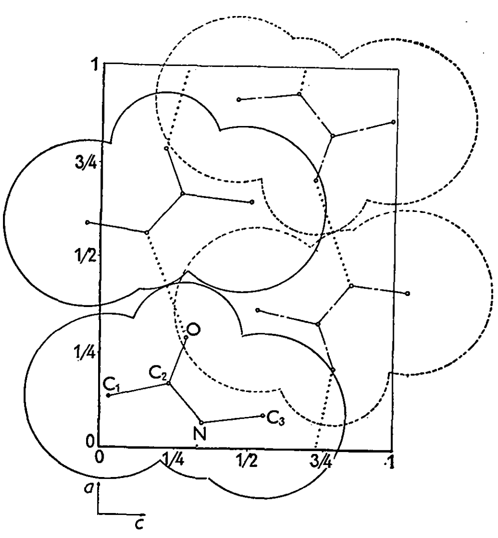


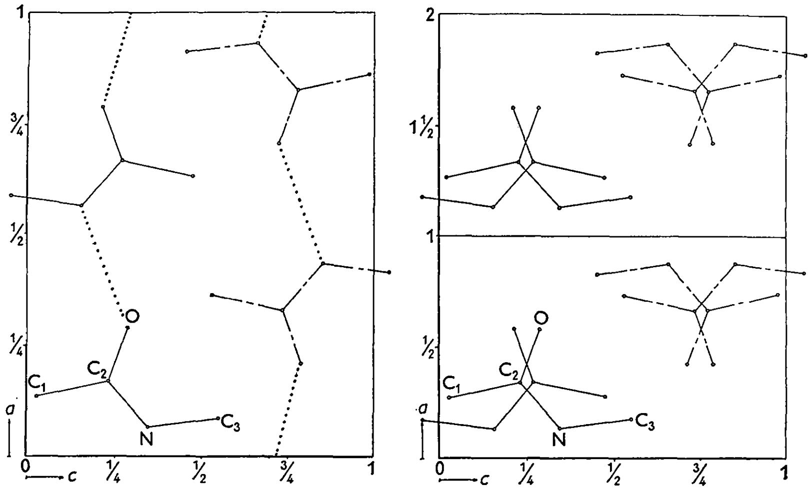
Fig. 2. Molecular arrangement: molecules drawn with heavy lines are at $y=\frac{1}{4}$; those drawn with dashed lines are at $y=\frac{3}{4}$. Hydrogen bonds are dotted.

Intermolecular contacts are normal, with one striking exception: the 3·51 Å from C_3 of molecule 1 to C_1 of molecule 2. This short methyl–methyl separation is probably made possible by the interleaving of hydrogen atoms of the two methyl groups, such as would result from a 60° rotation of one group relative to the other.

Solid phase transformation

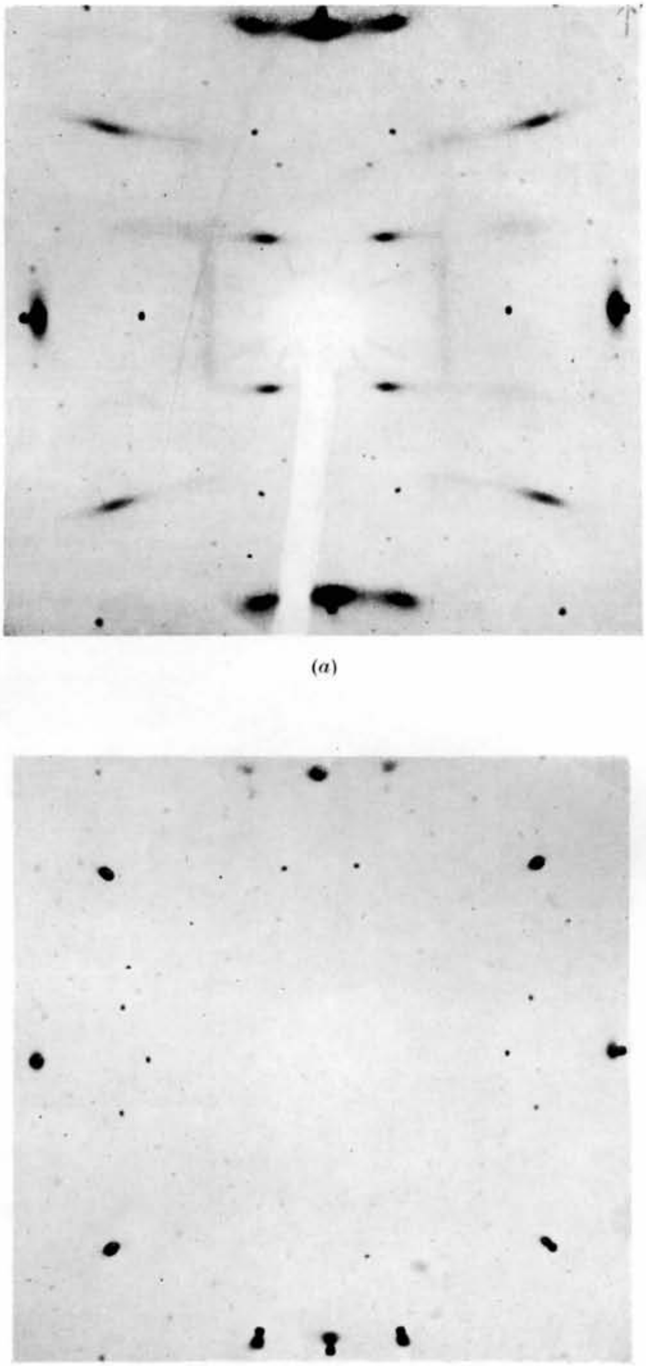
In the course of this work it was found that N-methyl acetamide undergoes a solid phase transition near 10 °C. The unit cell above the transition temperature resembles the low temperature cell except that the length of the *a* axis is cut to half its low temperature value; at 20 °C. $a=4{\cdot}85$, $b=6{\cdot}59$, $c=7{\cdot}30$ Å, all ±0·01 Å.

The high temperature modification is also ortho-



(*a*) (*b*)

Fig. 3. Molecular orientation. (*a*) Below transition: hydrogen bonds dotted. (*b*) Above transition: hydrogen bonds dotted.



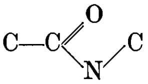
(*a*)

(*b*)

Fig. 4. Stationary crystal diagrams: Cu radiation, Ni filter. X-ray beam parallel to 010: (*a*) above transition (20 °C.). (*b*) below transition (−35 °C.).

rhombic, but contains only two molecules per unit cell. Reflections of the type ($0kl$) with k plus l odd, were not observed. The space group is $Pnmm$ or $Pn2_1m$. The results of the low temperature analysis indicated that the former is the more probable.

In $Pnmm$ the point symmetry of two-fold positions is mm with one mirror plane perpendicular to b and the other perpendicular to c. The molecules do not possess intrinsic mm symmetry of this sort. They can only achieve it by some form of disorder. It appears likely that in the high temperature form, individual molecules may assume randomly either of the following orientations (Fig. 3).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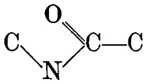
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The hydrogen bonds linking the molecules in the a direction are essentially unaffected by this type of disorder. The a glide of $Pnma$, operating on a pseudo molecule with mm symmetry, yields an identical duplicate at a position removed by $a/2$ from the original location. The a glide thus degenerates into a mirror plane and the length of the a axis is cut in half.

Comparisons of precession and oscillation photographs of the high and low temperature modifications lend support to this interpretation. Reflections with odd h indices (low temperature indices) are absent from the high temperature photographs. Reflections with h even have essentially identical intensities in both modifications. Even when film of the two forms were directly superimposed it was difficult to detect differences among intensities of reflections with even h indices (low temperature indices) except at large Bragg angles where the reflections of the low temperature form were slightly, but systematically, more intense.

Stationary crystal diagrams, using filtered radiation, with the X-ray beam parallel to [010], were taken at 20 °C. (Fig. 4(a)), and −35 °C. (Fig. 4(b)). The disappearance of the major portion of the diffuse scattering from the 4(b) photograph which was taken below the transition temperature, indicates clearly that the diffuse scattering is caused primarily by structural disorder rather than by the usual thermal factors. No effort was made to interpret the diffuse scattering quantitatively.

Steric factors (such as the relatively large size of the molecule and the small interlayer separation) appear to rule out the possibility of dynamic disorder involving actual rotation of individual molecules. The disorder appears to result primarily from 'static' randomness of molecular orientation.

The authors wish to thank Dr Frederic Holtzberg for assistance in the early stages of this work, and Prof. I. Fankuchen for illuminating discussions of various problems.

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Facteurs de Structure: Théorie des Inégalités Angulaires et des Restrictions de Signes

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A convenient method of notation is put forward. According to this notation the properties of the n-dimensional space built up with $\cos^{-1} U(H)$ are established. This is done in order to organize the search for structure factor signs by means of angular inequalities. The use of sign restrictions is also studied.

1. Introduction

Dans un mémoire précédent (v. Eller, 1955) nous avions souligné, et commencé à utiliser sous forme d'inégalités angulaires, les propriétés purement géométriques d'un espace dont le tenseur métrique admet pour sa matrice les mêmes éléments

$$U_{lc}=U(H_l-H_c)=U(H)=F(H)/\sum_i f_i(H)$$