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The Crystal Structure of Ethyl Carbamate

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The structure of ethyl carbamate (urethane, $C_2H_5.O.CONH_2$) has been determined using three-dimensional X-ray intensities measured with a proportional counter at two different temperatures. Atomic positions and anisotropic vibrational parameters have been refined by the method of least squares, and the vibrational parameters interpreted in terms of the rigid-body vibrations of the molecule.

Introduction

Several high-accuracy X-ray studies of the amide group have been made in recent years, including some in this laboratory using the three-circle diffractometer of Small & Travers (1961). In connection with these studies, the determination of the structure of ethyl carbamate is of interest in enabling a comparison to be made between the amidic C–O and C–N bond lengths in the carbamate group and those in other amides. Further interest lies in the length of the C–O bond connecting the carbamate group to the ethyl group, for studies of similar bonds in carboxylic acid esters (O'Gorman, Shand & Schomaker, 1950; Dougill & Jeffrey, 1953), tend to suggest that this bond is much longer than would be expected for a single C–O bond, although no really accurate evidence for this is yet available.

Intensity data measured for a crystal at room temperature *ca.* 25 °C showed that large atomic vibrations were present in ethyl carbamate crystals at this temperature. With a view to achieving greater accuracy from an increased number of measurements, the intensity measurements were repeated at −105 °C. Although more reflexions were observed at this temperature, the accuracy of the molecular parameters derived was not improved. Inaccuracies in the intensity measurements at the lower temperature arose from the design of the cooling system which was still under development at that time.

Crystal data

Crystals of ethyl carbamate, suitable for X-ray analysis, were obtained from a commercial sample by slow evaporation of an ethereal solution containing a small amount of light petroleum. The crystals were found to evaporate rapidly at normal temperatures, and it was necessary to seal them in Lindemann or 'Pantak' capillary tubes for all diffraction work. This process was usually hindered by the rather plastic nature of the crystals.

Preliminary Weissenberg photographs showed that ethyl carbamate crystallizes in the triclinic system, but accurate measurement of the unit-cell dimensions by the usual photographic methods was prohibited by a complete lack of observable reflexions at high Bragg angles. The suitability of diffractometer methods for precision cell dimension measurement has been demonstrated by Bond (1960) and so the instrument of Small & Travers was used in the following way for this purpose.

For a series of orders of reflexion from a certain set of crystal planes, line profiles were plotted with 2θ fixed and ω moving for each reflexion, the angles φ and χ being kept fixed throughout. To remove zero errors arising from both the instrument itself and missettings of φ and χ the 'observed' interplanar spacing for each measured value of θ_{obs} was plotted against

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$\cot\theta_{\text{obs}}$; this gave a straight-line graph of intercept d_{true} (the true spacing) and gradient αd_{true}, where

$$\theta_{\text{obs}}+\alpha=\theta_{\text{true}}.$$

At 25 °C, the spacings (100), (010), (001), $(10\bar{1})$ and (110) were measured in this way to give the cell dimensions by triangulation. At −105 °C, fourteen interplanar spaces were measured, the cell dimensions being determined by least-squares on the MERCURY computer at the University of Oxford. The resultant cell dimensions based on Cu $K\alpha$ ($\lambda=1{\cdot}5418$ Å) are:

At 25 °C,

$a=5{\cdot}023\pm0{\cdot}001,\ b=7{\cdot}044\pm0{\cdot}002,\ c=7{\cdot}763\pm0{\cdot}002$ Å

$\alpha=102°28'\pm2',\ \beta=102°35'\pm2',\ \gamma=77°41'\pm2'$

$V=257{\cdot}69\pm0{\cdot}05$ Å^3 .

At −105 °C,

$a=5{\cdot}051\pm0{\cdot}002,\ b=7{\cdot}011\pm0{\cdot}004,\ c=7{\cdot}543\pm0{\cdot}003$ Å

$\alpha=101°22'\pm3',\ \beta=104°35'\pm3',\ \gamma=76°39'\pm2'$

D_{obs} 1·16 $\quad D_{\text{calc}}$ 1·15 for $Z=2$.

Initially, photographic and counter intensity data were collected for the $(h0l)$ and $(0kl)$ zones, and an analysis of the statistical distribution of intensities in these zones revealed the presence of a centre of symmetry (Howells, Phillips & Rogers, 1950) indicating space group $P\bar{1}$. At a later stage, three-dimensional intensity data were collected by means of the diffractometer, the use of which has already been described in detail elsewhere (Beagley & Small, 1963). At 25 °C, only 715 out of a possible 1060 unique reflexions proved to be measurable, while at −105 °C, this number was increased to 850.

Approximate absorption corrections were applied to all three-dimensional data, by assuming the crystal to be a cylinder with its axis coincident with the φ axis of the diffractometer. The method of Albrecht (1939) was applied to the elliptical section of the crystal in the plane of the incident and reflected X-ray beams, for various values of θ and χ, individual absorption corrections being estimated by interpolation.

For the data at −105 °C, the graphical methods of Albrecht were replaced by computation on the MERCURY computer.

Determination and refinement of the structure

The structure was determined by the interpretation of sharpened Patterson projections on (010) and (100). The sharpening function was

$$M(S)=(1/\hat{f})^2\exp(-4\pi^2\sin^2\theta/7{\cdot}25\lambda^2)\ .$$

Refinement was carried out by Fourier, difference Fourier and least-squares methods, and was discontinued when the discrepancy indices were $R_{h0l}=0{\cdot}20$ and $R_{0kl}=0{\cdot}24$.

Refinement of the three-dimensional data, at both temperatures, was carried out on the MERCURY computer using the SFLS program of Dr J.S. Rollett. For the data at 25 °C, nine cycles of refinement with the weighting scheme

$$|F_o|>20,\ \sqrt{w}=20/|F_o|$$
$$|F_o|<20,\ \sqrt{w}=1$$

reduced R_{hkl} to 0·14. At this point the weighting scheme was changed to

$$w=1/[1+((|F_o|-2{\cdot}0)/5{\cdot}0)^2]$$

and refinement ceased with $R=0{\cdot}11$. A three-dimensional difference synthesis was computed with the program of Mr O.S. Mills, and this showed the positions of the seven hydrogen atoms in their expected places. For further refinement, the hydrogen atoms were included in the structure model and were given the temperature factors of their parent atoms. No attempt was made to refine the parameters of the hydrogen atoms, and refinement converged with $R_{hkl}=0{\cdot}64$. A second three-dimensional difference synthesis showed no significant feature at this point.

The data collected at −105 °C were used for refinement in a similar manner, and with the ultimate weighting scheme

$$w=1/[1+((|F_o|-2{\cdot}0)/2{\cdot}4)^2]$$

a final reliability index of $R_{hkl}=0{\cdot}87$ was obtained. The atomic coordinates of the hydrogen atoms are given in Table 1. The final positional and vibrational

Table 1. *Coordinates of hydrogen atoms*

	x/a	y/b	z/c
(*a*) 25 °C			
H(1)	−0·324	0·906	0·417
H(2)	−0·041	0·800	0·500
H(3)	−0·124	0·866	0·250
H(4)	−0·258	0·533	0·390
H(5)	−0·375	0·600	0·146
H(6)	0·417	0·216	0·158
H(7)	0·246	0·033	0·050
(*b*) −105 °C			
H(1)	−0·300	0·860	0·383
H(2)	0·042	0·767	0·500
H(3)	−0·104	0·883	0·283
H(4)	−0·296	0·543	0·358
H(5)	−0·363	0·593	0·142
H(6)	0·425	0·200	0·167
H(7)	0·250	0·033	0·067

Table 2. *Atomic coordinates from final least-squares cycle*

	x/a	y/b	z/c
(*a*) 25 °C			
C(1)	−0·14311	0·79092	0·36409
C(2)	−0·22885	0·59772	0·27468
C(3)	0·00198	0·28267	0·15368
N	0·24284	0·16657	0·12427
O(1)	0·02662	0·46424	0·23633
O(2)	−0·21885	0·22516	0·10746
(*b*) −105 °C			
C(1)	−0·13039	0·79270	0·36452
C(2)	−0·21887	0·59678	0·27521
C(3)	0·00727	0·28007	0·15288
N	0·25108	0·16633	0·12828
O(1)	0·03729	0·46255	0·23785
O(2)	−0·21542	0·22614	0·10596

parameters of the heavier atoms are shown in Tables 2 and 3 respectively.

For all refinement calculations, the atomic scattering factors used were those tabulated for carbon, oxygen and nitrogen by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955), and, for hydrogen by McWeeny (1951).

The vibrational analysis

The temperature factor in the least-squares refinement is

$$2^{-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)} .$$

With the use of the MERCURY program of Dr R. Sparks, these values of b_{ij} were converted to the magnitudes of the principal ellipsoids of vibration and their direction cosines relative to the axes a, b', c^*. Molecular axes L, M, N were chosen so that L was parallel to the C(3)–O(1) bond in the carbamate group, M was perpendicular to L and in the plane of the carbamate group, and N was perpendicular to both L and M; the origin was taken as the centroid of the molecule.

For each atom, the mean-square amplitudes of vibration in the directions L, M, N, together with their standard deviations as derived from the variance matrices for b_{ij} in the refinement, were calculated. (These are shown in Table 4.) Attempts were then made to analyse these amplitudes in terms of rigid-body vibrations of the molecule. It was found that, because of the hydrogen bonding to the carbamate group, there is an apparent shift in the centre of libration towards the carbamate group. This shift was found to be 1·27 Å at 25 °C, and 1·28 Å at −105 °C. The values obtained for the mean-square rigid-body translational amplitudes ($\tau^2L, \tau^2M, \tau^2N$) and librational amplitudes (ω^2L, ω^2M, ω^2N) are given in Table 5. The method of Cruickshank (1956) was used to correct the atomic coordinates for rotational oscillations.

Table 5. *Vibrational amplitudes* (Å^2 *and radians*^{2})

(*a*) At 25 °C			
τ_L^2	0·064 ± 0·003	ω_L^2	zero
τ_M^2	0·040 ± 0·002	ω_M^2	0·0136 ± 0·0039
τ_N^2	0·120 ± 0·030	ω_N^2	0·00688 ± 0·00083
(*b*) At −105 °C			
τ_L^2	0·028 ± 0·003	ω_L^2	zero
τ_M^2	0·021 ± 0·004	ω_M^2	0·0021 ± 0·0015
τ_N^2	0·061 ± 0·009	ω_N^2	0·00463 ± 0·00012

Results

The values obtained for the bond lengths and bond angles are shown in Fig. 3 and Table 6. The standard deviations in bond lengths and bond angles involving only C, N and O atoms take into account not only the standard deviations in position as estimated from the final least-squares cycle, but also the estimated standard deviations in the cell dimensions and the librational corrections. The standard deviations in

Table 3. *Vibrational parameters from final least-squares cycle*

	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
(*a*) 25 °C						
C(1)	0·22786	0·04679	0·05887	−0·00653	0·04135	−0·01302
C(2)	0·11756	0·04412	0·06690	−0·00698	0·03607	−0·00203
C(3)	0·07226	0·04577	0·04925	−0·00266	0·04005	−0·03295
N	0·05665	0·05508	0·06847	−0·01184	0·05196	−0·03097
O(1)	0·08495	0·04533	0·05868	−0·01064	0·03719	−0·04099
O(2)	0·06141	0·05065	0·07358	−0·01680	0·05014	−0·04169
(*b*) −105 °C						
C(1)	0·12263	0·01889	0·03260	−0·00261	0·01127	−0·01062
C(2)	0·06308	0·02090	0·02932	−0·00230	0·02068	−0·00083
C(3)	0·03521	0·01993	0·02057	0·00214	0·01709	−0·01876
N	0·03108	0·02770	0·03181	−0·00990	0·02803	−0·02321
O(1)	0·04824	0·01982	0·02566	−0·00405	0·01198	−0·02204
O(2)	0·03222	0·02255	0·03358	−0·00724	0·02697	−0·01831

Table 4. *Mean-square amplitudes of vibration* (Å^2)

	u_L^2	u_M^2	u_N^2
(*a*) 25 °C			
C(1)	0·071 ± 0·009	0·171 ± 0·016	0·131 ± 0·029
C(2)	0·069 0·011	0·089 0·018	0·147 0·022
C(3)	0·066 0·028	0·054 0·019	0·103 0·012
N	0·078 0·008	0·039 0·003	0·146 0·006
O(1)	0·061 0·013	0·066 0·014	0·130 0·007
O(2)	0·066 0·005	0·043 0·004	0·159 0·004
(*b*) −105 °C			
C(1)	0·030 ± 0·006	0·091 ± 0·009	0·064 ± 0·016
C(2)	0·033 0·010	0·046 0·024	0·059 0·038
C(3)	0·029 0·037	0·026 0·020	0·037 0·024
N	0·035 0·008	0·020 0·005	0·064 0·005
O(1)	0·026 0·007	0·039 0·023	0·054 0·019
O(2)	0·031 0·010	0·023 0·007	0·066 0·004

bonds to hydrogen were obtained from the earlier three-dimensional difference syntheses, using the method of Cruickshank (1949).

Table 6. *Bond lengths and bond angles*

Bond	25 °C	−105 °C
C(1)–C(2)	1·509 ± 0·006 Å	1·524 ± 0·006 Å
C(2)–O(1)	1·473 ± 0·004	1·472 ± 0·004
C(3)–O(1)	1·333 ± 0·004	1·342 ± 0·004
C(3)–O(2)	1·223 ± 0·003	1·219 ± 0·004
C(3)–N	1·349 ± 0·004	1·341 ± 0·004
C(1)–H(1)	1·15 ± 0·04	0·90 ± 0·04
C(1)–H(2)	1·05 ± 0·04	1·18 ± 0·04
C(1)–H(3)	1·15 ± 0·04	1·01 ± 0·04
C(2)–H(4)	1·14 ± 0·04	0·98 ± 0·04
C(2)–H(5)	1·11 ± 0·04	1·08 ± 0·04
N—H(6)	0·97 ± 0·03	0·92 ± 0·03
N—H(7)	0·98 ± 0·03	0·96 ± 0·03

Table 6 (*cont.*)

Angle	25 °C	−105 °C
C(1)–C(2)–O(1)	105·7 ± 0·6°	105·0 ± 0·3°
C(2)–O(1)–C(3)	116·8 ± 0·6	115·6 ± 0·3
O(1)–C(3)–O(2)	123·4 ± 0·6	123·4 ± 0·3
O(1)–C(3)–N	114·2 ± 0·5	111·7 ± 0·3
O(2)–C(3)–N	122·4 ± 0·5	124·9 ± 0·3
H(1)–C(1)–H(2)	88 ± 4	116 ± 3
H(2)–C(1)–H(3)	134 ± 4	118 ± 3
H(1)–C(1)–H(3)	99 ± 4	98 ± 3
H(1)–C(1)–C(2)	111 ± 3	96 ± 2
H(2)–C(1)–C(2)	115 ± 3	108 ± 2
H(3)–C(1)–C(2)	104 ± 3	119 ± 2
H(4)–C(2)–H(5)	124 ± 3	108 ± 3
H(4)–C(2)–C(1)	104 ± 2	112 ± 2
H(5)–C(2)–C(1)	116 ± 2	118 ± 2
H(4)–C(2)–O(1)	97 ± 2	109 ± 2
H(5)–C(2)–O(1)	106 ± 2	104 ± 2
H(6)–N—H(7)	118 ± 2	115 ± 2
H(6)–N—C(3)	121 ± 2	127 ± 1
H(7)–N—C(3)	121 ± 2	117 ± 1

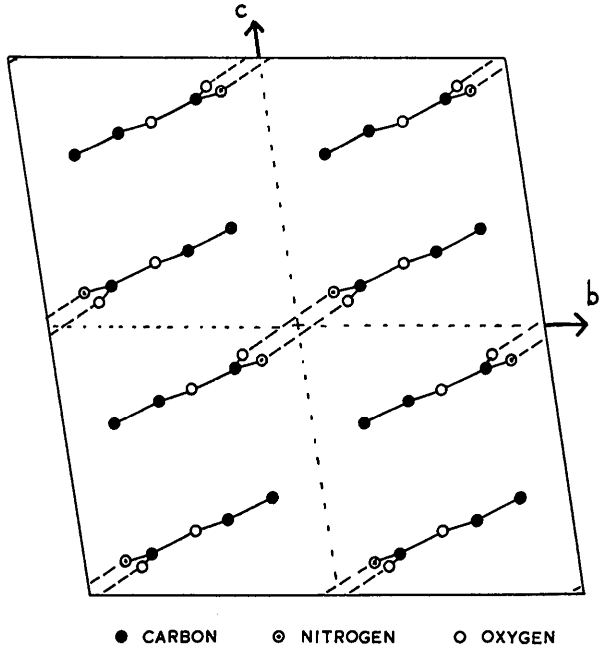

Fig. 1. Projection of the structure along the *a* axis. Hydrogen atoms have been omitted: broken lines indicate hydrogen bonds.

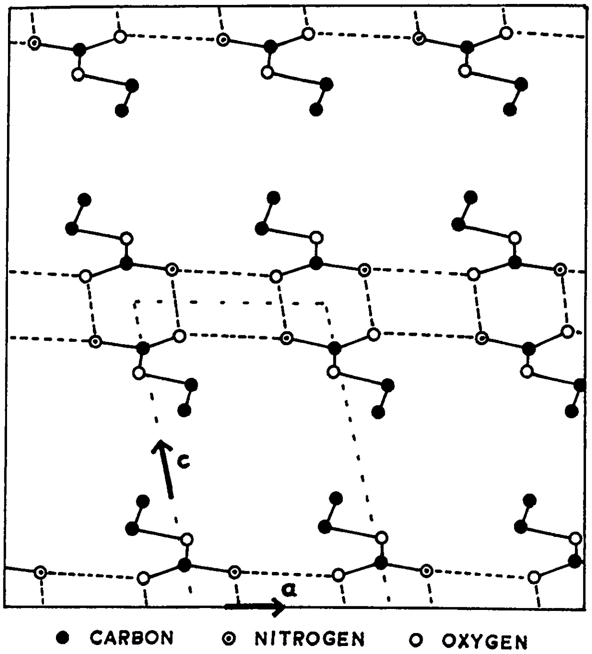

Fig. 2. Projection of the structure along the *b* axis. Hydrogen atoms have been omitted: broken lines indicate hydrogen bonds.

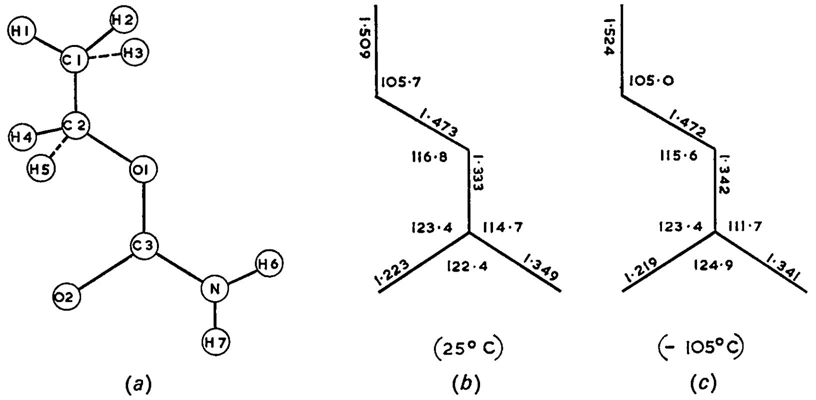

Fig. 3. (*a*) Diagram of molecule showing atom labelling scheme. (*b*) Bond lengths and angles at 25 °C. (*c*) Bond lengths and angles at −105 °C.

The C, N and O atoms in the carbamate group are coplanar within the limits of experimental error, the atoms of the ethyl group lying slightly but significantly outside this plane. The equations of the molecular plane, referred to the axes a,b',c^*, and as determined by least squares, are:

(*a*) at 25 °C,

$$-0{\cdot}13695x-0{\cdot}44866y+0{\cdot}88315z-0{\cdot}20681=0$$

(*b*) at −105 °C,

$$-0{\cdot}14909x-0{\cdot}43299y+0{\cdot}88896z-0{\cdot}19821=0\,.$$

The deviations of the heavier atoms from these planes are given in Table 7.

Table 7. *Deviations of C,N,O atoms from plane of carbamate group*

	25 °C	−105 °C
C(1)	−0·012 Å	−0·020 Å
C(2)	0·020	0·033
C(3)	0·0012	−0·0026
N	−0·0003	0·0008
O(1)	−0·0004	0·0008
O(2)	−0·0004	0·0010

The molecular arrangement

The crystal structure is very similar to that of monofluoroacetamide (Hughes & Small, 1962): it consists of chains of hydrogen-bonded dimers, roughly parallel to (01$\bar{2}$), the extension of the chains being in the direction of the *a* axis. Each oxygen [O(2)] and nitrogen atom forms two hydrogen bonds, thus using both hydrogen atoms in the group $-NH_2$.

The hydrogen bonds connecting each dimeric pair of centrosymmetrically related molecules are roughly perpendicular to the *a* axis, and have a mean (N···O)

Table 8. *Dimensions of the amide group in different compounds*

	C–N	C–O	NCO	Reference
Ethyl carbamate	1·345 Å	1·221 Å	123·6°	This work
e.s.d.	0·003	0·003	0·3	
Succinamide*	1·333	1·238	122·0	Davies & Pasternak (1956)
e.s.d.	0·002	0·002	0·2	
Oxamide*	1·315	1·243	125·7	Ayerst & Duke (1954)
e.s.d.	0·004	0·004	0·3	
Monofluoroacetamide	1·319	1·254	124·0	Hughes & Small (1962)
e.s.d.	0·005	0·005	0·4	
6-Amido-3-pyridazone	1·320	1·252	123·2	Beagley & Small (unpublished)
e.s.d.	0·008	0·007	0·6	
Ammonium oxamate	1·324	1·248	124·2	Beagley & Small (1963)
e.s.d.	0·002	0·002	0·2	
α-Pyrazinamide	1·312	1·244	123·1	Takaki, Sasada & Watanabe (1960)
e.s.d.	0·008	0·008	0·6	

* Not corrected for librational motion.

Table 9. *Dimensions of* C–O *bonds in various esters*

	C–O(*a*) (Å)	C–O(*b*) (Å)	C–O(*c*) (Å)	Reference
Ethyl carbamate	1·472	1·337	1·221	This work
e.s.d.	0·004	0·003	0·003	
Methyl chloroformate*	1·47	1·37	1·22	O'Gorman, Shand & Schomaker (1950)
e.s.d.	0·04	0·04	0·03	
Methyl formate*	1·46	1·36	1·22	
e.s.d.	0·04	0·04	0·03	
Methyl acetate*	1·47	1·36	1·19	
e.s.d.	0·04	0·04	0·03	
Dimethyl oxalate	1·46	1·31	1·19	Dougill & Jeffrey (1953)
e.s.d.	0·04	0·02	0·02	
Diethyl terephthalate	1·51	1·32	1·28	Bailey (1949)
e.s.d.	0·05	0·05	0·05	
Ethyl stearate	1·37	1·36	1·15	Aleby (1962)
e.s.d.	0·05	0·05	0·05	

* Electron diffraction studies.

Table 10(*a*). *Observed and calculated structure factors at* 25 °C

	50Fo	50Fo
001	763	905
002	890	-955
003	424	-463
004	295	-290
005	116	-106
006	48	-44
007	18	19
008	47	43
009	12	-2
010	606	-593
011	415	-450
012	813	-799
013	425	-439
014	265	-267
015	54	50
016	175	172
018	16	-17
$01\bar{1}$	709	802
$01\bar{3}$	427	444
$01\bar{4}$	489	-493
$01\bar{5}$	156	-156
$01\bar{6}$	37	-49
020	839	-777
021	631	-687
022	804	-786
023	96	87
024	443	420
025	109	104
028	12	-14
$02\bar{1}$	257	-280
$02\bar{2}$	41	5
$02\bar{3}$	378	379
$02\bar{4}$	691	696
$02\bar{5}$	99	100
$02\bar{6}$	154	-168
$02\bar{7}$	32	-34
030	796	-823
031	144	169
032	605	567
033	216	223
034	111	110
035	40	-28
036	54	-48
037	30	33
$03\bar{1}$	407	-405
$03\bar{2}$	293	-283
$03\bar{3}$	121	-97
$03\bar{5}$	78	62
$03\bar{6}$	143	134
$03\bar{8}$	41	-36
$03\bar{9}$	11	-7
040	352	320
041	205	209
042	258	258
043	86	-73
044	88	-90
045	72	87
047	45	-42
$04\bar{1}$	59	32
$04\bar{2}$	311	-295
$04\bar{3}$	90	-87
$04\bar{4}$	51	-61
$04\bar{5}$	39	-34
$04\bar{8}$	22	18
050	194	193
051	142	-148
052	95	-83
053	122	147
054	31	-33
055	84	-88
056	27	-21
$05\bar{1}$	150	141
$05\bar{2}$	108	101
$15\bar{3}$	24	19
$15\bar{4}$	61	-67
$15\bar{5}$	12	-14
060	57	-46
061	139	154
062	28	-24
063	93	-95
064	35	-38
$06\bar{1}$	150	-151
$06\bar{2}$	57	64
$06\bar{3}$	47	50
$06\bar{5}$	19	18
$06\bar{6}$	10	-9
071	45	-56
072	36	-36
074	18	21
$07\bar{1}$	96	100
$07\bar{2}$	20	-18
$07\bar{3}$	89	-82
$07\bar{5}$	18	16
081	22	25
$08\bar{3}$	34	32
101	705	758
102	944	-895
103	138	-139
104	167	153
105	36	47
108	18	16
$10\bar{1}$	535	-506
$10\bar{2}$	238	-247
$10\bar{3}$	307	-312
$10\bar{4}$	140	-150
$10\bar{5}$	24	34
$10\bar{6}$	12	-11
$10\bar{7}$	19	18
$10\bar{8}$	23	29
110	1170	-1211
111	354	-352
112	91	110
113	19	14
114	114	-124
115	28	-46
116	99	-93
118	44	-37
$11\bar{1}$	966	962
$11\bar{3}$	15	10
$11\bar{4}$	296	-291
$11\bar{5}$	150	-144
$11\bar{6}$	67	-81
$1\bar{1}0$	12	-6
$1\bar{1}1$	471	-418
$1\bar{1}2$	503	521
$1\bar{1}3$	236	230
$1\bar{1}4$	268	-299
$1\bar{1}5$	56	-44
$1\bar{1}6$	65	51
$1\bar{1}\bar{1}$	408	-406
$1\bar{1}\bar{2}$	275	-259
$1\bar{1}\bar{3}$	211	213
$1\bar{1}\bar{4}$	40	-27
$1\bar{1}\bar{6}$	77	82
$1\bar{1}\bar{9}$	17	-12
120	177	-192
121	61	12
122	522	-510
123	119	-121
124	308	300
125	30	17
126	108	-99
$12\bar{1}$	314	-316
$12\bar{2}$	533	-562
$12\bar{3}$	507	525
$12\bar{4}$	706	753
$12\bar{5}$	17	6
$12\bar{6}$	131	-129
$12\bar{7}$	36	-36
128	19	-20
$1\bar{2}0$	96	-94
$1\bar{2}1$	465	-459
$1\bar{2}2$	149	-184
$1\bar{2}3$	106	-113
$1\bar{2}4$	103	95
$1\bar{2}5$	72	71
$1\bar{2}6$	82	-72
$1\bar{2}7$	18	-15
$1\bar{2}\bar{1}$	582	541
$1\bar{2}\bar{2}$	66	86
$1\bar{2}\bar{3}$	75	69
$1\bar{2}\bar{4}$	102	129
$1\bar{2}\bar{5}$	40	27
$1\bar{2}\bar{7}$	65	-62
130	926	-869
131	191	-201
132	665	617
133	93	79
134	138	-138
137	17	23
$13\bar{1}$	199	-199
$13\bar{2}$	142	-146
$13\bar{3}$	80	-56
$13\bar{4}$	100	-103
$13\bar{5}$	162	161
$13\bar{6}$	207	206
$13\bar{8}$	37	-38
$1\bar{3}0$	189	187
$1\bar{3}1$	454	430
$1\bar{3}2$	31	27
$1\bar{3}3$	224	-240
$1\bar{3}4$	64	-49
$1\bar{3}6$	14	10
$1\bar{3}\bar{1}$	134	155
$1\bar{3}\bar{2}$	52	51
$1\bar{3}\bar{3}$	23	51
$1\bar{3}\bar{4}$	48	-54
$1\bar{3}\bar{5}$	207	-194
$1\bar{3}\bar{7}$	84	81
140	613	569
141	121	120
142	46	-50
145	41	45
147	25	-22
$14\bar{1}$	116	-122
$14\bar{2}$	526	-509
$14\bar{3}$	158	-162
$14\bar{4}$	47	-54
$14\bar{7}$	29	34
$14\bar{8}$	39	38
$1\bar{4}0$	43	42
$1\bar{4}1$	119	112
$1\bar{4}2$	120	112
$1\bar{4}3$	144	159
$1\bar{4}5$	78	-84
$1\bar{4}\bar{1}$	96	93
$1\bar{4}\bar{2}$	110	-104
$1\bar{4}\bar{3}$	423	-412
$1\bar{4}\bar{5}$	172	173
$1\bar{4}\bar{6}$	24	16
$1\bar{4}\bar{7}$	16	-11
150	74	69
151	31	46
153	67	78
154	19	-12
155	64	-68
$15\bar{1}$	96	87
$15\bar{2}$	247	245
$15\bar{3}$	44	-42
$15\bar{4}$	170	-179
$15\bar{5}$	42	-40
$1\bar{5}0$	135	-141
$1\bar{5}1$	89	83
$1\bar{5}2$	38	51
$1\bar{5}3$	57	50
$1\bar{5}4$	40	37
$1\bar{5}\bar{1}$	431	-453
$1\bar{5}\bar{2}$	13	-7
$1\bar{5}\bar{3}$	212	220
$1\bar{5}\bar{4}$	39	35
161	86	94
162	43	-37
163	100	-109
164	34	-45
$16\bar{1}$	25	25
$16\bar{2}$	63	68
$16\bar{3}$	31	25
$16\bar{4}$	76	68
$16\bar{5}$	6	1
$1\bar{6}1$	253	-255
$1\bar{6}2$	73	-78
$1\bar{6}3$	60	54
$1\bar{6}\bar{1}$	155	145
$1\bar{6}\bar{2}$	46	42
$1\bar{6}\bar{3}$	40	37
$1\bar{6}\bar{4}$	16	19
171	88	-98
172	57	-69
$17\bar{1}$	71	79
$17\bar{4}$	26	22
$1\bar{7}1$	55	49
$1\bar{7}3$	96	-90
$1\bar{7}4$	29	-25
$1\bar{7}\bar{1}$	45	46
$1\bar{7}\bar{2}$	21	30
180	49	-54
182	24	27
$18\bar{1}$	45	-48
$18\bar{3}$	38	37
$18\bar{5}$	16	-12
$1\bar{8}0$	21	21
$1\bar{8}\bar{1}$	30	28
200	508	-464
201	175	-165
202	319	-297
204	225	212
205	88	83
206	16	23
$20\bar{1}$	566	-520
$20\bar{2}$	326	-304
$20\bar{3}$	284	-283
$20\bar{4}$	257	250
$20\bar{5}$	332	336
$20\bar{6}$	58	58
210	617	-626
211	78	73
212	582	548
213	304	311
214	49	60
215	37	-44
216	18	1
218	35	-26
$21\bar{1}$	279	-245
$21\bar{2}$	223	-221
$21\bar{3}$	349	-347
$21\bar{4}$	137	-152
$21\bar{5}$	75	-79
$21\bar{6}$	56	64
$21\bar{7}$	87	91
210	418	-378
211	281	-276
212	210	-212
214	79	-73
215	19	5
216	45	42
$21\bar{1}$	675	-668
$21\bar{2}$	475	428
$21\bar{3}$	834	809
$21\bar{4}$	198	199
$21\bar{6}$	35	-28
$21\bar{7}$	22	-34
218	42	-35
220	595	552
221	638	598
222	130	133
223	106	-117
224	52	44
225	21	-30
226	128	-110
227	27	-24
$22\bar{1}$	31	-31
$22\bar{2}$	615	-608
$22\bar{3}$	39	-33
$22\bar{4}$	74	59
$22\bar{5}$	92	-94
$22\bar{6}$	41	-46
$22\bar{7}$	27	-26
229	12	70
$2\bar{2}0$	326	332
$2\bar{2}1$	538	-501
$2\bar{2}2$	240	-240
$2\bar{2}4$	34	-37
$2\bar{2}7$	12	-4
$2\bar{2}\bar{1}$	958	921
$2\bar{2}\bar{2}$	303	285
2.4	43	-38
$2\bar{2}\bar{5}$	53	-69
$2\bar{2}\bar{6}$	129	-124
$2\bar{2}\bar{7}$	99	-96
228	23	20
230	93	102
231	184	-177
232	169	175
233	64	-74
234	284	-302
235	81	-73
236	57	48
237	35	35
$23\bar{1}$	544	506
$23\bar{2}$	331	328
$23\bar{3}$	100	-106
$23\bar{4}$	265	-270
$23\bar{5}$	45	34
$23\bar{6}$	84	77
$23\bar{8}$	18	-18
$2\bar{3}0$	207	210
$2\bar{3}1$	468	426
$2\bar{3}2$	107	103
$2\bar{3}3$	216	-218
$2\bar{3}4$	63	-65
$2\bar{3}5$	42	34
$2\bar{3}\bar{1}$	46	65
$2\bar{3}\bar{2}$	24	19
$2\bar{3}\bar{3}$	37	-37
$2\bar{3}\bar{4}$	269	-271
$2\bar{3}\bar{5}$	244	-240
$2\bar{3}\bar{6}$	46	40
$2\bar{3}\bar{7}$	84	81
240	301	296
241	75	-88
242	476	-451
243	144	-140
244	72	84
245	81	86
246	39	47
$24\bar{1}$	111	-106
$24\bar{2}$	42	-42
$24\bar{3}$	151	163
$24\bar{4}$	78	71
$24\bar{5}$	51	-49
$24\bar{6}$	66	-54
$24\bar{7}$	26	22
$24\bar{8}$	30	28
$2\bar{4}0$	65	69
$2\bar{4}2$	77	66
$2\bar{4}3$	99	105
$2\bar{4}4$	14	19
$2\bar{4}5$	61	-64
$2\bar{4}\bar{1}$	30	46
$2\bar{4}\bar{2}$	318	-330
$2\bar{4}\bar{3}$	331	-352
$2\bar{4}\bar{4}$	60	57
$2\bar{4}\bar{5}$	132	124
$2\bar{4}\bar{6}$	61	49
$2\bar{4}\bar{7}$	28	25
250	349	-358
251	166	-166
253	135	135
254	59	56
$25\bar{1}$	29	-33
$25\bar{2}$	243	245
$25\bar{3}$	30	-34
$25\bar{4}$	63	-59
$25\bar{5}$	22	25
$2\bar{5}0$	209	-200
$2\bar{5}1$	56	57
$2\bar{5}2$	42	55
$2\bar{5}\bar{1}$	265	-264
$2\bar{5}\bar{2}$	53	54
$2\bar{5}\bar{3}$	76	96
$2\bar{5}\bar{4}$	73	67
$2\bar{5}\bar{5}$	67	58
262	54	52
264	24	16
$26\bar{1}$	86	-90
$26\bar{2}$	156	-164
$26\bar{4}$	121	108
$26\bar{6}$	-28	-26
$2\bar{6}0$	27	20
$2\bar{6}1$	114	-106
$2\bar{6}2$	78	-74
$2\bar{6}3$	35	32
$2\bar{6}\bar{1}$	37	31
$2\bar{6}\bar{2}$	64	55
$2\bar{6}\bar{3}$	70	68
$27\bar{1}$	75	74
$27\bar{3}$	37	-32
$27\bar{4}$	42	-41
$27\bar{6}$	25	29
$2\bar{7}\bar{1}$	41	42
$28\bar{3}$	31	30
300	102	101
301	140	-158
302	152	-148
303	33	-15
304	28	30
$30\bar{1}$	212	205
$30\bar{2}$	237	-224
$30\bar{3}$	302	-307
$30\bar{4}$	172	171
$30\bar{5}$	213	208
$30\bar{6}$	24	26
310	308	-335
311	32	17
312	151	148
313	60	54
314	36	38
315	21	23
$31\bar{1}$	281	-283
$31\bar{2}$	23	-11
$31\bar{3}$	59	63
$31\bar{4}$	120	-125
$31\bar{5}$	139	-136
$31\bar{6}$	75	76
$31\bar{7}$	90	88
$3\bar{1}0$	189	-178
$3\bar{1}1$	275	268
$3\bar{1}2$	123	121
$3\bar{1}3$	48	-58
$3\bar{1}4$	58	-59
$3\bar{1}5$	14	-14
$3\bar{1}\bar{1}$	395	-376
$3\bar{1}\bar{2}$	212	217
$3\bar{1}\bar{3}$	259	258
$3\bar{1}\bar{5}$	14	-12
$3\bar{1}\bar{8}$	45	-38
320	292	296
321	220	214
322	132	135
323	80	38
326	44	-43
$32\bar{1}$	18	11
$32\bar{2}$	381	-363
$32\bar{3}$	189	-217
$32\bar{4}$	47	-43
$32\bar{5}$	11	6
$32\bar{6}$	39	-44
$32\bar{7}$	49	-42
$32\bar{8}$	18	19
$32\bar{9}$	16	22
$3\bar{2}0$	123	119
$3\bar{2}1$	220	-226
$3\bar{2}2$	70	-68
$3\bar{2}3$	171	156
$3\bar{2}4$	75	69
$3\bar{2}5$	17	-16
$3\bar{2}\bar{1}$	123	126
$3\bar{2}\bar{2}$	84	-90
$3\bar{2}\bar{3}$	24	-20
$3\bar{2}\bar{4}$	49	54
$3\bar{2}\bar{6}$	90	-83
$3\bar{2}\bar{7}$	48	-54
330	255	243
331	58	70
332	48	44
333	23	-28
334	158	-151
335	72	-65
336	31	25
$33\bar{1}$	344	318
$33\bar{2}$	246	235
$33\bar{3}$	77	-66
$33\bar{4}$	210	-216
$33\bar{5}$	57	-70
$3\bar{3}0$	90	-107
$3\bar{3}2$	33	32
$3\bar{3}3$	79	-75
$3\bar{3}4$	19	-19
$3\bar{3}5$	60	51
$3\bar{3}6$	11	20
$3\bar{3}\bar{1}$	41	-34
$3\bar{3}\bar{2}$	75	81
$3\bar{3}\bar{3}$	55	58
$3\bar{3}\bar{4}$	105	-100
$3\bar{3}\bar{5}$	68	-78
$3\bar{3}\bar{6}$	25	22
340	116	114
341	72	-74
342	335	-324
343	166	-167
344	52	52
345	77	68
$34\bar{1}$	84	94
$34\bar{2}$	212	207
$34\bar{3}$	200	200
$34\bar{4}$	75	76
$34\bar{5}$	57	-49
$34\bar{6}$	66	-67
$3\bar{4}0$	57	61
$3\bar{4}2$	54	-58
$3\bar{4}\bar{1}$	65	70
$3\bar{4}\bar{2}$	69	-61
$3\bar{4}\bar{3}$	34	-41
$3\bar{4}\bar{4}$	24	26
$3\bar{4}\bar{5}$	19	20
$3\bar{4}\bar{6}$	34	25
350	377	-380
351	253	-852
353	134	127
354	58	52
$35\bar{1}$	47	-49
$35\bar{2}$	140	136
$35\bar{3}$	58	62
$35\bar{4}$	80	82
355	63	57
$3\bar{5}0$	26	-18
$3\bar{5}1$	36	37
$3\bar{5}\bar{2}$	27	25
$3\bar{5}\bar{2}$	23	21
361	138	137
362	90	81
363	33	28
364	33	32
$36\bar{1}$	218	-220
$36\bar{2}$	259	-246
$36\bar{4}$	99	87
$36\bar{6}$	14	13
$3\bar{6}\bar{3}$	14	-14
$37\bar{1}$	40	45
$37\bar{1}$	85	84
$37\bar{3}$	111	-107
374	105	-89
$38\bar{3}$	32	30
400	424	435
401	58	63
402	118	-124
403	60	-77
404	28	-35
405	27	-29
$40\bar{1}$	450	412
$40\bar{2}$	57	-47
$40\bar{3}$	227	-224
$40\bar{4}$	64	-89
$40\bar{5}$	53	-53
$40\bar{6}$	28	-29
410	144	-155
411	125	-126
412	93	-98
413	113	-110
414	24	-22
415	41	41
$41\bar{1}$	120	134
$41\bar{2}$	463	452
$41\bar{3}$	311	311
$41\bar{4}$	87	-92
$41\bar{5}$	164	-165
$41\bar{6}$	32	-31
$4\bar{1}1$	290	288
$4\bar{1}2$	227	226
$4\bar{1}3$	24	7
$4\bar{1}4$	61	-59
$4\bar{1}5$	17	-27
$4\bar{1}\bar{1}$	157	-156
$4\bar{1}\bar{2}$	120	-121
$4\bar{1}\bar{3}$	150	-154
$4\bar{1}\bar{4}$	108	-106
$4\bar{1}\bar{6}$	57	54
420	126	-128
421	204	-210
422	60	-68
423	88	88
424	67	73
$42\bar{1}$	112	-108
$42\bar{2}$	109	-113
$42\bar{3}$	94	99
$42\bar{4}$	233	249
$42\bar{5}$	136	122
$42\bar{6}$	65	-63
$42\bar{7}$	78	-67
$4\bar{2}0$	77	-73
$4\bar{2}1$	55	-52
$4\bar{2}3$	103	107
$4\bar{2}\bar{1}$	162	-169
$4\bar{2}\bar{2}$	146	-146
$4\bar{2}\bar{3}$	28	-28
$4\bar{2}\bar{4}$	68	71
$4\bar{2}\bar{5}$	80	82
$4\bar{2}\bar{6}$	23	22
430	77	-94
431	107	107
432	127	137
433	60	59
435	23	-19
$43\bar{1}$	178	-191
$43\bar{3}$	57	-44
$43\bar{4}$	52	-53
$43\bar{5}$	39	39
$43\bar{6}$	87	81
$43\bar{7}$	23	26
$4\bar{3}0$	90	-98
$4\bar{3}1$	80	-87
$4\bar{3}2$	26	-25
$4\bar{3}\bar{2}$	44	39
$4\bar{3}\bar{3}$	95	101
$4\bar{3}\bar{4}$	66	66
435	12	14
440	150	160
441	78	87
442	45	-39
443	50	-46
$44\bar{1}$	84	87
$44\bar{2}$	29	-48
$44\bar{3}$	90	-88
$44\bar{4}$	33	-21
$44\bar{5}$	22	-16
$44\bar{6}$	17	-21
$4\bar{4}\bar{2}$	31	-29
442	64	71
450	92	-79
451	90	-83
453	33	26
$45\bar{2}$	109	114
$45\bar{3}$	55	57
455	24	-22
$46\bar{1}$	58	46
$46\bar{1}$	105	-100
468	90	-85
$46\bar{4}$	57	61
$47\bar{1}$	48	44
$47\bar{3}$	77	-71
474	62	-50
500	191	179
501	45	33
502	45	-56
$50\bar{1}$	153	164
$50\bar{2}$	36	-6
$50\bar{3}$	116	-106
$50\bar{4}$	103	-98
$50\bar{5}$	60	-54
$50\bar{6}$	14	-10
510	69	-77
511	76	--80
512	35	-37
513	42	-37
$51\bar{1}$	111	104
$51\bar{2}$	268	277
$51\bar{3}$	178	185
$51\bar{4}$	52	-32
$51\bar{5}$	102	-103
$51\bar{6}$	67	-63
$5\bar{1}\bar{1}$	77	-63
$5\bar{1}\bar{2}$	92	-83
$5\bar{1}\bar{3}$	55	-55
$5\bar{1}\bar{6}$	23	20
520	102	-102
521	132	-129
523	52	45
$52\bar{1}$	90	-99
$52\bar{2}$	25	-41
$52\bar{3}$	144	144
$52\bar{4}$	230	234
$52\bar{5}$	106	108
$52\bar{6}$	44	-38
$52\bar{7}$	66	-57
$5\bar{2}1$	32	-26
$5\bar{2}\bar{1}$	19	-20
$5\bar{2}\bar{5}$	36	35
530	124	-130
531	70	62
532	100	108
533	28	32
$53\bar{1}$	199	-209
$53\bar{3}$	54	-59
$53\bar{5}$	97	99
$53\bar{6}$	123	109
$53\bar{7}$	33	33
$5\bar{3}0$	32	23
$5\bar{3}\bar{3}$	30	29
540	138	146
$54\bar{1}$	75	83
$54\bar{2}$	132	-150
$54\bar{3}$	182	-175
$54\bar{4}$	73	-70
550	28	32
$55\bar{2}$	105	113
$55\bar{4}$	83	-89
$55\bar{5}$	80	-79
$56\bar{4}$	47	53
600	12	-25
$60\bar{3}$	42	-37
$61\bar{4}$	36	-31
$62\bar{4}$	26	20

Table 10(*b*). *Observed and calculated structure factors at* −105 °C

	50Fo	50Fc
001	764	912
002	966	-1097
003	537	-515
004	443	-425
005	258	-246
006	115	-118
007	83	77
008	226	184
010	613	-609
011	465	-457
012	920	-951
013	612	-558
014	427	-399
015	116	106
016	401	392
017	59	57
011̄	751	846
013̄	506	521
014̄	704	-748
015̄	280	-260
016̄	100	-100
017̄	68	-54
019̄	34	37
020	899	-872
021	784	-724
022	1033	-990
023	152	136
024	701	658
025	237	203
028	61	-68
021̄	328	-265
022̄	68	-16
023̄	541	525
024̄	1052	1035
025̄	181	172
026̄	398	-396
027̄	113	-110
030	912	-982
031	209	205
032	697	734
033	342	312
034	229	244
035	74	-61
036	147	-140
037	65	65
031̄	565	-499
032̄	413	-353
033̄	181	-180
034̄	43	44
035̄	175	148
036̄	398	354
037̄	79	68
038	193	-175
040	464	427
041	311	296
042	437	424
043	130	-150
044	178	-164
045	143	148
046	58	-63
047	145	-148
041̄	76	60
042̄	526	-448
043̄	151	-142
044̄	124	-110
045̄	103	-105
048̄	100	108
050	353	329
051	239	-242
052	148	-133
053	227	232
054	80	-96
055	234	-226
056	68	-74
051̄	255	236
052̄	193	173
053̄	43	51
054̄	145	-156
055̄	34	-35
056̄	42	-47
057̄	63	-59
060	106	-106
061	257	272
062	47	-55
063	196	-202
064	96	-110
065	32	46
061̄	330	-298
062̄	138	142
063̄	138	148
064̄	57	51
065̄	66	66
066̄	22	-32
070	24	-5
071	112	-118
072	88	-100
073	50	63
074	65	66
071̄	219	217
072̄	72	63
073̄	320	-264
075̄	81	97
080	40	-44
081	71	76
081̄	29	-27
083̄	123	105
084̄	31	-39

	50Fo	50Fc
100	1567	1699
101	711	680
102	1016	-1035
103	83	-91
104	329	307
105	64	73
106	41	-46
107	43	-50
108	70	73
101̄	551	-530
103̄	308	-352
104̄	264	-287
105̄	21	2
106̄	44	-22
107̄	75	71
108	108	116
110	1111	-1269
111	318	-339
112	132	146
113	34	13
114	188	-194
115	67	-85
116	215	223
117	39	-29
118	169	-169
111̄	792	917
112̄	1794	2010
114̄	406	-412
115̄	270	-258
116̄	181	-198
117̄	31	-33
118	15	15
11̄1	562	-477
11̄2	660	566
11̄3	295	296
11̄4	497	-468
11̄5	46	-21
11̄6	214	174
11̄7	65	65
11̄8	13	-2
11̄1̄	429	-414
11̄2̄	380	-357
11̄3̄	252	267
11̄4̄	68	-65
11̄5̄	71	63
11̄6̄	186	176
11̄7̄	44	51
120	205	-220
121	116	18
122	638	-608
123	150	-147
124	516	509
126	269	-259
121̄	314	-358
122̄	607	-629
123̄	680	691
124̄	1120	1137
125̄	25	33
126̄	282	-317
127̄	116	-123
128	88	-87
12̄0	164	-157
12̄1	648	-578
12̄2	250	-254
12̄3	29	-195
12̄4	145	151
12̄5	150	136
12̄6	182	-171
12̄8	82	79
12̄1̄	695	640
12̄2̄	101	62
12̄3̄	103	130
12̄4̄	188	178
12̄5̄	85	96
12̄7̄	180	-176
128	33	-46
130	947	-1028
131	203	-182
132	883	855
133	72	50
134	253	-240
137	60	72
131̄	296	-258
132̄	199	-106
133̄	84	-95
134̄	79	-106
135̄	362	350
136̄	473	524
138̄	185	-193
139̄	26	-50
13̄0	303	296
13̄1	702	548
13̄2	45	12
13̄3	442	-429
13̄4	147	-132
13̄5	86	-65
13̄7	86	60
13̄8	69	-59
13̄1̄	178	207
13̄2̄	76	53
13̄3̄	113	95
13̄4̄	55	-45
13̄5̄	375	-380
13̄6̄	47	-51
13̄7̄	251	222

	50Fo	50Fc
140	858	826
141	121	124
142	42	-44
143	39	45
145	101	97
147	75	-72
141̄	154	-150
142̄	771	-768
143̄	285	-277
144̄	80	-103
147̄	133	148
148	202	207
14̄0	65	56
14̄1	213	184
14̄2	261	240
14̄3	289	282
14̄5	268	-255
14̄1̄	164	151
14̄2̄	124	-132
14̄3̄	705	-670
14̄4̄	52	-45
14̄5̄	343	350
14̄6̄	49	49
14̄7	30	-55
150	154	140
151	63	57
153	133	137
154	60	-56
155	152	-155
156	30	-35
151̄	142	134
152̄	438	438
153̄	87	-83
154̄	401	-423
155̄	125	-130
156̄	31	-29
158	23	25
15̄0	212	-218
15̄1	172	173
15̄2	90	85
15̄3	150	143
15̄4	133	121
15̄5	110	107
15̄6	16	-33
15̄7	143	-122
15̄1̄	791	-761
15̄2̄	72	-66
15̄3̄	427	394
15̄4̄	88	96
15̄5	38	17
161	158	167
162	119	-113
163	210	-217
164	84	-103
161̄	38	44
162̄	178	185
163̄	67	79
164̄	172	166
166̄	155	-190
167̄	31	-61
16̄0	72	-77
16̄1	608	-575
16̄2	170	-167
16̄3	171	161
16̄4	57	57
16̄5	61	64
16̄6	45	48
16̄1̄	303	294
16̄2̄	129	116
16̄3̄	116	103
16̄4̄	44	52
170	93	-80
171	206	-210
172	155	-163
173	32	-30
174	116	112
171̄	165	179
174̄	127	116
17̄0	78	87
17̄1	130	126
17̄2	47	-49
17̄3	340	-333
17̄4	101	-93
17̄5	113	118
17̄1̄	137	137
17̄2̄	94	87
17̄3̄	85	79
180	157	-161
181	28	-38
182	96	106
181̄	138	-137
183̄	135	128
200	532	-457
201	216	-173
202	404	-362
203	119	124
204	455	401
205	173	171
206	42	47
207	51	-48
201̄	637	-607
202̄	296	-260
203̄	373	-388
204̄	320	300
205̄	559	576
206̄	155	158
208̄	33	-32
209̄	26	-32

	50Fo	50Fc
210	694	-692
211	236	203
212	779	708
213	434	407
214	83	92
215	134	-126
217	35	-42
211̄	317	277
212̄	308	-218
213̄	430	-473
214̄	166	-173
215̄	133	-122
216̄	84	101
217̄	261	238
218̄	47	67
21̄0	388	-376
21̄1	314	-280
21̄2	352	-310
21̄4	123	-124
21̄6	168	144
21̄7	53	50
21̄1̄	820	-823
21̄2̄	438	375
21̄3̄	1118	1072
21̄4̄	324	325
21̄6̄	77	-68
21̄7̄	70	-70
21̄8	117	-128
220	597	625
221	745	687
222	159	152
223	208	-212
224	77	88
225	107	-92
226	370	-348
227	63	-63
221̄	60	50
222̄	700	-704
223̄	72	-64
224̄	104	102
225̄	191	-185
226̄	83	-89
227̄	56	-53
229̄	71	79
22̄0	317	304
22̄1	785	-718
22̄2	324	-274
22̄4	115	-103
22̄6	40	-47
22̄1̄	1209	1121
22̄2̄	436	404
22̄4̄	66	-68
22̄5̄	93	-105
22̄6̄	279	-274
22̄7̄	318	-286
22̄8̄	59	58
230	80	83
231	259	-236
232	270	276
233	194	-168
234	630	-615
235	109	-116
236	160	173
237	134	148
231̄	621	632
232̄	408	404
233̄	70	-85
234̄	487	-422
235̄	81	59
236̄	174	181
237̄	77	-66
238̄	52	-67
23̄0	330	317
23̄1	725	607
23̄2	115	120
23̄3	466	-429
23̄4	99	-94
23̄5	117	98
23̄1̄	76	76
23̄2̄	23	22
23̄4̄	439	-417
23̄5̄	503	-506
23̄6̄	76	68
23̄7̄	264	263
240	465	468
241	180	-182
242	662	-724
243	195	-183
244	180	-180
245	219	224
246	108	109
241̄	161	-167
242̄	92	-86
243̄	224	267
244̄	133	141
245̄	72	-82
246̄	140	-138
247̄	70	82
248̄	127	128
24̄0	99	97
24̄1	83	49
24̄2	162	149
24̄3	221	231
24̄4	32	34
24̄5	239	-217
24̄1̄	101	102
24̄2̄	489	-459
24̄3̄	698	-645
24̄4̄	61	66
24̄5̄	259	286
24̄6̄	145	148

	50Fo	50Fc
250	575	-581
251	209	-219
252	119	122
253	377	269
254	134	135
255	25	19
251̄	96	-98
252̄	445	444
253̄	47	-67
254̄	149	-158
255̄	57	71
256̄	25	13
257̄	39	-53
258	33	-26
25̄0	326	-328
25̄1	153	152
25̄2	86	79
25̄3	22	16
25̄5	58	62
25̄1̄	585	-516
25̄2̄	305	-312
25̄3̄	218	201
25̄4̄	157	162
25̄5̄	163	180
260	53	50
261	249	253
262	92	99
264	82	81
261̄	139	-135
262̄	305	-312
263̄	46	-38
264̄	243	284
266̄	118	-130
270	39	41
272	66	56
273	58	-71
271̄	171	181
273̄	38	-64
274̄	98	-104
276̄	122	137
27̄0	94	105
27̄2	26	16
27̄3	105	-120
27̄1̄	125	135
281	69	-76
281̄	22	-21
283̄	104	110
300	84	84
301	229	-199
302	216	-215
303	46	-11
304	37	43
305	29	-47
306	52	45
301̄	296	314
302̄	248	-173
303̄	476	-492
304̄	223	209
305̄	404	414
306̄	71	67
310	409	-371
311	73	77
312	209	193
313	40	12
314	101	100
315	71	65
311̄	399	-341
312̄	51	-55
313̄	96	-89
314̄	101	-111
315̄	259	-260
316̄	129	153
317̄	301	278
318	40	48
31̄0	89	-125
31̄1	479	468
31̄2	143	126
31̄3	127	-124
31̄4	121	-136
31̄5	51	-39
31̄1̄	475	-549,
31̄2̄	227	217
31̄3̄	413	414
31̄5̄	38	-42
31̄8	132	-146
320	226	338
321	250	198
322	210	204
323	44	38
326	155	-156
321̄	64	110
322̄	393	-417
323̄	276	-304
324̄	125	-127
325̄	21	-8
327̄	126	-108
328̄	68	74
329̄	139	140
32̄0	138	144
32̄1	387	-375
32̄3	420	389
32̄4	183	120
32̄5	86	-83
32̄6	66	-91
32̄1̄	207	197
32̄2̄	144	-143
32̄3̄	52	-51
32̄4̄	57	67
32̄5̄	49	44
32̄6̄	195	-182
32̄7̄	127	-168
32̄8̄	39	52

	50Fo	50Fc
330	323	307
331	56	43
332	66	63
333	48	-35
334	362	-346
335	146	-140
336	112	115
331̄	400	373
332̄	313	299
333̄	46	-19
334̄	290	-328
335̄	153	-159
339	50	-43
33̄0	187	-170
33̄2	63	70
33̄3	183	-185
33̄5	238	227
33̄1̄	82	-88
33̄2̄	80	83
33̄3̄	143	123
33̄4̄	156	-152
33̄5̄	159	-185
33̄6̄	54	58
33̄7̄	87	80
340	165	155
341	126	-125
342	605	-576
343	262	-253
344	170	166
345	196	187
341̄	71	68
342̄	288	310
343̄	314	338
344̄	142	146
345̄	96	-80
346̄	181	-180
347̄	41	-54
34̄0	61	58
34̄1	113	-104
34̄2	122	-132
34̄3	36	-34
34̄4	40	36
34̄5	70	-61
34̄1̄	172	148
34̄2̄	72	-80
34̄3̄	106	-101
34̄4̄	57	71
34̄5̄	36	38
34̄6̄	84	73
350	652	-665
351	348	-360
352	141	151
353	283	277
354	126	131
351̄	115	-113
352̄	252	236
353̄	60	59
354̄	166	179
355̄	175	185
356̄	19	22
357̄	64	-69
358	92	-69
35̄0	31	-27
35̄1	104	114
35̄2	43	26
35̄3	67	-67
35̄4	77	-70
35̄2̄	73	62
35̄4̄	78	85
360	67	63
361	292	288
362	170	184
363	62	58
364	113	115
361̄	358	-365
362̄	543	-541
363̄	40	-43
364̄	215	232
365̄	47	55
366̄	44	57
367̄	57	65
36̄0	36	35
36̄1̄	39	34
36̄2̄	109	105
370	165	166
371	110	106
372	172	177
371̄	224	214
373̄	276	-264
374̄	313	-307
376̄	149	156
380	180	186
381̄	96	101
382̄	75	94
383̄	116	116
400	575	543
402	236	-248
403	161	-156
404	81	-86
405	114	-115
401̄	586	664
403̄	337	-352
404̄	115	-119
405̄	90	-102
406̄	105	-112
408̄	71	77

Table 10(*b*) (*cont.*)

	50 Fo	50Fo
410	273	-254
411	170	-184
412	174	-168
413	241	-263
415	166	183
$41\bar{1}$	63	86
$41\bar{2}$	610	568
$41\bar{3}$	662	540
$41\bar{4}$	97	-74
$41\bar{5}$	327	-333
$4\bar{1}0$	67	66
$4\bar{1}1$	533	556
$4\bar{1}2$	338	360
$4\bar{1}3$	66	-56
$4\bar{1}4$	160	-179
$4\bar{1}5$	72	-90
$4\bar{1}\bar{1}$	203	-234
$4\bar{1}\bar{2}$	116	-135
$4\bar{1}\bar{3}$	239	-236
$4\bar{1}\bar{4}$	255	-226
$4\bar{1}\bar{6}$	102	113
$4\bar{1}\bar{7}$	120	101
420	213	-198
421	356	-374
422	44	-46
423	210	243
424	144	168
425	54	53
$42\bar{1}$	138	-123
$42\bar{2}$	230	-192
$42\bar{3}$	76	71
$42\bar{4}$	373	371
$42\bar{5}$	281	300
$42\bar{6}$	75	-93
$42\bar{7}$	225	-209

	50Fo	50Fc
420	74	-87
421	88	-93
423	311	317
424	178	179
425	55	-55
$42\bar{1}$	263	-267
$42\bar{2}$	268	-246
$42\bar{3}$	78	-60
$42\bar{4}$	89	92
$42\bar{5}$	162	173
426	72	77
430	40	-68
431	224	222
432	205	222
433	143	125
434	44	-50
435	71	-63
$43\bar{1}$	385	-326
$43\bar{2}$	103	-137
$43\bar{3}$	36	-36
$43\bar{4}$	144	-111
$43\bar{5}$	34	28
$43\bar{6}$	141	172
$43\bar{7}$	123	117
438	55	-65
430	164	-168
431	195	-186
432	36	-40
433	17	-18
431	103	-94
433	175	186
434	131	147
435	51	58

	50Fo	50Fo
440	216	230
441	148	152
442	83	-90
443	90	-91
444	25	25
$44\bar{1}$	199	163
$44\bar{3}$	211	-183
$44\bar{4}$	53	-73
$44\bar{5}$	27	-14
$44\bar{6}$	51	-67
$44\bar{8}$	60	72
$4\bar{4}1$	58	-66
$4\bar{4}2$	57	-71
$4\bar{4}3$	89	-96
$4\bar{4}\bar{1}$	121	134
$4\bar{4}\bar{2}$	128	149
$4\bar{4}\bar{3}$	93	85
450	190	-167
451	132	-136
452	64	52
453	58	47
$45\bar{1}$	101	109
$45\bar{2}$	180	183
$45\bar{3}$	82	109
$45\bar{4}$	51	53
$45\bar{5}$	47	-59
$45\bar{6}$	44	-43
$45\bar{7}$	13	-20
$4\bar{5}0$	83	95
$4\bar{5}1$	49	67
$4\bar{5}\bar{1}$	55	61

	50Fo	50Fo
460	64	51
461	103	103
$46\bar{1}$	194	-182
$46\bar{2}$	219	-215
$46\bar{3}$	61	63
$46\bar{4}$	122	143
$46\bar{5}$	45	76
470	31	42
471	39	-44
$47\bar{1}$	121	125
$47\bar{3}$	179	-191
$47\bar{4}$	180	-185
500	194	271
502	138	-129
503	62	-67
$50\bar{1}$	351	301
$50\bar{3}$	160	-156
$50\bar{4}$	178	-172
505	183	-155
$50\bar{6}$	40	-37
510	115	-168
511	127	-131
512	39	-43
513	98	-99
$51\bar{2}$	426	410
$51\bar{3}$	421	356
$51\bar{4}$	41	-26
$51\bar{5}$	246	-194
$51\bar{6}$	186	-153
$51\bar{7}$	128	-106
$5\bar{1}2$	135	133
$5\bar{1}\bar{1}$	91	-100
$5\bar{1}\bar{2}$	141	-145
$5\bar{1}\bar{3}$	123	-131

	50Fo	50Fc
520	143	-147
521	285	-244
522	98	-79
523	197	179
$52\bar{1}$	148	-159
$52\bar{2}$	153	-129
$52\bar{3}$	180	172
$52\bar{4}$	489	427
525	397	281
$52\bar{6}$	88	-70
527	237	-176
$5\bar{2}0$	83	-111
$5\bar{2}2$	52	47
530	136	-150
531	298	226
532	227	220
$53\bar{1}$	461	-371
$53\bar{2}$	225	-204
$53\bar{3}$	112	-110
$53\bar{4}$	56	-49
$53\bar{5}$	189	179
$53\bar{6}$	375	304
$53\bar{7}$	232	151
$5\bar{3}\bar{0}$	85	94
540	258	271
541	131	121
$54\bar{1}$	239	188
$54\bar{2}$	236	-198
$54\bar{3}$	458	-374
$54\bar{4}$	178	-164
$54\bar{7}$	131	122

	50Fo	50Fc
550	48	37
$55\bar{1}$	163	168
$55\bar{2}$	238	234
$55\bar{3}$	132	110
554	192	-166
$55\bar{5}$	368	-258
$55\bar{6}$	105	-96
560	42	21
$56\bar{2}$	39	44
$56\bar{3}$	161	136
$56\bar{4}$	143	148
$56\bar{5}$	60	51
600	33	-43
$60\bar{1}$	42	-54
$60\bar{2}$	105	-92
$60\bar{3}$	100	-98
610	21	-11
$61\bar{4}$	57	-60
$62\bar{2}$	48	-54
$62\bar{4}$	43	44
$63\bar{2}$	81	55
$63\bar{4}$	76	-60
$64\bar{1}$	153	113
$64\bar{2}$	48	-38
$64\bar{3}$	81	-70

length of 2·96 Å, with the hydrogen atom 0·97 Å from the nitrogen and 2·00 Å from the oxygen. The N–H bond makes an angle of 172° with the O···H direction.

The dimers are connected by further hydrogen bonds, roughly parallel to the *a* axis, with a mean (N···O) length of 2·68 Å. The N–H bond and O···H distances are 0·95 and 2·00 Å respectively, the angle N–H···O being 149°. The closest non-bonding approach is 2·89 Å, between the nitrogen atom of a particular molecule and the atom H(3) of the centrosymmetrically related molecule, translated one unit cell along the *b* axis. This distance represents, roughly, the distance between the chains of molecules in the direction of the *c* axis.

The hydrogen-bonding system clearly influences the rigid body vibrations of the molecule; it has a marked effect on librations in the plane of the molecule, as is shown by the apparent shift of 1·27 Å of the centre of libration from the centre of mass towards the carbamate group. The rigid-body translational vibrations are markedly greater in a direction perpendicular to the plane of the molecule than in directions parallel to this plane. The proportionate decrease in the amplitude of each of these vibrations on lowering the temperature from 25 °C to − 105 °C (Table 4) confirms the interpretation of the vibrational parameters as 'thermal'.

The molecule

A number of accurate determinations of the structure of the amide group have now been made, and it is of interest to compare the lengths of the C=O and C–N bonds in these structures with similar bonds in ethyl carbamate, C(3)–O(2) and C(3)–N (Table 8). The C=O and C–N bonds in ethyl carbamate are respectively shorter and longer than similar bonds in the amide group, although the sum of these lengths in both classes of compound is about the same.

Of further interest is a comparison of the lengths of the C–O bonds in ethyl carbamate with similar bonds in carboxylic esters: unfortunately, esters have not received the same attention as amides, and only vague tendencies can be shown by the results quoted here in Table 9. (In this Table, the three C–O bonds are lettered (*a*), (*b*) and (*c*) corresponding to the bonds C(2)–O(1), O(1)–C(3) and C(3)–O(2) respectively, in ethyl carbamate.) If the expected length of a paraffinic single C–O bond is 1·43 Å, then the ester C–O bonds (*a*) and (*b*) are respectively longer and shorter than expected, implying that the atom corresponding to O, takes part in the delocalization of electrons within the carbamate (or carbonyl) group, and that the C–O bond (*a*) has a total bond order of less than unity. In view of the apparent shortness of the C–C bond in ethyl carbamate, it could, perhaps, be assumed that the structure is not completely refined, particularly when the large thermal vibrations of the atoms C(1) and C(2) are taken into account.

The results in Table 9, however, do show some tendency for the C–O bond (*a*) to be rather long. This could be due to the fact that the atom O(1) in ethyl carbamate is mostly sp^2 hybridized, thus allowing an unhybridized *p*-orbital to join in the partial π bonding of C(3)–O(1). Since one of the lobes of the sp^2 orbital of O(1) is not used for bond formation, this 'lone pair' probably tends to fill an *s*-orbital, thus increasing the *p*-character of the other two lobes (Pauling, 1960) and it is possible that the partial π bonding of C(3)–O(1) prevents any increase in the length of the Osp^3 lobe along this bond, causing an extra increase in the length of C(2)–O(1).

The partial sp^2 nature of O(1) may account for the planarity of the molecule, for it requires that C(2) be coplanar with the carbamate group; rotation of the ethyl group about the bond C(2)–O(1) is probably prevented by steric hindrance between O(2) and the hydrogens attached to the atom C(2).

It is apparent that no gain in accuracy resulted from the measurement of a second set of intensities at a reduced temperature. The two possible reasons for this are, firstly, the formation of ice around the crystal, and secondly, the fact that the cooling apparatus was modified during the course of measurement. The reduced temperature determination was partly successful, however, in that it increased the number of available intensities, and reduced the errors arising from the librational corrections.

A complete list of observed and calculated structure amplitudes is given in Table 10.

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The Crystal and Molecular Structure of Newberyite, $MgHPO_4.3H_2O$

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Newberyite, $MgHPO_4.3H_2O$, from Skipton Caves, Victoria, Australia, belongs to the orthorhombic space group *Pbca* with eight molecules in a unit cell of dimensions $a = 10{\cdot}215$, $b = 10{\cdot}681$, $c = 10{\cdot}014$ Å, all ±0·002 Å. The crystal structure has been determined by Patterson projections and Fourier syntheses, and refined by three-dimensional least-squares methods to an R value of 0·044. The standard deviation in P–O and Mg–O bonds is 0·005 Å. In the phosphate group P–OH is 1·588 Å, the other P–O distances are 1·545, 1·542, 1·500 Å, and most of the O–P–O angles deviate considerably from the tetrahedral value. The distortion probably results from the participation of three phosphate oxygen atoms in the octahedral coordination of magnesium atoms. The Mg–O distances fall into two groups depending on whether the oxygen belongs to a water molecule or a phosphate group. In the latter case, the Mg–O bonds (mean value 2·049 Å) are significantly shorter than in the former (mean 2·118 Å) and probably are of greater ionic character. The crystal structure is very closely packed, with many short O···O contacts, some of which are hydrogen bonds.

Introduction

Newberyite or magnesium hydrogen orthophosphate trihydrate, $MgHPO_4.3H_2O$, is a naturally occurring mineral. It was first identified as a new species in Skipton Caves, Victoria, Australia, where it occurs as large crystals in bat guano. Other well-known deposits also associated with guano are in Mejillones, Chile, Ascension Island and the Tunnel du Comeran in Réunion. An unusual deposit in crystal relics of what was originally struvite has recently been found in Paoha Island, Mono Lake, California (Cohen & Ribbe, 1966). Parsons (1956) identified newberyite as a constituent of a urinary calculus and its occurrence in a few calculi has subsequently been reported elsewhere. We have found it a common constituent of certain collections of calculi studied in this laboratory, *e.g.* 57% of the stones from a collection of (allegedly) modern Indonesian bladder calculi and 31% of the stones examined from the Norwich Hospital Museum Collection of 19th-century bladder calculi contain newberyite (Lonsdale & Sutcr, 1966).

In many of the deposits both mineral and biological, struvite is associated with newberyite, and at Paoha Island the original struvite morphology, preserved by a coating of monetite, indicates that decomposition of