Acta Cryst. (1965). **19**, 440

The Crystal Structure of 3,5-Dibromo-*p*-aminobenzoic Acid at Room Temperature (25 °C approx) and at –150 °C

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(*Received* 29 *December* 1964)

Crystals of 3,5-dibromo-*p*-aminobenzoic acid, $Br_2C_6H_2(p\text{-}NH_2)COOH$, are orthorhombic, space group *Pman*, with eight molecules in a unit cell of dimensions $a=22{\cdot}46$, $b=19{\cdot}47$, $c=3{\cdot}94$ Å at room temperature and $a=22{\cdot}38$, $b=19{\cdot}46$, $c=3{\cdot}88$ Å at −150 °C. The structure analysis has been carried out at room temperature (25 °C) and at −150 °C by two-dimensional methods. Although there is one molecule per asymmetric unit, it consists of two independent sets of molecules, one basic molecule having mirror-image symmetry and the other having a diad symmetry. Within each set the molecules form dimers, the hydrogen bonds that link the two molecules in any one dimer being symmetrical.

For the bromine atoms anisotropic thermal parameters have been introduced; these have been refined by the method of least squares. Equations of ellipsoids of constant temperature factor and the mean-square and root-mean-square vibration amplitudes along the three principal axes have been calculated. Anisotropic thermal behaviour of the bromine atoms has been discussed on the basis of packing of the molecules in the unit cell.

Introduction

The crystal structure analysis of 3,5-dibromo-*p*-aminobenzoic acid, $Br_2C_6H_2(p\text{-}NH_2)COOH$, was undertaken with a view to deriving its structures at different temperatures – which is helpful in correlating various physical phenomena, for example, thermal expansion coefficients – and also to studying the thermal vibrations of atoms and molecules. It was also of interest to see the effect of unsymmetrical substitution in the benzene ring and compare it with similarly substituted benzene derivatives. A report of the preliminary structure has been published (Pant, 1962).

Experimental

Crystals were obtained by slow evaporation of a saturated solution of the substance in a mixture of equal amounts of ethyl alcohol and acetone. The crystals are colourless, shining and hard and usually break and develop strains on cutting. They are orthorhombic and grow as needles elongated along the *c* axis. Rotation and Weissenberg photographs were taken with Cu *Kα* radiation. The experimental arrangement, which was used to take Weissenberg photographs at low temperature, resembles that described by Kreuger (1955) with some modifications. The cooling gas was obtained by passing pure nitrogen gas through copper coils immersed in liquid oxygen. The temperature could be controlled by adjusting the pressure of the gas and was measured by a copper–constantan thermocouple. This was maintained steady at −150 ± 3 °C. To prevent frosting, the entire camera was enclosed inside a plastic cover and the air inside was kept dry by placing phosphorus pentoxide in it. The crystal and physical data are as follows:

$Br_2C_6H_2(p\text{-}NH_2)COOH$, mol. wt. 295, m.p. 333 °C
Orthorhombic
Axial lengths:

	25°C	−150°C	Coefficient of expansion × 10^6
$a=$	$22{\cdot}46 \pm 0{\cdot}02$ Å	$22{\cdot}38 \pm 0{\cdot}02$ Å	20 $°C^{-1}$
$b=$	$19{\cdot}47 \pm 0{\cdot}02$	$19{\cdot}46 \pm 0{\cdot}02$	3
$c=$	$3{\cdot}94 \pm 0{\cdot}01$	$3{\cdot}88 \pm 0{\cdot}01$	88

These were determined from high-angle reflexions in the zero-layer Weissenberg photographs along the *a* and *c* axes. Film shrinkage correction was applied by Srivastava's method (1959).

Density (by flotation)	2·26 $g.cm^{-3}$
Density (calculated)	2·27 $g.cm^{-3}$

Eight molecules per unit cell.

Linear absorption coefficient for Cu *Kα* radiation, $\mu=121{\cdot}0$ cm^{-1}. Total number of electrons per unit cell, $F(000)=1120$. Systematic absences are consistent with the space groups *P2an* and *Pman*. One statistical test of Howells, Phillips & Rogers (1950) showed it to be centrosymmetric, thus indicating that the more probable space group is *Pman*. Patterson and electron-density projections later confirmed this.

The numbers of observed reflexions at 25 °C and at −150 °C are respectively:

{ *hk*0 }	273 and 280 out of 305 theoretically possible,
{ 0*kl* }	80 and 91 out of 104 possible, and
{ *h*0*l* }	57 and 60 out of 68 possible.

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Intensity measurements were made, using the multiple-film technique, with the Moll recording microphotometer. These were corrected for the Lorentz and polarization factors and for absorption by Albrecht's method (1939). As no good crystal could be found for taking photographs about the *b* axis, the intensities of the *h*0*l* reflexions, particularly at room temperature, are rather less accurate. A few reflexions consistently showed extinction effects and were omitted from the refinement. Wilson's method (1942) was used to obtain the preliminary values for the scale factors and temperature factors. Anisotropic thermal parameters were, however, introduced for the bromine atoms during the later stages of refinement. The overall temperature-factor parameters for the three zones are as follows:

	25°C	−150°C
{ *hk*0 }	1·5 Å^2	0·7 Å^2
{ 0*kl* }	3·0	0·7
{ *h*0*l* }	1·5	0·7

Structure factors were calculated with the use of the atomic scattering factor curves of Berghuis, Haanappel, Potters, Loopstra, MacGillavry and Veenendaal (1955) for carbon, nitrogen and oxygen and that of Thomas & Umeda (1957) for bromine.

Determination of structure and refinement of atomic parameters

The *x* and *y* coordinates of the bromine atoms were obtained from the (001) Patterson projection, assuming the space group to be *P*2*an*. The positions of the other bromine atoms in the unit cell were marked by applying symmetry operations of the space group *P*2*an* and the presence of mirror planes perpendicular to the *a* axis was noticed. This confirmed the space group to be *Pman*, thus indicating that there is one molecule per asymmetric unit. However, from the facts that:

(*a*) a pair of bromine atoms, expected to belong to the same molecule, are related by mirror symmetry perpendicular to the *a* axis,

(*b*) another pair of bromine atoms, also expected to belong to the same molecule but different from the first, are related by a twofold axis of rotation parallel to the *a* axis, and

(*c*) the two pairs of bromine atoms are not related to each other by any symmetries of the space group, it became clear that the asymmetric unit consists of two half molecules, one lying across the mirror plane perpendicular to the *a* axis (hereafter referred to as molecule I) and the other along the twofold rotation axis parallel to the *a* axis (hereafter referred to as molecule II). The positions of the carbon, nitrogen and oxygen atoms were fixed by assuming usual bond lengths and angles and plane molecules. Signs of *F*(*hk*0) were calculated and the structure was refined by the usual iterative process until all the structure factors, except for a few small ones, stopped changing sign. The discrepancy index *R* was about 16·4%. The final (001) electron-density projection is shown in Fig. 1. Anisotropic thermal parameters were introduced at this stage for bromine atoms and *R* decreased to 11·2%. Further refinement of the *x* and *y* parameters was carried out by a few cycles of difference synthesis and least-squares.

The (010) Patterson projection gave the approximate *z* coordinates of the bromine atoms. The *z* coordinates of the other atoms were fixed from packing considerations. The (010) electron-density projection was refined by the usual iterative process. There is overlapping of atoms in the projections of the unit cell on the (010) and (100) planes. A few atoms are, however, clear in the (010) projection and a few others are clear in

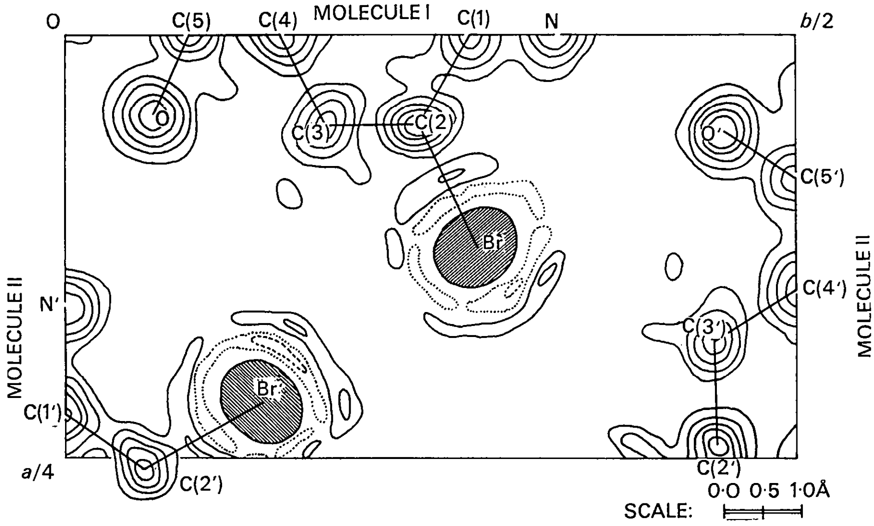


Fig. 1. (001) electron-density projection at room temperature. Contour intervals around the carbon, nitrogen and oxygen atoms 2 e.Å^{-2}. Bromine peaks inside 10 e.Å^{-2} contours shaded. Peak height 70 e.Å^{-2}. Diffraction ripples shown by contours at intervals of 2 e.Å^{-2}. Full lines: positive; dotted lines: zero; broken lines: negative.

the (100) projection. Therefore, to refine the *z* parameters, data of both the zones were utilized. The *z* parameters of a few atoms, which overlap in both the projections, were refined by the method of least squares by taking some cross terms into account. Refinement of the *z* parameters by difference synthesis and least squares was, however, effected after introducing and refining the thermal parameters of the bromine atoms, and this considerably improved the agreement between the observed and the calculated structure factors.

The X-ray photographs at low temperature showed that there had not been any appreciable change in the structure at low temperature. The low temperature structure was, therefore, assumed initially to have the same atomic positions as at room temperature and was then refined by difference synthesis and least squares from all the three projections. Only isotropic temperature factors were used. The final discrepancy indices, *R*, omitting reflexions showing strong and moderately strong extinctions, are given in Table 1, the final atomic parameters are listed in Table 2 and the observed and calculated structure factors in Table 3.

Table 1. *Discrepancy indices* (%)

R denotes the discrepancy index for observed reflexions only, whereas *R′* includes unobserved reflexions at half the minimum observable value.

	Room temperature (25°C)		−150°C	
	R	R′	R	R′
{*hk*0}	9·4	10·1	8·8	9·4
{0*kl*}	10·2	11·6	9·8	10·6
{*h*0*l*}	11·8	13·3	8·6	9·6

Refinement of thermal parameters

From the final (001) electron-density projection (Fig. 1) and the first (001) and (100) difference maps (Figs. 2 and 3 respectively) at room temperature it became

Table 2. *Fractional coordinates at given temperatures*

	25°C			−150°C		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Br	0·1275	0·2820	0·172	0·1280	0·2828	0·172
N	0	0·3352	0·038	0	0·3380	0·023
C(1)	0	0·2774	0·209	0	0·2766	0·213
C(2)	0·0527	0·2427	0·287	0·0537	0·2430	0·294
C(3)	0·0550	0·1776	0·481	0·0548	0·1805	0·481
C(4)	0	0·1510	0·574	0	0·1490	0·570
C(5)	0	0·0854	0·760	0	0·0850	0·753
O	0·0500	0·0595	0·843	0·0495	0·0573	0·837
Br′	0·2164	0·1329	0·812	0·2152	0·1328	0·816
N′	0·1615	0	0·500	0·1609	0	0·500
C(1′)	0·2254	0	0·500	0·2222	0	0·500
C(2′)	0·2556	0·0536	0·635	0·2546	0·0560	0·649
C(3′)	0·3198	0·0569	0·635	0·3173	0·0557	0·649
C(4′)	0·3486	0	0·500	0·3499	0	0·500
C(5′)	0·4132	0	0·500	0·4133	0	0·500
O′	0·4425	0·0495	0·628	0·4428	0·0506	0·638

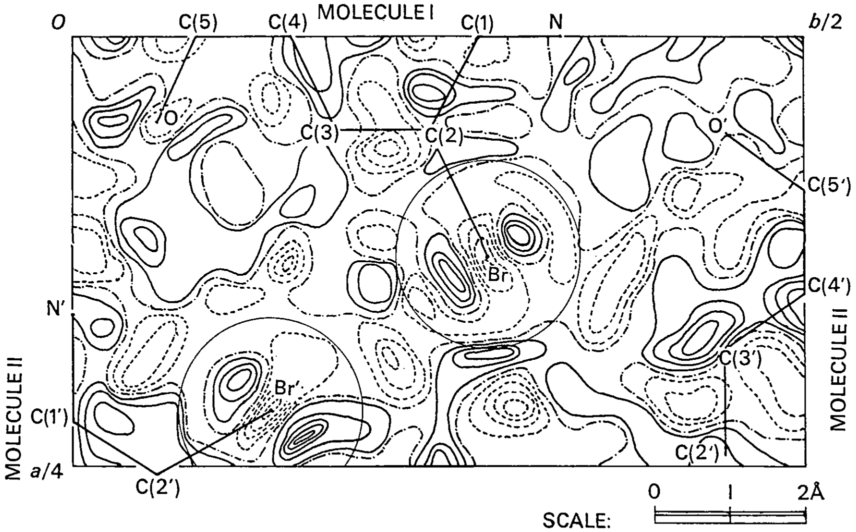


Fig. 2. First (001) difference map at room temperature. Contour interval 0·5 e.Å^{-2} except for bromine atoms where it is 1 e.Å^{-2}. Full lines: positive; chain lines: zero; broken lines: negative.

evident that the thermal movements of the atoms are anisotropic. An anisotropic temperature factor of the form

$$\exp\left[-(P\cos^2\varphi+Q\sin^2\varphi)\sin^2\theta/\lambda^2\right],$$

where P and Q are constants and φ is the angle between the normal to the reflecting plane and the direction of maximum vibration in projection, was therefore introduced for the bromine atoms for all the three zones. Directions of maximum vibration were fixed from the electron-density and difference maps. The values of P and Q were refined by the method of least-squares, initially with the use of the isotropic values for them. Structure factor equations were modified for

Table 3. *Observed and calculated structure factors*

			25°C		−150°C	
h	k	l	Fo	Fc	Fo	Fc
2	0	0	82	-99	—	-101
4	0	0	71	+53	69	+53
6	0	0	46	-42	35	-32
8	0	0	125	+111	116	+110
10	0	0	50	-33	44	-27
12	0	0	253	-272	253	-314
14	0	0	191	+199	218	+229
16	0	0	78	+80	84	+81
18	0	0	136	+134	147	+145
20	0	0	80	-74	82	-92
22	0	0	65	+75	74	+89
24	0	0	94	+107	160	+170
26	0	0	68	-80	127	-123
28	0	0	6	-13	<7	0
1	1	0	7	+2	—	+1
3	1	0	11	-4	12	-4
5	1	0	179	+200	167	+210
7	1	0	167	-164	180	-170
9	1	0	132	+111	132	+121
11	1	0	107	-93	100	-99
13	1	0	60	+47	47	+47
15	1	0	30	-26	23	-33
17	1	0	60	-53	74	-71
19	1	0	116	+106	141	+138
21	1	0	58	-51	77	-77
23	1	0	61	+53	71	+79
25	1	0	31	-32	41	-44
27	1	0	25	+32	38	+52
29	1	0	<2	+7	<4	-2
0	2	0	86	-119	—	-120
2	2	0	72	-66	—	-65
4	2	0	159	+190	158	+197
6	2	0	41	-44	40	-44
8	2	0	208	-231	207	-235
10	2	0	45	-42	47	-41
12	2	0	183	+186	182	+201
14	2	0	68	-69	77	-83
16	2	0	115	-114	127	-137
18	2	0	<7	+17	<12	+20
20	2	0	94	+91	100	+114
22	2	0	42	-35	55	-44
24	2	0	58	-68	94	-99
26	2	0	24	+25	41	+47
28	2	0	38	+38	65	+64
1	3	0	9	-2	13	+1
3	3	0	13	+11	7	+14
5	3	0	172	-206	172	-213
7	3	0	265	+313	239	+333
9	3	0	42	-26	46	-29
11	3	0	36	+29	22	+19
13	3	0	104	-91	87	-92
15	3	0	53	+49	49	+47
17	3	0	74	+68	99	+89
19	3	0	112	-112	145	-156
21	3	0	34	+29	49	+53
23	3	0	12	-8	13	-10
25	3	0	61	+75	90	+103
27	3	0	34	-43	64	-68
29	3	0	<2	+1	<3	-5
0	4	0	61	+54	57	+54
2	4	0	169	+189	160	+195
4	4	0	245	-337	224	-346
6	4	0	53	+43	41	+41
8	4	0	109	+109	114	+120
10	4	0	173	-178	187	-198
12	4	0	20	+23	32	+28
14	4	0	121	-113	124	-139
16	4	0	181	+186	195	+222
18	4	0	102	-96	114	-117
20	4	0	17	-17	32	-28
22	4	0	27	+21	42	+37
24	4	0	<7	+13	<12	+10
26	4	0	19	+16	34	+39
28	4	0	84	-95	164	-164
1	5	0	163	-193	178	-196
3	5	0	150	+165	161	+179
5	5	0	24	+20	19	+20
7	5	0	81	-74	84	-86
9	5	0	206	-217	212	-237
11	5	0	126	+132	133	+152
13	5	0	43	+31	45	+32
15	5	0	133	-126	150	-146
17	5	0	<7	-6	<13	-5
19	5	0	34	+27	47	+45
21	5	0	72	+63	87	+85
23	5	0	93	-104	146	-157
25	5	0	17	-15	15	-11
27	5	0	20	+22	45	+38
0	6	0	9	-9	8	-8
2	6	0	69	-79	72	-84
4	6	0	89	+83	80	+77
6	6	0	12	-5	<8	+5
8	6	0	27	-25	29	-39
10	6	0	69	+60	73	+70
12	6	0	55	+53	48	+47
14	6	0	55	+53	60	+71
16	6	0	117	-110	138	-129
18	6	0	57	+44	46	+44
20	6	0	<7	+1	<13	+12
22	6	0	<7	-13	21	-25
24	6	0	19	-20	<10	-17
26	6	0	22	+21	16	+8
28	6	0	20	+20	52	+44
1	7	0	152	+165	181	+179
3	7	0	221	-297	252	-323
5	7	0	78	+73	90	+78
7	7	0	30	-22	26	-25
9	7	0	220	+252	227	+278
11	7	0	185	-205	206	-233
13	7	0	<7	-8	<13	-20
15	7	0	92	+96	141	+142
17	7	0	59	+41	27	+32
19	7	0	37	-35	37	-33
21	7	0	108	-116	164	-168
23	7	0	105	+119	177	+183
25	7	0	24	-28	37	-47
27	7	0	18	-22	52	-51
0	8	0	107	+99	105	+106
2	8	0	190	-203	199	-215
4	8	0	69	+67	81	+79
6	8	0	17	-11	14	-17
8	8	0	14	+14	17	+6
10	8	0	120	+111	144	+139
12	8	0	82	-67	94	-93
14	8	0	139	+149	160	+176
16	8	0	158	-162	198	-201
18	8	0	53	+45	67	+80
20	8	0	39	-43	47	-58
22	8	0	<6	+7	22	-22
24	8	0	25	+22	52	+40
26	8	0	30	-21	52	-43
1	9	0	124	-116	120	-123
3	9	0	49	+44	62	+54
5	9	0	196	+192	208	+209
7	9	0	179	-185	200	-216
9	9	0	47	-40	52	-46
11	9	0	92	+94	103	+106
13	9	0	76	+79	91	+107
15	9	0	85	-91	115	-117
17	9	0	55	-41	54	-46
19	9	0	92	+87	121	+122
21	9	0	<6	-9	15	-9
23	9	0	46	-53	72	-77
25	9	0	38	-39	67	-74
27	9	0	39	+44	70	+89
0	10	0	101	-91	101	-89
2	10	0	17	+19	13	+21
4	10	0	179	-180	201	-206
6	10	0	72	+59	63	+59
8	10	0	101	+108	135	+138
10	10	0	28	+17	14	-10
12	10	0	<7	+7	<13	+14
14	10	0	32	-22	27	-19
16	10	0	40	+28	51	+46
18	10	0	59	-66	78	-83
20	10	0	27	-36	60	-67
22	10	0	31	-22	10	+2
24	10	0	27	+27	33	+20
26	10	0	29	+30	52	+40
1	11	0	79	+79	83	+86
3	11	0	8	-7	<10	-5
5	11	0	156	-166	177	-203
7	11	0	190	+207	229	+246
9	11	0	76	-74	97	-84
11	11	0	<7	+1	<13	+5
13	11	0	75	-73	84	-89
15	11	0	81	+73	88	+86
17	11	0	95	+106	146	+157
19	11	0	107	-108	162	-165
21	11	0	45	+48	79	+69
23	11	0	17	-16	22	-31
25	11	0	45	+45	65	+76
0	12	0	180	-192	235	-248
2	12	0	133	+130	157	+151
4	12	0	34	+27	46	+38
6	12	0	50	+50	53	+51
8	12	0	62	-60	78	-83
10	12	0	43	-36	47	-34
12	12	0	168	+174	225	+229
14	12	0	70	-65	102	-101
16	12	0	<8	-14	28	-19
18	12	0	24	-15	15	-20
20	12	0	76	+80	102	+124
22	12	0	13	+7	<10	-13
24	12	0	55	-55	105	-94
1	13	0	47	-32	50	-45
3	13	0	76	+68	74	+67
5	13	0	27	+29	32	+38
7	13	0	51	-46	50	-46
9	13	0	51	-54	63	-71
11	13	0	44	+29	61	+50
13	13	0	36	+25	23	+25
15	13	0	67	-57	67	-53
17	13	0	44	+31	49	+50
19	13	0	33	+27	46	+40
21	13	0	14	+18	9	+29
23	13	0	38	-37	55	-56
25	13	0	<2	-5	<4	-10
0	14	0	201	+213	268	+273
2	14	0	91	-94	118	-116
4	14	0	68	-60	87	-87
6	14	0	11	+9	18	+21
8	14	0	129	+124	177	+155
10	14	0	35	+32	53	+51
12	14	0	97	-102	156	-160
14	14	0	82	+73	134	+118
16	14	0	<8	+1	<14	+14
18	14	0	34	+20	14	+11
20	14	0	84	-89	117	-122
22	14	0	28	+34	40	+39
24	14	0	40	+56	117	+121
1	15	0	32	+34	42	+40
3	15	0	73	-62	82	-78
5	15	0	116	+107	158	+143
7	15	0	80	-81	126	-120
9	15	0	104	+105	134	+146
11	15	0	86	-83	94	-99
13	15	0	55	+40	52	+43
15	15	0	21	+14	22	+15
17	15	0	41	-29	63	-46
19	15	0	45	+46	98	+96
21	15	0	40	-48	109	-101
23	15	0	66	+62	99	+103
0	16	0	35	+35	46	+33
2	16	0	79	-74	104	-97
4	16	0	135	+127	198	+187
6	16	0	52	-53	82	-75
8	16	0	149	-151	219	-202
10	16	0	<8	-3	14	+3
12	16	0	<8	+9	13	+23
14	16	0	22	+14	25	+25
16	16	0	103	-110	169	-182
18	16	0	51	+51	79	+90
20	16	0	43	+46	90	+73
22	16	0	30	-24	56	-35
1	17	0	20	+22	46	+34
3	17	0	11	-8	15	-20
5	17	0	43	-33	56	-49
7	17	0	<7	-6	<10	+15
9	17	0	<7	-17	<14	-12
11	17	0	52	-45	80	-84
13	17	0	64	-51	69	-48
15	17	0	29	+16	39	+17
17	17	0	<2	+6	8	+18
19	17	0	24	+17	7	-10
21	17	0	33	-20	32	-17
0	18	0	74	+73	91	+90
2	18	0	56	+56	81	+80
4	18	0	107	-102	145	-154
6	18	0	41	+29	46	+33
8	18	0	60	+52	102	+99
10	18	0	58	-60	102	-95
12	18	0	<7	-1	<13	-2
14	18	0	38	-35	57	-69
16	18	0	87	+100	160	+164
18	18	0	52	-43	91	-68
20	18	0	<3	-1	22	-31
1	19	0	78	-77	134	-120
3	19	0	74	+73	137	+126
5	19	0	33	-32	55	-49
7	19	0	53	+51	69	+65
9	19	0	79	-76	129	-129
11	19	0	69	+71	121	+129
13	19	0	<6	+2	<11	0
15	19	0	34	-42	102	-91
17	19	0	16	-14	16	-10
19	19	0	<2	-16	27	-21
0	20	0	41	-35	68	-67
2	20	0	26	+28	52	+53
4	20	0	22	+19	20	+27
6	20	0	22	-11	10	0
8	20	0	30	-36	53	-68
10	20	0	25	-36	55	-53
12	20	0	74	+72	107	+112
14	20	0	51	-49	95	-75
16	20	0	<4	-1	<7	+3
1	21	0	42	+39	84	+82
3	21	0	29	-36	70	-73
5	21	0	14	-8	30	-21
7	21	0	25	+37	60	+65
9	21	0	59	+59	82	+92
11	21	0	51	-46	104	-91
13	21	0	<4	-5	28	-32
15	21	0	22	+22	71	+78
0	22	0	86	+93	145	+150
2	22	0	47	-50	78	-83
4	22	0	17	+22	52	+41
6	22	0	10	-18	20	-28
8	22	0	<6	+6	<10	-6
10	22	0	<5	0	<9	+28
12	22	0	40	-32	78	-74
14	22	0	37	+53	97	+91
1	23	0	42	-38	71	-68
3	23	0	<6	-9	<10	+1
5	23	0	64	+78	162	+151
7	23	0	74	-77	164	-159
9	23	0	27	+22	40	+37
11	23	0	13	+10	22	+13
0	24	0	29	+33	65	+66
2	24	0	17	-14	34	-36
4	24	0	<4	0	13	-6
6	24	0	<4	-2	<6	-5
8	24	0	<3	+3	11	+11
1	25	0	27	+17	39	+40
3	25	0	28	-27	45	-50
0	0	1	31	+43	45	+44
0	1	1	45	-36	49	-39
0	2	1	176	-196	195	-205
0	3	1	371	+454	387	+481
0	4	1	92	-85	103	-106
0	5	1	152	-174	160	-178
0	6	1	73	-81	79	-67
0	7	1	43	+33	47	+36
0	8	1	67	+46	78	+47
0	9	1	151	+155	185	+177
0	10	1	<18	-4	<18	-9
0	11	1	74	-80	99	-91
0	12	1	100	-101	135	-130
0	13	1	69	-60	88	-85
0	14	1	56	+59	85	+80
0	15	1	104	-110	139	-148
0	16	1	53	-44	71	-70
0	17	1	115	+128	177	+166
0	18	1	<20	-1	22	-20
0	19	1	54	-53	74	-68
0	20	1	68	-57	86	-80
0	21	1	17	-10	45	-20
0	22	1	<15	+4	<15	-8
0	23	1	24	+26	54	+55
0	24	1	14	+1	19	+6
0	0	2	170	-180	206	-210
0	1	2	63	-62	62	-65
0	2	2	117	+114	135	+127
0	3	2	118	+131	151	+151
0	4	2	48	+51	56	+52
0	5	2	158	-163	201	-206
0	6	2	86	+84	107	+117
0	7	2	61	-56	77	-73
0	8	2	53	-42	60	-56
0	9	2	81	+76	123	+122
0	10	2	47	+49	58	+63
0	11	2	<20	-16	32	-38
0	12	2	124	+123	171	+169
0	13	2	30	+26	43	+36
0	14	2	75	-80	107	-92
0	15	2	69	-66	95	-80
0	16	2	27	+20	38	+21
0	17	2	110	+112	183	+171
0	18	2	29	+21	42	+23
0	19	2	28	-32	57	-54
0	20	2	25	+25	51	+58
0	21	2	14	-11	45	-38
0	22	2	21	-16	35	-28
0	23	2	13	-10	29	-7
0	0	3	178	-176	264	-266
0	1	3	<20	-4	<20	0
0	2	3	77	+79	107	+119
0	3	3	31	-22	40	-35
0	4	3	<20	0	29	+23
0	5	3	63	+56	70	+73
0	6	3	<21	-15	42	-42
0	7	3	<21	+13	21	+18
0	8	3	72	-76	113	-121
0	9	3	30	-22	43	-12
0	10	3	38	-44	60	-65
0	11	3	<23	+7	<22	-15
0	12	3	77	+70	140	+120
0	13	3	<22	+1	<21	-2
0	14	3	85	-91	170	-168
0	15	3	<19	-11	<19	-4
0	16	3	<18	+8	<18	+8
0	17	3	19	-19	39	-40

Table 3 (*cont.*)

			25°C		−150°C	
h	k	l	Fo	Fc	Fo	Fc
0	18	3	16	-18	27	-16
0	19	3	<11	+7	16	+5
0	20	3	41	+44	65	+77
0	0	4	<20	-14	34	-33
0	1	4	<20	+9	<20	+8
0	2	4	<20	+3	<20	+8
0	3	4	58	-59	109	-118
0	4	4	<20	-4	<20	-1
0	5	4	46	+57	100	+121
0	6	4	24	+33	48	+49
0	7	4	19	+18	44	+39
0	8	4	<18	+19	28	+44
0	9	4	46	-48	103	-108
0	10	4	<17	-2	35	+45
0	11	4	19	+20	48	+41
0	12	4	26	+34	59	+81
0	13	4	<14	-5	<13	+1
0	14	4	<12	-1	<12	-20
0	15	4	26	+26	48	+56
0	0	5	28	+27	60	+82
0	1	5	<10	+3	15	+6
0	2	5	12	-18	30	-46
0	3	5	19	-28	39	-74
0	4	5	—	-18	—	-50
0	5	5	—	+4	—	+14
2	0	1	40	-54	56	-60
4	0	1	32	-33	37	-36
6	0	1	18	+14	26	+20
8	0	1	118	+128	131	+130
10	0	1	86	+74	86	+84
12	0	1	156	-135	167	-156
14	0	1	58	+58	81	+72
16	0	1	<20	+5	<12	-1
18	0	1	<21	+3	<12	0
20	0	1	65	-59	74	-71
22	0	1	<21	+19	15	+19
24	0	1	46	+43	68	+66
26	0	1	15	-9	30	-20
28	0	1	<10	+8	<5	+15
2	0	2	97	+97	94	+94
4	0	2	<16	-15	<10	-5
6	0	2	29	+27	30	+31
8	0	2	59	-55	60	-61
10	0	2	26	-36	35	-35
12	0	2	138	+147	167	+175
14	0	2	76	-66	97	-77
16	0	2	<22	-16	28	-20
18	0	2	<22	-25	33	-30
20	0	2	52	+46	63	+62
22	0	2	<19	-17	24	-22
24	0	2	39	-44	66	-63
26	0	2	32	+41	63	+58
2	0	3	67	+72	114	+99
4	0	3	50	+52	66	+65
6	0	3	20	+13	12	+11
8	0	3	80	-79	104	-95
10	0	3	30	-18	59	-32
12	0	3	143	+148	187	+201
14	0	3	92	-98	133	-133
16	0	3	20	+25	28	+29
18	0	3	37	-38	40	-44
20	0	3	56	+60	89	+88
22	0	3	18	-25	21	-21
2	0	4	24	+6	39	+23
4	0	4	22	+20	22	+25
6	0	4	<20	+12	<12	+18
8	0	4	16	-13	13	-12
10	0	4	<17	-8	<11	+19
12	0	4	17	+25	32	+47
14	0	4	22	+19	13	+21
16	0	4	22	-29	26	-38
18	0	4	5	+9	—	+22
2	0	5	15	-21	26	-41
4	0	5	<9	+9	—	+10

taking into account the effect of the non-parallel vibratons of atoms (Grenville-Wells, 1956). As suggested by Jeffrey & Cruickshank (1953), to reduce the effect of bond anisotropy, only high-angle reflexions having $\sin\theta > 0.60$ were used in their refinement. The final thermal-parameter values of the bromine atoms are listed in Table 4.

Table 4. *Thermal parameters* (Å^2)

	Br		Br′	
Projection	*P*	*Q*	*P*	*Q*
(001)	3·00	1·70	3·10	1·60
(100)	4·28	2·40	4·85	2·42
(010)	2·94	2·56	3·21	2·40

Estimation of accuracy

The standard deviations in atomic coordinates and interatomic distances were estimated (Lipson & Cochran, 1953) assuming $\sigma(F) = 0.094|F|$ for *hk*0 and $0.102\,|F|$ for 0*kl* reflexions and $p = 5$ Å^{-2}. Standard deviations in bond angles were estimated by the method of Darlow (1960). Calculations have been carried out for results at room temperature only. The standard deviations of the atomic parameters at low temperature are, however, expected to be smaller than those at room temperature since the value of *p* increases at low temperature. Molecular and crystal structures have, therefore, been discussed on the basis of the results at −150°C.

Table 5. *Intramolecular distances and bond angles**

Bond	25°C	−150°C
Br–Br$^{(m)}$	5·728 ± 0·011 Å	5·730 Å
C(2)–Br	1·901 ± 0·040	1·895
C(1)–N	1·311 ± 0·060	1·403
C(1)–C(2)	1·397 ± 0·054	1·404
C(2)–C(3)	1·480 ± 0·056	1·416
C(3)–C(4)	1·389 ± 0·054	1·413
C(4)–C(5)	1·472 ± 0·065	1·435
C(5)–O	1·274 ± 0·047	1·275
Br′–Br′$^{(2)}$	5·729 ± 0·022	5·723
C(2)′–Br′	1·893 ± 0·040	1·852
C(1′)–N′	1·435 ± 0·033	1·372
C(1′)–C(2′)	1·372 ± 0·042	1·431
C(2′)–C(3′)	1·443 ± 0·056	1·403
C(3′)–C(4′)	1·407 ± 0·042	1·429
C(4′)–C(5′)	1·450 ± 0·035	1·419
C(5′)–O′	1·272 ± 0·033	1·300

Angle	25°C	−150°C
N–C(1)–C(2)	121·9 ± 2·1°	120·9°
C(1)–C(2)–Br	120·2 ± 2·5	120·3
Br–C(2)–C(3)	115·9 ± 1·9	117·7
C(1)–C(2)–C(3)	123·8 ± 2·7	121·9
C(2)–C(3)–C(4)	115·1 ± 2·5	118·9
C(3)–C(4)–C(5)	117·1 ± 1·9	119·8
C(3)–C(4)–C(3)$^{(m)}$	125·6 ± 3·9	120·4
C(2)–C(1)–C(2)$^{(m)}$	115·9 ± 3·8	117·8
C(4)–C(5)–O	118·1 ± 2·0	119·6
O–C(5)–O$^{(m)}$	123·7 ± 4·1	120·7
N′–C(1′)–C(2′)	119·7 ± 1·5	120·4
C(1′)–C(2′)–Br′	122·3 ± 1·8	121·0
Br′–C(2′)–C(3′)	115·4 ± 2·3	118·4
C(1′)–C(2′)–C(3′)	119·9 ± 2·8	120·4
C(2′)–C(3′)–C(4′)	115·1 ± 2·7	120·7
C(3′)–C(4′)–C(5′)	117·4 ± 1·4	120·7
C(3′)–C(4′)–C(3′)$^{(2)}$	125·2 ± 2·8	118·5
C(2′)–C(1′)–C(2′)$^{(2)}$	120·7 ± 2·9	119·1
C(4′)–C(5′)–O′	121·2 ± 1·4	120·5
O′–C(5′)–O′$^{(2)}$	117·6 ± 2·7	119·1

* See Fig. 7 for different bonds and angles.

Table 6. *Equations of molecular planes*

	Equations		Deviations
Molecule I	$0.514y + 0.858z - 3.427 = 0$ at	25°C	0·003 to 0·054 Å
	$0.502y + 0.865z - 3.369 = 0$ at	−150°C	0·000 to 0·048
Molecule II	$0.443y - 0.897z + 1.766 = 0$ at	25°C	0·000 to 0·054
	$0.443y - 0.897z + 1.739 = 0$ at	−150°C	0·000 to 0·046

Description of the structure and discussion

Molecular structure

The bond lengths and angles in the two different molecules are listed in Table 5. The equations of the molecular planes, which were obtained by the method suggested by Schomaker, Waser, Marsh & Bergman (1959), and the minimum and maximum deviations of atoms from these planes are given in Table 6.

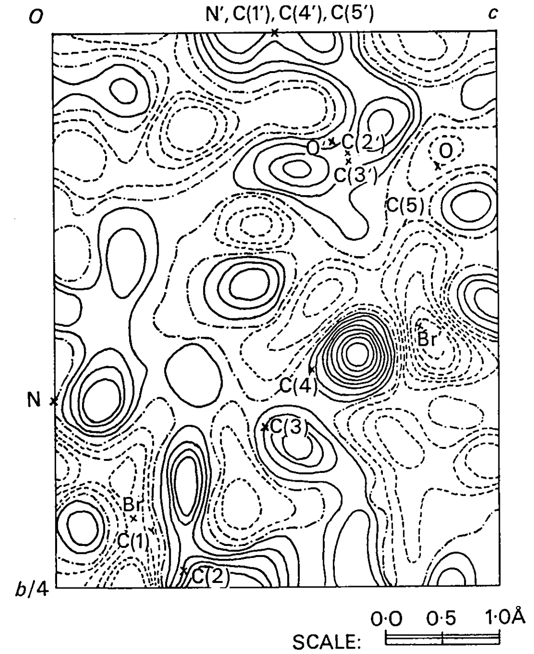


Fig. 3. First (100) difference map at room temperature. Contour interval 1 e.Å^{-2}. Density everywhere doubled owing to mirror planes parallel to (100). Full lines: positive; chain lines: zero; broken lines: negative.

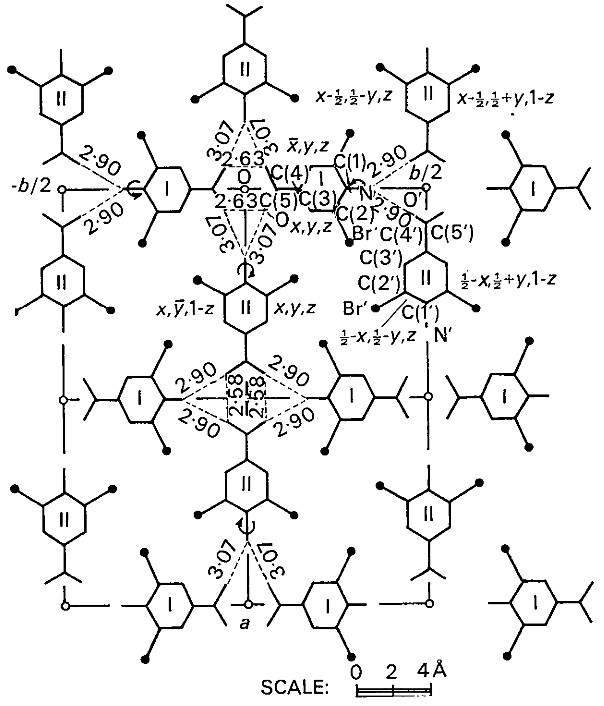


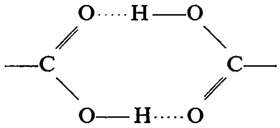
Fig. 4. Structure projected on (001) showing the intermolecular hydrogen bondings and the mode of vibrations of the dimers.

Within the accuracy of measurement both the molecules are planar and the corresponding bond lengths in the two crystallographically independent molecules have reasonable values at both temperatures. At room temperature, the discrepancy in the C–N bond lengths of the two molecules is quite large, but this does not appear to be significant as the two lengths have become almost equal (1·403 Å and 1·372 Å) at −150 °C. On account of the rather large uncertainties in the observed bond lengths and angles, a critical discussion of the molecular structure is not possible.

Crystal structure

The projections of the structure on the (001), (010) and (100) planes are shown in Figs. 4, 5 and 6 respectively. The short intermolecular distances (less than 4·0 Å) are listed in Table 7. The principal intermolecular contacts are between the oxygen atoms of the carboxyl groups of neighbouring molecules forming dimers, the mean distance between the oxygen atoms being 2·56 Å. These dimers are packed in the unit cell in such a way that their axes are alternately along and across the *a* axis. This explains the small values of the thermal expansion coefficients along the *a* and *b* axes. The other possibilities of hydrogen bonding are also being utilized. The nitrogen atom $N(0,y,z)$ of a molecule of type I is linked with two oxygen atoms $O'(\frac{1}{2}-x, \frac{1}{2}-y, z-1$ and $x-\frac{1}{2}, \frac{1}{2}-y, z-1)$ of molecules of type II by hydrogen bonds of length 2·840 Å, and is linked with two oxygen atoms $O'(\frac{1}{2}-x, \frac{1}{2}-y, z$ and $x-\frac{1}{2}, \frac{1}{2}-y, z)$ by van der Waals bonds of length 3·468 Å. Similarly, the nitrogen atom $N'(x, 0, \frac{1}{2})$ of a molecule of type II is linked with two oxygen atoms $O(x, y, z$ and $x, \bar{y}, 1-z)$ of molecules of type I by weak hydrogen bonds of length 3·028 Å, and is linked with two oxygen atoms $O(x, y, z-1$ and $x, \bar{y}, 2-z)$ by van der Waals bonds of length 3·751 Å. Along the *c* axis the molecules are held together by van der Waals bonds between the bromine atoms $Br(x, y, z)$ and $Br(x, y, z+1)$ of length $3{\cdot}88 \pm 0{\cdot}01$ Å.

The OH $\cdots$ O bonds between the molecules of a dimer are symmetrical since the two oxygen atoms are related either by mirror symmetry or by a twofold axis of rotation. Donohue (1952) has calculated the probable O–O distance for a symmetrical OH $\cdots$ O bond to be 2·30 Å from theoretical considerations. In the present case the average distance of 2·56 Å between these oxygen atoms, which is significantly different from the value of 2·30 Å, suggests that the hydrogen atom should be nearer to one of the oxygen atoms as shown below:



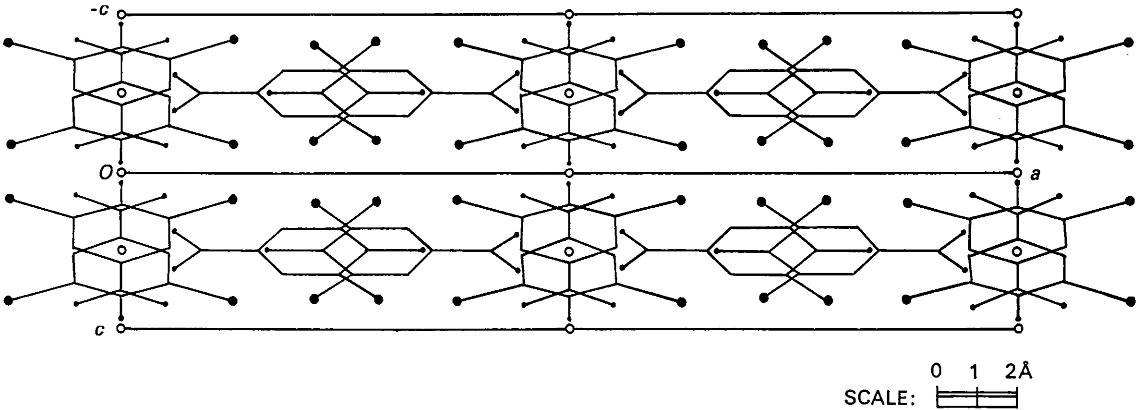


Fig. 5. Structure projected on (010).

This is, however, incompatible with the space group *Pman* and with the atomic arrangement in this case. Thus either the hydrogen atoms are located on special positions (on mirror planes and on twofold axes of rotation), or else the hydrogen atoms are disordered, with one half hydrogen, on the average, on each side. In view of the O–O distances the statistical distribution of the hydrogen atoms is most likely.

Anisotropic thermal motion

From the knowledge of the values of P and Q for all the three projections the equations of ellipsoids of constant temperature factor in reciprocal space with respect to the principal axes were obtained for both the bromine atoms. In terms of reciprocal coordinates (say x, y, z), the expression for the temperature factor can be written

$$\exp\{-(a_{11}x^2+a_{22}y^2+a_{33}z^2+2a_{12}xy+2a_{23}yz+2a_{13}xz)\}\,.$$

This reduces to $\exp\{-(a_{11}x^2+a_{22}y^2+2a_{12}xy)\}$ for $hk0$ reflexions, with similar terms for $h0l$ and $0kl$ reflexions. Thus

$$(P\cos^2\varphi+Q\sin^2\varphi)\sin^2\theta/\lambda^2\equiv a_{11}x^2+a_{22}y^2+2a_{12}xy\,.$$

The values of the terms a_{11}, a_{22} and a_{33} were obtained from two projections. Different values of a_{ij}'s for ellipsoids of constant temperature factor, $\exp(-0\cdot3)$, are listed in Table 8.

The values of a_{11} and a_{33} obtained from different projections are not in good agreement for either of the bromine atoms. This is probably due to the small number of reflexions (34 only) used in refining the values of P and Q from the $h0l$ reflexions. Therefore, except for taking the value of a_{13}, the values of a_{11} and a_{33} as obtained from $h0l$ reflexions were neglected. Taking the mean of the two values for a_{22}, the equations of ellipsoids of constant temperature factor, $\exp(-0\cdot3)$, for the bromine atoms Br and Br′ are respectively:

$$0\cdot687x^2+0\cdot947y^2+1\cdot400z^2-0\cdot346xy+0\cdot450yz+0\cdot074xz=1,\text{ and}$$

$$0\cdot773x^2+0\cdot940y^2+1\cdot557z^2+0\cdot520xy-0\cdot673yz+0\cdot263xz=1\,.$$

These equations were transformed to the equations with respect to the principal axes of the ellipsoids and the direction cosines of the directions of maximum, medium and minimum vibrations were obtained. The mean-square and root-mean-square amplitudes of vib-

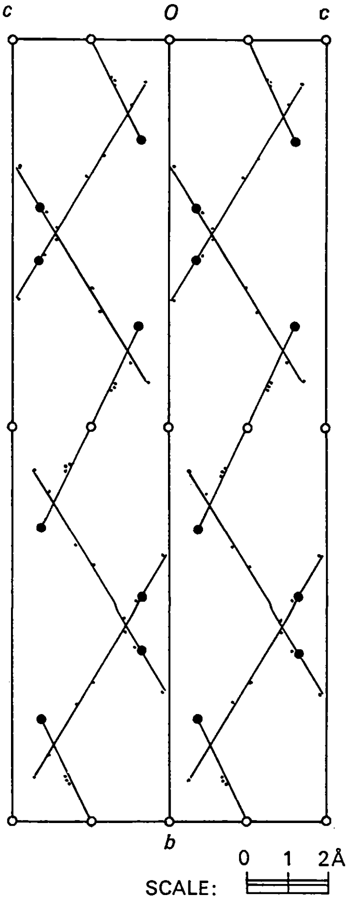


Fig. 6. Structure projected on (100).

ration along the principal axes of ellipsoids and the angles α, β, γ, δ and η, defined as follows, were calculated and are given in Tables 9 and 10 respectively:

α – the angle between the molecular plane and the direction of maximum vibration; β – the angle between the molecular plane and the direction of medium vibration; γ – the angle between the C–Br bond and the direction of medium vibration; δ – the angle between the C–Br bond and the direction of minimum vibration; η – the angle between the line joining the centre of the dimer to the corresponding bromine atom and the direction of medium vibration.

The angle α is nearly 90° for both the molecules, suggesting that the displacement of the bromine atoms is maximum approximately along the normal to the molecular planes, that is, roughly along the c axis. This is expected from crystal packing as well, since the binding forces along the c axis are of the weak van der Waals type. The oscillation of the dimers along their long axes, as shown by circular arrows in Fig. 4, will produce large displacements of the bromine atoms perpendicular to the molecular planes and, in fact, this mode of oscillation appears to be quite pronounced. This will not much disturb the NH · · · O hydrogen bonds between the two types of molecule since the nitrogen atoms lie on the axes of oscillation of the dimers and do not get displaced during oscillation; the oxygen atoms lie close to these axes and their positions also do not change much. For the bromine atom Br of molecule I the root-mean-square amplitude of vibration along the maximum vibration direction, that is, along the normal to the molecular plane, is 0·225 Å, and appears to be significantly less than that for the bromine atom Br′ of molecule II, 0·248 Å. This is expected in view of the difference in the N–O intermolecular distances in the two cases. The dimers of the

Table 7. *Short intermolecular contacts*

		25°C	−150°C
$O(x, y, z)$	$-O(x, \bar{y}, 2-z)$	$= 2{\cdot}627 \pm 0{\cdot}069$ Å	2·563 Å
$O(\bar{x}, y, z)$	$-O(\bar{x}, \bar{y}, 2-z)$	$= 2{\cdot}627 \pm 0{\cdot}069$	2·563
$O'(\frac{1}{2}-x, \frac{1}{2}-y, z)$	$-O'(x-\frac{1}{2}, \frac{1}{2}-y, z)$	$= 2{\cdot}582 \pm 0{\cdot}038$	2·560
$O'(\frac{1}{2}-x, y-\frac{1}{2}, 1-z)$	$-O'(x-\frac{1}{2}, y-\frac{1}{2}, 1-z)$	$= 2{\cdot}582 \pm 0{\cdot}038$	2·560
$N(0, y, z)$	$-O'(\frac{1}{2}-x, \frac{1}{2}-y, z)$	$= 3{\cdot}480 \pm 0{\cdot}043$	3·468
	$-O'(x-\frac{1}{2}, \frac{1}{2}-y, z)$	$= 3{\cdot}480 \pm 0{\cdot}043$	3·468
	$-O'(\frac{1}{2}-x, \frac{1}{2}-y, z-1)$	$= 2{\cdot}904 \pm 0{\cdot}043$	2·840
	$-O'(x-\frac{1}{2}, \frac{1}{2}-y, z-1)$	$= 2{\cdot}904 \pm 0{\cdot}043$	2·840
$N'(x, 0, \frac{1}{2})$	$-O(x, y, z)$	$= 3{\cdot}071 \pm 0{\cdot}032$	3·028
	$-O(x, \bar{y}, 1-z)$	$= 3{\cdot}071 \pm 0{\cdot}032$	3·028
	$-O(x, y, z-1)$	$= 3{\cdot}784 \pm 0{\cdot}032$	3·751
	$-O(x, \bar{y}, 2-z)$	$= 3{\cdot}784 \pm 0{\cdot}032$	3·751
$Br(x, y, z)$	$-Br'(x, y, z-1)$	$= 3{\cdot}799 \pm 0{\cdot}010$	3·775
	$-C(3')(\frac{1}{2}-x, \frac{1}{2}-y, z)$	$= 3{\cdot}837 \pm 0{\cdot}040$	3·845
	$-C(3')(\frac{1}{2}-x, \frac{1}{2}-y, z-1)$	$= 3{\cdot}941 \pm 0{\cdot}040$	3·936
$Br'(x, y, z)$	$-O(x, y, z)$	$= 4{\cdot}003 \pm 0{\cdot}031$	3·989
	$-C(3)(x, y, z)$	$= 3{\cdot}950 \pm 0{\cdot}040$	3·930

Table 8. *Constants of thermal ellipsoids*

Atom	Projection	a_{11}	a_{22}	a_{33}	$2a_{12}$	$2a_{23}$	$2a_{13}$
Br	(001)	0·206	0·287		−0·104		
	(010)	0·270		0·302			0·022
	(100)		0·280	0·420		0·135	
Br′	(001)	0·232	0·260		0·156		
	(010)	0·279		0·311			0·079
	(100)		0·303	0·467		−0·202	

Table 9. *Mean-square and root-mean-square amplitudes of vibrations*

	Maximum		Minimum		Medium	
Atom	$\overline{u^2}$	$(\overline{u^2})^{\frac{1}{2}}$	$\overline{u^2}$	$(\overline{u^2})^{\frac{1}{2}}$	$\overline{u^2}$	$(\overline{u^2})^{\frac{1}{2}}$
Br	0·054Å^2	0·225Å	0·021Å^2	0·145Å	0·035Å^2	0·187Å
Br′	0·062	0·248	0·018	0·133	0·039	0·197

Table 10. *Values of the angles* $\alpha, \beta, \gamma, \delta$ *&* η

Atom	α	β	γ	δ	η
Br	81·6°	5·5°	86·6°	3·4°	56·4°
Br′	88·8°	2·9°	72·9°	17·1°	70·3°

molecules of type I are held by stronger hydrogen bonds of length 2·90 Å at their ends, and therefore their oscillation is more restricted than that of the dimers of molecules of type II which are held by weaker bonds of length 3·07 Å at their ends.

The angle β is nearly zero for both the molecules. This suggests that the amplitudes in the medium vibration directions are due to the librational motion of the molecules about axes normal to their planes. Further, as is clear from the (001) electron-density map, the values of the angles η suggest that the axes of libration pass through the molecular centres and not through the centres of the dimers. Values of the angles η should have been nearly 90° if the dimers had been librating about axes normal to their planes and passing through their centres. In Fig. 7 the angles γ and η for both the molecules I and II are shown in the molecular plane.

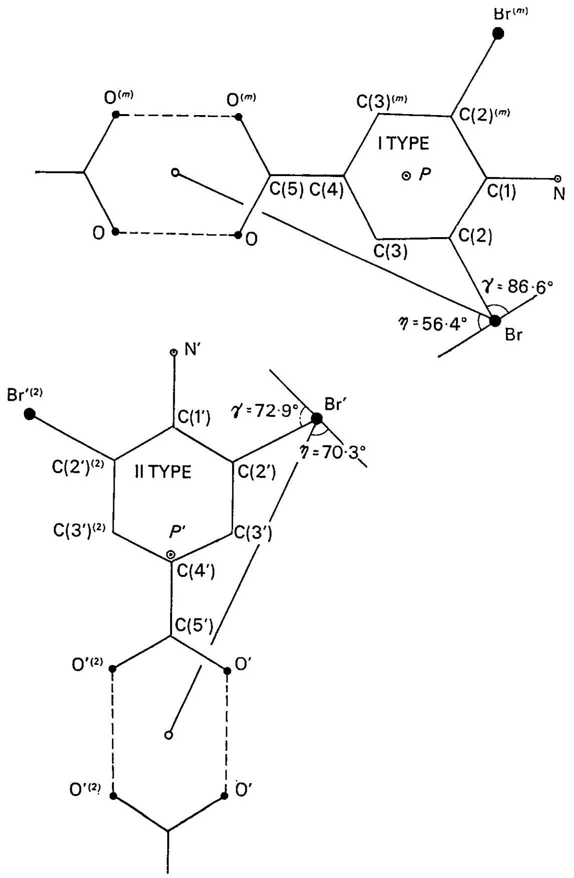


Fig. 7. Molecules showing the angles γ and η in the molecular planes. Axes of libration normal to the molecular planes pass through points P and P'. For bond lengths and angles see Table 5.

The angle γ is about 90° for the atom Br, showing that for molecule I the axis of libration passes near the molecular centre. For the bromine atom Br' the corresponding angle, 72·9°, is quite different, suggesting that for molecule II the axis of libration is away from the molecular centre. The reason for this is probably as follows:

On one side molecule I is bonded to another molecule of type I by OH · · · O hydrogen bonds of length 2·63 Å and to molecules of type II by weak NH · · · O hydrogen bonds of length 3·07 Å, whereas on the other side it is bonded to molecules of type II by NH · · · O hydrogen bonds of length 2·90 Å. Owing to these strong bonds on either side the axis of libration passes near the molecular centre. Molecule II is, however, held by strong OH · · · O hydrogen bonds of length 2·58 Å and NH · · · O hydrogen bonds of length 2·90 Å on one side and by weak NH · · · O bonds of length 3·07 Å on the other. Therefore the axis of libration moves closer to the side which is held more firmly. The approximate positions of the points, P, through which the axes of libration are expected to pass have been marked for both the molecules in Fig. 7.

I am much indebted to Professor K. Banerjee, Director, Indian Association for the Cultivation of Science, Calcutta for his valuable guidance and encouragement throughout the progress of the work. My thanks are due to Dr R. K. Sen and to my brother Dr L. M. Pant for many helpful suggestions and discussions. Finally I wish to express my thanks to the Council of Scientific and Industrial Research, Government of India, for the award of a Senior Research Fellowship.

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