Crystal Structure of m-Methylbenzamide

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The crystal structure of *m*-methylbenzamide, C_8H_9NO, has been investigated as a part of a study of the crystal structure of carboxyamide. The main interests of this study have been to determine the molecular configuration and to learn the features of the hydrogen bonding in the crystal.

In recent studies, the molecular configurations of salicylic acid(1), benzoic acid(2), nicotinic acid(3) and α-pyrazinamide(4) have been shown to be approximately planar, while nicotinamide(5) and benzamide(6) are non-planar, with an angle of 25∼26° between the amide group and the six-membered ring plane.

It is interesting to compare the crystal structure of *m*-methylbenzamide with the abovementioned crystal structures.

Experimental

m-Methylbenzamide crystals were obtained from an alcohol-water solution*[4]. They are colorless plates, with the a axis normal to the plates, and have a cleavage plane parallel to (1 0 0).

The crystallographic data obtained were as follows:

$a=8.93\pm0.03\,\text{Å}$ $b=16.02\pm0.03\,\text{Å}$

$c=5.12\pm0.02\,\text{Å}$ $\beta=95.0\pm0.6°$

Absent spectra: $(h0l)$ when h is odd
$(0k0)$ when k is odd

Space group: $P2_1/a$

Four molecules per unit cell

Volume of the unit cell: 729.6 Å^3

Density (flotation): $1.22_5\,\text{g. cm}^{-3}$
(calculation): $1.23_0\,\text{g. cm}^{-3}$

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1) W. Cochran, *Acta Cryst.*, **6**, 260 (1953).

2) G. A. Sim, J. M. Robertson and T. H. Goodwin, ibid., **8**, 157 (1955).

3) W. B. Wright and G. S. D. King, ibid., **6**, 305 (1953).

4) Y. Takaki, Y. Sasada and T. Watanabé, ibid., **13**, 693 (1960).

5) W. B. Wright and G. S. D. King, ibid., **7**, 285 (1954).

6) B. R. Penfold and J. C. B. White, ibid., **12**, 130 (1959).

*[4] The crystal used was supplied by the Sankyo Co., Ltd.

TABLE I. OBSERVED AND CALCULATED STRUCTURE FACTORS

h k l	F_o	F_c	*h k l*	F_o	F_c	*h k l*	F_o	F_c	*h k l*	F_o	F_c
0 2 0	8.53	−8.39	3 4 0	6.91	−7.19	6 0 0	6.66	−7.48	9 6 0	1.56	−1.64
4	9.61	−9.15	5	2.77	2.55	1	3.01	−2.46	7	1.05	1.16
6	14.02	−13.58	6	3.18	2.86	2	1.12	0.92	8	1.10	0.70
8	0.24	−0.59	7	5.57	−5.86	3	1.35	1.45	9	0.36	0.50
10	2.38	2.02	8	2.35	2.50	4	0.61	0.87	10	1.34	−1.67
12	2.32	1.86	9	0.20	0.08	5	1.24	1.07	11	0.59	−0.52
14	1.66	1.47	10	3.34	3.17	6	3.23	3.58	12	0.59	0.97
16	0.34	0.43	11	1.58	1.33	7	3.39	−3.21			
18	0.84	−0.62	12	3.99	−4.34	8	1.75	−1.78	10 0 0	0.37	0.27
20	1.04	−0.81	13	0.33	−0.46	9	0.67	0.50	1	0.37	0.17
			14	3.61	3.56	10	1.65	0.89	2	0.91	0.69
1 1 0	5.74	−5.87	15	0.76	0.82	11	0.39	0.20	3	1.00	1.28
2	2.24	1.65	16	0.92	−1.21	12	1.52	−1.61	4	1.42	−1.41
3	1.08	−0.88	17	0.42	0.05	13	1.27	1.16	5	0.35	−0.51
4	6.03	−6.41	18	0.72	−0.34	14	0.39	0.52	6	0.29	0.71
5	4.18	3.69	19	0.28	0.10	15	0.37	0.45	7	0.32	−0.20
6	5.53	−5.20	20	0.20	−0.87	16	0.32	−0.16	8	0.29	0.54
7	4.93	4.96				17	0.25	−0.08	9	0.55	0.61
8	7.26	7.09	4 0 0	4.44	−4.87				10	0.18	−0.79
9	0.79	−0.71	1	6.11	6.68	7 1 0	0.37	0.47			
10	0.45	−0.47	2	2.45	−1.99	2	1.44	1.46	11 1 0	0.28	−0.16
11	3.08	−3.14	3	4.71	4.73	3	0.65	0.60	2	0.51	1.08
12	0.77	0.87	4	2.88	2.98	4	2.89	2.92	3	0.26	−0.56
13	2.13	1.84	5	3.26	3.39	5	0.86	−1.05	4	0.62	−0.85
14	0.96	−0.81	6	0.31	0.46	6	0.39	0.41	5	1.00	1.45
15	1.55	−1.37	7	2.12	−1.89	7	0.39	0.18			
16	0.37	−0.27	8	1.36	1.23	8	2.40	−2.19	0 2 0	8.35	−8.37
17	0.37	0.15	9	3.04	−3.29	9	1.77	−1.68	4	8.75	−8.96
18	0.62	0.58	10	0.36	0.47	10	0.37	−0.01	6	14.00	−13.98
19	0.86	−0.59	11	2.24	−2.38	11	2.00	2.66	8	0.25	−0.84
20	1.00	−0.87	12	1.22	0.85	12	0.39	−0.18	10	2.40	1.98
			13	2.75	2.79	13	0.37	0.25	12	2.21	2.13
2 0 0	0.21	0.20	14	2.45	−2.09	14	0.35	−0.21	14	1.49	1.66
1	20.66	20.76	15	0.83	0.83	15	0.85	−0.88	16	0.34	0.41
2	10.84	10.76	16	0.39	0.49	16	0.23	−0.41	18	0.64	−0.84
3	12.05	12.15	17	0.37	0.13				20	1.02	−1.02
4	3.64	−2.84	18	0.32	−0.41	8 0 0	2.20	1.73			
5	5.05	5.21	19	0.29	−0.45	1	0.96	−0.87	0 0 1	20.14	−19.83
6	7.21	−7.17				2	1.23	−1.09	1	6.57	−6.73
7	6.62	−6.35	5 1 0	5.98	5.77	3	1.78	−1.64	2	4.26	4.31
8	0.62	−0.78	2	2.53	1.90	4	0.39	0.38	3	6.32	6.51
9	1.37	−1.77	3	1.88	1.89	5	0.39	0.11	4	5.40	5.51
10	1.74	0.98	4	1.65	−1.37	6	0.39	0.63	5	1.33	1.24
11	0.50	−0.96	5	6.82	−7.07	7	2.20	2.36	6	3.26	2.93
12	3.30	3.19	6	2.11	2.17	8	0.37	−0.02	7	5.17	−4.60
13	1.62	−1.57	7	1.67	−1.73	9	2.39	−2.49	8	5.07	−4.72
14	0.55	0.95	8	0.92	−0.57	10	1.02	−1.15	9	1.52	−1.50
15	1.94	1.91	9	1.63	1.46	11	0.84	0.65	10	0.30	−0.51
16	2.15	−1.97	10	0.39	−0.03	12	0.36	−0.80	11	1.04	−1.61
17	0.37	0.26	11	1.17	0.91	13	0.44	0.39	12	2.18	1.68
18	0.88	−0.60	12	0.39	0.58	14	0.72	0.70	13	3.63	3.18
19	0.33	0.13	13	1.66	−1.10				14	1.35	−1.03
20	0.74	0.56	14	1.71	−2.23	9 1 0	0.37	−0.10	15	2.93	3.28
			15	1.72	1.50	2	0.37	0.06	16	0.35	0.50
3 1 0	3.71	3.93	16	0.84	0.71	3	0.37	−0.54	17	1.31	−1.09
2	10.34	−10.54	17	0.33	0.17	4	1.84	2.14	18	0.34	−0.09
3	1.80	−0.93	18	0.26	0.40	5	0.39	−0.32	19	2.58	−1.97

Table I (Continued)

$h\ k\ l$	F_o	F_c	$h\ k\ l$	F_o	F_c	$h\ k\ l$	F_o	F_c	$h\ k\ l$	F_o	F_c
0 20 1	0.22	− 0.13	0 16 3	0.92	− 0.56	0 2 6	1.23	0.84	$\bar{4}$ 0 2	15.49	−14.96
			17	0.28	0.03	3	0.30	− 0.10	3	2.45	2.23
0 0 2	8.80	− 9.15	18	0.82	− 0.61	4	1.35	− 0.91	4	0.35	1.37
1	4.98	− 4.18				5	0.27	0.35	5	0.35	− 0.19
2	4.85	− 4.28	0 0 4	1.68	1.61	6	0.81	0.86	6	1.99	1.36
3	2.58	2.30	1	2.98	2.47	7	0.22	− 0.21			
4	1.57	− 1.05	2	2.36	1.59	8	0.17	0.25	6 0 0	6.66	− 7.50
5	3.17	− 2.84	3	1.08	0.80				1	1.35	− 2.15
6	7.81	7.42	4	0.82	− 0.09	0 0 1	20.12	−19.91	2	1.19	1.71
7	0.62	− 0.33	5	1.26	1.19	2	8.80	− 8.89	3	1.93	1.82
8	4.95	4.61	6	2.08	− 2.00	3	1.10	1.12	4	0.38	0.16
9	0.69	0.77	7	1.23	− 0.58	4	1.68	1.35	5	1.59	− 1.49
10	0.57	− 0.88	8	1.54	− 1.79	5	1.76	2.10			
11	4.15	4.02	9	3.08	− 3.29	6	1.94	− 1.69	$\bar{6}$ 0 1	4.70	7.13
12	4.25	− 4.08	10	0.35	− 0.04				2	3.17	2.64
13	2.96	− 2.96	11	1.74	1.75	2 0 0	0.20	0.21	3	1.57	− 2.94
14	0.50	− 0.42	12	1.21	1.50	1	5.55	− 4.84	4	1.20	− 1.07
15	1.41	− 1.33	13	1.08	0.83	2	1.00	1.45	5	1.19	1.09
16	0.35	− 0.51	14	0.55	0.36	3	2.71	1.93			
17	0.34	0.29	15	0.48	− 0.37	4	0.35	− 0.45	8 0 0	1.87	1.75
18	1.18	1.05	16	0.34	0.09	5	1.28	− 0.55	1	0.71	− 0.73
19	1.10	0.90				6	0.28	− 0.61	2	0.35	0.16
			0 0 5	1.76	2.02				3	0.35	− 0.28
0 0 3	1.10	1.19	1	0.85	− 0.57	$\bar{2}$ 0 1	2.56	− 2.85	4	0.24	− 0.05
1	1.11	1.74	2	3.56	− 3.25	2	1.54	− 0.15			
2	3.86	3.76	3	0.48	0.08	3	4.20	3.72	$\bar{8}$ 0 1	0.70	− 0.26
3	3.55	− 3.56	4	2.16	1.67	4	2.96	1.68	2	0.50	0.57
4	1.85	− 1.72	5	1.93	− 1.90	5	3.95	− 3.45	3	2.57	− 3.71
5	2.52	2.20	6	1.04	0.93	6	0.31	− 0.03	4	1.57	2.96
6	3.33	− 3.23	7	0.49	0.41				5	0.20	0.80
7	1.74	1.52	8	0.48	0.37	4 0 0	4.44	− 4.90			
8	0.33	0.39	9	1.40	1.03	1	2.09	0.53	10 0 0	0.34	0.30
9	3.18	2.82	10	1.22	− 0.62	2	0.81	1.24	1	0.33	0.51
10	0.79	0.47	11	0.10	− 0.36	3	1.69	− 1.24	2	0.27	− 0.79
11	4.19	− 4.13	12	0.52	− 0.53	4	1.12	− 1.16			
12	0.87	0.77	13	0.70	0.18	5	0.84	0.68	$\overline{10}$ 0 1	0.97	− 1.68
13	0.60	0.11				6			2	1.12	2.51
14	0.85	0.87	0 0 6	1.94	− 1.79				3	0.26	− 0.67
15	0.35	− 0.19	1	0.70	− 1.02	$\bar{4}$ 0 1	13.20	13.43			

The unit cell dimensions were determined from oscillation and Weissenberg photographs. The sets of intensities for $(h\,k\,0)$, $(0\,k\,l)$ and $(h\,0\,l)$ were obtained by the multiple-film Weissenberg technique, with CuK_α radiation and using a Ni filter. Intensities were estimated by visual comparison with a calibrated intensity scale.

Corrections for Lorentz and polarization factors were applied in the usual way, while that for absorption was disregarded. Preliminary scaling and temperature factors were determined by Wilson's method7) and were further improved during the later stages of the refinement.

Structure Determination

Approximate Structure on the (0 0 1) Projection.—It is to be expected from the axial length that an approximate crystal structure should be obtained without serious overlapping of the molecule from the electron-density projection on (0 0 1). A trial molecular model was set up as planar, with conventional bond lengths and angles. The approximate structure on the (0 0 1) projection was obtained by the trial and error method, using the structure factor maps successively. The ordinary Fourier syntheses were followed. In the calculation of structure factors, an isotropic temperature factor $\exp\{-3.0(\sin\theta/\lambda)^2\}$ was applied. After several successive Fourier refinements, the R-value $(R=\sum\{|F_o|-|F_c|\}/\sum|F_o|)$ became 0.25.

Approximate Structures on the (1 0 0) and (0 1 0) Projections. — The approximate structures on the (1 0 0) and (0 1 0) projections

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7) A. J. C. Wilson, *Nature*, **150**, 152 (1942).

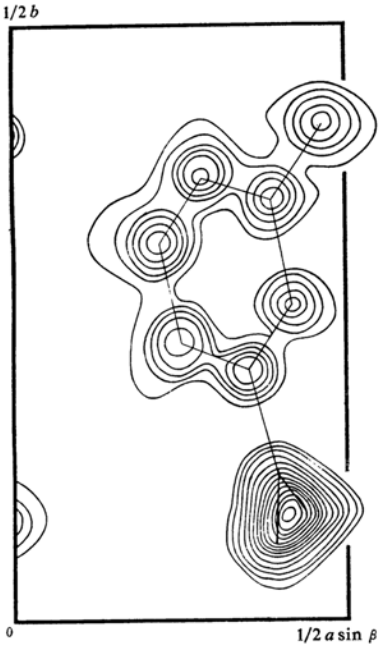

Fig. 1 (a)

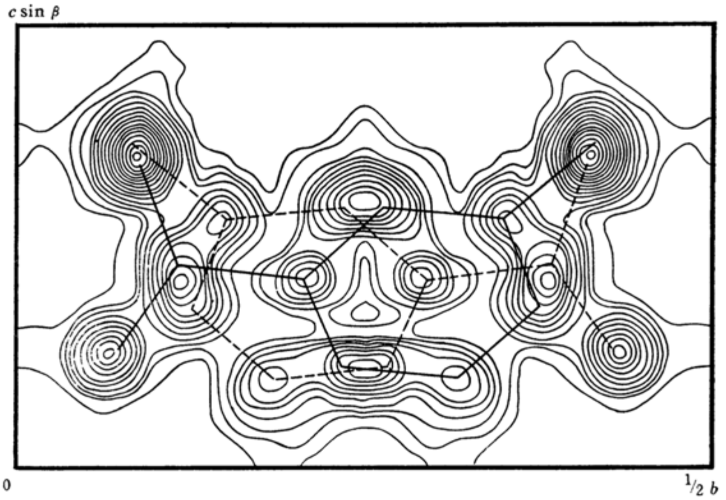

Fig. 1 (b)

Fig. 1. The final electron-density projections (a) along the c axis, (b) along the a axis. Contours are at an interval of 1 e. Å^{-2}, the lowest being at 2.0 e. Å^{-2}.

were given by assuming the planarity of the molecule with x and y coordinates obtained from the (0 0 1) projection. After several successive Fourier syntheses for the (1 0 0) and (0 1 0) projections, the R-values became 0.31 for $(0\,k\,l)$ and 0.44 for $(h\,0\,l)$. In the calculation of the structure factors, the isotropic temperature factor $\exp\{-3.0(\sin\theta/\lambda)^2\}$ was applied.

Refinement of Structure

Refinements of the structure were made by the method of modified (F_o-F_c) syntheses[8]. Preliminary hydrogen atoms were placed at the distance of 1.0 Å from each of the C_2, C_4, C_5 and C_6 atoms, and two hydrogen atoms in the amino group were placed at the distance of 1.0 Å from the nitrogen atom of the amino group on the N–O′ and N–O″ lines.

The locations of hydrogen atoms in the methyl group were obtained at the later stage of refinements. The isotropic temperature factor of each atom was corrected in each stage of the refinement. After ten successive (F_o-F_c) syntheses, the R-values reduced down to 0.11, 0.11 and 0.20 for $(h\,k\,0)$, $(0\,k\,l)$ and $(h\,0\,l)$ respectively. The observed and calculated structure factors are listed in Table I. The final atomic parameters are given in Table II, while the final Fourier maps are shown in Fig. 1.

TABLE II. ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS

Atom	Coordinates			Temperature factors		
	x/a	y/b	z/c	$(h\,k\,0)$	$(0\,k\,l)$	$(h\,0\,l)$
C_1	0.354	0.207	0.423	2.5	3.0	2.5
C_2	0.418	0.266	0.595	3.0	3.0	3.0
C_3	0.387	0.350	0.565	3.1	3.0	3.1
C_4	0.285	0.375	0.360	3.1	3.0	3.1
C_5	0.219	0.316	0.195	3.1	3.0	3.1
C_6	0.254	0.233	0.224	3.0	3.0	3.0
C_7	0.392	0.116	0.458	3.0	3.0	3.0
C_8	0.464	0.416	0.745	4.2	3.0	4.2
N	0.386	0.068	0.254	3.0	3.0	3.0
O	0.433	0.089	0.681	3.0	3.0	3.0
H_2	0.492	0.248	0.745	3.5	3.5	3.5
H_4	0.267	0.437	0.338	3.5	3.5	3.5
H_5	0.140	0.337	0.049	3.5	3.5	3.5
H_6	0.199	0.187	0.098	3.5	3.5	3.5
H_{M_1}	0.387	0.431	0.910	3.5	3.5	3.5
H_{M_2}	0.567	0.392	0.835	3.5	3.5	3.5
H_{M_3}	0.484	0.470	0.640	3.5	3.5	3.5
H_{N_1}	0.424	0.008	0.294	3.5	3.5	3.5
H_{N_2}	0.395	0.072	0.059	3.5	3.5	3.5

Throughout this study, the calculations of the structure factors were carried out on an NEAC 2101 electronic computer.

Description of the Structure and Discussion

Molecular Structure.—The bond lengths and angles found in *m*-methylbenzamide are shown in Fig. 2. None of the bond lengths observed in the benzene ring differ significantly from

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[8] T. Watanabé and Y. Takaki, to be published.

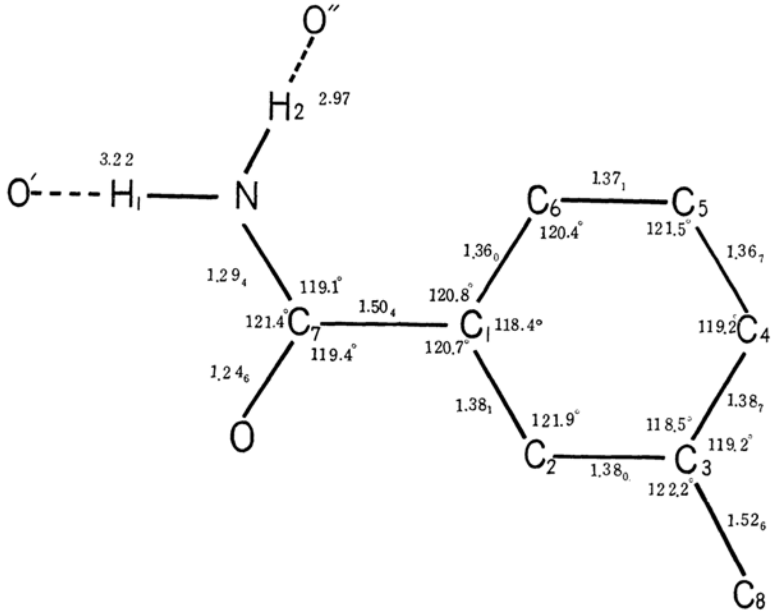

Fig. 2. Bond lengths (Å) and bond angles in *m*-methylbenzamide.

each other or from the mean observed value of 1.37_5 Å which is in good agreement with the mean C–C bond length, 1.38 Å, in the benzamide[6].

The C_1–C_7 bond length (1.50 Å) leading to the amide group is somewhat less than 1.54 Å, the standard length for a single bond. This value is, however, in good agreement with the 1.50, 1.52, 1.48, 1.48 and 1.48 Å observed in α-pyrazinamide[4], nicotinamide[5], benzamide[6], benzoic acid[2] and nicotinic acid[3] respectively, though it is somewhat less than that observed in oxalic acid dihydrate[9] (1.53 Å and α-oxalic acid[10] (1.56 Å).

The shortening of this C_1–C_7 bond may indicate that there is some double bond character caused by the resonance effect between the amide or acid group and the six-membered ring.

The bond length C_3–C_8 (1.52_6 Å) is in fairly good agreement with the standard single bond length.

TABLE III. DIMENSIONS OF THE AMIDE GROUP IN THE ANALOGOUS COMPOUNDS

	m-Methylbenzamide Å	Benzamide[6] Å	Nicotinamide[5] Å	α-Pyrazinamide[4] Å
C–N	1.29	1.31	1.34	1.31
C–O	1.25	1.24	1.22	1.24

The dimensions of the amide group agree closely with those observed in the analogous compounds. Some examples are shown in Table III.

The plane of the benzene ring can be represented by the equation:

$$0.550X' + 0.072Y - 0.403Z' - 1 = 0$$

where X', Y and Z' refer to the orthogonal axes a, b and c*, and the values of the coefficients are determined by means of the least squares. The perpendicular displacements of atoms from the mean plane are shown in Table IV.

TABLE IV. DISPLACEMENT OF EACH ATOM FROM THE MEAN PLANE OF THE BENZENE RING

	Å		Å
C_1	+0.006	C_6	+0.001
C_2	−0.013	C_7	+0.008
C_3	+0.007	C_8	+0.062
C_4	+0.006	N	+0.570
C_5	−0.012	O	−0.487

The mean value of the displacements for atoms in the benzene ring is 0.007_5 Å, that is, the benzene ring is concluded to be planar. On the other hand, the nitrogen atom and oxygen atom deviate significantly from the mean plane of the benzene ring, and the angle between the ring plane and the amide plane is 28.7°.

It has been shown that the amide planes in nicotinamide[5] and benzamide[6] make an angle

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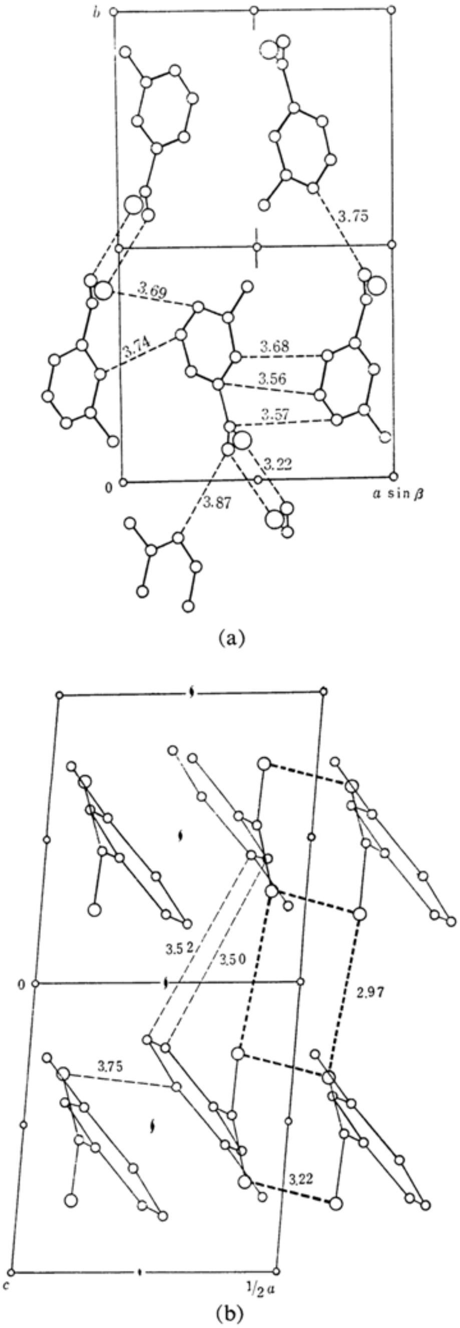
9) F. R. Ahmed and D. W. J. Cruickshank, *Acta Cryst.*, 6, 385 (1953).

10) E. G. Cox, M. W. Dougill and G. A. Jeffrey, *J. Chem. Soc.*, 1952, 4854.

about 25∼26° to their ring planes, while in salicylic acid[1], benzoic acid[2], nicotinic acid[3] and α-pyrazinamide[4] the molecules are approximately planar.

The twists of the amide group around the C_1-C_7 axis in *m*-methylbenzamide can be explained by the steric hindrance on the contact of H_6 in the benzene ring and H_{N2} in the amino group, as has been suggested by Penfold and White[6].



(a)

(b)

Fig. 3. Views of the arrangement of molecules (a) along the c axis, (b) along the b axis showing hydrogen bond as broken lines.

Crystal Structure. — The projection of the crystal structure along the c and b axes is shown in Fig. 3. The molecules are connected by the two NH–O hydrogen bonds, the first set 3.22 Å in length forming a dimer across the center of symmetry, and the second set 2.97 Å in length joining such dimers into endless chains extended along the c axis. The linkage of molecules by hydrogen bonding is of a type very similar to that found in the crystals of benzamide[6] and δ-pyrazinamide[12]. The hydrogen bond lengths in *m*-methylbenzamide are in agreement with those found for the NH-O type hydrogen bond, which have values ranging from 2.67 to 3.17 Å[11]. This crystal consists of endless chains linked by the NH–O hydrogen bonds, and the intermolecules between these chains are held in contact by the van der Waals force; such molecular arrangements as shown in Fig. 3 can reasonably explain the existence of the cleavage parallel to the (1 0 0) plane.

Summary

The crystal structure of *m*-methylbenzamide has been determined by two-dimensional X-ray methods. The atomic positions obtained from the trial and error method are refined by the modified $(F_o - F_c)$ synthesis[8].

1. The mean C–C distance in the benzene ring is 1.37_5 Å, while C_3–$C_8 = 1.52_6$, C_1–$C_7 = 1.50_4$, C_7–$N = 1.29_4$ and C_7–$O = 1.24_6$ Å.
2. The amide group twists around the C_1–C_7 axis with an angle of 28.7° because of the steric hindrance on the contact of H_6 and H_{N2}.
3. The molecules are connected by NH–O hydrogen bonds, 3.22 Å, forming dimers which are linked with each other by other NH–O hydrogen bonds, 2.97 Å, into endless chains.

The crystal structure is of a type analogous to benzamide[6] and δ-pyrazinamide[12].

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