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The Crystal Structure of *m*-Hydroxybenzamide

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Crystals of *m*-hydroxybenzamide are monoclinic with four molecules in a unit cell of dimensions $a=11.59$, $b=5.03$, $c=15.53$ Å, $\beta=136.1°$, space group $P\,2_1/c$. An approximate angular orientation of the molecule in the cell was quickly obtained by an application of the vector-set seeking method. The location of the molecule was then determined with the help of the orientation. The positional and anisotropic thermal parameters of the carbon, nitrogen and oxygen atoms were refined by means of the least-squares method with three-dimensional intensity data. The final R factor was 0.138. The carboxyamide group and benzene ring twist to each other about the C–C bond by an angle of 24.4°. The interatomic distances and bond angles are close to those expected. The molecules are linked by three types of hydrogen bonds to form the infinite double-layered sheets perpendicular to the c axis, and the crystal structure shows somewhat different features from those of the related compounds.

In the serial studies of the crystal structures of some aromatic carboxyamides, it has been found that there are several types of molecular arrangement connected by hydrogen bonds.[1-4] Although

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[1] Y. Takaki, Y. Sasada and T. Watanabe, *Acta Cryst.*, **13**, 693 (1960).

[2] C. Tamura, H. Kuwano and Y. Sasada, ibid., **14**, 693 (1961).

[3] S. Orii, T. Nakamura, Y. Takaki, Y. Sasada and M. Kakudo, This Bulletin, **36**, 788 (1963).

[4] Y. Sasada, T. Takano and M. Kakudo, ibid., **37**, 940 (1964).

the complete interpretation of these crystal structures in terms of interatomic interaction is impossible at the present stage, it will be of some significance to determine the crystal structures of carboxyamides with various substitutes.

In the previous paper, the authors have reported the structure of salicylamide (*o*-hydroxybenzamide).⁴⁾ In this compound, the hydroxy group in the ortho position to the carboxyamide group plays some role in the molecular association by hydrogen bonding, and in consequence the crystal structure shows somewhat different features from those already reported.

It might be interesting to compare the molecular linkage and molecular dimensions of *m*-hydroxybenzamide with those of salicylamide. The present paper will describ the threedimensional X-ray analysis of *m*-hydroxybenzamide.

Experimental and Crystal Data

Crystals were obtained from an alcohol-water solution as colorless hexagonal plates.

The unit cell dimensions were determined from oscillation and Weissenberg photographs about the b and c axes. The crystal and physical data found are as follows:

m-Hydroxybenzamide: $C_7H_7NO_2$, Molecular weight: 137.14.
Monoclinic: $a=11.59\pm0.03$, $b=5.03\pm0.03$, $c=15.53\pm0.03$ Å, $\beta=136.1\pm0.5°$.
Absent spectra: $(h0l)$ when l is odd, $(0k0)$ when k is odd.
Space group: $P\,2_1/c$.
Density (by flotation): 1.449 g.cm^{-3}.
Density (calculated): 1.451 g.cm^{-3}.
Four molecules per unit cell.
Volume of the unit cell: 627.78 Å^3.
Linear absorption coefficient for Cu$K\alpha$ radiation: $\mu=10.44$ cm^{-1}.
Total number of electron per unit cell: $F(000)=288$.

Equi-inclination Weissenberg photographs for 0—3 layers around the b axis were taken with filtered Cu$K\alpha$ radiation. In order to determine the approximate interlayer scales, Weissenberg photograph of $(hk0)$ zone was also taken. Intensities of the reflections were estimated visually against a calibrated intensity scale prepared using the same crystal. The multiple-film technique was used to correlate strong and weak reflections, ranging in relative intensities from 12000 to 1. The number of independent reflections observed was 706, representing about 70% of the total accessible reflections in the recorded layers. Corrections for Lorentz and polarization factors were applied in the usual way. The crystal used were square in cross section with rectangular dimensions 0.10×0.05 cm. Therefore, absorption and secondary extinction effect might be negligible, and corrections for them were omitted. The observed structure factors were first set onto an absolute scale by Wilson's method,⁵⁾ and the scale factors were further improved during the later stage of the refinement.

Structure Determination

Orientation of the Molecule.—In order to determine the orientation of the molecule, the vector-set seeking method described in the previous paper⁶⁾ was applied; the vector set of the planar molecular model was superposed on the Patterson projection on (010) and the best fitting between them was searched by varying stepwisely the angular orientation of the molecule. The maximum of the degree of fitting was found at $\theta=0°$, $\varphi=45°$ and $\psi=10°$, while there were some other high peaks in the fitting at the different rotations. It is naturally expected that the orientation of the molecule is given by the angles corresponding to the best fitting if the carboxyamide group is coplanar with the benzene ring. However, the coplanarity of the molecule may not necessarily be fulfilled in the present compound. Therefore, the orientation corresponding to the second highest peak was also saved for the subsequent refinement.

Location of the Molecule in the Unit Cell.—It was expected from the normal van der Waals radii that the atoms would be located only outside the circles centered at the symmetry elements of the unit cell, as shown in Fig. 1. The initial x and z coordinates of the atoms in the molecule for the possible orientations were assigned easily in a rather limited allowable region. They were adjusted by trial with the aid of the structure factor maps for some strong reflections. The discrepancy factor, $R=\sum||F_o|-|F_c||/\sum|F_o|$, was about 0.6 for both orientations at this stage.

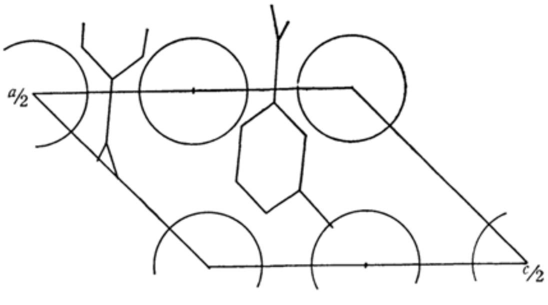

Fig. 1. Forbidden regions for the location of the molecule. The final position of the molecule is indicated.

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

6) Y. Katsube, Y. Sasada and M. Kakudo, This Bulletin, **39**, 6108 (1966).

TABLE I. THE FINAL ATOMIC COORDINATES AND TEMPERATURE FACTORS

Atom	x/a	y/b	z/c	$B_{ij}\times10^5$					
				B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	0.3662	0.2182	0.3524	738	2198	466	357	826	67
C(2)	0.1971	0.2519	0.2572	663	1671	493	−233	818	−115
C(3)	0.1292	0.4526	0.1706	731	1787	618	86	990	94
C(4)	0.2324	0.6251	0.1813	931	2873	529	1094	925	780
C(5)	0.4037	0.5984	0.2782	943	1836	722	439	1417	963
C(6)	0.4700	0.3985	0.3630	825	328	496	−68	1042	61
C(7)	0.6541	0.3551	0.4710	968	−28	679	178	1389	84
N	0.7492	0.5606	0.5089	916	402	634	−274	1005	−151
O(1)	0.7059	0.1305	0.5196	666	1426	626	438	889	433
O(2)	0.0940	0.0890	0.2466	627	2961	651	−476	889	309

	Attached to	x/a	y/b	z/c	B (Å^2)
H(1)	C(1)	0.4174	0.0472	0.4247	0.67
H(2)	O(2)	0.1334	−0.0943	0.2984	2.24
H(3)	C(3)	0.0003	0.4422	0.0890	3.45
H(4)	C(4)	0.1817	0.8009	0.1096	2.34
H(5)	C(5)	0.4749	0.7453	0.2688	5.44
H(6)	N	0.7033	0.7765	0.4826	5.62
H(7)	N	0.8769	0.5639	0.5939	1.90

In the Fourier projection for the model corresponding to the maximum peak in the vector-set seeking, all the atoms except those in the carboxyamide group were resolved. On the other hand, the Fourier projection for another orientation did not look encouraging to continue the refinement, because there appeared the regions of low electron density around the positions of the assumed atoms and areas of high density where no atom was placed.

The x and z coordinates in the former model were further refined by successive five Fourier syntheses. The R factor reduced to 0.27. Because of the overlapping of the atoms in the carboxyamide group, their coordinates were improved by the trial method, until the R factor dropped to 0.22.

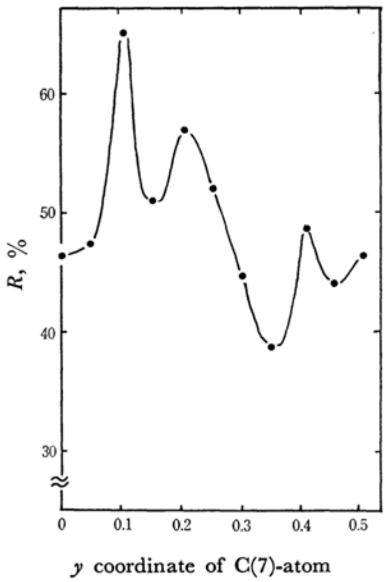

Fig. 2. Minimum residual calculation.

Determination of *y* Coordinates.—The y coordinates of the atoms were obtained by the one-dimensional minimum residual method.[7] The molecular model constructed from the fixed x and z coordinates was translated successively along the b axis; fifteen ($hk0$) reflections were included in the computation. It gave uniquely the y coordinates, as seen from Fig. 2, where the abscissa shows the coordinates of the reference atom C(7). Successive two Fourier refinements for ($hk0$) reduced the R factor to 0.30.

Three-dimensional Refinement.—Three positional parameters and one isotropic temperature factor for each atom were refined by least-squares method where off-diagonal matrix elements were neglected. The scale factors for the various layer lines were adjusted after every cycle. In the computation, 827 reflections in the four layers about the b axis, some of which were unobserved, were included. Five cycles of the refinement reduced the R factor to 0.23. At this stage, a three-dimensional (F_o-F_c) synthesis was made, but it did not show the positions of hydrogen atoms. Therefore, four hydrogen atoms were placed on the benzene ring plane and at a distance of 1.0 Å outward from the carbon atoms, and the hydrogen atoms of the hydroxy and the amino

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[7] A. K. Bhuiya and E. Stanley, *Acta Cryst.*, **17**, 746 (1964).

TABLE II. OBSERVED AND CALCULATED STRUCTURE FACTORS

K = 0	$\|F_o\|$	F_c
H = 0		
L 2	28.5	-27.9
4	53.0	57.0
6	23.3	22.5
8	25.6	25.2
10	13.0	-10.1
12	8.2	8.5
H = 1		
0	23.4	-23.8
2	26.0	-29.9
4	29.8	26.5
6	16.1	-14.1
8	3.6	-2.3
10	11.6	12.3
12	2.9	3.0
H = 2		
0	47.7	-51.0
2	65.0	-67.3
4	6.0	-7.1
6	14.6	-15.4
8	3.7	-5.5
10	3.9	-4.5
H = 3		
0	2.2	-1.4
2	51.0	50.3
4	6.6	-5.1
6	0	1.5
8	4.4	-3.7
H = 4		
0	9.8	-9.3
2	21.0	21.1
4	5.1	4.6
6	6.3	6.8
8	6.6	5.6
H = 5		
0	13.8	-13.4
2	8.4	-8.8
4	0	1.6
6	0	-1.5
8	1.4	0.1
H = 6		
0	12.8	-11.9
2	8.6	8.7
4	18.0	-16.3
H = 7		
0	8.1	-6.8
2	14.1	13.5
4	4.8	-3.4
H = 8		
0	10.1	8.5
2	0	-0.7
4	4.5	-3.5
H = 9		
0	4.6	4.4
2	1.4	-3.2
H = 1		
-2	35.7	-38.3
-4	0	0.3
-6	23.9	-23.6
-8	4.1	-4.8
-10	17.9	-18.2
-12	15.3	16.1
-14	11.3	-13.3
H = 2		
-2	4.3	2.9
-4	97.6	-100.9
-6	40.4	-43.5
-8	3.3	3.9
-10	10.0	-11.0
-12	15.9	-15.3
-14	10.6	9.3
H = 3		
-2	44.7	41.6
-4	52.4	56.7
-6	38.7	37.8
-8	17.5	16.2
-10	13.0	13.7
-12	2.2	3.0
-14	9.8	10.7
-16	8.4	-7.9
H = 4		
-2	47.3	45.5
-4	1.7	-1.5
-6	29.9	27.4
-8	10.5	-10.0
-10	35.8	31.6
-12	14.8	-13.5
-14	3.6	2.9
-16	6.0	5.7
H = 5		
-2	32.6	-26.9
-4	34.8	-33.3
-6	32.3	-29.3
-8	35.7	-34.0
-10	15.8	-14.0
-12	11.2	-11.0
-14	0	-0.6
-16	4.4	-4.7
H = 6		
-2	17.0	15.8
-4	9.9	-6.7
-6	17.2	15.3
-8	7.3	6.7
-10	4.5	4.1
-12	6.2	5.7
-14	7.9	-5.6
-16	3.3	2.4
-18	2.0	-2.1
H = 7		
-2	9.8	7.8
-4	10.4	11.4
-6	22.1	20.6
-8	21.0	-18.8
-10	31.4	31.0
-12	0	0
-14	9.7	9.4
-16	1.4	-0.1
-18	2.5	3.0
H = 8		
-2	1.4	-0.9
-4	15.9	-14.9
-6	6.3	-7.1
-8	8.5	-8.0
-10	7.1	-8.6
-12	10.4	-9.8
-14	5.3	-5.3
-16	1.9	1.7
-18	1.4	0.6
H = 9		
-2	6.8	-6.6
-4	2.6	-1.1
-6	21.3	20.9
-8	5.9	-5.9
-10	7.2	-7.9
-12	22.6	20.4
-14	4.8	-4.6
-16	5.9	-6.1
-18	0	0.6
H = 10		
-2	0	0.2
-4	5.7	7.0
-6	25.7	-24.0
-8	27.3	29.6
-10	9.3	-8.2
-12	6.7	7.1
-14	2.6	-2.0
-16	4.9	5.8
H = 11		
-2	4.3	-4.6
-4	1.8	1.3
-6	12.0	-11.9
-8	11.5	12.0
-10	29.8	-31.5
-12	2.1	2.7
-14	3.3	-4.4
-16	2.2	-1.0
-18	10.7	-14.3
H = 12		
-4	10.6	10.7
-6	3.4	-4.8
-8	0	-0.8
-10	18.8	19.6
-12	3.0	-3.4
-14	0	0.2
-16	5.4	5.6
-18	1.6	1.9
H = 13		
-6	1.7	2.9
-8	2.8	2.8
-10	3.9	4.5
-12	0	0
-14	7.6	8.0
-16	4.6	7.0
-18	0	-1.2
H = 14		
-12	5.0	-7.8
-14	3.8	-8.9
-16	9.7	-10.3
K = 1		
H = 0		
2	29.6	32.1
3	20.9	20.7
4	8.3	-8.3
5	1.2	-1.7
6	11.0	-11.4
7	0	0.8
8	8.9	8.5
9	12.6	14.5
10	0	0.1
11	9.2	-9.0
H = 1		
2	11.8	11.0
3	18.0	16.4
4	4.6	6.2
5	23.3	-21.9
6	21.4	19.5
7	2.9	3.3
8	18.5	-18.6
9	5.8	-6.8
10	8.0	8.0
H = 2		
0	29.5	-31.6
1	8.9	-9.5
2	2.9	2.5
3	3.3	3.8
4	23.8	-21.9
5	8.3	-9.6
6	4.5	3.6
7	13.5	16.0
H = 3		
0	20.0	-19.4
1	8.9	-9.7
2	4.9	4.3
3	3.8	3.0
4	6.0	6.1
5	0	-2.1
6	6.8	-8.1
H = 4		
0	11.3	12.6
1	13.9	-14.4
2	10.0	11.8
3	0	1.8
4	0	-1.2
5	6.8	-5.6
6	2.8	3.2
7	6.2	6.4
H = 5		
0	0	1.3
1	7.4	7.8
2	4.5	-4.7
3	8.3	8.5
4	6.8	-5.7
5	4.6	4.8
H = 6		
0	4.5	-5.4
1	4.7	-3.5
2	0	0.6
3	6.7	-8.2
H = 7		
0	0	0.9
1	4.8	-6.7
2	0	-1.6
3	4.2	-4.6
H = 8		
0	6.6	9.8
1	6.2	7.5
H = 9		
0	3.0	-2.6
1	5.8	7.1
H = 10		
0	4.6	5.7
H = 1		
-2	60.0	57.5
-3	31.6	32.0
-4	4.9	4.2
-5	17.6	16.4
-6	2.1	3.0
-7	11.2	-10.9
-8	0	-1.9
-9	13.6	12.1
-10	11.7	11.6
-11	4.8	4.7
-12	8.6	-9.2
-13	0	-0.1
-14	6.2	-2.7
H = 2		
-1	18.8	17.1
-2	14.0	12.0
-3	73.1	-76.3
-4	65.4	-74.9
-5	24.4	23.8
-6	28.9	27.5
-7	35.1	-32.1
-8	17.2	-16.6
-9	0	-0.1
-10	2.3	-3.4
-11	6.8	-8.4
-12	0	-2.3
-13	7.8	-6.7
-14	7.7	8.1
-15	2.9	-1.4
H = 3		
-1	0	-1.1
-2	4.7	3.6
-3	26.8	-21.0
-4	23.8	21.8
-5	32.3	32.9
-6	14.3	-12.2
-7	17.0	-16.8
-8	8.9	-8.1
-9	6.9	-4.8
-10	11.6	11.0
-11	0	0.2
-12	0	-1.7
-13	3.9	4.4
-14	0	1.6
-15	9.0	-8.6
H = 4		
-1	35.3	35.7
-2	23.8	19.7
-3	14.4	-15.2
-4	39.5	36.2
-5	17.1	15.0
-6	2.9	2.3
-7	31.4	29.3
-8	27.4	25.7
-9	14.5	15.6
-10	0	1.5
-11	7.8	7.1
-12	0	-0.3
-13	8.4	9.0
-14	0	0
-15	5.9	6.5
-16	3.4	3.4
-17	2.0	3.0
H = 5		
-1	0	2.0
-2	26.1	-23.7
-3	0	0.6
-4	15.5	-13.9
-5	27.4	20.6
-6	3.1	-3.4
-7	10.0	-10.1
-8	26.3	-23.4
-9	5.6	-5.7
-10	4.1	-5.0
-11	7.6	-8.3
-12	0	0.5
-13	4.8	3.4
-14	6.7	-5.7
-15	6.3	-7.2
-16	0	1.2
H = 6		
-1	4.2	-2.9
-2	8.4	-7.7
-3	0	3.9
-4	13.2	-11.9
-5	41.9	-37.2
-6	0	-2.1
-7	3.6	3.9
-8	14.0	-12.4
-9	17.0	-17.4
-10	7.3	-7.7
-11	7.6	-6.9
-12	0	2.2
-13	14.4	-15.7
-14	4.5	-4.4
-15	0	0
-16	0	0.4
-17	3.3	-3.8
-18	2.4	3.8
H = 7		
-1	9.4	-9.6
-2	23.1	24.9
-3	6.1	-4.5
-4	4.1	2.7
-5	6.2	-5.9
-6	17.8	16.7
-7	13.7	13.6
-8	24.5	23.4
-9	10.1	-7.0
-10	12.8	13.0
-11	10.9	11.7
-12	8.0	7.1
-13	8.3	9.4
-14	6.8	6.5
-15	8.1	8.7
-16	0	0
-17	0	-2.2
-18	0	1.2
H = 8		
-1	0	-0.6
-2	10.6	-13.2
-3	26.9	30.0
-4	4.6	5.8
-5	9.0	-12.1
-6	7.6	-7.3
-7	16.3	17.1
-8	4.3	5.0
-9	11.6	10.7
-10	11.8	-12.6
-11	4.6	5.1
-12	0	-1.0
-13	0	-1.1
-14	4.8	5.4
-15	4.7	5.5
-16	4.4	-5.6
-17	5.0	3.3
-18	0	-0.3
H = 9		
-1	4.4	-5.8
-2	6.6	-9.7
-3	8.7	9.0
-4	8.4	9.3
-5	0	-0.7
-6	23.3	-27.2
-7	0	2.4
-8	4.6	-5.3
-9	6.5	-7.8
-10	10.5	-12.3
-11	0	0.2
-12	0	-0.4
-13	9.7	-13.5
-14	19.3	-20.1
-15	3.8	3.0
-16	4.4	5.6
-17	10.7	-13.9
-18	3.4	-4.7
H = 10		
-3	6.2	-7.6
-4	0	-1.7
-5	4.7	-3.5
-6	8.3	8.4
-7	16.8	-19.1
-8	11.8	15.0
-9	4.8	1.1
-10	3.3	3.4
-11	0	-1.5
-12	6.8	5.4
-13	6.8	-7.8
-14	6.7	8.7
-15	0	-0.2
-16	6.1	8.3
-17	5.6	7.5
-18	4.8	-5.5
H = 11		
-5	5.9	7.1
-6	5.0	5.0
-7	5.6	5.2
-8	4.3	-4.2
-9	5.9	-6.6
-10	0	3.1
-11	6.7	8.9
-12	8.2	8.2
-13	4.7	4.2
-14	0	1.4
-15	0	-0.7
-16	4.2	-4.4
-17	6.8	6.8
-18	8.9	9.3
K = 2		
H = 0		
2	5.1	6.4
3	45.1	45.2
4	3.5	4.9
5	3.5	-3.1
6	6.0	6.9
7	17.6	17.6
8	0	-1.1
9	12.2	11.9
10	6.1	6.0
11	7.5	9.5
H = 1		
0	14.9	15.4
1	27.4	-27.8
2	12.1	-12.5
3	17.7	-15.8
4	8.1	8.8
5	18.8	-18.9
6	8.7	9.0
7	4.6	-4.9
8	3.9	-3.7
9	12.0	-13.0
10	0	0
11	5.2	-6.2
H = 2		
0	9.2	10.1
1	1.6	2.2
2	15.2	-17.5
3	4.1	4.4
4	3.2	2.9
5	25.3	-23.6
6	15.4	-15.5
7	4.8	5.0
8	4.7	4.2
9	7.0	-7.4
10	3.6	-4.7
H = 3		
0	12.4	-10.9
1	19.1	16.6
2	9.5	-8.8
3	6.3	6.9
4	11.0	13.2
5	31.4	30.7
6	8.8	-9.1
7	7.0	7.5
8	0	-1.7
H = 4		
0	0	0.9
1	5.0	5.3
2	11.5	11.7
3	11.3	-11.4
4	3.9	-3.8
5	0	0
6	4.5	7.8
7	3.3	-4.8
H = 5		
0	12.5	-14.7
1	24.5	-25.5
2	17.8	18.0
3	4.8	-4.6
4	5.5	-6.8
5	2.5	-3.1
6	0	0
7	9.8	-13.0
H = 6		
0	11.5	-12.6
1	29.0	26.8
2	0	-1.3
3	0	0.1
4	4.8	-5.8
5	4.1	5.2
6	2.5	3.5
H = 7		
0	8.4	9.9
1	5.4	6.0
2	0	-0.9
3	2.2	3.1
H = 8		
0	6.3	6.8
1	4.0	-4.5
2	0	-1.5
3	8.1	-9.3
H = 1		
-1	13.2	-13.5
-2	5.6	5.6
-3	12.5	-12.7
-4	18.9	-18.1
-5	8.1	-8.8
-6	4.1	2.8
-7	15.0	-13.4
-8	0	0.9
-9	9.0	9.8
-10	4.8	-5.7
-11	5.4	-7.8
H = 2		
-1	4.9	-7.9
-2	20.8	-19.6
-3	0	-0.5
-4	10.1	-6.8
-5	26.3	27.9
-6	3.2	-3.7
-7	15.6	15.4
-8	0	-0.1
-9	5.1	6.7
-10	6.7	-8.5
-11	10.1	12.4
-12	0	0.5
-13	4.2	5.9
H = 3		
-1	35.1	36.6
-2	0	1.1
-3	4.8	5.6
-4	10.9	11.0
-5	6.8	7.5
-6	22.3	-22.9
-7	10.8	-10.5
-8	13.8	14.0
-9	0	-1.5
-10	0	0.6
-11	0	-1.5
-12	4.0	3.8
-13	7.3	-8.3
H = 4		
-1	11.7	-13.5
-2	24.8	25.6
-3	6.0	-7.2
-4	6.4	-6.8
-5	21.5	-24.2
-6	11.7	11.9
-7	27.5	27.3
-8	8.8	8.9
-9	29.1	-29.5
-10	0	2.7
-11	0	-1.0
-12	4.8	-4.5
-13	0	1.6
-14	5.8	6.2
-15	3.1	-4.2
H = 5		
-1	13.8	-16.6
-2	4.8	3.3
-3	13.3	12.9
-4	4.8	3.7
-5	26.8	-27.5
-6	10.0	9.2
-7	2.0	2.9
-8	20.9	-21.6
-9	3.3	5.1
-10	13.4	12.3
-11	9.6	12.5
-12	3.9	-4.9
-13	0	-1.0
-14	0	0.5
-15	6.8	8.0
-16	3.4	-5.5
H = 6		
-1	3.6	-4.2
-2	2.4	3.0
-3	22.2	22.6
-4	14.2	-16.1
-5	5.8	-7.2
-6	6.4	-5.9
-7	13.5	14.7
-8	10.9	-13.8
-9	2.4	4.0
-10	5.7	8.0
-11	14.1	-12.9

TABLE II. (continued)

-12	16.4	-14.2
-13	0	-0.5
-14	0	0
-15	5.0	4.7
-16	3.0	2.7
-17	7.0	-7.2
H = 7		
-1	6.8	-7.6
-2	9.8	-9.9
-3	12.3	13 0
-4	0	1.4
-5	6.1	6.2
-6	8.8	11.1
-7	4.2	-5.3
-8	4.2	-4.8
-9	5.3	-5.3
-10	0	-2.7
-11	16.9	18.8
-12	5.5	7.1
-13	14.8	-15.2
-14	0	2.3
-15	0	-0.1
-16	0	-2.0
-17	0	-0.3
H = 8		
-3	18.1	-19.8
-4	12.9	14.5
-5	2.7	-2.8
-6	0	-2.3
-7	6.0	-6.8
-8	10.9	11.4
-9	4.7	4.2
-10	0	0.6
-11	3.8	-3.7
-12	14.8	16.3
-13	2.7	6.0
-14	8.2	-10.6
-15	4.5	5.6
-16	5.3	7.2
-17	4.1	6.4
H = 9		
-1	2.3	2.9
-2	0	1.6
-3	3.8	4.7
-4	6.2	-7.0
-5	3.9	3.6
-6	0	-1.9
-7	0	1.9
-8	3.9	3.9
-9	4.8	-6.2
-10	10.0	-11.4
-11	0	-0.6
-12	0	0.1
-13	3.3	3.0
-14	0	-1.3
-15	13.8	-15.0
-16	0	-0.1
-17	2.6	2.4
H = 10		
-1	6.5	8.4
-2	0	-0.9
-3	4.0	-4.7
-4	4.3	-5.6
-5	7.8	9.0
-6	0	-0.9
-7	0	-1.4
-8	0	-2.4
-9	8.3	10.7
-10	4.8	-7.3
-11	3.9	-8.1
-12	0	-0.6
-13	0	2.0
-14	0	0
-15	0	1.4
-16	6.1	-7.7
-17	3.9	-3.8
H = 11		
-7	3.5	-11.6
-8	4.5	3.8
-9	0	3.0
-10	5.0	5.3
-11	0	-2.8
-12	0	-0.8
-13	9.9	10.5
-14	3.5	5.3
-15	3.2	-3.5
-16	0	2.1
-17	9.1	9.6
-18	0	1.3
K = 3		
H = 0		
2	2.3	-1.8
3	8.2	6.7
4	9.6	9.3
5	7.7	6.6
6	6.9	-7.0
7	4.4	4.5
8	6.6	5.5
9	2.3	2.2
10	0	-1.9
11	3.6	3.1
12	6.5	4.7
H = 1		
0	8.1	10.2
1	4.2	4.7
2	12.2	-13.6
3	13.8	12.6
4	3.2	3.0
5	7.4	6.5
6	3.0	3.0
7	6.6	4.8
8	3.2	-3.5
9	12.9	11.5
10	3.6	-3.2
H = 2		
0	23.3	-28.1
1	12.6	-12.0
2	10.7	10.0
3	9.7	-7.7
4	6.1	-6.1
5	13.0	-12.5
6	10.5	-8.6
7	9.2	-7.5
8	0	-1.1
9	6.3	-6.5
10	5.8	5.4
H = 3		
0	10.8	-11.7
1	8.4	8.7
2	5.8	5.9
3	8.8	-8.6
4	0	1.2
5	3.3	-4.8
6	7.9	8.6
7	5.9	5.1
8	3.5	-3.5
H = 4		
0	5.7	-3.9
1	17.2	17.4
2	29.5	32.9
3	6.3	7.5
4	19.9	-19.2
5	13.4	12.4
6	8.0	8.0
7	3.3	3.3
H = 5		
0	11.0	-12.3
1	10.4	-11.3
2	8.1	-8.2
3	9.2	-8.7
H =6		
0	18.3	19.3
1	6.6	-7.2
2	13.4	-13.6
H = 7		
0	6.4	6.0
1	4.2	3.9
H = 8		
0	6.7	5.8
H = 9		
0	6.2	-8.1
H = 1		
-1	2.1	-1.7
-2	0	0.1
-3	8.3	-8.3
-4	5.2	3.0
-5	8.5	-7.3
-6	5.5	-6.1
-7	12.9	-12.0
-8	3.0	3.1
-9	9.4	-9.6
-10	3.5	-3.8
-11	5.9	-5.8
-12	0	-1.4
H = 2		
-1	18.1	-18.2
-2	3.0	3.3
-3	6.0	6.3
-4	14.2	-13.9
-5	5.0	-4.6
-6	5.1	5.6
-7	2.8	0.6
-8	6.2	-6.6
-9	4.6	7.0
H = 3		
-1	3.1	-1.8
-2	29.9	27.4
-3	4.0	-3.7
-4	2.3	-0.8
-5	7.5	8.1
-6	0	-0.2
-7	7.8	6.7
-8	2.9	3.4
-9	3.1	3.2
-10	14.1	14.7
-11	6.6	6.1
-12	10.0	-8.9
-13	4.0	2.1
-14	7.2	6.7
H = 4		
-1	6.5	6.0
-2	8.6	7.9
-3	5.6	5.8
-4	5.7	3.6
-5	13.6	11.4
-6	25.8	23.2
-7	7.7	-8.5
-8	9.2	-8.7
-9	8.2	-9.7
-10	5.6	3.5
-11	0	1.2
-12	0	-1.3
-13	8.6	-7.3
-14	0	2.6
-15	5.7	-5.6
H = 5		
-1	6.0	5.7
-2	4.6	-6.0
-3	10.3	-7.5
-4	10.7	-8.5
-5	13.6	-11.6
-6	10.8	-10.2
-7	13.8	13.0
-8	29.0	-27.3
-9	4.3	-4.3
-10	16.5	13.4
-11	0	0.7
-12	10.5	-9.9
-13	0	1.2
-14	7.0	-7.9
-15	0	0.3
H = 6		
-1	6.5	-6.5
-2	21.7	-19.5
-3	7.5	-6.8
-4	4.2	-3.9
-5	5.9	-4.7
-6	4.1	-2.9
-7	2.9	2.5
-8	15.0	14.0
-9	4.4	-4.3
-10	26.5	-24.0
-11	0	0.5
-12	13.3	11.8
-13	12.1	9.7
-14	0	0.4
-15	0	0.8
H = 7		
-1	6.6	5.4
-2	6.6	8.3
-3	17.5	16.1
-4	20.6	19.1
-5	0	-1.4
-6	6.3	6.0
-7	3.1	-0.9
-8	18.1	15.4
-9	10.2	8.4
-10	0	1.5
-11	13.3	-9.2
-12	27.0	23.8
-13	6.4	-5.7
-14	8.6	-7.9
-15	0	-2.3
-16	4.6	4.3
H = 8		
-1	0	-0.2
-2	0	-1.4
-3	3.8	-2.6
-4	0	-0.3
-5	3.3	3.8
-6	14.1	-13.0
-7	0	-0.2
-8	18.1	14.8
-9	3.3	3.9
-10	12.4	-11.8
-11	0	1.3
-12	12.3	-9.2
-13	0	0.7
-14	6.1	3.9
-15	5.5	5.4
-16	0	-0.4
H = 9		
-1	5.8	-5.4
-2	5.4	-5.3
-3	5.9	-5.7
-4	4.4	-4.6
-5	0	-1.9
-6	11.4	-10.4
-7	9.3	-8.7
-8	11.5	-10.1
-9	0	0.2
-10	13.2	-10.2
-11	0	2.0
-12	0	-2.3
-13	0	1.0
-14	9.4	-7.2
-15	0	0.6
-16	4.0	-4.2
-17	7.6	6.7
H = 10		
-10	15.6	14.8
-11	0	-1.6
-12	3.0	-4.2
-13	2.9	-3.9
-14	10.6	10.1
-15	6.3	-5.6
-16	3.2	3.7
-17	2.4	-1.4

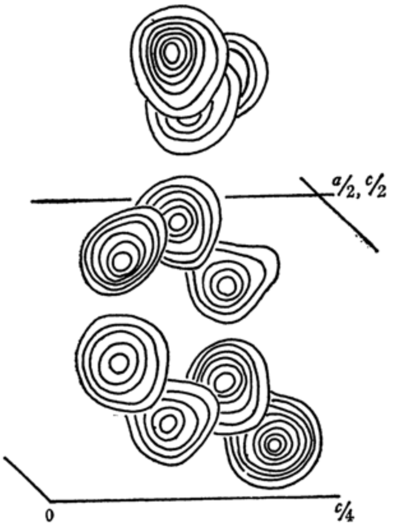

Fig. 3. The final electron density distribution. Composite diagram of sections parallel to the (010). Contours are at intervals of 1.0 eÅ^{-3}, the lowest one being 2.0 eÅ^{-3}.

groups were located at the positions expected from the hydrogen bonding. Further refinement of the structure was made by least-squares with a block-diagonal matrix approximation; anisotropic temperature factors in the form of

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

were assigned for the non-hydrogen atoms. Three cycles of the block-diagonal least-squares refinement yielded the R factor of 0.138 for all the independent reflections. If the unobserved reflections were omitted, the R factor became 0.118. Atomic scattering factors for the carbon, nitrogen and oxygen were taken from Berghuis, Haanapple, Potters, Loopstra, MacGillavry and Veenendaal,[8] and those for the hydrogen from McWeeny.[9] The final atomic coordinates and anisotropic temperature factors are given in Table I. Observed and calculated structure factors are listed in Table II. The final three-dimensional electron density distribution viewed down the b axis is shown in Fig. 3.

All numerical computations except for the final refinement were done on NEAC 2230 and NEAC 2206 computers with programs written by the authors. The least-squares method with block-diagonal approximation was made on an IBM 7090 with program written by T. Ashida.

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8) J. Berghuis, Ij. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry and A. L. Veenendaal, ibid., **8**, 478 (1955).

9) R. McWeeny, ibid., **4**, 513 (1951).

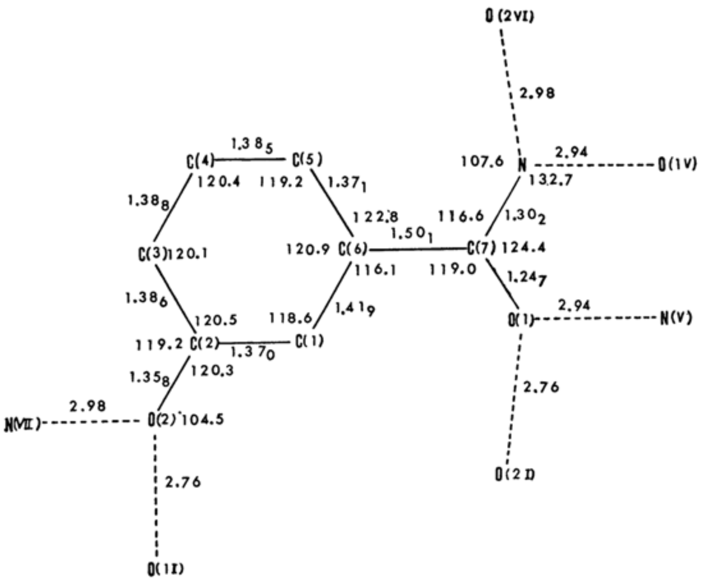

Fig. 4. Bond lengths (Å) and bond angles (°).

Description of the Structure and Discussion

Molecular Structure.—Bond lengths and bond angles found in the *m*-hydroxybenzamide molecule are shown in Fig. 4. The average standard deviations of the atomic coordinates are 0.014, 0.011 and 0.008 Å for carbon, nitrogen and oxygen atoms respectively. Therefore, the estimated standard deviations of the bond lengths are 0.020 Å in C–C, 0.018 Å in C–N and 0.016 Å in C–O. Although small fluctuations among the C–C bond lengths in the benzene ring are probably significant, detailed discussion about this will not be given because of low degree of accuracy. The average C–C bond length, 1.39 Å, and average C–C–C bond angle, 120.0°, in the benzene ring are in good agreement with the standard values. The dimensions of the carboxyamide group in the *m*-hydroxybenzamide, C–N$=1.30_2$ Å and C–O$=1.24_7$ Å, are close to those found in the related crystals: C–N$=1.31_2$ Å and C–O$=1.24_4$ Å in α-pyrazinamide,1) C–N$=1.29$ Å and C–O$=1.25$ Å in *m*-methylbenzamide,3) C–N$=1.30_9$ Å and C–O$=1.22_2$ Å in salicylamide,4) C–N$=1.34$ Å and C–O$=1.22$ Å in nicotinamide,10) C–N$=1.31$ Å, and C–O$=1.24$ Å in benzamide.11) The bond length between the ring carbon and hydroxy oxygen atoms is 1.35_8 Å, which does not differ significantly from the values found in the salicylamide, 1.36_1 Å, salicylic acid, 1.358 Å,12) and α-resorcinol, 1.36 Å.13)

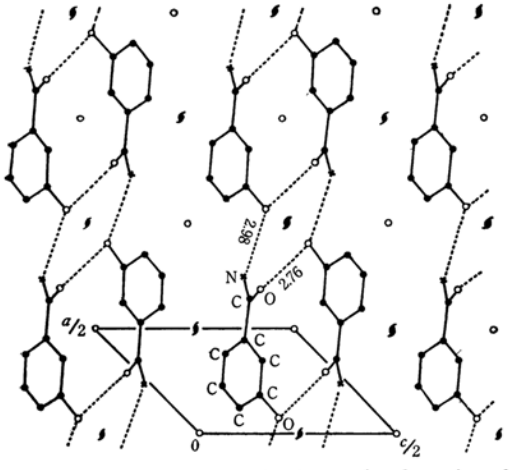

Fig. 5. Arrangement of the molecules viewed down the b axis.

The plane of the benzene ring (including C(7) and O(2)) can be represented by the equation:

$$y' = -0.0368x' - 1.2750z' + 4.3267$$

where $x' = x\sin\beta$, $y' = y$ and $z' = z + x\cos\beta$. The coefficients of the equation were determined by the least-squares method. The perpendicular displacements of the atoms from the mean plane are shown in Table III. The six carbon atoms in the benzene ring are coplanar within an experimental error. On the other hand, the carboxyamide group and the benzene ring twist to each

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

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

12) M. Sundarlingam and L. H. Jensen, ibid., **18**, 1053 (1965).

13) J. M. Robertson, *Proc. Roy. Soc.*, **A157**, 79 (1936).

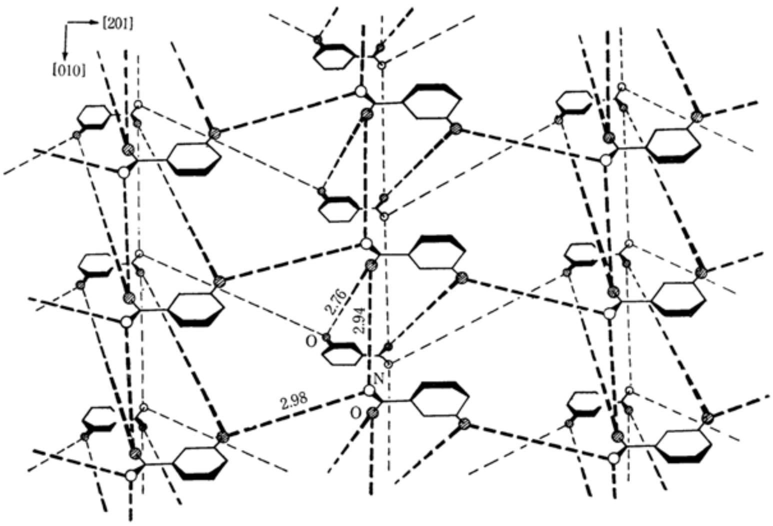

Fig. 6. A schematical drawing of the double-layered sheet formed by hydrogen bonds.

TABLE III. PERPENDICULAR DISPLACEMENTS OF ATOMS FROM THE MEAN PLANE OF THE BENZENE RING

Atom	Displacement Å
C(1)	0.025
C(2)	0.005
C(3)	0.006
C(4)	−0.001
C(5)	−0.007
C(6)	0.000
C(7)	−0.009
O(2)	−0.019

other around the C(6)–C(7) bond, and the angle between the planes of the benzene ring and the carboxyamide group is 24.4°. In many related crystals, the plane of the carboxyamide group makes an angle of about 25° with that of the benzene ring. This twist has been interpreted as the effect of steric hindrance between the hydrogen atom in the amino group and that in the ortho position of the ring.

Crystal Structure.—The crystal structure projected down the b axis is illustrated in Fig. 5, and the intermolecular distances less than 4.0 Å are listed in Table IV. There are three types of hydrogen bonds. The reference molecule at (x, y, z) is connected by the first set of OH···O (amide) of length 2.76 Å with the molecule at $(1-x, -y, 1-z)$, to form a molecular pair across the center of symmetry. The pairs are piled up infinitely along the b axis by the second set of NH···O (amide) of length 2.94 Å. The third hydrogen bonds, NH···O (hydroxy), of length 2.98 Å join the neighboring piles which are related to each other by the screw axis. Thus all the hydrogen atoms capable of participating the hydrogen bonding have been utilized and the endless double-layered sheets perpendicular to the c axis are formed as seen from Fig. 5. Figure 6 shows a schematical drawing of this double-layered sheet. This type of the molecular linkage by the hydrogen bonds has been first found in the present crystal.

TABLE IV. INTERMOLECULAR DISTANCES

From atom at x, y, z	To atom	In molecule	Distance(Å)
C(1)	C(1)	I	3.87
C(1)	C(6)	II	3.84
C(1)	C(7)	II	3.62
C(2)	C(7)	II	3.77
C(4)	C(7)	IV	3.62
C(5)	C(7)	IV	3.65
C(5)	C(6)	IV	3.72
C(5)	C(5)	IV	3.85
C(6)	C(6)	II	3.92
C(4)	N	IV	3.82
C(1)	O(1)	I	3.18
C(2)	O(1)	I	3.37
C(3)	O(2)	III	3.69
C(5)	O(1)	IV	3.82
C(7)	O(2)	VI	3.60
O(2)	N	II	3.30
O(2)	O(2)	III	3.38
	Hydrogen bond		
N	O(1)	V	2.94
N	O(2)	VI	2.98
O(2)	O(1)	I	2.76

Molecule		
Molecule	I at	$1-x,\ -y,\ 1-z$
	II	$1-x,\ 1-y,\ 1-z$
	III	$-x,\ {}^1/_2+y,\ {}^1/_2-z$
	IV	$1-x,\ {}^1/_2+y,\ {}^1/_2-z$
	V	$x,\ 1+y,\ z$
	VI	$1+x,\ {}^1/_2-y,\ {}^1/_2+z$

The intermolecular distances except the hydrogen bonds require no special comment, all corresponding to the van der Waals interaction. The molecular arrangement described here can reasonably explain the presence of cleavage parallel to the $(10\bar{4})$ plane.

The authors wish to express their thanks to Dr. Tamaichi Ashida for permitting the use of the programs of the least-squares with block-diagonal approximation. They are also indebted to Japan IBM Co., Ltd. which offerred machine time of an IBM 7090 under the University Contribution System.