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The Crystal Structure of *o*-Nitrobenzamide

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There are several types of molecular arrangement connected by hydrogen bonds[1-6] in the crystals of the derivatives of benzamide. It seems that a substituent group of benzamide influences the crystal structure. It is impossible, however, to discuss the effect of substituent on molecular arrangement at the present stage, because little is known about the crystal structure of the derivatives of benzamide. The present structure determination of *o*-nitrobenzamide has been undertaken as a part of a series of investigations on the crystal structures of aromatic carboxyamide.

Experimental

The crystal grown from alcohol solution was a transparent needle elongated along the *c* axis. The physical and crystal data are shown in Table 1. The unit cell dimensions were determined by the rotation and Weissenberg photographs about *b* and *c* axes. Intensities of 1494 independent reflections were measured visually on equi-inclination Weissenberg photographs of 0—3 layers around the *c* axis and of 0—8 layers around the *b* axis, with the use of Cu-K_α radiation. Intensities were corrected only for the usual Lorentz and polarization factors.

TABLE 1. CRYSTAL DATA

$C_6H_4(NO_2)(CONH_2)$		M.W.=166.14
Monoclinic		$P2_1/a$
a=12.01Å	b=12.79Å	c=5.03Å
α=90.0°	β=97.5°	γ=90.0°
D_{cal}=1.44g/cm³		
D_{obs}=1.43g/cm³	(by floatation)	

Structure Determination and Refinement

The orientation of the benzene ring was easily determined by the three-dimensional Patterson function. The three-dimensional coordinates of the atoms in the molecule for a probable orientation were at first determined by trial and successive Fourier methods. The coordinates of the atoms thus obtained were refined by the diagonal-matrix least-squares method with isotropic temperature factors. All the hydrogen atoms were revealed by (F_o-F_c) synthesis, at the stage of 0.15 of the R factor. Further refinements including hydrogen atoms were made by the block-diagonal-matrix least-squares method. The final R factor obtained was 0.136 for all the reflections but it was 0.108 excluding unobserved reflections. The atomic parameters are given in Table 2.

Structure Description and Discussion

The intramolecular bond lengths and angles are shown in Fig. 1. All the values seem to be reasonable.

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2) S. Orii, T. Nakamura, Y. Takaki, Y. Sasada, and M. Kakudo, This Bulletin, **36**, 788 (1963).
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5) Y. Kataube, Y. Sasada, and M. Kakudo, This Bulletin, **39**, 2576 (1966).
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TABLE 2. FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS

	x	y	z	$B_{11}\times10^5$	$B_{22}\times10^5$	$B_{33}\times10^4$	$B_{12}\times10^5$	$B_{13}\times10^4$	$B_{23}\times10^4$
C1	0.0769	0.3425	0.4306	476 (38)	359 (32)	239 (20)	24 (58)	−1 (13)	−1 (14)
C2	0.1295	0.4394	0.4522	780 (55)	382 (37)	494 (33)	−177 (74)	90 (21)	33 (18)
C3	0.2218	0.4522	0.6459	715 (57)	611 (50)	632 (41)	−436 (90)	40 (24)	−33 (24)
C4	0.2609	0.3709	0.8110	555 (49)	745 (55)	585 (38)	−339 (86)	−14 (21)	−82 (24)
C5	0.2091	0.2718	0.7816	501 (42)	573 (44)	388 (28)	−16 (71)	−33 (17)	27 (18)
C6	0.1164	0.2579	0.5908	483 (37)	276 (29)	236 (19)	105 (55)	21 (13)	−25 (13)
C7	0.0672	0.1506	0.5404	657 (43)	314 (31)	183 (18)	130 (61)	31 (14)	23 (13)
O1	−0.0303	0.3709	0.0212	1406 (62)	816 (42)	355 (21)	−0 (83)	−100 (18)	128 (16)
O2	−0.1080	0.2917	0.3302	557 (33)	741 (36)	503 (23)	−152 (58)	−52 (14)	8 (15)
O3	0.0442	0.1161	0.3125	1002 (40)	336 (23)	167 (13)	−137 (50)	25 (11)	−23 (9)
N1	−0.0276	0.3336	0.2465	755 (42)	340 (29)	309 (20)	331 (58)	−60 (14)	−12 (13)
N2	0.0547	0.0940	0.7588	923 (47)	410 (30)	190 (17)	−112 (63)	46 (14)	17 (12)
H1	0.107	0.485	0.296						
H2	0.254	0.537	0.630						
H3	0.328	0.380	0.982						
H4	0.223	0.229	0.934						
H5	−0.000	0.019	0.723						
H6	0.082	0.113	0.951						

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

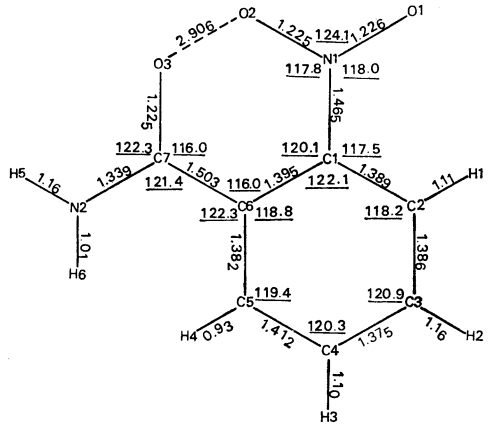

Fig. 1. Intramolecular distances (Å) and angles (°).

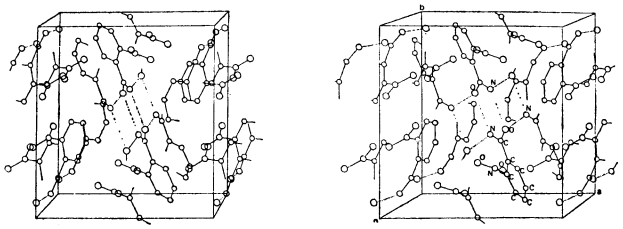

Fig. 3. The crystal structure of *o*-nitrobenzamide shown by a stereo pair, broken lines showing hydrogen bonds.

The average estimated standard deviation of bond lengths between non-hydrogen atoms is about 0.008 Å.

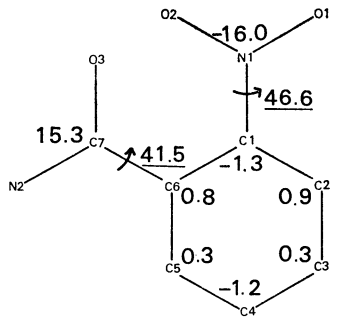

Fig. 2. The deviations ($\times10^2$Å) from the least-squares plane formed by the six carbon atoms of the benzene ring, and rotation angles of amide and nitro groups from the plane of the benzene ring.

The equation of the best plane of the benzene ring and the deviations of the atoms from the plane are given in Fig. 2. The planes of the amide and nitro groups rotate from that of the benzene ring at about 42 and 47 degrees, respectively. The arrangement of molecules in the unit cell is shown in Fig. 3 by a stereoscopic pair. There are two NH···O hydrogen bonds; the first set, 2.94 Å, forms a dimer across the center of symmetry, and the second set, 2.82 Å, links the dimers to form an endless chain extended along the *c* axis. A similar hydrogen bonding scheme has been found in the crystal of benzamide[1] and *m*-methylbenzamide.[2] The NO_2 group does not participate in the hydrogen bonds.