The Crystal Structure of the β Form of *p*-Chlorobenzamide

Taiichi HAYASHI, Kazuaki NAKATA,* Yoshito TAKAKI, and Kiichi SAKURAI
Department of Physics, Osaka Kyoiku University, Tennoji-ku, Osaka 543

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Synopsis. The crystal of the title compound is monoclinic, with space group $P2_1/a$, $a=9.11$, $b=9.54$, $c=8.18$ Å, $\beta=93.8°$, $Z=4$. The structure was solved by a packing analysis based on an ellipsoid-model and refined by block-diagonal least-squares calculations to $R=0.115$. The amide group makes a dihedral angle of 2.0° with the benzene ring.

p-Chlorobenzamide, C_7H_6ClNO, exhibits two polymorphs at room temperature.[1] They are triclinic with space group $P\bar{1}$ (α form) and monoclinic with $P2_1/a$ (β form). The structures of the α form at room temperature and −120 °C have been determined by Taniguchi *et al.*[2] Harada *et al.*[1] obtained crystals of the β form from an acetone solution, but they gave only crystal data. Therefore in this paper we deal with the structure determination of the β form.

Experimental

Many attempts were made to obtain crystals of the β form from acetone and other solutions, but they were all unsuccessful. Intensity data were then collected from Weissenberg photographs about the b axis ($k=0$—6) which have been prepared by Harada *et al.*,[1] although the quality of the photographs was rather poor. The intensities of 1067 reflections were measured visually and corrected for Lorentz and polarization factors. The cell dimensions were reconsidered on closer examination of the oscillation and Weissenberg photographs. The revised crystal data are: $a=9.11$ (10), $b=9.54$ (7), $c=8.18$ (15) Å, $\beta=93.8(5)°$, $Z=4$, space group $P2_1/a$.

A trial structure was successfully obtained from a packing analysis based on an ellipsoid-model[3] including a centrosymmetric dimer. The structure was refined by successive Fourier and by block-diagonal least-squares calculations[4] with a weighting scheme $w=1-\exp(-20\,s^2)$ with $s=\sin\theta/\lambda$. All the H atoms located from a difference Fourier map were included in the structure-factor calculations with an isotropic temperature factor of $B=4.0$ Å^2. The final R value was 0.115. The final atomic coordinates and thermal parameters are listed in Table 1.[5] All computations were made on an ACOS System 800 computer of the Computation Center of Osaka University.

Results and Discussion

Bond lengths and angles for the non-hydrogen atoms are shown in Fig. 1. The mean estimated standard deviations are 0.01 Å and 0.7°. The dihedral angle between the plane of the amide group and the mean plane of the benzene ring is 2.0°. This value is very close to that in *p*-nitrobenzamide[6] (2.3°), but unusually small as compared with those in the related amides, which vary from about 23°[7] to 29°.[8] The very small dihedral angle may give rise to a marked 'in-plane' bending of the C(1)–C(2) bond to reduce the interaction of the ortho-hydrogen with one of the NH_2 pro-

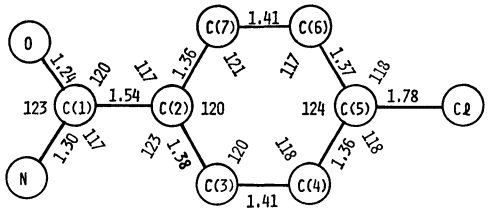

Fig. 1. A schematic diagram of the molecule showing the numbering of the atoms and the bond lengths (l/Å) and angles (ϕ/°).

TABLE 1. ATOMIC COORDINATES (×10³) AND THERMAL PARAMETERS (×10⁴) WITH THEIR ESTIMATED STANDARD DEVIATIONS

The anisotropic thermal parameters are of the form: $\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\}$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl	826 (2)	9 (3)	447 (2)	76 (2)	216 (5)	269 (4)	−33 (4)	−101 (4)	69 (7)
C(1)	225 (5)	6 (7)	86 (6)	77 (6)	36 (11)	179 (10)	−22 (11)	−9 (12)	−19 (15)
C(2)	377 (5)	0 (7)	181 (6)	75 (6)	60 (11)	161 (9)	8 (11)	11 (11)	19 (15)
C(3)	462 (6)	−120 (8)	188 (7)	93 (7)	89 (13)	186 (13)	7 (13)	1 (13)	−11 (17)
C(4)	601 (6)	−119 (9)	276 (7)	86 (7)	163 (16)	197 (12)	47 (15)	−27 (14)	−1 (21)
C(5)	649 (5)	4 (8)	343 (7)	63 (6)	102 (13)	188 (11)	−8 (12)	−19 (12)	22 (17)
C(6)	567 (6)	125 (9)	341 (7)	99 (7)	107 (14)	189 (11)	−49 (14)	−27 (14)	6 (18)
C(7)	427 (6)	120 (8)	254 (7)	87 (6)	67 (12)	213 (12)	−14 (13)	−17 (13)	6 (18)
N	177 (5)	−108 (7)	12 (6)	81 (6)	111 (11)	222 (11)	−13 (12)	−54 (12)	−24 (16)
O	152 (4)	116 (6)	87 (5)	86 (5)	89 (9)	259 (10)	33 (9)	−66 (11)	−37 (14)
H(3)	424	−210	136						
H(4)	675	−206	290						
H(6)	610	215	382						
H(7)	364	208	250						
H(N1)	92	−125	−50						
H(N2)	233	−201	−24						

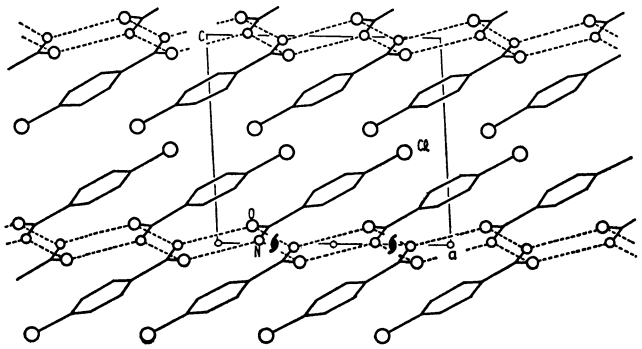

Fig. 2. The structure viewed along the b axis.

tons.[6] In fact, the difference between the C(1)–C(2)–C(3) and C(1)–C(2)–C(7) bond angles in the present compound and *p*-nitrobenzamide are remarkably large (6.0 and 6.7° respectively) as compared with those in the related amides.

The crystal structure viewed along the b axis is shown in Fig. 2. It consists of a stacking of hydrogen-bonded layers parallel to (001). Within a layer, two molecules are linked by NH···O hydrogen bonds of 3.06 Å to form a centrosymmetric dimer, and these dimers are linked by the other type of NH···O hydrogen bonds of 3.19 Å. This type of hydrogen-bond network (classified as 'screw-axis packing' by Leiserowitz and Schmidt[9]) is very rare in aromatic amides. The only case so far reported is that of *p*-chlorocinnamide.[10]

The Cl–Cl distance of 3.24 Å is appreciably shorter than those found in the α form of *p*-chlorobenzamide[2] at −120 °C (3.29 Å) and at room temperature (3.31 Å).

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