

The Crystal Structure of *o*-Bromobenzamide

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The crystal structure of *o*-bromobenzamide, C_7H_6NOBr , has been determined from two-dimensional X-ray intensity data estimated with a 'TV densitometer'. The crystals are monoclinic, space group $P2_1/a$ with $a=13.92$, $b=11.43$, $c=5.02$ Å, $\beta=107.3^\circ$, and four formula units in the cell. It is found that two molecules form a centrosymmetrical dimer, and these dimers are linked by hydrogen bonds into endless chains extended along the c axis.

Introduction

In previous papers,^{1,2)} as a method to facilitate an intensity measurement of X-ray film, the TV densitometer was proposed. A practical application of this apparatus has been attempted to the crystal structure determination of *o*-bromobenzamide. The present paper briefly describes the analysis of this crystal structure.

Experimental

Crystals of the compounds were kindly supplied by Professor Y. Takaki of Osaka Kyoiku University. Suitable crystals for a X-ray investigation were obtained by recrystallization from alcohol solution. The crystals are colorless needles elongated along the c axis. The systematic extinctions, $(0k0)$ absent with k odd and $(h0l)$ absent with h odd, indicated the space group to be $P2_1/a$. Cell dimensions were determined from oscillation and Weissenberg photographs of $(hk0)$ and $(h0l)$ using the higher reflexions. The values refined by least-squares method are $a=13.92\pm0.03$, $b=11.43\pm0.02$, $c=5.02\pm0.02$ Å, and $\beta=107^\circ\pm0.3^\circ$. Four molecules per unit cell correspond to the calculated density 1.74 g.cm⁻³.

Intensity data were obtained from multiple-film non-integrated Weissenberg photographs of $(hk0)$ and $(h0l)$ reflexions. Within the limiting sphere for Cu $K\alpha$ radiation, 169 out of 201 possible $(hk0)$ and 79 out of 89 possible $(h0l)$ reflexions were measured using the TV densitometer. The data were reduced to structure amplitudes in the usual way. No corrections were made for absorption or extinction.

Structure determination and refinement

Initial attempts were made to compute the Patterson function projected down the short c axis. The bromine atom was readily located by inspection of the Harker sections and was found at approximately $x/a=0.32$, $y/b=-0.054$. A Fourier synthesis for $(hk0)$ was computed with signs based on the bromine contribution only. From this analysis, carbon atoms of a benzene ring were reasonably well resolved, but, as shown in Fig. 1,

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the positions of an amide group were not deduced. Thus approximate x and y coordinates for these atoms were assigned from assumed bond lengths. An R value ($\sum ||F_o| - |F_c|| / |F_o|$) at this stage was 0.32 for ($hk0$) reflexions.

The Patterson projection on (010) was then computed. Approximate coordinates of the bromine atom were easily found at $x/a=0.32$, $z/c=-0.027$. The Fourier map based on the bromine atom showed the location for all carbon atoms, but the nitrogen and oxygen atoms in the amide group can not be located unambiguously. It was caused by the considerable overlaps of electron densities due to the crystal symmetry. The resulting structure factor calculation for ($h0l$) gave an R of 0.33 at this stage.

Refinement of the structure was made by means of difference Fourier syntheses

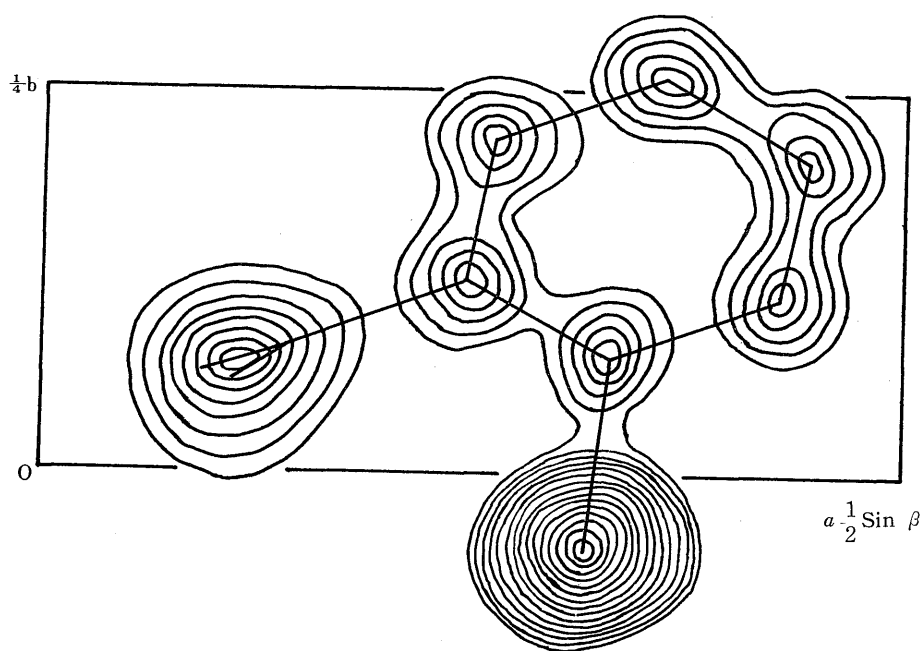


Fig. I The Fourier projection on (001). Contours are drawn at arbitrary intervals.

Table I. Atomic coordinates and temperature factors

Atom	x/a	y/b	z/c	($hk0$)	($h0l$)
C1	0.143	0.082	0.151	3.9	2.2
C2	0.246	0.128	0.276	3.8	2.2
C3	0.262	0.219	0.472	3.8	2.2
C4	0.359	0.258	0.588	3.8	2.2
C5	0.441	0.204	0.530	3.9	2.2
C6	0.424	0.114	0.337	3.8	2.2
C7	0.329	0.076	0.220	3.8	2.2
Br	0.316	-0.051	-0.027	6.2	4.3
Atom 1 (*)	0.092	0.064	0.328	4.0	3.0
Atom 2 (*)	0.110	0.058	-0.104	4.0	3.0

(*) One of these atoms corresponds to N and the other to O of the amide group.

using individual isotropic thermal parameters. After several cycles of the refinements, the R value decreased to 0.16 for both $(hk0)$ and $(h0l)$ reflections. However, at this stage, the nitrogen and oxygen atoms in the amide group can not be distinguished unambiguously. Further refinements were not performed in the present work because of the overlapping of the electron densities. The final Fourier projection on (001) is shown in Fig. 1. The atomic coordinates and temperature factors are listed in Table 1.

Description of the structure

The crystal structure is shown in projection along the *b* axis in Fig. 2.

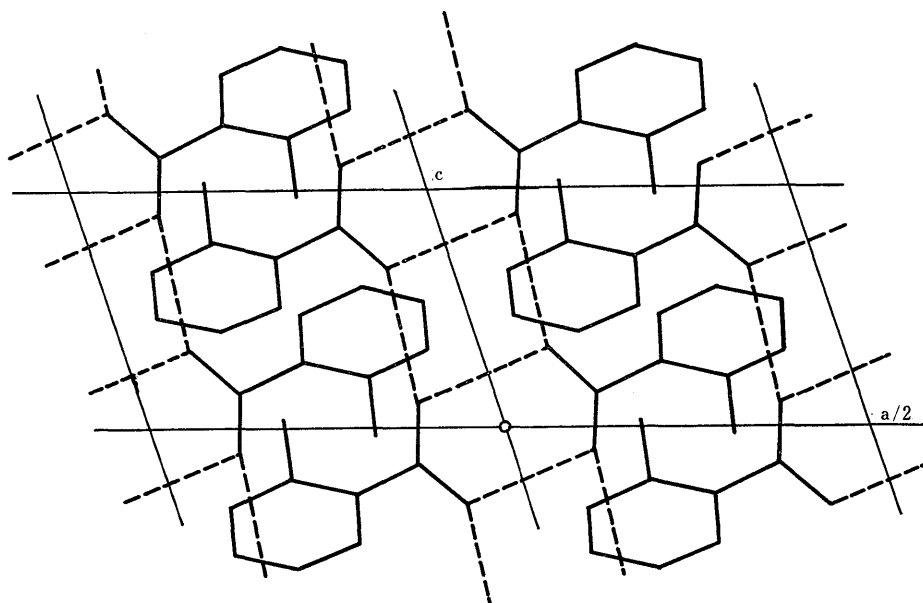


Fig. 2. Projection of the structure along the *b* axis.

The molecules are connected by two set of N-H...O type hydrogen bonds, the first set joining a pair of molecules across a center of symmetry to form a dimer, and the second set joining these dimers into endless chains extended along the *c* axis. This type of hydrogen bonding is the same as seen in benzamide^{3,4)} and its monosubstituted derivatives.⁵⁾ For further saying something conclusive about the crystal structure of the *o*-bromobenzamide, a knowledge of the more exact positions of light atoms would be essential. A three-dimensional X-ray diffraction study of the crystal has therefore been started.

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