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The Crystal Structure of *o*-(Bromomethyl)benzonitrile

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Abstract

o-(Bromomethyl)benzonitrile, C_8H_6BrN , is monoclinic with unit-cell dimensions $a = 12.69$ (3), $b = 8.16$ (4), $c = 7.24$ (2) Å and $\beta = 98.2$ (2)°. The space group is $P2_1/a$ and the calculated density with four formula units in the unit cell is 1.740 Mg m^{-3} . Intensities were collected on a Weissenberg camera using $Cu K\alpha$ radiation. The intensities of the reflections were visually estimated. The structure was determined by the heavy-atom technique and refined by the full-matrix least-squares method to $R = 0.095$ for 519 observed reflections. No angle in the benzyl ring differs significantly from the mean of 119.9° , nor C–C bond length from the mean of 1.41 Å; the lengths of C(1)–C(2) and C(7)–C(8) do not differ significantly.

Introduction

o-(Bromomethyl)benzonitrile, C_8H_6BrN , is important as a chemical reagent in the synthesis of heterocyclic compounds (Fuson, 1926). An X-ray investigation was undertaken to ascertain the stereochemistry of the molecule and the structure of the compound in the crystalline state.

Experimental

The crystals of the title compound used for this work were prepared by the method described by Fuson (1926). Single crystals were selected for X-ray diffraction work and being hygroscopic were sealed in Lindemann-glass capillaries of very low absorption.

The unit-cell dimensions were obtained from Weissenberg photographs using Ag lines superimposed as an internal standard. Preliminary optical and X-ray

examination of the crystals indicated that they are monoclinic. The space group was found to be $P2_1/a$ on the basis of systematic absences of reflections observed ($h0l$: $h = 2n + 1$; $0k0$: $k = 2n + 1$).

The unit-cell dimensions at room temperature ($\approx 303 \text{ K}$) are: $a = 12.69$ (3), $b = 8.16$ (4), $c = 7.24$ (2) Å and $\beta = 98.2$ (2)°. The density, 1.708 (5) Mg m^{-3} , measured by flotation in zinc chloride solution agrees with the value, 1.740 Mg m^{-3} , calculated for four formula units with $M_r = 195.9$ in the cell of volume 743.02 Å^3 . Three-dimensional intensity data were collected from equi-inclination Weissenberg photographs taken with $Cu K\alpha$ radiation by use of the multiple-film method. Intensities were measured by visual comparison with a calibrated intensity scale. The data were corrected for Lorentz, polarization and spot-extension effects (Phillips, 1954, 1956). The absorption correction was neglected but a type I extinction correction (Zachariasen, 1967) was applied in the last stages of refinement. The value of the extinction constant γ is 0.44 (6).

Structure determination and refinement

The structure was solved by identifying the Br–Br vectors in a three-dimensional Patterson synthesis. A three-dimensional Fourier synthesis based only on phases due to the Br-atom contribution revealed the positions of all the non-hydrogen atoms. The proposed structure was stereochemically satisfactory. The R factor at this stage was 0.21 .

The structure was then refined by the full-matrix least-squares method. The program used was the modified version of the *ORFLS* program of Busing, Martin & Levy (1962). The function minimized in the least-squares calculation was $\sum w(F_o - F_c)^2$, where the summation was over all reflections and w was the weighting factor. A plot of $w(\Delta F)^2$ as a function of

Table 1. Final fractional atomic coordinates ($\times 10^4$) with their standard deviations in parentheses

	x	y	z
Br	1732 (2)	1165 (2)	3936 (5)
N	3139 (17)	4510 (25)	1036 (41)
C(1)	852 (17)	2104 (18)	1895 (37)
C(2)	556 (13)	3827 (22)	2155 (38)
C(3)	-418 (16)	4175 (20)	2710 (40)
C(4)	-676 (15)	5826 (20)	3007 (42)
C(5)	0 (18)	7098 (24)	2803 (49)
C(6)	997 (16)	6795 (23)	2226 (46)
C(7)	1290 (12)	5126 (19)	1893 (39)
C(8)	2331 (23)	4742 (23)	1388 (47)

($\sin \theta$)/ λ and $|F_o|$ did not suggest any obvious weighting scheme, hence each reflection was given unit weight. The scattering factors for the C, N and Br atoms were taken from *International Tables for X-ray Crystallography* (1962). Subsequent cycles of full-matrix least-squares refinement with anisotropic temperature factors converged at a final *R* of 0.095. These calculations were performed on the CDC 3600 computer at the Tata Institute of Fundamental Research, Bombay.

Attempts were made to locate the H atoms from the difference map but their positions could not be precisely determined. The contribution of the H atoms is hence not included in the structure factors.

The positional parameters of the atoms together with their estimated standard deviations are given in Table 1.*

Description and discussion of the structure

Figs. 1 and 2 shows projections of the structure along the *c* and *a* axes respectively. Bond lengths and bond angles with standard deviations for non-hydrogen atoms are listed in Tables 2 and 3 respectively.

The equation of the least-squares plane through the atoms C(2), C(3), C(4), C(5), C(6) and C(7) of the benzyl group of the molecule is

$$0.907X' - 0.091Y' + 0.411Z' = 1.316 \text{ (plane } A\text{)}$$

where X', Y', Z' are coordinates in Å referred to a set of orthogonal axes given by $X' = X + Z \cos \beta$, $Y' = Y$, $Z' = Z \sin \beta$. The deviations of the atoms C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(1), N and Br from plane *A* are +0.011, +0.009, -0.009, -0.002, -0.008, +0.000, 0.063, 0.072, 0.133 and 1.013 Å

* Lists of structure factors, anisotropic thermal parameters and intermolecular contacts shorter than 3.5 Å have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33893 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

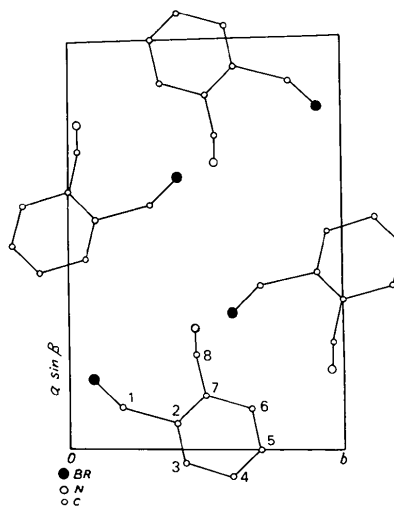


Fig. 1. Projection of the structure along the *c* axis.

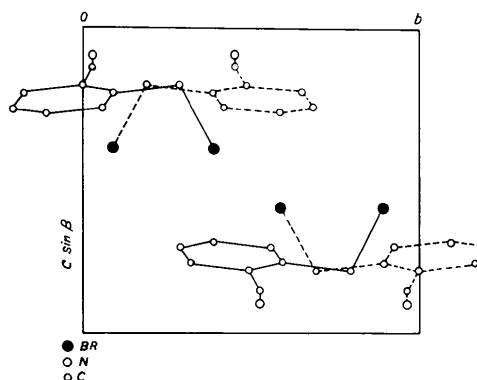


Fig. 2. Projection of the structure along the *a* axis.

Table 2. Bond lengths (Å) with their e.s.d.'s in parentheses

Br—C(1)	1.88 (0.022)	C(5)—C(6)	1.41 (0.033)
C(1)—C(2)	1.47 (0.024)	C(6)—C(7)	1.44 (0.025)
C(2)—C(3)	1.38 (0.028)	C(7)—C(2)	1.44 (0.024)
C(3)—C(4)	1.41 (0.025)	C(7)—C(8)	1.45 (0.034)
C(4)—C(5)	1.37 (0.027)	C(8)—N	1.11 (0.037)

Table 3. Bond angles ($^\circ$) with their e.s.d.'s in parentheses

Br—C(1)—C(2)	114.9 (1.37)	C(4)—C(5)—C(6)	120.1 (1.83)
C(1)—C(2)—C(3)	119.3 (1.54)	C(5)—C(6)—C(7)	118.6 (1.60)
C(1)—C(2)—C(7)	120.3 (1.43)	C(6)—C(7)—C(2)	119.1 (1.60)
C(3)—C(2)—C(7)	120.4 (1.77)	C(6)—C(7)—C(8)	120.8 (1.60)
C(2)—C(3)—C(4)	118.6 (1.66)	C(2)—C(7)—C(8)	120.1 (1.60)
C(3)—C(4)—C(5)	122.5 (1.72)	C(7)—C(8)—N	177.0 (2.78)

respectively. The plane through C(7) and cyano group atoms C(8) and N is

$$0.849X' - 0.468Y' + 0.247Z' = -0.594.$$

In the benzyl ring the mean valence angle 119.9° and the mean bond length 1.41 \AA are in agreement with the corresponding data found in the literature. No angle in the benzyl ring differs significantly from the mean of 119.9° , nor C—C bond length from the mean of 1.41 \AA . The lengths of C(1)—C(2) and C(7)—C(8) do not differ significantly.

The distortion in the angle Br—C(1)—C(2), $114.9 (1.37)^\circ$, from the tetrahedral value of 109.6° is due to an interaction between Br and N. There are no short interatomic contacts, which show that the structure is held by only van der Waals forces, which in turn are responsible for the high thermal vibrations of

the atoms and the decomposition observed when the substance is exposed to the atmosphere.

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Study of Photochromic Sydnones.

II. Structure of 4-Bromo-3-(3-pyridyl)sydnone

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Abstract

The structure and absolute configuration of $C_7H_4BrN_3O_2$ have been determined by the heavy-atom method; refinement led to $R = 0.029$ for 766 observed reflexions. The unit cell is orthorhombic, space group $P2_12_12_1$, with $a = 7.175 (2)$, $b = 17.018 (8)$, $c = 6.875 (3) \text{ \AA}$, $V = 839.5 (6) \text{ \AA}^3$, $Z = 4$. A significant intermolecular contact between Br and O(6), $2.979 (4) \text{ \AA}$, was found. The pyridyl rings of neighbouring molecules are stacked one over the other making a dihedral angle of 16.3° .

Introduction

The title compound changes its colour irreversibly under the influence of UV light ($\lambda < 400 \text{ nm}$). The original white colour was re-established after dissolution in ethanol and recrystallization (Nešpůrek & Šorm, 1977). This anomalous behaviour was observed only with sydnone halogen derivatives. Therefore we con-

sider it useful to estimate the role of the halogen substituent in the structure.

Experimental

Single crystals were synthesized by the method of Puranik & Suschitzky (1967) and grown by freezing from ethanol. The crystal used was ground to a sphere with $r = 0.15 \text{ mm}$.

Crystal data

$C_7H_4BrN_3O_2$, orthorhombic, $P2_12_12_1$, $a = 7.175 (2)$, $b = 17.018 (8)$, $c = 6.875 (3) \text{ \AA}$, $V = 839.5 (6) \text{ \AA}^3$, $Z = 4$, $D_m = 1.84 (3)$, $D_x = 1.92 \text{ Mg m}^{-3}$; FW 242, m.p. 407–409 K, $F(000) = 472$, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $\mu(\text{Mo } K\alpha) = 5.15 \text{ mm}^{-1}$; the density was determined by flotation in a Clerici solution; systematic absences: $h00$ for h odd; $0k0$ for k odd; $00l$ for l odd. The dimensions of the cell were determined by refining 16 reflexions measured with an automated diffractometer (Mo $K\alpha$, graphite monochromator) at room temperature.

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