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Structure of 4-Chlorobenzyl Alcohol

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Abstract. C₇H₇ClO, $M_r = 142.6$, monoclinic, $P2_1$, $a = 12.069$ (3), $b = 4.933$ (1), $c = 5.906$ (3) Å, $\beta = 102.63$ (3)°, $V = 343.1$ (2) Å³, $Z = 2$, $D_m = 1.380$, $D_x = 1.381$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.46$ mm⁻¹, $F(000) = 148$, $T = 298$ K, $R = 0.041$ for 645 unique reflections. The molecule takes a *trans* form with respect to the positions of the O hydrogen atom and the aryl group. The crystal structure is characterized by the chains of O—H...O hydrogen bonds extending along a 2₁ axis.

Introduction. The chlorine nuclear quadrupole resonance (NQR) study of the title compound has shown the presence of a phase transition from a low-temperature phase (LTP) to the room-temperature phase (RTP) at about 226 K (Hashimoto & Weiss, 1982). In the course of our thermoanalytical investigation on the phase transition, RTP was found to be supercooled without difficulty. The RTP to LTP transition temperature was about 205 K for crystals obtained by gradual evaporation of a benzene solution, while, for crystals which had undergone the phase transition several times, the transition temperature was observed in a region between 209 and 215 K depending upon the maximum

temperature up to which the specimen had been heated subsequently to the LTP to RTP transition. In general, a prolonged annealing of a specimen resulted in a lowering of the RTP to LTP transition temperature. As to the LTP to RTP transition, melt-grown crystals exhibited the transition at about 225 K, while the compound recrystallized from a benzene solution exhibited the transition at about 236 K. Similar complicated phase transitions were found for 4-bromo- and 4-methylbenzyl alcohols isomorphous to the title compound. Another point of interest is the rotational isomerism of the molecule predicted by IR and dipole-moment studies (Oki & Iwamura, 1959; Pandiarajan & Sekar, 1981). In order to obtain a definite structural base for the study of the nature of the phase transition and to determine the molecular conformation in the solid state, the crystal structure of the room-temperature phase was studied by single-crystal X-ray diffractometry.

Experimental. Colorless plate-like crystal (from benzene) set in a thin glass capillary to prevent sublimation. Density by pycnometry. Approximate crystal size 0.2 × 0.3 × 0.3 mm. Rigaku AFC-5 automated

four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Cell parameters determined by least-squares refinement of 25 reflections with $24 < 2\theta < 28^\circ$. Intensities of 747 independent reflections within $(\sin\theta)/\lambda < 0.650 \text{ \AA}^{-1}$ ($-14 \leq h \leq 14$, $0 \leq k \leq 6$, $0 \leq l \leq 7$) measured by ω - 2θ scan technique, scan speed 8° min^{-1} in ω . Crystal deterioration checked by monitoring intensities of three standard reflections, 300, 020 and 003, every 100 reflections: variations $< 3\%$. 645 reflections with $|F_o| > 3\sigma(F_o)$ used for structure analysis. Corrections for Lorentz-polarization, but not for absorption or extinction. Structure solved by the direct method with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by block-diagonal least squares (Ashida, 1979) with anisotropic thermal parameters for non-H atoms and isotropic ones for the H atom in the OH group; for the other H atoms the positional and isotropic thermal parameters were fixed ($B = 5.0 \text{ \AA}^2$). Final refinement gave $R = 0.041$, $wR = 0.041$ and $S = 2.46$; $w = [\sigma^2(F_o) - 0.150|F_o| + 0.012|F_o|^2]^{-1}$; $(\Delta/\sigma)_{\text{max}} = 0.07$. $\rho_{\text{max}} = 0.16$, $\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$ on final difference Fourier map. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations performed on an ACOS 1000 computer at the Information Processing Center of Kobe University with the *UNICS* (Sakurai & Kobayashi, 1979) system.

Discussion. The chlorine NQR spectrum of the compound predicted that the unit cell of the crystal should contain only one crystallographically independent chlorine atom, in accord with the present result.

Final atomic coordinates and thermal parameters are listed in Table 1,* and bond lengths and bond angles for non-H atoms are given in Table 2. The molecular structure drawn by *ORTEP* (Johnson, 1976) is shown in Fig. 1, together with the atom-numbering scheme. Bond lengths and bond angles show no unusual features. The benzene ring is planar within the e.s.d.'s, while C(7) and Cl deviate from the plane by 0.072 (6) and 0.029 (5) \AA , respectively.

Internal rotations around the C(1)–C(7) and C(7)–O bonds would give rise to two kinds of rotational isomerism. The first kind is concerned with the rotation around the latter bond. In this case, there may be two rotational isomers depending on whether the O hydrogen H(O) is *gauche* or *trans* to the aryl group. The other kind of isomer can be defined by the angle χ between the C(1)–C(7)–O plane and the benzene ring.

Studies of the IR spectrum (Oki & Iwamura, 1959) and dipole moment (Pandiarajan & Sekar, 1981) of the compound dissolved in carbon tetrachloride and benzene indicated that there exist both *trans* and *gauche* isomers in the nonpolar solvents and that the latter form is more stable than the former because of the O–H... π intramolecular hydrogen bonding. The present work shows that the molecule in the crystal takes the *trans* form [angle H(O)–O–C(7)–C(1) = $173 (3)^\circ$], less favorable for intramolecular hydrogen bonding.

For the free molecule of the *trans* isomer, the conformation with $\chi = 0$ or 90° seems to be stable. An atom-atom potential calculation based on a 6-exp function (Allinger, 1977) suggested that the latter is the most stable one, while a *trans* form with $\chi = 52.7 (5)^\circ$ is found in the crystal. Thus, intermolecular interactions must be responsible for the stabilization of the conformation in the crystal.

Table 1. Final atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}} (\text{\AA}^2)$
Cl	3973 (1)	6051	8569 (2)	4.69 (2)
C(1)	2081 (2)	-23 (6)	3455 (6)	3.61 (8)
C(2)	3120 (2)	983 (9)	3257 (5)	3.95 (8)
C(3)	3700 (3)	2850 (6)	4795 (6)	3.59 (9)
C(4)	3222 (2)	3723 (6)	6593 (5)	3.52 (8)
C(5)	2181 (3)	2776 (7)	6831 (6)	4.09 (10)
C(6)	1614 (3)	905 (9)	5260 (6)	4.51 (10)
C(7)	1500 (3)	-2171 (8)	1792 (7)	5.45 (12)
O	388 (2)	-1481 (5)	842 (5)	6.18 (8)

Table 2. Bond lengths (\AA) and bond angles ($^\circ$)

Cl–C(4)	1.743 (3)	C(1)–C(2)	1.378 (5)
C(1)–C(6)	1.387 (6)	C(1)–C(7)	1.509 (5)
C(2)–C(3)	1.373 (6)	C(3)–C(4)	1.383 (5)
C(4)–C(5)	1.377 (5)	C(5)–C(6)	1.379 (6)
C(7)–O	1.380 (5)		
C(2)–C(1)–C(6)	118.5 (3)	C(2)–C(1)–C(7)	119.9 (3)
C(6)–C(1)–C(7)	121.6 (3)	C(1)–C(2)–C(3)	121.8 (4)
C(2)–C(3)–C(4)	118.6 (3)	Cl–C(4)–C(3)	118.5 (3)
Cl–C(4)–C(5)	120.5 (3)	C(3)–C(4)–C(5)	121.1 (3)
C(4)–C(5)–C(6)	119.2 (3)	C(1)–C(6)–C(5)	120.9 (4)
C(1)–C(7)–O	111.3 (3)		

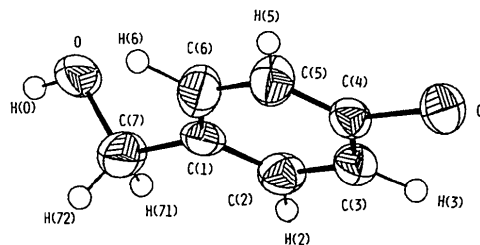


Fig. 1. An *ORTEP* drawing of the molecular structure with the numbering scheme. Non-hydrogen atoms are expressed as thermal ellipsoids at the 50% probability level and H atoms as spheres of radius 0.1 \AA .

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44492 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

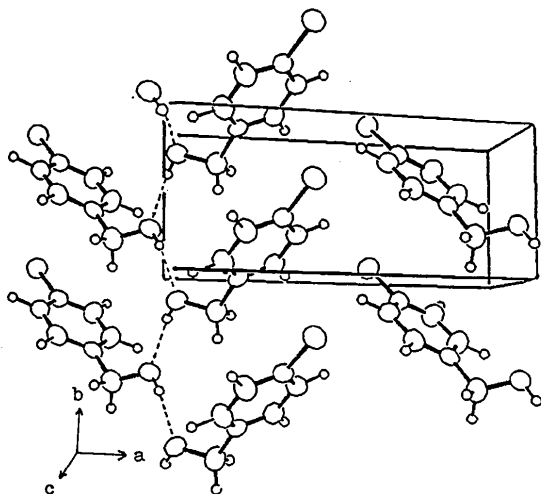


Fig. 2. An ORTEP drawing of the crystal structure viewed along the *c* axis. Broken lines denote hydrogen bonds.

The molecular packing projected along the *c* axis is illustrated in Fig. 2. The crystal structure of the compound is characterized by chains of O—H...O hydrogen bonds running along a 2_1 axis. The O...O distance of 2.746 (4) Å is within the usual range, although it is longer than the 2.66 Å found in methanol having similar hydrogen-bond chains (Tauer & Lipscomb, 1952). The molecules linked by the hydrogen-bond chains are held together by van der Waals interactions. The shortest intermolecular distance between Cl atoms is 3.641 (2) Å; Cl...H(71) (2.98 Å) is slightly less than the van der Waals contact. The Cl

atom of a molecule is placed just above the benzene ring of the adjacent molecule related by a *b* translation. However, the distance between the Cl atom and the mean plane of the benzene ring [3.694 (2) Å] is longer than the normal van der Waals contact, indicating the absence of specific interactions between them.

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Structure of 4-Chloro-7-nitro-2,1,3-benzoxadiazole

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Abstract. $C_6H_2ClN_3O_3$, $M_r = 199.55$, monoclinic, $P2_1$, $a = 13.420$ (1), $b = 5.410$ (2), $c = 10.703$ (1) Å, $\beta = 102.36$ (1)°, $V = 759.0$ (3) Å³, $Z = 4$, D_m not measured, $D_x = 1.746$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 4.7$ mm⁻¹, $F(000) = 400$, $T = 296$ K, final $R = 0.048$ for 1484 observed reflections. The two independent molecules of the asymmetric unit have different structures, resulting from different packing environments. There is a distinct double-bond fixation in the six-membered ring of the molecule. The non-

centrosymmetric crystal structure is consistent with the observation of second-harmonic generation.

Introduction. The structure of 2,1,3-benzoxadiazole (BFZ) has been of particular interest concerning the double-bond fixation in the six-membered ring. It has been shown that BFZ is more aromatic than the sulfur (BTD) and selenium (BSD) analogues which exhibit considerable quinoid character in the six-membered ring in crystals (Luzzati, 1951). Microwave study has,