Crystal Structure of Trichloroacetamide and Inequivalent Reorientations of CCl_3 Groups in the Crystal

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Synopsis. The crystal structure of trichloroacetamide has been determined by the single crystal X-ray diffraction method. Intermolecular contacts have been found to be responsible for the inequivalent reorientations of the CCl_3 groups of two crystallographically-independent molecules in the crystal.

It is well-known that CCl_3 groups in organic compounds undergo reorientations around the C_3 axis in crystalline state.[1] For several trichloromethyl derivatives, the magnitudes of the potential barrier height hindering the reorientation (V_0) have been determined by means of pulsed ^{35}Cl NQR method.[2-6] Chlorine NQR studies on trichloroacetamide (TCAA) indicated that the asymmetric unit of the crystal contains two independent CCl_3 groups with relatively different V_0 values (20.1 and 46.8 kJ mol^{-1}).[6,7] The origin of this difference has been unknown. Besides, our preliminary thermal analysis by a differential scanning calorimeter (DSC) showed that TCAA has a peculiar phase transition. Because of these reasons we decided to carry out the crystal structure analysis of TCAA.

Experimental

Recrystallizations of commercial trichloroacetamide (Nakarai Chemicals, LTD.) from diethyl ether gave colorless plate crystals (mp 415 K by DSC). A crystal with approximate dimensions of 0.5×0.4×0.3 mm^3 was used for the X-ray measurements. The unit cell parameters and intensities were measured on a Rigaku AFC-5 automatic four circle diffractometer with graphite-monochromatized Mo-K_α radiation. 1562 reflections within the range $2\theta<55°$ were collected by the ω-2θ scan technique. The ω scan width, scan rate and back ground counting time at both ends of a scan were $\omega=(1.4+0.35\tan\theta)°$, 8° min^{-1}, and 5.0 s, respectively. Lorentz and polarizetion corrections were made. Independent 1340 reflections with $|F_o|>3\sigma(F_o)$ were used in structure analysis. The structure was solved by the direct method (MULTAN 78)[8] and refined by the block-diagonal least-squares method (HBLS-V) with anisotropic temperature factors.[9] The function minimized was $\Sigma w(|F_o|-|F_c|)^2$. All the hydrogen atoms were found in the difference Fourier map and included in the refinement with isotropic temperature factors. The final R value was 0.058 (R_w=0.068). The weighting scheme adopted at the final stage was w=1.0 for $|F_o|\leq10.0$ and $w=[1.0+0.096(|F_o|-10.0)]^{-1}$ for $|F_o|>10.0$. Atomic scattering factors were taken from International Tables for X-Ray Crystallography.[10] The computations were carried out on an ACOS-1000 computer at Kobe University. Final atomic parameters are listed in Table 1.[11]

Crystal data: $C_2H_2Cl_3NO$, M=162.4, monoclinic, $P2_1$, a=10.415(2), b=5.785(1), c=10.182(2) Å, 3 =107.61° (2), Z=4, D_c=1.845 Mg m^{-3}, D_m=1.82 Mg^{-3}, μ=1.5 mm^{-1}, F(000)=320.

Results and Discussion

In accordance with the prediction of the NQR work,[7] the asymmetric unit of the crystal of TCAA contains two independent molecules (designated as Molecule A and B) shown in Fig. 1 (ORTEP-drawings).[12] The bond lengths, bond angles, and dihedral angles are listed in Table 2. The values of bond lengths and angles are comparable with those found in several amides.[13-17]

An ORTEP drawing of the crystal structure is shown in Fig. 2. A pair of N-H···O hydrogen bonds of lengths 2.982 and 3.019 Å couples Molecule A and B to form a dimer. Interestingly, the two molecules are related by a local two-fold axis. Each molecule of a dimer is also connected by other kinds of hydrogen bonds of lengths 2.915 and 2.957 Å to its nearest neighbors in the c direction. This results in a two-dimensional system of hydrogen bonds similar to those found in tetradecanamide and decanamide.[16,17]

Table 1. Final Atomic Coordinates (×10^4, H×10^3) with e. s. d.'s in Parentheses, and Equivalent Isotropic Thermal Parameters (Å^2)

	x	y	z	B_{eq}
Molecule A				
Cl(1)	9099(2)	492(4)	4132(2)	4.56(5)
Cl(2)	7538(2)	3985(4)	2342(2)	4.13(6)
Cl(3)	7462(2)	3642(4)	5122(2)	4.05(6)
C(1)	7576(6)	2056(12)	3670(6)	2.7(1)
C(2)	6447(6)	221(13)	3187(6)	2.8(2)
N	5925(6)	−649(12)	4120(5)	3.3(2)
O	6139(5)	−401(10)	1976(4)	3.6(1)
H(1)	608(9)	4(20)	494(9)	4.8(25)[a]
H(2)	518(7)	−183(16)	383(7)	2.2(16)[a]
Molecule B				
Cl(1)	2759(2)	764(5)	1200(4)	9.45(14)
Cl(2)	1283(3)	3814(8)	2388(3)	7.31(12)
Cl(3)	1251(2)	4410(6)	−379(2)	7.57(9)
C(1)	2240(6)	3617(13)	1270(6)	2.8(2)
C(2)	3545(5)	5112(11)	1795(6)	2.5(2)
N	4068(5)	5873(12)	850(5)	3.3(2)
O	4014(5)	5472(11)	3029(4)	3.8(1)
H(1)	367(9)	568(22)	−15(9)	4.4(23)[a]
H(2)	484(7)	660(17)	117(7)	2.5(18)[a]

a) Isotropic temperature factors.

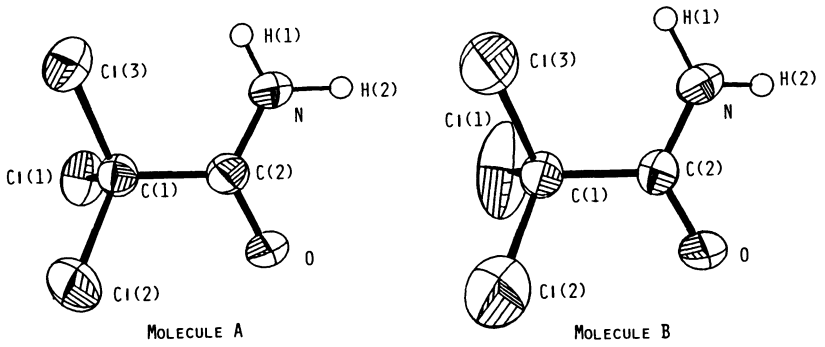

Fig. 1. ORTEP drawings of molecular structures with the numbering scheme. Non-hydogen atoms are expressed as thermal ellipsoids with 50% probability level and hydrogen atoms as spheres of radius 0.1 Å.

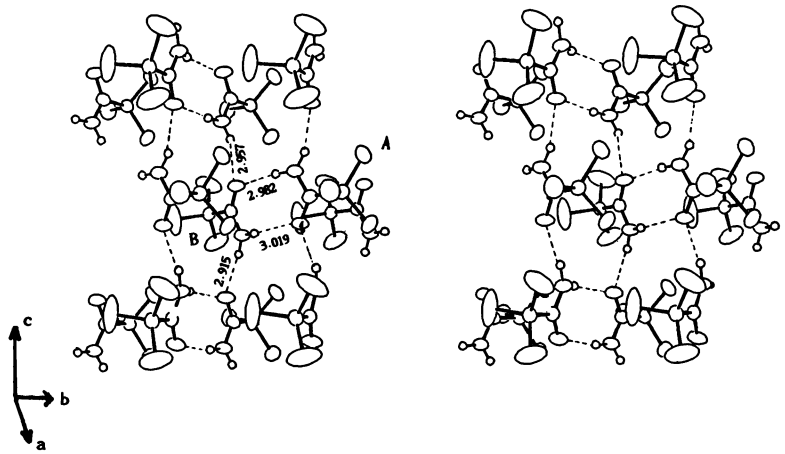

Fig. 2. An ORTEP drawing of the crystal structure of trichloroacetamide viewed along the normal to the bc plane. A: Molecule A; B: Molecule B.

Table 2. Bond Lengths, Bond Angles, and Dihedral Angles of Molecule A and B

	Molecule A	Molecule B
	l/Å	
C(1)-Cl(1)	1.762(8)	1.745(9)
C(1)-Cl(2)	1.745(7)	1.729(9)
C(1)-Cl(3)	1.775(7)	1.745(8)
C(1)-C(2)	1.550(10)	1.563(10)
C(2)-N	1.328(10)	1.316(10)
C(2)-O	1.230(9)	1.220(9)
	ϕ/deg	
Cl(1)-C(1)-Cl(2)	110.1(4)	109.7(4)
Cl(1)-C(1)-Cl(3)	109.0(4)	108.0(4)
Cl(2)-C(1)-Cl(3)	108.9(4)	109.0(4)
Cl(1)-C(1)-C(2)	105.6(5)	106.8(5)
Cl(2)-C(1)-C(2)	110.8(5)	110.7(5)
Cl(3)-C(1)-C(2)	112.5(5)	112.5(5)
C(1)-C(2)-O	117.5(6)	118.8(6)
C(1)-C(2)-N	117.9(6)	116.4(6)
N-C(2)-O	124.5(7)	124.8(7)
	χ/deg	
Cl(1)-C-C-N	91.2(7)	87.1(7)
Cl(2)-C-C-N	−149.6(6)	−153.6(6)
Cl(3)-C-C-N	−27.5(8)	−31.3(8)
Cl(1)-C-C-O	−85.6(7)	−92.2(7)
Cl(2)-C-C-O	33.6(8)	27.2(8)
Cl(3)-C-C-O	155.7(6)	149.5(6)

The gross feature of the solid is determined by van der Waals contacts of chlorine atoms in CCl_3 groups on both sides of the layer.

The crystal and molecular structures of TCAA suggest that the observed difference in V_0 is attributable to intermolecular contacts between CCl_3 groups and their neighboring atoms. Then, by rotating the group around its C_3 axis, we calculated the atom-atom potential energy (U) as a function of rotation angle (ϕ) on the basis of the following function[18]

$$U = \Sigma\varepsilon_i(2.90\times 10^5 \exp(-12.50/P_i) - 2.25P_i^6)$$

where P_i stands for the sum of van der Waals radii (Σr_i^*) divided by the distance (r_i) between interacting centers. The values of van der Waals radii and ε_i were taken from Ref. 19.

The results of the calculations shown in Fig. 3 indicate that the intermolecular Cl···Cl interactions dominate to determine the magnitude of the potential, and that the value of $V_0=U_{max}-U_{min}$ of Molecule A is considerably larger than that of Molecule B. These findings are consistent with the result of the NQR study. However, for both Molecule A and B, the calculated V_0 values are twice as high as the observed ones. Unfortunately, the discussion on the magnitude of V_0 will be artificial, because it depends strongly on the choice of van der Waals radius of chlorine atom.

As seen in Table 1, the magnitudes of the tem-

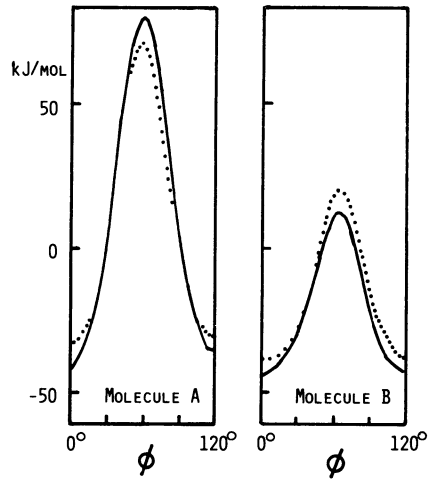

Fig. 3. Calculated atom-atom potential curves of CCl_3 groups in trichloroacetamide crystal as a function of rotation angle (ϕ), where the orientation with ϕ=0 corresponds to the structure determined by the present X-ray work. ——: Including interactions with all atoms within 4.1 Å (twice of the van der Waals radius of chlorine atom); ·····: including interactions only with chlorine atoms within 4.1 Å.

perature factor (B_{eq}) for Cl atoms in Molecule B are considerably larger than those in Molecule A. Moreover, the thermal ellipsoids of Cl atoms of Molecule B indicate the ease of the reorientation of the CCl_3 group around the C_3 axis (see Fig. 2). Thus, the CCl_3 group with the higher V_0 value may be assigned to Molecule A, although a complete assignment should be done by the Zeeman NQR study on a single crystal.

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