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The Crystal and Molecular Structures of 1:2 Complexes of N,N'-Dimethylpiperazine with 1-(o-Chlorophenyl)-1-phenyl-2-propyn-1-ol

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The N,N'-dimethylpiperazine molecule in the title crystals is bound by two chiral acetylenic alcohol molecules through the strong O-H...N hydrogen bonds. The symmetric 1:2 complex of N,N'-dimethylpiperazine with (+)- and (-)-1-(o-chlorophenyl)-1-phenyl-2-propyn-1-ol(CPPOH), which is useful for the optical purification of partially resolved CPPOH, has the denser packing of molecules in the crystal than the asymmetric 1:2 complex of N,N'-dimethylpiperazine with two (-)-CPPOH.

Recently, Toda and Tanaka have found that the partially resolved 1-(o-chlorophenyl)-1-phenyl-2-propyn-1-ol (CPPOH) can easily be purified optically by complexation with simple achiral amine such as N,N'-dimethylpiperazine.$^{1)}$ Interestingly, the N,N'-dimethylpiperazine forms a 1:2 molecular complex crystal with racemic mixture of (+)- and (-)-CPPOH (**1**). However, it was found that in an appropriate condition, the N,N'-dimethylpiperazine can also form another 1:2 complex crystal with optically pure CPPOH such as (-)-CPPOH (**2**). In order to obtain a clue to clarify the fact that makes the complex crystal formation of **1** much more easier than that of **2** the crystal structures of **1** and **2** have been determined by means of X-ray diffraction.

The crystal data of these two crystals are as follows: $C_6H_{14}N_2$,2($C_{15}H_{11}OCl$), F.W. 599.6, **1**: triclinic, space group $P\bar{1}$, a=10.752(4), b=9.057(4), c=8.350(5) Å, α =100.28(4), β =81.87(3), γ =102.38(2)°, V =777.0(7) $Å^3$, D_c=1.282 g cm^{-3} for Z=1; **2**: monoclinic, space group $P2_1$, a=17.511(2), b=7.606(1), c=13.311(2) Å, β =111.55 (1)°, V =1648.9(5) $Å^3$, D_c=1.208 g cm^{-3} for Z =2.

Molecular structures of the complexes **1** and **2** are shown in Fig 1.[2,3] The remarkable feature of the structure of the complex **1** is that the N,N'-dimethylpiperazine molecule takes a chair form, the center of which lies on a crystallographic center of symmetry, and one of the N atoms is bound with a (+)-CPPOH molecule and the other N atom with a (-)-CPPOH by the strong O-H...N hydrogen bonds to form a centrosymmetric 1:2 molecular complex [O(1)...N(1)=2.771(3), O(1)-H(1)=1.05(3), N(1)...H(1)=1.76(4) Å. The O(1), H(1), and N(1) atoms do not lie on a line[O(1)-H(1)...N(1)=161(3)°]. The asymmetric N,N'-dimethylpiperazine molecule in the complex **2** also takes a chair form, which is bound with two (-)-CPPOH molecules by the similar O-H...N hydrogen bonds[O(1A)...N(1)=2.768(5), O(1A)-H(1A) = 1.00(6), and H(1A)...N(1) = 1.77(6) Å, and O(1B)...N(2) = 2.730(6), O(1B)-H(1B)= 1.01(8), and H(1B)...N(2) = 1.72(8) Å] as those in **1**. The O(1A), H(1A), and N(1) atoms lie approximately on a line [O(1A)-H(1A)...N(1) = 175(5)°], and the O(1B), H(1B), and N(2) atoms also on a line [O(1B)-H(1B)...N(2)=173(7)°]. An asymmetric 1:2 molecular complex is thus formed in **2**.

Each crystal consists of the loose packing of the 1:2 molecular complexes of (+)-CPPOH...N,N'-dimethylpiperazine...(-)-CPPOH (**1**) or (-)-CPPOH...N,N'-dimethylpiperazine...(-)-CPPOH (**2**). However, because of the centrosymmetric structure of the complex, **1** has the crystal structure much more denser than **2**. This fact probably suggests the possibility of selective crystallization of **1** which makes the optical purification of partially resolved CPPOH by adding N,N'-dimethylpiperazine, an achiral diamine to it.

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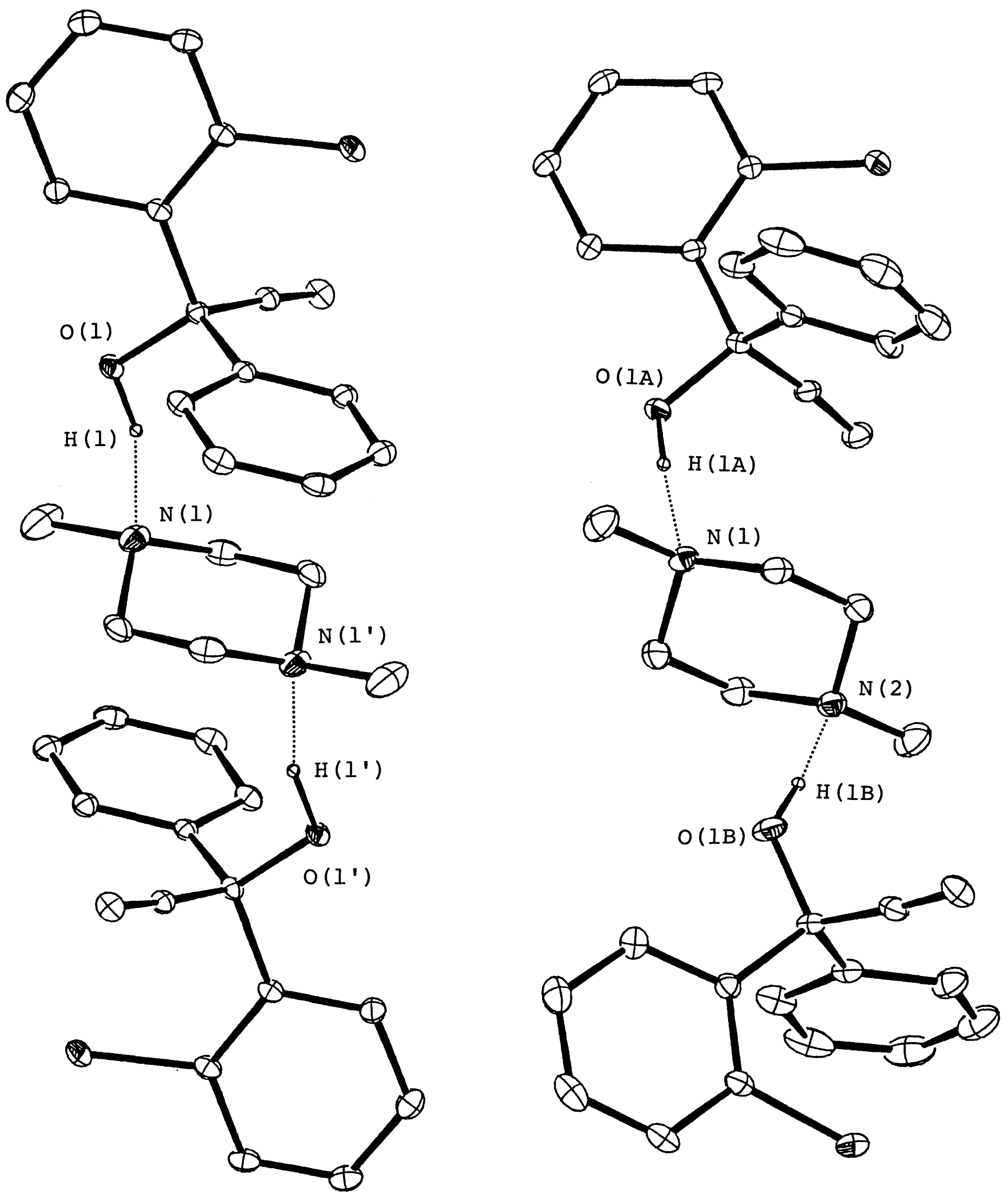

1 **2**

Fig. 1. A perspective view[2)] of the complexes **1** and **2**.
Nonhydrogen atoms are drawn as thermal ellipsoids with 10% probability level. All the hydrogen atoms except those engaged in the hydrogen bondings are omitted for clarity.

References

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3) The crystals used had approximate dimensions of 0.7 X 0.6 X 0.3 (**1**) and 0.7 X 0.6 X 0.3 mm(**2**). Unit cell dimensions and integrated intensities were measured on a Rigaku four-circle diffractometer at the Crystallographic Research Center, Institute for Protein Research, Osaka University. Intensity data were collected up to $2\theta = 120°$ by the θ-2θ scan technique at a θ rate of 4°/min and the scan width $\Delta\theta = (1.2 + 0.15\tan\theta)°$. Backgrounds were counted for 4 s at both ends of a scan. Three standard reflections measured after very 100 reflections to monitor the stability and orientation of the crystal showed no significant decay throughout the experiement for both crystals. Of the 2307 (**1**) and 2665 (**2**) independent reflections measured, number of reflections observed were 2188 (**1**) and 2603 (**2**) (($F_o > 2\sigma(F_o)$, where σ is the standard deviation obtained from the counting statistics). Usual Lorentz and polarization corrections were applied but absorption effect was ignored [μ(Cu K_α)= 21.7 for **1** and 20.3 cm^{-1} for **2**).
Both structures were solved by the direct method (MULTAN 78),[4] and refined anisotropically by the block-diagonal least-squares procedure (HBLS V).[5] The hydrogen atoms except those of methyl groups could be located on the diference Fourier map, which were refined with isotropic temperature factors. The final R indices are 0.060 (R_w=0.074) (**1**) and 0.077 (R_w=0.083) (**2**). The weighting schemes used at the final stage of the refinement were $w=(\sigma^2+a|F_o|+b|F_o|^2)^{-1}$, where a = -0.60828 and -3.88862 and b = 0.03603 and 0.18583 for **1** and **2**, respectively.
Atomic scattering factors used were taken from those of Intenational Tables for X-Ray Crystallography.[6] Computations were done on an ACOS S850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

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