# The Crystal and Molecular Structure of 1:2 Molecular Complex of 1,4-Diazabicyclo[3.3.3]octane (DABCO) with *p*-Cresol

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**Synopsis.** X-Ray crystal structure analysis of the title compound is described. $C_6H_{12}N_2$,$2C_7H_8O$, *F. W.* 328.5, monoclinic, space group *C*2/*c*, *a*=18.494(1), *b*=9.250(1), *c*=11.414(1) Å, $\beta$=103.67(1)°, *V*=1897.4(3) Å$^3$, $D_c$=1.150 g cm$^{-3}$ for *Z*=4. The DABCO molecule in the crystal is bound to two *p*-cresol molecules by the strong O-H ··· N hydrogen bonds, and the crystal is composed of *p*-cresol ··· DABCO ··· *p*-cresol complex units.

It has been reported that the optical resolution of tertiary alcohols, especially tertiary acetylenic alcohols, can easily be achieved by complexation with achiral amines, such as 1,4-diazabicyclo[3.3.3]octane (DABCO).[1] Recently, Toda and Tanaka found that DABCO also forms complex with phenols. In order to obtain structural informations on the complexation, the crystal structure of the 1:2 complex of DABCO and *p*-cresol has been determined by means of X-ray diffraction.

## Experimental

The crystal used had approximate dimensions of 0.75×0.5×0.25 mm, which was sealed in a thin-walled glass capillary tube in order to prevent sublimation. X-Ray diffraction data were collected on a Rigaku rotating anode four-circle diffractometer using nickel-filltered Cu $K\alpha$ radiation by the $\theta$-2$\theta$ scan technique up to 2$\theta$=120°. The scan rate was 4° min$^{-1}$ 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 every 100 reflections to monitor the stability and orientation of the crystal showed no significant decay through the experiment. Of the 1414 reflections measured, number of reflections observed was 1317 ($|F_o|>2\sigma$ ($F_o$), where $\sigma$ is the standard deviation obtained from the counting statistics). Usual Lorentz and polarization corrections were applied but absorption effect was ignored [$\mu$(Cu $K\alpha$)=5.94 cm$^{-1}$].

## Structure Solution and Refinement

The structure was solved by the direct method (*MULTAN* 78),[2] and was refined by the block-diagonal least-squares procedure (*HBLS* V).[3] The nonhydrogen atoms were refined anisotropically. The hydrogen atoms, which located on the difference Fourier map, were refined with isotropic temperature factors. The final *R* index was 0.073. The weighting scheme used at the final stage of the refinement was $w=[\sigma^2(F_o)+0.1582|F_o|+0.0013|F_o|^2]^{-1}$. Final atomic parameters are given in Tabler 1.†† Atomic scattering factors used were taken from International Tables for X-Ray Crystallography.[5] Computations were done on an ACOS 850S computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

## Results and Discussion

Molecular structure is shown in Fig. 1.[6] The remarkable feature of the structure is that the DABCO molecule, the center of which lies on a crystallographic two fold axis, is bound to two *p*-cresol molecules at its both ends by the strong O-H ··· N hydrogen bonds [O(1) ··· N(1)=2.713(3), O(1)-H(1)=1.03(4), H(1) ··· N(1)=1.69(4) Å, and O(1)-H(1) ··· N(1)=172(4)°] to form a linear 1:2 molecular complex of *p*-cresol ··· DABCO ··· *p*-cresol. The molecular symmetry of the central DABCO is 2 instead of $\bar{6}m2$ but has a similar structure as that determined by means of neutron diffraction at 298 K, and also as those observed in the 1:2 complex with (−)- and (+)-1-phenyl-1-(*o*-chlorophenyl)-2-propyn-1-ol.[7] The thermal ellipsoids of the C(8), C(9), and C(10) atoms are elongated along the direction approximately perpendicular to the N(1) ··· N(1′) axis of the molecule (equivalent isotropic temperature factors of these atoms are 13.8, 14.4, and

Table 1. Final Atomic Coordinates with Estimated Standard Deviations in Parentheses

a) Nonhydrogen atoms with equivalent isotropic temperature factors[4]

| Atom | *x* | *y* | *z* | $B_{eq}$/Å$^2$ |
|---|---|---|---|---|
| O(1) | 0.4491(2) | 0.7146(3) | -0.1068(2) | 6.65 |
| N(1) | 0.4744(2) | 0.7441(3) | 0.1361(3) | 5.99 |
| C(1) | 0.2166(2) | 1.0159(4) | -0.4304(3) | 6.7 |
| C(2) | 0.2787(2) | 0.9361(3) | -0.3431(3) | 5.28 |
| C(3) | 0.3256(2) | 0.8412(3) | -0.3840(3) | 5.36 |
| C(4) | 0.3829(2) | 0.7690(3) | -0.3053(3) | 5.42 |
| C(5) | 0.3937(2) | 0.7903(3) | -0.1810(3) | 5.17 |
| C(6) | 0.3478(2) | 0.8862(4) | -0.1383(3) | 5.85 |
| C(7) | 0.2913(2) | 0.9584(4) | -0.2193(3) | 5.99 |
| C(8) | 0.4242(4) | 0.6682(8) | 0.1938(4) | 13.8 |
| C(9) | 0.4541(4) | 0.6723(8) | 0.3335(5) | 14.4 |
| C(10) | 0.4824(3) | 0.8899(4) | 0.1807(4) | 8.7 |

b) Hydrogen atoms with isotropic temperature factors

| Atom | *x* | *y* | *z* | $B_{eq}$/Å$^2$ |
|---|---|---|---|---|
| H(3) | 0.318(2) | 0.826(3) | -0.480(3) | 3.5(6) |
| H(4) | 0.413(2) | 0.693(4) | -0.340(3) | 4.4(7) |
| H(6) | 0.357(2) | 0.903(4) | -0.045(3) | 5.0(8) |
| H(7) | 0.257(2) | 1.035(4) | -0.187(3) | 5.1(8) |
| H(81) | 0.418(3) | 0.552(5) | 0.163(5) | 9.(2) |
| H(82) | 0.369(3) | 0.720(7) | 0.173(5) | 13.(2) |
| H(91) | 0.459(3) | 0.558(6) | 0.366(5) | 12.(2) |
| H(92) | 0.419(4) | 0.724(6) | 0.378(6) | 11.(2) |
| H(101) | 0.428(3) | 0.942(6) | 0.163(5) | 9.(2) |
| H(102) | 0.516(3) | 0.939(6) | 0.134(4) | 9.(2) |
| H(1) | 0.456(2) | 0.734(5) | -0.016(4) | 7.(2) |
| H(11) | 0.181(2) | 1.061(4) | -0.388(4) | 7.(1) |
| H(12) | 0.185(3) | 0.954(6) | -0.495(4) | 10.(2) |
| H(13) | 0.237(3) | 1.098(5) | -0.480(4) | 7.(1) |

††Tables of anisotropic thermal parameters and observed and calculated structure factors are kept at the Chemical Society of Japan, Document No. 8769.

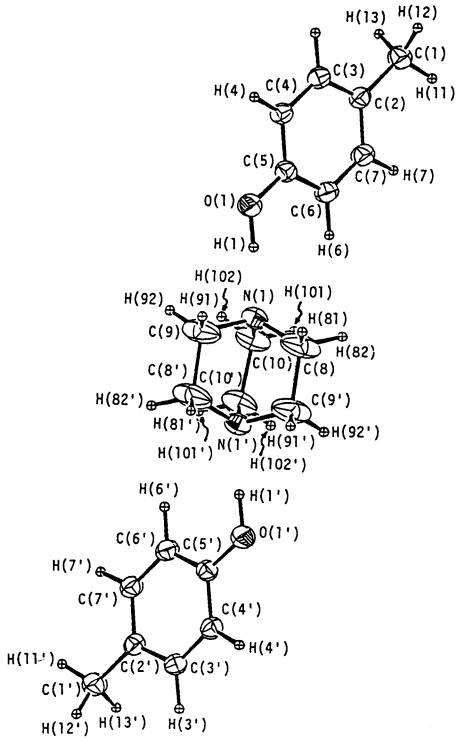


Fig. 1. A perspective view[6] of the 1:2 molecular complex of DABCO with *p*-cresol with the numbering scheme of atoms. Nonhydrogen atoms are drawn as thermal ellipsoids with 20% probability level, and hydrogen atoms with $B$=1.0 Å$^2$.

8.7 Å$^2$, respectively), which suggest a hindered rotation of the DABCO molecule along the N(1)···N(1′) axis. However, three C-N bond lengths [1.437(5), 1.442(7), and 1.447(8) Å] and C-N-C bond angles [108.6(4), 108.6(5), and 109.5(4)°] are respectively equal to the corresponding bond distances and bond angles determined by the neutron diffraction study[8] within the range of error, whereas, the C(8)-C(9′), C(8′)-C(9), and C(10)-C(10′) bond distances [1.56(1), 1.56(1), and 1.561(7) Å, respectively] are slightly smaller than those obtained by the same study. The *p*-cresol molecule attached to the DABCO by the hydrogen bonding has a normal structure.[9] The benzene ring is planar within 0.002 Å. The average C-C bond distance is 1.392 Å and the average C-C-C angle 120°. The C(6)-C(5)-O(1) angle [122.9(3)°] is larger than the C(4)-C(5)-O(1) [117.6(3)°].

As seen in Fig. 2, the crystal structure is composed of

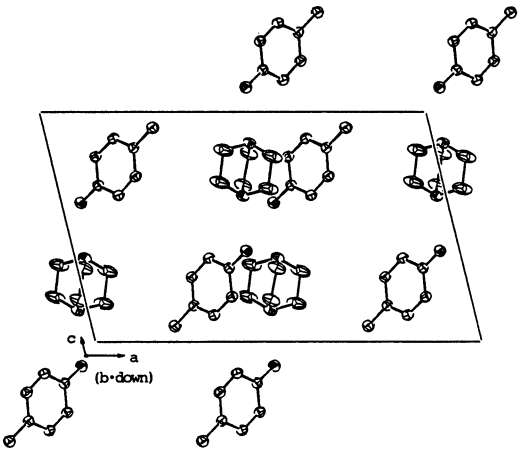


Fig. 2. Crystal structure[6] of the 1:2 molecular complex of DABCO with *p*-cresol projected along the b axis. Nonhydrogen atoms are drawn as thermal ellipsoids with 20% probability level. Hydrogen atoms are omitted for clarity.

a loose packing of the 1:2 complex. The closest intermolecular atomic contact[3.666(5) Å] is observed between the C(5) ($x$, $y$, $z$) and C(1) (0.5−$x$, −0.5+$y$, −0.5+$z$).

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