

## The Crystal and Molecular Structures of Two 1:2 Complexes of 1,4-Diazabicyclo[2.2.2]octane (DABCO) with 1-(*o*-Chlorophenyl)-1-phenyl-2-propyn-1-ol (CPPOH), and Those of Two 1:2 Complexes of *N,N'*-Dimethylpiperazine (DMP) with CPPOH

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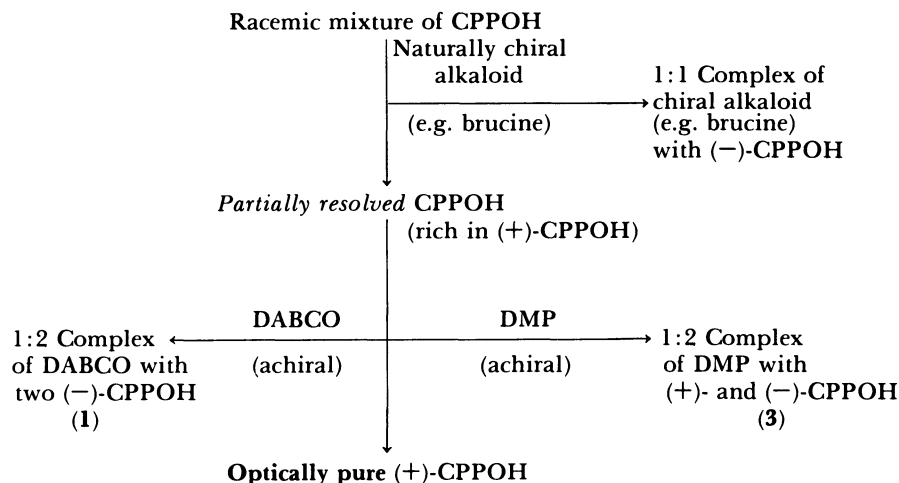
X-Ray crystal structure analysis of the title four complexes showed that crystals consist of CPPOH...achiral diamine...CPPOH units. In the first two crystals a DABCO molecule is bound by two (–)-CPPOH molecules (1) or by (+)- and (–)-CPPOH (2) to form 1:2 complex by strong intermolecular O–H...N hydrogen bonds [O–H...N=2.707(3) and 2.755(3) Å (1) and 2.704(4) and 2.747(4) Å (2)]. The latter two crystals are respectively formed by (+)-CPPOH...DMP... (–)-CPPOH complex (3) [O–H...N=2.771(3) Å] and (–)-CPPOH...DMP... (–)-CPPOH complex (4) [O–H...N=2.768(5) and 2.730(6) Å].

In a series of studies on the novel optical resolution of tertiary acetylenic alcohols by complexation with naturally chiral alkaloids,<sup>1–3</sup> Toda and Tanaka found that the partially resolved enantiomers, obtained after the separation of the 1:1 complex of optically pure enantiomers with alkaloid, can easily be purified by complexation with simple achiral diamines such as DABCO, *N,N'*-dialkylpiperazine, *N,N,N',N'*-tetramethylethylenediamine, or pyrazine to give the optically pure alcohols.<sup>4</sup> Among the complexation reactions mentioned above, achiral DABCO forms 1:2 complex selectively with two (–)-CPPOH molecules to give 1 crystal, and in result optically pure (+)-CPPOH remains in solution. On the other hand, achiral DMP easily forms 1:2 complex (3) with (+)- and (–)-CPPOH molecules. However, under appropriate but severe conditions, DABCO and DMP were found to form the other 1:2 complex crystals of (+)-CPPOH...DABCO... (–)-CPPOH (2) and (–)-CPPOH...DMP... (–)-CPPOH (4), respectively. In order to obtain a clue to clarify the fact that leads the selective

1:2 complex formation of achiral DABCO with two chiral (–)-CPPOH molecules, the crystal and molecular structures of 1 has been determined by means of X-ray diffraction. As a reference, the structure of 2, which is not formed under ordinary condition, has also been determined. The crystal and molecular structures of 1:2 complexes of DMP with two CPPOH molecules, (+)-CPPOH...DMP... (–)-CPPOH (3) and (–)-CPPOH...DMP... (–)-CPPOH (4, obtained under severe condition), which have been already reported briefly,<sup>5</sup> are compared with those of 1 and 2.

### Experimental

**Crystal Data.** C<sub>6</sub>H<sub>12</sub>N<sub>2</sub>,2(C<sub>15</sub>H<sub>11</sub>OCl), *F.W.* 597.6; **1**, monoclinic, space group *P*2<sub>1</sub>, *a*=15.785(2), *b*=11.511(1), *c*=8.878(1) Å, β=102.89(1)°, *V*=1565.6(3) Å<sup>3</sup>, *D<sub>c</sub>*=1.262 g cm<sup>-3</sup> for *Z*=2. **2**, monoclinic, space group *C*2/*c*, *a*=49.319(13), *b*=9.237(1), *c*=14.343(1) Å, β=105.96(1)°, *V*=6281.8(19) Å<sup>3</sup>, *D<sub>c</sub>*=1.264 g cm<sup>-3</sup> for *Z*=8. C<sub>6</sub>H<sub>14</sub>N<sub>2</sub>,2(C<sub>15</sub>H<sub>11</sub>OCl), *F.W.* 599.6; **3**, triclinic, space group *P* $\bar{1}$ , *a*=10.752(4), *b*=9.057(4),



$c=8.350(5)$  Å,  $\alpha=100.28(4)$ ,  $\beta=81.87(3)$ ,  $\gamma=102.38(2)^\circ$ ,  $V=777.0(7)$  Å<sup>3</sup>,  $D_c=1.282$  g cm<sup>-3</sup> for  $Z=1$ . **4**, monoclinic, space group  $P2_1$ ,  $a=17.511(2)$ ,  $b=7.606(1)$ ,  $c=13.311(2)$  Å,  $\beta=111.55(1)^\circ$ ,  $V=1648.9(5)$  Å<sup>3</sup>,  $D_c=1.208$  g cm<sup>-3</sup> for  $Z=2$ .

The crystals used has approximate dimensions of  $0.4 \times 0.3 \times 0.2$  mm (**1**) and  $0.5 \times 0.3 \times 0.2$  mm (**2**). X-Ray diffraction data were collected on a Rigaku four-circle diffractometer by the  $\theta$ - $2\theta$  scan technique ( $2\theta_{\max}=120^\circ$ ). For **1** and **4**,  $hkl$  and  $h\bar{k}l$  reflections were measured in order to determine the absolute configuration of (-)-CPPOH molecule. Nickel-filtered Cu  $K\alpha$  radiation was used ( $\lambda=1.5418$  Å). The  $\theta$ -scan rate was  $4^\circ$  min<sup>-1</sup> and the scan width  $\Delta\theta=(1.2+0.15 \tan \theta)^\circ$ . 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 throughout the experiment. Of the 2461 and 4663 independent reflections measured, 2393 and 3834 reflections were observed for **1** and **2**, respectively

( $|F_o| > 2\sigma(F_o)$ , where  $\sigma$  is the standard deviation obtained by the counting statistics of reflections). Usual Lorentz and polarization corrections were applied but absorption effect was ignored [ $\mu(\text{Cu } K\alpha)=21.4$  cm<sup>-1</sup> for both **1** and **2**]. X-Ray experiments on **3** and **4** crystals have been already described in the previous letter.<sup>6)</sup>

Bijvoet pair reflections were used for the determination of absolute configuration of (-)-CPPOH molecule in **1** and **4**. These pair reflections were also included in the Hamilton's  $R$  value test,<sup>6)</sup> but intensities of each pair reflections were averaged for the ordinary use of the structure determination.

### Structure Solution and Refinement

The structure of **1** was solved by the heavy atom method and that of **2** by the direct method (*MULTAN* 78).<sup>7)</sup> Both structures were refined anisotropically by the block-diagonal least-squares procedure (*HBL*S

Table 1. Final Atomic Coordinates and Equivalent Isotropic Temperature Factors<sup>8)</sup> for Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses

| Atom  | x           | y           | z           | $B_{eq}/\text{Å}^2$ |
|---|-------------|-------------|-------------|---------------------|
| (1) 1:2 Complex of DABCO with two (-)-CPPOH |             |             |             |                     |
| C(1A)                                       | -0.0422(2)  | 0.3264(3)   | 0.2884(4)   | 3.7                 |
| C(2A)                                       | -0.0115(2)  | 0.4396(3)   | 0.3612(4)   | 4.3                 |
| C(3A)                                       | 0.0176(3)   | 0.5260(3)   | 0.4258(5)   | 5.4                 |
| C(4A)                                       | -0.0378(2)  | 0.3316(3)   | 0.1163(3)   | 3.6                 |
| C(5A)                                       | -0.0860(2)  | 0.4087(3)   | 0.0108(4)   | 4.4                 |
| C(6A)                                       | -0.0775(3)  | 0.4149(4)   | -0.1425(4)  | 5.4                 |
| C(7A)                                       | -0.0198(3)  | 0.3416(4)   | -0.1921(4)  | 6.2                 |
| C(8A)                                       | 0.0256(3)   | 0.2598(4)   | -0.0916(5)  | 5.8                 |
| C(9A)                                       | 0.0179(2)   | 0.2555(3)   | 0.0616(4)   | 4.9                 |
| C(10A)                                      | -0.1322(2)  | 0.2925(3)   | 0.3087(4)   | 3.9                 |
| C(11A)                                      | -0.1717(3)  | 0.3488(3)   | 0.4126(4)   | 5.0                 |
| C(12A)                                      | -0.2517(3)  | 0.3086(4)   | 0.4382(5)   | 6.5                 |
| C(13A)                                      | -0.2904(3)  | 0.2129(4)   | 0.3583(5)   | 6.6                 |
| C(14A)                                      | -0.2505(3)  | 0.1555(4)   | 0.2536(5)   | 6.1                 |
| C(15A)                                      | -0.1726(3)  | 0.1962(3)   | 0.2301(4)   | 4.9                 |
| O(1A)                                       | 0.0139(1)   | 0.2375(2)   | 0.3665(3)   | 4.5                 |
| Cl(1A)                                      | -0.16303(6) | 0.50005(9)  | 0.06128(11) | 5.7                 |
| C(1B)                                       | 0.5403(2)   | 0.0482(3)   | 0.7575(4)   | 3.8                 |
| C(2B)                                       | 0.5102(2)   | -0.0398(3)  | 0.6350(4)   | 4.2                 |
| C(3B)                                       | 0.4851(3)   | -0.1084(4)  | 0.5361(4)   | 5.4                 |
| C(4B)                                       | 0.6410(2)   | 0.0442(3)   | 0.8022(4)   | 4.0                 |
| C(5B)                                       | 0.6882(2)   | -0.0508(3)  | 0.8717(4)   | 4.4                 |
| C(6B)                                       | 0.7778(2)   | -0.0557(4)  | 0.9117(5)   | 5.5                 |
| C(7B)                                       | 0.8232(3)   | 0.0388(4)   | 0.8755(5)   | 6.6                 |
| C(8B)                                       | 0.7806(3)   | 0.1352(4)   | 0.8062(5)   | 6.8                 |
| C(9B)                                       | 0.6884(2)   | 0.1375(4)   | 0.7700(5)   | 5.5                 |
| C(10B)                                      | 0.4993(2)   | 0.0288(3)   | 0.8950(4)   | 3.9                 |
| C(11B)                                      | 0.4367(2)   | -0.0559(3)  | 0.8960(4)   | 4.7                 |
| C(12B)                                      | 0.3981(3)   | -0.0688(4)  | 1.0209(5)   | 6.1                 |
| C(13B)                                      | 0.4224(3)   | 0.0010(5)   | 1.1478(5)   | 6.7                 |
| C(14B)                                      | 0.4855(3)   | 0.0874(5)   | 1.1496(5)   | 6.8                 |
| C(15B)                                      | 0.5237(2)   | 0.1003(4)   | 1.0242(4)   | 5.1                 |
| O(1B)                                       | 0.5183(2)   | 0.1615(2)   | 0.6958(3)   | 4.8                 |
| Cl(1B)                                      | 0.63560(6)  | -0.17730(9) | 0.91309(10) | 5.6                 |
| C(16)                                       | 0.2275(3)   | 0.1955(4)   | 0.3869(4)   | 5.6                 |
| C(17)                                       | 0.1901(3)   | 0.1965(4)   | 0.6351(5)   | 5.4                 |
| C(18)                                       | 0.2349(3)   | 0.3713(3)   | 0.5319(5)   | 5.6                 |
| C(19)                                       | 0.3244(3)   | 0.1778(4)   | 0.4592(4)   | 5.4                 |
| C(20)                                       | 0.2848(2)   | 0.1563(3)   | 0.7031(4)   | 4.8                 |
| C(21)                                       | 0.3286(2)   | 0.3427(4)   | 0.6255(5)   | 5.3                 |
| N(1)  | 0.1859(2)   | 0.2624(3)   | 0.4916(3)   | 4.4                 |
| N(2)  | 0.3438(2)   | 0.2160(3)   | 0.6206(3)   | 4.3                 |

Table 1. (Continued)

| Atom  | x          | y           | z          | $B_{eq}/\text{\AA}^2$ |
|---|------------|-------------|------------|-----------------------|
| <b>(2) 1:2 Complex of DABCO with (+)- and (-)-CPPOH</b> |            |             |            |                       |
| C(1A)   | 0.67481(8) | 0.1509(4)   | 0.3187(3)  | 3.1                   |
| C(2A)   | 0.64823(9) | 0.1834(4)   | 0.2424(3)  | 3.9                   |
| C(3A)   | 0.6263(1)  | 0.2081(5)   | 0.1862(4)  | 5.7                   |
| C(4A)   | 0.69572(8) | 0.0684(4)   | 0.2763(3)  | 2.9                   |
| C(5A)   | 0.70428(9) | 0.1127(4)   | 0.1962(3)  | 3.6                   |
| C(6A)   | 0.7242(1)  | 0.0362(5)   | 0.1632(3)  | 4.8                   |
| C(7A)   | 0.7356(1)  | -0.0894(5)  | 0.2106(4)  | 5.6                   |
| C(8A)   | 0.7276(1)  | -0.1365(5)  | 0.2895(3)  | 5.0                   |
| C(9A)   | 0.70761(9) | -0.0600(4)  | 0.3220(3)  | 3.7                   |
| C(10A)  | 0.68873(8) | 0.2895(4)   | 0.3678(3)  | 2.9                   |
| C(11A)  | 0.6806(1)  | 0.4262(4)   | 0.3323(3)  | 4.1                   |
| C(12A)  | 0.6942(1)  | 0.5493(5)   | 0.3804(4)  | 5.2                   |
| C(13A)  | 0.7153(1)  | 0.5349(5)   | 0.4648(3)  | 4.8                   |
| C(14A)  | 0.7234(1)  | 0.3988(5)   | 0.5025(3)  | 4.8                   |
| C(15A)  | 0.70979(9) | 0.2754(4)   | 0.4543(3)  | 3.9                   |
| O(1A)   | 0.66819(6) | 0.0590(3)   | 0.3877(2)  | 3.7                   |
| Cl(1A)  | 0.69161(3) | 0.27027(13) | 0.13346(8) | 5.3                   |
| C(1B)   | 0.57488(8) | 0.3400(4)   | 0.7882(3)  | 3.1                   |
| C(2B)   | 0.60295(9) | 0.3033(4)   | 0.8549(3)  | 3.8                   |
| C(3B)   | 0.6256(1)  | 0.2753(5)   | 0.9052(4)  | 5.3                   |
| C(4B)   | 0.55802(8) | 0.4310(4)   | 0.8417(3)  | 3.4                   |
| C(5B)   | 0.55105(9) | 0.3855(4)   | 0.9243(3)  | 3.8                   |
| C(6B)   | 0.5362(1)  | 0.4718(6)   | 0.9721(3)  | 5.2                   |
| C(7B)   | 0.5273(1)  | 0.6073(6)   | 0.9356(4)  | 5.7                   |
| C(8B)   | 0.5334(1)  | 0.6566(5)   | 0.8520(4)  | 5.4                   |
| C(9B)   | 0.5487(1)  | 0.5687(4)   | 0.8062(3)  | 4.1                   |
| C(10B)  | 0.55831(9) | 0.2042(4)   | 0.7439(3)  | 3.2                   |
| C(11B)  | 0.5713(1)  | 0.0690(4)   | 0.7506(3)  | 4.0                   |
| C(12B)  | 0.5559(1)  | -0.0504(5)  | 0.7040(3)  | 5.0                   |
| C(13B)  | 0.5281(1)  | -0.0324(5)  | 0.6518(4)  | 5.9                   |
| C(14B)  | 0.5154(1)  | 0.1022(6)   | 0.6432(4)  | 6.7                   |
| C(15B)  | 0.5305(1)  | 0.2213(5)   | 0.6898(3)  | 5.5                   |
| O(1B)   | 0.57934(7) | 0.4268(3)   | 0.7122(2)  | 3.9                   |
| Cl(1B)  | 0.56110(3) | 0.21371(12) | 0.97352(7) | 4.9                   |
| C(16)   | 0.6344(1)  | 0.3549(5)   | 0.4812(4)  | 5.2                   |
| C(17)   | 0.6112(1)  | 0.1306(6)   | 0.4745(4)  | 6.0                   |
| C(18)   | 0.6544(1)  | 0.1667(6)   | 0.5935(3)  | 5.9                   |
| C(19)   | 0.6170(1)  | 0.4099(5)   | 0.5513(4)  | 5.3                   |
| C(20)   | 0.5955(1)  | 0.1768(6)   | 0.5487(4)  | 6.2                   |
| C(21)   | 0.6391(1)  | 0.2291(5)   | 0.6653(3)  | 5.1                   |
| N(1)  | 0.63876(8) | 0.1283(3)   | 0.4941(2)  | 3.6                   |
| N(2)  | 0.61191(8) | 0.2913(3)   | 0.6109(2)  | 3.6                   |
| <b>(3) 1:2 Complex of DMP with (+)- and (-)-CPPOH</b>   |            |             |            |                       |
| C(1)  | 0.2600(2)  | 0.7065(3)   | 0.3562(3)  | 3.2                   |
| C(2)  | 0.3320(3)  | 0.8505(3)   | 0.3028(3)  | 3.5                   |
| C(3)  | 0.3817(3)  | 0.9687(4)   | 0.2598(4)  | 4.7                   |
| C(4)  | 0.3255(3)  | 0.5726(3)   | 0.2719(3)  | 3.3                   |
| C(5)  | 0.4526(3)  | 0.5689(3)   | 0.2857(3)  | 3.8                   |
| C(6)  | 0.5101(3)  | 0.4484(3)   | 0.2052(4)  | 4.5                   |
| C(7)  | 0.4422(3)  | 0.3301(3)   | 0.1065(4)  | 4.6                   |
| C(8)  | 0.3163(3)  | 0.3294(4)   | 0.0932(4)  | 5.0                   |
| C(9)  | 0.2584(3)  | 0.4491(3)   | 0.1754(3)  | 4.1                   |
| C(10)   | 0.2429(2)  | 0.7153(3)   | 0.5425(3)  | 3.2                   |
| C(11)   | 0.3041(3)  | 0.8378(3)   | 0.6470(3)  | 3.8                   |
| C(12)   | 0.2817(3)  | 0.8416(4)   | 0.8156(4)  | 4.6                   |
| C(13)   | 0.1986(3)  | 0.7222(4)   | 0.8807(4)  | 5.1                   |
| C(14)   | 0.1372(3)  | 0.6014(4)   | 0.7780(4)  | 4.9                   |
| C(15)   | 0.1589(3)  | 0.5966(3)   | 0.6092(4)  | 4.1                   |
| O(1)  | 0.1358(1)  | 0.6757(2)   | 0.2999(2)  | 3.7                   |
| Cl(1)   | 0.54804(6) | 0.71576(9)  | 0.40454(9) | 4.9                   |
| C(16)   | -0.1079(3) | 0.8840(4)   | 0.4830(5)  | 6.5                   |
| C(17)   | 0.0534(3)  | 1.0619(4)   | 0.3582(4)  | 6.0                   |

Table 1. (Continued)

| Atom                                      | x           | y           | z            | $B_{eq}/\text{\AA}^2$ |
|---|-------------|-------------|--------------|-----------------------|
| C(18)                                     | -0.0703(5)  | 0.8445(6)   | 0.1927(6)    | 10.7                  |
| N(1)                                      | -0.0081(3)  | 0.9026(3)   | 0.3456(3)    | 5.7                   |
| (4) 1:2 Complex of DMP with two (-)-CPPOH |             |             |              |                       |
| C(1A)                                     | -0.0131(3)  | 0.2562(6)   | 0.1959(4)    | 3.7                   |
| C(2A)                                     | 0.0111(3)   | 0.1285(6)   | 0.1295(4)    | 3.9                   |
| C(3A)                                     | 0.0271(4)   | 0.0323(7)   | 0.0707(4)    | 5.1                   |
| C(4A)                                     | 0.0588(3)   | 0.3825(6)   | 0.2496(4)    | 3.5                   |
| C(5A)                                     | 0.1339(3)   | 0.3294(6)   | 0.3248(4)    | 4.0                   |
| C(6A)                                     | 0.1975(3)   | 0.4472(7)   | 0.3734(4)    | 4.7                   |
| C(7A)                                     | 0.1868(3)   | 0.6225(8)   | 0.3449(5)    | 5.2                   |
| C(8A)                                     | 0.1140(3)   | 0.6768(7)   | 0.2694(5)    | 5.1                   |
| C(9A)                                     | 0.0503(3)   | 0.5605(6)   | 0.2224(4)    | 4.5                   |
| C(10A)                                    | -0.0403(3)  | 0.1675(7)   | 0.2799(4)    | 4.2                   |
| C(11A)                                    | -0.0494(3)  | -0.0129(7)  | 0.2845(4)    | 5.0                   |
| C(12A)                                    | -0.0766(4)  | -0.0896(11) | 0.3582(6)    | 7.5                   |
| C(13A)                                    | -0.0952(4)  | 0.0127(12)  | 0.4295(5)    | 8.4                   |
| C(14A)                                    | -0.0871(4)  | 0.1955(13)  | 0.4276(5)    | 8.0                   |
| C(15A)                                    | -0.0599(4)  | 0.2734(9)   | 0.3520(4)    | 5.7                   |
| O(1A)                                     | -0.0793(2)  | 0.3589(5)   | 0.1254(3)    | 4.2                   |
| Cl(1A)                                    | 0.15269(8)  | 0.11505(19) | 0.36437(11)  | 5.6                   |
| C(1B)                                     | -0.4886(3)  | -0.1713(7)  | -0.1988(4)   | 4.2                   |
| C(2B)                                     | -0.5023(3)  | -0.3130(8)  | -0.1322(4)   | 4.8                   |
| C(3B)                                     | -0.5118(4)  | -0.4201(9)  | -0.0732(5)   | 6.3                   |
| C(4B)                                     | -0.5679(3)  | -0.0658(7)  | -0.2509(4)   | 4.1                   |
| C(5B)                                     | -0.6392(3)  | -0.1332(7)  | -0.3248(4)   | 4.6                   |
| C(6B)                                     | -0.7101(4)  | -0.0360(9)  | -0.3701(5)   | 5.9                   |
| C(7B)                                     | -0.7108(4)  | 0.1359(11)  | -0.3389(6)   | 7.5                   |
| C(8B)                                     | -0.6415(5)  | 0.2090(9)   | -0.2643(6)   | 7.1                   |
| C(9B)                                     | -0.5713(4)  | 0.1090(8)   | -0.2214(5)   | 5.8                   |
| C(10B)                                    | -0.4564(3)  | -0.2407(7)  | -0.2828(4)   | 4.6                   |
| C(11B)                                    | -0.4306(4)  | -0.4152(10) | -0.2840(5)   | 6.7                   |
| C(12B)                                    | -0.3999(5)  | -0.4688(12) | -0.3590(7)   | 8.9                   |
| C(13B)                                    | -0.3935(4)  | -0.3574(15) | -0.4333(6)   | 9.5                   |
| C(14B)                                    | -0.4189(4)  | -0.1872(14) | -0.4360(5)   | 8.9                   |
| C(15B)                                    | -0.4499(4)  | -0.1239(11) | -0.3587(5)   | 6.7                   |
| O(1B)                                     | -0.4301(2)  | -0.0539(6)  | -0.1280(3)   | 5.7                   |
| Cl(1B)                                    | -0.64471(9) | -0.3500(3)  | -0.36675(12) | 6.5                   |
| C(16)                                     | -0.2557(4)  | 0.0582(8)   | 0.0970(4)    | 5.3                   |
| C(17)                                     | -0.2745(4)  | 0.2349(8)   | -0.0564(5)   | 5.9                   |
| C(18)                                     | -0.2685(4)  | 0.3733(10)  | 0.1093(6)    | 7.7                   |
| C(19)                                     | -0.2267(4)  | -0.0883(9)  | 0.0471(5)    | 5.9                   |
| C(20)                                     | -0.2450(4)  | 0.0892(9)   | -0.1057(5)   | 5.7                   |
| C(21)                                     | -0.2327(5)  | -0.2258(11) | -0.1202(6)   | 8.1                   |
| N(1)                                      | -0.2375(3)  | 0.2277(6)   | 0.0608(4)    | 4.8                   |
| N(2)                                      | -0.2640(3)  | -0.0817(6)  | -0.0707(4)   | 4.8                   |

V).<sup>9</sup> The function minimized was  $\sum w\Delta F^2$ . The hydrogen atoms which could be located on the difference Fourier maps were refined with isotropic temperature factors. The final  $R$  indices are 0.045 ( $R_w=0.038$ ) and 0.063 ( $R_w=0.092$ ) for **1** and **2**, respectively. The weighting schemes used at the final stage of the refinement were  $w=(\sigma^2+a|F_o|+b|F_o|^2)^{-1}$ , where  $a=-0.65941$  and  $0.12269$  and  $b=0.03381$  and  $0.00105$  for **1** and **2**, respectively.

The structures of **3** and **4** have been determined in a similar manner as mentioned above.<sup>9</sup>  $R=0.060$  ( $R_w=0.074$ ) (**3**) and  $R=0.077$  ( $R_w=0.083$ ) (**4**).

The absolute configuration of the (-)-CPPOH molecule has been determined by examining the magnitude of structure factors of Bijvoet pair reflec-

tions of the **1** and **4** crystals, and the chirality of the asymmetric C(1) atom of the (-)-CPPOH in both complexes was found as  $R$ . Hamilton's  $R$  value test for the **1** and **4** is consistent with this result.

Final atomic parameters of **1**, **2**, **3**, and **4** are given in Table 1.<sup>††</sup> Atomic scattering factors used were taken from those of International Tables for X-Ray Crystallography, Vol. IV.<sup>10</sup> Computations were done on an ACOS S850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

<sup>††</sup> Tables of anisotropic thermal parameters and those of observed and calculated structure factors of **1**, **2**, **3**, and **4** are kept at the Chemical Society of Japan, Document No. 8871.

## Results and Discussion

**Crystal Structures.** The packings of molecules in **1** and **2** crystals<sup>11)</sup> are depicted in Fig. 1, which are compared with those of **3** and **4**. The remarkable feature of the structure is that all these crystals consist of discrete 1:2 host-guest complexes of CPPOH...achiral diamine...CPPOH consolidated by O-H...N hydrogen bonds. Each DABCO molecule is bound to two (-)-CPPOH in **1** and bound to (+)- and (-)-CPPOH molecules in **2** by strong hydrogen bondings [O-H...N=2.707(3) and 2.755(3) Å (**1**) and 2.704(4) and 2.747(4) Å (**2**) (Fig. 2, (a) and (b))]. This 1:2 complex formation seems to be similar to that of achiral DMP with (+)- and (-)-CPPOH (**3**) and two (-)-CPPOH molecules (**4**) (Fig. 2, (c) and (d)). The geometry about the hydrogen bondings in **1** and **2** complexes are compared with those in **3** and **4** in Table 2. In **1** and **2**, the H(1) atom of CPPOH locates at the direction of lone pair electrons of the N atom which occupies the apex of the pyramid made by one N and three C atoms at one end of DABCO. The O(1), H(1), and N atoms of each of the hydrogen bonds lie approximately on a line. In **3** and **4**, the H(1) atom of CPPOH is approximately at the direction of lone pair electrons of one of the N atoms of DMP. The O(1), H(1), and N atoms of each of the hydrogen bonds are not on a line in **3** [O-H(1)...N=161(3)°].

In **1** crystal very close inter-complex atomic contacts are observed. The closest distance, 3.160(5) Å was found between the hydroxyl oxygen atom of one complex, O(1A)(*x*, *y*, *z*) and the acetylenic carbon atom of the adjacent complex, C(3A)(-*x*, -0.5+*y*, 1-*z*). The second closest contact, 3.290(5) Å was observed between the chlorine atom of the *o*-chlorophenyl group of one complex, Cl(1B)(*x*, *y*, *z*) and the carbon atom of the phenyl group of the other complex, C(14B)(1-*x*, -0.5+*y*, 2-*z*). On the other hand, no close contact shorter than 3.465(5) Å [Cl(1A)(*x*, *y*, *z*)...C(13A)(*x*, 1-*y*, -0.5+*z*)] was observed in **2**. In addition to this, most of the close inter-complex contact distances involved

with hydrogen atoms in **1** are shorter than those in **2**. These facts suggest that the stronger inter-complex interaction leads the selective crystallization of (-)-CPPOH...DABCO...(-)-CPPOH (**1**), which makes the optical resolution of (-)-CPPOH enantiomers from the partially resolved CPPOH.

In **3** and **4** crystals, however, no short inter-complex contact distances are found between non-hydrogen atoms. Instead, intercomplex atomic contacts involved with hydrogen atoms in **3** are mostly shorter than those in **4**, and the **3** crystal has the denser structure ( $D_c=1.282$  g cm<sup>-3</sup>) than **4** ( $D_c=1.208$  g cm<sup>-3</sup>).

**Molecular Structures.** Selected bond distances and bond angles in **1**, **2**, **3**, and **4** are listed in Table 3.

**1-(*o*-Chlorophenyl)-1-phenyl-2-propyn-1-ol(CPPOH).** The C(2)-C(3) acetylenic bonds have distances of 1.187(5) and 1.180(5) Å (**1**) and 1.179(6) and 1.181(6) Å (**2**), which are slightly shorter than the standard C-C triple bond distance, 1.204(2) Å. The C(1)-C(2)-C(3) angles are smaller than 180° [175.5(4) and 178.8(4)° (**1**) and 175.9(4) and 177.6(4)° (**2**)].

Two benzene rings of *o*-Cl-Ph and Ph groups are planar, which make angles of 88.6(1) and 89.1(1)° in **1** and 80.4(1) and 89.1(1)° in **2**. The corresponding angles in **3** and **4** are 82(1)° and 87.7(1) and 85.8(1)°, respectively. Among the bond angles around the C(5) atom, the C(4)-C(5)-Cl(1) angle is approximately equal to the C(4)-C(5)-C(6), which are larger than the C(6)-C(5)-Cl(1) throughout the complexes **1** to **4** (Table 2).

The (-)-1-(*o*-bromophenyl)-1-phenyl-2-propyn-1-ol molecule in its 1:1 complex with brucine and also that with (-)-sparteine<sup>3)</sup> have similar structure as (-)-CPPOH in the present complexes of **1** and **2**.

**1,4-Diazabicyclo[2.2.2]octane (DABCO).** The DABCO molecule completely lost its original  $\bar{6}m2$  symmetry by the formation of 1:2 complex with CPPOH. However, in the 1:2 complex with *p*-cresol, it was observed that the molecular symmetry of DABCO decreased down to 2. All the thermal ellipsoids of carbon atoms of DABCO are much larger than those of the other carbon atoms, and they also show remarkable elonga-

Table 2. Hydrogen Bondings in the 1:2 Complexes of DABCO and DMP with CPPOH. Estimated Standard Deviations in Parentheses

|                         | 1                    | 2                    | 3        | 4                    |
|-------------------------|----------------------|----------------------|----------|----------------------|
| Distance [ <i>l</i> /Å] |                      |                      |          |                      |
| O(1).....N              | 2.707(3)<br>2.755(3) | 2.704(4)<br>2.747(4) | 2.771(3) | 2.768(5)<br>2.730(6) |
| O(1)-H(1)               | 1.05(4)<br>1.06(4)   | 1.07(6)<br>1.03(5)   | 1.05(3)  | 1.00(6)<br>1.01(8)   |
| H(1).....N              | 1.66(4)<br>1.70(4)   | 1.63(6)<br>1.71(5)   | 1.76(4)  | 1.77(6)<br>1.72(8)   |
| Angle [ $\phi$ /°]      |                      |                      |          |                      |
| O(1)-H(1).....N         | 177(4)<br>176(4)     | 178(5)<br>179(4)     | 161(3)   | 175(5)<br>173(7)     |

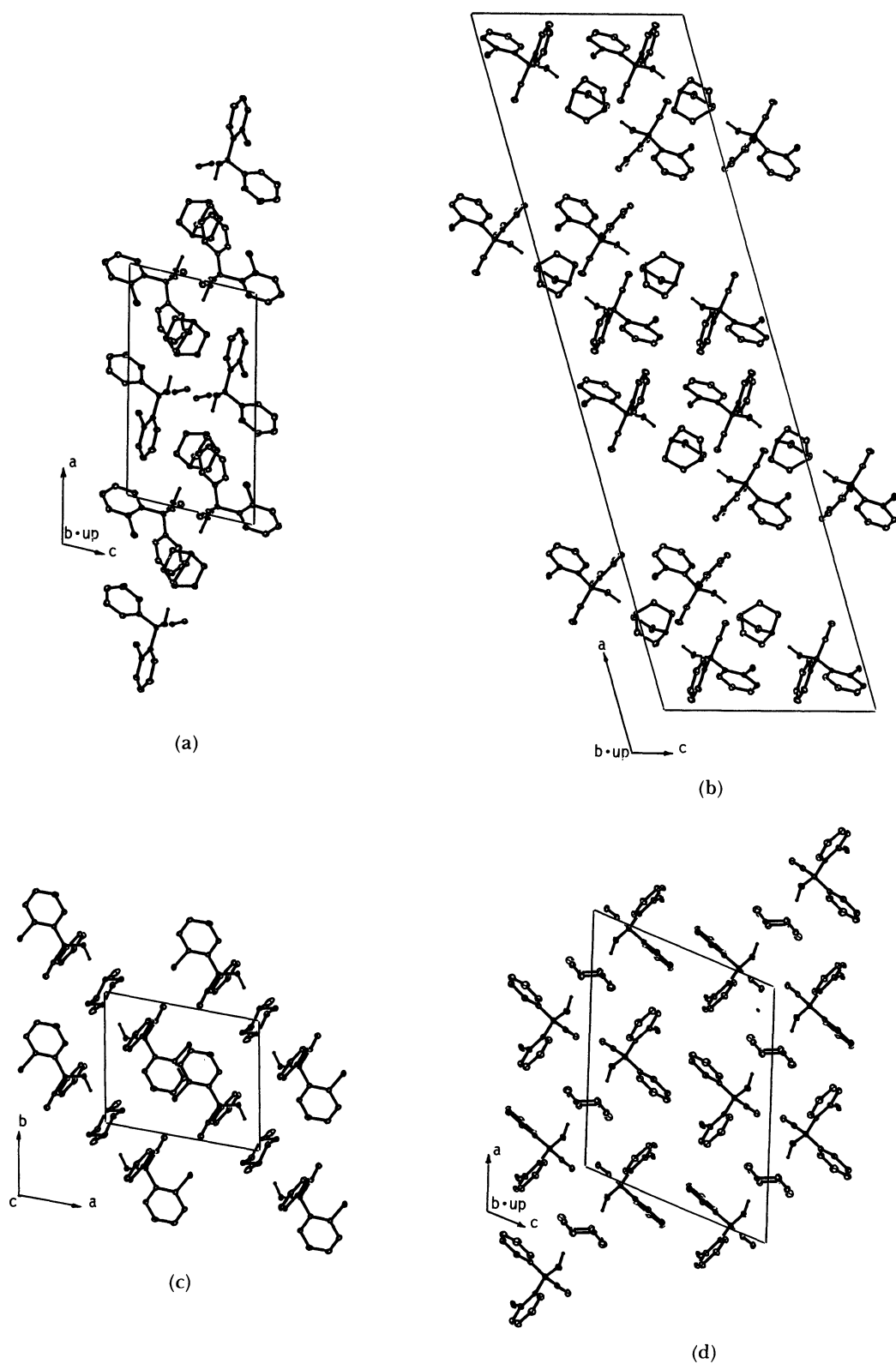


Fig. 1. Packing of 1:2 complex molecules<sup>11)</sup> in the 1(a) and 2(b) crystals are compared with that of 3(c) and 4(d). Non-hydrogen atoms are drawn as thermal ellipsoids with 10% probability level, and hydrogen atoms only engaged in hydrogen bondings are shown as spheres with  $B=1.0 \text{ \AA}^2$ .

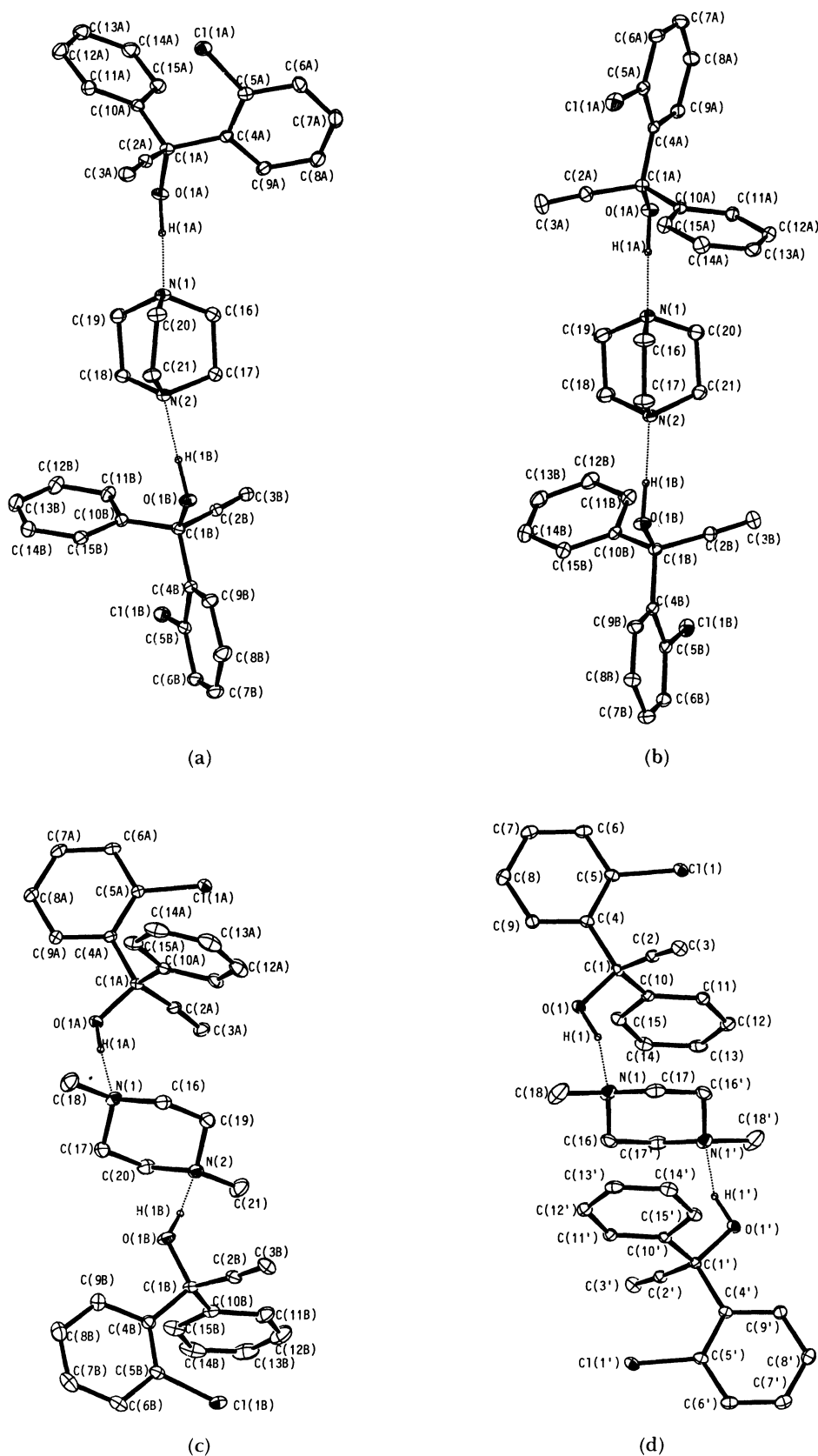


Fig. 2. A perspective view<sup>1D</sup> of **1(a)** and **2(b)** complexes with the numbering scheme of atoms compared with that of **3(c)** and **4(d)**. Non-hydrogen atoms are drawn as thermal ellipsoids with 10% probability level, and hydrogen atoms only engaged in hydrogen bonding are shown as spheres with  $B=1.0 \text{ \AA}^2$ .

Table 3. Selected Bond Distances and Bond Angles in the 1:2 Complex of DABCO with Two (-)-CPPOH (1) and that with (+)- and (-)-CPPOH (2) Compared with Those in the 1:2 Complex of *N,N'*-Dimethylpiperazine with (+)- and (-)-CPPOH (3) and That with Two (-)-CPPOH (4). Estimated Standard Deviations in Parentheses

|  | 1        | 2        | 3                     | 4         |
|--|----------|----------|-----------------------|-----------|
| Bond distances [ <i>l</i> /Å]                              |          |          |                       |           |
| 1-( <i>o</i> -Chlorophenyl)-1-phenyl-2-propyn-1-ol (CPPOH) |          |          |                       |           |
| C(1)-O(1)  | 1.425(4) | 1.409(4) | 1.434(3)              | 1.427(5)  |
|  | 1.426(4) | 1.417(5) |                       | 1.424(7)  |
| C(1)-C(2)  | 1.485(4) | 1.489(5) | 1.475(3)              | 1.476(6)  |
|  | 1.482(4) | 1.490(5) |                       | 1.469(7)  |
| C(1)-C(4)  | 1.543(4) | 1.536(5) | 1.544(3)              | 1.536(6)  |
|  | 1.549(4) | 1.529(5) |                       | 1.532(7)  |
| C(1)-C(10)   | 1.521(4) | 1.530(4) | 1.529(3)              | 1.525(6)  |
|  | 1.518(4) | 1.536(5) |                       | 1.520(7)  |
| C(2)-C(3)  | 1.187(5) | 1.179(6) | 1.182(4)              | 1.177(7)  |
|  | 1.180(5) | 1.181(6) |                       | 1.185(9)  |
| C(4)-C(5)  | 1.385(4) | 1.390(4) | 1.395(3)              | 1.388(6)  |
|  | 1.385(4) | 1.387(5) |                       | 1.373(7)  |
| C(4)-C(9)  | 1.402(4) | 1.403(5) | 1.384(3)              | 1.395(6)  |
|  | 1.374(5) | 1.400(5) |                       | 1.393(8)  |
| C(5)-C(6)  | 1.397(5) | 1.393(5) | 1.392(4)              | 1.390(7)  |
|  | 1.378(5) | 1.384(6) |                       | 1.379(9)  |
| C(5)-Cl(1)   | 1.737(3) | 1.735(4) | 1.743(3)              | 1.708(5)  |
|  | 1.753(3) | 1.753(4) |                       | 1.732(6)  |
| C(6)-C(7)  | 1.381(6) | 1.384(6) | 1.371(4)              | 1.380(8)  |
|  | 1.377(6) | 1.380(7) |                       | 1.374(10) |
| C(7)-C(8)  | 1.380(6) | 1.368(6) | 1.373(4)              | 1.365(8)  |
|  | 1.369(6) | 1.390(7) |                       | 1.373(11) |
| C(8)-C(9)  | 1.391(5) | 1.392(5) | 1.392(4)              | 1.381(7)  |
|  | 1.417(6) | 1.389(7) |                       | 1.379(9)  |
| C(10)-C(11)  | 1.382(4) | 1.379(5) | 1.389(3)              | 1.385(7)  |
|  | 1.386(5) | 1.395(5) |                       | 1.405(9)  |
| C(10)-C(15)  | 1.385(4) | 1.388(5) | 1.392(4)              | 1.389(8)  |
|  | 1.392(5) | 1.385(6) |                       | 1.380(9)  |
| C(11)-C(12)  | 1.409(6) | 1.401(6) | 1.389(4)              | 1.369(9)  |
|  | 1.385(5) | 1.401(6) |                       | 1.359(11) |
| C(12)-C(13)  | 1.375(6) | 1.368(6) | 1.386(4)              | 1.356(12) |
|  | 1.365(6) | 1.378(7) |                       | 1.338(14) |
| C(13)-C(14)  | 1.398(6) | 1.384(6) | 1.372(4)              | 1.399(13) |
|  | 1.404(7) | 1.383(7) |                       | 1.365(15) |
| C(14)-C(15)  | 1.373(5) | 1.405(5) | 1.390(4)              | 1.394(11) |
|  | 1.385(6) | 1.393(7) |                       | 1.413(13) |
| 1,4-Diazabicyclo[2.2.2]octane (DABCO)                      |          |          |                       |           |
| C(16)-N(1)   | 1.467(5) | 1.466(6) | 1.463(5)              | 1.452(7)  |
| C(17)-N(1)   | 1.469(4) | 1.452(6) | 1.445(4)              | 1.453(8)  |
| C(18)-N(1)   | 1.473(5) | 1.451(6) | 1.485(6)              | 1.482(9)  |
| C(19)-N(2)   | 1.462(5) | 1.454(6) |                       | 1.461(8)  |
| C(20)-N(2)   | 1.474(4) | 1.474(6) |                       | 1.459(8)  |
| C(21)-N(2)   | 1.479(5) | 1.470(5) |                       | 1.484(9)  |
| C(16)-C(19)  | 1.533(6) | 1.567(7) | 1.481(5) <sup>a</sup> | 1.480(9)  |
| C(17)-C(20)  | 1.550(5) | 1.540(7) |                       | 1.475(9)  |
| C(18)-C(21)  | 1.560(5) | 1.546(7) |                       |           |
| <i>N,N'</i> -Dimethylpiperazine (DMP)                      |          |          |                       |           |
| Bond angles [ $\phi$ /°]                                   |          |          |                       |           |
| 1-( <i>o</i> -Chlorophenyl)-1-phenyl-2-propyn-1-ol (CPPOH) |          |          |                       |           |
| C(2)-C(1)-C(4)   | 108.2(3) | 111.1(3) | 109.9(2)              | 108.9(4)  |
|  | 108.0(3) | 109.9(3) |                       | 109.6(5)  |
| C(2)-C(1)-C(10)  | 113.3(3) | 111.3(3) | 112.6(2)              | 112.5(4)  |
|  | 111.3(3) | 112.0(3) |                       | 112.1(5)  |
| C(2)-C(1)-O(1)   | 108.1(3) | 108.1(3) | 107.8(2)              | 108.0(4)  |
|  | 109.4(3) | 108.1(3) |                       | 107.3(5)  |
| C(4)-C(1)-C(10)  | 112.0(3) | 109.4(3) | 111.4(2)              | 111.0(4)  |
|  | 112.7(3) | 110.8(3) |                       | 111.6(5)  |
| C(4)-C(1)-O(1)   | 110.4(3) | 106.8(3) | 106.4(2)              | 107.1(4)  |
|  | 105.8(3) | 107.2(3) |                       | 106.5(4)  |



Table 3. (Continued)

|                                | 1        | 2        | 3        | 4         |
|--------------------------------|----------|----------|----------|-----------|
| C(10)-C(1)-O(1)                | 104.7(3) | 110.0(3) | 108.4(2) | 109.1(4)  |
|                                | 109.4(3) | 108.8(3) |          | 109.5(5)  |
| C(1)-C(2)-C(3)                 | 175.5(4) | 175.9(5) | 175.4(3) | 175.6(5)  |
|                                | 178.8(4) | 177.6(4) |          | 175.9(6)  |
| C(1)-C(4)-C(5)                 | 123.6(3) | 124.8(3) | 123.1(3) | 123.5(4)  |
|                                | 123.8(3) | 124.0(3) |          | 124.2(5)  |
| C(1)-C(4)-C(9)                 | 119.2(3) | 118.3(3) | 120.1(3) | 119.6(4)  |
|                                | 119.8(4) | 119.1(3) |          | 119.8(5)  |
| C(5)-C(4)-C(9)                 | 117.2(3) | 116.9(3) | 116.8(3) | 116.9(4)  |
|                                | 116.3(3) | 116.9(4) |          | 116.0(5)  |
| C(4)-C(5)-C(6)                 | 122.1(4) | 122.2(3) | 121.9(3) | 122.2(5)  |
|                                | 124.4(4) | 122.5(4) |          | 123.2(6)  |
| C(4)-C(5)-Cl(1)                | 121.5(3) | 121.9(3) | 121.7(2) | 121.6(4)  |
|                                | 120.9(3) | 120.6(3) |          | 121.0(4)  |
| C(6)-C(5)-Cl(1)                | 116.4(3) | 115.9(3) | 116.4(2) | 116.2(4)  |
|                                | 114.7(3) | 116.8(4) |          | 115.8(5)  |
| C(5)-C(6)-C(7)                 | 119.4(4) | 119.2(4) | 119.9(3) | 119.3(5)  |
|                                | 117.7(4) | 119.3(5) |          | 119.0(6)  |
| C(6)-C(7)-C(8)                 | 119.6(4) | 120.1(5) | 119.4(3) | 119.4(5)  |
|                                | 120.9(4) | 120.2(5) |          | 120.0(7)  |
| C(7)-C(8)-C(9)                 | 120.6(4) | 120.5(4) | 120.6(3) | 121.4(5)  |
|                                | 119.5(5) | 119.4(4) |          | 119.6(7)  |
| C(4)-C(9)-C(8)                 | 120.9(4) | 121.0(4) | 121.4(3) | 120.8(5)  |
|                                | 121.1(4) | 121.7(4) |          | 122.2(6)  |
| C(1)-C(10)-C(11)               | 122.0(3) | 123.2(3) | 123.1(3) | 122.9(5)  |
|                                | 122.6(3) | 121.4(3) |          | 122.9(5)  |
| C(1)-C(10)-C(15)               | 118.8(3) | 117.6(3) | 117.9(3) | 118.3(5)  |
|                                | 118.9(3) | 118.1(4) |          | 117.9(5)  |
| C(11)-C(10)-C(15)              | 119.0(3) | 119.1(4) | 119.0(3) | 118.8(5)  |
|                                | 118.5(3) | 120.3(4) |          | 119.2(6)  |
| C(10)-C(11)-C(12)              | 120.4(4) | 120.7(4) | 120.5(3) | 122.0(6)  |
|                                | 121.3(4) | 119.6(4) |          | 120.5(7)  |
| C(11)-C(12)-C(13)              | 119.3(4) | 120.1(4) | 120.1(3) | 119.5(7)  |
|                                | 120.2(4) | 119.5(5) |          | 121.1(8)  |
| C(12)-C(13)-C(14)              | 120.4(5) | 120.2(5) | 119.7(3) | 120.4(8)  |
|                                | 119.5(5) | 121.1(5) |          | 120.3(10) |
| C(13)-C(14)-C(15)              | 119.4(4) | 119.8(4) | 120.6(3) | 120.0(8)  |
|                                | 120.1(5) | 119.7(5) |          | 120.9(10) |
| C(10)-C(15)-C(14)              | 121.5(4) | 120.2(4) | 120.1(3) | 119.3(7)  |
|                                | 120.4(4) | 119.8(5) |          | 118.1(8)  |
| C(1)-O(1)-H(1)                 | 123(3)   | 112(4)   | 109(2)   | 121(4)    |
|                                | 114(3)   | 112(3)   |          | 122(4)    |
|                                |          | DABCO    |          | DMP       |
| N(1)-C(16)-C(19) <sup>b)</sup> | 110.5(3) | 108.8(4) | 111.0(3) | 111.4(5)  |
| N(1)-C(17)-C(20) <sup>c)</sup> | 110.1(3) | 111.7(4) | 110.9(3) | 111.0(5)  |
| N(1)-C(18)-C(21)               | 109.5(3) | 110.7(4) |          |           |
| N(2)-C(19)-C(16)               | 109.9(4) | 110.2(4) |          | 111.4(5)  |
| N(2)-C(20)-C(17)               | 109.2(3) | 108.6(4) |          | 111.7(5)  |
| N(2)-C(21)-C(18)               | 109.4(3) | 109.5(4) |          |           |
| C(16)-N(1)-C(17)               | 109.7(3) | 107.7(4) | 108.7(3) | 108.9(5)  |
| C(16)-N(1)-C(18)               | 108.3(3) | 110.1(4) | 107.4(3) | 111.0(5)  |
| C(17)-N(1)-C(18)               | 108.0(3) | 108.7(4) | 113.2(3) | 110.5(5)  |
| C(19)-N(2)-C(20)               | 109.2(3) | 109.9(4) |          | 108.0(5)  |
| C(19)-N(2)-C(21)               | 109.0(3) | 109.1(4) |          | 111.0(5)  |
| C(20)-N(2)-C(21)               | 108.6(3) | 108.1(4) |          | 106.5(5)  |

a) C(16)-C(17') in **3**. b) N(1)-C(16)-C(17') in **3**. c) N(1)-C(17)-C(16') in **3**.

tion along the direction perpendicular to the N(1)...N(2) axis of DABCO molecule. This suggests an existence of hindered rotation of the molecule along the N(1)...N(2) axis, similar to that in the 1:2 complex of DABCO with *p*-cresol.<sup>12)</sup> The C-N bond distances

are equal in each molecule [av. 1.469 Å(1) and av. 1.461 Å(2)] and also equal to that observed in uncomplexed DABCO by the neutron diffraction study [1.470(7) Å]<sup>13)</sup> within the range of errors. The C-C distances [av. 1.548 Å (1) and av. 1.554 Å (2)] are

larger than those in DABCO crystal [1.513(5) Å]. The C–N–C and N–C–C bond angles of **1** and **2** showed no significant difference respectively from the corresponding angles of DABCO in the crystal [108.4(2) and 110.5(4)°].

***N,N'*-Dimethylpiperazine (DMP)**. The DMP molecule in **3** takes a chair form, the center of which lies on a crystallographic center of symmetry. In **4**, the DMP molecule is also in a chair form but not centrosymmetric structure.

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