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1:1 and 1:2 Complexes Between Diaza-18-crown-6 and 2,7-Dihydroxynaphthalene

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Abstract. 1:1 Complex, $C_{12}H_{26}N_2O_4.C_{10}H_8O_2$, $M_r = 422.53$, monoclinic, $P2_1/c$, $a = 17.813$ (3), $b = 7.563$ (2), $c = 18.297$ (2) Å, $\beta = 97.80$ (1)°, $V = 2442.3$ (6) Å^3, $Z = 4$, $D_x = 1.149$ g cm^{-3}, λ(Mo $K\alpha$) $= 0.71073$ Å, $\mu = 0.78$ cm^{-1}, $F(000) = 912$, $T = 295$ K, $R = 0.0687$ for 1964 observed reflections. 1:2 Complex, $C_{12}H_{26}N_2O_4.2C_{10}H_8O_2$, $M_r = 582.70$, monoclinic, $P2_1/n$, $a = 11.957$ (2), $b = 7.551$ (1), $c = 18.474$ (2) Å, $\beta = 105.85$ (1)°, $V = 1604.4$ (3) Å^3, $Z = 2$, $D_x = 1.206$ g cm^{-3}, λ(Mo $K\alpha$) $= 0.71073$ Å, $\mu = 0.81$ cm^{-1}, $F(000) = 624$, $T = 295$ K, $R = 0.0424$ for 1745 observed reflections. The conformations of the diaza-18-crown-6 molecules are analogous to the D_{3d} conformation of 18-crown-6. In the 1:1 complex the dihydroxynaphthalene bridges two independent diaza-18-crown-6 molecules by hydrogen bonding to the diaza N atoms. In the 1:2 complex one hydroxyl O(7) hydrogen bonds to the diaza N atom while the other hydroxyl O(2) hydrogen bonds to O(7) of an adjacent molecule.

Introduction. Diaza-18-crown-6 (IUPAC name: 1,4,-10,13-tetraoxa-7,16-diazacyclooctadecane) forms stable complexes with neutral organic molecules containing proton donors (Watson, Galloy, Grossie, Vögtle & Müller, 1984; Vögtle, Müller & Watson, 1984). The hydrogen bonds always involve the diaza N atoms. If the guest donor is sufficiently acidic, proton transfer occurs yielding a diaza-18-crown-6 dication (Watson, Vögtle & Müller, 1988a). In a recent investigation (Watson, Vögtle & Müller, 1988b), it was found that diaza-18-crown-6 could be used to selectively precipitate some polyhydroxy guests from mixtures of oligohydroxy phenols. Chemical analysis of a complex formed with 2,7-dihydroxynaphthalene indicated a host:guest ratio

of 2:3. Since this is a rather unusual ratio for guests of this type, we believed the structure would be of interest. Upon careful control of the guest:host stoichiometries we isolated 1:1 and 1:2 complexes but no trace of a 2:3 complex. An initial 2:3 host:guest ratio leads to an approximate equimolar mixture of 1:2 and 1:1 complexes giving a 2:3 chemical analysis.

Experimental. Data were collected on a Nicolet $R3m/\mu$ update of a $P2_1$ diffractometer ($3 \le 2\theta \le 45°$) in the Wyckoff mode (2θ fixed, ω varied) using a variable scan rate (4 to 29.3° min^{-1}) and graphite-monochromated Mo $K\alpha$ radiation. Lorentz–polarization corrections and a ψ-scan-based empirical absorption correction were applied; structure solved by direct methods and refined by block-cascade least-squares techniques. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = [\sigma^2(F_o) + gF_o^2]^{-1}$. Computer programs for Desktop 30 Microeclipse and Nova 4/C configuration (Nicolet Instrument Corporation, 1986); scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974).

1:1 Complex: Obtained by refluxing a 1:1 molar ratio of the two components in a minimum quantity of ethyl acetate, colorless crystals $0.15 \times 0.38 \times 0.52$ mm, 25 reflections ($32.03 \le 2\theta \le 40.93°$) used to determine unit-cell dimensions; systematic absences ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$) and Laue symmetry $2/m$ consistent with space group $P2_1/c$; 3189 independent reflections ($-19 \le h \le 19$, $0 \le k \le 8$, $0 \le l \le 19$), $1964 \ge 3\sigma(I)$; transmission factors 0.920 to 0.966; all H atoms located in a difference map, OH and NH H atoms refined isotropically, all other H atoms allowed to ride on attached atom, one isotropic thermal parameter refined for naphthalene H atoms and another for H atoms of one crown, H atoms of crown with large thermal parameters assigned isotropic value of attached atom; $R = 0.0687$, $wR = 0.0534$ for 286 parameters

and 1964 reflections ($R = 0.1112$, $wR = 0.0570$ for 3189 reflections), $S = 1.673$, $(\Delta/\sigma)_{max} = 0.030$; the largest peaks in the final difference map of -0.29 and $+0.21$ e Å^{-3}, $g = 0.0015$. Table 1 gives the atomic positional parameters and U_{eq} values while Tables 3,4 and 5 give bond lengths, valence angles and torsion angles. Fig. 1 is a drawing of the 1:1 complex.

1:2 Complex: Obtained by refluxing a 2:1 molar ratio of the two components in a minimum quantity of ethyl acetate, colorless crystals, $0.38 \times 0.50 \times 0.50$ mm, 25 reflections ($42.04 \le 2\theta \le 48.96°$) used to determine unit-cell dimensions; systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) and Laue symmetry $2/m$ consistent with space group $P2_1/n$; 2095 independent reflections ($-12 \le h \le 12$, $0 \le k \le 8$, $0 \le l \le 19$), $1745 \ge 3\sigma(I)$; transmission factors 0.879 to 0.916; all H atoms located in difference map, OH and NH H atoms refined isotropically, all other H atoms allowed to ride on attached atom, one isotropic thermal parameter refined for naphthalene H atoms and another for crown H atoms; $R = 0.0424$, $wR = 0.0546$ for 204 parameters and 1745 reflections ($R = 0.0696$, $wR = 0.0748$ for 2095 reflections), $S = 1.508$, $(\Delta/\sigma)_{max} = 0.015$; largest peaks in the final difference map of -0.12 and $+0.17$ e Å^{-3}, $g = 0.00070$. Table 2 gives the atomic positional parameters and U_{eq} values while bond lengths, valence angles and torsion angles are listed in Tables 3, 4 and 5. Fig. 2 is a drawing of the 1:2 complex.*

Discussion. The diaza-18-crown-6 molecules exhibit conformations analogous to the D_{3d} conformation of the 18-crown-6 molecule (see Table 5) (Elbasyoung, Brügge, Von Deuten, Dickel, Knöchel, Koch, Kopf, Melzer & Rudolf, 1983). In the 1:1 complex there are two independent diaza-18-crown-6 molecules lying on centers of symmetry. In crown [N(9)...] the six electron-donating atoms lie on an average 0.217 (5) Å above and below the mean plane while the donors in crown [N(18)...] are on average 0.239 (5) Å from the mean plane. These values are consistent with those reported for other 18-crown-6 molecules in the D_{3d} conformation (Vögtle et al., 1984). The two molecules exhibit significantly different thermal parameters although the number of intermolecular interactions of less than 2.80 Å is about the same. The dihydroxy-naphthalene molecule bridges the two independent diaza-18-crown-6 molecules forming hydrogen bonds to the diaza N atoms; $H(7)\cdots N(9) = 1.89$ (3), $O(7)\cdots N(9) = 2.702$ (5) Å, $O(7)-H(7)\cdots N(9) = 174$ (2)°;

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å$^2 \times 10^3$) for the 1:1 complex

	x	y	z	U_{eq}*
C(1)	2339 (2)	2081 (4)	132 (2)	51 (1)
C(2)	2882 (2)	3123 (5)	−98 (2)	56 (2)
O(2)	2930 (2)	3192 (4)	−827 (1)	83 (1)
C(3)	3376 (2)	4088 (5)	418 (2)	65 (2)
C(4)	3303 (2)	3978 (5)	1148 (2)	69 (2)
C(4a)	2751 (2)	2906 (5)	1408 (2)	56 (2)
C(5)	2666 (2)	2741 (6)	2163 (2)	70 (2)
C(6)	2145 (2)	1652 (6)	2384 (2)	69 (2)
C(7)	1659 (2)	657 (5)	1873 (2)	61 (2)
O(7)	1162 (2)	−389 (4)	2159 (1)	85 (1)
C(8)	1713 (2)	811 (5)	1139 (2)	55 (1)
C(8a)	2261 (2)	1915 (4)	887 (2)	48 (1)
N(9)	129 (2)	−2206 (4)	1233 (2)	68 (1)
C(10)	−565 (3)	−2227 (7)	1578 (2)	88 (2)
C(11)	−820 (3)	−408 (7)	1716 (2)	88 (2)
O(12)	−1032 (1)	442 (4)	1034 (1)	66 (1)
C(13)	−1224 (3)	2231 (6)	1111 (3)	82 (2)
C(14)	−1489 (3)	3009 (6)	380 (3)	85 (2)
O(15)	−878 (1)	3099 (3)	−29 (2)	69 (1)
C(16)	−1086 (3)	3945 (6)	−723 (3)	90 (2)
C(17)	−394 (3)	3996 (5)	−1101 (2)	89 (2)
N(18)	5967 (2)	4621 (5)	1282 (2)	89 (2)
C(19)	6272 (3)	2805 (7)	1465 (3)	122 (3)
C(20)	6493 (4)	1973 (8)	801 (4)	135 (3)
O(21)	5904 (2)	1869 (4)	261 (3)	102 (2)
C(22)	6096 (4)	1091 (8)	−419 (4)	134 (4)
C(23)	5418 (4)	1060 (11)	−966 (4)	148 (4)
O(24)	5221 (2)	2729 (5)	−1187 (2)	111 (2)
C(25)	4558 (4)	2706 (9)	−1727 (3)	125 (3)
C(26)	4305 (3)	4550 (10)	−1883 (3)	130 (3)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å$^2 \times 10^3$) for the 1:2 complex

	x	y	z	U_{eq}*
C(1)	786 (2)	6633 (2)	8107 (1)	41 (1)
C(2)	498 (2)	7147 (2)	7374 (1)	44 (1)
O(2)	−561 (1)	6625 (2)	6916 (1)	60 (1)
C(3)	1270 (2)	8123 (3)	7089 (1)	58 (1)
C(4)	2336 (2)	8540 (3)	7545 (1)	65 (1)
C(4a)	2676 (2)	8025 (3)	8306 (1)	46 (1)
C(5)	3783 (2)	8430 (3)	8797 (1)	59 (1)
C(6)	4068 (2)	7941 (3)	9530 (1)	53 (1)
C(7)	3277 (2)	7012 (2)	9820 (1)	42 (1)
O(7)	3621 (1)	6600 (2)	10565 (1)	57 (1)
C(8)	2209 (2)	6572 (2)	9362 (1)	41 (1)
C(8a)	1884 (1)	7070 (2)	8595 (1)	36 (1)
N(9)	2164 (2)	4771 (2)	1115 (1)	47 (1)
C(10)	2117 (2)	5745 (3)	1790 (1)	53 (1)
C(11)	1536 (2)	7492 (3)	1589 (1)	59 (1)
O(12)	363 (1)	7211 (2)	1204 (1)	56 (1)
C(13)	−269 (2)	8832 (3)	1077 (1)	76 (1)
C(14)	−1477 (2)	8501 (3)	658 (1)	74 (1)
O(15)	−1537 (1)	7990 (2)	−89 (1)	64 (1)
C(16)	−2686 (2)	7870 (3)	−546 (1)	67 (1)
C(17)	−2657 (2)	7013 (3)	−1264 (1)	63 (1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

$H(2)\cdots N(18)$ $(1-x, 1-y, -z) = 2.04$ (4), $O(2)\cdots N(18) = 2.781$ (6) Å, $O(2)-H(2)\cdots N(18) = 176$ (3)°. Because the arrangement of hydroxyl groups is not collinear (e.g. as in guest molecules with centers of

Table 3. *Bond lengths (Å) for the* 1:1 *and* 1:2 *complexes*

	1:1	1:2
C(1)–C(2)	1·358 (5)	1·359 (2)
C(1)–C(8a)	1·412 (5)	1·414 (2)
C(2)–O(2)	1·349 (5)	1·375 (2)
C(2)–C(3)	1·405 (5)	1·392 (3)
C(3)–C(4)	1·361 (6)	1·359 (3)
C(4)–C(4a)	1·406 (5)	1·407 (3)
C(4a)–C(5)	1·416 (6)	1·418 (3)
C(4a)–C(8a)	1·416 (5)	1·406 (3)
C(5)–C(6)	1·344 (6)	1·354 (3)
C(6)–C(7)	1·404 (6)	1·397 (3)
C(7)–O(7)	1·345 (5)	1·359 (2)
C(7)–C(8)	1·364 (6)	1·368 (2)
C(8)–C(8a)	1·409 (5)	1·413 (2)
N(9)–C(10)	1·463 (6)	1·498 (6)*	1·463 (2)
C(10)–C(11)	1·481 (7)	1·469 (9)	1·490 (3)
C(11)–O(12)	1·409 (5)	1·342 (7)	1·405 (2)
O(12)–C(13)	1·408 (6)	1·459 (9)	1·424 (2)
C(13)–C(14)	1·479 (6)	1·460 (10)	1·462 (3)
C(14)–O(15)	1·404 (6)	1·357 (7)	1·415 (3)
O(15)–C(16)	1·425 (5)	1·434 (7)	1·406 (2)
C(16)–C(17)	1·492 (7)	1·481 (10)	1·486 (3)
C(17)–N(9')	1·464 (5)	1·408 (7)	1·466 (3)

* N(9) = N(18), C(10) = C(19), *etc.*

Table 4. *Selected bond angles* (°) *for the* 1:1 *and* 1:2 *complexes*

	1:1	1:2
C(1)–C(2)–O(2)	118·3 (3)	118·2 (2)
C(3)–C(2)–O(2)	121·5 (3)	120·8 (1)
C(6)–C(7)–O(7)	115·7 (3)	117·0 (1)
C(8)–C(7)–O(7)	125·2 (3)	123·0 (2)
C(10)–N(9)–C(17')	112·1 (3)	112·3 (4)*	114·1 (1)
N(9)–C(10)–C(11)	111·4 (3)	109·9 (6)	110·8 (1)
C(10)–C(11)–O(12)	108·8 (3)	110·7 (4)	109·0 (2)
C(11)–O(12)–C(13)	113·1 (3)	114·2 (4)	111·4 (2)
O(12)–C(13)–C(14)	110·5 (3)	108·7 (5)	110·1 (2)
C(13)–C(14)–O(15)	108·8 (3)	110·1 (5)	110·0 (2)
C(14)–O(15)–C(16)	111·7 (3)	109·7 (4)	112·6 (2)
O(15)–C(16)–C(17)	107·0 (3)	108·5 (4)	107·9 (2)
C(16)–C(17)–N(9')	110·6 (3)	113·6 (4)	109·8 (2)

* For correspondence N(9) = N(18), C(10) = C(19), *etc.*

Table 5. *Torsion angles* (°) *for diaza-*18-*crown-*6-*molecules*

	1:1	1:2
N(9)–C(10)–C(11)–O(12)	65·8 (4)	58·8 (5)*	66·1 (2)
C(10)–C(11)–O(12)–C(13)	−175·0 (3)	−178·6 (4)	173·0 (2)
C(11)–O(12)–C(13)–C(14)	−176·3 (3)	178·5 (5)	178·5 (2)
O(12)–C(13)–C(14)–O(15)	−67·8 (4)	−68·9 (7)	−69·6 (2)
C(13)–C(14)–O(15)–C(16)	−176·6 (3)	−179·5 (5)	−172·5 (2)
C(14)–O(15)–C(16)–C(17)	178·4 (3)	−172·9 (5)	−169·6 (2)
O(15)–C(16)–C(17)–N(9')	61·8 (4)	66·9 (6)	61·0 (2)
C(16)–C(17)–N(9')–C(10')	−178·4 (3)	−175·5 (5)	179·0 (2)
C(17)–N(9')–C(10')–C(11')	178·8 (3)	−177·4 (4)	−176·4 (2)

* N(9) = N(18), *etc.*

symmetry), the bridging leads to the formation of infinite zigzag chains throughout the structure. The naphthalene plane makes angles of 86·6 (9)° with the mean planes of the electron-donor atoms in each of the two independent diaza-18-crown-6 moieties.

In the 1:2 complex the usual centrosymmetric monomeric cluster is formed through hydrogen bonding of a hydroxyl to the crown N; however, one hydroxyl now hydrogen bonds to the hydroxyl of an adjacent 1:2 complex, N(9)···H(7)(x, y, −1 + z) = 1·66 (2), N(9)··· O(7) = 2·635 (2) Å, O(7)–H(7)···N(9) = 172 (1)°; O(7)···H(2)(0·5 + x, 1·5 − y, 0·5 + z) = 1·95 (2), O(7)···O(2) = 2·766 (2) Å, O(2)–H(2)···O(7) = 164 (2)°. The naphthalene planes make an angle of 85·5 (4)° with the mean plane of the six donor atoms. The donor atoms lie on an average of 0·220 (3) Å above and below the mean plane.

The bond lengths of one diaza-18-crown-6 molecule in the 1:1 complex are equivalent to those in the 1:2 complex. (For exact correspondence the arbitrary direction of numbering must be reversed.) The distances in the other diaza-18-crown-6 (the molecule with the large thermal motion) show significant differences. The nonequivalent N–C bonds of 1·498 (6) and 1·408 (7) Å are particularly unsatisfactory; however, a more symmetric placement of the N atom does not
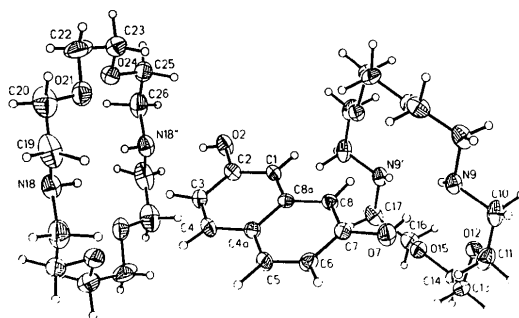

Fig. 1. Drawing of the 1:1 complex between 2,7-dihydroxy-naphthalene and diaza-18-crown-6. Thermal ellipsoids are drawn at the 30% probability level while H atoms are represented by spheres of arbitrary size.
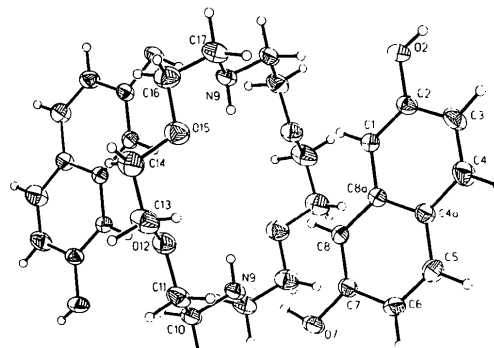

Fig. 2. Drawing of the 2:1 complex between 2,7-dihydroxynaphthalene and diaza-18-crown-6. Thermal ellipsoids are drawn at the 35% probability level while H atoms are represented by spheres of arbitrary size.
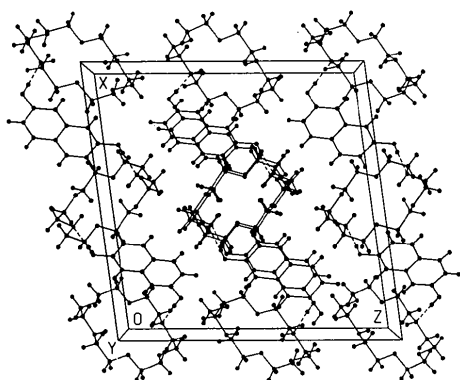
Fig. 3. Packing diagram for the 1:1 complex. Hydrogen bonds are shown as dashed lines.
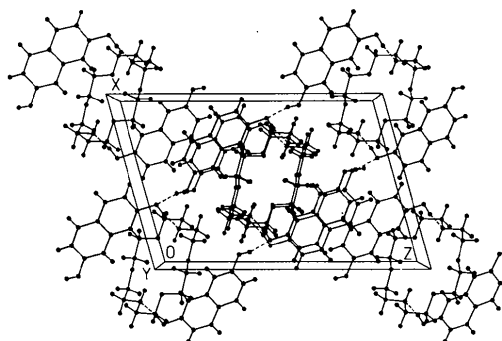

Fig. 4. Packing diagram for the 1:2 complex. Hydrogen bonds are shown as dashed lines.

refine, the two crown molecules are not related *via* a mirror plane containing C(4a)—C(8a), nor is an alternate space group apparent. The low residual electron density does not indicate alternate positions; however, solvent loss may be possible. Except for the C(2)—O(2) and C(7)—O(7) distances, the two dihydroxynaphthalene molecules are statistically equivalent, and both molecules are essentially planar (r.m.s.d. = 0·011 Å). Packing diagrams of the 1:1 and 1:2 complexes are shown in Figs. 3 and 4.

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The Absolute Configuration of (+)-Isoconcinndiol

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Abstract. 6-Bromo-α-ethenyldecahydro-2-hydroxy-α,2,5,5,8a-pentamethyl-1-naphthalenepropanol, $C_{20}H_{35}BrO_2$, $M_r = 387·4$, orthorhombic, $P2_12_12_1$, $a = 6·830 (1)$, $b = 12·736 (2)$, $c = 23·289 (2)$ Å, $V = 2026 (5)$ Å^3, $Z = 4$, $D_x = 1·27$ Mg m^{-3}, $\lambda(Cu K\alpha) = 1·5418$ Å, $\mu = 2·82$ mm^{-1}, $F(000) = 824$, $T = 293$ K, final $R = 0·051$ for 682 observed reflections. (+)-Isoconcinndiol was isolated from the mollusc *Aplysia dactylomela*. Its structure and absolute configuration are those of (3S,8R,13S)-labd-14-ene-8,13-diol. Hydrogen bonds O(2)H···O(1) [2·68 (1) Å, 165·4 (6)°] and O(1)H···O(2)$(x-\frac{1}{2}, -y+\frac{1}{2}, -z+1)$ [2·65 (1) Å, 166·9 (6)°] link the crystal structure.

Introduction. The brominated diterpene isoconcinndiol was first isolated from the marine alga *Laurencia snyderae*, var. *guadalupensis* (Dawson) (Howard & Fenical, 1980). The structure of the compound was proposed as shown in (1), mainly on the basis of its spectral data. A recent report (Murai, Abiko & Masamune, 1984) concerning the synthesis of the C(13) diastereoisomers of racemic (1), agrees that