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Acta Cryst. (1982). **B38**, 3157–3159

A 1,4,7,10,13,16-Hexaoxacyclooctadecane(18-crown-6)–4,4′-Biphenyldiol Dihydrate Ternary Complex

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(*Received* 8 *March* 1982; *accepted* 7 *July* 1982)

Abstract. $C_{12}H_{24}O_6.C_{12}H_{10}O_2.2H_2O$, $M_r = 486{\cdot}6$, monoclinic, $P2_1/c$, $a = 9{\cdot}264\,(1)$, $b = 11{\cdot}007\,(2)$, $c = 14{\cdot}165\,(2)$ Å, $\beta = 109{\cdot}10\,(1)°$, $U = 1364{\cdot}8\,(4)$ Å^3, $Z = 2$, $D_c = 1{\cdot}18$ Mg m^{-3}, μ(Cu $K\alpha$) = $0{\cdot}844$ mm^{-1}. Full-matrix least-squares refinement (calculated and observed H-atom positions were included in the structure-factor calculations but the parameters were not refined) based on 1138 observed reflections led to a final R of 0·073 and R_w of 0·035. The 18-crown-6 ether sits on a center of symmetry. The six O atoms are alternately 0·23 (2) Å above and below the mean plane and form an approximate hexagon with averaged sides of 2·83 (1) Å. The two water molecules are each hydrogen bonded to two O atoms of the crown ether. The planar 4,4′-biphenyldiol molecules sit on centers of symmetry and are hydrogen-bonded to the water molecules. The 4,4′-biphenyldiol molecules bridge two crown ethers *via* hydrogen bonds to water molecules.

Introduction. The weak interactions between crown ethers and neutral organic molecules are of chemical and biological interest. The mediation of these interactions by water molecules is of particular interest because of the importance of water in living organisms. The study of such interactions may lead to a better understanding of secondary interactions that occur at biological receptor sites. The change in the hydrophobic or hydrophilic nature of a site and the imposed stereospecificity are areas of interest. The specific role of water as an integral component of molecular recognition has not been emphasized. Although a number of structures of 18-crown-6 ethers with charged species have been described, only the neutral complexes with dimethyl acetylenedicarboxylate (1:1) (Goldberg, 1975), dimethyl sulfone (1:1) (Weber & Vögtle, 1980), urea (1:5) (Harkema, Van Hummel, Daasvatn & Reinhoudt, 1981), benzenesulfonamide (1:2) (Knochel, Kopf, Oehler & Rudolph, 1978) and phenyl carbamate (1:2) (Galloy, Watson, Vögtle & Müller, 1982) have been reported.

Recently the structures of two ternary complexes composed of a cryptand, a salt and a small neutral molecule have been reported (de Boer, Reinhoudt, Uiterwijk & Harkema, 1982; Hilgenfeld & Saenger, 1981). The present structure and a ternary complex of a cryptand, hydroquinone and water (Vögtle, Puff, Friedricks & Müller, 1982) are the first comprehensive reports on neutral ternary complexes involving cryptands.

A crystal of dimensions 0·33 × 0·17 × 0·17 mm was selected for all X-ray measurements. Intensity data were collected on a Syntex $P2_1$ diffractometer system by the θ:2θ scanning technique using a variable scan speed, Cu $K\alpha$ radiation ($\lambda = 1{\cdot}54178$ Å) and a graphite monochromator. Room-temperature lattice parameters were refined by a least-squares procedure utilizing 13 reflections whose angles were measured by a centering routine associated with the diffractometer. A periodically monitored reflection showed no significant change in intensity. Of the 2113 independent reflections measured ($2\theta < 120°$) 1239 had intensities greater than $3\sigma(I)$. Lorentz and polarization corrections were applied, but no absorption corrections were made.

An E map phased by *MULTAN* 78 (Main, Lessinger, Woolfson, Germain & Declercq, 1978) revealed the positions of all non-H atoms. After several cycles of refinement H-atom positions were calculated and compared with those obtained from a difference

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Fourier map. Full-matrix least-squares refinement was terminated at a final R value of 0·073 and R_w of 0·035 where $R = \sum \| F_o| - |F_c\| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. The function minimized in the refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(F_o)^2$.

Atomic scattering factors were calculated by the XRAY 76 program (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Atomic positional parameters and $U_{\rm eq}$ values are presented in Table 1 while interatomic distances and valence angles are listed in Table 2.*

Table 1. *Positional parameters* ($\times 10^4$) *and* U_{eq} ($\times 10^3$)

	x	y	z	$U_{\rm eq}$* (Å^2)
O(1)	633 (5)	1561 (4)	−1472 (3)	77 (3)
C(2)	1253 (9)	884 (7)	−2099 (4)	105 (6)
C(3)	2547 (7)	142 (8)	−1437 (3)	107 (7)
O(4)	1977 (4)	−782 (4)	−990 (3)	81 (3)
C(5)	3163 (8)	−1470 (8)	−312 (6)	109 (8)
C(6)	2521 (10)	−2434 (7)	138 (6)	120 (8)
O(7)	1846 (5)	−1951 (4)	786 (3)	83 (3)
C(8)	1232 (9)	−2838 (6)	1268 (6)	103 (7)
C(9)	595 (10)	−2257 (7)	1977 (4)	100 (7)
O(10)	1263 (3)	569 (2)	1150 (2)	75 (2)
O(11)	3521 (3)	2063 (3)	2138 (2)	73 (3)
C(12)	3886 (6)	2876 (5)	1531 (4)	55 (4)
C(13)	3183 (5)	2886 (5)	519 (4)	64 (4)
C(14)	3607 (6)	3716 (5)	−73 (3)	61 (4)
C(15)	4755 (6)	4565 (4)	327 (4)	45 (4)
C(16)	5433 (5)	4538 (5)	1349 (4)	63 (4)
C(17)	5027 (7)	3709 (5)	1944 (3)	73 (5)

* $U_{\rm eq} = (U_{11} \times U_{22} \times U_{33})^{1/3}$.

Table 2. *Interatomic distances* (Å) *and valence angles* (°)

O(1)–C(2)	1·417 (9)	O(10)···O(4′)	2·945 (8)
O(1)–C(9′)	1·365 (8)	O(10)···O(11)	2·669 (8)
C(2)–C(3)	1·499 (9)	O(11)–C(12)	1·358 (7)
C(3)–O(4)	1·390 (9)	C(12)–C(13)	1·367 (7)
O(4)–C(5)	1·418 (8)	C(12)–C(17)	1·377 (8)
C(5)–C(6)	1·460 (13)	C(13)–C(14)	1·381 (8)
C(6)–O(7)	1·376 (11)	C(14)–C(15)	1·390 (7)
O(7)–C(8)	1·413 (9)	C(15)–C(15′)	1·502 (8)
C(8)–C(9)	1·468 (12)	C(15)–C(16)	1·376 (8)
O(10)···O(7)	2·905 (8)	C(16)–C(17)	1·377 (7)
C(9′)O(1)C(2)	113·9 (5)	O(11)C(12)C(17)	119·0 (4)
O(1)C(2)C(3)	107·4 (5)	C(13)C(12)C(17)	118·5 (5)
C(2)C(3)O(4)	109·7 (6)	C(12)C(13)C(14)	120·6 (5)
C(3)O(4)C(5)	111·9 (5)	C(13)C(14)C(15)	122·0 (4)
O(4)C(5)C(6)	110·3 (6)	C(14)C(15)C(15′)	121·5 (4)
C(5)C(6)O(7)	110·5 (6)	C(14)C(15)C(16)	116·0 (5)
C(6)O(7)C(8)	113·5 (5)	C(15′)C(15)C(16)	122·4 (4)
O(7)C(8)C(9)	110·2 (6)	C(15)C(16)C(17)	122·5 (4)
C(8)C(9)C(1′)	109·8 (5)	C(16)C(17)C(12)	120·4 (4)
O(11)C(12)C(13)	122·5 (4)		

Discussion. Fig. 1 is an *ORTEP* drawing (Johnson, 1971) of the title compound. The hexaether lies at an inversion center and exhibits an approximate D_{3d} symmetry. The torsion angles around the 18-crown-6 ether are similar to those reported for the phenyl carbamate complex (Galloy *et al.*, 1982). The torsion angles about the C—C bonds average 69° which corresponds to a *gauche* conformation of the ethyleneoxy units, while those about the C—O bonds average 178° indicating planarity of these segments. The C—O and C—C distances average 1·397 (9) and 1·476 (10) Å while the C—O—C and O—C—C angles average 113·1 (5) and 108·7 (6)° respectively. The shortening of the bonds and the average values of the angles are consistent with the reported values for other 18-crown-6 complexes (Dunitz, Dobler, Seiler & Phizackerley, 1974). The six O atoms of the hexaether are alternately about 0·23 Å above and below the mean plane and form a nearly planar hexagon with an average O···O separation of 2·83 (1) Å. Two water molecules are hydrogen bonded to each 18-crown-6 ether and are related by the inversion center. The O(10)···O(4′) and O(10)···O(7) distances are 2·905 (8) and 2·945 (8) Å respectively. The H-atom positions are not refined and probably represent a too idealized geometry; however, the relevant parameters are O(10)–H(10*a*) = 1·02, H(10*a*)···O(4′) = 1·92 Å, O(10)H(10*a*)O(4′) = 179° and H(10*b*)–O(10) = 1·03, H(10*b*)···O(7) = 1·87 Å, O(10)H(10*b*)O(7) = 178°.

The 4,4′-biphenyldiol molecule lies on a center of symmetry and least-squares planes fitted to the phenyl rings indicate a dihedral angle of less than 1°. A least-squares plane fitted to the entire 4,4′-biphenyldiol molecule shows a maximum deviation of 0·02 Å from the plane which is very unusual for biphenyl systems. The calculated H(14)···H(16′) and H(16)···H(14′) separations are 2·13 Å. The hydroxyl groups are involved in hydrogen bonding with the water molecules, O(10)···O(11) = 2·669 (8) Å. The 4,4′-biphenyldiol molecule bridges two 18-crown-6 ether molecules *via* hydrogen bonding to the water molecules.

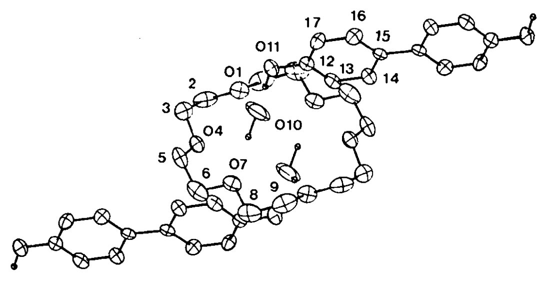

Fig. 1. *ORTEP* drawing of the ternary complex. Thermal ellipsoids are drawn at the 20% probability level. H atoms on the ether and phenyl rings have been omitted for clarity.

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* Lists of H-atom positional coordinates, anisotropic thermal parameters, torsion angles and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38059 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The present structure is an interesting example of a substrate molecule unable to bind efficiently to a host site but capable of binding through the mediation of water molecules. Such processes may be of importance in the secondary binding interactions of substrates to enzyme or receptor sites. The bond is strong enough to orient the substrate but weak enough to be broken readily through changes of conformation or solvation.

We thank The Robert A. Welch Foundation (P-074) for their financial support. This is FASTBIOS contribution No. 95.

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Acta Cryst. (1982). B**38**, 3159–3161

9,9'-Bibicyclo[3.3.1]nonylidene

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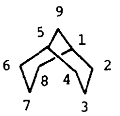
(*Received* 26 *March* 1982; *accepted* 1 *July* 1982)

Abstract. $C_{18}H_{28}$, $M_r = 244{\cdot}42$, monoclinic, $C2/m$, $a = 14{\cdot}257\ (6)$, $b = 15{\cdot}015\ (6)$, $c = 6{\cdot}895\ (2)$ Å, $\beta = 93{\cdot}21\ (3)^\circ$, $V = 1474\ (1)$ Å^3, $Z = 4$, $D_c = 1{\cdot}10$ Mg m^{-3}, μ(Mo $K\alpha$) = 0·057 mm^{-1}. Full-matrix least-squares refinement (non-H atoms anisotropic, H atoms isotropic) based on 790 observed reflections led to an R of 0·045 and R_w of 0·078. The two independent molecules sit on sites of C_{2h} ($2/m$) symmetry. In one molecule the twofold crystallographic axis is along the C=C bond while in the other it is perpendicular to this bond. The bicyclo[3.3.1]non-9-ylidene molecules exhibit all-chair conformations with transannular H···H contacts of 1·99 (3) and 1·81 (8) Å.

Introduction. In the liquid state bicyclo[3.3.1]nonane (1) exists as an equilibrium mixture of the dichair, boat–chair and diboat conformations with the dichair conformation being more stable by about 11·3 kJ mol^{-1} (Fisch, Smallcombe, Gramain, McKervey & Anderson, 1970; Russell & Keske, 1970). With *endo* substituents at C(3) and C(7), the boat–chair conformation is most stable (Binsch & Roberts, 1965). The close approach of the C(3) and C(7) *endo* H atoms is reflected in the unusually high C—H bending and stretching frequencies of 2990 and 1490 cm^{-1}, respectively (Eglington, Martin & Parker, 1965). The structures of 1-(p-bromobenzenesulfonyloxymethyl)-5-methylbicyclo[3.3.1]nonan-9-ol (Brown, Martin & Sim, 1965) and 3-azabicyclo[3.3.1]nonane hydrobromide (Dobler & Dunitz, 1964) have been reported. Both structures exhibit chair–chair conformations in the solid state with estimated H(3)···H(7) distances of 1·7 and 1·8 Å, respectively. The crowded molecular environment also affects the NMR chemical shifts. The compressed protons are deshielded and exhibit nuclear Overhauser effects. Transannular hydride shifts have been observed in these systems (Appleton & Graham, 1965).



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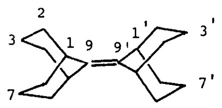

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