Interaction of Dihydroxy Host Systems with Glycols. A Comparative Study of the Crystal Structures of 1:1 Molecular Complexes of 1,4-Butanediol with 2,5-Bis(4-chlorophenyl)hydroquinone and *trans*-9,10-Dihydroxy-9,10-diphenyl-9,10-dihydroanthracene★

FUMIO TODA and KOICHI TANAKA
Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790, Japan

and

THOMAS C. W. MAK★★
Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

Abstract. The title compounds crystallize in space group $C2/c$ with $Z = 4$; $C_{18}H_{12}O_2Cl_2 \cdot HO(CH_2)_4OH$, $a = 16.186(3)$, $b = 7.626(1)$, $c = 16.939(3)$ Å, $\beta = 91.32(2)°$, $R_F = 0.048$ for 1743 observed $MoK\alpha$ reflections; $C_{26}H_{20}O_2 \cdot HO(CH_2)_4OH$, $a = 11.881(3)$, $b = 13.009(4)$, $c = 16.689(4)$ Å, $\beta = 110.67(2)°$, $R_F = 0.066$ for 1783 data points. Both structures feature centrosymmetric hydrogen-bonded $(OH)_4$ rings formed by molecular components located in special positions. Different packing modes account for the observed conformations (g^+ag^- and aaa, respectively) of 1,4-butanediol and its possible replacement by 1,2-ethanediol as a guest in the former crystal structure.

Key words: crystal structure, hydroquinone, *p*-terphenyl, dihydroanthracene, hydrogen bonding, host-guest compound, molecular complex, adduct.

1. Introduction

Recent studies on molecular inclusion by hydroxy host systems have shown that 2,5-bis(2,4-dimethylphenyl)hydroquinone (**1**), 2,5-bis-(4-chlorophenyl)hydroquinone (**2**), *trans*-9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene (**3**), and 9-hydroxy-9-(1-propynyl)fluorene (**4**) as well as its 2,7-dichloro (**5**) and 2,7-dibromo (**6**) derivatives form crystalline complexes with a variety of monohydric alcohols and glycols [1]. The hydrophobic nature of hosts **1–6** has been exploited to achieve selective extraction of ethanol from its aqueous solution of various concentration [1], thereby offering promise of a potentially useful means of gaining inexpensive energy from the fermentation of biomass. On the premise that detailed knowledge of the crystal structures of the adducts could pave the way for the rational design of new and more effective host systems, we embarked on a systematic X-ray crystallographic investigation

★ Dedicated to Professor H. M. Powell.
★★ Author for correspondence.

and reported the structures of the 1 : 2 complex of **1** with ethanol [2], the 1 : 1 complex of **3** with ethanol [3], and the 1 : 2 complex of **3** with methanol [4].

1 X = Y = Me	**3**	**4** X = H
2 X = Cl, Y = H		**5** X = Cl
		6 X = Br
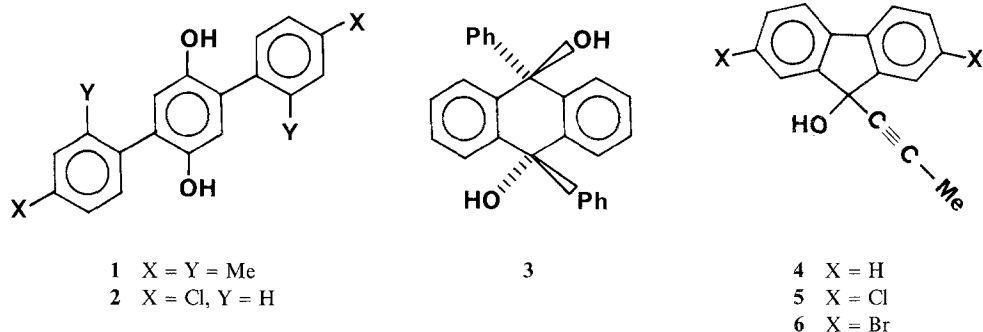
Crystallization studies have established that 1 : 1 adducts are formed by 1,2-ethanediol with **1** and **2**, and by 1,4-butanediol with **1–3** [1]. In order to provide a structural basis for the complexation of glycols containing an even number of methylene groups, we have determined the crystal structures of $2 \cdot HO(CH_2)_4OH$ (**7**) and $3 \cdot HO(CH_2)_4OH$ (**8**) as described in the present contribution.

2. Experimental

Compounds **2** [5] and **3** [6] were synthesized according to literature methods. Complexes **7** and **8** were each obtained as colorless prisms from slow evaporation of a mixture of an ether solution of the corresponding host and purified 1,4-butanediol. Infrared and NMR(JEOL FX-100S) spectra: **7**, $v_{OH}(cm^{-1})$, 3350, 3050, $\delta(CDCl_3)$ 7.22(s, C_6H_4Cl, 8H), 6.82(s, $C_6H_2(OH)_2$, 2H), 3.65(m, CH_2, 4H), 1.66(m, CH_2, 4H); **8**, v_{OH} 3280, 3380, δ 7.2–7.5(m, Ar, 18H), 3.67(m, CH_2, 4H), 1.65(m, CH_2, 4H). X-ray analyses of **7** and **8** were conducted in the same manner, and the crystal data and processing parameters are summarized in Table I.

A selected crystal was sealed in a 0.5 mm Lindemann glass capillary, transferred to a goniometer head, and mounted on a Nicolet R3m four-circle diffractometer. Determination of the crystal class and orientation matrix was performed according to established procedures [7]. Accurate unit-cell dimensions were derived from a least-squares fit of the angular settings for 25 reflections in the range $14 < 2\theta < 20°$. Intensity data were collected at an ambient laboratory temperature of 22 °C using graphite-monochromatized $MoK\alpha$ radiation ($\lambda = 0.71069$ Å), a NaI(Tl) scintillation counter, and a pulse height analyser. The crystal remained stable throughout the diffraction experiment as three standard reflections monitored every 50 data measurements showed only random fluctuations within $\pm 1\%$ of their mean values.

The raw intensities were processed with the learnt-profile procedure [8], and redundant and equivalent reflections were averaged to yield a set of structure amplitudes following corrections for Lorentz and polarization factors. For each complex the statistical distributions of the normalized structure factors strongly indicated the presence of a center of symmetry, and structure solution in space group $C2/c$ was achieved by direct phase determination based on negative quartets [9].

Table I. Data collection and processing parameters.

Compound	7		8	
Molecular formula	$C_{22}H_{22}O_4Cl_2$		$C_{30}H_{30}O_4$	
Molecular weight	421.32		454.57	
Cell constants	$a = 16.186(3)$ Å	$\beta = 91.32(2)°$	$a = 11.881(3)$ Å	$\beta = 110.67(2)°$
	$b = 7.626(1)$ Å	$V = 2090.3(6)$ Å^3	$b = 13.009(4)$ Å	$V = 2413.4(8)$ Å^3
	$c = 16.939(3)$ Å	$Z = 4$	$c = 16.689(4)$ Å	$Z = 4$
Density (flotation in CCl_4/hexane)	1.342 g cm^{-3}		1.249 g cm^{-3}	
Density (calcd.)	1.339 g cm^{-3}		1.251 g cm^{-3}	
Space group	$C2/c$		$C2/c$	
Radiation	graphite-monochromatized Mo$K\alpha$, $\lambda = 0.71069$ Å			
Crystal size	$0.40 \times 0.30 \times 0.20$ mm		$0.40 \times 0.38 \times 0.32$ mm	
Absorption coefficient	3.33 cm^{-1}		0.76 cm^{-1}	
Scan type and speed	$\omega - 2\theta$; 2.02–8.37 deg min^{-1}			
Scan range	1° below $K\alpha_1$ to 1° above $K\alpha_2$			
Background counting	stationary counts for one-half of scan time at each end of scan			
Collection range	$h, k, \pm l$; $2\theta_{max} = 52°$		$h, k, \pm l$; $2\theta_{max} = 52°$	
Unique data measured	2036		2350	
Observed data with $|F| > 3\sigma(|F|)$, n	1743		1783	
Number of variables, p	127		154	
$R_F = \Sigma \||F_o| - |F_c|\|/\Sigma|F_o|$	0.048		0.066	
Weighting scheme	$w = [\sigma^2(F_o) + 0.0003|F_o|^2]^{-1}$		$w = [\sigma^2(F_o) + 0.0012|F_o|^2]^{-1}$	
$R_{wF} = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$	0.059		0.091	
$S = [\Sigma w(|F_o| - |F_c|)^2/(n - p)]^{1/2}$	2.23		1.87	
Residual peaks in final difference map	0.26 to -0.44 eÅ^{-3}		0.33 to -0.42 eÅ^{-3}	

All non-hydrogen atoms were varied anisotropically in structure refinement. The aromatic and methylene H atoms were generated geometrically (C—H fixed at 0.96 Å) and allowed to ride on their respective parent C atoms. Both hydroxy H atoms were located from a difference Fourier map and held stationary in subsequent least-squares cycles. Isotropic temperature factors were assigned to all H atoms.

Computations were performed on a Data General Corporation Nova 3/12 minicomputer using the SHELXTL program package [10]. Analytic expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [11]. Blocked-cascade least-squares refinement [12] converged to the R indices listed in Table I, which also shows the residual electron-density extrema in the final difference maps.

3. Results and Discussion

Perspective views, each with atom labelling, of the asymmetric units in **7** and **8** are shown in Figures 1 and 2, respectively. The final positional parameters for both structures are listed in Table II. Bond lengths, bond angles, and selected torsion angles are given in Table III.

In the crystal structure of **7** (Figure 3), the hydroquinone (**2**) and glycol molecules occupy special positions of symmetry 2 and $\bar{1}$, respectively. These two molecular components are alternately linked by hydrogen bonds, giving rise to a three-dimensional packing mode dictated by $(OH)_4$ rings centered at a second set of centrosymmetric sites. Each phenolic group forms a significantly stronger donor hydrogen bond [2.674(3) Å] than an acceptor bond [2.788(3) Å] with its neighboring glycolic groups in the cyclic $(OH)_4$ system. The central and outer benzene rings in **2** are individually planar (maximum deviations from their mean planes 0.0024 and 0.0007 Å, respectively), making a dihedral angle of 37.4°, which may be compared
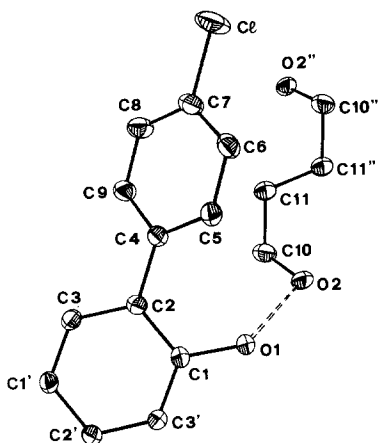
Fig. 1. Perspective view and atom labelling of the asymmetric unit in **7**. The thermal ellipsoids are drawn at the 30% probability level, and the broken double line represents an $O(1)\cdots H - O(2)$ hydrogen bond.
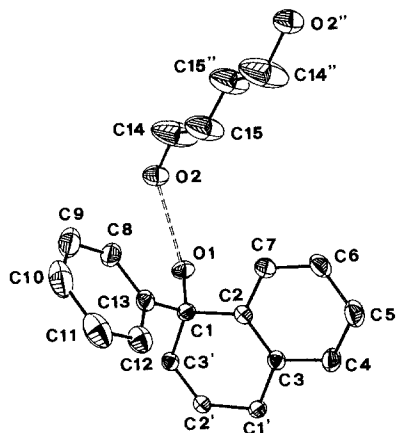
Fig. 2. Perspective view and atom labelling of the asymmetric unit in **8**. The thermal ellipsoids are drawn at the 30% probability level, and the broken double line represents an $O(1)\cdots H - O(2)$ hydrogen bond.
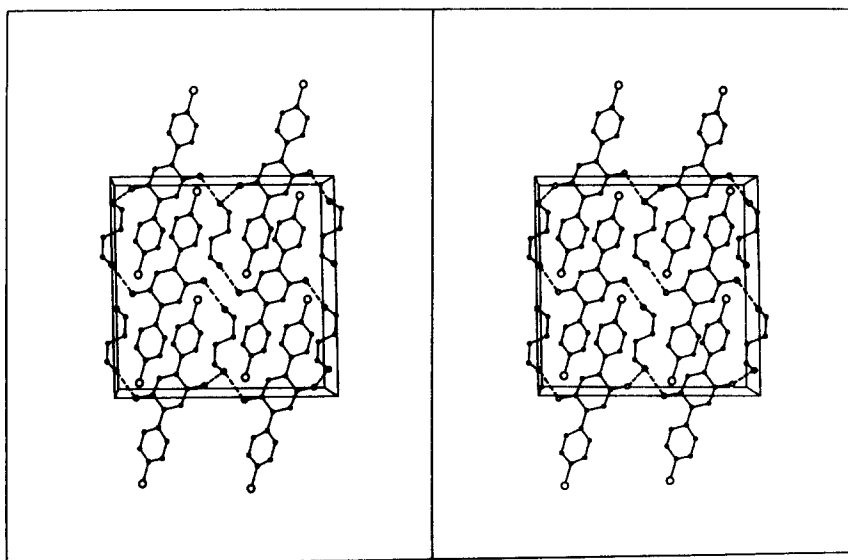

Fig. 3. Stereo view of the crystal structure of the 1 : 1 adduct (**7**) of 2,5-bis(4-chlorophenyl)-hydroquinone and 1,4-butanediol. The origin of the unit cell lies at the lower left corner, with a pointing upwards, b towards the reader, and c from left to right. Hydrogen bonds are indicated by broken lines, and all H atoms have been omitted.

to the corresponding values of 62 and $-43°$ in 1,4-dimethoxy-2,4', 4''-trihydroxy-p-terphenyl whose terminal rings are unrelated by symmetry [13]. The $O(1) - C(1) - C(3)'$ angle is considerably larger than the $O(1) - C(1) - C(2)$ angle, in accord with the well established steric influence of the phenolic H atom [14]. Steric repulsion between adjacent hydroxy and p-chlorophenyl groups are manifested in the unequal exo-ring bond angles at C(2) and C(4)

Table II. Atomic coordinates ($\times 10^5$ for Cl; $\times 10^4$ for other atoms), equivalent isotropic temperature factors[a] ($\text{Å}^2 \times 10^4$ for Cl; $\times 10^3$ for C and O atoms), and assigned isotropic thermal parameters[b] ($\text{Å}^2 \times 10^3$ for H atoms).

Atom	x	y	z	U_{eq}/U_{iso}
$C_{18}H_{12}O_2Cl_2 \cdot HO(CH_2)_4OH$ (7)				
Cl	43928(4)	67717(10)	38877(4)	774(3)
O(1)	295(1)	6571(2)	4114(1)	45(1)
C(1)	146(1)	6593(2)	3311(1)	34(1)
C(2)	826(1)	6598(2)	2812(1)	32(1)
C(3)	650(1)	6594(3)	1999(1)	36(1)
C(4)	1700(1)	6610(2)	3105(1)	33(1)
C(5)	1962(1)	7594(3)	3763(1)	38(1)
C(6)	2784(1)	7649(3)	3998(1)	42(1)
C(7)	3360(1)	6724(3)	3581(1)	43(1)
C(8)	3127(1)	5741(3)	2929(1)	47(1)
C(9)	2301(1)	5692(3)	2698(1)	41(1)
O(2)	1025(1)	3859(2)	4986(1)	50(1)
C(10)	1400(1)	2510(3)	4539(1)	56(1)
C(11)	2326(1)	2606(3)	4583(1)	49(1)
H(O1)	− 140	6550	4370	80
H(O2)	860	4830	4660	80
H(3)	1103	6582	1643	50
H(5)	1563	8241	4056	60
H(6)	2954	8331	4449	60
H(8)	3532	5099	2641	60
H(9)	2139	5009	2244	60
H(10a)	1227	1397	4741	70
H(10b)	1222	2617	3996	70
H(11a)	2545	1689	4261	70
H(11b)	2496	3724	4383	70
$C_{26}H_{20}O_2 \cdot HO(CH_2)_4OH$ (8)				
O(1)	1261(2)	754(1)	4631(1)	51(1)
C(1)	2008(2)	1535(2)	4464(2)	38(1)
C(2)	3206(2)	1569(2)	5207(1)	38(1)
C(3)	3654(2)	2440(2)	5690(2)	38(1)
C(4)	4775(2)	2398(2)	6363(2)	54(1)
C(5)	5420(3)	1499(2)	6550(2)	62(1)
C(6)	4977(2)	623(2)	6075(1)	56(1)
C(7)	3885(2)	667(2)	5413(2)	50(1)
C(8)	1699(3)	371(2)	3168(2)	60(1)
C(9)	1922(3)	124(3)	2427(2)	77(1)
C(10)	2666(3)	713(3)	2162(2)	87(2)
C(11)	3180(3)	1579(3)	2618(2)	81(2)
C(12)	2962(3)	1844(3)	3359(2)	59(1)
C(13)	2226(2)	1230(2)	3642(2)	44(1)
O(2)	167(2)	− 1229(2)	4406(3)	71(1)
C(14)	941(4)	− 2058(4)	4591(6)	167(4)
C(15)	2099(4)	− 2068(3)	4873(4)	124(3)
H(O1)	860	1010	4970	80
H(O2)	600	− 560	4350	80
H(4)	5086	3003	6697	70

[a] Calculated as one-third of the trace of the orthogonalized U_{ij} matrix.
[b] Exponent takes the form: $- 8\pi^2 U_{iso} \sin^2 \theta/\lambda^2$.

Table II (continued)

Atom	x	y	z	U_{eq}/U_{iso}
H(5)	6184	1480	7010	70
H(6)	5425	− 8	6204	70
H(7)	3581	57	5084	70
H(8)	1178	− 55	3354	90
H(9)	1542	− 468	2101	90
H(10)	2836	526	1660	90
H(11)	3696	2004	2426	90
H(12)	3316	2453	3672	90
H(14a)	697	− 2458	4074	180
H(14b)	743	− 2422	5024	180
H(15a)	2295	− 1760	4416	160
H(15b)	2343	− 1619	5361	160

(Table III). Planarity of the carbon skeleton of the glycol molecule is necessitated by its $\bar{1}$ site symmetry, and the observed O(2)—C(10)—C(11)—C(11)″ torsion angle deviates little from the value of 60° for the $g^+ ag^-$ conformation★ [15]. The measured bond distances in both **2** and 1,4-butanediol (Table III) are in accord with expected values.

Figure 4 illustrates the crystal structure of **8**, which also features hydrogen-bonded (OH)$_4$ rings centered at special positions of $\bar{1}$ symmetry. The tertiary hydroxy group forms a stronger donor hydrogen bond than an acceptor bond with its adjacent glycolic functions, but both
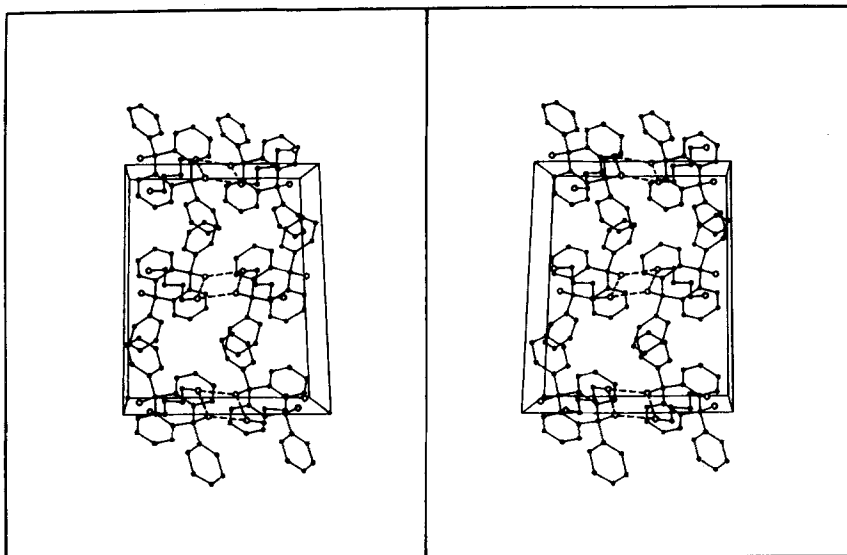

Fig. 4.   Stereo view of the crystal structure of the 1:1 adduct (**8**) of *trans*-9,10-dihydroxy-9, 10-diphenyl-9,10-dihydroanthracene and 1,4-butanediol. The origin of the unit cell lies at the lower left corner, with *a* pointing towards the reader, *b* from left to right, and *c* upwards. Hydrogen bonds are indicated by broken lines, and all H atoms have been omitted.

★ Conformational isomers are designated by combinations of *anti* (*a*), *right-handed gauche* (g$^+$), and *left-handed gauche* (g$^-$).

Table III. Bond distances (Å), bond angles (deg), and selected torsion angles (deg)

$C_{18}H_{12}O_2Cl_2 \cdot HO(CH_2)_4OH$ (**7**) [host in Wyckoff position $4e$ (site symmetry 2), guest in $4d(\bar{1})$, and $(OH)_4$ ring in $4b(\bar{1})$]

O(1)—C(1)	1.377(2)	C(1)—C(2)	1.402(2)
C(1)—C(3)'	1.381(2)	C(2)—C(3)	1.399(2)
C(2)—C(4)	1.489(2)	C(4)—C(5)	1.401(2)
C(5)—C(6)	1.381(3)	C(6)—C(7)	1.377(3)
C(7)—C(8)	1.380(3)	C(8)—C(9)	1.385(3)
C(9)—C(4)	1.395(3)	C(7)—Cl	1.740(2)
O(2)—C(10)	1.422(3)	C(10)—C(11)	1.500(3)
C(11)—C(11)″	1.516(4)		
O(1)···H—O(2)	2.788(3)	O(1)—H···O(2)‴	2.674(3)
O(1)—C(1)—C(2)	118.2(2)	O(1)—C(1)—C(3)'	121.1(2)
C(2)—C(1)—C(3)'	120.6(1)	C(1)—C(2)—C(3)	116.7(2)
C(1)—C(2)—C(4)	123.5(1)	C(3)—C(2)—C(4)	119.9(2)
C(2)—C(3)—C(1)'	122.7(2)	C(2)—C(4)—C(5)	122.5(2)
C(2)—C(4)—C(9)	120.0(2)	C(9)—C(4)—C(5)	117.4(2)
C(4)—C(5)—C(6)	121.2(2)	C(5)—C(6)—C(7)	119.8(2)
C(6)—C(7)—C(8)	120.9(2)	C(7)—C(8)—C(9)	119.0(2)
C(8)—C(9)—C(4)	121.8(2)	C(6)—C(7)—Cl	119.6(2)
C(8)—C(7)—Cl	119.5(2)	O(2)—C(10)—C(11)	112.1(2)
C(10)—C(11)—C(11)″	113.0(2)		
C(1)—O(1)···O(2)	126.5(2)	C(1)—O(1)···O(2)‴	116.1(2)
C(10)—O(2)···O(1)	115.8(3)	C(10)—O(2)···O(1)‴	124.9(3)
O(2)···O(1)···O(2)‴	86.7(3)		
C(1)—C(2)—C(4)—C(5)	−39.0(3)	O(2)—C(10)—C(11)—C(11)″	61.1(3)

Symmetry transformations: ' $-x, y, \frac{1}{2} - z$; ″ $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; ‴ $-x, 1 - y, 1 - z$

$C_{26}H_{20}O_2 \cdot HO(CH_2)_4OH$ (**8**) [host in Wyckoff position $4d$ (site symmetry $\bar{1}$), guest in $4c(\bar{1})$, and $(OH)_4$ ring in $4a(\bar{1})$]

O(1)—C(1)	1.440(3)	C(1)—C(2)	1.523(3)
C(1)—C(3)'	1.523(3)	C(1)—C(13)	1.535(4)
C(2)—C(3)	1.384(3)	C(3)—C(4)	1.407(3)
C(4)—C(5)	1.372(4)	C(5)—C(6)	1.381(4)
C(6)—C(7)	1.377(3)	C(7)—C(2)	1.396(3)
C(13)—C(8)	1.385(4)	C(8)—C(9)	1.390(5)
C(9)—C(10)	1.356(6)	C(10)—C(11)	1.376(6)
C(11)—C(12)	1.395(5)	C(12)—C(13)	1.384(4)
O(2)—C(14)	1.380(5)[a]	C(14)—C(15)	1.287(6)[a]
C(15)—C(15)″	1.436(8)[a]		
O(1)···H—O(2)	2.853(4)	O(1)—H···O(2)‴	2.787(4)
O(1)—C(1)—C(2)	109.0(2)	O(1)—C(1)—C(3)'	109.5(2)
O(1)—C(1)—C(13)	107.5(2)	C(2)—C(1)—C(13)	109.4(2)
C(13)—C(1)—C(3)'	108.4(2)	C(2)—C(1)—C(3)'	113.0(2)
C(1)—C(2)—C(3)	123.7(2)	C(1)—C(2)—C(7)	117.9(2)
C(2)—C(3)—C(1)'	123.3(2)	C(2)—C(3)—C(4)	119.6(2)
C(4)—C(3)—C(1)'	117.1(2)	C(3)—C(4)—C(5)	120.7(2)
C(4)—C(5)—C(6)	120.2(2)	C(5)—C(6)—C(7)	119.1(2)
C(6)—C(7)—C(2)	122.1(2)	C(7)—C(2)—C(3)	118.4(2)
C(1)—C(13)—C(8)	122.3(3)	C(1)—C(13)—C(12)	118.7(2)
C(12)—C(13)—C(8)	119.0(3)	C(13)—C(8)—C(9)	120.3(3)
C(8)—C(9)—C(10)	120.7(3)	C(9)—C(10)—C(11)	119.7(4)

Table III (continued)

C(10)—C(11)—C(12)	120.5(4)	C(11)—C(12)—C(13)	119.8(3)
O(2)—C(14)—C(15)	129.2(4)[a]	C(14)—C(15)—C(15)″	128.9(5)[a]
C(1)—O(1)···O(2)	153.6(3)	C(1)—O(1)···O(2)‴	119.9(3)
C(14)—O(2)···O(1)	116.2(4)[a]	C(14)—O(2)···O(1)‴	122.5(4)[a]
O(2)···O(1)···O(2)‴	86.3(3)		
C(8)—C(13)—C(1)—O(1)	3.2(3)	O(2)—C(14)—C(15)—C(15)‴	174.7(9)[a]
C(2)—C(1)—C(13)—C(8)	121.4(2)	C(2)—C(1)—O(1)—H(O1)	84.3(5)

Symmetry transformations: ′ $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; ″ $\frac{1}{2} - x, -\frac{1}{2} - y, 1 - z$; ‴ $-x, -y, 1 - z$

[a] Subject to larger errors than indicated due to large thermal vibration or positional disorder of C(14) and C(15).

bonds are longer than corresponding ones formed by the phenolic group in **7**. The dihydro-anthracene (**3**) and 1,4-butanediol molecules, which occupy other independent centro-symmetric sites, are linked into infinite chains pointing alternatively in the [110] and [$\bar{1}$10] directions, resulting in a chain-and-layer structure with hydrogen bonding concentrated about the (002) planes and van der Waals contacts lying in between. Molecule **3** possesses a planar central 1,4-cyclohexadiene ring, and its dimensions and stereochemistry closely match those observed in neat *trans*-9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene and its 1:1 ethanol and 1:2 methanol adducts [3,4]. In the 1,4-butanediol molecule, the apparent pronounced anisotropic thermal motion of C(14) and C(15) (Figure 2) and abnormal bond distances and angles involving these atoms (Table III) most likely arise from minor positional disorder rather than a large vibrational effect. The glycol molecule adopts an almost fully extended *aaa* conformation as indicated by the measured value of 174.7(9)° for the O(2)—C(14)—C(15)—(15)″ torsion angle.

The salient features common to the crystal structures of **7** and **8** are the effective utilization of crystallographic point symmetry elements and the occurrence of hydrogen bonded (OH)₄ rings. The disparity in size and shape of the 2,5-bis(4-chlorophenyl)hydroquinone and *trans*-9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene host species, particularly their site symmetries (2 and $\bar{1}$ respectively), gives rise to two distinct modes of molecular packing in the same space group (*C2/c*), as well as vastly different conformations adopted by the 1,4-butanediol guest species. In both structures, crystallographically imposed $\bar{1}$ symmetry of the guest molecule precludes the complexation of glycols having an odd number of methylene groups. In **7**, the crystal lattice presumably remains invariant when the guest species is replaced by its lower homolog 1,2-ethanediol, since adjustments in molecular packing are facilitated by conformational flexibility of the *p*-terphenyl skeleton of the host system. This hypothesis is also consistent with the fact that **1** and **2** form analogous adducts with the same glycols. In **8**, steric repulsion of the bulky host molecules forces the glycol guest species into a fully extended *aaa* conformation; obviously 1,2-ethanediol cannot serve as a guest since its chain length is much too short, but 1,6-hexanediol may turn out to be usable. It is of interest to note that the crystal structure of **8** bears a striking resemblance to that of the 3.2CH₃OH adduct [4], in which a pair of oppositely oriented and non-bonded methanol molecules plays the same role as the present 1,4-butanediol guest species.

References

1. F. Toda, K. Tanaka, G. Ulibarri Daumas, and M. C. Sanchez: *Chem. Lett.* 1521 (1983).
2. F. Toda, K. Tanaka, and T. C. W. Mak: *Chem. Lett.* 1699 (1983).

3. F. Toda, K. Tanaka, and T. C. W. Mak: *Tetrahedron Lett.* **25**, 1359 (1984).

4. F. Toda, K. Tanaka, S. Nagamatsu, and T. C. W. Mak: *Isr. J. Chem.* in press.

5. E. Browning and R. Adams: *J. Am. Chem. Soc.* **52**, 4098 (1930).

6. C. K. Ingold and P. G. Marshall: *J. Chem. Soc.* 3080 (1926).

7. R. A. Sparks: in *Crystallographic Computing Techniques* (Ed. F. R. Ahmed), p. 452. Munksgaard, Copenhagen (1976).

8. R. Diamond: *Acta Crystallogr.* **A25**, 43 (1969).

9. G. T. De Titta, J. W. Edmonds, D. A. Langs, and H. Hauptman: *Acta Crystallogr.* **A31**, 472 (1975).

10. G. M. Sheldrick: in *Computational Crystallography* (Ed. D. Sayre), p. 506. Oxford University Press, New York (1982).

11. *International Tables for X-ray Crystallography*, pp. 55, 99, 149. Kynoch Press, Birmingham (1974).

12. J. W. Shilling: in *Crystallographic Computing* (Ed. F. R. Ahmed), p. 201. Munksgaard, Copenhagen (1970).

13. G. D. Andreetti, G. Bocelli, and P. Sgarabotto, *Cryst. Struct. Commun.* **3**, 145 (1974).

14. S. C. Wallwork and H. M. Powell, *J. Chem. Soc., Perkin Trans. 2,* 641 (1980) and references cited therein.

15. J. Dale: *Stereochemistry and Conformational Analysis*, pp. 94, 100. Verlag Chemie, Weinheim (also Universitets-forlaget, Oslo) (1978).