Molecular Complexes of Hydroxy Host Systems with Alcohols. X-Ray Crystal Structures of 1,1,6,6-Tetrakis(2,4-dimethylphenyl)-2,4-hexadiyne-1,6-diol–Ethanol (1:2), 1,1-Bis(2,4-dimethylphenyl)-2-butyn-1-ol–Ethanol (1:1), and 9-(1-Propynyl)-9-fluorenol–Methanol (1:1)

Fumio Toda,* Koichi Tanaka, and Thomas C. W. Mak*†

Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790
†*Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong*
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The structures of a 1:2 molecular complex(I) of 1,1,6,6-tetrakis(2,4-dimethylphenyl)-2,4-hexadiyne-1,6-diol with ethanol, a 1:1 complex(II) of 1,1-bis(2,4-dimethylphenyl)-2-butyn-1-ol with ethanol, and a 1:1 complex (III) of 9-hydroxy-9-(1-propynyl)fluorene with methanol have been determined by X-ray crystallography. The crystal data are: I, $C_{42}H_{50}O_4$, P$\bar{1}$, a=8.249(3), b=9.522(5), c=14.803(8)Å, α=100.95(4), β=110.82(4), γ=113.08(3)°, Z=1, and R_f=0.105 for 1834 observed Mo$K\alpha$ data; II, $C_{22}H_{28}O_2$, P$\bar{1}$, a=8.142(2), b=11.281(3), c=12.262(4)Å, α=102.76(2), β=97.08(2), γ=111.19(2)°, Z=2, and R_f=0.073 for 2104 data; III, $C_{17}H_{16}O_2$, P2_1/a, a=8.641(5), b=10.883(5), c=30.63(2)Å, β=92.88(4)°, Z=8, R_f=0.154 for 1885 data. The crystal structures of I and II are closely related and both feature planar hydrogen-bonded $(OH)_4$ rings centered at centrosymmetric sites. In III, the fluorene and methanol molecules belong to two independent sets, and the molecular components in each set are alternately linked by hydrogen bonds to form infinite zigzag chains parallel to the a axis.
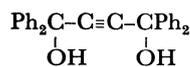
Previously, we reported that 1,1,4,4-tetraphenyl-2-butyne-1,4-diol (**1**) and 1,1,6,6-tetraphenyl-2,4-hexadiyne-1,6-diol (**2a**) form 1:1 and 1:2 crystalline inclusion compounds with various guest molecules, which show the presence of strong hydrogen bonds *via* their IR spectra.[1,2] X-Ray single-crystal analysis of the complexes **1**·$(CH_3)_2CO$[2] and **2a**·$(CH_3)_2CO$[3] disclosed that the acetone moiety is included in a channel and surrounded by phenyl groups, being bound to the anti-oriented OH groups of the host through hydrogen bonding.

If surrounding of the guest species by phenyl rings is important for the stabilization of the complex, an effective host molecule might be derived by employing a more bulky aromatic substituent. Proceeding along this line of reasoning, we subsequently found that 1,1,6,6-tetrakis(2,4-dimethylphenyl)-2,4-hexadiyne-1,6-diol (**2b**) forms a stable 1:2 complex (I) with ethanol, even though **2a** fails to do so. The complexation Phenomenon is potentially useful for the isolation of ethanol from aqueous solution. However, complex I turned out to be too stable for the extraction of ethanol by the usual method, and it appeared that the 2,4-dimethylphenyl group might hinder the escape of ethanol molecules from the channels in the crystalline complex.
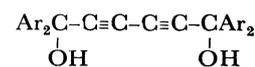
We then designed 1,1-diphenyl-2-propyn-1-ol (**3a**), 1,1-bis(2,4-dimethylphenyl)-2-propyn-1-ol (**3b**), and 1,1-bis(2,4-dimethylphenyl)-2-butyn-1-ol (**3c**) as potentially useful host molecules which would include ethanol more loosely than **2b** because one side of the molecular skeleton is opened. Actually, we did find that ethanol can easily be removed from its complexes with **3b** and **3c** by evaporation, even though **3a** does not include ethanol. Another variation in the design of related host systems is achieved by making the two aromatic rings coplanar, as in 9-(1-propynyl)-9-fluorenol (**4**), which has been shown to be an effective re-

agent for extracting ethanol from its aqueous solution.[4]

In order to test the above hypotheses and as part of our continuing studies on the synthesis and structural characterization of inclusion compounds, we have determined the crystal structures of I, a 1:1 complex (II) of **3c** with ethanol, and a 1:1 complex (III) of **4** with methanol, which are reported in the present paper. The analogous ethanol adduct turned out to be too unstable for X-ray analysis.
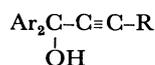

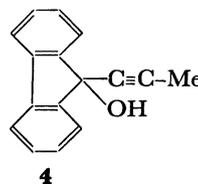$$Ph_2C-C\equiv C-CPh_2$$
$$\underset{OH}{|}\qquad\underset{OH}{|}$$

1

$$Ar_2C-C\equiv C-C\equiv C-CAr_2$$
$$\underset{OH}{|}\qquad\qquad\underset{OH}{|}$$

2a: Ar = Ph

b: Ar = 2,4-dimethylphenyl

$$Ar_2C-C\equiv C-R$$
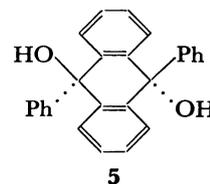$$\underset{OH}{|}$$

3a: Ar = Ph; R = H

b: Ar = 2,4-dimethylphenyl; R = H

c: Ar = 2,4-dimethylphenyl; R = Me

4

5

Experimental

1,1-Bis(2,4-dimethylphenyl)-2-propyn-1-ol (3b). A solution of Na (49 g) in liquid NH_3 (1.5 l) was stirred at $-33\,°C$ for 3 h in the presence of a catalytic amount of $Fe(NO_3)_3\cdot 9H_2O$. The resulting $NaNH_2$ suspension was cooled to *ca.* $-60\,°C$ and acetylene gas bubbled through it for 2 h, and then a solution of 2,2',4,4'-tetramethylbenzophenone (380 g) in THF (500 ml) was added and stirred for 2 h. The residue left after the evaporation of NH_3 was decomposed with dil HCl and extracted with ether. The ether solution

TABLE 1. DATA COLLECTION AND PROCESSING PARAMETERS

Complex	I	II	III
Molecular formula	$C_{42}H_{50}O_4$	$C_{22}H_{28}O_2$	$C_{17}H_{16}O_2$
Molecular weight	618.85	324.46	252.31
Cell constants	a=8.249(3)Å α=100.95(4)°	a=8.142(2)Å α=102.76(2)°	a=8.641(3)Å β=92.88(3)°
	b=9.522(5) β=110.82(4)	b=11.281(3) β=97.08(2)	b=10.883(4) V=2877(2)Å³
	c=14.803(8) γ=113.08(3)	c=12.262(4) γ=111.19(2)	c=30.63(1) Z=8
	V=923.6(8)Å³ Z=1	V=998.3(4) Z=2	
Density (flotation in KI/H₂O)	1.11 gcm⁻³	1.09 gcm⁻³	1.18 gcm⁻³
Density (calcd)	1.113 gcm⁻³	1.079 gcm⁻³	1.165 gcm⁻³
Space Group	P$\bar{1}$	P$\bar{1}$	P2₁/a
Absorption coefficent	0.65 cm⁻¹	0.63 cm⁻¹	0.70 cm⁻¹
Crystal size	0.50×0.50×0.50 mm	0.48×0.44×0.42 mm	0.50×0.42×0.38 mm
Scan type and speed		ω—2θ; 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	$h,\pm k,\pm l; 2\theta_{max}$=45°	$h,\pm k,\pm l; 2\theta_{max}$=50°	$h,k,\pm l; 2\theta_{max}$=45°
Unique data measured	2095	2777	2784
Observed data with $|F_o|>3\sigma(|F_o|)$, n	1834	2104	1885
Number of variables, p	206	231	175
$R_f=\sum\|F_o\|-\|F_c\|/\sum\|F_o\|$	0.105	0.073	0.154
Constant g in weighting scheme $w=[\sigma^2(F_o)+g\|F_o\|^2]^{-1}$	0.001	0.002	0.002
$R_g=[\sum w(\|F_o\|-\|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$	0.152	0.098	0.185
$S=[\sum w(\|F_o\|-\|F_c\|)^2/(n-p)]^{1/2}$	3.664	1.714	2.626
Residual extrema in final difference map	+0.49 to −0.23 e Å⁻³	+0.47 to −0.21 e Å⁻³	+0.69 to −0.42 e Å⁻³

was washed with water and dried over Na₂SO₄. Evaporation of the solvent gave crude **3b**, recrystallization of which from benzene resulted in pure **3b** (350 g, 87%) as colorless needles, mp 61—63°C, NMR (CDCl₃), 6.9—7.8 (6H, m, Ar), 2.83 (1H, s, =CH), 2.57 (1H, s, OH), 2.30 (6H, s, Me), and 2.02 (6H, s, Me). Found: C, 86.11; H, 7.48%. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63%.

Recrystallization of **3b** in ethanol gave a 1:1 complex which melted at 40—48°C. NMR (CDCl₃) 6.9—7.8 (6H, m, Ar), 3.68 (2H, q, J=6.8 Hz, CH₂), 2.83 (1H, s, CH), 2.30 (6H, s, Me), 2.02 (6H, s, Me), and 1.21 (3H, t, J=6.8 Hz, Me). Found: C, 81.15; H, 8.37%, Calcd for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44%.

1,1-Bis(2,4-dimethylphenyl)-2-butyn-1-ol (3c).   To a NaNH₂ suspension prepared from Na (49 g) and liquid NH₃ (1.5 l), 1,2-dichloropropane (80 g) was added and stirred for 1 h. To this solution, 2,2′4,4′-tetramethylbenzophenone (140 g) dissolved in THF (200 ml) was added and stirred for 2 h. The residue left after the evaporation of NH₃ was decomposed with dil HCl and extracted with ether. The ether solution was washed with water and dried over Na₂SO₄. Evaporation of the solvent gave crude **3c** as an oil, crystallization of which from ethanol yielded a 1:1 complex (140 g, 76%), **II**, colorless prisms, mp 64—65°C. NMR (CDCl₃) 6.8—7.7 (6H, m, Ar), 3.68 (2H, q, J=6.8 Hz, CH₂), 2.27 (6H, s, Me), 1.98 (6H, s, Me), 1.82 (3H, s, Me), and 1.21 (3H, t, J= 6.8 Hz, Me). Found: C, 85.89; H, 5.70%. Calcd for $C_{22}H_{28}O_2$: C, 86.12; H, 5.68%.

1,1,6,6-Tetrakis(2,4-dimethylphenyl)-2,4-hexadiyne-1,6-diol (2b). A solution of **3b** (100 g) and CuCl (10 g) in acetone (500 ml) containing pyridine (50 ml) was stirred under O₂ atmosphere for 12 h. When 3 M⁺ HCl (500 ml) was added to the reaction mixture, **2b** crystallized out. Recrystallization from benzene gave pure **2b** as colorless prisms (90 g, 90%), mp 192—193 °C.

† 1 M= 1 mol dm⁻³.

NMR (CDCl₃) 6.90—7.73 (12H, m, Ar), 2.29 (12H, s, Me), and 1.98 (12H, s, Me,). Found: C, 86.47; H, 7.44%. Calcd for $C_{38}H_{38}O_2$: C, 86.65; H, 7.27%.

Recrystallization of **2b** from ethanol resulted in a 1:2 complex, **I**, which does not have a clear mp. NMR (CDCl₃) 6.90—7.73 (12H, m, Ar), 3.68 (4H, q, J=6.8 Hz, CH₂), 2.29 (12H, s, Me), 1.98 (12H, s, Me), and 1.21 (6H, t, J=6.8 Hz, Me). Found: C, 81.39; H, 7.87%. Calcd for $C_{42}H_{50}O_4$: c, 81.51; H, 8.14%.

X-Ray Data Collection.   All three complexes turned milky upon exposure to air, and each selected crystal was therefore enclosed in an alcohol atmosphere inside a 0.5 mm Lindemann glass capillary. Determination of the crystal class and orientation matrix was performed on a Nicolet R3m four-circle diffractometer according to established procedures[5] using graphite-monochromatized Mo $K\alpha$ radiation (λ=0.71069 Å). Accurate unit-cell parameters were derived from a least-squares fit of the angular settings for 25 reflections in the range 14°<2θ<18°. Reflection intensities were recorded at an ambient laboratory temperature of 22 °C, and three standards monitored every 50 data measurements showed only random fluctuations within ±2% of their mean values. The crystal data and processing parameters for I—III are sumarized in Table 1.

Structure Determination and Refinement

The raw intensities were processed with the learnt-profile procedure,[6] and redundant and equivalent reflections were averaged to yield a set of structure amplitudes following corrections for Lorentz and polarization factors. No absorption correction was applied. For each complex the statistical distributions of the normalized structure factors strongly favoured a
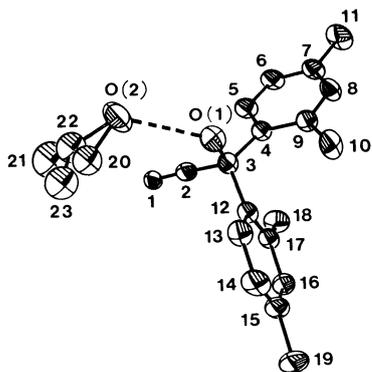
Fig. 1. Perspective view and atom labelling of the asymmetric unit in I. Both orientations of the disordered ethyl group are shown, and the broken line represents an O(1)···O(2) hydrogen bond.

centrosymmetric space group, and structure solution was achieved by direct phase determination based on negative quartets.[7]

In complex I, the 1,1,6,6-tetrakis(2,4-dimethylphenyl)-2,4-hexadiyne-1,6-diol molecule is situated at a center of symmetry, and the carbon atoms of the ethanol molecule exhibit two-fold orientational disorder as illustrated in Fig. 1. The disordered atoms C(20)–C(23) were assigned half weight and isotropic temperature factors, whereas the remaining non-hydrogen atoms were varied anisotropically. The aromatic H atoms were generated geometrically (C–H bond length fixed at 0.96 Å) and allowed to ride on their respective parent C atoms.

In complex II the methyl group of the ethanol moiety is two-fold disordered and was accordingly represented by two isotropic "half-carbon" atoms. Anisotropic thermal parameters were assigned to all other non-hydrogen atoms. The aromatic H atoms were treated with the riding model, and the methyl groups were handled as rigid groups in including the contribution of the hydrogen atoms with isotropic temperature factors.

In complex III, there exist two sets of crystallographically independent molecules in the unit cell. In view of the unfavourable data-to-parameter ratio in this structure, all non-hydrogen atoms were refined isotropically except those belonging to the 1-propynyl and hydroxyl groups and the methanol molecules. To further reduce the number of variables, the benzene rings of the fluorene moiety were treated as regular hexagons of edge 1.395 Å. The aromatic H atoms were assigned isotropic temperature factors and allowed to ride on their respective parent C atoms.

Computations were performed on a Data General Corporation Nova 3/12 minicomputer using the SHELXTL program package.[8] Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated.[9] Blocked-cascade least-squares refinement[10] converged to the R indices and parameters listed in Table 1.

Results and Discussion

Perspective views, each with atom labelling, of the asymmetric units in complexes I, II, and III are shown in Figs. 1, 2, and 3, respectively. The final atomic parameters are listed in Tables 2—4. The dimensions of the 3c host molecule in II closely match the corresponding values for one-half of molecule 2b in I, and those for the two independent 4 molecules in III are in satisfactory agreement (Table 5).

In the crystal structure of I (Fig. 4), the hexadiyne-diol molecule 2b occupies a centrosymmetric site at the center of the unit cell, and its hydroxyl groups are linked by hydrogen bonds to neighboring ethanol molecules, generating a layer structure which features $(OH)_4$ rings centered at a second set of centrosymmetric sites at (0,0,1/2). The dimensions of the planar, hydrogen-bonded $(OH)_4$ ring are: O(1)···O(2)=2.723(8) Å, O-(1)···O(2)′=2.669(7) Å, and O(2)···O(1)···O(2)′=84.2(2)°, where the primed superscript denotes the symmetry
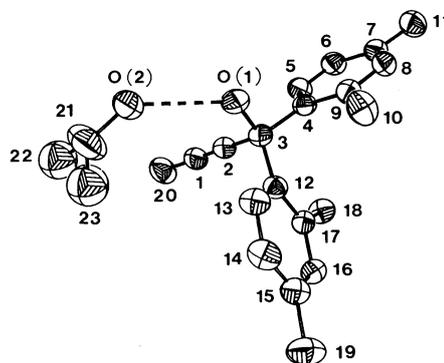

Fig. 2. Perspective view and atom labelling of the two molecular components in II. Both orientations of the disordered methyl group are shown, and the O(1)···O(2) hydrogen bond is represented by a broken line.
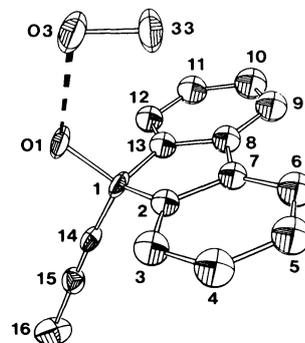

Fig. 3. Perspective view and atom labelling of one set (Type A) of molecular components in III, the O(1)···O(3) hydrogen bond being shown as a broken line. Atom labels for the other fluorene and methanol molecules (Type B) in the asymmetric unit are derived by incrementing the numbering of the corresponding oxygen and methanol carbon atoms by 1, and that of the remaining carbon atoms by 16.
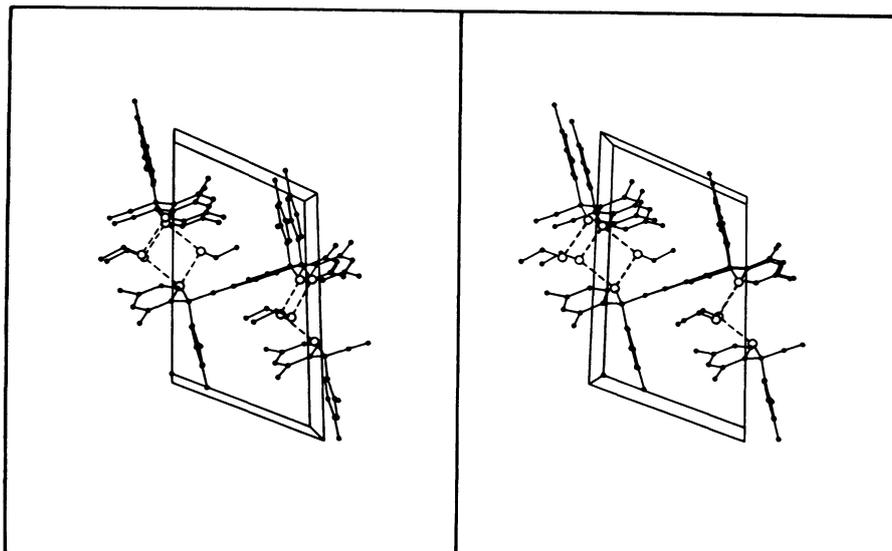
Fig. 4. Stereo view of the crystal structure of the 1:2 adduct (I) of 1,1,6,6-tetrakis(2,4-dimethylphenyl)-2,4-hexadiyne-1,6-diol (2b) with ethanol. The origin of the unit cell lies at the lower left corner, with a pointing towards the reader, b slantwise from left to right, and c upwards. The disordered ethyl group is shown in one of its two orientations, and hydrogen bonds are represented by broken lines.
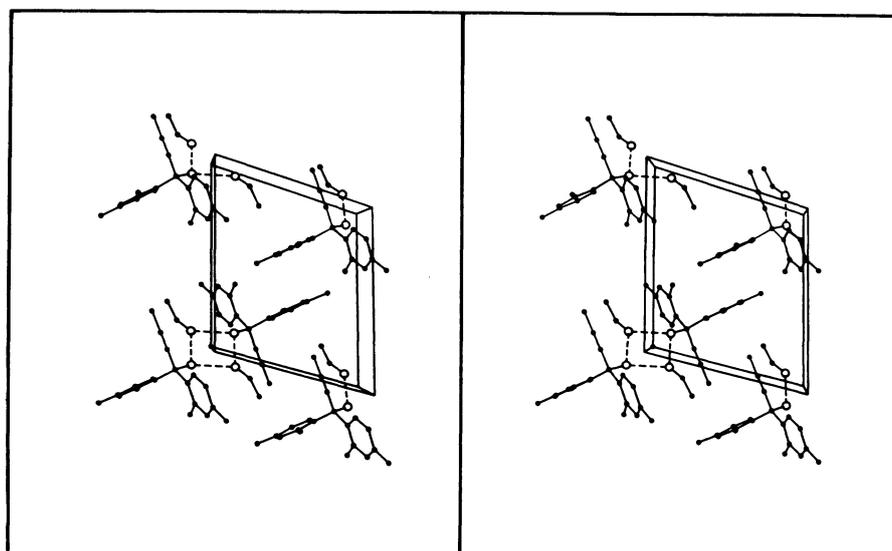

Fig. 5. Stereo view of the crystal structure of the 1:1 adduct (II) of 1,1-bis(2,4-dimethylphenyl)-2-butyn-1-ol (3c) with ethanol. The origin of the unit cell lies at the lower left corner, with a pointing towards the reader, b slantwise from left to right, and c upwards. The disordered methyl group of the ethanol molecule is shown in one of its two half-populated sites, and hydrogen bonds are represented by broken lines.

transformation $(-x, -y, 1-z)$. In the crystal lattice, van der Waals' contacts between the hydrophobic groups occur mainly across the (001) set of planes, midway between which are located the $(OH)_4$ rings and acetylenic functions.

In the crystal structure of II (Fig. 5), two butynol (3c) and two enthanol molecules are likewise alternately linked into a planar, hydrogen-bonded $(OH)_4$ ring centered at (1/2, 0, 0), with dimensions $O(1)\cdots O(2)=$

$2.700(5)$ Å, $O(1)\cdots O(2)'=2.686(4)$ Å, and $O(2)\cdots O(1)\cdots O-(2)'=91.9(1)°$, where the primed superscript indicates the transformation $(1-x, -y, -z)$. The crystal lattice thus comprises a packing of clearly discernible "dimeric" (butynol-ethanol)$_2$ aggregates.

The salient features common to the crystal structures of I and II are the effective utilization of crystallographic inversion centers and the occurrence of hydrogen-bonded $(OH)_4$ rings, which have been found

TABLE 2. ATOMIC COORDINATES ($\times$ 10⁴) AND THERMAL PARAMETERS[a] ($\text{Å}^2 \times 10^3$) FOR COMPLEX I

Atom	x	y	z	U_{eq}/U
O(1)	72(5)	516(4)	3762(3)	69(2)*
C(1)	4272(7)	4228(5)	4658(3)	56(3)*
C(2)	2996(7)	2837(6)	4044(4)	58(3)*
C(3)	1287(6)	1162(5)	3276(4)	52(2)*
C(4)	2005(6)	−45(5)	3015(3)	49(2)*
C(5)	3968(7)	358(6)	3634(4)	64(3)*
C(6)	4648(7)	−745(6)	3475(4)	68(3)*
C(7)	3389(7)	−2285(6)	2735(4)	63(3)*
C(8)	1449(7)	−2680(6)	2130(4)	65(3)*
C(9)	685(7)	−1649(6)	2229(4)	56(3)*
C(10)	−1523(7)	−2260(7)	1521(4)	79(3)*
C(11)	4148(10)	−3499(8)	2604(5)	98(4)*
C(12)	61(6)	1449(5)	2329(4)	50(2)*
C(13)	−1720(7)	1399(7)	2233(4)	68(3)*
C(14)	−2787(8)	1761(7)	1421(5)	81(3)*
C(15)	−2160(8)	2166(7)	735(4)	70(3)*
C(16)	−440(7)	2175(6)	820(4)	64(3)*
C(17)	737(7)	1867(5)	1621(4)	53(3)*
C(18)	2639(8)	1970(7)	1645(4)	72(3)*
C(19)	−3374(10)	2570(8)	−136(5)	105(4)*
O(2)	442(9)	2029(6)	5638(4)	126(4)*
C(20)	−437(21)	3150(16)	5640(10)	87(4)
C(21)	1479(34)	4609(28)	6446(18)	143(8)
C(22)	1110(27)	3808(23)	6181(13)	96(5)
C(23)	−834(25)	3906(21)	5795(12)	109(5)

a) Asterisk indicates equivalent isotropic temperature factor U_{eq} calculated as one-third of the trace of the orthogonalized U matrix. The exponent of the istropic temperature factor takes the form: $-8\pi^2 U \sin^2\theta/\lambda^2$.

TABLE 3. ATOMIC COORDINATES ($\times$ 10⁴) AND THERMAL PARAMETERS[a] ($\text{Å}^2 \times 10^3$) FOR COMPLEX II

Atom	x	y	z	U_{eq}/U
O(1)	4788(3)	1319(2)	1133(2)	80(1)*
C(1)	3226(5)	3181(3)	−152(3)	73(2)*
C(2)	3546(4)	2764(3)	621(3)	66(1)*
C(3)	4087(4)	2293(3)	1580(3)	59(1)*
C(4)	2484(4)	1555(3)	2064(3)	59(1)*
C(5)	739(4)	1235(3)	1479(3)	69(1)*
C(6)	−763(5)	542(3)	1841(3)	73(2)*
C(7)	−586(5)	131(3)	2808(3)	69(2)*
C(8)	1177(5)	430(3)	3380(3)	69(2)*
C(9)	2714(4)	1137(3)	3037(3)	63(1)*
C(10)	4539(5)	1405(4)	3740(4)	89(2)*
C(11)	−2202(5)	−601(4)	3234(4)	92(2)*
C(12)	5642(4)	3512(3)	2463(3)	56(1)*
C(13)	7418(4)	3632(3)	2537(3)	70(2)*
C(14)	8843(5)	4740(4)	3249(3)	77(2)*
C(15)	8583(5)	5784(3)	3918(3)	69(2)*
C(16)	6807(4)	5660(3)	3843(3)	62(1)*
C(17)	5339(4)	4559(3)	3125(3)	55(1)*
C(18)	3471(4)	4569(4)	3087(3)	72(2)*
C(19)	10153(6)	6993(4)	4677(4)	100(2)*
C(20)	2841(6)	3685(4)	−1101(3)	99(2)*
O(2)	6536(6)	1340(3)	−601(4)	144(2)*
C(21)	7894(8)	2199(6)	−935(6)	144(4)*
C(22)	7497(18)	2781(14)	−1782(13)	144(4)
C(23)	7878(21)	3383(16)	−944(14)	168(5)

a) Asterisk indicates equivalent isotropic temperature factor U_{eq} calculated as one-third of the trace of the orthogonalized U matrix. The exponent of the istropic temperature factor takes the form: $-8\pi^2 U \sin^2\theta/\lambda^2$.

TABLE 4. ATOMIC COORDINATES ($\times$ 10⁴) AND THERMAL PARAMETERS[a] ($\text{Å}^2 \times 10^3$) FOR COMPLEX III

Atom	x	y	z	U_{eq}/U
Type A molecules				
O(1)	591(8)	6636(6)	1270(3)	56(3)*
C(1)	1452(13)	5512(9)	1178(4)	49(4)*
C(2)	420(8)	4607(6)	975(3)	48(3)
C(3)	−406(8)	4658(6)	573(3)	64(4)
C(4)	−1311(8)	3661(6)	430(3)	75(4)
C(5)	−1390(8)	2612(6)	690(3)	73(4)
C(6)	−563(8)	3561(6)	1093(3)	71(4)
C(7)	342(8)	3558(6)	1235(3)	49(3)
C(8)	1284(9)	3746(7)	1632(2)	55(3)
C(9)	1585(9)	3012(7)	2000(2)	75(4)
C(10)	2582(9)	3431(7)	2340(2)	87(5)
C(11)	3277(9)	4583(7)	2313(2)	79(4)
C(12)	2976(9)	5317(7)	1945(2)	61(4)
C(13)	1979(9)	4899(7)	1604(2)	53(3)
C(14)	2783(14)	5865(10)	917(4)	42(4)*
C(15)	3827(15)	6088(10)	707(4)	52(5)*
C(16)	5158(16)	6342(14)	423(5)	85(6)*
O(3)	−2449(10)	6520(7)	1502(3)	83(4)*
C(33)	−2972(16)	5317(11)	1507(5)	76(6)*
Type B molecules				
O(2)	5161(8)	3396(7)	3729(3)	62(3)*
C(17)	6054(12)	4485(10)	3827(4)	50(4)*
C(18)	5057(8)	5418(6)	4030(3)	48(3)
C(19)	4352(8)	5318(6)	4428(3)	69(4)
C(20)	3478(8)	6291(6)	4580(3)	75(4)
C(21)	3309(8)	7366(6)	4334(3)	84(5)
C(22)	4014(8)	7467(6)	3936(3)	82(4)
C(23)	4888(8)	6493(6)	3784(3)	50(3)
C(24)	5719(9)	6312(7)	3395(3)	61(4)
C(25)	5907(9)	7089(7)	3040(3)	74(4)
C(26)	6794(9)	6710(7)	2696(3)	107(5)
C(27)	7492(9)	5554(7)	2708(3)	95(5)
C(28)	7304(9)	4777(7)	3063(3)	68(4)
C(29)	6417(9)	5156(7)	3407(3)	55(3)
C(30)	7440(14)	4204(11)	4080(4)	54(5)*
C(31)	8605(16)	3994(11)	4302(4)	56(5)*
C(32)	10035(16)	3692(16)	4559(5)	91(7)*
O(4)	2030(10)	3403(8)	3508(4)	89(4)*
C(34)	1497(17)	4657(12)	3420(5)	88(6)*

a) Asterisk indicates equivalent isotropic temperature factor U_{eq} calculated as one-third of the trace of the orthogonalized U matrix. The exponent of the istropic temperature factor takes the form: $-8\pi^2 U \sin^2\theta/\lambda^2$.

previously in related complexes such as the 1:1 adduct of 9,10-diphenyl-9,10-dihydro-r-9,t-10-anthracenediol (5) with 1,4-butanediol.[12] In both structures the environment around the ethyl carbon atoms of the ethanol molecule is relatively spacious, especially in I, allowing for the equal population of two energetically similar orientations. Interestingly, two neighboring $CH_3-C\equiv C-$ groups in II are related by inversion and play the same role as a $-C\equiv C-C\equiv C-$ fragment in I (see Figs. 4 and 5), and the structural relationship is analogous to that between the crystalline adducts $5 \cdot 2CH_3OH^{[13]}$ and $5 \cdot HO(CH_2)_4OH,^{[12]}$ in which a pair of oppositely oriented methanol molecules are topologically equivalent to a 1,4-butanediol species.

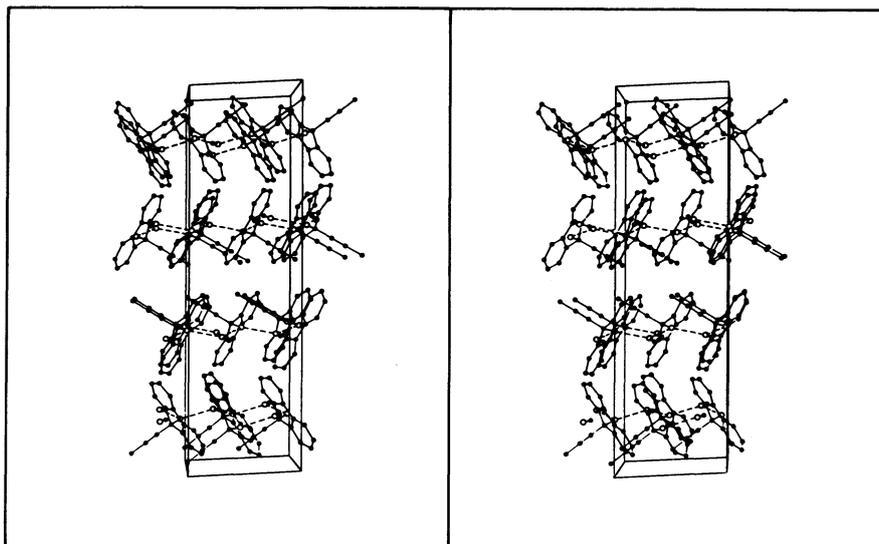Figure 6 illustrates the crystal structure of III, which

Fig 6.   Stereo view of the crystal structure of the 1:1 adduct (III) of 9-hydroxy-9-(1-propynyl)fluorene (4) with methanol. The origin of the unit cell lies at the upper right corner, with a pointing from left to right, b towards the reader, and c downwards. Hydrogen bonds are represented by broken lines.

TABLE 5.   SELECTED BOND DISTANCES $(l/\text{Å})$ AND ANGLES $(\phi/°)$ IN THE HOST MOLECULES

	I	II
C(3)-O(1)	1.447(7)	1.449(5)
C(3)-C(4)	1.533(9)	1.539(5)
C(3)-C(12)	1.555(7)	1.553(3)
C(3)-C(2)	1.494(5)	1.476(5)
C(2)-C(1)	1.208(5)	1.189(6)
C(1)-C(1)'	1.347(7)	—
C(1)-C(20)	—	1.451(6)
O(1)-C(3)-C(4)	107.0(4)	105.3(2)
O(1)-C(3)-C(12)	109.2(4)	108.8(3)
O(1)-C(3)-C(2)	107.5(4)	107.5(3)
C(4)-C(3)-C(12)	115.3(4)	115.4(3)
C(2)-C(3)-C(4)	111.9(4)	113.0(3)
C(2)-C(3)-C(12)	105.6(4)	106.5(2)
	III, Molecule A	III, Molecule B*
C(1)-O(1)	1.47(1)	1.44(1)
C(1)-C(2)	1.45(1)	1.49(1)
C(1)-C(13)	1.52(1)	1.53(1)
C(1)-C(14)	1.49(2)	1.43(2)
C(14)-C(15)	1.16(2)	1.21(2)
C(15)-C(16)	1.50(2)	1.47(2)
O(1)-C(1)-C(2)	110.0(8)	109.5(8)
O(1)-C(1)-C(13)	109.7(8)	110.4(9)
O(1)-C(1)-C(14)	107.5(8)	111.4(9)
C(2)-C(1)-C(13)	102.8(7)	100.0(8)
C(2)-C(1)-C(14)	114.9(9)	114.0(9)
C(13)-C(1)-C(14)	111.7(9)	111.0(9)

*Values matching those in molecule A are displayed. To obtain the atom numbers for O and C atoms in molecule B, add 1 and 16, respectively, to those shown in Fig. 3.

contains two independent sets of fluorene (4) and methanol molecules; the molecular species in each set are linked by hydrogen bonds to form infinite zigzag chains parallel to the a axis. The measured parameters of the two independent systems of hydrogen-bonded

chains are: $O(1)\cdots O(3)=2.76(1)\text{Å}$, $O(1)\cdots O(3)^i=2.70(1)$ Å, $O(3)\cdots O(1)\cdots O(3)^i=124.0(4)°$, $O(1)\cdots O(3)\cdots O(1)^{ii}=119.5(4)°$, $O(4)\cdots O(2)\cdots O(4)^{iii}=122.9(4)°$, and $O(2)\cdots O(4)\cdots O(2)^{iv}=122.6(4)°$, where the superscripts i, ii, iii, and iv denote the symmetry transformations $(1/2+x, 1/2-y, z)$, $(-1/2+x, 11/2-y, z)$, $(1/2+x, 1/2-y, z)$ and $(-1/2+x, 1/2-y, z)$ respectively. With reference to Figs. 3 and 6, it is noted that the hydrogen-bonded chains generated from Type A fluorene [O(1)-C(16)] and methanol molecules [O(3)-C(33)] lie close to the planes $z=1/8$ and 5/8, whereas similar chains belonging to the other system are in the proximity of the planes $z= 3/8$ and 7/8. The van der Waals' contacts between hydrophobic groups thus occur mainly accross the (004) set of planes.

Elucidation of the crystal structures of the complexes I, II, and III in the present study provides a rationale for the formation of analogous alcohol adducts by the relevant host species 2b, 3c, and 4. In each instance the alkyl group of the alcohol guest component is accommodated in a spacious void, so that its substitution by a more bulky alcohol would not be expected to significantly affect the overall pattern of molecular packing and hydrogen bonding.

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