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Structures and Photochemistry of Inclusion Compounds of 9,10-Dihydro-9,10-ethenoanthracene-11,12-bis(diphenylmethanol)

Tai Yu Fu, John R. Scheffer and James Trotter*

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Z1. E-mail: jtrt@xray4.chem.ubc.ca

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Abstract

Crystal structures have been determined for inclusion complexes of the host molecule 9,10-dihydro-9,10-ethenoanthracene-11,12-bis(diphenylmethanol), with acetone, ethanol and toluene as guest solvent molecules. The host molecule exhibits an intramolecular O—H···O hydrogen bond in each of the complexes, with intermolecular hydrogen bonds to the acetone and ethanol guests. Different photoproducts are obtained from solution and solid-state photolyses; the solid-state reaction involves a relatively small amount of molecular rearrangement, for which a mechanism is proposed.

1. Introduction

Crystal structures and photochemical reactivity have been correlated for inclusion complexes of the dibenzobarrelene derivative (1) (Fig. 1), in which the phosphine oxide groups can act as hydrogen-bond acceptors (Fu, Liu, Olovsson, Scheffer & Trotter, 1997). A new inclusion host has now been designed (2), with the same molecular skeleton as (1), but differing in that the sensor Ph_2COH groups are hydrogen-bond donors. Crystal structures of three inclusion complexes of (2) have been determined and correlated with the photochemical reactivity.

2. Experimental

The synthesis of (2) involves a Diels–Alder reaction followed by a phenyllithium reaction (Fig. 1).† The diol (2) includes different solvent molecules upon recrystallization and three complexes were prepared, (2).acetone, (2).EtOH and (2).toluene.

The three complexes are very stable in the solid state at room temperature, but, on heating in an inert atmosphere, they decompose and the solvent molecules escape from the crystal lattice at elevated temperature.

Table 1. *Summary of DSC results of the complexes of diol (2) (K)*

Complex	Solvent evolution temperature	Final melting point
(2).acetone	377.9–393.1	493.3
(2).EtOH	375.8–424.9	511.9
(2).toluene	382.6–402.1	511.9

The DSC analyses of these complexes, summarized in Table 1, indicate 1:1 complexes; the loss of solvent was also detected by a complementary TGA experiment (details in deposition data). It is interesting to note that the final melting point of (2) obtained from (2).acetone

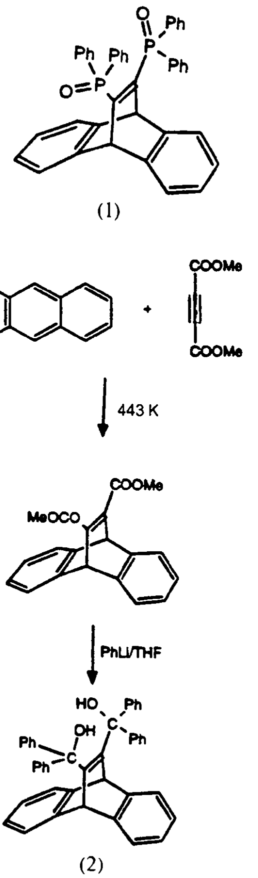

Fig. 1. Compound (1) and synthesis of diol (2).

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† Lists of atomic coordinates, anisotropic displacement parameters, complete geometry, structure factors and details of synthesis and photochemistry, and packing diagrams have been deposited with the IUCr (Reference: FG0007). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 2. *Experimental details*

	(2).acetone	(2).EtOH	(2).toluene
Crystal data			
Chemical formula	$C_{42}H_{32}O_2.C_3H_6O$	$C_{42}H_{32}O_2.C_2H_6O$	$C_{42}H_{32}O_2.C_7H_8$
Chemical formula weight	626.79	614.78	660.85
Cell setting	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a (Å)	10.210 (1)	13.623 (3)	10.703 (2)
b (Å)	21.152 (3)	15.960 (5)	10.208 (3)
c (Å)	16.462 (1)	15.950 (2)	34.057 (2)
β (°)	95.916 (7)	98.54 (2)	98.604 (8)
V (Å^3)	3536.2 (7)	3429 (1)	3679 (1)
Z	4	4	4
D_x (Mg m^{-3})	1.177	1.191	1.193
Radiation type	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
Wavelength (Å)	1.5418	1.5418	1.5418
No. of reflections for cell parameters	24	24	24
θ range (°)	44.1–51.5	45.0–54.3	25.4–43.0
μ (mm^{-1})	0.564	0.57	0.55
Temperature (K)	294	294	294
Crystal form	Prism	Prism	Prism
Crystal size (mm)	0.50 × 0.30 × 0.20	0.40 × 0.20 × 0.15	0.20 × 0.10 × 0.10
Crystal color	Colorless	Colorless	Colorless
Data collection			
Diffractometer	Rigaku AFC-6*S*	Rigaku AFC-6*S*	Rigaku AFC-6*S*
Data collection method	ω–2θ scans	ω–2θ scans	ω–2θ scans
Absorption correction	ψ scans (North, Phillips & Mathews, 1968)	ψ scans (North, Phillips & Mathews, 1968)	ψ scans (North, Phillips & Mathews, 1968)
$T_{\min}$	0.945	0.905	0.853
$T_{\max}$	0.998	0.999	1.000
No. of measured reflections	7883	7575	8395
No. of independent reflections	7449	7261	7980
No. of observed reflections	4831	4799	3414
Criterion for observed reflections	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$
$R_{\rm int}$	0.014	0.013	0.022
$\theta_{\max}$ (°)	77.62	78.02	77.59
Range of h, k, l	$0 \rightarrow h \rightarrow 12$ $0 \rightarrow k \rightarrow 26$ $-20 \rightarrow l \rightarrow 20$	$-3 \rightarrow h \rightarrow 17$ $-9 \rightarrow k \rightarrow 20$ $-20 \rightarrow l \rightarrow 19$	$0 \rightarrow h \rightarrow 13$ $0 \rightarrow k \rightarrow 12$ $-43 \rightarrow l \rightarrow 42$
No. of standard reflections	3	3	3
Frequency of standard reflections	Every 200 reflections	Every 200 reflections	Every 200 reflections
Intensity decay (%)	4	0.5	20
Refinement			
Refinement on	F	F	F
R	0.0430	0.0560	0.0525
wR	0.0460	0.0600	0.0690
S	2.810	3.800	2.100
No. of reflections used in refinement	4831	4799	3414
No. of parameters used	471	425	461
H-atom treatment	All H-atom parameters refined (except acetone H)	All H-atom parameters refined (except ethanol H)	Only hydroxyl H atoms refined
Weighting scheme	$w = 1/[\sigma^2(F_o) + 0.00001\vert F_o\vert^2]$	$w = 1/[\sigma^2(F_o) + 0.00000\vert F_o\vert^2]$	$w = 1/[\sigma^2(F_o) + 0.00044\vert F_o\vert^2]$
$(\Delta/\sigma)_{\max}$	0.31	0.04	0.02
$\Delta\rho_{\max}$ (e Å^{-3})	0.15	0.34	0.30
$\Delta\rho_{\min}$ (e Å^{-3})	−0.15	−0.35	−0.20
Extinction method	Zachariasen (1967)	Zachariasen (1967)	Zachariasen (1967)
Extinction coefficient	$2.7 (5) \times 10^{-6}$	$3.7 (5) \times 10^{-6}$	$0.5 (3) \times 10^{-6}$
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Table 6.1.1.2)	*International Tables for Crystallography* (1992, Vol. C, Table 6.1.1.2)	*International Tables for Crystallography* (1992, Vol. C, Table 6.1.1.2)
Computer programs			
Data collection	*MSC/AFC* (MSC, 1988)	*MSC/AFC* (MSC, 1988)	*MSC/AFC* (MSC, 1988)
Cell refinement	*MSC/AFC* (MSC, 1988)	*MSC/AFC* (MSC, 1988)	*MSC/AFC* (MSC, 1988)
Data reduction	*TEXSAN* (MSC, 1995)	*TEXSAN* (MSC, 1995)	*TEXSAN* (MSC, 1995)
Structure solution	*MITHRIL84* (Gilmore, 1984)	*SHELXS86* (Sheldrick, 1985)	*SHELXS86* (Sheldrick, 1985)
Structure refinement	*TEXSAN* (MSC, 1995)	*TEXSAN* (MSC, 1995)	*TEXSAN* (MSC, 1995)
Preparation of material for publication	*TEXSAN* (MSC, 1995)	*TEXSAN* (MSC, 1995)	*TEXSAN* (MSC, 1995)

is different from (2), from (2).EtOH and (2).toluene. Perhaps the solvent-free (2) formed from heating the acetone complex has a different polymorphic form from that of the other two complexes.

The crystal structures of the three complexes (2).acetone, (2).EtOH and (2).toluene were determined by direct methods (*TEXSAN*; Molecular Structure Corporation, 1995). Details are summarized in Table 2. The toluene

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
(2).acetone				
O(1)	0.2962 (1)	0.21001 (7)	0.20797 (9)	0.0516 (4)
O(2)	0.4399 (1)	0.12036 (7)	0.27571 (8)	0.0568 (4)
O(3*a*)	0.4397 (6)	0.0541 (2)	0.4201 (3)	0.115 (2)
O(3*b*)	0.316 (2)	0.0583 (4)	0.3970 (5)	0.164 (4)
C(1)	0.8535 (2)	0.2628 (1)	0.1497 (1)	0.0624 (7)
C(2)	0.9761 (2)	0.2342 (2)	0.1632 (1)	0.0767 (9)
C(3)	0.9891 (2)	0.1700 (2)	0.1541 (1)	0.0815 (9)
C(4)	0.8810 (2)	0.1327 (1)	0.1313 (1)	0.0670 (7)
C(5)	0.5555 (2)	0.1337 (1)	−0.0665 (1)	0.0633 (7)
C(6)	0.5154 (2)	0.1712 (2)	−0.1336 (1)	0.0768 (8)
C(7)	0.4994 (2)	0.2353 (2)	−0.1252 (1)	0.0748 (8)
C(8)	0.5248 (2)	0.2639 (1)	−0.0490 (1)	0.0629 (7)
C(9)	0.6031 (2)	0.24799 (10)	0.1051 (1)	0.0457 (5)
C(10)	0.6281 (2)	0.1295 (1)	0.0890 (1)	0.0483 (5)
C(11)	0.5136 (2)	0.21011 (8)	0.1577 (1)	0.0401 (5)
C(12)	0.5332 (2)	0.14765 (8)	0.1527 (1)	0.0414 (5)
C(13)	0.7443 (2)	0.2259 (1)	0.1261 (1)	0.0504 (6)
C(14)	0.7582 (2)	0.1609 (1)	0.1171 (1)	0.0523 (6)
C(15)	0.5801 (2)	0.1617 (1)	0.0091 (1)	0.0499 (6)
C(16)	0.5657 (2)	0.2267 (1)	0.0177 (1)	0.0493 (5)
C(17)	0.4107 (2)	0.24726 (8)	0.2005 (1)	0.0413 (5)
C(18)	0.4875 (2)	0.09332 (9)	0.2040 (1)	0.0468 (5)
C(19)	0.3582 (2)	0.30139 (9)	0.1442 (1)	0.0483 (5)
C(20)	0.2777 (2)	0.2867 (1)	0.0735 (1)	0.0600 (7)
C(21)	0.2280 (3)	0.3332 (1)	0.0207 (2)	0.0798 (9)
C(22)	0.2566 (3)	0.3952 (2)	0.0376 (2)	0.096 (1)
C(23)	0.3351 (3)	0.4110 (1)	0.1072 (2)	0.098 (1)
C(24)	0.3862 (2)	0.3642 (1)	0.1602 (2)	0.0708 (7)
C(25)	0.4659 (2)	0.27190 (8)	0.2845 (1)	0.0415 (5)
C(26)	0.3789 (2)	0.2904 (1)	0.3391 (1)	0.0595 (7)
C(27)	0.4225 (2)	0.3137 (1)	0.4151 (1)	0.0672 (7)
C(28)	0.5543 (2)	0.3202 (1)	0.4377 (1)	0.0619 (7)
C(29)	0.6422 (2)	0.3026 (1)	0.3847 (1)	0.0616 (7)
C(30)	0.5982 (2)	0.2779 (1)	0.3086 (1)	0.0523 (6)
C(31)	0.6101 (2)	0.05422 (9)	0.2332 (1)	0.0549 (6)
C(32)	0.7023 (2)	0.0800 (1)	0.2914 (2)	0.0719 (8)
C(33)	0.8171 (3)	0.0488 (2)	0.3169 (2)	0.101 (1)
C(34)	0.8419 (4)	−0.0092 (2)	0.2846 (2)	0.118 (1)
C(35)	0.7532 (4)	−0.0358 (2)	0.2272 (2)	0.108 (1)
C(36)	0.6368 (3)	−0.0042 (1)	0.2013 (2)	0.0764 (8)
C(37)	0.3766 (2)	0.05473 (9)	0.1585 (1)	0.0514 (6)
C(38)	0.3189 (3)	0.0057 (1)	0.1983 (2)	0.0746 (8)
C(39)	0.2153 (3)	−0.0285 (1)	0.1595 (2)	0.090 (1)
C(40)	0.1676 (3)	−0.0152 (1)	0.0804 (2)	0.0849 (9)
C(41)	0.2240 (2)	0.0323 (1)	0.0402 (2)	0.0769 (8)
C(42)	0.3272 (2)	0.0673 (1)	0.0791 (1)	0.0626 (7)
C(43*a*)	0.3933 (9)	0.0828 (4)	0.4746 (5)	0.099 (3)
C(43*b*)	0.308 (2)	0.0881 (5)	0.4556 (7)	0.096 (4)
C(44*a*)	0.305 (3)	0.130 (1)	0.455 (1)	0.36 (1)
C(44*b*)	0.236 (2)	0.0703 (4)	0.5244 (8)	0.206 (7)
C(45*a*)	0.4151 (9)	0.0640 (3)	0.5602 (3)	0.130 (3)
C(45*b*)	0.362 (2)	0.1546 (7)	0.4573 (7)	0.101 (3)
(2).EtOH				
O(1)	0.0371 (1)	0.0841 (1)	0.8631 (1)	0.0516 (5)
O(2)	0.0606 (1)	0.1453 (1)	1.0137 (1)	0.0530 (5)
O(3)	−0.0533 (2)	−0.0708 (2)	0.8293 (1)	0.0804 (8)
C(1)	0.2500 (2)	0.4041 (2)	0.8596 (2)	0.0560 (9)
C(2)	0.2874 (3)	0.4645 (2)	0.9177 (2)	0.0661 (10)
C(3)	0.2325 (3)	0.4923 (2)	0.9778 (2)	0.0654 (10)
C(4)	0.1392 (2)	0.4597 (2)	0.9818 (2)	0.0545 (8)
C(5)	−0.1394 (2)	0.4145 (2)	0.8015 (2)	0.0580 (9)
C(6)	−0.1752 (3)	0.4256 (2)	0.7149 (2)	0.073 (1)
C(7)	−0.1200 (3)	0.3982 (2)	0.6550 (2)	0.074 (1)
C(8)	−0.0284 (2)	0.3602 (2)	0.6781 (2)	0.0585 (9)
C(9)	0.1022 (2)	0.3079 (2)	0.8028 (2)	0.0433 (7)
C(10)	0.0014 (2)	0.3572 (1)	0.9142 (1)	0.0416 (7)
C(11)	0.0711 (2)	0.2352 (1)	0.8569 (1)	0.0382 (6)
C(12)	0.0230 (2)	0.2614 (1)	0.9195 (1)	0.0374 (6)
C(13)	0.1566 (2)	0.3721 (1)	0.8616 (1)	0.0435 (7)
C(14)	0.1018 (2)	0.3995 (1)	0.9231 (2)	0.0436 (7)
C(15)	−0.0492 (2)	0.3760 (1)	0.8248 (2)	0.0457 (7)
C(16)	0.0060 (2)	0.3490 (1)	0.7631 (1)	0.0448 (7)
C(17)	0.0924 (2)	0.1469 (1)	0.8262 (1)	0.0417 (6)
C(18)	−0.0088 (2)	0.2127 (1)	0.9936 (1)	0.0412 (6)
C(19)	0.0513 (2)	0.1450 (1)	0.7313 (1)	0.0476 (7)
C(20)	0.1106 (3)	0.1547 (2)	0.6684 (2)	0.0613 (9)
C(21)	0.0686 (4)	0.1579 (2)	0.5833 (2)	0.080 (1)
C(22)	−0.0309 (4)	0.1511 (3)	0.5603 (2)	0.094 (1)
C(23)	−0.0911 (3)	0.1427 (2)	0.6212 (3)	0.089 (1)
C(24)	−0.0504 (2)	0.1394 (2)	0.7072 (2)	0.0659 (10)
C(25)	0.2023 (2)	0.1234 (2)	0.8464 (1)	0.0442 (7)
C(26)	0.2341 (2)	0.0485 (2)	0.8153 (2)	0.0577 (9)
C(27)	0.3300 (2)	0.0213 (2)	0.8363 (2)	0.069 (1)
C(28)	0.3970 (2)	0.0688 (2)	0.8900 (2)	0.071 (1)
C(29)	0.3681 (2)	0.1435 (2)	0.9205 (2)	0.069 (1)
C(30)	0.2703 (2)	0.1708 (2)	0.8991 (2)	0.0563 (9)
C(31)	−0.1139 (2)	0.1782 (2)	0.9708 (2)	0.0523 (8)
C(32)	−0.1851 (2)	0.2188 (2)	0.9162 (2)	0.069 (1)
C(33)	−0.2813 (3)	0.1894 (3)	0.8990 (3)	0.094 (1)
C(34)	−0.3056 (3)	0.1161 (4)	0.9339 (3)	0.124 (2)
C(35)	−0.2348 (4)	0.0715 (4)	0.9853 (3)	0.134 (2)
C(36)	−0.1392 (3)	0.1026 (3)	1.0044 (2)	0.098 (1)
C(37)	0.0015 (2)	0.2700 (2)	1.0719 (1)	0.0456 (7)
C(38)	−0.0793 (3)	0.3025 (2)	1.1039 (2)	0.068 (1)
C(39)	−0.0670 (3)	0.3570 (2)	1.1723 (2)	0.087 (1)
C(40)	0.0269 (3)	0.3805 (2)	1.2080 (2)	0.084 (1)
C(41)	0.1074 (3)	0.3491 (2)	1.1778 (2)	0.075 (1)
C(42)	0.0946 (2)	0.2937 (2)	1.1089 (2)	0.0598 (9)
C(43)	−0.0409 (8)	−0.1096 (4)	0.7570 (3)	0.241 (4)
C(44)	−0.0365 (6)	−0.1039 (5)	0.6874 (4)	0.227 (4)
(2).toluene				
O(1)	0.0854 (2)	0.0390 (3)	0.40162 (7)	0.0725 (8)
O(2)	0.1966 (2)	0.1697 (2)	0.34871 (7)	0.0726 (7)
C(1)	0.6293 (3)	−0.1062 (3)	0.42670 (10)	0.068 (1)
C(2)	0.7362 (3)	−0.0744 (4)	0.4102 (1)	0.080 (1)
C(3)	0.7296 (4)	−0.0644 (4)	0.3697 (1)	0.082 (1)
C(4)	0.6158 (3)	−0.0852 (3)	0.34497 (10)	0.068 (1)
C(5)	0.3137 (3)	−0.3915 (3)	0.33030 (10)	0.069 (1)
C(6)	0.2871 (4)	−0.5086 (3)	0.3475 (1)	0.084 (1)
C(7)	0.2942 (4)	−0.5184 (4)	0.3881 (1)	0.086 (1)
C(8)	0.3275 (3)	−0.4103 (3)	0.4121 (1)	0.073 (1)
C(9)	0.3909 (3)	−0.1641 (3)	0.41512 (8)	0.0554 (9)
C(10)	0.3776 (3)	−0.1467 (3)	0.34068 (8)	0.0543 (9)
C(11)	0.2902 (3)	−0.0638 (3)	0.39666 (8)	0.0517 (9)
C(12)	0.2885 (3)	−0.0504 (3)	0.35723 (8)	0.0500 (8)
C(13)	0.5159 (3)	−0.1262 (3)	0.40266 (9)	0.0528 (9)
C(14)	0.5093 (3)	−0.1165 (3)	0.36142 (9)	0.0557 (9)
C(15)	0.3461 (3)	−0.2833 (3)	0.35365 (8)	0.0556 (9)
C(16)	0.3542 (3)	−0.2928 (3)	0.39505 (9)	0.0572 (10)
C(17)	0.2038 (3)	−0.0045 (3)	0.42405 (8)	0.0555 (9)
C(18)	0.2149 (3)	0.0488 (3)	0.32871 (9)	0.0564 (9)
C(19)	0.2626 (3)	0.1159 (3)	0.44660 (8)	0.0560 (10)
C(20)	0.1882 (3)	0.1973 (3)	0.4660 (1)	0.075 (1)
C(21)	0.2388 (4)	0.3050 (4)	0.4872 (1)	0.084 (1)
C(22)	0.3653 (4)	0.3342 (3)	0.4897 (1)	0.076 (1)
C(23)	0.4408 (3)	0.2553 (4)	0.4709 (1)	0.073 (1)
C(24)	0.3894 (3)	0.1476 (3)	0.44938 (9)	0.065 (1)
C(25)	0.1689 (3)	−0.1114 (3)	0.45193 (9)	0.061 (1)
C(26)	0.0922 (4)	−0.2148 (4)	0.4368 (1)	0.085 (1)
C(27)	0.0624 (4)	−0.3146 (4)	0.4606 (2)	0.104 (2)
C(28)	0.1067 (4)	−0.3142 (4)	0.5005 (2)	0.098 (2)
C(29)	0.1812 (4)	−0.2148 (4)	0.5159 (1)	0.093 (1)
C(30)	0.2126 (4)	−0.1140 (4)	0.49215 (10)	0.077 (1)
C(31)	0.0867 (3)	−0.0022 (4)	0.30979 (8)	0.063 (1)
C(32)	0.0539 (4)	−0.1328 (4)	0.3096 (1)	0.079 (1)
C(33)	−0.0627 (5)	−0.1741 (5)	0.2900 (1)	0.106 (2)
C(34)	−0.1485 (5)	−0.0856 (8)	0.2712 (1)	0.121 (2)
C(35)	−0.1178 (5)	0.0427 (8)	0.2723 (2)	0.130 (2)
C(36)	−0.0011 (4)	0.0862 (4)	0.2910 (1)	0.097 (1)
C(37)	0.2960 (4)	0.0879 (3)	0.2970 (1)	0.073 (1)
C(38)	0.2727 (4)	0.0382 (5)	0.2584 (1)	0.106 (2)
C(39)	0.3508 (7)	0.0742 (8)	0.2315 (2)	0.158 (3)
C(40)	0.4504 (9)	0.160 (1)	0.2419 (3)	0.200 (4)
C(41)	0.4724 (6)	0.2074 (7)	0.2790 (3)	0.166 (3)
C(42)	0.3974 (4)	0.1705 (4)	0.3074 (1)	0.107 (2)

Table 3. (*cont.*)

	x	y	z	U_{eq}
C(43)	0.139 (2)	−0.061 (3)	0.1327 (3)	0.38 (1)
C(44)	0.180 (2)	−0.191 (1)	0.1351 (4)	0.232 (6)
C(45)	0.300 (2)	−0.182 (1)	0.1223 (3)	0.225 (6)
C(46)	0.3751 (8)	−0.069 (3)	0.1077 (4)	0.312 (8)
C(47)	0.288 (2)	0.006 (2)	0.1143 (4)	0.267 (8)
C(48)	0.195 (1)	0.0517 (10)	0.1226 (3)	0.193 (5)
C(49)	0.0412 (9)	−0.061 (2)	0.1451 (4)	0.339 (8)

Table 4. *Hydrogen-bonding parameters (Å, °)*

	O···O	O—H	H···O	O—H···O
(2).acetone				
O(1)-H(1)···O(2) (intra)	2.580 (2)	0.94 (3)	1.71 (3)	151 (2)
O(2)—H(2)···O(3*a*)	2.760 (4)	0.86 (3)	1.96 (3)	154 (2)
O(2)—H(2)···O(3*b*)	2.800 (6)	0.86 (3)	1.99 (3)	155 (2)
(2).EtOH				
O(1)—H(1)···O(2) (intra)	2.569 (2)	0.97 (3)	1.65 (3)	156 (2)
O(2)—H(2)···O(3^{i})	2.787 (3)	0.88 (4)	1.91 (4)	176 (3)
O(3)—H(3)···O(1)	2.779 (3)	0.86 (5)	1.97 (5)	156 (4)
(2).toluene				
O(2)—H···O(1) (intra)	2.662 (4)	1.16 (6)	1.51 (6)	175 (5)
O(1)—H(1)	No hydrogen bond	1.12 (9)	–	–

Symmetry codes: (i) $-x, -y, 2-z$.

complex showed about 20% decomposition during the data collection. H atoms were refined for the host molecules (2) (only hydroxyl H atoms for the toluene complex). The guest molecules have large displacement parameters, which probably correspond to disorder as well as to high thermal motion. The dimensions of the guests are also poorly determined; for the toluene molecule, for example, unrestrained refinement gave a reasonably well defined planar molecule, but with somewhat unrealistic dimensions, particularly for C(47), and these parameters are given in Table 3 (restrained refinement gave more reasonable dimensions, but with a slightly higher R value). For the acetone complex, two sites were used for the acetone guest molecule (occupancies 60:40).

3. Discussion

The molecular structures of diol (2) in the three complexes are very similar (Table 3 and Fig. 2), all being characterized by intramolecular hydrogen bonding between the two alcohol moieties (Table 4). The C(11)=C(12) double-bond system shows some deviation from planarity, with C(9)—C(11)=C(12)—C(10) torsion angles of 6.3 (3), 6.3 (2) and 5.2 (3)° in the ethanol, acetone and toluene complexes, respectively, and C(17)—C(11)=C(12)—C(18) angles of 14.3 (4), 18.1 (3) and 12.9 (5)° (both enantiomers are present in each crystal structure). These deviations are probably a result of steric repulsions between the bulky diphenylmethanol substituent groups and may be compared with the slightly larger deviations (P—C=C—P torsion angles of 21–24°) in the phosphine oxide complexes (1).

The crystal packing in the three complexes is very different (packing diagrams – see deposition data*). For (2).acetone there is an intermolecular hydrogen bond formed between the disordered acetone molecule and

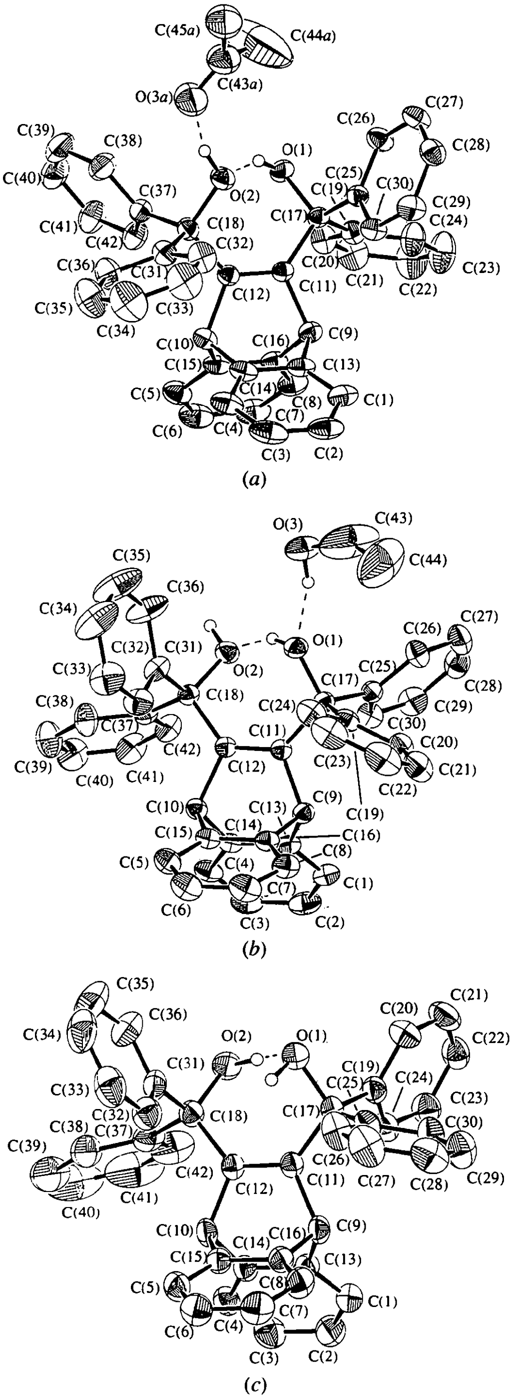

Fig. 2. Views of the complexes (*a*) (2).acetone, (*b*) (2).ethanol and (*c*) (2).toluene (30% ellipsoids; Johnson, 1976).

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* See deposition footnote on p. 300.

the diol molecule (Table 4). There is still a considerable amount of void space in the crystal lattice, which a third party molecule may be able to occupy. In accordance with this, yellow prismatic crystals of a three-component complex of diol (2):benzoquinone:acetone (2:1:2) have been prepared by recrystallizing diol (2) in the presence of excess benzoquinone from acetone solution. The complex was characterized by proton NMR, but it decomposes within hours in air after isolation from the recrystallizing solution and no further work on this complex was performed. Complex (2).EtOH possesses a hydrogen-bonding network with two diol and two ethanol molecules linked *via* a 12-membered ring (Table 4 and Fig. 3). Complex (2).toluene has a packing arrangement with the toluene molecule surrounded by aromatic rings of the diol (2) and located under the 'roof' of the dibenzobarrelene group. There is, however, no strong interaction between the toluene molecule and the diol moiety.

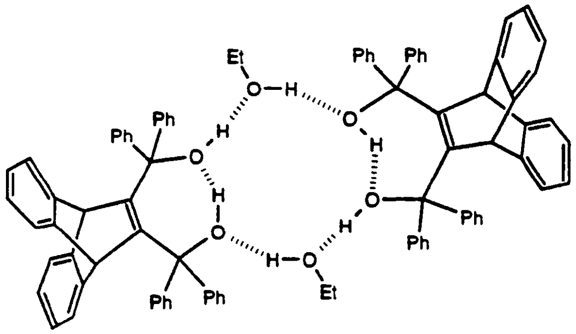

Fig. 3. Hydrogen bonding in the complex (2).EtOH (there is an inversion center, 0,0,1, at the center of the diagram).

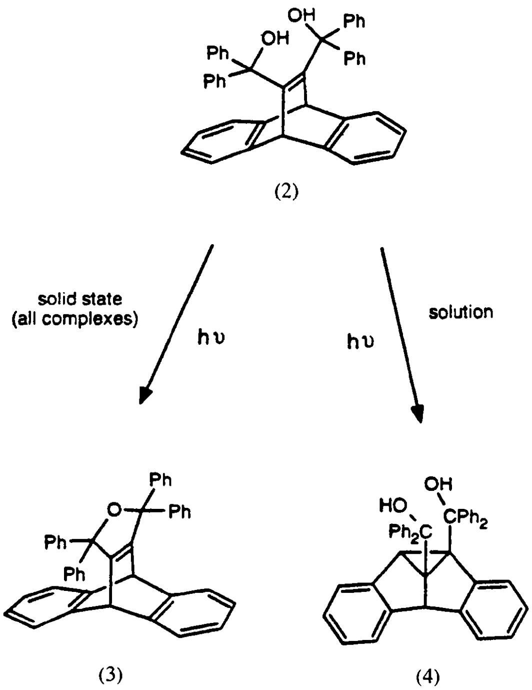

Fig. 4. Photochemistry of diol (2).

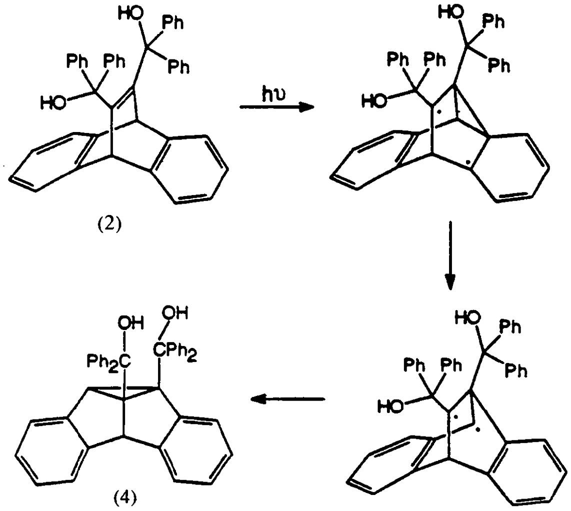

Fig. 5. Di-π-methane rearrangement of diol (2).

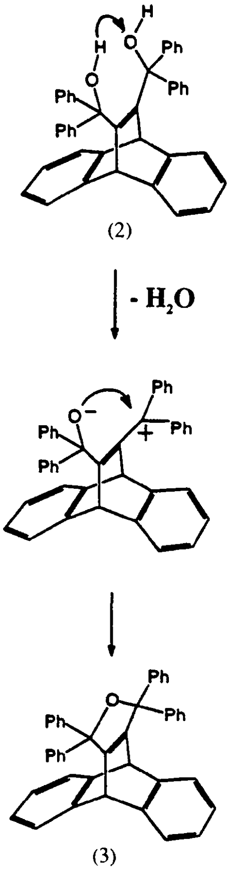

Fig. 6. Photosolvolysis mechanism for photocyclization of diol (2).

All three complexes possess essentially the same photochemistry in the solid state (Fu, Olovsson, Scheffer & Trotter, 1995). For example, the powder form of (2).acetone (200 mg) was photolyzed at $\lambda \geq 290$ nm for 24 h and photoproduct (3) (Fu, Olovsson, Scheffer & Trotter, 1996) was isolated after chromatography in 15% yield; photolysis of either the ethanol or the toluene complex gave similar results (Fig. 4). However, it was found that upon irradiation in benzene, acetone or ethanol solution, diol (2) undergoes the di-π-methane rearrangement and gives (4) as the only product (Fig. 4); the mechanism of the formation of (4) is shown in Fig. 5.

The mechanism for the photocyclization of diol (2) to give ether (3) most likely involves initiation by a photochemically induced heterolysis of one of the C—O bonds (Shukla & Wan, 1991; Wan & Shukla, 1993); this process, assisted by intramolecular transfer of the proton involved in the intramolecular O—H···O hydrogen bond, results in the loss of water and the formation of a carbonium ion (Fig. 6). This mechanism is supported by the fact that photosolvolyses of benzyl derivatives with a variety of leaving groups, including halides, nitriles, acetates, carbamates, ethers, trialkylammonium salts and dialkylsulfonium salts, are well known (Cristol & Bindel, 1983; Das, 1993). The involvement of carbonium ions in these reactions is widely accepted. The final step in the mechanism involves capture of the carbonium ion by the remaining alkoxide group.

The difference between the photochemical reactivity in crystal and solution phases for diol (2) can be explained by the topochemical principle. Although the di-π-methane rearrangement of diol (2) proceeds in solution, it involves substantial atomic and molecular movement of bulky groups (Fig. 5). Such a reaction is topochemically disfavored in the solid state [although the even bulkier (1) does undergo such a reaction in the solid state]. The photocyclization reaction (Fig. 6), on the other hand, requires a relatively small degree of molecular rearrangement around the diol moieties; the O···C intramolecular distances involved in the formation of new O—C bonds are in the range 2.96–3.15 Å and are reduced to a normal bond distance of 1.466 Å during the photoreaction. This reaction therefore predominates in the solid state.

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References

Cristol, S. J. & Bindel, T. H. (1983). *Org. Photochem.* **6**, 327–415.

Das, P. K. (1993). *Chem. Rev.* **93**, 119–144.

Fu, T. Y., Liu, Z., Olovsson, G., Scheffer, J. R. & Trotter, J. (1997). *Acta Cryst.* **B53**, 293–299.

Fu, T. Y., Olovsson, G., Scheffer, J. R. & Trotter, J. (1995). *Tetrahedron Lett.* **36**, 4353–4356.

Fu, T. Y., Olovsson, G., Scheffer, J. R. & Trotter, J. (1996). *Acta Cryst.* **C52**, 2347–2349.

Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structure.* University of Göttingen, Germany.

Shukla, D. & Wan, P. (1991). *Trends Org. Chem.* **2**, 143–153.

Wan, P. & Shukla, D. (1993). *Chem. Rev.* **93**, 571–584.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.