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

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Abstract

Inclusion complexes of 9,10-dihydro-9,10-ethenoanthracene-11,12-bis(diphenylphosphine oxide) (1) as host are synthesized using a variety of guest solvent molecules and the photochemistry of the host molecule is studied in solution and in the crystalline complexes. The crystal structures of four complexes are determined and correlated with their photochemical reactivity. In each case only one dibenzosemibullvalene photoproduct is obtained in the photolysis. Since three of the complexes studied crystallize in the chiral space group $P2_12_12_1$, irradiation of single crystals produces a chiral photoproduct in >90% enantiomeric excess. Determination of the absolute configurations of reactants and products allows elucidation of the key structural features that control the enantiospecific solid-state photorearrangements.

1. Introduction

The design and applications of new host molecules in molecular recognition and materials science is a topic of much current interest (*Inclusion Compounds*, 1984, 1991; *Advances in Supramolecular Chemistry*, 1990, 1992). Studies have shown that good host molecules are bulky and pack inefficiently with voids and contain appended sensor groups that coordinate to the guests (Weber & Czugler, 1988); the host–guest inclusion compounds have been termed **coordinatoclathrates**. By introducing into the host molecule substituents that are capable of donating hydrogen bonds, many different coordinatoclathrate inclusion compounds have been prepared and studied. An alternative approach involves using a hydrogen-bond acceptor, such as a phosphine oxide, in the host molecule (Etter & Baures, 1988).

Photochemical interest in inclusion complexes stems from advantages offered by such systems: a well defined small **reaction cavity** for a reactant guest molecule is provided, and molecular packing and hence the selectivity of phototransformations of **guests** can be controlled by using a variety of hosts (Ramamurthy, 1991). An alternative approach to utilizing inclusion compounds in photochemistry involves photoreactive **host** molecules; photochemistry in the crystalline state can be studied by synthesizing a large number of different crystals with the same photoreactive host molecule, simply by introducing different photostable guest molecules. The effect of the crystalline environment on the photochemistry in the solid state can then be studied and compared without the complications of differences in intrinsic reactivity among different compounds. The present paper describes studies of inclusion complexes of the photoreactive host molecule (1) (Fig. 1), which possesses the features that are necessary for a good host: its roof-shaped molecular structure and the four phenyl groups make the crystal packing inefficient and help to create voids in the parent lattice, and the two phosphine oxide groups can act as hydrogen bond acceptors that will coordinate to the guests.

2. Experimental

2.1. *Synthesis and photochemistry*

Compound (1) was synthesized by a Diels–Alder reaction (Fig. 1; details in the depository material†) and found to form complexes with a wide variety of solvent molecules, including acetone, 2-butanone, 2- and 3-pentanone, methyl vinyl ketone, THF, dimethoxyethane, ethyl acetate, ethanol, 1-propanol, 2-propanol and *tert*-butanol (Fu, Liu, Scheffer & Trotter, 1993).

Thermally, the inclusion complexes begin to effloresce at ~393 K and eventually the empty host melts at 510–511.5 K; weight loss corresponds to 1:1 host:guest molar ratios for all the complexes. The (1).acetone complex, for example, loses acetone over the range 373–425 K, with higher temperatures required to drive off hydrogen-bond donor guests (ethanol *etc.*; TGA/DSC data in the deposition material). Photolysis of (1) and its complexes under a variety of conditions produces (2) as the only photoproduct (Fig. 1).

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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: FG0006). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

2.2. *X-ray analysis*

Crystal structures were determined for four complexes (Table 1) by direct methods (*TEXSAN*; Molecular Structure Corporation, 1995). H atoms were fixed in idealized sites (hydroxyl H atoms not located). The ethanol complex (1).EtOH and the propanol complexes (1).Pr^{n}OH and (1).Pr^{i}OH are isomorphous and crystallize in the chiral space group $P2_12_12_1$ ($Z = 4$); the ethyl acetate complex (1).EtOAc crystallizes in the monoclinic space group $P2_1/c$ ($Z = 4$). The correct chiralities for the chiral crystals were determined by inclusion of anomalous dispersion terms. The guest molecules have large displacement parameters, which probably correspond to disorder as well as high thermal motion (the dimensions of the guests are also poorly determined, particularly for the ethanol molecule). For the isopropanol complex, the oxygen and both terminal C atoms in the guest molecule were each split over two sites (occupancies 0.5:0.5); one of the disordered carbon sites may have some oxygen occupancy, since a short intermolecular contact suggests hydrogen bonding at this site.

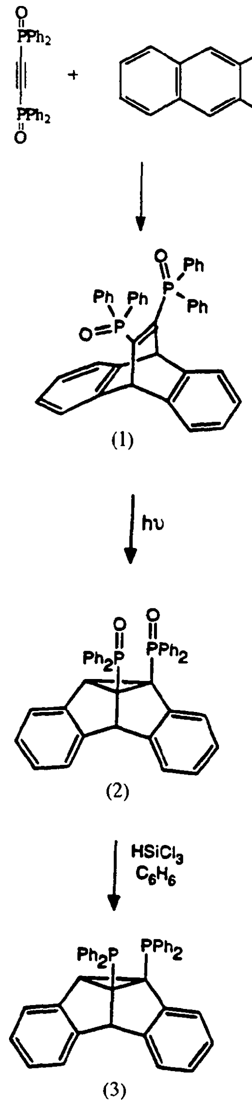

Fig. 1. Synthesis and photochemistry of (1).

3. Discussion

All four inclusion compounds studied by X-ray methods exhibit similar conformations and dimensions for the host molecule (1) (Fig. 2 and Table 2). Each structure contains an intramolecular dipole–dipole interaction between the two phosphine oxide moieties (Fig. 2), with P═O···P═O contacts (Table 3) close to van der Waals distances. Evidently, from the variety of inclusion complexes obtained, hydrogen bonding is not essential for complex formation. However, hydrogen bonding is indicated by IR spectroscopy in those complexes involving guests with hydrogen-donor functional groups, where no sharp O—H stretching bands are observed and *R*—O(H)···O—P intermolecular distances of 2.75–2.83 Å indicate weak intermolecular hydrogen bonding between guest (donor, OH) and host (receptor, OP) in the inclusion complexes (Table 3).

The three alcohol complexes of (1) are isomorphous; the alcohol molecules in each crystal are situated in a channel-like structure along **c** (packing diagrams in deposition data).* These channels provide space, not only for the alcohol molecules, but also for the sensor (P═O) groups for intermolecular hydrogen bonding. A similar channel structure is also present in complex (1).EtOAc along **b**.

3.1. *Photochemistry*

Compound (1) undergoes the di-π-methane rearrangement (Zimmerman, 1991) upon irradiation in solution (acetone, chloroform, benzene, ethanol) and in the solid state (all the crystalline inclusion complexes) to give dibenzosemibullvalene (2) as the only product (Fig. 1). The quantum yield in deuterated chloroform is moderately high ($\Phi = 0.28$). The photoreaction in the solid inclusion complexes is a crystal-to-glass process [the photolyzed crystals are transparent, resemble single crystals and lose their imprisoned solvent molecules upon heating above 373 K; the photolyzed crystalline complexes of (1) with ethanol and ethyl acetate give no Bragg reflections on exposure to X-rays]. Photoproduct (2) has been characterized spectroscopically* as well as by reduction to the corresponding bis(phosphine) (3), whose structure was established by X-ray analysis (Fu, Scheffer & Trotter, 1996).

Since photoproduct (2) is a chiral compound, an absolute asymmetric di-π-methane rearrangement may

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* See deposition footnote on p. 293.

Table 1. *Experimental details*

	(1).EtOH	(1).Pr^nOH	(1).Pr^iOH	(1).EtOAc
Crystal data				
Chemical formula	$C_{40}H_{30}O_2P_2.C_2H_6O$	$C_{40}H_{30}O_2P_2.C_3H_8O$	$C_{40}H_{30}O_2P_2.C_3H_8O$	$C_{40}H_{30}O_2P_2.C_4H_8O_2$
Chemical formula weight	650.69	664.72	664.72	692.73
Cell setting	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1/c$
a (Å)	17.983 (2)	18.191 (1)	18.076 (2)	18.223 (2)
b (Å)	20.682 (3)	20.748 (2)	20.904 (2)	9.435 (3)
c (Å)	9.384 (6)	9.436 (2)	9.432 (6)	21.946 (2)
β (°)				103.430 (7)
V (Å^3)	3490 (2)	3561.5 (6)	3563 (1)	3670.2 (9)
Z	4	4	4	4
D_x (Mg m^{-3})	1.238	1.240	1.239	1.254
Radiation type	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
Wavelength (Å)	1.5418	1.5418	1.5418	1.5418
No. of reflections for cell parameters	25	24	24	21
θ range (°)	28.5–40.8	27.6–40.3	12.6–24.0	43.0–50.9
μ (mm^{-1})	1.419	1.412	1.411	1.414
Temperature (K)	294	294	294	294
Crystal form	Prism	Prism	Prism	Plate
Crystal size (mm)	0.40 × 0.20 × 0.20	0.25 × 0.20 × 0.20	0.10 × 0.10 × 0.10	0.30 × 0.15 × 0.05
Crystal color	Colorless	Colorless	Colorless	Colorless
Data collection				
Diffractometer	Rigaku AFC-6*S*	Rigaku AFC-6*S*	Rigaku AFC-6*S*	Rigaku AFC-6*S*
Data collection method	ω–2θ scans	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)	ψ scans (North, Phillips & Mathews, 1968)
T_{min}	0.885	0.949	0.961	0.796
T_{max}	0.996	0.999	0.997	1.000
No. of measured reflections	4024	4119	4110	8247
No. of independent reflections	4024	4119	4110	8001
No. of observed reflections	3274	2907	2615	5327
Criterion for observed reflections	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$
R_{int}	–	–	–	0.13
θ_{max} (°)	77.50	77.64	77.71	78.58
Range of h, k, l	$0 \rightarrow h \rightarrow 22$ $0 \rightarrow k \rightarrow 26$ $0 \rightarrow l \rightarrow 11$	$0 \rightarrow h \rightarrow 23$ $0 \rightarrow k \rightarrow 26$ $0 \rightarrow l \rightarrow 11$	$0 \rightarrow h \rightarrow 22$ $0 \rightarrow k \rightarrow 26$ $0 \rightarrow l \rightarrow 11$	$0 \rightarrow h \rightarrow 23$ $0 \rightarrow k \rightarrow 11$ $-27 \rightarrow l \rightarrow 27$
No. of standard reflections	3	3	3	3
Frequency of standard reflections	Every 500 reflections	Every 200 reflections	Every 200 reflections	Every 200 reflections
Intensity decay (%)	1.63	0.12	0.93	1.05
Refinement				
Refinement on	F	F	F	F
R	0.0386	0.0396	0.0415	0.0490
wR	0.0411	0.0390	0.0413	0.0580
R (opposite chirality)	0.046	0.040	0.045	–
wR (opposite chirality	0.048	0.039	0.043	–
S	2.564	2.102	2.066	2.980
No. of reflections used in refinement	3274	2907	2615	5327
No. of parameters used	425	434	439	452
H-atom treatment	H-atom parameters not refined	H-atom parameters not refined	H-atom parameters not refined	H-atom parameters not refined
Weighting scheme	$w = 1/[\sigma^2(F_o)]$	$w = 1/\sigma^2(F_o)$	$w = 1/[\sigma^2(F_o) + 0.00002\lvert F_o\rvert^2]$	$w = 1/[\sigma^2(F_o) + 0.00003\lvert F_o\rvert^2]$
$(\Delta/\sigma)_{max}$	0.0474	0.0090	0.0350	0.0180
$\Delta\rho_{max}$ (e Å^{-3})	0.28	0.22	0.23	0.27
$\Delta\rho_{min}$ (e Å^{-3})	−0.24	−0.20	−0.17	−0.41
Extinction method	Zachariasen (1967)	Zachariasen (1967)	Zachariasen (1967)	Zachariasen (1967)
Extinction coefficient	0.501 (9) × 10^{-5}	0.252 (7) × 10^{-5}	0.099 (6) × 10^{-5}	0.1448 × 10^{-5}
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)	*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)	*MSC/AFC* (MSC, 1988)
Cell refinement	*MSC/AFC* (MSC, 1988)	*MSC/AFC* (MSC, 1988)	*MSC/AFC* (MSC, 1988)	*MSC/AFC* (MSC, 1988)
Data reduction	*TEXSAN* (MSC, 1995)	*TEXSAN* (MSC, 1995)	*TEXSAN* (MSC, 1995)	*TEXSAN* (MSC, 1995)
Structure solution	*SIR*92 (Altomare *et al.* 1993)	*SIR*92 (Altomare *et al.* 1993)	*SHELXS*86 (Sheldrick, 1985)	*DIRDIF*92 *PATTY* (Beurskens, 1992)
Structure refinement	*TEXSAN* (MSC, 1995)	*TEXSAN* (MSC, 1995)	*TEXSAN* (MSC, 1995)	*TEXSAN* (MSC, 1995)
Preparation of material for publication	*TEXSAN* (MSC, 1995)	*TEXSAN* (MSC, 1995)	*TEXSAN* (MSC, 1995)	*TEXSAN* (MSC, 1995)

be carried out in the solid state. Single crystal photolysis of (1).EtOH (space group $P2_12_12_1$) at room temperature gives photoproduct (2) in >90% enantiomeric excess, particularly with a slow reaction on a single crystal, but reasonably high enantiomeric excess (~70%) is obtained with ground crystals at room temperature (cooling increases the enantiomeric excess to 90%). Photolyses of (1).Pr^nOH and (1).Pr^iOH crystals give similar results, but solution photolyses and photolysis of solid (1).EtOAc give racemic (2).

The absolute configurations of crystals of compounds (1).EtOH, (1).Pr^nOH, (1).Pr^iOH and (3) (all space group $P2_12_12_1$) were all determined. Making the reasonable assumption that the absolute configuration of photoproduct (2) does not change upon reduction to (3), the absolute configurations of (1) in the inclusion complexes and of photoproduct (2) can be correlated and details of the mechanism of the photolyses derived. Compound (1) has no chirality, but fortuitous crystallization of the alcohol–guest inclusion complexes in space group $P2_12_12_1$ gives chiral crystals. Any sample of crystals is likely to have an equal amount of the two enantiomorphic crystals, but larger amounts of enantiomorphically pure crystals are obtained by seeding crystallization solutions with ground single crystals. One single crystal of (1).EtOH was used in the X-ray analysis. The chirality is exhibited in a deviation from planarity of the C(11)═C(12) double-bond system, the P(1)—C(11)—C(12)—P(2) torsion angle having an absolute value of +24° for the particular crystal studied (Fig. 3). The crystal used for the X-ray analysis was then photolyzed and gave 89% enantiomeric excess of (−)-(4b*S*,8b*S*,8c*S*,8d*S*)-(2) (dibenzosemibullvalene numbering system), see Fig. 3. For the (1).Pr^nOH and (1).Pr^iOH compounds, the particular crystals used in the X-ray analyses had configurations with P—C═C—P torsion angles −23 and −21°, and photolyses of these crystals gives (+)-(2).

Based on Zimmerman's mechanism for the di-π-methane rearrangement it is proposed that

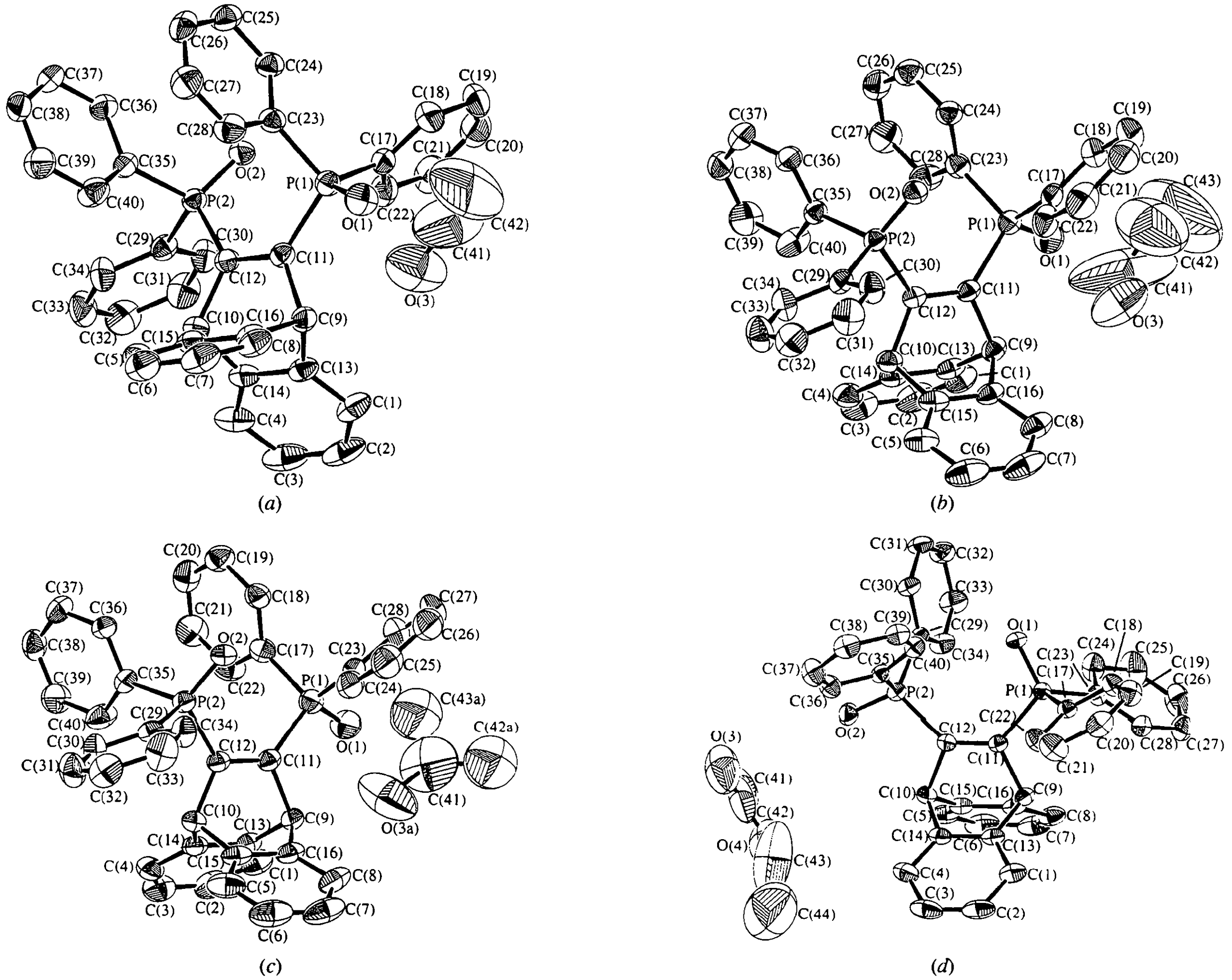
(*a*) (*b*) (*c*) (*d*)

Fig. 2. Views of the complexes (*a*) (1).EtOH, (*b*) (1).Pr^nOH, (*c*) (1).Pr^iOH and (*d*) (1).EtOAc (33% ellipsoids; Johnson, 1976).

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

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

	x	y	z	$U_{\rm eq}$
(1).EtOH				
P(1)	0.01981 (5)	0.10376 (4)	0.7556 (1)	0.0462 (2)
P(2)	0.19793 (5)	0.18189 (4)	0.68914 (10)	0.0404 (2)
O(1)	−0.0501 (1)	0.0963 (1)	0.8390 (3)	0.0690 (9)
O(2)	0.1824 (1)	0.1275 (1)	0.5917 (3)	0.0482 (7)
O(3)	−0.1810 (3)	0.1227 (3)	0.9786 (7)	0.193 (3)
C(1)	−0.0635 (2)	0.3176 (2)	0.6188 (4)	0.070 (1)
C(2)	−0.0479 (3)	0.3727 (3)	0.5393 (5)	0.090 (2)
C(3)	0.0205 (4)	0.4019 (2)	0.5477 (6)	0.095 (2)
C(4)	0.0760 (3)	0.3768 (2)	0.6356 (5)	0.075 (1)
C(5)	0.1028 (2)	0.3099 (2)	1.0861 (5)	0.067 (1)
C(6)	0.0604 (3)	0.3030 (2)	1.2094 (5)	0.078 (2)
C(7)	−0.0078 (3)	0.2726 (2)	1.2059 (5)	0.080 (2)
C(8)	−0.0357 (2)	0.2493 (2)	1.0786 (4)	0.060 (1)
C(9)	−0.0163 (2)	0.2350 (2)	0.8074 (4)	0.0474 (10)
C(10)	0.1128 (2)	0.2877 (2)	0.8151 (4)	0.0483 (10)
C(11)	0.0467 (2)	0.1884 (2)	0.7640 (4)	0.0410 (8)
C(12)	0.1143 (2)	0.2169 (1)	0.7632 (4)	0.0413 (9)
C(13)	−0.0093 (2)	0.2931 (2)	0.7085 (4)	0.051 (1)
C(14)	0.0604 (2)	0.3229 (2)	0.7149 (4)	0.052 (1)
C(15)	0.0751 (2)	0.2866 (2)	0.9595 (4)	0.049 (1)
C(16)	0.0045 (2)	0.2570 (2)	0.9565 (4)	0.048 (1)
C(17)	0.0074 (2)	0.0791 (2)	0.5726 (5)	0.053 (1)
C(18)	−0.0260 (3)	0.0199 (2)	0.5481 (6)	0.077 (2)
C(19)	−0.0404 (3)	−0.0003 (3)	0.4090 (8)	0.096 (2)
C(20)	−0.0215 (3)	0.0389 (3)	0.2983 (7)	0.100 (2)
C(21)	0.0100 (3)	0.0984 (3)	0.3225 (5)	0.086 (2)
C(22)	0.0256 (2)	0.1185 (2)	0.4586 (5)	0.064 (1)
C(23)	0.0931 (2)	0.0579 (2)	0.8359 (4)	0.048 (1)
C(24)	0.1367 (2)	0.0132 (2)	0.7653 (4)	0.0509 (10)
C(25)	0.1907 (2)	−0.0207 (2)	0.8390 (5)	0.066 (1)
C(26)	0.2020 (2)	−0.0098 (2)	0.9826 (5)	0.067 (1)
C(27)	0.1580 (3)	0.0342 (2)	1.0517 (5)	0.078 (2)
C(28)	0.1043 (3)	0.0678 (2)	0.9813 (5)	0.067 (1)
C(29)	0.2418 (2)	0.2483 (2)	0.5954 (4)	0.0442 (10)
C(30)	0.2265 (2)	0.2547 (2)	0.4527 (4)	0.060 (1)
C(31)	0.2590 (3)	0.3036 (2)	0.3751 (5)	0.077 (2)
C(32)	0.3072 (3)	0.3469 (2)	0.4383 (6)	0.078 (2)
C(33)	0.3229 (2)	0.3402 (2)	0.5798 (6)	0.079 (2)
C(34)	0.2908 (2)	0.2913 (2)	0.6599 (4)	0.062 (1)
C(35)	0.2582 (2)	0.1617 (2)	0.8364 (4)	0.0436 (9)
C(36)	0.3151 (2)	0.1182 (2)	0.8098 (4)	0.056 (1)
C(37)	0.3644 (2)	0.1012 (2)	0.9147 (5)	0.066 (1)
C(38)	0.3573 (2)	0.1269 (2)	1.0479 (5)	0.064 (1)
C(39)	0.3015 (3)	0.1694 (2)	1.0758 (4)	0.071 (1)
C(40)	0.2517 (2)	0.1860 (2)	0.9708 (4)	0.065 (1)
C(41)	−0.2099 (7)	0.0648 (4)	1.003 (2)	0.269 (7)
C(42)	−0.220 (1)	0.0253 (5)	1.004 (3)	0.43 (1)
(1).Pr^{n}OH				
P(1)	0.02475 (6)	0.10631 (5)	0.2443 (1)	0.0491 (3)
P(2)	0.20128 (5)	0.18127 (5)	0.3119 (1)	0.0416 (2)
O(1)	−0.0446 (2)	0.0996 (1)	0.1627 (4)	0.075 (1)
O(2)	0.1844 (1)	0.1268 (1)	0.4067 (3)	0.0503 (8)
O(3)	−0.1792 (4)	0.1265 (4)	0.032 (1)	0.238 (4)
C(1)	−0.0251 (3)	0.2546 (2)	−0.0775 (5)	0.065 (1)
C(2)	0.0042 (4)	0.2793 (3)	−0.2024 (6)	0.084 (2)
C(3)	0.0716 (3)	0.3084 (3)	−0.2019 (5)	0.084 (2)
C(4)	0.1120 (3)	0.3142 (2)	−0.0772 (5)	0.069 (2)
C(5)	0.0817 (3)	0.3778 (2)	0.3703 (5)	0.073 (2)
C(6)	0.0271 (4)	0.4031 (3)	0.4545 (6)	0.097 (2)
C(7)	−0.0421 (4)	0.3746 (3)	0.4582 (6)	0.091 (2)
C(8)	−0.0575 (3)	0.3197 (2)	0.3784 (5)	0.069 (1)
C(9)	−0.0090 (2)	0.2373 (2)	0.1923 (5)	0.052 (1)
C(10)	0.1192 (2)	0.2889 (2)	0.1913 (5)	0.050 (1)
C(11)	0.0524 (2)	0.1906 (2)	0.2373 (4)	0.0426 (10)
C(12)	0.1192 (2)	0.2181 (2)	0.2398 (4)	0.042 (1)
C(13)	0.0133 (2)	0.2599 (2)	0.0457 (4)	0.052 (1)
C(14)	0.0830 (2)	0.2889 (2)	0.0458 (4)	0.051 (1)
C(15)	0.0660 (2)	0.3236 (2)	0.2900 (4)	0.054 (1)
C(16)	−0.0026 (2)	0.2949 (2)	0.2911 (4)	0.052 (1)
C(17)	0.0126 (2)	0.0813 (2)	0.4259 (5)	0.057 (1)
C(18)	−0.0212 (3)	0.0225 (3)	0.4491 (7)	0.084 (2)
C(19)	−0.0347 (4)	0.0026 (3)	0.5898 (9)	0.106 (3)
C(20)	−0.0161 (4)	0.0404 (4)	0.6974 (8)	0.111 (3)
C(21)	0.0165 (3)	0.0993 (3)	0.6754 (6)	0.096 (2)
C(22)	0.0319 (3)	0.1202 (3)	0.5389 (5)	0.069 (2)
C(23)	0.0962 (2)	0.0594 (2)	0.1637 (4)	0.051 (1)
C(24)	0.1380 (2)	0.0140 (2)	0.2324 (5)	0.055 (1)
C(25)	0.1907 (3)	−0.0206 (2)	0.1588 (6)	0.068 (2)
C(26)	0.2016 (3)	−0.0096 (2)	0.0170 (6)	0.072 (2)
C(27)	0.1604 (3)	0.0349 (3)	−0.0517 (6)	0.081 (2)
C(28)	0.1067 (3)	0.0697 (2)	0.0190 (5)	0.070 (2)
C(29)	0.2472 (2)	0.2456 (2)	0.4075 (4)	0.046 (1)
C(30)	0.2305 (2)	0.2540 (2)	0.5479 (5)	0.064 (2)
C(31)	0.2643 (3)	0.3006 (3)	0.6270 (6)	0.086 (2)
C(32)	0.3170 (3)	0.3400 (3)	0.5658 (7)	0.083 (2)
C(33)	0.3340 (3)	0.3320 (3)	0.4285 (7)	0.085 (2)
C(34)	0.2999 (3)	0.2844 (2)	0.3478 (5)	0.067 (1)
C(35)	0.2602 (2)	0.1610 (2)	0.1654 (4)	0.045 (1)
C(36)	0.3167 (2)	0.1176 (2)	0.1892 (5)	0.061 (1)
C(37)	0.3644 (3)	0.1009 (2)	0.0842 (6)	0.072 (2)
C(38)	0.3576 (3)	0.1268 (2)	−0.0467 (6)	0.069 (2)
C(39)	0.3029 (3)	0.1695 (3)	−0.0729 (5)	0.083 (2)
C(40)	0.2541 (3)	0.1866 (2)	0.0305 (5)	0.073 (2)
C(41)	−0.191 (2)	0.082 (1)	−0.073 (2)	0.52 (2)
C(42)	−0.198 (1)	0.035 (1)	0.007 (3)	0.36 (1)
C(43)	−0.249 (2)	0.003 (1)	−0.106 (4)	0.58 (2)
(1).Pr^{i}OH				
P(1)	0.02159 (5)	0.10022 (4)	0.2487 (1)	0.0555 (2)
P(2)	0.19590 (4)	0.18219 (4)	0.31083 (9)	0.0452 (2)
O(1)	−0.0481 (1)	0.0908 (1)	0.1679 (3)	0.0811 (8)
O(2)	0.1827 (1)	0.12821 (9)	0.4080 (2)	0.0544 (6)
O(3*a*)	−0.167 (1)	0.110 (1)	−0.021 (2)	0.24 (1)
O(3*b*)	−0.191 (1)	0.115 (1)	0.055 (2)	0.181 (6)
C(1)	−0.0384 (2)	0.2443 (2)	−0.0756 (4)	0.067 (1)
C(2)	−0.0118 (3)	0.2693 (2)	−0.2005 (4)	0.083 (1)
C(3)	0.0546 (3)	0.3015 (2)	−0.2034 (4)	0.082 (1)
C(4)	0.0957 (2)	0.3088 (2)	−0.0787 (4)	0.068 (1)
C(5)	0.0640 (2)	0.3713 (2)	0.3696 (4)	0.083 (1)
C(6)	0.0073 (3)	0.3937 (2)	0.4545 (5)	0.104 (2)
C(7)	−0.0589 (3)	0.3629 (3)	0.4605 (5)	0.101 (2)
C(8)	−0.0711 (2)	0.3083 (2)	0.3817 (4)	0.079 (1)
C(9)	−0.0195 (2)	0.2285 (1)	0.1932 (4)	0.0532 (9)
C(10)	0.1062 (2)	0.2848 (1)	0.1906 (4)	0.0520 (8)
C(11)	0.0456 (1)	0.1848 (1)	0.2371 (3)	0.0456 (7)
C(12)	0.1108 (2)	0.2149 (1)	0.2395 (3)	0.0430 (7)
C(13)	0.0015 (2)	0.2519 (2)	0.0467 (4)	0.0528 (9)
C(14)	0.0692 (2)	0.2832 (1)	0.0450 (4)	0.0521 (9)
C(15)	0.0515 (2)	0.3174 (2)	0.2891 (3)	0.0571 (9)
C(16)	−0.0156 (2)	0.2860 (2)	0.2936 (4)	0.0598 (10)
C(17)	0.0950 (2)	0.0557 (1)	0.1690 (4)	0.0540 (9)
C(18)	0.1384 (2)	0.0117 (1)	0.2387 (4)	0.059 (1)
C(19)	0.1921 (2)	−0.0223 (2)	0.1630 (4)	0.070 (1)
C(20)	0.2027 (2)	−0.0118 (2)	0.0210 (5)	0.077 (1)
C(21)	0.1592 (3)	0.0315 (2)	−0.0477 (4)	0.086 (2)
C(22)	0.1063 (2)	0.0651 (2)	0.0240 (4)	0.077 (1)
C(23)	0.0108 (2)	0.0771 (2)	0.4305 (4)	0.0600 (9)
C(24)	0.0277 (2)	0.1165 (2)	0.5425 (4)	0.072 (1)
C(25)	0.0138 (3)	0.0975 (2)	0.6797 (5)	0.100 (2)
C(26)	−0.0165 (3)	0.0393 (3)	0.7081 (6)	0.115 (2)
C(27)	−0.0341 (3)	−0.0007 (2)	0.5981 (7)	0.110 (2)
C(28)	−0.0211 (2)	0.0174 (2)	0.4574 (5)	0.089 (1)
C(29)	0.2391 (2)	0.2494 (1)	0.4012 (4)	0.0492 (9)
C(30)	0.2910 (2)	0.2885 (2)	0.3396 (4)	0.068 (1)
C(31)	0.3233 (2)	0.3377 (2)	0.4183 (5)	0.087 (1)
C(32)	0.3031 (3)	0.3466 (2)	0.5556 (5)	0.089 (1)
C(33)	0.2509 (2)	0.3081 (2)	0.6180 (4)	0.091 (2)
C(34)	0.2196 (2)	0.2590 (2)	0.5428 (4)	0.069 (1)
C(35)	0.2555 (2)	0.1632 (1)	0.1626 (3)	0.0470 (8)
C(36)	0.3120 (2)	0.1204 (1)	0.1857 (4)	0.0577 (9)
C(37)	0.3599 (2)	0.1046 (2)	0.0798 (4)	0.071 (1)
C(38)	0.3536 (2)	0.1321 (2)	−0.0498 (5)	0.073 (1)
C(39)	0.2965 (2)	0.1742 (2)	−0.0758 (4)	0.083 (1)
C(40)	0.2481 (2)	0.1894 (2)	0.0293 (4)	0.072 (1)
C(41)	−0.2040 (6)	0.0540 (5)	−0.014 (2)	0.271 (6)
C(42*a*)	−0.271 (1)	0.0303 (10)	0.047 (2)	0.250 (6)

Table 2. (*cont.*)

	x	*y*	*z*	U_{eq}
C(42*b*)	−0.269 (1)	0.0573 (9)	−0.112 (2)	0.250
C(43*a*)	−0.1650 (10)	0.0044 (9)	−0.025 (2)	0.234 (6)
C(43*b*)	−0.182 (1)	0.0287 (10)	0.138 (2)	0.234
(1).EtOAc				
P(1)	0.35158 (4)	0.52595 (7)	0.10296 (3)	0.0341 (2)
P(2)	0.27166 (4)	0.55736 (7)	0.24576 (3)	0.0347 (2)
O(1)	0.3987 (1)	0.6052 (2)	0.15567 (8)	0.0437 (5)
O(2)	0.2081 (1)	0.5668 (2)	0.27735 (8)	0.0456 (5)
O(3)	0.1900 (3)	0.2250 (7)	0.4039 (2)	0.210 (3)
O(4)	0.1094 (3)	0.1590 (9)	0.3161 (2)	0.192 (3)
C(1)	0.1677 (2)	0.1511 (3)	0.0472 (1)	0.0549 (9)
C(2)	0.1336 (2)	0.0372 (3)	0.0697 (2)	0.069 (1)
C(3)	0.1039 (2)	0.0530 (4)	0.1207 (2)	0.072 (1)
C(4)	0.1082 (2)	0.1821 (3)	0.1520 (1)	0.0582 (10)
C(5)	0.0496 (2)	0.6312 (3)	0.0997 (2)	0.0576 (9)
C(6)	0.0194 (2)	0.7046 (4)	0.0454 (2)	0.072 (1)
C(7)	0.0478 (2)	0.6900 (4)	−0.0065 (2)	0.071 (1)
C(8)	0.1082 (2)	0.5993 (3)	−0.0062 (1)	0.0570 (9)
C(9)	0.2027 (2)	0.4169 (3)	0.0577 (1)	0.0394 (7)
C(10)	0.1492 (1)	0.4470 (3)	0.1546 (1)	0.0400 (7)
C(11)	0.2612 (1)	0.4737 (3)	0.1153 (1)	0.0349 (6)
C(12)	0.2332 (1)	0.4889 (3)	0.1663 (1)	0.0342 (7)
C(13)	0.1716 (1)	0.2797 (3)	0.0772 (1)	0.0413 (7)
C(14)	0.1425 (1)	0.2952 (3)	0.1297 (1)	0.0416 (7)
C(15)	0.1091 (1)	0.5395 (3)	0.1005 (1)	0.0431 (7)
C(16)	0.1382 (2)	0.5239 (3)	0.0476 (1)	0.0425 (7)
C(17)	0.3958 (1)	0.3652 (3)	0.0847 (1)	0.0379 (7)
C(18)	0.4550 (2)	0.3739 (3)	0.0549 (1)	0.0513 (9)
C(19)	0.4956 (2)	0.2546 (4)	0.0470 (2)	0.060 (1)
C(20)	0.4788 (2)	0.1263 (4)	0.0696 (2)	0.063 (1)
C(21)	0.4215 (2)	0.1165 (3)	0.1002 (2)	0.069 (1)
C(22)	0.3796 (2)	0.2359 (3)	0.1075 (1)	0.0536 (9)
C(23)	0.3279 (2)	0.6303 (3)	0.0319 (1)	0.0414 (8)
C(24)	0.3191 (2)	0.7741 (3)	0.0388 (2)	0.064 (1)
C(25)	0.2987 (3)	0.8597 (4)	−0.0135 (2)	0.092 (2)
C(26)	0.2865 (3)	0.8026 (5)	−0.0722 (2)	0.084 (1)
C(27)	0.2966 (2)	0.6616 (4)	−0.0794 (1)	0.067 (1)
C(28)	0.3167 (2)	0.5751 (3)	−0.0279 (1)	0.0521 (9)
C(29)	0.3118 (1)	0.7302 (3)	0.2413 (1)	0.0361 (7)
C(30)	0.3778 (2)	0.7722 (3)	0.2824 (1)	0.0461 (8)
C(31)	0.4008 (2)	0.9127 (3)	0.2834 (1)	0.0556 (9)
C(32)	0.3587 (2)	1.0105 (3)	0.2441 (1)	0.0590 (10)
C(33)	0.2933 (2)	0.9686 (3)	0.2025 (2)	0.0623 (10)
C(34)	0.2700 (2)	0.8292 (3)	0.2011 (1)	0.0522 (9)
C(35)	0.3432 (2)	0.4399 (3)	0.2884 (1)	0.0380 (7)
C(36)	0.3257 (2)	0.3699 (3)	0.3390 (1)	0.0518 (9)
C(37)	0.3774 (2)	0.2820 (4)	0.3766 (2)	0.065 (1)
C(38)	0.4473 (2)	0.2603 (3)	0.3641 (1)	0.0577 (9)
C(39)	0.4651 (2)	0.3265 (3)	0.3139 (1)	0.0508 (9)
C(40)	0.4141 (2)	0.4170 (3)	0.2765 (1)	0.0428 (8)
C(41)	0.0990 (5)	0.395 (1)	0.3522 (4)	0.198 (4)
C(42)	0.1361 (4)	0.249 (1)	0.3600 (4)	0.168 (4)
C(43)	0.1408 (8)	0.006 (2)	0.3160 (5)	0.292 (8)
C(44)	0.0861 (10)	−0.087 (2)	0.2931 (8)	0.39 (1)

Table 3. *Intra- and intermolecular contacts in the four crystalline complexes of (1)*

	(1).EtOH	(1).Pr^{n}OH	(1).Pr^{i}OH	(1).EtOAc
P═O· · ·P═O contact (Å)	3.339 (2)	3.311 (2)	3.329 (2)	3.406 (6)
P═O· · ·(H)O—*R* distance (Å)	2.75 (1)	2.80 (1)	2.83 (3)	

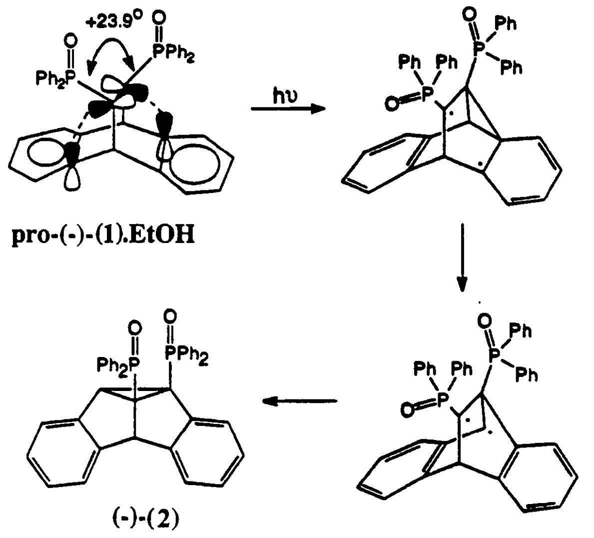

Fig. 3. Absolute configuration correlations in the solid-state photolysis of (1).EtOH.

the initial benzovinyl bridging that will give the (−)-(2) product is favored by a positive P(1)—C(11)═C(12)—P(2) dihedral angle [+24° for (1).EtOH]. The geometry with this positive dihedral angle will lead to a better orbital overlap between the interacting orbitals in the transition state for the (−)-2 product, as well as to a diminution of the steric interaction between the bulky diphenylphosphine oxide groups (Fig. 3). In the alternative pathways leading to the unobserved enantiomer the diphenylphosphine oxide groups would be driven toward each other during the benzo-vinyl bridging. A similar explanation has successfully accounted for the absolute steric course of other solid-state di-π-methane photorearrangements (Garcia-Garibay, Scheffer, Trotter & Wireko, 1989; Gudmundsdottir, Scheffer & Trotter, 1994).

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