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Enantioselective Photoreactions of Cycloocta-2,4,6-trien-1-one and Cycloocta-2,4-dien-1-one in Their Inclusion Complexes with (*R*,*R*)-(−)-1,6-Bis(*o*-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol: Mechanistic Study Based on X-ray Crystal Structure Analyses

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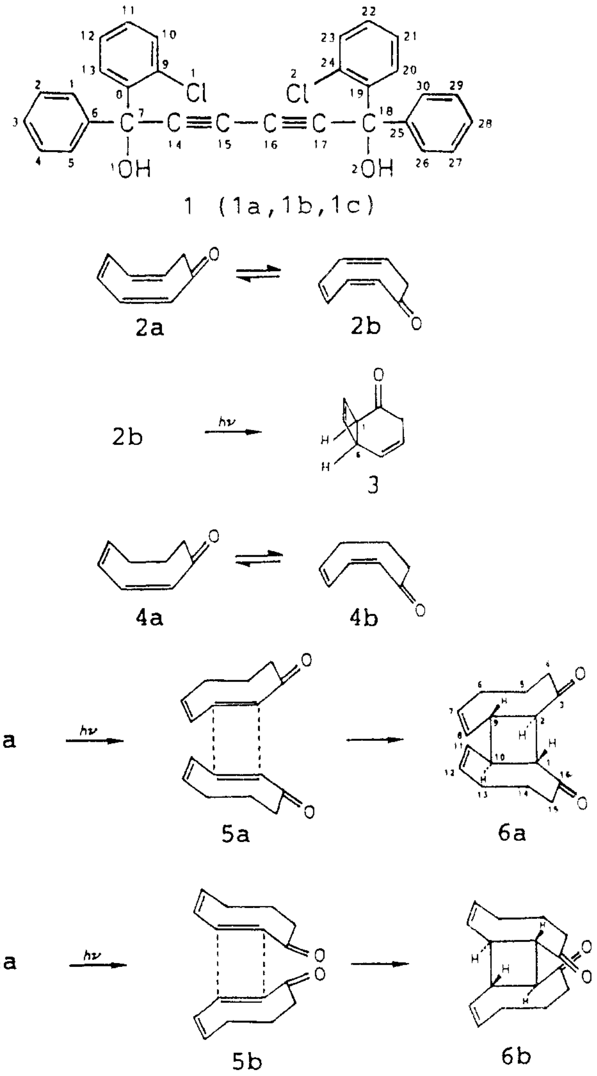
A host molecule, (*R*,*R*)-(−)-1,6-bis(*o*-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol (**1**), includes two enantiomers (**2a** and **2b**) of a guest molecule, cycloocta-2,4,6-trien-1-one (**2**), and gives the crystalline complex I (host:guest = 1:2). On the other hand, **1** includes one of the two enantiomers (**4a** and **4b**) of cycloocta-2,4-dien-1-one (**4**) and produces the crystalline complex II (3:2). Irradiation of I and II in the solid state gives an optically active intramolecular photocyclization product, (−)-bicyclo[4.2.0]octa-4,7-dien-2-one (**3**), and an intermolecular photodimerization product, (−)-*trans-anti-trans*-tricyclo[8.6.0.0^{2,9}]hexadeca-7,11-diene-3,16-dione (**6a**), respectively. Mechanisms of the enantioselective photoreactions of **2** in I and **4** in II were studied by X-ray crystal structural analyses. In both complexes I and II, one host links two guests through the O–H- - -O hydrogen bond. There are two enantiomers in complex I, in which one enantiomer, **2a**, is enclosed loosely and another one, **2b**, tightly. On the other hand, in complex II, there is a column composed only of host molecules, the column plays a role as chiral hydrophobic spacer, and one enantiomer, **4a**, is included stereoselectively. Mechanisms of the enantioselective photoreactions of **2** in I and **4a** in II are demonstrated.

We have found that 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol includes many kinds of organic compounds[2,3] and forms crystalline complexes stoichiometrically. Since the complexation occurs selectively, it can be used for isolation and refinement of isomeric compounds.[4,5] Furthermore an enantioselective reaction can be expected in the crystalline complex when the reactant is crystallized with an optically active host compound. According to this idea, we designed the host compound **1**, which could form cyrstalline complexes with a variety of guest compounds and had excellent enantioselective ability.[6]

Cycloocta-2,4,6-trien-1-one exists as an equilibrium mixture of **2a** and **2b** in solution, and conversion between the two optical conformers is fast around room temperature with an activation energy of 11.9 kcal/mol.[7] Photoreaction of **2** in pentane solution is known to give racemic **3** in 31% yield after irradiation for 21 days.[8] When 1:2 crystalline complex I of **1** and **2** was irradiated for 7 days, however, 50% conversion occurred and (−)-**3** was obtained in 28% yield. The photoreaction of **2** in I is clearly shown to proceed not only enantioselectively but also much more efficiently. On the other hand, irradiation of **4** in pentane for 1 h gives racemic **6**[9] in 10% yield along with polymeric materials.[10] However, irradiation of 3:2 complex II of **1** and **4** for 48 h gave (−)-**6** in 78% ee[11] and 55% yield.

Scheme I



By the host–guest complexation method, one isomer of an enantiomeric mixture can be isolated as a component of an inclusion compound.[12] In order to understand the mechanisms of the enantioselective photoreactions of **2** and

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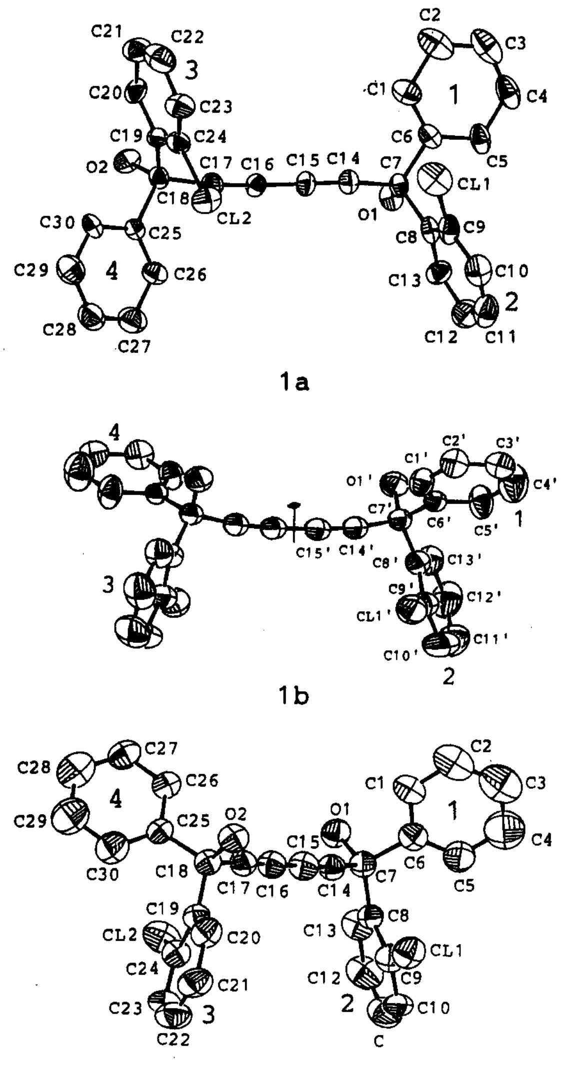

Figure 1. Molecular structure and numbering of the host molecule ((*R*,*R*)-(−)-1,6-bis(*o*-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol) **1a** in complex I and **1b** and **1c** in complex II. Numbering of the phenyl rings is shown in large letters.

4, X-ray crystal structures of I and II were studied.

Results and Discussion

About Symmetry in the Host Molecules 1a–c and Crystallographic Symmetry. As illustrated in Scheme I and numbered in Figure 1, the host molecule **1** is symmetrical, i.e., the absolute configurations around C7 and C18 are both *R*, and each terminal bears a hydroxyl, a phenyl, and an *o*-chlorophenyl group. The left side of the molecule could coincide with the right side by rotation of either half of the molecule by 180° around an axis at the center of the C15–C16 bond. therefore, this molecule itself has 2-fold rotation symmetry. On the other hand, a crystal by three-dimensional repeating of a unit cell belongs one of 230 space groups and each space group has its own symmetries, namely, a center of symmetry, a mirror plane, glide planes, rotation axes, and screw axes. By observing X-ray diffractions from a crystal, we can determine the unit cell dimensions and space group of the crystal. As the space group of complex I is $P2_1$, there is a 2-fold screw axis along the *b* axis. The structural unit consisting of one host (**1a**) and two guests (**2a** and **2b**) is called an asymmetric unit, and two structural units are related by a 2-fold screw axis and make up a unit cell ($Z = 2$). We can assume the existence of 2-fold rotation symmetry in the host molecule **1**, but there is no such symmetry in the crystal structure of I. This is a case in which the symmetry in a molecule does not coincide with that in a crystal. On the other hand, about the complex II, the space group of $C2$ and $Z = 4$ indicate that one-half of the host and one guest molecule are in an asymmetric unit. The crystallographic 2-fold rotation axes are parallel to the *b* axis at 0, $^1/_2$, and 1 along either or both the *a* and *c* axes. The host **1b** has 2-fold rotation symmetry in the molecule (Figure 1, **1b**), and its rotation axis coincides with that in the crystal lattice ($x = {}^1/_2$, $z = 1$, Figure 5). On the other hand, the host **1c** appears to have 2-fold rotation symmetry (Figure 1, **1c**), but it is pseudo one and two **1c** molecules are related by a crystallographic 2-fold rotation axis at $x = {}^1/_2$, $z = {}^1/_2$ in Figure 5.

Molecular Structures of the Host (1a) and Guest (2a and 2b) in Complex I. The molecular structure and numbering of **1a** (i.e., **1**) in I are shown in Figure 1. Bond lengths and angles are available as supplementary material. The molecule is composed of a linear diacetylene skeleton with hydrophobic phenyl and *o*-chlorophenyl residues and hydroxyl groups which act as hydrogen-bond donors at both the right and left sides. Four atoms in the diacetylene linkage, C14, C15, C16, and C17, are nearly in a straight line, which, however, bends at C14 and C17. Two hydroxyl groups are directed near to the same side and act as hydrogen-bond donors. Each phenyl and *o*-chlorophenyl group is planar, and their dihedral angles between planes 1 and 2 and planes 3 and 4 are 86.7° and 73.3°, respectively. Distances of the C–C bonds which connect the diacetylene linkage and the phenyl or *o*-chlorophenyl rings, range from 1.529 (13) Å to 1.577 (12) Å. This means that the phenyl and *o*-chlorophenyl rings can rotate about the C6–C7, C7–C8, C18–C19, and C18–C25 bonds. Significantly short C–C single bonds in the diacetylene linkage, C7–C14 = 1.445 (13) Å, C15–C16 = 1.412 (13) Å, and C17–C18 = 1.441 (12) Å, indicate electron transfer from the triple bond to the single bond; therefore, rotation about the diacetylene skeleton is not so easy as that about C6–C7, C7–C8, C18–C19, and C18–C25.

The molecular structure, naming, and bond lengths and angles of the guest, **2a** and **2b** (i.e., **2**), in I are shown in Figure 2. Each of **2a** and **2b** is a flipping optical conformer in the liquid state as illustrated in Scheme I. Interestingly both conformers are also found in the crystalline host–guest (1:2) complex I. The molecular structures of **2a** and **2b** in I are roughly related by a mirror plane. As shown in Figure 2, the thermal factors of **2a** are much larger than those of **2b**. The molecular structure of **2a** can be explained by three planes, that is, through C36A, C37A, C38A, C31A, C32A, and O3A, through C34A, C35A, C36A, and C37A, and through C32A, C33A, C34A, and C35A. The conformations about three double bonds, C33A–C34A, C35A–C36A, and C37A–C38A, are all cis. The molecular structure of **2b** is different from that of **2a**. In this molecule, C36B, C37B, C38B, C31B, and O3B are in the first plane, C34B, C35B, C36B, and C37B are in the second one, and C32B, C33B, C34B, and C35B are in the third one. Consequently, **2a** is a half-chair form, and **2b** a boat form.

Crystal Structure of Complex I. The crystal structure of I is shown in Figure 3. As shown in Figure 3, two hydroxyl groups of **1a** point to the same direction and work as the hydrogen-bond donors to **2a** and **2b** (O1- - -O3B = 2.739 (10) Å, O2- - -O3A = 2.784 (12) Å). Moreover, a set of the guest molecules **2a** and **2b** is included in the hy-

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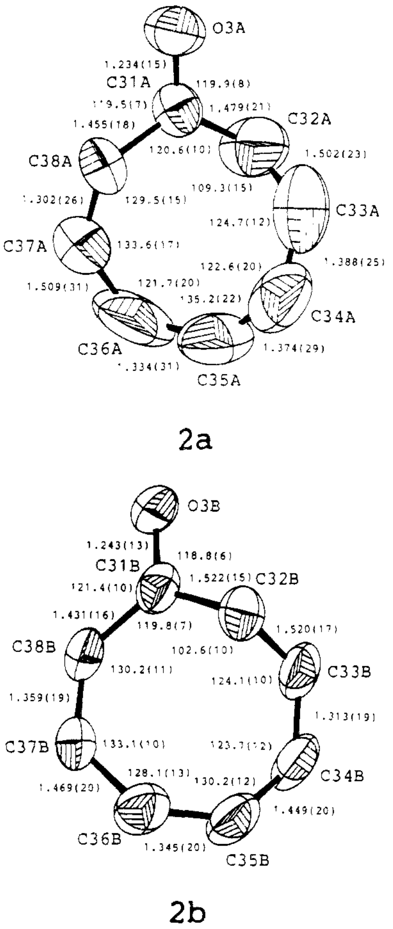


Figure 2. Molecular structure, numbering, and bond lengths and angles of the guest molecules (2a and 2b) in I, drawn by ORTEP at 50% probability. The bond lengths (Å) and angles (deg) are shown with their esd's in parentheses.

drophobic phenyl and *o*-chlorophenyl groups of neighboring **1a** molecules interacting with each other and with the neighboring **1a** by van der Waals contacts. Generally speaking, the thermal motion of the guests is larger than that of the host, and the ratio of their average thermal factors is 2:1.3:1 for **2a**, **2b**, and **1a**, respectively. The larger thermal factor in **2a** than **2b** indicates that there is much more space around **2a** than around **2b**.

Reaction Mechanism of Intramolecular Photocyclization of 2 in Complex I. As mentioned above, **2a** and **2b** are fixed by the host–guest hydrogen bonds and are included in the hydrophobic cavity stabilized by van der Waals contacts in the crystalline complex I. The photocyclization reaction of **2** in solution produces the racemic **3**,[8] but irradiation of crystalline complex I gives the optically active (−)-**3**. Although the optical purity of (−)-**3** could not be observed, consideration using a molecular model of **2** in the crystalline environment leads to the conclusion that the cyclization reaction of **2a** and **2b** in I should result in the generation of (*S*,*S*)-(−)-**3** in 50% ee, because **2b** produces (*S*,*S*)-(−)-**3** in 100% ee and **2a** with large temperature factors may produce racemic products (0% ee) as in the solution.

Molecular Structure of the Hosts (1b and 1c) and Guest (4a) in Complex II. The molecular structures and numbering of **1b** and **1c** in II are shown in Figure 1. There are two types of host molecule, namely, **1b** and **1c**, which are found in II as the host–guest (**1b**–**4a**) complex and in host–host (**1c**–**1c**) polymer formation through hydrogen bonds as shown in Figure 7. Bond lengths and angles of **1b** and **1c** are also available as supplementary material. About the bond lengths, angles, and planarity of the phenyl and *o*-chlorophenyl groups, there are no significant differences among the hosts in complexes I (**1a**) and II (**1b** and **1c**) except the angle of C16–C17–C18 of 178.8 (6)° in **1c** indicating that the left side of the diacetylene linkage of **1c** does not bend. Large differences are found in the corresponding torsion angles of **1a** in I and of **1b** and **1c** in II. As illustrated in Figure 1 and summarized in Table I, the directions of the two hydroxyl groups of each host molecule are different for I and II. The torsion angles of O1–C7- - -C18–O2 are −32.5°, −84.8°, and −116.1° for **1a**, **1b**, and **1c**, respectively. The former two torsion angles are those of the host:guest = 1:2 molecular complexes I and II, respectively, and the last one is that of the host–host dimmer in II. Judging from the bond distances among atoms in the diacetylene linkage, the left- and right-side terminals made up of the hydroxyl, phenyl, and *o*-chlorophenyl groups could rotate independently around the axes at the C18–C17 and C14–C7 bonds. The overall structures about the terminal of **1a** in I are similar to those of **1b** and **1c** in II. Owing to the bulky chlorine atom at the ortho position of the phenyl group, the torsion angles of O1–C7–C8–C9 and O2–C18–C19–C24 are roughly 180°, that is, there is a trans conformation in both I and II. The dihedral angles between the planes of the phenyl and *o*-chlorophenyl groups are also summarized in Table I for complexes I and II. The phenyl and *o*-chlorophenyl planes attached to the same terminal or different terminals are roughly arranged orthogonally. Moreover, the two *o*-chlorophenyl rings attached to different terminals are roughly parallel to each other for I and II. As shown in Figure 1, **1b**, a crystallographic 2-fold rotation axis runs through the center of **1b**. The molecular structure, numbering, and bond lengths and angles of **4a** are shown in Figure 4. The molecular shape of **4a** is a boat form which is characterized by two planes through C36, C37, C38, and C31 and through C34, C35, C36, and C37. The C–C double

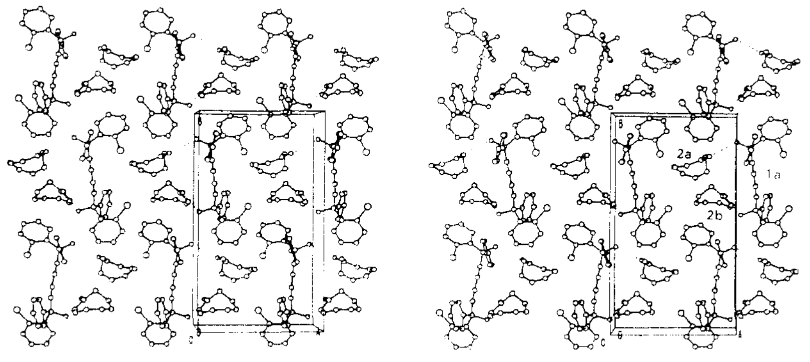


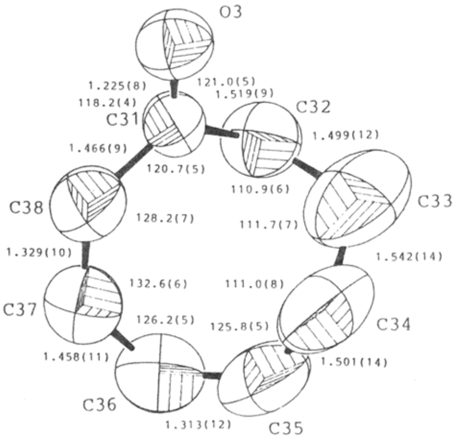
Figure 3. Stereoscopic view of the crystal structure of I (host:guest = 1:2) along the *c* axis. Hydrogen bonds are indicated by dotted lines.

Table I. Torsion Angles and Dihedral Angles Involving Phenyl and *o*-Chlorophenyl Groups in 1a in Complex I and in 1b and 1c in Complex II[a]

	torsion angle, deg		
	1a	**1b**	**1c**
O1–C7–C18–O2	−32.5		−116.1
(O1′–C7′–C7″–O1″)		−84.8	
C1–C6–C7–C14	−8.4	−18.9	−50.2
C5–C6–C7–C14	177.2	164.1	130.5
C1–C6–C7–O1	112.1	97.6	65.3
C5–C6–C7–O1	−62.2	−79.3	−114.1
O1–C7–C8–C9	174.4	−175.9	−171.9
O1–C7–C8–C13	−6.6	4.8	8.9
C14–C7–C8–C9	−68.9	−56.5	−54.1
C14–C7–C8–C13	110.1	124.2	126.7
O2–C18–C25–C26	80.5	–	72.7
O2–C18–C25–C30	95.6	–	−103.0
C17–C18–C25–C26	158.0	–	−45.0
C17–C18–C25–C30	−25.9	–	139.3
O2–C18–C19–C24	173.0	–	−174.0
O2–C18–C19–C20	−9.1	–	6.9
C17–C18–C19–C24	−69.2	–	−57.1
C17–C18–C19–C20	108.7	–	123.8

	dihedral angle, deg		
	1a	**1b**	**1c**
1–2*	86.7	88.0	71.9
1–3*	88.3	61.9	87.8
1–4	19.0	56.4	53.3
2*–3*	7.2	33.4	32.6
2*–4	74.5	(61.9)	89.4
3*–4	73.3	(88.0)	76.0

[a] Plane numbers are shown in Figure 1. A plane number with an asterisk indicates an *o*-chlorophenyl group.



4a

Figure 4. Molecular structure, numbering, and bond lengths and angles of **4a** in II, drawn by ORTEP at 50% probability. The bond lengths (Å) and angles (deg) are shown with their esd's in parentheses.

bond lengths of C35–C36 and C37–C38 are 1.313 (12) and 1.329 (10) Å, respectively, and the C–C single bond lengths of C31–C38 = 1.466 (9) Å and C36–C37 = 1.458 (11) Å are shorter than those of C31–C32 = 1.519 (9) Å, C32–C33 = 1.499 (12) Å, C34–C35 = 1.501 (14) Å, and C33–C34 = 1.542 (14) Å.

Crystal Structure of Complex II. As shown in Figure 5, the crystal structure of II is well explained by a layer structure. One layer is composed only of the host **1c** molecules. The **1c** molecules are connected through host–host O–H- - -OH hydrogen bonds and π–π stacking of C2···C27($-X+2,Y,-Z+1$) = 3.289 (10) Å and C4···C29($-X+2,Y-1,-Z+1$) = 3.508 (11) Å between the phenyl groups whose dihedral angle is 11°, and they construct a chiral hydrophobic column enclosing their hydrophilic groups. A framework of the left-handed double-helical structure along the *b* axis is shown in Figure 7. Between the hydrophobic layers, another layer composed of the host–guest (**1b**–**4a**) pair through the O1′–H- - -O3 hydrogen bonds of 2.831 (6) Å is sandwiched and arranges along [0,0,1]. Two-fold symmetry in **1b** coincides with the crystallographic 2-fold symmetry. As the torsion angle of O1′–C7′- - -C7″–O1″ (see Figure 1, **1b**, and Figure 6) is −84.8°, photodimerizative sites of **4a** are so far separated as C37- - -C37 = 9.780 (10) Å and C38- - -C38 = 8.929 (10) Å by 2-fold rotation symmetry, and 7.780 Å by a unit translation toward the *b* axis. The average thermal motion

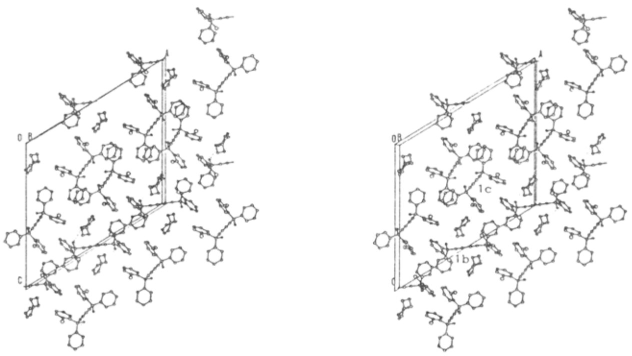
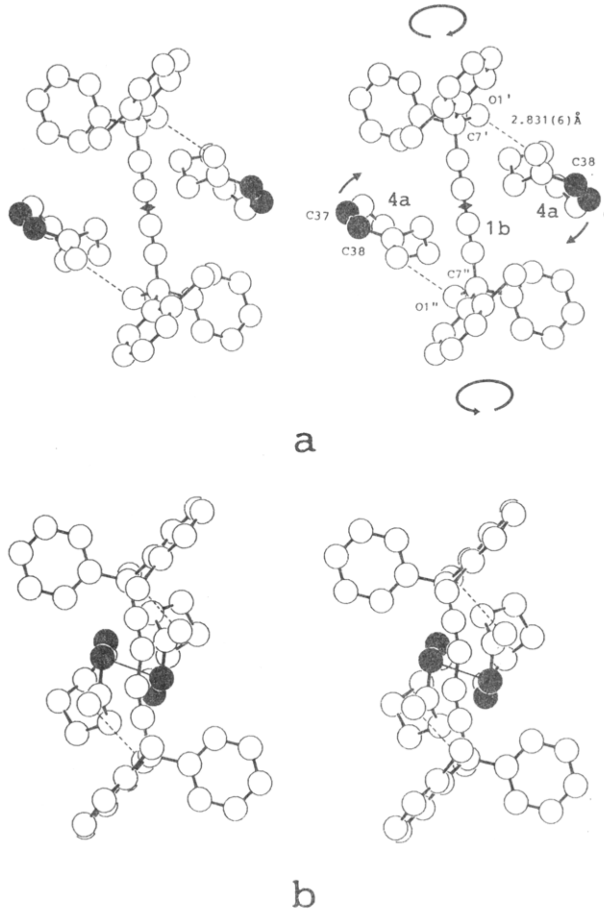


Figure 5. Stereoscopic view of the crystal structure of II (host:guest = 3:2) along the *b* axis. Hydrogen bonds are indicated by dotted lines.



a

b

Figure 6. (a) Stereoscopic view of the molecular structure of **1b** and **4a** in II. (b) Stereoscopic view of a model structure which is rotated along the arrows in part a. The reaction sites (C37 and C38) are indicated by solid circles, a thin line shows the formation of a new C38–C38 bond, and the hydrogen bonds are indicated by dotted lines.

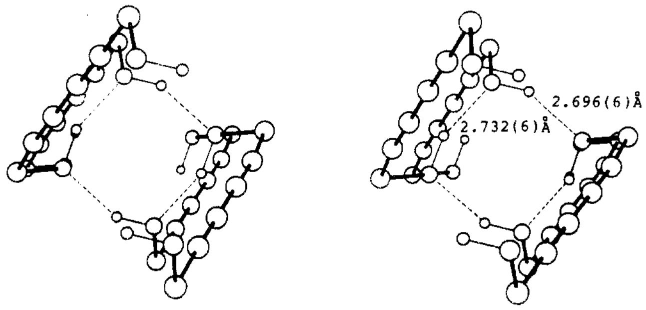


Figure 7. Stereoscopic drawing of the left-handed double helical polymer formation through the OH- - -O hydrogen bonds between **1c**'s. Only the diacetylene linkages of **1c** are drawn. Hydrogen bonds are indicated by dotted lines.

of the guest is about 1.5 times larger than that of the hosts.

Reaction Mechanism of Intermolecular Photodimerization of 4a in Complex II. As illustrated in Scheme I, photoirradiation of **4a** in II gives optically active **6a**. However, the intermolecular reaction-site distances between the C37 atoms or the C38 atoms of **4a** in II are 8–10 Å as mentioned above. Even though the separation distance is two times longer than the 4.2-Å distance recommended for polymerization in the solid state,[13] the enantioselective photodimerization reaction does occur in II just as in Scheme I.[9] The photodimerization reaction seems to start from rotation of **1b** and **4a** while keeping the **1b**- - -**4a** hydrogen bond around the the diacetylene linkage until the two reaction sites of **4a** come close to make new coordinate bonds. We confirmed by distance calculations that the right and left **1b**- - -**4a** pairs could be rotated as indicated by arrows in Figure 6a around the diacetylene linkage without an abnormally short contact with 1c, and the rotational angle of 35° for each **1b**- - -**4a** pair brings them within the distance for the possible intermolecular dimerization reaction; but this rotation is not sufficient to produce the intermolecular photodimerization product. As shown in Figure 6a, the **4a** molecules themselves must rotate until two sites come to face each other, while keeping the **1b**- - -**4a** hydrogen bond. The synchronous rotation of **1b** and **4a** in the chiral hydrophobic environment of **1c** could produce the chiral photodimerization product **6a** in Scheme I. In this case, however, boat-form **4a** isomerizes initially by irradiation to chair-form **5a** of *R* configuration through the flipping down of its ene moiety and its dimerization gives finally **6a** of 1*R*,2*R*,9*S*,10*S* configuration. As the ketone moiety of **4a** is fixed in II by formation of the **1b**- - -**4a** hydrogen bond, the ene moiety[9] would be more easily flipped down and then **6a** of the former configuration would be produced (Figure 6b).

Another possibility of the photodimerization reaction of **4a** in II is between two **4a**'s related by a unit translation along the *b* axis, but this possibility seems to be low, because in this case the **1b**- - -**4a** hydrogen bond must be broken first. Moreover, one of the two **4a**'s must rotate to produce new coordinate bonds between two C37=C38 reaction sites (Figure 5).

Experimental Section

When a solution of **1** (0.966 g, 2 mmol) and **2** (0.48 g, 4 mmol) in ether–hexane (1:1, 5 mL) was kept at room temperature for 12 h, a 1:2 complex (I) of **1** and **2** was obtained as pale yellow prisms (1.1 g, 92%), mp 67–69 °C. When a solution of **1** (2.42 g, 5 mmol) and **4** (0.61 g, 5 mmol) in ether–hexane (1:1, 5 mL) was kept at room temperature for 12 h, a 3:2 complex (II) of **1** and **4** was obtained as colorless needles (2.2 g, 78%), mp 105–108 °C.

Table II. Summary of Crystal Data and Intensity Collection

	complex I	complex II
cryst color	pale yellow	colorless
formula	$(C_{30}Cl_2H_{20}O_2)\cdot 2(C_8H_8O)$	$1.5(C_{30}Cl_2H_{20}O_2)\cdot(C_8H_{10}O)$
fw	711.7	874.3
cryst system	monoclinic	monoclinic
space group	$P2_1$	$C2$
a, Å	11.073 (5)	27.241 (6)
b, Å	19.591 (3)	7.780 (3)
c, Å	8.786 (1)	24.145 (5)
α, deg		
β, deg	94.86 (2)	121.26 (1)
γ, deg		
V, Å^3	1899 (1)	4374 (2)
Z	2	4
D_{measd}, Mg m^{-3}	1.285 (2)	1.286 (1)
D_{calcd}, Mg m^{-3}	1.259	1.286
μ, cm^{-1}	18.81	22.71
cryst size, mm	0.6 × 0.3 × 0.2	0.6 × 0.3 × 0.2
data range, deg	$0 < 2\theta < 125$	$0 < 2\theta < 125$
scan mode	$\omega-2\theta$	$\omega-2\theta$
scan speed in ω, deg min^{-1}	4	4
obsd data	2480	3798
data with $F_o > 3\sigma(F_o)$	2318	3472
R	0.059	0.043

Irradiation[14] of finely powdered I (1.1 g) in the solid state for 168 h gave a crude reaction product. Purification of the crude reaction product by column chromatography on silica gel using $CHCl_3$ as solvent gave recovered **2** (0.55 g, 50%) and (–)-**3**, which on distillation gave (–)-**3** (0.052 g, 14%, bp 200 °C/20 mmHg, $[\alpha]_D$ –62.9° (*c* 0.12, $CHCl_3$)). However, its optical purity could not be determined.

Irradiation[14] of finely powdered II (2 g) in the solid state for 48 h gave a crude reaction product. Purification of the crude product by column chromatography on silica gel using $CHCl_3$ as solvent gave (–)-**6**, which on distillation gave pure (–)-**6** of 78% ee (0.16 g, 55%, bp 200 °C/1 mmHg, $[\alpha]_D$ –34.7° (*c* 0.11, $CHCl_3$)). The optical purity was determined by HPLC using chiral-phase Chiral Cell OC.[11]

Details of the crystal data for the respective complexes and their data-collection parameters are summarized in Table II. For crystals both of I and of II, X-ray experiments were performed according to common procedures. The X-ray data were observed on an automated Rigaku AFC-5 diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.5418 Å) at 40 kV and 30 mA, using crystals enclosed in a thin-walled glass capillary. The precise cell parameters were determined by a least-squares fit of 2θ angles for 25 reflections (35° < 2θ < 40°). The $\omega-2\theta$ scan method was employed for the intensity measurement, and the background was counted for 5 s at both sides of the peaks. Three standard reflections were monitored at 100-reflection intervals and showed a random variation of 5% with no significant trends. Lorentz and polarization corrections were applied for intensity data, but no corrections were made for the absorption and extinction effects.

Both structures I and II were solved by a direct method (program MULTAN78)[15] and refined by a block-diagonal least-squares method (program HBLS)[16] with anisotropic thermal parameters for non-hydrogen atoms. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where a unit weight was applied throughout the refinement. All the hydrogen atoms were obtained on a difference

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(13) Schmidt, G. M. *Pure Appl. Chem.* **1971**, *27*, 647.

(14) All irradiations of the complex were carried out in the solid state at room temperature by using a 100-W high-pressure Hg lamp.

(15) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. W. *MULTAN78, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*; Universities of York, England, and Louvain, Belgium, 1978.

(16) Ashida, T. UNICS, The Universal Crystallographic Computing System, Osaka, 1979.

Fourier map and were included in subsequent refinements with isotropic thermal factors. Final atomic parameters are available as supplementary material. Atomic scattering factors were taken from *International Tables for X-ray Crystallography*.[17] All the computations were carried out on Mitsubishi MX-2000 and IBM-3081 GX3 computers at Shimane University.

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Supplementary Material Available: Tables of bond lengths and angles of **1a–c**, atomic coordinates with isotropic thermal parameters of non-hydrogen atoms, and final atomic coordinates with isotropic thermal parameters of hydrogen atoms for complexes I and II (12 pages); listing of observed and calculated structure factor amplitudes for complexes I and II (25 pages). Ordering information is given on any current masthead page.

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[17] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

Photochemistry of 2,5,7,7-Tetraphenyl-7-boratabicyclo[4.1.0]hepta-2,4-diene (a Boratanorcaradiene Anion): No Evidence for Diphenylborene Anion

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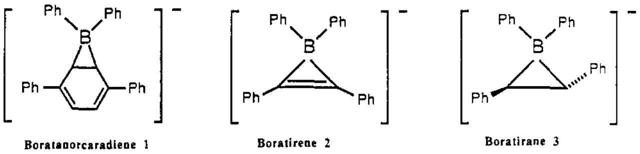
Irradiation of 2,5,7,7-tetraphenyl-7-boratabicyclo[4.1.0]hepta-2,4-diene anion (1, a boratanorcaradiene, as its potassium or tetramethylammonium salt) with UV light leads to formation of *p*-terphenyl in high yield. This observation led us to consider the possibility that diphenylborene anion (Ph_2B^-, an analogue of diphenylcarbene) might also be formed in this reaction. We designed and carried out a series of spectroscopic and chemical experiments to detect and characterize the borene. None of these experiments provides evidence for the formation of diphenylborene from this reaction. We suggest that the formation of *p*-terphenyl from the photolysis of 1 is initiated by an electron-transfer (photoionization) process. We also reexamined experiments reported earlier that were claimed to show that diphenylborene is formed from the irradiation or overirradiation of tetraphenylborate. Each of these experiments is ambiguous and cannot be relied upon to demonstrate the formation of the borene by this route.

Recently there has been considerable interest and some controversy concerning the photochemistry of tetraarylborate salts $\{M^+[Ar_4B]^-\}$. In the first experiments in this area, Grisdale and co-workers studied the photolysis of tetraphenylborate anion in protic solvents and concluded that unisolated bridged-boron intermediates are formed.[1] Later, Eisch and co-workers claimed that irradiation of tetraphenylborate anion (254 nm) in tetrahydrofuran (THF) or dimethoxyethane (DME) solution caused it to fragment to biphenyl and diphenylborene $[Ph_2B]^-$, a carbene analogue of some interest.[2] This conclusion was based on the results of a trapping experiment with diphenylacetylene and the observation that D_2 is evolved when the photolysis mixture is quenched with deuteriated acetic acid. Our reinvestigation of the photolysis of tetraphenylborate convinced us that Eisch's experiments had been misinterpreted.[3] We concluded that there was no valid experimental evidence that diphenylborene is formed from photolysis of tetraphenylborate.

In subsequent work, we succeeded in isolating and characterizing by X-ray crystallography the blood-red bridged-boron product (boratanorcaradiene, Chart I) formed from the irradiation of a tetraarylborate.[4] Also, we succeeded in the preparation, isolation, and characterization by X-ray crystallography[5] of the boratirene anion 2 claimed by Eisch to be the product of reaction of diphenylborene with diphenylacetylene when the irradiation of tetraphenylborate is performed in the presence of the acetylene.

Chart I



In a recent paper in this Journal, Eisch and co-workers painstakingly reconsidered the experiments that led to the earlier report that diphenylborene is formed from photolysis of tetraphenylborate.[6] They are compelled by the data to modify their earlier conclusion. These workers claim now that diphenylborene is a red compound, stable in DME solution for hours, formed from the "... prolonged irradiation of the Schuster intermediate (a boratanorcaradiene)".

We report herein results from the study of the photochemistry of 2,5,7,7-tetraphenyl-7-boratabicyclo[4.1.0]-hepta-2,4-diene (1, a boratanorcaradiene) and a search for facts that might substantiate a claim that its photolysis generates diphenylborene. This study provides no experimental evidence to support the conclusion that the photolysis of boratanorcaradienes generates diphenylborene either as a transient species or as a compound

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