Enantioselective Photocyclization of Acrylanilides and *N*-Ethyl-*N*-methylbenzoylformamide in Inclusion Crystals with (*R*,*R*)-(−)-[*trans*]-2,3-Bis(α-hydroxydiphenylmethyl)-1,4-dioxaspiro-[4.4]nonane and -[4.5]decane. Mechanistic Study Based on X-Ray Crystal Structure Analyses

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X-Ray structure analyses of the inclusion complexes indicated that the high stereo- and enantioselectivities in photocyclization of cyclohex-1-enecarboic acid methyl-phenyl-amide (**3**), *N*-methyl, *N*-{(*E*)-methylmethacryloyl}anilide (**5**), *N*-methyl, *N*-(methacryloyl)anilide (**8**), and *N*-ethyl-*N*-methylbenzoylformamide (**10**) are the result of their chiral conformations in the clathrate crystalline environment with the title chiral hosts [(−)-**1** and (−)-**2**, respectively]. The chirality of acrylanilides and benzoylformamide can be indicated by the sign of the torsion angle in the backbone of the molecule, C–N–C(=O)–C and O=C(–Ph)–C(=O)–N, respectively. A partial single-crystal-to-single-crystal transformation of 1 : 1 complex of **10** with (−)-**1** was performed by photoirradiation to observe in situ the photoproduct.

The photocyclization reaction of acrylanilide to 3,4-dihydroquinolin-2-one has long been studied for the preparation of heterocyclic compounds.[1] However, no attempt for enantiocontrol of this reaction has been reported, except for one enantioselective photocyclization of anilide **3** in benzene-diethyl ether containing (+)-di(*p*-toluoyl)tartaric acid, which affords a mixture of *trans*-**4** and its *cis*-isomer in low optical purity.[2] Recently, we reported highly enantioselective photocyclization reactions of anilides **3**, **5**, and **8** to the corresponding almost optically pure 3,4-dihydroquinolin-2-ones **4**, **6**, and **9** by utilizing the inclusion crystals with optically active host compounds **1** and **2**.[3] The enantioselective photocyclizations of *N*,*N*-dialkylphenylglyoxylamides (*N*,*N*-dialkylbenzoylformamides) to β-lactam derivatives in inclusion compounds with optically active hosts have also been reported.[4] As can be seen in Table 1, the absolute configurations of the major photoproducts are dependent on the hosts, although hosts **1** and **2** only differ in the size of the cycloalkane moiety, i.e. five-membered and six-membered rings, respectively. To elucidate the mechanism of the enantio- and stereo-selectivities, the structures of the inclusion crystals (**I**, **II**, **IV**, **V**, **VII**, and **VIII**) have been determined by X-ray analyses. The crystal structure of **III** and its partial single-crystal-to-single-crystal transformation were reported previously.[5]

The clathrate compound **I** shows a polymorphism. Elongated thin prisms **I** were obtained from a butyl ether solution and bulky prisms **I′** from a toluene solution. The major photoproduct for **I** and **I′** is **(+)-4** and (−)-**4**, respectively.

Results and Discussion

Stereo- and Enantioselectivities. The photoirradiation of a 1 : 1 inclusion complex **I** of anilide **3** with five-membered ring host (−)-**1** in the solid state gave an optically active photocyclization product, **(+)-4**, in 70%ee (Table 1). On the other hand, the same photoirradiation of a 1 : 1 inclusion complex **II** of **3** with six-membered ring host (−)-**2** gave (−)-**4** in 98%ee (Chart 1). Recently, it was revealed that complex **I′**, which is a polymorph of **I** and isostructural with **II** obtained by the different solvent for recrystallization (vide infra), gave (−)-**4** predominantly. The photoirradiation of a 1 : 1 complex **III** of anilide **5** with (−)-**1** gave the major product (−)-**6** in 98%ee, whereas the photoirradiation of a 1 : 2 : H_2O complex **IV** of **5** with (−)-**2** afforded the major product **(+)-6** in 95%ee. Although the major photoproduct from guest **5** in **III** and **IV** was *trans*-**6**, a racemic mixture of *cis*-**7** was also obtained at 16 and 4% yields for **III** and **IV**, respectively. This may be due to an imperfect control of the photoreaction at the lattice defects, since the photoreaction in solution gave *cis*-lactams as well as *trans*-lactams.[2] The reversed enantioselectivity of the photoproduct was also observed for 1 : 1 inclusion compounds **V** and **VI** of anilide **8** with hosts (−)-**1** and (−)-**2**, respectively. The dihydroquinolinone derivative (−)-**9** was obtained in 98%ee from

Table 1. Photoreactivities of Anilides **3**, **5**, **8**, and Glyoxylamide **10** in Clathrate Crystals

Compound	I[a]	II	III	IV[b]	V	VI	VII	VIII
Host·guest	(−)-**1**·**3**	(−)-**2**·**3**	(−)-**1**·**5**	(−)-**2**·**5**	(−)-**1**·**8**	(−)-**2**·**8**	(−)-**1**·**10**	(−)-**2**·**10**
Radiation time (h)[c]	50	50	150	150	15	15	53	38
Major photoproduct	(+)-**4**	(−)-**4**	(−)-**6**	(+)-**6**	(−)-**9**	(+)-**9**	(−)-**11**	(+)-**12**
and the yield (%)[d]	62	70	46	29	64	41	21	48
Optical purity (%ee)[e]	70	98	98	95	98	8	99	98

a) This compound shows polymorphism. Major product for **I** and **I′** is (+)-**4** and (−)-**4**, respectively. b) **2**·**5**·H_2O (2 : 1 : 1). None solvent and host : guest (1 : 1) for other compounds. c) A suspension of powdered sample in water was irradiated by using a 100-W high-pressure Hg lamp for **I**, **II**, **V**, and **VI**. Powdered sample was irradiated with a 400-W high-pressure Hg lamp in the solid state at room temperature for **III**, **IV**, **VII**, and **VIII**. d) Isolated yield in the pure state. The minor photoproduct is (−)-*cis*-**7** (16% yield, 36%ee) for **III**, (−)-*cis*-**7** (4% yield, 8%ee) for **IV**, (−)-**13** (2% yield, 11%ee) for **VII**, and (−)-**14** (25% yield, 45%ee) for **VIII**. e) Optical purity was determined by HPLC.

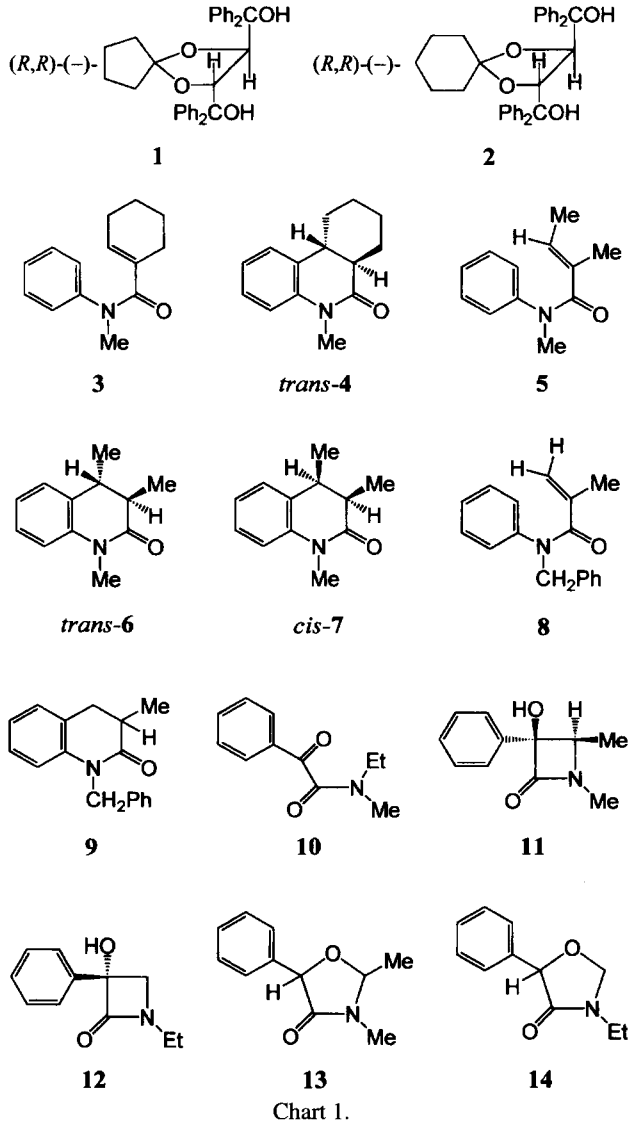


Chart 1.

V, and (+)-**9** in 8%ee from **VI**. The exceptionally low enantioselectivity in **VI** may be due to a severe disorder of the crystal structure. Not only the intramolecular rotation of the methacryl moiety, but also the inversion of the sign of torsion angle in the backbone of the anilide **8**, are expected in **VI** (vide infra).

Optically active β-lactams and oxazolidinones have been obtained selectively by the photoirradiation of 1 : 1 inclusion complexes (**VII** and **VIII**) of glyoxylamide **10** with (−)-**1** and (−)-**2**. The photoirradiation of **VII** and **VIII** gave β-lactams (−)-**11** of 99%ee and (+)-**12** of 98%ee as the major product, respectively.

Molecular Structures of Acrylanilides. Experimental details of X-Ray analyses are listed in Table 2, and the selected geometric parameters in Table 3. The conformations of guest **3** in **I** and **II** (Figs. 1a and 1b), as well as those of guest **5** in **III** and **IV** (Figs. 2a and 2b) are evidently mirror image with each other. The C–N–C(=O)–C torsion angle in the backbone of the anilide is important to describe the

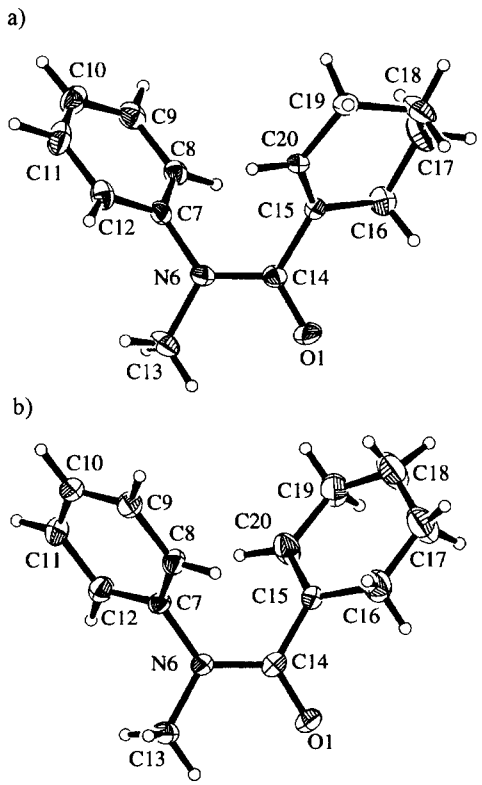


Fig. 1. The molecular structures of guest **3** in (a) **I** and (b) **II** with displacement ellipsoids at the 20% probability level. The rotational disorder of the cyclohexyl moiety exists in **II**, but not in **I**.

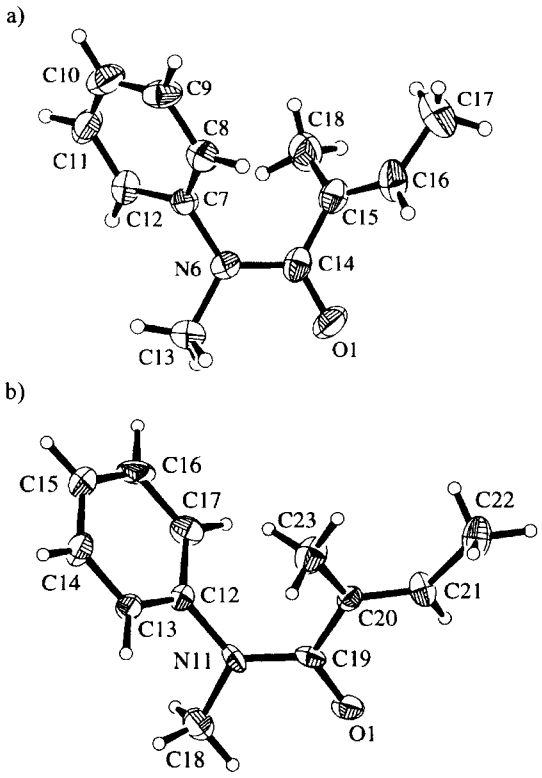
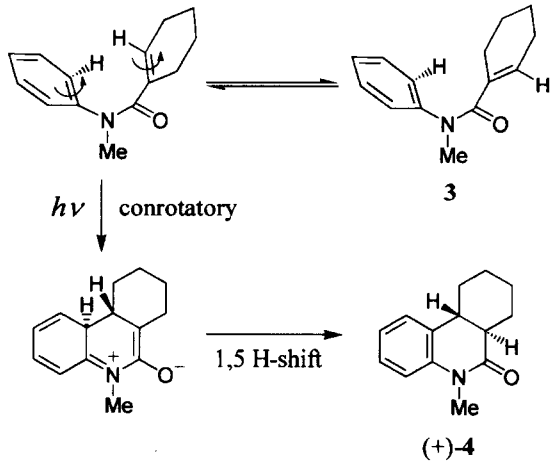


Fig. 2. The molecular structures of guest **5** in (a) **III**[5] and (b) **IV** with displacement ellipsoids at the 20% probability level. There is no rotational disorder of the methylmethacryl moiety in **III** and **IV**.

chirality. For example, −19.5(7)° for C7–N6–C14–C15 in **III**, and +18.5(11)° for C12–N11–C19–C20 in **IV**.

Disorder due to the intramolecular rotation was observed for the cyclohexyl moiety of guest **3** in **I′** and **II**, and for the methacryl moiety of guest **8** in **V** (Table 3). The position of unsaturated bond of guest **5** in **III** and **IV** is not suitable for photocyclization, and intramolecular rotation around the C(=O)–C(=C) bond in α,β-unsaturated kenone is expected before the photocyclization. In fact, the photocyclization of guest **5** in **III** was observed in situ by a partial single-crystal-to-single-crystal transformation.[5]

The mechanism of enantioselective photocyclization of acrylanilides **3**, **5**, and **8** is essentially identical, and illustrated in Scheme 1 for guest **3** in **I**. The molecular structure of **3** at the beginning is seen in Fig. 1a. The bond sequence of C8–C7–N6–C14–C15–C20 can be recognized as a part of the right-handed helix, which corresponds to the positive value of C7–N6–C14(=O1)–C15 torsion angle. By an intramolecular rotation around the C14–C15 bond axis, the positions of the C16 and C20 atoms will be exchanged, but the sign of the C–N–C(=O)–C torsion angle will not be changed. By photoirradiation, the helical bond sequence C=C–N–C(=O)–C=C becomes flat as the two C=C bond approach each other. When the conjugated trienes are converted to a 6-membered ring, the hydrogens at the 1 and 6 positions will corotate in such a way that they do not come into collision. Afterwards, a 1,5 hydrogen shift will occur in a suprafacial



Scheme 1.

manner, and the *trans*-isomer will be obtained. The absolute configuration of the main photoproduct for guest **3** in **I** can be deduced as above, and combined with the observed (+) sign of the angle of rotation. This assignment agrees with the known absolute configuration of **4**.[2] The molecular structure of **3** in **II** (and that in **I′**) is mirror image of that in **I**. Therefore, the other enantiomer of the photoproduct, (−)-**4**, was obtained predominantly from **II**.

In Fig. 2a, the C18–C15–C14–N6–C7–C8 moiety of guest **5** in **III** can be recognized as a part of the left-handed helix. This chirality will be conserved when the positions of C16 and C18 atoms are exchanged with each other by the rotation around the C14–C15 bond axis. The phenyl group will also rotate around the C7–N6 bond axis to form a C8–C16 covalent bond. In Fig. 2b, the C23–C20–C19–N11–C12–C17 moiety of guest **5** in **IV** is the part of right-handed helix. Therefore, the different chiralities of the initial molecular configuration of **5** in **III** and **IV** reflect in the enantiomeric absolute configurations of the photoproduct, (−)-**6** and (+)-**6**, respectively. In Fig. 3, the C22–C21–C20–N6–C7–C8 moiety of guest **8** in **V** is a part of the left-handed helix. Therefore, the absolute configuration of the photoproduct,

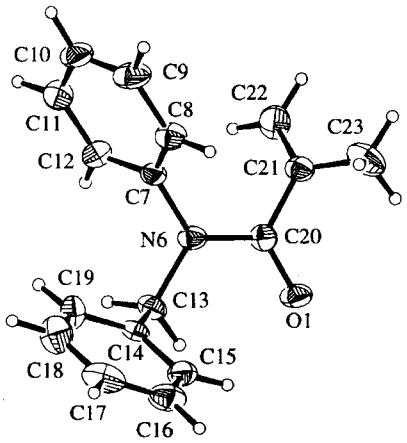


Fig. 3. The molecular structure of guest **8** in **V** with displacement ellipsoids at the 20% probability level. There is the rotational disorder of the methacryl moiety in **V**.

Table 2. Experimental Details of X-Ray Analyses of Inclusion Compounds **I**, **I′**, **II**, **IV**, **V**, **VII**, **VII′**, and **VIII**

	I	**I′**[a)]	**II**	**IV**	**V**
Chemical formula	$C_{33}H_{32}O_4 \cdot C_{14}H_{17}NO$	$C_{33}H_{32}O_4 \cdot C_{14}H_{17}NO$	$C_{34}H_{34}O_4 \cdot C_{14}H_{17}NO$	$2(C_{34}H_{34}O_4) \cdot C_{12}H_{15}NO \cdot H_2O$	$C_{33}H_{32}O_4 \cdot C_{17}H_{17}NO$
Chemical formula weight	707.91	707.91	721.94	1220.55	743.94
Cell setting	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1$	$P2_1$	$P2_1$	$P2_1$	$P2_12_12_1$
a/Å	13.660(2)	10.192(2)	10.205(3)	9.505(3)	19.385(2)
b/Å	9.251(2)	20.523(2)	20.948(6)	34.392(3)	21.884(2)
c/Å	14.957(1)	10.426(1)	10.467(4)	10.254(3)	9.657(2)
β/°	92.39(1)	116.53(1)	117.75(3)	94.65(2)	
V/Å^3	1888.5(5)	1951.2(5)	1980.2(12)	3341.0(15)	4096.7(10)
Z	2	2	2	2	4
D_X/Mg m^{-3}	1.245	1.205	1.211	1.213	1.206
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073
μ/mm^{-1}	0.080	0.077	0.077	0.079	0.077
Temperature/K	298	298	298	298	298
Crystal size/mm	0.6 × 0.4 × 0.1	0.6 × 0.5 × 0.5	0.5 × 0.5 × 0.2	0.75 × 0.3 × 0.1	0.5 × 0.4 × 0.2
Data collection method	θ–2θ scans	θ–2θ scans	θ–2θ scans	ω scans	θ–2θ scans
Absorption correction	$0.97 < T < 0.99$	None	None	None	None
No. of measured reflections	3700	3750	3804	6367	4049
No. of independent reflections	3546	3544	3596	5991	4049
No. of observed reflections	2497	2724	2638	3276	2260
θ_{max}/°	25.0	25.0	25.0	25.0	25.0
Range of h,k,l	$0 \rightarrow h \rightarrow 16$	$0 \rightarrow h \rightarrow 12$	$0 \rightarrow h \rightarrow 12$	$0 \rightarrow h \rightarrow 11$	$0 \rightarrow h \rightarrow 23$
	$0 \rightarrow k \rightarrow 11$	$0 \rightarrow k \rightarrow 24$	$0 \rightarrow k \rightarrow 25$	$0 \rightarrow k \rightarrow 41$	$0 \rightarrow k \rightarrow 26$
	$-18 \rightarrow l \rightarrow 18$	$-12 \rightarrow l \rightarrow 12$	$-12 \rightarrow l \rightarrow 12$	$-12 \rightarrow l \rightarrow 12$	$0 \rightarrow l \rightarrow 11$
Refinement method	F	F	F	F	F
$R(F)$ $[\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)]$	0.057	0.053	0.051	0.067	0.066
wR	0.059	0.057	0.049	0.059	0.059
S	1.19	1.15	1.08	1.27	1.29
No. of reflections used	2497	2724	2638	3276	2260
No. of parameters refined	477	477	486	814	505
$(\Delta/\sigma)_{max}$	0.02	0.004	0.01	0.02	0.02
$\Delta\rho_{max}$/e Å^{-3}	0.24	0.17	0.18	0.28	0.22
$\Delta\rho_{min}$/e Å^{-3}	−0.26	−0.27	−0.18	−0.28	−0.22

Table 2. (Continued)

	VI	VII	VII′[b]	VIII
Chemical formula	$C_{34}H_{34}O_4 \cdot C_{17}H_{17}NO$	$C_{33}H_{32}O_4 \cdot C_{11}H_{13}NO_2$	$C_{33}H_{32}O_4 \cdot C_{11}H_{13}NO_2$	$C_{34}H_{34}O_4 \cdot C_{11}H_{13}NO_2$
Chemical formula weight	757.97	683.84	683.84	697.87
Cell setting	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
a/Å	10.243(3)	18.536(4)	18.496(4)	9.453(3)
b/Å	9.856(2)	23.101(3)	23.466(4)	40.907(5)
c/Å	21.109(3)	8.508(3)	8.523(5)	9.917(3)
β/°	97.84(2)			91.57(2)
V/Å^3	2111.1(8)	3643(2)	3699(2)	3834(2)
Z	2	4	4	4
D_X/Mg m^{-3}	1.192	1.247	1.228	1.209
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Cu $K\alpha$
λ/Å	0.71073	0.71073	0.71073	1.54184
μ/mm^{-1}	0.076	0.082	0.081	0.635
Temperature/K	298	296	296	248
Crystal size/mm	0.7 × 0.2 × 0.1	0.7 × 0.5 × 0.3	0.7 × 0.5 × 0.3	0.7 × 0.2 × 0.2
Data collection method	θ–2θ scans	θ–2θ scans	θ–2θ scans	θ–2θ scans
Absorption correction	None	$0.95 < T < 0.98$	$0.95 < T < 0.9$	$0.76 < T < 0.89$
No. of measured reflections	4182	4668	4741	7752
No. of independent reflections	3935	4668	4741	7275
No. of observed reflections	1487	2179	1154	6473
θ_{max}/°	25.0	27.5	27.5	75.0
Range of h,k,l	$0 \rightarrow h \rightarrow 12$	$0 \rightarrow h \rightarrow 24$	$0 \rightarrow h \rightarrow 24$	$-11 \rightarrow h \rightarrow 0$
	$0 \rightarrow h \rightarrow 12$	$0 \rightarrow k \rightarrow 29$	$0 \rightarrow k \rightarrow 30$	$0 \rightarrow k \rightarrow 51$
	$-25 \rightarrow l \rightarrow 25$	$0 \rightarrow l \rightarrow 11$	$0 \rightarrow l \rightarrow 11$	$-12 \rightarrow l \rightarrow 12$
Refinement method	Not solved[c]	F	F	F^2
$R(F)$ [$\|F_o\| > 3\sigma(\|F_o\|)$]		0.060	0.113	0.041
wR		0.125	0.154	0.122
S		1.07	1.29	1.05
No. of reflections used		4668	1154	7275
No. of parameters refined		460	205	937
$(\Delta/\sigma)_{max}$		0.02	0.02	0.004
$\Delta\rho_{max}$/e Å^{-3}		0.67	0.47	0.34
$\Delta\rho_{min}$/e Å^{-3}		−0.67	−0.41	−0.17

a) **I′** is a polymorph of **I**. b) **VII′** is the structure of **VII** after photoirradiation. c) Structure solution of **VI** was failed due to the weak high-angle reflections suggesting severe disorder.

Table 3. Selected Geometric Parameters (Å, °)

I	O1–C14	1.236(6)	C15–C16	1.505(9)
	N6–C7	1.433(8)	C15–C20	1.329(9)
	N6–C13	1.467(7)	C8···C20	3.569(10)
	N6–C14	1.357(7)	C7–N6–C14–C15	+17.8(6)
	C14–C15	1.486(6)		
I′[a)]	O1–C14	1.235(4)	C15–C16	1.428(7)*
	N6–C7	1.433(5)	C15–C20	1.374(5)*
	N6–C13	1.460(6)	C8···C20	3.606(5)*
	N6–C14	1.352(4)	C7–N6–C14–C15	−20.2(4)
	C14–C15	1.493(5)		
II	O1–C14	1.243(5)	C15–C16	1.410(7)*
	N6–C7	1.445(6)	C15–C20	1.402(6)*
	N6–C13	1.468(6)	C8···C20	3.484(6)*
	N6–C14	1.350(5)	C7–N6–C14–C15	−18.6(4)
	C14–C15	1.489(6)		
III[5)]	O1–C14	1.243(6)	C15–C16	1.347(9)
	N6–C7	1.442(6)	C15–C18	1.475(9)
	N6–C13	1.472(7)	C8···C16	3.732(9)#
	N6–C14	1.352(6)	C7–N6–C14–C15	−19.5(7)
	C14–C15	1.491(8)		
IV	O1–C19	1.242(13)	C20–C21	1.308(17)
	N11–C12	1.451(14)	C20–C23	1.519(15)
	N11–C18	1.463(16)	C17···C21	4.40(2)#
	N11–C19	1.342(15)	C12–N11–C19–C20	+18.5(11)
	C19–C20	1.492(16)		
V	O1–C20	1.246(12)	C21–C22	1.361(14)*
	N6–C7	1.440(11)	C21–C23	1.397(15)*
	N6–C13	1.501(11)	C8···C22	3.56(1)*
	N6–C20	1.358(13)	C7–N6–C20–C21	−15.8(8)
	C20–C21	1.487(14)		
VII	O1–C8	1.206(9)	C8···C17	2.92(1)
	O2–C15	1.244(9)	O1···H17B	2.74
	N7–C15	1.32(1)	C8–O1···H17B	66.0
	N7–C17	1.44(1)	O1–C8–C15–N7	−70(1)
	C8–C15	1.53(1)	C8–C15–N7–C16	174.4(7)
VIII	O1–C15	1.192(6)	C26–C33	1.512(8)
	O2–C22	1.223(8)	C26···C34	2.86(1)
	O3–C26	1.220(7)	O1···H23B	2.78
	O4–C33	1.242(8)	C15–O1···H23B	80.3
	N13–C22	1.359(9)	O3···H34C	2.81
	N13–C23	1.464(10)	C26–O3···H34C	76.7
	N14–C33	1.376(9)	O1–C15–C22–N13	81.6(8)
	N14–C34	1.49(1)	C15–C22–N13–C23	−4.6(9)
	C15–C22	1.535(8)	O3–C26–C33–N14	83.7(8)
	C15···C23	2.885(9)	C26–C33–N14–C34	−6.5(9)

a) **I′** is a polymorph of **I**. *These bond distances are affected by the rotational disorder (see text). #Initial molecular configuration in **III** and **IV** is not suitable for photocyclization.

(−)-**9**, is similar to those obtained from **II** and **III**, (−)-**4**, and (−)-**6**, respectively.

A semi-empirical molecular orbital calculation was carried out by MOPAC/PM3 method for the guest molecules **3**, **5**, and **8** in gas phase.[6] The energy barriers of the intramolecular rotation of the *N*-alkene substituents were estimated to 25, 25, and 18 kJ mol^{-1} for **3**, **5**, and **8**, respectively. For comparison, a similar calculation was made for the ring inversion of a cyclohexane molecule, and the barrier was estimated to 31 kJ mol^{-1}. The reported value, determined by NMR method is 46 kJ mol^{-1}, and the frequency of the ring inversion of cyclohexane was evaluated to 53 s^{-1} at 206 K.[7] It is safe to say that the rotational barriers for guests **3**, **5**, and **8** are equal to or less than that of cyclohexane.

The intramolecular rotation of guest molecules in the clathrate crystals seems to be allowed by chance due to an increase of temperature of the crystal by the photoirradiation. Photocyclization of a guest molecule will produce

some buffer zone near the reaction cavity of the neighboring unit-cell.[8] Consequently, the photoreaction may proceed like dominoes. The high enantioselectivities of the reactions in **I**—**V** indicate that the inversion of the sign of the C–N–C(=O)–C torsion angle in the backbone of the guest molecules is surpressed in the crystals. However, this seems not true in **VI** due to a severe disorder or large thermal motion suggested from the weak high-angle reflections in the X-ray measurement (Table 2).

Molecular Structures of Glyoxylamide. The PhCOCO moiety of the guest **10** in **VII** takes a twisted structure, which is an origin of the chilarity (Fig. 4a). If it adopted a planar conformation, one of the phenyl H atoms will be very close to the carbonyl O atom or an *N*-alkyl H atom. The CON(Me)Et moiety takes a planar conformation and the *N*-methyl group lies in *trans* position to the benzoyl moiety. In **VIII**, there are two independent guest molecules, which take a similar structure with each other, and the *N*-methyl group is in *cis* position to the benzoyl moiety (Fig. 4b). The different conformations of **10** in **VII** and **VIII** apparently cause the different photoproducts. The C···C distances which will be connected via photocyclization to yield β-lactam derivatives are 2.92(1) Å for C8···C17 in **VII**, and 2.86(1) and 2.89(1) Å for C26···C34 and C15···C23, respectively, in **VIII**. The distance between the keto O atom and the γ-H atom which will be abstracted is 2.7—2.8 Å, with the C–O···H angle of 66—80° as shown in Table 3. The structure of the PhCOCON moiety of **10** in **VII** is enantiomorphic to that in **VIII**. The O=C(–Ph)–C(=O)–N torsion angle of the glyoxylamide is −70(1)° for O1–C8–C15–N7 in **VII**, and +81.6(8) and +83.7(8)° in **VIII**.

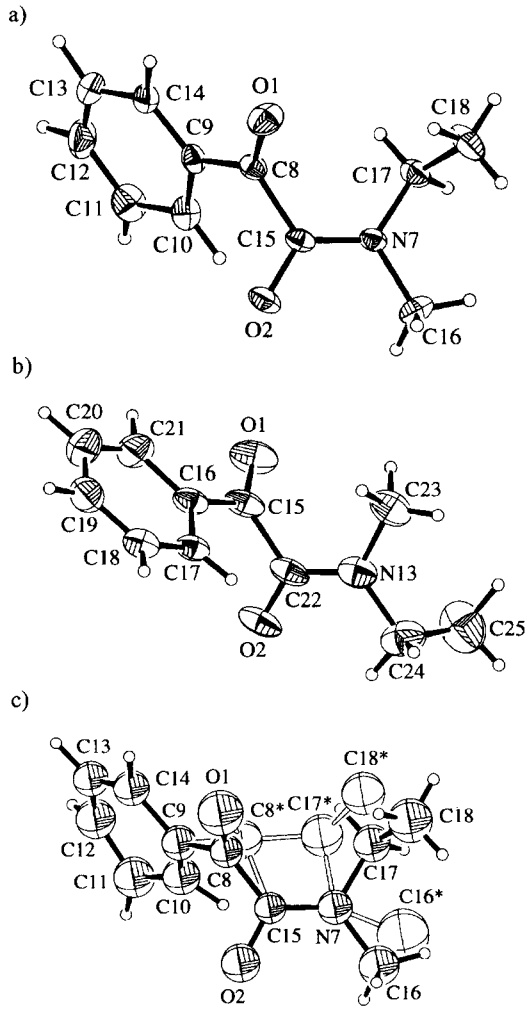


Fig. 4. The molecular structures of (a) guest **10** in **VII**, (b) one of the two independent guest **10** in **VIII**, and (c) the disordered structure of guest **10** in **VII′**, where the starred atoms and unfilled bonds indicate the photoproduct **11** of ca. 40%. Displacement ellipsoids are at the 20% probability level.

Photoirradiation of a single-crystal of **VII** was carried out. The wavelength of the incident light was limited to be longer than ca. 340 nm to progress the solid-state reaction homogeneously.[9] The structure of the guest molecule in **VII′** (**VII** after photoirradiation) is shown in Fig. 4c. This is a disordered structure, and the populations of the starting glyoxylamide **10** and the product β-lactam **11** were estimated to be 60 and 40%, respectively. Figure 4c shows that the positional parameters of the phenyl group of the guest were almost unchanged by the photocyclization, and that the *N*-ethyl group approached to the carbonyl C atom to make a C–C bond. The important point was that the reaction was confirmed to be topochemical.

Crystal Structures. The structures of the host molecules in **III** and **IV** are compared in Fig. 5. The configurations of the 4,5-bis(α-hydroxydiphenylmethyl)-1,3-dioxolane framework of hosts **1** and **2** are similar, and there is an intramolecular O–H···O hydrogen bond. A positional disorder of C49 in **III** indicates a puckering of the cyclopentane ring. In contrast to the five-membered ring, the cyclohexane moiety of **2** is more rigid and takes a chair form. The cyclohexane ring can take two possible orientations to the remaining part of the host, and the interconversion occurs frequently in solution, but not in crystals. In **I**—**V**, hosts are connected with the guest ketone oxygen by the O–H···O hydrogen bond. Furthermore in **IV**, a unit of **2**–water–**5**–**2** is created by the hydrogen bonds. In **VII** and **VIII**, the hosts are connected with the ketone oxygen of the guest **10** (the O2 in **VII**) by the hydrogen bond.

Polymorphism was observed for the inclusion complex of **3** with (−)-**1**. Crystals of **I** and **I′** were grown from butyl ether and toluene solutions, respectively. Both **I** and **I′** are monoclinic, space group $P2_1$ with $Z = 2$, but the lattice constants and packing are different (Fig. 6). The smaller density of **I′**, 1.205 Mg m^{-3}, than that of **I**, 1.245 Mg m^{-3}, indicates that the packing efficiency in **I′** is less than that in **I**. This corresponds to the larger displacement ellipsoids of the molecules in **I′** than in **I**. The crystal **I′** is isostructural with **II**. However, **II** did not show any polymorphism. Bulky prisms of **II** were grown both from toluene and butyl ether solutions.

Crystals of *N*-isopropyl-*N*-methylphenylglyoxylamide with host (−)-**1** (host : guest = 2 : 1) were isostructural to those with host (−)-**2**, although the photoproducts obtained

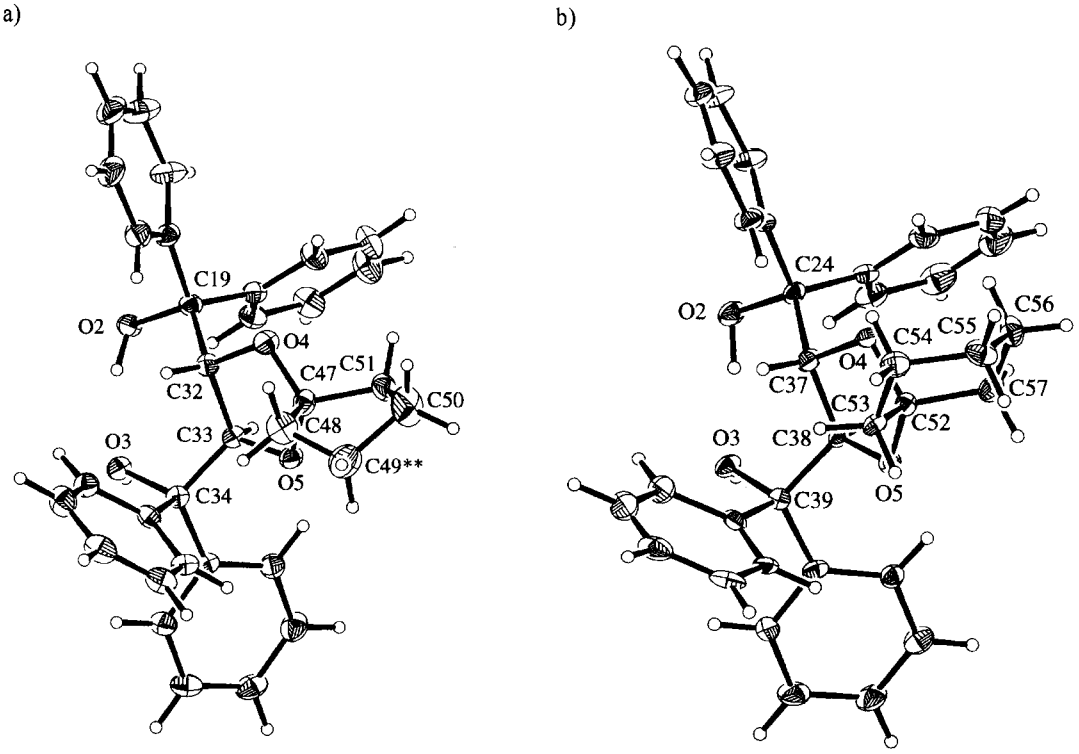


Fig. 5. The molecular structures of (a) host **1** in **III**,[5] and (b) one of two independent host **2** in **IV** with displacement ellipsoids at the 20% probability level. One of the two possible positions of the C49 atom of host **1** in **III** is neglected for clarity.

from these inclusion compounds were not the same.[10] Further investigations are in progress to clarify this phenomena.[11]

There are four possible configurations for *N*-ethyl-*N*-methylphenylglyoxylamide **10**, and interconversion is taken place by a rotation around the PhC(=O)–C(=O) and/or C(=O)–N-(Me)Et bond axes. The intramolecular rotations seem to occur dynamically in solution. When the guest molecules are incorporated into the crystals with a chiral host, the most suitable conformation of the guest will be selected for packing efficiency. As a result, the conformations of **10** in **VII** and **VIII** are different.

Conclusions. The chiral conformations of the guest molecules in the inclusion crystals reflect to the absolute configurations of the photoproducts. The key point is that the central C–N–C(=O)–C torsion angle in the backbone of the acrylanilides hardly changes its sign in the solid state, even if the *N*-alkene substituent rotates to some extent. In general, hosts **1** and **2** form different crystal structures, in which the guest molecules may take different chiral configurations. However, there is no necessity for guests to be mirror images with each other in the inclusion compounds of hosts **1** and **2**. In fact, the polymorphous crystals, **I** and **I′**, gave major photoproducts having different chirality.

Experimental

(a) Synthesis. Optically active hosts (−)-**1** and (−)-**2** were derived from tartaric acid.[12] Preparation of inclusion compounds was carried out by recrystallization from solutions. The ratio of all inclusion compounds was determined by elemental analysis. All melting points were determined using a Yanaco micro melting-point apparatus and were uncorrected. All $[\alpha]_D$ values were measured with a JASCO DIP-1000 polarimeter. The optical purities were determined by HPLC using hexane/2-propanol (9 : 1) or hexane/ethanol (95 : 5) solvent and a column (0.46 cm×25 cm) containing the chiral solid phase, Chiralcel OC, OD, OJ, or Chiralpak As (Daicel Chemical Industries, Ltd., Himeji, Japan). ^{1}H NMR spectra were recorded in $CDCl_3$ on JEOL PMX-60Si or JNM-LA300 spectrometer.

Preparation of a 1 : 1 Inclusion Complex I of (−)-1 and 3. When a solution of (−)-**1** (2.29 g, 4.64 mmol) and **3**[13] (1.00 g, 4.64 mmol) in ether–hexane (4 : 1) (50 ml) was kept at room temperature for 2 d, a 1 : 1 complex **I** of (−)-**1** and **3** was obtained as colorless needles (3.0 g, 91%; mp 118—121 °C). Found: C, 79.53; H, 7.12; N, 1.77%. Calcd for $C_{47}H_{49}NO_5$: C, 79.74; H, 6.98; N, 1.98%.

Preparation of a 1 : 1 Inclusion Complex II of (−)-2 and 3. When a solution of (−)-**2** (2.35 g, 4.64 mmol) and **3** (1.00 g, 4.64 mmol) in benzene–hexane (1 : 3) (20 ml) was kept at room temperature for 2 d, a 1 : 1 complex **II** of (−)-**2** and **3** was obtained as colorless needles (3.3 g, 98%; mp 121—124 °C). Found: C, 79.63; H, 7.52; N, 1.76%. Calcd for $C_{48}H_{51}NO_{10}$: C, 79.86; H, 7.12; N, 1.94%.

Preparation of a 1 : 1 Inclusion Complex III of (−)-1 and 5. When a solution of (−)-**1** (2.50 g, 5.08 mmol) and **5**[1] (0.96 g, 5.08 mmol) in ether–hexane (4 : 1) (25 ml) was kept at room temperature for 2 d, a 1 : 1 complex **III** of (−)-**1** and **5** was obtained as colorless needles (2.92 g, 84%; mp 95—98 °C). Found: C, 79.16; H, 7.09; N, 1.93%. Calcd for $C_{45}H_{47}NO_5$: C, 79.27; H, 6.95; N, 2.05%.

Preparation of a 2 : 1 : 1 Inclusion Complex IV of (−)-2, 5, and H_2O. When a solution of (−)-**2** (2.68 g, 5.28 mmol) and **5** (1.00 g, 5.28 mmol) in benzene–hexane (2 : 1) (30 ml) was kept at room temperature for 2 d, a 2 : 1 : 1 complex **IV** of (−)-**2**, **5**, and H_2O was obtained as colorless needles (2.83 g, 88%; mp not clear). Found: C, 78.69; H, 7.14; N, 1.13%. Calcd for $C_{80}H_{85}NO_{10}$: C,

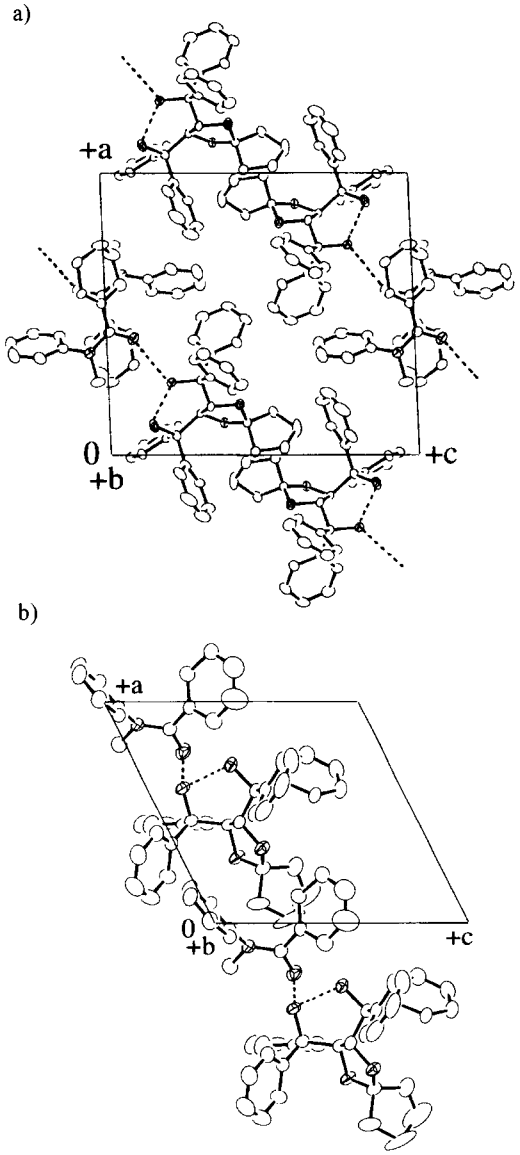


Fig. 6. Projection of crystal structures of (a) **I** along *b* ($-1/2 < y < 1/2$), and (b) **I′** along *b* ($-1/4 < y < 1/4$). Dashed lines represent hydrogen bonds.

78.73; H, 7.02; N, 1.15%.

Preparation of a 1 : 1 Inclusion Complex V of (−)-1 and 8. When a solution of (−)-**1** (2.00 g, 4.1 mmol) and **8**[14] (1.00 g, 4.1 mmol) in ether–hexane (3 : 1) (15 ml) was kept at room temperature for a day, a 1 : 1 complex **V** of (−)-**1** and **8** was obtained as colorless needles (2.7 g, 81%; mp 123—124 °C). Found: C, 80.56; H, 6.60; N, 1.73%. Calcd for $C_{50}H_{49}NO_5$: C, 80.73; H, 6.64; N, 1.88%.

Preparation of a 1 : 1 Inclusion Complex VI of (−)-2 and 8. When a solution of (−)-**2** (2.50 g, 4.93 mmol) and **8** (1.28 g, 5.09 mmol) in benzene–hexane (3 : 2) (25 ml) was kept at room temperature for 2 d, a 1 : 1 complex **VI** of (−)-**2** and **8** was obtained as colorless needles (3.35 g, 89%; mp 102 °C). Found: C, 80.68; H, 6.76; N, 1.51%. Calcd for $C_{51}H_{51}NO_5$: C, 80.82; H, 6.78; N, 1.85%.

Preparation of 10. To an ice-cooled solution of *N*-ethyl-*N*-methylamine (7.50 g, 44.5 mmol) and triethylamine (30 mL) in dry ether (60 mL) was added a solution of benzoylformyl chloride[15] (4.50 g, 44.5 mmol) in dry ether (10 mL), and the mixture was stirred for 3 h in an ice bath. After filtration of triethylammonium chloride, the filtrate was washed with dilute HCl and aqueous $NaHCO_3$ and dried over $MgSO_4$. The crude product obtained by evaporation of the solvent was chromatographed on silica gel using toluene to give **3** as colorless oil (4.61 g, 54% yield): IR (Nujol) ν_{max} 1680 and 1645 cm^{-1}; ^1H NMR δ = 1.16 (t, 3H), 1.25 (t, 3H), 2.92 (s, 3H), 3.09 (s, 3H), 3.30 (q, 2H), 3.58 (q, 2H), 7.48 (t, 2H), 7.63 (t, 1H), 7.93 (d, 2H). Since **10** was obtained as an oily material, this was identified by elemental analysis of this inclusion compounds with the hosts **1** and **2**.

Preparation of a 1 : 1 Inclusion Complex VII of (−)-1 and 10. When a solution of **10** (1.70 g, 3.46 mmol) and (−)-**1** (0.66 g, 3.46 mmol) in ether (20 mL) was kept at room temperature for 12 h, a 1 : 1 complex **VII** was obtained as colorless needles (1.23 g, 52% yield, mp 127—130 °C): IR (Nujol) ν_{max} 3310, 3250, 1680, and 1635 cm^{-1}. Anal. Calcd for $C_{44}H_{45}NO_6$: C, 77.28; H, 6.63; N, 2.05%. Found: C, 77.35; H, 6.71; N, 2.08%.

Preparation of a 1 : 1 Inclusion Complex VIII of (−)-2 and 10. By the same procedure as described above, a 1 : 1 complex **VIII** was obtained as colorless needles (43% yield, mp 139—142 °C): IR (Nujol) ν_{max} 3305, 1680, and 1630 cm^{-1}. Anal. Calcd for $C_{45}H_{47}NO_6$: C, 77.45; H, 6.79; N, 2.01%. Found: C, 77.41; H, 6.98; N, 1.94%.

Photoreaction of Inclusion Complex I. Photoirradiation of a suspension of powdered 1 : 1 complex **I** (3.0 g) in water (150 ml) containing a small amount of sodium alkyl sulfate as a surfactant was carried out for 50 h using a 100-W high-pressure Hg lamp under stirring. The reaction product was filtered, air dried, and chromatographed on silica gel using CH_2Cl_2 as an eluent to give (+)-*trans*-**4** (0.56 g, 62% yield, mp 122—125 °C, $[\alpha]_D$ +126° (*c* 0.5), 70%ee). The enantiomeric excess was determined by a HPLC analysis using Daicel CHIRALPAK AS (hexane : EtOH 95 : 5, 0.3 ml min^{-1}, 230 nm). The (+)-**4** isomer eluted at 20.6 min.

Photoreaction of Inclusion Complex II. Photoirradiation of a suspension of powdered 1 : 1 complex **II** (3.2 g) in water (150 ml) containing a small amount of sodium alkyl sulfate as a surfactant was carried out for 50 h using a 100-W high-pressure Hg lamp under stirring. The reaction product was filtered, air dried, and chromatographed on silica gel using CH_2Cl_2 as an eluent to give (−)-*trans*-**4** (0.67 g, 70% yield, mp 123—125 °C, $[\alpha]_D$ −177° (*c* 0.5), 98%ee). The enantiomeric excess was determined by a HPLC analysis using Daicel CHIRALPAK AS (hexane : EtOH 95 : 5, 0.3 ml min^{-1}, 230 nm). The (−)-**4** isomer eluted at 18.9 min.

Photoreaction of Inclusion Complex III. Photoirradiation of a powdered 1 : 1 complex **III** (1.0 g) was carried out in the solid state for 150 h using a 400-W high-pressure Hg lamp. The reaction mixture was chromatographed on silica gel with benzene–THF (15 : 1) as solvent to give a mixture of (−)-*trans*-**6** (0.13 g, 46% yield, mp 98—100 °C, $[\alpha]_D$ −68.0° (*c* 0.05), 98%ee; ^1H NMR δ = 1.12 and 1.24 (3H each, d, *J* = 6 Hz, CH_3), 2.57 and 2.73 (1H each, dd, *J* = 6, 4 Hz, CH), 3.37 (3H, s, NCH_3), 6.8—7.4 (4H, m, ArH)) and (−)-*cis*-**7** (0.04 g, 16% yield, oil, $[\alpha]_D$ −15.3° (*c* 0.1), 36%ee. ^1H NMR δ = 1.07 and 1.20 (3H each, d, *J* = 4 Hz, CH_3), 2.97 and 3.17 (^1H each, dd, *J* = 4.8, 4 Hz, CH), 3.33 (3H, s, NCH_3), 6.8—7.4 (4H, m, ArH)). The enantiomeric excess of (−)-*trans*-**6** was determined by a HPLC analysis using Daicel CHIRALCEL OD (hexane : 2-PrOH 9 : 1, 0.2 ml min^{-1}, 230 nm). The (−)-**6** isomer eluted at 34.0 min.

Photoreaction of Inclusion Complex IV. Photoirradiation of a powdered 1 : 1 complex **IV** (1.8 g) was carried out in the solid state for 150 h using a 400-W high-pressure Hg lamp. The reaction

mixture was chromatographed on silica gel with CCl_4-THF (20 : 1) as solvent to give a mixture of (+)-*trans*-**6** (0.08 g, 29% yield, mp 96—99 °C, $[\alpha]_D$ +66.0° (*c* 0.05), 95%ee) and (−)-*cis*-**7** (0.01 g, 4% yield, oil, $[\alpha]_D$ −5.6° (*c* 0.01), 8%ee). The enantiomeric excess of (+)-*trans*-**6** was determined by a HPLC analysis using Daicel CHIRALCEL OD (hexane : 2-PrOH 9 : 1, 0.2 ml min^{-1}, 230 nm). The **(+)-6** isomer eluted at 31.8 min.

Photoreaction of Inclusion Complex V. Photoirradiation of a suspension of powdered 1 : 1 complex **V** (2.7 g) in water (150 ml) containing a small amount of sodium alkyl sulfate as a surfactant was carried out for 15 h using a 100-W high-pressure Hg lamp under stirring. The reaction product was filtered, air dried, and chromatographed on silica gel using CH_2Cl_2 as an eluent to give **(−)-9** (0.58 g, 64% yield, mp 51—52 °C, $[\alpha]_D$ −51.4° (*c* 0.25), 98%ee). The enantiomeric excess was determined by a HPLC analysis using Daicel CHIRALCEL OJ (hexane : 2-PrOH 9 : 1, 0.3 ml min^{-1}, 230 nm). The **(−)-9** isomer eluted at 39.2 min.

Photoreaction of Inclusion Complex VI. Photoirradiation of a suspension of powdered 1 : 1 complex **VI** (3.0 g) in water (150 ml) containing a small amount of sodium alkyl sulfate as a surfactant was carried out for 15 h using a 100-W high-pressure Hg lamp under stirring. The reaction product was filtered, air dried, and chromatographed on silica gel using CH_2Cl_2 as an eluent to give **(+)-9** (0.40 g, 41% yield, mp 80—81 °C, $[\alpha]_D$ +5.9° (*c* 0.55), 8%ee). The enantiomeric excess was determined by a HPLC analysis using Daicel CHIRALCEL OJ (hexane : 2-PrOH 9 : 1, 0.3 ml min^{-1}, 230 nm). The **(+)-9** isomer eluted at 53.7 min.

Photoreaction of Inclusion Complex VII. Photoirradiation of finely powdered 1 : 1 complex **VII** (1.23 g, 1.80 mmol) in the solid state through a Pyrex filter using a 400-W high-pressure Hg lamp for 53 h at room temperature gave a crude reaction product. Purification of the crude reaction product by column chromatography on a silica gel using AcOEt–toluene (3 : 8) as an eluent gave **(−)-11** of 99%ee as colorless needles (0.072 g, 21% yield, mp 186—189 °C, $[\alpha]_D$ −16° (*c* 0.7, MeOH)): IR (neat) ν_{max} 3220 and 1740 cm^{-1}, ^1H NMR δ = 1.39 (d, *J* = 6 Hz, 3H), 2.87 (s, 3H), 3.52 (d, *J* = 5 Hz, 1H), 3.75 (q, *J* = 6 Hz, 1H), 7.31—7.45 (m, 5H) and **(−)-13** of 11%ee as colorless oil (0.039 g, 2% yield, $[\alpha]_D$ −3° (*c* 0.13, MeOH)): IR (neat) ν_{max} 1700 cm^{-1}. ^1H NMR δ = 1.53 (d, *J* = 5 Hz, 3H), 2.85 (s, 3H), 5.18 (s, 1H), 5.22 (q, *J* = 5 Hz, 1H), 7.32—7.47 (m, 5H). The enantiomeric excess was determined by a HPLC analysis using Daicel CHIRALCEL OC (hexane : 2-PrOH 9 : 1, 1.0 ml min^{-1}, 220 nm). The **(−)-11** isomer eluted at 24 min.

Photoreaction of Inclusion Complex VIII. Photoirradiation of complex **VIII** for 38 h as described above gave **(+)-12** of 98%ee as colorless plates (48% yield, mp 50—61 °C, $[\alpha]_D$ +38° (*c* 2.7, MeOH), IR (Nujol) ν_{max} 3340 and 1735 cm^{-1}. ^1H NMR δ = 1.17 (t, *J* = 7 Hz, 3H), 3.29-3.37 (m, 2H), 3.45 (d, *J* = 5 Hz, 1H), 3.57 (d, *J* = 5 Hz, 1H), 5.62 (s, 1H), 7.26—7.41 (m, 5H) and **(−)-14** of 45%ee as colorless oil (25% yield, $[\alpha]_D$ −19° (*c* 1.4, MeOH)): IR (neat) ν_{max} 1705 cm^{-1}; ^1H NMR δ = 1.15 (t, *J* = 7 Hz, 3H), 3.35—3.38 (m, 2H), 5.12 (s, 1H), 5.18 (s,1H), 5.20 (s, 1H), 7.31—7.45 (m, 5H). The enantiomeric excess was determined by a HPLC analysis using Daicel CHIRALCEL OC (hexane : 2-PrOH 9 : 1, 1.0 ml min^{-1}, 220 nm). The **(+)-12** isomer eluted at 21 min.

(b) Crystallography. Solvents for recrystallization were butyl ether for **I** and **II**, ethyl ether for **V**, **VI**, and **VII**, and toluene for **IV**, **VIII**, and **I′**. The X-ray intensities were measured on a Rigaku AFC-5S or AFC-7R four-circle diffractometer with Mo $K\alpha$ radiation except for **VIII**, which was measured with Cu $K\alpha$ radiation. The hydroxy H atoms of the host molecules and H atoms of water for crystallization in **IV** were located on difference syntheses. All of the other H atom positions were calculated geometrically. The absolute structures of the crystals were assigned based on the known absolute configuration of the hosts, **(−)-1** and **(−)-2**, which were derived from (*R*,*R*)-(+)-tartaric acid. The terminal CH_3–C(=CH_2)– moiety of guest **8** in **V** (Fig. 3) shows almost equivalent C21–C22 and C21–C23 bond distances, i.e. 1.361(14) and 1.397(15) Å. It indicates a rotational disorder of the methacryl moiety. The cyclohexyl moiety of guest **3** also have a similar rotational disorder in **I′** and **II**, but not in **I**. Programs used to solve and refine structures were CRYSTAN-GM and TEXSAN.[16]

Photoirradiation of a single-crystal of **VII** was carried out. The light from a 250 W ultra-high-pressure Hg lamp was led to a crystal using a flexible light guide made with quartz and through a long-pass filter UV34 (*T* = 10% at 330 nm; *T* = 40% at 340 nm). By the photoirradiation, cell axis *b* increased significantly along with the crystal decay. The crystal structure of **VII** after photoirradiation for 7 h is denoted as **VII′**. The structure of guest **10** in **VII′** was disordered (Fig. 4c). The population of the newly appeared atoms (C16*–C18*) of the photoproduct **11** was estimated to be 40% based on their thermal parameters. All non-H atoms were refined isotropically for **VII′** to suppress the number of parameters.

X-Ray structural information (atomic coordinates, anisotropic thermal parameters, bond lengths and bond angles) on **I**, **I′**, **II**, **IV**, **V**, **VII**, **VII′**, and **VIII** are deposited as Document No. 73050 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Chambridge CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers CCDC 145861-145868.

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