Structures and Photoreactivities of *N*-Isopropyl-*N*-methylphenylglyoxylamide Included in Two Clathrate Crystals as a Guest

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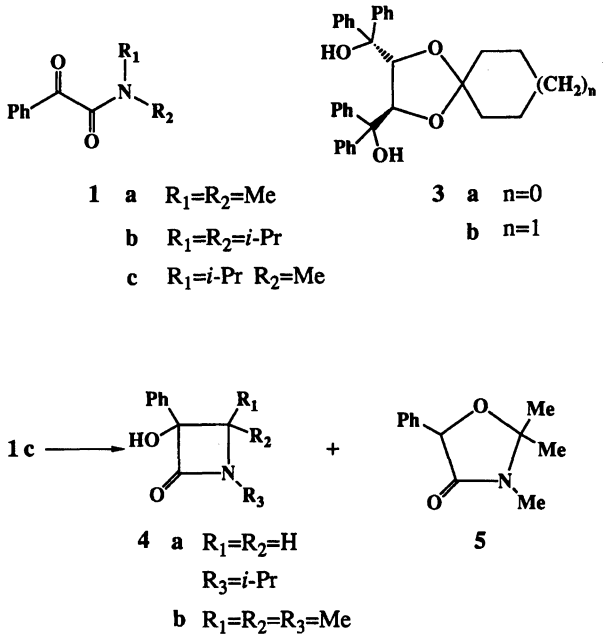
The achiral *N*-isopropyl-*N*-methylphenylglyoxylamide molecule forms 1 : 2 host–guest complexes with the two kinds of the chiral host molecules derived from tartaric acid. The guest molecules in both of the clathrate crystals, I and II, are converted to the chiral β-lactam and oxazolidinone on exposure to a Hg lamp. The crystal structures of I and II, which are very similar to each other, were determined by X-rays: (I) Bis[(*R*,*R*)-(−)-*trans*-2,3-bis(diphenylhydroxymethyl)-1,4-dioxaspiro(4.4)nonane]*N*-isopropyl-*N*-methylphenylglyoxylamide, $(C_{33}H_{32}O_4)_2\cdot(C_{12}H_{15}NO_2)$, $f_w=1190.49$, $a=10.404(2)$, $b=34.056(3)$, $c=9.434(3)$ Å, $\beta=94.87(2)°$, $V=3331(1)$ Å^3, Final *R* became 0.056. (II) Bis[(*R*,*R*)-(−)-*trans*-2,3-bis(diphenylhydroxymethyl)-1,4-dioxaspiro(4.5)decane]*N*-isopropyl-*N*-methylphenylglyoxylamide, $(C_{34}H_{34}O_4)_2\cdot(C_{12}H_{15}NO_2)$, $f_w=1218.54$, $a=10.4616(5)$, $b=34.358(2)$, $c=9.469(4)$ Å, $\beta=94.798(3)°$, $V=3391.4(3)$ Å^3, Final *R* became 0.052. The guest molecule in each crystal is hydrogen bonded to the two host molecules. The absolute configurations of the chiral products seem to depend on the conformations of the guest molecules in I and II.

It has been found that *N*,*N*-dimethylphenylglyoxylamide (**1a**) included as a guest molecule in the clathrate crystal with chiral 1,6-bis(*o*-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol (**2**) as a host molecule is converted enantioselectively to β-lactam on exposure to UV light.[1] The molecules of *N*,*N*-diisopropylphenylglyoxylamide (**1b**) in Scheme 1 crystallize in a chiral space group and the enantiomeric crystals are transformed to optically almost pure β-lactam by photoirradiation.[2] Recently new chiral host molecules, **3a** and **3b**, were prepared from tartaric acid.[3] These molecules easily form inclusion complexes with **1a** and **1c**.[4] Hereafter the clathrate crystals of **3a** and **1c**, and **3b** and **1c** are abbreviated as I and II, respectively.



Scheme 1. Reaction scheme of phenylglyoxylamide to β-lactam and oxazolidinone.

On exposure to a high-pressure Hg lamp at room temperature, the powdered sample of crystal I gave β-lactam **4a** and oxazolidinone **5**.[4] The crystal II, on the other hand, gave **4b** and **5**. This work was undertaken to elucidate the reason why the two crystals revealed different reactivities.

Experimental

The crystal data and experimental details are summarized in Table 1. The Lorentz and polarization corrections were applied for both crystals, but the absorption correction was done only for I. The structure of II was solved by the direct method with MULTAN78[5] and the atomic parameters of II were used for the initial values for I since the two structures are very similar to each other. The structures were refined by the full-matrix least-squares method with the program SHELX76.[6] The weighting schemes were $w=[\sigma(|F_o|)^2]^{-1}$ and $[\sigma(|F_o|)^2+0.004(|F_o|)^2]^{-1}$ for I and II, respectively. Positions of several hydrogen atoms were obtained on difference maps and others were calculated geometrically. The anisotropic and isotropic temperature factors were used for non-hydrogen and hydrogen atoms, respectively, in the final refinement. The positional parameters of hydrogen atoms were constrained to have the C–H and O–H distances of 1.00 and 0.90 Å, respectively. Atomic scattering factors were taken from International Tables for Crystallography.[7] Final atomic parameters for I and II are given in Tables 2 and 3, respectively. #

#The tables of the anisotropic temperature factor for non-hydrogen atoms, the parameters of hydrogen atoms, the F_o-F_c, and bond distances and angles are deposited as Document No. 67022 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Table 1. Crystal Data and Experimental Conditions

	I	II
Chemical formula	$(C_{33}H_{32}O_4)_2 \cdot (C_{12}H_{15}NO_2)$	$(C_{34}H_{34}O_4)_2 \cdot (C_{12}H_{15}NO_2)$
Formula weight	1190.49	1218.54
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
Z	2	2
a/Å	10.404(2)	10.4616(5)
b/Å	34.056(3)	34.358(2)
c/Å	9.434(3)	9.469(4)
β/°	94.87(2)	94.798(3)
V/Å^3	3331(1)	3391.4(3)
D_x/Mg m^{-3}	1.19	1.19
Diffractometer	AFC-5R	AFC-4
Radiation	Cu $K\alpha$	Cu $K\alpha$
λ/Å	1.54184	1.54184
μ(Cu $K\alpha$)/mm^{-1}	5.42	5.41
$F(000)$	1268	1300
Color of crystal	Colorless	Colorless
Shape of crystal	Plate-like	Plate-like
Crystal dimensions/mm^3	0.2×0.3×0.4	0.1×0.15×0.3
No. and range of 2θ for cell parameters	25 ($45<2\theta<50°$)	25 ($45<2\theta<60°$)
T/K	296	296
$2\theta_{max}$/°	125	125
Range of h, k, and l	$-12\leq h\leq 12$ $0\leq k\leq 39$ $0\leq l\leq 11$	$-12\leq h\leq 12$ $0\leq k\leq 39$ $0\leq l\leq 11$
Scan technique	$\omega/2\theta$	$\omega/2\theta$
Scan width	$(1.5+0.15 \tan\theta)°$	$(1.0+0.15 \tan\theta)°$
Scan rate/° (θ) min^{-1}	8	2
Systematic absences	$0k0$, k odd	$0k0$, k odd
No. of unique reflections	5396	5510
No. of observed reflections [$\lvert F_o\rvert>3\sigma(\lvert F_o\rvert)$]	3286	5163
R	0.056	0.052
wR	0.049	0.056
S	1.250	0.883
$(\Delta/\sigma)_{max}$	0.001	0.024
$\Delta\rho/e$ Å^{-3}	−0.22, 0.21	−0.25, 0.24

Results and Discussion

Crystal Structure. Figure 1 shows the crystal structure of I viewed along the a-axis. The absolute structure is matched to that of the host molecule. The guest molecule is hydrogen bonded to the host molecules, A and B, through O(1)···H(1A)–O(1A) and O(2)···H(1B)–O(1B). The O(1)···H(1A), O(2)···H(1B), and O(1)···O(1A), O(2)···O(1B) distances and the O(1)···H(1A)–O(1A), O(2)···H(1B)–O(1B) angles are 1.95(6), 1.82(4), and 2.769(7), 2.715(7) Å and 152(6), 175(4)°, respectively.

Figure 2 shows the crystal structure of II, which is very similar to that of I. The corresponding hydrogen bond geometries are as follows: O(1)···H(1A) and O(2)···H(1B), 1.98(6) and 2.0(2) Å; O(1)···O(1A) and O(2)···O(1B), 2.780(4) and 2.707(5) Å; O(1)···H(1A)–O(1A) and O(2)···H(1B)–O(1B), 147(5) and 139(14)°.

Molecular Structure. The molecular structures of I and II with the numbering of the atoms is shown in Figs. 3 and 4, respectively. The same numbering is applied to the guest molecules in both crystals. The selected bond distances and angels of I and II are listed in Table 4. The corresponding distances and angles are in good agreement with each other.

The structures of the two host molecules are very similar to each other. The torsion angles of C(16A)–C(14A)–C(15A)–C(17A), C(16B)–C(14B)–C(15B)–C-

Table 2. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters for I

$$B_{eq} = \left(8\pi^2/3\right) \sum_i \sum_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$$

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
O(1)	0.7683(5)	0.3064(2)	0.3512(6)	6.7	C(39A)	0.6398(7)	0.7414(3)	−0.1055(9)	5.7
O(2)	0.6499(5)	0.3903(1)	0.3262(5)	5.9	C(40A)	0.6524(8)	0.7772(3)	−0.0378(8)	6.6
N(1)	0.7427(6)	0.3760(2)	0.5460(7)	5.0	C(41A)	0.7056(7)	0.7787(2)	0.1036(8)	5.2
C(1)	0.8031(7)	0.3414(2)	0.3367(7)	4.7	C(42A)	0.7825(8)	0.6230(2)	0.4609(10)	5.6
C(2)	0.7286(7)	0.3723(2)	0.4086(9)	4.9	C(43A)	0.6191(7)	0.6558(3)	0.5876(8)	5.9
C(3)	0.6571(10)	0.4043(3)	0.6109(10)	7.9	C(44A)	0.6534(10)	0.6066(3)	0.4075(12)	7.8
C(4)	0.8425(8)	0.3546(2)	0.6376(8)	5.4	C(45A)	0.5636(11)	0.6193(4)	0.5140(12)	11.0
C(5)	0.9397(11)	0.3832(3)	0.7078(13)	11.7	O(1B)	0.6523(4)	0.4509(1)	1.1393(5)	3.9
C(6)	0.7807(10)	0.3285(3)	0.7432(12)	8.5	O(2B)	0.8192(4)	0.4704(1)	0.9479(5)	4.4
C(7)	0.9029(7)	0.3525(3)	0.2477(8)	5.2	O(3B)	0.4528(4)	0.5289(1)	0.9973(4)	3.3
C(8)	0.9450(8)	0.3913(3)	0.2509(9)	7.0	O(4B)	0.5682(4)	0.5391(1)	0.8071(4)	3.2
C(9)	1.0482(10)	0.4021(4)	0.1701(12)	9.2	C(13B)	0.4794(6)	0.5575(2)	0.8926(7)	3.6
C(10)	1.0979(11)	0.3736(5)	0.0861(13)	10.9	C(14B)	0.5669(6)	0.5062(2)	1.0243(6)	2.7
C(11)	1.0530(11)	0.3361(5)	0.0805(12)	11.3	C(15B)	0.6226(5)	0.5054(2)	0.8775(6)	2.9
C(12)	0.9562(8)	0.3251(3)	0.1609(8)	7.0	C(16B)	0.5283(6)	0.4676(2)	1.0958(7)	3.2
O(1A)	1.0937(4)	0.7448(1)	0.5189(5)	4.2	C(17B)	0.7713(6)	0.5050(2)	0.8793(6)	3.3
O(2A)	0.9325(4)	0.76957	0.3005(5)	4.3	C(18B)	0.4586(5)	0.4744(2)	1.2293(6)	2.8
O(3A)	0.8442(4)	0.6783(1)	0.6202(4)	3.8	C(19B)	0.4662(6)	0.5090(2)	1.3035(7)	4.3
O(4A)	0.7255(4)	0.6909(1)	0.4135(5)	3.8	C(20B)	0.4165(7)	0.5133(2)	1.4336(8)	4.8
C(13A)	0.7463(7)	0.6625(2)	0.5240(8)	4.3	C(21B)	0.3576(7)	0.4815(3)	1.4927(8)	5.1
C(14A)	0.9003(5)	0.7122(2)	0.5590(6)	3.1	C(22B)	0.3450(8)	0.4463(3)	1.4185(9)	6.0
C(15A)	0.8428(6)	0.7113(2)	0.4027(6)	3.2	C(23B)	0.3965(7)	0.4435(2)	1.2888(8)	4.7
C(16A)	1.0494(6)	0.7094(2)	0.5854(7)	3.2	C(24B)	0.4525(7)	0.4406(2)	0.9896(7)	3.5
C(17A)	0.8127(6)	0.7508(2)	0.3263(7)	3.5	C(25B)	0.4998(9)	0.4050(2)	0.9505(9)	6.1
C(18A)	1.1055(6)	0.6742(2)	0.5200(7)	3.7	C(26B)	0.4303(11)	0.3807(3)	0.8550(11)	8.3
C(19A)	1.0978(7)	0.6378(2)	0.5802(8)	4.5	C(27B)	0.3158(12)	0.3930(4)	0.7938(10)	8.2
C(20A)	1.1478(9)	0.6045(3)	0.5120(13)	7.3	C(28B)	0.2613(11)	0.4281(3)	0.8310(10)	7.5
C(21A)	1.2048(10)	0.6091(4)	0.3885(14)	8.5	C(29B)	0.3291(8)	0.4521(3)	0.9318(9)	5.7
C(22A)	1.2128(9)	0.6448(4)	0.3286(11)	8.5	C(30B)	0.8306(6)	0.5424(2)	0.9527(7)	3.3
C(23A)	1.1637(7)	0.6774(3)	0.3925(8)	5.6	C(31B)	0.8359(6)	0.5775(2)	0.8795(8)	4.0
C(24A)	1.0961(6)	0.7128(2)	0.7456(7)	3.7	C(32B)	0.8883(7)	0.6106(3)	0.9454(9)	5.6
C(25A)	1.0154(7)	0.7165(2)	0.8534(7)	4.4	C(33B)	0.9388(8)	0.6095(3)	1.0837(11)	6.6
C(26A)	1.0671(8)	0.7228(2)	0.9933(8)	5.2	C(34B)	0.9354(8)	0.5745(3)	1.1576(10)	6.7
C(27A)	1.1980(8)	0.7252(2)	1.0240(9)	5.6	C(35B)	0.8796(7)	0.5413(2)	1.0939(8)	4.8
C(28A)	1.2798(7)	0.7204(2)	0.9192(8)	4.8	C(36B)	0.8215(6)	0.5026(2)	0.7309(7)	3.2
C(29A)	1.2292(6)	0.7140(2)	0.7799(7)	4.2	C(37B)	0.9525(7)	0.4985(2)	0.7265(8)	5.5
C(30A)	0.7336(7)	0.7772(2)	0.4178(7)	4.1	C(38B)	1.0040(8)	0.4940(2)	0.5949(9)	5.8
C(31A)	0.6045(8)	0.7702(3)	0.4278(8)	5.6	C(39B)	0.9279(9)	0.4953(2)	0.4695(9)	6.0
C(32A)	0.5316(12)	0.7931(3)	0.5144(11)	8.4	C(40B)	0.7981(8)	0.5003(2)	0.4762(8)	5.7
C(33A)	0.5907(14)	0.8230(4)	0.5892(11)	9.9	C(41B)	0.7448(7)	0.5042(2)	0.6041(7)	4.9
C(34A)	0.7200(13)	0.8310(3)	0.5792(11)	8.9	C(42B)	0.3546(7)	0.5701(2)	0.8130(8)	5.1
C(36A)	0.7464(6)	0.7454(2)	0.1780(7)	3.4	C(43B)	0.5320(8)	0.5949(2)	0.9660(8)	4.8
C(37A)	0.7302(7)	0.7100(2)	0.1100(8)	4.7	C(44B)	0.3039(11)	0.6033(4)	0.9017(12)	9.5
C(35A)	0.7929(11)	0.8082(2)	0.4931(9)	6.5	C(45B)	0.4090(10)	0.6149(3)	1.0120(11)	8.4
C(38A)	0.6788(7)	0.7076(3)	−0.0317(8)	5.6					

(17B) for I and II are −95.2(7), −94.5(6)° and −93.5(3), −96.6(3)°, respectively. The conformations of the two hydroxyl groups I are in good agreement with the corresponding ones of II. The torsion angles of O(1A)–C(16A)–C(14A)–C(15A), O(1B)–C(16B)–C(14B)–C(15B) and O(2A)–C(17A)–C(15A)–C(14A), O(2B)–C(17B)–C(15B)–C(14B) are 63.3(7), 72.8(6)° and 71.0(7), 62.4(7)° for I and 60.6(3), 73.0(3)° and 72.5(3), 64.0(3)° for II, respectively. Since the host molecules in I and II are different from each other only in the number of atoms of spiro ring, the shapes of the molecules are very similar to each other. This may cause nearly

Table 3. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters for II

$$B_{eq} = \left(8\pi^2/3\right) \sum_i \sum_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$$

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
O(1)	0.7681(3)	0.30577(8)	0.3446(3)	5.4	C(40A)	0.7255(7)	0.8308(2)	0.5957(6)	7.8
O(2)	0.6494(3)	0.3888(1)	0.3107(4)	6.6	C(41A)	0.7932(6)	0.8080(1)	0.5063(5)	5.8
N(1)	0.7444(4)	0.3770(1)	0.5321(4)	5.0	C(42A)	0.7711(4)	0.6255(1)	0.4650(4)	3.7
C(1)	0.8014(4)	0.3395(1)	0.3259(4)	4.0	C(43A)	0.6201(3)	0.6634(1)	0.6058(4)	3.9
C(2)	0.7281(4)	0.3714(1)	0.3931(5)	4.4	C(44A)	0.6570(4)	0.6089(1)	0.3745(5)	4.8
C(3)	0.6623(8)	0.4059(2)	0.5923(8)	9.3	C(45A)	0.5062(4)	0.6465(1)	0.5142(5)	4.7
C(4)	0.8421(5)	0.3557(2)	0.6243(5)	6.2	C(46A)	0.5385(4)	0.6068(1)	0.4563(6)	5.4
C(5)	0.9442(9)	0.3834(3)	0.6903(9)	12.8	O(1B)	0.6471(2)	0.44951(8)	1.1285(3)	4.0
C(6)	0.7833(7)	0.3317(2)	0.7324(7)	8.8	O(2B)	0.8146(2)	0.47181(8)	0.9432(3)	4.2
C(7)	0.9004(4)	0.3504(1)	0.2336(4)	4.8	O(3B)	0.4447(2)	0.52683(7)	0.9927(2)	3.0
C(8)	0.9455(5)	0.3885(2)	0.2299(6)	6.9	O(4B)	0.5589(2)	0.53833(7)	0.8027(2)	3.2
C(9)	1.0419(7)	0.3967(3)	0.1430(9)	9.4	C(13B)	0.4601(3)	0.5539(1)	0.8829(3)	2.9
C(10)	1.0914(7)	0.3668(3)	0.0624(7)	9.5	C(14B)	0.5589(3)	0.5053(1)	1.0186(3)	2.9
C(11)	1.0465(7)	0.3296(3)	0.0668(7)	8.9	C(15B)	0.6151(3)	0.50461(9)	0.8728(3)	2.9
C(12)	0.9499(5)	0.3215(2)	0.1503(5)	6.3	C(16B)	0.5238(3)	0.4658(1)	1.0849(3)	2.9
O(1A)	1.0906(2)	0.74562(8)	0.5225(3)	3.7	C(17B)	0.7638(3)	0.50636(9)	0.8745(3)	2.8
O(2A)	0.9303(2)	0.77024(8)	0.3074(3)	4.2	C(18B)	0.4518(3)	0.4713(1)	1.2185(3)	3.1
O(3A)	0.8455(2)	0.67829	0.6197(2)	3.3	C(19B)	0.4550(4)	0.5050(1)	1.2969(4)	4.1
O(4A)	0.7220(2)	0.69299(7)	0.4181(2)	3.3	C(20B)	0.4018(4)	0.5067(1)	1.4257(4)	4.6
C(13A)	0.7396(3)	0.6645(1)	0.5270(4)	3.1	C(21B)	0.3446(4)	0.4749(1)	1.4790(4)	4.7
C(14A)	0.8995(3)	0.71236(9)	0.5628(3)	2.7	C(22B)	0.3386(5)	0.4411(1)	1.4015(5)	5.5
C(15A)	0.8415(3)	0.71247(9)	0.4068(3)	2.8	C(23B)	0.3907(5)	0.4392(1)	1.2731(5)	4.6
C(16A)	1.0467(3)	0.7109(1)	0.5891(3)	2.9	C(24B)	0.4484(4)	0.4401(1)	0.9770(4)	3.8
C(17A)	0.8110(3)	0.7525(1)	0.3342(3)	3.1	C(25B)	0.3249(5)	0.4503(1)	0.9230(5)	5.1
C(18A)	1.1020(3)	0.6753(1)	0.5155(3)	3.2	C(26B)	0.2577(6)	0.4271(2)	0.8230(6)	7.0
C(19A)	1.0924(4)	0.6387(1)	0.5754(4)	4.1	C(27B)	0.3108(8)	0.3936(2)	0.7765(6)	8.4
C(20A)	1.1357(4)	0.6064(1)	0.5052(5)	5.2	C(28B)	0.4313(8)	0.3821(2)	0.8324(7)	8.6
C(21A)	1.1872(4)	0.6107(2)	0.3761(5)	5.7	C(29B)	0.4997(5)	0.4059(1)	0.9304(6)	6.0
C(22A)	1.1979(5)	0.6470(2)	0.3181(5)	5.7	C(30B)	0.8183(3)	0.5432(1)	0.9486(3)	3.1
C(23A)	1.1548(4)	0.6790(1)	0.3879(4)	4.4	C(31B)	0.8195(4)	0.5783(1)	0.8766(4)	3.9
C(24A)	1.0941(3)	0.7124(1)	0.7461(4)	3.3	C(32B)	0.8708(4)	0.6116(1)	0.9427(6)	5.2
C(25A)	1.0146(4)	0.7155(1)	0.8554(4)	3.8	C(33B)	0.9196(5)	0.6099(2)	1.0805(6)	6.3
C(26A)	1.0646(5)	0.7209(1)	0.9941(4)	5.0	C(34B)	0.9183(5)	0.5753(2)	1.1548(5)	6.0
C(27A)	1.1961(5)	0.7236(1)	1.0257(4)	5.1	C(35B)	0.8690(4)	0.5421(1)	1.0883(4)	4.7
C(28A)	1.2751(4)	0.7205(1)	0.9187(5)	4.8	C(36B)	0.8121(3)	0.5045(1)	0.7262(4)	3.2
C(29A)	1.2262(3)	0.7146(1)	0.7792(4)	3.7	C(37B)	0.7370(4)	0.5060(1)	0.6004(4)	4.1
C(30A)	0.7411(3)	0.7476(1)	0.1855(4)	3.3	C(38B)	0.7899(5)	0.5029(1)	0.4709(5)	5.2
C(31A)	0.7245(4)	0.7125(1)	0.1153(4)	4.2	C(39B)	0.9194(5)	0.4976(2)	0.4673(5)	5.7
C(32A)	0.6721(5)	0.7114(2)	−0.0250(4)	5.2	C(40B)	0.9967(5)	0.4971(2)	0.5906(5)	6.2
C(33A)	0.6327(5)	0.7451(2)	−0.0926(4)	5.4	C(41B)	0.9437(4)	0.5002(2)	0.7202(5)	5.0
C(34A)	0.6469(6)	0.7803(2)	−0.0240(5)	6.0	C(42B)	0.3350(3)	0.5561(1)	0.7913(4)	3.6
C(35A)	0.6996(5)	0.7812(1)	0.1152(4)	5.0	C(43B)	0.4999(4)	0.5934(1)	0.9434(4)	3.6
C(36A)	0.7325(4)	0.7782(1)	0.4271(4)	3.8	C(44B)	0.2285(4)	0.5731(1)	0.8739(4)	4.1
C(37A)	0.6051(4)	0.7718(1)	0.4366(5)	5.0	C(45B)	0.3944(4)	0.6118(1)	1.0218(5)	4.6
C(38A)	0.5344(6)	0.7944(2)	0.5254(6)	7.7	C(46B)	0.2671(4)	0.6136(1)	0.9303(5)	4.9
C(39A)	0.5967(8)	0.8240(2)	0.6045(6)	8.8					

the same structure for the two inclusion complexes.

The structures of the guest molecules in I and II are very similar to each other. The C–N distances of the amide moieties are shorter than the usual C–N single bond distance, 1.475 Å. The torsion angles of O(1)–C(1)–C(2)–O(2) and C(1)–C(2)–N(1)–C(4) are −102.5(8) and 8(1)° for I and −102.2(5) and 6.3(6)° for II, respectively. These values are consistent with the corresponding ones of the phenylglyoxylamide derivatives, −88.1 and 5° for the pure crystal of **1b**[2] and −101 and

Table 4. Selected Bond Distances (l/Å) and Angles (ϕ/°)

	I	II		I	II
O(1)–C(1)	1.256(9)	1.226(5)	C(16A)–C(18A)	1.492(10)	1.543(5)
O(2)–C(2)	1.243(9)	1.239(5)	C(16A)–C(24A)	1.552(9)	1.528(5)
N(1)–C(2)	1.298(11)	1.327(6)	C(17A)–C(30A)	1.534(10)	1.540(5)
N(1)–C(3)	1.480(12)	1.460(8)	C(17A)–C(36A)	1.518(9)	1.532(5)
N(1)–C(4)	1.484(10)	1.481(6)	O(1B)–C(16B)	1.437(8)	1.434(4)
C(1)–C(2)	1.502(11)	1.509(6)	O(2B)–C(17B)	1.413(8)	1.434(4)
C(1)–C(7)	1.440(11)	1.459(6)	O(3B)–C(13B)	1.430(8)	1.415(4)
C(4)–C(5)	1.515(14)	1.526(11)	O(3B)–C(14B)	1.420(7)	1.410(4)
C(4)–C(6)	1.518(14)	1.487(9)	O(4B)–C(13B)	1.422(8)	1.436(4)
O(1A)–C(16A)	1.452(8)	1.442(4)	O(4B)–C(15B)	1.419(7)	1.436(4)
O(2A)–C(17A)	1.439(8)	1.430(4)	C(13B)–C(42B)	1.507(10)	1.511(5)
O(3A)–C(13A)	1.412(8)	1.435(4)	C(13B)–C(43B)	1.531(10)	1.518(5)
O(3A)–C(14A)	1.436(8)	1.425(3)	C(14B)–C(15B)	1.546(8)	1.545(5)
O(4A)–C(13A)	1.425(9)	1.422(4)	C(14B)–C(16B)	1.547(9)	1.552(5)
O(4A)–C(15A)	1.415(7)	1.429(4)	C(15B)–C(17B)	1.546(8)	1.556(5)
C(13A)–C(42A)	1.529(11)	1.512(5)	C(16B)–C(18B)	1.523(9)	1.537(5)
C(13A)–C(43A)	1.516(11)	1.510(5)	C(16B)–C(24B)	1.528(9)	1.519(5)
C(14A)–C(15A)	1.545(8)	1.550(4)	C(17B)–C(30B)	1.552(9)	1.534(5)
C(14A)–C(16A)	1.552(8)	1.541(4)	C(17B)–C(36B)	1.538(9)	1.533(5)
C(15A)–C(17A)	1.547(9)	1.559(5)			
O(1)–C(1)–C(7)	122.7(7)	123.7(4)	O(3A)–C(13A)–O(4A)	105.5(5)	105.3(2)
C(2)–C(1)–C(7)	120.3(7)	118.5(3)	O(3A)–C(13A)–C(42A)	113.4(6)	110.4(3)
O(2)–C(2)–N(1)	126.1(7)	125.3(4)	O(4A)–C(13A)–C(42A)	109.8(6)	110.3(3)
O(2)–C(2)–C(1)	113.6(7)	114.8(4)	O(3A)–C(13A)–C(43A)	114.1(6)	109.6(3)
N(1)–C(2)–C(1)	120.0(6)	119.8(3)	O(4A)–C(13A)–C(43A)	107.9(6)	108.3(3)
N(1)–C(4)–C(5)	110.3(7)	111.0(6)	O(1B)–C(16B)–C(14B)	101.6(5)	102.7(3)
N(1)–C(4)–C(6)	110.8(7)	112.0(5)	O(2B)–C(17B)–C(15B)	109.0(5)	107.8(3)
C(2)–N(1)–C(3)	117.1(6)	117.1(4)	C(15B)–C(14B)–C(16B)	120.4(5)	118.0(3)
C(2)–N(1)–C(4)	123.2(6)	122.5(4)	C(14B)–C(15B)–C(17B)	116.2(5)	116.4(3)
C(3)–N(1)–C(4)	119.6(7)	120.4(4)	O(3B)–C(14B)–C(15B)	102.8(4)	103.5(2)
O(1A)–C(16A)–C(14A)	103.3(5)	104.6(2)	O(3B)–C(14B)–C(16B)	107.2(5)	107.7(3)
O(2A)–C(17A)–C(15A)	108.8(5)	107.8(3)	O(4B)–C(15B)–C(14B)	103.8(4)	103.3(2)
C(15A)–C(14A)–C(16A)	116.9(5)	117.4(3)	O(4B)–C(15B)–C(17B)	111.8(5)	110.1(3)
C(14A)–C(15A)–C(17A)	118.3(5)	107.4(2)	O(3B)–C(13B)–O(4B)	105.4(5)	106.0(3)
O(3A)–C(14A)–C(15A)	103.3(5)	103.1(2)	O(3B)–C(13B)–C(42B)	109.2(5)	110.0(3)
O(3A)–C(14A)–C(16A)	108.8(5)	109.5(2)	O(4B)–C(13B)–C(42B)	114.6(5)	110.0(3)
O(4A)–C(15A)–C(14A)	102.0(5)	101.7(2)	O(3B)–C(13B)–C(43B)	109.8(5)	110.8(3)
O(4A)–C(15A)–C(17A)	108.6(5)	107.4(2)	O(4B)–C(13B)–C(43B)	113.5(6)	110.2(3)

Table 5. Intramolecular Contacts of Guest Molecules (l/Å)

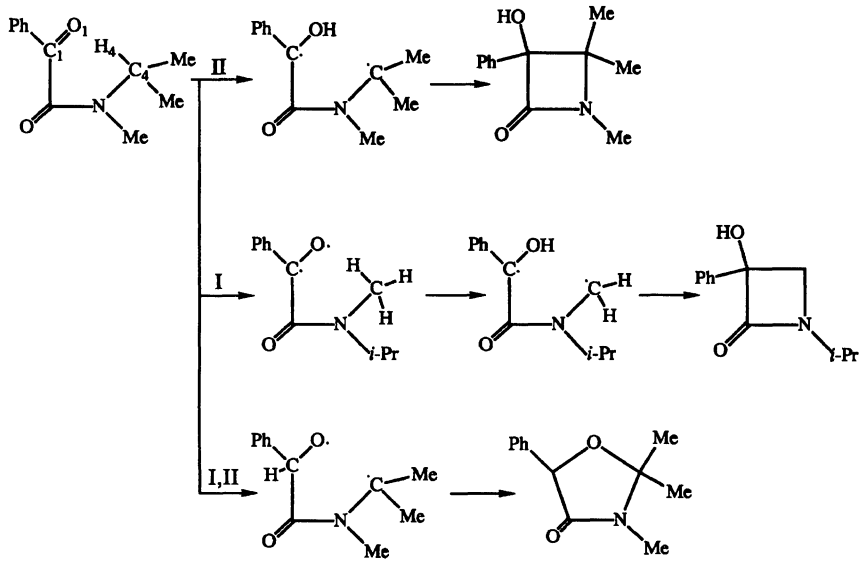
	C(1)···C(4)	O(1)···H(4)	O(1)···C(4)	C(1)···H(4)	Reference
I	2.87(1)	2.56(5)	3.20(1)	2.34(5)	This work
II	2.876(6)	2.556(6)	3.196(6)	2.347(6)	This work
III	2.86	2.79	3.18	2.53	1)
IV	2.87	2.78	3.42	2.23	2)

III: *N,N*-Dimethylglyoxylamide; IV: *N,N*-Diisopropylglyoxylamide.

3° for the inclusion crystal of **1a**,[2] respectively.

The above conformation of the guest molecules brings about intramolecular short contacts, which are listed in Table 5, together with the corresponding distances of *N,N*-dimethyl derivative in the clathrate crystal and *N,N*-diisopropyl derivatives in the pure crystal. The C(1)···C(4) distances are significantly shorter than the sum of the van der Waals radii, 3.5 Å.

If the photocyclization occurs between C(1) and C(4) as observed in the *N,N*-dimethyl and *N,N*-diisopropyl derivatives, the H(4) atom is extracted by O(1) to form a hydroxyl group. The configuration of the chiral



Scheme 2. Three possible routes of cyclization.

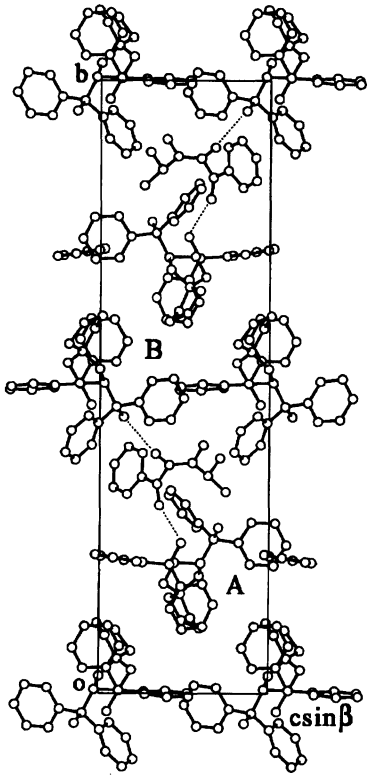


Fig. 1. Crystal structure of I viewed along the a-axis. Broken lines indicate the hydrogen bonds.

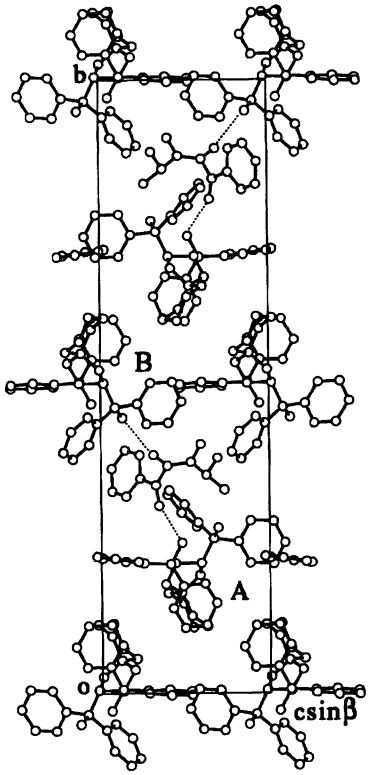


Fig. 2. Crystal structure of II viewed along the a-axis. Broken lines indicates the hydrogen bonds.

carbon, C(1), of the four-membered ring thus formed should be R from the topochemical point of view, as shown in Fig. 5. Since the absolute configuration of the produced β-lactam has not been determined for the present N-isopropyl-N-methyl derivative, it is not clear which sign of the optical rotation the R configuration gives. However, since dextrorotatory β-lactam from **1a** and **1b** has the R configuration, the R configuration of the present β-lactam **4a** and **4b** may have plus sign. For the crystal II the produced β-lactam **4b** has plus sign, although the reaction yield is 17% and the optical yield is 61% ee. Thus the reaction seems to proceed via the right route in Fig. 5. This mechanism is in good agreement with that observed in N,N-diisopropyl derivative.[2] However, from the crystal I the β-lactam **4a** with minus sign was obtained with 100% ee, although the reaction yield was 11%. The reaction may proceed following the rotations around the central two bonds as shown in the

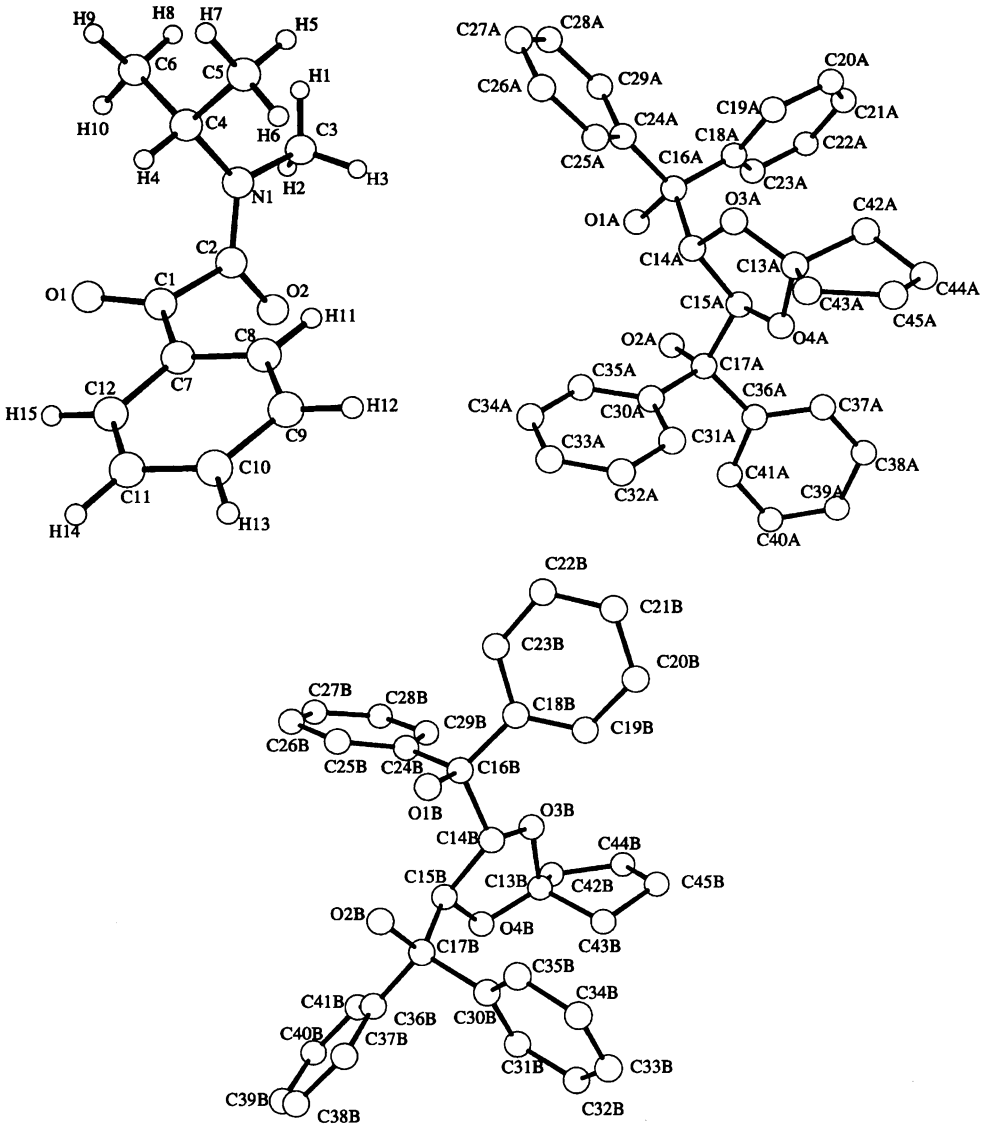


Fig. 3. Molecular structures and the numbering of atoms in I, a) the guest; b) the host A and c) host B.

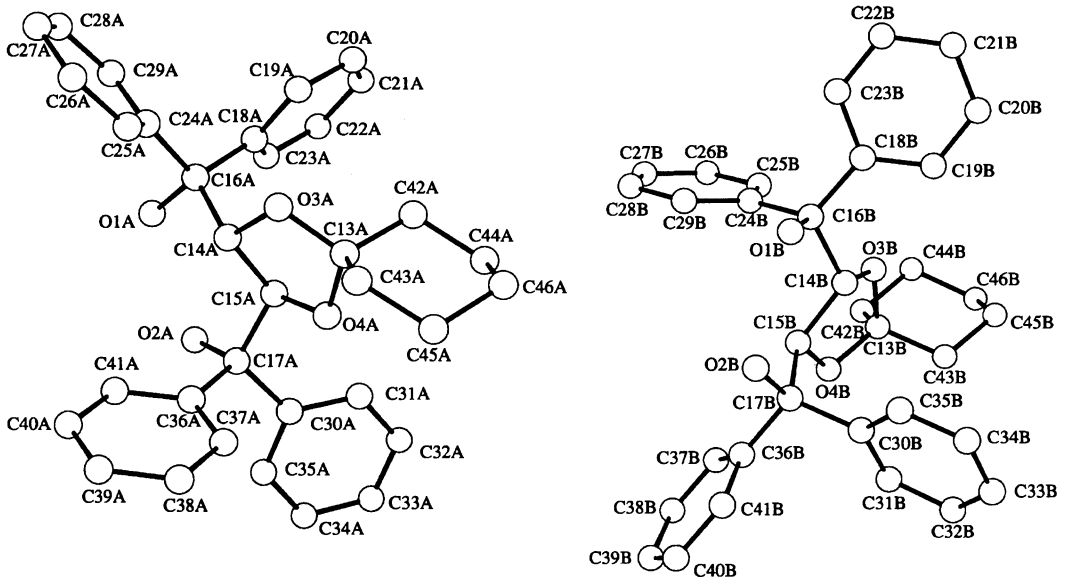


Fig. 4. Molecular structures and the numbering of atoms in II, a) the host A and b) host B.

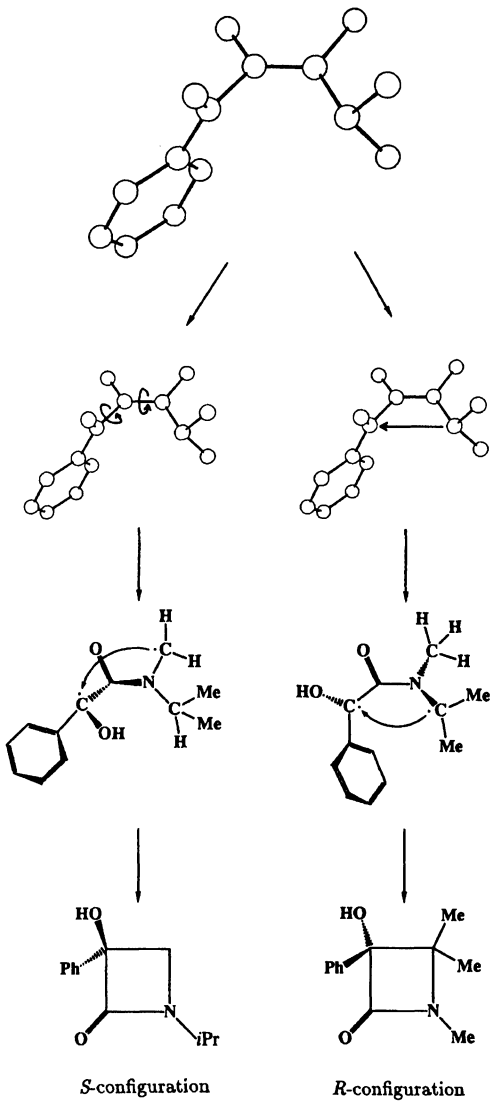


Fig. 5. A possible process of cyclization to form the chiral β-lactam.

left route in Fig. 5. Since the two crystals are very similar to each other and the conformations of the guest molecules in two crystals are approximately the same, it is obscure why **4a** with *S* configuration was made in the crystal I. This indicates that another factor should be taken into account to explain the difference.

For the present host–guest crystals, oxazolidinone was obtained. As shown in the Scheme 2, this may be produced if the H(4) is extracted by C(1) and the oxygen and carbon radicals may be made on exposure to UV light. Since the O(1) in either crystal is hydrogen-bonded to the host molecule, the produced oxygen radical would be stabilized. Therefore, the oxazolidinone derivative can be made in the inclusion compounds to more extend than that in the pure crystals. Since the hydrogen atom, H(4), appears to attack C(1) from the right side of the carbonyl plane in Fig. 6, the absolute configuration of C(1) should be *S* for both crystals, although the absolute configuration of the oxazolidinone

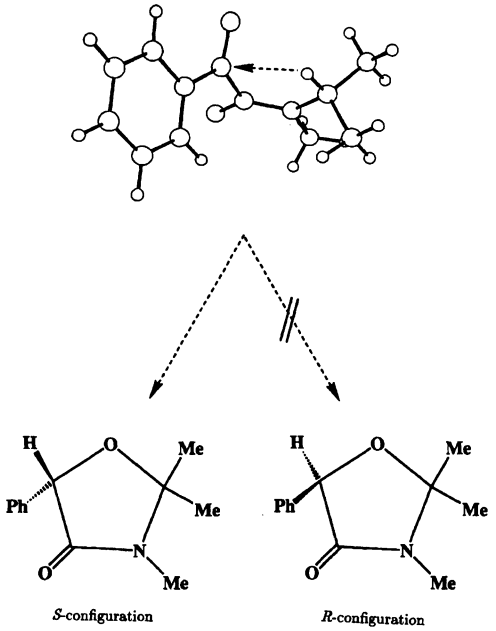


Fig. 6. A possible process to the chiral oxazolidinone.

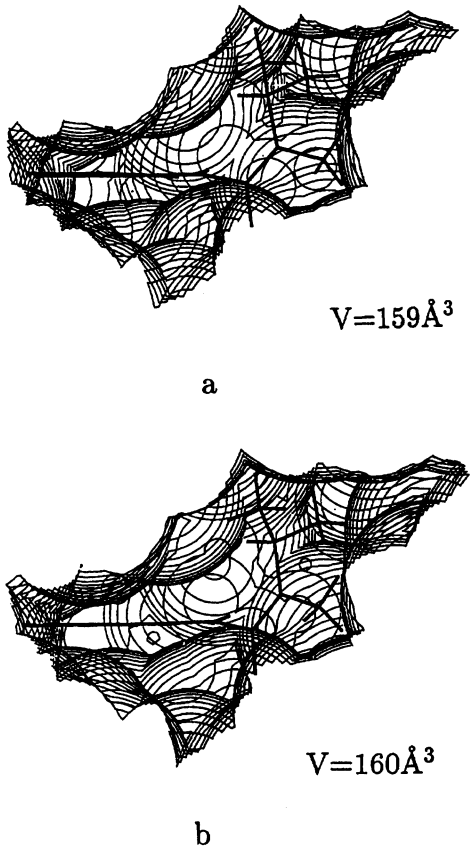


Fig. 7. Cavities of the guest molecules in a) I and b) II.

has not been determined. The produced oxazolidinone has minus sign of optical rotation for both inclusion crystals, although the optical yield was not so high. Somewhat low optical yield of the present oxazolidinone derivative, 39%ee for I and 43 %ee for II, may be due

to the rotation of the benzoyl group around C(1)–C(2) bond.

In order to explain the difference in chemical yields of the β-lactam and oxazolidinone between I and II, the reaction cavities were drawn for the guest molecules in the two crystals. As shown in Fig. 7, the two cavities have nearly the same shape, and the volumes are calculated to be 159 and 160 $Å^3$ for the guest molecules of I and II, respectively. The guest molecule in each crystal is in contact with the spiro rings. The flexibilities of the spiro rings are different between the five and six membered rings. This indicates that the softness of the cavity wall may be taken into account to explain the difference in reactivity between the two crystals. Further experiments are in progress.

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