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Optically Active *Anti* Head-to-head Coumarin Dimer. Resolution, Absolute Configuration, and Molecular Structure

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(±)-*Anti* head-to-head coumarin dimer was successfully resolved into a pair of optically active forms in good yields and in high optical purity by the fractional crystallization of both lactone-opened diamides with optically active 1-phenylethylamine followed by hydrolysis and relactonization. The absolute configuration of $(-)_{589}$-*anti* head-to-head coumarin dimer was confirmed to be (3*R*,3′*R*,4*R*,4′*R*) by X-ray crystal structure analysis, which showed puckering of the cyclobutane ring (32.5°) and some short nonbonded distances (2.15—2.60 Å).

In the previous papers it was shown that the lactone rings in *anti* head-to-head coumarin dimer, which can be easily prepared by the photochemical dimerization of coumarin,[1] are susceptible to nucleophilic ring-opening,[2] and the reaction was successfully applied to ring-opening polyaddition.[3] Although the optically active dimer may be useful as an optically active reagent with high reactivity and as an optically active diacid component in organic and polymer syntheses, respectively, no attempt at optical resolution of the dimer was reported. We have now optically resolved the dimer and determined the absolute configurations as reported in the preliminary paper.[4] This paper describes the optical resolution in detail and the absolute configuration on the basis of X-ray crystal structure analysis.

Results and Discussion

Optical Resolution of Anti *Head-to-head Coumarin Dimer (1).* It is known that *anti* head-to-head coumarin dimer (**1**) and the lactone-ring-opened derivative, *t*-3,*c*-4-bis(2-hydroxyphenyl)-*r*-1,*t*-2-cyclobutanedicarboxylic acid, are interconvertible.[1] The fractional crystallization of the salts of the cyclobutanedicarboxylic acid with chiral amines such as 1-phenylethylamine, brucine, strychnine, and quinidine has been carried out in an attempt to obtain optically active **1**, but all the trials resulted in failure. On the other hand, in our laboratory the relactonization of mono(lactone-ring-opened) *N*-butylamide of **1** has been found to occur smoothly on heating in solution.[5] The optical resolution of the diamide, prepared from **1** and an optically active amine by ring-opening reaction, was tried with the expectation that the diamide would be easily converted to the dimer (**1**).

When **1** was allowed to react with two molar amounts of (*S*)-(−)-1-phenylethylamine in dioxane at room temperature, white precipitate deposited. On the basis of elemental analysis, and ^{1}H NMR and IR spectral data, the precipitate was found to be one (**2a**) of a pair of diastereomeric diamides (79% yield). The residue, obtained from the filtrate on concentration, was crystallized from acetone/methanol (10/1 v/v) to give the other diastereomer (**2b**) in 81% yield. HPLC analyses of **2a** and **2b** thus-obtained each showed one peak only. The peak corresponding to the other diastereomer could not be detected, indicating that both of **2a** and **2b** were almost diastereomerically pure. Consequently both of the diastereomeric diamides could be obtained in good chemical yields and in high diastereomeric purity by crystallization from dioxane or acetone/methanol without recrystallization since their solubilities were extremely different.

Hydrolysis of **2** in ethanol/concd hydrochloric acid under refluxing proceeded without difficulty, and **2** was shown to be hydrolyzed completely within 20 h by TLC check. On heating the reaction mixture in acetic acid as described in the literature,[1] relactonization took place easily to give optically active **1**. The relactonization also proceeded efficiently on heating a toluene solution of the reaction mixture in the presence of a catalytic amount of *p*-toluenesulfonic acid.

Thus, $(+)_{589}$- and $(-)_{589}$-**1** were obtained from **2a** and **2b**, respectively. They were found to be almost optically pure since HPLC analyses of the diamides produced by the reaction of (+)- and (−)-**1** thus-obtained with (*S*)-(−)-1-phenylethylamine showed only one peak of the corresponding diastereomeric diamide. The result indicates that no racemization nor epimerization occurs in the course of the hydrolysis, the relactonization, and the nucleophilic ring-opening with an amine.

Absolute Configuration of (−)-1 Determined by X-Ray Crystal Structure Analysis. To determine the absolute configuration of optically active **1**, an X-ray crystal structure analysis of (−)-**1** was carried out. Differences of the calculated structure factors of ten selected Friedel pairs, *i.e.*, $\Delta F_c=|F_c(hkl)|-|F_c(\bar{h}\bar{k}\bar{l})|$ are compared in Table 1 with those of the observed

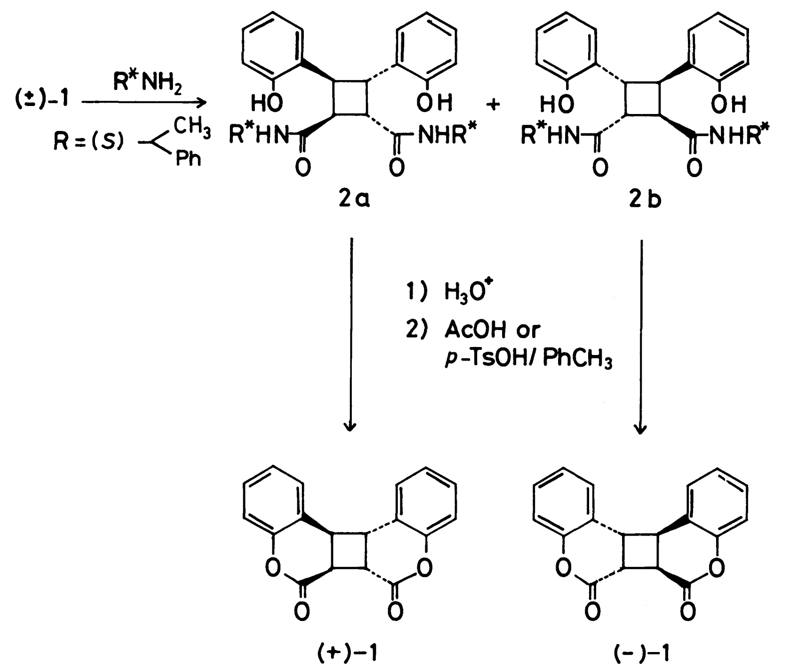

Table 1. Relation of $|F|$ in friedel pairs

h	k	l	$\langle F_c\rangle$	$\langle F_o\rangle$	ΔF_c	ΔF_o	$\sigma(\Delta F_o)$
6	8	1	12.5	16.4	0.6	2.1	0.9
1	11	1	20.3	24.1	0.4	0.4	0.4
5	5	2	23.8	16.3	0.8	1.9	0.8
3	5	2	21.1	23.2	0.7	1.1	0.4
2	1	3	24.9	20.2	−0.7	−0.7	0.3
9	8	3	14.0	12.2	−0.3	−1.4	0.7
1	8	6	16.9	21.3	−0.8	−1.0	0.8
2	5	6	49.8	51.1	−1.0	−1.2	0.5
1	4	9	33.5	26.7	0.6	1.1	0.6
1	7	9	36.1	41.2	0.7	0.7	0.6

All $|F_c|$s are multiplied by 10.0 in the absolute scale.

Table 2. Fractional atomic coordinates with their estimated deviations in parentheses and equivalent isotropic temperature factors (B/Å^2) of non-hydrogen atoms

	x	y	z	B_{eq}[a]
O(1)	0.5802(3)	−0.0163(2)	0.8124(2)	5.5
C(2)	0.4660(3)	−0.0947(3)	0.7404(3)	4.7
C(3)	0.3448(3)	−0.0134(2)	0.7624(2)	4.6
C(4)	0.3098(3)	0.0180(3)	0.8773(2)	4.1
C(5)	0.4664(5)	0.0616(3)	1.0378(2)	5.9
C(6)	0.6038(5)	0.0571(3)	1.0950(3)	7.1
C(7)	0.7250(5)	−0.0016(3)	1.0572(3)	7.2
C(8)	0.7168(4)	−0.0555(3)	0.9625(3)	6.3
C(9)	0.5786(4)	−0.0491(3)	0.9071(3)	4.9
C(10)	0.4527(4)	0.0088(3)	0.9420(2)	4.5
O(11)	0.4721(3)	−0.1494(2)	0.6624(2)	5.9
O(1′)	0.2094(3)	0.1882(2)	0.6193(2)	5.1
C(2′)	0.3506(4)	0.1481(3)	0.6361(3)	5.1
C(3′)	0.3881(3)	0.1064(3)	0.7424(2)	4.2
C(4′)	0.2869(3)	0.1351(2)	0.8381(2)	4.0
C(5′)	0.0026(4)	0.1602(2)	0.8716(3)	5.3
C(6′)	−0.1454(4)	0.1880(3)	0.8373(3)	5.9
C(7′)	−0.1674(4)	0.2157(3)	0.7338(3)	6.1
C(8′)	−0.0480(4)	0.2171(3)	0.6627(3)	5.4
C(9′)	0.0968(4)	0.1870(3)	0.6991(3)	4.5
C(10′)	0.1265(3)	0.1598(2)	0.8031(2)	4.3
O(11′)	0.4369(3)	0.1464(3)	0.5634(2)	7.6

a) The equivalent isotropic temperature factors were computed using the following expression; $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2)$. The B_{ij}'s are defined by; $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+klB_{23}+hlB_{13}+hkB_{12})]$.

ones, $\Delta F_o=|F_o(hkl)|-|F_o(\bar{h}\bar{k}\bar{l})|$. All the signs of ΔF_o are consistent with those of ΔF_c, indicating that the absolute configuration of (−)-**1** is correctly expressed by the atomic coordinates in Table 2 referred to a right-handed coordinate system. The configuration is drawn in Fig. 1, where the numbering system is also shown. From Fig. 1 the absolute configuration of (−)-**1** is concluded to be (3*R*, 3′*R*, 4*R*, 4′*R*).

Molecular Structure of (−)-1. The bond distances and angles are listed in Table 3. The dihedral angles between planes C(3′)-C(3)-C(4) and C(3′)-C(4′)-C(4), and between C(3)-C(4)-C(4′) and C(3)-C(3′)-C(4′) are the same value of 32.5°, showing that the cyclobutane ring in **1** crystal is puckered.

Some short nonbonded distances are found for C(2)···C(3′) (2.602(5) Å), C(3)···C(2′) (2.579(5) Å), C(4)···C(10′) (2.565(4) Å), and C(10)···C(4′) (2.515(4) Å), in addition to short ones in the cyclobutane ring, *i.e.*, C(3)···C(4′) (2.150(4) Å) and C(4)···C(3′) (2.152(4) Å), resulting from the puckering of the cyclobutane ring. This puckering and subsequent short contacts might be the reason for the instability and/or the high reactivity of lactones in **1**.

^{1}H NMR Study of (−)-1. ^{1}H NMR spectrum of (−)-**1** (Fig. 2a) showed a singlet of four protons (Ha, Hb, Hc, Hd) on the cyclobutane ring at δ 3.86. But, in ^{1}H NMR spectra of the both lactone-ring-opened derivatives, such as (−)-*t*-3,*c*-4-bis(2-hydroxyphenyl)-*r*-1,*t*-2-cyclobutanedicarboxylic acid (Fig. 2b) and its dimethyl and diethyl esters, two *pseudo* doublets were observed at δ 3.5—3.6 and 4.6—4.7. As the signal of methine protons adjacent to an aryl group is known to appear at lower region in a magnetic field than that of methine protons adjacent to a carboxyl group, the lower signal is assigned to the signal of Hb′ and Hd′, and the higher one to that of Ha′ and Hc′, respectively (see Fig. 2). The large up-field shift of the signal of Hb and Hd in comparison with that of Hb′ and Hd′ would be explained by the shielding effect of the facing aryl group. HGS molecular models show that Hb and Hd are in the shielding zone of the facing aryl group on the assumption of some puckering of the cyclobutane ring.

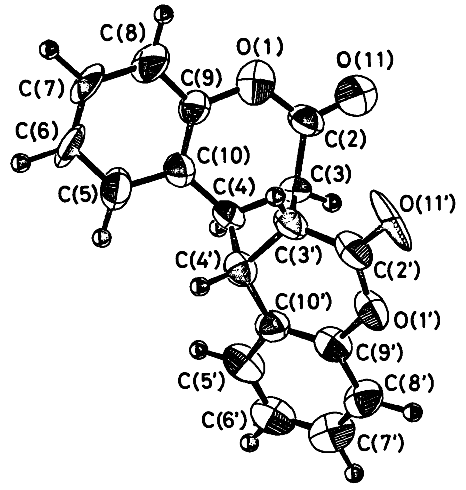

Fig. 1. Computer drawing of (−)-**1**.

The puckering, which would exist in a solution as well as in the crystalline state, conforms well to the up-field shift of Hb and Hd signals in the ^{1}H NMR spectrum of (−)-**1**.

CD Study of (+)-1. The absolute configuration of (+)-**1** was considered to be determinable on the basis of the CD exciton chirality theory,[6] if two phenolic

Table 3. Bond distances (l/Å) and angles (θ/°)

O (1)-C (2)	1.361 (4)	O (1′)-C (2′)	1.345 (4)
O (1)-C (9)	1.401 (4)	O (1′)-C (9′)	1.412 (4)
C (2)-C (11)	1.206 (4)	C (2′)-C (11′)	1.193 (5)
C (2)-C (3)	1.491 (4)	C (2′)-C (3′)	1.485 (5)
C (3)-C (4)	1.545 (4)	C (3′)-C (4′)	1.546 (4)
C (4)-C (10)	1.497 (4)	C (4′)-C (10′)	1.499 (4)
C (10)-C (5)	1.399 (5)	C (10′)-C (5′)	1.387 (5)
C (5)-C (6)	1.396 (6)	C (5′)-C (6′)	1.406 (5)
C (6)-C (7)	1.373 (6)	C (6′)-C (7′)	1.375 (6)
C (7)-C (8)	1.383 (6)	C (7′)-C (8′)	1.379 (5)
C (8)-C (9)	1.397 (5)	C (8′)-C (9′)	1.395 (5)
C (9)-C (10)	1.387 (5)	C (9′)-C (10′)	1.391 (4)
C (3)-C (3′)	1.564 (4)		
C (4)-C (4′)	1.558 (4)		
C (2)-O (1)-C (9)	121.2 (3)	C (2′)-O (1′)-C (9′)	121.1 (3)
O (1)-C (2)-C (3)	117.6 (3)	O (1′)-C (2′)-C (3′)	118.5 (3)
O (1)-C (2)-O (11)	117.5 (3)	O (1′)-C (2′)-O (11′)	117.3 (3)
C (3)-C (2)-O (11)	124.9 (3)	C (3′)-C (2′)-O (11′)	124.2 (3)
C (2)-C (3)-C (4)	119.4 (3)	C (2′)-C (3′)-C (4′)	120.7 (3)
C (3)-C (4)-C (10)	109.7 (2)	C (3′)-C (4′)-C (10′)	110.2 (3)
C (4)-C (10)-C (5)	121.3 (3)	C (4′)-C (10′)-C (5′)	122.6 (3)
C (4)-C (10)-C (9)	121.4 (3)	C (4′)-C (10′)-C (9′)	121.4 (3)
C (5)-C (10)-C (9)	117.3 (3)	C (5′)-C (10′)-C (9′)	116.9 (3)
C (10)-C (5)-C (6)	120.5 (3)	C (10′)-C (5′)-C (6′)	121.3 (3)
C (5)-C (6)-C (7)	120.0 (3)	C (5′)-C (6′)-C (7′)	119.2 (3)
C (6)-C (7)-C (8)	121.7 (3)	C (6′)-C (7′)-C (8′)	121.8 (3)
C (7)-C (8)-C (9)	117.2 (3)	C (7′)-C (8′)-C (9′)	117.4 (3)
C (8)-C (9)-C (10)	123.3 (3)	C (8′)-C (9′)-C (10′)	123.4 (3)
O (1)-C (9)-C (10)	123.3 (3)	O (1′)-C (9′)-C (10′)	123.9 (3)
C (2)-C (3)-C (3′)	116.8 (3)		
C (4)-C (3)-C (3′)	87.6 (3)		
C (10)-C (4)-C (4′)	110.7 (3)		
C (3)-C (4)-C (4′)	87.7 (3)		

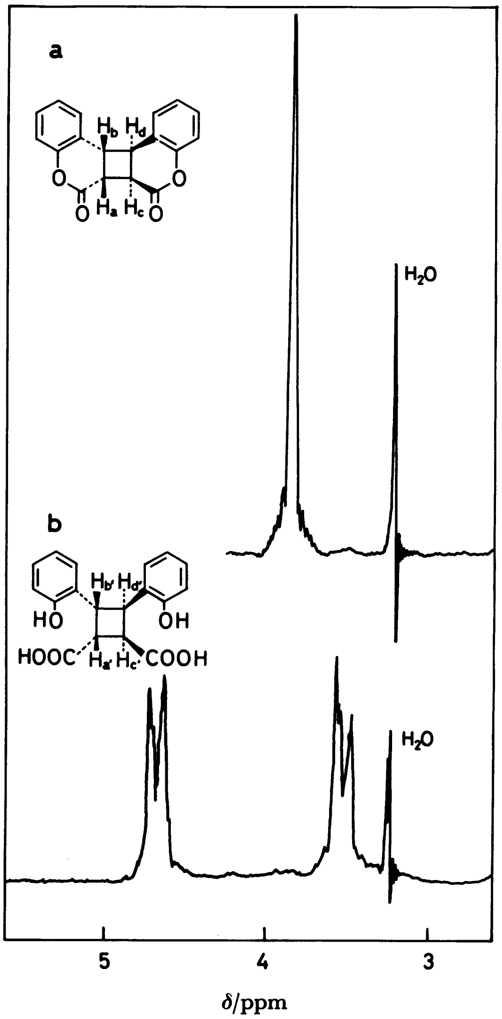

Fig. 2. The partial ^{1}H NMR spectra of (a) *anti* head-to-head coumarin dimer and (b) its both lactone-ring-opened derivative, *t*-3, *c*-4-bis(2-hydroxyphenyl)-*r*-1,*t*-2-cyclobutanedicarboxylic acid.

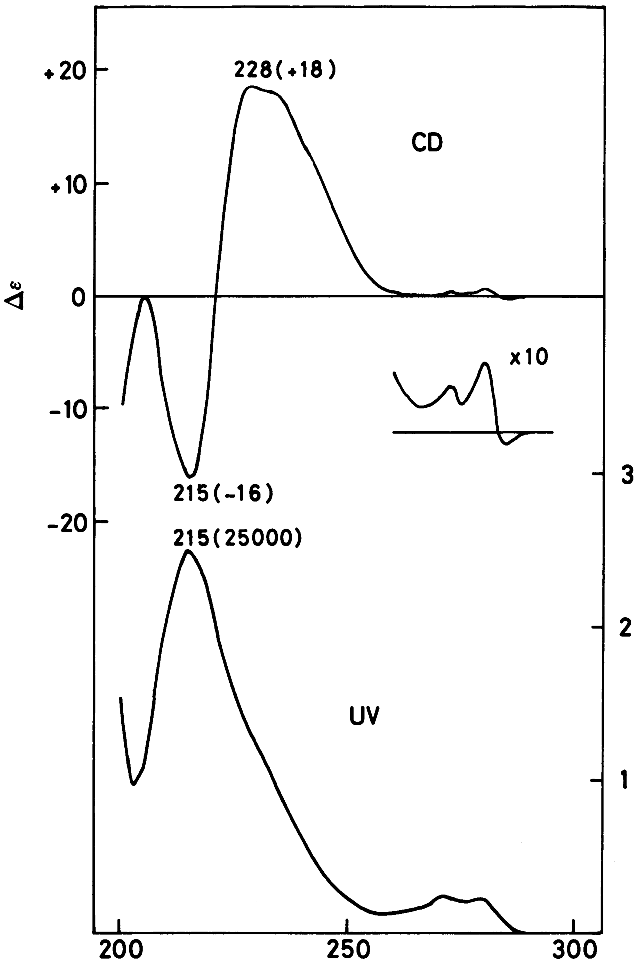

Fig. 3.

carbon–oxygen bonds in (+)-1 are non-parallel. The UV spectrum of (+)-1 in acetonitrile (Fig. 3) showed an absorption maximum at 215 nm, which would be attributable to ^{1}L$_a$←^{1}A transition directed along the long axis of the acyloxyphenyls, namely, along the phenolic carbon–oxygen bonds.[6,7] The CD spectrum of (+)-1 in acetonitrile (Fig. 3) showed a strong positive first Cotton effect at 228 nm and a negative second one at 215 nm, indicating a right-handed screw of the carbon–oxygen bonds.[8] Assuming that the predominant conformation of the lactone rings of (+)-1 in a solution is a *pseudo*-boat form as well as that in the crystalline state (Fig. 1), an HGS molecular model constracted on the basis of a right-handed screw of the carbon–oxygen bonds shows that the absolute configuration of (+)-1 is (3*S*, 3′*S*, 4*S*, 4′*S*), which is in good agreement with the result of the X-ray crystal structure analysis.

In the previous paper[4] the absolute configuration of (+)-1 has been reported to be (3*R*,3′*R*,4*R*, 4′*R*), which is the opposite of that indicated above. The erroneous conclusion would result from the mistaken assumption that the predominant conformation of the lactone rings of (+)-1 is a *pseudo*-chiar form.

Experimental

Melting points were determined on a Laboratory Devices Mel-Temp apparatus and are uncorrected. The IR spectra were measured on a JASCO IRA-1 Spectrophotometer. The ^{1}H NMR and UV spectra were recorded on a Hitachi R-40 Spectrometer (90 MHz) and on a Hitachi Model 100-60 Spectrophotometer, respectively. The specific rotations were measured on a JASCO DIP-181 digital polarimeter. The HPLC analyses were carried out on a LiChrosorb SI-60 column (4×250 mm, 0.5 ml/min) using a UV detector (280 nm).

Materials. (±)-*Anti* head-to-head coumarin dimer (1) was prepared by the method described in the literature.[1] Optically active 1-phenylethylamine (Yamakawa Chemical Industrial Co. Ltd.) was used without purification.

Synthesis and Separation of Diastereomeric Diamides (2a and 2b). To a solution of (±)-1 (58.46 g, 0.20 mol) in dry dioxane (870 ml) was added (*S*)-(−)-1-phenylethylamine (48.47 g, 0.40 mol). On stirring the mixture at room temperature, a white precipitate appeared gradually. After stirring for 12 h at the temperature, the precipitate was collected by filtration, washed thoroughly with dioxane (70 ml×2), and dried over P_2O_5 to give 42.29 g (79%) of one of diastereomeric diamides (**2a**): mp 237—238 °C; $[\alpha]^{21}_D$ −19.0° (*c* 0.50, 99% MeOH); IR (KBr) 3360, 3200, 1635, 1520, 1450, 750, and 695 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 1.26 (6H, d, *J*=7 Hz), 3.74 (2H, *pseudo* d, *J*=7 Hz), 4.5—4.9 (4H, m), 6.4—7.2 (18 H, m), 7.64 (2H, d, *J*=7 Hz), and 9.42 (2H, s).

Found: C, 76.54; H, 6.27; N, 5.17%. Calcd for $C_{34}H_{34}N_2O_4$: C, 76.38; H, 6.40; N, 5.23%.

The filtrate was concentrated to dryness under reduced pressure, and the residue was crystallized from acetone/methanol (1,500 ml/150 ml), giving 35.54 g (67%) of the other diastereomeric diamide (**2b**): mp 246—247 °C; $[\alpha]^{21}_D$ −177.3° (*c* 0.51, 99% MeOH); IR (KBr) 3360, 3200, 1630, 1520, 1445, 750, and 695 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 0.85 (6H, d, *J*=7 Hz), 3.72 (2H, *pseudo* d, *J*=7 Hz), 4.5—4.9 (4H, m), 6.6—7.3 (18H, m), 7.43 (2H, d, *J*=7 Hz), and 9.56 (2H, s).

Found: C, 76.66; H, 6.16; N, 5.19%. Calcd for $C_{34}H_{34}N_2O_4$: C, 76.38; H, 6.40; N, 5.23%.

The evaporation of the filtrate followed by crystallization from acetone/methanol (600 ml/60 ml) gave 7.66 g (14%) of **2b** as a second crop. The total yield of **2b** was 43.20 g (81%). The diastereomeric purities of **2a** and **2b** were found to be more than 99% on the basis of HPLC analysis (eluent: benzene/ethyl acetate=60/40 v/v).

*Hydrolysis and Relactonization of **2a** and **2b**.* The suspension of **2b** (5.35 g, 0.01 mol) in 99% ethanol/concd hydrochloric acid (100 ml/50 ml) was refluxed for 20 h to give a clear solution. After concentration, water (200 ml) was added to the residue and it was extracted with ethyl acetate (150 ml×3). The extracts were dried over anhydrous sodium sulfate and concentrated under reduced pressure. To the remaining oil acetic acid (150 ml) was added, and the solution refluxed for 20 h. After evaporation of the solvent to dryness, purification of the crude product by silica-gel chromatography (eluent: benzene then benzene/ethyl acetate=90/10 v/v) followed by recrystallization from ethyl acetate/hexane (60/40 v/v) gave 1.92 g (66%) of (−)-**1**: mp 168.5—169 °C; $[\alpha]^{21}_D$ −9.0°, $[\alpha]^{21}_{435}$ −65.8° (*c* 1.00, benzene); IR (KBr) 1760, 1490, 1450, 775, and 765 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 3.86 (4H, s) and 6.9—7.4 (8H, m).

Similar treatment of **2a** gave (+)-**1** in 64% yield: mp 168—169 °C; $[\alpha]^{21}_D$ +9.0°, $[\alpha]^{21}_{435}$ +66.0° (*c* 1.00, benzene); IR (KBr) 1760, 1490, 1450, 775, and 765 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 3.86 (4H, s) and 6.9—7.4 (8H, m).

The relactonization also proceeded in toluene in the presence of *p*-toluenesulfonic acid. A toluene solution (120 ml) of the crude product, obtained by the similar hydrolysis of **2a** (5.35 g, 0.01 mol), and *p*-toluenesulfonic acid (156 mg, 1 mmol) was refluxed for 48 h. After cooling, the mixture was washed with water (100 ml×2), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. Chromatographic purification followed by recrystallization in a similar manner gave 1.48 g (51%) of (+)-**1**.

To determine the optical purities of (+)- and (−)-**1**, small quantities of the dimers were again converted into both lactone-ring-opened diamides by the reaction with (*S*)-(−)-1-phenylethylamine in dioxane; they were found to be almost optically pure since the HPLC analyses of the diamides derived from them showed the sole formation of **2a** or **2b**, respectively.

Optically active **1** melting at 193—193.5 °C was sometimes obtained, while its ^{1}H NMR spectrum, HPLC retention time, and $[\alpha]_D$ value were identical with those of optically active **1** melting at 168—169 °C.

X-Ray Crystal Structure Determination. Colorless plate-shaped crystals of (−)-**1** (mp 168.5—169 °C) were grown from an acetone solution by slow evaporation at room temperature. The space group was determined from Weissenberg photographs. The precise lattice constants and intensity data were derived from measurements on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Cu-*Kα* radiation. The specimen used was a fragment of a plate, 0.20×0.20×0.20 mm. The density was measured by the floatation method in a mixture of cyclohexane and carbon tetrachloride. All reflections within the range of $\theta<75°$ were collected by use of the $\omega-2\theta$ scan mode with variable scan rate from 1.43 to 5°/min, of which 1593 were greater than $3\sigma(|F_o|)$ and were used for structure determination. No correction was made for absorption. Crystallographic data of (−)-**1**: $C_{18}H_{12}O_4$, M.W. 292.3. Orthorhombic, $P2_12_12_1$, a=8.711(1), b=12.493(4), c=12.728(3) Å, V=1385.1 Å^3. Z=4, D_x=1.407, D_m=1.40 g/cm^3.

The structure was solved by the direct method and was refined by the block-diagonal least-squares method.[8] The final refinement including isotropic hydrogen atoms reduced the *R* value to 0.055.[9] Atomic scattering factors were taken from International Tables for X-Ray Crystallography (1974). The final atomic coordinates are given in Table 2.

To determine the absolute configuration of (−)-**1**, structure factors of all the Friedel pairs (hkl and $\overline{h}\overline{k}\overline{l}$) were calculated using the parameters in Table 2. Among them, ten Friedel pairs were selected manually in order of difference in the intensities, and their intensities were measured on the diffractometer under the same conditions as those of the data collection described above.

UV and CD Measurements. The UV spectrum of a solution of (+)-**1** in acetonitrile (1.00×10^{-4} mol dm^{-3}) was recorded on a Shimadzu UV-260 Spectrophotometer. The CD spectrum of a solution of (+)-**1** in acetonitrile (3.23×10^{-4} mol dm^{-3}) was measured on a JASCO J-500 Automatic Spectropolarimeter under the following conditions using a 1 mm quartz cell: sensitivity 2m° cm^{-1}; time constant 8 s; wave length expansion 5 nm cm^{-1}; chart speed 2 cm min^{-1}; integration time 8 times.

The CD spectra of solutions of (+)-**1** in acetonitrile (4.04×10^{-5}, 8.07×10^{-5}, 8.07×10^{-6} mol dm^{-3}) were also measured, giving similar results to that shown in Fig. 3.

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