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Crystal Structures of the Cyclic Oligoesters from 6,8-Dioxabicyclo[3.2.1]octan-7-one. 1. The Cyclic Dimer and the Optically Active Cyclic Tetramer

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Abstract: The crystal structures of the cyclic dimer from racemic 6,8-dioxabicyclo[3.2.1]octan-7-one and the cyclic tetramer from the optically active (+)-(1*R*,5*R*)-6,8-dioxabicyclo[3.2.1]octan-7-one were studied by the X-ray method. The dimer crystal is monoclinic $P2_1/c$ with $a = 8.460$ (2) Å, $b = 7.254$ (1) Å, $c = 9.460$ (1) Å, and $\beta = 104.45$ (1)°. The tetramer crystal is monoclinic $P2_1$ with $a = 11.611$ (1) Å, $b = 10.417$ (2) Å, $c = 11.172$ (1) Å, and $\beta = 95.76$ (1)°. Their stereo configuration was determined, and the mechanism of ring-opening polymerization was verified. The tetramer molecule holds the acetonitrile molecule in its cavity to provide a good example of complexation caused by the dipole–dipole interaction.

Introduction

In the studies of ring-opening polymerization of bicyclic compounds containing a tetrahydropyran ring, racemic 6,8-dioxabicyclo[3.2.1]octan-7-one (**1**) was found to give 10-, 20-, and 25-membered cyclic oligoesters (**2**–**5**),[1–3] while the optically active monomer, (+)-(1*R*,5*R*)-6,8-dioxabicyclo[3.2.1]octan-7-one, gives only 20- and 25-membered ones.[4]

Preliminary X-ray studies of these oligoesters were carried out and summarized in Table I. The cyclic dimer or 10-membered cyclic ester crystallizes in a monoclinic cell. The cyclic tetramer and pentamer (20- and 25-membered cyclic esters) have several different crystal forms depending on the optical property of the compounds and on the crystallization conditions. It is desirable to determine these crystal structures not only to establish stereochemical structures of the cyclic oligoesters but also to investigate the reaction mechanisms of the ring-opening polymerization. The present report is concerned with the crystal structures of the cyclic dimer from the racemic 6,8-dioxabicyclo[3.2.1]octan-7-one and the cyclic tetramer from the optically active (+)-(1*R*,5*R*)-6,8-dioxabicyclo[3.2.1]octan-7-one.

Experimental Section

Cyclic Dimer. The crystal with dimensions 0.7 mm × 0.7 mm × 0.5 mm was used in the intensity measurements by a Hilger & Watts automatic four-circle diffractometer. Data were collected by the ω–2θ step scanning technique with Zr-filtered Mo Kα radiation. Structure amplitudes were obtained for 1374 unique reflections up to $2\theta = 55°$, of which 1329 were nonzero. Lorentz and polarization corrections were applied, but no absorption correction was made.

The structure was solved by the direct method using the program MULTAN[5] and refined by the block-diagonal least-squares method (HBLS V).[6] Difference Fourier synthesis revealed all the H atoms at the expected positions. Anisotropic thermal parameters were applied to nonhydrogen atoms and isotropic ones to the hydrogen atoms. The function minimized was $\sum\omega(\Delta F)^2$, with $\omega = 1/\sigma^2(F)$, where $\sigma(F)$ is the standard deviation based on counting statistics. The final R value was 0.076 for all the reflections and 0.075 for nonzero reflections. The final atomic parameters are listed in Tables II–IV. The labeling of the atoms is given in Figure 1.

Cyclic Tetramer. The crystal of dimensions 0.4 mm × 0.4 mm × 0.1 mm was used for the X-ray experiment. Rigaku four-circle diffractometer equipped with a rotating anode X-ray generator was used for the data collection. ω–2θ continuous scan mode was applied by using monochromatized Mo Kα with a scan range of $\Delta\omega = 1.0° + 0.35 \tan \theta°$ and a scan speed of 10°/min ($2\theta < 46°$) and 5°/min ($2\theta > 46°$). Data were collected up to $2\theta = 55°$ for total 3277 reflections, of which 2983 were nonzero. Lorentz and polarization corrections were applied, but no absorption correction was made.

Structure was solved by the direct method using the program MULTAN.[5] All the nonhydrogen atoms excluding 6 atoms of acetonitrile and a tetrahydropyran ring were located on the first E map, and the remaining atoms were found on the ΔF synthesis. The structure was refined by the block-diagonal least-squares method (HBLS V).[6] The function minimized was $\sum\omega(\Delta F)^2$, with $\omega = 0.45$ for $|F_o| = 0$ and $\omega = [\sigma^2(F) - 0.010|F_o| + 0.001|F_o|^2]^{-1}$ for $|F_o| > 0$, where $\sigma(F)$ is the standard deviation based on counting statistics. The final R value was 0.066 for all the reflections and 0.051 for nonzero reflections. The atomic scattering factors were taken from ref 7. The coordinates and anisotropic thermal factors, other than hydrogen, are listed in Tables V and VI. The hydrogen positional parameters are listed in Table VII. The isotropic thermal factor $B = 3.72$ Å^2 was assigned to all the hydrogen atoms.

Results and Discussion

Molecular Dimensions. The ORTEP[8] stereodrawings of **2** and **4*R*** are given in Figures 2 and 3. The bond lengths and angles are listed in Tables VIII and IX, while the conformation angles are listed in Table X for the 20-membered rings and in Table XI for the 6-membered ring.

The most interesting aspect of the molecular dimensions is the asymmetry of the two C–O bond lengths in the tetrahydropyran ring. The bond length of C(1)–O(1) is 1.436 (2) Å for **2** and 1.431 (4)–1.438 (4) Å, mean 1.433 Å, for **4*R***, while the bond length C(5)–O(1) is 1.409 (2) Å for **2** and 1.399 (4)–1.416 (5) Å, mean 1.405 Å, for **4*R***. The observed shortening of the C(5)–O(1) bond, comparing with the average C–O single bond 1.43 Å, resembles the anomeric effect[9] on the pyranose ring. Both experimental and theoretical studies have shown that the shortening of the anomeric C–O bond of the pyranose ring arises from the delocalization of the 2p lone pair electrons at oxygen atoms of the acetal bond sequence –O–C–O–, to compensate for the polarization of the σ orbitals due to the electron negativity differences.[10,11]

Unlike the acetal moiety in pyranose, the electron withdrawing

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(4) M. Okada, H. Sumitomo, and I. Tajima, *J. Am. Chem. Soc.*, **101**, 4013 (1979): In the previous papers 1–4, it was erroneously reported that a 30-membered cyclic hexamer was produced from both racemic and optically active 6,8-dioxabicyclo[3.2.1]octan-7-one, on the basis of the molecular weight determination by vapor pressure osmometry. Recent X-ray analysis has disclosed that it is actually a 25-membered cyclic pentamer. The error was due to the formation of a molecular complex of the cyclic pentamer with chloroform, whose molecular weight was close to that of the cyclic hexamer.

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Table I. Crystals of Cyclic Oligoesters from 6,8-Dioxabicyclo[3.2.1]octan-7-one[a]

		crystallizatn solvent	cryst data
dimer, **2**		CH_3CN	$P2_1/c$ ($Z = 2$), $a = 8.460$ (2) A, $b = 7.254$ (1) A, $c = 9.460$ (1) A, $\beta = 104.45$ (1)°
tetramer:	**4**, form I (unstable)	$CHCl_3$	$Pcmn$ ($Z = 8$), $a = 16.297$ (1) A, $b = 16.319$ (1) A, $c = 17.839$ (14) A
	4, form II	CH_3CN	$Pccn$ ($Z = 8$), $a = 14.290$ (8) A, $b = 15.997$ (8) A, $c = 24.096$ (31) A
	4, form III	CH_3CN	$C2/c$ ($Z = 8$), $a = 44.53$ (3) A, $b = 5.979$ (2) A, $c = 22.562$ (9) A, $\beta = 108.41$ (3)°
	4*R*	CH_3CN	$P2_1$ ($Z = 2$), $a = 11.611$ (1) A, $b = 10.417$ (2) A, $c = 11.172$ (1) A, $\beta = 95.76$ (1)°
pentamer:	**5**, form I (unstable)	CH_3CN	unknown
	5, form II	CH_3CN	$P2_1/c$ ($Z = 4$), $a = 13.11$ A, $b = 6.19$ A, $c = 45.99$ A, $\beta = 92$°
	5*R*	CH_3CN	$P2_12_12_1$ ($Z = 4$), $a = 10.050$ (2) A, $b = 14.764$ (2) A, $c = 24.268$ (4) A

[a] For the synthesis of **2**, **4**, and **5** racemic monomer is used, and for **4*R*** and **5*R*** optically active monomer (1*R*,5*R*)-6,8-dioxabicyclo[3.2.1]-octan-7-one is used.

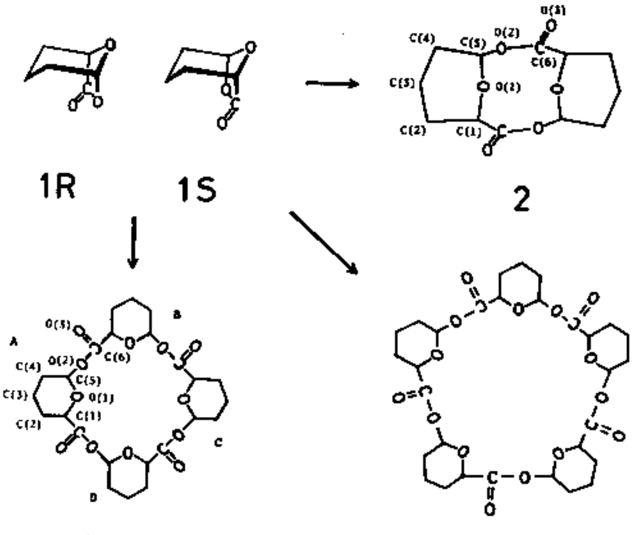

Figure 1. 6,8-Dioxabicyclo[3.2.1]octan-7-one and its cyclic oligoesters.

Table II. Atomic Positional Parameters and Their Esd's in Parentheses (×10⁴) for the Dimer

	x	*y*	*z*
C(1)	7573 (2)	−226 (2)	3306 (1)
C(2)	6082 (2)	893 (2)	3380 (1)
C(3)	6582 (2)	2551 (2)	4397 (1)
C(4)	7885 (2)	3659 (2)	3933 (1)
C(5)	9269 (2)	2471 (2)	3724 (1)
C(6)	8280 (2)	−1275 (2)	4721 (1)
O(1)	8781 (1)	878 (1)	2874 (1)
O(2)	9807 (1)	−1877 (1)	4825 (1)
O(3)	7528 (1)	−1594 (2)	5610 (1)

Table III. Hydrogen Positional (×10³) and Isotropic Thermal (×10) Parameters with Their Esd's in Parentheses for the Dimer

	x	*y*	*z*	*B*, A²	bonded to
H(1)	719 (2)	−120 (2)	246 (1)	17 (4)	C(1)
H(2)	525 (2)	9 (2)	373 (1)	13 (3)	C(2)
H(3)	549 (2)	136 (2)	237 (2)	19 (4)	C(2)
H(4)	710 (2)	211 (2)	546 (1)	11 (3)	C(3)
H(5)	552 (2)	329 (3)	435 (2)	36 (5)	C(3)
H(6)	836 (2)	458 (3)	468 (1)	24 (4)	C(4)
H(7)	735 (2)	434 (3)	299 (1)	22 (4)	C(4)
H(8)	1031 (2)	289 (3)	351 (2)	47 (6)	C(5)

Table IV. Anisotropic Thermal Parameters and Their Esd's in Parentheses (×10⁴) for the Dimer[a]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	85 (2)	102 (3)	67 (1)	−14 (4)	29 (3)	−25 (4)
C(2)	85 (2)	142 (3)	77 (1)	10 (5)	17 (3)	1 (4)
C(3)	96 (2)	139 (3)	84 (2)	44 (5)	44 (4)	−14 (4)
C(4)	117 (3)	111 (3)	102 (2)	30 (5)	18 (4)	14 (4)
C(5)	86 (2)	115 (3)	81 (2)	−1 (4)	26 (3)	37 (4)
C(6)	93 (2)	92 (3)	84 (2)	−14 (4)	42 (3)	−8 (4)
O(1)	101 (1)	134 (2)	63 (1)	0 (3)	55 (2)	6 (2)
O(2)	87 (1)	108 (2)	70 (1)	9 (3)	32 (2)	7 (2)
O(3)	111 (2)	219 (3)	135 (1)	46 (4)	122 (3)	145 (4)

[a] The temperature factor is in the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table V. Atomic Positional Parameters and Their Esd's in Parentheses (×10⁴) for the Tetramer

atom	*x*	*y*	*z*
C(1)A	4384 (2)	1862 (3)	5507 (2)
C(2)A	5055 (3)	2287 (3)	6741 (2)
C(3)A	6304 (3)	2559 (4)	6512 (3)
C(4)A	6819 (3)	1397 (4)	5939 (3)
C(5)A	6045 (3)	939 (3)	4855 (3)
C(6)A	5814 (2)	1567 (3)	2784 (2)
O(1)A	4898 (2)	757 (2)	5080 (2)
O(2)A	6093 (1)	1911 (2)	3938 (1)
O(3)A	5677 (2)	490 (2)	2453 (2)
C(1)B	5694 (2)	2758 (3)	2025 (2)
C(2)B	6819 (2)	3483 (3)	1982 (3)
C(3)B	6595 (3)	4649 (3)	1184 (3)
C(4)B	6004 (3)	4260 (4)	−365 (3)
C(5)B	4996 (3)	3384 (4)	662 (3)
C(6)B	2970 (2)	3702 (3)	202 (2)
O(1)B	5233 (1)	2359 (2)	856 (1)
O(2)B	4058 (1)	4148 (2)	471 (1)
O(3)B	2730 (2)	2765 (3)	−366 (2)
C(1)C	2147 (2)	4585 (3)	755 (2)
C(2)C	2077 (3)	5913 (3)	175 (3)
C(3)C	1214 (3)	6713 (3)	780 (3)
C(4)C	56 (3)	6023 (4)	735 (3)
C(5)C	205 (2)	4657 (3)	1195 (3)
C(6)C	343 (2)	3617 (3)	3086 (3)
O(1)C	1045 (1)	3970 (2)	651 (2)
O(2)C	515 (1)	4708 (2)	2475 (2)
O(3)C	−160 (2)	2708 (2)	2656 (2)
C(1)D	912 (2)	3736 (3)	4357 (2)
C(2)D	408 (2)	4793 (3)	5083 (3)
C(3)D	1035 (3)	4793 (3)	6354 (3)
C(4)D	972 (3)	3459 (4)	6904 (3)
C(5)D	1343 (2)	2439 (3)	6087 (3)
C(6)D	3144 (2)	1519 (3)	5699 (2)
O(1)D	805 (1)	2512 (2)	4901 (1)
O(2)D	2589 (1)	2564 (2)	6050 (2)
O(3)D	2709 (2)	500 (2)	5501 (2)
C(1)S	3081 (2)	2723 (4)	2956 (3)
C(2)S	2649 (3)	1776 (4)	2695 (3)
N(1)S	2065 (5)	578 (6)	2406 (5)

effect of the adjacent carbonyl group is notable in this molecule. Electron withdrawal in the C(5)–O(2) bond partially empties the 2p orbital on C(5) and facilitates the delocalization of the 2p-type lone pair on O(1) to provide the double-bond character with C(5)–O(1) bond. On the other hand, no such feedback of lone pair electrons is observed from the O(2) side.

No such symmetry at the C–O bonds of the ring was observed in Nonactin[12] in which an additional carbon atom exists between the ester group and the ring (in this case, tetrahydrofuran ring).

Complexation of 4*R* with an Acetonitrile. As is shown in Figure 3, **4*R*** holds an acetonitrile molecule in its cavity. In the figure,

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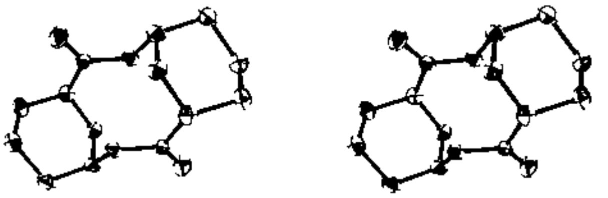

Figure 2. Stereodrawing of 2. The thermal ellipsoids are drawn at the 50% probability level.

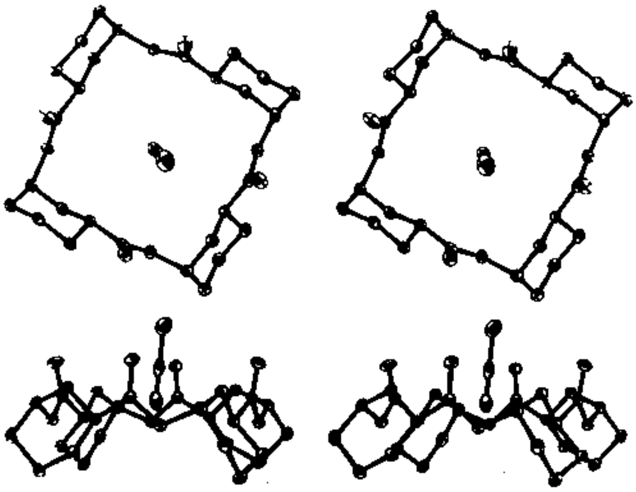

Figure 3. Stereodrawing of the molecular complex of 4*R* with an acetonitrile viewed from the directions parallel to (top) and perpendicular to (bottom) its noncrystallographic fourfold symmetry axis. The thermal ellipsoids are drawn at the 50% probability level.

Table VI. Thermal Parameters ($\times 10^4$) and Their Esd's in Parentheses for the Tetramer[a]

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)A	68 (2)	70 (3)	66 (2)	8 (4)	3 (4)	7 (5)
C(2)A	84 (3)	101 (4)	55 (2)	16 (5)	−10 (4)	−8 (5)
C(3)A	80 (2)	113 (4)	73 (2)	−3 (6)	−32 (4)	0 (6)
C(4)A	81 (3)	125 (4)	72 (3)	51 (6)	−28 (4)	10 (6)
C(5)A	80 (2)	74 (3)	74 (2)	37 (5)	2 (4)	20 (5)
C(6)A	70 (2)	72 (3)	65 (2)	19 (5)	−4 (4)	−16 (5)
O(1)A	79 (1)	70 (2)	70 (1)	20 (3)	−2 (2)	4 (3)
O(2)A	84 (2)	74 (2)	57 (1)	8 (3)	−2 (2)	−4 (3)
O(3)A	196 (3)	72 (2)	79 (2)	6 (5)	−55 (4)	−14 (4)
C(1)B	66 (2)	72 (3)	59 (2)	11 (4)	0 (3)	−14 (4)
C(2)B	73 (2)	87 (3)	85 (3)	−4 (5)	17 (4)	−13 (5)
C(3)B	76 (2)	83 (3)	115 (3)	7 (5)	47 (5)	32 (6)
C(4)B	91 (3)	111 (4)	94 (3)	56 (6)	78 (5)	63 (6)
C(5)B	84 (2)	109 (4)	60 (2)	45 (6)	24 (4)	8 (5)
C(6)B	86 (3)	83 (3)	56 (2)	15 (5)	−12 (4)	11 (5)
O(1)B	89 (2)	79 (2)	55 (1)	19 (3)	−4 (2)	−15 (3)
O(2)B	68 (1)	88 (2)	64 (1)	18 (3)	7 (2)	−1 (3)
O(3)B	101 (2)	122 (3)	120 (2)	28 (5)	−19 (4)	−106 (5)
C(1)C	66 (2)	69 (3)	58 (2)	−5 (4)	−18 (3)	10 (4)
C(2)C	89 (3)	77 (3)	104 (3)	6 (5)	13 (5)	52 (6)
C(3)C	100 (3)	73 (3)	104 (3)	28 (6)	−8 (5)	34 (6)
C(4)C	81 (3)	101 (4)	89 (3)	47 (6)	−36 (5)	9 (6)
C(5)C	60 (2)	92 (3)	80 (3)	6 (5)	−28 (4)	−8 (5)
C(6)C	48 (2)	74 (3)	101 (3)	−14 (4)	3 (4)	7 (5)
O(1)C	64 (1)	81 (2)	79 (2)	−7 (3)	−17 (3)	−21 (3)
O(2)C	67 (1)	74 (2)	80 (2)	−12 (3)	−6 (2)	4 (3)
O(3)C	95 (2)	93 (2)	122 (2)	−62 (4)	−44 (4)	25 (5)
C(1)D	54 (2)	68 (3)	83 (2)	−4 (4)	11 (4)	26 (5)
C(2)D	68 (2)	84 (3)	84 (3)	21 (5)	20 (5)	−5 (6)
C(3)D	88 (3)	92 (4)	98 (3)	30 (6)	36 (5)	−26 (6)
C(4)D	77 (3)	121 (4)	83 (3)	9 (6)	27 (4)	11 (6)
C(5)D	66 (2)	90 (3)	90 (3)	−11 (5)	20 (4)	27 (6)
C(6)D	77 (2)	74 (3)	60 (2)	5 (5)	−13 (4)	25 (4)
O(1)D	70 (1)	67 (2)	88 (2)	−12 (3)	6 (3)	32 (3)
O(2)D	63 (1)	75 (2)	94 (2)	3 (3)	6 (3)	3 (4)
O(3)D	94 (2)	72 (2)	130 (2)	−8 (4)	6 (4)	19 (4)
C(1)S	87 (2)	189 (5)	105 (3)	46 (7)	24 (4)	101 (7)
C(2)S	86 (3)	166 (5)	72 (3)	101 (7)	20 (4)	42 (7)
N(1)S	138 (6)	164 (7)	162 (6)	101 (12)	−15 (10)	−69 (12)

[a] Thermal parameters are in the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table VII. Hydrogen Positional Parameters and Their Esd's in Parentheses ($\times 10^3$) for the Tetramer

atom	*x*	*y*	*z*	bonded to
H(1)	439 (3)	256 (4)	498 (3)	C(1)A
H(2)	468 (3)	307 (4)	711 (3)	C(2)A
H(3)	504 (3)	163 (4)	741 (3)	C(2)A
H(4)	640 (3)	332 (4)	606 (3)	C(3)A
H(5)	682 (3)	276 (4)	735 (3)	C(3)A
H(6)	770 (3)	162 (4)	568 (3)	C(4)A
H(7)	693 (3)	66 (4)	664 (3)	C(4)A
H(8)	635 (3)	11 (4)	456 (3)	C(5)A
H(9)	512 (3)	334 (4)	231 (3)	C(1)B
H(10)	714 (3)	372 (4)	275 (3)	C(2)B
H(11)	741 (3)	296 (4)	160 (3)	C(2)B
H(12)	612 (3)	524 (4)	151 (3)	C(3)B
H(13)	732 (3)	511 (4)	103 (3)	C(3)B
H(14)	568 (3)	508 (4)	−50 (3)	C(4)B
H(15)	659 (3)	383 (4)	−52 (3)	C(4)B
H(16)	468 (3)	296 (4)	−71 (3)	C(5)B
H(17)	236 (3)	470 (4)	153 (3)	C(1)C
H(18)	284 (3)	631 (4)	22 (3)	C(2)C
H(19)	181 (3)	578 (4)	−66 (3)	C(2)C
H(20)	151 (3)	685 (4)	162 (3)	C(3)C
H(21)	111 (3)	760 (4)	39 (3)	C(3)C
H(22)	−54 (3)	650 (4)	116 (3)	C(4)C
H(23)	−31 (3)	594 (4)	−9 (3)	C(4)C
H(24)	−49 (3)	410 (4)	100 (3)	C(5)C
H(25)	171 (3)	391 (4)	431 (3)	C(1)D
H(26)	48 (3)	561 (4)	466 (3)	C(2)D
H(27)	−43 (3)	463 (4)	505 (3)	C(2)D
H(28)	183 (3)	504 (4)	634 (3)	C(3)D
H(29)	63 (3)	541 (4)	693 (3)	C(3)D
H(30)	144 (3)	344 (4)	767 (3)	C(4)D
H(31)	9 (3)	332 (4)	704 (3)	C(4)D
H(32)	144 (3)	157 (4)	644 (3)	C(5)D
H(33)	245 (3)	12 (4)	179 (3)	C(1)S
H(34)	190 (3)	7 (4)	310 (3)	C(1)S
H(35)	129 (3)	71 (4)	192 (3)	C(1)S

Table VIII. Bond Lenghs (A) and Angles (Deg) for 2

	Bond Lengths		
C(1)–C(2)	1.516 (3)	C(5)–O(1)	1.409 (2)
C(2)–C(3)	1.532 (3)	C(1)–O(1)	1.436 (2)
C(3)–C(4)	1.516 (3)	C(5)–O(2)	1.463 (2)
C(4)–C(5)	1.506 (3)	C(6)–O(2)	1.343 (2)
C(6)–C(1)	1.479 (2)	C(6)–O(3)	1.197 (2)
	Bond Angles		
C(6)–C(1)–C(2)	112.1 (2)	C(5)–O(1)–C(1)	115.1 (1)
C(6)–C(1)–O(1)	112.1 (1)	C(4)–C(5)–O(2)	106.1 (1)
O(1)–C(1)–C(2)	111.9 (1)	O(1)–C(5)–O(2)	107.7 (1)
C(1)–C(2)–C(3)	110.3 (2)	C(5)–O(2)–C(6)	113.9 (1)
C(2)–C(3)–C(4)	109.9 (2)	O(2)–C(6)–O(3)	123.8 (1)
C(3)–C(4)–C(5)	112.3 (2)	O(2)–C(6)–C(1)	112.7 (1)
C(4)–C(5)–O(1)	114.7 (1)	O(3)–C(6)–C(1)	123.5 (1)

the molecule is viewed from the directions parallel to and perpendicular to its noncrystallographic fourfold symmetry axis. The 20-membered ring is roughly square, consisting of the sides of trans zigzag atom chains (C(5)–O(1)–C(1)–C(6)–O(2)–C(5)) with the two consecutive gauche bonds (O(2)–C(5)–O(1)) at each corner. The sizes of the square-shaped ring are 5.941–5.975 Å (mean 5.961 Å) in terms of C(5)–C(5) distances.

The four carbonyl bonds are almost parallel to the fourfold axis. The angles between the facing carbonyl bonds are 24.4 and 22.5°, meaning that the carbonyl bonds are inclined at about 11.7° from the fourfold axis toward the outside of the ring. The main-chain conformation is by itself not the most stable one, since the molecule is highly polar in the direction of the fourfold axis. This polarity is compensated for by the dipole–dipole interactions between the carbonyl bonds and a $C\equiv N$ bond of the solvent molecule located at the center of the cavity. The polarities of the four C–O bonds made by O(1) and O(2) roughly balance themselves.

The complexation is a good example caused by the dipole–dipole interaction. The $C\equiv N$ bond of the solvent molecule sticks into the cavity until the nitrile carbon atom reaches 0.16 Å below the average plane consisting of the four carbonyl oxygen atoms. The

Table IX. Bond Lengths (A) and Angles (Deg) for 4R

	A	B	C	D	mean
C(1)–C(2)	1.529 (5)	1.521 (5)	1.534 (5)	1.527 (5)	1.528
C(2)–C(3)	1.532 (6)	1.521 (6)	1.522 (6)	1.538 (6)	1.528
C(3)–C(4)	1.528 (6)	1.528 (6)	1.528 (6)	1.532 (6)	1.529
C(4)–C(5)	1.519 (6)	1.506 (6)	1.525 (6)	1.500 (6)	1.513
C(6)–C(1)	1.510 (5)	1.512 (5)	1.519 (5)	1.512 (5)	1.513
C(5)–O(1)	1.399 (4)	1.402 (5)	1.404 (4)	1.416 (5)	1.405
C(1)–O(1)	1.438 (4)	1.431 (4)	1.432 (4)	1.431 (4)	1.433
C(5)–O(2)	1.454 (4)	1.466 (5)	1.449 (4)	1.465 (5)	1.459
C(6)–O(2)	1.354 (4)	1.358 (4)	1.358 (4)	1.351 (4)	1.355
C(6)–O(3)	1.195 (5)	1.189 (5)	1.195 (5)	1.194 (4)	1.193
C(6)–C(1)–C(2)	113.5 (3)	113.5 (3)	112.9 (3)	114.1 (3)	113.5
C(6)–C(1)–O(1)	106.6 (2)	106.4 (3)	107.1 (2)	106.3 (2)	106.6
O(1)–C(1)–C(2)	111.5 (2)	111.3 (2)	111.4 (2)	111.5 (2)	111.4
C(1)–C(2)–C(3)	108.8 (3)	108.8 (3)	108.6 (3)	108.9 (3)	108.8
C(2)–C(3)–C(4)	110.2 (3)	110.5 (3)	110.4 (3)	109.6 (3)	110.2
C(3)–C(4)–C(5)	111.2 (3)	112.3 (3)	111.2 (3)	111.9 (3)	111.4
C(4)–C(5)–O(1)	113.6 (3)	114.2 (3)	113.2 (3)	114.2 (3)	113.8
C(5)–O(1)–C(1)	113.7 (2)	113.0 (2)	113.2 (2)	113.6 (2)	113.4
C(4)–C(5)–O(2)	106.6 (3)	107.8 (3)	108.1 (3)	107.5 (3)	107.5
O(1)–C(5)–O(2)	109.3 (2)	109.1 (3)	109.6 (3)	108.4 (3)	109.1
C(5)–O(2)–C(6)	118.1 (2)	117.0 (2)	115.8 (2)	116.3 (2)	116.8
O(2)–C(6)–O(3)	124.2 (3)	124.6 (3)	123.9 (3)	124.8 (3)	124.4
O(2)–C(6)–C(1)	108.7 (3)	108.4 (3)	109.5 (3)	109.1 (3)	108.9
O(3)–C(6)–C(1)	127.0 (3)	126.9 (3)	126.6 (3)	126.0 (3)	126.6
C(1)S–C(2)S	1.448 (8)				
C(2)S–N(1)S	1.138 (7)				
C(1)S–C(2)S–N(1)S	177.4 (5)				

Table X. Conformation Angles of the 20-Membered Ring (Deg) for 4R

	A	B	C	D	mean
O(2)–C(6)–C(1)–O(1)	−174.3 (2)	−171.5 (2)	−169.4 (2)	−173.8 (2)	−172.3
C(6)–C(1)–O(1)–C(5)	177.4 (2)	175.8 (2)	176.5 (2)	177.3 (2)	176.8
C(1)–O(1)–C(5)–O(2)	−64.2 (3)	−66.4 (3)	−65.3 (3)	−66.5 (3)	−65.6
O(1)–C(5)–O(2)–C(6)	−78.8 (3)	−79.7 (3)	−75.5 (3)	−77.0 (3)	−77.8
C(5)–O(2)–C(6)–C(1)	168.9 (2)	177.0 (2)	169.3 (2)	173.2 (2)	172.1

Table XI. Conformation Angles of the Tetrahydropyran Ring (Deg) for 4R

	A	B	C	D	mean
O(1)–C(1)–C(2)–C(3)	57.4 (4)	59.4 (4)	58.5 (4)	58.3 (4)	58.4
C(1)–C(2)–C(3)–C(4)	−54.4 (5)	−53.3 (4)	−54.4 (4)	−54.5 (4)	−54.2
C(2)–C(3)–C(4)–C(5)	51.3 (4)	48.1 (4)	51.1 (4)	50.5 (4)	50.3
C(3)–C(4)–C(5)–O(1)	−51.1 (4)	−48.2 (4)	−51.0 (4)	−49.7 (4)	−50.0
C(4)–C(5)–O(1)–C(1)	54.7 (4)	54.2 (4)	55.5 (3)	53.4 (4)	54.5
C(5)–O(1)–C(1)–C(2)	−58.2 (3)	−60.1 (3)	−59.6 (3)	−57.9 (3)	−59.0

distances between the atoms of carbonyl carbon and nitrile nitrogen are 3.251–3.435 Å (mean 3.339 Å), while the distances between the atoms of carbonyl oxygen and nitrile carbon are 3.418–3.816 Å (mean 3.564 Å).

Molecular Configuration and Ring-Opening Polymerization Mechanism. The molecule **2** is on the crystallographic center of symmetry. Of the six diastereomers possible for the cyclic dimer, the structure determined is the centrosymmetric one whose configuration is *SSRR* with respect to the asymmetric carbon atoms C(1), C(5), C(1′), and C(5′). The bonds C(1)–C(6) and C(5)–O(2) from tetrahydropyran ring are both in axial positions. The implication of this structure to the study of the ring-opening polymerization is reported elsewhere.[2]

Four tetrahydropyran rings of **4*R***, on the other hand, are in the chair form with C(1)–C(6) bonds in equatorial position and C(5)–O(2) bonds in axial position. The chirality of the **4*R*** molecule cannot be determined by this analysis alone, but the C(1) asymmetric carbon retains the configuration through the reaction, so the absolute configuration of the **4*R*** is proved to be $(1R,5S)_4$. This is very important in the consideration of the mechanism of the ring-opening polymerization of **1*R***.

There are two possible modes of bond cleavage of **1*R*** when it is ring-opened by cationic species, namely, alkyl–oxygen fission (C(=O)O—C bond) and acyl–oxygen fission (C(=O)—OC bond). In fact, in the acid-catalyzed hydrolysis of 1,3-dioxolan-4-one (5-membered cyclic acetal esters), two different mechanisms, unimolecular alkyl–oxygen fission($A_{AL}1$-like mechanism) and bimolecular acyl–oxygen fission ($A_{AC}2$ mechanism), have been proposed on the basis of kinetic data.[13] The fact that the absolute configuration of all the acetal carbons of **4*R*** is opposite to that of the corresponding carbon of **1*R*** clearly reveals that the ring-opening polymerization of **1*R*** takes place by the attack of monomer to the partially positively charged acetal carbon atom of the terminal oxonium ion of a growing chain from the direction opposite to the breaking C–O bond, in other words, by an S_N2 type mechanism involving the exclusive alkyl–oxygen fission.

Furthermore, it is of particular interest that **4*R*** forms a molecular complex with acetonitrile in which an acetonitrile molecule is located in the cavity of **4*R***, because the cationic polymerization of **1*R*** gives rise to **4*R***, along with **5*R*** only in acetonitrile, while it preferentially or exclusively produces **5*R*** in methylene chloride, chloroform, and 1-nitropropane.[4] It is therefore suggested that in the polymerization of **1*R*** in acetonitrile, the solvent molecule itself directly participates in the formation of **4*R***, presumably by acting as a kind of template to facilitate the ring closure of a linear growing chain to **4*R*** and/or by complexing with **4*R*** to prevent its transformation to **5*R***.

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(13) P. Salomaa, *Acta Chem. Scand.*, **20**, 1263 (1966).