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Crystal Structures of the Cyclic Oligoesters from 6,8-Dioxabicyclo[3.2.1]octan-7-one. 3. The Cyclic Pentamer

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Abstract: The crystal structures of the complexes of the cyclic pentamers from both optically active and racemic 6,8-dioxabicyclo[3.2.1]octan-7-one with acetonitrile or acetone have been determined by the single-crystal X-ray diffraction method. The former belongs to the orthorhombic space group $P2_12_12_1$ with cell dimensions a = 10.050 (1) Å, b = 14.764 (2) Å, c = 24.268 (4) Å, and Z = 4. The final R value was 0.112 for all the reflections and 0.083 for nonzero reflections. The space group of the latter is also $P2_12_12_1$ with cell dimensions a = 9.863 (5) Å, b = 14.727 (4) Å, c = 24.335 (9) Å, and Z = 4. The final R value was 0.081 for all the reflections and 0.077 for nonzero reflections. The two structures are isomorphous with each other and the pentamer, which is a nearly regular pentagonal shaped molecule, includes an acetonitrile or acetone molecule in its cavity. In spite of the differences in shape and size from the previously analyzed tetramer, which is a regular tetragonal shaped molecule, the present molecule has similar main-chain conformation angles, showing the molecules of this group have rather rigid main-chain conformation. The solvent molecules are so aligned that their dipole moments are opposite to that of the pentamer molecule. But this antiparallel arrangement of dipoles is not so perfect as was seen in the case of the tetramers.

Cationic ring-opening oligomerization of 6,8-dioxabicyclo[3.2.1]octan-7-one yields cyclic oligoesters di-, tetra-, and pentamers[1-4] (Figure 1). Among them, we have so far studied the crystal structures of the di- and tetramers.[5] The dimer **2**, which is produced only from racemic monomer **1**, was proved to be a meso compound having an inversion center in the molecule. On the other hand, the tetramers, which are produced from both **1** and **1R** ((+)-(1*R*,5*R*)-6,8-dioxabicyclo[3.2.1]octan-7-one), have several crystal forms, of which two structures were reported. One is the optically active tetramer (**4R**)[5] from **1R** and the other is an optically inactive tetramer form III crystal (**4** form III) from **1**.[6]

In this paper, we deal with the structures of the cyclic pentamers. While **5R** from **1R** crystallizes only in one crystal form, **5** from **1** has been known to crystallize in at least two different forms. Since type I crystals of **5** are unstable and type II are extremely fine needle, their structures have not yet been solved. However, recent attempts to recrystallize them from an acetone solution gave a suitable crystal (form III) for X-ray analysis. Inspection of the X-ray photographs revealed that this crystal was isomorphous with the crystal of **5R** from acetonitrile solution. (Crystal data are given in Table I.) It is apparent that **5** from **1** is not a meso compound but a racemic mixture of **5R** and **5S** and the optical resolution occurs during the crystallization process. In spite of the isostructural relationship of **5R** and **5** (form III), they were expected to include different solvent molecules, i.e., acetonitrile or acetone. Therefore, we attempted to analyze both crystals.

One of the most interesting results found in the structure analysis of the cyclic tetramer was its unique interactions with polar solvent molecules: the cyclic tetramer forms an inclusion complex with an acetonitrile molecule by dipole–dipole interactions. It is all the more interesting to know the complexation mode of the pentamer, which has a larger cavity and seemingly more flexible conformation.

These molecules, on the other hand, bear a structural resemblance to nonactin, a naturally occurring ionophore. Actually, **4**(**4R**) and **5**(**5R**) are known to interact with alkali metals or alkaline-earth metals in solution.[7] Establishment of the structural characteristics, shape, and size of the molecule and molecular cavity is requisite for better understanding of the ion extraction properties of these synthetic macrolides.

Table I. Crystal Data

	5R	5
included molecule	acetonitrile	acetone
space group	$P2_12_12_1$	$P2_12_12_1$
a, Å	10.050 (1)	9.863 (5)
b, Å	14.764 (2)	14.727 (4)
c, Å	24.268 (4)	24.335 (9)
Z	4	4
D_{calcd}, g·cm^{-3}	1.257	1.313
D_{obsd}, g·cm^{-3}	1.28	1.29

Experimental Section

5R and Acetonitrile Complex. A crystal of dimensions 0.4 mm × 0.3 mm × 0.2 mm was used for the X-ray experiment. A Rigaku four-circle diffractometer equipped with a rotating anode X-ray generator was used for the data collection and the ω–2θ continuous scan mode was adopted 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 ($2\theta \leq 42°$) and 3°/min ($2\theta > 42°$). Data were collected up to $2\theta = 45°$ for a total of 2706 reflections, of which 2355 were nonzero. Lorentz and polarization corrections were applied, but no absorption correction was made.

The structure was solved by the direct methods program MULTAN.[8] An E map showed most of the non-hydrogen atoms. The remaining atoms were located by successive ΔF synthesis. The structure was refined by the block-diagonal least-squares method. Anisotropic temperature factors were assigned to all the non-hydrogen atoms. Isotropic temper-

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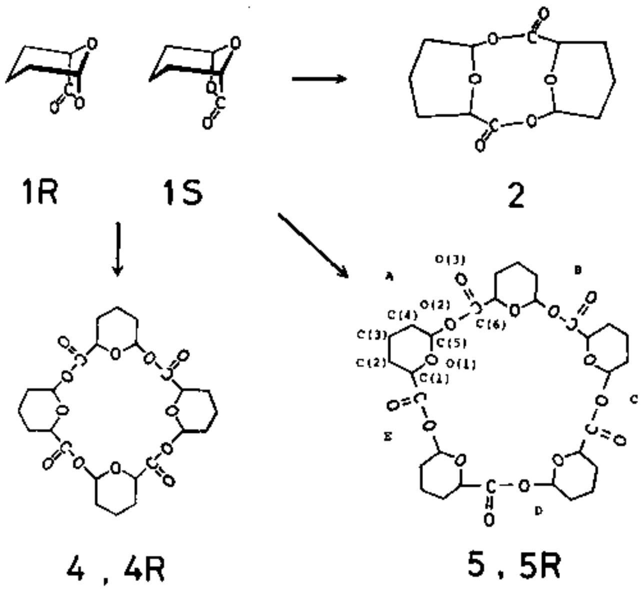

Figure 1. 6,8-Dioxabicyclo[3.2.1]octane-7-one and its cyclic oligoesters.

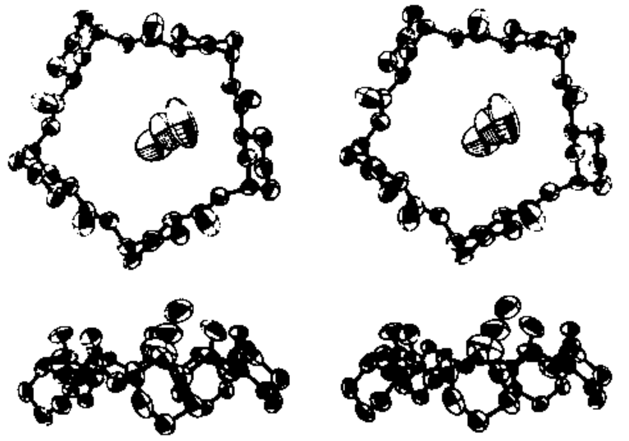

Figure 2. Stereodrawing of the molecular complex of **5** with an acetone viewed from the directions parallel to (top) and perpendicular to (bottom) its noncrystallographic fivefold symmetry axis.

ature factors for hydrogen atoms were held constant, equal to B_{eq} of their carrier atoms. The function minimized was $\sum w(\Delta F)^2$, with $w = 0.0662$ for $|F_o| = 0$ and $w = [\sigma^2(F) + 0.2074|F_o| + 0.003|F_o|^2]^{-1}$ for $F_o \neq 0$ where $\sigma(F)$ is the standard deviation based on counting statistics. The final R value was 0.112 for all the reflections and 0.083 for nonzero reflections. The final atomic parameters are listed in Tables II and III.

5 and Acetone Complex. The size of the crystal was 0.2 mm × 0.2 mm × 0.1 mm. Since preliminary photographic work had shown a substantially high temperature factor, the diffractometer experiment was performed at −84 °C. Monochromatized Cu Kα was used with an ω–2θ scan mode and a scan speed of 10°/min. Data were collected up to $2\theta = 115°$ for a total of 2756 reflections, of which 2662 were nonzero.

The atomic parameters of the non-hydrogen atoms of **5R**, excluding those of the solvent molecule, were used for the first-phase calculation. The acetone molecule and the hydrogen atoms were located on the ΔF synthesis. In the least-squares refinement, the weighting scheme was $\sum w(\Delta F)$, with $w = 0.1296$ for $|F_o| = 0$ and $w = [\sigma^2(F) + 0.1161|F_o| + 0.003|F_o|^2]^{-1}$ for $|F_o| \neq 0$. The final R value was 0.081 for all the reflections and 0.077 for nonzero reflections. The atomic scattering factors were taken from ref 9. The final atomic parameters are deposited in the supplementary material.

Results and Discussion

Optical Resolution. We did not determine the absolute configuration of **5**, but to make a comparison with **5R** easy, we depicted the absolute configuration of **5** as identical with that of **5R**. Recent X-ray analysis of form III crystals of **4** revealed that they are also a racemic mixture of **4R** and **4S**.[6]

Table II. The Atomic Positional Parameters and Their Esd's in Parentheses (X10^4) for the Acetonitrile Complex

atom	x	y	z	B_{eq},[a] A^2
C(1)A	−723 (8)	−353 (6)	1613 (3)	4.1 (4)
C(2)A	1 (11)	−854 (7)	2075 (4)	5.8 (5)
C(3)A	−425 (10)	−1834 (7)	2129 (4)	5.5 (5)
C(4)A	−1933 (11)	−1858 (8)	2185 (4)	6.1 (5)
C(5)A	−2620 (9)	−1304 (6)	1753 (3)	4.6 (4)
C(6)A	−3458 (9)	−1824 (7)	902 (4)	5.0 (4)
O(1)A	−2140 (5)	−408 (4)	1701 (2)	4.3 (2)
O(2)A	−2430 (6)	−1768 (4)	1243 (2)	4.8 (3)
O(3)A	−4491 (8)	−1471 (6)	962 (3)	7.7 (4)
C(1)B	−3054 (8)	−2419 (6)	412 (3)	4.4 (4)
C(2)B	−2686 (11)	−3345 (7)	585 (4)	5.4 (4)
C(3)B	−2400 (11)	−3896 (6)	51 (4)	5.2 (4)
C(4)B	−3572 (11)	−3896 (6)	−322 (4)	5.3 (4)
C(5)B	−3993 (9)	−2932 (6)	−440 (3)	4.6 (4)
C(6)B	−3288 (9)	−1870 (6)	−1112 (3)	4.5 (4)
O(1)B	−4163 (6)	−2409 (5)	28 (3)	4.9 (3)
O(2)B	−2965 (6)	−2547 (4)	−777 (2)	4.6 (3)
O(3)B	−4357 (6)	−1491 (4)	−1143 (3)	5.1 (3)
C(1)C	−2109 (8)	−1629 (6)	−1476 (3)	4.0 (3)
C(2)C	−1761 (10)	−2419 (7)	−1854 (5)	5.8 (5)
C(3)C	−642 (10)	−2120 (9)	−2244 (4)	6.5 (5)
C(4)C	−1026 (10)	−1250 (9)	−2538 (4)	6.2 (5)
C(5)C	−1469 (9)	−524 (6)	−2129 (3)	4.6 (4)
C(6)C	−126 (10)	616 (6)	−1708 (4)	5.4 (5)
O(1)C	−2420 (6)	−825 (4)	−1753 (2)	4.5 (3)
O(2)C	−280 (6)	−268 (4)	−1828 (3)	5.3 (3)
O(3)C	−885 (9)	1186 (5)	−1832 (4)	9.4 (5)
C(1)D	1146 (11)	748 (6)	−1390 (4)	5.4 (5)
C(2)D	2372 (10)	383 (8)	−1725 (4)	6.6 (5)
C(3)D	3617 (11)	606 (8)	−1406 (4)	5.8 (5)
C(4)D	3695 (11)	1606 (9)	−1295 (4)	6.7 (6)
C(5)D	2434 (12)	1928 (7)	−1011 (4)	6.3 (5)
C(6)D	1859 (9)	2012 (6)	−48 (4)	4.8 (4)
O(1)D	1253 (7)	1686 (4)	−1287 (3)	5.8 (3)
O(2)D	2403 (7)	1539 (4)	−473 (3)	5.6 (3)
O(3)D	1305 (9)	2701 (5)	−114 (3)	7.6 (4)
C(1)E	2066 (8)	1506 (6)	478 (3)	4.3 (4)
C(2)E	3554 (10)	1423 (9)	601 (4)	6.1 (5)
C(3)E	3728 (10)	1002 (10)	1182 (4)	6.9 (6)
C(4)E	2916 (10)	1514 (8)	1601 (4)	5.7 (5)
C(5)E	1494 (10)	1601 (7)	1429 (4)	5.6 (5)
C(6)E	−372 (8)	615 (7)	1596 (4)	4.8 (4)
O(1)E	1347 (6)	1962 (4)	897 (3)	5.1 (3)
O(2)E	922 (6)	696 (4)	1444 (3)	5.2 (3)
O(3)E	−1059 (7)	1245 (5)	1712 (4)	7.6 (4)
C(1)S	−3484 (25)	327 (16)	−419 (14)	19.3 (20)
C(2)S	−2275 (18)	135 (15)	−300 (11)	14.6 (14)
N(1)S	−1187 (19)	116 (16)	−292 (9)	17.6 (16)

[a] The B_{eq} values are the equivalent isotropic temperature factor.

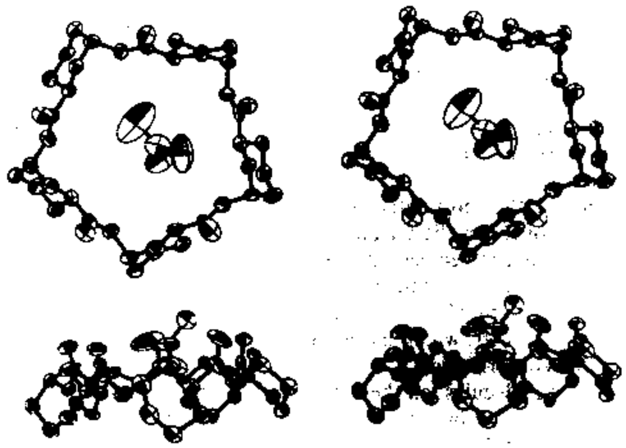

Figure 3. Stereodrawing of the molecular complex of **5R** with an acetonitrile molecule.

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

atom	*x*	*y*	*z*	bonded to
H(1)	−56 (10)	−46 (7)	125 (4)	C(1)A
H(2)	−28 (11)	−52 (7)	249 (4)	C(2)A
H(3)	99 (11)	−78 (7)	192 (4)	C(2)A
H(4)	11 (12)	−214 (7)	252 (5)	C(3)A
H(5)	−14 (11)	−223 (7)	185 (4)	C(3)A
H(6)	−215 (11)	−152 (7)	252 (4)	C(4)A
H(7)	−245 (11)	−259 (7)	214 (4)	C(4)A
H(8)	−354 (10)	−122 (7)	185 (4)	C(5)A
H(9)	−220 (10)	−212 (7)	18 (4)	C(1)B
H(10)	−329 (11)	−375 (7)	86 (4)	C(2)B
H(11)	−188 (11)	−339 (7)	93 (4)	C(2)B
H(12)	−209 (11)	−445 (7)	11 (4)	C(3)B
H(13)	−143 (11)	−383 (7)	−14 (4)	C(3)B
H(14)	−430 (11)	−434 (7)	−19 (4)	C(4)B
H(15)	−344 (11)	−415 (7)	−66 (4)	C(4)B
H(16)	−476 (11)	−283 (7)	−67 (4)	C(5)B
H(17)	−134 (10)	−149 (7)	−119 (4)	C(1)C
H(18)	−249 (11)	−255 (6)	−206 (4)	C(2)C
H(19)	−161 (11)	−301 (7)	−167 (4)	C(2)C
H(20)	−45 (10)	−274 (7)	−252 (4)	C(3)C
H(21)	21 (11)	−197 (7)	−206 (4)	C(3)C
H(22)	−172 (11)	−133 (7)	−275 (4)	C(4)C
H(23)	−30 (11)	−99 (7)	−273 (4)	C(4)C
H(24)	−185 (6)	−2 (7)	−233 (4)	C(5)C
H(25)	104 (11)	45 (7)	−96 (4)	C(1)D
H(26)	237 (11)	69 (7)	−214 (4)	C(2)D
H(27)	242 (11)	−37 (7)	−183 (4)	C(2)D
H(28)	444 (11)	45 (7)	−167 (4)	C(3)D
H(29)	371 (11)	32 (7)	−100 (4)	C(3)D
H(30)	389 (11)	193 (7)	−177 (4)	C(4)D
H(31)	437 (11)	168 (7)	−100 (4)	C(4)D
H(32)	245 (11)	248 (7)	−95 (4)	C(5)D
H(33)	152 (11)	83 (7)	39 (4)	C(1)E
H(34)	378 (11)	198 (7)	58 (4)	C(2)E
H(35)	394 (11)	100 (7)	31 (4)	C(2)E
H(36)	473 (11)	99 (7)	127 (4)	C(3)E
H(37)	353 (11)	47 (7)	118 (4)	C(3)E
H(38)	334 (11)	211 (7)	162 (4)	C(4)E
H(39)	294 (11)	117 (7)	196 (4)	C(4)E
H(40)	89 (11)	201 (7)	167 (4)	C(5)E
H(41)	−425 (12)	−8 (7)	−9 (4)	C(1)S
H(42)	−366 (12)	18 (8)	−81 (5)	C(1)S
H(43)	−368 (12)	105 (8)	−37 (4)	C(1)S

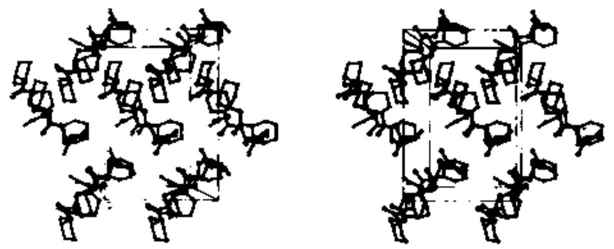

Figure 4. Crystal packing of **5**.

It is interesting that only **2** is a meso compound. The steric repulsion, as model inspection shows, may prohibit the formation of *R-S-R-S* or *R-R-S-S* type products for cyclic tetra- or pentamer.

Molecular Structure of 5 and 5R. ORTEP stereodrawings of **5** and **5R** with the enclosed solvent molecules are shown in Figures 2 and 3. Crystal packing of **5** is given in Figure 4. The bond lengths and angles are given in Tables IV and V, and the conformational angles are listed in Tables VI and VII. No significant difference is detected in bond lengths or angles among oligomers **4R**, **5**, and **5R**. The effect of the low-temperature experiment (−84 °C) with **5** appeared as a shortening of the intermolecular distances.

The cyclic pentamer has, as a whole, a C_5 symmetry, consisting of a trans zigzag chain of C(5)–O(1)–C(1)–C(6)–O(2)–C(5) and two consecutive gauche conformations of O(2)–C(5)–O(1). The root-mean-square deviation from the approximate C_5 symmetry is 0.30 Å for **5** and 0.34 Å for **5R**.

The conformational difference between **4R**, whose symmetry is C_4, and **5R** is surprisingly small. The largest difference in torsion angles is observed in O(1)–C(5)–O(2)–C(6) where C(5) makes up the corner of the polygons. The mean values of the corresponding angles are −92° for **5R** and −89° for **5**, whereas **4R** has a value of −78°.

C(5)–C(5) distances, which define the sizes of the polygons, are 5.99 (2)–6.02 (2) Å [mean 6.00 Å] for **5R** and 5.96 (1)–6.04 (1) Å [mean 6.00 Å] for **5**, which is slightly longer than the corresponding value of 5.96 Å for **4R**. This is due to the more perfect trans zigzag chain of C(5)–O(1)–C(1)–C(6)–O(2)–C(5) than that in **4R**.

As was evidenced by the small difference between the conformations of the tetramer and the pentamer, the 20- and 25-

Table IV. The Bond Lengths (A) and Angles (Deg) for the Acetonitrile Complex

	A	B	C	D	E	means
C(1)–C(2)	1.53 (1)	1.48 (1)	1.53 (2)	1.57 (2)	1.53 (2)	1.53
C(2)–C(3)	1.52 (2)	1.59 (2)	1.54 (2)	1.51 (2)	1.55 (2)	1.54
C(3)–C(4)	1.52 (2)	1.49 (2)	1.52 (2)	1.50 (2)	1.51 (2)	1.51
C(4)–C(5)	1.50 (2)	1.51 (1)	1.53 (2)	1.52 (2)	1.49 (2)	1.51
C(5)–O(1)	1.41 (1)	1.38 (1)	1.39 (1)	1.41 (1)	1.41 (1)	1.40
C(1)–O(1)	1.44 (1)	1.45 (1)	1.40 (1)	1.41 (1)	1.42 (1)	1.42
C(6)–C(1)	1.53 (1)	1.52 (1)	1.51 (2)	1.49 (1)	1.47 (1)	1.50
C(5)–O(2)	1.43 (1)	1.44 (1)	1.45 (1)	1.43 (1)	1.46 (1)	1.44
C(6)–O(2)	1.33 (1)	1.33 (1)	1.35 (1)	1.36 (1)	1.36 (1)	1.35
C(6)–O(3)	1.17 (1)	1.21 (1)	1.18 (1)	1.17 (1)	1.19 (1)	1.18
C(1)–C(2)–C(3)	113.0 (9)	108.6 (9)	108.6 (10)	108.1 (9)	108.7 (10)	109.4
C(2)–C(3)–C(4)	108.2 (9)	109.6 (9)	110.3 (10)	110.5 (10)	110.6 (11)	109.8
C(3)–C(4)–C(5)	112.6 (9)	111.8 (9)	111.2 (10)	110.2 (11)	111.9 (10)	111.5
C(6)–C(1)–O(1)	106.8 (7)	107.7 (7)	106.4 (9)	107.7 (7)	107.2 (7)	107.2
C(6)–C(1)–C(2)	112.1 (8)	110.4 (8)	110.9 (9)	110.1 (8)	112.1 (8)	111.1
O(1)–C(1)–C(2)	109.5 (7)	112.6 (8)	114.3 (8)	111.6 (9)	113.4 (8)	112.3
C(4)–C(5)–O(1)	114.6 (8)	113.8 (8)	113.7 (8)	114.1 (10)	113.0 (9)	113.8
C(1)–O(1)–C(5)	113.8 (6)	115.2 (7)	115.6 (7)	113.4 (8)	115.2 (8)	114.6
O(1)–C(5)–O(2)	109.0 (7)	109.6 (7)	108.6 (7)	108.3 (9)	109.3 (8)	109.0
C(4)–C(5)–O(2)	106.4 (8)	106.2 (7)	105.7 (8)	107.9 (10)	107.0 (8)	106.6
C(5)–O(2)–C(6)	117.8 (7)	118.1 (7)	117.2 (8)	119.7 (8)	117.8 (8)	118.1
O(2)–C(6)–O(3)	125.8 (10)	126.9 (9)	124.4 (10)	122.2 (9)	123.4 (10)	124.5
O(2)–C(6)–C(1)	108.3 (8)	110.0 (7)	109.5 (8)	109.6 (8)	108.8 (8)	109.2
O(3)–C(6)–C(1)	125.9 (10)	123.1 (8)	126.1 (10)	128.2 (10)	127.7 (10)	126.2
C(1)S–C(2)S	1.28 (4)					
C(2)S-N(1)S	1.09 (4)					
C(1)S–C(2)S-N(1)S	163.3 (32)					

Table V. The Bond Lengths (A) and Angles (Deg) for the Acetone Complex

	A	B	C	D	E	means
C(1)–C(2)	1.51 (1)	1.53 (1)	1.54 (1)	1.52 (1)	1.52 (1)	1.52
C(2)–C(3)	1.56 (1)	1.53 (1)	1.52 (1)	1.51 (1)	1.54 (1)	1.53
C(3)–C(4)	1.51 (1)	1.54 (1)	1.53 (1)	1.49 (1)	1.53 (1)	1.52
C(4)–C(5)	1.52 (1)	1.53 (1)	1.52 (1)	1.51 (1)	1.50 (1)	1.52
C(5)–O(1)	1.39 (1)	1.39 (1)	1.38 (1)	1.41 (1)	1.37 (1)	1.39
C(1)–O(1)	1.43 (1)	1.46 (1)	1.44 (1)	1.44 (1)	1.44 (1)	1.44
C(6)–C(1)	1.52 (1)	1.50 (1)	1.51 (1)	1.49 (1)	1.51 (1)	1.51
C(5)–O(2)	1.44 (1)	1.45 (1)	1.46 (1)	1.46 (1)	1.48 (1)	1.46
C(6)–O(2)	1.37 (1)	1.35 (1)	1.34 (1)	1.36 (1)	1.34 (1)	1.35
C(6)–O(3)	1.18 (1)	1.19 (1)	1.19 (1)	1.20 (1)	1.18 (1)	1.19
C(1)–C(2)–C(3)	109.9 (6)	109.0 (6)	110.4 (6)	110.2 (6)	110.9 (6)	110.1
C(2)–C(3)–C(4)	107.8 (6)	107.7 (6)	108.2 (6)	110.5 (6)	107.3 (7)	108.3
C(3)–C(4)–C(5)	111.3 (6)	111.1 (6)	111.3 (7)	111.9 (7)	112.1 (6)	111.6
C(6)–C(1)–O(1)	104.9 (6)	107.9 (6)	106.0 (6)	105.6 (6)	108.6 (6)	106.6
C(6)–C(1)–C(2)	112.2 (6)	112.6 (6)	114.1 (6)	111.9 (6)	111.4 (6)	112.4
O(1)–C(1)–C(2)	110.4 (6)	111.7 (6)	110.4 (6)	112.7 (6)	112.7 (6)	111.6
C(4)–C(5)–O(1)	113.4 (6)	114.7 (6)	113.6 (6)	114.2 (7)	116.4 (6)	114.4
C(1)–O(1)–C(5)	114.8 (5)	114.1 (5)	115.9 (5)	113.3 (6)	113.6 (5)	114.3
C(4)–C(5)–O(2)	106.6 (6)	105.3 (6)	106.2 (6)	105.8 (7)	105.3 (6)	105.8
O(1)–C(5)–O(2)	109.9 (6)	108.8 (6)	107.9 (6)	109.0 (6)	109.9 (6)	109.1
C(5)–O(2)–C(6)	116.6 (5)	115.7 (5)	117.2 (5)	117.6 (6)	117.5 (5)	116.9
O(2)–C(6)–O(3)	124.5 (7)	125.5 (6)	125.6 (7)	125.7 (7)	125.9 (7)	125.4
O(2)–C(6)–C(1)	106.8 (6)	107.1 (5)	109.2 (6)	108.0 (6)	108.8 (6)	108.0
O(3)–C(6)–C(1)	128.7 (7)	127.3 (6)	125.2 (7)	126.3 (7)	125.3 (7)	126.6
C(1)S–C(2)S	1.46 (2)					
C(2)S–C(3)S	1.36 (3)					
C(2)S–O(1)S	1.19 (2)					
C(1)S–C(2)S–O(1)S	117 (1)					
C(3)S–C(2)S–O(1)S	125 (2)					
C(1)S–C(2)S–C(3)S	118 (2)					

Table VI. The Conformation Angles for the Acetonitrile Complex (Deg)

	A	B	C	D	E	means
25-Membered Ring						
O(2)–C(6)–C(1)–O(1)	−176 (1)	−170 (1)	179 (1)	−173 (1)	−172 (1)	−174
C(6)–C(1)–O(1)–C(5)	−177 (1)	−179 (1)	−177 (1)	−177 (1)	−177 (1)	−177
C(1)–O(1)–C(5)–O(2)	−65 (1)	−68 (1)	−66 (1)	−66 (1)	−65 (1)	−66
O(1)–C(5)–O(2)–C(6)	−98 (1)	−83 (1)	−97 (1)	−90 (1)	−92 (1)	−92
C(5)–O(2)–C(6)–C(1)	−175 (1)	−174 (1)	179 (1)	−174 (1)	−177 (1)	−176
Tetrahydropyran Ring						
O(1)–C(1)–C(2)–C(3)	57 (1)	55 (1)	54 (1)	57 (1)	52 (1)	55
C(1)–C(2)–C(3)–C(4)	−53 (1)	−55 (1)	−53 (1)	−56 (1)	−52 (1)	−54
C(2)–C(3)–C(4)–C(5)	49 (1)	52 (1)	52 (1)	54 (1)	53 (1)	52
C(3)–C(4)–C(5)–O(1)	−51 (1)	−51 (1)	−50 (1)	−53 (1)	−53 (1)	−52
C(4)–C(5)–O(1)–C(1)	54 (1)	51 (1)	51 (1)	55 (1)	54 (1)	53
C(5)–O(1)–C(1)–C(2)	−55 (1)	−55 (1)	−54 (1)	−56 (1)	−55 (1)	−55

Table VII. The Conformation Angles for the Acetone Complex (Deg)

	A	B	C	D	E	means
25-Membered Ring						
O(2)–C(6)–C(1)–O(1)	−178.0 (5)	−172.6 (5)	−179.5 (5)	−175.4 (5)	−175.1 (5)	−176.1
C(6)–C(1)–O(1)–C(5)	179.9 (5)	−176.5 (5)	−177.5 (5)	−179.1 (6)	−175.1 (5)	−177.7
C(1)–O(1)–C(5)–O(2)	−64.3 (7)	−67.3 (7)	−64.7 (7)	−66.1 (8)	−68.4 (7)	−66.2
O(1)–C(5)–O(2)–C(6)	−92.9 (7)	−85.5 (7)	−93.2 (7)	−87.2 (8)	−86.4 (7)	−89.0
C(5)–O(2)–C(6)–C(1)	−178.5 (5)	−171.4 (5)	−178.8 (5)	−173.2 (5)	−178.0 (5)	−176.0
Tetrahydropyran Ring						
O(1)–C(1)–C(2)–C(3)	57.7 (8)	59.1 (8)	55.6 (8)	54.1 (8)	55.4 (8)	56.4
C(1)–C(2)–C(3)–C(4)	−56.1 (8)	−58.7 (7)	−56.4 (8)	−53.2 (8)	−53.9 (9)	−55.7
C(2)–C(3)–C(4)–C(5)	52.6 (8)	54.2 (8)	54.1 (8)	51.8 (9)	51.2 (9)	52.8
C(3)–C(4)–C(5)–O(1)	−52.7 (8)	−50.9 (8)	−52.4 (9)	−51.7 (10)	−51.8 (9)	−51.9
C(4)–C(5)–O(1)–C(1)	54.8 (8)	50.4 (8)	52.7 (8)	52.1 (9)	51.1 (8)	52.2
C(5)–O(1)–C(1)–C(2)	−57.6 (8)	−54.7 (8)	−53.9 (8)	−53.7 (8)	−52.8 (8)	−54.5

membered rings of these compounds are rather rigid. No large conformational adjustment seems to be done in including the solvent molecule. This rigidity of the main chain may be more clearly understood by comparison with the nactin structures, which show several different main-chain conformations. The rigidity of the present cyclic oligoesters may be attributable to the fact that the main chain consists of two kinds of rigid groups, tetrahydropyran ring and ester plane, and no aliphatic C–C bond intervenes between them.

Complexation of 5 with Acetone and 5R with Acetonitrile. As is shown in Figures 2 and 3, the mode of complexation of 5 and **5R** with solvent molecules resembles that of **4R** in that they

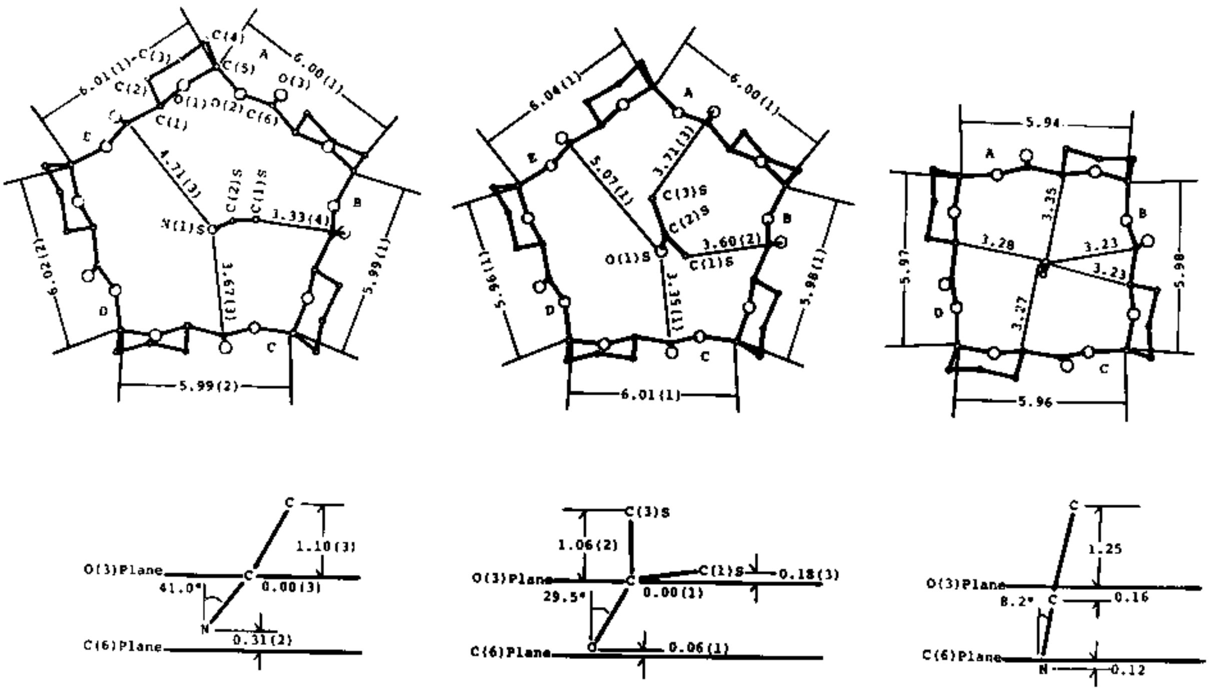

Figure 5. The position and the orientation of the enclosed solvent molecules with respect to **5R**, **5**, and **4R** molecules (left to right). The explanation is in the text.

arrange their C═O dipoles on one side of the molecule and the dipole moment of the enclosed solvent on the other side.

However, a more detailed inspection reveals that there are some differences in the complexation due to different molecular sizes. The radius of the molecular cavity, which is approximated by the inscribed circle of the pentagon consisting of the C(5)–C(5) sides, is 4.13 Å. Taking into account the van der Waals radius of the methylene group, the actual radius of the cavity of the pentamer is 2.13 Å. The corresponding radius in **4R** is 0.96 Å. Consequently, the temperature factors of the solvent molecules included in the pentamer are significantly larger.

As shown in Figure 5, in **5** and **5R** the included solvent molecule is not located at the center of the molecular cavity and is tilted away from the fivefold axis. The nitrile bond in the acetonitrile molecule is inclined at 41.0° and the carbonyl bond of the acetone molecule is inclined at 29.5° from the fivefold axis toward the outside of the ring. In the case of the **4R** molecule, the corresponding angle was 8.2°. These shifts in the pentamers are caused mainly by the van der Waals interactions with the adjacent molecules. The shortest interactions between the cyclic pentamer molecule and the solvent molecule are N(1)S–C(6)C (3.67 (3) Å) and C(1)S–O(3)B (3.33 (4) Å) in **5R** and O(1)S—C(6)C (3.35 (1) Å), C(1)S–O(3)B (3.60 (2) Å), and C(3)S–O(3)A (3.71 (3) Å) in **5**. The solvent molecule is included in **5R** in such a way that the nitrile nitrogen atom is placed 0.31 (2) Å above the average plane of the C(6)'s and 0.07 (2) Å above the average plane of the O(1)'s and the nitrile carbon atom is placed on the average plane of the O(3)'s. On the other hand, the acetone molecule is included in the **5** molecule in such a way that the carbonyl oxygen atom is placed 0.06 (1) Å above the average plane of the C(6)'s and 0.14 (1) Å below the average plane of the O(1)'s and the carbonyl carbon atom is placed 0.03 (1) Å below the average plane of the O(3)'s. In the case of **4R** the acetonitrile molecule sticks into the cavity to such an extent that the nitrile carbon atom is 0.16 Å below the average plane of the O(3)'s.

Thus, the cyclic tetramer and pentamer hold the same molecule without changing their conformation in spite of the different size of the cavity. This is caused by the rigidity of the molecule mentioned before.

Another important point to note about the molecule is that the molecule consists of repeating units whose absolute configuration is fixed, as it is designated as $(1R,5S)_4$ or $(1R,5S)_5$. This is sharply contrasted by the fact that nonactin, as expressed by S_4 symmetry, has two kinds of units alternately changing absolute configuration. The repeat of the same absolute configuration and the rigidity of the molecule combined to make carbonyl bonds align in one direction, giving a polarity to the molecule. This polarity contributes to the characteristic interaction of the molecules of this group with the polar solvent molecules.

Registry No. 5, 82977-29-5; **5R**, 82977-30-8.

Supplementary Material Available: The atomic parameters for the acetone complex, listing of the observed and calculated structure factors, and anisotropic thermal parameters of non-hydrogen atoms (30 pages). Ordering information is given on any current masthead page.