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

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

properties of these synthetic macrolides.

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 θ 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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(3) Okada, M.; Sumitomo, H.; Tajima, I. *Polym. Bull.* **1978**, *1*, 41–5.

(4) Okada, M.; Sumitomo, H.; Tajima, I. *J. Am. Chem. Soc.* **1979**, *101*, 4013–4.

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(7) Tajima, I.; Okada, M.; Sumitomo, H. *J. Am. Chem. Soc.* **1981**, *103*, 4096–100.

(8) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. "MULTAN78, a System of Computer Programs for the Automatic Solution of Crystal Structure from X-ray Diffraction Data"; University of York: York, England, 1978.

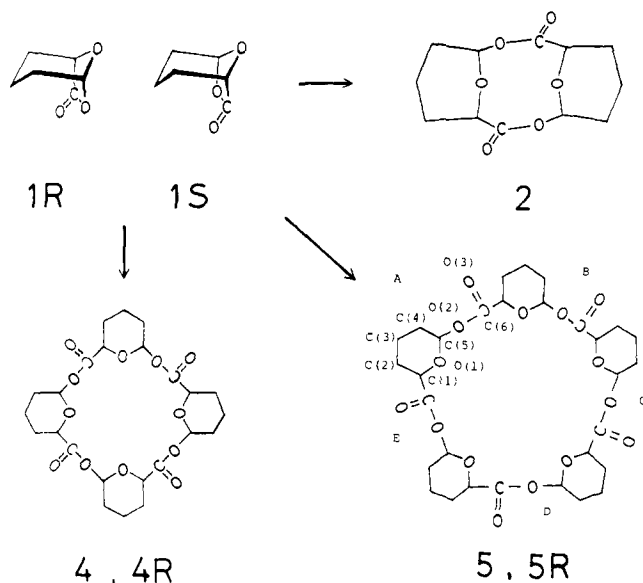[‡] Faculty of Engineering.
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Figure 1. 6,8-Dioxabicyclo[3.2.1]octane-7-one and its cyclic oligoesters.
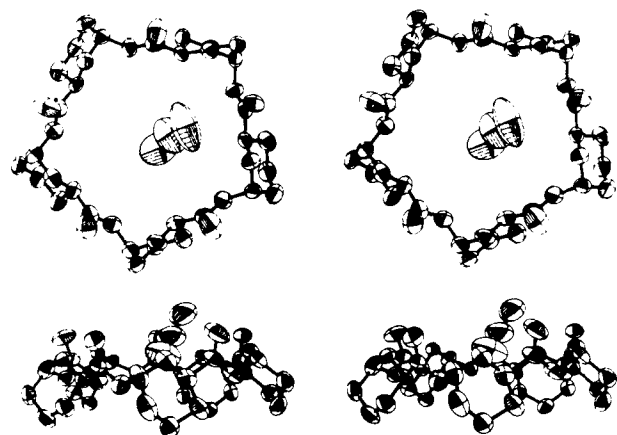

Figure 2. Stereodrawing of the molecular complex of **5** with an acetone viewed from the directions parallel to (top) and perpendicular to (bottom) its noncrystallographic fivefold symmetry axis.

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 2θ = 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

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

atom	x	y	z	B_{eq},^{a} Å^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.

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]

Communications to the Editor
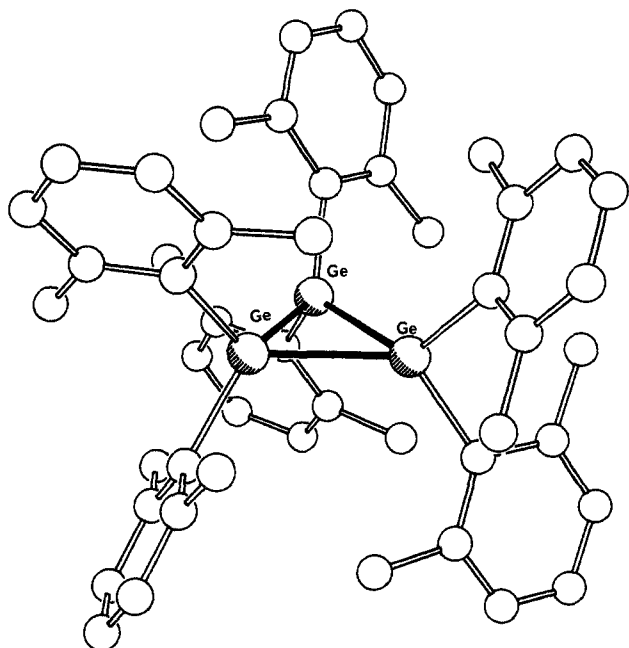
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Figure 2. Crystal structure of **3**. Ge–Ge bond lengths (Å): 2.543, 2.543, 2.537. Ge–Ge bond angles (deg): 59.9, 60.1. C–Ge bond lengths (Å): 1.977–2.015.
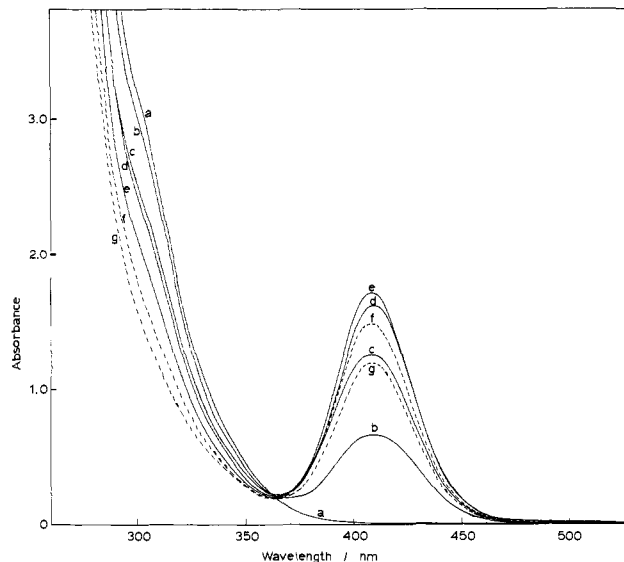

Figure 3. Photolysis of **3** (2.6×10^{-1} mM in cyclohexane-d_6) followed by ultraviolet spectroscopy: (a) before irradiation; (b) after 7 s of irradiation; (c) 20 s; (d) 30 s; (e) 40 s; (f) 50 s; (g) 66 s.

routine, and of these 5084 had $|F_o| > 3\sigma(|F_o|)$ and were considered to be observed. The structure was solved by the heavy-atom method, and the nonhydrogen atoms were refined anisotropically. The hydrogen atoms, with the exception of the methyl groups, which were refined as rigid bodies, were placed at calculated positions and allowed to ride on their parent carbons. Refinement was by full-matrix least-squares analysis to $R = 0.074$. The cyclohexane molecules are disordered and partially occupy three independent positions in the asymmetric unit. In one site two principal orientations were found.

As shown in Figure 2, the three germanium atoms form an essentially equilateral triangle with Ge–Ge bond lengths of 2.543 (1), 2.543 (1), and 2.537 (1) Å, respectively,[12] and bond angles of between 59.9 (1) and 60.1 (1)°. The planes formed by each of the pairs of Ge–Ar bonds are all rotated in the same sense by between 7.2 and 8.6° from the normal to the plane of the germaniums. The Ge–Ar bonds are in the range 1.977 (8)–2.015 (12) Å. Thus, the molecule has approximate D_3 symmetry, in contrast to the symmetry exhibited by the silicon analogue **1**, where the three silicon atoms form an isosceles triangle. The Ge–Ge bond length of **3** are apparently the longest every found for the bond of this type,[12] and the slow rotation of the phenyl rings along the C–Ge bonds shown above by ^{1}H NMR spectra is expected from the steric congestion created between several pairs of the methyl groups.

Photoconversion of 3 to 4. Irradiation of **3** in cyclohexane-d_{12} with a low-pressure mercury lamp at room temperature provides a new (yellow) product (**4**) as evidenced by the appearance of a set of ^{1}H NMR signals: δ 2.18 (s), 6.83 (d, $J = 7.2$ Hz), 6.96 (t, $J = 7.2$ Hz), with a relative intensity of 6:2:1. Since **4** is also labile under this condition and undergoes slow photoinduced polymerization, the concentration of **4** reaches a maximum (approximately 65% yield)[13] when **3** is 75%[13] consumed.[14] Ultraviolet

spectroscopy also serves the purpose of following this photochemical reaction (see Figure 3), and indeed the electronic spectrum of pure **4** can be calculated with resonable accuracy (error in $\epsilon \simeq 10\%$) as the concentration of **4** and **3** is estimated by ^{1}H NMR spectroscopy (see Figure 1).[15] The addition of degassed methanol to a photolysate (60% conversion of **3**) immediately causes decoloration of the solution and provides $Ar_2HGe–Ge(OMe)Ar_2$ (**7**)[16] in 65% yield in addition to recovered **3**.[17] From this spectral and chemical evidence, we conclude that **4** is indeed tetrakis(2,6-dimethylphenyl)digermene. 2,6-Dimethylphenylgermylene, assumed to be the other photofragment, has not been trapped, and it is yet to be determined if this species dimerizes to form **4**. Pyrolysis of **3** at 160 to 165 °C provides Ar_3GeH (**8**)[18] as well as a small quantity of **4**.

(12) The Ge–Ge bond lengths are 2.465 Å in $(Ph_2Ge)_4$ (a) (Ross, L.; Dräger, M. *J. Organomet. Chem.* **1980**, *199*, 195), 2.463 and 2.457 Å in $(Ph_2Ge)_6$ (b) (Dräger, M.; Ross, L. *Z. Anorg. Allg. Chem.* **1981**, 476, 95), and 2.374 Å in $(Me_2Ge)_6$ (c) (Jensen W.; Jacobson, R *Cryst. Struct. Commun.* **1975**, *4*, 299). The Ge–C bond lengths are 1.951–1.976 Å in a, 1.959–1.981 Å in b, and 1.92–1.97 Å in c.

(13) Hexamethylethane was used as internal standard in order to estimate the concentration of **3** and **4**.

(14) A mass spectrum (electron impact, 70 eV) of this photolysis shows the parent peaks corresponding to $(Ar_2Ge)_2$ with the proper relative intensities,[9] whereas that of **3** measured under the identical conditions indicates the presence of the overlapping $[(Ar_2Ge)_2 - 1]$ and $(Ar_2Ge)_2$ peaks in this region. It is clearly noticeable that a peak at m/z 559 corresponding to $[(Ar_2Ge)_2 - 1]$ is missing in the spectrum of the photolysate.[9]

(15) Due to the extreme sensitivity of compound **4** to O_2 and moisture, we have not been able to isolate pure **4**. All handling was done in a drybox with O_2 concentration less than 5 ppm. Attempted purification of **4** taking advantage of the solubility difference between **4** and **3** in several hydrocarbon solvents raised the purity of **4** to 75%.

(16) **7**: IR (CHCl$_3$) ν for Ge–H 2020 cm^{-1}; mass spectrum (field desorption) M$^+$· cluster m/z 592–606 matchable to that calculated for C_{33}-$H_{40}Ge_2O$;[9] ^{1}H NMR (250 MHz, benzene-d_6) δ 2.27 (s, 12 H), 2.35 (s, 12 H), 3.48 (s, 3 H), 5.79 (s, 1 H), 6.80 (d, $J = 7.5$ Hz, 4 H), 6.87 (d, $J = 7.5$ Hz, 4 H), 7.01 (t, $J = 7.5$ Hz, 2 H), 7.03 (t, $J = 7.5$ Hz, 2 H).

(17) Compound **3** is infinitely stable in its methanolic solution.

(18) **8**: IR (CHCl$_3$) ν for Ge–H 2030 cm^{-1}; mass spectrum (field desorption) M$^+$· cluster m/z 386–394, in agreement with that calculated for $C_{24}H_{28}Ge$;[9] ^{1}H NMR (250 MHz, cyclohexane-d_{12}) δ 2.15 (s, 18 H), 5.92 (s, 1 H), 6.87 (d, 6 H), 7.03 (t, 3 H).

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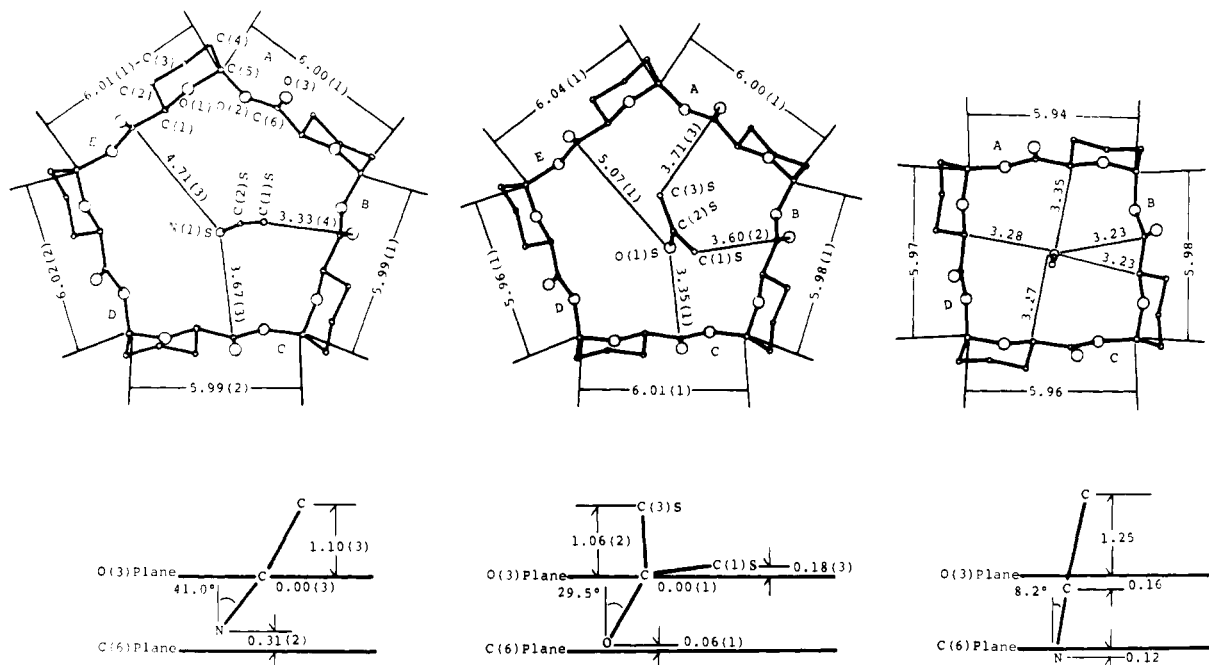
Figure 5. The position and the orientation of the enclosed solvent molecules with respect to **5R**, **5**, and **4R** molecules (left to right). The explanation is in the text.

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.