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Synthesis and X-ray Crystallographic Characterization of Spiro Orthocarbonates

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Received January 22, 1992

In this study we have synthesized two spiro orthocarbonates, which can be polymerized with volume expansion, and determined their crystal structures. The crystal data are as follows: 3,4,10,11-Di(9,10-dihydro-9,10-ethanoanthracenyl)-1,6,8,13-tetraoxa-6.6-tridecane 5: $a = 16.898$ (1), $b = 9.299$ (1), $c = 24.359$ (2) Å, $\beta = 123.73$ (7)°, space group $P2_1/c$ and $R = 0.073$ for 2954 reflections; compound 8: $a = 15.244$ (4), $b = 15.293$ (3), $c = 10.772$ (3) Å, $\beta = 99.45$ (2)°, space group $P2_1/c$ and $R = 0.082$ for 2346 reflections. The seven-membered rings of compound 5 are chair forms and all the six-membered rings are boat shaped. For a six-membered spiro orthocarbonate, 3,9-Di(9-fluorenylidenyl)-1,4,6,9-tetraoxa-5,5-undecane 8, fluorene groups [C(1) atom through C(13) atom] are planar within ± 0.09 Å and the six-membered rings have chair conformations. The whole molecule has pseudo-C_2 symmetry. The water molecules in the crystal are linked with each other through the hydrogen bond with distance of 2.790 (20) Å.

Introduction

Monomers that will polymerize with no shrinkage or volume expansion are highly desirable for practical applications of polymeric materials, such as strain free composites, precision castings, dental filling and semi-conductor encapsulations. Spiro orthocarbonate, which is a bicycle compound, was found to expand volume on ring opening polymerization in which for every bond that goes from a van der Waals' distance to a covalent distance, at least two bonds would go from a covalent distance to a near van der Waals' distance. Therefore the volume shrinkage on a bond formation can be compensated with the volume expansion on two bonds breakage.

Baily and coworkers[1-3] reported the preparation of various spiro orthocarbonates and the practical applications such as in epoxy resin modifier, dental filling and elastomers. We also prepared several spiro orthocarbonates which have bulk and rigid side groups such as anthracene, naphthalene and benzene rings[4-6]. Here we report the syntheses of two spiro orthocarbonates and their crystal structures determined by single crystal X-ray diffraction method.
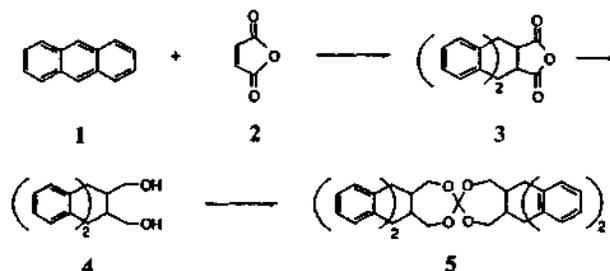
Figure 1. The synthesis of spiro orthocarbonate based on anthracene

Synthesis

In this study we have synthesized two new spiro orthocarbonates 5 and 8 as shown in Figures 1 and 2. The Diels-Alder adduct 3 was prepared in 91% yield from the reaction of anthracene and maleic anhydride in benzene following the published procedure[7]. The diol 4 was first prepared in 80% yield by treatment of compound 3 with $BF_3/NaBH_4$ in diglyme[8]. However it has been found that this reaction can

Figure 2. The synthesis of spiro orthocarbonate based on fluorene
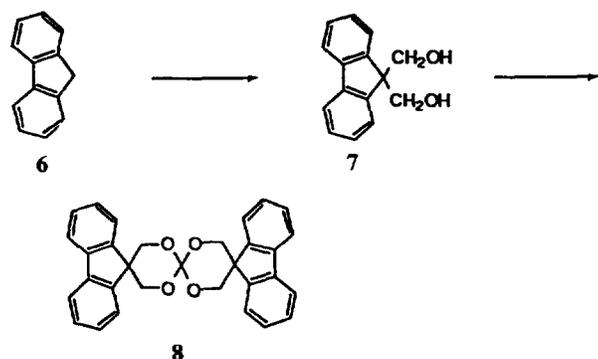
be carried out in dried THF instead of diglyme without any noticeable difference in yield. The highly reactive and versatile spiro orthocarbonates were synthesized by the reaction of diol with (nBu)$_2$SnO followed by treatment with carbon disulfide using the Sakai's procedure.[9] Sakai reported that the larger membered spiro orthocarbonate was relatively unstable due to ring strain in the two large membered rings and was decomposed to cyclic ether and polycarbonate. Therefore seven- and eight-membered spiro orthocarbonates could not be to synthesized. However, recently we have reported that when aromatic rings are contained as spiro rings, larger-membered spiro orthocarbonate could be obtained in good yield by using the Sakai method[5,6]. The spiro orthocarbonate 5 has been synthesized in 78% yield by treatment of diol 4 with (nBu)$_2$SnO followed by treatment of carbon

disulfide. The structure of compound 5 has been confirmed by IR and NMR spectrum. In the IR spectrum the strong OH stretching band of the diol was disappeared and the intensity of C-O stretching band was greatly increased at 1200-1000 cm^{-1} region.

The absence of any carbonyl stretching band also supports the formation of spiro orthocarbonate instead of direct formation of polycarbonate.

In this study, another spiro orthocarbonate, which has bulky and rigid fluorenyl side group, was prepared as shown on Figure 2. The diol 7 was synthesized in 74% yield from the reaction of fluorene, paraformaldehyde and sodium ethoxide in DMSO following the procedures published by Wesslen[10]. To facilitate the reaction, dipolar aprotic DMSO was used as solvent and the reaction time was 5 min at ice-bath temperature. The yield of diol 7 was not increased with the increase in reaction time and product was found to be a mixture of 2 or 3 compounds with the shorter reaction time. The preparation of spiro orthocarbonate 8 from diol 7 was conducted by the same method as the preparation of compound 5. The structure of compound 8 was confirmed by IR and ^{1}H-NMR spectra.

X-Ray Crystallographic Studies

All X-ray data were collected with a Nonius CAD-4 Diffractometer. Further details are in Table 1. All calculations were carried out on an IBM 386 compatible PC using the Shelx-76[11] and Shelxs-86[11] programs. The atomic form factors were from "International Tables of Crystallography"[12].

Table 1. Summary of Crystal Data, Intensity Collection and Least-Squares Refinement Statistics

	5	8
formula	$C_{37}H_{32}O_4 \cdot CH_2Cl_2$	$C_{31}H_{24}O_4 \cdot H_2O$
M_w	625	478
space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$
a, Å	16.898 (1)	15.244 (4)
b, Å	9.299 (1)	15.293 (3)
c, Å	24.359 (2)	10.772 (3)
β, deg.	123.73 (7)	99.45 (2)
Z	4	4
V, Å^3	3183.31	2477.16
μ (Mo-Kα), cm^{-1}	2.01	0.52
density, g/cm^3	1.30 (calc.)	1.28 (calc.) 1.35 (meas.)
diffractometer	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4
radiation	Mo-Kα(graphite monochromater, λ=0.7107 Å)	Mo-Kα(graphite momochromater, λ=0.7107 Å)
crystal size, mm	0.8×0.4×0.3	0.8×0.3×0.2
cell-constant determination	25 reflections(23°<2θ<29°)	16 reflections(20°<2θ<26°)
range of h, k, and l	$-18 \leq h \leq 15$	$-16 \leq h \leq 15$
	$0 \leq k \leq 9$	$0 \leq k \leq 16$
	$0 \leq l \leq 27$	$0 \leq l \leq 10$
2θ range, deg.	4-48	2-44
scan type	ω/2θ	ω/2θ
scan width, deg	0.65+0.34 tanθ	0.8+0.35 tanθ
no. of observed reflection	2954$|F_o|>4\sigma|F_o|$	2346$|F_o|>4\sigma|F_o|$
R, R_w	0.073, 0.076	0.082, 0.096
w	$3.11/[\sigma^2(F_o)+0.0006(F_o)^2]$	$1.00/[\sigma^2(F_o)+0.0004(F_o)^2]$

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Table 2. Fractionnal Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for 5*. The e.s.d.'s are in the Parentheses

$U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$ ($\text{Å} \times 10^5$)

Atom	x	y	z	U_{eq}
O(1)	903 (2)	3596 (3)	3240 (1)	54
O(2)	2535 (2)	3194 (3)	3855 (1)	52
C(1)	1639 (3)	2686 (5)	3646 (2)	48
C(2)	740 (4)	3952 (6)	2613 (2)	52
C(3)	1302 (3)	5263 (5)	2664 (2)	44
C(4)	2398 (3)	5022 (5)	3081 (2)	46
C(5)	2705 (4)	3489 (6)	3348 (2)	50
C(6)	986 (4)	5820 (5)	1965 (2)	50
C(7)	2800 (3)	5453 (6)	2663 (2)	51
C(1A)	1535 (4)	7208 (5)	2089 (2)	49
C(2A)	2516 (3)	6998 (5)	2466 (2)	50
C(3A)	3123 (5)	8173 (6)	2634 (3)	65
C(4A)	2732 (5)	9523 (7)	2418 (3)	71
C(5A)	1764 (5)	9736 (7)	2051 (3)	69
C(6A)	1155 (5)	8566 (6)	1888 (2)	59
C(1B)	1323 (3)	4739 (5)	1673 (2)	47
C(2B)	2293 (3)	4546 (5)	2053 (2)	47
C(3B)	2708 (4)	3565 (6)	1859 (3)	62
C(4B)	2130 (5)	2790 (7)	1280 (3)	74
C(5B)	1182 (5)	2994 (7)	909 (3)	72
C(6B)	755 (4)	3974 (6)	1098 (2)	62
O(1')	1605 (2)	2609 (3)	4197 (1)	55
O(2')	1439 (2)	1369 (3)	3309 (1)	50
C(2')	2299 (4)	1798 (6)	4748 (2)	50
C(3')	1950 (3)	277 (5)	4698 (2)	44
C(4')	1796 (3)	−592 (5)	4094 (2)	42
C(5')	2068 (4)	189 (6)	3677 (2)	47
C(6')	2621 (3)	−601 (5)	5345 (2)	51
C(7')	2347 (3)	−2036 (5)	4351 (2)	47
C(1A')	2125 (3)	−2013 (5)	5248 (2)	51
C(2A')	1978 (3)	−2778 (5)	4710 (2)	46
C(3A')	1497 (4)	−4082 (6)	4532 (2)	59
C(4A')	1163 (4)	−4602 (7)	4904 (3)	70
C(5A')	1317 (4)	−3865 (7)	5437 (3)	69
C(6A')	1779 (4)	−2580 (7)	5606 (3)	63
C(1B')	3524 (3)	−908 (5)	5388 (2)	53
C(2B')	3390 (3)	−1700 (5)	4855 (2)	51
C(3B')	4142 (4)	−2073 (6)	4818 (3)	61
C(4B')	5055 (4)	−1696 (7)	5329 (2)	80
C(5B')	5200 (4)	−922 (7)	5858 (3)	79
C(6B')	4450 (4)	−514 (7)	5892 (3)	68
Cl(1)	4454 (3)	−117 (9)	1842 (2)	401
Cl(2)	4475 (2)	885 (5)	816 (2)	311
C(S)	4059 (7)	−382 (11)	1045 (5)	178

*Tables for anisotropic thermal parameters of the non-hydrogen atoms, coordinates of hydrogen atoms, and structure factor tables are available from the author (YJP).

The single crystals of **5** were obtained by slow evaporation of concentrated methylenechloride solution. The crystal was

Table 3. Fractionnal Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for 8*. The e.s.d.'s are in the Parentheses

$U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$ ($\text{Å} \times 10^5$)

Atom	x	y	z	U_{eq}
O(1)	4814 (2)	3034 (2)	1796 (2)	42
O(2)	4521 (2)	2018 (2)	3249 (2)	43
C(1)	2653 (3)	2404 (3)	1365 (4)	50
C(2)	1806 (4)	2278 (4)	705 (5)	63
C(3)	1113 (4)	2814 (4)	878 (5)	69
C(4)	1246 (3)	3508 (4)	1708 (5)	63
C(5)	2008 (4)	4980 (3)	3836 (5)	60
C(6)	2487 (4)	5463 (3)	4819 (5)	61
C(7)	3348 (4)	5257 (3)	5300 (5)	59
C(8)	3781 (3)	4573 (3)	4801 (4)	51
C(9)	3644 (3)	3359 (2)	3072 (4)	38
C(10)	2800 (3)	3087 (3)	2208 (4)	42
C(11)	2098 (3)	3645 (3)	2375 (4)	47
C(12)	2429 (3)	4290 (3)	3343 (4)	44
C(13)	3312 (3)	4103 (3)	3801 (4)	41
C(14)	4345 (3)	3719 (3)	2331 (5)	43
C(15)	4059 (3)	2632 (3)	3936 (4)	43
C(16)	5168 (3)	2422 (3)	2673 (4)	39
O(1')	5548 (1)	1796 (1)	2007 (2)	43
O(2')	5803 (1)	2846 (1)	3555 (2)	42
C(1')	6501 (3)	312 (2)	5574 (4)	60
C(2')	6914 (4)	−336 (3)	6353 (4)	76
C(3')	7799 (4)	−505 (3)	6390 (4)	85
C(4')	8302 (4)	−33 (3)	5665 (4)	78
C(5')	9089 (3)	1337 (3)	3745 (4)	71
C(6')	9234 (3)	1982 (4)	2908 (5)	81
C(7')	8549 (3)	2512 (3)	2354 (4)	74
C(8')	7694 (3)	2418 (3)	2620 (3)	56
C(9')	6682 (2)	1505 (2)	3890 (3)	41
C(10')	6988 (2)	785 (2)	4828 (3)	46
C(11')	7888 (2)	621 (2)	4874 (3)	53
C(12')	8237 (2)	1230 (2)	4017 (3)	54
C(13')	7537 (2)	1765 (2)	3453 (3)	45
C(14')	5996 (2)	1128 (2)	2828 (3)	46
C(15')	6246 (3)	2260 (2)	4500 (3)	45
O(W)	215 (7)	−798 (8)	601 (19)	86

*Tables for anisotropic thermal parameters of the non-hydrogen atoms, coordinates of hydrogen atoms, and structure factor tables are available from the author (YJP).

unstable in the air, and immediately placed in the capillary. The space group was uniquely determined as $P2_1/c$ from the systematic absences in $0k0$ for $k = 2n+1$ and in $h0l$ for $l = 2n+1$. Intensity data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods. The hydrogen atoms attached to methylenechloride molecule could not be located in the difference Fourier maps. The structure was refined by least-squares methods, with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were included in the refinement with the isotropic thermal parameters. The
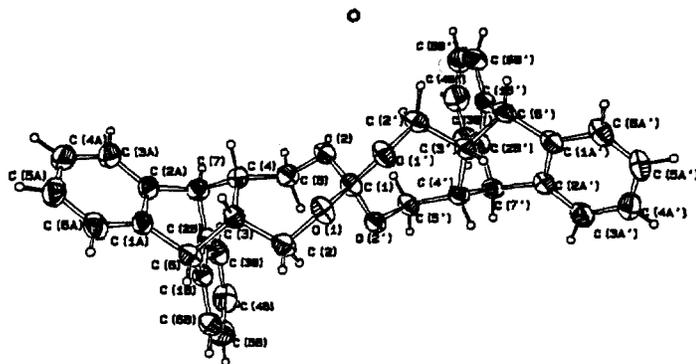
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Figure 3. Molecular conformation with atomic numbering in 5.

Table 4. Bond Lengths (Å) and Angles (°) for 5. The e.s.d.'s are in Parentheses. The values in first column are for unprimed atoms, and those in second one for primed atoms

O(1)-C(1)	1.369 (5)	1.375 (5)
O(1)-C(2)	1.433 (5)	1.413 (6)
O(2)-C(1)	1.387 (5)	1.407 (5)
O(2)-C(5)	1.439 (6)	1.442 (6)
C(2)-C(3)	1.507 (7)	1.511 (7)
C(3)-C(4)	1.557 (6)	1.570 (6)
C(3)-C(6)	1.564 (6)	1.566 (6)
C(4)-C(5)	1.532 (7)	1.513 (7)
C(4)-C(7)	1.558 (6)	1.555 (6)
C(6)-C(1A)	1.519 (7)	1.504 (6)
C(6)-C(1B)	1.513 (7)	1.498 (6)
C(7)-C(2A)	1.506 (7)	1.495 (6)
C(7)-C(2B)	1.498 (6)	1.519 (6)
C(1A)-C(2A)	1.393 (7)	1.387 (6)
C(1A)-C(6A)	1.377 (7)	1.396 (7)
C(2A)-C(3A)	1.396 (8)	1.389 (7)
C(3A)-C(4A)	1.380 (9)	1.392 (8)
C(4A)-C(5A)	1.374 (10)	1.360 (9)
C(5A)-C(6A)	1.396 (9)	1.360 (9)
C(1B)-C(2B)	1.374 (6)	1.397 (6)
C(1B)-C(6B)	1.377 (6)	1.399 (7)
C(2B)-C(3B)	1.384 (7)	1.368 (7)
C(3B)-C(4B)	1.391 (9)	1.386 (8)
C(4B)-C(5B)	1.345 (10)	1.374 (9)
C(5B)-C(6B)	1.391 (9)	1.368 (8)
Cl(1)-C(S)		1.684 (11)
Cl(2)-C(S)		1.622 (11)
O(1')-C(1)-O(1)		102.9 (3)
O(1')-C(1)-O(2)		106.8 (3)
O(2')-C(1)-O(1)		106.8 (3)
O(2')-C(1)-O(2)		111.6 (3)
O(2)-C(1)-O(1)	115.1 (4)	113.4 (3)
O(2)-O(1)-C(1)	118.2 (3)	119.5 (3)
C(3)-C(2)-O(1)	111.1 (3)	110.0 (4)
C(4)-C(3)-C(2)	113.8 (4)	114.3 (4)
C(4)-C(5)-O(2)	111.1 (4)	112.8 (4)
C(5)-O(2)-C(1)	116.6 (3)	116.4 (3)
C(5)-C(4)-C(3)	114.3 (4)	115.4 (4)

C(6)-C(3)-C(2)	111.1 (3)	112.8 (4)
C(6)-C(3)-C(4)	108.7 (4)	109.0 (4)
C(7)-C(4)-C(3)	109.2 (3)	108.4 (3)
C(7)-C(4)-C(5)	110.4 (4)	110.3 (4)
C(1A)-C(6)-C(3)	105.3 (3)	105.6 (3)
C(1A)-C(2A)-C(7)	113.3 (4)	113.7 (4)
C(2A)-C(7)-C(4)	106.1 (4)	106.5 (3)
C(2A)-C(1A)-C(6)	112.5 (4)	112.8 (4)
C(3A)-C(2A)-C(7)	127.0 (4)	125.6 (4)
C(3A)-C(2A)-C(1A)	119.7 (5)	120.7 (4)
C(4A)-C(3A)-C(2A)	118.8 (6)	118.5 (5)
C(5A)-C(4A)-C(3A)	121.6 (6)	121.0 (6)
C(5A)-C(6A)-C(1A)	119.2 (6)	120.7 (5)
C(6A)-C(1A)-C(6)	126.6 (5)	128.5 (4)
C(6A)-C(1A)-C(2A)	120.9 (5)	118.7 (5)
C(6A)-C(5A)-C(4A)	119.8 (6)	120.4 (6)
C(1B)-C(6)-C(3)	107.6 (4)	107.1 (3)
C(1B)-C(6)-C(1A)	108.1 (4)	107.6 (4)
C(1B)-C(2B)-C(7)	113.9 (4)	112.0 (4)
C(2B)-C(7)-C(4)	106.7 (4)	108.3 (4)
C(2B)-C(7)-C(2A)	108.4 (4)	107.3 (3)
C(2B)-C(1B)-C(6)	112.9 (4)	113.8 (4)
C(3B)-C(2B)-C(7)	126.2 (4)	126.8 (4)
C(3B)-C(2B)-C(1B)	119.8 (4)	121.2 (4)
C(4B)-C(3B)-C(2B)	118.9 (5)	119.2 (5)
C(5B)-C(4B)-C(3B)	120.8 (6)	120.4 (5)
C(5B)-C(6B)-C(1B)	118.6 (5)	119.8 (5)
C(6B)-C(1B)-C(6)	126.1 (4)	127.7 (4)
C(6B)-C(1B)-C(2B)	121.0 (4)	118.6 (4)
C(6B)-C(5B)-C(4B)	120.9 (6)	120.8 (6)
Cl(2)-C(S)-Cl(1)	108.7 (6)	

refinement converged with $R = 0.073$ for 2954 reflections. Table 2 contains the final atomic coordinates for 5.

The single crystals of **8** were obtained by slow evaporation of concentrated methylenechloride solution. The space group was $P2_1/c$. The structure was solved and refined by the methods used for 5. All of the hydrogen atoms excepting those for water molecule were detected in a difference electron density map. The refinement converged with $R = 0.082$ for the 2346 reflections used. Table 3 contains the final atomic coordinates for **8**.

The molecular conformation of 5 with atomic numbering is shown in Figure 3. The benzene rings are designated as A, B, A', B'. The bond distances and angles are listed in Table 4. Table 5 contains the selected torsion angles. The seven-membered rings are chair forms with the pseudo-C_2 conformations. The asymmetry parameters[13] are 2.4 for the unprimed, and 6.9 for the primed part of the molecule. All of the six-membered rings are boat shaped. The relative dihedral angles between two adjacent benzene rings are A-B = 54.0° and A'-B' = 65.1°, whereas that between A and A' is 95.5° and B and B' is 163.1°. The crystal packing is shown in Figure 4.

Bond distances and angles of **8** with their estimated standard deviations are listed in Table 6. These values are normal as expected for the type of bonds involved. The conformation

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Table 5. Selected Torsion Angles of **5**. The e.s.d.'s are in the Parentheses. The values in first column are for unprimed atoms, and those in second one for primed atoms

Seven-membered Rings

O(2)-C(1)-O(1)-C(2)	62.8 (4)	67.8 (4)
C(1)-O(1)-C(2)-C(3)	−89.4 (4)	−91.9 (5)
O(1)-C(2)-C(3)-C(4)	67.2 (4)	64.0 (4)
C(2)-C(3)-C(4)-C(5)	1.6 (4)	3.2 (4)
C(3)-C(4)-C(5)-O(2)	−70.0 (4)	−69.3 (4)
C(4)-C(5)-O(2)-C(1)	87.0 (4)	84.2 (4)
C(5)-O(2)-C(1)-O(1)	−60.9 (4)	−60.3 (4)

Six-membered Rings

C(3)-C(4)-C(7)-C(2A)	57.4 (4)	57.1 (4)
C(4)-C(7)-C(2A)-C(1A)	−60.6 (4)	−61.2 (4)
C(7)-C(2A)-C(1A)-C(6)	−0.2 (4)	0.3 (4)
C(2A)-C(1A)-C(6)-C(3)	61.3 (4)	60.5 (4)
C(1A)-C(6)-C(3)-C(4)	−59.3 (4)	−58.8 (4)
C(6)-C(3)-C(4)-C(7)	1.3 (4)	1.3 (3)
C(3)-C(4)-C(7)-C(2B)	−58.0 (4)	−58.0 (4)
C(4)-C(7)-C(2B)-C(1B)	60.4 (4)	59.5 (4)
C(7)-C(2B)-C(1B)-C(6)	−0.7 (4)	1.0 (4)
C(2B)-C(1B)-C(6)-C(3)	−59.0 (4)	−59.8 (4)
C(1B)-C(6)-C(3)-C(4)	55.8 (4)	56.1 (4)
C(6)-C(3)-C(4)-C(7)	1.3 (4)	1.3 (3)
C(1A)-C(2B)-C(7)-C(2B)	53.7 (4)	54.6 (4)
C(2A)-C(7)-C(2B)-C(1B)	−53.4 (4)	−55.1 (4)
C(7)-C(2B)-C(1B)-C(6)	−0.7 (4)	1.0 (4)
C(2B)-C(1B)-C(6)-C(1A)	54.2 (4)	53.8 (4)
C(1B)-C(6)-C(1A)-C(2A)	−53.5 (4)	−54.7 (4)
C(6)-C(1A)-C(2A)-C(7)	−0.2 (4)	0.3 (4)
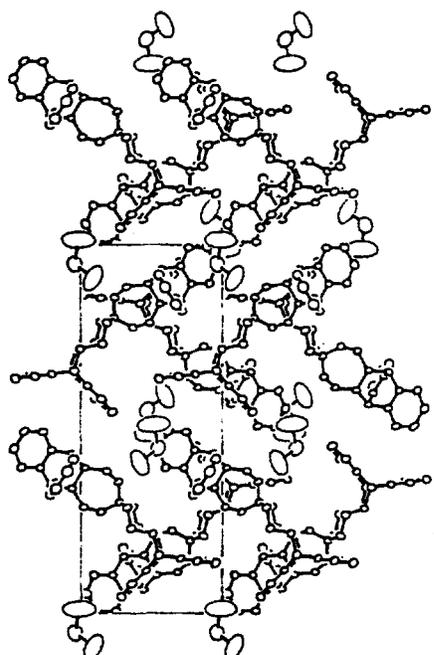
Figure 4. The crystal structure of **5** in projection down the a-axis.

Table 6. Bond Lengths (Å) and Angles (°) for **8**. The e.s.d.'s are in Parentheses. The values in first column are for unprimed atoms, and those in second one for primed atoms

|		
O(1)-C(14)	1.441 (6)	1.447 (4)
O(1)-C(16)	1.376 (5)	1.380 (5)
O(2)-C(15)	1.447 (5)	1.438 (4)
O(2)-C(16)	1.393 (5)	1.400 (5)
C(1)-C(2)	1.381 (7)	1.387 (6)
C(1)-C(10)	1.377 (6)	1.389 (5)
C(2)-C(3)	1.374 (9)	1.378 (8)
C(3)-C(4)	1.381 (8)	1.379 (7)
C(4)-C(11)	1.393 (6)	1.388 (6)
C(5)-C(6)	1.395 (7)	1.384 (7)
C(5)-C(12)	1.386 (7)	1.396 (5)
C(6)-C(7)	1.366 (8)	1.367 (7)
C(7)-C(8)	1.391 (7)	1.381 (6)
C(8)-C(13)	1.391 (6)	1.384 (5)
C(9)-C(10)	1.517 (6)	1.509 (4)
C(9)-C(13)	1.515 (6)	1.516 (4)
C(9)-C(14)	1.537 (6)	1.531 (4)
C(9)-C(15)	1.520 (6)	1.533 (5)
C(10)-C(11)	1.404 (6)	1.401 (4)
C(11)-C(12)	1.463 (6)	1.470 (4)
C(12)-C(13)	1.386 (6)	1.388 (4)
O(2)-C(16)-O(1)	112.4 (4)	111.7 (3)
C(9)-C(14)-O(1)	112.4 (3)	112.7 (2)
C(9)-C(15)-O(2)	110.5 (3)	110.6 (2)
C(16)-O(1)-C(14)	112.5 (3)	111.6 (3)
C(16)-O(2)-C(15)	112.3 (3)	112.6 (3)
C(3)-C(2)-C(1)	121.5 (5)	121.3 (5)
C(4)-C(3)-C(2)	120.8 (5)	120.8 (4)
C(7)-C(6)-C(5)	121.1 (5)	121.4 (4)
C(8)-C(7)-C(6)	121.0 (5)	120.1 (4)
C(9)-C(10)-C(1)	130.0 (4)	129.8 (3)
C(9)-C(13)-C(8)	128.1 (4)	129.2 (3)
O(1')-C(16)-O(1)		105.4 (3)
O(1')-C(16)-O(2)		108.2 (3)
O(2')-C(16)-O(1)		107.5 (3)
O(2')-C(16)-O(2)		111.4 (3)
C(10)-C(1)-C(2)	118.9 (4)	118.4 (4)
C(10)-C(11)-C(4)	120.6 (4)	120.8 (3)
C(11)-C(4)-C(3)	118.3 (5)	118.6 (5)
C(11)-C(10)-C(1)	120.0 (4)	120.0 (3)
C(11)-C(10)-C(9)	110.0 (4)	110.2 (3)
C(11)-C(12)-C(5)	131.3 (4)	131.6 (3)
C(12)-C(5)-C(6)	118.5 (5)	118.8 (4)
C(12)-C(11)-C(4)	130.7 (4)	130.9 (3)
C(12)-C(11)-C(10)	108.7 (4)	108.4 (3)
C(12)-C(13)-C(8)	121.0 (4)	120.4 (3)
C(12)-C(13)-C(9)	111.0 (4)	110.4 (3)
C(13)-C(8)-C(7)	118.1 (4)	119.6 (4)
C(13)-C(9)-C(10)	101.7 (3)	102.3 (2)
C(13)-C(12)-C(5)	120.3 (4)	119.7 (3)
C(13)-C(12)-C(11)	108.4 (4)	108.7 (3)
C(14)-C(9)-C(10)	111.8 (4)	112.7 (2)
C(14)-C(9)-C(13)	108.7 (3)	108.7 (3)
C(15)-C(9)-C(10)	113.6 (3)	113.2 (3)
C(15)-C(9)-C(13)	111.9 (4)	111.6 (3)
C(15)-C(9)-C(14)	109.0 (4)	108.2 (3)
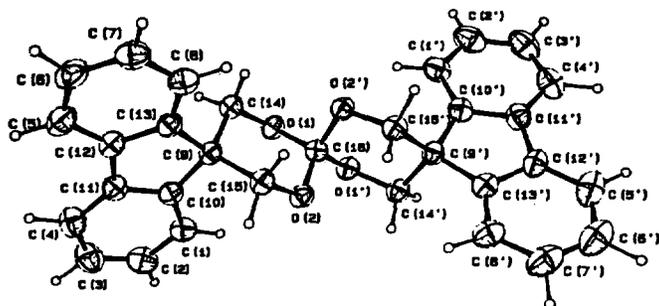
Figure 5. Molecular Conformation with Atomic Numbering in **8**.

Table 7. Selected Torsion Angles of **8**. The e.s.d.'s are in the Parentheses. The values in first column are for unprimed atoms, and those in second one for primed atoms

C(16)-O(1)-C(14)-C(9)	−52.6 (4)	−52.6 (4)
O(1)-C(14)-C(9)-C(15)	47.1 (4)	48.2 (3)
C(14)-C(9)-C(15)-O(2)	−48.6 (4)	−48.7 (3)
C(9)-C(15)-O(2)-C(16)	56.7 (4)	56.8 (3)
C(15)-O(2)-C(16)-O(1)	−61.9 (4)	−62.6 (3)
O(2)-C(16)-O(1)-C(14)	59.3 (4)	60.3 (3)
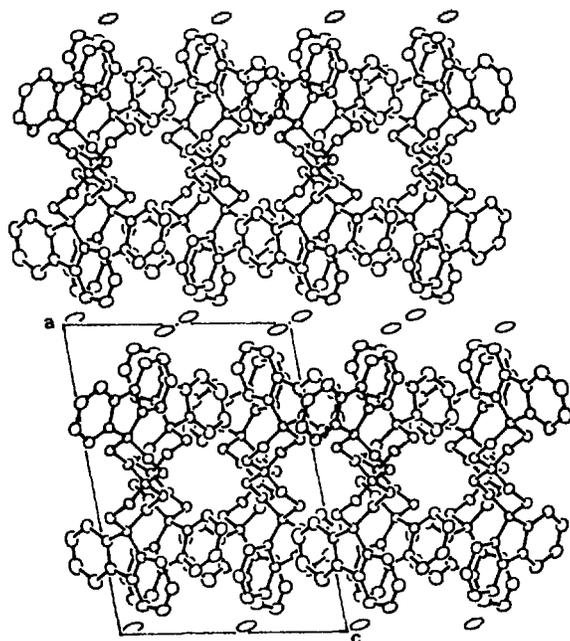
Figure 6. The Crystal Structure of **8** in projection down the *b*-axis.

of the molecule with atomic numbering is shown on Figure 5. Both fluorene groups [from C(1) atom to C(13) atom] are planar within ±0.09 Å. Two opposite side fluorene groups make the dihedral angle of 85° with each other. The six-membered rings have chair conformations (see Table 7 for the selected torsion angles). The whole molecule in the structure has the pseudo-C_2 symmetry. The crystal packing is shown in Figure 6. The two centrosymmetrically related

water molecules are hydrogen bonded with a distance of 2.790 Å.

Experimental

Melting points were measured by Sybron thermolyne apparatus with polarizing microscope and were not corrected. IR spectra were obtained using a Shimazu IR-435 spectrophotometer, and ^{1}H-NMR spectra were recorded on Varian EM-360 instrument with TMS as internal standard. Solvents were purified by the published procedures before use and reagent grade chemicals were used as obtained.

The Diel-Alder adduct **3** of anthracene and maleic anhydride was prepared by the Bachmann's method[7] with modification. A mixture of anthracene (2.50 g, 0.14 mole) and maleic anhydride (35.0 g, 0.36 mole) in benzene (300 m*l*) was refluxed for 5 h then cooled to room temperature. Precipitated solid was collected, washed with cold benzene three times and dried at 100℃ for overnight under vacuum. A recrystallization from ethylacetate gave a total of 35.9 g (91%) of colorless crystalline solid; mp. 265-267℃ (lit[7]. 265℃); IR (KBr) 1860 and 1775 cm^{-1} (C=O stretching); ^{1}H-NMR (CDCl₃) 7.50-7.15 (m, 8H, ArH), 4.83 (t, 2H, ArCHAr), 3.50 ppm (t, 2H, CH).

9,10-Dihydro-9,10-ethanoanthracene-11,12-dimethanol 4. To a well stirred solution of NaBH₄ (2.72 g, 74 mmole) in diglyme or THF, powdered compound **3** (11.0 g, 40 mmole) was added in several portions at room temperature under a nitrogen atmosphere. A solution of BF₃·etherate (11.7 m*l*) in diglyme or THF (30 m*l*) was added dropwise during a 30 min period, then heated for 2h at 65℃ in an oil bath. The reaction mixture was poured into cold water (500 m*l*) and the resulting white solid was collected, washed with water 5 times, and then dried overnight at 100℃ under vacuum. A recrystallization from a mixture of diglyme and hexane gave a total 8.52 g (80%) of colorless needle; mp. 225-226℃ (lit[8]. 225-226℃); IR (KBr) 3280 cm^{-1} (OH stretching); ^{1}H-NMR (CDCl₃) 7.38-7.00 (m, 8H, ArH), 4.67 (d, 2H, ArCHAr), 4.50 (d, 2H, CH₂), 3.30 (d, 2H, CH₂), 2.83 (m, 2H, CH), 2.10 ppm (br, 2H, OH).

3,4,10,11-Di(9,10-dihyro-9,10-ethanoanthracenyl)-1,6,8,13-tetraoxa-6,6-tridecane 5. A mixture of compound **4** (4.00 g 0.15 mole) and *n*-butyltin oxide (3.75 g) in toluene (100 m*l*) was refluxed for 6 h to collect water in a Dean-Stark moisture trap. After collection of the calculated amount of water the moisture trap was removed and then 1.1 m*l* of carbon disulfide was added dropwise and heating was extended overnight. White solid precipitated upon cooling was collected, washed with toluene several times. The mother liquid and washing were combined and concentrated to 100 m*l*, then cooled to room temperature. The resulting precipitate was collected and combined with the first crop. A recrystallization from a mixture of dried methylene chloride and anhydrous methanol gave a total of 3.17 g (78%) of colorless crystalline solid; mp. 301-302℃; IR (KBr) 1170 cm^{-1} (C-O stretching); ^{1}H-NMR (CDCl₃) 7.24 (s, 16H, ArH), 4.00 (d, 4H, ArCHAr), 3.70-3.00 (m, 8H, CH₂), 2.50 ppm (m, 4H, CH).

9,9-Bis(hydroxymethyl)fluorene 7. To a well stirred solution of paraformaldehyde (8.0 g) in DMSO (100 m*l*), a solution of NaOEt (1.11 g, 16.8 mmole) in absolute ethanol

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was added rapidly and then a solution of fluorene (16.0 g, 0.1 mole) in DMSO (100 m*l*) was added during 30 sec period with stirring in an ice bath. After 5 min stirring, the reaction mixture was neutralized with dil. HCl, added 400 m*l* of water and then extracted with ethyl acetate. The organic layer was separated, washed with water then dried over anhyd. Na_2SO_4. The yellow oily residue, obtained by evaporation of solvent, was triturated with benzene. The resulting colorless precipitate was collected and recrystallized from benzene to produce 16.1 g (74%) of crystalline solid; mp. 144-145°C (lit[9]. 144-145°C); IR (KBr) 3300 cm^{-1} (OH stretching); ^{1}H-NMR (CDCl$_3$) 7.48 (s, 8H, ArH), 4.85 (t, 2H, OH), 3.33 ppm (s, 4H, CH$_2$).

3,9-Di(9-fluorenylidenyl)-1,4,6,9-tetraoxa-5,5-undecane 8. A mixture of compound 7 (5.0 g, 22 mmole) and *n*-butyltin oxide (6.05 g, 24 mmole) in toluene (100 m*l*) was refluxed for 12 h to collect water in Dean-Stark moisture trap. After collection of water the moisture trap was removed and then 5 m*l* of carbon disulfide was added dropwise and heating was extended overnight at 100°C. The yellow oily residue, resulted upon removal of solvent, was triturated with methanol to give white solid. A recrystallization from methylene chloride and methanol gave 4.81 g (94%) of colorless crystalline solid; mp. 212-213°C; IR (KBr) 1230 and 1140 cm^{-1} (C-O stretching); ^{1}H-NMR (DMSO d$_6$) 7.88 (m, 16H, ArH), 4.31 ppm (s, 8H, CH$_2$).

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Large Unilamellar Phospholipid Vesicles as a Model Substrate for Phospholipase D

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The hydrolytic susceptibility of large unilamellar vesicle (LUV) toward cabbage phospholipase D (PLD) was studied. The activity of PLD was determined by pH stat titration method. Using phosphatidylcholine LUV as substrate a pH optimum of 6.96 was observed. For maximal activity the optimal temperature of 31°C and 10 mM of Ca^{2+} were required. The apparent K_m value estimated was 2.5 mM. The hydrolytic activity of PLD toward PC LUV was somewhat high despite the absence of activator in assay system and this high susceptibility of PC LUV may be attributed to the structural properties of LUV. The effect of amphiphatic substances such as dicetyl phosphate and phosphatidic acid on the enzyme activity were also examined in mixed LUVs.

Introduction

Since the discovery of the spherically closed structure of amphiphatic substances, phospholipid vesicles have been used as model systems for various biological membranes.[1] And at the same time various methods have been developed to form morphologically different vesicles such as multilamellar vesicle, small unilamellar vesicle, and large unilamellar vesicle (LUV).[2] For some lipolytic enzymes, lipid vesicle was selectively used as substrate. Since the water insoluble lipid substrates form aggregates in aqueous media, any hydrolytic enzymes acting upon lipid substrates react with lipids at a water-lipid interface and hence are affected by the physical properties of the interface.[3-5]