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Isolation and Spectral and Structural Characterization of Bisphenol A Cyclic Dimer, Trimer, and Tetramer Carbonates

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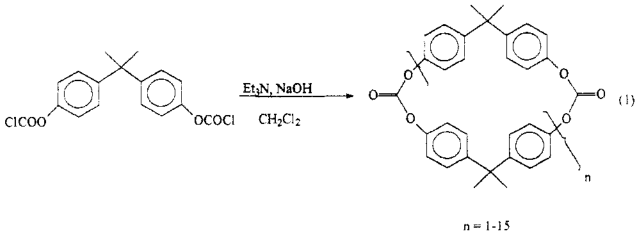
ABSTRACT: Cyclic dimer, trimer, and tetramer carbonates of 2,2-bis(4-hydroxyphenyl)propane (BPA) were isolated from a mixture of cyclics obtained by hydrolysis/condensation of BPA bischloroformate. The compounds were characterized by ^1H and ^{13}C NMR, DSC, and FTIR. Single-crystal X-ray structures were solved for the cyclic dimer and tetramer, as well as for diphenyl carbonate. Analysis of the crystal structures reveals that three distinct conformations about the carbonyl carbon are present, two trans-trans forms, one of which is similar to that found in diphenyl carbonate, and a single cis-trans form, seen only in the cyclic dimer.

Introduction

Experimental and theoretical studies of the conformations of the polycarbonate of 2,2-bis(4-hydroxyphenyl)propane (BPA) have been the object of considerable interest since the early work of Williams and Flory.[1] Some of the molecular geometry features of diphenyl carbonate have been published, although full X-ray data have not yet appeared.[2] Because polycarbonate has low conformational barriers to rotation, phenyl ring-flipping and cis-trans isomerization of the carbonate group have been invoked as mechanisms for energy absorption by polycarbonate which provide impact strength below the glass transition temperature.[3] The crystal structure of a model compound, the bis-phenyl carbonate of BPA (BPA-BPC), including a conformational analysis of polycarbonate, appeared recently.[4] That molecule was found to crystallize in two forms, one immobile, and one in which phenyl ring-flipping occurred. A crystal structure of a complex of BPA-BPC with two molecules of a thiopyrilium salt has also been reported, although the precision was poor due to the quality of the crystal.[5] In the complexed structure, a cis-trans orientation of the phenyl groups about the carbonyl was seen; in the uncomplexed form, a trans-trans conformation is present.[4] Several calculational[6] and physical[7] methods have been used to analyze conformational features of BPA polycarbonate. Estimations of the energy differences between cis-trans and trans-trans conformations of the aromatic groups about the carbonate have been investigated by a variety of techniques, including ab initio calculations,[8] NMR spectroscopy,[9] and infrared spectroscopy.[10]

The efficient preparation of cyclic oligomeric carbonates via a triethylamine-catalyzed hydrolysis-condensation of BPA bischloroformate under interfacial conditions was recently reported.[11,12] Kinetic control in that reaction allows preparation of a mixture of cyclic oligomers in high yields (eq 1). The anionically-initiated ring-opening polymerization reactions of the cyclic oligomers, which provide polycarbonates with very high molecular weight, were also reported.[13] The cyclic oligomers obtained from such reactions are a mixture of ring sizes, ranging from dimer to hexadecamer. The lower oligomeric cyclic oligomers are easily separated and purified. The preparation of the cyclic tetramer carbonate of BPA had been described earlier, but no structural features and little spectroscopic information were reported at that time.[14] The cyclic trimer was also reported, but with no characterization.[15] Since our work is the first reporting the formation of BPA cyclic *dimer* carbonate, we were interested in determining its structural and physical properties, as well as comparing the dimer to the trimer and tetramer. This paper reports the preparation, isolation, and spectral features of cyclic dimer, trimer, and tetramer carbonates of BPA, as well as the crystal structures of the cyclic dimer and tetramer. The structural features are compared to diphenyl carbonate and to polycarbonate.



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Results and Discussion

Typical cyclization of BPA bischloroformate affords a product mixture comprising about 85% cyclic oligomers and 15% high molecular weight polymer.[10,11] The cyclic fraction contains oligomers from dimer to about hexadecamer, but with the lower cyclics predominating (>90% of the cyclics have a degree of polymerization of less than 10). Although the formation of cyclic dimer should be statistically favored, ring strain disfavors its formation, and it is normally present in levels of 3-10%. The level of cyclic dimer can be increased to 15-20% by adding free BPA to the cyclization reaction or by operating at somewhat higher dilution (0.10 M). Cyclic trimer, tetramer, and pentamer, which are essentially strain-free, are typically formed in yields of 15-20% each. The even-numbered cyclics crystallize more easily than do the odd oligomers. Upon standing in a 1:1 CH_2Cl_2-acetone solution at 10 wt %, a mixture of cyclic dimer, tetramer, and hexamer precipitates. Further crystallizations provide pure crystals of each. Cyclic trimer and pentamer can be isolated and purified by chromatography, but X-ray quality crystals have not been obtained. Although cyclic trimer produced very large cubic crystals on crystallization from benzene, loss of solvent after isolation and drying destroyed the crystal symmetry before X-ray data could be collected, even at -100 °C.

A comparison of the physical and spectroscopic properties of cyclic dimer, trimer, and cyclic tetramer is interesting. Each of the pure discrete cyclics are high melting solids (visual melting points: cyclic dimer = 339

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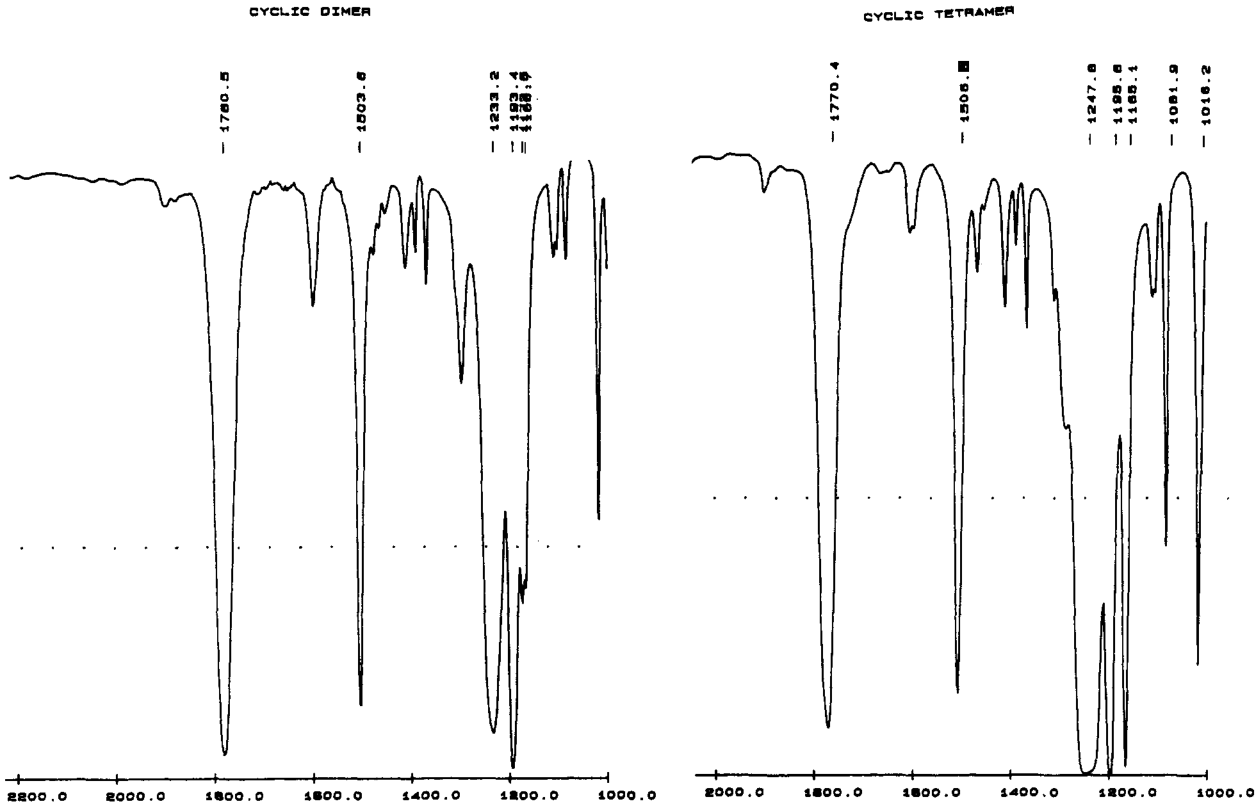

Figure 1. FTIR of BPA cyclic dimer carbonate (left) and cyclic tetramer carbonate (right).

°C; cyclic trimer = 350 °C; cyclic tetramer = 375 °C). Ring strain in the dimer is evident from a shift in the carbonyl absorption band of about 10 cm^{-1}, which occurs at 1780.5 cm^{-1} (Figure 1). The cyclic tetramer carbonyl band occurs at 1770.4 cm^{-1}, which is similar to the frequency observed in polycarbonate (1770.6 cm^{-1}). Cyclic trimer has a similar C═O (1771.0). Both the cyclic tetramer and the cyclic trimer have strong COC bands at 1249 cm^{-1}, with a shoulder at 1230 cm^{-1}. The cyclic dimer has a strong COC band observed at 1233.1 cm^{-1}, with no evidence of the band at 1249 cm^{-1}. These bands correlate well with those observed for amorphous polycarbonate,[10] which has a C═O maximum at 1767 cm^{-1}, with a shoulder at 1785 cm^{-1}, and COC vibrations at 1252 and 1223 cm^{-1}. Crystalline polycarbonate, which has a higher degree of cis–trans isomer present, shows increased intensities of the bands at 1785 cm^{-1} (carbonyl) and 1223 cm^{-1} (COC).[10] In addition, the cyclic trimer and tetramer have sharp bands at 1155.6 and 1154.9 cm^{-1}, respectively, while the cyclic dimer has a pair of bands at 1173.5 and 1157.4 cm^{-1}, of approximate equal intensity.

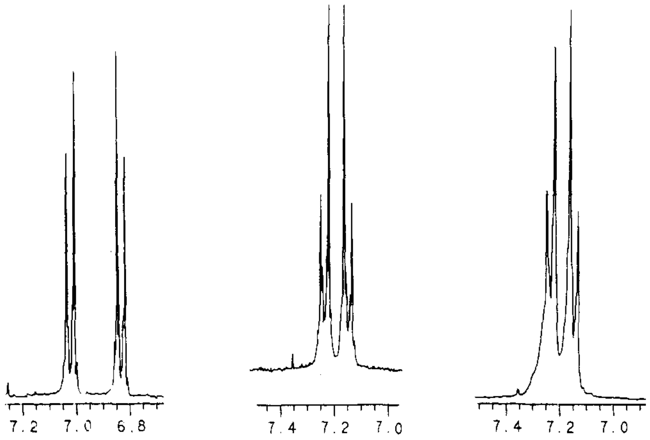

Figure 2. ^1H NMR of BPA cyclic dimer (left), cyclic trimer (middle), and cyclic tetramer (right) carbonates.

The ^1H NMR spectrum also indicates a compact ring size in cyclic dimer. The aromatic CH protons are shifted significantly upfield, from normal values of 7.16 and 7.25 ppm (in polycarbonate) to 6.832 and 7.022 ppm, due to shielding by the ring current of the ring on the opposite side of the macrocycle (Figure 2). Cyclic trimer has chemical shifts slightly shifted, to 7.09 and 7.14 ppm, while cyclic tetramer has chemical shifts similar to those found in polycarbonate, at 7.16 and 7.24 ppm. The ^{13}C NMR spectra are also interesting. The cyclic tetramer has chemical shifts comparable to polycarbonate, with the carbonyl at 152.16, the substituted aromatic carbons at 148.36 and 148.99, and the hydrogen-bearing aromatics at 127.99 and 120.38 (polycarbonate has resonances at 152.1, 148.9, 148.2, 127.9, and 120.3). Cyclic trimer is similar, with resonances at 152.40, 149.15, 148.5, 127.84, and 120.58. Cyclic dimer, on the other hand also shows some changes in chemical shift. Most notably, the carbonyl peak is apparently accidently equivalent to one of the substituted aromatic resonances, which appear at 148.84 and 149.68 ppm. The hydrogen-bearing aromatic carbons appear at nearly normal locations of 119.51 and 127.55 ppm (Figure 3).

Differential scanning calorimetry (DSC) of the cyclic dimer shows an unusual endotherm at 158 °C (ΔH = 18.4 J/g), which coincides with the glass transition temperature of polycarbonate, and may be indicative of a change in the crystal lattice; no change is seen visually. Second and third endotherms are apparent at 300 and 336 °C, which correspond to the visual melting point at 339 °C. The third endotherm (336 °C) is followed by an exotherm, indicating polymerization after melting (Figure 4). On second heating in the DSC, only a glass transition for high molecular weight polycarbonate is observed, at 161 °C. Visibly, no change occurs in a sample heated on a glass slide, until about 300 °C, when the sample containing large crystals appears to soften, melt, and then gel.

DSC of cyclic trimer shows a single sharp melting point at 353.7 °C (lit.[15] mp = 350 °C), with an endotherm of 69.8

Table I. Details of Data Collection and Refinement

structure	dimer	tetramer	diphenyl carbonate
crystal system	monoclinic	monoclinic	orthorhombic
lattice constants			
a (Å)	7.718(5)	8.320(8)	6.077(2)
b (Å)	8.695(4)	32.11(2)	7.297(1)
c (Å)	19.693(9)	11.99(1)	23.429(7)
β (deg)	94.53(5)	102.43(8)	
space group	$P2_1/n$	$P2_1/a$	$P2_12_12_1$
Z	2 dimers	2 tet. + 2 solv.	4
μ (cm^{-1})	1.0	0.9	1.1
unit cell vol (Å^3)	1317.4	3125.5	1039
unit cell mass (amu)	1017.2	2459.1	856.9
calcd density (g/cm^3)	1.28	1.31	1.37
data collecn	$4 < 2\theta < 45$	$4 < 2\theta < 50$	$4 < 2\theta < 50$
min, max hkl	(00–22), (9 10 22)	(00–15), (10 39 15)	(000), (8 9 28)
check reflns	(-1 -14), (-1 -1 0)	(0 6 0), (-1 -4 2)	(0 0 4), (1 1 -3)
reflns collected	1961	6017	1123
obsd reflns	1074	2620	948
	$F > 3\sigma(F)$	$F > 4\sigma(F)$	$F > 2\sigma(F)$
parameters refined	172	391	145
R	0.0704	0.0931	0.0543
wR, $w^{-1} = \sigma2(F) + gF^2$	0.0481	0.1156	0.0687
g	0.0004	0.002	0.00254

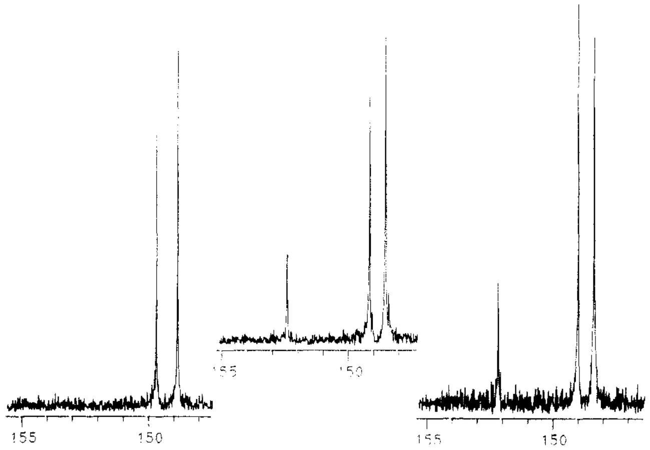

Figure 3. ^{13}C NMR of BPA cyclic dimer (left), cyclic trimer (middle), and cyclic tetramer (right) carbonates.

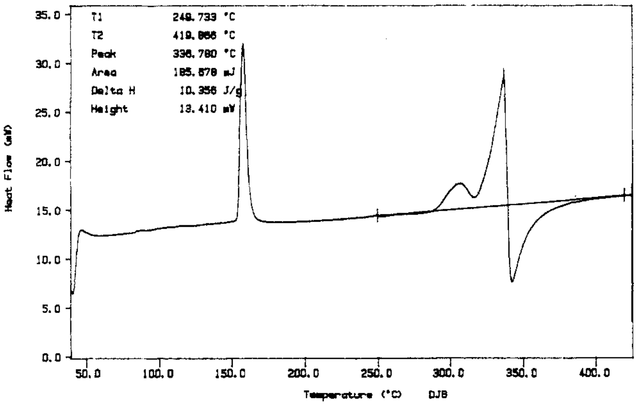

Figure 4. Differential scanning calorimetry of BPA cyclic dimer carbonate (heat rate = 40 °C/min).

J/g. Although complete polymerization occurred on melting, only a very slight exotherm was noted; a second heat showed the glass transition temperature for high molecular weight polycarbonate (162.6 °C). The DSC of cyclic tetramer was similar, with a melting point of 339.6 °C, and with little polymerization exotherm on heating. Second heating showed a glass transition temperature of 154 °C. The high melting point observed in the literature[14] (375 °C) was obtained on acid-washed glass slides, which prevent polymerization.

Table II. Torsional Angles from X-ray Data (deg)

Diphenyl Carbonate	
C(9)–C(8)–O(1)–C(7) = –54.38	C(8)–O(1)–C(7)–O(2) = 176.5
C(13)–C(8)–O(1)–C(7) = 133.13	C(8)–O(1)–C(7)–O(3) = –4.46
C(2)–C(1)–O(2)–C(7) = 58.83	C(1)–O(2)–C(7)–O(3) = 6.17
C(6)–C(1)–O(2)–C(7) = –127.58	C(1)–O(2)–C(7)–O(1) = –174.78
Cyclic Dimer	
C(2)–C(1)–O(1)–C(7) = –106.46	C(8)–O(2)–C(7)–O(3) = 22.45
C(6)–C(1)–O(1)–C(7) = 71.89	C(8)–O(2)–C(7)–O(1) = –159.8
C(9)–C(8)–O(2)–C(7) = 119.66	C(1)–O(1)–C(7)–O(3) = –166.03
C(13)–C(8)–O(2)–C(7) = –66.62	C(1)–O(1)–C(7)–O(2) = 16.06
C(5)–C(4)–C(14)–C(11) = –59.34	C(10)–C(11)–C(14)–C(4) = –39.52
C(3)–C(4)–C(14)–C(11) = 113.96	C(12)–C(11)–C(14)–C(4) = 141.62
C(5)–C(4)–C(14)–C(15) = –177.19	C(10)–C(11)–C(14)–C(15) = 82.10
C(5)–C(4)–C(14)–C(16) = 61.51	C(10)–C(11)–C(14)–C(16) = –159.04
C(3)–C(4)–C(14)–C(15) = –3.59	C(12)–C(11)–C(14)–C(15) = –96.77
C(3)–C(4)–C(14)–C(16) = 22.09	C(12)–C(11)–C(14)–C(16) = 22.09
Cyclic Tetramer	
C(19)–C(20)–O(4)–C(23) = 122.84	C(20)–O(4)–C(23)–O(6) = 0.26
C(21)–C(20)–O(4)–C(23) = –62.98	C(20)–O(4)–C(23)–O(5) = –179.22
C(25)–C(24)–O(5)–C(23) = –132.81	C(24)–O(5)–C(23)–O(6) = 4.61
C(29)–C(24)–O(5)–C(23) = 51.90	C(24)–O(5)–C(23)–O(4) = –175.91
C(18)–C(17)–C(14)–C(16) = 71.50	C(10)–C(11)–C(14)–C(16) = –166.13
C(18)–C(17)–C(14)–C(15) = –171.21	C(10)–C(11)–C(14)–C(15) = 74.11
C(22)–C(17)–C(14)–C(16) = –105.13	C(12)–C(11)–C(14)–C(16) = 16.51
C(22)–C(17)–C(14)–C(15) = 12.08	C(12)–C(11)–C(14)–C(15) = –102.94
C(2)–C(1)–O(3)–C(7) = –29.46	C(1)–O(3)–C(7)–O(2) = 5.51
C(6)–C(1)–O(3)–C(7) = 152.09	C(1)–O(3)–C(7)–O(1) = 1173.06
C(9)–C(8)–O(1)–C(7) = –52.00	C(8)–O(1)–C(7)–O(2) = –3.17
C(13)–C(8)–O(1)–C(7) = 134.86	C(1)–O(3)–C(7)–O(3) = 175.41
C(26)–C(27)–C(30)–C(32) = 179.01	C(3)–C(4)–C(30)–C(31) = –62.97
C(26)–C(27)–C(30)–C(31) = –62.19	C(3)–C(4)–C(30)–C(32) = 178.45
C(28)–C(27)–C(30)–C(32) = –5.73	C(5)–C(4)–C(30)–C(31) = 117.09
C(28)–C(27)–C(30)–C(31) = 113.06	C(5)–C(4)–C(30)–C(32) = –1.48

Single-crystal X-ray structures were solved for cyclic dimer, tetramer, and for diphenyl carbonate. Details of the data collection and refinement may be found in Table I. Atom coordinates, bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates may be found in Appendices 1–3 (supplementary material). Some torsional angles are listed in Table II. Diphenyl carbonate forms orthorhombic crystals with four molecules in a unit cell. The unit cell mass of 856.9 amu and dimensions give a density of 1.37 g/cm^3. The structure is almost symmetrical, with a trans–trans conformation of the phenyl rings about the carbonyl (Figure 5). The dihedral angles from the aromatic C—O—C(=O)—O are 174.8 and 176.5°, which indicates that the carbonyl oxygen and the aromatic rings are nearly eclipsed. As a consequence of that conformation, the plane of the carbonyl group is skewed by 59.1 and 53.1° from the planes of the aromatic rings (Figure 6). The carbonyl bond length is

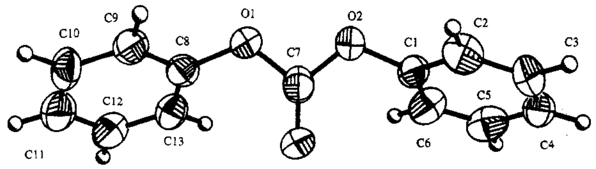

Figure 5. X-ray structure of diphenyl carbonate.

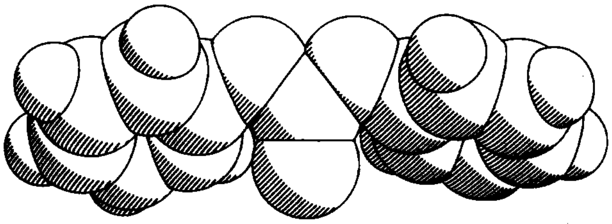

Figure 6. Space-filling model of diphenyl carbonate based on X-ray data.

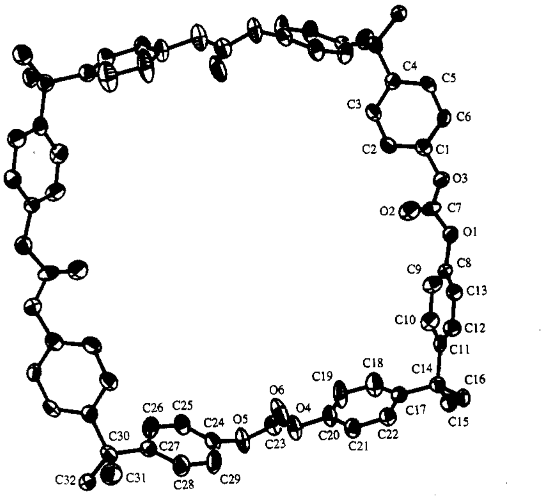

Figure 7. X-ray structure of BPA cyclic tetramer carbonate.

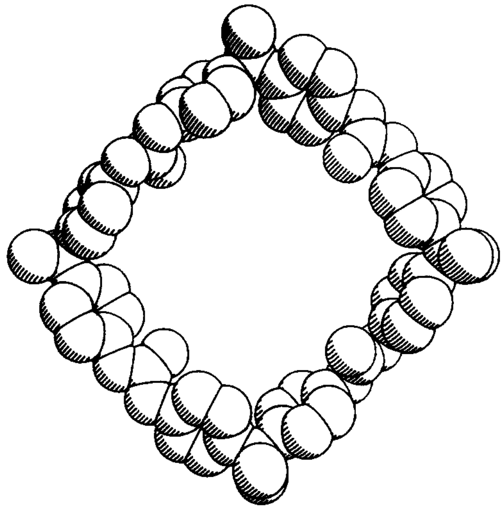

Figure 8. Space-filling model of BPA cyclic tetramer based on X-ray data.

1.198 Å, and the O═C—O single bonds are 1.34 Å. The O—C(═O)—O bond angle is 105.35°, and the O—C═O bond angles are 127.01 and 127.64°. These values differ somewhat from those reported earlier,[2] possibly because our measurements were taken at −100 °C. The conformation of diphenyl carbonate is dissimilar to that of BPA–BPC, which showed a perpendicular orientation of the phenyl rings and carbonyl group to be favored and also showed somewhat shorter carbonyl bonds (1.15 and 1.17 Å).[4] We also find that the oxygens attached to the aromatic rings are angled several degrees below the plane of the aromatic (5.9 and 6.9°) with respect to the carbonyl group.

Solution of the crystal structure of cyclic tetramer was also made difficult by the molecule's tendency to include solvent molecules. However, a stable crystal was formed using *m*-xylene as the crystallization solvent. BPA cyclic tetramer carbonate crystallized in a monoclinic form, which included two tetramer molecules and two solvent molecules in the unit cell. The unit cell mass of 2459.1 and volume of 3125.5 Å^3 gave a calculated density of 1.31 g/cm, very similar to diphenyl carbonate. Surprisingly, BPA cyclic tetramer carbonate showed two types of conformations about the carbonate (Figure 7). One of the conformations is very similar to diphenyl carbonate and shows a nearly symmetrical positioning of the phenyl rings in planes skewed 51.9 and 59.7° from the plane of the carbonyl group. That conformation has dihedral angles from the aromatic C—O—C(═O)—O of 175.91 and 179.22°, again indicating trans–trans geometry. The carbonyl bond length is somewhat shorter, at 1.182 Å, and the O═C—O single bonds are about the same length, 1.35 and 1.3335 Å. The O—C(═O)—O bond angle is exactly the same, 105.3°, and the O—C—O bond angles are similar, 126.69 and 128.07°. The second type of conformation has the phenyl rings attached to the carbonate functionality in planes which are rotated 70.8° relative to one another. Thus, the plane of one of the aromatic rings is forced nearly into the plane of the carbonyl, with an interplane angle of only 25.4°, while the other ring is at an angle of 50.6° relative to the carbonyl. The bond lengths and angles are barely affected by this rotation. The C═O is 1.193 Å, and the C—O single bonds are 1.342 and 1.331 Å, the O—C(═O)—O bond angle is unchanged at 105.2°, and the O—C—O bonds are 127.8 and 127.2°. The two types of conformations about the carbonyl are somewhat clearer in the space-filling representation of Figure 8. The oxygen atoms attached to the phenyl rings are again displaced from the plane of the aromatic, away from the carbonyl by several degrees (6.1, 1.4, 5.3, and 4.3°).

The cyclic tetramer is a very large, open cyclic structure, with a cavity measuring 14–16 Å across, between parallel benzene rings. The outside diameter of the cyclic (from *gem*-dimethyl to *gem*-dimethyl) is 20.7 Å. The carbonyl groups lie opposed to one another, and thus are not repulsive, with distances of 14.92 and 13.8 Å between opposing pairs of carbonyl carbons. Because the ring is so large, it is anticipated that no hindrance to ring-flipping or cis–trans—trans–trans isomerization about the carbonyl would occur. Solution FTIR, in fact (vide supra), indicates the presence of substantial cis–trans carbonyl conformation.

BPA cyclic dimer presents a completely different structure. Due to ring strain, the dimer is forced to assume a cis–trans relationship of the aromatic rings about the carbonate functionality (Figure 9). In that conformation, the four aromatic rings form an array with the transannular benzene rings in a coplanar but staggered conformation. This arrangement, in which the aromatic CH protons are located directly over the center of a benzene ring on the opposite side of the macrocycle, accounts for the large shift seen in the proton NMR. The ring is fairly small, only 3.87 Å across the cavity from aromatic ring to aromatic ring, on the short axis, and 8.20 Å on the long axis, or 9.23 Å between the two carbonyl carbons. The outside diameter of the cyclic is only 10.9 Å, from *gem*-dimethyl across the ring to the opposing *gem*-dimethyl (Figure 10).

The carbonyl C═O in cyclic dimer is 1.191 Å in length, approximately the same as in cyclic tetramer, but the O═C—O single bonds are 1.364 and 1.335 Å long, showing

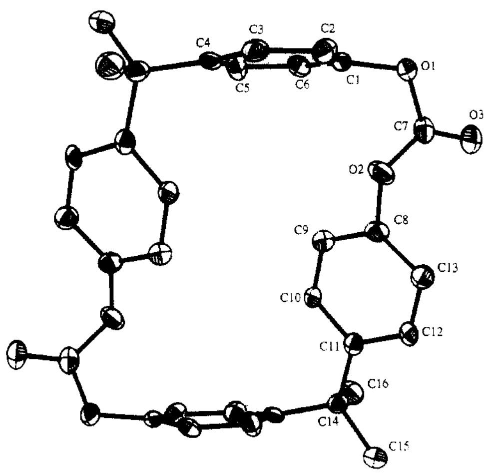

Figure 9. X-ray structure of BPA cyclic dimer carbonate.

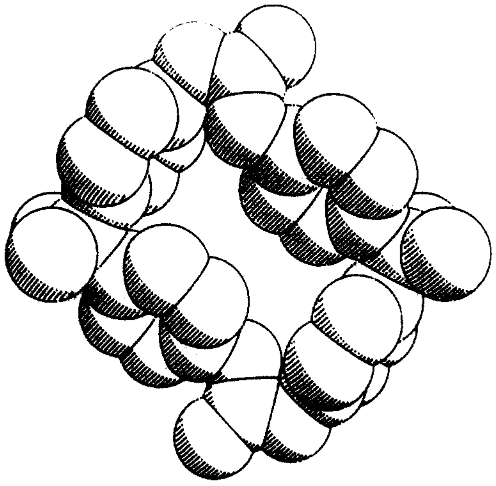

Figure 10. Space-filling model of BPA cyclic dimer based on X-ray data.

the effects of different structure. Evidence of ring strain is seen in the bond angles, which show an increase in the O—C(=O)—O angle to 109.55°, one normal O—C—O angle at 128.27° C, and one squeezed to 122.14°. The dihedral angles about the aromatic C—C—C(=O)—O bonds of 159.8 and 16.06° indicate a cis–trans conformation of the carbonate. The planes of the aromatic rings are rotated by 50.05 and 78.7° from the plane of the carbonyl group. Another feature resulting from ring strain is a twisting in the aromatic rings. A twist angle of 6.2° in the ring is evident from the crystal structure. The oxygens attached to the aromatic rings are out of the plane of the phenyl rings to different degrees; the cis-oxygen is 1.5° *toward* the carbonyl, while the trans oxygen is 5.7° away from the carbonyl.

The cyclic dimer also gives a monoclinic crystal, with two dimers in the unit cell; no solvent was included. The unit cell volume of 1317.4 Å^3 and mass of 1017.2 amu gave a calculated density of 1.28 g/cm^{-1}.

Conclusion

Recent studies have used infrared spectroscopy and solid-state ^{13}C NMR to probe the conformational states of polycarbonates. Despite the interest in transitions in conformation between the cis–trans geometry and the more stable trans–trans form, direct observation of a cis–trans aromatic carbonate by solution NMR or FTIR has not been available. Other than the thiopyrillium salt complex of BPA–BPC, BPA cyclic dimer carbonate is the first material reported which has exclusively cis–trans orientation about the carbonate. The cyclic tetramer adopts a crystal form with only trans–trans conformations about the carbonate functionality, although it appears that some cis–trans form is present in solution. The flexibility of the cyclic tetramer which allows cis–trans isomerism, should make it an excellent model for polycarbonate. Preliminary molecular modeling studies[16] indicate that the cyclic trimer will adopt a form with both cis–trans and trans–trans conformations present and that interconversion is rapid in solution at room temperature.

Experimental Section

Materials and Instruments. Reagent-grade solvents and chemicals were used without further purification. The procedure for preparation of a mixture of BPA cyclic oligomers has been reported previously.[11,12] Proton and ^{13}C NMR were recorded on a GE QE-300 300-MHz spectrometer, in CDCl$_3$, and are reported in parts per million vs TMS. FTIR spectra were measured on a Nicolet 5DXC spectrophotometer, in CDCl$_3$. Melting points were measured using a Mettler hot stage apparatus and a microscope.

Bisphenol A Carbonate Cyclic Tetramer. One hundred grams of polymer-free macrocyclic carbonates were dissolved in 500 mL of hot 70:29:1 acetone/CH$_2$Cl$_2$/2-propanol. Upon standing, 95% pure cyclic tetramer crystallized. Recrystallization from benzene afforded 15.0 g of pure cyclic tetramer with mp = 368–372 °C. FTIR shows no OH and a strong C=O at 1770.3 cm^{-1}. ^{1}H NMR has a slightly broadened singlet at 1.66 ppm and a collapsed A$_2$B$_2$ pattern at 7.20 and 7.24 ppm. ^{13}C NMR: 31.00 (methyls), 42.64 (quaternary carbon), 120.38 and 127.99 (unsubstituted aromatic), 148.36 and 148.99 (substituted aromatic), and 152.16 (carbonyl carbons). High-resolution mass spectrum has a parent at 1016.3772, calcd 1016.3708. Anal. Calcd for C$_{16}$H$_{14}$O$_3$: C, 75.57; H, 5.55. Found: C, 75.58; H, 5.21.

Bisphenol A Carbonate Cyclic Dimer. The tetramer-poor filtrate from above was evaporated and the residue dissolved in hot toluene. Cooling caused cyclic dimer and trimer to crystallize. Trimer was removed by washing with 60/40 acetone/hexane, which when recrystallized from benzene gave 13.4 g of white solid with mp = 345–350 °C. The transparent plates obtained from benzene occluded benzene, and a crystal structure could not be solved. The residue after removal of cyclic trimer was 98% pure cyclic dimer. Recrystallization from toluene afforded 5.8 g of pure dimer with mp = 330–335 °C. FTIR had no OH and a strong C=O at 1780.9 cm^{-1}. ^{1}H NMR had a singlet at 1.73 and an A$_2$B$_2$ pattern at 6.81 and 7.02 ppm (J = 9 Hz). ^{13}C NMR: 28.39 (methyls), 42.22 (quaternary carbon), 119.51 and 127.56 (unsubstituted aromatic), 148.84 and 149.68 (substituted aromatic); the carbonyl carbon was shifted upfield and revealed by integration to be accidentally equivalent to the 148.68 absorption. High-resolution mass spectrum calcd for C$_{32}$H$_{28}$O$_6$ 508.1886, found 508.1897. Anal. Calcd: C, 75.57; H, 5.55. Found: C, 75.61; H, 5.86.

Crystal Structure Determination. The crystals were sealed in glass capillaries for the analysis. Data were collected, in $\omega/2\theta$ mode, on a Nicolet P3/F automated diffractometer, at ~−100 °C, with graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å). The crystal dimensions were approximately 0.2 × 0.2 × 0.2 mm. Lattice parameters were determined from 12 reflections from 6 to 22°2θ. Two standard reflections were monitored in each case with a standard deviation in observed intensity of ~1%. No absorption correction was applied. The structures were solved by direct methods using SHELXTL.[17] Full-matrix refinement was carried out, minimizing the quantity $\sum w(F_o - F_c)^2$. Hydrogen positions were located by difference Fourier synthesis. In the final stages of refinement, C–H bond lengths and H–C–H angles were fixed at 0.96 Å and 109.5°. A fixed isotropic thermal parameter of 0.06 Å^2 was used for all H atoms. All non-hydrogen atoms were refined anisotropically. The scattering factors and f', f'' were supplied by the computer programs. Details of the data collection and refinement can be found in Table I. Atom coordinates, bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates may be found in Appendices 1–3 (supplementary material).

Supplementary Material Available: Appendices 1-3, containing atom coordiantes, band lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates (26 pages). Ordering information is given on any current masthead page.

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