polymer papers

X-ray crystallographic studies of sterically strained cyclic oligocarbonate precursors for polymerization

Steve A. Dobrowski, Howell G. M. Edwards, Anthony F. Johnson, Utai Meekum and Len Shields*
Chemistry and Chemical Technology, Department of Chemical Engineering, University of Bradford, West Yorkshire BD7 1DP, UK
(Received 12 November 1993; revised 5 April 1994)

Crystals of the dimeric and trimeric cyclic oligocarbonates of bisphenol A have been prepared by recrystallization from benzene, and these have been examined by X-ray diffractometry. The trimeric oligomer crystals have been shown to include solvate molecules of benzene, and were efflorescent, so that special precautions and measuring conditions were required in order to elucidate the crystal structure. The conformations of the cyclic oligocarbonates are strained, and the release of this steric strain on ring opening combined with a favourable entropic conversion are the proposed motivating factors in the polymerization of these precursors to a linear polycarbonate chain structure.

(Keywords: cyclic oligocarbonates; X-ray structures; steric strain)

INTRODUCTION

The cyclic oligomeric carbonates of 4,4′-isopropylidene-diphenol (bisphenol A) were first prepared in low yields using high-dilution techniques[1–6]. More recently, these cyclic oligomers, ranging from dimer to eicosamer, have been prepared in higher yields by using pseudo-high-dilution techniques involving an amine-catalysed hydrolysis/condensation of the aromatic bischloroformate of bisphenol A[7].

These cyclic oligocarbonates can be rapidly polymerized and copolymerized between 250 and 280°C through the use of initiators, which become incorporated into the solid product. Heat alone is sufficient above 300°C to induce polymerization. The oligomers are readily polymerized in solution using a variety of basic initiators[8–10].

The ability of cyclic ethers, lactams and lactones to ring-open depends to a considerable extent on the size of the ring. The principal driving force for the polymerization of small rings is the release of conformational strain in the monomer; the extent to which this factor contributes to the driving force is reflected in the enthalpy of polymerization. However, the polymerization of the cyclic oligocarbonates is reported to be nearly thermoneutral[7], signifying that bond making and breaking during polymerization is not the most important thermodynamic factor in the reaction. This paper explores the extent to which the dimeric and trimeric cyclic oligocarbonates are strained, and crystal structures for these cyclic oligocarbonates are reported for the first time. The relation between structure and the facility for the rapid polymerization of the cyclic oligocarbonates is discussed.

EXPERIMENTAL

The cyclic oligocarbonates were prepared as a mixture, and the dimeric and trimeric components were obtained as individual species by recrystallization[7]. Each of these oligomers was further purified, as described below, to give single crystals. The purity of each component was determined by h.p.l.c.[10].

Preparation of crystals

The cyclic oligomer mixture (approximately 0.20 g) was dissolved by refluxing in benzene (BDH, GPR grade, 10 ml) for 15 min. The solution was then brought to room temperature over a period of at least 4 h and crystals were obtained by gently tapping the outside surface of the flask. The colourless crystals of the dimer that formed were removed by filtration and washed with cold benzene (2 × 10 ml). The trimer crystals were retained under benzene; extraction of the crystals from benzene resulted in the loss of crystalline form due to the efflorescence of crystalline benzene solvate.

X-ray studies

A single crystal of the dimeric oligomer was examined directly using a Stoe four-circle diffractometer. For the trimeric oligomer, a single crystal in its benzene crystallization solution was transferred into a glass capillary tube in which one end was drawn down and sealed; a fine wire was used to remove any trapped air bubbles at the bottom of the capillary before the other end was sealed. This crystal under benzene was examined using a Stoe imaging plate diffractometer[11]; in summary, the imaging plate consists of a 180 mm diameter flat plate disc with Eu/BaFCl sensor[12,13], and a simple phi-axis

---

[*] To whom correspondence should be addressed

0032-3861/94/22/4707–05

Table 1 Crystal structure data[a]

	Dimer	Trimer/solvate
Molecular formula	$2[(CH_3)_2C(C_6H_4)_2CO_3]$	$3[(CH_3)_2C(C_6H_4)_2CO_3]\cdot\frac{1}{2}C_6H_6$
RMM	508	1035
Space group	$P2_1/n$	$P2_1/n$
a(Å)	7.791(2)	14.680(13)
b(Å)	8.582(5)	13.821(8)
c(Å)	20.027(10)	29.609(32)
β(deg)	94.3(2)	98.73(8)
Volume (Å^3)	1335.3	5937.6
Calculated density (g cm^{-3})	1.263	1.157
No. of reflections	2732	12538
No of unique reflections	1117	5187
No. of reflections used	1117	3156, $I/\sigma(I)>3$
Structure determination	Shelx86	Shelx86
Refinement program	Crystals (Oxford)	Shelx76
Convergence (shift/e.s.d.)	<0.003	<0.05
R(unweighted)	0.0317	0.0751
R(weighted)	0.0293, $w=1/\sigma(F)$	0.0635, $w=1/\sigma(F^2)$

[a] Values in parentheses are e.s.d. (significant digits)

Table 2 Dimer—fractional atomic coordinates[a] and isotropic temperature factors (Å^2)

Atom	x/a	y/b	z/c	U(iso)
O(1)	0.0330(2)	0.4895(2)	0.66840(8)	0.0479
O(2)	1.0867(3)	0.7024(2)	0.3927(1)	0.0638
O(3)	0.8160(2)	0.624(2)	0.40643(9)	0.0554
C(1)	0.6225(3)	0.8783(3)	0.6539(1)	0.0425
C(2)	0.5831(4)	1.0539(3)	0.6503(2)	0.0533
C(3)	0.7648(4)	0.8497(4)	0.7093(2)	0.0549
C(4)	0.6880(3)	0.8161(3)	0.5880(1)	0.0394
C(5)	0.7630(3)	0.9085(3)	0.5415(1)	0.0461
C(6)	0.8165(3)	0.8480(3)	0.4817(1)	0.0484
C(7)	0.7925(3)	0.6930(3)	0.4691(1)	0.0454
C(8)	0.7261(4)	0.5960(4)	0.5150(2)	0.0546
C(9)	0.6760(4)	0.6577(3)	0.5744(1)	0.0513
C(10)	0.4562(3)	0.7893(3)	0.6660(1)	0.0387
C(11)	0.4408(4)	0.6849(3)	0.7177(1)	0.0461
C(12)	0.2987(3)	0.5875(3)	0.7202(1)	0.0475
C(13)	0.1710(3)	0.5991(3)	0.6708(1)	0.0404
C(14)	0.1735(3)	0.7098(3)	0.6217(1)	0.0481
C(15)	0.3167(3)	0.8030(3)	0.6195(1)	0.0468
C(16)	0.9683(4)	0.6213(3)	0.3796(1)	0.0471

[a] Values in parentheses are e.s.d. (significant digits)

vertical drive goniometer[14]. The latent X-ray image is decoded by photoluminescent stimulation of the plate by a helium–neon laser and sequential recording of the fluorescent intensities of the reflections at a photomultiplier. The crystalline solids differed in their behaviour when attempts were made to recover them from benzene. It was observed that, whereas the dimeric crystal retained its crystallinity after filtration from benzene, the trimer crystals became opaque and lost their crystallinity on exposure to the atmosphere; this was confirmed by measuring the decay of a list of X-ray reflections on the four-circle diffractometer. The rate of benzene efflorescence and associated loss of crystallinity was approximately 50% per hour.

The parameter matrix was anisotropic for the non-hydrogen atoms, and the hydrogen atoms were conventionally placed after each cycle of least-squares refinement. In the trimer/solvate, the parameters of the benzene solvate molecules were refined in a separate matrix block. Crystal structure data are shown in *Tables 1* to *6*. Additional refinement details, structure factors, anisotropic temperature parameters and molecular structural bond lengths and angles may be obtained from the corresponding author or from Cambridge Crystallographic Data Centre, Cambridge, CB2 1EW, UK.

DISCUSSION

The planar rigidity of the carbonate group imposes the most significant constraints on the conformational potentialities of the cyclic diphenyl isopropylidene carbonate. It has been estimated from semi-empirical quantum conformational energy calculations on diphenylcarbonate ester[15] that the *trans–trans* conformer is more stable than the *cis–trans* conformer in the region of 4 to 8 kJ mol^{-1}, with the *cis–cis* conformer out of consideration on steric grounds. The estimated activation energy barrier to the transition of *trans–trans* to *cis–trans* conformer was 16.5 kJ mol^{-1}. In the structures reported here, the dimer is *cis–trans* and the trimer is *trans–trans* around the ring (*Figures 1* and *2*). In the X-ray crystallographic structure determination[16] of a model monomer, 4,4′-isopropylidenediphenyl carbonate ester, the conformation is *cis–trans*, which appears to throw into doubt the reliability of the calculations. If it is assumed that, the larger the ring, the more conformationally relaxed the monomer unit is, then the *trans–trans* version would appear to be the more stable conformer. However, other considerations need to be assessed, including the steric restraint to free rotation of the phenyl planes relative to the carbonate plane and the isopropylidene centre, and the bond angles at the carbonate and isopropylidene apices of the dimer and trimer molecular polygons. The carbonate and phenyl planes in both the dimeric and trimeric oligomers are rigidly planar with very small deviations from planarity (*Table 5*). In the force-field calculations and crystallographic studies of Flory *et al.*[17]

Table 3 Trimer/solvate—fractional atomic coordinates[a] and isotropic temperature factors (Å^2)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U* (iso)
O1	0.5134 (4)	−0.2401 (2)	0.2843 (2)	0.160 (5)
O2	0.4790 (3)	−0.3849 (2)	0.3112 (1)	0.093 (2)
O3	0.4002 (2)	−0.2607 (2)	0.3257 (1)	0.081 (2)
O4	0.5000 (2)	0.3123 (2)	0.1791 (1)	0.092 (2)
O5	0.5888 (2)	0.3196 (2)	0.1280 (1)	0.097 (3)
O7	0.8994 (2)	−0.3264 (2)	0.1057 (1)	0.091 (2)
O6	0.5716 (3)	0.1766 (2)	0.1611 (1)	0.123 (4)
O8	0.8077 (3)	−0.1974 (2)	0.1111 (1)	0.102 (3)
O9	0.9195 (3)	−0.1994 (2)	0.0667 (1)	0.092 (2)
C1	0.3037 (3)	0.1419 (2)	0.3121 (1)	0.071 (3)
C2	0.8637 (4)	0.2032 (3)	0.0224 (1)	0.090 (4)
C3	0.7932 (3)	−0.5561 (3)	0.2500 (1)	0.067 (3)
C4	0.4694 (4)	−0.2892 (3)	0.3056 (2)	0.088 (4)
C5	0.5535 (4)	0.2606 (3)	0.1566 (1)	0.081 (4)
C6	0.8676 (5)	−0.2365 (3)	0.0960 (2)	0.091 (4)
C7	0.3248 (4)	0.1874 (3)	0.3601 (1)	0.092 (5)
C8	0.2027 (4)	0.1594 (3)	0.2927 (2)	0.093 (4)
C9	0.9511 (5)	0.2656 (4)	0.0387 (2)	0.108 (5)
C10	0.8340 (6)	0.2169 (4)	−0.0297 (2)	0.114 (7)
C11	0.8782 (4)	−0.5599 (3)	0.2885 (2)	0.101 (4)
C12	0.7671 (4)	−0.6609 (3)	0.2357 (2)	0.092 (4)
C13	0.3611 (3)	0.1872 (3)	0.2781 (1)	0.067 (3)
C14	0.4087 (3)	0.2749 (3)	0.2854 (1)	0.074 (3)
C15	0.4556 (4)	0.3140 (3)	0.2525 (1)	0.077 (4)
C16	0.4548 (3)	0.2662 (3)	0.2121 (1)	0.071 (3)
C17	0.4080 (4)	0.1801 (3)	0.2030 (1)	0.077 (4)
C18	0.3627 (4)	0.1420 (3)	0.2362 (1)	0.080 (4)
C19	0.6549 (4)	0.2856 (3)	0.1025 (1)	0.081 (4)
C20	0.6478 (5)	0.3173 (3)	0.0582 (2)	0.094 (5)
C21	0.7121 (5)	0.2909 (3)	0.0318 (2)	0.099 (5)
C22	0.7889 (4)	0.2342 (3)	0.0496 (1)	0.084 (4)
C23	0.7937 (4)	0.2058 (3)	0.0952 (1)	0.090 (5)
C24	0.7291 (4)	0.2299 (3)	0.1218 (1)	0.085 (4)
C25	0.8832 (4)	0.0942 (3)	0.0321 (1)	0.084 (4)
C26	0.9666 (4)	0.0589 (3)	0.0534 (2)	0.088 (4)
C27	0.9769 (4)	−0.0389 (4)	0.0647 (1)	0.096 (4)
C28	0.9040 (5)	−0.1002 (3)	0.0543 (1)	0.085 (5)
C29	0.8227 (5)	−0.0698 (3)	0.0314 (2)	0.095 (5)
C30	0.8118 (5)	0.0283 (4)	0.0208 (1)	0.096 (5)
C31	0.8663 (4)	−0.3792 (3)	0.1411 (1)	0.086 (3)
C32	0.0398 (4)	−0.4728 (3)	0.1315 (2)	0.074 (4)
C33	0.8168 (4)	−0.5303 (3)	0.1664 (2)	0.086 (4)
C34	0.8187 (3)	−0.4957 (3)	0.2108 (1)	0.077 (3)
C35	0.8452 (4)	−0.3989 (3)	0.2186 (1)	0.077 (4)
C36	0.8688 (4)	−0.3405 (3)	0.1844 (2)	0.080 (4)
C37	0.7095 (4)	−0.5105 (3)	0.2666 (1)	0.080 (4)
C38	0.6418 (4)	−0.4642 (3)	0.2356 (1)	0.077 (4)
C39	0.5646 (4)	−0.4234 (3)	0.2492 (2)	0.080 (4)
C40	0.5544 (4)	−0.4288 (3)	0.2948 (2)	0.080 (4)
C41	0.6173 (5)	−0.4785 (3)	0.3257 (2)	0.081 (5)
C42	0.6919 (4)	−0.5200 (3)	0.3116 (1)	0.085 (5)
C43	0.3771 (4)	−0.1610 (3)	0.3224 (1)	0.078 (4)
C44	0.4421 (4)	−0.0913 (3)	0.3373 (2)	0.080 (4)
C45	0.4140 (4)	0.0054 (3)	0.3339 (2)	0.094 (4)
C46	0.3266 (4)	0.0336 (3)	0.3162 (1)	0.075 (3)
C47	0.2636 (4)	−0.0398 (3)	0.3027 (1)	0.089 (4)
C48	0.2897 (4)	−0.1364 (3)	0.3054 (1)	0.092 (4)
C49	0.4169 (7)	0.6083 (6)	0.0881 (3)	0.123 (7)
C50	0.4864 (10)	0.5434 (5)	0.0934 (3)	0.157 (10)
C51	0.5718 (8)	0.5708 (7)	0.1091 (3)	0.112 (7)
C52	0.5938 (6)	0.6632 (7)	0.1186 (2)	0.146 (6)
C53	0.5232 (9)	0.7304 (5)	0.1123 (3)	0.163 (11)
C54	0.4326 (7)	0.6995 (6)	0.0987 (3)	0.151 (7)
C55	0.2103 (7)	0.0143 (10)	0.1403 (5)	0.150 (7)
C57	0.1474 (9)	0.4296 (5)	0.3433 (4)	0.148 (9)
C58	0.1201 (8)	0.4689 (7)	0.3792 (6)	0.145 (9)
C59	0.2426 (11)	0.0564 (8)	0.1018 (4)	0.162 (10)
C60	0.3286 (13)	0.0299 (12)	0.0928 (3)	0.157 (12)
C61	0.5598 (19)	0.0516 (19)	0.310 (8)	0.149 (15)
C62	0.5578 (14)	−0.0484 (16)	0.0345 (7)	0.185 (16)
C63	0.5081 (21)	0.0903 (14)	0.0030 (12)	0.157 (16)
C64	0.7212 (14)	0.6073 (14)	0.0080 (4)	0.176 (13)
C65	0.2227 (17)	0.3902 (14)	0.0654 (5)	0.200 (18)
C66	0.7123 (19)	0.6706 (15)	−0.0765 (4)	0.229 (22)
C67	0.6480 (12)	0.6987 (8)	−0.0516 (5)	0.187 (15)
C68	0.6532 (12)	0.6636 (10)	−0.0097 (4)	0.189 (13)
C69	0.7848 (17)	0.5719 (11)	−0.0197 (10)	0.240 (20)

[a] Values in parentheses are e.s.d. (significant digits)

Table 4 Bond angles[a] (deg) for O–C–O and Φ–C–Φ

	O–C–O	Φ–C–O
Theoretical[14]	105.8	109.8
Diphenyl carbonate[16]	108	
Model monomer[15]	113	120
Dimer	109.6 (2)	107.4 (2)
Trimer	108.1 (5)	108.4 (5)
	108.3 (5)	107.4 (5)
	106.6 (5)	108.6 (5)

[a] Values in parentheses are e.s.d. (significant digits)

Table 5 Interplanar torsional angles (ϕ) and interplanar dihedral angles (θ)

	$\phi, \phi / \theta$ (deg)	
	Φ–CO$_3$–Φ	Φ–C–Φ
Theoretical[14]	44, 44 / 88	48, 48 / –
Diphenyl carbonate[16]	45, 45 / 90	
Diphenylisopropylidene[16]		46, 46 / –
Dimer	77.9, 47.3 / 73.3	64.7, 38.4 / 73.3
Trimer	52.1, 55.8 / 91.4	40.9, 62.9 / 85.6
	60.9, 48.9 / 76.4	41.9, 63.7 / 85.6
	37.7, 40.2 / 70.3	53.5, 32.5 / 63.5

Table 6 Root mean square deviation from planarity of the phenyl planes and carbonate planes. Deviation $=(\Sigma z^2/n)^{1/2}$, where z is the vertical displacement of the atom above or below the best plane, summed over the n atoms constituting the plane

Plane	Dimer (Å)	Trimer (Å)
CO$_3$	0.005	0.007, 0.010, 0.004
Φ (phenyl)	0.025	0.004, 0.009, 0.014
	0.016	0.003, 0.020, 0.006

on the *trans–trans* conformer of diphenyl carbonate ester, the phenyl planes are rotated clockwise and anticlockwise about the carbonate plane by 45°, generating a phenyl interplanar dihedral angle of 90°. In the X-ray crystallographic study[16] of the model monomer, the rotations are 88.6° and 81°, so that the phenyl planes are almost at right angles to the carbonate plane. In phenyl benzoate the phenyl plane is rotated 61.5° to the carboxylate group[18]. Our results show that the torsions deviate significantly from the theoretically estimated values and the measured model monomer values, and if we take the model monomer conformation as the more relaxed form, then there are grounds for attributing some of the cyclic strain to the restricted rotation of the phenyl planes about

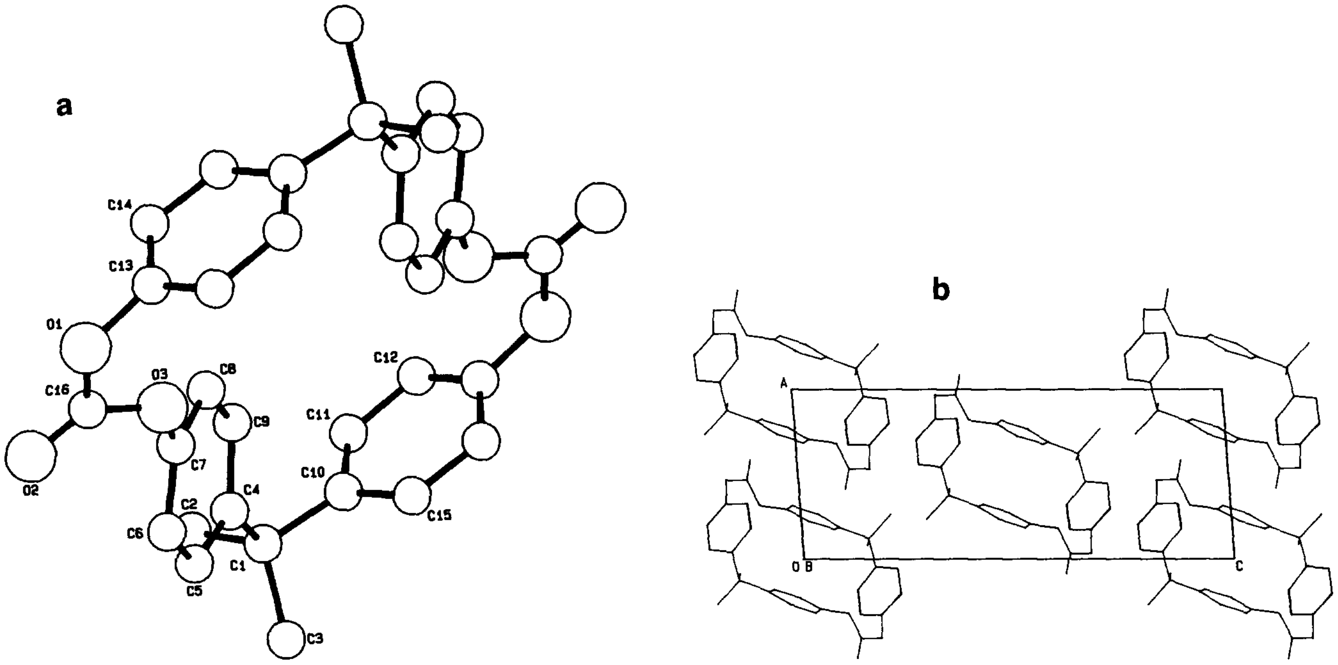

Figure 1 (a) Structure and conformation of the diphenyl isopropylidene carbonate dimer, (b) Crystal structure arrangement of the dimer as seen down the unique stacking *b* axis

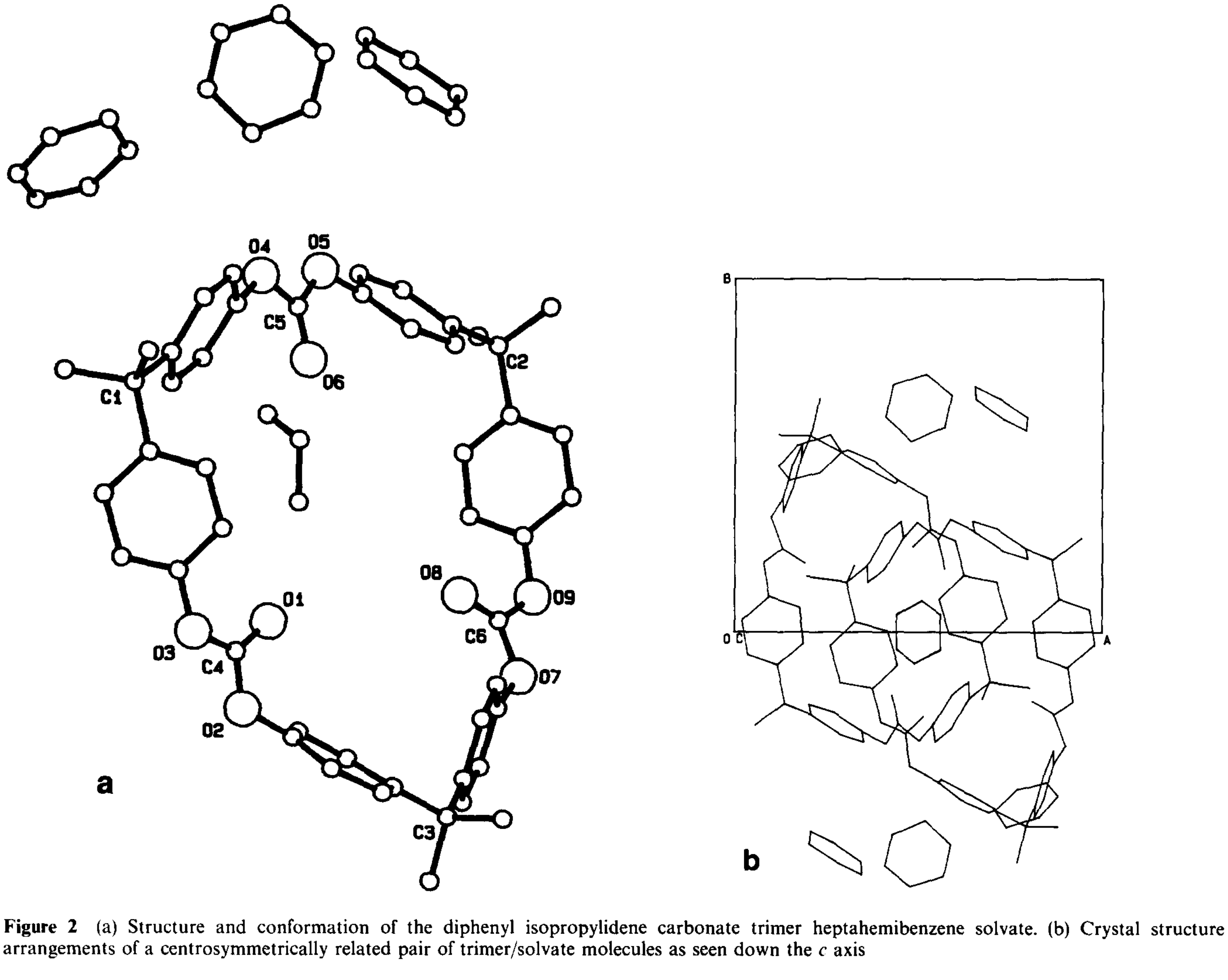

Figure 2 (a) Structure and conformation of the diphenyl isopropylidene carbonate trimer heptahemibenzene solvate. (b) Crystal structure arrangements of a centrosymmetrically related pair of trimer/solvate molecules as seen down the *c* axis

the carbonate planes (*Table 4*). The estimated values for the barrier to the synchronous free rotation of the phenyl planes about the carbonate plane are small (16 kJ mol^{-1}), so that this factor will not be the principal contributor to the conformational strain energies of the cyclic oligomers.

The phenyl rotations about the isopropylidene centre are estimated[17] to be about 46°, thus relieving the potential *ortho*-hydrogen repulsion between the two phenyl groups. The effect is to establish a dihedral angle between the phenyl planes attached to the isopropylidene centre of approximately 90°. This conformation is similarly observed, with variations, in our structural analyses (*Table 4*). The estimated values for the barrrier to free synchronous rotations in this case are ca. 38 to 42 kJ mol^{-1}.

However, the most important contributor to the steric strain energy in these molecular polygons should be the distortions at the turning points of the molecular polygons, namely, the carbonate and isopropylidene centres, expressed in the diphenyl ester O–C–O bond angles and phenyl–C–phenyl bond angles. In the dimer and trimer cyclic oligomers the O–C–O bond angles are consistently larger, and the Φ–C–Φ bond angles consistently smaller, than the estimated values (*Table 3*). Thus the strain potential is minimized by the carbonate centres opening up the O–C–O angle; significantly, this opening is greater for the smaller ring, enforcing a small contraction of the Φ–C–Φ bond angles from the desirable tetrahedral bond angle at the isopropylidene centre.

On polymerization, linear esterification replaces ring esterification so that the enthalpy contribution to the free energy of the process comprises a relatively small release of steric strain energy. The fact that the molten-state polymerization is so facile indicates the unusual situation where the ring oligomers are less structurally ordered than the linear polymers. At the temperatures of polymerization, 250 to 300°C, the thermal relaxation of the linear chains provides for a diminished system entropy and hence an entropically driven polymerization process.

REFERENCES

1 Schnell, H. and Bottenbruch, L. Ger. Pat. 1229101, 1966

2 Schnell, H. and Bottenbruch, L. Belg. Pat. 620, 1962

3 Schnell, H. and Bottenbruch, L. *Makromol. Chem.* 1962, **57**, 1

4 Prochaska, R. J. US Pat. 3247214, 1966

5 Moody, L. S. US Pat. 3155683, 1964

6 Brunell, D. J., Boden, E. P. and Shannon, T. G. *J. Am. Chem. Soc.* 1990, **112**, 2399

7 Evans, T. L. and Carpenter, J. C. *Polym. Prepr.* 1990, **31**(1), 18

8 Stewart, K. R. *Polym. Prepr.* 1989, **30**(2), 575

9 Evans, T. L., Berman, C. B., Carpenter, J. C., Choi, D. Y. and William, D. A. *Polym. Prepr.* 1989, **30**(2), 573

10 Keul, H., Deisel, F. and Hocker, H. *Makromol. Chem., Rapid Commun.* 1991, **12**, 133

11 Schutt, W., Herdtwerk, E., Hahn, F. and Kreissel, F. R. *J. Organomet. Chem.* 1993, **443**, C33

12 Miyahara, J. and Kato, H. *Japan. Soc. Appl. Phys.* 1984, **53**, 884

13 Takahashi, K., Miyahara, J. and Shibahara, Y. *J. Electrochem. Soc.* 1985, **132**, 1492

14 Arndt, U. W. and Wonacott, A. J. 'The Rotation Method in Crystallography', North-Holland, Amsterdam, 1977

15 Bicerano, J. and Clark, H. A. *Macromolecules* 1988, **21**, 585

16 Dulmage, W. L., Light, W. A., Marino, S. J., Salzberg, C. D., Smith, D. L. and Staudenmayer, W. J. *J. Appl. Phys.* 1978, **49**(11), 5543

17 Erman, B., Marvin, D. C., Irvine, P. A. and Flory, P. J. *Macromolecules* 1982, **15**, 664

18 Adams, J. M. and Morsi, S. E. *Acta. Crystallogr. (B)* 1976, **32**, 1345