

The Crystal Structures of Two Cyclic Polyurethane Oligomers, Cyclobisurethane and Cyclotetraurethane

BY JOHN J. BERES* AND LEROY E. ALEXANDER†

Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213, U.S.A.

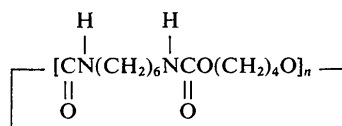
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The crystal structures of cyclobisurethane, $C_{12}H_{22}N_2O_4$, and cyclotetraurethane, $C_{24}H_{44}N_4O_8$, have been determined by single-crystal X-ray diffraction analysis. Intensities were collected with an automated XRD-5 diffractometer using $Cu K\alpha$ radiation. Cyclobisurethane crystallizes in the monoclinic space group $C2/c$, with $a=17.330$ (2), $b=8.866$ (1), $c=17.944$ (3) Å, $\beta=91.77$ (1)°, and $Z=8$. Cyclotetraurethane crystallizes in monoclinic space group $P2_1/c$, with $a=16.463$ (4), $b=9.929$ (2), $c=9.464$ (2) Å, $\beta=110.19$ (3)°, and $Z=2$. The structures were solved by direct methods and refined by full-matrix least squares to final R values of 0.056 and 0.055 respectively. The molecules of both structures are linked two-dimensionally into sheets by $C=O \cdots H-N$ hydrogen bonds. However, in cyclobisurethane all urethane groups participate in hydrogen bonding, whereas in cyclotetraurethane one carbonyl oxygen accepts two hydrogens, one from each of the crystallographically nonequivalent nitrogens. The carbonyl oxygen not participating in hydrogen bonding appears to interact weakly with a methylene hydrogen of a molecule in an adjoining layer. Cyclobisurethane furnishes conformational models for regular adjacent reentry chain folding in the corresponding polyurethane system. The hydrogen-bonding patterns from both structures provide possible models for hydrogen bonding within hard segment domains of segmented urethane elastomers. The structures of these two polyurethane oligomers are compared with those of the analogous cyclic polyhexamethylene adipamide oligomers.

Introduction

The present investigation concludes a series of X-ray crystallographic studies of model compounds of linear polymers. The three previous studies, which were concerned with cyclic polyamide oligomers (Northolt & Alexander, 1968, 1971; Northolt, 1970), sought to elucidate conformational features having possible or probable applicability to the corresponding polymer

systems, in particular the dimensions of the amide groups, hydrogen-bonding modes, and chain-fold models (Alexander, 1972). In the present investigation these objectives are extended to the analogous polyurethanes through structural studies of the cyclic monomer (cyclobisurethane) and dimer (cyclotetraurethane),



where $n=1$ and 2 respectively.

* From a thesis submitted in partial fulfillment of the requirements for the Ph.D. degree. Present address: Army Materials and Mechanics Research Center, Watertown, Massachusetts 02172.

† To whom correspondence should be addressed.

Table 1. Crystal data

	Dimer	Monomer
Space group	$P2_1/c$	$C2/c$
a (Å)	16.463 (4)	17.330 (2)
b (Å)	9.929 (2)	8.866 (1)
c (Å)	9.464 (2)	17.944 (3)
β (°)	110.19 (3)	91.77 (1)
M	516.64	258.32
$F(000)$	560	280
D_m ($g\ cm^{-3}$)*	1.178	1.252
D_x ($g\ cm^{-3}$)	1.182	1.245
Z	2	8
μ for $Cu K\alpha$ (cm^{-1})	7.4	7.8
m.p. (°C)	198	164
Crystal dimensions (mm)	0.275 × 0.275 × 0.045	0.27 × 0.33 × 0.41
Reflections observed	1334	1904
Reflections unobserved†	152	128
$(\sin \theta)/\lambda$ limit (Å ⁻¹)	0.4959	0.5600

* Determined by the flotation method.

† $I \leq 1.5\sigma_I$.

Experimental

Historically, these oligomers were originally isolated from the addition products of 1,4-butanediol and hexamethylene diisocyanate by Zahn & Dominik (1961*a*). The crystalline oligomers for the present work were extracted from polyurethane chips with dimethylformamide, purified by gel filtration, and supplied to us by P. Kusch and H. Zahn, Technischen Hochschule, Aachen, Germany.

A suitable plate-like crystal of the cyclic dimer was mounted with a diagonal (c^*) parallel to the goniometer axis. The space group and initial values of the unit-cell dimensions were determined photographically at room temperature with nickel-filtered Cu $K\alpha$ radiation. From the monoclinic symmetry and systematic absences the space group was uniquely determined as $P2_1/c$ (C_{2h}^2). The diffractometrically measured 2θ values of 21 reflections were refined by least squares.† The crystal data appear in Table 1.

Clear, colorless crystals of the monomer, resembling truncated pyramids fused to rhombohedral bases, were grown by slow evaporation of saturated methanol solutions of the compound as received. With a crystal mounted parallel to its c^* axis, X-ray photography at 22°C with Cu $K\alpha$ radiation showed the symmetry to be monoclinic and the systematic absences to be hkl with $h+k=2n+1$ and $h0l$ with $l=2n+1$. The absence of a piezoelectric signal favored the centrosymmetric space group $C2/c$ (C_{2h}^2) over the noncentrosymmetric, Cc (C_s^4), both of which disagree with the orthorhombic space group chosen by Haas (1961). The unit-cell constants, refined by least squares from 16 diffractometrically measured 2θ values, along with other crystal data, are given in Table 1.

Reflection intensities from each crystal were measured by the $\theta-2\theta$ scan technique using a General Electric automated diffractometer with Eulerian geometry and pulse-height discrimination. The procedure followed for data gathering and processing has been described (Northolt & Alexander, 1968). No correction for absorption was made. For the monomer the collection and processing were controlled by a PDP-8/e computer interfaced to the diffractometer.

Structure determination and refinement

Both structures were solved by direct methods. Refinement was accomplished by standard Fourier and full-matrix least-squares techniques. In the least-squares refinement of atomic parameters the function minimized was $\sum w(F_o - F_c)^2$, the weight w being defined by $1/\sigma_{F_o}^2$. For the dimer the atomic scattering factors employed were those given in *International Tables for X-ray Crystallography* (1962) for neutral

† Unless otherwise noted, the computer programs used were from the X-RAY System of Crystallographic Programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

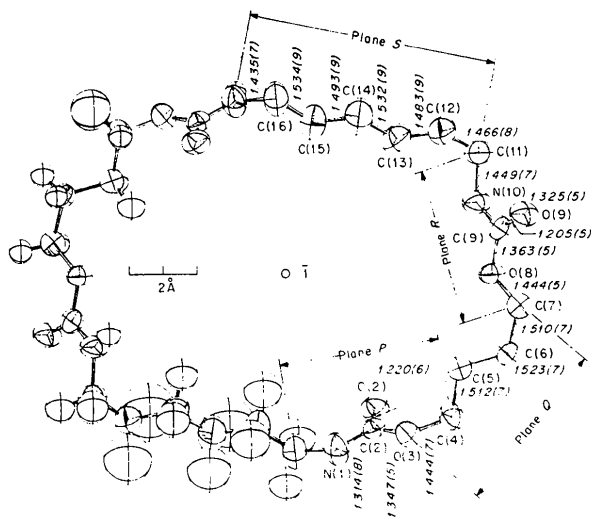


Fig. 1. Parallel projection of cyclotetraurethane onto the least-squares molecular plane T . Bond lengths between non-hydrogen atoms in Å with e.s.d.'s in parentheses. Thermal ellipsoids enclose 50% probability (Johnson, 1970).

oxygen, nitrogen, and carbon; for the monomer the scattering factors for these atoms were generated Hartree-Fock wave functions (Stewart *et al.*, 1972). For both structures the hydrogen scattering factors were those of Stewart, Davidson & Simpson (1965). All hydrogen atoms were located by difference Fourier syntheses.

All observed reflections were included in the least-squares refinement along with those unobserved reflections for which $F_c > F_o$. No corrections were made for primary or secondary extinction because there was no conspicuous disagreement between observed and calculated structure factors for the strong reflections of low Miller indices.* The average final shifts per error in the parameter refinements were 0.09 and 0.171 for the dimer and monomer respectively, and the maximum shift per error was 0.8 for both compounds.

The final agreement indices, based only on observed reflections, are for the dimer and monomer respectively:

$$R = \frac{[\sum |F_o| - |F_c|]}{[\sum |F_o|]} = 0.055 \text{ and } 0.056,$$

$$wR = \left\{ \frac{\sum [w(F_o - F_c)]^2}{\sum (wF_o)^2} \right\}^{1/2} = 0.042 \text{ and } 0.058,$$

$$S = \left\{ \frac{\sum [w(F_o - F_c)]^2}{(m-n)} \right\}^{1/2} = 1.4 \text{ and } 1.9.$$

In the above expressions m is the number of reflections included in the least-squares refinement ($m = 1366$ and 1928 for the dimer and monomer respectively), and n is the number of variables refined ($n = 251$ for both structures). The significant departure of S from unity

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31684 (23 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

may be assumed to result from an underestimation of the weights employed in the least-squares refinement or from systematic errors in the data or structural model (Brown, 1969).

Table 2. *Dimer: atomic coordinates and temperature factor coefficients*

E.s.d.'s are in parentheses; x, y, z are in fractions of the unit-cell dimensions; U_{ij} are in $\text{\AA}^2 \times 10^4$.

	x	y	z
O(2)	0.2199 (2)	0.1792 (3)	0.7955 (3)
O(3)	0.3088 (2)	0.3096 (3)	0.9833 (3)
O(8)	0.3769 (1)	0.5263 (2)	0.5264 (3)
O(9)	0.4139 (2)	0.7166 (3)	0.4307 (3)
N(1)	0.1834 (3)	0.2446 (5)	0.9920 (5)
N(10)	0.3074 (3)	0.5781 (4)	0.2895 (4)
C(2)	0.2356 (3)	0.2401 (4)	0.9138 (5)
C(4)	0.3767 (3)	0.3083 (5)	0.9193 (6)
C(5)	0.3708 (3)	0.4283 (4)	0.8179 (5)
C(6)	0.4496 (3)	0.4317 (4)	0.7684 (5)
C(7)	0.4487 (3)	0.5475 (5)	0.6645 (5)
C(9)	0.3692 (3)	0.6178 (5)	0.4151 (5)
C(11)	0.2853 (3)	0.6545 (6)	0.1509 (6)
C(12)	0.2146 (3)	0.7507 (6)	0.1303 (7)
C(13)	0.1301 (4)	0.6876 (7)	0.1137 (8)
C(14)	0.0567 (4)	0.7880 (7)	0.0961 (9)
C(15)	-0.0287 (4)	0.7218 (7)	0.0706 (9)
C(16)	-0.1019 (3)	0.8241 (7)	0.0482 (7)

Description of the structures

Dimer, cyclotetraurethane

Fig. 1 displays the molecule along the normal to the least-squares molecular plane. The right-hand side shows the numbering scheme for the nonhydrogen atoms, while the left shows all atoms of that half of the molecule. The hydrogens (unlabeled in Fig. 1) are designated by three digits, the first two of which identify the parent nonhydrogen atom while the last differentiates two hydrogens bonded to the same carbon atom (see Table 2).

The positional and thermal parameters for the atoms of the parametral molecule are given in Table 2. The thermal parameters labeled U have the form of mean-square displacements. The estimated standard deviations (σ) given in parentheses are those derived from the least-squares refinement, which are known to be unrealistically small (Stewart & Hall, 1971).

The thermal parameters for hydrogen atoms 041, 121, 122, and 142 correspond to anharmonic vibrations, and they are much larger than those of the analogous cyclic amide (Northolt, 1970). For hydrogen atoms the electron density is 0.3 e \AA^{-3} when $B=14$ (Northolt & Alexander, 1968), or, in terms of mean-square displacements, $U=0.1773 \text{ \AA}^2$. The carbon atoms

Table 2 (cont.)

$$T = \exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(2)	729 (20)	742 (21)	442 (17)	170 (16)	207 (16)	-1 (16)
O(3)	637 (19)	636 (20)	591 (18)	-71 (17)	264 (16)	-1 (15)
O(8)	564 (18)	458 (18)	425 (17)	-66 (14)	63 (15)	83 (14)
O(9)	739 (20)	453 (19)	649 (20)	-173 (17)	180 (15)	67 (15)
N(1)	637 (30)	1074 (37)	586 (31)	-105 (25)	306 (28)	-227 (29)
N(10)	672 (27)	616 (30)	581 (29)	-215 (25)	42 (22)	166 (25)
C(2)	545 (30)	582 (32)	514 (30)	174 (26)	197 (29)	171 (26)
C(4)	664 (36)	558 (36)	790 (39)	-43 (29)	339 (32)	50 (34)
C(5)	533 (29)	458 (31)	496 (29)	2 (25)	166 (25)	-30 (26)
C(6)	482 (28)	497 (31)	472 (28)	-3 (24)	134 (24)	-28 (26)
C(7)	558 (32)	464 (34)	542 (33)	-24 (26)	190 (28)	-43 (29)
C(9)	491 (29)	463 (30)	540 (32)	58 (24)	179 (26)	-12 (28)
C(11)	688 (38)	757 (40)	606 (37)	-88 (31)	105 (30)	184 (33)
C(12)	678 (37)	916 (43)	1054 (45)	75 (34)	262 (31)	369 (38)
C(13)	742 (41)	926 (49)	1103 (53)	178 (39)	192 (37)	346 (47)
C(14)	770 (42)	1198 (56)	1346 (58)	55 (41)	388 (40)	128 (50)
C(15)	630 (39)	1176 (56)	1120 (56)	15 (38)	271 (36)	65 (51)
C(16)	602 (37)	1171 (49)	866 (44)	-97 (36)	325 (33)	-135 (41)

$$T = \exp (-8\pi^2 U \sin^2 \theta / \lambda^2).$$

	x	y	z	$U (\text{\AA}^2 \times 10^2)$	x	y	z	$U (\text{\AA}^2 \times 10^2)$	
H(011)	0.197 (2)	0.275 (4)	1.065 (4)	3.9 (1.6)	H(111)	0.272 (2)	0.588 (4)	0.068 (4)	9.0 (1.7)
H(101)	0.282 (2)	0.505 (4)	0.286 (4)	5.4 (1.5)	H(112)	0.340 (2)	0.688 (4)	0.137 (4)	8.1 (1.4)
H(041)	0.446 (3)	0.313 (5)	1.015 (5)	14.5 (1.9)	H(121)	0.195 (3)	0.807 (6)	0.018 (7)	21.5 (2.8)
H(042)	0.367 (2)	0.241 (3)	0.861 (4)	5.1 (1.5)	H(122)	0.191 (4)	0.844 (8)	0.216 (7)	29.5 (3.6)
H(051)	0.318 (2)	0.423 (3)	0.719 (4)	7.1 (1.2)	H(131)	0.121 (3)	0.621 (4)	0.037 (5)	10.7 (2.2)
H(052)	0.369 (2)	0.510 (3)	0.871 (3)	5.1 (1.2)	H(132)	0.135 (2)	0.632 (4)	0.214 (4)	9.4 (1.5)
H(061)	0.503 (2)	0.451 (3)	0.862 (3)	5.0 (1.0)	H(141)	0.044 (3)	0.845 (6)	0.001 (6)	17.7 (3.1)
H(062)	0.454 (2)	0.343 (3)	0.714 (3)	4.3 (1.0)	H(142)	0.040 (4)	0.874 (7)	0.187 (7)	24.8 (3.2)
H(071)	0.502 (2)	0.553 (3)	0.639 (3)	5.0 (1.1)	H(151)	-0.029 (3)	0.664 (6)	-0.015 (6)	14.8 (2.8)
H(072)	0.443 (2)	0.617 (3)	0.709 (4)	4.3 (1.4)	H(152)	-0.018 (3)	0.681 (5)	0.182 (5)	13.5 (2.2)
					H(161)	-0.101 (3)	0.888 (4)	-0.031 (5)	10.4 (1.9)
					H(162)	-0.092 (3)	0.894 (4)	0.148 (5)	12.3 (1.8)

to which these hydrogens are bonded also have large thermal parameters, and the hydrogen atoms on one side of the molecular plane are more affected than those on the other side. A kind of spatial disordering may be occurring, which, under the limitations of this present study, cannot be differentiated from true thermal motion.

The least-squares molecular plane, upon which the parallel projection of Fig. 1 is based, is described by the equation

$$-1.17684x + 8.51949y + 4.75136z = 6.63542,$$

which was calculated from the 32 atoms of the ring. Applying the χ^2 distribution test (Stout & Jensen, 1968), one calculates that the probability of the 32 ring atoms being coplanar is less than 1%. By this same test, none of the elements of the molecule shown in Fig. 1 is rigorously planar. However, for purposes of discussion, it is convenient to assume that they approximate planes. Element *P* makes an angle of approximately 60° with the molecular plane *T*. Elements *P* and *Q* are nearly mutually perpendicular, which can also be seen from the torsion (internal rotation) angle C(2)-O(3)-C(4)-C(5) in Table 3. All other torsion angles are antiperiplanar, synperiplanar, or synclinal (Klyne & Prelog, 1960) except angles C(15)*-C(16)*-N(1)-C(2) and C(9)-N(10)-C(11)-C(12), which are anticlinal. An asterisk denotes an atom related to an atom of the same number by a center of symmetry.

Bond lengths between the C, N, and O atoms are given in Fig. 1. In the hexamethylene segment of the dimer, where it has been noted that some anomalous thermal parameters are found, bonds C(11)-C(12), C(12)-C(13), and C(14)-C(15) are shorter than the generally accepted value for C(sp^3)-C(sp^3) bonds,

1.531 Å (Lide, 1962). Nearly all other chemically equivalent bond lengths involving two nonhydrogen atoms agree with each other to within 2σ . The notable exceptions are the carbonyl C=O and ether C-O bonds, which agree with each other to within 3σ .

Table 3. Torsion (internal rotation) angles in degrees

Estimated standard deviations after Stanford & Waser (1972) are in parentheses.

Approximate description of torsion angles (Klyne & Prelog, 1960):

$0^\circ \pm 30^\circ$	\pm synperiplanar (\pm sp)
$+60^\circ \pm 30^\circ$	+ synclinal (+ sc)
$+120^\circ \pm 30^\circ$	+ anticlinal (+ ac)
$180^\circ \pm 30^\circ$	\pm antiperiplanar (\pm ap)
$-120^\circ \pm 30^\circ$	- anticlinal (- ac)
$-60^\circ \pm 30^\circ$	- synclinal (- sc)

	Dimer	Monomer
C(15)*C(16)*N(1) C(2)	-120.0 (5)	-150.2 (3)
C(16)*N(1) C(2) O(2)	1.7 (7)	-0.8 (5)
C(16)*N(1) C(2) O(3)	-177.2 (4)	178.5 (3)
N(1) C(2) O(3) C(4)	175.7 (3)	-170.5 (3)
O(2) C(2) O(3) C(4)	-3.2 (6)	8.8 (4)
C(2) O(3) C(4) C(5)	94.6 (4)	77.2 (3)
O(3) C(4) C(5) C(6)	173.2 (3)	66.3 (4)
C(4) C(5) C(6) C(7)	179.2 (4)	-168.8 (3)
C(5) C(6) C(7) O(8)	-65.6 (4)	63.6 (4)
C(6) C(7) O(8) C(9)	-176.3 (3)	78.7 (4)
C(7) O(8) C(9) O(9)	-5.5 (5)	-4.0 (4)
C(7) O(8) C(9) N(10)	172.8 (3)	176.1 (3)
O(8) C(9) N(10)C(11)	-179.1 (4)	175.6 (3)
O(9) C(9) N(10)C(11)	-0.9 (7)	-4.3 (5)
C(9) N(10) C(11)C(12)	-92.9 (5)	-138.2 (3)
N(10) C(11) C(12)C(13)	-64.7 (6)	62.0 (5)
C(11) C(12) C(13)C(14)	178.5 (5)	60.7 (5)
C(12) C(13) C(14)C(15)	176.6 (5)	165.1 (3)
C(13) C(14) C(15)C(16)	-178.1 (5)	64.1 (4)
C(14) C(15) C(16)N(1)*	173.7 (5)	61.1 (4)

* Atoms generated in dimer by symmetry center at $(0, \frac{1}{2}, \frac{1}{2})$

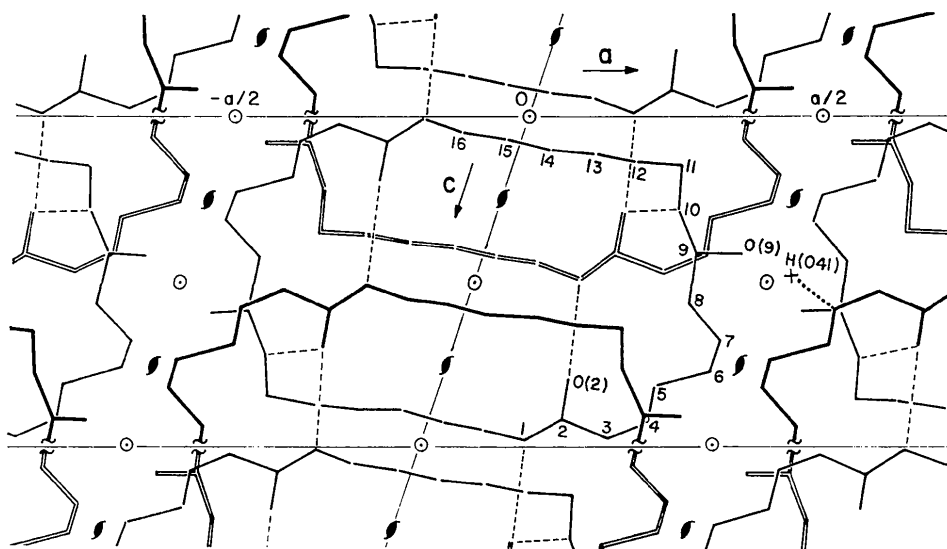


Fig. 2. Schematic parallel projection of crystal structure of cyclotetraurethane as viewed along *b*. Circles represent centers of symmetry, dashed lines hydrogen bonds.

An examination of the numerous intramolecular contacts and near contacts involving 1, 4 or greater

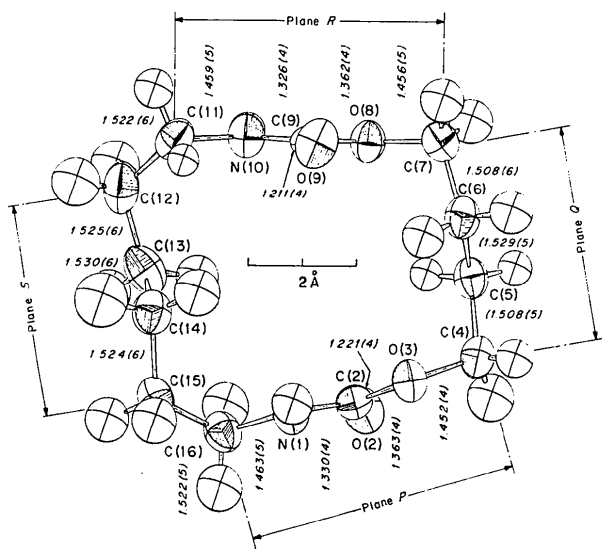


Fig. 3. Parallel projection of cyclobisurethane onto the least-squares molecular plane *T*. Bond lengths between non-hydrogen atoms in Å with e.s.d.'s in parentheses. Thermal ellipsoids enclose 50% probability (Johnson, 1970).

interactions less than 4Å shows the ring to be very open, with no transannular contacts. Contacts are especially close near the regions where chain bending occurs, that is, primarily between urethane groups and the polymethylene elements. These contacts are not

Table 4. Monomer: atomic coordinates and temperature factor coefficients

E.s.d.'s are in parentheses; *x, y, z* are in fractions of the unit-cell dimensions; U_{ij} are in $\text{Å}^2 \times 10^4$.

	<i>x</i>	<i>y</i>	<i>z</i>
O(2)	0.3701 (1)	0.8249 (3)	0.2342 (1)
O(3)	0.4053 (1)	0.8034 (3)	0.1138 (1)
O(8)	0.2794 (1)	0.3642 (3)	0.1210 (1)
O(9)	0.2308 (1)	0.4670 (3)	0.0139 (1)
N(1)	0.2999 (2)	0.9332 (4)	0.1392 (2)
N(10)	0.1589 (2)	0.4442 (3)	0.1166 (2)
C(2)	0.3585 (2)	0.8533 (4)	0.1683 (2)
C(4)	0.4636 (2)	0.6953 (4)	0.1385 (2)
C(5)	0.4286 (2)	0.5410 (4)	0.1482 (2)
C(6)	0.3993 (2)	0.4725 (4)	0.0744 (2)
C(7)	0.3506 (2)	0.3330 (5)	0.0827 (2)
C(9)	0.2224 (2)	0.4293 (4)	0.0780 (2)
C(11)	0.0899 (2)	0.5200 (5)	0.0867 (2)
C(12)	0.0553 (2)	0.6198 (5)	0.1461 (3)
C(13)	0.1073 (3)	0.7474 (5)	0.1748 (2)
C(14)	0.1295 (2)	0.8587 (5)	0.1140 (2)
C(15)	0.1635 (2)	1.0073 (5)	0.1424 (2)
C(16)	0.2401 (2)	0.9966 (5)	0.1857 (2)

Table 4 (cont.)

$$T = \exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(2)	647 (16)	672 (17)	295 (12)	138 (13)	-43 (11)	-20 (11)
O(3)	436 (13)	523 (15)	376 (12)	45 (11)	52 (10)	45 (11)
O(8)	407 (13)	510 (14)	454 (13)	28 (11)	9 (10)	83 (11)
O(9)	567 (16)	846 (20)	296 (13)	-7 (14)	-6 (11)	89 (13)
N(1)	466 (17)	586 (19)	354 (16)	94 (15)	4 (13)	32 (14)
N(10)	459 (17)	492 (18)	407 (17)	47 (14)	15 (13)	124 (14)
C(2)	429 (19)	398 (19)	401 (19)	-41 (16)	24 (15)	-21 (15)
C(4)	381 (19)	545 (23)	464 (20)	27 (17)	9 (16)	-5 (18)
C(5)	441 (19)	504 (22)	370 (18)	66 (17)	-14 (16)	38 (16)
C(6)	454 (20)	586 (24)	390 (19)	0 (18)	68 (16)	-9 (17)
C(7)	478 (22)	498 (24)	659 (26)	81 (19)	37 (19)	-49 (20)
C(9)	437 (19)	363 (18)	406 (19)	-57 (15)	-37 (15)	-26 (15)
C(11)	401 (20)	550 (24)	578 (23)	-44 (18)	-90 (17)	82 (20)
C(12)	440 (23)	730 (30)	803 (30)	131 (22)	146 (21)	219 (25)
C(13)	741 (27)	575 (25)	431 (21)	167 (22)	77 (19)	47 (18)
C(14)	539 (22)	604 (24)	430 (20)	29 (19)	43 (17)	1 (19)
C(15)	512 (21)	563 (23)	482 (21)	119 (19)	14 (17)	-40 (19)
C(16)	522 (21)	536 (23)	413 (20)	80 (18)	10 (16)	-83 (18)

$$T = \exp (-8\pi^2 U \sin^2 \theta / \lambda^2).$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U (\text{Å}^2 \times 10^2)$		<i>x</i>	<i>y</i>	<i>z</i>	$U (\text{Å}^2 \times 10^2)$
H(011)	0.297 (2)	0.947 (5)	0.089 (2)	8.6 (1.4)	H(111)	0.106 (2)	0.582 (4)	0.041 (2)	4.9 (0.9)
H(101)	0.157 (2)	0.410 (4)	0.162 (2)	4.7 (1.0)	H(112)	0.054 (2)	0.446 (4)	0.065 (2)	6.2 (1.1)
H(041)	0.489 (2)	0.739 (4)	0.194 (2)	7.3 (1.1)	H(121)	0.013 (2)	0.658 (5)	0.125 (2)	8.4 (1.4)
H(042)	0.498 (2)	0.695 (4)	0.093 (2)	5.2 (1.0)	H(122)	0.039 (2)	0.549 (5)	0.195 (2)	8.5 (1.3)
H(051)	0.386 (2)	0.552 (4)	0.188 (2)	4.6 (0.9)	H(131)	0.081 (2)	0.797 (5)	0.220 (2)	8.8 (1.3)
H(052)	0.467 (2)	0.479 (4)	0.175 (2)	5.0 (1.0)	H(132)	0.161 (2)	0.710 (4)	0.203 (2)	5.8 (1.1)
H(061)	0.369 (2)	0.555 (4)	0.043 (2)	6.0 (1.1)	H(141)	0.074 (2)	0.884 (5)	0.072 (2)	10.1 (1.4)
H(062)	0.448 (2)	0.438 (4)	0.037 (2)	6.7 (1.1)	H(142)	0.165 (2)	0.808 (5)	0.077 (2)	7.9 (1.3)
H(071)	0.333 (2)	0.268 (4)	0.025 (2)	7.6 (1.1)	H(151)	0.171 (2)	1.074 (5)	0.091 (2)	9.0 (1.3)
H(072)	0.374 (2)	0.262 (5)	0.107 (2)	6.4 (1.2)	H(152)	0.124 (2)	1.060 (5)	0.185 (2)	8.2 (1.3)
					H(161)	0.258 (2)	1.101 (4)	0.211 (2)	5.8 (1.0)
					H(162)	0.234 (2)	0.918 (4)	0.231 (2)	6.1 (1.1)

relieved because of the high rotational barriers within the urethane group. There are few intermolecular contacts, the only close approaches within layers of the structure occurring between the atoms involved in hydrogen bonding, while between layers the only conspicuously close approach is between H(041) and O(9), which are specially depicted in Fig. 2.*

Fig. 2 represents a parallel projection of the crystal structure as viewed along the b axis. The parametral molecule, with nonhydrogen atoms numbered, is centrally located about the point $0, \frac{1}{2}, \frac{1}{2}$. The c -glide planes at $b = \frac{1}{4}$ and $\frac{3}{4}$ produce the nearest neighbors above (heavy lines) and below (open double lines) the parametral molecule. The molecules make an angle of about $\pm 30^\circ$ with the ac plane, which orients urethane group N(1)–C(2)–O(2)–O(3) and its symmetry-generated neighbors nearly parallel to that plane. These generated molecules then hydrogen bond into two-dimensional sheets, producing a natural cleavage plane parallel to plane bc . The hydrogen-bonding scheme is unusual among the various cyclic oligomers (amides and urethanes) studied in this laboratory in that only one of the two unique carbonyl oxygens participates in C=O...H–N hydrogen bonding. Hydrogen bonds are donated to O(2) from neighboring c -glide related urethane groups and from neighboring urethane groups that are not symmetrically generated from N(1)–C(2)–O(2)–O(3). Thus O(9) is not hydrogen bonded to another urethane group, as can be seen in Fig. 2.

Monomer, cyclobisurethane

Fig. 3 is a projection of the molecule on the least-squares molecular plane showing the labeling scheme for the nonhydrogen atoms. The unlabeled hydrogen atoms retain the same three-digit identification code as explained for the dimer. The positional and thermal parameters for the atoms of the parametral molecule are given in Table 4. The thermal parameters are of the order of size of those of the analogous cyclic hexamethylene adipamide monomer $c(\text{B}-\text{A})_1$ (Northolt & Alexander, 1968). All hydrogen atoms and carbonyl oxygens have isotropic thermal parameters equal to or larger than those of the atoms to which they are bonded.

The least-squares molecular plane, upon which the parallel projection of Fig. 3 is based, is described by the equation

$$0.0931x - 1.8561y + 17.5351z = 1.0175,$$

* In Fig. 2 the specially designated atom H(041) is symmetry-related by the screw axis at $\frac{1}{2}, y, \frac{3}{4}$ to the parametral H(041) atom with coordinates $x = 0.446$, $y = 0.313$, $z = 1.015$ which is not shown in the figure.

which was calculated from the 16 atoms of the ring. Applying the χ^2 distribution test, one finds that the probability of the 16 ring atoms being coplanar is less than 1%. By the same criterion none of the elements of the molecule shown in Fig. 3 is rigorously planar. The four approximately planar elements P , Q , R , and S are nearly perpendicular to the molecular plane T , the hydrocarbon planes Q and S are nearly parallel (1.5°), and the urethane planes P and R meet at an angle of 20° . The deviations from planarity within elements P , Q , R , and S may also be expressed by the torsion angles (Table 3). The torsion angles about the central bonds, C(5)–C(6) and C(13)–C(14), of elements Q and S deviate respectively about 11 and 15° from planar. Most of the torsion angles can be classified as synclinal or antiperiplanar except for the rotations about the C(hydrocarbon)–N bonds, which are anticlinal (Table 3). These angles are discussed below.

Bond lengths between the nonhydrogen atoms are shown in Fig. 3. The molecule possesses a pseudotwofold axis that bisects bonds C(13)–C(14) and C(5)–C(6). In the hydrocarbon elements, bonds C(4)–C(5) and C(6)–C(7) of length 1.508 Å are appreciably shorter than the average of the other bonded distances, 1.525 ± 0.001 Å, which is comparable to the C(sp^3)–C(sp^3) value of 1.531 Å. All C–C–C bond angles fall within 3σ of the ideal 113° value for alkanes (Wertz &

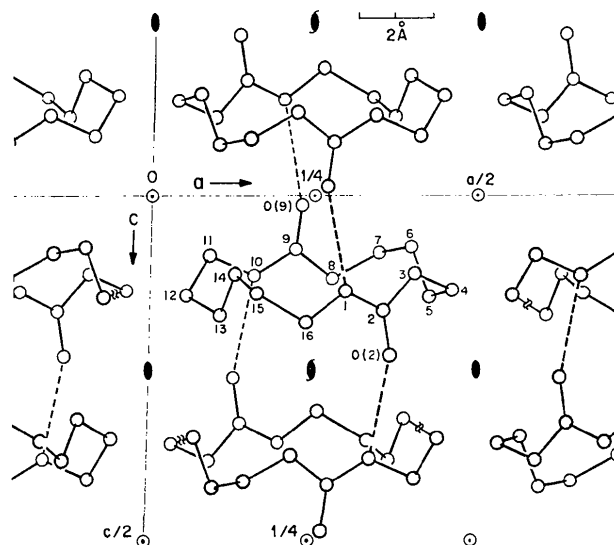


Fig. 4. Parallel projection of cyclobisurethane structure as viewed along b . Circles represent centers of symmetry, dashed lines hydrogen bonds.

Table 5. Comparison of hydrogen-bond lengths (Å) and angles (degrees)

	N...O	H...O	N-H	\angle N-H...O	\angle C=O...N	\angle C=O...H
Urethane	2.827 (6)	2.13 (4)	0.72 (4)	164.8 (3.8)	134.7 (3)	137.9 (1.1)
(Cyclic dimer)	2.943 (5)	2.11 (4)	0.84 (4)	175.6 (3.8)	119.9 (3)	121.1 (1.2)
Urethane	2.921 (4)	2.04 (4)	0.91 (4)	169.1 (3.1)	141.4 (2)	139.4 (1.0)
(Cyclic monomer)	2.935 (4)	2.08 (4)	0.87 (4)	161.8 (3.8)	162.5 (2)	158.4 (1.2)

Allinger, 1974) except for C(4)–C(5)–C(6). The average C–C–C angle, $114.1 \pm 0.1^\circ$, is larger than the tetrahedral value, which is to be expected (Williams, Stang & Schleyer, 1968). In cyclodecane, for example, Baeyer strain opens these angles to a mean value of about 116.5° (Dunitz, 1968). The average C–H bond length (1.06 ± 0.01 Å) and H–C–H bond angle ($105.5 \pm 0.9^\circ$) agree with the corresponding average bond lengths and angles of $c(\text{B-A})_n$, which are 1.052 ± 0.013 Å and $108.7 \pm 2^\circ$ respectively (Northolt & Alexander, 1968).

All intramolecular contacts across the ring are larger than the sums of the van der Waals radii of the atoms involved (Bondi, 1964). High barriers to internal rotation about certain bonds produce close contacts. The first examples are the barriers about the C(2)–O(3) and the O(8)–C(9) bonds, which produce close contacts between O(2) and C(4), 2.659 (4) Å, and between O(9) and C(7), 2.662 (5) Å, as well as between C(2) and C(5), 3.050 (5) Å, and between C(6) and O(9), 3.085 (4) Å. Another example is the high rotational barrier about the amide bonds N(1)–C(2) and C(9)–N(10), which will not relieve close approaches of C(16) and O(2), 2.833 (4) Å, and O(9) and C(11), 2.843 (4) Å.

Fig. 4 is a parallel projection of the molecular packing of the crystal structure as viewed along the b axis. The molecules hydrogen bond in sheets parallel to the bc plane. The parametral molecule near the center of the figure is coupled by C=O...H–N hydrogen bonds to its enantiomer across the symmetry center at $\frac{1}{2}, \frac{3}{4}, 0$. The twofold screw axis at $\frac{1}{2}, y, \frac{1}{4}$ produces two neighboring molecules within the layer, represented here as one molecule with two broken bonds. These two neighbors then hydrogen bond to the parametral molecule. Other than the hydrogen-bond distances, the only noteworthy close intermolecular contact between layers is between H(041) and H(041) across the twofold axis at $\frac{1}{2}, y, \frac{1}{4}$, with a separation of 2.04 (5) Å.

There are three near contacts within a layer: the two contacts between C(9) and H(071) and between O(9) and H(071) across the symmetry center at $\frac{1}{2}, \frac{3}{4}, 0$ [2.70 (4) and 2.44 (4) Å, respectively] and the third between H(161) and H(132) across the 2_1 screw axis [2.27 (5) Å]. From the sparseness and comparative looseness of the intermolecular approaches one may conclude that the intramolecular contacts are more significant in molding the molecular conformation than are the intermolecular ones.

Figs. 1, 3, and 4 were plotted with program ORTEP (Johnson, 1965) on the Univac 1108 computer at Carnegie-Mellon University.

Discussion of structural features

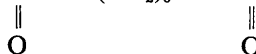
Table 5 lists the hydrogen-bonding parameters, which compare favorably with those of other urethane structures (Bracher & Small, 1967; Ganis, Avitabile, Migdal & Goodman, 1971; Adams & Small, 1973; Gieren, Hoppe & Fleischmann, 1973; Coiro, Mazza &

Mignucci, 1974), and those of cyclic amides (Northolt, 1970; Northolt & Alexander, 1968).

A few qualitative comparisons can be made between these cyclic urethane and amide oligomers. The urethane hydrogen bonds are amide-like in that no bonds are donated to the ring oxygens, which are potential acceptors. The molecules of the urethane monomer hydrogen-bond into sheets, whereas the cyclic monomer of nylon 66 (Northolt & Alexander, 1968) hydrogen bonds into columns. Both the cyclic amide (Northolt, 1970) and urethane dimers pack with two neighboring molecules nearly contacting each other through the opening in the center of the ring of a third molecule. These two compounds crystallize in the same space group but are not isomorphous. The amide dimer consists of two distinct conformers, while the urethane dimer has just one.

Structural implications for urethane polymers

Compared with the polyamide oligomers studied in our laboratory, the cyclic urethane monomer and dimer at present offer less possibility of structural application to the related polyurethanes since these polymers have not been crystallized and, hence, the necessary X-ray data are lacking. To the authors' knowledge the only information available is the fiber period, 19.1 Å, and the unit-cell base, 9.30×8.34 Å, proposed by Zahn (1951). Nevertheless, some suggestions may be deduced from the results of the present study, particularly in regard to possible chain-fold conformations. The urethane analogue of nylon 66, Durethan U_{18} , seems likely to exhibit chain folding. The homologous series of linear urethane oligomers, $\text{HO}-(\text{CH}_2)_4-[\text{O}-\text{C}-\text{NH}-(\text{CH}_2)_6-\text{NH}-\text{C}-\text{O}-(\text{CH}_2)_4]_n-\text{OH}$, was found



to have a constant long period as measured by small-angle X-ray scattering of 75 Å for $n \geq 5$ (Kern, Davidovits, Rauterkus & Schmidt, 1961; Zahn & Dominik, 1961*b*), which suggests that the chains do fold back on themselves when they reach this length.

From the oligomeric amide studies (Northolt & Alexander, 1968, 1971; Northolt, 1970) it was possible to draw conclusions about the suitability of certain fold patterns for adjacent reentry (Alexander, 1972) because the known polymer structures provided numerical values of the required fold spans, registry shifts, polarities, and azimuths characterizing pairs of neighboring polymer chains. Of these parameters the unit cell of Zahn supplies only tentative values of the required fold spans, namely: $a/2 = 4.65$, $c/2 = 4.17$ Å, one-half the short and long cell diagonals = 4.72 and 7.46 Å, respectively. These values may be compared with the observed spans of 3.864 Å for the tetramethylene element and 5.238 Å for the hexamethylene element of the cyclic urethane monomer, each of which possesses the torsion-angle sequence sc-sc-ap-sc-sc. These fold models are almost identical

with those observed in the corresponding cyclic polyhexamethyleneadipamide monomer (Alexander, 1972).

The open 32-membered rings of the cyclic urethane dimer in principle provide some potential model conformations for nonadjacent reentry folding in the polymer. Furthermore, these fold models are required to possess antiparallel stems by reason of the centrosymmetry of the dimer molecule. More realistically, however, it seems unprofitable to speculate further on this topic both because of the large number of degrees of freedom involved in such larger folds, or loops, and because of the tentative nature of Zahn's unit cell.

An interesting and commercially important class of polymers is the segmented urethane elastomer, a block copolymer of a urethane with a polyether or polyester. The latter segments provide elasticity and are referred to as soft segments, while the urethane elements are called hard segments because hydrogen bonding links them together into inflexible domains (Bonart, 1968; Bonart & Morbitzer, 1970; Clough & Schneider, 1968), which in favorable circumstances exhibit crystalline properties (Bonart, Morbitzer & Hentze, 1969). The hard-segment domains are considered to be lamellae, but too thin (about 25 Å) to support a folded-chain structure (Bonart & Müller, 1974).

One may use the hydrogen-bonding patterns of the cyclic urethane oligomers, which have the same chemical formulas as hard-segment domains, as a pattern for the hydrogen bonding within a hard-segment domain. The hydrogen-bonding scheme of the cyclic monomer links neighboring chains together that are antiparallel to one another. The cyclic dimer possesses a bonding pattern in which the neighboring chains are parallel to each other due to their relationship along the *c*-glide plane. The other hydrogen bond in the dimer cannot propagate sheet-like domains.

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