X-Ray Crystal Structure Analyses and Conformational Studies of *cis*-Cyclo-octane-1,5-diol and Cyclo-octane-1,5-dione

By **Richard W. Miller** and **Andrew T. McPhail,*** Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706, U.S.A.

Single-crystal *X*-ray analyses of *cis*-cyclo-octane-1,5-diol (1) and cyclo-octane-1,5-dione (2) have established that the eight-membered rings in both compounds adopt boat-chair conformations in the solid state. The observed geometries accord well with those derived by force-field methods. Monoclinic crystals of (1) belong to space group *Cc*, a = 9.119(4), b = 11.717(5), c = 8.118(4) Å, β = 108.35(5)°, Z = 4. Crystals of (2) are orthorhombic, space group $P2_12_12_1$, a = 13.195(6), b = 11.425(5), c = 5.258(3) Å, Z = 4. Both crystal structures were solved by direct methods and refined by full-matrix least-squares calculations to R 0.035 for (1) and 0.078 for (2) over 740 and 850 statistically significant reflections, respectively, measured by diffractometer.

CONFORMATIONAL properties of medium rings have been of interest for a number of years. The inherent strains, unusual reactivity, and conformational mobility render these systems of especial merit for structural studies. Thus, energetically accessible conformations for this class of compounds and their modes of interconversions have been extensively investigated by means of strain-energy calculations,[1-6] while n.m.r. measurements have been used to elucidate solution conformations and their interconversion barriers.[7-9]

Cyclo-octane and its simple derivatives have been shown to exist predominantly in the boat-chair (BC) conformation,[4,7,8] a form characterized by severe transannular H · · · H repulsions, and valency and torsion-angle strain. These unfavourable aspects may be alleviated to some extent through replacement of a methylene by a carbonyl group which results in elimination of one of three transannular H · · · H interactions, enlargement of an endocyclic valency angle, and introduction of a favourable eclipsed orientation for the carbonyl group. Allinger *et al.*[10] have not only calculated that the strain energy of cyclo-octane exceeds that of cyclo-octanone by 3.27 kcal mol^{-1} but also their calculations demonstrate that the carbonyl group in the latter should preferentially occupy the symmetry equivalent 1 or 5 ring sites (BC-1 or BC-5) as shown in Figure 1. Introduction of a second carbonyl group into the ring should further serve to reduce ring strain. On the basis of i.r. and dipole-moment measurements, Dale *et al.*[11] concluded that cyclo-octane-1,5-dione occurs in the solid state, as well as in solution, as an extended crown form with the carbonyl groups in a parallel orientation and occupying the 1 and 5 ring sites (CC-1,5), although he conceded that the data could also be accommodated by the boat-chair (BC-1,5) form with similarly placed carbonyl functions. Recent dynamic n.m.r. work supports the assignment of the BC-1,5 conformation to the 1,5-dione. Anet *et al.*[8] have performed line-shape analysis on the variable-temperature spectra of the 2,2,4,4,6,6,8,8-octadeuterio-derivative of cyclo-octane-1,5-dione and interpreted the results in terms of ring pseudorotation ($\Delta G^{\ddagger}$ 6.1 kcal mol^{-1}) and ring inversion ($\Delta G^{\ddagger}$ 7.0 kcal mol^{-1}) processes; the pattern of signals in the spectra was consistent with a boat-chair BC-1,5 conformation over the temperature range studied.

Although there is a considerable amount of indirect structural data accumulated in the form of strain-energy calculations and n.m.r. measurements, remarkably few definitive *X*-ray determinations have been performed on simple cycloalkane derivatives; moreover, the only cycloalkanone for which an *X*-ray analysis has been reported to date is cyclodeca-1,6-dione.[12] In order to provide further structural information on these systems, we have performed single-crystal *X*-ray analyses of two

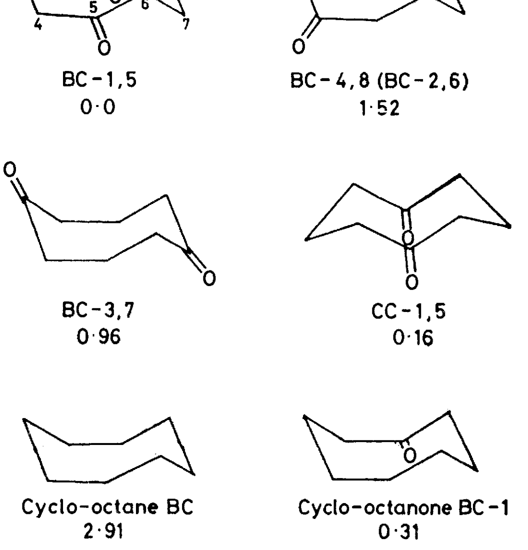
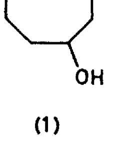
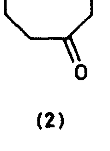


FIGURE 1 Some conformations of cyclo-octane-1,5-dione, cyclo-octane, and cyclo-octanone; the number underneath each conformer represents the calculated energy difference (in kcal mol^{-1}) between that conformer and the boat-chair (BC-1,5) conformation



(1)



(2)

simple representative cyclo-octane derivatives, *viz. cis*-cyclo-octane-1,5-diol (1) and cyclo-octane-1,5-dione (2), as well as strain-energy calculations on (2), cyclo-octane, and cyclo-octanone by use of White and Bovill's programmes.[5]

EXPERIMENTAL

Proton-decoupled ^{13}C n.m.r. spectra (p.p.m., downfield from $SiMe_4$) were obtained at 15.0 MHz on a JEOL FX-60 spectrometer by use of the Fourier-transform technique.

cis-Cyclo-octane-1,5-diol (1) (Aldrich) was recrystallized from methanol. Cyclo-octane-1,5-dione (2) was prepared from (1) by a literature procedure [13] and recrystallized from chloroform.

Crystal Data.—(*a*) *cis*-Cyclo-octane-1,5-diol (1), M = 144.2. Monoclinic, $a = 9.119(4)$, $b = 11.717(5)$, $c = 8.118(4)$ Å, $\beta = 108.35(5)°$, U = 823.3 Å^3, D_m(flotation) = 1.15 g cm^{-3}, $Z = 4$, D_c = 1.162 g cm^{-3}, $F(000) = 320$. Cu-K_α radiation, λ = 1.541 8 Å; μ(Cu-K_α) = 6.6 cm^{-1}. Space group Cc (C_s^4) or $C2/c$ (C_{2h}^6) from systematic absences: hkl when $h + k \neq 2n$, $h0l$ when $l \neq 2n$; shown to be the former by structure solution and refinement.

(*b*) Cyclo-octane-1,5-dione (2), M = 140.2. Orthorhombic, $a = 13.195(6)$, $b = 11.425(5)$, $c = 5.258(3)$ Å, U = 792.7 Å^3, D_m(flotation) = 1.16 g cm^{-3}, $Z = 4$, D_c = 1.175 g cm^{-3}, $F(000) = 304$. Cu-K_α radiation, μ(Cu-K_α) = 7.3 cm^{-1}. Space group $P2_12_12_1$ (D_4^2) uniquely from systematic absences: $h00$ when $h \neq 2n$, $0k0$ when $k \neq 2n$, $00l$ when $l \neq 2n$.

Crystallographic Measurements.—Initial unit-cell dimensions and space-group information were obtained from oscillation and Weissenberg photographs taken with Cu-K_α radiation and precession photographs with Mo-K_α (λ = 0.710 7 Å) radiation. For the intensity meazurements crystals of dimensions *ca.* 0.50 × 0.80 × 0.20 mm for (1) and *ca.* 0.30 × 0.80 × 0.10 mm for (2) were oriented on an Enraf-Nonius CAD 3 automated diffractometer (Ni-filtered Cu-K_α radiation). Refined unit-cell parameters were calculated for each crystal by least-squares treatment of the θ, χ, and ϕ angles for 40 reflections widely separated in reciprocal space. All unique reflections to θ 67° were surveyed by use of the θ—2θ scanning technique with scanwidths $(1.20 + 0.50\tan\theta)°$ in both cases; stationary background measurements were made at each end of the scan range for times equal to half the scan duration. In each case the intensity of a standard reflection remeasured after each batch of 99 reflections to monitor instrument and crystal stability showed no significant variation. Of the 740 reflections measured for (1) and 850 for (2), only those (670 and 549) having $I > 2.0\sigma(I)$ [$\sigma^2(I)$ = scan count + total background count] were considered observed and corrected for the usual Lorentz and polarization effects for use in the structure analyses and refinements. Absorption corrections, established from the ϕ-dependence of the intensities of the $\bar{2}04$ for (1) and 004 for (2) reflections measured at χ 90°, were also applied to these data.

Structure Analyses.—Both crystal structures were solved by use of MULTAN [14] incorporating a recent 'magic integer' modification.[15] For (1), the non-centrosymmetric space group Cc was assumed to be the correct choice at the outset since $Z = 4$ in the alternative $C2/c$ would demand that the molecules possessed either C_i or C_2 symmetry, both of which are in conflict with the expected C_s boat-chair form. The structure models thus derived were refined at first with isotropic and subsequently with anisotropic thermal parameters for the non-hydrogen atoms to R 0.082 for (1) and 0.096 for (2). Hydrogen atom positions were then obtained from difference-Fourier syntheses, and for (1) their positional and isotropic thermal parameters were refined in the subsequent least-squares iterations; for (2) only the hydrogen positions were varied as attempts to refine their thermal parameters led to physically unacceptable values. The refinements converged to R 0.035 for (1) and 0.078 for (2). Final positional parameters for non-hydrogen atoms are listed in Table 1. Anisotropic thermal parameters for non-hydrogen atoms and fractional co-ordinates for hydrogen atoms have been deposited along with Tables of observed and calculated structure amplitudes, intermolecular distances, strain-energy parameters, and ^{13}C n.m.r. spectra in Supplementary Publication No. SUP 22572 (17 pp.).*

For all structure-factor calculations, atomic scattering factors for carbon and oxygen were taken from ref. 16 and for hydrogen from ref. 17. In the least-squares calculations $\Sigma w\Delta^2$ was minimized with weights w assigned according to the scheme: $\sqrt{w} = 1$ for $|F_o| \leqslant K$ and $\sqrt{w} = K/|F_o|$ for $|F_o| > K$ [K = 7.0 for (1), 4.7 for (2)].

RESULTS AND DISCUSSION

Interatomic distances, and valency and torsion angles, are listed in Table 2. Molecular dimensions derived for cyclo-octane and (2) by force-field calculations are also included. The solid-state conformations found for (1) and (2) are of the boat-chair type, as shown in Figures 2 and 3, but with different substituent positions; in (1) the carbon atoms bearing the hydroxy-groups occupy sites 3 and 7 of the BC-1,5 conformer whereas in (2) the carbonyl groups are at sites 1 and 5. The arrangements of molecules of (1) and (2) in their unit cells are shown in Figures 4 and 5. The room-temperature ^{13}C n.m.r. spectral information is com-

TABLE 1

Fractional co-ordinates (× 10^4) for non-hydrogen atoms, with estimated standard deviations in parentheses

Atom	x	y	z
(*a*) For (1)			
C(1)	5 850(—)	1 441(2)	5 020(—)
C(2)	7 157(3)	804(2)	4 637(3)
C(3)	8 107(2)	1 476(2)	3 709(3)
C(4)	7 209(3)	2 252(2)	2 235(3)
C(5)	7 168(3)	3 521(2)	2 267(3)
C(6)	6 403(3)	3 865(2)	4 009(4)
C(7)	7 149(3)	3 418(2)	5 840(3)
C(8)	6 353(3)	2 389(2)	6 359(3)
O(1)	4 970(2)	659(2)	5 709(2)
O(5)	8 710(2)	3 971(1)	3 284(2)
(*b*) For (2)			
C(1)	7 999(4)	8 697(5)	3 860(12)
C(2)	8 930(5)	9 147(5)	2 671(14)
C(3)	9 511(5)	8 295(6)	1 038(18)
C(4)	9 930(5)	7 230(5)	2 391(16)
C(5)	9 155(5)	6 476(5)	3 647(12)
C(6)	8 228(6)	6 084(5)	2 141(14)
C(7)	7 268(5)	6 767(7)	2 935(16)
C(8)	7 254(4)	8 030(7)	2 302(13)
O(1)	7 826(4)	8 884(4)	6 085(9)
O(5)	9 278(4)	6 146(5)	5 847(10)

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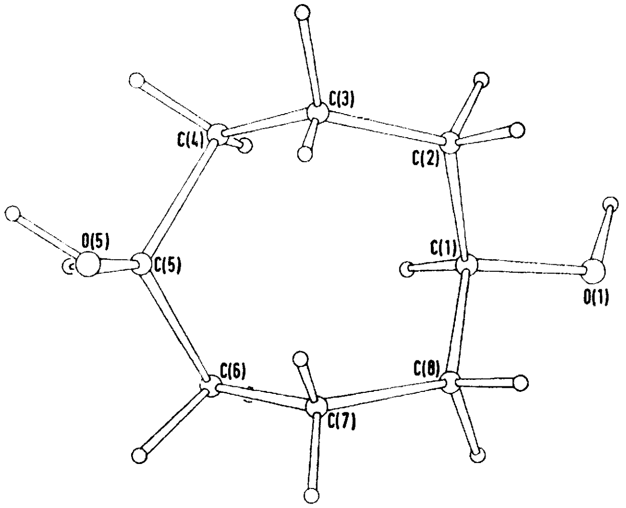


FIGURE 2 Solid-state conformation of cyclo-octane-1,5-diol (1); small circles denote hydrogen atoms

patible with either pseudorotation or ring inversion or a combination of both processes.

The solid-state cyclo-octane ring conformation found in all simple derivatives studied to date is the boat-chair form, although in heavily substituted or heterocyclic

TABLE 2

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

	(1)	Cyclo-octane	(2)	(2) (calc.)
(*a*) Bond lengths				
C(1)–C(2)	1.519(3)	1.531	1.471(9)	1.512
C(1)–C(8)	1.521(3)	1.531	1.489(9)	1.512
C(1)–O(1)	1.441(2)		1.211(8)	1.223
C(2)–C(3)	1.532(3)	1.532	1.507(10)	1.530
C(3)–C(4)	1.521(3)	1.532	1.514(10)	1.530
C(4)–C(5)	1.531(3)	1.533	1.491(9)	1.512
C(5)–C(6)	1.522(4)	1.533	1.524(10)	1.512
C(5)–O(5)	1.436(3)		1.227(8)	1.223
C(6)–C(7)	1.520(4)	1.532	1.545(11)	1.532
C(7)–C(8)	1.534(4)	1.532	1.481(11)	1.532
(*b*) Valency angles				
C(2)–C(1)–C(8)	115.2(1)	116.3	119.7(6)	117.1
C(2)–C(1)–O(1)	109.6(2)		120.4(6)	121.4
C(8)–C(1)–O(1)	105.4(1)		119.8(5)	121.5
C(1)–C(2)–C(3)	116.7(2)	116.9	116.2(5)	116.1
C(2)–C(3)–C(4)	116.5(2)	115.3	115.9(7)	114.6
C(3)–C(4)–C(5)	116.5(2)	114.3	115.0(5)	116.2
C(4)–C(5)–C(6)	118.1(2)	116.3	119.3(6)	117.1
C(4)–C(5)–O(5)	110.2(2)		120.2(6)	121.4
C(6)–C(5)–O(5)	105.8(2)		120.4(6)	121.5
C(5)–C(6)–C(7)	116.3(2)	114.3	111.7(5)	114.0
C(6)–C(7)–C(8)	115.8(2)	115.3	116.2(6)	115.2
C(1)–C(8)–C(7)	116.1(2)	116.9	111.5(6)	114.0
(*c*) Torsion angles				
C(8)–C(1)–C(2)–C(3)	−67.9(2)	−65.5	−47.5(6)	−49.8
O(1)–C(1)–C(2)–C(3)	173.5(2)		133.9(6)	133.0
C(2)–C(1)–C(8)–C(7)	66.3(2)	65.5	107.5(6)	106.9
O(1)–C(1)–C(8)–C(7)	−172.8(2)		−73.8(6)	−75.9
C(1)–C(2)–C(3)–C(4)	−41.7(2)	−43.5	−62.8(6)	−60.0
C(2)–C(3)–C(4)–C(5)	99.2(2)	102.6	59.6(6)	60.0
C(3)–C(4)–C(5)–C(6)	−62.8(2)	−69.9	50.1(7)	49.8
C(3)–C(4)–C(5)–O(5)	58.9(2)		−132.1(7)	−133.0
C(4)–C(5)–C(6)–C(7)	63.3(2)	69.9	−105.0(6)	−106.9
O(5)–C(5)–C(6)–C(7)	−60.6(2)		77.2(6)	75.9
C(5)–C(6)–C(7)–C(8)	−101.4(2)	−102.6	67.3(7)	63.5
C(6)–C(7)–C(8)–C(1)	44.1(2)	43.5	−69.2(6)	−63.5

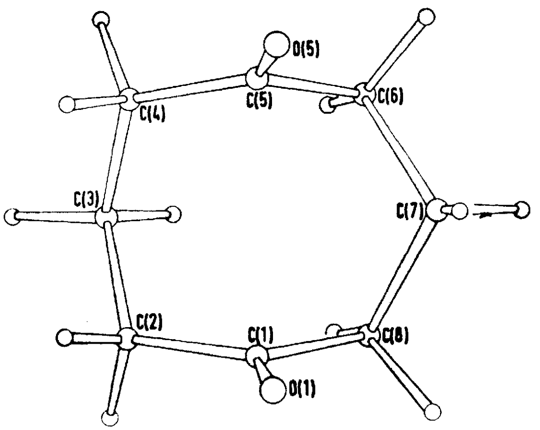


FIGURE 3 Solid-state conformation of cyclo-octane-1,5-dione (2); small circles denote hydrogen atoms

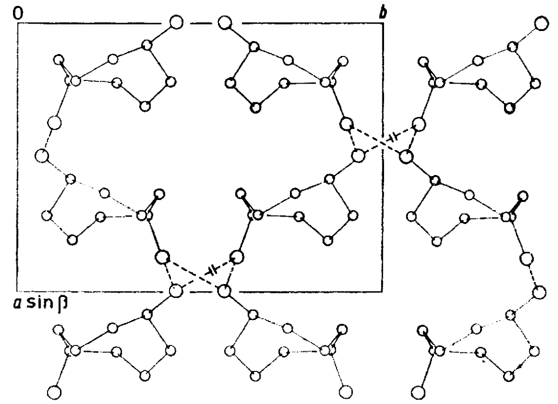


FIGURE 4 Packing of cyclo-octane-1,5-diol (1) molecules in the crystal, viewed in projection along the *c* axis; broken lines denote O–H · · · O hydrogen bonds

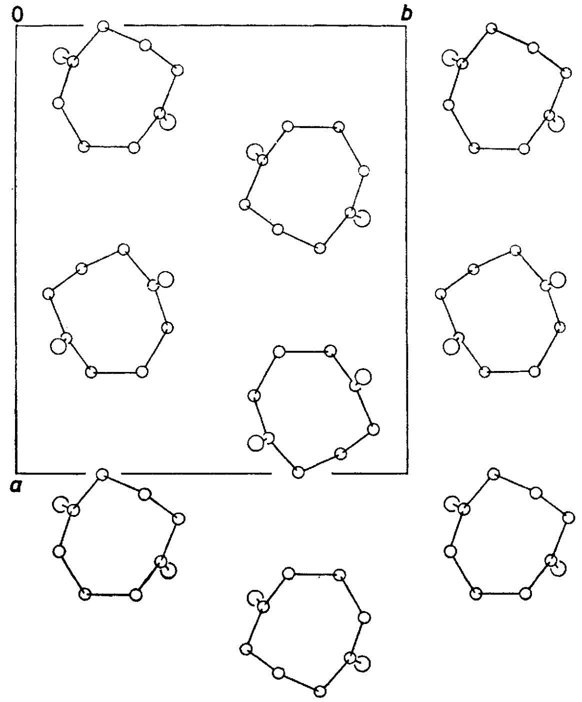
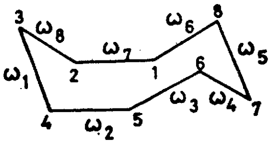


FIGURE 5 Packing of cyclo-octane-1,5-dione (2) molecules in the crystal, viewed in projection along the *c* axis

molecules some form of the crown conformation has also been observed.[9,18] The ring conformation in crystals of diol (1) is very similar to that calculated for cyclo-octane by use of force-field methods (Table 2), the principal differences lying in the region around C(5) (site 3 of the BC-1,5 form) where the torsion angles ω_4 and ω_5 at 63.3 and $-62.8°$ in (1) are significantly smaller than those of $\pm 70°$ calculated for cyclo-octane. The observed flattening in (1) occurs to accommodate the C(5) axial hydroxy-group, the orientation of which is indicated by an α angle of $-71.0°$ [α is the angle that the substituent bond vector makes with the mean ring plane (see Table 3)].[19] Flattening is similarly manifested by the small increase in the endocyclic valency angles at C(5) [118.1 in (1) *vs.* 116.7° in cyclo-octane]. The observed asymmetry in the exocyclic C–C–O(H) valency angles [109.6(2), 105.4(1) at C(1); 110.2(2), 105.8(2)° at C(5)] is a reflection of non-bonded H · · · H interactions between the ring methylene groups and the substituent hydroxy-groups.

TABLE 3

Calculated and observed torsion angles (°) for several eight-membered rings in the boat-chair conformation



Compound	Substituent α [a,b]	Ring $\langle\theta sp^3\rangle$	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ω_7	ω_8	ΔBC [c]
Cyclo-octane (3) (calc.)[d]	None	115.7	66	44	−103	70	−70	103	−44	−66	0.0
Cyclo-octane-1,5-dione (2) [d] (calc.)	O(1) −71.2 O(5) −71.2	115.0	60	50	−107	64	−64	107	−50	−60	0.0
Cyclo-octane-1,5-dione (2) [d]	O(1) −70.3 O(5) −71.0	114.4	59.6	50.1	−105.0	67.3	−69.2	107.5	−47.5	−62.8	2.6
Cyclo-octane-1,5-diol (1) [d]	O(3) 22.4 O(7) −67.5	116.4	66.3	44.1	−101.4	63.3	−62.8	99.2	−41.7	−67.9	1.7
trans-Cyclo-octane-1,2-dicarboxylic acid (4) [e]	C(6) −3.6 C(7) 32.2	116.0	62	47	−106	71	−70	101	−43	−63	2.8
cis-Cyclo-octane-1,2-di-carboxylic acid (5) [f]	C(1) −25.4 C(2) 39.9	116.8	60	48	−105	67	−66	96	−38	−69	7.3
trans-1,4-Dichlorocyclo-octane (6) [g]	Cl(2) 39.3 Cl(7) −63.6	116.4	62	48	−101	60	−63	100	−41	−68	4.3
3,6-Spiro-octylidene-1,2,4,5-tetraoxacyclohexane (7) [h]	O(2) 30.4 O(2) −57.6	116.5	70	37	−98	66	−64	101	−49	−61	6.5
1-Aminocyclo-octanecarboxylic acid hydrobromide (8) [i]	C(2) 36.6 N(2) −49.1	117.1	67	41	−98	67	−65	98	−46	−63	2.8

[a] For convenience of comparison substituent sites are labelled according to the above boat-chair system rather than by the usual chemical numbering scheme. [b] The angle α in the present paper is defined as the angle that the substituent bond vector makes with the mean ring plane and lies in the range $-90° < \alpha < +90°$, where for $\alpha = 0°$ the bond vector lies in the plane and for $\alpha = \pm 90°$ the bond vector lies perpendicular to the ring plane (*cf.* ref. 19). [c] $\Delta BC = \frac{1}{4}(|\omega_1 + \omega_8| + |\omega_2 + \omega_7| + |\omega_3 + \omega_6| + |\omega_4 + \omega_5|)$. [d] Present work. [e] M. Dobler, J. D. Dunitz, and A. Mugnoli, *Helv. Chim. Acta*, 1966, **49**, 2492. [f] H. Burgi and J. D. Dunitz, *Helv. Chim. Acta*, 1968, **51**, 1514. [g] J. V. Egmond and C. Romers, *Tetrahedron*, 1969, **25**, 2693. [h] P. Groth, *Acta Chem. Scand.*, 1971, **21**, 2695. [i] R. Srinivasan and T. Srikishnan, *Tetrahedron*, 1971, **27**, 1009.

Strain-energy calculations for (2) point to the BC-1,5 conformer as the minimum energy form among the various BC conformers, although the extended crown form CC-1,5 is, in fact, calculated to be only slightly higher in energy; the energy difference between these two forms is increased after allowance is made for inductive effects.[20] INDO [21] calculations indicate that a substantial induced positive charge (0.1 e) on atoms C(3) and C(7) induces a negative charge on their bonded hydrogen atoms with concomitant increase in the effective van der Waals radius of these hydrogen atoms. Relative to the BC-1,5 conformer, the extended crown form has several destabilizing interactions between hydrogen atoms at C(3) and C(7) and the axial carbonyl oxygen atoms. Calculations provide a measure of the extent to which stabilization occurs in the eight-membered ring through introduction of one or two keto-groups [E_{strain}: cyclo-octane 11.49, cyclo-octanone 8.89, cyclo-octane-1,5-dione (BC-1,5) 8.58 kcal mol^{-1}]; this fact is also reflected in the corresponding reduction which occurs in the mean sp^3 valency angle in the ring (cyclo-octane 115.7, cyclo-octanone 115.1, cyclo-octane-1,5-dione 115.0°).

The calculated structure for (2) agrees very well with that found experimentally (mean deviation in bond lengths 0.022 Å, in valency angles 1.5°, in torsion angles 1.8°). The C=O groups have a parallel orientation and lie approximately perpendicular to the mean ring plane with α values of 70.3 and 71.0° for the C(1)=O(1) and C(5)=O(5) bonds compared with calculated values of 71.2° for both; this arrangement accords with that deduced by Anet *et al.*[8] for the solution conformation. The dipole moment determined from INDO calculations [21] by use of the final *X*-ray derived co-ordinates for (2), $\mu_{\text{calc.}}$ 5.31 Debye, is close to that of 4.81 Debye found experimentally by Dale *et al.*[11]

One measure of fit to the boat-chair (BC-1,5) C_s symmetry-related torsion angles is provided by the deviation parameters ΔBC (Table 3) which we have evaluated for the cyclo-octane rings in a number of

TABLE 4

Puckering parameters [a] for several eight-membered rings in the boat-chair conformation

Cpd [b]	q_2 [c]	q_3 [c]	q_4 [c]	Q [c]	ϕ_2 [c]	ϕ_3 [c]	θ_2 [d]	θ_3 [d]	ΔBCP [e]
(3)	1.011	0.622	0.355	1.239	180.0	180.0	31.6	73.4	
(2) (calc.)	1.042	0.591	0.332	1.243	180.0	180.0	29.6	74.5	0.78
(2)	0.953	0.621	0.341	1.187	178.3	178.8	33.1	73.3	1.13
(1)	1.048	0.583	0.317	1.240	179.6	179.1	29.1	75.2	1.40
(4)	0.986	0.608	0.382	1.220	181.2	178.6	31.7	71.8	1.08
(5)	1.005	0.599	0.334	1.216	181.9	184.7	30.8	74.1	2.03
(6)	1.093	0.572	0.327	1.277	177.3	178.0	27.6	75.2	2.63
(7)	1.039	0.597	0.329	1.242	184.6	183.0	29.9	74.6	2.63
(8)	1.021	0.590	0.353	1.231	181.1	182.9	30.0	73.3	1.43

[a] Ref. 19; the atom sequence used here for the derivation of the puckering parameters is C(3), C(4), C(5), C(6), C(7), C(8), C(1), C(2) for the boat-chair form shown above. [b] See Table 3 for the identities of compounds (1)—(8), sources of data and position numbering. [c] $q_m\cos\phi_m = 0.5 \sum_{j=1}^{8} z_j\cos[2\pi m(j-1)/8]$, $q_m\sin\phi_m = -0.5 \sum_{j=1}^{8} z_j\sin[2\pi m(j-1)/8]$, for $m = 2, 3$; $q_4 = 0.5 \sum_{j=1}^{8} (-1)^{j-1}z_j$; Q (the total puckering amplitude) $= (\sum_{m=2}^{4} q_m^2)^{\frac{1}{2}} = (\sum_{j=1}^{8} z_j^2)^{\frac{1}{2}}$, where z_j is the displacement (Å) of atom j from the mean ring plane. [d] $\theta_3 = \cos^{-1}(q_4/Q)$; $\theta_2 = \tan^{-1}(q_3/q_2)$. [e] $\Delta BCP = \frac{1}{4}(|\phi_{2s} - \phi_2| + |\phi_{3s} - \phi_3| + |\theta_{2s} - \theta_2| + |\theta_{3s} - \theta_3|)$, where the subscripts 2s and 3s refer to the standard cyclo-octane (3) values.

substituted compounds. The small values found for ΔBC in each case examined attest to the fact that the boat-chair form is maintained remarkably well throughout and thus is the preferred conformation. A further monitor of conformational fit, based on deviations from the mean ring plane, has been developed by Cremer and Pople,[19] although its previous use has been restricted primarily to five- and six-membered ring systems. For eight-membered rings each conformation may be uniquely defined in terms of five parameters, ϕ_2, ϕ_3, θ_2, θ_3, and Q. The ϕ angles indicate the molecular symmetry; for systems with C_s symmetry ϕ angles assume values of 180 or 360° ideally, while for C_2 symmetry forms ideal values are 90 or 270°. The θ angles arise from the unique distribution of deviations from the mean ring plane for each conformer, and Q is a measure of the puckering of the ring system under consideration. For the boat-chair conformation the appropriate ϕ values are $\phi_2 = \phi_3 = 180°$, while the θ values are ideally those determined from the calculated cyclo-octane model, *viz.* $\theta_2 = 31.6$ and $\theta_3 = 73.4°$. Again, the deviation parameters (ΔBCP) for the surveyed systems are quite small (Table 4).

In crystals of (1) (Figure 4) the molecules are held together by O(1)-H · · · O(5) hydrogen bonds linking molecules related by the *c*-glide (2.72 Å) and *C*-face-centring (2.77 Å) operations. For (2) (Figure 5), dipolar interactions dominate, with the shortest intermolecular separations involving the C(1)=O(1) dipole [O(1) · · · C(1) 3.31 Å]; the efficiency of the dipolar packing is evidenced by the similar calculated densities for (1) and (2) (1.162 and 1.173 g cm^{-3}).

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