

Table 3. Structural differences between the complex and the individual molecule of saccharin

	Present structure	Free molecule
Bond distances (Å)		
S(1)—N(2)	1.610 (3)	1.663 (4)
N(2)—C(3)	1.332 (3)	1.369 (5)
C(3)—O(13)	1.252 (3)	1.214 (5)
C(3)—C(9)	1.506 (3)	1.474 (5)
Bond angles (°)		
C(8)—S(1)—N(2)	97.0 (3)	92.2 (6)
C(9)—C(3)—O(13)	121.6 (3)	126.5 (6)
S(1)—N(2)—C(3)	111.3 (3)	115.1 (6)
N(2)—C(3)—C(9)	113.9 (3)	109.6 (6)
Maximum displacement of saccharin ring (Å)	0.025 (4)	0.007 (5)

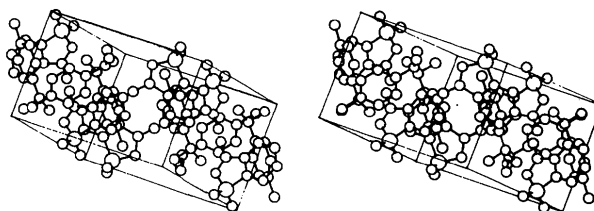


Fig. 2. Stereo packing diagram.

notes the crystal packing (Fig. 2). Molecules of the complex are linked together by weak van der Waals interactions.

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compare well with those found in *p*-toluidinium hydrochloride (Colapietro, Domenicano & Portalone, 1982) and in diisothiocyanatobis(*p*-toluidine)zinc (Caira & Nassimbeni, 1976). The dihedral angle between the two rings (saccharin and toluidine) is 41°.

Intermolecular bonding. The H atom on the toluidine amino group is directed toward the saccharin ketone oxygen, forming a strong hydrogen bond: O(13)⋯N(40) = 2.676 (3), O(13)⋯H(60) = 1.84 (6) Å and O(13)⋯H(60)—N(40) = 165 (6)°. This hydrogen bond between the anionic and cationic parts domi-

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Structure of Oxacycloheptane (Oxepane) at 105 K

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Abstract. C₆H₁₂O, *M_r* = 100.16, monoclinic, *C2/c*, *a* = 22.669 (8), *b* = 6.466 (4), *c* = 8.154 (6) Å, β = 92.11 (5)°, *V* = 1194.4 Å³, *Z* = 8, *D_x* = 1.114 g cm⁻³, λ(Mo *Kα*) = 0.71069 Å, μ = 0.79 cm⁻¹, *F*(000) = 448, *T* = 105 K, final *R*(*F*) = 0.085 for 1368 independent observed reflections. In the crystal the seven-membered ring adopts an approximate twist-chair conformation with the pseudo-twofold axis passing through C(2), so that a *C*-type twist-chair ring is present. The average C—O and C—C bond lengths are 1.429 (4) and 1.528 (4) Å. Application of the Cremer–Pople concept leads to the surprising result that the ring-puckering parameters of this conformation are intermediate between twist chair (TC) and twist boat (TB) in the pseudo-rotation circle.

Introduction. A series of crystal structure investigations on small unsubstituted cyclic ethers has so far resulted in the determination of the structures of ethylene oxide (Luger, Zaki, Buschmann & Rudert, 1986), oxetane (Luger & Buschmann, 1984), tetrahydrofuran (Luger & Buschmann, 1983) and dioxane (Buschmann, Müller & Luger, 1986) (ring sizes *n* = 3, 4, 5, 6). It was of interest to include the seven-membered ring oxacycloheptane, C₆H₁₂O, also called oxepane. In comparison with five- and six-membered rings the seven-membered ring should have a higher flexibility, so that one might expect any of a number of possible conformations to occur, including the chair (C), the boat (B), the twist chair (TC), the twist boat (TB) and intermediate forms (Bocian &

Strauss, 1977). Oxacycloheptane is a liquid at room temperature, the melting point being 210 K. A differential thermoanalysis showed that there are two plastic phases between 210 and 180 K. At 180 K there is a transition into an ordinary crystalline phase. The first plastic crystalline phase is cubic ($a = 10.9 \text{ \AA}$, space group $P\bar{4}3n$), the lattice of the second phase could not be determined. The crystal structure below 180 K is monoclinic with space group $C2/c$.

Experimental. A single crystal of oxacycloheptane was grown by the method described by Luger & Buschmann (1984), at a temperature a few degrees below the transition point of 180 K, on a DEC Micro PDP computer-controlled Siemens four-circle diffractometer. The diffractometer was equipped with an N_2 gas stream cooling device built according to Dietrich & Dierks (1970). Inspection of several reflection profiles indicated only moderate crystal quality. Moreover, a few unindexed reflections suggested that more than one crystal was present in the capillary. It was known from previous crystallization experiments (Buschmann, Müller & Luger, 1986) that passing through plastic phases during crystal growth can cause problems. So, after several unsuccessful attempts to improve the crystal quality by recrystallization, a moderate crystal had to be accepted. The crystal quality, symmetry and general characteristics remained unchanged when the temperature was further lowered to 105 K for the final X-ray measurement. A cylindrical single crystal, $\sim 2 \text{ mm}$ long, sealed within a Lindemann glass tube (0.3 mm diameter, 0.01 mm wall thickness) was used in measurements.

Lattice parameters from least-squares refinement of 20 reflections with $20 < 2\theta < 35^\circ$. One set of independent reflections was measured in ω - 2θ scan mode up to $(\sin\theta/\lambda)_{\max} = 0.704 \text{ \AA}^{-1}$ with Zr-filtered Mo $K\alpha$ radiation. 1611 reflections measured, of which 243 were unobserved with $I < 2\sigma(I)$; $h - 31$ to 32 , $k - 9$ to 0 , $l 0$ to 11 . Two standard reflections (800 and $0\bar{2}0$) measured every 40 min showed insignificant statistical intensity variations. Reflection intensities corrected for Lorentz and polarization factors, and for changes in the crystal volume exposed to the X-ray beam. The latter correction depends on the angle between the 'endless' crystal cylinder and the primary X-ray beam, and varied between 1.00 and 0.88 (Luger, 1984). No absorption correction. Structure solved readily by *MULTAN77* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). All H atoms were found with the help of a difference Fourier synthesis. Usual parameters submitted to full-matrix least-squares refinement with the *XTAL* system (Hall & Stewart, 1987). Quantity minimized $\sum(w|F_o| - |F_c|)^2$. Unobserved reflections included if $|F_c| > |F_o|$.

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^2$) for oxacycloheptane at 105 K

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
O(1)	0.37892 (9)	-0.0104 (3)	0.0411 (2)	2.67 (6)
C(2)	0.3250 (1)	0.0157 (5)	0.1239 (4)	2.83 (9)
C(3)	0.3140 (1)	0.2361 (5)	0.1849 (4)	2.89 (9)
C(4)	0.3371 (1)	0.4071 (5)	0.0746 (4)	2.88 (9)
C(5)	0.4025 (1)	0.4550 (5)	0.1072 (4)	2.85 (9)
C(6)	0.4448 (1)	0.2843 (5)	0.0589 (4)	2.70 (9)
C(7)	0.4299 (1)	0.0713 (5)	0.1270 (4)	2.61 (8)
H(21)	0.295 (1)	-0.023 (4)	0.046 (3)	1.8 (7)
H(22)	0.324 (1)	-0.083 (5)	0.221 (4)	2.7 (8)
H(31)	0.273 (2)	0.257 (6)	0.214 (5)	6 (1)
H(32)	0.334 (1)	0.245 (5)	0.301 (3)	1.8 (7)
H(41)	0.327 (1)	0.379 (5)	-0.034 (4)	1.8 (7)
H(42)	0.312 (2)	0.539 (5)	0.112 (4)	3.6 (9)
H(51)	0.410 (1)	0.592 (6)	0.062 (4)	3.2 (9)
H(52)	0.413 (1)	0.488 (4)	0.227 (4)	2.2 (8)
H(61)	0.478 (2)	0.323 (8)	0.127 (5)	8 (1)
H(62)	0.444 (1)	0.273 (5)	-0.062 (4)	3.7 (9)
H(71)	0.465 (2)	-0.047 (6)	0.108 (4)	4 (1)
H(72)	0.430 (1)	0.075 (5)	0.240 (4)	2.4 (8)

Final $R = 0.085$ and $wR = 0.087$, based on 1368 reflections and 112 variables, $S = 3.61$, $w = 1/\sigma^2(F)$, maximum $(\Delta/\sigma) = 0.03$, largest peak in final difference map $= 0.48$, largest hole $= 0.39 e \text{ \AA}^{-3}$. * The relatively high R value results from the moderate crystal quality obtained from low-temperature crystal growth as described above. Atomic scattering factors for C and N atoms from Cromer & Mann (1968), H-atom scattering factors from Stewart, Davidson & Simpson (1965).

Discussion. Final atomic coordinates and equivalent isotropic displacement factors (Hamilton, 1959) are given in Table 1. A stereo representation (Johnson, 1976) of the oxepane molecular structure in the crystal is shown in Fig. 1. Tables 2 and 3 list bond lengths, bond angles and ring torsion angles. The average length of the two O—C bonds is 1.429 \AA with deviations of $\pm 0.001 \text{ \AA}$ and that of the five C—C bonds is 1.528 \AA with a maximum deviation of $+0.005 \text{ \AA}$. In the low-temperature phase of dioxane these values were $1.431 (2)$ and $1.513 (2) \text{ \AA}$; in two recently determined methyl β -D-glucosidans (Foster, James & Stevens, 1989) with oxepane rings fused to five-membered rings, averages of $1.420 (4)$ and $1.519 (5) \text{ \AA}$ were observed. Looking at the ring bond angles of the oxacycloheptane molecule the angle at atom C(7) is 110.0° , while the other six angles are close to 114.4° with a maximum deviation of 1.1° .

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52928 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

As Fig. 1 and the ring torsion angles (Table 3) show, the molecule adopts an approximate TC conformation in the crystal, the pseudo-twofold axis passing through C(2) and the middle of the C(5)—C(6) bond. Force-field calculations on cycloheptane (Hendrickson, 1967) suggest that the TC form is the energetically favoured conformation for the seven-membered ring. For oxacycloheptane the ring may be present in several TC forms because of the heteroatom. According to Bocian & Strauss (1977), the TC forms of type *B* and type *C* are energetically preferred; for type *B*, by definition, the pseudo-twofold axis runs through C(3) and for type *C* through C(2). Of the eight monocyclic oxacycloheptane derivatives whose crystal structures have been investigated so far (Cambridge Structural Database, September 1988 release; Allen *et al.*, 1979), six exhibit an approximate TC form and two a distorted chair form. Of the six TC-like forms three correspond to type *B* and three to type *C*. The unsubstituted oxacycloheptane ring described here belongs to type *C*, see Table 4.

Comparing the geometries of all oxacycloheptane rings, a remarkable variety of conformations is observed. However, if the rings of the *B*-type TC-like form are transformed to their mirror image isomer and then superimposed so that the pseudo-twofold axes are coincident (in which case not all O atoms are in the same positions), a rather good geometrical agreement is obtained for all seven TC-like forms (Fig. 2).

Cameron & Scheeren (1977) and Moritani, Sasahara, Kashino & Haisa (1987) also found TC-like conformations in unsubstituted seven-membered rings with an N heteroatom, when carrying out structure determinations on some hexamethylene ammonium salts. Also, in polycyclic septanosides, recently investigated by Foster, James & Stevens (1989), the TC conformation (type *C*) is observed for the oxepane ring.

In contrast to these organic rings there are inorganic seven-membered rings of different conformation. Unsubstituted rings formed by S atoms alone, S_7 , or by Se and S atoms, Se_5S_2 , were investigated by Steudel, Steidel, Pickardt & Schuster (1980) and Steudel, Papavassiliou, Strauss & Laitinen

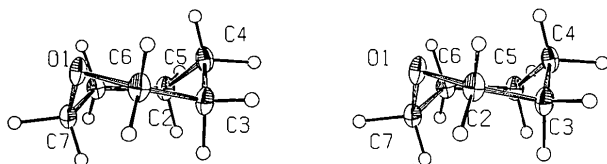


Fig. 1. An ORTEP stereoview of the oxacycloheptane molecule. The thermal ellipsoids are plotted at the 36.5% probability level.

Table 2. Bond lengths (Å) and angles (°) for oxacycloheptane at 105 K

O(1)—C(2)	1.428 (4)	O(1)—C(7)	1.430 (3)
C(2)—C(3)	1.533 (4)	C(3)—C(4)	1.530 (4)
C(4)—C(5)	1.527 (4)	C(5)—C(6)	1.525 (4)
C(6)—C(7)	1.527 (4)		
C(2)—O(1)—C(7)	114.6 (2)	C(4)—C(5)—C(6)	115.1 (3)
O(1)—C(2)—C(3)	114.6 (2)	C(5)—C(6)—C(7)	114.1 (3)
C(2)—C(3)—C(4)	114.7 (3)	O(1)—C(7)—C(6)	110.0 (2)
C(3)—C(4)—C(5)	113.3 (3)		

Table 3. Torsion angles of oxacycloheptane at 105 K (°) and theoretical values (Bocian & Strauss, 1977) for the TC form *C* (°)

	Experimental	Theoretical
O(1)—C(2)—C(3)—C(4)	34.1 (4)	44.4
C(2)—C(3)—C(4)—C(5)	-83.9 (3)	-90.9
C(3)—C(4)—C(5)—C(6)	68.4 (4)	67.7
C(4)—C(5)—C(6)—C(7)	-51.0 (4)	-50.8
C(5)—C(6)—C(7)—O(1)	73.0 (3)	72.9
C(6)—C(7)—O(1)—C(2)	-98.6 (3)	-96.4
C(7)—O(1)—C(2)—C(3)	49.5 (3)	43.0

Table 4. Summary of ring conformations for monocyclic oxepane rings

Refcode	q_2 (Å)	φ_2 (°)	q_3 (Å)	φ_3 (°)	Configuration type of TC form
AHIDIT	0.565	242.6	0.645	141.9	$^4sTC_{6,0}$ <i>B</i>
MAGSEP	0.548	231.7	0.635	139.0	$^4sTC_{6,0}$ <i>B</i>
ACGLSP	0.552	232.6	0.622	141.6	$^4sTC_{6,0}$ <i>B</i>
BERFAF	0.549	158.8	0.615	117.7	$^5sTC_{3,4}$ <i>C</i>
BUJRED	0.523	170.7	0.537	118.1	$^5sTC_{3,4}$ <i>C</i>
BUJXIN	0.655	170.1	0.627	117.9	$^5sTC_{3,4}$ <i>C</i>
OXEPAN	0.557	166.9	0.648	117.8	— <i>C</i>
BUFFOX	0.522	345.7	0.645	54.8	$^2C_{5,6}$ —
MTAGLU	—	—	—	—	$^3C_{1,2}$ —

References: AHIDIT, $C_5H_{12}O_5$, 1,6-anhydro-L-iditol (Luger, Reinhardt & Paulsen, 1975); MAGSEP, $C_{15}H_{22}O_{10}$, methyl 2,3,4,5-tetra-*O*-acetyl- α -D-glucoseptanoside (McConnell & Stevens, 1974); ACGLSP, $C_{15}H_{22}O_{10}$, methyl 2,3,4,5-tetra-*O*-acetyl- α -D-galactoseptanoside (Choong, McConnell, Stephenson & Stevens, 1980); BERFAF, $C_{15}H_{22}O_{10}$, methyl 2,3,4,5-tetra-*O*-acetyl- β -D-alloseptanoside (James & Stevens, 1982a); BUJRED, $C_7H_{14}O_6$, methyl- α -L-idoseptanoside (Grainger, Rukvichai & Stevens, 1982); BUJXIN, $C_{15}H_{22}O_{10}$, methyl 2,3,4,5-tetra-*O*-acetyl- α -L-idoseptanoside (James & Stevens, 1982b); OXEPAN, $C_7H_{14}O$, oxacycloheptane (this work); BUFFOX, $C_7H_{14}O_6$, methyl β -D-glucoseptanoside (Foster, James & Stevens, 1983); MTAGLU, $C_{15}H_{22}O_{10}$, methyl 2,3,4,5-tetra-*O*-acetyl- β -D-glucoseptanoside (Beale, Stephenson & Stevens, 1971).

(1986). The crystal structure determinations gave a chair-like conformation for these compounds: three torsional angles near 45° are obviously less favorable than one of 0° which allows all other torsional angles to have values between 76 and 109°, as all the ring atoms possess lone-pair electrons.

According to the ring-puckering concept of Cremer & Pople (1975) the conformation of a seven-membered ring can be numerically described by four

ring-puckering parameters q_2 , q_3 , φ_2 , φ_3 . For a pure TC form $q_2 = 0$ holds. An analysis of the parameters obtained for oxacycloheptane [$q_2 = 0.557$ (3), $q_3 = 0.648$ (3) Å, $\varphi_2 = 166.9$ (3), $\varphi_3 = 117.8$ (3)°] shows that, according to this concept, the seven-membered ring can be accurately described as an intermediate form between the TC and the TB forms, with 54% TC and 46% TB character. When the ring-puckering parameters for the other oxacycloheptane rings (shown in Fig. 2) are calculated, intermediate conformations are also observed. The proportional agreements with respect to the TB form amount to between 46 and 51%. Surprisingly, this result even holds for the theoretical TC forms of type *B* and *C* (Bocian & Strauss, 1977), so that when using the Cremer-Pople concept as a quantitative basis, the oxacycloheptane derivatives described in the literature can no longer be characterized as having TC conformation, but must be assigned conformations almost midway between TC and TB on the pseudorotation circle.

A unit-cell stereo representation is shown in Fig. 3. In the crystal lattice there are two intermolecular O...H contacts close to or less than the van der Waals O...H distances of 2.72 Å [van der Waals radii of 1.52 Å for O and 1.20 Å for H are assumed (Bondi, 1964)]. These contacts (see the dotted lines in

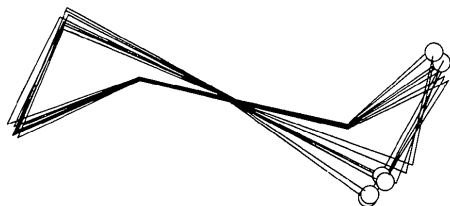


Fig. 2. Six oxacycloheptane rings with TC-like conformation from different crystal structures superimposed on the unsubstituted ring by their pseudo-twofold axes; the O atoms are denoted by circles.

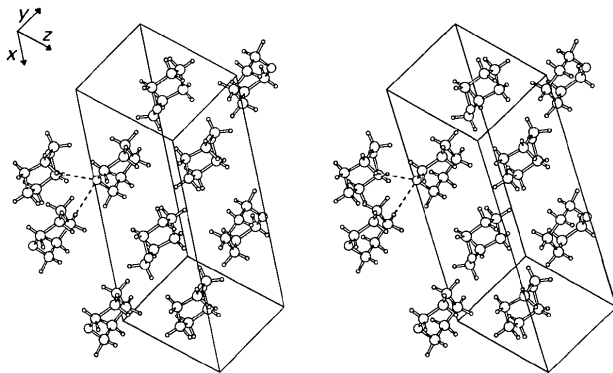


Fig. 3. Unit cell of oxacycloheptane. Intermolecular C—H...O contacts are drawn as dotted lines.

Fig. 3) are O(1)...H(32)($x, -y, -\frac{1}{2} + z$) = 2.65 (3) and O(1)...H(51)($x, -1 + y, z$) = 2.67 (4) Å. Similar intermolecular C—H...O interactions were found in the oxetane and ethylene oxide crystal structures.

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Structures of Di-*p*-tolyl Terephthalate (C₂₂H₁₈O₄) and 1,4-Phenylene Di-*p*-toluate (C₂₂H₁₈O₄)

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Abstract. Di-*p*-tolyl terephthalate (CA), $M_r = 346.2$, monoclinic, $C2/m$, $a = 7.920$ (1), $b = 8.957$ (1), $c = 13.017$ (1) Å, $\beta = 98.425$ (6)°, $V = 913.4$ (2) Å³, $Z = 2$, $D_x = 1.259$ (1) g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 6.6$ cm⁻¹, $F(000) = 364$, $T = 298$ K, $R = 0.056$ for 673 reflections. 1,4-Phenylene di-*p*-toluate (CB), $M_r = 346.2$, monoclinic, $P2_1/c$, $a = 6.127$ (3), $b = 7.555$ (1), $c = 19.360$ (4) Å, $\beta = 102.39$ (3)°, $V = 875.4$ (2) Å³, $Z = 2$, $D_x = 1.313$ (1) g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 6.9$ cm⁻¹, $F(000) = 364$, $T = 298$ K, $R = 0.054$ for 905 reflections. Consistent with their mesogenic properties, molecules CA and CB have a strongly anisometric shape. A common feature of their crystal packing is the almost parallel orientation of their molecular axes; layers in this direction are formed in CA but not in CB. The torsion angle C10—C9—O1—C8 of CB is 76.2 (4)° while the corresponding angle for CA is ~90°, owing to different conformations.

Introduction. The title compounds are both mesogenic. They are characterized by the atomic groups $A = -\phi-OOC-\phi-COO-\phi-$ and $B = -\phi-COO-\phi-OOC-\phi-$ ($-\phi-$ = *p*-phenylene) that have been extensively utilized in the synthesis of low-molecular-weight mesogenic compounds (Dewar & Goldberg, 1970; Schroeder & Bristol, 1973; Kelker & Hatz, 1980) and polymeric (Lenz, 1985) mesogenic compounds.

The detailed examination of the relationship between molecular structure and mesogenic properties of a number of compounds containing groups *A* or *B* has indicated that quite a relevant role is played

by the stereochemical nature of the atomic groups linked to *A* or *B*; for instance, structures of the type $R-OOC-A-COO-R$ are more frequently smectogenic while nematic phases are given preferentially by structures $R-COO-A-OOC-R$. In addition, systematic differences in the mesophasic properties have been observed between *A*- and *B*-type compounds containing identical terminal groups (Dewar & Goldberg, 1970), since *A*-type compounds exhibit higher nematic to isotropic liquid transition temperatures. To a first approximation, electric polarizability and steric hindrance appear to be the relevant factors, the latter being probably less effective.

The title compounds have been chosen for a complete structural study in order to detect molecular structure and packing differences in a pair of nematogenic *A*- and *B*-type compounds containing terminal groups that have moderate effects on the electronic structure of the molecular cores.

Experimental. The title compounds were prepared by condensation of terephthaloyl chloride with *p*-cresol (CA) and *p*-toluoyl chloride with hydroquinone (CB). The reactions were carried out at room temperature using 1,2-dichloroethane as solvent and equimolar amounts of triethylamine as the catalyst and HCl acceptor. After precipitation and recrystallization from methanol the nature and the purity of the compounds were controlled by TLC, ¹H NMR and IR methods. The phase behaviour was examined by DSC and polarizing microscopy. Compound CA melts at 473.3 K to a nematic liquid (mobile schlieren