C11—C12—C13	120.9 (2)	P—C31—C36	116.4 (2)
C11—C12—O11	116.0 (2)	C32—C31—C36	118.6 (2)
C13—C12—O11	123.1 (2)	C31—C32—C33	120.6 (2)
C12—C13—C14	119.5 (3)	C31—C32—O31	116.4 (2)
C13—C14—C15	121.1 (3)	C33—C32—O31	123.0 (2)
C14—C15—C16	119.7 (3)	C32—C33—C34	118.7 (3)
C11—C16—C15	120.9 (2)	C33—C34—C35	122.0 (3)
C12—O11—C17	119.1 (2)	C34—C35—C36	118.5 (3)
O11—C17—C18	108.8 (2)	C31—C36—C35	121.4 (2)
C17—C18—O12	113.7 (3)	C32—O31—C37	118.4 (2)
C18—O12—C19	115.4 (3)	O31—C37—C38*A*	118.2 (4)
P—C21—C22	118.0 (2)	O31—C37—C38*B*	96.2 (3)
P—C21—C26	122.8 (2)	C37—C38*A*—O32*A*	106.4 (4)
C22—C21—C26	119.1 (2)	C37—C38*B*—O32*B*	100.9 (5)
C21—C22—C23	119.9 (2)	C38*A*—O32*A*—C39*A*	112.5 (5)
C21—C22—O21	115.9 (2)	C38*B*—O32*B*—C39*B*	110.8 (6)
C23—C22—O21	124.2 (2)	O1···O2···O22	93.8
O1—P—C11—C16	−117.8	C17—C18—O12—C19	−94.2
O1—P—C21—C26	−124.6	C23—C22—O21—C27	−6.7
O1—P—C31—C36	−1.9	O21—C27—C28—O22	−76.4
C13—C12—O11—C17	19.3	C27—C28—O22—C29	−179.3
O11—C17—C18—O12	76.9		

Table 3. *Contact distances (Å)*

O1···O2	2.877 (3)	P···O11	2.899 (2)
O2···O22	3.021 (3)	P···O21	2.876 (2)
O1···O21	3.019 (2)	P···O31	3.046 (2)
O1···O11	3.005 (2)		

During solution of the structure, it became apparent that several atoms on one side chain (C38, O32 and C39) were disordered. These atoms were refined as pairs of disordered atoms with a common isotropic temperature factor for each pair of disordered atoms and with occupancies constrained to add to 1.00. During the refinement process, it was noted that the occupancies of the 'major' site for each atom had refined to the same value. Therefore occupancies of C38*A*, O32*A* and C39*A* were held equal [refined value 0.567 (3)]. Although we did not refine C37 as disordered, we did note a peak in all difference maps within 0.5 Å of C37, which suggests that this atom too is disordered. The decision to refine C37 as non-disordered may explain the unusual distances between C37 and the two images of C38.

Data collection: *P*3 *Software* (Siemens, 1989). Cell refinement: *P*3 *Software*. Data reduction: *SHELXTL-Plus* (VMS) (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus* (VMS). Program(s) used to refine structure: *SHELXTL-Plus* (VMS). Molecular graphics: *Chemdraw* 2.1.2. Software used to prepare material for publication: Microsoft *Word* 5.1a.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1225). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Torturing the 7-Oxabicyclo[2.2.1]heptane Skeleton with an Oxetane Ring: 4,7-Dioxatricyclo[3.2.1.0^{3,6}]octane at 190 K

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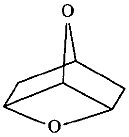
Abstract

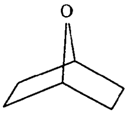
The low-temperature phase of 4,7-dioxatricyclo[3.2.1.0^{3,6}]octane, $C_6H_8O_2$, has been structurally characterized by X-ray diffraction at 190 K. Only minor bond differentiation is observed here compared to oxetane and 7-oxabicylo[2.2.1]heptanes.

Comment

Annulation of a molecule with small rings leads to bond-angle deformations that are sometimes accompanied by bond-length changes. A recent example is the bond alternation of the benzene unit in tris(bicyclo[2.2.1]hexeno)benzene (Bürgi, Baldridge, Hardcastle, Frank, Gantzel, Siegel & Ziller, 1995). During our studies of the chemistry of 7-oxabicyclo[2.2.1]heptenes (Vogel, Fatton, Gasparini & le Drian, 1990; le Drian & Vogel, 1988), we found that the oxetane unit in 4,7-dioxatricyclo[3.2.1.0^{3,6}]octane derivatives was not very reactive. For the title parent diether, (1), we observed that strong acids such as CF_3SO_3H or HSO_3F in CD_2Cl_2 quantitatively protonate the ethereal function of the oxetane moiety, giving the corresponding oxetanium ion which was stable up to 233 K. This demonstrated that the oxetane moiety of (1) is significantly more basic than its 7-oxabicyclo[2.2.1]heptane unit (le Drian & Vogel, 1993). Although 7-oxabicyclo[2.2.1]heptane, (2), is not a highly strained ether (strain energy: 6–7 kcal mol^{-1}; Bedford, Beezer, Mortimer & Springall, 1963; see also Hall, DeBlauwe & Pyriadi, 1975), annulation by the oxetane ring as in (1) was expected to increase the strain significantly owing to bond-angle deformation (Figs. 1 and 2). In the hope of learning more about the properties of (1) which is astonishingly high melting (m.p. 646–648 K) for a molecule of this size, and because there is no example of such a tricyclic system in the Cambridge Structural Database (CSD) (Allen *et al.*, 1987), we have determined its structure by X-ray diffraction.



(1)



(2)

The molecule of (1) has crystallographic *m* symmetry; for this reason, the atom numbering in Fig. 1 does not follow IUPAC rules.

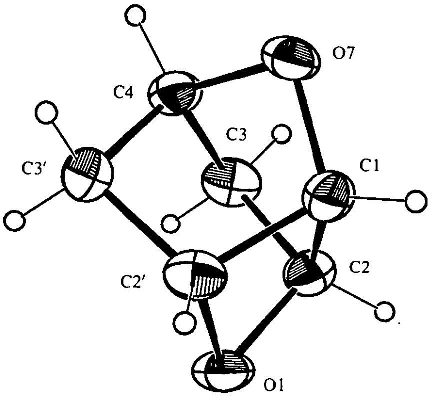


Fig. 1. *ORTEP*II (Johnson, 1976) plot of 4,7-dioxatricyclo[$3.2.1.0^{3,6}$]-octane with 50% displacement ellipsoids showing the atom-numbering scheme.

Comparison of our geometric data for (1) with those reported for oxetane (Luger & Buschmann, 1984; see also Allen *et al.*, 1987) shows that the pucker of the oxetane unit of (1) [26.9 (2)°] is more pronounced than in oxetane itself (8.7° at 140 K and 10.7° at 90 K). However, the CSD indicates that this is not unusual (values range from 0–49°).

The 7-oxabicyclo[2.2.1]heptane skeleton is strongly distorted to adapt to the oxetane unit as shown by the comparison of bond angles C2—C1—C2′ [82.92 (9)°] and C3—C4—C3′ [109.5 (1)°] in (1). This tends to elongate the C1—C2 and C2—O1 bonds of its oxetane unit compared with oxetane itself, although the effect is not dramatic. Interestingly, there is a bond-length differentiation for the 7-oxabicyclo[2.2.1]heptane C—O bonds which makes the C1—O7 bond shorter than the C4—O7 bond [1.420 (2) *versus* 1.443 (2) Å].

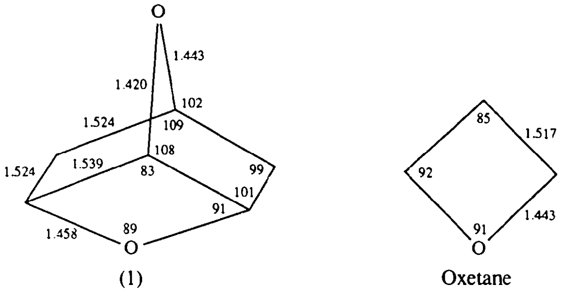


Fig. 2. Comparison of the bond lengths and angles (Å, °) in the structures of (1) (190 K) and oxetane (140 K).

In conclusion, most of the stress introduced by annulation of the 7-oxabicyclo[2.2.1]heptane by an oxetane ring as in (1) is accommodated by bond-angle deformation of the 7-oxabicyclo[2.2.1]heptane skeleton.

Experimental

A crystal of (1) was obtained as a plate by slow sublimation *in vacuo* after several days at approximately 250 K in a sealed thin walled glass capillary mounted on the diffractometer. The crystal was then cooled to 190 K and no further sublimation took place.

Crystal data

$C_6H_8O_2$
$M_r = 112.13$
Monoclinic
$C2/m$
$a = 9.634 (3)$ Å
$b = 6.5478 (8)$ Å
$c = 8.474 (1)$ Å
$\beta = 98.86 (2)°$
$V = 528.2 (3)$ Å^3
$Z = 4$
$D_x = 1.41$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 16–18°$
$\mu = 0.098$ mm^{-1}
$T = 190$ K
Irregular plate
0.35 × 0.25 × 0.25 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.976$, $T_{max} = 0.999$
1106 measured reflections
555 independent reflections

508 observed reflections [$I > 3\sigma(I)$]
$R_{int} = 0.018$
$\theta_{max} = 25.90°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 8$
$l = -10 \rightarrow 10$
3 standard reflections
frequency: 50 min
intensity decay: 2.6%

Refinement

Refinement on F
$R = 0.032$
$wR = 0.051$
$S = 2.81$
508 reflections
62 parameters
All H-atom parameters refined
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0004F_o^4]$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: 0.25×10^{-4}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.5187 (1)	0	0.2475 (1)	0.0336 (3)
O7	0.1876 (1)	0	0.1265 (1)	0.0316 (3)
C1	0.3253 (2)	0	0.0858 (2)	0.0296 (4)
C2	0.4136 (1)	−0.1557 (2)	0.1945 (1)	0.0306 (3)
C3	0.3213 (1)	−0.1901 (2)	0.3229 (1)	0.0331 (3)
C4	0.2292 (1)	0	0.2976 (2)	0.0293 (4)
H1	0.325 (2)	0	−0.029 (2)	0.032 (4)
H2	0.453 (1)	−0.276 (2)	0.147 (1)	0.043 (3)
H3	0.264 (2)	−0.312 (2)	0.302 (1)	0.060 (4)
H4	0.376 (1)	−0.201 (2)	0.430 (1)	0.035 (3)
H5	0.147 (2)	0	0.351 (2)	0.044 (5)

Table 2. *Selected geometric parameters (Å, °)*

O1—C2	1.458 (1)	C2—H2	0.98 (1)
O7—C1	1.420 (2)	C3—C4	1.524 (1)
O7—C4	1.443 (2)	C3—H3	0.97 (2)
C1—C2	1.539 (1)	C3—H4	0.98 (1)
C1—H1	0.98 (2)	C4—H5	0.97 (2)
C2—C3	1.524 (2)		
C2—O1—C2$^{\rm i}$	88.69 (8)	C3—C2—H2	118.4 (8)
C1—O7—C4	96.8 (1)	C2—C3—C4	99.8 (1)
O7—C1—C2	107.78 (9)	C2—C3—H3	111.7 (8)
O7—C1—H1	112. (1)	C2—C3—H4	112.3 (7)
C2—C1—C2$^{\rm i}$	82.92 (9)	C4—C3—H3	110.1 (9)
C2—C1—H1	121.1 (6)	C4—C3—H4	114.2 (7)
O1—C2—C1	90.88 (8)	H3—C3—H4	109 (1)
O1—C2—C3	109.71 (9)	O7—C4—C3	101.94 (8)
O1—C2—H2	113.0 (7)	O7—C4—H5	110. (1)
C1—C2—C3	101.28 (9)	C3—C4—C3$^{\rm i}$	109.5 (1)
C1—C2—H2	119.8 (7)	C3—C4—H5	115.6 (4)

Symmetry code: (i) $x, -y, z$.

Backgrounds were obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974)

Data collection: *CAD*-4 (Enraf–Nonius, 1977). Cell refinement: *CAD*-4. Data reduction: *PROCESS MolEN* (Fair, 1990). Program(s) used to solve structure: direct methods (*MULTAN*; Main *et al.*, 1980). Program(s) used to refine structure: *LSFM MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIF VAX MolEN*.

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BK1244). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,4-Dinitrophenyl Phenyl Sulfone

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Abstract

The crystal structure of the title compound, $C_{12}H_8N_2O_6S$, has been determined by single-crystal X-ray diffraction. The compound crystallizes in the noncentro-

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