Autoassembly of cage structures
6.* X-ray diffraction study of the conformation of 1,4-dimethyl-2,5-dioxabicyclo[2.2.2]octane-3,6-dione

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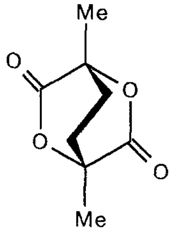
The molecular structure of 1,4-dimethyl-2,5-dioxabicyclo[2.2.2]octane-3,6-dione (**1**) has been determined by X-ray diffraction analysis. The skeleton of dilactone **1** has a synchro(+,+,+)-twist conformation with dihedral angles φ = 4.0° for the hydrocarbon bridge bonds and φ = 4.4, 4.6° for the lactone bridge bonds.

Kzey words: dilactone, conformation, molecular structure, X-ray diffraction analysis.

This work was performed as part of a systematic study of the conformation of bridged dilactones possessing C_2 symmetry. For 2,5-dioxabicyclo[2.2.2]octane-3,6-diones of type (**1**), either a preference for the *twist* conformation of the skeleton due to the decrease in torsional strain (similar to bicyclo[2.2.2]octane (**2**), data of gas phase electron diffraction[2]) or stabilization of the eclipsed conformation through $n_\pi(O)—\pi^*(C=O)$ conjugation (similar to bicyclo[2.2.2]octa-2,5-diene (**3**), gas phase electron diffraction[3]) are expected.



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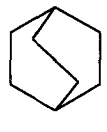
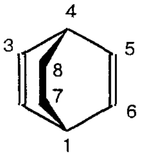
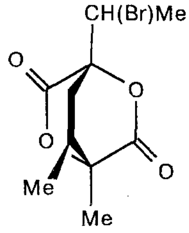


2 (D_3)



3 (C_{2v})



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In the only known study on the structure of dilactones of this type (according to the Cambridge Structural Database, CSD[4]), carried out for bromodilactone (**4**), the precise geometric characteristics of the molecule were not determined.[5] The main aim of this work is to establish the conformation of dilactone **1** in the crystalline state.

Experimental

Dilactone **1** was synthesized according to the procedure reported previously.[1] The principal crystallographic characteristics for molecule **1** are: $C_8H_{10}O_4$, M = 110.2, a = 7.969(2), b = 11.191(5), c = 10.068(1) Å, γ = 65.47(2)°, V = 816.8(7) Å^3, Z = 4, d_{calc} = 1.39 g/cm^3, space group is $P2_1/b$.

The intensities of 827 reflections with $I > 3\sigma(I)$ were collected on an automated DAR-UM diffractometer. Absorption was ignored ($\mu(CuK_\alpha)$ = 9.6 cm^{-1}). The structure of **1** was solved by the direct method. The full-matrix least-squares refinement with anisotropic thermal parameters for C and O atoms and isotropic thermal parameters for H atoms reduced the R value to 0.063. All calculations were carried out using the Rentgen-75 program (see Ref. 6). Atomic coordinates are given in Table 1; bond lengths and bond angles are listed in Tables 2 and 3.

Results and Discussion

The molecular structure of dilactone **1** is shown in Fig. 1.

According to the dihedral angles in the C(1)O(1)C(2)C(3), C(3)O(3)C(4)C(1), and

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* For the previous paper in the series see Ref. 1.

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Table 1. Atomic coordinates for molecule **1** ($\times 10^4$ for O and C atoms and $\times 10^3$ for atoms H)

Atom	*x*	*y*	*z*
O(1)	−1031(4)	6752(2)	−220(2)
O(2)	1812(4)	5501(2)	−866(3)
O(3)	294(5)	6384(3)	2286(2)
O(4)	−2574(5)	6932(3)	2965(2)
C(1)	−2060(6)	7692(3)	818(4)
C(2)	818(7)	6217(4)	−59(4)
C(3)	1335(6)	6662(4)	1233(3)
C(4)	−1573(8)	6982(4)	2118(4)
C(5)	−1387(7)	8766(4)	843(4)
C(6)	648(7)	8161(4)	1153(4)
C(7)	−4089(7)	8137(5)	483(5)
C(8)	3338(8)	5895(6)	1546(5)
H(51)	−216(4)	945(3)	150(4)
H(52)	−156(4)	912(3)	−6(3)
H(61)	137(4)	830(3)	58(3)
H(62)	98(4)	840(3)	194(4)
H(71)	−484(5)	885(5)	112(4)
H(72)	−432(5)	860(5)	−33(5)
H(73)	−428(5)	738(5)	71(5)
H(81)	406(5)	595(4)	927(4)
H(82)	353(6)	618(5)	234(5)
H(83)	364(6)	481(5)	165(4)

Table 2. Bond lengths (*d*/ Å) for molecule **1**

Bond	*d*	Bond	*d*
C(1)—O(1)	1.464(3)	C(3)—O(3)	1.458(5)
O(1)—C(2)	1.350(5)	O(3)—C(4)	1.365(6)
C(2)—O(2)	1.184(4)	C(4)—O(4)	1.185(6)
C(2)—C(3)	1.510(5)	C(1)—C(4)	1.496(5)
C(1)—C(5)	1.507(7)	C(3)—C(6)	1.535(5)
C(5)—C(6)	1.508(7)	—	—
C(1)—C(7)	1.518(7)	C(3)—C(8)	1.499(6)

Table 3. Bond angles (ω/deg) for molecule **1**

Angle	ω	Angle	ω
C(1)O(1)C(2)	114.7(3)	C(3)O(3)C(4)	113.9(3)
O(1)C(2)C(3)	110.6(3)	O(3)C(4)C(1)	111.0(4)
O(1)C(2)O(2)	120.3(3)	O(3)C(4)O(4)	121.3(4)
C(3)C(2)O(2)	128.1(4)	C(1)C(4)O(4)	128.6(5)
C(2)C(3)O(3)	107.4(4)	C(4)C(1)O(1)	107.5(2)
C(4)C(1)C(5)	108.0(4)	C(2)C(3)C(6)	107.0(3)
C(4)C(1)C(7)	112.0(4)	C(2)C(3)C(8)	111.3(3)
O(1)C(1)C(5)	107.5(3)	O(3)C(3)C(6)	107.2(3)
O(1)C(1)C(7)	106.3(3)	O(3)C(3)C(8)	106.9(3)
C(5)C(1)C(7)	115.1(3)	C(6)C(3)C(8)	116.7(4)
C(1)C(5)C(6)	108.5(3)	C(3)C(6)C(5)	109.3(3)

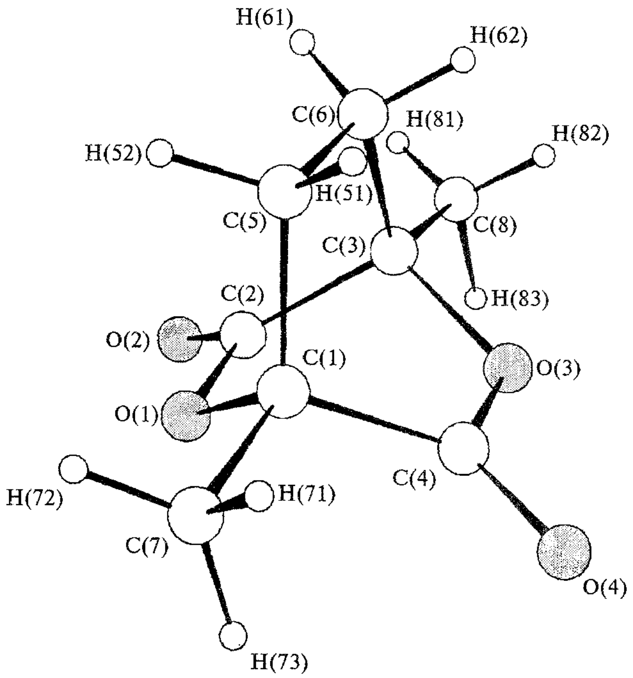


Fig. 1. Structure of molecule **1**

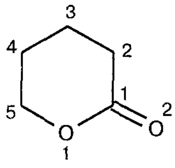
Torsion angle	φ
C(1)O(1)C(2)O(2)	−175.7
O(1)C(2)C(3)C(6)	−61.8
C(2)C(3)C(6)C(5)	55.1
O(1)C(1)C(5)C(6)	−60.2
H(51)C(5)C(6)H(62)	6
H(52)C(5)C(6)H(62)	131
O(1)C(2)C(3)O(3)	53.0
C(2)C(3)O(3)C(4)	−58.3
C(2)O(1)C(1)C(5)	58.0
H(51)C(5)C(6)H(61)	−116
H(52)C(5)C(6)H(61)	8

C(1)C(5)C(6)C(3) bridges (4.4, 4.6, and 4.0°, respectively), the six-membered fragments in **1** have a slightly twisted boat conformation, and the overall conformation of the structure of the skeleton of the above-mentioned enantiomer of dilactone **1** is a synchro(+,+,+)-twist. According to the interplanar angles and the folding angles about the lines O(1)...C(4) (49.7°) and O(3)...C(2) (49.3°), O(1)...C(5) (52.4°) and C(2)...C(6) (53.7°), and O(3)...C(6) (53.3°) and C(4)...C(5) (52.9°), the dilactone fragment is flattened compared to the δ-monolactone fragments. This is in agreement with the flattening of the diene monocycle in molecule **3** (ϕ = 123.4°).[3] Increasing the dihedral angle between the planes defined by the atoms C(1)O(1)C(2)O(2)C(3) and C(3)O(3)C(4)O(4)C(1) of the lactone groups to 124.9° reduces the energy of the sterically strained molecule **1** owing to the increase in the O(1)...C(4) and O(3)...C(2) distances to 2.392(4) Å and 2.387(5) Å, respectively. The O(1)...C(5) and O(3)...C(6) distances decrease to 2.409(9) Å and 2.397(3) Å and become comparable to the C(2)...C(6) (2.448(6) Å) and C(4)...C(5) (2.430(6) Å) distances, which causes the planes defined by the atoms C(1)C(5)C(6)C(3) and O(1)C(2)O(3)C(4) to be orthogonal (ϕ = 90.1°).

The rigid bicyclic skeleton of molecule **1** causes the endocyclic bond angles at the lactone carbon (C(2) and C(4)) and oxygen (O(1) and O(3)) atoms (Table 3) to be substantially lower than the average values (according to the CSD data) for δ-lactones (**5**)[7] for the angles

O(1)C(1)C(2) (118.4(2)°) and C(1)O(1)C(5) (122.9(3)°). This is accompanied by an increase in the sum of the exocyclic bond angles at the C(2) ($\Sigma\omega_{exo}$ = 248.4°) and C(4) (249.9°) carbon atoms in molecule **1** compared to the normal value of 240°. This change in the bond angles should cause[8] the enhancement of the p-character of the orbitals of the C(2) and C(4) carbon atoms involved in the endocyclic bonds and correspondingly the elongation of these bonds, as well as the enhancement of the s-character of the orbitals of these atoms involved in the exocyclic bonds, *i.e.*, their shortening.

The O(1)—C(2) and O(3)—C(4) bonds in molecule **1** (Table 2) are longer than the C(1)—O(1) bond (1.337(8) Å,[7] 1.336 Å[9]) in δ-lactones **5** (according to the CSD data), whereas the C(2)=O(2) and C(4)=O(4) bonds in molecule **1** are shorter than the C(1)=O(2) bond (1.204(7) Å,[7] 1.196 Å[9]) in δ-lactones **5**.



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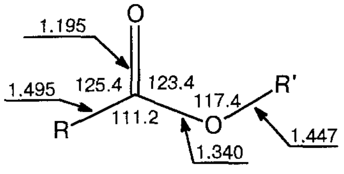
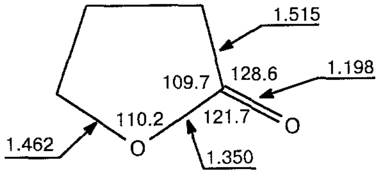


6, R—R' = Alk*



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Similarly, the decrease in the sum of the endocyclic bond angles at the C(1) ($\Sigma\omega_{endo}$ = 320.0°) and C(3) (321.6°) atoms of dilactone **1** compared to the normal value of 328.5° should cause the enhancement of the p-character of the orbitals of the «internal» bonds at these carbon atoms and result in their elongation.[8] However, the C(1)—O(1), C(3)—O(3), C(1)—C(4), and C(2)—C(3) bond lengths in molecule **1** are close to the average values of the corresponding O(1)—C(5) (1.462(13) Å [7]) and C(1)—C(2) (1.514(15),[7] 1.504 Å [9]) bonds in δ-lactones according to the CSD data, though they are larger than those of the corresponding bonds in acyclic esters (**6**).

Based on the close values of the sums of the exocyclic bond angles ($\Sigma\omega_{exo}$) at the carbonyl carbon atoms in molecule **1** and esters **6** ($\Sigma\omega_{exo}$ = 248.4°),[7] one may conclude that the n_π(O)—π^*(C=O) conjugation in the lactone fragments of molecule **1** decreases despite the fact that they are nearly coplanar.

The increase in $\Sigma\omega_{exo}$ at the C(1), C(3) and C(2), C(4) atoms is also favorable for decreasing 1,3-repulsion between the exo-substituents and the atoms of the bicycle,[10] as well as for the steric interaction of the lone electron pairs of the O atoms in the *E* form of the lactone groups.[11]

By and large, the structural parameters of both lactone groups of molecule **1** are closer to the average parameters of γ-(**7**)[8] than to those for δ-lactones, which is confirmed by the observed difference in the exo bond angles at the C(2) ($\Delta\omega_{exo}$ = 7.8°) and C(4) (7.3°) atoms; this difference agrees more closely with γ-lactones (6.9°) than with δ-lactones (4.5°).[7]

Intermolecular interactions apparently have no effect on the conformation of molecule **1** in the crystal because no shortened contacts between molecules are observed.

Hence, according to X-ray structural data, the structure of dilactone **1** in the crystal has the synchro(+,+,+)-twist form stabilized through the mutual compensation of steric effects and n_π(O)—π^*(C=O) conjugation. This form of molecule **1** (φ = 4.0—4.6°) is intermediate between the conformations of saturated bicycle **2** (φ = 12.0(1.5)°), which has D_3 [2] symmetry, and diene **3** (φ = 0.1(0.3)°), which has C_{2v}[2] symmetry.

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* X-ray structural data.[7]