X-ray diffraction study of DL-1,4-dimethyl-2,5-dioxabicyclo[2.2.1]heptane-3,6-dione: the sense of twist and folding

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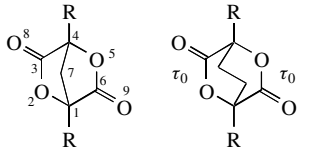
The title dilactone exists in a crystalline state (110 K) as enantiomeric synchro-(+,+)-(*R*,*R*)- and synchro-(–,–)-(*S*,*S*)-twist forms ($\tau_0 = |1.8°|$) with the retention of C_2 symmetry, linked by infinite zig-zag heterochiral chains (space group *C*2/*c*) by mutual H-bonds of the CH_2–H···O=C type.

Zelinsky's dilactone **1** has a long history of interest in the synthesis,[1–5] optical resolution,[6] spectroscopy (CD, VCD)[6,7] and theoretical (MP2/6-31G*)[6] studies. However, its structure was not determined by X-ray diffraction (XRD), MW or GED in contrast to its bridged homologue **3** (XRD).[8] At the same time, the geometry of norbornane **5** and norborna-2,5-diene **6**, possessing the parent bicyclo[2.2.1]frame rigid system, was investigated thoroughly by the XRD analysis of their plastic crystals.[9,10]

Dilactone **1** also tends to form plastic crystals owing to its globular shape.[11] However, the polarity of **1** and intermolecular H-bonds prevent such a formation. Nevertheless, in an effort to increase the crystal structure ordering, the XRD analysis of **1**† was performed at a low temperature.

The aim of this study was to compare the structural characteristics of **1** with available XRD and theoretical data for bicycles **3**,[8,12] **6**[10] and γ-lactones.[13,14] [XRD data for the structure of **2** are unknown (see refs. 5, 7) and those for **5** are unaccurate[9]].

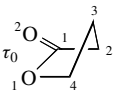


1 R = Me
2 R = H

3 R = Me
4 R = H

5

6



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† *Crystallographic data for* **1**: at 110(2) K crystals of $C_7H_8O_4$ **1** are monoclinic, space group *C*2/*c*, $a = 10.379(16)$ Å, $b = 8.943(15)$ Å, $c = 8.477(13)$ Å, $\beta = 114.22(6)°$, $V = 717.6(19)$ Å^3, $Z = 4$, $M = 156.13$, $d_{calc} = 1.445$ g cm^{-3}, μ(MoKα) = 1.20 cm^{-1}, $F(000) = 328$. Intensities of 1236 reflections were measured on a Smart 1000 CCD diffractometer at 110 K [λ(MoKα) = 0.71072 Å, ω-scans with a 0.3° step in ω and 10 s per frame exposure, $2\theta < 55°$], and 618 independent reflections ($R_{int} = 0.0157$) were used in the further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. Hydrogen atoms were located from the Fourier synthesis and refined in the isotropic approximation. The refinement converged to $wR_2 = 0.1302$ and GOF = 1.091 for all independent reflections [$R_1 = 0.0447$ was calculated against F for 546 observed reflections with $I > 2\sigma(I)$]. The number of the refined parameters was 67 (the ratio of the refined parameters for observed reflections was more than 7). All calculations were performed using SHELXTL PLUS 5.0 on IBM PC AT. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2001. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/81.

The main characteristic feature of the molecular structure of dilactone **1** with C_2 symmetry in a crystal† is the sense of its skeleton twist as synchro-(+,+) ($\tau_0 = 1.8°$) and synchro-(–,–) ($\tau_0 = –1.8°$) for (*R*,*R*)- (Figure 1) and (*S*,*S*)-enantiomeric forms, respectively, which is in accordance with the *ab initio* model (MP2/6-31G*, $\tau_0 = 0.9°$)[6] of enantiomer (*R*,*R*)-**1**.

The analogous twist character for a bicyclo[2.2.2]skeleton was observed for dilactone (±)-**3** in a crystal without the retention of C_2 symmetry ($\tau_0 = |4.4|$ and $|4.6|°$)[8] and confirmed by DFT (B3LYP/6-31G*) models of homochiral dilactones (*R*,*R*)-**3** and (*R*,*R*)-**4** [a single synchro-(+,+,+)-twist form, $\tau_0 = 2.9°$ (**3**), 3.1° (**4**)].[12]

As expected, the planarity of the lactone group [C–C(O)–O–C, τ_0] and the folding of the dilactone ring [the fold angle between mean planes of lactone groups is $\phi = 109.0°$ (XRD),† 110.2° (MP2)[6]] in **1** increased as compared with **3** [$\phi = 124.9°$ (XRD)[8]].

Considering the framework of dilactones **1**, **2** as a fusion of two γ-lactone rings in the envelope form, it is of interest to compare the sense of their lactone groups twist with that in γ-lactones, which mainly exist in the envelope conformation (XRD).[14] However, neither statistical XRD data[14] of γ-lactones nor an experimental study of γ-butyrolactone **7** by MW spectroscopy[15] cannot evaluate the character of twist related to the enantiomeric conformation[16] of the γ-lactone ring. For this reason, we performed DFT calculations‡ of **1**, **2** and **7**, according to which the lactone group of the enantiomeric envelope conformation of a molecule of **7** is reversely twisted ($\tau_0 = –2.1°$) as compared with that of the γ-lactone envelope conformation in (*R*,*R*)-**1** ($\tau_0 = 1.2°$), **2** ($\tau_0 = 1.4°$) of the same enantiomeric form.

This interesting effect is displayed in chiroptical properties, namely in the opposite sign of the *n*–π* Cotton effect (CE) of (*R*,*R*)-**1**[6] and γ-lactones[17] with the same enantiomeric conformation ring (see **7**). Previous correlations[17,18] between the sign of the *n*–π* CE and the γ-lactone ring enantiomeric conformation did not take into account the sense of twisting of the lactone group. On the other hand, a correlation between the twist sign of the C–NH–CO–C system in lactams and the sign of the *n*–π* CE was a subject of special interest,[18] and had an opposite relationship [(+)-τ_0, (+)-CE (*n*–π*) and *vice versa*][18] as compared with that for lactones.

As can be seen in Figure 1, a strong compression of endocyclic bond angles at bridgehead C(1)/C(4) [$\sum\omega_{endo} = 303.5°$ (XRD), 305.3° (MP2)[6] and 304.7° (DFT)‡] and carbonyl C(3)/

‡ The geometries of dilactones (*R*,*R*)-**1**, **2**, bicycle **6** and γ-butyrolactone **7** were completely optimised at the density functional theoretical level (DFT) with the conventional 6-31G* basis set using procedures implemented in the Gaussian 94 program system.[21] For the DFT calculations, a hybrid approach based on Becke's three parameter functional[22] was employed (Becke3LYP). Convergence criteria for the density matrix were set to 1×10^{-8}. All calculations were performed on an SGI Power Challenge computer. The calculated energies (in hartrees) and dipole moments (in debyes) are –572.46501 and 4.78 (**1**), –493.81629 and 4.63 (**2**), –271.47728 (**6**), –306.49261 and 4.48 (**7**), respectively.

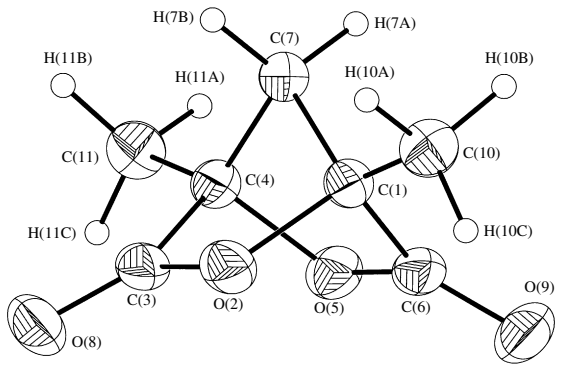

Figure 1 Molecular structure of dilactone **1**. Atoms C(4), O(5), C(6), O(9), and C(11) are symmetrically equivalent to atoms C(1), O(2), C(3), O(8), and C(10), respectively. Selected bond lengths (Å): C(1)–O(2) 1.491(3), C(1)–C(6) 1.536(3), C(1)–C(7) 1.530(3), C(1)–C(10) 1.490(3), O(2)–C(3) 1.366(3), C(3)–O(8) 1.193(2); selected bond and dihedral angles (°): C(1)–O(2)–C(3) 106.3(1), C(1)–C(6)–O(5) 106.3(2), C(1)–C(7)–C(4) 92.8(2), O(2)–C(1)–C(6) 102.6(2), O(2)–C(1)–C(7) 101.7(2), O(2)–C(1)–C(10) 110.0(2), C(6)–C(1)–C(7) 99.3(2), C(6)–C(1)–C(10) 117.5(2), C(7)–C(1)–C(10) 123.0(2), O(2)–C(3)–O(8) 123.2(2), C(4)–C(3)–O(8) 130.4(2), C(1)–O(2)–C(3)–C(4) (τ_0) 1.8, C(1)–O(2)–C(3)–O(8) –179.8.

C(6) carbon atoms [105.5° (MP2)[6] and 105.6° (DFT)‡] beyond their normal values (109.5° and 120°) leads to an increase in the *p*- and *s*-character of these carbon hybrid orbitals in 'internal' and 'external' bonds and hence to lengthening and shortening of these bonds, respectively. A comparison of the crystal structure of **1** with statistical XRD data for γ-lactones [C(1)–O(1) 1.350(9) Å, C(1)=O(2) 1.198(7) Å, C(1)–C(2) 1.515(7) Å, C(4)–O(1) 1.462(8) Å; see numbering for **7**][14] and bonds of the types $(C)_3$–*C*–*Me* (1.534 Å) and $(C)_3$–*C*–CH_2–C (1.538 Å)[13] confirms this tendency, except for shortened C(7)–C(1)/C(4) bridged bonds of **1** (Figure 1), whose length corresponds to the average XRD value for C sp^3–C sp^3 type bonds (1.530 Å).[13] The shortening of C(7)–C(1)/C(4) bridged bonds (C sp^3–C sp^3 type) as compared with C(1)–C(6)/C(4)–C(3) bonds (C sp^3–C sp^2 type) of the dilactone ring of **1** in a crystal, is in agreement with the MP2 (1.527 Å and 1.531 Å)[6] and DFT models (1.537 Å and 1.543 Å).‡ Interestingly, for norbornadiene **6**, the sequence of bond lengths of the C sp^3–C sp^3 [bridged C(7)–C(1)/C(4) bonds: 1.555(1) (XRD),[10] 1.552 (MP2)[10] and 1.560 Å (DFT)‡] and C sp^3–C sp^2 types [C(1)–C(2)/C(6) bonds: 1.536(1) (XRD),[10] 1.533 (MP2)[10] and 1.545 Å (DFT)‡] is reverse, as compared with dilactone **1**.

On the other hand, an increase in the folding of the dilactone ring boat of **1** {decreased C(1)···C(4) distance [2.216 (XRD), 2.220 (MP2)[6] and 2.213 Å (DFT)‡] and the angle of folding [ϕ = 110.7° (DFT)‡]} and almost equal characterictic top angles C(1)–C(7)–C(4) [92.8(2)° (XRD), 92.2° (MP2)[6] and 92.1° (DFT)‡] are observed, as compared with the boat of a six-membered ring [C(1)···C(4) 2.247 Å, ϕ = 115.1° (DFT)‡] and the bridged angle value in norbornadiene **6** [C(1)–C(7)–C(4) 92.5(1)° (XRD), 92.4° (MP2)[10] and 92.0° (DFT)‡], respectively.

An increased folding of the boat ring in **1** should also result in an increased strain in the skeleton of **1**, as compared to **6**. However, the strained folded frame structure of dilactone **1** is probably stabilised by the dominated through-bond intramolecular interaction of ester groups,[19] in spite of preferred through-space intramolecular interactions between two ethylenic moieties[10,20] in **6**.

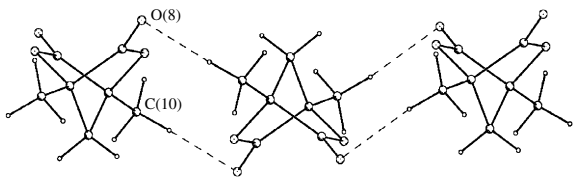

Figure 2 Hydrogen-bonded heterochiral chain in the crystal structure of **1**. Geometry parameters of short C(10)–H(10B)···O(8) contacts: H···O 2.40 Å, C···O 3.393(3) Å, C–H···O 155°, H···O=C 122.7°.

Thus, the experimental sense of twist of dimethyl-dilactones (**1**†, **3**[8]) in crystals is confirmed by *ab initio* models for **1**–**4** in a free state. In addition to data on the torsional energy surface of (*R*,*R*)-**2**[16] and (*R*,*R*)-**4**[12] obtained by the MM2(91) method, these results show that the above twist sense for lactone groups in bridged dilactones **1**–**4** is a common tendency to form a ground-state conformation. The preference of the found enantiomeric forms over the possible diastereomeric *synchro*-(+,+)-(*R*,*R*)- and *synchro*-(–,–)-(*S*,*S*)-twist forms can be explained by more favourable intramolecular dipole–dipole interaction of C=O groups.[12,16]

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