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cis-1,2,3,6-Tetrahydrophthalic anhydride at 173 K

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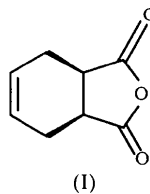
Abstract

The title compound, C₈H₈O₃, (I), crystallizes with two nearly identical molecules in the asymmetric unit. Each molecule has a boat conformation and non-crystallographic mirror symmetry. The structure was determined in connection with a study of the possible chemical decomposition of the compound in different solvents and in contact with the atmosphere. A similar boat conformation was found in five of six structures retrieved from the Cambridge Structural Database which contain (I) as a moiety. The present structure exhibits nearly the same packing motif as the recently found monoclinic polymorph [Ben Fredj, Ben Redjeb, Ben Amor & Driss (1998). *Acta Cryst.* **C54**, 1710–1712].

Comment

The structure of the title compound, (I), was determined by X-ray structure analysis during investigations on

the possibility of chemical decomposition in solution, especially hydrolysis. Solutions of (I) in toluene, hexane, acetone, ether and tetrahydrofuran were exposed to air and diffused daylight for one week. During the time of examination no decomposition could be observed.



There are only a few applications for (I) in chemistry and industry, but it offers very attractive properties as an intermediate or starting material in chemical synthesis because it provides an easy access to other cyclohexene-1,2-dicarboxylic anhydrides and their analogues (Bailey & Amstutz, 1956). Furthermore, it is easily obtainable from maleic anhydride and butadiene. Also, in contrast to many other [4+2]-cycloaddition adducts, its formation is thermally irreversible which provides an explanation for the very good yields in the synthesis described below. (I) was first described by Diels & Alder (1928). They obtained it in theoretical yield by dissolving butadiene and maleic anhydride in a small amount of benzene and leaving this mixture for 12 h in an autoclave at room temperature. Finally, they heated it for 5 h to 373 K. The reported yield could not be reproduced by other authors, but yields better than 90% of the theoretical value have been reported (Kohler & Jansen, 1938; Jenkins & Costello, 1946; Fieser & Novello, 1942). As expected, no *trans* adduct is formed during the synthesis. Another application of (I) was reported by Fieser & Novello (1942), using it as a starting material for the synthesis of a benzantracene compound.

(I) crystallizes with two nearly identical molecules in the asymmetric unit. A least-squares fit between all non-H atoms gives an r.m.s. deviation of 0.021 Å. Each molecule has approximate mirror symmetry. Additional symmetry elements between the similar moieties could not be detected. Bond lengths and angles do not show any extraordinary values. The molecules have a boat conformation with a central plane (C4, C5, C8, C9 and C4A, C5A, C8A, C9A, respectively), a bow plane (C9, C1, O2, C3, C4 and C9A, C1A, O2A, C3A, C4A, respectively) and a stern plane (C5, C6, C7, C8 and C5A, C6A, C7A, C8A, respectively). The dihedral angles are 61.02(6) and 61.17(6)° between the central plane and the bow plane, and 47.28(6) and 48.08(6)° between the central plane and the stern plane. A search of the Cambridge Structural Database (Allen & Kennard, 1993; Version 5.15, April 1998) revealed that (I) appears as a moiety of six structures. In five of them (Lee, Peng, Lush, Mu & Liu, 1988; Lee, Peng,

Lush & Liu, 1988; Tripathy *et al.*, 1991; Maddaluno *et al.*, 1996; Mukherjee *et al.*, 1994) the same boat conformation as in the title compound was found with a mean angle of $60(2)^\circ$ between the central and bow planes, and $50(1)^\circ$ between the central and stern planes. There is only one exception (Lee, Peng, Lush, Mu & Liu, 1988): in dicarbonyl-(η^5 -cyclopentadienyl)-[(cyclohexene-4,5-dicarboxylic anhydride-3-yl)methyl]iron(II) the C=C double bond of the cyclohexene ring is tilted away from the five-membered ring, so that a chair-like conformation of the bicyclic system results.

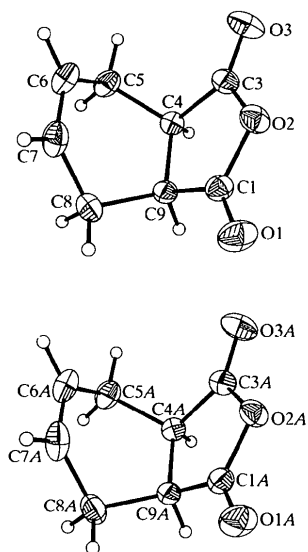


Fig. 1. A perspective view (not the relative orientation in the crystal) of the independent molecules of the title compound with the atom-numbering scheme. Displacement ellipsoids are at the 50% probability level.

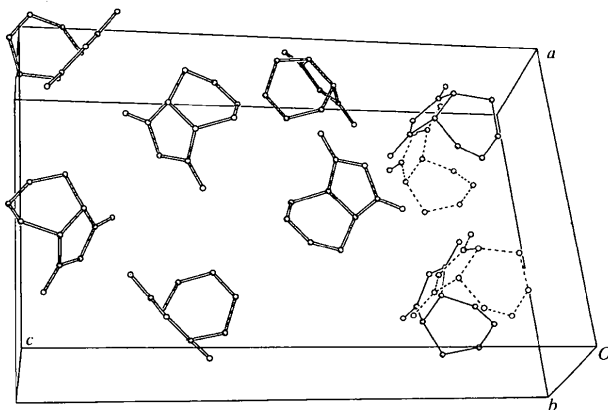


Fig. 2. Packing diagram showing the superimposition of the monoclinic structure on the orthorhombic structure and cell. Where the molecular positions coincide (in six out of eight molecules) the bonds are shown as double lines. For the other two molecules, full lines represent the orthorhombic structures, dotted lines the monoclinic.

The title compound shows polymorphism: recently Ben Fredj *et al.* (1998) crystallized it from water-free toluene and found a monoclinic structure in space group $P2_1/a$ [hereinafter (I_{mon})]. The matrix $\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0.5 & 0 \end{pmatrix}$ transforms the cell parameters of (I_{mon}) almost exactly to those of (I), and the packing of both structures is very similar. Fig. 2 reveals that after transforming (I_{mon}) to the orthorhombic cell, six of the eight molecules in the unit cell occupy almost exactly the same positions, whereas the remaining two are mutually related by a non-crystallographic mirror plane.

Experimental

To a solution of sublimed maleic anhydride in benzene, gaseous butadiene was added over a period of 30 to 40 min under heating and stirring. A temperature of 343 to 348 K was reached and on completion of the addition of butadiene, the mixture was continuously stirred for 2 h at this temperature. The resultant solution was cooled overnight in a refrigerator and the precipitated product was isolated by filtration. A second fraction was obtained from the filtrate by adding petrol-ether and further filtration. The combined fractions were purified by washing with cooled petrol-ether. Suitable crystals for the X-ray structure determination were obtained by slow evaporation from an ether solution.

Crystal data

$\text{C}_8\text{H}_8\text{O}_3$
 $M_r = 152.14$
 Orthorhombic
 $Pca2_1$
 $a = 13.322(1) \text{ \AA}$
 $b = 5.167(1) \text{ \AA}$
 $c = 20.938(1) \text{ \AA}$
 $V = 1441.3(3) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.402 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 8192 reflections
 $\theta = 1-25^\circ$
 $\mu = 0.108 \text{ mm}^{-1}$
 $T = 173(2) \text{ K}$
 Plate
 $0.55 \times 0.51 \times 0.15 \text{ mm}$
 Colourless

Data collection

Siemens CCD three-circle diffractometer
 ω scans
 Absorption correction: empirical; *SADABS* (Sheldrick, 1996)
 $T_{\text{min}} = 0.943$, $T_{\text{max}} = 0.984$
 31 023 measured reflections
 4333 independent reflections

3958 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\text{max}} = 31.27^\circ$
 $h = -19 \rightarrow 18$
 $k = -7 \rightarrow 7$
 $l = -30 \rightarrow 30$
 433 standard reflections
 frequency: 1200 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.085$
 $S = 1.056$
 4333 reflections
 200 parameters

$\Delta\rho_{\text{max}} = 0.246 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.138 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL*
 Extinction coefficient: 0.0092 (12)

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 0.2161P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

Scattering factors from *International Tables for Crystallography* (Vol. C)
 Absolute structure: Flack (1983)
 Flack parameter = 0.3 (6)

The data collection nominally covered a sphere of reciprocal space by a combination of seven sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω . The crystal-to-detector distance was 4.5 cm. Coverage of the unique set is 100% complete to at least 28° in θ . Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters [$U(H) = 1.2U_{eq}(C)$] using a riding model with C—H(tertiary) = 1.00, C—H(secondary) = 0.99 or Csp^2 —H = 0.95 Å. The structure contains only C, H and O atoms and since Mo $K\alpha$ radiation was used, the absolute structure could not be determined.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XP (SHELXTL-Plus)*; Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1235). Services for accessing these data are described at the back of the journal.

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$\Delta^{8,9}$ -Decarboxyfibleucin from *Fibraurea chloroleuca* Miers

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Abstract

In the title compound, 2-(3-furyl)-1,4,6,6a,7,10,10a,10b-octahydro-6a,10b-dimethyl-2*H*-naphtho[2,1-*c*]pyran-7,4-dione, C₁₉H₂₀O₄, one of the fused cyclohexane rings adopts a half-chair conformation and the other a sofa conformation. The conformation of the pyran ring is intermediate between sofa and half-chair. Screw-related molecules along the *c* axis form an infinite one-dimensional chain.

Comment

The compounds fibraurin, (I), and fibleucin, (II), isolated from the medicinal plant *Fibraurea chloroleuca* Miers (Ito & Furukawa, 1969), have been found to possess antitumour and antifungal activities (Nakanishi *et al.*, 1965). We wished to prepare derivatives from both of them, which might be more water soluble and exhibit enhanced antifungal activity. Opening either of the lactone rings in these compounds seemed like a reasonable option. However, attempted transesterification of the mixture with titanium tetraisopropoxide as the catalyst (Seebach *et al.*, 1982) indicated that fibleucin alone was slowly and poorly transformed into two products. Preliminary gas chromatography–mass spectrometry studies indicated that both these products were decarboxylated fibleucin. Currently, there is only one report in the literature of decarboxylation of a similar compound, namely, columbin to decarboxy-columbin (Barton & Elad, 1956). Decarboxylation of fibleucin, but not of fibraurin, was subsequently found to proceed smoothly and completely in boiling xylene. This reaction allowed the facile separation of fibraurin from a mixture of fibraurin and fibleucin. The products were easily isolated by thin layer chromatography. The major product from the decarboxylation of fibleucin was shown by spectroscopic studies to be $\Delta^{9,10}$ -decarboxy-

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