

Dimethyl 3,6-dioxatetracyclo[6.1.0.0^{2,4}.0^{5,7}]nonane-2,9-dicarboxylateTuncer Hökelek,^{a*} Murat Çelik,^b
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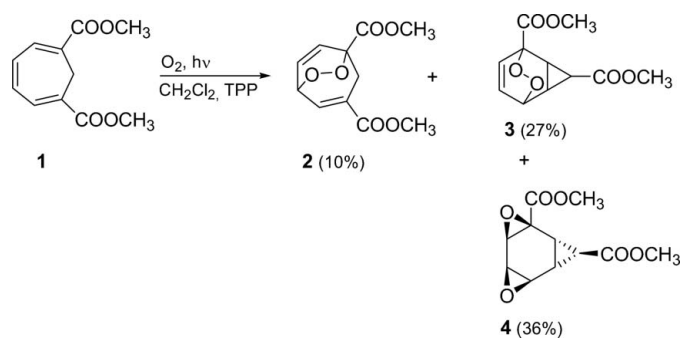
Key indicators

Single-crystal X-ray study
 $T = 296$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.040
 wR factor = 0.117
Data-to-parameter ratio = 11.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, $\text{C}_{11}\text{H}_{12}\text{O}_6$, has a norcarane structure, which is obtained by the photooxygenation reaction of a cycloheptatriene derivative. The cyclohexane ring is planar. The intermolecular $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds are effective in stabilizing the crystal structure, in which they form parallel infinite chains along the b axis.

Comment

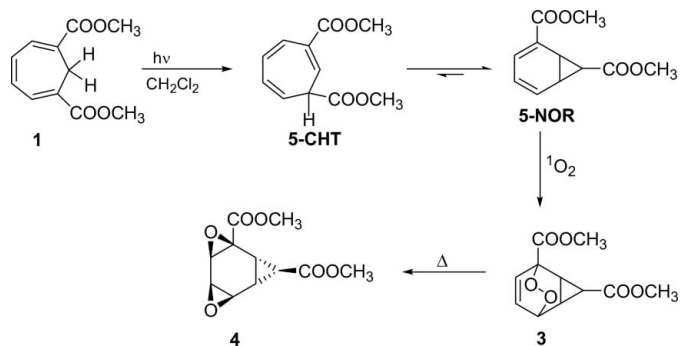
Troponone and tropolone have fascinated organic chemists for well over 50 years. A number of syntheses of tropolone derivatives have been developed (Asao & Oda, 1985). In this connection, with the development of new synthetic strategies for tropolones, we recently studied the applicability of bicyclic endoperoxides derived by the cycloaddition of singlet oxygen to the appropriate cyclic dienes and synthesized a number of new troponone and tropolone derivatives (Güney *et al.*, 2005; Daştan *et al.*, 2001; Çelik *et al.*, 2000). The cycloheptatriene derivative 1 was submitted to the photooxygenation reaction with tetraphenylporphyrin (TPP) as sensitizer in CH_2Cl_2 at room temperature. After 17 h, ^1H NMR analysis indicated complete consumption of 1 and the formation of endoperoxides 2 and 3 and the bis-epoxide 4.



The expected cycloaddition product, 2, was formed from the [2 + 4]-cycloaddition of singlet oxygen to the diene unit of the cycloheptatriene system. However, the products 3 and 4 are not formed from the original skeleton. We assume that the starting material 1 first undergoes a photochemically allowed 1,7-suprafacial hydrogen shift under the reaction conditions and forms the isomeric cycloheptatriene derivative 5-CHT. Since one of the carboxymethyl groups in 5-CHT is now attached to the sp^3 -hybridized C7 atom, it can stabilize the norcaradiene structure and shift the cycloheptatriene–norcaradiene equilibrium (Balci, 1992) to the side of norcaradiene 5-NOR. The resulting norcaradiene 5-NOR has a planar diene unit. Therefore, it can add singlet oxygen much

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faster than the diene unit in cycloheptatriene. Addition of singlet oxygen to norcaradiene 5-NOR results in the formation of the norcaradiene endoperoxide 3. The norcaradiene endoperoxides are not very stable. They can easily undergo homolytic oxygen–oxygen bond cleavage followed by the addition of the resulting oxygen radicals to the adjacent double bond to form the title compound, 4. The structural assignments of the compounds were established by ^1H and ^{13}C NMR spectra and the crystal structure of 4 is reported here.



Compound 4 has a norcarane structure, containing two carboxymethyl groups and two epoxide groups (Fig. 1). The cyclohexane ring *A* (C1–C6) is planar, as evidenced by the torsion angles, with the C–C bond lengths lying in the range 1.463 (3)–1.487 (3) Å and C–C–C bond angles in the range 119.54 (19)–120.3 (2)°. The planarity of ring *A* may be due to the existence of the two epoxides *B* (C1/C2/O5) and *C* (C3/C4/O6) and one cyclopropane *D* (C5–C7). The planarity of the cyclohexane ring is a rare occurrence and, to the best of our knowledge, there are only a few reported structures (Kabuto *et al.*, 1973; Little & Druck, 1974; Vogel *et al.*, 1977) containing planar cyclohexane rings. The orientations of the epoxide and cyclopropane groups with respect to the planar cyclohexane ring are given by the dihedral angles $A/B = 74.1 (1)^\circ$, $A/C = 73.1 (1)^\circ$ and $A/D = 73.2 (1)^\circ$.

In the carboxymethyl groups, O2–C8 [1.327 (3) Å] and C7–C8 [1.471 (3) Å] bonds are a little shorter than the corresponding ones O4–C10 [1.335 (2) Å] and C1–C10 [1.498 (3) Å]. On the other hand, the O1–C8–C7 [125.2 (2)°] bond angle is enlarged while the O1–C8–O2 [123.6 (2)°] and O2–C8–C7 [111.22 (19)°] angles are narrowed with respect to O3–C10–C1 [123.3 (2)°], O3–C10–O4 [124.2 (2)°] and O4–C10–C1 [112.48 (18)°], respectively.

The crystal packing is stabilized by intermolecular C–H...O [H71...O1ⁱ = 2.53 (3) Å, C7...O1ⁱ = 3.342 (3) Å, C7–H71...O1ⁱ = 144 (2)°; symmetry code: (i) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$] hydrogen bonds, which form parallel infinite chains extended along the *b* axis and stacked along the *a* axis (Fig. 2). Dipole–dipole and van der Waals interactions are also effective in the molecular packing.

Experimental

Dimethyl cyclohepta-3,5,7-triene-1,3-dicarboxylate (1) was synthesized according to the literature (Vogel *et al.*, 1980, 1986). A CH_2Cl_2 solution (30 ml) of substituted cycloheptatriene 1 (3 g, 14.42 mmol)

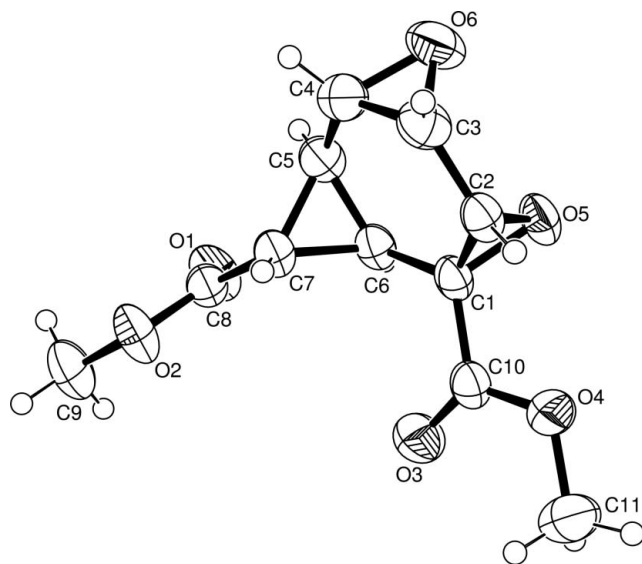


Figure 1
An ORTEP-3 (Farrugia, 1997) drawing of the title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

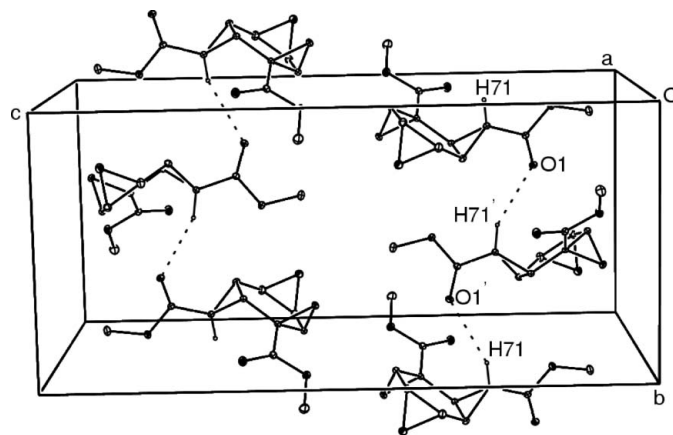


Figure 2
Packing diagram, viewed down the *a* axis. Hydrogen bonds are shown as dashed lines.

and TPP (50 mg, 0.075 mmol) was irradiated with a projector lamp (500 W), while a slow stream of dry O_2 was passed through it continuously. The progress of the photo-oxygenation was monitored by ^1H NMR spectroscopy until consumption of the starting material was essentially complete (17 h). The solvent was evaporated at room temperature. Column chromatography (silica gel, Et_2O /hexane 30:70) of the crude product gave the bicyclic endoperoxides 2 (yield 0.3 g, 10%, m.p. 372–374 K) and 3 (yield 0.81 g, 27%, m.p. 377–378 K) and *syn*-bisepoxide 4 (yield 1.08 g, 36%, m.p. 402–403 K). Compound 4 was recrystallized from *n*-hexane/ CH_2Cl_2 (1:1).

Crystal data

$\text{C}_{11}\text{H}_{12}\text{O}_6$
 $M_r = 240.21$
 Orthorhombic, *Pbca*
 $a = 12.3492 (9) \text{ \AA}$
 $b = 9.0553 (14) \text{ \AA}$
 $c = 19.813 (2) \text{ \AA}$
 $V = 2215.6 (4) \text{ \AA}^3$

$Z = 8$
 $D_x = 1.440 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 0.12 \text{ mm}^{-1}$
 $T = 296 (2) \text{ K}$
 Block, colourless
 $0.4 \times 0.25 \times 0.15 \text{ mm}$

Data collection

Enraf–Nonius CAD-4
diffractometer
Non-profiled ω scans
Absorption correction: none
1983 measured reflections
1983 independent reflections

1360 reflections with $I > 2\sigma(I)$
 $\theta_{\max} = 25.6^\circ$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.117$
 $S = 1.03$
1983 reflections
176 parameters
H atoms treated by a mixture of
independent and constrained
refinement

$w = 1/[\sigma^2(F_o^2) + (0.0564P)^2 + 0.581P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.21 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.18 \text{ e } \text{Å}^{-3}$
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0097 (10)

Table 1

Selected geometric parameters (Å, °).

O1—C8	1.200 (3)	O5—C2	1.436 (3)
O2—C9	1.445 (3)	O5—C1	1.448 (2)
O3—C10	1.199 (2)	O6—C3	1.440 (3)
O4—C11	1.445 (3)	O6—C4	1.445 (3)
C8—O2—C9	116.47 (18)	O5—C2—C1	59.65 (13)
C10—O4—C11	115.74 (18)	O5—C2—C3	118.63 (19)
C2—O5—C1	61.53 (13)	O6—C3—C4	59.70 (15)
C3—O6—C4	60.94 (15)	O6—C3—C2	117.3 (2)
O5—C1—C2	58.82 (13)	O6—C4—C3	59.36 (14)
O5—C1—C6	116.46 (17)	O6—C4—C5	117.2 (2)
O5—C1—C10	115.46 (16)		
C2—C1—C6—C5	−1.3 (3)	C2—C3—C4—C5	−0.1 (4)
C3—C2—C1—C6	2.9 (3)	C4—C5—C6—C1	−1.0 (3)
C1—C2—C3—C4	−2.2 (3)	C6—C5—C4—C3	1.7 (3)

Atom H6 and methyl H atoms were positioned geometrically, with C—H = 0.96 and 0.98 Å for methyl and methine H atoms, respec-

tively, and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$, where $x = 1.5$ for methyl H and $x = 1.2$ for methine H atoms. The remaining H atoms were located in a difference map and refined isotropically [C—H = 0.94 (2)–0.97 (2) Å].

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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