$w = 1/[\sigma^2(F_o^2) + (0.0871P)^2 + 0.3698P]$
where $P = (F_o^2 + 2F_c^2)/3$

Absolute configuration: Flack (1983)
Flack parameter = −0.3 (2)

Table 3. *Selected geometric parameters (Å, °) for (2)*

S1—C1	1.800 (9)	O2—C10	1.477 (8)
S1—C3	1.883 (7)	O3—C12	1.185 (10)
O1—C3	1.413 (8)	O4—C16	1.360 (5)
O1—C2	1.429 (9)	O4—C19	1.416 (9)
O2—C12	1.337 (9)		
C1—S1—C3	92.3 (4)	C2—C1—S1	105.0 (6)
C3—O1—C2	111.5 (6)	O1—C3—S1	104.6 (4)
C12—O2—C10	116.5 (6)	C8—C3—S1	109.5 (5)
C16—O4—C19	118.2 (6)	C4—C3—S1	108.4 (5)

For (1), the space group $P\bar{1}$ was determined from the statistical analysis, intensity distribution and successful solution and refinement of the structure. Based on the systematic absences, statistical analysis, intensity distribution, successful solution and refinement of the structure, the space group $P2_1$ was assigned to (2). The phenyl rings in both structures were constrained to refine as regular hexagons.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1994); program(s) used to solve structures: *SAPI*91 (Fan, 1991); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1317). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1963–1966

cis-anti-cis-Tricyclo[6.4.0.0^{2,7}]dodecane-3,12-dione and *cis-anti-cis*-Tricyclo[6.4.0.0^{2,7}]dodecane-3,9-dione

ANGELA TAYLOR, EDMUND J. EISENBRAUN, CLINTON E. BROWNE AND ELIZABETH M. HOLT

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, USA. E-mail: chememh@mvs.okstate.edu

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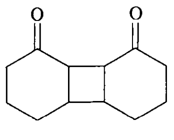
Abstract

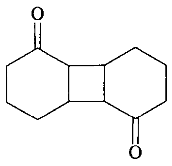
The single-crystal X-ray structures of two photochemical products of 2-cyclohexenone have identified them as the head-to-head and head-to-tail *cis-anti-cis* dimers ($C_{12}H_{16}O_2$) formed by 2+2 addition. The cyclobutane ring is twisted in the head-to-head isomer but flat in the head-to-tail compound.

Comment

The photochemical dimerization of 2-cyclopentenone or 2-cyclohexenone has been shown to proceed *via* an excited triplet state to give dimers of head-to-head (HH) and head-to-tail (HT) orientation along with photorearrangement, photoreduction and photocycloaddition products (Schuster, 1989; Schuster & Insogna, 1991). The relative positions of substituents at the adjacent junctures of the four-membered central ring and two different five- or six-membered rings are identified by *anti* or *syn* terminology (Fig. 1). The relative positions of substituents at the junction of one four- and one five- or six-membered ring are identified by *cis* or *trans*.

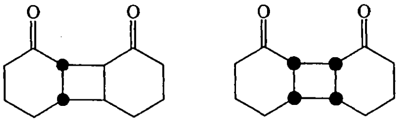


(1)

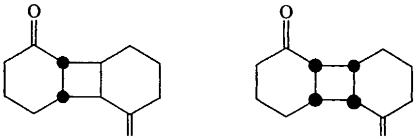


(2)

The dimerization of 2-cyclopentenone appears to lead exclusively to *cis* isomers. With the enlargement of the cyclo-enone ring to six members, there are reports of *trans* isomers (Eaton, 1962; Lem *et al.*, 1993).



HH *cis-anti-cis* HH *cis-syn-cis*



HT *cis-anti-cis* HT *cis-syn-cis*

Fig. 1. Photochemical products of cyclohexenone

The major photodimers, (1), m.p. 352–353 K, and (2), m.p. 326–328 K, of 2-cyclohexenone were described in 1964 (Valentine, Turro & Hammond, 1964) and their structure assignments, (1), HH *cis-anti-cis*, and (2), HT *cis-anti-cis*, were proposed in 1967 (Lam, Valentine & Hammond, 1967). The HT photodimer, (2), predominates when photolysis is carried out on a neat liquid or in non-polar solvents (Lam, Valentine & Hammond, 1967; Wagner & Buchek, 1969; Schuster, 1989). However, in polar solvents, the HH photodimer, (1), predominates (Wagner & Buchek, 1969).

We have observed four substances of molecular weight 192.2 upon GC–MS analysis of the products of ultraviolet irradiation of 2-cyclohexenone and shown these major products to be those predicted: the *cis-anti-cis* HH, (1), and *cis-anti-cis* HT, (2), dimers. Oddly enough, the single-crystal X-ray structures of these two compounds have not appeared in the literature until now.

Structural details of interest for the two structures are the relative planarity of the cyclobutane ring, the relative lengths of the bonds forming sides of this ring, and the conformations of the six-membered rings.

The HH dimer, (1), has a puckered cyclobutane ring [dihedral angle between the planes C4′, C8″, C4″ and C8′, C8″, C4″ of 155.4 (4)°] as does the HH *cis-anti-cis* dimer produced from irradiation of 3-phenylcyclopent-2-enone (dihedral angle 152.4°) (Shaw, Fratini & Adams, 1974). However, the HH *cis-anti-cis* dimer of 3-methylcyclopent-2-enone crystallizes with a planar cyclobutane ring (Yvon, 1974). The centrosymmetric HT dimer, (2), displays a flat cyclobutane ring as does the centrosymmetric HT *cis-anti-cis* dimer of cyclopent-2-enone (Margulis, 1965).

It has been noted that dimers of cyclohexene, *i.e.* tricyclo[6.4.0.0^{2,7}]dodecanes, have alternating C—C bond lengths within the cyclobutane moiety: in *trans-anti-trans* molecules, those C—C bonds which are also part of cyclohexane rings (intra) are shorter (1.539 Å) than those between six-membered rings (inter) (1.557 Å), whereas in the *trans-syn-trans* model, the intra C—C bonds (1.539 Å) are expected to be longer than the inter ones (1.505 Å) (Salomon *et al.*, 1974).

Both title compounds display an alternation of C—C bond lengths within the cyclobutane ring: the HH *cis-anti-cis* isomer, (1), has intra C—C bonds [C4′—C8″ 1.547 (4) and C4″—C8′ 1.548 (4) Å] which are longer than the inter C—C bonds [C8″—C8′ 1.538 (3) and C4′—C4″ 1.540 (4) Å], whereas the HT *cis-anti-cis* molecule has longer inter C—C bond lengths [C4′—C4″^{i} 1.545 (3) Å; symmetry code: (i) $-x, -y, 1-z$] than intra ones [C4′—C4″ 1.524 (3) Å]. Comparison with similar cyclobutane C—C bond distances in known HH and HT *cis-anti-cis* cyclopent-2-enone reveals no consistent pattern of alternation of bond length.

Compounds (1) and (2) have six-membered rings in flattened chair conformations as expected.

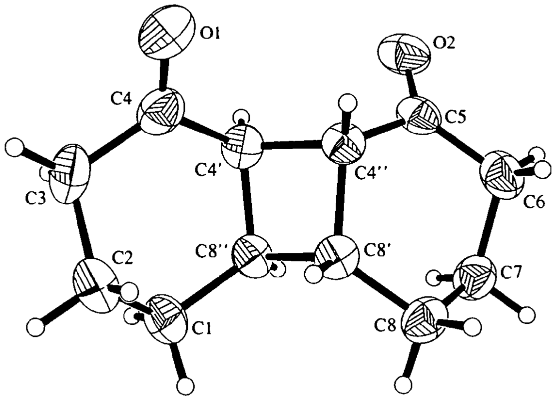


Fig. 2. Projection view of *cis-anti-cis*-tricyclo[6.4.0.0^{2,7}]dodecane-3,12-dione (HH) (ellipsoids are drawn at the 50% probability level).

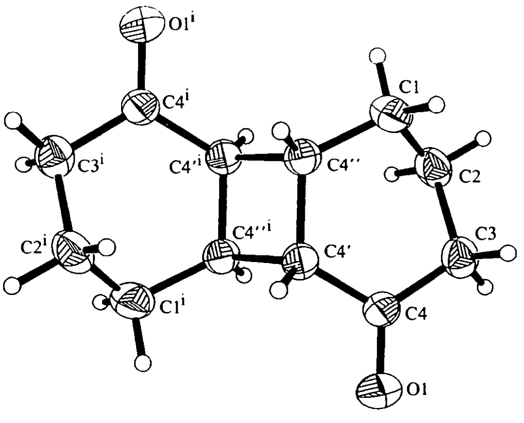


Fig. 3. Projection view of *cis-anti-cis*-tricyclo[6.4.0.0^{2,7}]dodecane-3,9-dione (HT) (ellipsoids are drawn at the 50% probability level).

Experimental

Freshly distilled 2-cyclohexenone (48 g in 950 ml hexane) was magnetically stirred and photodimerized for 80 h using a Pyrex-filtered 450 W Hanovia lamp. The crude product was steam distilled to remove volatile impurities. The product diones were also slowly steam distilled. Gas chromatography (Varian 3700 using hydrogen-flame detection and fitted with a 15 M, J&W, DB-5MS, 1.0 micron film thickness, 0.25 mm ID capillary column operating between 333–573 K) showed the steam-distilled fraction to be a complex mixture containing several major peaks later shown to include (2) and (1). Distillation (383–393 K/0.1 mm Hg) of the steam distillation residue gave a colorless oil (35 g) which showed four closely grouped but distinct peaks with the two middle peaks [(2) and (1) in order of appearance] predominating. The GC trace was free of other peaks. GC–MS (Hewlett-Packard) studies showed the first three peaks to have m/z = 192 and $m/2$ = 96 characteristic of diones (2) and (1) (Ziffer, Fales, Milne & Field, 1970). Chromatography of the distilled oil (30 g) on acidic alumina (300 g, E. Merck, activity 1) with hexane was carried out as previously described (Browne, Buchanan & Eisenbraun, 1977) to give, after 2 h of extraction, crystalline (2) accompanied by 10–15% of (1). Recrystallization of this initial fraction from ether/hexane or rechromatography gave pure (2), m.p. 328–330 K. Additional extractions with hexane gave oily crystals of mixtures showing four peaks. The oily crystals were combined and blotted with filter paper to remove adhering oil. This treatment or prolonged centrifuging gave a thick paste of colorless microcrystals which showed (2) and (1) with the former predominating. The paste was wrapped in multiple layers of filter paper and squeezed in a vice between Teflon-faced wooden blocks. Repeated pressing until oil no longer was expressed, turned the crystals into a hard colorless cake. GC analysis of the cake showed (1) to be the major peak. Recrystallization of this mixture from ether/hexane gave needles and plates [mainly (2)] adhering to the upper part of the beaker upon solvent evaporation. The crystals deposited at the bottom of the beaker appeared as square blocks from which pure (1), m.p. 350–352 K, was obtained on subsequent recrystallization from ether/hexane.

Compound (1)

Crystal data

$C_{12}H_{16}O_2$
M_r = 192.2
Orthorhombic
Pbca
a = 10.703 (2) Å
b = 10.990 (1) Å
c = 17.584 (5) Å
V = 2068.3 (7) Å^3
Z = 8
D_x = 1.236 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 63 reflections
θ = 3.694–12.433°
μ = 0.082 mm^{-1}
T = 298 K
Rhomb
0.200 × 0.155 × 0.150 mm
Colorless

Data collection

Syntex *P*4 four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2996 measured reflections
2336 independent reflections
852 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.077

$\theta_{\rm max}$ = 27.49°
$h = -1 \rightarrow 13$
$k = -1 \rightarrow 14$
$l = -1 \rightarrow 22$
3 standard reflections every 97 reflections intensity decay: 0.01%

Refinement

Refinement on F^2
$R(F)$ = 0.059
$wR(F^2)$ = 0.156
S = 0.725
2336 reflections
129 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.1363P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.001

$\Delta\rho_{\rm max}$ = 0.15 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.16 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0013 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (1)*

O1—C4	1.209 (3)	C4′—C8″	1.547 (4)
O2—C5	1.199 (3)	C4″—C5	1.515 (4)
C1—C2	1.509 (4)	C4″—C8′	1.548 (4)
C1—C8″	1.519 (4)	C5—C6	1.489 (4)
C2—C3	1.532 (5)	C6—C7	1.519 (4)
C3—C4	1.480 (5)	C7—C8	1.510 (4)
C4—C4′	1.494 (4)	C8—C8′	1.517 (4)
C4′—C4″	1.540 (4)	C8′—C8″	1.538 (3)
C2—C1—C8″	112.9 (2)	O2—C5—C6	123.1 (3)
C1—C2—C3	109.9 (3)	O2—C5—C4″	121.3 (3)
C4—C3—C2	110.2 (3)	C6—C5—C4″	115.5 (3)
O1—C4—C3	122.2 (3)	C5—C6—C7	110.2 (3)
O1—C4—C4′	121.2 (3)	C8—C7—C6	110.6 (2)
C3—C4—C4′	116.5 (3)	C8′—C8—C7	112.9 (2)
C4—C4′—C4″	114.3 (2)	C8—C8′—C8″	118.9 (2)
C4—C4′—C8″	115.0 (2)	C8—C8′—C4″	118.2 (2)
C4″—C4′—C8″	88.79 (18)	C8″—C8′—C4″	88.80 (18
C5—C4″—C4′	115.6 (2)	C1—C8″—C8′	119.5 (2)
C5—C4″—C8′	115.6 (2)	C1—C8″—C4′	118.1 (2)
C4′—C4″—C8′	88.40 (18)	C8′—C8″—C4′	88.54 (18

Compound (2)

Crystal data

$C_{12}H_{16}O_2$
M_r = 192.2
Monoclinic
$P2_1/n$
a = 8.342 (3) Å
b = 5.661 (3) Å
c = 10.553 (4) Å
β = 93.23 (1)°
V = 497.6 (4) Å^3
Z = 2
D_x = 1.283 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 35 reflections
θ = 5.34–12.36°
μ = 0.086 mm^{-1}
T = 298 K
Chunk
0.21 × 0.20 × 0.19 mm
Colorless

Data collection

Syntex *P*4 four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1287 measured reflections
870 independent reflections
456 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.073

$\theta_{\rm max}$ = 24.99°
$h = -1 \rightarrow 9$
$k = -1 \rightarrow 6$
$l = -12 \rightarrow 12$
3 standard reflections every 97 reflections intensity decay: 0.01%

Refinement

Refinement on F^2
$R(F) = 0.055$
$wR(F^2) = 0.139$
$S = 0.891$
870 reflections
66 parameters
$w = 1/[\sigma^2(F_o^2) + (0.048P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.15$ e Å^{-3}
$\Delta\rho_{\min} = -0.14$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.010 (10)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C4	1.207 (3)	C4—C4′	1.483 (4)
C1—C4′′	1.490 (4)	C4′—C4′′	1.524 (3)
C1—C2	1.493 (4)	C4′—C4′′′$^{\rm i}$	1.545 (3)
C2—C3	1.508 (4)	C4′′—C4′$^{\rm i}$	1.545 (3)
C3—C4	1.467 (4)		
C4′′—C1—C2	112.3 (3)	C4—C4′—C4′′	119.0 (2)
C1—C2—C3	109.9 (3)	C4—C4′—C4′′′$^{\rm i}$	113.0 (2)
C4—C3—C2	112.3 (2)	C4′′—C4′—C4′′′$^{\rm i}$	90.22 (19)
O1—C4—C3	121.0 (3)	C1—C4′′—C4′	116.6 (3)
O1—C4—C4′	119.8 (2)	C1—C4′′—C4′$^{\rm i}$	117.5 (2)
C3—C4—C4′	119.2 (2)	C4′—C4′′—C4′$^{\rm i}$	89.78 (19)

Symmetry code: (i) $-x, -y, 1 - z$.

Variable scan rate, a θ–2θ scan mode with a scan width of 0.6° below $K\alpha_1$ and 0.6° above $K\alpha_2$ to a maximum 2θ value of 50°. H-atom positions were calculated using idealized geometry and constrained to this geometry.

For both compounds, data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1038). Services for accessing these data are described at the back of the journal.

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6-Hydroxy-5,7-dimethoxy-4-methylcoumarin

Amarjit Singh,[a] Rajesh Kumar,[a] Virinder S. Parmar[a] and William Errington[b]

[a]*Department of Chemistry, University of Delhi, Delhi 110 007, India, and* [b]*Department of Chemistry, University of Warwick, Coventry CV4 7AL, England. E-mail: w.errington@warwick.ac.uk*

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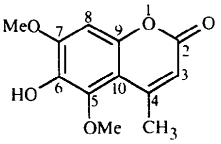
Abstract

The synthesis and structure of the title compound, $C_{12}H_{12}O_5$, are described. The molecule is approximately flat with the exception of the 5-methoxy group which is twisted at 70.1 (3)° with respect to the aromatic ring. The molecules pack together with intermolecular hydrogen bonding between the O4 and O2(x, y, $z - 1$) atoms.

Comment

Coumarins constitute an important group of natural products and many of their analogues are found to be biologically active (Murray, Medez & Brown, 1982). 4-Methylcoumarins have been found to possess a wide range of biological activities *viz.* choleretic, analgesic, antispermatogenic and diuretic properties (Deana, 1983; Yang *et al.*, 1981). We have found that 18 4-methylcoumarins bearing different functionalities inhibit effectively the rat liver microsome mediated aflatoxin B_1-DNA binding *in vitro* (Raj *et al.*, 1996). Encouraged by these findings, we have synthesized a series of novel 4-methylcoumarins for structure–activity studies. This paper reports the synthesis and structure of a new coumarin in this series, namely, 6-hydroxy-5,7-dimethoxy-4-methylcoumarin, (I).



(I)