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The Crystal and Molecular Structure of Tricyclo[5,3,0,$0^{2,6}$]decane-4,9-dione, a Photochemical Product of Cyclodeca-3,8-diene-1,6-dione

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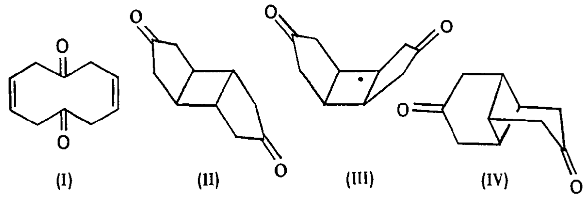
Irradiation of *cis,cis*-cyclodeca-3,8-diene-1,6-dione leads to a tricyclic *anti* product $C_{10}H_{12}O_2$. Crystals are orthorhombic, space group *Pbca*, with $a=10{\cdot}852$ (4), $b=13{\cdot}086$ (4), and $c=11{\cdot}739$ (5) Å, $Z=8$. 1490 independent reflexions were measured on an automated diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The structure was solved by direct methods and refined by block-diagonal and full-matrix least-squares methods to $R=0{\cdot}046$. The non-planar cyclobutane ring has a dihedral angle of 163·1°, and the two C–C bonds in this ring not involved in ring fusion are significantly shorter (1·546, 1·542 Å) than in similar compounds.

Introduction

Chemical analysis suggested that the irradiation of a solution of *cis,cis*-cyclodeca-3,8-diene-1,6-dione (I) leads to the *anti* tricyclo[5,3,0,$0^{2,6}$]dione (II) rather than the *syn* (III) or the cross-bonded (IV) (Shani, 1968, 1972).


(I) (II) (III) (IV)

However, some unusual chemical properties and a non-zero dipole moment (Shani & Ta-Shma, 1974) raised doubts as to the correctness of this assignment. Since the discrepancy could not be resolved on the basis of preliminary space-group assignment and cell constants, a full structure determination was carried out.

Experimental

Crystals from material provided by Dr A. Shani were obtained by slow evaporation of an ether solution at *ca.* 5°C. Weissenberg and precession photographs indicated orthorhombic symmetry with systematic absences characteristic of space group *Pbca*: 0*kl*, *k* odd; *h*0*l*, *l* odd; *hk*0, *h* odd. Lattice constants were obtained from a least-squares fit of 15 reflexions with 2θ values ranging between 8 and 36° (Mo $K\bar{\alpha}$).

Intensities were measured on a Syntex $P\bar{1}$ automated diffractometer with graphite-monochromated Mo radiation. 1490 reflexions for which $2\theta \le 50{\cdot}0°$ were measured by a $\theta:2\theta$ scan. After Lorentz and polarization corrections, 412 reflexions had $F_o \le 2{\cdot}5\sigma(F_o)$ and were considered unobserved.

Crystal data

$C_{10}H_{12}O_2$	F.W. 164·2
Orthorhombic	$\varrho_{\text{calc}}=1{\cdot}31$ g cm^{-3}
Space group *Pbca*	$\varrho_{\text{meas}}=1{\cdot}29$ g cm^{-3} (flotation, CCl_4–isooctane)

Table 1. *Final positional and thermal parameters for non-hydrogen* ($\times 10^4$) *and hydrogen* ($\times 10^3$) *atoms*

E.s.d.'s in parentheses are in units of the least significant digit. Hydrogen atoms are numbered according to the atoms to which they are bonded. Anisotropic thermal parameters are in the form $\exp\left[-2\pi^2\sum_i\sum_j a_ia_jh_ih_ju^{ij}\right]$; isotropic, $\exp\left[-8\pi^2 \sin^2 \theta/\lambda^2\right]$.

	x	y	z	u^{11}	u^{22}	u^{33}	u^{12}	u^{23}	u^{13}
C(1)	1993 (2)	1360 (2)	−614 (2)	399 (12)	392 (12)	449 (12)	−3 (10)	40 (10)	−14 (10)
C(2)	3351 (2)	975 (2)	−632 (2)	383 (13)	503 (12)	484 (13)	−31 (10)	0 (11)	78 (10)
C(3)	2000 (2)	1281 (2)	699 (2)	394 (12)	429 (13)	443 (12)	−45 (10)	17 (10)	38 (10)
C(4)	3423 (2)	1136 (2)	667 (2)	402 (13)	464 (13)	465 (13)	55 (10)	20 (10)	−34 (10)
C(5)	1219 (2)	586 (2)	−1244 (2)	457 (14)	562 (14)	517 (16)	−57 (11)	−15 (11)	−29 (11)
C(6)	1959 (2)	−382 (2)	−1231 (2)	711 (16)	466 (13)	407 (13)	−87 (12)	−53 (10)	32 (11)
C(7)	3288 (2)	−129 (2)	−1032 (3)	610 (16)	613 (16)	592 (16)	128 (13)	−112 (14)	34 (14)
C(8)	1734 (2)	2243 (2)	1364 (2)	448 (14)	591 (13)	507 (13)	54 (11)	−81 (10)	24 (10)
C(9)	2907 (2)	2848 (2)	1343 (2)	574 (13)	484 (15)	364 (17)	−52 (12)	−10 (13)	6 (12)
C(10)	3961 (2)	2153 (2)	1048 (3)	409 (17)	648 (12)	632 (14)	−84 (10)	−77 (9)	−31 (11)
O(6)	1546 (2)	−1230 (1)	−1371 (2)	1061 (14)	508 (14)	840 (16)	−152 (11)	−107 (12)	−51 (11)
O(9)	3002 (2)	3750 (1)	1543 (2)	971 (15)	496 (11)	805 (13)	−121 (10)	−135 (8)	140 (11)

Table 1 (*cont.*)

	x	y	z	U^{iso}
H(Cl)	189 (2)	208 (2)	−87 (2)	20 (7)
H(C2)	390 (2)	137 (1)	−107 (2)	25 (7)
H(C3)	156 (2)	68 (1)	95 (2)	19 (7)
H(C4)	377 (2)	54 (1)	108 (2)	25 (7)
H(C5)	108 (2)	80 (2)	−204 (2)	37 (8)
H′(C5)	41 (2)	49 (1)	−93 (2)	28 (7)
H(C7)	363 (2)	−60 (2)	−50 (2)	43 (9)
H′(C7)	375 (3)	−17 (2)	−172 (2)	52 (9)
H(C8)	156 (2)	208 (2)	215 (2)	50 (9)
H′(C8)	108 (2)	266 (1)	105 (2)	29 (7)
H(C10)	445 (2)	247 (2)	46 (2)	43 (8)
H′(C10)	449 (2)	208 (2)	170 (2)	60 (10)

$a=10{\cdot}852(4)$ Å
$b=13{\cdot}086(4)$
$c=11{\cdot}739(5)$
$\lambda(\text{Mo }K\alpha)=0{\cdot}70926$ Å
$Z=8$
$F(000)=704$
$\mu=0{\cdot}972\ \text{cm}^{-1}$ (Mo $K\alpha$)

Structure determination and refinement

The structure was solved with the program *MULTAN*. All 12 heavy atoms appeared in the E map corresponding to the model with the highest figure of merit and the lowest residual (Germain, Main & Woolfson, 1971).

Least-squares refinement of the heavy atoms proceeded smoothly through three cycles (full-matrix) with isotropic temperature factors ($\sin\theta/\lambda \le 0{\cdot}30$), and three cycles (full-matrix) with anisotropic temperature factors ($\sin\theta/\lambda \le 0{\cdot}45$). Expected hydrogen atom positions were calculated from geometrical considerations and were included in the next two cycles with individual isotropic temperature factors; to save computer time the molecule was divided into three blocks. One final cycle of full-matrix refinement resulted in values for R of 0·046 (0·052 including 'unobserveds') and R' of 0·011. The function minimized was $\sum w(|kF_o|^2-|F_c|^2)^2$ where w is $1{\cdot}0/\sigma^2(F_o^2)$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1965). The least-squares program used is a local version of *ORFLS* (Busing, Martin & Levy, 1963). Final positional parameters and temperature factors are given in Table 1, and observed and calculated structure factors in Table 2.

Table 2. *Observed and calculated structure factors*

The three columns list respectively l, $10kF_o$ and $10F_c$. U signifies reflexions for which $F_o \le 2{\cdot}5\ \sigma(F_o)$. Asterisks indicate reflexions not included in least-squares refinement.

[illegible]

Results and discussion

Bond lengths and angles for the heavy atoms are shown in Fig. 1. Those involving hydrogen atoms are all normal (average bond length 0·97 Å). All chemically equivalent bond lengths and angles agree to within three standard deviations save the non-carbonyl internal angles in the two cyclopentanone rings, where the discrepancies are probably due to differences in ring conformation (see below). C(1)–C(3) and C(2)–C(4) are normal for sp^3–sp^3 hybridization which this system approximates but are considerably shorter than the equivalent bonds in the photodimers of cyclopentanone (1·59 Å) (Margulis, 1965) and its 3-phenyl derivative (1·579,1·581 Å) (Shaw, Fratini & Adams, 1974).

The cyclobutane ring is folded about an axis through the transannular atoms with a dihedral angle of 163·1 °; this is the largest value observed to date for crystallographic site symmetry 1. All other features of the ring compare favourably with those of earlier studies (Shirrell & Williams, 1973).

Although the cyclopentanone rings are *anti* to each other in accordance with the chemical analysis, the folding of the cyclobutane ring precludes a molecular inversion centre and accounts for the non-zero dipole moment of the material. A further contribution to the dipole moment may come from the small but significant differences between chemically equivalent torsion angles in the cyclopentanone rings.

The best planes of the cyclopentanone rings make angles of 107 and 108° with the best plane of the cyclobutane ring, as would be expected from nearly tetrahedral hybridization of the latter, although strictly speaking none of these moieties is or would be expected to be planar. The folding of the cyclopentanone rings about the axes C(5)· · ·C(7) and C(8)· · ·C(10) is such that both oxygen atoms are *endo* to the cyclobutane ring. Both carbonyl groups, comprising three carbon atoms and the oxygen, are planar within 0·004 Å.

The crystal is composed of sheets of molecules nearly perpendicular to **a** (Fig. 2). The intra-sheet relationship of carbonyl groups suggests a predominance of dipole–dipole interactions in this region of the structure whereas regions between sheets are limited to contacts of the H· · ·H type, only two of which are shorter than 2·6 Å, suggesting that van der Waals forces dominate here.

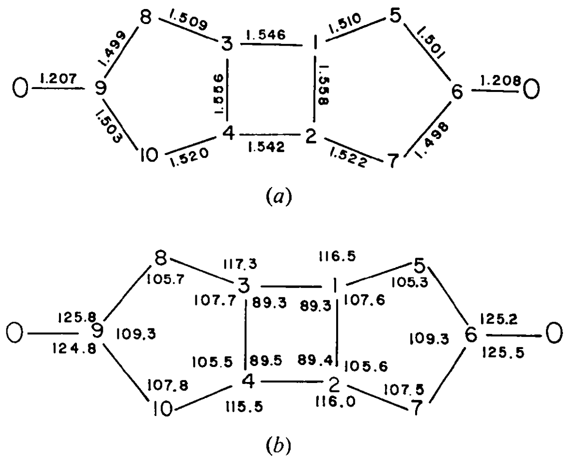


Fig. 1. Molecular dimensions for tricyclo[5,3,0,$0^{2,6}$]decane-4,9-dione. (*a*) Bond lengths (Å); average e.s.d. 0·003 Å. (*b*) Bond angles (°); average e.s.d. 0·2°.

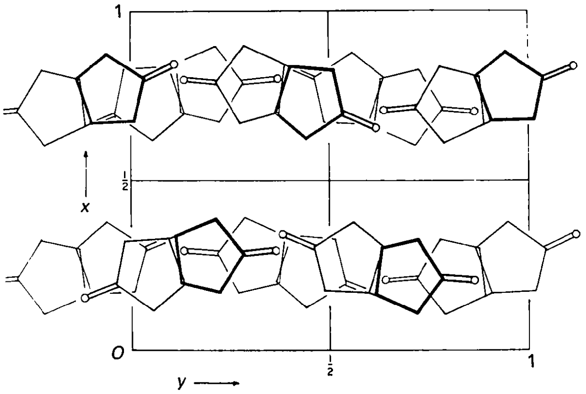


Fig. 2. View of the structure along the *c* axis.

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