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Acta Cryst. (1995). **C51**, 2685–2687

Photochemistry of Dimethyl 1,8-Dichloro-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate

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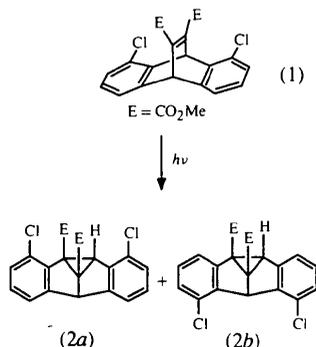
(Received 31 March 1995; accepted 16 June 1995)

Abstract

The molecule of the title compound, (1), $C_{20}H_{14}Cl_2O_4$, has geometry and dimensions similar to those of related materials; one ester group is fully conjugated with the C=C double bond and the other is non-conjugated. Photolysis of (1) produces two dibenzosemibullvalenes, the reaction being controlled mainly by intramolecular steric effects of the Cl substituents.

Comment

The 1,8-dichlorodibenzobarrelene diester (1) undergoes the di- π -methane reaction both in solution and in the solid state to give two regioisomeric dibenzosemibullvalenes, (2a) and (2b). The molecular structure of (1) was established by X-ray analysis and those of the photoproducts (2a) and (2b) from NMR data (Yang, 1993; Jones, Rettig, Scheffer, Trotter & Yang, 1995). The ratio (2a):(2b) is about 30:70 in solution and 10:90 in solid-state photolyses.



The molecular structure of (1) (Fig. 1 and Table 2) is similar to that of related materials (Jones *et al.*, 1995). The external angles at the ring junctions are enlarged as a result of steric strain, those adjacent to the Cl substituents being larger [mean $127.8(2)^\circ$] than the remote angles [mean $125.9(2)^\circ$]; the Cl—C—C(junction) angles are also slightly larger [mean $120.7(1)^\circ$] than the Cl—C1—C2 type angles [mean $119.2(1)^\circ$]. The two methoxycarbonyl groups exhibit different amounts of conjugation with the C11=C12 double bond. The group adjacent to the Cl substituents has a C=C—C=O dihedral angle of $-177.3(2)^\circ$ (for the molecule of Table 1 and Fig. 1; the crystals are racemic), $\cos^2(\text{angle}) = 1.00$, and is thus fully conjugated. This conformation probably results from possible Cl...O steric repulsions if the group were rotated from the conjugated position. The remote ester group has a dihedral angle of $-94.0(2)^\circ$, $\cos^2(\text{angle}) = 0.00$, and is thus non-conjugated. The C—CO₂Me bond distances reflect these differences in conjugation, being $1.478(2)$ Å for the conjugated group and $1.492(2)$ Å for the non-conjugated group (Allen, 1981).

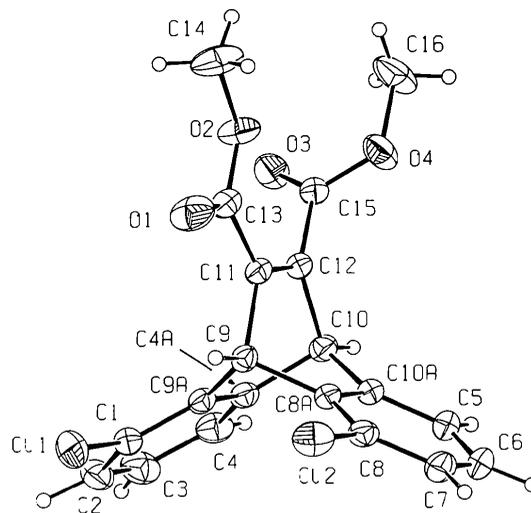


Fig. 1. View of the molecule with 33% probability displacement ellipsoids.

The major photoproduct (particularly in the solid state) is (2b); this is formed by initial vinyl–benzo bridging involving a benzo C atom *meta* to the Cl substituents [nearer the viewer in the above scheme; C12...C4a or C12...C10a in Fig. 1]. From considerations of the electronic effects of the Cl substituents, initial *ortho* bridging is predicted, as a result of greater electron density at the *ortho* C atom and of more extensive electron delocalization in the resulting biradical (Santiago, Houk, Snow & Paquette, 1976; Snow, Cottrell & Paquette, 1977; Jones *et al.*, 1995); thus, considering the electronic effects of the Cl substituents, (2a) is predicted to be the major photoproduct.

Compound (1) contains moderately severe non-bonded Cl...H(bridgehead) steric repulsions of distance 2.84 Å (compared with a van der Waals distance of 2.95 Å). As for the 1,5-dichloro derivative (Jones *et al.*, 1995), molecular-modelling calculations suggest relief of one of these repulsions in the reaction pathway leading to the major photoproduct (2*b*). Hence, steric effects again seem to dominate. Bridging is also thought to be favored at the vinyl C atom which carries the less-conjugated ester group and this would again favor photoproduct (2*b*). This latter effect is probably of some importance, since the amount of (2*b*) is greatest in the solid-state photolysis, where the ester conformations are constrained by the crystal lattice.

Experimental

The title compound was prepared according to the procedures described by Yang (1993).

Crystal data

C₂₀H₁₄Cl₂O₄

$M_r = 389.23$

Triclinic

$P\bar{1}$

$a = 8.106(1) \text{ \AA}$

$b = 14.788(1) \text{ \AA}$

$c = 7.866(1) \text{ \AA}$

$\alpha = 100.93(1)^\circ$

$\beta = 103.28(1)^\circ$

$\gamma = 90.86(1)^\circ$

$V = 899.4(2) \text{ \AA}^3$

$Z = 2$

$D_x = 1.437 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation

$\lambda = 1.54178 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 53.7\text{--}58.7^\circ$

$\mu = 3.5 \text{ mm}^{-1}$

$T = 294 \text{ K}$

Prism

$0.35 \times 0.25 \times 0.22 \text{ mm}$

Colorless

Data collection

AFC-6S diffractometer

ω - 2θ scans

Absorption correction:

refined from ΔF

(DIFABS; Walker &

Stuart, 1983)

$T_{\min} = 0.33$, $T_{\max} = 0.46$

3922 measured reflections

3655 independent reflections

3273 observed reflections

$[I > 3\sigma(I)]$

$R_{\text{int}} = 0.013$

$\theta_{\text{max}} = 77.6^\circ$

$h = 0 \rightarrow 10$

$k = -18 \rightarrow 18$

$l = -9 \rightarrow 9$

3 standard reflections

monitored every 150

reflections

intensity decay: 8.2%

Refinement

Refinement on F

$R = 0.036$

$wR = 0.052$

$S = 3.96$

3273 reflections

292 parameters

All H-atom parameters

refined

$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\text{max}} = 0.25$

$\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$

Extinction correction:

Zachariasen (1968) type

2 Gaussian isotropic

Extinction coefficient:

0.23×10^{-4}

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C11	0.66399 (7)	0.02604 (4)	0.18909 (7)	0.0643 (3)
C12	0.15462 (7)	0.17078 (4)	0.08722 (7)	0.0613 (3)
O1	0.6436 (2)	0.3274 (1)	0.1692 (2)	0.072 (1)
O2	0.7589 (2)	0.4333 (1)	0.4113 (2)	0.063 (1)
O3	0.8764 (2)	0.4096 (1)	0.8216 (2)	0.061 (1)
O4	0.6476 (2)	0.4894 (1)	0.7537 (2)	0.062 (1)
C1	0.6833 (2)	0.0639 (1)	0.4159 (3)	0.044 (1)
C2	0.7745 (3)	0.0132 (1)	0.5344 (3)	0.057 (1)
C3	0.7932 (3)	0.0431 (1)	0.7139 (3)	0.062 (1)
C4	0.7235 (2)	0.1232 (1)	0.7817 (3)	0.051 (1)
C4a	0.6336 (2)	0.1727 (1)	0.6620 (2)	0.038 (1)
C5	0.2252 (2)	0.2546 (1)	0.6834 (3)	0.050 (1)
C6	0.0636 (2)	0.2366 (1)	0.5710 (3)	0.059 (1)
C7	0.0418 (2)	0.2121 (1)	0.3899 (3)	0.056 (1)
C8	0.1837 (2)	0.2027 (1)	0.3165 (3)	0.043 (1)
C8a	0.3460 (2)	0.2192 (1)	0.4268 (2)	0.036 (1)
C9	0.5145 (2)	0.2106 (1)	0.3722 (2)	0.035 (1)
C9a	0.6129 (2)	0.1446 (1)	0.4794 (2)	0.036 (1)
C10	0.5512 (2)	0.2632 (1)	0.7113 (2)	0.038 (1)
C10a	0.3649 (2)	0.2464 (1)	0.6096 (2)	0.038 (1)
C11	0.6100 (2)	0.3049 (1)	0.4484 (2)	0.036 (1)
C12	0.6294 (2)	0.3320 (1)	0.6250 (2)	0.036 (1)
C13	0.6712 (2)	0.3548 (1)	0.3266 (2)	0.043 (1)
C14	0.8088 (5)	0.4911 (3)	0.2993 (6)	0.092 (1)
C15	0.7336 (2)	0.4140 (1)	0.7425 (2)	0.040 (1)
C16	0.7454 (4)	0.5735 (2)	0.8554 (5)	0.084 (1)

Table 2. Selected bond lengths (\AA) and angles ($^\circ$)

C—Cl	1.735, 1.735 (2)
C11=C12	1.342 (2)
C—C (aromatic)	1.369–1.398 (3)
C—CO ₂ Me	1.478 (2), 1.491 (2)
C=O	1.195, 1.191 (2)
C—OMe	1.327, 1.323 (2)
O—Me	1.452, 1.455 (3)
C—C (external)	127.6, 127.9; 125.5, 126.3 (2)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1990). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1082). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tricyclo[22.2.2.2^{11,14}]triaconta-11,13,24,26,27,29-hexaene-6,19-dione

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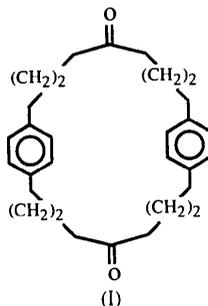
(Received 9 May 1995; accepted 27 June 1995)

Abstract

The title molecule, C₃₀H₄₀O₂, contains a centrosymmetric 26-membered ring and has a conformation in which O···γ-H distances are in the range 4.6–5.0 Å, too long for H-atom abstraction, and in accord with the lack of photochemical reactivity in the solid state.

Comment

The title compound, (I), was examined as part of a study of the photochemistry of macrocyclic diketones (Lewis, Rettig, Scheffer, Trotter & Wireko, 1990; Lewis, Rettig, Scheffer & Trotter, 1991). Photolysis in solution gives three Norrish type II photoproducts (cyclization and cleavage), but the compound is not photochemically reactive in the solid state.



The molecule crystallizes with a conformation in which the O···γ-H distances are in the range 4.6–5.0 Å

[O···H on C(4) and C(13) in Fig. 1], much too long for H-atom abstraction. Other conformations presumably give rise to the reactivity in solution (Lewis *et al.*, 1990).

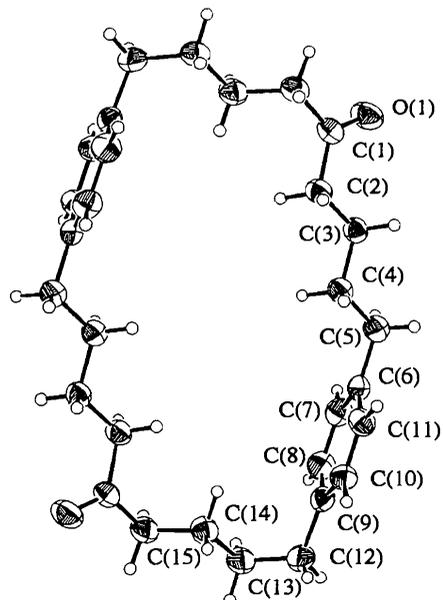


Fig. 1. View of the title molecule showing the crystallographic numbering system. Displacement ellipsoids are drawn at the 33% probability level.

Experimental

Crystals of the title compound were obtained according to the procedure described by Yang (1993).

Crystal data

C₃₀H₄₀O₂

M_r = 432.64

Monoclinic

*P*2₁/*c*

a = 9.920 (1) Å

b = 11.209 (1) Å

c = 11.755 (1) Å

β = 96.93 (1)°

V = 1297.5 (1) Å³

Z = 2

D_x = 1.107 Mg m⁻³

Cu Kα radiation

λ = 1.54178 Å

Cell parameters from 25 reflections

θ = 34.1–44.1°

μ = 0.48 mm⁻¹

T = 294.2 K

Prism

0.45 × 0.25 × 0.20 mm

Colorless

Data collection

AFC-6S diffractometer

ω–2θ scans

Absorption correction:

ψ scans (TEXSAN);

Molecular Structure

Corporation, 1990)

T_{min} = 0.92, *T_{max}* = 1.00

2945 measured reflections

2640 independent reflections

1552 observed reflections

[*I* > 3σ(*I*)]

R_{int} = 0.039

θ_{max} = 77.5°

h = 0 → 12

k = 0 → 13

l = –14 → 14

3 standard reflections

monitored every 250

reflections

intensity decay: none