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Crystal Structure and Photochemistry of Dimethyl 9,10-Dichloro-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate

Phani Raj Pokkuluri, John R. Scheffer and James Trotter*

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Z1

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Abstract

Photolysis of the title 9,10-dichlorodibenzobarrelene-11,12-diester, (1), results in formation of a semibullvalene, dimethyl 4b,8b-dichloro-4b,8b,8c,8d-tetrahydrodibenzo[*a,f*]cyclopropa[*cd*]pentalene-8c,8d-dicarboxylate (2), and an additional photoproduct, dimethyl 4b,10-dichloro-4b,9,9a,10-tetrahydro-9,10-epidioxydibenzo[*a,f*]pentalene-9,9a-dicarboxylate (3), which contains an unusual peroxo-ring structure. The structures of (1), (2) and (3) have been determined by X-ray analysis. Formation of (2) can be rationalized in terms of a di-π-methane rearrangement of (1) *via* biradical intermediates, and (3) is most likely a secondary photoproduct, formed from (2) *via* bond fission followed by trapping of molecular oxygen [no (3) is formed in carefully deoxygenated systems]. Crystals of (1) exhibit photochromism, probably as the result of formation of an (unidentified) radical ion.

Comment

In a continuation of studies of the photochemistry of dibenzobarrelene diesters (Pokkuluri, Scheffer & Trotter, 1993*a,b*), the photolysis of the 9,10-dichloro-11,12-dimethyl diester [(1), Fig 1] has been examined. In acetone solution and in the solid state, mainly one photoproduct, (2), is isolated, while photolysis in acetonitrile solution gives (2) and an additional product, (3). X-ray crystal analyses of (1), (2) and (3) have established a normal dibenzosemibullvalene structure for (2), and an unusual peroxo-ring structure for (3) (Fig. 1).

Fig. 2 shows views of the molecules (1), (2) and (3). The structure and dimensions of the molecule of the dibenzobarrelene diester (1) are very similar to those of other derivatives (Pokkuluri *et al.*, 1993*a,b*). The bond angles external to the aromatic rings (mean 127.6°) and the inter-annular benzene–barrelene angles (mean 112.4°) are distorted to about the same extent as in the other derivatives. The C11—C12 distance [1.337 (4) Å] is normal for a double bond. The two ester groups are rotated out of the plane of the double bond to different extents; the C12—C11—C13—O2 and C11—C12—C15—O4 torsion angles are −129.6 (4) and −104.2 (4)°, respectively. Thus the ester group at C11 shows some conjugation with the C11═C12 double bond ($\cos^2\varphi = 0.41$), while the group at C12 is essentially unconjugated ($\cos^2\varphi = 0.06$), the difference probably being due to intermolecular packing effects. The difference in conjugation is barely reflected in the C—CO_2Me bond distances, which are essentially equal at 1.492 (4) and 1.497 (4) Å.

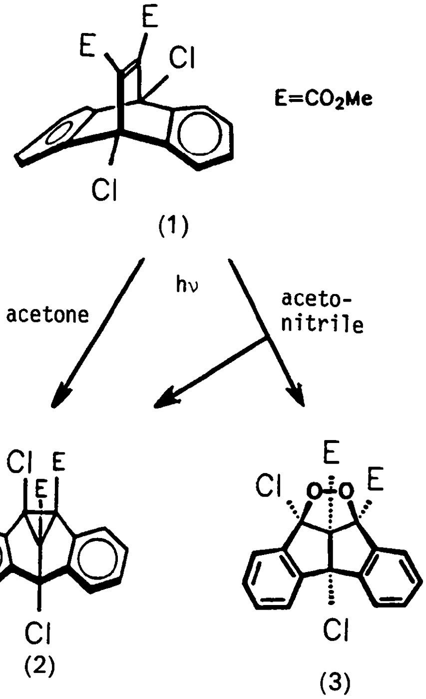
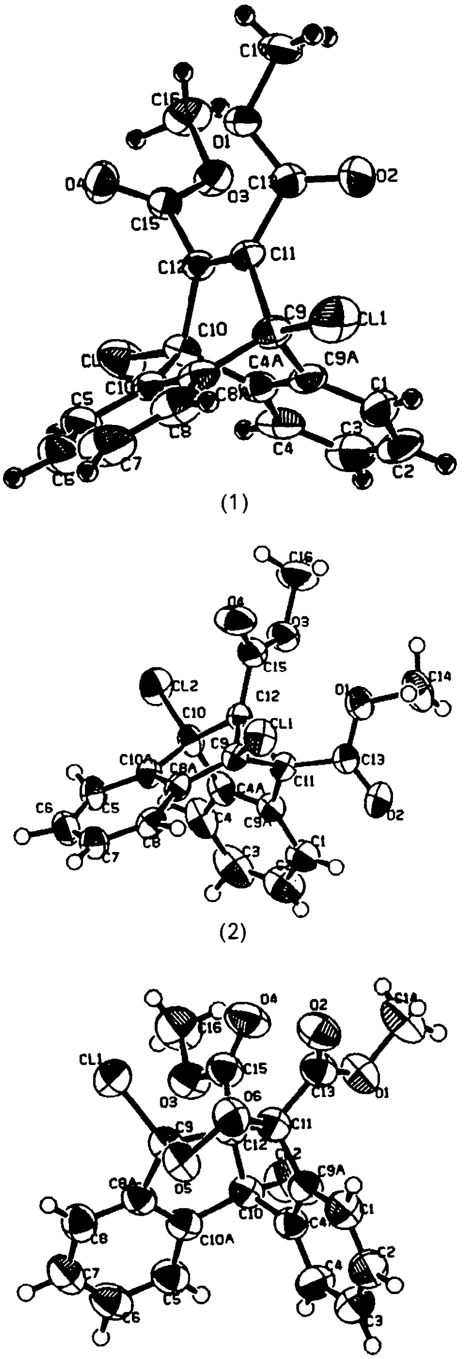


Fig. 1. Photolysis of compound (1).

The ring system in the dibenzosemibullvalene photoproduct (2) (Fig. 2) shows the usual additional strain as a result of the formation of the three-membered ring (Pokkuluri *et al.*, 1993*b*). The angles at the five/six-membered ring junctions are further from 120° [mean 128.7 (external), 109.9° (internal)] and the angles in the three-membered ring are in the range 57.9–63.7 (2)°. The ring junction angles in (3) average 127.7 and 111.5°. Compound (3) contains an additional peroxo group as part of a five-membered ring. This ring has a half-chair conformation with the two O atoms displaced above and below the plane of the three C atoms, and a C—O—O—C dihedral angle of 53° (Table 2) [O—O = 1.464 (4) Å, C—O—O = 102.0 (3)°].



(1)

(2)

(3)

Fig. 2. Views (50% thermal ellipsoids) of (1), (2) and (3) [stereo versions are shown in the deposited material; the dibenzobarrelene numbering system of (1) is retained for (2) and (3)].

Photolysis results

Formation of product (2) can be rationalized readily in terms of the di-π-methane rearrangement of (1) *via* the T_1 triplet state (Fig. 3) which is expected to produce only one semibullvalene as a racemate. The molecule of (2) contains four chiral centers and crystals of (2) belong to space group $P2_12_12_1$; hence spontaneous resolution must occur during crystallization.

Compound (3) is most likely a secondary photoproduct, formed *via* photochemical bond fission of the strained cyclopropane ring in (2) to produce a 1,3-biradical, stabilized through conjugation with the aromatic rings, which is trapped by traces of molecular oxygen present in the photolysis mixture (Fig. 3). Compound (3) is not formed from the biradicals proposed in the di-π-methane pathway, which would give different peroxo compounds. This hypothesis is supported by independent photolysis of (2) which yields (3) and an additional unidentified minor product. In addition, carefully deoxygenated solutions of (1) produce only (2) on photolysis, and degassed solutions of (2) show no reaction on photolysis. An intermediate peroxo-ring compound (not isolated) analogous to (3) has been proposed in the photolysis of a dibenzoyl-dibenzobarrelene (Asokan, Kumar, Das, Rath & George, 1991). Photolysis of crystals of (1) (in nitrogen or in air) leads exclusively to (2), and crystals of (2) are photostable, hence oxygen addition does not occur in the crystal lattice.

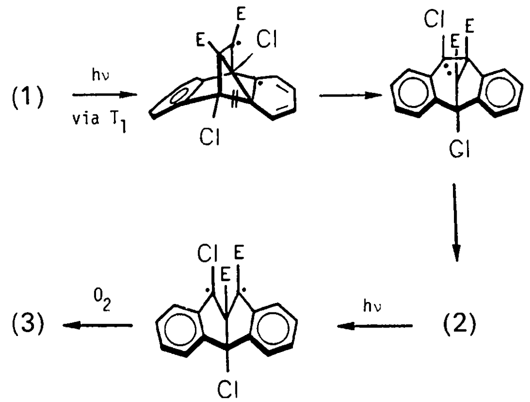


Fig. 3. Proposed reaction mechanism for the formation of photoproducts (2) and (3).

Solid-state photochromism of (1)

An additional feature of interest is that crystals of (1) are photochromic, a purple–blue color developing on irradiation (Pyrex filter, $\lambda \geq 290$ nm). The color fades when irradiated crystals are allowed to stand in the dark at room temperature (heating speeds up the decolorization) and the process can be repeated with no photoreaction (prolonged irradiation does produce brown or yellow coloration and some photoreaction to products which are detectable by GC). The phenomenon is not observed in solution, so that the purple color is due to the formation of some species in the solid state.

The solid-state UV–vis. spectrum of irradiated (1) [KBr pellet, 4 mg (1)/152 mg KBr] shows a weak absorption band at 582 nm ($A = 0.12$), which is consistent with the observed purple color, and which is absent before irradiation and after the color fades. An ESR signal is observed, the intensity of the signal decreasing as the color fades. The g values are consistent with the presence of an organic radical species (Thompson, 1973). It is tempting to speculate that the radical species responsible for the photochromism is one of the biradicals postulated in the di-π-methane rearrangement pathway (Fig. 3). However, these biradicals would not be expected to show absorption in the visible region of the spectrum, and a radical ion seems a more likely source of the absorption and of the purple color. A previous study of a photochromic chloro-organic compound (Zweegers & Varma, 1979) suggested a possible radical ion, formed by heterolytic fission of a C—Cl bond, but this does not seem so likely for (1). The photochromism of (1) is related to some phenomenon in the solid state, but the detailed reasons are not clear.

Experimental

Compound (1)

Crystal data

$C_{20}H_{14}Cl_2O_4$
$M_r = 389.23$
Monoclinic
$P2_1/a$
$a = 14.767$ (1) Å
$b = 8.243$ (2) Å
$c = 15.130$ (1) Å
$\beta = 105.36$ (1)°
$V = 1775.9$ (5) Å^3
$Z = 4$
$D_x = 1.46$ Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 31$-$40°$
$\mu = 3.54$ mm^{-1}
$T = 294$ K
Prism
0.3 × 0.3 × 0.2 mm
Colorless
Crystal source: synthesis (see supplementary material)

Data collection

Rigaku AFC-6 diffractometer
ω-2θ scans
Absorption correction: empirical
$T_{\min} = 0.56$, $T_{\max} = 1.00$
2974 measured reflections
2634 independent reflections
2041 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.015$
$\theta_{\max} = 60°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 9$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 150 reflections intensity variation: negligible

Refinement

Refinement on F
Final $R = 0.046$
$wR = 0.064$
$S = 1.62$
2041 reflections
292 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}
Extinction correction: *TEXSAN* (Molecular Structure Corporation, 1990)
Extinction coefficient: 0.98×10^{-5}
Atomic scattering factors from *TEXSAN*

Compound (2)

Crystal data

$C_{20}H_{14}Cl_2O_4$
$M_r = 389.23$
Orthorhombic
$P2_12_12_1$
$a = 10.420$ (3) Å
$b = 17.652$ (1) Å
$c = 9.697$ (2) Å
$V = 1783.6$ (5) Å^3
$Z = 4$
$D_x = 1.45$ Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 45$-$52°$
$\mu = 3.53$ mm^{-1}
$T = 294$ K
Prism
0.4 × 0.25 × 0.2 mm
Colorless
Crystal source: photochemical reaction

Data collection

Rigaku AFC-6 diffractometer
ω-2θ scans
Absorption correction: empirical
$T_{\min} = 0.85$, $T_{\max} = 1.00$
2199 measured reflections
2199 independent reflections
1824 observed reflections [$I > 3\sigma(I)$]
$\theta_{\max} = 77.6°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 12$
3 standard reflections monitored every 150 reflections intensity variation: negligible

Refinement

Refinement on F
Final $R = 0.039$
$wR = 0.061$
$S = 2.04$
1824 reflections
292 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}
Extinction correction: *TEXSAN* (Molecular Structure Corporation, 1990)
Extinction coefficient: 0.43×10^{-5}
Atomic scattering factors from *TEXSAN*

Compound (3)

Crystal data

$C_{20}H_{14}Cl_2O_6$
$M_r = 421.24$
Triclinic
$P\bar{1}$
$a = 9.012$ (4) Å
$b = 13.272$ (8) Å
$c = 7.869$ (6) Å
$\alpha = 94.07$ (6)°
$\beta = 97.79$ (5)°
$\gamma = 88.34$ (4)°
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 24 reflections
$\theta = 32$-$43°$
$\mu = 3.38$ mm^{-1}
$T = 294$ K
Plate
0.40 × 0.35 × 0.10 mm
Colorless

$V = 930\ (1)$ Å^3
$Z = 2$
$D_x = 1.50$ Mg m^{-3}

Crystal source: photochemical reaction

Data collection

Rigaku AFC-6 diffractometer
ω-2θ scans
Absorption correction: empirical
$T_{\min} = 0.66$, $T_{\max} = 1.00$
4021 measured reflections
3773 independent reflections
2861 observed reflections
$[I > 3\sigma(I)]$

$R_{\rm int} = 0.032$
$\theta_{\max} = 77.7°$
$h = 0 \rightarrow 11$
$k = -17 \rightarrow 17$
$l = -10 \rightarrow 10$
3 standard reflections
monitored every 150 reflections
intensity variation: 12% decay

Refinement

Refinement on F
Final $R = 0.087$
$wR = 0.121$
$S = 3.7$
2861 reflections
254 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.01$

$\Delta\rho_{\max} = 0.53$ e Å^{-3}
$\Delta\rho_{\min} = -0.70$ e Å^{-3}
Extinction correction: *TEXSAN* (Molecular Structure Corporation, 1990)
Extinction coefficient: 0.47×10^{-4}
Atomic scattering factors from *TEXSAN*

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j B_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Compound (1)				
Cl1	0.31594 (7)	0.0278 (1)	0.14796 (7)	5.37 (5)
Cl2	−0.02635 (6)	−0.0346 (1)	0.30044 (7)	4.97 (5)
O1	0.3442 (1)	−0.2035 (3)	0.4054 (2)	3.6 (1)
O2	0.3945 (2)	0.0245 (3)	0.3539 (2)	4.8 (1)
O3	0.1938 (2)	−0.0540 (3)	0.4767 (1)	3.6 (1)
O4	0.1338 (2)	−0.2909 (3)	0.4158 (2)	4.3 (1)
C1	0.2023 (3)	0.3302 (5)	0.1856 (3)	4.6 (2)
C2	0.1520 (4)	0.4662 (5)	0.2030 (3)	5.9 (2)
C3	0.0752 (4)	0.4495 (6)	0.2373 (3)	5.4 (2)
C4*A*	0.0941 (2)	0.1633 (4)	0.2385 (2)	3.2 (1)
C4	0.0462 (3)	0.2981 (5)	0.2553 (3)	4.4 (2)
C5	−0.0184 (3)	−0.1858 (5)	0.1150 (3)	4.4 (2)
C6	−0.0178 (4)	−0.2556 (6)	0.0330 (3)	6.0 (2)
C7	0.0588 (4)	−0.2426 (6)	−0.0005 (3)	6.2 (2)
C8*A*	0.1380 (3)	−0.0865 (4)	0.1301 (2)	3.4 (1)
C8	0.1370 (4)	−0.1589 (6)	0.0474 (3)	4.7 (2)
C9	0.2166 (2)	0.0139 (4)	0.1926 (2)	3.2 (1)
C9*A*	0.1723 (2)	0.1782 (4)	0.2035 (2)	3.4 (1)
C10*A*	0.0589 (2)	−0.1000 (4)	0.1634 (2)	3.3 (1)
C10	0.0719 (2)	−0.0136 (4)	0.2546 (2)	3.0 (1)
C11	0.2387 (2)	−0.0640 (4)	0.2879 (2)	2.7 (1)
C12	0.1624 (2)	−0.0827 (4)	0.3187 (2)	2.7 (1)
C13	0.3352 (2)	−0.0760 (4)	0.3506 (2)	3.1 (1)
C14	0.4270 (3)	−0.2004 (7)	0.4838 (3)	4.8 (2)
C15	0.1617 (2)	−0.1572 (4)	0.4087 (2)	2.8 (1)
C16	0.2011 (4)	−0.1185 (7)	0.5681 (3)	5.1 (2)
Compound (2)				
Cl1	0.9407 (1)	0.91072 (7)	0.9148 (1)	4.28 (4)
Cl2	1.2136 (1)	1.02687 (7)	1.3421 (1)	5.19 (5)
O1	0.7446 (3)	0.9769 (2)	1.1353 (4)	4.5 (1)
O2	0.7082 (3)	0.8555 (2)	1.1848 (5)	5.3 (2)
O3	0.9250 (3)	1.0800 (2)	1.2571 (3)	4.3 (1)
O4	1.0080 (5)	1.0793 (2)	1.0448 (4)	6.1 (2)
C1	0.8975 (5)	0.8094 (3)	1.4114 (5)	4.4 (2)
C2	0.9519 (7)	0.7862 (4)	1.5351 (6)	6.0 (3)
C3	1.0671 (7)	0.8158 (4)	1.5809 (5)	6.2 (3)
C4*A*	1.0738 (4)	0.8957 (3)	1.3832 (4)	3.5 (2)
C4	1.1308 (5)	0.8713 (3)	1.5052 (5)	4.7 (2)
C5	1.3379 (4)	0.8738 (3)	1.2093 (5)	3.8 (2)
C6	1.3892 (4)	0.8195 (3)	1.1208 (5)	4.3 (2)
C7	1.3163 (4)	0.7884 (3)	1.0152 (5)	4.0 (2)
C8	1.1894 (4)	0.8107 (3)	0.9953 (4)	3.6 (2)
C8*A*	1.1391 (3)	0.8660 (2)	1.0819 (4)	2.9 (1)
C9*A*	0.9596 (4)	0.8650 (2)	1.3372 (4)	3.2 (1)
C9	1.0129 (3)	0.9035 (2)	1.0773 (4)	3.0 (1)
C10*A*	1.2136 (4)	0.8961 (2)	1.1872 (4)	3.1 (1)
C10	1.1305 (4)	0.9477 (2)	1.2752 (4)	3.3 (1)
C11	0.9196 (4)	0.9037 (2)	1.2064 (4)	3.1 (1)
C12	1.0135 (3)	0.9669 (2)	1.1800 (4)	2.9 (1)
C13	0.7787 (4)	0.9090 (2)	1.1754 (4)	3.3 (1)
C14	0.6125 (5)	0.9878 (4)	1.0935 (8)	5.6 (3)
C15	0.9814 (4)	1.0478 (2)	1.1489 (5)	3.7 (2)
C16	0.893 (1)	1.1582 (4)	1.246 (1)	6.6 (4)
Compound (3)				
Cl1	0.6155 (1)	0.3993 (1)	0.4796 (2)	5.75 (6)
Cl2	0.9743 (1)	0.2680 (1)	1.0073 (1)	5.46 (5)
O1	0.5911 (3)	0.1385 (3)	0.9550 (4)	5.5 (1)
O2	0.4057 (4)	0.1332 (3)	0.7329 (5)	6.1 (2)
O3	0.7612 (4)	0.4260 (2)	0.8647 (4)	5.3 (1)
O4	0.5518 (4)	0.3424 (3)	0.8774 (5)	6.5 (2)
O5	0.7040 (3)	0.2118 (2)	0.4317 (4)	4.8 (1)
O6	0.5843 (3)	0.1701 (2)	0.5124 (4)	4.9 (1)
C1	0.7610 (5)	−0.0188 (3)	0.6567 (7)	5.1 (2)
C2	0.8861 (6)	−0.0815 (4)	0.6730 (7)	5.8 (2)
C3	1.0254 (6)	−0.0417 (4)	0.7316 (8)	5.9 (2)
C4	1.0422 (5)	0.0602 (4)	0.7708 (7)	5.2 (2)
C4*A*	0.9166 (5)	0.1226 (3)	0.7538 (5)	4.2 (2)
C5	1.1502 (5)	0.3032 (4)	0.6833 (6)	4.9 (2)
C6	1.2064 (5)	0.3512 (4)	0.5579 (8)	5.8 (2)
C7	1.1123 (6)	0.3851 (4)	0.4200 (7)	5.7 (2)
C8	0.9604 (6)	0.3723 (4)	0.4033 (6)	5.1 (2)
C8*A*	0.9043 (5)	0.3238 (3)	0.5296 (5)	4.3 (2)
C9	0.7456 (5)	0.2986 (3)	0.5403 (5)	4.2 (2)
C9*A*	0.7778 (5)	0.0831 (3)	0.6983 (5)	4.2 (2)
C10	0.9111 (4)	0.2354 (3)	0.7848 (5)	4.2 (2)
C10*A*	0.9970 (4)	0.2902 (3)	0.6690 (5)	4.1 (2)
C11	0.6566 (4)	0.1643 (3)	0.6860 (5)	4.1 (2)
C12	0.7428 (4)	0.2646 (3)	0.7255 (5)	3.9 (1)
C13	0.5329 (5)	0.1454 (3)	0.7908 (6)	4.6 (2)
C14	0.4848 (7)	0.1307 (5)	1.0759 (8)	7.3 (3)
C15	0.6734 (5)	0.3472 (3)	0.8346 (6)	4.7 (2)
C16	0.7076 (8)	0.5110 (4)	0.9636 (8)	7.3 (3)

Table 2. *Selected bond lengths* (Å) *and torsion angles* (°) (*mean values where appropriate*)

	(1)	(2)	(3)
C=C	1.337 (4)		
C—C (aromatic)	1.361-1.407 (6)	1.37-1.39 (1)	1.371-1.385 (7)
C—CO$_2$Me	1.492, 1.497 (4)	1.506, 1.498 (6)	1.510, 1.517 (6)
C—C (other)	1.529-1.533 (5)	1.473-1.585 (5)	1.493-1.560 (6)
C—Cl	1.774, 1.775 (3)	1.751 (4) (3-ring), 1.767 (5)	1.800 (5) (peroxo ring), 1.793 (4)
C=O	1.194 (4)	1.193 (5)	1.190 (5)
C—OMe	1.323 (4)	1.319 (5)	1.328 (5)
O—Me	1.460 (4)	1.436 (6)	1.442 (6)
O—O			1.464 (4)
C—O			1.426 (5)
O5—C9—C12—C11			−14.1 (4)
C9—C12—C11—O6			−17.6 (4)
C12—C11—O6—O5			42.0 (4)
C11—O6—O5—C9			−52.7 (4)
O6—O5—C9—C12			40.5 (4)

The structures of (1) and (2) were determined by direct methods (*TEXSAN*; Molecular Structure Corporation, 1990).

For (2), the material produced in the photochemical reaction is presumably racemic, so it can be assumed that spontaneous resolution occurred in the crystallization process. The actual crystal studied has the absolute configuration shown in Figs. 1 and 2 (the opposite enantiomer had $R = 0.055$).

In (3), minor disorder is indicated by difference map peaks of up to 0.5 e Å^{-3}, particularly near the Cl atoms, but these could not be interpreted in terms of any meaningful geometry; this is the likely reason for the high R factor.

We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond lengths and angles, details of synthesis and photolysis, UV-vis. and ESR spectra, and molecular and packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71297 (79 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1036]

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Structure of Dimethyl 9-Formyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate

JIANXIN CHEN, PHANI RAJ POKKULURI, JOHN R. SCHEFFER AND JAMES TROTTER*

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Z1

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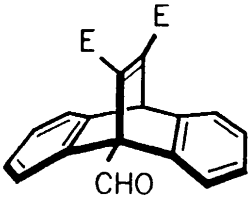
Abstract

The structure of the title compound has been determined. The molecular structure and dimensions are normal, with the carboxyl group adjacent to the formyl substituent not conjugated with the C11=C12 double bond and the remote carboxyl group fully conjugated.

Comment

The general molecular structure and dimensions of (1) (Fig. 1 and Table 2) are similar to those of related materials (Pokkuluri, Scheffer & Trotter, 1993). The carboxyl group adjacent to the CHO substituent on C9 is rotated out of the plane of the C11=C12 double bond [C12—C11—C13—O2 = 96.9 (3)°, cos^2 (angle) = 0.01], presumably as a result of steric repulsions [C11—C9—C17 = 115.6 (2)°], and hence is not conjugated with the C=C bond; the remote carboxyl group is fully conjugated [C11—C12—C15—O4 = −179.0 (3)°, cos^2 (angle) = 1.00]. The differences are reflected in the C—CO$_2$Me bond lengths of 1.489 (3) (non-conjugated) and 1.477 (3) Å (conjugated).



(1)

Photolysis of (1) yields a normal di-π-methane semibullvalene-type photoproduct (Chen, Pokkuluri, Scheffer & Trotter, 1990).

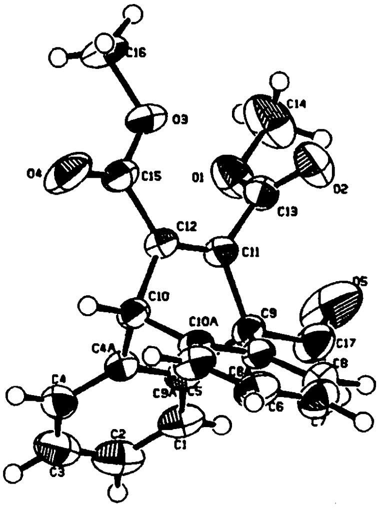


Fig. 1. View of the molecule (50% probability ellipsoids; stereo version in the supplementary material).

Experimental

Crystal data

$C_{21}H_{16}O_5$
$M_r = 348.35$
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å