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Dimethyl 1-Chloro-4b,8b,8c,8d-tetrahydrodibenzo[*a*,*f*]cyclopropa[*cd*]pentalene-8c,8d-dicarboxylate

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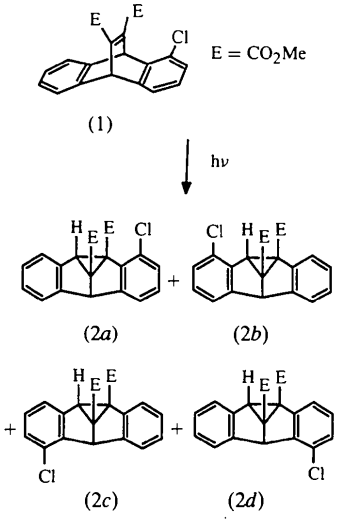
Abstract

The title compound, $C_{20}H_{15}ClO_4$, is one of the photoproducts of the photolysis of a 1-chlorodibenzobarrelene diester. The geometry and dimensions of the title molecule are similar to those of related materials.

Comment

The 1-chlorodibenzobarrelene diester (1) undergoes a di-π-methane reaction in solution and in the solid state; four regioisomeric dibenzosemibullvalene photoproducts [(2*a*)–(2*d*)] are possible. The products are difficult to separate by column chromatography, with broad overlapping GC signals. Only one product could be isolated and its molecular structure was determined by X-ray analysis to be that of (2*a*). The details of the photochemical pathways have not been established.



The mechanism for the formation of (2*a*) from (1) involves formation of a new C11—C9a bond (dibenzobarrelene numbering system), the breaking of bond C9—C9a and finally formation of a C9—C12 bond. The molecular structure of (2*a*) (Fig. 1 and Table 2) is similar to that of related materials (Garcia-Garibay, Scheffer, Trotter & Wireko, 1990; Pokkuluri, Scheffer & Trotter, 1993). The external angles at the ring junctions are large [128.4–130.4 (1)°] as a result of the additional steric strain due to the formation of the three-membered ring, with the largest angle adjacent to the Cl substituent.

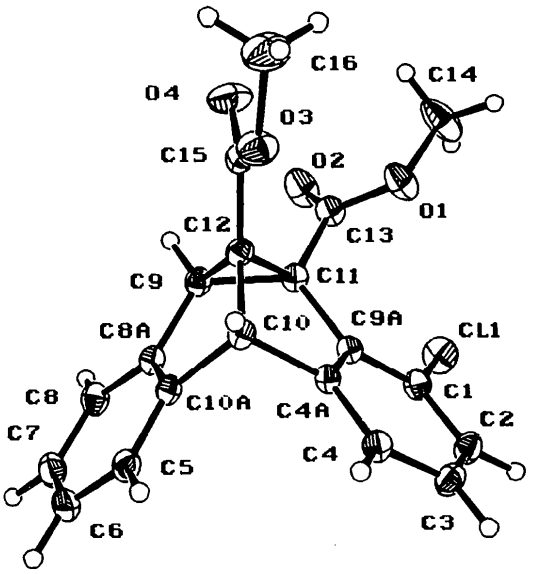


Fig. 1. View of the molecule with 33% probability displacement ellipsoids; the dibenzobarrelene numbering system is used.

Experimental

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

Crystal data

$C_{20}H_{15}ClO_4$
M_r = 354.79
Triclinic
$P\bar{1}$
a = 9.756 (1) Å
b = 10.556 (1) Å
c = 8.830 (1) Å
α = 107.22 (1)°
β = 105.31 (1)°
γ = 95.40 (1)°
V = 823.0 (1) Å^3
Z = 2
D_x = 1.432 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 25 reflections
θ = 48.2–55.5°
μ = 2.3 mm^{-1}
T = 294 K
Prism
0.40 × 0.35 × 0.25 mm
Colorless

Data collection

AFC-6*S* diffractometer
ω–2θ scans
R_{int} = 0.023
θ_{max} = 77.5°

Absorption correction:
ψ scan (*TEXSAN*; Molecular Structure Corporation, 1990)
T_{min} = 0.85, T_{max} = 1.00
3556 measured reflections
3323 independent reflections
2996 observed reflections [$I > 3\sigma(I)$]
$h = 0 \rightarrow 12$
$k = -13 \rightarrow 13$
$l = -10 \rightarrow 10$
3 standard reflections
monitored every 150 reflections
intensity decay: none

Refinement

Refinement on F
R = 0.035
wR = 0.046
S = 4.2
2996 reflections
227 parameters
H atoms refined as riding, C—H = 0.98 Å
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max}$ = 0.02
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}
Extinction correction: Zachariasen (1968) type 2 Gaussian isotropic
Extinction coefficient: 0.14×10^{-4}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Cl1	0.33673 (5)	−0.01704 (5)	0.03519 (6)	0.0505 (3)
O1	0.5148 (1)	0.1164 (1)	0.4323 (2)	0.045 (1)
O2	0.5649 (1)	0.2909 (1)	0.3478 (2)	0.053 (1)
O3	0.3360 (1)	0.2885 (1)	0.7822 (2)	0.050 (1)
O4	0.5145 (1)	0.3905 (1)	0.7187 (2)	0.058 (1)
C1	0.2053 (2)	−0.0100 (1)	0.1359 (2)	0.033 (1)
C2	0.0940 (2)	−0.1216 (1)	0.0806 (2)	0.038 (1)
C3	−0.0132 (2)	−0.1178 (1)	0.1566 (2)	0.040 (1)
C4	−0.0126 (2)	−0.0039 (1)	0.2858 (2)	0.033 (1)
C4a	0.1004 (1)	0.1048 (1)	0.3413 (2)	0.027 (1)
C5	−0.0957 (2)	0.3434 (1)	0.3372 (2)	0.035 (1)
C6	−0.1383 (2)	0.4269 (2)	0.2446 (2)	0.041 (1)
C7	−0.0402 (2)	0.4930 (2)	0.1917 (2)	0.043 (1)
C8	0.1040 (2)	0.4773 (2)	0.2304 (2)	0.038 (1)
C8a	0.1465 (2)	0.3949 (1)	0.3236 (2)	0.031 (1)
C9	0.2940 (2)	0.3708 (1)	0.3912 (2)	0.032 (1)
C9a	0.2111 (1)	0.1029 (1)	0.2679 (2)	0.027 (1)
C10	0.1215 (1)	0.2421 (1)	0.4725 (2)	0.028 (1)
C10a	0.0476 (1)	0.3296 (1)	0.3781 (2)	0.029 (1)
C11	0.3255 (1)	0.2270 (1)	0.3592 (2)	0.029 (1)
C12	0.2842 (1)	0.2995 (1)	0.5147 (2)	0.030 (1)
C13	0.4819 (2)	0.2181 (2)	0.3780 (2)	0.035 (1)
C14	0.6612 (2)	0.0938 (3)	0.4512 (3)	0.068 (1)
C15	0.3923 (2)	0.3334 (1)	0.6814 (2)	0.036 (1)
C16	0.4328 (3)	0.3068 (3)	0.9466 (3)	0.072 (1)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

C—Cl	1.738 (2)
C—C(aromatic)	1.381–1.398 (2)
C—CO_2Me	1.506 (2), 1.485 (2)
C=O	1.198, 1.197 (2)
C—OMe	1.332, 1.333 (2)
O—Me	1.444, 1.453 (2)
C—C—C(external)	128.8, 128.4, 130.4, 129.2 (1)

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: FG1085). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dimethyl 4b,8b,8c,8d-Tetrahydrodibenzo[*a,f*]cyclopropa[*cd*]pentalene-8b-carboxylate-8c-thionocarboxylate and the Corresponding 8c-Thiolocarboxylate

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Abstract

The title compounds, methyl 8c-[methoxy(thiocarbonyl)]-4b,8b,8c,8d-tetrahydrodibenzo[*a,f*]cyclopropa[*cd*]pentalene-8b-carboxylate, $C_{20}H_{16}O_3S$, and methyl 8c-[(methylthio)]carbonyl-4b,8b,8c,8d-tetrahydrodibenzo[*a,f*]cyclopropa[*cd*]pentalene-8b-carboxylate, $C_{20}H_{16}O_3S$, are the photoproducts in the photolysis of the dibenzobarrelene thiono and thiolo esters. The geometry and dimensions of the molecules are similar