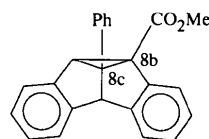Ito, Y., Nishimura, H., Umehara, Y., Yamada, Y., Tone, M. & Matsuura, T. (1983). *J. Am. Chem. Soc.* **105**, 1590–1597.

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Methyl 8c-Phenyl-4b,8b,8c,8d-tetrahydrodibenzo[a,f]cyclopropa[cd]pentalene-8b-carboxylate

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Abstract

The title molecule, $C_{24}H_{18}O_2$, is the sole product of photolysis of a phenyl–methoxycarbonyl–dibenzobarrelene derivative, has a dibenzosemibullvalene structure, 8c-phenyl and 8b-methoxycarbonyl substituents, and normal bond lengths and angles.

Comment

Photolysis of dibenzobarrelene (9,10-dihydro-9,10-ethenoanthracene) derivatives proceeds *via* the di-π-methane reaction to produce dibenzosemibullvalene photoproducts. For unsymmetrically substituted 11,12-derivatives, two isomeric dibenzosemibullvalene photoproducts (and their enantiomers) are possible, the proportions of the products being greatly influenced by the nature of the substituent groups (Rattray, Yang, Gudmundsdottir & Scheffer, 1993). The proposed mechanism (Zimmerman, 1991) involves initial bond formation between a vinyl (C11 or C12) and a benzo C atom, to form a biradical, with one of the radical sites at the second vinyl C atom. The polar nature and the radical-stabilizing ability of the 11,12-substituents are important

in determining which of the two reaction pathways is more favourable. For $CO_2Me/CXYMe$ derivatives (X = S, Y = O; X = O, Y = S), for example, initial bond formation involves the C atom bearing the CO_2Me substituent, with the intermediate biradical stabilized by resonance with the CSOMe or COSMe groups (Jones, Rattray, Scheffer & Trotter, 1995); as a result, only the 8c-thiono and 8c-thiolo dibenzosemibullvalene products are formed.

(I)

The CH_3/CO_2Me dibenzobarrelene derivative gives only the 8b-CH_3/8c-CO_2Me product, again in accord with radical stabilization by delocalization of the radical electron over the CO_2Me group (Rattray *et al.*, 1993). By contrast, the only photoproduct from photolysis of the Ph/CO_2Me derivative has been shown to be the 8c-Ph/8b-CO_2Me dibenzosemibullvalene (Fig. 1); this is in accord with the greater radical-stabilizing ability of the phenyl substituent. The photoproduct molecule, (I) (Fig. 1) has a normal folded dibenzosemibullvalene skeleton, with a three-membered ring, and normal bond lengths and angles.
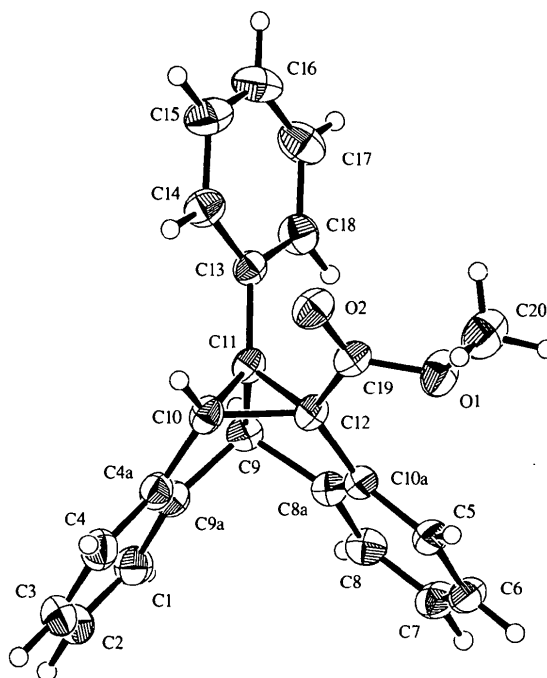

Fig. 1. View of the molecule (33% ellipsoids; dibenzobarrelene numbering system).

Experimental

The material is obtained by photolysis of a 9,10-dihydro-9,10-ethenoanthracene derivative, with 11,12 phenyl and methoxy-carbonyl substituents [Rattray *et al.*, 1993, compound (1-10); Rattray, 1992; details are in the supplementary material].

Crystal data

$C_{24}H_{18}O_2$	Cu $K\alpha$ radiation
$M_r = 338.40$	$\lambda = 1.5418$ Å
Orthorhombic	Cell parameters from 21
$Pbca$	reflections
$a = 15.266\,(2)$ Å	$\theta = 49.6–57.0°$
$b = 16.262\,(3)$ Å	$\mu = 0.598$ mm^{-1}
$c = 14.1071\,(15)$ Å	$T = 294$ K
$V = 3502.1\,(7)$ Å^3	Octahedron
$Z = 8$	$0.40 \times 0.40 \times 0.40$ mm
$D_x = 1.283$ Mg m^{-3}	Colourless
D_m not measured	

Data collection

Rigaku AFC-6S diffractometer	2722 reflections with $I > 3\sigma(I)$
ω–2θ scan	$\theta_{max} = 77.62°$
Absorption correction:	$h = 0 \rightarrow 19$
ψ scans (North, Phillips & Mathews, 1968)	$k = 0 \rightarrow 20$
	$l = 0 \rightarrow 17$
$T_{min} = 0.765$, $T_{max} = 0.787$	3 standard reflections
3413 measured reflections	every 200 reflections
3413 independent reflections	intensity decay: 1.5%

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.26$ e Å^{-3}
$R(F) = 0.041$	$\Delta\rho_{min} = -0.21$ e Å^{-3}
$wR(F^2) = 0.118$	Extinction correction:
$S = 2.22$	Zachariasen (1967)
3413 reflections	Extinction coefficient:
236 parameters	$4.4\,(4) \times 10^{-6}$
H atoms not refined	Scattering factors from
$w = 1/[\sigma^2(F_o^2)$	*International Tables for*
$+ 0.00022(F_o^2)^2]$	*Crystallography* (Vol. C)
$(\Delta/\sigma)_{max} = 0.001$	

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR*92 (Altomare, Cascarano, Giacovazzo & Guagliardi, 1993). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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N,N-Diethyl-N'-methyl-4b,8b,8c,8d-tetrahydrodibenzo[a,f]cyclopropa[cd]pentalene-8b,8c-dicarboxamide

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Abstract

The title compound, $C_{23}H_{24}N_2O_2$, is a product of photolysis of an unsymmetrical dibenzobarrelene diamide and has a dibenzosemibullvalene structure with normal molecular geometry and dimensions. Molecules are linked by one N—H$\cdots$O hydrogen bond.

Comment

Dibenzobarrelene 11,12-diesters undergo di-π-methane rearrangements in solution and in the solid state to give dibenzosemibullvalene diesters. Unsymmetrically substituted dibenzobarrelenes (with two different ester groups) give two possible dibenzosemibullvalene photoproducts and variations in product ratios have been interpreted in terms of differing electronic and intra- and intermolecular steric effects (Scheffer, Trotter, Garcia-Garibay & Wireko, 1988; Garcia-Garibay, Scheffer,