Experimental

The material is obtained by photolysis of a 9,10-dihydro-9,10-ethenoanthracene derivative, with 11,12 phenyl and methoxycarbonyl 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
$w = 1/[\sigma^2(F_o^2) + 0.00022(F_o^2)^2]$	International Tables for 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: *SIR92* (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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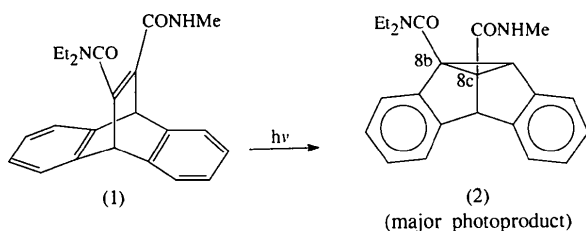
Abstract

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,

Trotter & Wireko, 1990). The photochemistry of the unsymmetrical diamide, (1), has been studied to determine whether dibenzobarrelenes with two different amide substituents behave in a similar fashion to the diesters. The products of photolysis of (1) are two possible isomeric dibenzosemibullvalenes, and in addition possible H-atom abstraction products (Jones, Rattray, Rettig, Scheffer & Trotter, 1996).
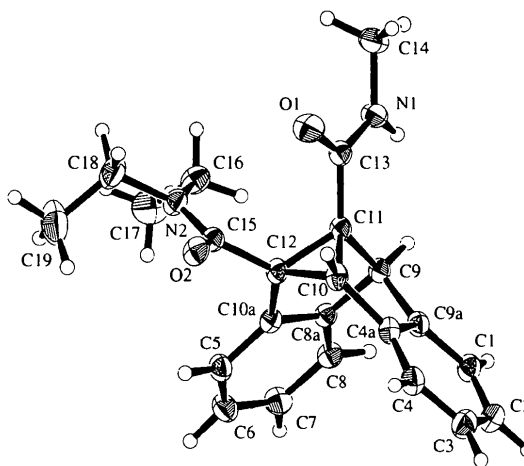

(1)   (2)
           (major photoproduct)

Fig. 1. A view of the title molecule (dibenzobarrelene numbering system). Displacement ellipsoids are drawn at the 33% probability level.

Photolysis of (1) in solution results in the formation of three principal products, in the ratio 50:30:15. The major product is easily separated from the two minor products by column chromatography, but establishment of its molecular structure proved difficult since it exhibits unusual NMR data (Rattray, 1992; see supplementary material). The proton NMR spectrum of the solution exhibits a double set of peaks in the intensity ratio 2:1, suggesting the presence of two compounds. However, the material could not be further purified. In addition, the photoproduct was synthesized by two alternative methods, one photochemical and one nonphotochemical (see Rattray, 1992, for details); all methods gave identical material, with the unusual NMR spectrum.

The structure has therefore been determined from a single crystal by X-ray analysis and proves to be the dibenzosemibullvalene, (2) (Fig. 1). Another single crystal from the same batch of crystals was dissolved in deuterochloroform and gave the same NMR spectrum as previously observed. A single compound is therefore responsible for the dual set of NMR peaks and the reasons for this unusual spectroscopic behaviour are not readily apparent. One possibility is the presence in solution of conformational isomers as a result of restricted rotation about single bonds. When the spectrum is measured at higher temperatures, the two sets of peaks start to coalesce (which could be a result of a faster rate of interconversion of two magnetically distinct conformations), but the peaks also broaden and a spectrum with a single set of peaks was not obtained. Hence, the reason for the doubled peaks is not established.

Compound (2) contains a dibenzosemibullvalene ring structure, which is folded, and contains a three-membered ring (Fig. 1). Bond lengths and angles are normal and are available in the supplementary material. Molecules are linked by one N1—H$\cdots$O2 hydrogen bond.

The two minor photoproducts from the irradiation of (1) were recovered as a mixture after separation of the major photoproduct, (2), by column chromatography. Successive crystallization yielded first the minor (15%) product and then the third (30%) product. IR, NMR and MS (mass spectrometry) data for the 15% product, together with independent synthesis (Rattray, 1992) showed it to be an H-atom abstraction product, similar to those obtained from monoamides (Jones *et al.*, 1996). Similar data (no unusual NMR data) for the 30% product established that it is the isomeric dibenzosemibullvalene [(2), with an interchange of 8b and 8c substituents].

Experimental

Compound (2) was obtained by photolysis of a dibenzobarrelene derivative (Rattray, 1992; details are in the supplementary material).

Crystal data

$C_{23}H_{24}N_2O_2$	Cu $K\alpha$ radiation
$M_r = 360.45$	$\lambda = 1.5418$ Å
Monoclinic	Cell parameters from 22
$P2_1/n$	reflections
$a = 8.766\,(2)$ Å	$\theta = 47.3–56.2°$
$b = 17.885\,(2)$ Å	$\mu = 0.597$ mm^{-1}
$c = 12.612\,(2)$ Å	$T = 294$ K
$\beta = 103.661\,(11)°$	Prismatic
$V = 1921.4\,(4)$ Å^3	$0.50 \times 0.20 \times 0.15$ mm
$Z = 4$	Colourless
$D_x = 1.246$ Mg m^{-3}	
D_m not measured	

Data collection

Rigaku AFC-6S diffractometer	2867 reflections with
eter	$I > 3\sigma(I)$

ω–2θ scans
Absorption correction:
  ψ scans (North, Phillips
  & Mathews, 1968)
  $T_{min} = 0.671$, $T_{max} = 0.914$
4325 measured reflections
3930 independent reflections

$R_{int} = 0.065$
$\theta_{max} = 77.52°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 22$
$l = -15 \rightarrow 15$
3 standard reflections
  every 200 reflections
  intensity decay: 0.08%

Refinement

Refinement on F^2
$R(F) = 0.043$
$wR(F^2) = 0.119$
$S = 1.78$
3930 reflections
249 parameters
H atoms: H on N1 refined,
  others fixed
$w = 1/[\sigma^2(F_o^2)$
  $+ 0.00031(F_o^2)^2]$

$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}
Extinction correction:
  Zachariasen (1967)
Extinction coefficient:
  0.53 (6) × 10^{-5}
Scattering factors from
  International Tables for
  Crystallography (Vol. C)

Table 1. *Hydrogen-bonding geometry (Å, °)*

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N1—H1⋯O2^i	0.90 (2)	2.03 (2)	2.910 (2)	166 (2)

Symmetry code: (i) $\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992). 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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Phenanthrene-9-carboxylic Acid

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Abstract

The title compound, $C_{15}H_{10}O_2$, crystallized in the centrosymmetric space group $C2/c$. Hydrogen bonding is of the cyclic dimer type about a center of symmetry. The carboxyl H and O atoms are ordered. The phenanthrene core is almost planar and the dihedral angle between the core plane and the carboxyl group plane is only 1.8 (1)°. The bay H atoms, H4 and H5, lie close to the core plane and 2.02 (2) Å from each other; the refinement places them on opposite sides of the core plane, but this result has little statistical significance.

Comment

This is one of a series of reports on hydrogen bonding in polyaromatic carboxylic acids. Among earlier reports are those on anthracene-9-carboxylic acid and anthracene-1-carboxylic acid (Fitzgerald & Gerkin, 1997*a,b*). Phenanthrene-9-carboxylic acid, (I), crystallized in the centrosymmetric space group $C2/c$. The hydrogen bonding is of the cyclic dimer type about a center of symmetry. A diagram of the dimer showing our numbering scheme appears in Fig. 1. Geometric details of the hydrogen bond are given in Table 2. Those data and data from Table 1 make clear that both the carboxyl H atom and the carboxyl O atoms are ordered.

(I)
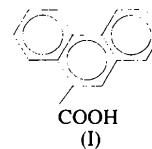
With respect to pseudo-mirror symmetry, the phenanthrene core in this acid shows an r.m.s. deviation of 0.014 Å within the seven pairs of distances which would be identical under mirror symmetry, the e.s.d.'s of the individual distances being 0.002–0.003 Å. For the five pairs of distances unique to the outer rings of the core, the corresponding r.m.s. deviation is 0.005 Å. Thus it appears that the presence of the carboxyl group on the central ring interferes substantially with the pseudo-symmetry of the core. Interestingly, however, in phenanthrene itself, as reported by Kay, Okaya & Cox (1971), pseudo-symmetry is not much better satisfied, the r.m.s.