

Table 3. Selected bond lengths (Å) and angles (°)

	(4)	(13)
C=C	1.315 (3), 1.331 (2)	1.326 (3)
C—C (aromatic)	1.368–1.395 (3)	1.372–1.401 (3)
C—C (three ring)	—	1.508–1.559 (2)
C—CO	1.470–1.504 (2)	1.490–1.508 (2)
C—C (other)	1.519–1.536 (2)	1.478–1.561 (2)
C=O	1.203, 1.213 (2)	1.200, 1.214 (2)
C—OMe	1.335 (2)	1.331 (2)
O—Me	1.440 (2)	1.442 (2)
Ring angles		
Aromatic rings	118.8–120.8 (2)	117.7–121.6 (2)
Aromatic/five-ring junction (external)	126.9, 127.0 (2)	129.0, 128.5 (1)
Three-membered ring	—	58.8–62.1 (1)

Data collection, cell refinement, data reduction, structure solution and refinement, and graphical representation used the *TEXSAN* program package (Molecular Structure Corporation, 1985). *TEXSAN* includes modified versions of *MITHRIL* (Gilmore, 1984), *DIFABS* (Walker & Stuart, 1983), *ORFLS* (Busing, Martin & Levy, 1962) and *ORTEP* (Johnson, 1976), with scattering factors (*International Tables for X-ray Crystallography*, 1974, Vol. IV) and extinction correction (Zachariasen, 1963).

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

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, and stereo molecular and packing diagrams of (4) and (13) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71724 (57 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1059]

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*Acta Cryst.* (1994). **C50**, 581–583

## The Photolysis Product of Dimethyl 9,10-Diphenyl-1,4-dihydro-1,4-ethenoanthracene-11,12-dicarboxylate

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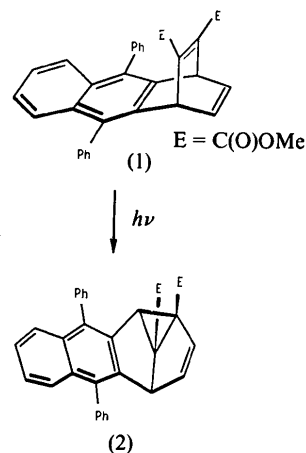
(Received 19 April 1993; accepted 6 October 1993)

### Abstract

Photolysis of the title compound (1) produces a semibullvalene photoproduct dimethyl 3,8-diphenyl-2a,2b,8b,8c-tetrahydrocyclopropa[1',2',3':3,3a,4]pentaleno[1,2-*b*]-naphthalene-2a,8c-dicarboxylate (2) via a di- $\pi$ -methane rearrangement. The molecule of (2) contains a three-membered ring and has geometry and dimensions similar to those of related materials.

### Comment

Reaction of 9,10-diphenylanthracene and dimethyl acetylenedicarboxylate<sup>†</sup> gives only the 1,4-ethenoanthracene product (1).<sup>‡</sup> Photolysis of (1) in solution or in the solid state<sup>†</sup> gives only one photoproduct, whose structure has now been established by X-ray methods as the semibullvalene (2); formation of (2) can be rationalized on the ba-



sis of di- $\pi$ -methane rearrangement (Pokkuluri, Scheffer & Trotter, 1993*a,b*). The general geometry and dimensions of molecule (2) are similar to those of related materials (Pokkuluri *et al.*, 1993*b*).

<sup>†</sup> See deposited material.

<sup>‡</sup> The molecule of (1) has been numbered for correlation with the related 9,10-ethenoanthracene compounds, and this numbering system has been retained for (2).

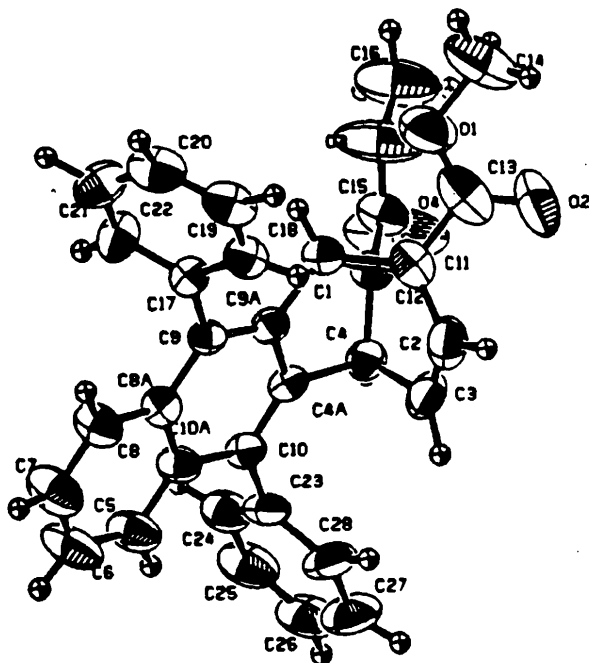


Fig. 1. View of the molecule with 50% probability ellipsoids, showing the 1,4-ethanoanthracene numbering system.

## Experimental

### Crystal data

C<sub>32</sub>H<sub>24</sub>O<sub>4</sub>

*M<sub>r</sub>* = 472.54

Monoclinic

C2/c

*a* = 29.368 (1) Å

*b* = 13.378 (2) Å

*c* = 13.186 (2) Å

β = 111.52 (1)°

*V* = 4819.4 (4) Å<sup>3</sup>

*Z* = 8

*D<sub>x</sub>* = 1.30 Mg m<sup>-3</sup>

Cu Kα radiation

λ = 1.5418 Å

Cell parameters from 25 reflections

θ = 25–40°

μ = 0.64 mm<sup>-1</sup>

*T* = 294 K

Prism

0.3 × 0.2 × 0.2 mm

Colourless

### Data collection

Rigaku AFC-6 diffractometer

ω/2θ scans

Absorption correction:

DIFABS (Walker & Stuart, 1983)

*T<sub>min</sub>* = 0.87, *T<sub>max</sub>* = 1.16

5409 measured reflections

4961 independent reflections

2261 observed reflections

[*I* > 3σ(*I*)]

*R<sub>int</sub>* = 0.06

θ<sub>max</sub> = 77.7°

*h* = -37 → 37

*k* = 0 → 17

*l* = 0 → 17

3 standard reflections

monitored every 150 reflections

intensity variation: none

### Refinement

Refinement on *F*

*R* = 0.068

*wR* = 0.088

*S* = 2.3

Δρ<sub>max</sub> = 0.25 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.27 e Å<sup>-3</sup>

Extinction correction: not applied

2261 reflections

325 (+ 68 H-atom) parameters

*w* = 1/σ<sup>2</sup>(*F*)

(Δ/σ)<sub>max</sub> = 0.01

Atomic scattering factors

from TEXSAN (Molecular Structure Corporation, 1985)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
C1	0.1839 (2)	0.2452 (4)	0.7414 (4)	0.044 (3)
C2	0.2242 (2)	0.2347 (6)	0.5964 (5)	0.072 (4)
C3	0.1980 (2)	0.3104 (5)	0.5384 (5)	0.067 (4)
C4	0.1771 (2)	0.3731 (4)	0.6068 (4)	0.051 (3)
C4a	0.1271 (2)	0.3242 (3)	0.5835 (3)	0.042 (3)
C5	-0.0022 (2)	0.2942 (5)	0.4077 (5)	0.066 (4)
C6	-0.0410 (2)	0.2316 (5)	0.3921 (5)	0.085 (4)
C7	-0.0346 (2)	0.1489 (5)	0.4611 (5)	0.077 (4)
C8	0.0089 (2)	0.1308 (4)	0.5407 (4)	0.058 (3)
C8a	0.0493 (2)	0.1940 (3)	0.5609 (4)	0.043 (3)
C9	0.0954 (2)	0.1773 (3)	0.6457 (3)	0.038 (2)
C9a	0.1337 (2)	0.2409 (3)	0.6570 (3)	0.041 (2)
C10	0.0838 (2)	0.3439 (3)	0.5031 (3)	0.043 (2)
C10a	0.0426 (2)	0.2802 (3)	0.4893 (4)	0.047 (3)
C11	0.2293 (2)	0.2396 (4)	0.7114 (4)	0.058 (3)
C12	0.2069 (2)	0.3408 (4)	0.7238 (4)	0.048 (3)
C13	0.2784 (3)	0.2095 (4)	0.7902 (7)	0.080 (4)
C14	0.3276 (3)	0.1643 (7)	0.9645 (7)	0.123 (6)
C15	0.2318 (2)	0.4165 (4)	0.8071 (4)	0.058 (3)
C16	0.2809 (3)	0.4499 (5)	0.9889 (5)	0.118 (5)
C17	0.1028 (2)	0.0894 (3)	0.7204 (4)	0.041 (3)
C18	0.1380 (2)	0.0177 (4)	0.7261 (4)	0.053 (3)
C19	0.1440 (2)	-0.0657 (4)	0.7913 (5)	0.063 (4)
C20	0.1156 (3)	-0.0785 (4)	0.8520 (5)	0.070 (4)
C21	0.0818 (3)	-0.0080 (5)	0.8509 (5)	0.072 (4)
C22	0.0765 (2)	0.0760 (4)	0.7866 (5)	0.058 (3)
C23	0.0787 (2)	0.4323 (4)	0.4292 (4)	0.052 (3)
C24	0.0576 (2)	0.5197 (4)	0.4449 (5)	0.063 (3)
C25	0.0547 (3)	0.6004 (5)	0.3775 (6)	0.080 (5)
C26	0.0712 (3)	0.5959 (7)	0.2957 (6)	0.096 (5)
C27	0.0935 (3)	0.5094 (7)	0.2795 (5)	0.095 (6)
C28	0.0967 (2)	0.4267 (5)	0.3452 (4)	0.071 (4)
O1	0.2779 (2)	0.1760 (4)	0.8832 (4)	0.100 (3)
O2	0.3150 (2)	0.2110 (4)	0.7651 (5)	0.101 (4)
O3	0.2523 (2)	0.3820 (3)	0.9026 (3)	0.125 (4)
O4	0.2346 (3)	0.4996 (3)	0.7884 (4)	0.158 (5)

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

C=C	1.331 (9)	C=O	1.235 (8), 1.148 (6)
C—C (aromatic)	1.34–1.46 (1)	C—OMe	1.311 (8), 1.267 (6)
C—C (three ring)	1.504–1.540 (7)	O—Me	1.468 (8), 1.458 (7)
C—CO <sub>2</sub> Me	1.491 (8), 1.476 (7)		
C—C (other)	1.47–1.53 (1)		

### Ring angles

Aromatic rings	116.8–123.4 (4)
Aromatic/five-ring junction (external)	129.2, 130.7 (4)
Three-membered ring	58.7–61.1 (3)

The methyl group H atoms were fixed; H26 was fixed, since refinement gave an unacceptably high displacement parameter. Difference map peaks of about 0.3 e Å<sup>-3</sup> indicate possible minor disorder in one ester group (O1 and O14). Data collection, cell refinement, data reduction, structure solution and refinement, and graphical representation used the TEXSAN program package (Molecular Structure Corporation, 1985). TEXSAN includes modified versions of MITHRIL (Gilmore, 1984), DIFABS (Walker & Stuart, 1983), ORFLS (Busing, Martin & Levy, 1962) and ORTEP (Johnson, 1976), with scattering factors (*International Tables for X-ray Crystallography*, 1974, Vol. IV) and extinction correction (Zachariasen, 1963).

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

Details of synthesis and photolysis, stereo molecular and packing diagrams, and lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71715 (47 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1057]

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## *N*-[2-(2-Formylphenyl)ethyl]-2-nitroaniline

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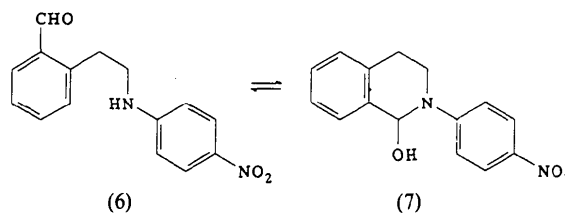
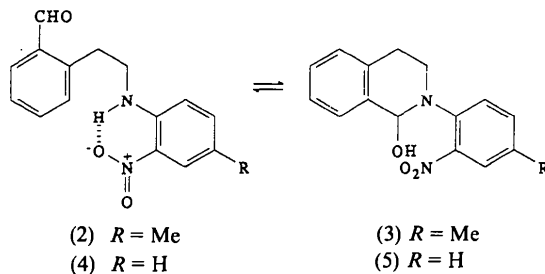
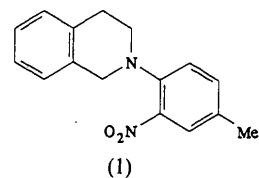
(Received 22 June 1993; accepted 7 October 1993)

## Abstract

The structure of the molecule,  $C_{15}H_{14}N_2O_3$ , consists of essentially planar and parallel nitroaniline and benzaldehyde fragments [dihedral angle  $2.7$  ( $4^\circ$ )], linked through an ethylene bridge between the aniline N atom and an *ortho* C atom of the benzaldehyde fragment. The aldehyde and nitro substituents are essentially coplanar with their respective rings. Intramolecular hydrogen bonding occurs between the amino and nitro groups; there are no significant intermolecular interactions.

## Comment

The reaction between *N*-(4-methyl-2-nitrophenyl)-1,2,3,4-tetrahydroisoquinoline (1) with oxygen yielded *N*-[2-(2-formylphenyl)ethyl]-4-methyl-2-nitroaniline (2) (Shawcross & Stanforth, 1990). In principle, this product aldehyde may exist as the hemi-aminal (3), but proton NMR spectroscopy firmly established the aldehyde structure (2). We anticipated that the aldehyde would be preferred to the hemi-aminal because of intramolecular hydrogen bonding between the amine group and the adjacent nitro group. Consequently, the title compound (4) has been prepared (Hedley & Stanforth, 1992) in order to establish by X-ray crystallography both the structural form and the presence of intramolecular hydrogen bonding. In a previous report (Streith & Fizet, 1977), NMR spectroscopy indicated that the aldehyde (4) and not the corresponding hemi-aminal (5) was present. It is noteworthy that (7), which has also been prepared, exists in the hemi-aminal and not in the aldehyde form (6), presumably because intramolecular hydrogen bonding is not possible in this case (Stanforth, 1993).



The structure determination shows clearly that the aldehyde form is present and that intramolecular hydrogen bonding occurs between the amine and nitro groups. The  $O19 \cdots N11$  distance is  $2.578$  (8),  $O19 \cdots H11$  is  $1.920$  (9) Å and the  $O19 \cdots H11 - N11$  angle is  $129.4$  ( $3^\circ$ ), giving a six-membered ring involving the hydrogen bond.

An ethylene bridge links the two ring systems of the molecule; the bridge connects an *ortho* C atom of the benzaldehyde fragment to the amino N atom of the nitroaniline fragment. The two rings are essentially planar (r.m.s. deviation  $0.008$  Å for both) and parallel [dihedral