C9	0.9900 (2)	0.8810 (2)	0.3334 (3)	0.040 (1)
C9a	0.9367 (2)	0.9655 (2)	0.3165 (3)	0.042 (1)
C10	1.0974 (3)	0.9577 (2)	0.1190 (3)	0.042 (1)
C10a	1.0295 (3)	0.8818 (2)	0.0666 (3)	0.040 (1)
C11	1.1363 (2)	0.8888 (2)	0.3458 (3)	0.038 (1)
C12	1.1942 (2)	0.9291 (2)	0.2358 (3)	0.038 (1)
C13	1.1786 (3)	0.8429 (2)	0.4772 (3)	0.045 (1)
C14	0.9542 (3)	0.8344 (2)	0.4742 (3)	0.051 (2)
C15	1.3328 (3)	0.9480 (2)	0.2113 (3)	0.042 (1)
C16	1.5485 (3)	0.9143 (4)	0.2626 (6)	0.072 (3)
O1	1.0744 (2)	0.8086 (1)	0.5395 (2)	0.056 (1)
O2	1.2843 (2)	0.8318 (2)	0.5270 (3)	0.066 (1)
O3	1.4126 (2)	0.9002 (2)	0.2843 (3)	0.060 (1)
O4	1.3682 (2)	1.0024 (2)	0.1365 (4)	0.086 (2)

Table 2. *Selected geometric parameters (Å, °)*

C1—C2	1.368 (5)	C9—C9a	1.516 (4)
C1—C9a	1.393 (4)	C9—C11	1.524 (3)
C2—C3	1.393 (6)	C9—C14	1.530 (4)
C3—C4	1.400 (5)	C10—C10a	1.519 (4)
C4—C4a	1.377 (4)	C10—C12	1.527 (4)
C4a—C9a	1.398 (4)	C11—C12	1.337 (4)
C4a—C10	1.529 (4)	C11—C13	1.473 (4)
C5—C6	1.392 (5)	C12—C15	1.485 (4)
C5—C10a	1.373 (4)	C13—O1	1.342 (4)
C6—C7	1.366 (5)	C13—O2	1.196 (4)
C7—C8	1.395 (5)	C14—O1	1.441 (4)
C8—C8a	1.382 (4)	C15—O3	1.321 (4)
C8a—C9	1.534 (4)	C15—O4	1.185 (4)
C8a—C10a	1.399 (4)	C16—O3	1.439 (4)
C2—C1—C9a	119.4 (3)	C4a—C9a—C9	112.4 (2)
C1—C2—C3	120.8 (3)	C4a—C10—C10a	106.3 (2)
C2—C3—C4	120.1 (3)	C4a—C10—C12	107.0 (2)
C3—C4—C4a	118.9 (3)	C10a—C10—C12	105.0 (2)
C4—C4a—C9a	120.6 (3)	C5—C10a—C8a	120.2 (3)
C4—C4a—C10	126.7 (3)	C5—C10a—C10	127.0 (3)
C9a—C4a—C10	112.7 (2)	C8a—C10a—C10	112.8 (2)
C6—C5—C10a	119.5 (3)	C9—C11—C12	115.7 (2)
C5—C6—C7	120.3 (3)	C9—C11—C13	108.1 (2)
C6—C7—C8	121.1 (3)	C12—C11—C13	136.1 (2)
C7—C8—C8a	118.5 (3)	C10—C12—C11	111.8 (2)
C8—C8a—C9	127.5 (2)	C10—C12—C15	117.8 (2)
C8—C8a—C10a	120.4 (3)	C11—C12—C15	130.5 (2)
C9—C8a—C10a	112.1 (2)	C11—C13—O1	108.4 (2)
C8a—C9—C9a	105.2 (2)	C11—C13—O2	130.7 (3)
C8a—C9—C11	104.5 (2)	O1—C13—O2	120.9 (3)
C8a—C9—C14	118.4 (2)	C9—C14—O1	106.2 (2)
C9a—C9—C11	106.9 (2)	C12—C15—O3	113.8 (2)
C9a—C9—C14	117.6 (2)	C12—C15—O4	123.0 (3)
C11—C9—C14	102.9 (2)	O3—C15—O4	123.2 (3)
C1—C9a—C4a	120.1 (3)	C13—O1—C14	113.4 (2)
C1—C9a—C9	127.5 (3)	C15—O3—C16	116.5 (3)

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), *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).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, and stereo molecular and packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71734 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1060]

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An Ethenonaphthalene and One of its Photolysis Products

Phani Raj Pokkuluri, John R. Scheffer, James Trotter and Melvin Yap

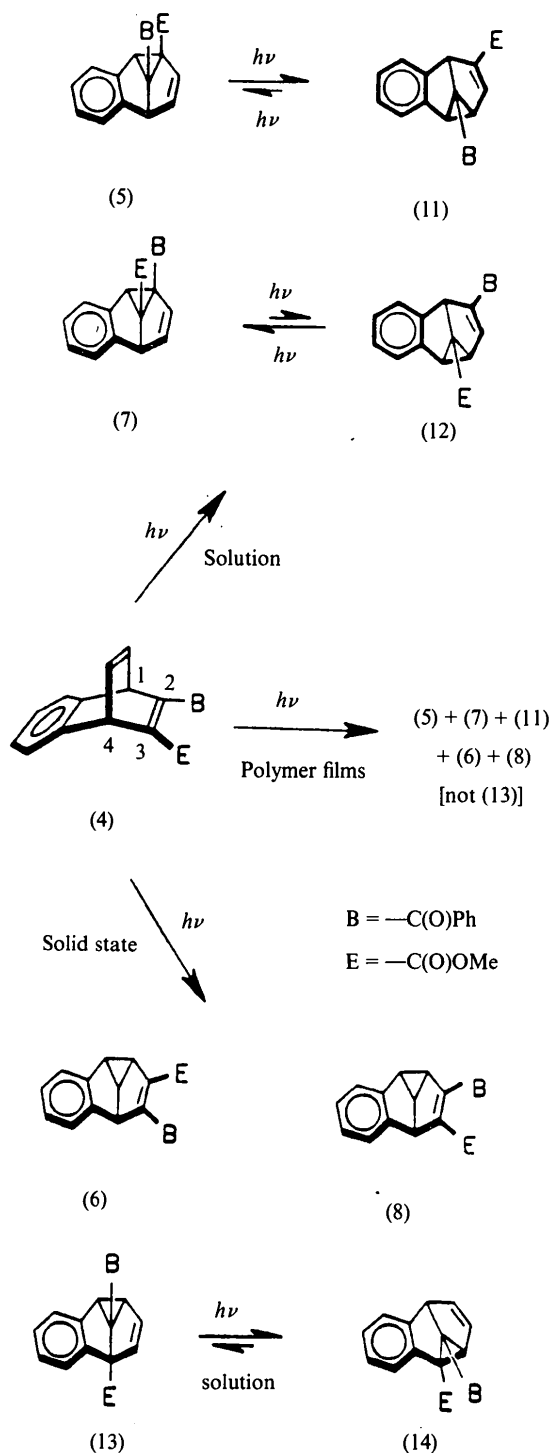*Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Z1*

Abstract

Photolysis of methyl 2-benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (4) produces two di-π-methane photoproducts in solution, but three different products in the solid state. The structures of (4) and an unusual solid-state photoproduct methyl 6c-benzoyl-2a,2b,6b,6c-tetrahydrobenzo[*a*]cyclopropa[*cd*]pentalene-6b-carboxylate (13) have been determined by X-ray crystal analyses.

Comment

Photolysis of methyl 2-benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (4) in solution gives two primary di-π-methane-type photoproducts, (5) and (7), with the 1,3-shift isomers (11) and (12) forming as the photolysis proceeds [see scheme below where compounds are numbered according to Pokkuluri, Scheffer, Trotter & Yap (1992)]. In solid-state photolysis, three different photoproducts are formed, (6), (8) and (13), the last of which cannot be formed *via* a standard di-π-methane mechanism. The structures of (4) and (13) have been determined by X-ray methods; the molecular structures and dimensions are similar to those of related materials (Pokkuluri,
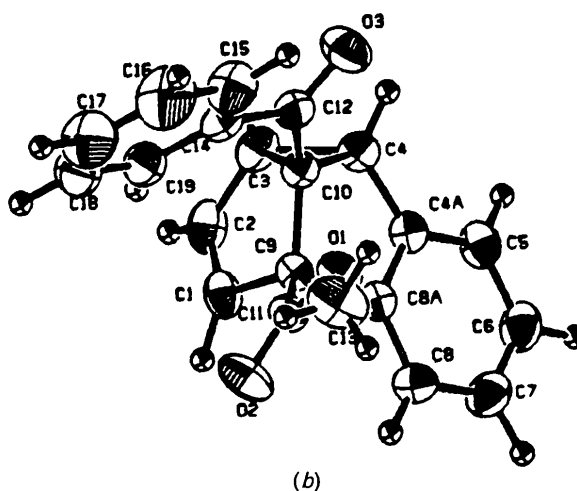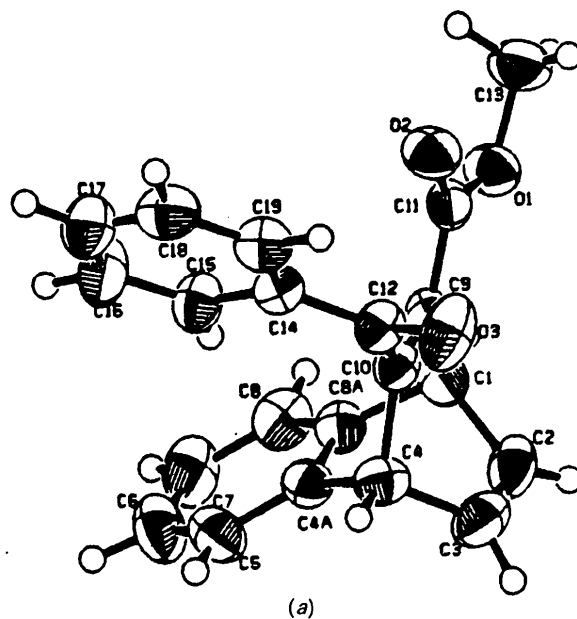
Fig. 1. Views of the molecules of (a) (4) and (b) (13) with 50% probability ellipsoids. The numbering system corresponds to that used in 1,4-ethenoanthracenes.

B = —C(O)Ph

E = —C(O)OMe

Experimental

Compound (4) was synthesized according to the procedure described by Pokkuluri et al. (1992). Compound (13) was synthesized via the solid-state photolysis of compound (4) (Pokkuluri et al., 1992).

Compound (4)

Crystal data

$C_{21}H_{16}O_3$	$D_x = 1.30$ Mg m^{-3}
$M_r = 316.36$	Cu $K\alpha$ radiation
Triclinic	$\lambda = 1.5418$ Å

Scheffer & Trotter, 1993). The different behaviours in solution and solid state can be rationalized on the basis of reaction mechanisms which involve large movements of the benzoyl and ester substituents in the solution reactions; these large movements are topochemically hindered in the solid state by intermolecular H· · ·O contacts of about 2.7–2.8 Å (Pokkuluri et al., 1992).

$P\bar{1}$
$a = 9.772$ (1) Å
$b = 11.034$ (2) Å
$c = 8.174$ (1) Å
$\alpha = 92.58$ (1)°
$\beta = 111.50$ (1)°
$\gamma = 97.96$ (1)°
$V = 807.8$ (2) Å^3
$Z = 2$

Cell parameters from 11 reflections
$\theta = 60.7–61.8°$
$\mu = 0.66$ mm^{-1}
$T = 294$ K
Prism
$0.5 \times 0.4 \times 0.3$ mm
Colourless

Data collection

Rigaku AFC-6 diffractometer
$\omega/2\theta$ scans
Absorption correction:
ψ scans
$T_{min} = 0.89$, $T_{max} = 1.0$
3474 measured reflections
3280 independent reflections
2887 observed reflections
[$I > 3\sigma(I)$]

$R_{int} = 0.011$
$\theta_{max} = 77.4°$
$h = 0 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = -10 \rightarrow 10$
3 standard reflections
monitored every 150 reflections
intensity variation: none

Refinement

Refinement on F
$R = 0.042$
$wR = 0.080$
$S = 2.7$
2887 reflections
282 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.01$

$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}
Extinction correction:
Zachariasen (1963)
Extinction coefficient:
0.39×10^{-4}
Atomic scattering factors from *TEXSAN* (Molecular Structure Corporation, 1985)

Compound (13)

Crystal data

$C_{21}H_{16}O_3$
$M_r = 316.36$
Orthorhombic
Pbca
$a = 33.023$ (2) Å
$b = 11.210$ (1) Å
$c = 8.637$ (2) Å
$V = 3197$ (1) Å^3
$Z = 8$
$D_x = 1.314$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 23 reflections
$\theta = 48.4–56.5°$
$\mu = 0.66$ mm^{-1}
$T = 294$ K
Prism
$0.5 \times 0.4 \times 0.3$ mm
Colourless

Data collection

Rigaku AFC-6 diffractometer
$\omega/2\theta$ scans
Absorption correction:
ψ scans
$T_{min} = 0.92$, $T_{max} = 1.00$
3730 measured reflections
3730 independent reflections
2261 observed reflections
[$I > 3\sigma(I)$]

$\theta_{max} = 77.5°$
$h = 0 \rightarrow 42$
$k = 0 \rightarrow 14$
$l = -11 \rightarrow 0$
3 standard reflections
monitored every 150 reflections
intensity variation: none

Refinement

Refinement on F
$R = 0.042$
$wR = 0.063$
$S = 2.0$
2661 reflections
282 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.01$

$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}
Extinction correction:
Zachariasen (1963)
Extinction coefficient:
0.37×10^{-5}
Atomic scattering factors from *TEXSAN* (Molecular Structure Corporation, 1985)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (4)

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

	x	y	z	U_{eq}
C1	−0.0201 (1)	0.3299 (1)	0.6166 (2)	0.050 (1)
C2	−0.0951 (2)	0.2189 (2)	0.4772 (2)	0.066 (1)
C3	−0.1036 (2)	0.1125 (2)	0.5423 (2)	0.066 (1)
C4	−0.0366 (2)	0.1236 (1)	0.7430 (2)	0.051 (1)
C4a	−0.1186 (1)	0.2128 (1)	0.8039 (2)	0.047 (1)
C5	−0.1968 (2)	0.1909 (2)	0.9127 (2)	0.062 (1)
C6	−0.2658 (2)	0.2836 (2)	0.9532 (3)	0.074 (1)
C7	−0.2536 (2)	0.3957 (2)	0.8901 (3)	0.072 (1)
C8	−0.1743 (2)	0.4180 (2)	0.7802 (2)	0.059 (1)
C8a	−0.1084 (1)	0.3250 (1)	0.7363 (2)	0.046 (1)
C9	0.1319 (1)	0.3004 (1)	0.7317 (2)	0.042 (1)
C10	0.1237 (1)	0.1928 (1)	0.7978 (2)	0.042 (1)
C11	0.2744 (1)	0.3812 (1)	0.7659 (2)	0.043 (1)
C12	0.2526 (1)	0.1346 (1)	0.9091 (2)	0.046 (1)
C13	0.3930 (2)	0.5564 (2)	0.6882 (3)	0.070 (1)
C14	0.3066 (1)	0.1587 (1)	1.1039 (2)	0.043 (1)
C15	0.2288 (2)	0.2207 (1)	1.1832 (2)	0.055 (1)
C16	0.2762 (2)	0.2370 (2)	1.3653 (2)	0.073 (1)
C17	0.4025 (2)	0.1937 (2)	1.4696 (2)	0.071 (1)
C18	0.4815 (2)	0.1339 (2)	1.3918 (2)	0.063 (1)
C19	0.4336 (2)	0.1147 (1)	1.2096 (2)	0.053 (1)
O1	0.2574 (1)	0.4764 (1)	0.6693 (1)	0.055 (1)
O2	0.3932 (1)	0.3624 (1)	0.8665 (1)	0.058 (1)
O3	0.3024 (2)	0.0637 (1)	0.8369 (2)	0.072 (1)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (13)

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

	x	y	z	U_{eq}
C1	0.90428 (5)	−0.1270 (1)	0.6771 (2)	0.042 (1)
C2	0.88165 (5)	−0.1128 (2)	0.5516 (2)	0.047 (1)
C3	0.85968 (5)	0.0021 (1)	0.5543 (2)	0.043 (1)
C4	0.88239 (4)	0.1231 (1)	0.5727 (2)	0.037 (1)
C4a	0.92703 (4)	0.1269 (1)	0.5871 (2)	0.035 (1)
C5	0.95485 (5)	0.1930 (1)	0.5024 (2)	0.044 (1)
C6	0.99560 (5)	0.1887 (2)	0.5456 (2)	0.052 (1)
C7	1.00810 (5)	0.1173 (2)	0.6664 (2)	0.051 (1)
C8	0.98039 (4)	0.0477 (1)	0.7496 (2)	0.043 (1)
C8a	0.93987 (4)	0.0559 (1)	0.7093 (2)	0.033 (1)
C9	0.90394 (4)	−0.0143 (1)	0.7745 (2)	0.032 (1)
C10	0.86672 (4)	0.0567 (1)	0.7122 (2)	0.033 (1)
C11	0.90724 (4)	−0.0307 (1)	0.9473 (2)	0.034 (1)
C12	0.83250 (4)	0.1032 (1)	0.8077 (2)	0.036 (1)
C13	0.89584 (9)	0.0642 (2)	1.1882 (2)	0.063 (1)
C14	0.81256 (4)	0.0223 (1)	0.9214 (2)	0.039 (1)
C15	0.79151 (6)	0.0726 (2)	1.0440 (2)	0.057 (1)
C16	0.77260 (7)	0.0003 (2)	1.1515 (3)	0.079 (1)
C17	0.77399 (7)	−0.1227 (2)	1.1353 (3)	0.076 (1)
C18	0.79435 (6)	−0.1730 (4)	1.0132 (3)	0.065 (1)
C19	0.81418 (5)	−0.1014 (1)	0.9072 (2)	0.047 (1)
O1	0.89607 (3)	0.0681 (1)	1.0213 (1)	0.040 (1)
O2	0.91990 (5)	−0.1188 (1)	1.0098 (1)	0.060 (1)
O3	0.82042 (4)	0.2046 (1)	0.7900 (2)	0.058 (1)

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).

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

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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-π-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† gives only the 1,4-ethenoanthracene product (1).‡ Photolysis of (1) in solution or in the solid state† 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-

E = C(O)OMe (1)

hν

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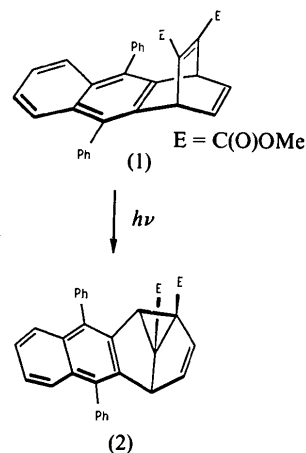
sis of di-π-methane rearrangement (Pokkuluri, Scheffer & Trotter, 1993*a,b*). The general geometry and dimensions of molecule (2) are similar to those of related materials (Pokkuluri *et al.*, 1993*b*).

† See deposited material.
‡ 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).