

C2—C1—C6	119,4 (3)	C8B—C9B—C10B	127,5 (3)
C2—C1—C7B	122,6 (4)	C11B—C10B—C9B	122,0 (4)
C6—C1—C7B	118,1 (3)	C11B—C10B—C15B	123,5 (4)
C1—C2—C3	121,4 (4)	C9B—C10B—C15B	114,4 (4)
C4—C3—C2	118,3 (3)	C10B—C11B—C18B	125,3 (5)
C4—C3—C7C	124,3 (3)	C10B—C11B—C12B	121,6 (5)
C2—C3—C7C	117,3 (4)	C18B—C11B—C12B	113,0 (4)
C3—C4—C5	121,7 (3)	C13B—C12B—C11B	114,3 (5)
C4—C5—C6	118,7 (4)	C14B—C13B—C12B	123,0 (*)
C4—C5—C7A	123,0 (3)	C13B—C14B—C15B	128,0 (9)
C6—C5—C7A	118,2 (3)	C17B—C15B—C14B	110,1 (6)
C1—C6—C5	120,5 (3)	C17B—C15B—C16B	107,7 (4)
O7A—C7A—C8A	122,6 (4)	C17B—C15B—C10B	110,8 (4)
O7A—C7A—C5	120,0 (4)	C14B—C15B—C16B	109,7 (5)
C8A—C7A—C5	117,4 (3)	C14B—C15B—C10B	109,2 (4)
C9A—C8A—C7A	122,0 (3)	C16B—C15B—C10B	109,4 (4)
C8A—C9A—C10A	130,2 (3)	O7C—C7C—C8C	120,2 (3)
C11A—C10A—C9A	116,8 (3)	O7C—C7C—C3	119,5 (4)
C11A—C10A—C15A	123,4 (5)	C8C—C7C—C3	120,4 (4)
C9A—C10A—C15A	119,8 (5)	C9C—C8C—C7C	120,4 (5)
C10A—C11A—C18A	125,7 (5)	C8C—C9C—C10C	134,0 (5)
C10A—C11A—C12A	120,7 (4)	C11C—C10C—C9C	117,6 (4)
C18A—C11A—C12A	113,7 (5)	C11C—C10C—C15C	122,2 (3)
C13A—C12A—C11A	112,3 (7)	C9C—C10C—C15C	120,2 (4)
C14A—C13A—C12A	113,3 (7)	C10C—C11C—C12C	122,9 (4)
C13A—C14A—C15A	118,5 (7)	C10C—C11C—C18C	124,7 (4)
C17A—C15A—C10A	111,1 (4)	C12C—C11C—C18C	112,3 (4)
C17A—C15A—C16A	110,1 (5)	C13C—C12C—C11C	112,5 (4)
C17A—C15A—C14A	111,2 (5)	C14C—C13C—C12C	123,8 (7)
C10A—C15A—C16A	110,8 (4)	C13C—C14C—C15C	127,4 (8)
C10A—C15A—C14A	109,0 (5)	C16C—C15C—C17C	109,5 (5)
C16A—C15A—C14A	104,5 (5)	C16C—C15C—C14C	110,7 (6)
O7B—C7B—C8B	121,9 (4)	C16C—C15C—C10C	109,8 (4)
O7B—C7B—C1	119,6 (4)	C17C—C15C—C14C	106,7 (5)
C8B—C7B—C1	118,4 (3)	C17C—C15C—C10C	111,5 (5)
C9B—C8B—C7B	122,3 (3)	C14C—C15C—C10C	108,6 (5)

Valla, A., Andriamialisoa, Z., Giraud, M. & Ginderow, D. (1993). *Naturwissenschaften*. Soumis.
Wolga, J. (1987). Eur. Patent FR 0 300 887.

Acta Cryst. (1994). **C50**, 576–578

12-Methyl 9-Hydroxymethyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate Lactone

JIANXIN CHEN, PHANI RAJ POKKULURI, JOHN R. SCHEFFER AND JAMES TROTTER

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

(Received 4 May 1993; accepted 6 October 1993)

Abstract

The structure of an achiral ester-lactone, C₂₀H₁₄O₄ (1), which crystallizes spontaneously in space group *P*₂₁₂₁₂₁, has been determined. Solid-state photolysis gives two products, one of which is produced as a racemate, while the other is formed in near-quantitative enantiomeric excess; the optical activity of the latter product probably results from intermolecular steric effects.

Comment

The general molecular structure and dimensions of (1) are similar to those of related materials (Pokkuluri, Scheffer & Trotter, 1993). The carboxyl groups are both conjugated with the C11=C12 double bond; the C11—C12—C15—O4 torsion angle is $-157.2(3)^\circ$ [$\cos^2(\text{angle}) = 0.85$] and C12—C11—C13—O2 is $+4.0(6)^\circ$ [$\cos^2(\text{angle}) = 0.995$] [$\cos^2(\text{angle})$ is a measure of the amount of conjugative interaction]. The five-membered lactone ring is a distorted C14-envelope [maximum ring torsion angle $10.8(4)^\circ$].

Compound (1) crystallizes in space group *P*₂₁₂₁₂₁ and so appears to resolve spontaneously on crystallization (although anomalous-dispersion terms are not large enough to enable possible twinning to be checked). Solution photolysis of (1) produces only racemic (2), while photolysis of single crystals produces racemic (2) (87%) plus optically active (3) (13%) (Chen, Pokkuluri, Scheffer & Trotter, 1990). The preponderance of photoproduct (2) can be rationalized on the basis of intramolecular steric repulsions between the C14 H atoms and the H atoms bonded to C1 and C8 [H14A...H1 = 2.43 (8) (not too short), H14B...H8 = 2.06 (6) Å (very short)]. These repulsions are relieved by bond formations C11...C8a or C11...C9a, which are required to form the

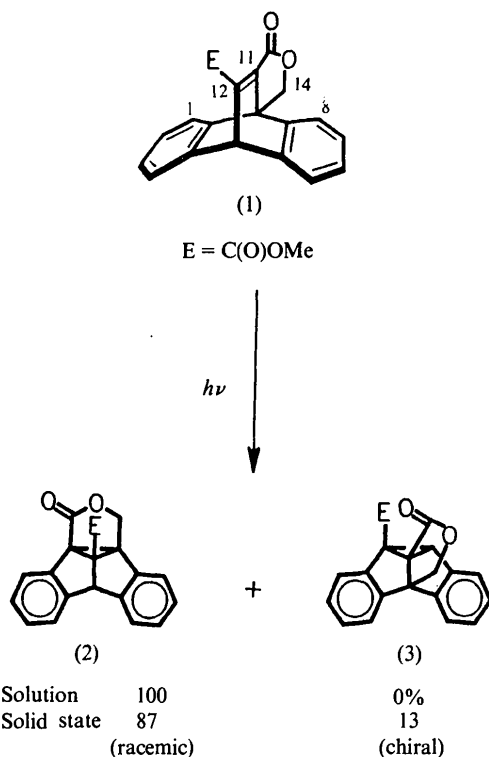
La structure a été résolue avec le programme *SHELXS86* (Sheldrick, 1985) et l'affinement avec une version modifiée de *ORFLS* (Busing, Martin & Levy, 1962). Pour les figures, utilisation du programme *ORTEPII* (Johnson, 1976). Ordinateur: IBM 3090 du CIRCE sous le système d'exploitation AIX/370.

Les listes des facteurs de structure, des facteurs d'agitation thermique anisotrope et des coordonnées des atomes d'hydrogène ont été déposées au dépôt d'archives de la British Library Document Supply Centre (Supplementary Publication No. SUP 71759: 33 pp.). On peut en obtenir des copies en s'adressant à: The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre. [Référence de CIF: DU1065]

Références

- Addae-Mensah, I., Waibel, R. & Achenbach, H. (1985). *Liebigs Ann. Chem.* pp. 1284–1287.
Berkovitch-Yellin, Z. & Leiserowitz, L. (1984). *Acta Cryst.* **B40**, 159–165.
Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Rapport ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, EU.
Dalvi, R. R. & Sere, A. (1988). *Ind. J. Crude Drug. Res.* **26**, 117–120.
Diallo, A., Vanhaellen-Frastré, R. & Vanhaelen, M. (1991). *Phytochemistry*, **30**, 4153–4156.
Johnson, C. K. (1976). *ORTEPII*. Rapport ORNL-5138. Oak Ridge National Laboratory, Tennessee, EU.
O'Connor, A. H. (1973). *Acta Cryst.* **B29**, 1903–1909.
Sheldrick, G. M. (1985). *SHELXS86*. Programme pour la Détermination des Structures Cristallines. Univ. de Göttingen, Allemagne.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
Thackeray, M. M. & Gafner, G. (1975). *Acta Cryst.* **B31**, 335–338.

two enantiomers of (2); (3) is formed via C12...C4a or C12...C10a bond formations, which leave the H...H repulsions almost intact and hence are less-favourable pathways.



The optical activity of photoproduct (3) probably results from an intermolecular steric effect. The C...C bond formation involved in the production of (3) results in a

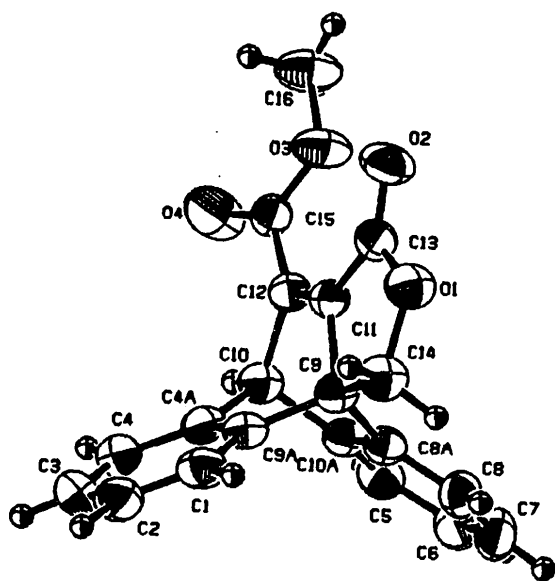


Fig. 1. View of the molecule showing 50% probability ellipsoids.

large movement of the C15 carbomethoxy group, which is impeded on one side of the molecule (but not on the other) by an H atom from a neighbouring molecule (O3...H = 2.49 Å). Both sides of the lactone ring are tightly packed, which accounts for the lack of enantioselectivity in the formation of photoproduct (2).

Experimental

The compound was synthesized according to the procedure described by Chen (1991).

Crystal data

C₂₀H₁₄O₄
M_r = 318.33
 Orthorhombic
*P*2₁2₁2₁
a = 10.349 (1) Å
b = 16.620 (1) Å
c = 8.9933 (6) Å
V = 1546.9 (2) Å³
Z = 4
D_x = 1.366 Mg m⁻³

Cu *K*α radiation
 λ = 1.5418 Å
 Cell parameters from 25 reflections
 θ = 37–47°
 μ = 0.74 mm⁻¹
T = 294 K
 Needle
 0.4 × 0.3 × 0.2 mm
 Colourless

Data collection

Rigaku AFC-6 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: not applied
 (*T*_{min} = 0.95, *T*_{max} = 1.0)
 1785 measured reflections
 1785 independent reflections
 1529 observed reflections
 [*I* > 3σ(*I*)]

θ_{\max} = 77.6°
 h = 0 → 13
 k = 0 → 20
 l = 0 → 11
 3 standard reflections monitored every 150 reflections
 intensity variation: none

Refinement

Refinement on *F*
R = 0.038
wR = 0.055
S = 1.77
 1529 reflections
 274 parameters
 All H-atom parameters refined
 $w = 1/\sigma^2(F)$
 (Δ/σ)_{max} = 0.004

$\Delta\rho_{\max}$ = 0.23 e Å⁻³
 $\Delta\rho_{\min}$ = -0.19 e Å⁻³
 Extinction correction: Zachariasen (1963)
 Extinction coefficient: 5.9 × 10⁻⁶
 Atomic scattering factors from TEXSAN (Molecular Structure Corporation, 1985)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
C1	0.8396 (3)	1.0018 (2)	0.4002 (4)	0.051 (2)
C2	0.8031 (3)	1.0790 (2)	0.3682 (5)	0.061 (2)
C3	0.8619 (2)	1.1216 (2)	0.2532 (5)	0.063 (2)
C4	0.9597 (3)	1.0856 (2)	0.1686 (4)	0.052 (2)
C4a	0.9956 (2)	1.0077 (2)	0.2004 (3)	0.042 (1)
C5	1.0256 (3)	0.8520 (2)	-0.0757 (3)	0.047 (1)
C6	0.9582 (4)	0.7812 (2)	-0.1043 (4)	0.055 (2)
C7	0.8946 (4)	0.7424 (2)	0.0078 (4)	0.057 (2)
C8	0.8991 (3)	0.7710 (2)	0.1536 (4)	0.049 (2)
C8a	0.9678 (2)	0.8406 (2)	0.1822 (3)	0.040 (1)

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).

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 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]

References

- Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.
- Chen, J. (1991). PhD thesis, Univ. of British Columbia, Vancouver, Canada.
- Chen, J., Pokkuluri, P. R., Scheffer, J. R. & Trotter, J. (1990). *Tetrahedron Lett.* **31**, 6803–6806.
- Gilmore, G. J. (1984). *J. Appl. Cryst.* **17**, 42–46.
- Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Pokkuluri, P. R., Scheffer, J. R. & Trotter, J. (1993). *Acta Cryst.* **B49**, 107–116.
- Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1994). **C50**, 578–581

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

(Received 27 April 1993; accepted 6 October 1993)

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,