

Ethyl 1-Ethyl-7-methoxy-3,4-dioxo-2-phenanthrenecarboxylate, C₂₀H₁₈O₅

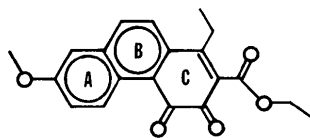
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(Received 30 April 1984; accepted 3 July 1984)

Abstract. $M_r = 338.36$, monoclinic, $P2_1/c$, $a = 14.815(3)$, $b = 8.009(1)$, $c = 13.911(6)$ Å, $\beta = 90.90(5)^\circ$, $V = 1650.4(13)$ Å³, $Z = 4$, $D_m = 1.35(1)$, $D_x = 1.36$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.091$ mm⁻¹, $F(000) = 712$, $T = 291$ K. Final $R = 0.075$ for 851 reflections. The phenanthrene ring system is planar (mean deviation, 0.034 Å). The bond distance between the carbonyl C atoms in the α,β -quinone is characteristically elongated (1.544 Å). Twelve molecules contribute to the unit-cell content, all occupying sites in two different sets of parallel planes. The angle between the sets of planes is 9.4° .

Introduction. A method discovered by Layton (1956) for the preparation of cyclic compounds from stable ozonides appears suitable for the synthesis of steroid-type structures having O atoms in the potential eleven and twelve positions of the steroid nucleus. The ozonization of the appropriate indone, which was sequentially synthesized by a Friedel–Crafts reaction and a Stobbe condensation followed by cyclization, was the method of preparation for the precursor of the needed phenanthrenequinone. Reduction of the ozonide by hydrogen and platinum(IV) oxide led to the formation of the title compound (Hwang, 1962). The first two complete single-crystal crystallographic investigations of stable ozonides were carried out recently (Oliver, Mullica, Milligan, Karban, McAtee & Belew, 1979; Mullica, Korp, Milligan, Belew, McAtee & Karban, 1979). Our keen interest in ozonides and compounds which may serve as intermediates in the preparation of steroids has propagated the structural analysis of the title compound.



Experimental. Dark deep-red crystal, irregular shape (approx. $0.41 \times 0.28 \times 0.24$ mm), D_m at room temperature by flotation method in aqueous ZnCl₂, glass-fiber mount, monochromated Mo $K\alpha$ radiation

* Deceased 18 February 1984.

and Si(Li) solid-state detector (Mullica, Beall, Milligan & Oliver, 1979); standard CAD-4 centering, indexing and data-collection programs, lattice constants and the orientation matrix refined by least-squares fit of 25 reflections; correction for Lorentz and polarization effects; intensity data collected by θ - 2θ scan technique, variable scan rate of 0.38 to 3.35° min⁻¹; intensities of two check reflections (262 and 415) measured every 2 h revealed only random deviations ($<1.6\%$) from mean intensities; 3238 unique reflections ($3^\circ < 2\theta < 50^\circ$; range of hkl : $0 \rightarrow 16, 0 \rightarrow 9, -17 \rightarrow 17$), 851 with $I > 3\sigma(I)$ used in refinement, $R_{\text{int}} = 0.012$; direct-methods program *MULTAN* 11/82 (Main, 1982) used to solve structure using $275 E \geq 1.35$, E map selected by the highest combined figure of merit; 20 non-hydrogen atoms located from E map, remainder by difference Fourier methods; H-atom positions were located in part by difference Fourier synthesis and calculations except for H atoms associated with C(17), which could not be located with any confidence; full-matrix least-squares refinement on F yielded $R = 0.075$, $R_w = 0.075$, $w = \sigma^{-2}(F_o)$ with $\sigma(F_o) = \{I_p + I_b + [0.02(I_p - I_b)]^2\}^{1/2}$ where I_p and I_b are the number of counts in the peak and background respectively, $S = 2.69$, max. shift/error in final least-squares cycle 7.78×10^{-2} ; max. and min. peaks in final ΔF map 0.3 and -0.3 e Å⁻³; scattering factors taken from *International Tables for X-ray Crystallography* (1974); investigation used programs contained in *VAXSDP* (Enraf–Nonius, 1982). Final atomic positional parameters with equivalent isotropic thermal parameters and bond distances and angles are found in Tables 1† and 2, respectively.

Discussion. Fig. 1 shows a labeled *ORTEP* (Johnson, 1971) stereoscopic drawing of the title compound. The 14-membered phenanthrene ring system is planar having a mean deviation from the least-squares plane of 0.034 Å. The bond lengths and angles of rings A (C 1–6) and B (C5–10) in the phenanthrene system are

† Lists of structure factor amplitudes, H-atom coordinates, anisotropic thermal parameters, selected torsional angles, and least-squares planes, and a stereoview of the unit-cell packing have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39620 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

within expected values with mean values of 1.396 Å and 120°, respectively. The C ring (C9–14) in the system shows apparent anomalies, namely bond lengths of 1.544 (10) and 1.343 (9) Å for C(11)–C(12) and

Table 1. Atomic positional parameters ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$)

U_{eq} is defined as one third the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U_{eq}(\text{Å}^2)$
C(1)	10710 (7)	-1376 (14)	6246 (7)	53 (4)
C(2)	11628 (7)	-1450 (14)	6108 (7)	61 (4)
C(3)	12121 (7)	26 (15)	5971 (7)	60 (4)
C(4)	11726 (7)	1520 (14)	5930 (7)	57 (4)
C(5)	10773 (7)	1580 (13)	6063 (7)	50 (4)
C(6)	10264 (6)	152 (12)	6223 (6)	40 (3)
C(7)	10351 (7)	3154 (14)	6069 (8)	64 (4)
C(8)	9446 (7)	3321 (13)	6238 (8)	59 (4)
C(9)	8916 (7)	1888 (13)	6413 (7)	46 (3)
C(10)	9304 (6)	330 (12)	6396 (6)	40 (3)
C(11)	8730 (7)	-1093 (12)	6517 (7)	46 (3)
C(12)	7726 (7)	-847 (14)	6760 (7)	56 (4)
C(13)	7401 (7)	822 (14)	6795 (7)	58 (4)
C(14)	7932 (7)	2132 (13)	6593 (7)	48 (4)
C(15)	6404 (8)	1027 (15)	6994 (8)	79 (5)
C(16)	5295 (9)	917 (24)	8137 (10)	155 (8)
C(17)	5177 (10)	1968 (28)	9008 (12)	211 (9)
C(18)	7543 (7)	3878 (14)	6553 (8)	62 (4)
C(19)	7345 (8)	4453 (15)	5573 (8)	81 (5)
C(20)	13584 (8)	1126 (17)	5750 (9)	103 (5)
O(3)	13038 (5)	-254 (10)	5895 (5)	81 (3)
O(11)	8943 (5)	-2550 (9)	6438 (6)	79 (3)
O(12)	7251 (5)	-2060 (10)	6909 (6)	87 (3)
O(15)	6241 (5)	832 (13)	7893 (5)	114 (4)
O(15A)	5842 (5)	1388 (14)	6388 (7)	131 (4)

Table 2. Bond distances (Å) and angles (°)

C(1)–C(2)	1.378 (9)	C(11)–C(12)	1.544 (10)
C(1)–C(6)	1.391 (9)	C(11)–O(11)	1.214 (8)
C(2)–C(3)	1.404 (10)	C(12)–C(13)	1.422 (10)
C(3)–C(4)	1.332 (10)	C(12)–O(12)	1.219 (8)
C(3)–O(3)	1.383 (8)	C(13)–C(14)	1.343 (9)
C(4)–C(5)	1.427 (9)	C(13)–C(15)	1.516 (11)
C(5)–C(6)	1.390 (9)	C(14)–C(18)	1.513 (10)
C(5)–C(7)	1.408 (10)	C(15)–O(15)	1.287 (10)
C(6)–C(10)	1.453 (9)	C(15)–O(15A)	1.211 (10)
C(7)–C(8)	1.371 (9)	C(16)–C(17)	1.488 (15)
C(8)–C(9)	1.414 (10)	C(16)–O(15)	1.450 (11)
C(9)–C(10)	1.374 (9)	C(18)–C(19)	1.465 (9)
C(9)–C(14)	1.496 (9)	C(20)–O(3)	1.385 (9)
C(10)–C(11)	1.434 (9)		
C(2)–C(1)–C(6)	120.2 (8)	C(10)–C(11)–C(12)	120.0 (8)
C(1)–C(2)–C(3)	120.0 (8)	C(10)–C(11)–O(11)	126.7 (9)
C(2)–C(3)–C(4)	122.2 (8)	C(12)–C(11)–O(11)	113.3 (9)
C(2)–C(3)–O(3)	112.8 (9)	C(11)–C(12)–C(13)	117.1 (8)
C(4)–C(3)–O(3)	125.0 (9)	C(11)–C(12)–O(12)	119.8 (9)
C(3)–C(4)–C(5)	117.3 (8)	C(13)–C(12)–O(12)	123.1 (8)
C(4)–C(5)–C(6)	122.3 (8)	C(12)–C(13)–C(14)	121.9 (8)
C(4)–C(5)–C(7)	118.1 (9)	C(12)–C(13)–C(15)	116.1 (8)
C(6)–C(5)–C(7)	119.6 (8)	C(14)–C(13)–C(15)	121.9 (9)
C(1)–C(6)–C(5)	118.0 (8)	C(9)–C(14)–C(13)	120.5 (8)
C(1)–C(6)–C(10)	123.2 (9)	C(9)–C(14)–C(18)	119.0 (8)
C(5)–C(6)–C(10)	118.8 (8)	C(13)–C(14)–C(18)	120.4 (8)
C(5)–C(7)–C(8)	121.6 (8)	C(13)–C(15)–O(15)	111.2 (9)
C(7)–C(8)–C(9)	119.9 (8)	C(13)–C(15)–O(15A)	124.0 (11)
C(8)–C(9)–C(10)	120.0 (8)	O(15)–C(15)–O(15A)	124.7 (10)
C(8)–C(9)–C(14)	117.9 (8)	C(17)–C(16)–O(15)	110.1 (10)
C(10)–C(9)–C(14)	122.1 (8)	C(14)–C(18)–C(19)	113.3 (7)
C(6)–C(10)–C(9)	120.2 (8)	C(3)–O(3)–C(20)	117.3 (7)
C(6)–C(10)–C(11)	121.7 (8)	C(15)–O(15)–C(16)	114.7 (8)
C(9)–C(10)–C(11)	118.1 (8)		

C(13)–C(14), respectively. An examination of the literature reveals that these obvious deviations from a normal conjugated ring are characteristic of an α,β -unsaturated quinone. In the case of 1,2-naphthoquinones, the bond distances between the carbonyl C atoms range from 1.50 to 1.53 Å while double-bond lengths may range from 1.34 to 1.41 Å (Bechtel, Chasseau, Gaultier & Hauw, 1976; Boeyens, 1976).

In the reported structural determination of the parent compound, phenanthrene, an interaction is found between the H atom associated with C(4) and the H atom related to C(5) which forces C(4) out of the molecular plane (Kay, Okaya & Cox, 1971; Mason, 1961). The contact distance between the H atoms is 2.04 Å, which is much shorter than the 2.4 Å distance derived from the summation of the van der Waals radii. In the current structure, a corresponding interaction is noted between the H atom attached to C(1) and the carbonyl O atom, O(11). The observed contact distance of 2.054 Å is slightly longer than the corresponding distance in phenanthrene. This close contact is the likely cause for the slight deviation from the mean plane of C(11) and the aberrant bond angles about C(11).

The plane containing the exocyclic carboxylic acid function forms an angle of 74.5° with the phenanthrene ring system. This angle can be attributed to the bulk of the acid function and esterified ethyl group. Similarly, the angle formed by the C(18)–C(19) bond of the ethyl group attached to C(14) is oriented almost perpendicular to the ring, as shown by torsion angles of 81.0 (11) [C(9)–C(14)–C(18)–C(19)] and -99.5 (11)° [C(13)–C(14)–C(18)–C(19)]. Coplanarity is exhibited by the methoxy group attached to C(3) and the phenanthrene nucleus. This is evidenced by the experimental torsion angles of -1.1 (15) [C(4)–C(3)–O(3)–C(20)] and 179.5 (8)° [C(2)–C(3)–O(3)–C(20)].

Twelve molecules contribute to the unit-cell contents ($Z = 4$) and are oriented so as to lie in two sets of parallel molecular groupings. The interplanar angle

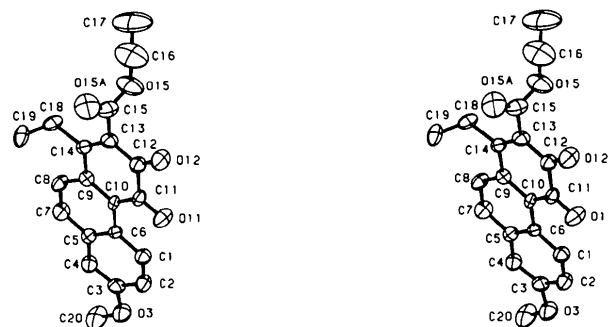


Fig. 1. Stereoview with the numbering scheme according to a steroid nucleus. Thermal ellipsoids are drawn at 35% of thermal probability. Hydrogens have been omitted for clarity.

between the two sets of parallel planes is 9.4° . The occurrence of two sets of parallel planes is not uncommon and is found in both phenanthrene and anthracene (Mason, 1961). The interplanar angles observed in these two structures are 56 and 52° , respectively. The angular magnitudes of the compounds are much larger than the interplanar angle observed in our crystallographic investigation of the title compound. This difference can be attributed to the altered molecular packing caused by the exocyclic substituents.

The authors wish to acknowledge the financial support of this work, in part, by the Robert A. Welch Foundation (Grant No. AA-668) and Baylor University.

References

BECHTEL, F., CHASSEAU, D., GAULTIER, J. & HAUV, C. (1976). *Acta Cryst.* B32, 1738–1748.

- BOEYENS, J. C. A. (1976). *J. Cryst. Mol. Struct.* 6, 217–222.
 Enraf-Nonius (1982). *VAX Structure Determination Package*. Delft, Holland.
 HWANG, TSE-RU (1962). Thesis. Baylor Univ.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–151. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1971). *ORTEPII*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.
 KAY, M. I., OKAYA, Y. & COX, D. E. (1971). *Acta Cryst.* B27, 26–33.
 LAYTON, R. (1956). Thesis. Univ. of Virginia.
 MAIN, P. (1982). Editor, *MULTAN 11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England.
 MASON, R. (1961). *Mol. Phys.* 4, 413–415.
 MULLICA, D. F., BEALL, G. W., MILLIGAN, W. O. & OLIVER, J. D. (1979). *J. Appl. Cryst.* 12, 263–266.
 MULLICA, D. F., KORB, J. D., MILLIGAN, W. O., BELEW, J. S., MCATEE, J. L. JR & KARBAN, J. (1979). *J. Chem. Soc. Perkin Trans. 2*, pp. 1703–1707.
 OLIVER, J. D., MULLICA, D. F., MILLIGAN, W. O., KARBAN, J., MCATEE, J. L. JR & BELEW, J. S. (1979). *Acta Cryst.* B35, 2273–2276.

Acta Cryst. (1984). C40, 1925–1927

Structure of a Derivative of Mitindomide, the Maleimide–Benzene Photoadduct,* $C_{20}H_{20}N_2O_8$

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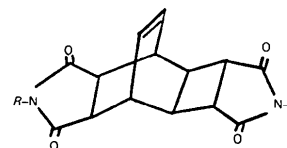
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(Received 9 April 1984; accepted 10 July 1984)

Abstract. $M_r = 416.39$, orthorhombic, $Pca2_1$, $a = 16.646$ (7), $b = 15.890$ (4), $c = 7.222$ (2) Å, $U = 1910$ (1) Å³, $Z = 4$, $D_m = 1.444$, $D_x = 1.448$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.71$ cm⁻¹, $T = 298$ K, $F(000) = 872$. Final $R = 0.0646$ for 2322 observed reflections measured on a diffractometer. The structure of the adduct (I) was determined *via* the diacetate of the bis(hydroxymethyl) derivative (III). The monomeric units clearly show that the imide rings have the *exo-endo* configuration, confirming the 1,2 photoaddition as *exo* and the 1,4 Diels–Alder addition as *endo*. The two imide rings are nearly coplanar (dihedral angle = 4.1°) and the distance between the two nitrogens is 7.79 Å.

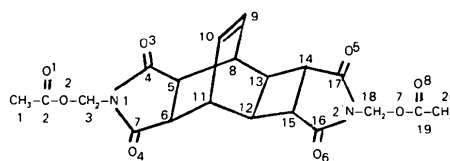
Introduction. The photosensitized reaction of maleimide with a large excess of benzene yields an insoluble adduct (I) (Bradshaw, 1966; Arkhipova, Zhubanov & Saidenova, 1972) whose structure has been presumed

based on analogy with the known photoadduct of maleic anhydride and benzene (Bryce-Smith, Vickery & Frey, 1967; Grovenstein, Rao & Taylor, 1961). Since this compound (I) shows strong and reproducible antitumor activity in a number of test systems (Lomax & Narayanan, 1981), it was important to confirm this structural assignment.



(I) $R = H$

(II) $R = \text{CH}_2\text{OH}$



(III)

* 4,6,11,13-Tetraoxo-5,12-diazapentacyclo[7.5.2.0^{2,8}.0^{3,7}.0^{10,14}]-hexadec-15-ene-5,12-diyldimethylene diacetate.

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