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Spectroscopic and crystal structure analyses of methyl 1-phenyl-3,4-dioxo-2-naphthalenecarboxylate, $C_{18}H_{12}O_4$[1]

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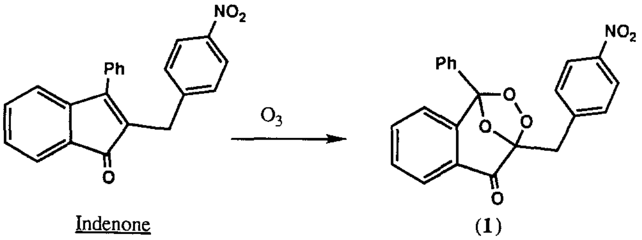
The crystal and molecular structure of methyl 1-phenyl-3,4-dioxo-2-naphthalenecarboxylate, $C_{18}H_{12}O_4$, has been determined from three-dimensional, single-crystal X-ray diffraction data. The compound crystallizes in the monoclinic space group *Cc*(No. 9, C_s^4) with $a = 9.837(2)$, $b = 16.397(3)$, $c = 8.706(1)$ Å, $\beta = 94.88(1)°$, $Z = 4$, $D_m = 1.38(1)$ Mg m^{-3}, and $D_x = 1.388$ Mg m^{-3}. The phasing model was determined by direct methods and the final full-matrix least-squares refinement yielded $R = 0.0363$ and $R_w = 0.0405$ for 1374 unique reflections. Optical, infrared, NMR, and UV-VIS analyses have also been carried out. The molecules in the crystal lattice are held together by van der Waals forces.

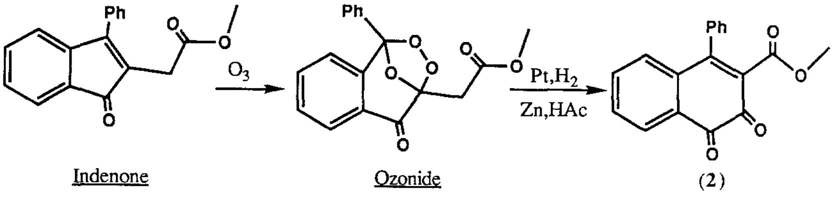
Introduction

Since the explicit elucidation of the first unambiguous crystal and molecular structure of an ozonide (Mullica *et al.*, 1979) was reported, keen interest in stable ozonides employed in the synthesis of steroid intermediates has been consistently increased. In addition to the isolation and structural analysis of stable ozonides, the structural knowledge and content of the starting indenone compounds and the resultant products obtained by the reduction of the derivative ozonides, are considered essential.

The synthesis of the stable ozonide H-(4-nitrophenylmethyl)-1-phenyl-1,4-epoxy-1H-2,3-benzodioxepin-5(4H)-one **(1)**, which crystallizes in space group $P2_1/c$, is found elsewhere (Mullica *et al.*, 1979). The following is presented for comparative purposes (Scheme 1). Scheme 2 shows the formation of the title compound **(2)**.



Scheme 1



Scheme 2

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[1] 3-Carbomethoxy-4-phenyl-1,2-naphthoquinone.

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The X-ray crystallographic study of **(2)** has been carried out with the view of determining the geometric and structural change produced by the ozonolysis of the staring indenone, methyl 3-phenylindenone-2-acetate. The ultimate goal of this study is to augment our knowledge related to the synthesis of steroid intermediates.

Experimental

The appropriate starting indenone was sequentially synthesized by a Friedel-Crafts reaction, a Stobbe condensation and cyclization (Layton, 1956). The indenone was treated with an oxygen-ozone mixture to yield the intermediate ozonide (Belew and Layton, 1956) which was then reduced by PtO_2 and H_2. The product was dissolved in glacial acetic acid and zinc dust was added. After filtration, distillation, and evaporation, the residue was crystallized from ethanol forming bright orange crystals of the title compound (Layton, 1956). Analysis-found: C, 73.85; H, 4.35%. $C_{18}H_{12}O_4$ requires: C, 73.96; H, 4.14%.

The flotation method was employed to determine the experimental density, 1.38(1) Mg m^{-3} (calc., 1.388 Mg m^{-3}). The melting point of **(2)** is 199–200°C. UV-VIS spectroscopic results lends credence to the formation of a 1,2 naphthoquinone (λ_{max}: 254, 333, and 408 nm). Convincing evidence of this formation is seen by a direct and striking comparison to the UV-VIS research by Macbeth *et al.* (1935) with 4-methoxy-1,2-naphthoquinone and that of Goldschmidt and Graef (1928) with 1,2-naphthoquinone. An infrared spectrum obtained over the frequency range of 4000–400 cm^{-1} on a Mattson-fourier Transform IR analyzer using the KBr pressed-pellet technique, displayed three bands at 1667, 1695, and 1730 cm^{-1} which account for the two ketone and ester carbonyl groups, respectively. Elsewhere, the spectrum revealed peaks that were straightforward and no evidence of hydrogen bonding was observed. A ^1H NMR spectrum of **(2)** shows an apparent singlet at 3.55 ppm with peak integration accounting for three protons (the methyl group) and multi-peaks down field (7.09–7.11, 7.27, 7.35–7.39, 7.49–7.53, 7.54–7.60, 8.20–8.22 ppm) with peak integration accounting for the remaining nine protons. These data presented no pertinent information related to the formation of the 1,2-naphthoquinone. However, a ^{13}C NMR spectrum revealed three distinctive peaks at 164.35, 176.75, and 177.69 ppm which account for the ester carbonyl and the two ketone carbonyl groups in the structure, respectively. The NMR spectra were obtained on a Bruker AMX 360 NMR spectrometer. A conoscopic study of single crystals of **(2)** provided evidence that the system was biaxial (anisotropic in nature, optically birefringent). Crystal rotation between two crossed polarizers on a Ziess Photomicroscope II was used for the optical examination.

A single crystal (0.22 × 0.30 × 0.47 mm) selected on the basis of optical homogeneity was mounted on an Enraf-Nonius CAD4-F diffractometer equipped with a dense graphite monochromator, take-off angle of 5.8°. Using the ω-2θ scan method, the intensities were measured at a varied scan rate of 0.28–3.35° min^{-1}. Data were collected in the range of $3.0° < 2\theta < 140°$ using Cu $K\bar{\alpha}$ radiation, $\lambda_{mean} = 1.54184$ Å (292K). Of the 2872 measured reflections (*h*: $-2 \rightarrow 11$, *k*: $-4 \rightarrow 19$, *l*: $-10 \rightarrow 10$), 1388 were independent ($R_{int} = 0.018$) of which 1374 fitted $F > 6.0\ \sigma(F)$. The intensities were corrected for Lorentz and polarization effects. Systematic absences (*hkl*: $h + k = 2n + 1$, *h*0*l*: $h, l = 2n + 1$) are consistent with space group Cc (No. 9). The calculated combined figure of merit value lends credence to a non-centrosymmetric lattice choice. A crystallographic analysis (direct methods) of the reduce and averaged data employing SHELXTL-PC-89 (1989) revealed the location of all nonhydrogen atoms. The disclosure of the hydrogen atomic positions was obtained through difference Fourier mapping. The model was refined by the full-matrix least-squares method (SHELXTL-PC-89, 1989). After entering the hydrogen atomic positions which were only isotropically refined, applying a secondary extinction correction, and refining non-hydrogen atoms in the anisotropic mode, final reliability factors were obtained, $R = \Sigma\, \Delta F/\Sigma|F_o| = 0.0363$ and $R_w = \Sigma\sqrt{w}\, \Delta F/\Sigma\sqrt{w}|F_o| = 0.0405$ ($R_{all} = 0.0366$) where ΔF equals $\|F_o| - |F_c\|$ and the weighting factor $w = 1/[\sigma^2(F_o) + 0.0031F^2]$. The 'goodness-of-fit' value (Σ_2) is 1.01 (see Table 1). As a result of **(2)** crystallizing in the polar space group Cc, the absolute configuration was assigned based on the chirality/polarity parameter, η (Rogers, 1981). The value of η refined to 0.97(8) and is an indication of the correctness of the configuration. A value of η close to +1 signifies a correctly assigned configuration and a value close to −1 implies an incorrect configuration and the configuration must be inverted. From a final electron density map, only a random fluctuating background was observed (max., 0.23 and min., −0.21 e^- Å^{-3}). Atomic scattering factors and associated anomalous dispersion correction factors were taken from the usual source (*International Tables*, 1974). Final fractional atomic coordinates according to the number scheme in Fig. 1 and isotropic equivalent thermal parameters are listed in Table 2.

Table 1. Experimental and statistical summaries

	Single Crystal
Molecular formula	$C_{18}H_{12}O_4$
Crystal system	Monoclinic
Space group	*Cc* (No. 9, C_s^4)
Radiation	Cu $K\bar{\alpha}$
λ_{mean} (Å)	1.54184
a (Å)	9.837(2)
b (Å)	16.397(3)
c (Å)	8.706(1)
β (°)	94.88(1)
V (Å^3)	1399.2(4)
D_m (Mg m^{-3})	1.38(1)
D_x (Mg m^{-3})	1.388
M_r	292.3
Z	4
F(000) (e$^-$)	608
Crystal size (mm)	0.22 × 0.30 × 0.47
μ (Cu$K\bar{\alpha}$)(mm^{-1})	0.770
$\Delta\theta$ (°)	1.5 − 70.0
$\Delta\omega$ (°) ($\omega - 2\theta$ scan)	0.60 + 0.14 tan θ
R_{int}	0.018
R	0.0363
$R_w(R_{all})$	0.0405 (0.0366)
Unique reflections	1374
g (e^{-2}) (×10^{-5})	2.24(7)
η	0.97(8)
Residual density (e$^-$Å^{-3})	
Maximum	0.23
Minimum	−0.16
Gnft (Σ_2)	1.01

Table 2. Fractional atomic coordinates (×10^4) and isotropic equivalent thermal parameters (Å^2 × 10^3) with esd's in parentheses

Atom	x	y	z	U_{eq}[a]
C(1)	5737(3)	−871(1)	4164(3)	48(1)
C(2)	6198(3)	−1673(1)	4073(3)	57(1)
C(3)	7320(3)	−1845(1)	3277(3)	63(1)
C(4)	7996(3)	−1226(1)	2587(3)	56(1)
C(5)	7560(3)	−422(1)	2691(3)	45(1)
C(6)	6397(3)	−232(1)	3475(3)	40(1)
C(7)	5927(2)	622(1)	3589(3)	38(1)
C(8)	6739(2)	1251(1)	3221(3)	42(1)
C(9)	8054(3)	1117(1)	2567(3)	48(1)
C(10)	8362(2)	239(1)	2063(3)	48(1)
C(11)	4554(3)	776(1)	4120(3)	40(1)
C(12)	3397(3)	424(1)	3344(3)	53(1)
C(13)	2120(3)	585(2)	3817(4)	65(1)
C(14)	1961(3)	1090(1)	5068(3)	62(1)
C(15)	3102(3)	1443(1)	5838(3)	54(1)
C(16)	4397(3)	1289(1)	5363(3)	44(1)
C(17)	6296(3)	2126(1)	3353(3)	46(1)
C(18)	6602(4)	3332(2)	4806(4)	80(1)
O(1)	9260(3)	135(1)	1200(3)	70(1)
O(2)	8853(3)	1663(1)	2354(3)	72(1)
O(3)	5452(3)	2444(1)	2479(3)	61(1)
O(4)	6984(3)	2492(1)	4525(3)	62(1)
H(1)[b]	4948(8)	−758(8)	4704(8)	79(1)
H(2)	5753(8)	−2110(8)	4552(8)	80(1)
H(3)	7638(8)	−2413(8)	3212(8)	80(1)
H(4)	8782(8)	−1336(8)	2038(8)	79(1)
H(12)	3479(8)	67(8)	2476(8)	79(1)
H(13)	1321(8)	368(8)	3278(8)	80(1)
H(14)	1076(8)	1184(8)	5386(8)	80(1)
H(15)	3000(8)	1802(8)	6711(8)	79(1)
H(16)	5175(8)	1526(8)	5905(8)	80(1)
H(18a)	7168(8)	3525(8)	5681(8)	81(1)
H(18b)	5656(8)	3367(8)	5033(8)	81(1)
H(18c)	6717(8)	3669(8)	3915(8)	81(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

[b] Hydrogen atoms were refined isotropically.

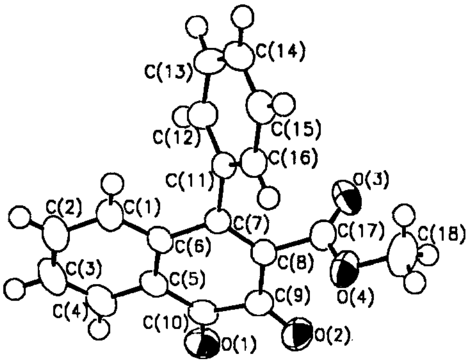

Fig. 1. The methyl 1-phenyl-3,4-dioxo-2-naphthalenecarboxylate molecule showing the atomic numbering scheme.

Results and discussion

Tables 3 and 4 list the bond distances and angles with their standard deviations for the title compound. The interatomic bond lengths and angles associated with rings I and II (see Table 5), i.e., rings C(1)-C(6) and C(11)-C(16), are well within the range of expected values [1.379-1.416 Å, mean value is 1.391(10) Å; 117.8-121.2°, mean value is 120.0(9)°]. In the carbon ring [C(5)-C(10)], there are apparent anomalies, namely C(9)—C(10) = 1.542(3) and C(7)—C(8) = 1.358(3) Å. A literature search reveals that these obvious deviations from a normal conjugated ring are characteristic of unsaturated 1,2 naphthoquinones, C—C bonds between the carbonyls range from 1.50 to 1.55 Å and the range of double-bond distances may vary from 1.34 to 1.41 Å (Bechtel *et al.*, 1976; Boeyens, 1976; Mullica *et al.*, 1984). The remaining C—C bond distances [mean, 1.476(4) Å] in the C(5)-C(10) ring are in direct agreement with published values found in BIDICS (1969–1981). The bond lengths of C(sp^2)—O(4) = 1.320(3) Å

Table 3. Interatomic bond distances (Å) with esd's in parentheses

Atoms	Distances	Atoms	Distances
C(1)—H(1)	0.959 (9)	C(1)—C(2)	1.396(3)
C(1)—C(6)	1.395 (3)	C(2)—H(2)	0.954 (11)
C(2)—C(3)	1.382 (4)	C(3)—H(3)	0.986 (13)
C(3)—C(4)	1.379 (4)	C(4)—H(4)	0.960 (9)
C(4)—C(5)	1.392 (3)	C(5)—C(6)	1.416 (4)
C(5)—C(10)	1.473 (3)	C(6)—C(7)	1.481 (3)
C(7)—C(8)	1.358 (3)	C(7)—C(11)	1.486 (3)
C(8)—C(9)	1.474 (4)	C(8)—C(17)	1.507 (3)
C(9)—C(10)	1.542 (3)	C(9)—O(2)	1.216(3)
C(10)—O(1)	1.219 (4)	C(11)—C(12)	1.398 (3)
C(11)—C(16)	1.389 (3)	C(12)—H(12)	0.964 (10)
C(12)—C(13)	1.381 (4)	C(13)—H(13)	0.949 (9)
C(13)—C(14)	1.388 (4)	C(14)—H(14)	0.949 (9)
C(14)—C(15)	1.384 (4)	C(15)—H(15)	0.973 (10)
C(15)—C(16)	1.396 (4)	C(16)—H(16)	0.948 (9)
C(17)—O(3)	1.197 (3)	C(17)—O(4)	1.320 (3)
C(18)—H(18a)	0.958 (9)	C(18)—H(18b)	0.969 (9)
C(18)—H(18c)	0.966 (10)	C(18)—O(4)	1.455 (3)

and C(sp^3)—O(4) = 1.455(3) Å correspond quite well to similar bonds in ethyl 1-ethyl-7-methoxy-3,4-dioxo-2-phenanthrenecarboxylate (Mullica *et al.*, 1984). The average carboxyl bond length of 1.211(10) Å is in excellent agreement with published work (BIDICS, 1969–1981) and with the summation of the involved double bond radii of carbon (0.665 Å) and oxygen (0.55 Å) atoms obtained from the work of Demitras *et al.* (1972), 1.215 Å.

It is noteworthy to mention that the plane containing the exocyclic carboxylic acid function forms an angle of 74.8° with the naphthalene ring system (ring III, see Table 5) and that the phenyl ring (I) forms an angle of 63.9° with plane III. Plane I and II exhibit good planarity of the tested atoms with mean standard deviations of 0.006 and 0.003 Å, respectively. Plane III, the naphthalene ring system, has a mean deviation of 0.109 Å which is quite reasonable for a 1,2-naphthoquinone with a phenyl and a carbomethoxy group. Selective torsion angles and molecular planes are presented in Table 5. Figure 2 displays the molecular packing within the unit cell. The molecules within the crystal lattice are held together by van der Waals forces (m.p., 199–200°C), since no intermolecular contact distances are shorter than the sum of the respective van der Waals radii of the atoms (Pauling, 1960).

Table 4. Bond angles (°) with esd's in parentheses

Atoms	Angle	Atoms	Angle
H(1)—C(1)—C(2)	119.4(8)	H(1)—C(1)—C(6)	119.5(8)
C(2)—C(1)—C(6)	121.2(2)	C(1)—C(2)—H(2)	121.3(7)
C(1)—C(2)—C(3)	119.9(2)	H(2)—C(2)—C(3)	118.7(7)
C(2)—C(3)—H(3)	119.6(6)	C(2)—C(3)—C(4)	120.2(2)
H(3)—C(3)—C(4)	120.2(6)	C(3)—C(4)—H(4)	121.2(8)
C(3)—C(4)—C(5)	120.4(3)	H(4)—C(4)—C(5)	118.4(8)
C(4)—C(5)—C(6)	120.4(2)	C(4)—C(5)—C(10)	119.7(2)
C(6)—C(5)—C(10)	119.8(2)	C(1)—C(6)—C(5)	117.8(2)
C(1)—C(6)—C(7)	121.5(2)	C(5)—C(6)—C(7)	120.7(2)
C(6)—C(7)—C(8)	120.6(2)	C(6)—C(7)—C(11)	118.6(2)
C(8)—C(7)—C(11)	120.9(2)	C(7)—C(8)—C(9)	122.1(2)
C(7)—C(8)—C(17)	121.6(2)	C(9)—C(8)—C(17)	116.1(2)
C(8)—C(9)—C(10)	116.7(2)	C(8)—C(9)—O(2)	123.3(2)
C(10)—C(9)—O(2)	119.9(2)	C(5)—C(10)—C(9)	117.2(2)
C(5)—C(10)—O(1)	124.4(2)	C(9)—C(10)—O(1)	118.4(2)
C(7)—C(11)—C(12)	120.3(2)	C(7)—C(11)—C(16)	120.6(2)
C(12)—C(11)—C(16)	119.1(2)	C(11)—C(12)—H(12)	120.7(5)
C(11)—C(12)—C(13)	120.1(2)	H(12)—C(12)—C(13)	119.3(5)
C(12)—C(13)—H(13)	121.1(6)	C(12)—C(13)—C(14)	120.9(2)
H(13)—C(13)—C(14)	117.9(6)	C(13)—C(14)—H(14)	119.6(6)
C(13)—C(14)—C(15)	119.3(3)	H(14)—C(14)—C(15)	121.1(6)
C(14)—C(15)—H(15)	119.9(5)	C(14)—C(15)—C(16)	120.2(2)
H(15)—C(15)—C(16)	119.9(5)	C(11)—C(16)—C(15)	120.4(2)
C(11)—C(16)—H(16)	119.9(6)	C(15)—C(16)—H(16)	119.8(6)
C(8)—C(17)—O(3)	123.7(2)	C(8)—C(17)—O(4)	111.1(2)
O(3)—C(17)—O(4)	125.2(2)	H(18a)—C(18)—H(18b)	108.8(8)
H(18a)—C(18)—H(18c)	110.5(9)	H(18b)—C(18)—H(18c)	108.1(8)
H(18a)—C(18)—O(4)	107.8(8)	H(18b)—C(18)—O(4)	110.9(8)
H(18c)—C(18)—O(4)	110.9(7)	C(17)—O(4)—C(18)	116.0(2)

Table 5. Selective torsion angles (°) and molecular planes (Å)

Torsion angles (°)

Atom 1	Atom 2	Atom 3	Atom 4	Angle
O(1)	C(10)	C(5)	C(4)	14.0(4)
O(1)	C(10)	C(9)	O(2)	−13.9(4)
O(2)	C(9)	C(8)	C(7)	−173.3(3)
O(2)	C(9)	C(8)	C(17)	10.9(4)
O(3)	C(17)	O(4)	C(18)	4.2(4)
C(18)	O(4)	C(17)	C(8)	−177.5(2)
C(7)	C(6)	C(5)	C(4)	−180.0(4)
C(7)	C(6)	C(1)	C(2)	−179.0(2)
C(7)	C(11)	C(12)	C(13)	−178.3(2)
C(7)	C(11)	C(16)	C(15)	178.8(2)
C(6)	C(7)	C(8)	C(17)	−178.9(2)
C(11)	C(7)	C(8)	C(17)	0.8(3)

Molecular planes (Å)

Plane (I): C(1)—C(6), mean deviation is 0.006.
Plane (II): C(11)—C(16), mean deviation is 0.003.
Plane (III): C(1)—C(10), mean deviation is 0.109.

Angle between planes (I) and (III) is 63.9°.

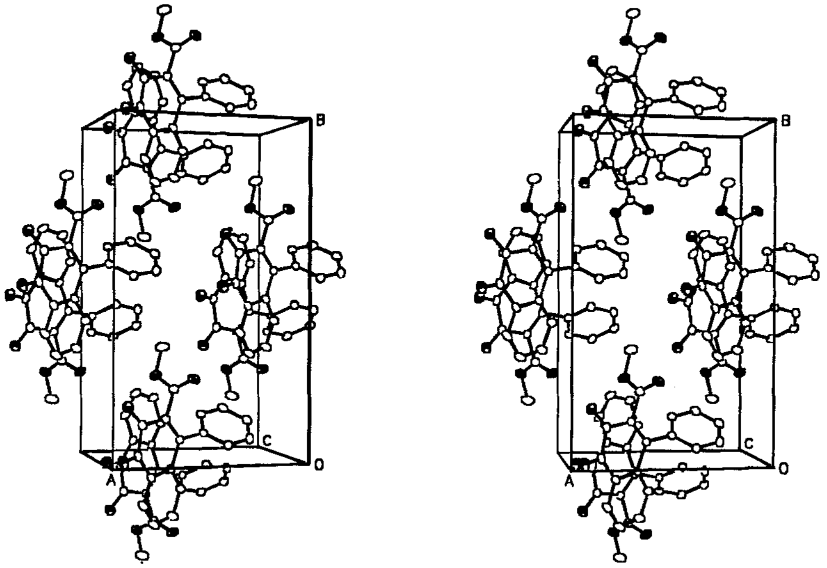

Fig. 2. Stereoscopic view of the molecular packing arrangement in the unit cell.

Acknowledgements

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Anisotropic thermal parameters and structure factor data have been deposited with the British Library, Boston Spa, Wetherby, West Yorkshire, UK as supplementary publication No. 67076 (11 pages).