

Refinement

Refinement on *F**R* = 0.070*wR* = 0.071*S* = 1.38

781 reflections

119 parameters

H atoms riding with
common group *U**w* = 1/[$\sigma^2(F) + 0.002568F^2$] $(\Delta/\sigma)_{\max} = 0.05$ $\Delta\rho_{\max} = 0.56 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.35 \text{ e } \text{\AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
S1	0.4122 (4)	0.8415 (3)	0.1496 (3)	0.0524 (8)
S2	0.6223 (4)	0.8107 (4)	0.3704 (4)	0.068 (1)
O1	0.1709 (10)	0.8862 (9)	-0.1258 (9)	0.072 (3)
O2	-0.0423 (12)	0.7027 (11)	-0.3606 (10)	0.091 (3)
N1	0.0865 (11)	0.7359 (11)	-0.2140 (10)	0.051 (3)
N2	0.4227 (15)	0.7338 (12)	0.6082 (12)	0.081 (4)
C1	0.3248 (14)	0.4720 (11)	0.0925 (13)	0.051 (3)
C2	0.2257 (16)	0.3082 (13)	-0.0068 (15)	0.061 (4)
C3	0.0847 (16)	0.2801 (14)	-0.1690 (15)	0.065 (4)
C4	0.0383 (14)	0.4224 (13)	-0.2382 (13)	0.055 (3)
C5	0.1406 (12)	0.5878 (11)	-0.1382 (11)	0.040 (3)
C6	0.2872 (12)	0.6198 (11)	0.0278 (11)	0.041 (3)
C7	0.5007 (15)	0.7626 (12)	0.5107 (13)	0.058 (4)

Table 2. Selected geometric parameters (\AA , °)

S2—S1	2.059 (3)	C6—S1	1.791 (8)
C7—S2	1.702 (12)	N1—O1	1.229 (9)
N1—O2	1.221 (9)	C5—N1	1.465 (11)
C7—N2	1.143 (12)	C2—C1	1.352 (13)
C6—C1	1.386 (11)	C3—C2	1.352 (14)
C4—C3	1.382 (14)	C5—C4	1.367 (12)
C6—C5	1.389 (11)		
C6—S1—S2	103.4 (3)	C7—S2—S1	101.2 (3)
O2—N1—O1	123.5 (8)	C5—N1—O1	118.4 (7)
C5—N1—O2	118.1 (8)	C6—C1—C2	120.3 (9)
C3—C2—C1	122.5 (9)	C4—C3—C2	119.6 (10)
C5—C4—C3	117.7 (9)	C4—C5—N1	116.4 (8)
C6—C5—N1	120.0 (8)	C6—C5—C4	123.6 (8)
C1—C6—S1	123.3 (7)	C5—C6—S1	120.4 (6)
C5—C6—C1	116.3 (8)	N2—C7—S2	178.2 (9)

Data collection: Nicolet (1980) *P3* diffractometer software. Cell refinement: *P3* diffractometer software. Data reduction: *RDNIC* (Howie, 1980). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXS76* (Sheldrick, 1976). Molecular graphics: *ORTEX* (McArdle, 1994). Software used to prepare material for publication: *XPUB* (Low, 1980).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1016). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-Methylphthalic Anhydride

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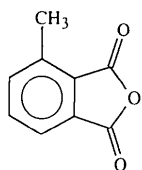
Abstract

Molecules of the title compound, C₉H₆O₃, are not wholly planar, having a dihedral angle of 2.0(1)° between the two ring planes. The fused heterocyclic five-membered ring causes significant distortions in the bond angles within the benzene ring. The methyl group is displaced by 0.06(1) Å from the least-squares plane through the aromatic ring.

Comment

A large number of derivatives of the title compound have been reported as a result of interest either in their use for the synthesis of epoxy resins and in the manufacture of ceramic and powder metallurgical products (Bayer & Nagl, 1993), or because they form charge-transfer complexes with a number of polycyclic compounds (Wilkerson, Chodak & Strouse, 1975; Baumer & Starodub, 1984; Bulgarovskaya, Zavodnik, Bel'skii & Vozzhennikov, 1989). In view of the potential utilization

of these compounds, the properties of which clearly depend on the nature of the substituents on the rings, we decided to analyse the title compound, (I), by X-ray diffraction.



(I)

Bond distances and angles within the title compound compare well with those reported for unsubstituted phthalic anhydride (Bates & Cutler, 1977). Our results confirm the influence of small-ring fusion on the geometry of benzene (Allen, 1981), already observed in phthalic anhydride, and in tetrachloro- and tetrabromophthalic anhydride (Ito, Moriya, Kashino & Haisa, 1975; Gowda & Rudman, 1982; Uchida, Nakano & Kozawa, 1982); the presence of the fused heterocyclic five-membered ring causes a significant distortion in the bond angles but not in the bond distances of the benzene ring. Moreover, the presence of the methyl group increases the narrowing of the C6—C7—C8 angle to 114.5 (6)° compared with a value of 117.0 (4)° for the C3—C4—C5 angle opposite. The two rings are inclined towards each other with a dihedral angle of 2.0 (1)°. The methyl C10 atom is displaced by 0.06 (1) Å from the least-squares plane through the aromatic ring.

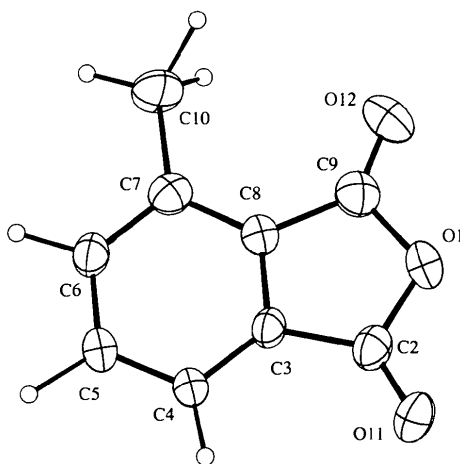


Fig. 1. Projection of the title compound showing 30% probability displacement ellipsoids.

Experimental

Crystals of 3-methylphthalic anhydride were obtained from ethanolic solution according to the method of Grenier-Loustalot (1995).

Crystal data

C₉H₆O₃
M_r = 162.14
 Orthorhombic
*Pna*2₁
a = 9.504 (2) Å
b = 15.059 (3) Å
c = 5.295 (2) Å
V = 757.8 (4) Å³
Z = 4
D_x = 1.421 Mg m⁻³

Cu Kα radiation
 λ = 1.54178 Å
 Cell parameters from 30 reflections
 θ = 11.2–42.9°
 μ = 0.911 mm⁻¹
T = 293 (2) K
 Prism
 0.52 × 0.06 × 0.04 mm
 Colourless

Data collection

Siemens AED diffractometer
 Lehman & Larsen (1974) scans
 Absorption correction: none
 809 measured reflections
 809 independent reflections
 387 observed reflections [*I* > 2σ(*I*)]
 θ_{max} = 70.07°
h = 0 → 11
k = 0 → 18
l = 0 → 6
 1 standard reflection monitored every 50 reflections
 intensity decay: 55%

Refinement

Refinement on *F*²
R(*F*) = 0.0323
wR(*F*²) = 0.0746
S = 0.647
 806 reflections
 134 parameters
 All H-atom parameters refined
w = 1/[σ²(*F*_o²) + (0.0129*P*)²]
 where *P* = (*F*_o² + 2*F*_c²)/3
 (Δ/σ)_{max} = 0.482
 Δρ_{max} = 0.10 e Å⁻³
 Δρ_{min} = -0.09 e Å⁻³
 Extinction correction: *SHELXL93* (Sheldrick, 1993)
 Extinction coefficient: 0.0084 (7)
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
 Absolute configuration: Flack (1983) parameter = 0.1 (5); not determined reliably

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
O1	0.2251 (3)	0.06205 (14)	0.0184 (7)	0.0726 (10)
C2	0.1503 (4)	0.0169 (2)	-0.1690 (10)	0.0609 (13)
C3	0.1948 (3)	-0.0763 (2)	-0.1651 (9)	0.0488 (11)
C4	0.1473 (4)	-0.1467 (2)	-0.3043 (9)	0.0576 (13)
C5	0.2075 (4)	-0.2289 (2)	-0.2555 (9)	0.0625 (13)
C6	0.3103 (4)	-0.2380 (2)	-0.0681 (8)	0.0570 (13)
C7	0.3578 (4)	-0.1672 (2)	0.0780 (8)	0.0577 (13)
C8	0.2945 (3)	-0.0858 (2)	0.0217 (8)	0.0468 (10)
C9	0.3141 (4)	0.0006 (3)	0.1437 (9)	0.0649 (14)
C10	0.4730 (6)	-0.1791 (4)	0.2721 (11)	0.079 (2)
O11	0.0678 (3)	0.05567 (13)	-0.3007 (7)	0.0790 (11)
O12	0.3851 (3)	0.0265 (2)	0.3144 (7)	0.0954 (13)

Table 2. Selected geometric parameters (Å, °)

O1—C2	1.398 (5)	C5—C6	1.399 (5)
O1—C9	1.418 (4)	C6—C7	1.392 (5)
C2—O11	1.201 (4)	C7—C8	1.398 (4)
C2—C3	1.466 (4)	C7—C10	1.513 (6)
C3—C4	1.368 (5)	C8—C9	1.465 (5)
C3—C8	1.377 (4)	C9—O12	1.193 (5)
C4—C5	1.388 (4)		

C2—O1—C9	108.6 (3)	C6—C7—C8	114.5 (4)
O11—C2—O1	120.5 (3)	C6—C7—C10	121.4 (4)
O11—C2—C3	131.5 (5)	C8—C7—C10	124.1 (4)
O1—C2—C3	108.0 (4)	C3—C8—C7	122.7 (3)
C4—C3—C8	122.3 (3)	C3—C8—C9	108.2 (3)
C4—C3—C2	129.7 (4)	C7—C8—C9	129.1 (4)
C8—C3—C2	107.9 (4)	O12—C9—O1	118.6 (4)
C3—C4—C5	117.0 (4)	O12—C9—C8	134.1 (4)
C4—C5—C6	120.5 (4)	O1—C9—C8	107.3 (4)
C7—C6—C5	123.0 (3)		

The amplitude of the Lehman & Larsen (1974) scans is given by $(0.55 + 0.55 \tan \theta)^\circ$. A decrease in the intensity of the standard reflection of about 55% was found during the data collection time and a correction for this decay was included in the data reduction procedure. Data were also corrected for Lorentz and polarization effects but not for absorption. All the calculations were performed on a 466DE Dell computer with the *CRYSRULER* (Rizzoli, Sangermano, Calestani & Andreotti, 1987) package. Refinement was on F^2 for all reflections except for 3 reflections with very negative F^2 or flagged by the user for potential systematic errors. The unreliable determination of the Flack (1983) parameter arose because of the severe decay suffered by the crystal. It was not possible to acquire the anomalous-diffraction data which could have improved the determination.

Data collection: Belletti, Cantoni & Pasquinelli (1992). Cell refinement: Belletti, Cantoni & Pasquinelli (1992). Data reduction: Belletti, Cantoni & Pasquinelli (1992). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1019). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Ethyl 3-(3-Bromo-4-hydroxyphenyl)-2(E)-(hydroxyimino)propanoate

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Abstract

The crystal structure determination of the title compound, C₁₁H₁₂BrNO₄, m.p. 408.5–409.3 K, shows the oxime geometry to be *E* (*trans*). In the crystal structure, two molecules form a head-to-tail hydrogen-bonded cyclic dimer, with the hydrogen bonds between the phenol H atom of one molecule and the carboxylate O atom of the other. The dimers are hydrogen bonded *via* the oximes to form a repeating chain.

Comment

Over the last twenty-five years several metabolites of tyrosine have been isolated from a variety of marine sponges of the order Verongida (Berquist & Wells, 1983; Ireland *et al.*, 1989). In most cases metabolism involves bromination of the tyrosine aromatic ring and oxidation of the amine to an oxime. The tyrosine oximes are then further metabolized to form spirocyclic isoxazolines, biphenyl ethers and semiquinols. Recently, we began to investigate a biomimetic synthesis of these metabolites from tyrosine, including methods for oxidation of the amine to the corresponding oxime.

Treatment of the tyrosine ethyl ester (1) with 1 equivalent of sodium tungstate and 10 equivalents of hydrogen peroxide in aqueous ethanol (Kahr & Berther, 1960) gave the corresponding oxime (2) in an 85% yield as a single geometric isomer (determined by spectroscopic analysis). Controlled bromination of the resulting oxime (2) gave either a monobromo oxime, a dibromo oxime, or a spiroisoxazoline (Boehlow & Spilling, 1995). While the oxidative cyclization of the oxime gave indirect evidence for the *E* geometry (Boehlow & Spilling, 1995; for other examples, see Kacan, Koyuncu & McKillop, 1993; Forrester, Thomson & Woo, 1978*a,b*; Noda, Niwa