Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

2-Methoxy-6-methyl-3-nitro-4-(2-nitroprop-1-enyl)phenyl acetate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.046
wR factor = 0.144
Data-to-parameter ratio = 12.3

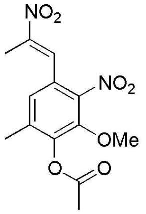
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 15 April 2005
Accepted 3 May 2005
Online 14 May 2005

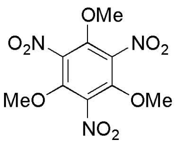
In the title compound, $C_{13}H_{14}N_2O_7$, steric crowding around the aromatic ring results in significant out-of-plane twisting of the nitro, methoxy, acetoxy and 2-nitropropenyl functional groups. These distortions are explained by comparison with less congested substituted benzene analogues.

Comment

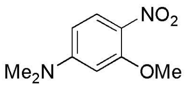
β–Nitrostyrenes and their derivatives are important starting materials for the synthesis of a variety of amines, ketoximes, hydroxylamines and aldoximes (Barrett & Graboski, 1986). They also have recognized antimicrobial and antifungal activities (Worthen & Bond, 1970) and have potential for further development as anticancer drugs (Kim *et al.*, 2003; Kaap *et al.*, 2003). Our interest in this class of compounds stems from their use as common precursors for the preparation of substituted indole derivatives by reductive cyclization of an appropriate nitrostyrene precursor with an *o*-nitro group on the aromatic ring (Rogers *et al.*, 1987; Sinhababu *et al.*, 1985). The title compound, (I), was isolated as the sole product from a nitration reaction of 4-acetoxy-3-methoxy-5-methyl-β-methylnitrostyrene. Our target was the 6-nitro derivative as a precursor for the preparation of novel methylated eumelanin pigments. Instead, we found that the 2-nitro isomer, (I), was formed preferentially.



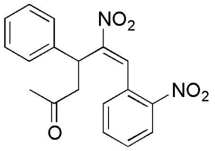
(I)



(II)



(III)



(IV)

An examination of the structure of (I) reveals a crowded aromatic ring system with non-bonding interactions between adjacent substituents, resulting in a distorted conformation. Bond lengths, angles and torsion angles are in listed Table 1. The 2-nitro group is twisted out of the plane of the ring [C3—C2—N2—O3 = 48.6 (4)°], as is the 3-methoxy group [C4—C3—O5—C13 = 78.7 (3)°]. A similar distortion is evident in the structure of the equally congested (II) (see scheme), where the Ar—NO_2 torsion angles are in the range 63.4–79.0° and the Ar—OMe torsions span the range 72.0–81.1° (Anulewicz-Ostrowska *et al.*, 1999). By contrast, in the structure of the simpler analogue (III), the nitro and methoxy groups are essentially coplanar with the ring (Borbulevych *et al.*, 2002).

The acetoxy group is wedged between methoxy and methyl substituents and similarly twists out of the plane of the ring to

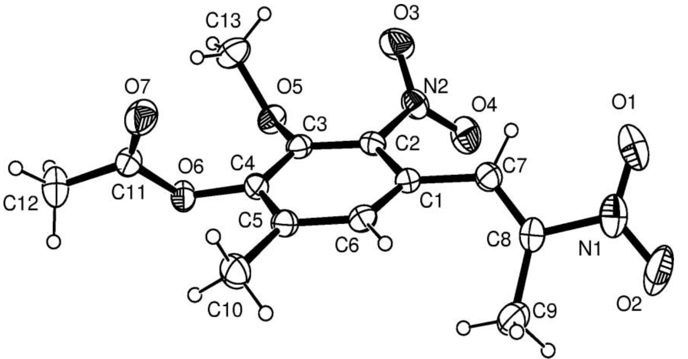


Figure 1
ORTEP-3 plot (Farrugia, 1997) of (I) (30% probability ellipsoids).

avoid its neighbouring groups [C5—C4—O6—C11 = 71.6 (3)°]. The bulkier 2-nitropropenyl group is twisted out of the plane of the aromatic ring [C6—C1—C7—C8 = 42.2 (4)°] to avoid the H atom in the 6-position as well as the nitro group in the 2-position. In the structure of the related but less congested (IV) (Peseke *et al.*, 1999), the nitroalkene substituent is twisted by 57.2°, but significantly the 2-nitro group is coplanar and conjugated with the aromatic ring.

The C—O bonds to the methoxy [C3—O5 = 1.363 (3) Å] and acetoxy [C4—O6 = 1.408 (3) Å] substituents exhibit partial double-bond character [*c.f.* single bond C13—O5 = 1.434 (4) Å], which suggests that conjugation with the aromatic ring is maintained despite rotation about the connecting C—O bond. The C2—N2 bond [1.464 (4) Å] in (I) lies in the middle of the range of known Ar—NO$_2$ bonds (*ca* 1.43–1.49 Å). Typically, Ar—NO$_2$ bonds are sensitive to the presence and position (*ortho*/*para* or *meta*) of other potentially electron-donating or -withdrawing groups around the ring. The out-of-plane twisting appears to have little effect on the Ar—NO$_2$ bond length in (I).

In conclusion, the nitro, methoxy and acetoxy functional groups of (I) are twisted significantly out of the plane of the aromatic ring due to interactions with neighbouring substituents on each side of the group. The bulkier 2-nitropropenyl group is also twisted from the plane but this group has only one adjacent non-H substituent. The distortions come at an electronic cost, in that conjugation between the aromatic ring and the nitro and 2-nitropropenyl groups is lost.

Experimental

4-Hydroxy-3-methoxy-5-methylbenzaldehyde (3.32 g, 20 mmol), EtNO$_2$ (4.5 g, 60 mmol) and NH$_4$OAc (3.08 g, 40 mmol) were refluxed for 2 h in glacial acetic acid (40 ml). After cooling, the reaction mixture was poured over ice and vacuum filtration gave the product as a solid (3.53 g, 15.8 mmol, 79%). This was acetylated by reaction with excess acetic anhydride for 1 h at *ca* 353 K, using dimethylaminopyridine as a catalyst. The desired product was obtained by pouring over ice and filtration yielded 3.22 g (12.1 mmol, 77%). A portion of this solid (1.59 g, 6 mmol) was dissolved in 1,2-dichloroethane (25 ml) and reacted with fuming HNO$_3$ (*ca* 10 ml) at 273 K for 4 h, after which the reaction was poured over ice. The organic layer was separated and the aqueous phase was extracted with ethyl acetate (3 × 50 ml). The organic layers were combined and dried over sodium sulfate, then concentrated *in vacuo*. X-ray quality crystals of (I) were grown by slow evaporation of an ethyl acetate solution at 273 K. ^{1}H NMR (CDCl$_3$): δ 2.23 (*d*, 3H, 2.23 Hz, Ar—CH$_3$), 2.29 (*d*, 3H, 2.28 Hz, ArC=CH$_3$NO$_2$), 2.38 (*s*, 3H, CH$_3$CO$_2$Ar), 3.89 (*s*, 3H, CH$_3$—OAr), 6.95 (*m*, 1H, Ar H), 7.81 (*m*, 1H, ArCH=C). ^{13}C NMR (CDCl$_3$): δ 14.0, 16.5, 20.3, 62.7, 123.9, 125.8, 126.6, 136.3, 143.4, 144.1, 145.4, 150.9 and 167.6.

Crystal data

$C_{13}H_{14}N_2O_7$
M_r = 310.26
Triclinic, $P\overline{1}$
a = 8.274 (3) Å
b = 9.125 (2) Å
c = 10.623 (2) Å
α = 76.31 (2)°
β = 81.34 (2)°
γ = 66.51 (3)°
V = 713.3 (3) Å^3
Z = 2
D_x = 1.445 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 16 reflections
θ = 11.3–13.3°
μ = 0.12 mm^{-1}
T = 293 (2) K
Prism, colourless
0.40 × 0.33 × 0.13 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.952, $T_{\max}$ = 0.983
2684 measured reflections
2497 independent reflections
1306 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.023
$\theta_{\max}$ = 25.0°
$h = 0 \rightarrow 9$
$k = -9 \rightarrow 10$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: −3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.144
S = 1.01
2497 reflections
203 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.072P)^2 + 0.0191P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.002
$\Delta\rho_{\max}$ = 0.19 e Å^{-3}
$\Delta\rho_{\min}$ = −0.23 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—C6	1.377 (4)	C3—C4	1.389 (4)
C1—C2	1.405 (4)	C4—C5	1.380 (4)
C2—C3	1.388 (4)	C5—C6	1.396 (4)
C6—C1—C2	116.7 (3)	C5—C4—C3	122.4 (3)
C3—C2—C1	122.2 (3)	C4—C5—C6	117.2 (3)
C2—C3—C4	117.9 (3)	C1—C6—C5	123.5 (3)
C6—C1—C7—C8	42.2 (4)	C3—C2—N2—O4	−131.4 (3)
C1—C7—C8—N1	−176.5 (3)	C2—C3—O5—C13	−108.0 (3)
C7—C8—N1—O2	−169.2 (3)	O7—C11—O6—C4	7.1 (4)
C7—C8—N1—O1	12.1 (4)	C5—C4—O6—C11	71.6 (3)
C3—C2—N2—O3	48.6 (4)		

All H atoms were treated as riding, with C—H distances ranging from 0.93 to 0.96 Å and $U_{\rm iso}$(H) values equal to 1.5 (methyl H atoms) or 1.2 (all other atoms) times $U_{\rm eq}$ of the parent atom.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Version 1.64.02; Farrugia, 1999).

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Financial assistance by the Australian Research Council to PM (Discovery DP0345309) is gratefully acknowledged.

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