4-Allyl-2-methoxy-5-nitrophenyl acetate

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Key indicators

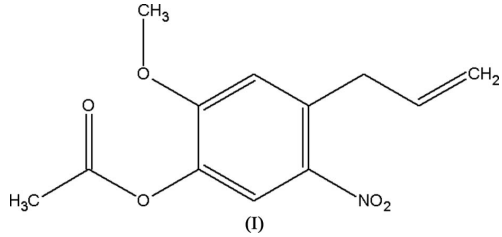
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.003 Å
R factor = 0.045
wR factor = 0.113
Data-to-parameter ratio = 15.0

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

Molecules of the title compound, $C_{12}H_{13}NO_5$, are linked into chains *via* weak C—H$\cdots\pi$(allyl) interactions and these chains are linked into sheets *via* C—H$\cdots$O contacts; the sheets, in turn, are interconnected *via* carbonyl–carbonyl and nitro–π stacking interactions to form a three-dimensional crystal structure.

Comment

Polyphenolic acids found in wines have acquired great importance owing to their possible role in the prevention of cancer as well as their generation of a series of cellular responses to stress. These properties are thought to arise due to the capacity of these acids to participate in processes associated with the capture of free radicals (Bors *et al.*, 2002). It has been stated that the anti-oxidant capacity of these compounds increases with the number of hydroxyl groups present in the molecule. This observation led our research group to investigate other naturally occurring compounds possessing similar structural characteristics. A prominent example is that of a natural product, eugenol (4-allyl-2-methoxyphenol), which is known to possess anti-oxidant properties (Wie *et al.*, 1997; Fujisawa *et al.*, 2002). We report here the synthesis and crystal structure of the title compound, (I), which was obtained by treating 4-allyl-2-methoxiacetate with a mixture of sulfuric acid and nitric acid in dichloromethane solution. It is important to emphasize that in the above reaction both isomers were formed, (I) and 4-allyl-2-methoxy-3-nitrophenylacetate, but that upon recrystallization from a mixture of ethyl acetate/*n*-hexane, we managed to separate completely one of the products, whose structure has been determined by NMR and X-ray diffraction.



(I)

A perspective view of (I) is shown in Fig. 1. The large thermal motion of atom C7 is thought to account for the unusually short C7═C8 bond length [1.204 (4) Å; Table 1]; the reference value is 1.300 (27) Å (Allen *et al.*, 1987). The nitro group is coplanar with the C1–C6 aromatic ring, which allows for the formation of intramolecular hydrogen bonds involving both O atoms as detailed in Table 2. Even so, the

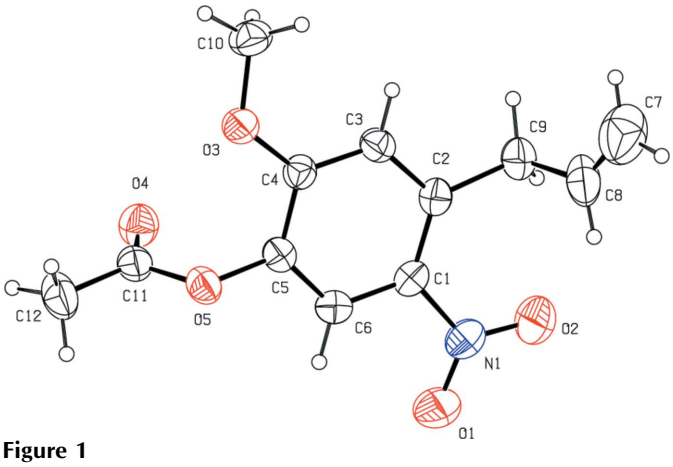


Figure 1
Molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level and showing the atom-labeling scheme.

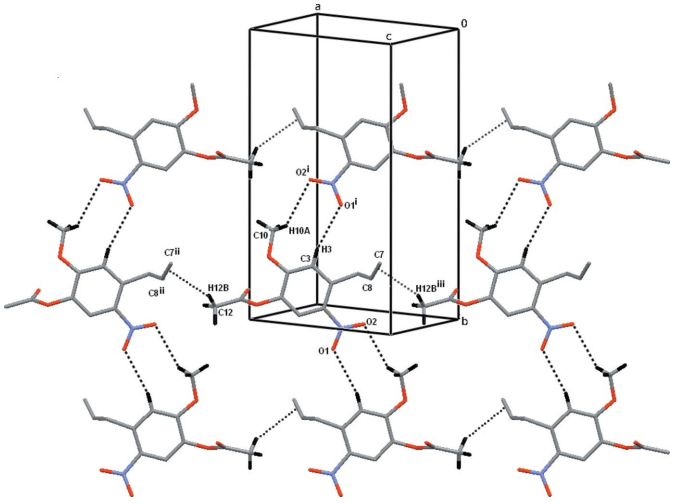


Figure 2
Part of the crystal structure, showing the formation of sheets parallel to the $(\bar{1}01)$ plane. C—H$\cdots\pi$ and C—H$\cdots$O interactions are shown as dotted and dashed lines, respectively. H atoms not involved in these interactions have been omitted. [Symmetry codes: (i) $1-x, -\frac{1}{2}+y, \frac{3}{2}-z$; (ii) $1+x, y, 1+z$; (iii) $-1+x, y, -1+z$].

nitro group is tilted towards atom C6, as seen in the N1—C1—C6 angle of 115.61 (19)°.

There are no conventional intermolecular hydrogen bonds in (I) and the entire supramolecular structure is constructed only by weak interactions. Chains along the $[\bar{1}01]$ direction are formed *via* C—H$\cdots\pi$(allyl) interactions (the distance from H12*B* to the C7^{ii}=C8^{ii} bond is 2.79 Å) and these chains are linked *via* two C—H$\cdots$O contacts forming sheets parallel to the $(\bar{1}01)$ plane (see Fig. 2). These sheets are connected into a three-dimensional network *via* interactions of the type shown in Fig. 3. Thus, a carbonyl–carbonyl interaction (Allen *et al.*, 1998) exists where the C—O dipole is attracted by the C—O dipole at $(2-x, 2-y, 2-z)$. Furthermore, there are nitro–π stacking interactions, where the distance from atom O1^{v} to the center of the phenyl ring at $(1-x, -\frac{1}{2}+y, \frac{3}{2}-z)$ is 3.53 Å (symmetry code as in Fig. 3). This is another example where

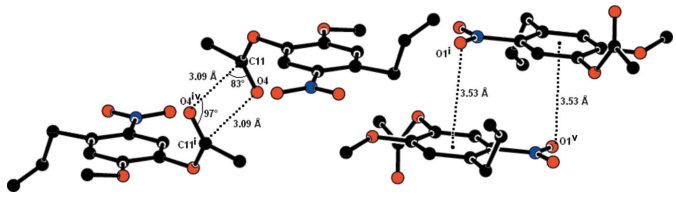


Figure 3
Detail of the carbonyl–carbonyl and the nitro-π-stacking interactions (dotted lines) linking sheets (see text). H atoms have been omitted. [Symmetry codes: (i) $1-x, -\frac{1}{2}+y, \frac{3}{2}-z$; (iv) $2-x, 2-y, 2-z$; (v) $x, \frac{3}{2}-y, -\frac{1}{2}+z$.]

the strong electron-withdrawing NO_2 group interacts with the π system of a phenyl ring (Kaafarani *et al.*, 2003).

Experimental

To a stirred solution of 4-allyl-2-methoxyphenyl acetate (200 mg, 0.97 mmol) in dichloromethane (5 ml) was added carefully, at 273 K, 2 ml of a mixture prepared by adding concentrated nitric acid (25 ml, 0.364 mol) to concentrated sulfuric acid (1 ml, 0.727 mol). The reaction was allowed to continue for 30 minutes and, after this period, the complete disappearance of the starting product was confirmed by means of thin layer chromatography (AcOEt:*n*-hexane 1:3). The reaction was stopped by adding water (15 ml). The organic layer was washed with water (3 × 20 ml) in order to extract excess acid and dried with Na_2SO_4. The solution was then filtered and the solvent evaporated at low pressure to obtain an oily product, which was purified by flash chromatography (AcOEt:*n*-hexane), resulting in 89 mg (35%) of a mixture of pure isomers. The mixture of isomers was recrystallized from a mixture of AcOEt/*n*-hexane (1:3) and crystals of (I) suitable for X-ray analysis were obtained. ^{1}H NMR (400 MHz, $CDCl_3$, p.p.m.): δ 2.32 (*s*, 3H, CH_3CO), 3.76 (*d*, 2H, J = 6.4 Hz, H9), 3.91 (*s*, 3H, OCH_3), 5.14 (*m*, 2H, H7), 5.98 (*ddt*, 1H, J = 16.6, 10.3 and 6.4 Hz, H8), 6.85 (*s*, 1H, H6), 7.83 (*s*, 1H, H3); ^{13}C NMR (100 MHz, $CDCl_3$, p.p.m.): δ 20.44 (C12), 37.70 (C9), 56.34 (C10), 114.17 (C3), 117.44 (C7), 120.66 (C6), 134.82 (C8), 136.05 (C2), 137.66 (C5), 140.88 (C1), 155.09 (C4), 168.36 (C11).

Crystal data

$C_{12}H_{13}NO_5$
M_r = 251.23
Monoclinic, $P2_1/c$
a = 10.209 (2) Å
b = 15.651 (3) Å
c = 7.8920 (17) Å
β = 104.822 (4)°
V = 1219.0 (4) Å^3
Z = 4
D_x = 1.369 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 298 K
Polyhedral, yellow
0.37 × 0.36 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: none
9643 measured reflections
2482 independent reflections
1177 reflections with $I > 2\sigma(I)$
R_{int} = 0.068
θ_{max} = 26.4°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.113
S = 0.81
2482 reflections
165 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—N1	1.219 (3)	O5—C5	1.388 (3)
O2—N1	1.207 (3)	O5—C11	1.373 (3)
O3—C4	1.346 (3)	N1—C1	1.465 (3)
O3—C10	1.424 (2)	C7—C8	1.204 (4)
O4—C11	1.185 (3)		
N1—C1—C2	122.36 (19)	C2—C1—C6	122.0 (2)
N1—C1—C6	115.61 (19)		
O2—N1—C1—C6	−176.9 (2)	O2—N1—C1—C2	4.8 (3)
O1—N1—C1—C2	−175.2 (2)	O1—N1—C1—C6	3.2 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···O1	0.93	2.31	2.641 (3)	100
C8—H8···O2	0.93	2.58	3.035 (3)	111
C9—H9*A*···O2	0.97	2.29	2.753 (3)	108
C10—H10*A*···O2^{i}	0.96	2.83	3.396 (3)	119
C3—H3···O1^{i}	0.93	2.72	3.637 (3)	167

Symmetry code: (i) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$.

H atoms were placed in geometrically idealized positions and constrained to ride on their parents atoms, with C—H = 0.93–0.97 Å, and with U_{iso}(H) equal to 1.2 (1.5 for methyl) times U_{eq} of the parent atom.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-PC* (Sheldrick, 1994); software used to prepare material for publication: *PLATON* (Spek, 2003) and *MERCURY* (Bruno *et al.*, 2002).

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