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3-Nitrocinnamic acid

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.046
wR factor = 0.146
Data-to-parameter ratio = 11.5

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

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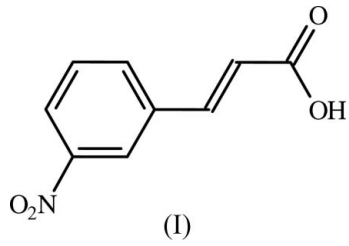
The title compound, $C_9H_7NO_4$, forms centrosymmetric dimers through intermolecular O—H···O hydrogen bonds in the crystal structure. The nitro group deviates slightly from coplanarity with the benzene ring. The benzene ring and the carboxylic acid group are in an *E* configuration about the ethylenic double bond.

Comment

Various cinnamic acid derivatives form substrate intermediates with the enzyme papain (Huber, 1985). *m*-Nitrocinnamic acid crystallizes in two modifications and the unit-cell dimensions of these polymorphs have been reported previously (Schmidt, 1964). In this paper, we report the crystal structure of the β polymorph of *m*-nitrocinnamic acid, (I).



(I)

A perspective view of (I), with the atomic numbering scheme, is shown in Fig. 1. The bond lengths and angles agree well with literature values (Allen *et al.*, 1987). The C1—C7—C8—C9 torsion angle of 179.5 (2)° indicates that the benzene ring and the carboxylic acid group are in an *E* configuration about the C7═C8 bond and the propenoic acid moiety exists in an extended conformation. The alkenecarbonyl conforma-

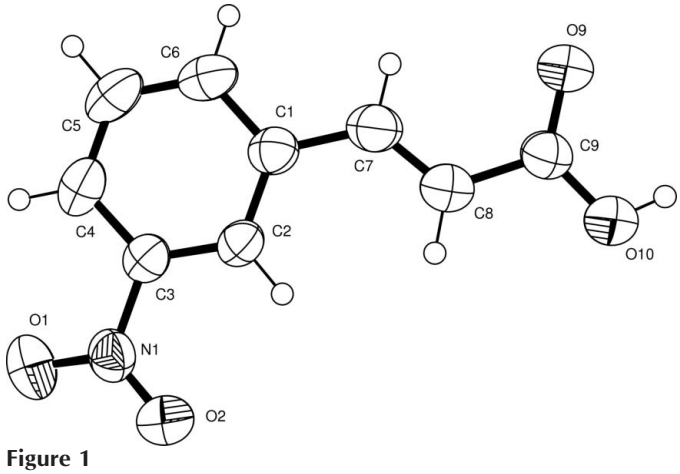


Figure 1
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

tion [C7—C8—C9—O9 = −2.5 (4)°] is synperiplanar, which is the most common conformation for *trans*-cinnamic acids (Leiserowitz, 1976).

The dihedral angle between the 3-nitro group and the benzene ring is 8.9 (9)°. In a related structure, *viz*. *p*-nitrocinnamic acid (Kageyama *et al.*, 1993), the nitro group is coplanar (2.2°) with the benzene ring. With respect to the plane of the benzene ring, the 3-nitro group is oriented at an angle of 45.3° in 4-dimethylamino-3-nitrocinnamic acid (Huber, 1985), 3.6° in 3,5-dinitrocinnamic acid and 2.3° in the 3,5-dinitrocinnamic acid 2,5-dimethoxycinnamic acid complex (Desiraju & Sharma, 1991), 3.0° in the 3,5-dinitrocinnamic acid 4-(*N*,*N*-dimethylamino)benzoic acid complex and 6.1° in the 3,5-dinitrocinnamic acid 4-(*N*,*N*-dimethylamino)cinnamic acid complex (Sharma *et al.*, 1993).

The angle between the mean plane of the benzene ring and the mean plane of the propenoic acid moiety is 3.5 (7)° in (I) and 2.6° in 4-dimethylamino-3-nitrocinnamic acid (Huber, 1985). The corresponding angles in 4-chlorocinnamic acid (Glusker *et al.*, 1975), 4-iodocinnamic acid (Goud *et al.*, 1993), *p*-nitrocinnamic acid (Kageyama *et al.*, 1993), 3,5-dinitrocinnamic acid and the 3,5-dinitrocinnamic acid 2,5-dimethoxycinnamic acid complex (Desiraju & Sharma, 1991) are 14.1, 13.8, 4.7, 28.7 and 6.4°, respectively. In the 3,5-dinitrocinnamic acid 4-(*N*,*N*-dimethylamino)cinnamic acid complex, the propenoic acid group is twisted by 7.6° out of the mean plane of the benzene ring (Sharma *et al.*, 1993).

In the crystalline state, the molecules form O—H···O hydrogen-bonded dimers across an inversion centre (Table 1). These dimers are stacked along the shortest cell axis and lead to an $R_2^2(8)$ motif (Fig. 2) (Bernstein *et al.*, 1995).

Experimental

The title compound, (I), was prepared by dissolving *m*-nitrobenzaldehyde (6 g, 0.04 mol) and malonic acid (8.3 g, 0.08 mol) in a mixture of 5 ml of pyridine and 0.25 ml of piperidine. The solution was allowed to reflux for 1 h, with rapid evolution of CO_2. The resulting title compound was recrystallized from ethanol.

Crystal data

$C_9H_7NO_4$
M_r = 193.16
Monoclinic, $P2_1/n$
a = 3.7756 (2) Å
b = 9.4584 (13) Å
c = 24.295 (4) Å
β = 90.875 (8)°
V = 867.52 (18) Å^3
Z = 4
D_x = 1.479 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 20–30°
μ = 1.02 mm^{-1}
T = 293 (2) K
Block, colourless
0.30 × 0.20 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.751, T_{max} = 0.823
1733 measured reflections
1478 independent reflections
1068 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 67.9°
$h = 0 \rightarrow 4$
$k = 0 \rightarrow 11$
$l = -29 \rightarrow 29$
3 standard reflections
frequency: 120 min
intensity decay: none

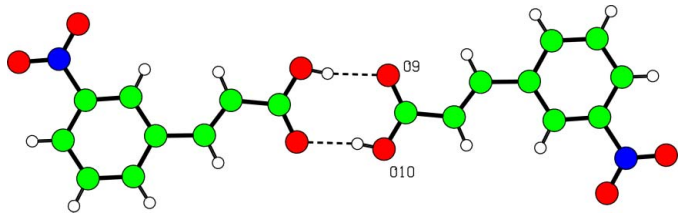


Figure 2
The O—H···O hydrogen-bonded (dashed lines) dimer in the structure of (I).

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.146
S = 1.03
1478 reflections
129 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0726P)^2 + 0.3649P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0054 (11)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O10—H10···O9^{i}	0.82	1.83	2.636 (3)	169

Symmetry code: (i) $-x+1, -y-1, -z$.

All the H atoms were placed in idealized positions (C—H = 0.93 Å and O—H = 0.82 Å) and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(parent atom).

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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