organic papers

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Key indicators

Single-crystal X-ray study
T = 130 K
Mean σ(C–C) = 0.009 Å
R factor = 0.063
wR factor = 0.111
Data-to-parameter ratio = 6.4

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

The β-form of *trans*-3-(2-nitrophenyl)prop-2-enoic acid at 130 K

The crystal structure of a non-centrosymmetric polymorphic modification of the title compound, $C_9H_7NO_4$, determined at 130 K, shows the presence of 2_1 screw-generated one-dimensional zigzag chains formed through catemeric $C(4)$ *syn–anti* carboxylic acid hydrogen-bonding associations.

Comment

A large number of the *trans*-cinnamic acids, including those with aromatic ring substituents, undergo topotactic photo-dimerization reactions (Cohen & Schmidt, 1964; Cohen *et al.*, 1964; Atkinson *et al.*, 2002). The stable α-forms of these acids give α-truxillic acids, the metastable β-forms give β-truxinic acids, while the γ-forms give no reaction (Cohen *et al.*, 1964). Thus irradiation of the title compound, (I) (common name 2-nitro-*trans*-cinnamic acid), gives the substituted β-truxinic acid [3,4-bis(2-nitrophenyl)cyclobutane-1,2-dicarboxylic acid]. The unit-cell data for β-2-nitro-*trans*-cinnamic acid were reported by Schmidt (1964) among a set of 15 β-*trans*-cinnamic acids, all having one cell dimension between 3.8 and 4.1 Å. This molecular separation allowed their classification as β-acids among the three forms, correlating with the two-dimensional packing which gives the stated 3.6–4.1 Å ethylenic C=C separations required for photodimerization to occur. This reaction proceeds *via* either head-to-tail inter-action (α-forms) or head-to-head interaction (β-forms) (Atkinson *et al.*, 2002). Understandably, very few crystal structures of these acids, including (I), have been previously reported. Examples of β-acid structures include 4-chloro-*trans*-cinnamic acid (Glusker *et al.*, 1975), 4-formyl-*trans*-cinnamic acid (Nakanishi *et al.*, 1985) and 3-nitro-*trans*-cinnamic acid (Udaya Lakshmi *et al.*, 2005).

(I)
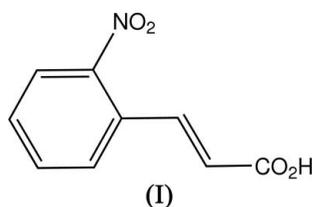
We have now determined the structure of (I) using diffraction data obtained at 130 K from a CCD-detector-equipped diffractometer and it is reported here. The unit-cell dimensions and space group determined for (I) are different from those of Schmidt (1964) for the β form (a = 3.76 Å, b = 7.2 Å2, c = 31.5 Å, β = 91.6°, space group $P2_1/c$, Z = 4). Acid (I) has comparable cell parameters (but with *ca* 1/2*c* for Z = 2) and may be assumed to represent a non-centrosymmetric
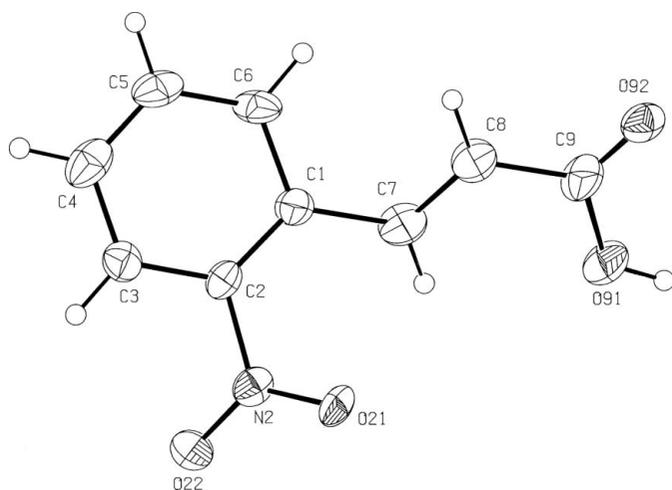
Figure 1
Molecular conformation and atom-naming scheme for (I). Atoms are shown as 40% probability displacement ellipsoids.
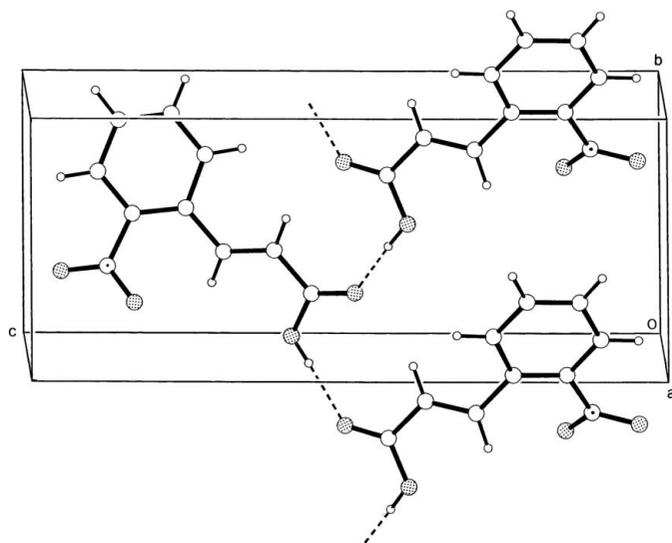
Figure 2
Syn–anti hydrogen-bonding associations (broken lines), which extend the structure of (I) into one-dimensional zigzag chains along the *b* cell direction.

polymorph of the room-temperature centrosymmetric β-form of Schmidt. The structure determination shows that the molecules are not planar (Fig. 1), with the nitro group and the essentially planar propenoic acid substituent group both rotated significantly out of the plane of the benzene ring [torsion angles C1—C2—N2—O22 = −154.0 (6)° and C2—C1—C7—C8 = −147.8 (8)°]. However, the molecular conformation is influenced by the presence of intramolecular interactions between the C7 ethylenic H and both a nitro O [C7···O21 = 2.721 (8) Å and C7—H7···O21 = 101°] and a carboxyl O [C7···O91 = 2.767 (8) Å and C7—H7···O91 = 100°]. The carboxylic acid groups of the 2_1 screw-related molecules associate through single hydrogen bonds [O91···O92^i = 2.632 (7)Å and O91—H91···O92^i = 180°; symmetry code (i) $-x + 2, y - \frac{1}{2}, -z + 1$], giving a *syn–anti* C(4)

catemeric motif (Leiserowitz, 1976) which extends the structure into one-dimensional zigzag chains along the *b* cell direction (Fig. 2). This type of association is found in only a small number of carboxylic acids where, among the mono- and dicarboxylic acids without other functional groups, occurrence of the cyclic $R_2^2(8)$ motif has a probability of 95.5% (Allen *et al.*, 1998). This includes other known photodimerizable β-examples (Glusker *et al.*, 1975; Nakanishi *et al.*, 1985; Udaya Lakshmi *et al.*, 2005). The stacking of the molecules in the chains in (I) provides head-to-head interaction down the short *a*-axial direction, which is consistent with the requirement for β-photodimerization.

Experimental

The title compound was obtained by slow evaporation of a solution of the commercial acid from 80% 2-propanol–water as pale brown crystals [literature m.p. 513 K (Rappoport, 1967)].

Crystal data

$C_9H_7NO_4$	$Z = 2$
$M_r = 193.16$	$D_x = 1.537$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 3.6850$ (18) Å	$\mu = 0.12$ mm^{-1}
$b = 7.074$ (4) Å	$T = 130$ (2) K
$c = 16.073$ (8) Å	Plate, pale brown
$\beta = 94.978$ (11)°	$0.30 \times 0.20 \times 0.03$ mm
$V = 417.4$ (4) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	810 independent reflections
	578 reflections with $I > 2\sigma(I$
φ and ω scans	$R_{int} = 0.096$
Absorption correction: none	$\theta_{max} = 25.0°$
2152 measured reflections	

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.063$	$w = 1/[\sigma^2(F_o^2) + (0.0161P)^2]$
$wR(F^2) = 0.111$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.81$	$(\Delta/\sigma)_{max} < 0.001$
810 reflections	$\Delta\rho_{max} = 0.21$ e Å^{-3}
127 parameters	$\Delta\rho_{min} = -0.23$ e Å^{-3}

The carboxylic acid proton was located by difference methods and constrained in the refinement (O—H = 0.90 Å). Other H atoms were included in the refinement at calculated positions (C—H = 0.95 Å) and treated as riding. $U_{iso}(H) = 1.2U_{eq}(C,O)$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997) in *WinGX* (Farrugia, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997) in *WinGX*; molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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