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A rare *syn–anti* catemer in 4-nitrophenylpropiolic acid

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Key indicators

Single-crystal X-ray study
T = 223 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.058
wR factor = 0.163
Data-to-parameter ratio = 15.4

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

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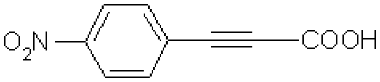
The crystal structure of 4-nitrophenylpropiolic acid, $C_9H_5NO_4$, is described. The carboxylic acid functional group adopts the rare *syn–anti* conformation and the molecules are arranged in a catemeric chain.

Comment

Most carboxylic acids without other hydrogen-bonding substituents form centrosymmetric dimers in the solid state (Kolotuchin *et al.*, 1995). This functional group can, however, also be arranged as catemers (Leiserowitz, 1976). The catemer motif is uncommon. Even rarer are structures where the carboxylic acid group adopts both *syn* and *anti* conformations in the crystal structure, these conformations alternating along an infinite O—H···O mediated array. This is referred to as the *syn–anti* conformation. In such a situation, the carboxyl groups may be either ordered or disordered (Kuduva *et al.*, 1999; Das *et al.*, 2003), but the general packing of the molecules is similar in the two cases. In a continuation of our previous work on 4-halosubstituted phenylpropiolic acids (Das *et al.*, 2003), we studied the title compound, (I).



(I)

Molecule (I) crystallizes in space group $P2_1/n$ with one molecule in the crystallographic asymmetric unit. The electron-withdrawing substituent in the *para* position of the benzene ring directs the structure towards the catemer because of the activation of the aromatic CH groups towards C—H···O hydrogen-bond formation, which supports the formation of such a catemer. The molecular geometry of (I) is shown in Fig. 1. The carboxylic acid H atom is disordered between O1 and O2, with 50% occupancy at each site. Such

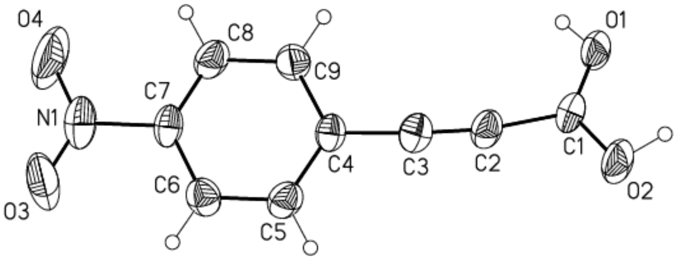


Figure 1
An *ORTEPII* view (Johnson, 1976) and the atom-numbering scheme for (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Both components of the disordered carboxylic acid H atom are shown.

disorder was also observed in 4-chlorophenylpropiolic acid (Desiraju *et al.*, 1990). The nitro group is coplanar with the benzene ring, but the carboxyl group deviates from this plane. Notable interactions are C9—H9···O2, C6—H6···O3 and C5—H5···O4, as detailed in Table 1.

Experimental

The title compound, (I), was prepared by standard procedures from the corresponding cinnamic acid. Single crystals for the X-ray diffraction study were obtained by slow evaporation of a solution in a 1:1 mixture of $CHCl_3$ and MeCN.

Crystal data

$C_9H_5NO_4$	$D_x = 1.514$ Mg m^{-3}
$M_r = 191.14$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 2334 reflections
$a = 3.726$ (2) Å	$\theta = 3.0$–26.9°
$b = 7.511$ (5) Å	$\mu = 0.12$ mm^{-1}
$c = 29.983$ (18) Å	$T = 223$ (2) K
$\beta = 91.937$ (12)°	Block, yellow
$V = 838.6$ (9) Å^3	0.32 × 0.21 × 0.12 mm
$Z = 4$	

Data collection

Siemens SMART CCD area-detector diffractometer	2065 independent reflections
φ and ω scans	1200 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)	$R_{\rm int} = 0.055$
$T_{\rm min} = 0.962$, $T_{\rm max} = 0.986$	$\theta_{\rm max} = 28.4$°
5168 measured reflections	$h = -4 \rightarrow 4$
	$k = -10 \rightarrow 9$
	$l = -21 \rightarrow 40$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.058$	$w = 1/[\sigma^2(F_o^2) + (0.0814P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.163$	$(\Delta/\sigma)_{\rm max} < 0.001$
$S = 1.03$	$\Delta\rho_{\rm max} = 0.29$ e Å^{-3}
2065 reflections	$\Delta\rho_{\rm min} = -0.31$ e Å^{-3}
134 parameters	

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O1$^{\rm i}$	0.75 (5)	1.90 (5)	2.635 (3)	168 (6)
O2—H2···O2$^{\rm ii}$	0.92 (6)	1.78 (6)	2.660 (3)	158 (6)
C5—H5···O4$^{\rm iii}$	0.94	2.56	3.345 (4)	142
C6—H6···O3$^{\rm iv}$	0.94	2.57	3.367 (4)	143
C9—H9···O2$^{\rm v}$	0.94	2.70	3.425 (3)	134

Symmetry codes: (i) $-1-x, -y, -z$; (ii) $-1-x, -1-y, -z$; (iii) $x, y-1, z$; (iv) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (v) $x, 1+y, z$.

All H atoms except carboxylic acid H atoms were positioned geometrically (C—H = 0.94 Å) and refined with riding constraints and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). Carboxylic acid H-atom positions were found in a difference Fourier map and refined with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O).

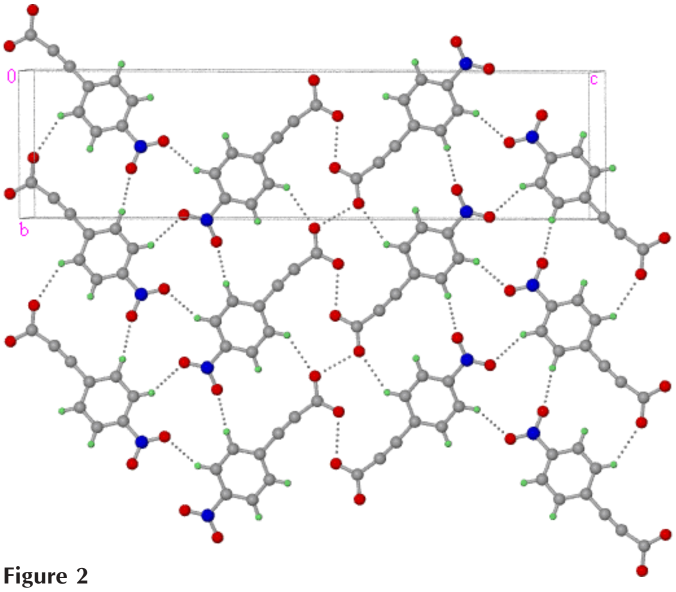


Figure 2
Packing diagram of (I). For clarity, carboxylic acid H atoms have been omitted. Hydrogen bonds are shown as dashed lines.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000) and *X-SEED* (Barbour, 2001); software used to prepare material for publication: *SHELXTL*.

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