

(2Z)-3-(5-Hydroxy-4-oxo-4H-chromen-3-yl)acrylonitrile

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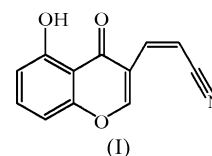
The title compound, C₁₂H₇NO₃, consists of a chromone moiety substituted in position 3 with an acrylonitrile group in a *Z* configuration. The two planar groups are twisted with respect to one another. The only significant hydrogen bond in the structure is an intramolecular O—H···O bond. π – π contacts connecting aromatic groups and C—H···O intermolecular weak interactions lead to a supramolecular layer arrangement.

Comment

Organic and organic–inorganic hybrid layered crystals have received significant attention due to their restricted space for reactions or molecular recognition, as well as their chemical and physical properties (Clearfield, 1988; Lee *et al.*, 2003). Recently, robust organic layered structures of (1-naphthylmethyl)ammonium *n*-alkanoates, with adjustable interlayer distances, have been reported (Sada *et al.*, 2004). It is not easy to construct robust structures with weak intermolecular interactions and only a few examples have ever been reported, *e.g.* an organic clay mimic based on the two-dimensional array of calixarene derivatives (Coleman *et al.*, 1988) and laminated crystalline materials of *N,N*-dialkylammonium salts of 1,3,5-benzenetricarboxylic acid (Melendez *et al.*, 1996; Melendez & Zaworotko, 1997; Sharma *et al.*, 1997; Biradha *et al.*, 1998; Zaworotko, 2001). Taking into account that supramolecular construction may be achieved not only with strong hydrogen bonds such as O—H···O and N—H···O, but also with C—H···O bonds, rationalization of the packing observed can be useful for the recognition of supramolecular synthons of importance in crystal engineering (Desiraju, 1996).

Recently, some authors have reported that hydrocarbons are weak H-atom donors. However, addition of electron-withdrawing groups strengthens them to the point where their interaction energies with H-atom acceptors could lie within

the range of conventional hydrogen bonds. The cyano group, among other functional groups, has been described as an electron-withdrawing agent that imparts sufficient acidity to the CH group to allow hydrogen bonding (Scheiner *et al.*, 2001; Cabaleiro-Lago *et al.*, 2000; Desiraju, 1996). On the other hand, the chromone system (4*H*-1-benzopyran-4-one) has received attention because of the possibility that the heterocyclic moiety may present some aromatic character (Polly & Taylor, 1999), and also because many chromone derivatives show interesting biological properties, including antitumour activity *in vivo* (Valenti *et al.*, 1996; Rajski & Williams, 1998) and phosphatase inhibition (Shim *et al.*, 2003). Moreover, some heteroarylacrylonitriles have also shown cytotoxic activities (Saczewsky *et al.*, 2004). Therefore, the combination of acrylonitrile and chromone moieties in one single molecule gives the possibility of achieving novel bioactive compounds. However, there are no reports to date dealing with the synthesis of chromone attached to an acrylonitrile framework.



The structure of the title compound, (I), was initially assigned by NMR spectroscopy. In order to confirm its double-bond geometry, as well as to obtain more detailed information on its structural conformation, the X-ray structure determination of (I) (Fig. 1) has been carried out and the results are presented here. The planar geometry of the benzopyran ring system supports the observation regarding the aromatic character of chromone reported previously for the benzopyrane ring (Polly *et al.*, 1999; Rybarczyk-Pirek & Nawrot-Modranka, 2004), that there is an elongation of the C6—C9 bond and a decrease of the valence angle because atom C9 is engaged in a formal C=O bond. On the other hand, the shortest bond length and the largest angle are observed for atom C7.

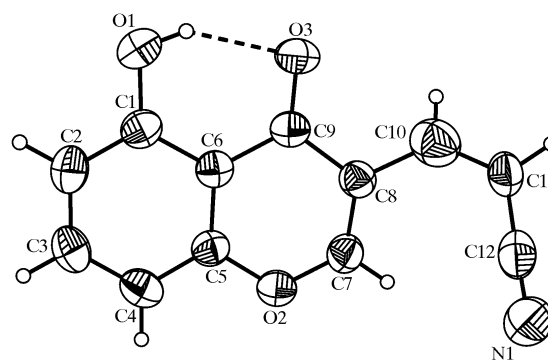


Figure 1

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

Similar variations of the geometric parameters have been reported also for other compounds (Thinagar *et al.*, 2003; Wallet & Gaydou, 1992; Adams *et al.*, 1991). These distances can be compared with the typical aromatic bond length of 1.384 (13) Å (Allen *et al.*, 1987). Both rings are planar to within 0.02 (1) Å of the maximum deviation. The planar acrylonitrile moiety (atoms C10, C11, C12 and N1) is twisted around C8–C10 with respect to the chromone system, subtending a dihedral angle of 38.1°; such an arrangement of these two groups reduces the possibility of resonance between them.

The packing of (I) is stabilized by extensive weak C–H···O intermolecular interactions. The structure presents a strong intramolecular hydrogen bond connecting atoms H1 and O3 (Table 1). In addition, a C–H···O hydrogen bond (Table 1) generates chains along [010] (Figs. 2 and 3). The only other significant intermolecular interactions are the π – π contacts which govern the stacking of aromatic groups along the [100] direction. Symmetry-related moieties at $(1-x, 2-y, -z)$ and $(2-x, 2-y, -z)$ extend parallel to each other at a graphitic distance of 3.45 (1) Å and a slippage angle of less than 20°, defining well connected columns which run parallel to *a*.

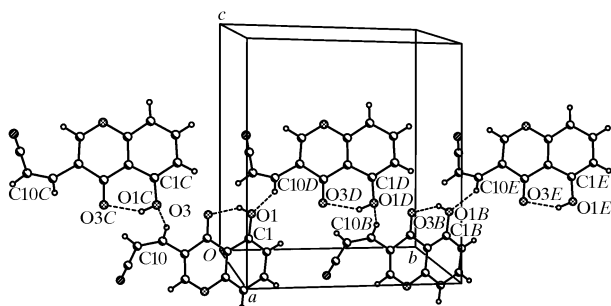


Figure 2
A packing view of (I), showing the formation of a chain along [010]. [Symmetry codes: (B) $x, 1+y, z$; (C) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (D) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (E) $1-x, \frac{3}{2}+y, \frac{1}{2}-z$.]

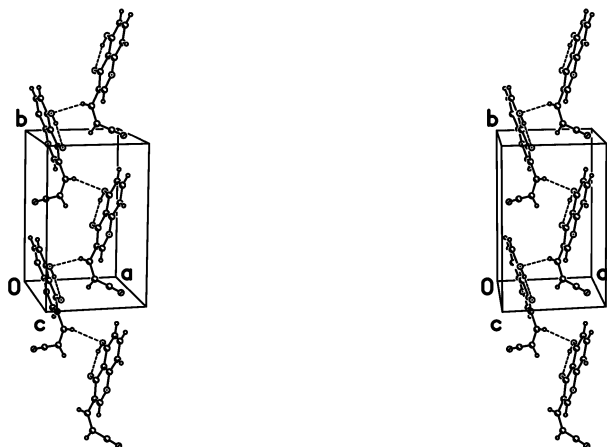


Figure 3
A stereopacking view of (I), showing the [010] chains.

Experimental

Triphenylphosphoranylideneacetonitrile (0.5 g) was added to a solution of 5-hydroxy-4-oxo-4*H*-1-benzopyran-3-carbaldehyde (5-hydroxy-3-formylchromone) (0.3 g) in toluene (50 ml) and the resulting solution was heated under reflux for 2 h, yielding a mixture of the two geometrical isomers. This mixture was chromatographed on silica gel (hexane–ethyl acetate–acetone, 4:1:0.01) to afford the pure *Z* and *E* compounds. The title compound (60% yield) was crystallized as pale-yellow needles by adding hexane over an ethyl acetate solution of the compound until opalescence. Analysis calculated for $C_{12}H_7NO_3$: C 67.6, H 3.3, N 6.6%; found: C 67.0, H 3.0, N 6.9%.

Crystal data

$C_{12}H_7NO_3$	Mo $K\alpha$ radiation
$M_r = 213.19$	Cell parameters from 999 reflections
Monoclinic, $P2_1/c$	$\theta = 2.5\text{--}26.2^\circ$
$a = 7.2251$ (11) Å	$\mu = 0.11\text{ mm}^{-1}$
$b = 11.1930$ (17) Å	$T = 293$ (2) K
$c = 12.2219$ (18) Å	Polyhedron, pale yellow
$\beta = 101.099$ (2)°	$0.35 \times 0.30 \times 0.25\text{ mm}$
$V = 969.9$ (3) Å ³	
$Z = 4$	
$D_x = 1.460\text{ Mg m}^{-3}$	

Data collection

Bruker SMART CCD area-detector diffractometer	$R_{\text{int}} = 0.041$
φ and ω scans	$\theta_{\text{max}} = 27.9^\circ$
6913 measured reflections	$h = -9 \rightarrow 9$
2172 independent reflections	$k = -14 \rightarrow 14$
1494 reflections with $I > 2\sigma(I)$	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.041$	$w = 1/[\sigma^2(F_o^2) + (0.0638P)^2]$
$wR(F^2) = 0.113$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.99$	$(\Delta/\sigma)_{\text{max}} < 0.001$
2172 reflections	$\Delta\rho_{\text{max}} = 0.17\text{ e \AA}^{-3}$
146 parameters	$\Delta\rho_{\text{min}} = -0.20\text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
$O1\text{--}H1\cdots O3$	0.82	1.91	2.6327 (14)	147
$C10\text{--}H10\cdots O1^i$	0.93	2.51	3.3286 (17)	147

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

All H atoms were located from difference maps and then treated as riding, with O–H distances of 0.82 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$, and C–H distances of 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 2002); cell refinement: SMART; data reduction: SAINT-Plus NT (Bruker, 2002); program(s) used to solve structure: XS in SHELXTL-NT (Bruker, 2002); program(s) used to refine structure: XL in SHELXTL-NT; molecular graphics: XP in SHELXTL-PC (Sheldrick, 1994); software used to prepare material for publication: SHELXTL-NT.

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