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7-Nitro-2,3-dihydro-1*H*-cyclopenta[*b*]chromen-1-one

Fang-Jun Huo, Cai-Xia Yin and Pin Yang*

Institute of Molecular Science, Chemical Biology and Molecular Engineering, Laboratory of Education Ministry, Shanxi University, Taiyuan, Shanxi 030006, People's Republic of China

Correspondence e-mail: yangpin@sxu.edu.cn

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Key indicators

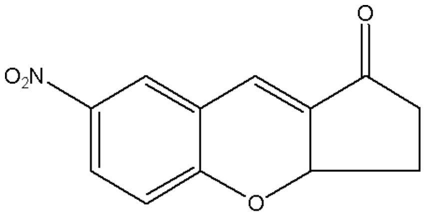
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.052
wR factor = 0.125
Data-to-parameter ratio = 10.1

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

In the crystal structure of the title compound, $C_{12}H_9NO_4$, the disordered pyran ring adopts a half-chair conformation. Weak intermolecular C—H···O hydrogen bonds link molecules into centrosymmetric dimers, which generate $R_2^1(6)$, $R_2^2(10)$ and $R_2^2(14)$ rings. In addition, π–π stacking interactions are present.

Comment

Chromenes (2*H*-1-benzopyrane derivatives) are frequently found in naturally occurring heterocycles, many of which exhibit biological activity (Bowers *et al.*, 1976) and have been widely employed as important intermediates in the synthesis of many natural products and medicinal agents (Cassidy *et al.*, 1992; Cruz-Almanza *et al.*, 1994; Wang & Finn, 2000). Furthermore, these common structural elements can yield a new family of potassium-channel activating drugs (Atwal *et al.*, 1995; Salamon *et al.*, 2002). Thus, various synthetic methods for the formation of these compounds have been reported (Chang & Grubbs, 1998; Gopal & Rajagopalan, 1987; Kaye & Nocanda, 2000; Lee *et al.*, 2003; Parker & Mindt, 2001). In this paper, we report the crystal structure of a new chromene compound, *viz*. the title compound, (I).



(I)

Selected geometric parameters of the title compound are listed in Table 1. An ellipsoid plot of the molecule is shown in Fig. 1. The molecule contains three fused rings. Atoms C3, C4 and C5 of the pyran ring are disordered over two sites, with a ratio of 0.72 (9):0.28 (9) for the major and minor components, respectively. The disorder represents an inversion of the chirality at atom C3 and the resulting geometric disorder of atoms C4 and C5. Although the minor component of disorder is the psuedo-mirror image of the major component, the following least-squares plane calculations are for the major component only. All atoms except for C3 are planar within ±0.1094 (4), while atom C3 deviates from the plane of the other atoms by 0.5645 (8) Å. The pyran ring adopts a half-chair conformation. Although the molecule contains a chiral centre at C3, the crystal belongs to a centrosymmetric space group and is thus a racemate. The pairs of enantiomers related

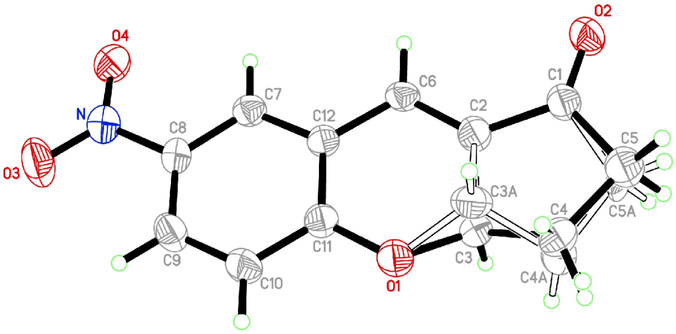


Figure 1
A view of the molecular structure of (I), with the atom-numbering scheme. The suffix A denotes the minor disorder component.

by the inversion centre are linked *via* C—H···O hydrogen bonds (Fig. 2 and Table 2). These weak interactions generate graph-set motifs of $R^1_2(6)$, $R^2_2(10)$ and $R^2_2(14)$ (Bernstein *et al.*, 1995). The molecules are packed face-to-face to form layers (see Fig. 2.). One significant intermolecular set of π–π contacts, elucidated by *PLATON* (Spek, 2003), involves the π system of the C7–C12 ring (with centroid *Cg*). The interaction is characterized by the perpendicular distances between the parallel planes (3.453 Å), the corresponding distances between their centroids [Cg–Cg^{ii} = 4.0590 (17) Å; symmetry code: (ii) $1 - x$, $2 - y$, $1 - z$] and the angle between these vectors (31.7°).

Experimental

The title compound was synthesized by Baylis–Hillman reactions. At room temperature, a clear solution of 5-nitrosalicylaldehyde (1 mmol), cyclopent-2-enone (2 mmol) and imidazole (1 mmol) in tetrahydrofuran (THF, 1.5 ml) was mixed with deionized water (1.5 ml). The mixture was stirred at ambient temperature for 72 h to complete the reaction. The mixture was diluted by water (10 ml) and extracted with ethyl acetate. The organic layer was concentrated under reduced pressure. After the usual work up, chromatography of the crude product on silica gel, using ethyl acetate and petroleum (1:4) as eluant, gave pure product (I) with a yield of 48%. The compound (50 mg) was dissolved in $CHCl_3$ (1.5 ml). The solution was allowed to evaporate slowly at room temperature for several days. Yellow crystals suitable for X-ray crystallography were formed.

Crystal data

$C_{12}H_9NO_4$
$M_r = 231.20$
Monoclinic, $P2_1/n$
$a = 6.0584$ (11) Å
$b = 19.717$ (4) Å
$c = 8.9513$ (16) Å
$\beta = 98.257$ (4)°
$V = 1058.2$ (3) Å^3
$Z = 4$
$D_x = 1.451$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4356 reflections
$\theta = 2.5$–22.4°
$\mu = 0.11$ mm^{-1}
$T = 293$ (2) K
Block, yellow
0.20 × 0.20 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.978$, $T_{max} = 0.989$
4356 measured reflections
1850 independent reflections
1165 reflections with $I > 2\sigma(I)$
$R_{int} = 0.064$
$\theta_{max} = 25.0°$
$h = -7 \rightarrow 6$
$k = -23 \rightarrow 20$
$l = -10 \rightarrow 9$

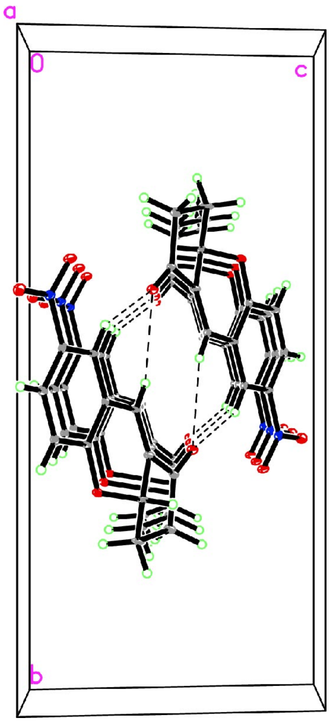


Figure 2
Part of the packing of the title compound, viewed down the *a* axis. Hydrogen bonds are shown as dashed lines. Minor disorder components have been omitted for clarity.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.125$
$S = 0.98$
1850 reflections
183 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0544P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}
Extinction correction: none

Table 1
Selected geometric parameters (Å, °).

O1—C11	1.353 (3)	C2—C3	1.537 (4)
O1—C3*A*	1.430 (4)	C2—C3*A*	1.539 (4)
O1—C3	1.431 (3)	C3—C4	1.514 (9)
O2—C1	1.211 (3)	C4—C5	1.537 (4)
C1—C2	1.468 (3)	C3*A*—C4*A*	1.514 (9)
C1—C5*A*	1.510 (5)	C4*A*—C5*A*	1.537 (4)
C1—C5	1.510 (5)	C6—C12	1.449 (3)
C2—C6	1.320 (3)	C11—C12	1.405 (3)
C11—O1—C3*A*	118.6 (4)	C4—C3—C2	100.1 (5)
C11—O1—C3	117.9 (2)	C3—C4—C5	108.0 (7)
O2—C1—C2	125.8 (2)	C1—C5—C4	102.9 (7)
O2—C1—C5*A*	129.7 (10)	O1—C3*A*—C4*A*	111.9 (15)
C2—C1—C5*A*	103.6 (10)	O1—C3*A*—C2	110.2 (3)
O2—C1—C5	125.1 (5)	C4*A*—C3*A*—C2	105.7 (13)
C2—C1—C5	109.0 (5)	C3*A*—C4*A*—C5*A*	99.8 (17)
C6—C2—C1	131.2 (2)	C1—C5*A*—C4*A*	111.3 (15)
C6—C2—C3	120.9 (2)	C2—C6—C12	118.7 (2)
C1—C2—C3	107.8 (2)	O1—C11—C10	117.2 (2)
C6—C2—C3*A*	117.6 (5)	O1—C11—C12	122.0 (2)
C1—C2—C3*A*	103.9 (3)	C7—C12—C6	123.2 (2)
O1—C3—C4	112.7 (6)	C11—C12—C6	118.3 (2)
O1—C3—C2	110.2 (2)		

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

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C6}-\text{H6}A\cdots\text{O2}^{\text{i}}$	0.93	2.57	3.380 (3)	146
$\text{C7}-\text{H7}A\cdots\text{O2}^{\text{i}}$	0.93	2.56	3.390 (3)	149

Symmetry code: (i) $-x, 2-y, 2-z$.

H atoms were placed in calculated positions and allowed to ride on their parent atoms, with $U_{\text{iso}}(\text{H})$ values set to $1.5U_{\text{eq}}$(parent atom) for the Csp^3-bound H atoms and $1.2U_{\text{eq}}$(parent atom) for Csp^2-bound H atoms. The C—H distances were fixed in the range 0.93–0.98 Å.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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