

Nancy E. Magaña-Vergara,<sup>a</sup>  
Francisco J. Martínez-Martínez,<sup>a</sup>  
Itzia I. Padilla-Martínez,<sup>a</sup>  
Herbert Höpfl<sup>b</sup> and  
Efrén V. García-Báez<sup>a\*</sup>

<sup>a</sup>Unidad Profesional Interdisciplinaria de Biotecnología, Instituto Politécnico Nacional, Avenida Acueducto s/n, Barrio La Laguna Ticomán, México DF 07340, Mexico, and <sup>b</sup>Centro de Investigaciones Químicas, Universidad Autónoma del estado de Morelos, Cuernavaca Morelos, Mexico

Correspondence e-mail:  
vgarcia@acei.upibi.ipn.mx

#### Key indicators

Single-crystal X-ray study  
 $T = 100$  K  
Mean  $\sigma(C-C) = 0.003$  Å  
 $R$  factor = 0.056  
 $wR$  factor = 0.142  
Data-to-parameter ratio = 12.0

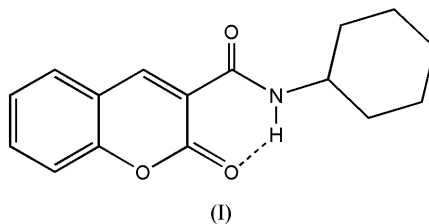
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## *N*-Cyclohexyl-2-oxo-2*H*-1-benzopyran-3-carboxamide

The title compound,  $C_{16}H_{17}NO_3$ , crystallizes in the space group  $P\bar{1}$ , with one molecule in the asymmetric unit. The amide H atom is engaged in an intramolecular N—H $\cdots$ O contact to the O atom of one of the two carbonyl groups. The molecules form centrosymmetric dimers through self-complementary C—H $\cdots$ O hydrogen-bonding interactions defining the  $R_2^2(14)[R_2^1(6)]$  motif. The supramolecular structure is achieved by aryl C—H $\cdots$  $\pi$  interactions, as well as face-to-face  $\pi$ – $\pi$  stacking interactions between lactone and benzenoid rings.

#### Comment

Coumarins are nowadays an important group of organic compounds that are used as additives to food and cosmetics (O’Kennedy & Thornes, 1997), optical brightening agents (Zahradnik, 1992), and dispersed fluorescent and laser dyes (Maeda, 1994). Coumarin derivatives usually occur as secondary metabolites present in seeds, roots, and leaves of many plant species. Their function is far from clear, though suggestions include waste products, plant-growth regulators, fungistats and bacteriostats (Murray *et al.*, 1982). There are many X-ray structures of coumarin derivatives reported in the literature (Allen, 2002), but very few of them concern supramolecular structures (Gnanaguru *et al.*, 1985). In particular, a crystallographic study of 3-carboxycoumarins and 3-amidocoumarins was reported in the context of crystal engineering (García-Báez *et al.*, 2002). These compounds are described as two fused rings with opposed polarity, which are associated through parallel displaced  $\pi$ -stacking interactions.

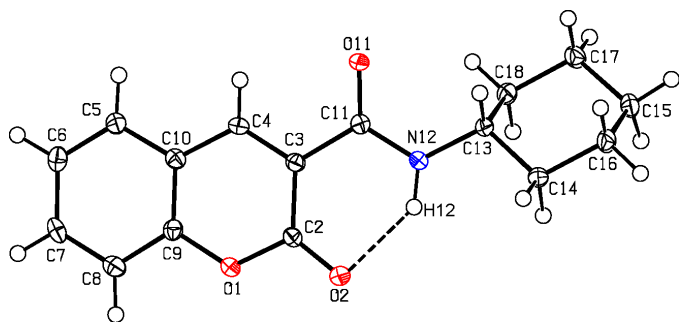


Following on from this study, the molecular and supramolecular structure of the title compound, (I), is reported (Fig. 1). Bond lengths and angles in (I) are in the ranges of those found in comparable structures retrieved from the Cambridge Structure Database (Allen, 2002) (Table 1). The amide H atom H12 is antiperiplanar to the carbonyl O atom O11 [O11—C11—N12—H12 = 173.56 (15)°], forming an intramolecular hydrogen bond to the lactone carbonyl atom O2 (see Table 2). This motif is a characteristic of 3-carboxyamido-coumarins (García-Báez *et al.*, 2002). Hydrogen-bonded

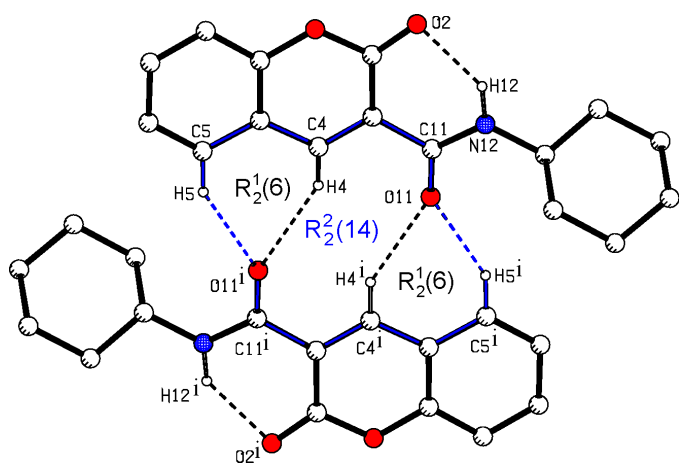
Received 29 September 2004

Accepted 5 November 2004

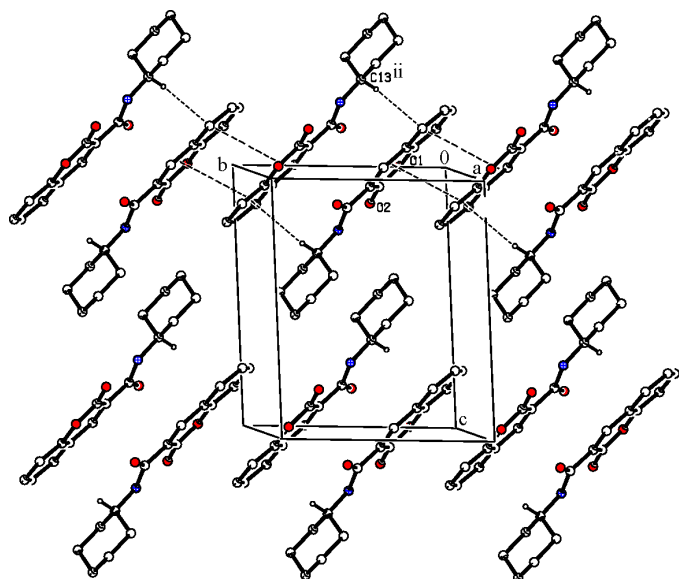
Online 13 November 2004



**Figure 1**  
The molecular structure of the title compound, (I), with displacement ellipsoids drawn at the 30% probability level. The intramolecular N—H···O contact is shown as a dashed line.



**Figure 2**  
The crystal structure of (I), showing the hydrogen-bonded dimers together with the graph-set notation. C—H···O interactions are shown as dashed lines [symmetry code: (i)  $1 - x, 1 - y, -z$ ].



**Figure 3**  
The crystal structure of (I), showing the  $\pi$ – $\pi$  stacking interactions between lactone and benzenoid (Bz) rings and the C13–H13···Bz interaction along the  $[\bar{1}22]$  direction as dashed lines [symmetry code: (ii)  $-x, 1 - y, -z$ ].

dimers are formed by the self-complementary interactions C4–H4···O11<sup>i</sup> and C5–H5···O11<sup>i</sup> (Table 2) defining the hydrogen-bonding motif  $R_2^2(14)[R_2^2(6)]$ , according to the graph-set notation (Bernstein *et al.*, 1995), along the  $[2\bar{4}5]$  direction (Fig. 2 and Table 2).

The supramolecular structure is mainly achieved through  $\pi$ – $\pi$  stacking interactions (Hunter *et al.*, 1991; Singh & Thornton, 1990) between the lactone and the benzenoid rings along the  $[\bar{1}22]$  direction (Fig. 3). The centroid-to-centroid and interplanar distances [3.5845 (13) and 3.349 (19) Å], as well as the angle between the centroid of the first ring and the normal to the second ring mean plane [ $21(1)^\circ$ ] at the  $(-x, -y, -z)$  symmetry position indicate an almost face-to-face  $\pi$ – $\pi$  stacking arrangement, which is the preferred stacking between electron-rich and electron-deficient aromatic rings (Williams, 1993).

The additional weak C13–H13··· $\pi$  interaction involving the benzenoid coumarin ring (Bz) and the cyclohexyl H atom H13 [C13–H13···Bz = 3.071 (19) Å and  $133.3(14)^\circ$ ] completes the crystal packing.

## Experimental

The title compound was obtained by the reaction of ethylcoumarin carboxylate (0.5 g, 2.2 mmol) with 0.25 ml of cyclohexylamine (1:1) in 15 ml of ethanol for 48 h. The product crystallized from the reaction mixture as a white solid. Colorless crystals suitable for X-ray analysis were obtained after recrystallization from ethanol (m.p. 425–527 K); IR (KBr)  $\nu/\text{cm}^{-1}$ : 3320 (N–H), 1705 (NC=O); 1655 (OC=O), 1610 (C=C);  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  8.91 (*s*, 1 H, H4), 7.71–7.35 (*m*, 3H, H5–8), 4.01 (1H, H13), 1.22 to 2.01 (10H, H14–H18);  $^{13}\text{C}$  NMR (DMSO- $d_6$ ):  $\delta$  161.4 (C11), 160.3 (C2), 154.0 (C9), 148.0 (C4), 133.8 (C7), 125.1 (C6), 118.6 (C3), 118.6 (C10), 116.5 (C8), 48.5 (C13), 30.9 (C16), 25.5 (C15), 24.6 (C14).

## Crystal data

$\text{C}_{16}\text{H}_{17}\text{NO}_3$   
 $M_r = 271.31$   
Triclinic,  $P\bar{1}$   
 $a = 6.0870(14)$  Å  
 $b = 9.529(2)$  Å  
 $c = 12.021(3)$  Å  
 $\alpha = 93.682(4)^\circ$   
 $\beta = 96.977(4)^\circ$   
 $\gamma = 103.543(4)^\circ$   
 $V = 669.7(3)$  Å<sup>3</sup>

$Z = 2$   
 $D_x = 1.345$  Mg m<sup>−3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 600 reflections  
 $\theta = 20$ – $25^\circ$   
 $\mu = 0.09$  mm<sup>−1</sup>  
 $T = 100(2)$  K  
Plate, colorless  
 $0.43 \times 0.41 \times 0.03$  mm

## Data collection

Bruker SMART area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
Absorption correction: none  
7666 measured reflections  
2997 independent reflections

2550 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.035$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -7 \rightarrow 7$   
 $k = -12 \rightarrow 12$   
 $l = -15 \rightarrow 15$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.056$   
 $wR(F^2) = 0.142$   
 $S = 1.10$   
2997 reflections  
249 parameters  
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0662P)^2 + 0.1763P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.36$  e Å<sup>−3</sup>  
 $\Delta\rho_{\text{min}} = -0.26$  e Å<sup>−3</sup>

**Table 1**

Selected geometric parameters (Å, °).

O1—C2	1.371 (2)	N12—C11	1.350 (2)
O2—C2	1.214 (2)	N12—C13	1.459 (2)
O11—C11	1.230 (2)	C3—C4	1.354 (2)
C2—O1—C9	122.59 (14)	O11—C11—C3	120.27 (15)
C11—N12—C13	121.00 (14)	N12—C11—C3	117.21 (15)
O2—C2—C3	126.54 (15)	N12—C13—C14	110.73 (14)
O1—C2—O2	116.00 (15)	N12—C13—C18	110.81 (13)
O11—C11—N12	122.51 (15)		
H12—N12—C11—O11	173.6 (15)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N12—H12...O2	0.92 (2)	1.99 (2)	2.7426 (19)	138.7 (18)
C4—H4...O11 <sup>i</sup>	0.905 (19)	2.510 (19)	3.317 (2)	148.7 (15)
C5—H5...O11 <sup>i</sup>	0.953 (19)	2.470 (19)	3.319 (2)	148.4 (15)

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

All H atoms were located in a difference map and their positional and isotropic displacement parameters were refined.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); 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); software used to prepare material for publication: *SHELXL97* and *WinGX2003* (Farrugia, 1999).

This work was supported by CGPI-IPN (Coordinación General de Posgrado e Investigación del Instituto Politécnico Nacional).

## References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bruker (2000). *SMART, SAINT and SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- García-Báez, E. V., Martínez-Martínez, F. J., Höpfl, H. & Padilla-Martínez, I. I. (2002). *Cryst. Growth Des.* **3**, 35–45.
- Gnanaguru, K., Venkatesan, K. & Ramamarthy, V. (1985). *J. Org. Chem.* **50**, 2337–2346.
- Hunter, C. A., Singh, J. & Thornton, J. M. (1991). *J. Mol. Biol.* **218**, 837–846.
- Maeda, M. (1994). *Laser Dyes*. New York: Academic Press.
- Murray, R. D. H., Mendez, J. & Brown, S. A. (1982). *The Natural Coumarins: Occurrence, Chemistry and Biochemistry*. New York: Wiley and Sons.
- O’Kennedy, R. & Thornes, R. D. (1997). *Coumarins: Biology, Applications and Mode of Action*. Chichester: Wiley and Sons.
- Sheldrick G. M. (1997). *SHELXS97 and SHELXL97*. University of Göttingen, Germany.
- Singh, J. & Thornton, J. M. (1990). *J. Mol. Biol.* **211**, 595–515.
- Williams, J. H. (1993). *Acc. Chem. Res.* **26**, 593–598.
- Zahradnik, M. (1992). *The Production and Application of Fluorescent Brightening Agents*. Chichester: Wiley and Sons.