



Received 19 September 2015

Accepted 25 September 2015

Edited by A. J. Lough, University of Toronto,
Canada

Keywords: crystal structure; chromones; pharmacological activity; supramolecular structure; hydrogen bonding

CCDC references: 1427459; 1427458;
1025355

Supporting information: this article has
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A comparison of the structures of some 2- and 3-substituted chromone derivatives: a structural study on the importance of the secondary carboxamide backbone for the inhibitory activity of MAO-B

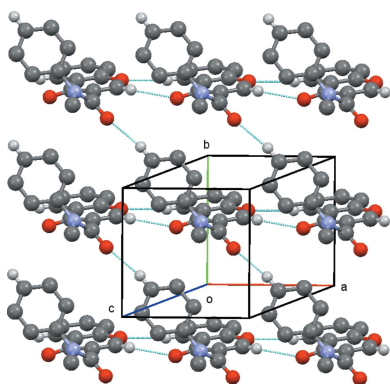
Ligia R. Gomes,^{a,b} John Nicolson Low,^{c*} Fernando Cagide,^d Alexandra Gaspar^d and Fernanda Borges^d

^aFP-ENAS-Faculdade de Ciências de Saúde, Escola Superior de Saúde da UFP, Universidade Fernando Pessoa, Rua Carlos da Maia, 296, P-4200-150 Porto, Portugal, ^bREQUIMTE/Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal, ^cDepartment of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, AB24 3UE, Scotland, and ^dCIQUP/Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal. *Correspondence e-mail: jnlow111@gmail.com

The crystal structures of the 3-substituted tertiary chromone carboxamide derivative, C₁₇H₁₃NO₃, *N*-methyl-4-oxo-*N*-phenyl-4*H*-chromene-3-carboxamide (**1**), and the chromone carbonyl pyrrolidine derivatives, C₁₄H₁₃NO₃, 3-(pyrrolidine-1-carbonyl)-4*H*-chromen-4-one (**3**) and 2-(pyrrolidine-1-carbonyl)-4*H*-chromen-4-one (**4**) have been determined. Their structural features are discussed and compared with similar compounds namely with respect to their MAO-B inhibitory activities. The chromone carboxamide presents a *-syn* conformation with the aromatic rings twisted with respect to each other [the dihedral angle between the mean planes of the chromone system and the exocyclic phenyl ring is 58.48 (8)°]. The pyrrolidine derivatives also display a significant twist: the dihedral angles between the chromone system and the best plane formed by the pyrrolidine atoms are 48.9 (2) and 23.97 (12)° in (**3**) and (**4**), respectively. Compound (**3**) shows a short C—H···O intramolecular contact forming an *S*(7) ring. The supramolecular structures for each compound are defined by weak C—H···O hydrogen bonds, which link the molecules into chains and sheets. The Cambridge Structural Database gave 45 hits for compounds with a pyrrolidinecarbonyl group. A simple statistical analysis of their geometric parameters is made in order to compare them with those of the molecules determined in the present work.

1. Chemical context

Chromone (1-benzopyran-4-one) is the building block of a large family of natural and synthetic compounds of the utmost importance in medicinal chemistry (Gaspar *et al.*, 2014). Within this group of heterocycles, chromone carboxamide derivatives have been found to display interesting biological activities, namely as adenosine receptor ligands (Gaspar *et al.*, 2012) and as MAO-B inhibitors (Gaspar *et al.*, 2012; Gomes *et al.*, 2015*b*; Cagide *et al.*, 2015). From the library synthesized so far, chromones (**1**)–(**6**) were selected for the present study, see Scheme. Previous data acquired on the development of new MAO-B inhibitors allowed us to conclude that 2-substituted chromones carboxamides based on the *N*-phenyl-4-oxo-4*H*-2-chromone carboxamide (**6**) skeleton have no significant IMAO-B activity whereas 3-substituted carboxamides based on the *N*-phenyl-4-oxo-4*H*-3-chromone carboxamide (**5**) core have been shown to be potent and selective inhibitors (Cagide *et al.*, 2015). Structure–activity relationship (SAR) studies



revealed the significance of phenylcarboxamide as a key structure. Structural investigations made so far show that the derivatives of **(5)** have very similar conformations and indicate that the displayed IMAO-B activity is mostly dependent on electronic factors modulated by the nature and position of the substituent group attached to the exocyclic phenyl substituent (Gomes *et al.*, 2015a,b). Despite this, those studies do not allow inferences to be made about (i) the importance of the carboxamide group, including the amidic hydrogen atom or (ii) the configuration of the amide due to the C–N rotamer, in the molecular docking. Thus new compounds were synthesised and structurally characterized *viz.* *N*-methyl-4-oxo-*N*-phenyl-4*H*-chromene-3-carboxamide (**1**) and its isomer *N*-methyl-4-oxo-*N*-phenyl-4*H*-chromene-2-carboxamide (**2**), both tertiary carboxamides, as opposed to the secondary carboxamides **(5)** and **(6)** and 3-(pyrrolidine-1-carbonyl)-4*H*-chromen-4-one (**3**) and 2-(pyrrolidine-1-carbonyl)-4*H*-chromen-4-one (**4**), which instead of the carboxamide have a carbonyl pyrrolidine linked to the chromone (see Scheme). Compounds **(2)**, **(5)** and **(6)**, *N*-methyl-4-oxo-*N*-phenyl-4*H*-chromene-2-carboxamide, *N*-phenyl-4-oxo-4*H*-3-chromone carboxamide and *N*-phenyl-4-oxo-4*H*-2-chromone carboxamide, have previously been characterized by X-ray diffraction (Gomes *et al.* 2013, Cagide *et al.*, 2015 and Reis *et al.*, 2014, respectively). They will be used in this study for comparative purposes.

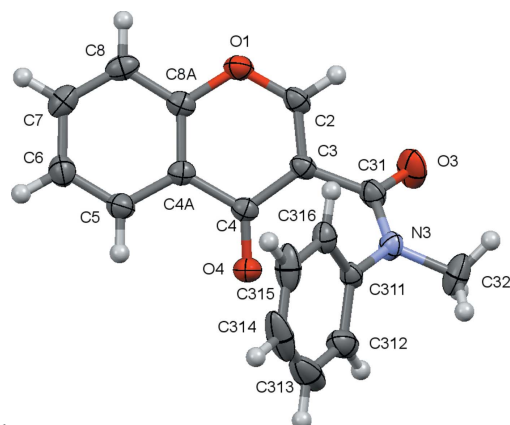
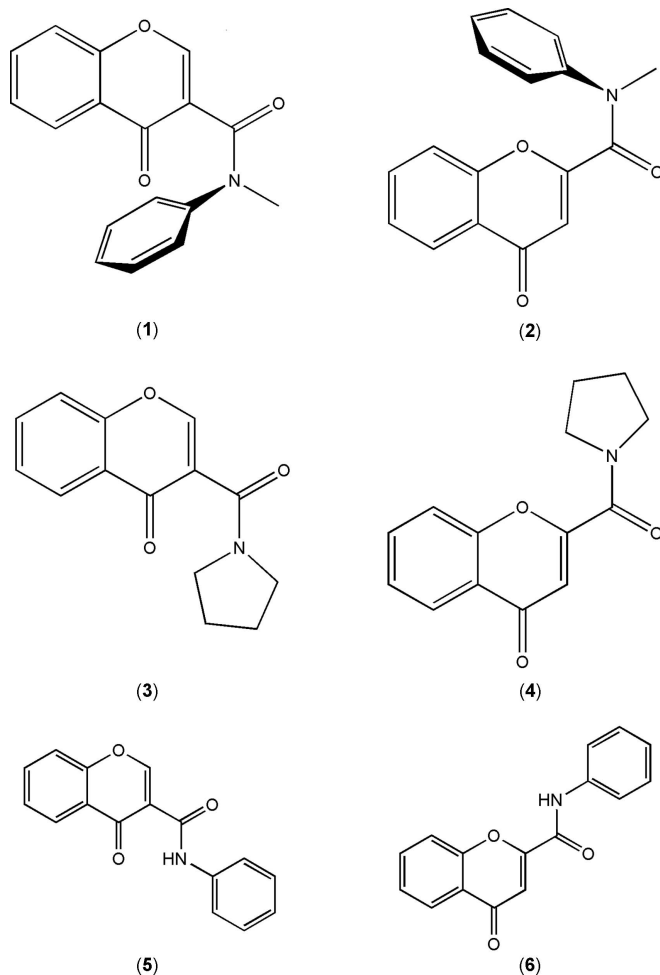


Figure 1
A view of the asymmetric unit of **(1)** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 70% probability level.

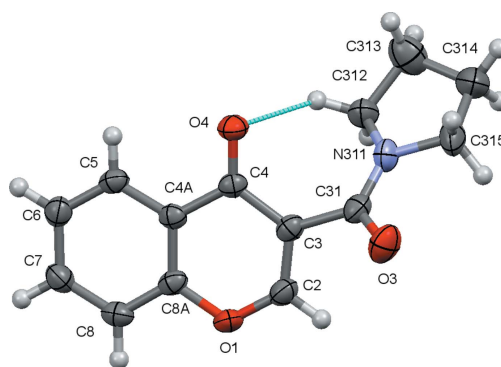


Figure 2
A view of the asymmetric unit of **(3)** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 70% probability level.

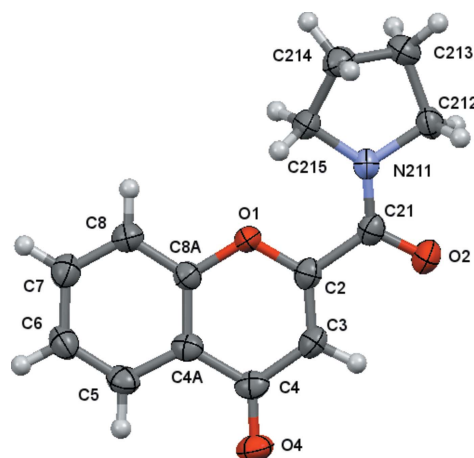


Figure 3
A view of the asymmetric unit of **(4)** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 70% probability level.

2. Structural commentary

2.1. Molecular Conformations

As mentioned above, the compounds discussed in this work are presented in the Scheme. Compounds **(2)**, **(5)** and **(6)** have previously been characterized. The ellipsoid plots for the remaining structures, *e.g.* for **(1)**, **(3)** and **(4)**, are given in Figs. 1–3. The results of the biological tests show that only **(5)**

exhibits significant IMAO-B activity. Its isomer (**6**) is much less active while the remaining ones are inactive towards MAO-B, suggesting that substitution on position number 3 of the chromone is required and it must be a secondary carboxamide. As will be discussed, the presence of a tertiary amide induces significant conformational changes to the compounds that can explain the lack of activity for those compounds.

Compound (**1**) is a phenyl chromone carboxamide similar to (**5**) where the amidic hydrogen atom has been replaced by a methyl substituent. Since the nitrogen atom of the amide tends to be planar due to the partial sp^2 hybridization of the C–N bond and, owing to the high rotational barrier around that bond, amides often exhibit *–anti/–syn* conformations with respect to the C–N rotamer. The inactive chromone carboxamides (**1**) and (**2**) present *–syn* conformations whereas chromone (**5**) (active) and (**6**) (inactive) are in the *–anti* form. In (**5**) and (**6**) the aromatic rings are roughly co-planar [dihedral angles between the mean planes of the aromatic rings are 10.77 (4) (Cagide *et al.*, 2015) and 6.57 (7)° (Reis *et al.*, 2013), respectively], while in compounds (**1**) and (**2**) the aromatic rings are twisted with respect to each other [dihedral angles between the mean planes of the chromone and the exocyclic phenyl rings are 58.48 (8) and 73.86 (5)° (Gomes *et al.*, 2013), respectively]. The twisting is probably driven by the minimization of steric hindrance that would arise from the proximity of the rings.

Molecules (**3**) and (**4**) present a chromone residue and an exocycle pyrrolidine ring separated by a carbonyl spacer. The pyrrolidine ring in (**3**) assumes a mostly envelope shape as it is puckered at C313, with $\theta(2) = 0.349$ (5) Å and $\varphi(2) = 78.8$ (7)°. In (**4**) the pyrrolidine conformation is between an envelope and a half-chair, the ring being twisted at C213–C214, with $\theta(2) = 0.380$ (3) Å and $\varphi(2) = 91.0$ (3)°. The inactive pyrrolidines (**3**) and (**4**) also display a high degree of torsion; the dihedral angles between the chromone and the best plane formed by the pyrrolidine atoms are 48.9 (2) and 23.97 (12)° respectively. A close analysis of the $-(C=O)-N$ bond lengths for (**3**) [1.337 (4) Å] and (**4**) [1.340 (3) Å] shows that these values are comparable with those presented for the corresponding bonds in the carboxamides (**1**) [1.361 (2) Å] and (**2**) [1.3528 (14) Å], indicating partial sp^2 hybridization of the nitrogen atom in (**3**) and (**4**). Furthermore, a search made in the Cambridge Structural Database (Groom & Allen, 2014) for structures containing the pyrrolidinecarbonyl unit (see *Database survey* section below) shows that the C–N distances range between 1.294 and 1.361 Å [the mean value is 1.335 (2) Å], suggesting that in carbonyl pyrrolidines the C–N bond displays partial hybridization (Laursen *et al.*, 2013).

2.2. Intramolecular C–H···O bonding

There is no intramolecular hydrogen bonding in compounds (**1**) and (**2**). This contrasts with what occurs in (**5**) and (**6**) where, due to the presence of the imidic nitrogen atom, the molecules display N–H···O intramolecular $S(6)$ rings and, due to the *–anti* configuration, they present weak $C_{arom}-$

Table 1
Hydrogen-bond geometry (Å, °) for (**1**).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2–H2···O4 ⁱ	0.95	2.47	3.253 (3)	140
C5–H5···O1 ⁱⁱ	0.95	2.49	3.432 (3)	172
C314–H314···O3 ⁱⁱⁱ	0.95	2.33	3.255 (3)	164

Symmetry codes: (i) $x + 1, y, z$; (ii) $x - 1, y, z$; (iii) $x - 1, y + 1, z$.

H···O hydrogen bonds (the carbonyl group of the amide acting as acceptor for the *ortho*-carbon atom of the benzyl ring), resulting in second $S(6)$ rings (Cagide *et al.*, 2015; Reis *et al.*, 2014). In (**3**) there is a short intramolecular contact C312–H312···O4 in which the pyrrolidine carbon atom acts as a donor to the carbonyl oxygen atom, O4, of the chromone, forming an $S(7)$ ring. The search of the CSD (Groom & Allen, 2014) described below found five molecules containing a pyrrolidine carbonyl moiety that exhibit similar intramolecular hydrogen bonding. In conclusion, apart from precluding the formation of an intramolecular N–H···A bond, substitution of the amidic hydrogen atom by a methyl group in the carboxamide or the insertion of a carboxypyrrolidine unit in the chromone causes a large change in the conformational geometry of the molecules that prevents a link to the active site of the MAO-B enzyme.

3. Supramolecular features

Details of the hydrogen bonding are given in Tables 1, 2 and 3.

In compound (**1**) the C2–H2···O4($x + 1, y, z$) and C5–H5···O1($x + 1, y, z$) hydrogen bonds link the molecules into $R_2^2(8)$ rings which link the molecules into chains running parallel to the a axis, Fig. 4. These chains are then linked by the C314–314···O3($x - 1, y + 1, z$) hydrogen bond, Fig. 5, to form sheets lying parallel to [001], Fig. 6. A centrosymmetric sheet interpenetrates the first sheet, and these two sheets are

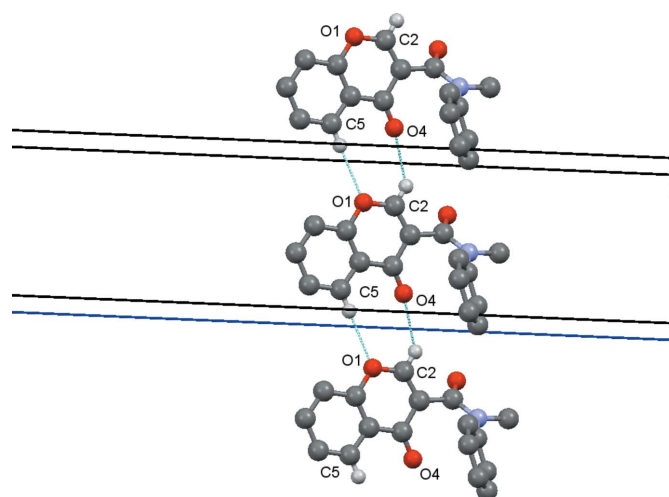


Figure 4
Compound (**1**): the chain of $R_2^2(8)$ rings running parallel to the a axis. Hydrogen atoms not involved in the hydrogen bonding are omitted.

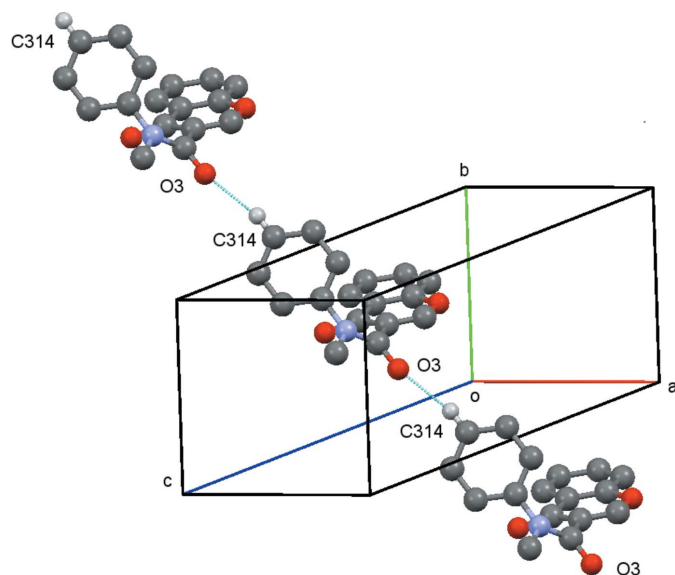


Figure 5
Compound (1): the chain formed by the C314–314...O3 hydrogen bond. Hydrogen atoms not involved in the hydrogen bonding are omitted.

linked by π - π stacking between the chromone rings [centroid-centroid distance = 3.557 (2) Å].

In compound (3) the molecules are linked by C–H...O interactions and by C–H... π interactions. The C8–H8...O4($-x + \frac{3}{2}, -y + 1, z + \frac{1}{2}$) and C314–H31E...O3($-x + \frac{3}{2}, -y + 2, z - \frac{1}{2}$) contacts both form $C(6)$ chains running parallel to the c axis which are propagated by the twofold screw axes at $(\frac{3}{4}, \frac{1}{2}, z)$ and $(\frac{3}{4}, 1, z)$, respectively, Figs. 7 and 8. These combine

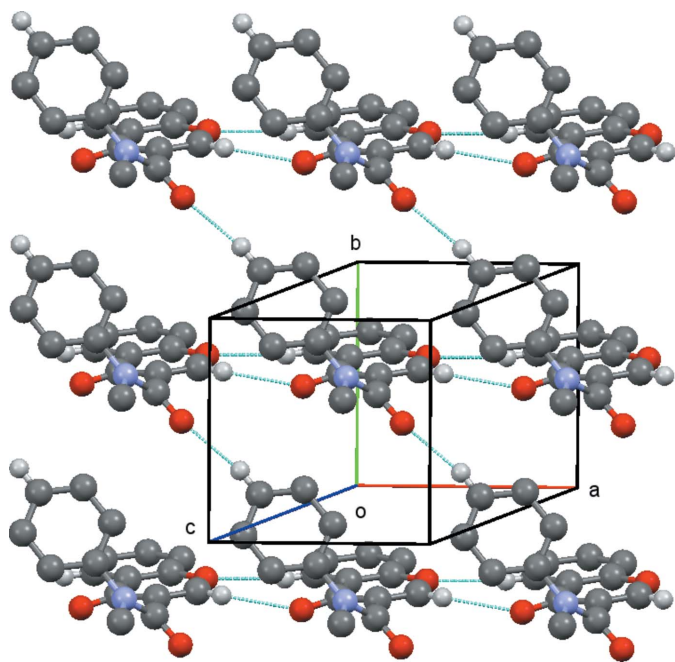


Figure 6
Compound (1): view of the sheets which lie parallel to [001] formed by the combination of the chains shown in Figs. 4 and 5. Hydrogen atoms not involved in the hydrogen bonding are omitted.

Table 2
Hydrogen-bond geometry (Å, °) for (3).

C_g is the centroid of the benzene ring C4A/C5–C8/C8A

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C312–H31A...O4	0.99	2.29	3.082 (5)	136
C2–H2...O4 ⁱ	0.95	2.47	3.338 (4)	152
C6–H6...O4 ⁱⁱ	0.95	2.48	3.389 (4)	161
C8–H8...O4 ⁱⁱⁱ	0.95	2.57	3.514 (4)	170
C314–H31E...O3 ^{iv}	0.99	2.42	3.128 (5)	128
C313–H31D...C _g ^v	0.99	2.59	3.570 (6)	170

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

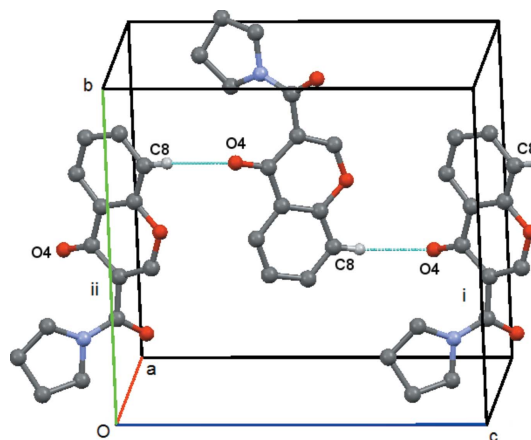


Figure 7
Compound (3): molecular $C(6)$ chain running parallel to the c axis. Molecules i and ii are at $(-x + \frac{3}{2}, -y + 1, z + \frac{1}{2})$ and $(-x + \frac{3}{2}, -y + 1, z - \frac{1}{2})$, respectively. Hydrogen atoms not involved in the hydrogen bonding are omitted.

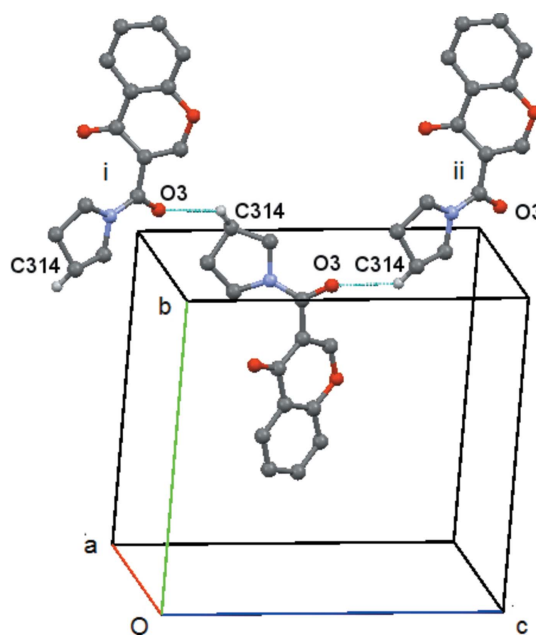


Figure 8
Compound (3): molecular $C(6)$ chain running parallel to the c axis. Molecules i and ii are at $(-x + \frac{3}{2}, -y + 2, z - \frac{1}{2})$ and $(-x + \frac{3}{2}, -y + 2, z + \frac{1}{2})$, respectively. Hydrogen atoms not involved in the hydrogen bonding are omitted.

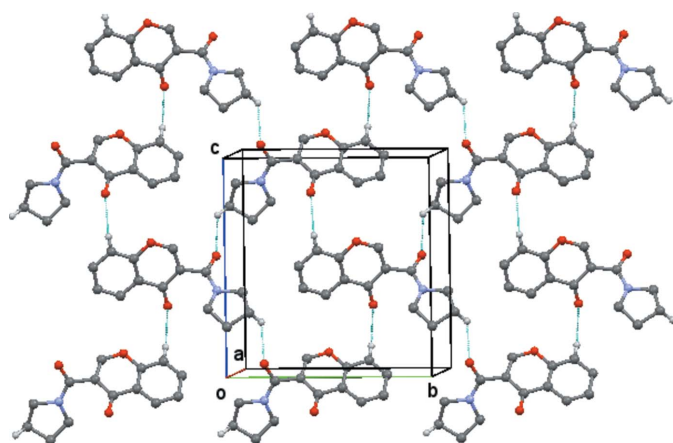


Figure 9
Compound (3): corrugated sheet in the *bc* plane formed by the interactions of the two *C*(6) chains shown in Figs. 7 and 8. Hydrogen atoms not involved in the hydrogen bonding are omitted.

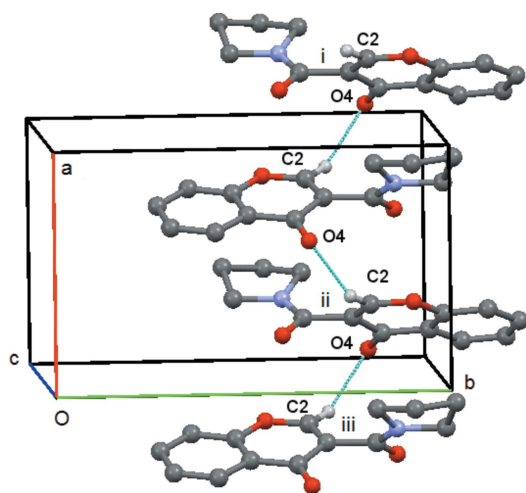


Figure 10
Compound (3): molecular *C*(5) chain running parallel to the *a* axis. Molecules i, ii and iii are at $(x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1)$, $(x - \frac{1}{2}, -y + \frac{3}{2}, -z + 1)$ and $(x - 1, y, z)$, respectively. Hydrogen atoms not involved in the hydrogen bonding are omitted.

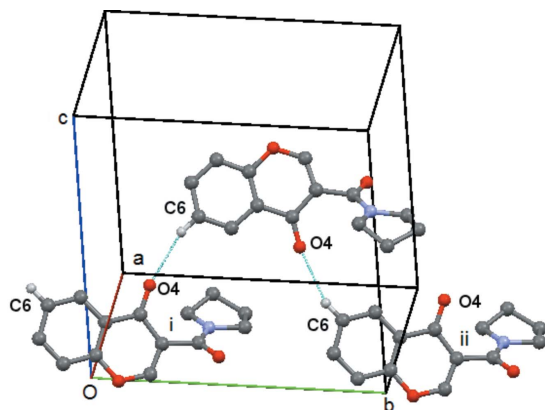


Figure 11
Compound (3): molecular *C*(6) chain running parallel to the *b* axis. Molecules i and ii are at $(-x + 1, y - \frac{1}{2}, -z + \frac{1}{2})$ and $(-x + 1, y + \frac{1}{2}, -z + \frac{1}{2})$, respectively. Hydrogen atoms not involved in the hydrogen bonding are omitted.

Table 3
Hydrogen-bond geometry (Å, °) for (4).

<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>
C8—H8···O2 ⁱ	0.95	2.55	3.137 (3)	121
C214—H21C···O4 ⁱⁱ	0.99	2.47	3.340 (3)	146

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

to form a corrugated sheet in the *bc* plane, Fig. 9. The C2—H2···O4($x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$) interaction links the molecules into *C*(5) chains running along the *a* axis propagated by the twofold screw axis at $(x, \frac{3}{4}, \frac{1}{2})$, Fig. 10. The C6—H6···O4($-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$) interaction links the molecules into *C*(6) chains running along the *b* axis which are propagated by the twofold screw axis at $(\frac{1}{2}, y, \frac{1}{4})$, Fig. 11. There is also a C—H··· π interaction C313—H31D···Cg($x - 2, y + \frac{1}{2}, -z + \frac{1}{2}$). These interactions combine to form a complex three-dimensional network.

In compound (4) there is a short contact between C214—H21C and O4($-x + 1, -y + \frac{1}{2}, z - \frac{1}{2}$). This forms a *C*(9) chain which runs along the *c* axis, propagated by the twofold screw axis at $(\frac{1}{2}, \frac{1}{4}, z)$, Fig. 12. There is also a short contact between C8—H8 and O2($x + \frac{1}{2}, -y - \frac{1}{2}, z$) but in this case the angle at H8 is 121° and so this interaction will be relatively weak. It forms a *C*(7) chain parallel to the *a* axis propagated by the glideplane at $\frac{1}{4}$ along the *b* axis, Fig. 13. There are no C—H··· π or π — π interactions.

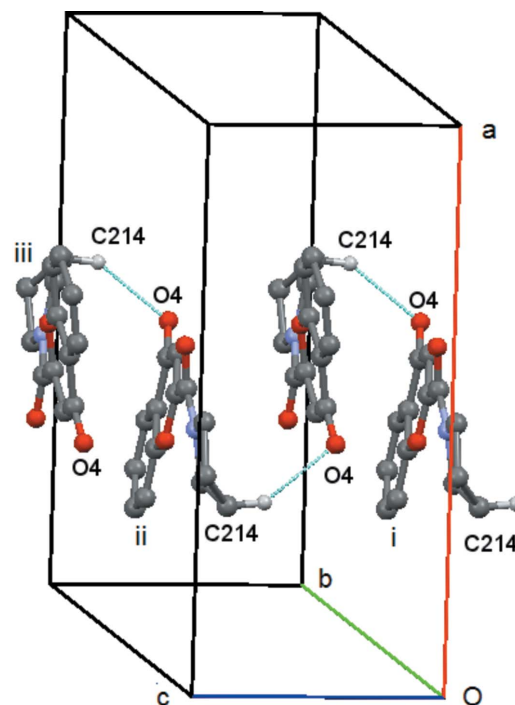


Figure 12
Compound (4): molecular *C*(9) chain running parallel to the *c* axis. Molecules i, ii and iii are at $(-x + 1, -y + \frac{1}{2}, z - \frac{1}{2})$, $(-x + 1, -y + \frac{1}{2}, z + \frac{1}{2})$ and $(x, y, z + 1)$, respectively. Hydrogen atoms not involved in the hydrogen bonding are omitted.

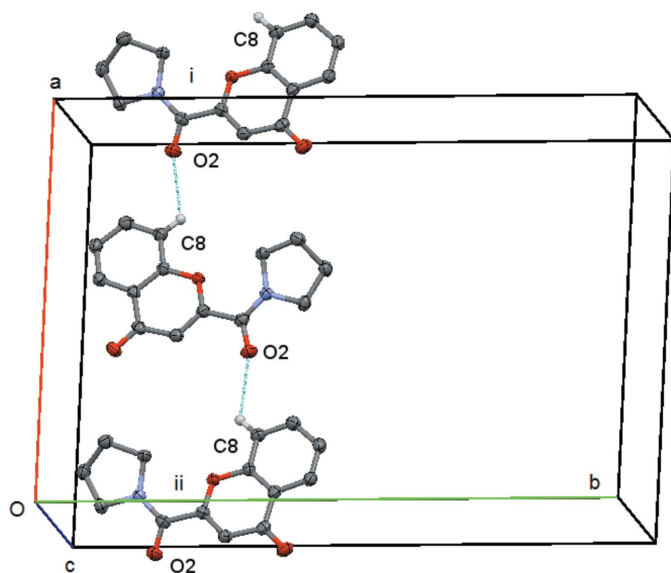


Figure 13
Compound (4): molecular $C(7)$ chain running parallel to the a axis. Molecules *i* and *ii* are at $(x + \frac{1}{2}, -y - \frac{1}{2}, z)$ and $(x - \frac{1}{2}, -y - \frac{1}{2}, z)$, respectively. Hydrogen atoms not involved in the hydrogen bonding are omitted.

4. Database survey

A search of the Cambridge Structural Database (Groom & Allen, 2014) gave 45 hits for the pyrrolidinecarbonyl group for structures with $R \leq 0.10$ (see supplementary data for the search fragment). The mean value for the C—O bond length was 1.235 (2) Å with a range of 1.209–1.282 Å. The values for (3) and (4) are 1.239 (4) and 1.230 (2) Å, respectively. The mean C—N bond length is 1.335 (2) Å with a range of 1.294–1.361 Å. The values for (3) and (4) are 1.337 (4) and 1.340 (3) Å, respectively. The values for these compounds are close to the mean values in each case.

The torsion angles around the C(carbonyl) and N(pyrrolidine) bond involving the carbonyl O atom lie in ranges between -9.15 and 8.023° with a mean value of close to zero and between -161.33 and 166.71° with a mean value close to 180° for both the C atoms attached to the N atom within the pyrrolidine group. The respective torsion angles for (3) [-0.5 (5) and 171.9 (3) $^\circ$] and those for (4) [1.1 (3) and -175.3 (2) $^\circ$] are well within the ranges specified above.

Intramolecular C—H \cdots O short contacts similar to that in (3) are found in five compounds in the CSD: LISLAB, 1-(1-pyrrolidinylcarbonyl)cyclopropyl sulfamate (Morin *et al.*, 2007), PEQHAU, 2-[3'-(4''-chlorophenyl)-4',6'-dimethoxyindol-7'-yl]glyoxyl-1-pyrrolidine (Black *et al.*, 1997), QIBBEJ, [2-hydroxy-5-(2-hydroxybenzoyl)phenyl](pyrrolidin-1-yl)-methanone (Holtz *et al.*, 2007), SINHAZ, 2-methoxy-1-(1-pyrrolidinylcarbonyl)naphthalene (Sakamoto *et al.*, 2007) and TAJDIR, (4*S*,5*S*)-4,5-bis(pyrrolidinylcarbonyl)-2,2-dimethyl-1,3-dioxolane (Garcia *et al.*, 1991), Fig. 10. In LISLAB and TAJDIR, $S(6)$ rings are formed. In QIBBEJ and SINHAZ, an $S(7)$ ring similar to that in (2) is formed. In PEQHAU, an $S(8)$ ring is formed, Fig. 14.

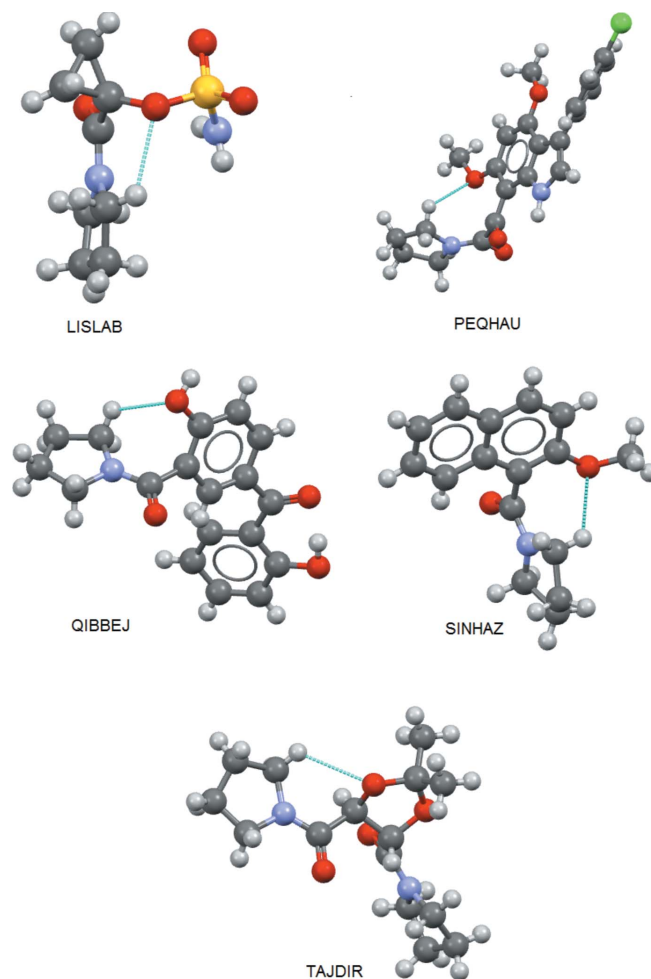


Figure 14
View of compounds in the CSD with C—H \cdots O short intramolecular contacts involving an *o*-pyrrolidine hydrogen atom.

5. Synthesis and crystallization

***N*-methyl-4-oxo-*N*-phenyl-4*H*-chromene-3-carboxamide**, (1) was synthesized in a low yield (10%) by a one-pot reaction using 4-oxo-4*H*-chromene-3-carboxylic acid as starting material. The activation of the carboxylic acid was obtained by the coupling reagent bromotripyrrolidinophosphonium hexafluorophosphate (PyBrOP) and the amide obtained by reacting the ester derivative with *N*-methylaniline. The crude product was purified by flash chromatography (ethyl acetate and ethyl acetate/CH₂Cl₂ in an 4:1 ratio). Crystals suitable for X-ray diffraction were obtained from ethyl acetate.

3-(Pyrrolidine-1-carbonyl)-4*H*-chromen-4-one, (3) and **2-(pyrrolidine-1-carbonyl)-4*H*-chromen-4-one**, (4) were synthesized in moderate yields, 57% and 45%, by a one-pot reaction using 4-oxo-4*H*-chromene-3-carboxylic and 4-oxo-4*H*-chromene-2-carboxylic acids, respectively, as starting materials. The synthetic strategy encompasses the activation of the chromone carboxylic acids by reaction with phosphorus(V) oxychloride with formation *in situ* of an acid chloride intermediate. The acid chlorides react with pyrrolidine giving the desired amides. Crystals suitable for X-ray

Table 4
Experimental details.

	(1)	(3)	(4)
Crystal data			
Chemical formula	C ₁₇ H ₁₃ NO ₃	C ₁₄ H ₁₃ NO ₃	C ₁₄ H ₁₃ NO ₃
<i>M_r</i>	279.28	243.25	243.25
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Orthorhombic, <i>P</i> 2 ₁ 2 ₁	Orthorhombic, <i>Ab</i> a2
Temperature (K)	100	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.716 (4), 6.809 (4), 29.425 (17)	7.430 (3), 11.963 (6), 12.648 (6)	15.337 (6), 21.940 (8), 6.808 (3)
α , β , γ (°)	90, 94.784 (7), 90	90, 90, 90	90, 90, 90
<i>V</i> (Å ³)	1340.9 (14)	1124.2 (9)	2290.8 (16)
<i>Z</i>	4	4	8
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.10	0.10	0.10
Crystal size (mm)	0.25 × 0.07 × 0.06	0.22 × 0.07 × 0.03	0.50 × 0.04 × 0.02
Data collection			
Diffractometer	Rigaku Saturn724+	Rigaku Saturn724+	Rigaku Saturn724+
Absorption correction	Multi-scan (<i>CrystalClear-SM Expert</i> ; Rigaku, 2012)	Multi-scan (<i>CrystalClear-SM Expert</i> ; Rigaku, 2012)	Multi-scan (<i>CrystalClear-SM Expert</i> ; Rigaku, 2012)
<i>T</i> _{min} , <i>T</i> _{max}	0.572, 1.000	0.978, 0.997	0.952, 0.998
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	6206, 3032, 2304	7547, 3294, 3066	9598, 3374, 3079
<i>R</i> _{int}	0.043	0.031	0.034
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.648	0.731	0.731
Refinement			
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.056, 0.133, 1.07	0.069, 0.152, 1.07	0.048, 0.102, 1.11
No. of reflections	3032	3294	3374
No. of parameters	190	163	163
No. of restraints	0	0	1
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.30, -0.25	0.51, -0.44	0.32, -0.21

Computer programs: *CrystalClear-SM Expert* (Rigaku, 2012), *SHELXS* (Sheldrick, 2015), *SHELXL2014/17* (Sheldrick, 2015) *PLATON* (Spek, 2009) *Flipper 25* (Oszlányi & Sütő, 2004) *OLEX2* (Dolomanov *et al.*, 2009), *OSCAIL* (McArdle *et al.*, 2004), *ShelXle* (Hübschle *et al.*, 2011) and *Mercury* (Macrae *et al.*, 2006).

diffraction for both compounds were obtained from a solution of CH₂Cl₂/*n*-hexane solvent 1:1, m.p. for (3): 421–426K; m.p. for (4): 382–386K.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. H atoms were treated as riding atoms with C–H(aromatic) = 0.95 Å and C–H(CH₂) = 0.99 Å with *U*_{iso} = 1.2*U*_{eq}(C), and C–H(methyl) = 0.98 Å with *U*_{iso} = 1.5*U*_{eq}(C). The methyl hydrogen atoms were generated in idealized positions and checked on a final difference map.

Acknowledgements

The authors thank the staff at the National Crystallographic Service, University of Southampton (Coles & Gale, 2012), for the data collection, help and advice and the Foundation for Science and Technology (FCT) of Portugal (QUI/UI0081/2015). FC (SFRH/BPD/74491/2010) is supported by an FCT grant.

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A comparison of the structures of some 2- and 3-substituted chromone derivatives: a structural study on the importance of the secondary carboxamide backbone for the inhibitory activity of MAO-B

Ligia R. Gomes, John Nicolson Low, Fernando Cagide, Alexandra Gaspar and Fernanda Borges

Computing details

For all compounds, data collection: *CrystalClear-SM Expert* (Rigaku, 2012); cell refinement: *CrystalClear-SM Expert* (Rigaku, 2012); data reduction: *CrystalClear-SM Expert* (Rigaku, 2012). Program(s) used to solve structure: *SHELXS* (Sheldrick, 2015), *PLATON* (Spek, 2009), *Flipper 25* (Oszlányi & Sütő, 2004) and *Olex2* (Dolomanov *et al.*, 2009) for (1); *SHELXS* (Sheldrick, 2015), *PLATON* (Spek, 2009), *Flipper 25* (Oszlányi & Sütő, 2004) and *Olex2* (Dolomanov *et al.*, 2009) for (3); *SHELXS* (Sheldrick, 2015), *PLATON* (Spek, 2009), *Flipper 25* (Oszlányi & Sütő, 2004) and *Olex2* (Dolomanov *et al.*, 2009) for (4). For all compounds, program(s) used to refine structure: *OSCAIL* (McArdle *et al.*, 2004), *ShelXle* (Hübschle *et al.*, 2011) and *SHELXL2014/17* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *OSCAIL* (McArdle *et al.*, 2004), *SHELXL2014/17* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

(1) *N*-Methyl-4-oxo-*N*-phenyl-4*H*-chromene-3-carboxamide

Crystal data

$C_{17}H_{13}NO_3$	$Z = 4$
$M_r = 279.28$	$F(000) = 584$
Monoclinic, $P2_1/c$	$D_x = 1.383 \text{ Mg m}^{-3}$
$a = 6.716 (4) \text{ \AA}$	Mo $K\alpha$ radiation, $\lambda = 0.71075 \text{ \AA}$
$b = 6.809 (4) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$c = 29.425 (17) \text{ \AA}$	$T = 100 \text{ K}$
$\beta = 94.784 (7)^\circ$	Rod, colourless
$V = 1340.9 (14) \text{ \AA}^3$	$0.25 \times 0.07 \times 0.06 \text{ mm}$

Data collection

Rigaku Saturn724+ diffractometer	6206 measured reflections
Radiation source: Rotating Anode	3032 independent reflections
Confocal monochromator	2304 reflections with $I > 2\sigma(I)$
Detector resolution: 28.5714 pixels mm^{-1}	$R_{\text{int}} = 0.043$
profile data from ω -scans	$\theta_{\text{max}} = 27.4^\circ$, $\theta_{\text{min}} = 3.0^\circ$
Absorption correction: multi-scan	$h = -8 \rightarrow 8$
(<i>CrystalClear-SM Expert</i> ; Rigaku, 2012)	$k = -8 \rightarrow 8$
$T_{\text{min}} = 0.572$, $T_{\text{max}} = 1.000$	$l = -17 \rightarrow 38$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.056$
 $wR(F^2) = 0.133$
 $S = 1.07$
 3032 reflections
 190 parameters
 0 restraints

Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0336P)^2 + 1.136P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.6806 (2)	0.7176 (2)	0.54188 (5)	0.0226 (3)
O3	0.6513 (2)	0.4530 (2)	0.66760 (5)	0.0351 (4)
O4	0.1517 (2)	0.5956 (2)	0.59524 (5)	0.0219 (3)
N3	0.4090 (3)	0.6598 (2)	0.68645 (5)	0.0204 (4)
C2	0.6722 (3)	0.6736 (3)	0.58634 (7)	0.0206 (4)
H2	0.7952	0.6604	0.6045	0.025*
C3	0.5026 (3)	0.6467 (3)	0.60699 (6)	0.0181 (4)
C4	0.3091 (3)	0.6483 (3)	0.58017 (6)	0.0176 (4)
C4A	0.3200 (3)	0.7089 (3)	0.53230 (6)	0.0175 (4)
C5	0.1473 (3)	0.7317 (3)	0.50257 (7)	0.0225 (4)
H5	0.0196	0.7139	0.5136	0.027*
C6	0.1615 (3)	0.7800 (3)	0.45738 (7)	0.0262 (5)
H6	0.0437	0.7970	0.4376	0.031*
C7	0.3497 (3)	0.8040 (3)	0.44074 (7)	0.0250 (5)
H7	0.3586	0.8342	0.4095	0.030*
C8	0.5213 (3)	0.7842 (3)	0.46923 (7)	0.0228 (4)
H8	0.6488	0.8018	0.4581	0.027*
C8A	0.5041 (3)	0.7376 (3)	0.51492 (6)	0.0184 (4)
C31	0.5272 (3)	0.5798 (3)	0.65592 (7)	0.0218 (4)
C32	0.4238 (4)	0.5723 (3)	0.73235 (7)	0.0329 (6)
H32A	0.3328	0.6409	0.7513	0.049*
H32B	0.3872	0.4331	0.7302	0.049*
H32C	0.5612	0.5848	0.7461	0.049*
C311	0.2721 (3)	0.8175 (3)	0.67737 (6)	0.0180 (4)
C312	0.0764 (3)	0.7959 (4)	0.68895 (7)	0.0296 (5)
H312	0.0338	0.6752	0.7011	0.036*
C313	-0.0547 (4)	0.9506 (5)	0.68268 (8)	0.0428 (7)

H313	-0.1879	0.9361	0.6908	0.051*
C314	0.0046 (4)	1.1271 (4)	0.66470 (8)	0.0450 (8)
H314	-0.0873	1.2330	0.6605	0.054*
C315	0.1985 (4)	1.1481 (3)	0.65283 (8)	0.0352 (6)
H315	0.2394	1.2679	0.6399	0.042*
C316	0.3337 (3)	0.9941 (3)	0.65974 (6)	0.0225 (4)
H316	0.4679	1.0098	0.6524	0.027*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0171 (7)	0.0268 (8)	0.0242 (7)	0.0015 (6)	0.0046 (6)	-0.0019 (6)
O3	0.0367 (10)	0.0375 (9)	0.0303 (8)	0.0219 (8)	-0.0014 (7)	0.0022 (7)
O4	0.0176 (7)	0.0269 (8)	0.0215 (7)	-0.0015 (6)	0.0035 (5)	0.0009 (6)
N3	0.0232 (9)	0.0203 (8)	0.0178 (8)	0.0059 (7)	0.0024 (7)	0.0032 (6)
C2	0.0162 (10)	0.0218 (10)	0.0236 (10)	0.0045 (8)	-0.0001 (8)	-0.0030 (8)
C3	0.0151 (10)	0.0187 (9)	0.0206 (9)	0.0021 (8)	0.0018 (7)	-0.0025 (7)
C4	0.0164 (10)	0.0161 (9)	0.0203 (9)	0.0013 (8)	0.0024 (7)	-0.0019 (7)
C4A	0.0180 (10)	0.0153 (9)	0.0195 (9)	0.0008 (8)	0.0032 (7)	-0.0026 (7)
C5	0.0181 (10)	0.0257 (11)	0.0238 (10)	-0.0004 (9)	0.0025 (8)	-0.0009 (8)
C6	0.0254 (11)	0.0299 (12)	0.0227 (10)	0.0018 (10)	-0.0019 (8)	0.0010 (8)
C7	0.0343 (12)	0.0213 (10)	0.0202 (9)	-0.0002 (9)	0.0063 (9)	0.0007 (8)
C8	0.0254 (11)	0.0181 (10)	0.0263 (10)	0.0004 (9)	0.0101 (8)	-0.0027 (8)
C8A	0.0178 (10)	0.0148 (9)	0.0227 (9)	0.0012 (8)	0.0024 (8)	-0.0029 (7)
C31	0.0190 (10)	0.0226 (10)	0.0235 (10)	0.0049 (9)	-0.0005 (8)	0.0002 (8)
C32	0.0523 (16)	0.0281 (12)	0.0183 (10)	0.0063 (11)	0.0021 (10)	0.0045 (8)
C311	0.0160 (10)	0.0215 (10)	0.0162 (8)	0.0055 (8)	-0.0006 (7)	-0.0028 (7)
C312	0.0219 (11)	0.0415 (13)	0.0257 (10)	0.0011 (10)	0.0035 (9)	-0.0075 (9)
C313	0.0223 (12)	0.071 (2)	0.0347 (13)	0.0161 (13)	-0.0016 (10)	-0.0213 (13)
C314	0.0448 (16)	0.0515 (17)	0.0355 (13)	0.0353 (14)	-0.0166 (12)	-0.0195 (12)
C315	0.0542 (16)	0.0229 (11)	0.0257 (11)	0.0127 (11)	-0.0121 (11)	-0.0039 (9)
C316	0.0254 (11)	0.0232 (10)	0.0181 (9)	0.0021 (9)	-0.0023 (8)	-0.0017 (8)

Geometric parameters (Å, °)

O1—C2	1.348 (2)	C7—C8	1.374 (3)
O1—C8A	1.377 (2)	C7—H7	0.9500
O3—C31	1.229 (2)	C8—C8A	1.395 (3)
O4—C4	1.233 (2)	C8—H8	0.9500
N3—C31	1.361 (3)	C32—H32A	0.9800
N3—C311	1.425 (3)	C32—H32B	0.9800
N3—C32	1.472 (3)	C32—H32C	0.9800
C2—C3	1.347 (3)	C311—C316	1.386 (3)
C2—H2	0.9500	C311—C312	1.393 (3)
C3—C4	1.464 (3)	C312—C313	1.375 (3)
C3—C31	1.506 (3)	C312—H312	0.9500
C4—C4A	1.476 (3)	C313—C314	1.385 (4)
C4A—C8A	1.391 (3)	C313—H313	0.9500

C4A—C5	1.402 (3)	C314—C315	1.384 (4)
C5—C6	1.381 (3)	C314—H314	0.9500
C5—H5	0.9500	C315—C316	1.391 (3)
C6—C7	1.403 (3)	C315—H315	0.9500
C6—H6	0.9500	C316—H316	0.9500
C2—O1—C8A	118.54 (16)	O1—C8A—C8	116.18 (18)
C31—N3—C311	125.50 (16)	C4A—C8A—C8	122.26 (19)
C31—N3—C32	116.47 (17)	O3—C31—N3	121.05 (18)
C311—N3—C32	118.03 (17)	O3—C31—C3	119.82 (18)
C3—C2—O1	124.97 (19)	N3—C31—C3	119.13 (17)
C3—C2—H2	117.5	N3—C32—H32A	109.5
O1—C2—H2	117.5	N3—C32—H32B	109.5
C2—C3—C4	120.15 (18)	H32A—C32—H32B	109.5
C2—C3—C31	116.29 (18)	N3—C32—H32C	109.5
C4—C3—C31	122.62 (17)	H32A—C32—H32C	109.5
O4—C4—C3	123.61 (18)	H32B—C32—H32C	109.5
O4—C4—C4A	122.49 (18)	C316—C311—C312	120.02 (19)
C3—C4—C4A	113.82 (17)	C316—C311—N3	121.05 (18)
C8A—C4A—C5	118.01 (18)	C312—C311—N3	118.83 (19)
C8A—C4A—C4	120.47 (17)	C313—C312—C311	119.6 (2)
C5—C4A—C4	121.47 (18)	C313—C312—H312	120.2
C6—C5—C4A	120.51 (19)	C311—C312—H312	120.2
C6—C5—H5	119.7	C312—C313—C314	121.0 (2)
C4A—C5—H5	119.7	C312—C313—H313	119.5
C5—C6—C7	120.01 (19)	C314—C313—H313	119.5
C5—C6—H6	120.0	C315—C314—C313	119.5 (2)
C7—C6—H6	120.0	C315—C314—H314	120.2
C8—C7—C6	120.68 (19)	C313—C314—H314	120.2
C8—C7—H7	119.7	C314—C315—C316	120.1 (2)
C6—C7—H7	119.7	C314—C315—H315	119.9
C7—C8—C8A	118.51 (19)	C316—C315—H315	119.9
C7—C8—H8	120.7	C311—C316—C315	119.8 (2)
C8A—C8—H8	120.7	C311—C316—H316	120.1
O1—C8A—C4A	121.54 (17)	C315—C316—H316	120.1
C8A—O1—C2—C3	0.1 (3)	C7—C8—C8A—O1	179.39 (17)
O1—C2—C3—C4	5.2 (3)	C7—C8—C8A—C4A	0.7 (3)
O1—C2—C3—C31	174.45 (18)	C311—N3—C31—O3	174.8 (2)
C2—C3—C4—O4	168.55 (19)	C32—N3—C31—O3	-6.1 (3)
C31—C3—C4—O4	0.0 (3)	C311—N3—C31—C3	-6.0 (3)
C2—C3—C4—C4A	-8.3 (3)	C32—N3—C31—C3	173.13 (19)
C31—C3—C4—C4A	-176.85 (17)	C2—C3—C31—O3	-42.0 (3)
O4—C4—C4A—C8A	-169.94 (18)	C4—C3—C31—O3	126.9 (2)
C3—C4—C4A—C8A	7.0 (3)	C2—C3—C31—N3	138.8 (2)
O4—C4—C4A—C5	7.5 (3)	C4—C3—C31—N3	-52.3 (3)
C3—C4—C4A—C5	-175.54 (18)	C31—N3—C311—C316	-54.2 (3)
C8A—C4A—C5—C6	0.5 (3)	C32—N3—C311—C316	126.7 (2)

C4—C4A—C5—C6	-177.09 (19)	C31—N3—C311—C312	129.5 (2)
C4A—C5—C6—C7	0.9 (3)	C32—N3—C311—C312	-49.6 (3)
C5—C6—C7—C8	-1.4 (3)	C316—C311—C312—C313	0.1 (3)
C6—C7—C8—C8A	0.7 (3)	N3—C311—C312—C313	176.53 (19)
C2—O1—C8A—C4A	-1.6 (3)	C311—C312—C313—C314	0.5 (3)
C2—O1—C8A—C8	179.71 (17)	C312—C313—C314—C315	0.1 (4)
C5—C4A—C8A—O1	-179.89 (17)	C313—C314—C315—C316	-1.2 (3)
C4—C4A—C8A—O1	-2.3 (3)	C312—C311—C316—C315	-1.3 (3)
C5—C4A—C8A—C8	-1.2 (3)	N3—C311—C316—C315	-177.58 (18)
C4—C4A—C8A—C8	176.34 (18)	C314—C315—C316—C311	1.8 (3)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H2 \cdots O4 ⁱ	0.95	2.47	3.253 (3)	140
C5—H5 \cdots O1 ⁱⁱ	0.95	2.49	3.432 (3)	172
C314—H314 \cdots O3 ⁱⁱⁱ	0.95	2.33	3.255 (3)	164

Symmetry codes: (i) $x+1, y, z$; (ii) $x-1, y, z$; (iii) $x-1, y+1, z$.

(3) 3-(Pyrrolidine-1-carbonyl)-4H-chromen-4-one

Crystal data

$C_{14}H_{13}NO_3$
 $M_r = 243.25$
 Orthorhombic, $P2_12_12_1$
 $a = 7.430$ (3) \AA
 $b = 11.963$ (6) \AA
 $c = 12.648$ (6) \AA
 $V = 1124.2$ (9) \AA^3
 $Z = 4$
 $F(000) = 512$

$D_x = 1.437$ Mg m^{-3}
 Mo $K\alpha$ radiation, $\lambda = 0.71075$ \AA
 Cell parameters from 4253 reflections
 $\theta = 2.3\text{--}31.2^\circ$
 $\mu = 0.10$ mm^{-1}
 $T = 100$ K
 Lath, colourless
 $0.22 \times 0.07 \times 0.03$ mm

Data collection

Rigaku Saturn724+
 diffractometer
 Radiation source: Rotating Anode
 Confocal monochromator
 Detector resolution: 28.5714 pixels mm^{-1}
 profile data from ω -scans
 Absorption correction: multi-scan
 (*CrystalClear-SM Expert*; Rigaku, 2012)
 $T_{min} = 0.978$, $T_{max} = 0.997$

7547 measured reflections
 3294 independent reflections
 3066 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.031$
 $\theta_{max} = 31.3^\circ$, $\theta_{min} = 2.3^\circ$
 $h = -8 \rightarrow 10$
 $k = -17 \rightarrow 15$
 $l = -18 \rightarrow 18$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.069$
 $wR(F^2) = 0.152$
 $S = 1.07$
 3294 reflections
 163 parameters
 0 restraints

Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0459P)^2 + 1.1472P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.51$ e \AA^{-3}
 $\Delta\rho_{min} = -0.44$ e \AA^{-3}

Absolute structure: Flack x determined using
 946 quotients $[(I^-)-(I)]/[(I^+)+(I)]$ (Parsons *et al.*,
 2013)
 Absolute structure parameter: -0.1 (6)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.8069 (3)	0.5658 (2)	0.58566 (17)	0.0247 (5)
O3	0.6707 (4)	0.8949 (2)	0.5280 (2)	0.0362 (6)
O4	0.5779 (3)	0.66383 (19)	0.30612 (18)	0.0255 (5)
N311	0.7972 (4)	0.8846 (2)	0.3665 (2)	0.0292 (6)
C2	0.7960 (5)	0.6739 (3)	0.5573 (2)	0.0254 (7)
H2	0.8374	0.7277	0.6068	0.030*
C3	0.7316 (4)	0.7126 (3)	0.4646 (2)	0.0224 (6)
C4	0.6548 (4)	0.6348 (3)	0.3885 (2)	0.0215 (6)
C4A	0.6710 (4)	0.5165 (3)	0.4186 (2)	0.0212 (6)
C5	0.6124 (4)	0.4305 (3)	0.3517 (2)	0.0236 (6)
H5	0.5596	0.4485	0.2855	0.028*
C6	0.6304 (5)	0.3197 (3)	0.3812 (3)	0.0263 (7)
H6	0.5910	0.2620	0.3351	0.032*
C7	0.7069 (5)	0.2928 (3)	0.4790 (3)	0.0271 (7)
H7	0.7185	0.2166	0.4992	0.033*
C8	0.7659 (5)	0.3762 (3)	0.5466 (3)	0.0259 (6)
H8	0.8178	0.3581	0.6131	0.031*
C8A	0.7474 (4)	0.4865 (3)	0.5153 (2)	0.0223 (6)
C31	0.7301 (5)	0.8378 (3)	0.4541 (3)	0.0259 (6)
C312	0.8921 (6)	0.8294 (3)	0.2780 (3)	0.0318 (8)
H31A	0.8245	0.7634	0.2523	0.038*
H31B	1.0147	0.8057	0.2991	0.038*
C313	0.8989 (7)	0.9193 (3)	0.1957 (4)	0.0430 (10)
H31C	0.7881	0.9192	0.1522	0.052*
H31D	1.0043	0.9093	0.1487	0.052*
C314	0.9147 (8)	1.0274 (4)	0.2587 (3)	0.0477 (12)
H31E	0.8685	1.0916	0.2175	0.057*
H31F	1.0414	1.0421	0.2784	0.057*
C315	0.7994 (5)	1.0074 (3)	0.3571 (3)	0.0360 (8)
H31G	0.8542	1.0424	0.4203	0.043*
H31H	0.6763	1.0374	0.3474	0.043*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0315 (12)	0.0273 (11)	0.0153 (9)	-0.0027 (10)	-0.0022 (9)	-0.0007 (8)
O3	0.0401 (14)	0.0323 (13)	0.0362 (14)	0.0008 (11)	0.0038 (12)	-0.0126 (11)
O4	0.0296 (12)	0.0265 (11)	0.0202 (10)	0.0029 (10)	-0.0052 (9)	0.0009 (9)
N311	0.0379 (16)	0.0207 (12)	0.0288 (14)	-0.0021 (12)	-0.0007 (13)	-0.0022 (11)
C2	0.0289 (16)	0.0275 (15)	0.0196 (14)	-0.0026 (13)	-0.0011 (13)	-0.0041 (12)
C3	0.0221 (14)	0.0245 (14)	0.0208 (14)	0.0004 (12)	0.0003 (12)	-0.0033 (11)
C4	0.0209 (13)	0.0247 (14)	0.0188 (13)	0.0017 (11)	0.0018 (11)	-0.0011 (11)
C4A	0.0195 (13)	0.0259 (14)	0.0180 (13)	-0.0005 (12)	0.0013 (11)	0.0002 (11)
C5	0.0246 (14)	0.0289 (15)	0.0174 (13)	-0.0008 (12)	0.0003 (12)	-0.0013 (11)
C6	0.0300 (17)	0.0246 (15)	0.0243 (15)	-0.0042 (12)	0.0012 (13)	-0.0017 (12)
C7	0.0325 (17)	0.0236 (14)	0.0252 (15)	-0.0005 (13)	0.0028 (14)	0.0053 (12)
C8	0.0274 (15)	0.0310 (16)	0.0193 (14)	0.0007 (13)	-0.0019 (13)	0.0044 (12)
C8A	0.0205 (14)	0.0292 (15)	0.0171 (13)	-0.0013 (12)	0.0008 (11)	-0.0012 (11)
C31	0.0267 (15)	0.0261 (15)	0.0250 (14)	-0.0003 (13)	-0.0040 (13)	-0.0043 (12)
C312	0.045 (2)	0.0271 (16)	0.0229 (15)	-0.0047 (16)	0.0005 (15)	0.0001 (13)
C313	0.047 (2)	0.042 (2)	0.040 (2)	0.0007 (19)	0.010 (2)	0.0069 (17)
C314	0.076 (3)	0.036 (2)	0.030 (2)	-0.019 (2)	-0.009 (2)	0.0046 (16)
C315	0.042 (2)	0.0226 (15)	0.044 (2)	-0.0042 (15)	-0.0086 (17)	0.0010 (14)

Geometric parameters (\AA , $^\circ$)

O1—C2	1.345 (4)	C6—H6	0.9500
O1—C8A	1.374 (4)	C7—C8	1.386 (5)
O3—C31	1.239 (4)	C7—H7	0.9500
O4—C4	1.238 (4)	C8—C8A	1.384 (4)
N311—C31	1.337 (4)	C8—H8	0.9500
N311—C315	1.474 (4)	C312—C313	1.498 (5)
N311—C312	1.480 (5)	C312—H31A	0.9900
C2—C3	1.348 (4)	C312—H31B	0.9900
C2—H2	0.9500	C313—C314	1.524 (6)
C3—C4	1.455 (4)	C313—H31C	0.9900
C3—C31	1.504 (4)	C313—H31D	0.9900
C4—C4A	1.471 (4)	C314—C315	1.529 (6)
C4A—C8A	1.396 (4)	C314—H31E	0.9900
C4A—C5	1.401 (4)	C314—H31F	0.9900
C5—C6	1.383 (5)	C315—H31G	0.9900
C5—H5	0.9500	C315—H31H	0.9900
C6—C7	1.399 (5)		
C2—O1—C8A	118.2 (2)	O1—C8A—C4A	121.4 (3)
C31—N311—C315	119.2 (3)	C8—C8A—C4A	122.4 (3)
C31—N311—C312	128.2 (3)	O3—C31—N311	121.8 (3)
C315—N311—C312	112.2 (3)	O3—C31—C3	119.0 (3)
O1—C2—C3	125.7 (3)	N311—C31—C3	119.2 (3)
O1—C2—H2	117.2	N311—C312—C313	102.8 (3)

C3—C2—H2	117.2	N311—C312—H31A	111.2
C2—C3—C4	119.7 (3)	C313—C312—H31A	111.2
C2—C3—C31	114.9 (3)	N311—C312—H31B	111.2
C4—C3—C31	125.1 (3)	C313—C312—H31B	111.2
O4—C4—C3	124.0 (3)	H31A—C312—H31B	109.1
O4—C4—C4A	121.7 (3)	C312—C313—C314	104.4 (3)
C3—C4—C4A	114.3 (3)	C312—C313—H31C	110.9
C8A—C4A—C5	117.8 (3)	C314—C313—H31C	110.9
C8A—C4A—C4	120.5 (3)	C312—C313—H31D	110.9
C5—C4A—C4	121.7 (3)	C314—C313—H31D	110.9
C6—C5—C4A	120.7 (3)	H31C—C313—H31D	108.9
C6—C5—H5	119.7	C313—C314—C315	104.5 (3)
C4A—C5—H5	119.7	C313—C314—H31E	110.9
C5—C6—C7	119.9 (3)	C315—C314—H31E	110.9
C5—C6—H6	120.0	C313—C314—H31F	110.9
C7—C6—H6	120.0	C315—C314—H31F	110.9
C8—C7—C6	120.6 (3)	H31E—C314—H31F	108.9
C8—C7—H7	119.7	N311—C315—C314	103.2 (3)
C6—C7—H7	119.7	N311—C315—H31G	111.1
C8A—C8—C7	118.6 (3)	C314—C315—H31G	111.1
C8A—C8—H8	120.7	N311—C315—H31H	111.1
C7—C8—H8	120.7	C314—C315—H31H	111.1
O1—C8A—C8	116.2 (3)	H31G—C315—H31H	109.1
C8A—O1—C2—C3	-0.2 (5)	C5—C4A—C8A—O1	-179.5 (3)
O1—C2—C3—C4	4.3 (5)	C4—C4A—C8A—O1	1.0 (4)
O1—C2—C3—C31	178.5 (3)	C5—C4A—C8A—C8	-0.3 (5)
C2—C3—C4—O4	173.1 (3)	C4—C4A—C8A—C8	-179.8 (3)
C31—C3—C4—O4	-0.4 (5)	C315—N311—C31—O3	-0.5 (5)
C2—C3—C4—C4A	-5.3 (4)	C312—N311—C31—O3	171.9 (3)
C31—C3—C4—C4A	-178.8 (3)	C315—N311—C31—C3	-178.7 (3)
O4—C4—C4A—C8A	-175.6 (3)	C312—N311—C31—C3	-6.3 (5)
C3—C4—C4A—C8A	2.8 (4)	C2—C3—C31—O3	-46.6 (4)
O4—C4—C4A—C5	4.9 (5)	C4—C3—C31—O3	127.2 (4)
C3—C4—C4A—C5	-176.7 (3)	C2—C3—C31—N311	131.6 (3)
C8A—C4A—C5—C6	-0.1 (5)	C4—C3—C31—N311	-54.6 (5)
C4—C4A—C5—C6	179.4 (3)	C31—N311—C312—C313	168.7 (4)
C4A—C5—C6—C7	0.4 (5)	C315—N311—C312—C313	-18.4 (4)
C5—C6—C7—C8	-0.4 (5)	N311—C312—C313—C314	32.8 (5)
C6—C7—C8—C8A	0.0 (5)	C312—C313—C314—C315	-36.0 (5)
C2—O1—C8A—C8	178.2 (3)	C31—N311—C315—C314	169.9 (3)
C2—O1—C8A—C4A	-2.5 (4)	C312—N311—C315—C314	-3.6 (4)
C7—C8—C8A—O1	179.6 (3)	C313—C314—C315—N311	24.0 (4)
C7—C8—C8A—C4A	0.3 (5)		

Hydrogen-bond geometry (Å, °)

Cg is the centroid of the benzene ring C4A/C5–C8/C8A

<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>
C312—H31A···O4	0.99	2.29	3.082 (5)	136
C2—H2···O4 ⁱ	0.95	2.47	3.338 (4)	152
C6—H6···O4 ⁱⁱ	0.95	2.48	3.389 (4)	161
C8—H8···O4 ⁱⁱⁱ	0.95	2.57	3.514 (4)	170
C314—H31E···O3 ^{iv}	0.99	2.42	3.128 (5)	128
C313—H31D···Cg ^v	0.99	2.59	3.570 (6)	170

Symmetry codes: (i) $x+1/2, -y+3/2, -z+1$; (ii) $-x+1, y-1/2, -z+1/2$; (iii) $-x+3/2, -y+1, z+1/2$; (iv) $-x+3/2, -y+2, z-1/2$; (v) $x-1/2, -y+3/2, -z+1$.(4) 2-(Pyrrolidine-1-carbonyl)-4*H*-chromen-4-one

Crystal data

C₁₄H₁₃NO₃ $M_r = 243.25$ Orthorhombic, *Aba2* $a = 15.337$ (6) Å $b = 21.940$ (8) Å $c = 6.808$ (3) Å $V = 2290.8$ (16) Å³ $Z = 8$ $F(000) = 1024$ $D_x = 1.411$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å

Cell parameters from 3760 reflections

 $\theta = 2.3$ – 31.2° $\mu = 0.10$ mm⁻¹ $T = 100$ K

Needle, colourless

 $0.50 \times 0.04 \times 0.02$ mm

Data collection

Rigaku Saturn724+

diffractometer

Radiation source: Rotating Anode

Confocal monochromator

Detector resolution: 28.5714 pixels mm⁻¹profile data from ω -scans

Absorption correction: multi-scan

(CrystalClear-SM Expert; Rigaku, 2012) $T_{\min} = 0.952, T_{\max} = 0.998$

9598 measured reflections

3374 independent reflections

3079 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.034$ $\theta_{\max} = 31.3^\circ, \theta_{\min} = 2.3^\circ$ $h = -21 \rightarrow 17$ $k = -29 \rightarrow 31$ $l = -9 \rightarrow 8$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.048$ $wR(F^2) = 0.102$ $S = 1.11$

3374 reflections

163 parameters

1 restraint

Hydrogen site location: inferred from

neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 1.0329P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.32$ e Å⁻³ $\Delta\rho_{\min} = -0.21$ e Å⁻³Absolute structure: Flack x determined using1043 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et**al.*, 2013)

Absolute structure parameter: 1.2 (5)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.60596 (8)	0.22901 (6)	0.4803 (2)	0.0186 (3)
O2	0.42149 (9)	0.32316 (7)	0.4657 (3)	0.0254 (4)
O4	0.42290 (10)	0.09521 (7)	0.4038 (3)	0.0244 (4)
C2	0.52132 (12)	0.24216 (9)	0.4484 (3)	0.0176 (4)
C3	0.45851 (13)	0.19980 (9)	0.4233 (3)	0.0193 (4)
H3	0.3999	0.2124	0.4038	0.023*
C4	0.47910 (13)	0.13519 (9)	0.4255 (3)	0.0191 (4)
C4A	0.57164 (13)	0.12141 (9)	0.4559 (3)	0.0182 (4)
C5	0.60362 (13)	0.06129 (9)	0.4609 (4)	0.0207 (4)
H5	0.5647	0.0281	0.4423	0.025*
C6	0.69058 (14)	0.05020 (9)	0.4923 (4)	0.0227 (5)
H6	0.7113	0.0094	0.4973	0.027*
C7	0.74912 (15)	0.09874 (9)	0.5172 (4)	0.0220 (4)
H7	0.8093	0.0906	0.5375	0.026*
C8	0.71978 (14)	0.15805 (9)	0.5122 (3)	0.0203 (4)
H8	0.7592	0.1911	0.5286	0.024*
C8A	0.63128 (13)	0.16867 (9)	0.4826 (3)	0.0174 (4)
C21	0.49892 (13)	0.30951 (9)	0.4482 (3)	0.0186 (4)
N211	0.56212 (11)	0.35131 (7)	0.4300 (3)	0.0185 (4)
C212	0.53740 (13)	0.41656 (8)	0.4348 (4)	0.0203 (4)
H21G	0.5017	0.4259	0.5522	0.024*
H21H	0.5043	0.4280	0.3156	0.024*
C213	0.62437 (14)	0.44949 (9)	0.4428 (4)	0.0233 (5)
H21E	0.6442	0.4548	0.5801	0.028*
H21F	0.6207	0.4899	0.3789	0.028*
C214	0.68522 (14)	0.40700 (10)	0.3296 (4)	0.0231 (5)
H21C	0.6780	0.4123	0.1861	0.028*
H21D	0.7469	0.4146	0.3648	0.028*
C215	0.65665 (13)	0.34367 (9)	0.3941 (4)	0.0208 (4)
H21A	0.6676	0.3132	0.2896	0.025*
H21B	0.6874	0.3309	0.5152	0.025*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0133 (6)	0.0152 (6)	0.0271 (8)	-0.0003 (5)	-0.0021 (6)	0.0001 (7)
O2	0.0154 (7)	0.0248 (7)	0.0360 (10)	0.0030 (5)	-0.0001 (7)	0.0003 (8)
O4	0.0199 (8)	0.0242 (7)	0.0289 (10)	-0.0073 (6)	0.0007 (7)	-0.0016 (7)
C2	0.0166 (9)	0.0184 (8)	0.0177 (10)	0.0008 (7)	0.0000 (8)	-0.0008 (9)
C3	0.0155 (9)	0.0211 (9)	0.0213 (11)	-0.0005 (7)	0.0013 (8)	0.0010 (10)
C4	0.0191 (10)	0.0209 (9)	0.0173 (11)	-0.0035 (7)	0.0021 (8)	-0.0006 (9)
C4A	0.0188 (9)	0.0181 (8)	0.0177 (11)	-0.0024 (7)	0.0028 (8)	0.0002 (9)
C5	0.0212 (10)	0.0175 (8)	0.0235 (11)	-0.0027 (7)	0.0028 (9)	0.0009 (9)
C6	0.0245 (11)	0.0167 (9)	0.0267 (12)	0.0018 (7)	0.0039 (9)	0.0013 (10)
C7	0.0185 (10)	0.0230 (10)	0.0244 (12)	0.0018 (8)	0.0010 (9)	0.0030 (10)

C8	0.0179 (10)	0.0197 (9)	0.0233 (11)	-0.0014 (7)	-0.0008 (8)	0.0002 (9)
C8A	0.0172 (9)	0.0161 (8)	0.0189 (10)	0.0002 (7)	-0.0004 (8)	0.0009 (8)
C21	0.0174 (9)	0.0199 (9)	0.0185 (11)	0.0022 (7)	-0.0011 (8)	-0.0006 (9)
N211	0.0160 (8)	0.0163 (7)	0.0231 (10)	0.0013 (6)	-0.0010 (7)	-0.0011 (8)
C212	0.0216 (10)	0.0167 (9)	0.0225 (11)	0.0034 (7)	-0.0021 (9)	0.0005 (9)
C213	0.0242 (10)	0.0165 (9)	0.0291 (13)	-0.0021 (7)	-0.0011 (9)	0.0011 (10)
C214	0.0190 (11)	0.0238 (11)	0.0263 (12)	-0.0028 (8)	-0.0009 (9)	0.0022 (10)
C215	0.0143 (9)	0.0185 (9)	0.0295 (12)	0.0004 (7)	-0.0004 (8)	0.0008 (9)

Geometric parameters (Å, °)

O1—C2	1.347 (2)	C8—C8A	1.392 (3)
O1—C8A	1.380 (2)	C8—H8	0.9500
O2—C21	1.230 (2)	C21—N211	1.340 (3)
O4—C4	1.239 (2)	N211—C215	1.480 (3)
C2—C3	1.349 (3)	N211—C212	1.481 (2)
C2—C21	1.517 (3)	C212—C213	1.518 (3)
C3—C4	1.452 (3)	C212—H21G	0.9900
C3—H3	0.9500	C212—H21H	0.9900
C4—C4A	1.466 (3)	C213—C214	1.528 (3)
C4A—C8A	1.395 (3)	C213—H21E	0.9900
C4A—C5	1.408 (3)	C213—H21F	0.9900
C5—C6	1.373 (3)	C214—C215	1.522 (3)
C5—H5	0.9500	C214—H21C	0.9900
C6—C7	1.403 (3)	C214—H21D	0.9900
C6—H6	0.9500	C215—H21A	0.9900
C7—C8	1.377 (3)	C215—H21B	0.9900
C7—H7	0.9500		
C2—O1—C8A	118.59 (15)	O2—C21—C2	117.10 (17)
O1—C2—C3	124.10 (18)	N211—C21—C2	120.19 (17)
O1—C2—C21	115.27 (16)	C21—N211—C215	130.26 (16)
C3—C2—C21	120.60 (17)	C21—N211—C212	118.31 (16)
C2—C3—C4	121.05 (19)	C215—N211—C212	111.34 (15)
C2—C3—H3	119.5	N211—C212—C213	103.65 (16)
C4—C3—H3	119.5	N211—C212—H21G	111.0
O4—C4—C3	122.60 (19)	C213—C212—H21G	111.0
O4—C4—C4A	122.99 (19)	N211—C212—H21H	111.0
C3—C4—C4A	114.41 (17)	C213—C212—H21H	111.0
C8A—C4A—C5	117.71 (18)	H21G—C212—H21H	109.0
C8A—C4A—C4	120.01 (18)	C212—C213—C214	103.19 (17)
C5—C4A—C4	122.28 (17)	C212—C213—H21E	111.1
C6—C5—C4A	120.57 (18)	C214—C213—H21E	111.1
C6—C5—H5	119.7	C212—C213—H21F	111.1
C4A—C5—H5	119.7	C214—C213—H21F	111.1
C5—C6—C7	120.39 (19)	H21E—C213—H21F	109.1
C5—C6—H6	119.8	C215—C214—C213	103.63 (19)
C7—C6—H6	119.8	C215—C214—H21C	111.0

C8—C7—C6	120.3 (2)	C213—C214—H21C	111.0
C8—C7—H7	119.8	C215—C214—H21D	111.0
C6—C7—H7	119.8	C213—C214—H21D	111.0
C7—C8—C8A	118.71 (19)	H21C—C214—H21D	109.0
C7—C8—H8	120.6	N211—C215—C214	103.08 (17)
C8A—C8—H8	120.6	N211—C215—H21A	111.1
O1—C8A—C8	115.90 (17)	C214—C215—H21A	111.1
O1—C8A—C4A	121.82 (17)	N211—C215—H21B	111.1
C8—C8A—C4A	122.28 (18)	C214—C215—H21B	111.1
O2—C21—N211	122.71 (18)	H21A—C215—H21B	109.1
C8A—O1—C2—C3	1.8 (3)	C5—C4A—C8A—O1	-179.9 (2)
C8A—O1—C2—C21	179.99 (19)	C4—C4A—C8A—O1	-0.3 (3)
O1—C2—C3—C4	-1.2 (4)	C5—C4A—C8A—C8	0.4 (3)
C21—C2—C3—C4	-179.3 (2)	C4—C4A—C8A—C8	180.0 (2)
C2—C3—C4—O4	179.6 (2)	O1—C2—C21—O2	-163.5 (2)
C2—C3—C4—C4A	-0.2 (3)	C3—C2—C21—O2	14.8 (3)
O4—C4—C4A—C8A	-178.9 (2)	O1—C2—C21—N211	16.3 (3)
C3—C4—C4A—C8A	0.9 (3)	C3—C2—C21—N211	-165.4 (2)
O4—C4—C4A—C5	0.6 (4)	O2—C21—N211—C215	-175.3 (2)
C3—C4—C4A—C5	-179.5 (2)	C2—C21—N211—C215	5.0 (4)
C8A—C4A—C5—C6	0.4 (4)	O2—C21—N211—C212	1.1 (3)
C4—C4A—C5—C6	-179.1 (2)	C2—C21—N211—C212	-178.7 (2)
C4A—C5—C6—C7	-0.9 (4)	C21—N211—C212—C213	171.5 (2)
C5—C6—C7—C8	0.6 (4)	C215—N211—C212—C213	-11.5 (3)
C6—C7—C8—C8A	0.1 (3)	N211—C212—C213—C214	31.0 (2)
C2—O1—C8A—C8	178.7 (2)	C212—C213—C214—C215	-39.4 (2)
C2—O1—C8A—C4A	-1.0 (3)	C21—N211—C215—C214	163.8 (2)
C7—C8—C8A—O1	179.6 (2)	C212—N211—C215—C214	-12.8 (3)
C7—C8—C8A—C4A	-0.7 (3)	C213—C214—C215—N211	31.8 (2)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C8—H8 \cdots O2 ⁱ	0.95	2.55	3.137 (3)	121
C214—H21C \cdots O4 ⁱⁱ	0.99	2.47	3.340 (3)	146

Symmetry codes: (i) $x+1/2, -y+1/2, z$; (ii) $-x+1, -y+1/2, z-1/2$.