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2-Amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile

John N. Low,[a]*† Justo Cobo,[b] Manuel Nogueras,[b] Adolfo Sánchez,[b] Jairo Quiroga[c] and Carlos Cisneros[c]

[a]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, [b]Departamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, and [c]Grupo de Investigación de Compuestos Heterocíclicos, Departamento de Química, Universidad de Valle, AA 25360 Cali, Colombia
Correspondence e-mail: jnlow111@hotmail.com

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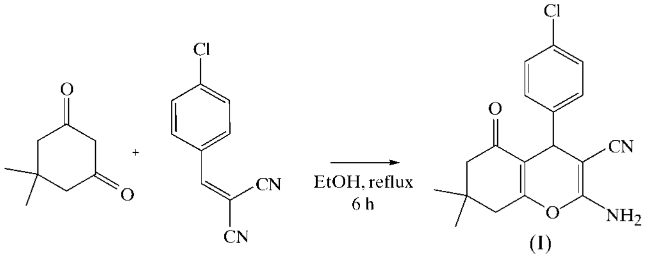
The supramolecular structure of the title compound, $C_{18}H_{17}ClN_2O_2$, is determined by the intersection of two chains formed by N—H···O and N—H···N hydrogen bonds, forming a two-dimensional sheet.

Comment

The structure of 2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile, (II), has been reported by Tu *et al.* (2001). We report here the structure of the title 4-(4-chlorophenyl)- analogue, (I).



In (II), an N—H···N hydrogen bond links the molecules into dimers, which are then linked to form a three-dimensional network *via* an N—H···O(oxo) hydrogen bond; the supramolecular structure of (I), however, is completely different. In (I) (Fig. 1, where the *S* enantiomer has been arbitrarily chosen as the asymmetric unit), the basic supramolecular motifs are two chains. An N2—H2*B*···N31 hydrogen bond forms a *C*(6) chain (Bernstein *et al.*, 1995), which runs parallel to [001], linking molecules related by the *c*-glide plane at $y = \frac{1}{4}$. These chains are then linked together by a *C*(8) chain, formed by the N2—H2*A*···O5 hydrogen bond, which runs parallel to [201]. The combination of these two chains generates a sheet of $R_4^4(24)$ rings (Fig. 2). This sheet lies in the range $0 < y < \frac{1}{2}$, and another antiparallel sheet lies in the range $\frac{1}{2} < y < 1.0$.

Atom N31 in the molecule at (x, y, z) acts as an acceptor, *via* atom H2*B*, for amino atom N2 in the molecule at $(x, \frac{1}{2} - y, z - \frac{1}{2})$. Atom O5 in the molecule at (x, y, z) acts as an acceptor, *via* atom H2*A*, for amino atom N2 in the molecule at $(x - 1, \frac{1}{2} - y, z - \frac{1}{2})$. Atom N31 in the molecule at $(x - 1, \frac{1}{2} - y, z - \frac{1}{2})$ acts as an acceptor, *via* atom H2*B*, for amino atom N2 in the molecule at $(x - 1, y, z - 1)$. Finally, atom N2 in the molecule at $(x - 1, y, z - 1)$ acts as a donor, *via* atom H2*A*, to atom O5 in the molecule at $(x, \frac{1}{2} - y, z - \frac{1}{2})$, thus completing the ring.

There is also a contact between atom Cl4 and atom O1 at $(2 - x, -y, 1 - z)$, with a Cl···O distance of 3.192 (2) Å, which is less than the sum of the van der Waals radii of Cl and O (3.27 Å; Gilli, 1994). The C44—Cl4···O1 angle is 159.34 (8)°. A search of the Cambridge Structure Database (CSD, Version

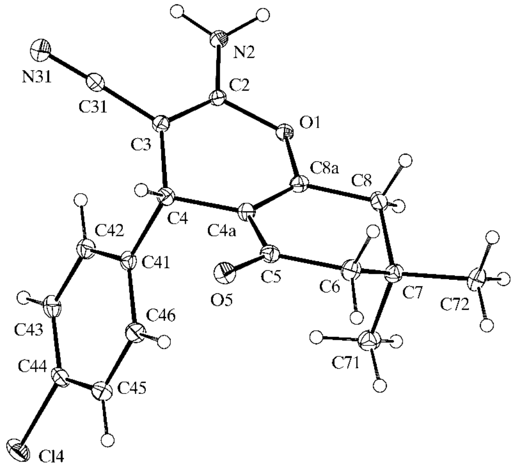


Figure 1
A view of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

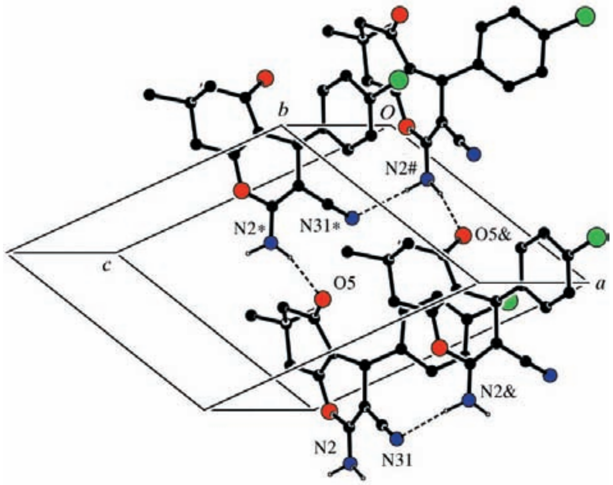


Figure 2
The $R_4^4(24)$ ring in (I), formed by the intersection of the *C*(6) and *C*(8) chains. Atoms labelled with an asterisk (*), hash (#) or ampersand (&) are at the symmetry positions $(x - 1, \frac{1}{2} - y, z - \frac{1}{2})$, $(x - 1, y, z - 1)$ and $(x, \frac{1}{2} - y, z - \frac{1}{2})$, respectively.

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† Postal address: Department of Electronic Engineering and Physics, University of Dundee, Dundee DD1 4HN, Scotland.

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of April 2002; Allen, 2002), gives 68 hits for Cl···O(ring) contacts. Of these contacts, only three are less than the sum of the van der Waals radii, and all the others range between 3.294 and 4.247 Å. Thus, contacts less than 3.27 Å are rare. In 3,4,5,6,7-pentachloro-8-oxatricyclo[4.3.0.0^{3,7}]non-4-ene (refcode JEMXUU; Shnulin *et al.*, 1989), the Cl···O distance is 3.049 Å and the angle at Cl is 153.8°. In *N*-(2,6-dichlorophenyl)-1,2-epimino-3,4-epoxycyclopentane (refcode KOJJUO; Rousselle *et al.*, 1991), the Cl···O distance is 3.114 Å and the angle at Cl is 165.7°. In *N*-(2,2-dichlorovinyl)-1,2-epimino-4,5-epoxy-cyclopentane (refcode XZCVIN10; Van Meerssche *et al.*, 1977), the Cl···O distance is 2.961 Å and the angle at Cl is 179.0°. It is also worth noting that in (I) and the compounds cited above, the angles at Cl are all greater than 153°, whereas the angles at Cl for the rest of the compounds in the search range between 60 and 170°, randomly.

There are no unusual bond lengths and angles in (I), which are in agreement with those found in (II).

Experimental

A solution of *p*-chlorobenzylidenemalonodinitrile (1 mmol) and 5,5-dimethylcyclohexane-1,3-dione (1 mmol) in absolute ethanol (10 ml) was heated under reflux for 6 h according to the method of Tu *et al.* (2001). The resulting precipitate was isolated by filtration, washed with ethanol, dried and recrystallized from ethanol (yield 80%, m.p. 491 K). Analysis, required for $C_{18}H_{17}ClN_2O_2$: C 65.8, H 5.2, N 8.5%; found: C 65.7, H 5.2, N 8.6%.

Crystal data

$C_{18}H_{17}ClN_2O_2$
$M_r = 328.79$
Monoclinic, $P2_1/c$
$a = 9.3867$ (3) Å
$b = 16.5328$ (5) Å
$c = 11.3189$ (3) Å
$\beta = 118.118$ (2)°
$V = 1549.25$ (8) Å^3
$Z = 4$

$D_x = 1.410$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3487 reflections
$\theta = 3.2$–27.5°
$\mu = 0.26$ mm^{-1}
$T = 120$ (1) K
Plate, colourless
0.20 × 0.08 × 0.08 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.950$, $T_{\max} = 0.980$
12 189 measured reflections

3487 independent reflections
2262 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.066$
$\theta_{\max} = 27.5°$
$h = -12 \rightarrow 12$
$k = -18 \rightarrow 21$
$l = -14 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.130$
$S = 1.02$
3487 reflections
210 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.066P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C3—C31	1.415 (3)	C31—N31	1.151 (3)
N31—C31—C3	177.9 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O5$^{\rm i}$	0.92	2.00	2.894 (3)	165
N2—H2*B*···N31$^{\rm ii}$	0.92	2.26	3.118 (3)	155

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

Space group $P2_1/c$ was deduced from the systematic absences. H atoms were treated as riding atoms, with C—H distances in the range 0.95–1.00 Å and N—H distances of 0.92 Å. These latter atoms were DFIXed to this value based on positions found in a difference map, and then AFIXed in the final cycles (*SHELXL*97; Sheldrick, 1997). It is worth noting that the amino group is not planar in (I), and therefore the use of AFIX 93 would give a false position for the amino H atoms.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97; molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1236). Services for accessing these data are described at the back of the journal.

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