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4-Chloro-3-nitrocoumarin: an unusual non-bonding C—Cl···O=C interaction

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Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.003 Å
R factor = 0.047
wR factor = 0.198
Data-to-parameter ratio = 13.7

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

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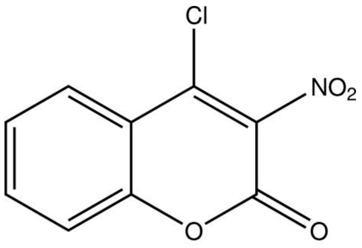
In the title compound, 4-chloro-3-nitro-2*H*-chromen-2-one, $C_9H_4ClNO_4$, the coumarin core has a planar conformation. The Cl atom accepts one of the bifurcated lone pairs of the keto O atom with sp^2 hybridization state. The other lone pair is donated to the pyran ring of a neighboring molecule.

Comment

Coumarin and its 3,4-substituted derivatives, such as warfarin and trioxalen, have attracted research interest in the fields of bioorganic and medicinal chemistry (Clatanoff *et al.*, 1954; Sehgal, 1974; Fujii & Hirayama, 1998). In particular, a series of 3-nitrocoumarins exhibit a variety of potent inhibitions of phospholipase C (Perrella *et al.*, 1994; Tisi *et al.*, 2001). One of the derivatives, the title compound, (I), is a starting material for the inhibitors and [*c*]-fused heterocyclocoumarin derivatives (Amantini *et al.*, 2003). In the present study, an X-ray analysis of (I) was performed in order to determine the inherent conformation and its correlation with chemical properties.



(I)

An *ORTEP-3* (Farrugia, 1997) drawing of (I), together with the atomic numbering, is shown in Fig. 1. Selected bond lengths, bond angles and torsion angles are given in Table 1. The coumarin core has a planar conformation, with a mean deviation of 0.020 (2) Å from the least-squares plane defined by the two six-membered rings, which form a dihedral angle of 2.24 (8)°. Electron localization was found at the short C3—C4 [1.342 (3) Å] bond. Atom Cl4 deviates from the mean plane by only 0.054 (1) Å, while the nitro group is nearly perpendicular to the plane [dihedral angle = 98.0 (2)°]. The Cl4—C4 bond length [1.709 (2) Å] is slightly shorter than the typical Csp^2—Cl bond distance [1.734 (19) Å; International Tables for Crystallography Vol. C, 1999].

In the crystal structure, the planar chromones are stacked opposite each other along the $[10\overline{1}]$ direction, as shown in Fig. 2. Between these stacked molecules, π–π interactions are found [$Cg1\cdots Cg2^{iii} = Cg2\cdots Cg1^{iii}$ = 3.678 (1) Å; symmetry code: (iii) $-x, 1-y, 1-z$; $Cg1$ and $Cg2$ are the centroids of

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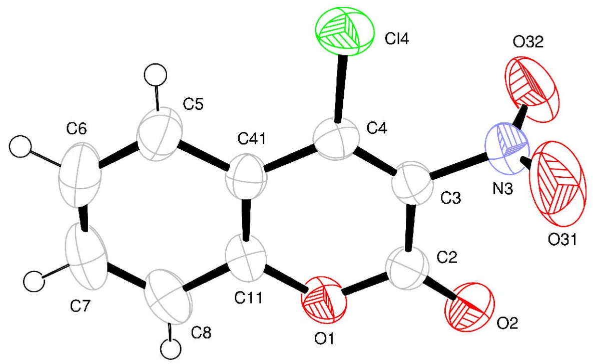

Figure 1
ORTEP-3 (Farrugia, 1997) drawing representing non-H atoms as 50% probability ellipsoids.

the pyran and benzene rings, respectively]. A non-bonding interaction is also found between atoms Cl4 and O2^{i}, where atom Cl4 accepts one of the bifurcated lone-pair electrons of atom O2 with sp^2 hybridization state. The other lone pair is donated to the conjugated ring system [$O2\cdots Cg1^{ii}$ = 3.444 (2) Å and $C2—O2\cdots Cg1^{ii}$ = 123.9 (1)°; symmetry code: (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$]. The crystal structure is also stabilized by the $C6—H6\cdots O1^{iv}$ interaction [symmetry code: (iv) $-x, \frac{1}{2} + y, \frac{1}{2} - z$]. The herringbone structure is stabilized by hydrogen bonding and the above non-bonding interactions.

It is thought that the high electronegativity of the nitro group causes electron localization at the 3,4-position in the coumarin core. This localization increases the dienophilicity of the coumarin core in the Diels–Alder reaction. Furthermore, the nitro group produces the low electron density around atom Cl4, as a result of which atom Cl4 tends to accept a lone-pair electron from a neighboring molecule. This configuration is supported by the high nucleophilic attack of the Cl4 atom against, for example, alcohols.

Experimental

Compound (I) was purchased from Tokyo Chemical Industry Co. Ltd. Rod-like yellow crystals of (I) were obtained by vapor-phase diffusion of *n*-hexane into a chloroform solution at 283 (5) K.

Crystal data

$C_9H_4ClNO_4$
M_r = 225.59
Monoclinic, $P2_1/c$
a = 8.5110 (4) Å
b = 13.526 (1) Å
c = 8.6612 (5) Å
β = 114.119 (5)°
V = 910.0 (1) Å^3
Z = 4
D_x = 1.646 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 30.0–35.0°
μ = 3.71 mm^{-1}
T = 297.2 K
Rod, yellow
0.3 × 0.2 × 0.2 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.433, T_{max} = 0.478
2084 measured reflections
1876 independent reflections
1727 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.032
θ_{max} = 74.9°
$h = -10 \rightarrow 0$
$k = 0 \rightarrow 16$
$l = -9 \rightarrow 10$
3 standard reflections every 300 reflections intensity decay: none

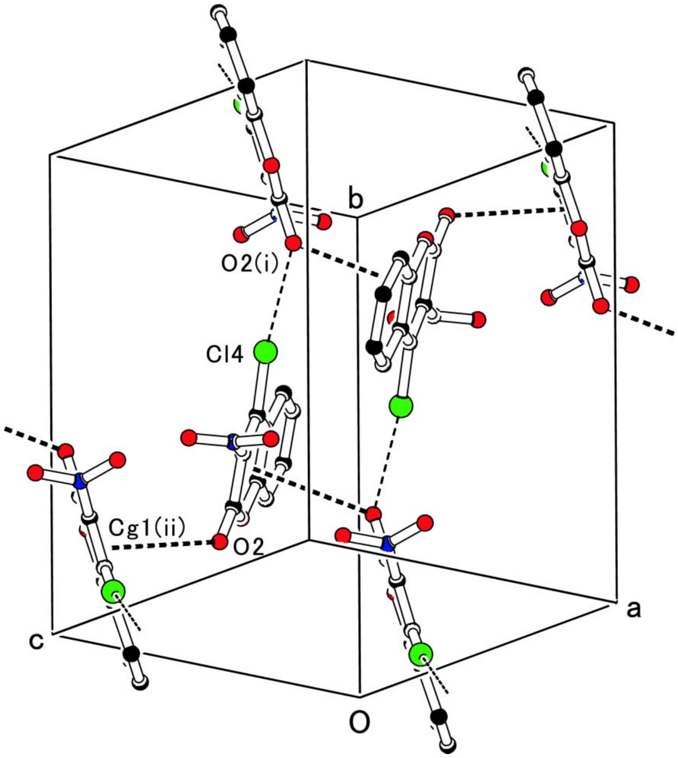

Figure 2
The crystal structure of (I). Dashed lines indicate O···Cl and O···π interactions. [Symmetry codes: (i) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$.]

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.198
S = 1.21
1876 reflections
137 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + [0.157(\mathrm{Max}(F_o^2,0] + 2F_c^2)/3)^2]$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}
Extinction correction: type 2 Gaussian isotropic (Zachariasen, 1967)
Extinction coefficient: 0.39 (6)

Table 1
Selected geometric parameters (Å, °).

Cl4—C4	1.709 (2)	C3—C4	1.342 (3)
C2—C3	1.454 (3)	C4—C41	1.438 (3)
Cl4···O2^{i}	2.981 (2)		
N3—C3—C2	114.6 (2)	Cl4—C4—C3	120.7 (1)
N3—C3—C4	122.6 (2)	Cl4—C4—C41	119.5 (1)
O31—N3—C3—C4	101.0 (3)	O32—N3—C3—C2	101.5 (2)

Symmetry code: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$.

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

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···O1^{iv}	0.95	2.51	3.449 (3)	172

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

All of the H atoms were located in difference Fourier maps and refined isotropically, but then fixed.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1988); cell refinement: *CAD-4 Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1993); program(s) used to solve structure: *SIR88* (Burla *et al.*, 1989); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *TEXSAN*.

References

Amantini, D., Fringuelli, F., Piermatti, O., Pizzo, F. & Vaccaro, L. (2003). *J. Org. Chem.* **68**, 9263–9268.

Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.

Clatanoff, C. V., Triggs, P. O. & Meyer, O. O. (1954). *AMA Arch. Intern. Med.* **94**, 213–220.

Enraf–Nonius (1988). *CAD-4 Software*. Enraf–Nonius, Delft, The Netherlands.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Fujii, I. & Hirayama, N. (1998). *Anal. Sci.* **14**, 871-872.

Molecular Structure Corporation (1993). *TEXSAN*. Version 1.6. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Perrella, F. W., Chen, S.-F., Behrens, D. L. & Kaltenbach, R. F. III (1994). *J. Med. Chem.* **37**, 2232–2237.

Sehgal, V. N. (1974). *Arch. Dermatol.* **109**, 578.

Tisi, R., Coccetti, P., Banfi, S. & Martegani, E. (2001). *Cell Biochem. Funct.* **19**, 229–235.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.