Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

{3-[(4-Chloroanilino)carbonyl]-2-[(3,4-dichlorophenyl)imino]-8-methyl-2*H*-pyrano[2,3-*c*]pyridin-5-yl}methyl acetate

Sergiy M. Kovalenko,[a] Vyacheslav N. Baumer,[b]* Iryna O. Zhuravel[a] and Valentyn P. Chernykh[d]

[a]Department of Organic Chemistry, Ukrainian National University of Pharmacy, 4 Blyukher Str., Kharkiv 61002, Ukraine, [b]Institute for Single Crystals, National Academy of Sciences of Ukraine, 60 Lenin Ave., Kharkiv 61001, Ukraine, and [d]Ukrainian National University of Pharmacy, 4 Blyukher Str., Kharkiv 61002, Ukraine

Correspondence e-mail:
baumer@xray.isc.kharkov.com

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.043
wR factor = 0.071
Data-to-parameter ratio = 13.0

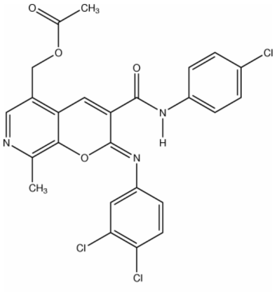
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 9 December 2003
Accepted 5 January 2004
Online 17 January 2004

The coplanar arrangement of rings in the title molecule, $C_{25}H_{18}Cl_3N_3O_4$, is accompanied by the formation of short intramolecular O···H (2.20 and 2.26 Å) contacts. A strong N—H···N hydrogen bond [N···N = 2.698 (4) Å and N—H···N = 142°] is present and, as a result, the exocyclic bond angles at the C atoms in the 2- and 3-positions of the pyranone ring are slightly distorted. The coplanar rings form a layered structure in which a short intermolecular Cl···Cl($-x$, $1 - y$, $1 - z$) contact of 3.280 (2) Å is observed.

Comment

The title compound, (I), belongs to the class of iminocoumarin derivatives and analogs, which have hitherto received relatively little attention (Baumer *et al.*, 1993, 2003; O'Callaghan *et al.*, 1996; Kovalenko *et al.*, 1999).



(I)

In our previous publications (Zubkov *et al.*, 1994; Kovalenko *et al.*, 1999) on the reactivity and structure analysis of substituted 2-iminocoumarin-3-carboxamides, it was shown that reaction with aromatic amines led to the formation of 2-*N*-*R*-imino derivatives. The present work is concerned with the synthesis of new aza-analogs of these compounds. Condensation of pyridoxal hydrochloride with *N*-arylcyanoacetamides in the presence of excess piperidine was found to yield 2-imino-5-hydroxymethylene-8-methyl-2*H*-pyrano[2,3-*c*]pyridin-3-*N*-arylcarboxamides. Treatment of these compounds with acetic anhydride led to O-acetate derivatives, of which the title compound is an example.

The rings in the title compound are coplanar to within 0.05 Å [maximum deviation of 0.093 (1) Å for O1], resulting in some steric hindrance in the molecule. Hindrance between the pyranone and dichlorophenyl moieties is caused by a short intramolecular O1···H11 contact of 2.20 Å [the sum of the van der Waals radii is 2.36 Å (Zefirov, 1997)], leading to a noticeable increase of the C2—N1—C10 and N1—C10—C11 bond angles (Table 1). In addition, the formation of an intramolecular N2—H2···N1 hydrogen bond [N1···N2 = 2.698 (4) Å and N—H···N = 142°] causes a slight increase in the N1—C2—C3 and C2—C3—C16 angles. Furthermore, the short H18···O2 contact (2.26 Å) results in a noticeable

DOI: 10.1107/S1600536804000078

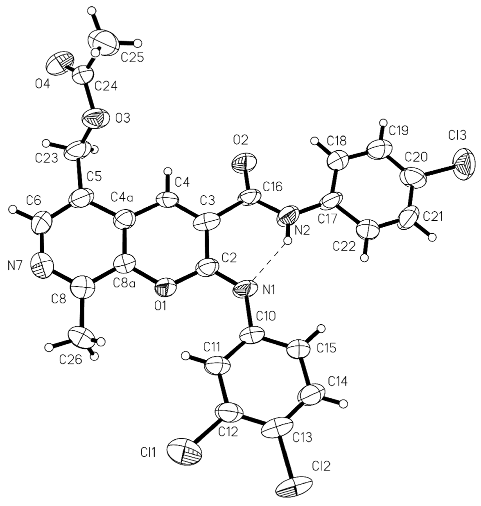


Figure 1

A view of the title molecule, with displacement ellipsoids drawn at the 50% probability level and the atom-numbering scheme. The intramolecular hydrogen bond is indicated by a dashed line.

increase of the O2—C16—N2, C16—N2—C17 and N2—C17—C18 angles.

One peculiarity of the title molecule should be mentioned. The Cl1—C12 bond [1.684 (2) Å] is substantially shorter than the value of 1.720 Å given by Bürgi & Dunitz (1994) for *ortho*-dichloro-substituted benzene derivatives. The observed shortening can be explained if the molecular arrangement in the crystal structure is taken into account. The molecules in the crystal structure form planar layers, between which lie the acetate groups. Within these layers, the Cl atoms are involved in short contacts [Cl1···Cl2 = 3.133 (2) Å and Cl1···Cl1($-x$, $1 - y$, $1 - z$) = 3.280 (2) Å; the sum of the van der Waals radii is 3.80 Å (Zefirov, 1997)]. The interactions between the Cl atoms may cause a decrease of electron density in the C—Cl σ bonds, resulting in the observed shortening of these bonds.

Experimental

The method of preparation has been described by Zubkov *et al.* (1994).

Crystal data

$C_{25}H_{18}Cl_3N_3O_4$
$M_r = 530.77$
Triclinic, $P\bar{1}$
$a = 9.020$ (2) Å
$b = 11.390$ (3) Å
$c = 12.890$ (3) Å
$\alpha = 73.95$ (2)°
$\beta = 86.18$ (2)°
$\gamma = 67.49$ (2)°
$V = 1174.5$ (5) Å^3

$Z = 2$
$D_x = 1.501$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 20$–22°
$\mu = 0.43$ mm^{-1}
$T = 293$ (2) K
Polyhedron, yellow
0.25 × 0.20 × 0.20 mm

Data collection

Siemens *P*3/PC diffractometer
$2\theta/\theta$ scans
4323 measured reflections
4106 independent reflections
1737 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.077$
$\theta_{\rm max} = 25.0°$

$h = -9 \rightarrow 10$
$k = 0 \rightarrow 13$
$l = -14 \rightarrow 15$
2 standard reflections every 98 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.071$
$S = 0.92$
4106 reflections
317 parameters
H-atom parameters constrained

$w = \exp[2.00(\sin\theta/\lambda)^2]/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\rm max} = 0.01$
$\Delta\rho_{\rm max} = 0.19$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.15$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0060 (5)

Table 1

Selected geometric parameters (Å, °).

Cl1—C12	1.684 (2)	C10—C15	1.371 (3)
Cl2—C13	1.711 (2)	C10—C11	1.386 (3)
Cl3—C20	1.751 (2)	C11—C12	1.395 (3)
O1—C2	1.366 (2)	C12—C13	1.394 (3)
O1—C8*A*	1.376 (2)	C13—C14	1.390 (3)
C2—N1	1.279 (2)	C14—C15	1.381 (3)
C2—C3	1.464 (3)	C16—O2	1.212 (2)
C3—C4	1.341 (3)	C16—N2	1.302 (2)
C3—C16	1.545 (3)	N2—C17	1.425 (2)
C4—C4*A*	1.427 (3)	C17—C18	1.375 (3)
C4*A*—C8*A*	1.392 (3)	C17—C22	1.406 (3)
C4*A*—C5	1.414 (3)	C18—C19	1.387 (3)
C5—C6	1.397 (3)	C19—C20	1.356 (3)
C5—C23	1.519 (3)	C20—C21	1.361 (3)
C6—N7	1.321 (3)	C21—C22	1.350 (3)
N7—C8	1.315 (3)	C23—O3	1.418 (2)
C8—C8*A*	1.406 (3)	O3—C24	1.315 (2)
C8—C26	1.487 (3)	C24—O4	1.191 (2)
N1—C10	1.421 (2)	C24—C25	1.473 (3)
C2—O1—C8*A*	121.61 (15)	C11—C12—C13	120.26 (19)
N1—C2—O1	120.56 (17)	C11—C12—Cl1	119.59 (16)
N1—C2—C3	121.67 (18)	C13—C12—Cl1	120.15 (17)
O1—C2—C3	117.78 (16)	C14—C13—C12	118.55 (19)
C4—C3—C2	119.94 (18)	C14—C13—Cl2	120.00 (17)
C4—C3—C16	116.52 (18)	C12—C13—Cl2	121.45 (17)
C2—C3—C16	123.52 (17)	C15—C14—C13	120.6 (2)
C3—C4—C4*A*	121.48 (19)	C10—C15—C14	121.0 (2)
C8*A*—C4*A*—C5	116.69 (18)	O2—C16—N2	125.55 (19)
C8*A*—C4*A*—C4	117.66 (17)	O2—C16—C3	117.77 (17)
C5—C4*A*—C4	125.60 (19)	N2—C16—C3	116.67 (17)
C6—C5—C4*A*	117.2 (2)	C16—N2—C17	127.15 (18)
C6—C5—C23	121.17 (18)	C18—C17—C22	118.21 (18)
C4*A*—C5—C23	121.60 (19)	C18—C17—N2	124.27 (17)
N7—C6—C5	124.2 (2)	C22—C17—N2	117.49 (17)
C8—N7—C6	120.23 (19)	C17—C18—C19	120.13 (19)
N7—C8—C8*A*	119.7 (2)	C20—C19—C18	120.0 (2)
N7—C8—C26	118.31 (19)	C19—C20—C21	120.6 (2)
C8A—C8—C26	122.01 (19)	C19—C20—Cl3	119.91 (17)
O1—C8*A*—C4*A*	121.37 (17)	C21—C20—Cl3	119.52 (17)
O1—C8*A*—C8	116.83 (18)	C22—C21—C20	120.6 (2)
C4*A*—C8*A*—C8	121.78 (19)	C21—C22—C17	120.5 (2)
C2—N1—C10	128.40 (17)	O3—C23—C5	107.66 (16)
C15—C10—C11	119.32 (19)	C24—O3—C23	116.97 (15)
C15—C10—N1	114.36 (18)	O4—C24—O3	122.77 (16)
C11—C10—N1	126.29 (18)	O4—C24—C25	125.64 (19)
C10—C11—C12	120.21 (19)	O3—C24—C25	111.54 (18)
C8*A*—O1—C2—N1	175.58 (15)	O2—C16—N2—C17	−1.8 (3)
O1—C2—C3—C16	−177.48 (15)	C3—C16—N2—C17	178.01 (15)
C23—C5—C6—N7	−177.21 (18)	C16—N2—C17—C18	10.5 (3)
O1—C2—N1—C10	−0.3 (3)	C16—N2—C17—C22	−171.66 (17)
C4—C3—C16—O2	−7.2 (2)	C4*A*—C5—C23—O3	−67.6 (2)
C2—C3—C16—O2	174.48 (16)	C5—C23—O3—C24	−159.29 (17)
C4—C3—C16—N2	173.03 (16)	C23—O3—C24—O4	−4.5 (3)
C2—C3—C16—N2	−5.3 (2)	C23—O3—C24—C25	178.07 (18)

All H atoms were located in a difference map and treated as riding [$C_{\rm methyl}$—H = 0.96 Å, other C—H = 0.93 Å and N—H = 0.84 Å]. The $U_{\rm iso}$(H) values were set to $1.2U_{\rm eq}$ of the carrier atom.

Data collection: *P*3 (Siemens, 1989); cell refinement: *P*3; data reduction: *XDISK* and *XPREP* (Siemens, 1991); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1991); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Baumer, V. N., Karasev, A. A. & Sizova, Z. A. (2003). *Acta Cryst.* E**59**, o54–o56.

Baumer, V. N., Ponomaryov, O. A., Novikov, A. I., Lakin, E. E. & Kuznetsov, V. P. (1993). *Adv. Mater. Optics Electron.* **2**, 191–195.

Bürgi, H.-B. & Dunitz, J. D. Editors (1994). *Structure Correlation*, Vol. 2, pp. 771–777. Weinheim/New York/Basel/Cambridge/Tokyo: VCH Verlag.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Kovalenko, S. N., Baumer, V. N., Rusanova, S. V. & Chernykh, V. P. (1999). *Z. Kristallogr.* **214**, 580–583.

O'Callaghan, C. N., McMurry, T. B. H., O'Brien, J. E., Draper, S. M. & Wilcock, D. J. (1996). *J. Chem. Soc. Perkin Trans.* 1, pp. 1067–1071.

Sheldrick, G. M. (1997). *SHELXL*97. Release 97-2. University of Göttingen, Germany.

Siemens (1989). *P*3. Siemens Analytical X-ray Instruments Inc., Karlsruhe, Germany.

Siemens (1991). *XDISK*, *XPREP* and *XP*. Siemens Analytical X-ray Instruments Inc., Karlsruhe, Germany.

Zefirov, Yu. V. (1997). *Kristallografiya*, **42**, 936–959. (In Russian.)

Zubkov, V. A., Kovalenko, S. N., Chernykh, V. P. & Ivkov, S. M. (1994). *Khim. Get. Soedin. SSSR*, **6**, 760–766. (In Russian.)