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3,6-Diethyl-*N*,*N*′-bis(3-methylphenyl)-1,6-dihydro-1,2,4,5-tetrazine-1,4-dicarboxamide. Erratum

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In the paper by Shi, Hu & Rao [*Acta Cryst.* (2004), E**60**, o1065–o1066], the title is given incorrectly. The chemical name should appear as '3,6-Diethyl-*N*,*N*′-bis(3-methylphenyl)-1,4-dihydro-1,2,4,5-tetrazine-1,4-dicarboxamide'.

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5-Benzyl-7,9-dimethoxy-3-phenyl-5*H*-pyrazolo[4,3-*c*]quinolin-1-ium chloride acetic acid solvate

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Key indicators

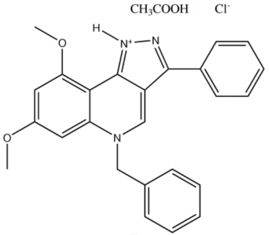
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.046
wR factor = 0.083
Data-to-parameter ratio = 14.1

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

The asymmetric unit of the title compound, $C_{25}H_{22}N_3O_2^+\cdot Cl^-\cdot C_2H_4O_2$, is composed of a 5-benzyl-7,9-dimethoxy-3-phenyl-5*H*-pyrazolo[4,3-*c*]quinolin-1-ium cation, a chloride anion and an acetic acid solvent molecule. The positive charge of the cation is located on the pyrazole ring, resulting in aromatization of the bonds in the pyrazolo[4,3-*c*]quinoline tricyclic system. The pyrazolium H atom forms a bifurcated hydrogen bond with the O atom of the 6-methoxy group [N···O = 2.741 (2) Å and N—H···O = 117°] and with the carbonyl O atom of the acetic acid molecule [N···O = 2.826 (2) Å and N—H···O = 134°]. Another hydrogen bond is observed between the acetic acid hydroxy group and the chloride anion [Cl···O = 2.972 (2) Å and O—H···Cl = 172°].

Comment

Structural analogues of pyrazolo[4,3]quinoline have been studied for their biological activity as benzodiazepine receptor ligands (Palazzino *et al.*, 1987) and PDE-4 inhibitors (Crespo *et al.*, 2000). To increase the number of available synthetic functionally reduced pyrazoloquinolines, a method for obtaining novel 5-alkyl-3-aryl-5*H*-pyrazolo[4,3-*c*]quinolines from 3-aroyl-4-quinolinones has been developed; the title compound, (I), is an example. The X-ray crystallographic study of (I) was carried out to determine its molecular structure and also to locate the protonation site in the pyrazolo[4,3-*c*]quinoline tricyclic system.



(I)

The asymmetric unit of (I) is composed of the 5-benzyl-7,9-dimethoxy-3-phenyl-5*H*-pyrazolo[4,3-*c*]quinolin-1-ium cation, one chloride anion and one acetic acid solvent molecule. The cation consists of two planar fragments. The first, composed of the pyrazoloquinoline tricyclic system together with the phenyl ring attached at the 3-position, is planar to within 0.024 Å. Deviations from this plane for methoxy-group atoms O1, O2, C27 and C28 are 0.061 (2), −0.101 (2), −0.022 (4) and 0.036 (3) Å, respectively. The second plane is the phenyl ring of the benzyl fragment (r.m.s. deviation = 0.014 Å). These two planar fragments make a dihedral angle of 83.03 (6)°. Methylene atom C20 deviates by 0.167 (3) Å from the former plane and by 0.095 (3) Å from the latter, due to steric hindrance of atoms H8 and H20*a* (H8···H20*a* = 2.10 Å) and atoms C8 and C21 [C8···C21 = 3.226 (3) Å].

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Protonation of atom N1 leads to aromatization of the bonds in the pyrazoline fragment and further conjugation of pyrazoline and the phenyl rings (Table 1). The C3—C14 bond length of 1.467 (3) Å coincides with the value of 1.470 Å quoted by Bürgi & Dunitz (1994) for a bond between aromatic and sp^2-hybridized C atoms. As a result of conjugation, the coplanarity of the pyrazoline and phenyl rings is accompanied by a shortening of the intramolecular distances N2⋯H19 (2.46 Å) and H5⋯H15 (2.04 Å) [the sums of van der Waals radii are 2.66 and 2.32 Å, respectively (Zefirov, 1994)]. This shortening leads to a widening of the C4—C3—C14 bond angle to 131.5 (2)°, whereas, for example, in the structure of 2-phenyl-5-furyl-1,3,4-oxadiazole, in which similar shortened contacts are not observed, the corresponding angle is 121.5 (3)° (Patsenker *et al.*, 1999).

Atom H1 of the pyrazoline ring makes a bifurcated hydrogen bond with atom O2 of a methoxy group and atom O3 of the acetic acid molecule. Furthermore, a hydrogen bond is observed between the chloride anion and the carboxyl H atom of the acetic acid molecule [see Table 2; van der Waals radii for Cl, H and O atoms are 1.90, 1.16 and 1.29 Å, respectively, as quoted by Zefirov (1994)]. In the crystal structure, there are no remarkable van der Waals interactions involving short intermolecular distances. The structure is layered, with the first planar fragment (see above) and the methoxy groups parallel to the $(10\overline{1})$ plane. The interlayer spaces are filled only by the anions and the phenyl rings of the benzyl groups. Perhaps as a result, atoms belonging to the latter show increased anisotropic displacement parameters (Fig. 1).

Experimental

5-Benzyl-7,9-dimethoxy-3-phenyl-5*H*-pyrazolo[4,3-*c*]quinolin-1-ium chloride was obtained by reaction of 3-benzoyl-1*H*-quinolin-4-one with benzyl chloride in the presence of sodium hydride, followed by cyclization with hydrazine monohydrochloride in acetic acid. Crystals of the title compound were grown during slow cooling, from 373 K to room temperature, of an acetic acid solution of the product; this was further filtered, washed with hexane and dried at room temperature.

Crystal data

$C_{25}H_{22}N_3O_2^+\cdot Cl^-\cdot C_2H_4O_2$
$M_r = 491.96$
Monoclinic, $C2/c$
$a = 21.224\ (7)$ Å
$b = 15.830\ (4)$ Å
$c = 15.550\ (5)$ Å
$\beta = 109.42\ (3)°$
$V = 4927\ (3)$ Å^3
$Z = 8$

$D_x = 1.326$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 36 reflections
$\theta = 12.0$–$13.0°$
$\mu = 0.19$ mm^{-1}
$T = 293\ (2)$ K
Plate, colourless
$0.50 \times 0.20 \times 0.15$ mm

Data collection

Siemens *P*3/*PC* diffractometer
$2\theta/\theta$ scans
Absorption correction: by integration (*XPREP*; Siemens, 1991)
$T_{\min} = 0.951$, $T_{\max} = 0.964$
4692 measured reflections
4509 independent reflections
2075 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.054$
$\theta_{\max} = 25.5°$
$h = -25 \rightarrow 24$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 18$
2 standard reflections every 98 reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.083$
$S = 0.99$
4509 reflections
320 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.02P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.14$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0054 (3)

Table 1
Selected geometric parameters (Å, °).

O1—C9	1.372 (2)	C11—C12	1.408 (2)
O1—C27	1.413 (2)	C12—C13	1.414 (3)
O2—C11	1.362 (2)	C14—C19	1.378 (3)
O2—C28	1.429 (2)	C14—C15	1.384 (3)
N1—C13	1.341 (2)	C15—C16	1.396 (3)
N1—N2	1.353 (2)	C16—C17	1.351 (4)
N2—C3	1.312 (2)	C17—C18	1.383 (4)
C3—C4	1.458 (3)	C18—C19	1.390 (3)
C3—C14	1.467 (3)	C20—C21	1.495 (3)
C4—C5	1.345 (2)	C21—C22	1.376 (3)
C4—C13	1.404 (2)	C21—C26	1.378 (3)
C5—N6	1.348 (2)	C22—C23	1.377 (4)
N6—C7	1.408 (2)	C23—C24	1.360 (4)
N6—C20	1.502 (2)	C24—C25	1.339 (4)
C7—C8	1.388 (3)	C25—C26	1.385 (3)
C7—C12	1.407 (2)	O3—C30	1.216 (3)
C8—C9	1.368 (2)	O4—C30	1.297 (3)
C9—C10	1.397 (3)	C29—C30	1.416 (4)
C10—C11	1.358 (3)		
C9—O1—C27	118.94 (15)	C7—C12—C13	116.80 (16)
C11—O2—C28	118.18 (16)	C11—C12—C13	125.21 (17)
C13—N1—N2	112.76 (15)	N1—C13—C4	106.08 (17)
C3—N2—N1	107.45 (15)	N1—C13—C12	131.94 (17)
N2—C3—C4	108.99 (16)	C4—C13—C12	121.97 (16)
N2—C3—C14	119.45 (17)	C19—C14—C15	118.72 (19)
C4—C3—C14	131.52 (17)	C19—C14—C3	119.38 (19)
C5—C4—C13	118.83 (17)	C15—C14—C3	121.89 (19)
C5—C4—C3	136.40 (17)	C14—C15—C16	119.8 (2)
C13—C4—C3	104.66 (15)	C17—C16—C15	121.0 (3)
C4—C5—N6	121.47 (16)	C16—C17—C18	119.8 (3)
C5—N6—C7	121.89 (15)	C17—C18—C19	119.6 (2)
C5—N6—C20	118.10 (14)	C14—C19—C18	120.9 (2)
C7—N6—C20	119.83 (15)	C21—C20—N6	112.36 (15)
C8—C7—C12	120.81 (16)	C22—C21—C26	117.8 (2)
C8—C7—N6	120.22 (16)	C22—C21—C20	121.7 (2)
C12—C7—N6	118.96 (17)	C26—C21—C20	120.5 (2)
C9—C8—C7	118.20 (17)	C21—C22—C23	120.8 (3)
C8—C9—O1	123.34 (18)	C24—C23—C22	119.2 (3)
C8—C9—C10	123.22 (18)	C25—C24—C23	122.0 (3)
O1—C9—C10	113.44 (17)	C24—C25—C26	118.6 (3)
C11—C10—C9	117.73 (17)	C21—C26—C25	121.4 (2)
C10—C11—O2	124.98 (17)	O3—C30—O4	119.8 (3)
C10—C11—C12	122.04 (18)	O3—C30—C29	124.4 (3)
O2—C11—C12	112.98 (18)	O4—C30—C29	115.7 (3)
C7—C12—C11	117.97 (18)		
C27—O1—C9—C8	−4.9 (4)	N2—C3—C14—C15	176.7 (2)
C27—O1—C9—C10	174.8 (2)	C4—C3—C14—C15	−0.7 (4)
C28—O2—C11—C10	7.0 (3)	C5—N6—C20—C21	102.8 (2)
C28—O2—C11—C12	−173.02 (18)	C7—N6—C20—C21	−72.4 (2)
N2—C3—C14—C19	−2.2 (3)	N6—C20—C21—C22	128.21 (18)
C4—C3—C14—C19	−179.7 (2)	N6—C20—C21—C26	−54.4 (2)

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N1—H1⋯O3	0.86	2.16	2.826 (2)	134
N1—H1⋯O2	0.86	2.25	2.741 (2)	117
O4—H4⋯Cl1	0.98	2.00	2.972 (2)	172

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All H atoms were located in a difference map and treated as riding, with N—H = 0.86 Å and C—H in the range 0.93–0.97 Å. $U_{\rm iso}$(H) was set equal to $1.2U_{\rm eq}$ of the carrier atom.

Data collection: P3 (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., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

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

Crespo, M. I., Gracia, J., Puig, C., Vega, A., Bou, J., Beleta, J., Domenech, T., Ryder, H., Segarra, V. & Palacios, J. M. (2000). *Bioorg. Med. Chem. Lett.* **10**, 2661–2664.

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

Palazzino, G., Cecchi, L., Melani, F., Colotta, V., Filacchioni, G., Martini, C. & Lucacchini, A. (1987). *J. Med. Chem.* **30**, 1737–1742.

Patsenker, L. D., Baumer, V. N. & Kuznetsov, V. P. (1999). *Functional Mater.* **6**, 110–115.

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. (1994). *Kristallografiya*, **39**, 1025–1031. (In Russian.)

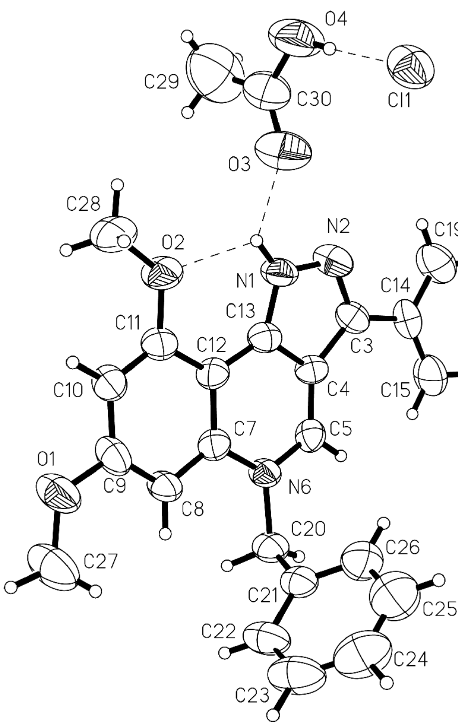

Figure 1

A view of (I), with displacement ellipsoids drawn at the 50% probability level and the atom-numbering scheme. Hydrogen bonds are indicated by dashed lines.

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