Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

10-Ethyl-4-oxo-2,3,4,10-tetrahydropyrimido[4,5-*b*]quinolin-2-iminium 4-toluenesulfonate: a polarized electronic structure in the cation and a hydrogen-bonded sheet structure

Jorge Trilleras,[a] Jairo Quiroga,[a] John N. Low,[b] Justo Cobo[c] and Christopher Glidewell[d]*

[a]Departamento de Química, Universidad de Valle, AA 25360 Cali, Colombia, [b]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, [c]Departamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, and [d]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland
Correspondence e-mail: cg@st-andrews.ac.uk

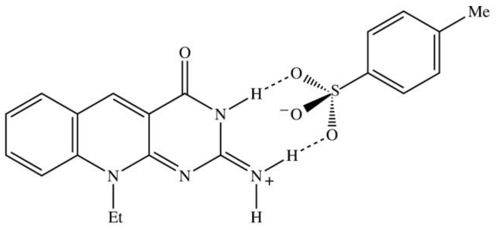
Received 4 June 2008
Accepted 4 June 2008
Online 14 June 2008

In the title compound, $C_{13}H_{13}N_4O^+\cdot C_7H_7O_3S^-$, the bond distances within the cation provide evidence for the delocalization of the positive charge in a manner reminiscent of guanidinium cations. Three independent N—H···O hydrogen bonds link the ions into centrosymmetric four-ion aggregates, and these are further linked into sheets by a single C—H···O hydrogen bond. This study shows how a single hydrogen bond can link centrosymmetric entities into a continuous sheet structure.

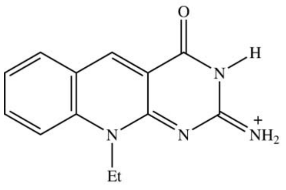
Comment

The synthesis and study of fused pyrimidine compounds is of interest due to the wide variety of their biological and pharmacological properties. In particular, pyrimidinoquinolines have found application as antitumour agents (Chua *et al.*, 2008; Weissman & Yang, 2007), biocidal agents (Kumar *et al.*, 2002) and antiallergic agents (Althuis *et al.*, 1980). Compounds of this type have been prepared from 4,6-dichloro-5-formylpyrimidines using a two-step sequence consisting of a monosubstitution with aromatic amines (Quiroga *et al.*, 2008) followed by an acid-catalysed Bradsher-type cyclocondensation. The title compound, (I), was isolated in small quantity from an attempt to induce such a cyclocondensation using 4-toluenesulfonic acid under microwave irradiation.

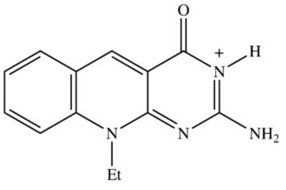
The title compound is a salt for which the asymmetric unit was selected so that the two independent ions are linked within the asymmetric unit by two N—H···O hydrogen bonds, which are both almost linear (Fig. 1 and Table 2). The dihedral angle between the mean plane of the tricyclic ring system of the cation and the aryl ring of the anion is only 5.4 (2)°, so that the non-H atoms of the ring systems within the asymmetric unit are almost coplanar. The main deviations from the near planarity are found for the O atoms of the sulfonate group and the ethyl group pendent from the cation, the plane of which is almost orthogonal to that of the adjacent ring (Table 1).



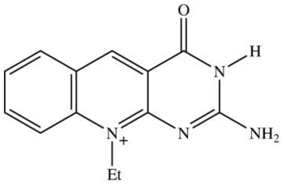
(I)



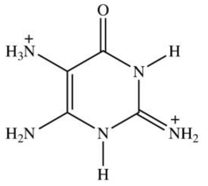
(I*a*)



(I*b*)



(I*c*)



(II)

Within the cation, the peripheral and exocyclic bond distances (Table 1) exhibit some interesting values. Amongst the peripheral C—C distances, the C4a—C5, C6—C7 and C8—C9 bonds are all significantly shorter than the remainder, indicating a degree of double-bond fixation. Of the C—N distances, the exocyclic C2—N2 distance is the shortest by some margin, the ring C2—N1 and C10a—N1 distances are longer than C2—N2 and fairly similar to each other, the C2—N3 and C10a—N10 distances are longer still and are also similar to each other, the amidic C4—N3 bond is long for its type with a distance more typical of C—N bonds in bis-acyl imines (Allen *et al.*, 1987), while C9a—N10 is the longest of all the C—N bonds. The C2—N2 distance is, in fact, rather typical of those found in guanidinium cations (Allen *et al.*, 1987) and

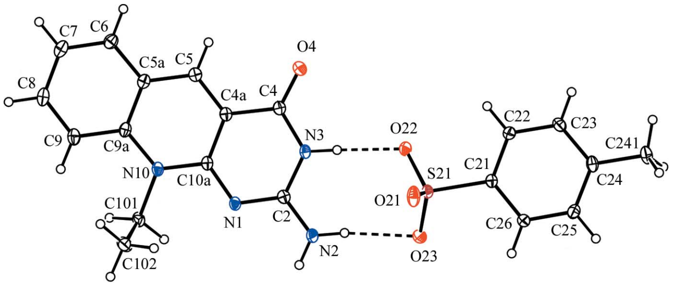


Figure 1
The two independent ions in the asymmetric unit of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

doi:10.1107/S0108270108016995

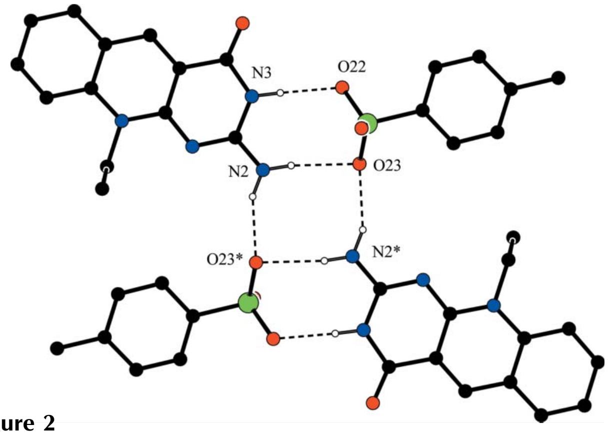


Figure 2
Part of the crystal structure of compound (I), showing a centrosymmetric four-ion aggregate. For the sake of clarity, H atoms bonded to C atoms have been omitted, as has the unit-cell outline. Atoms marked with an asterisk (*) are at the symmetry position $(-x, 1 - y, 1 - z)$.

is close in value to the corresponding bond in the cation, (II), of its sulfate salt [1.3195 (9) Å; Cambridge Structural Database (Allen, 2002) refcode HACDEU; Bieri *et al.*, 1993]. This distance is also consistent with the character of the C4—N3 bond, and these observations suggest that the positive charge which is formally localized at N2 is, in fact, best described as delocalized over atoms N2, N3 and N10, as in forms (I*a*)–(I*c*) (see scheme). The cation can thus be regarded as a protonated iminouracil derivative.

As noted above, the two independent ions within the asymmetric unit of (I) are linked by two N—H···O hydrogen bonds, both of which are almost linear. In addition, pairs of these units are linked by a third N—H···O hydrogen bond (Table 2) to form a centrosymmetric four-ion aggregate in which the central $R_4^2(8)$ (Bernstein *et al.*, 1995) ring is flanked by two symmetry-equivalent $R_2^2(8)$ rings (Fig. 2). These aggregates can be regarded as the basic building block for the structure as a whole and a single C—H···O hydrogen bond (Table 2) links these building blocks into sheets.

The aryl C23 atoms at (x, y, z) and $(-x, 1 - y, 1 - z)$ are components of the aggregate centred at $(0, \frac{1}{2}, \frac{1}{2})$. These two atoms act as hydrogen-bond donors to sulfonate O21 atoms at $(\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z)$ and $(-\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, respectively, which themselves are components of the aggregates centred at $(\frac{1}{2}, 1, 1)$ and $(-\frac{1}{2}, 0, 0)$, respectively. Similarly, the O21 atoms at (x, y, z) and $(-x, 1 - y, 1 - z)$ accept hydrogen bonds from the C23 atoms at $(-\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z)$ and $(\frac{1}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z)$, respectively, which are components of the aggregates centred at $(-\frac{1}{2}, 1, 0)$ and $(\frac{1}{2}, 0, 1)$. Propagation of this interaction by the space group links the centrosymmetric four-ion aggregates into a sheet parallel to $(10\overline{1})$ and built from a combination of $R_2^2(8)$, $R_4^2(8)$ and $R_8^8(40)$ rings (Fig. 3). Thus, a single hydrogen bond is sufficient to link the centrosymmetric four-ion entities into a two-dimensional structure. There are no direction-specific interactions between adjacent sheets. By contrast, in HACDEU, where there are nine independent N—H bonds all participating in hydrogen-bond formation, the overall hydrogen-bonded supramolecular structure is three-dimensional.

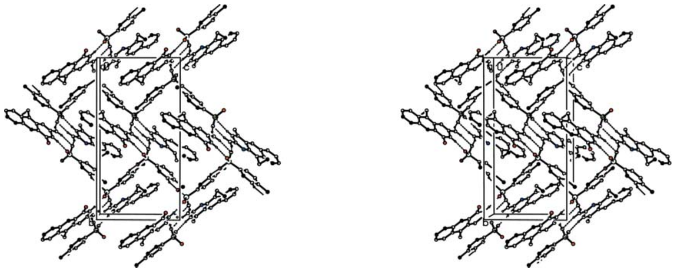


Figure 3
A stereoview of part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded sheet parallel to $(10\overline{1})$. For the sake of clarity, H atoms bonded to C atoms and not participating in the sheet formation have been omitted.

Experimental

A mixture of 2-amino-4-chloro-6-(*N*-ethyl-*N*-phenylamino)pyrimidine-5-carbaldehyde (0.18 mmol) and 4-toluenesulfonic acid monohydrate (0.18 mmol) in ethanol (3 ml) was subjected to microwave irradiation in a sealed tube under magnetic stirring, using a CEM monomode microwave reactor (maximum power 300 W, ramp time 15 min, hold time 10 min and maximum temperature 573 K). The reaction mixture was then cooled in a refrigerator and the resulting solid, which proved to be a mixture of several products, was collected by filtration. Recrystallization from ethanol afforded a few crystals of the title compound as brown blocks, which proved to be suitable for single-crystal X-ray diffraction (m.p. 537–538 K).

Crystal data

$C_{13}H_{13}N_4O^+\cdot C_7H_7O_3S^-$
$M_r = 412.46$
Monoclinic, $P2_1/n$
$a = 9.0213$ (7) Å
$b = 20.2880$ (18) Å
$c = 10.3932$ (6) Å
$\beta = 90.245$ (5)°
$V = 1902.2$ (2) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.21$ mm^{-1}
$T = 120$ (2) K
0.41 × 0.40 × 0.39 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.920$, $T_{max} = 0.924$
43973 measured reflections
4370 independent reflections
3363 reflections with $I > 2\sigma(I)$
$R_{int} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.127$
$S = 1.08$
4370 reflections
265 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.67$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}

The space group $P2_1/n$ was uniquely assigned from the systematic absences. All H atoms were located in difference maps and then treated as riding atoms in geometrically idealized positions, with C—H = 0.95 (aryl), 0.98 (CH_3) or 0.99 Å (CH_2) and N—H = 0.88 Å, and with $U_{iso}(H) = kU_{eq}$(carrier), where $k = 1.5$ for the methyl groups and 1.2 for all other H atoms.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *OSCAIL* (McArdle, 2003) and *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.346 (2)	C8—C9	1.376 (3)
C2—N3	1.364 (2)	C9—C9a	1.410 (3)
N3—C4	1.377 (2)	C9a—N10	1.390 (2)
C4—C4a	1.473 (3)	N10—C10a	1.365 (2)
C4a—C5	1.362 (3)	C10a—N1	1.335 (2)
C5—C5a	1.415 (3)	C4a—C10a	1.430 (3)
C5a—C6	1.410 (3)	C5a—C9a	1.416 (3)
C6—C7	1.369 (3)	C2—N2	1.312 (3)
C7—C8	1.397 (3)	C4—O4	1.217 (2)
C9a—N10—C101—C102	−86.8 (2)	C10a—N10—C101—C102	91.7 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O23^{i}	0.88	2.03	2.855 (2)	156
N2—H2B···O23	0.88	2.11	2.976 (2)	166
N3—H3···O22	0.88	1.92	2.799 (2)	174
C23—H23···O21^{ii}	0.95	2.37	3.299 (3)	164

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

The authors thank the Servicios Técnicos de Investigación of the Universidad de Jaén and the staff for data collection. JC thanks the Consejería de Innovación, Ciencia y Empresa (Junta de Andalucía, Spain) and the Universidad de Jaén for financial support. JT and JQ thank COLCIENCIAS and UNIVALLE (Universidad del Valle, Colombia) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3244). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.

Althuis, T. H., Kadin, S. B., Czuba, L. J., Moore, P. F. & Hess, H. J. (1980). *J. Med. Chem.* **23**, 262–269.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Bieri, J. H., Prewo, R. & Linden, A. (1993). Private communication to the CSD (refcode HACDEU). CCDC, Union Road, Cambridge, England.

Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.

Chua, P., Pierre, F. & Whitten, J. P. (2008). PCT Int. Appl. WO 2008028168.

Duisenberg, A. J. M., Hooft, R. W. W., Schreurs, A. M. M. & Kroon, J. (2000). *J. Appl. Cryst.* **33**, 893–898.

Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.

Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.

Kumar, R. N., Suresh, T. & Mohan, P. S. (2002). *Asian J. Chem.* **14**, 1405–1408.

McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.

Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.

Quiroga, J., Trilleras, J., Insuasty, B., Abonía, R., Nogueras, M., Marchal, A. & Cobo, J. (2008). *Tetrahedron Lett.* **49**, 3257–3259.

Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Weissman, A. & Yang, Y. (2007). PCT Int. Appl. WO 2007146375.