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5-Amino-1-benzyl-4-cyano-3-methylimidazolium toluene-*p*-sulfonate

Raja Dey,[a]* Tapati Banerjee,[b] Vratislav Langer,[c] Sibdas Ray[d] and Priyobroto Roychowdhury[b]

[a]Centre for Structural Biology, Department of Chemical and Biological Engineering, Chalmers University of Technology, Box 462, Gothenburg 40530, Sweden, [b]Department of Physics, University of Calcutta, 92 APC Road, Calcutta 700 009, India, [c]Department of Chemical and Biological Engineering, Division of Materials and Surface Chemistry, Subdivision of Inorganic Environmental Chemistry, Chalmers University of Technology, SE-41296 Gothenburg, Sweden, and [d]Department of Chemistry, University of Calcutta, 92 APC Road, Calcutta 700 009, India

Correspondence e-mail: raja.dey@chembio.chalmers.se

Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.002 Å
R factor = 0.050
wR factor = 0.127
Data-to-parameter ratio = 23.8

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

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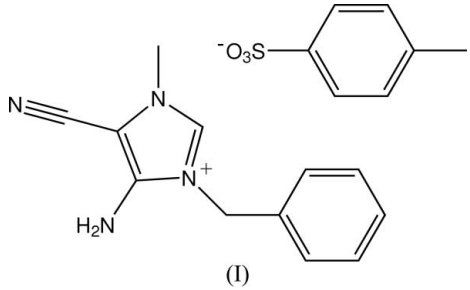
The title compound, $C_{12}H_{13}N_4^+\cdot C_7H_7O_3S^-$, contains an imidazolium cation and a toluene-*p*-sulfonate anion in the asymmetric unit. Hydrogen-bonded dimers are formed between the cyano and amino groups of inversion-related imidazolium cations.

Comment

The most important approach in the treatment of respiratory allergic reactions, such as asthma, is the inhibition of the intracellular cyclic adenosine monophosphate (cAMP) and phosphodiesterase (PDE), leading to an increase of the cAMP level to a physiologically optimum value. Most bronchodilator compounds contain a planar, preferably heterocyclic, nucleus associated with a carbonyl group and a substituent of a basic, neutral or weakly acidic character (Lunt, 1982). Structural analyses of a series of active antihistamines have indicated the presence of a network of intramolecular hydrogen bonds between the amide group and the heterocyclic ring, resulting in the formation of pseudo-planar aromatic systems (Lunt, 1982; Ford *et al.*, 1986). Structural investigations of active anti-allergics, such as chloropheniramine, bromopheniramine, promethazine and others, have indicated the importance of the bulky groups such as diphenylmethylbenzyl and similar bicyclic groups in this class of compounds. In order to study the changes in the geometry of an imidazole ring as a result of its protonation to give an imidazolium cation, we have chosen the 1,3-dialkylimidazolium system as a model. The synthesis of the present compound was undertaken as a part of our research studying differently substituted 5-amino imidazole derivatives as possible PDE inhibitors (Sen *et al.*, 1977).



(I)

The molecular structure of the title complex, (I), is shown in Fig. 1. The C5—N4 bond distance of 1.3458 (18) Å indicates conjugation of the lone pair of electrons of the amino group with the imidazole ring, an observation consistent with the structure of 5-amino-1-(2-chloroethyl)-4-cyanoimidazole, *i.e.* 1.370 (4) Å (Banerjee *et al.*, 1999). The electron-withdrawing effect of the cyano group and the lack of intramolecular

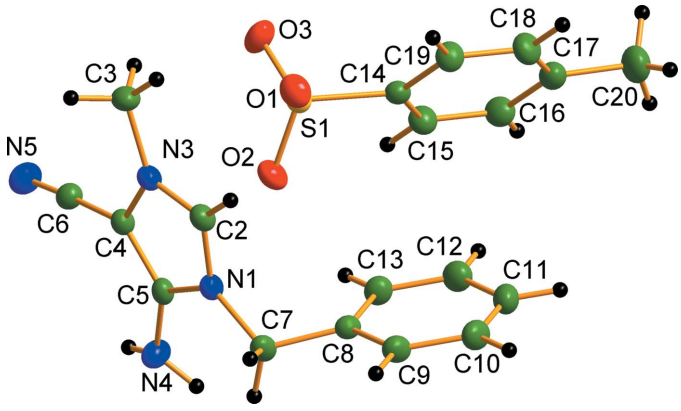


Figure 1
Structure of (I) showing the atomic numbering scheme and 50% probability displacement ellipsoids.

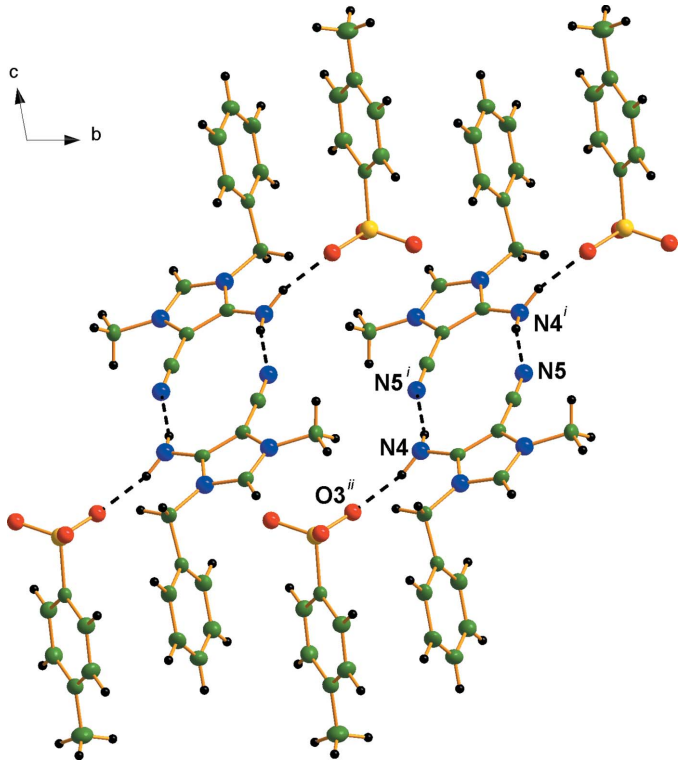


Figure 2
Packing of (I), viewed along the *a* axis, showing the intermolecular hydrogen bonding. C atoms are shown in green, N in blue, O in red, S in yellow and H in black. For symmetry codes see Table 1.

hydrogen bonding in the imidazole group results in a net accumulation of electrons in the 1-benzyl region of the compound. This explains the differences in the bond distances of the imidazole ring from those found in other 5-amino-imidazole-4-carboxamide derivatives (Adamiak & Saenger, 1979; Simon *et al.*, 1980; Allen *et al.*, 1987; Banerjee, Roychowdhury, Chattopadhyay *et al.*, 1991; Banerjee, Roychowdhury, Yamane *et al.*, 1991; Banerjee *et al.*, 1999). The lengthening of the N3—C3 bond distance to 1.4680 (18) Å compared with the Csp^3—N (planar) distance of 1.454 (11) Å (Allen *et al.*, 1987) that is normally observed for such bonds indicates delocalization of π-electron density within the imidazolium ring. However, this delocalization is not uniform; for example, it is clear that the N1—C2 [1.3524 (18) Å] and C2—N3 [1.3161 (18) Å] bonds have greater double bond character than the N1—C5 [1.3805 (17) Å] and N3—C4 [1.4008 (17) Å] bonds. The C4—C5 bond [1.3879 (19) Å] shows reduced double bond character with respect to the corresponding bond distance [1.360 (14) Å] found in imidazole residues (Allen *et al.*, 1987). A similar distribution of bond distances has been found in other 4-cyanoimidazolium compounds (Barni *et al.*, 1997). The pattern of N1—C7 and C7—C8 bonds [*i.e.* 1.4795 (17) Å and 1.5121 (19) Å, respectively] and angles [*i.e.* C8—C7—N1 = 113.2 (1)°] is consistent with the relief of steric strain about atom C7. A similar angle [112.8 (2)°] has been found in the structure of 5-amino-1-diphenylmethylimidazole-4-carboxamide (Banerjee, Roychowdhury, Chattopadhyay *et al.*, 1991). The six-membered ring lies almost perpendicular to the plane of the imidazole ring, the dihedral angle being 89.9 (1)°. The pronounced angular dissymmetry observed in the exocyclic angles at position-C5 [*i.e.* N4—C5—N1 is 124.02 (12) and N4—C5—C4 is 130.04 (13)°] has been attributed to the formation of intramolecular hydrogen bonds between the amino group and the vicinal carboxyamide group (Adamiak & Saenger, 1979; Freeman & Hutchinson, 1979*a*,*b*; Afshar *et al.*, 1987; Banerjee, Roychowdhury, Chattopadhyay *et al.*, 1991). However, this dissymmetry has also been observed in similar amino-substituted heterocyclic nuclei lacking this intramolecular N—H···O hydrogen bond (Banerjee *et al.*, 1999; Lynch, 2001) and therefore appears to be a characteristic feature of hetero-nuclei structures. The cyano group is almost coplanar with the imidazole ring, the dihedral angle being 10.0 (3)°. The molecular geometry of the toluene-*p*-sulfonate group agrees well with that found in the literature (Batsanov *et al.*, 2001; Smith *et al.*, 2004, 2005).

The crystal structure is stabilized by an extensive network of intermolecular hydrogen bonds. Sulfonyl atom O3 is hydrogen bonded to the amino N atom through an N—H···O hydrogen bond; geometric details of the hydrogen bonds are listed in Table 1. The imidazolium rings of the centrosymmetrically related cations form dimers through N4—H41···N5^{i} hydrogen bonds, as may be seen in Fig. 2. The short and straight C2—H2···O2^{iii} non-classical hydrogen bond, presumably strengthened by the local positive charge around atom C2, also plays an important role in stabilizing the crystal structure of (I).

Experimental

The title compound, (I), was synthesized in the Department of Chemistry, University of Calcutta (Sen *et al.*, 1977). Diffraction-quality single crystals were obtained by slow evaporation of an ethanol solution of the compound at room temperature.

Crystal data

$C_{12}H_{13}N_4^+\cdot C_7H_7O_3S^-$
M_r = 384.45
Triclinic, $P\overline{1}$
a = 5.8760 (1) Å
b = 7.5163 (1) Å
c = 21.3393 (2) Å
α = 100.047 (1)°
β = 92.570 (1)°
γ = 93.006 (1)°
V = 925.34 (2) Å^3
Z = 2
D_x = 1.380 Mg m^{-3}
D_m = 1.368 Mg m^{-3}
D_m measured by flotation in a mixture of benzene and bromoform
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
θ = 1.9–32.9°
μ = 0.20 mm^{-1}
T = 173 (2) K
Plate, colorless
0.65 × 0.22 × 0.09 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
T_{min} = 0.879, T_{max} = 0.982
16651 measured reflections
6461 independent reflections
4943 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 32.9°
$h = -8 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = -32 \rightarrow 32$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.127
S = 1.02
6461 reflections
272 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0588P)^2 + 0.3521P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.71 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N4—H41···N5^{i}	0.86 (2)	2.24 (2)	3.0777 (19)	166 (2)
N4—H42···O3^{ii}	0.90 (2)	1.90 (2)	2.7677 (17)	161 (2)
C2—H2···O2^{iii}	0.95	2.02	2.9582 (18)	168
C7—H7*A*···O1^{ii}	0.99	2.36	3.2205 (19)	145
C13—H13···O2	0.95	2.49	3.3588 (18)	151
C19—H19···O1	0.95	2.56	2.9263 (19)	103

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $x, y-1, z$; (iii) $x+1, y, z$.

C-bound H atoms were positioned geometrically, with C—H = 0.95 (aromatic H), 0.99 (methylene H) and 0.98 Å (methyl H), and refined as riding, with individual isotropic displacement parameters. The amino H atoms were located in difference Fourier maps and refined freely (see Table 1 for bond distances).

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *SADABS* (Sheldrick, 2002); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXTL*.

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