

## The C—H···O hydrogen bond in (dicyanomethyl)ammonium *p*-toluenesulfonate

Thomas Steiner

Institut für Chemie – Kristallographie, Freie Universität Berlin, Takustraße 6, D-14195 Berlin, Germany

Correspondence e-mail: steiner@chemie.fu-berlin.de

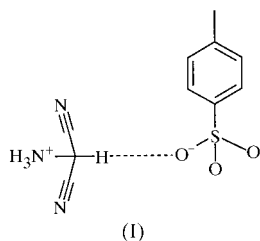
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In the title compound,  $C_3H_4N_3^+ \cdot C_7H_7O_3S^-$ , the activated C—H group of the cation forms a short but bent C—H···O hydrogen bond with a sulfonate O atom of the anion; C···O = 3.075 (5) Å and C—H···O = 130°.

### Comment

C—H···O hydrogen bonds are known to have a very wide range of geometries and strengths. With highly polar C—H groups, such as in  $CHCl_3$ ,  $C\equiv C-H$ ,  $CH(NO_2)_3$  etc., C—H···O interactions may have similar geometries to conventional O/N—H···O hydrogen bonds. On the other hand, with weakly polar methyl groups, C—H···O interactions have long contact distances and are only slightly directional. All intermediate situations exist between these extremes (see, e.g., Steiner, 1997; Steiner & Desiraju, 1998; Desiraju & Steiner, 1999). When studying the stronger kinds of C—H···O interactions, methyl groups which carry two or even three strongly electron-withdrawing substituents are of interest (Pedireddi & Desiraju, 1992). In this context, the (dicyanomethyl)-ammonium cation is of obvious interest. In the *p*-toluenesulfonate salt, (I), formation of a short C—H···O hydrogen bond may be expected.



In the crystal structure of (I), the three ammonium H atoms form N—H···O hydrogen bonds with the sulfonate group (Table 2). As expected, the activated C—H group of the cation also interacts with a sulfonate O atom (Fig. 1). The C···O distance is very short at 3.075 (5) Å, but the geometry is strongly bent. Based on a normalized H-atom position (C—H = 1.08 Å), the H···O distance is 2.27 Å and the C—

H···O angle is 130°. When compared to the shortest C—H···O interactions known, which have H···O distances around and below 2.0 Å (e.g. Bock *et al.*, 1993; Kariuki *et al.*, 1997), this may not appear to be so short. However, upon closer examination, it is seen that the C—H donor is involved in two additional intermolecular interactions with hydrogen-bond geometry, but both have substantially longer distances (Table 2). The crystal packing as a whole is shown in Fig. 2 to illustrate the typical segregation of polar and apolar groups in the lattice. An important factor responsible for the poor C—H···O angle might be the competition between C—H and the neighbouring ammonium group for acceptors. The ammonium group certainly plays the more dominant role in determining intermolecular geometries, and optimizing N—H···O geometries might prevent the C—H···O angle from being linear.

To see how the C—H···O hydrogen bond in (I) compares with related interactions of dicyanomethyl C—H donors, a database search was performed (Cambridge Structural Database, version 5.20; Allen & Kennard, 1993). In the 15 relevant crystal structures found, the shortest occurring (C—)H···O distance is 2.12 Å (in a crown-ether complex of dicyanomethane; Grootenhuys *et al.*, 1986), with more typical values being greater than 2.2 Å. This indicates that  $(CN)_2C-H$  is a good hydrogen-bond donor in general, but clearly falls behind the classical strong C—H donors like  $CHCl_3$  and  $C\equiv C-H$ .

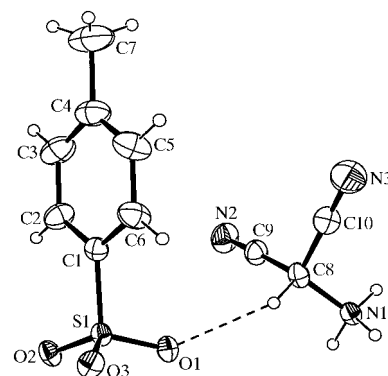


Figure 1

The molecular structure of (I) with displacement ellipsoids drawn at the 30% probability level.

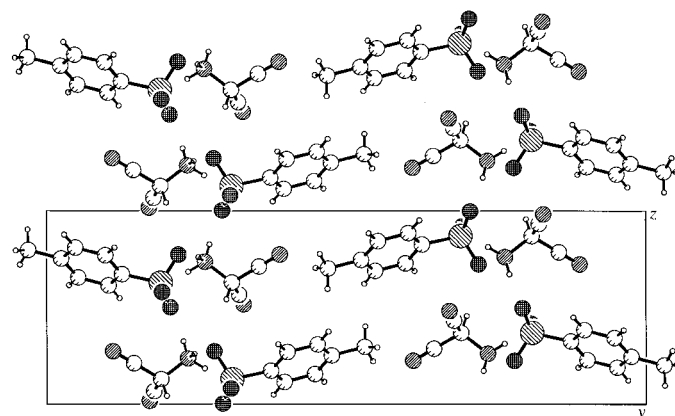


Figure 2

The crystal packing shown in a projection on the *yz* plane.

Experimental

Compound (I) was obtained from Lancaster Synthesis and was recrystallized from MeOH by slow evaporation of the solvent.

Crystal data

$C_3H_4N_3^+ \cdot C_7H_7O_3S^-$	$D_x = 1.384 \text{ Mg m}^{-3}$
$M_r = 253.28$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
$a = 5.604 (9) \text{ \AA}$	$\theta = 8.2\text{--}14.9^\circ$
$b = 25.90 (5) \text{ \AA}$	$\mu = 0.27 \text{ mm}^{-1}$
$c = 8.427 (12) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 96.40 (14)^\circ$	Plate, colourless
$V = 1216 (4) \text{ \AA}^3$	$0.80 \times 0.30 \times 0.05 \text{ mm}$
$Z = 4$	

Data collection

Stoe four-circle diffractometer	$h = -7 \rightarrow 4$
$\omega$ scans	$k = -25 \rightarrow 33$
3001 measured reflections	$l = -10 \rightarrow 10$
2660 independent reflections	3 standard reflections
2162 reflections with $I > 2\sigma(I)$	frequency: 90 min
$R_{int} = 0.019$	intensity decay: 3%
$\theta_{max} = 27.0^\circ$	

Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0656P)^2 + 0.4531P]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.126$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.03$	$\Delta\rho_{max} = 0.45 \text{ e \AA}^{-3}$
2660 reflections	$\Delta\rho_{min} = -0.39 \text{ e \AA}^{-3}$
171 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

N1—C8	1.473 (4)	C8—C10	1.469 (4)
N2—C9	1.127 (4)	C8—C9	1.473 (4)
N3—C10	1.120 (4)		
C10—C8—C9	110.3 (2)	C9—C8—N1	109.7 (2)
C10—C8—N1	111.1 (2)		

H atoms bonded to C atoms of the anion were treated in the default riding model with  $U_{eq}$  values allowed to vary. The H atoms of the cation were located in difference Fourier calculations and refined isotropically [ $U_{eq}$  values: H(N1) = 0.043–0.057 and H(C8) = 0.040  $\text{\AA}^2$ ].

Table 2

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1A $\cdots$ O2 <sup>i</sup>	0.91 (3)	1.84 (3)	2.741 (4)	175 (2)
N1—H1B $\cdots$ O3 <sup>ii</sup>	0.93 (3)	1.78 (3)	2.701 (4)	168 (2)
N1—H1C $\cdots$ O1 <sup>iii</sup>	0.92 (3)	1.87 (3)	2.778 (5)	167 (3)
C8—H8 $\cdots$ O1	0.95 (3)	2.35 (2)	3.075 (5)	132.3 (19)
C8—H8 $\cdots$ O2 <sup>iii</sup>	0.95 (3)	2.73 (2)	3.373 (5)	125.8 (17)
C8—H8 $\cdots$ N2 <sup>iv</sup>	0.95 (3)	2.78 (3)	3.409 (6)	124.2 (17)

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

Data collection: Stoe diffractometer software; cell refinement: Stoe diffractometer software; data reduction: Stoe diffractometer software; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1169). Services for accessing these data are described at the back of the journal.

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