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Synthesis and Crystal Structure of 1,3-Dimethyl Benzotriazolium Trifluoromethane Sulfonate

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The isolation of stable carbenes of the Arduengo (**1a**) and Wanzlick (**2a**) type has prompted us to look for stable nitrenium ions of the related structural type 1,3-dimethyl benzotriazolium trifluoromethane sulfonate (**3**$^+$). The title compound was isolated and structure was characterized by X-ray methods.

Keywords: Crystal structure; carbenes; sulfonate

INTRODUCTION

Nitrenium ions R_2N^+: containing a cationic divalent nitrogen atom, are isoelectronic with carbenes R_2C:. Nitrenium ions are involved as highly reactive intermediates in a wide variety of organic reactions [1–4]. For example, when substituted with aromatic groups, nitrenium ions are postulated to be the ultimate carcinogens in the carcinogenesis initiated by aromatic amines [5]. Recent time-resolved UV and IR spectral studies of some short lived aryl nitrenium ions provide important results on their structure and reactivity. Although, electronically different molecules of the type mentioned above are usually extremely short lived, Arduengo et al. [6] and others [7], following the initial work of Wanzlick et al. [8], recently isolated and structurally characterized stable crystalline carbenes (**1a** and **2a**), opening the route for a rich coordination chemistry [7]. We

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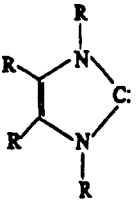
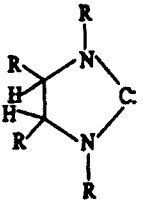
have earlier synthesized [9] and characterized some stable crystals of structurally related nitrenium ions or more precisely, ion pairs of nitrenium, but not of the type $\mathbf{3}^{+}$. The difference between the present molecule and 1,3-dimethyl benzotriazolium iodide [9] is the counter ion which comprises of a group of atoms rather than a single atom (I-). The study was undertaken to understand the chemistry and reactions of nitrenium ions with metal ions and/or nucleophiles to know the reactivity, and to get an insight into its implications in carcinogenesis. The title compound $\mathbf{3}^{+}$was synthesized as per **Scheme-1** and characterized by X-ray studies. Further, by carrying out the reactions of the title compound ($\mathbf{3}^{+}$), information regarding the nature of the reactive intermediates in carcinogenesis will be obtained.

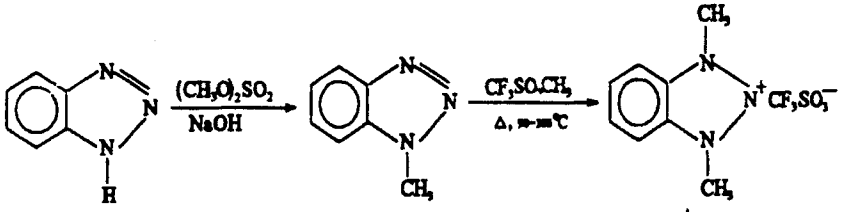


1a



2a

Stable carbenes of the Arduengo (1a) and Warnfick (2a) type



1 Benzotriazole

2 Methylbenzotriazole

3^{+} 1,3-Dimethylbenzotriazole trifluoromethane sulphonate

SCHEME 1

SYNTHESIS AND X-RAY STUDIES OF 3^+

Synthesis of methylbenzotriazol(2)

70 ml of 2 M Sodium hydroxide was added to 9 gm of Benzotriazol (**1**) while stirring, then 10 gm (7.2 ml) of dimethyl sulfate was added, stirred for 15 minutes (at room temperature) and then the temperature was raised to approximately 80°C with continuous stirring for half an hour. The solution was cooled and the organic layer was separated with ether. The combined ether solution was treated with approximately 5–10 ml of ammonia solution and again the ether layer was separated. The ether layer was dried with $MgSO_4$, rotavap off ether and the crystalline solid(**2**) was collected by filtration. The other product was discarded. The melting point was 63°C.

Synthesis of 1,3-dimethylbenzotriozoulium trifluoromethane sulfonate(3^+)

2 gm of (7.5 m.mol) of 1-Methyl-benzotriazol (**2**) was added to 3.4 ml (4.93 gm, 30 m.mol) of trifluoromethane sulfonate and heated to 90–100°C. The compound completely dissolved at approximately 90–100°C resulting in a light brown coloured solution. On cooling this solution to a temperature below 40°C, the crystalline solid appeared. It was filtered by vacuum filtration, and the product ($\mathbf{3^+}$) was recrystallised in ethanol. The yield was 1.5 gm (70%) and melting point was 122–123°C.

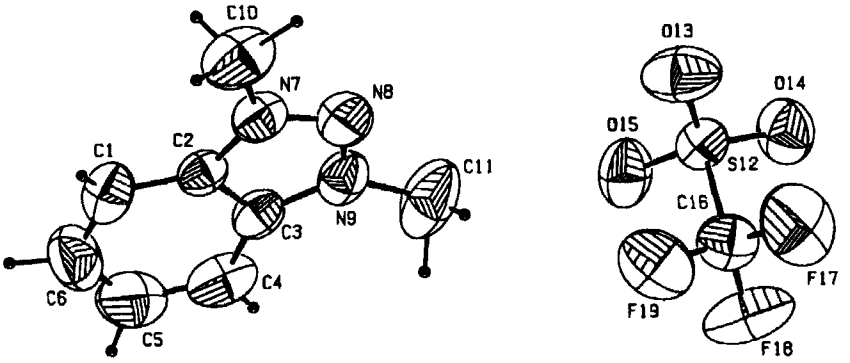


FIGURE 1 ORTEP of the molecule at 50% probability

TABLE I Experimental Details

Empirical formula	$C_9H_{10}F_3N_3O_3S$
Formula weight	297.26
Temperature	293(2)°K
Wavelength	0.71069Å
Crystal system, Space group	Monoclinic, $P2_1/c$(#14)
Cell dimensions	a = 6.864(2) Å
	b = 11.319(2) Å
	c = 16.557(3) Å
	β = 91.253(19)°
Volume	1285.9(5)Å^3
Z, $\rho_{(cal)}$	4, 1.535 Mg/m^3
μ(Mo$K\alpha$)	0.296 mm^{-1}
F_{000}	608
Crystal size	0.3 × 0.2 × 0.15 mm
Theta range for data collection	2.18° to 24.99°
Index ranges	$0 \le h \le 8$
	$0 \le k \le 13$
	$-19 \le l \le 19$
Reflections collected/unique	1836/1836
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1836 / 0 / 203
Goodness-of-fit on F^2	1.060
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0615, $wR2$ = 0.1917
R indices (all data)	$R1$ = 0.0801, $wR2$ = 0.2144
Extinction coefficient	0.021(6)
Largest diff. peak and hole	0.323 and –0.375 e.Å^{-3}

Characterisation

^{1}NMR=(300 MHz, DMSO-d6): δ =4.61(S,6H, (-CH_3)$_2$; 8.36–7.96 (2 m, 4H-aromatic) ^{13}C NMR=(75.5 MHz, DMSO-d6); δ = 37.5 (Methyl) 113.76, 130.6, 134.9 C H N (MW: 297.0) Theoretical: C 36.36%, H 3.37%, N 14.14% Observed: 36.68 3.56 14.52.

RESULTS AND DISCUSSION

X-ray crystal structure studies of **3**$^+$: Table I contains the details of crystal data, data collection and refinement. The final coordinates with equivalent isotropic temperature factors for all atoms are given in Table II. Tables III and 4 give the bond distances and angles of non-hydrogen atoms. Figure 1 represents the

ORTEP [10] diagram of the molecule with thermal ellipsoids at 50% probability. Figure 2 represents the packing of the molecules down a-axis.

TABLE II Fractional coordinates and equivalent thermal parameters of the non-hydrogen atoms

Atom	x	y	z	U_{eq} (Å^2)
C1	−0.7906(7)	1.1497(4)	0.1946(3)	0.0714(13)
C2	−0.6333(5)	1.0722(3)	0.1996(2)	0.0499(9)
C3	−0.4943(6)	1.0684(4)	0.1415(2)	0.0547(10)
C4	−0.5049(9)	1.1429(5)	0.0732(3)	0.0763(15)
C5	−0.6598(11)	1.2154(5)	0.0690(4)	0.0910(18)
C6	−0.7990(10)	1.2196(5)	0.1272(4)	0.0887(17)
N7	−0.5782(6)	0.9894(3)	0.2542(2)	0.0624(10)
N8	−0.4160(6)	0.9358(3)	0.2347(2)	0.0727(11)
N9	−0.3655(5)	0.9844(3)	0.1666(2)	0.0641(10)
C10	−0.6760(11)	0.9521(6)	0.3273(3)	0.0930(19)
C11	−0.1897(9)	0.9426(8)	0.1266(6)	0.117(3)
S12	0.28709(14)	0.72922(9)	0.13380(6)	0.0570(5)
O13	0.2161(6)	0.7045(4)	0.2121(2)	0.0985(13)
O14	0.4854(4)	0.6982(3)	0.1210(2)	0.0822(10)
O15	0.2318(4)	0.8410(3)	0.1022(2)	0.0826(10)
C16	0.1525(7)	0.6276(4)	0.0699(3)	0.0710(13)
F17	0.1829(6)	0.5167(3)	0.0932(2)	0.1292(15)
F18	0.1980(6)	0.6373(3)	−0.00641(18)	0.1216(13)
F19	−0.0391(4)	0.6445(3)	0.0737(2)	0.1050(11)

Hydrogen bonds and cation-anion interactions are prominent in the packing so as to minimize the total energy. Packing of molecules down a-axis shows stacking. The cationic part of the molecule is completely planar. Also phenyl and five membered rings are independently planar.

The crystal structure shows that the anion $CF_3SO_3^-$ is not directly connected to the positively charged part of the cation. $CF_3SO_3^-$ holds cation by means of C-H···O hydrogen bond [11]. The intermolecular hydrogen bond between atoms C10-H10C···O14 has length 3.187(8)Å and angle 135° with symmetry code $-x$, $0.5+y$, $0.5-z$ (C10-H10C = 0.89Å, H10C-O14 = 2.50(7)Å). These bonds are shown as dashed lines in the packing diagram (Figure 2).

The bond distances and bond angles compare well with those of 1,3-dimethyl benzotriazolium iodide. The counter ion in the present structure, in spite of being a group of atoms, does not play a significant role on the geometry of the

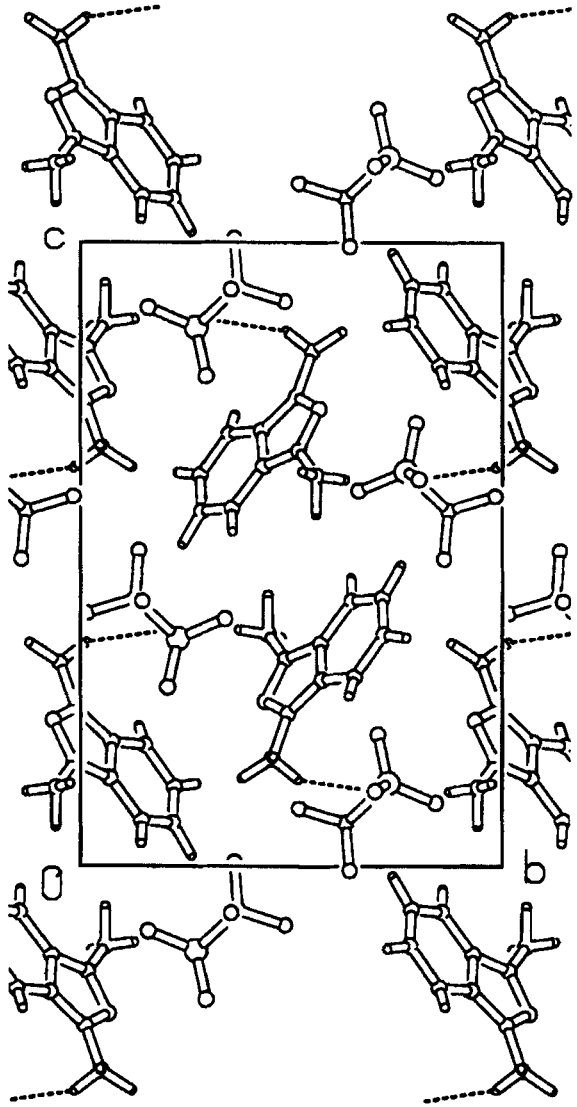


FIGURE 2 Packing of molecules down *a* axis. Dashed lines represent the hydrogen bonds

nitrenium ions. However it has some effect on the N7-C2 bond due to the presence of the hydrogen bond between the counter ion and the carbon atom attached to N7. The title compound is saturated and highly stable for crystal structure studies.

TABLE III Bond Lengths (Å)

Atoms	*Length*	*Atoms*	*Length*
C1-C6	1.368(8)	N8-N9	1.308(5)
C1-C2	1.392(6)	N9-C11	1.467(7)
C2-N7	1.350(5)	S12-O15	1.418(3)
C2-C3	1.371(5)	S12-O13	1.422(4)
C3-N9	1.357(5)	S12-O14	1.426(3)
C3-C4	1.411(6)	S12-C16	1.803(5)
C4-C5	1.344(8)	C16-F18	1.313(5)
C5-C6	1.373(9)	C16-F17	1.328(5)
N7-N8	1.314(5)	C16-F19	1.332(5)
N7-C10	1.460(6)		

TABLE IV Bond Angles (°)

Atoms	*Angle*	*Atoms*	*Angle*
C6-C1-C2	115.6(5)	N8-N9-C11	119.3(6)
N7-C2-C3	105.0(3)	C3-N9-C11	128.6(6)
N7-C2-C1	133.1(4)	O15-S12-O13	114.7(2)
C3-C2-C1	121.9(4)	O15-S12-O14	114.4(2)
N9-C3-C2	105.4(4)	O13-S12-O14	115.7(2)
N9-C3-C4	133.3(4)	O15-S12-C16	102.9(2)
C2-C3-C4	121.3(4)	O13-S12-C16	103.2(2)
C5-C4-C3	115.7(5)	O14-S12-C16	103.5(2)
C4-C5-C6	123.1(5)	F18-C16-F17	108.6(4)
C1-C6-C5	122.4(5)	F18-C16-F19	106.8(4)
N8-N7-C2	112.5(3)	F17-C16-F19	105.7(4)
N8-N7-C10	118.5(5)	F18-C16-S12	112.4(3)
C2-N7-C10	128.9(4)	F17-C16-S12	111.0(3)
N9-N8-N7	105.1(4)	F19-C16-S12	112.0(3)
N8-N9-C3	112.0(3)		

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