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SYNTHESIS AND CRYSTAL STRUCTURE OF 1-METHYL-3-(4-NITROPHENYL)-1,2,3 TRIAZOLIUM PERCHLORATE

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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-methyl-3-(4-nitrophenyl)-1,2,3 triazolium perchlorate (**6**). The title compound ($C_9\ H_{11}\ Cl\ N_4\ O_6$) was isolated and structure was investigated by X-ray crystallography. It crystallizes in the monoclinic space group $P2_1/c$ with cell parameters $a = 9.704(1)$ Å, $b = 12.580(2)$ Å, $c = 13.684(8)$ Å, $Z = 4$. The molecules appear to be stacked.*

Keywords: nitrenium ions; carbenes; triazolium perchlorates; crystal structure

INTRODUCTION

Nitrenium ions are involved as highly reactive intermediates in a wide variety of organic reaction [1]. For example, aromatic nitrenium ion (Figure 1) with $R_1 =$ aryl, $R_2 = H$ or C(O), CH_3, or SO_3 are considered as ultimate carcinogens in carcenogenesis initiated by aromatic amines [2]. Nitrenium ions are isoelectronic with carbenes R_2C containing a cationic [3] divalent nitrogen atom R_2N^+. Recent time-resolved studies allowed the UV and IR spectra of some short-lived aryl nitrenium ions to be measured and

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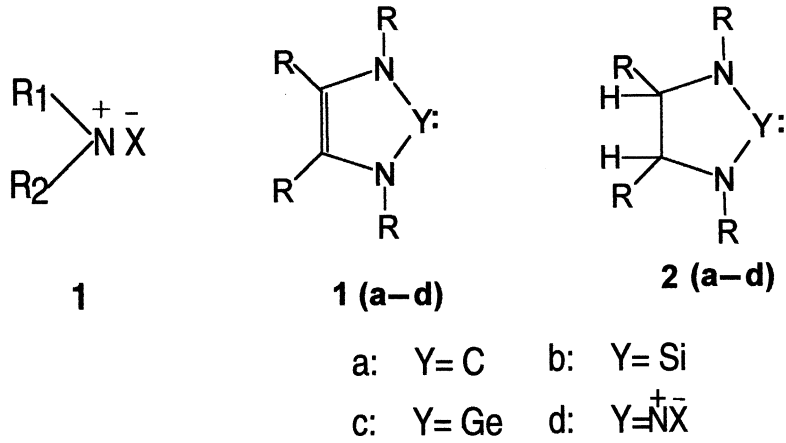


FIGURE 1 Stable carbene of the Arduengo (**1a**) and Wanzlick (**2a**) type.

provided important results on their structure and reactivity [4]. Although electronically deficient molecules of the types mentioned above are extremely short-lived, Arduengo [5(a)] and Wanzlick [5(b)] et al. recently isolated and structurally characterized stable crystalline carbenes (Figure 1) concomitantly. Stable crystals of nitrenium ions more precisely, ion pair of nitrenium ions were synthesized and their crystal structures were determined [6]. From experimental data and theoretical calculations it emerged that these molecules are stabilized by electronic delocalization [7]. Intramolecular rearrangement reaction of nitrenium ions have been reported and established as useful intermediates in wide variety of biological applications [8].

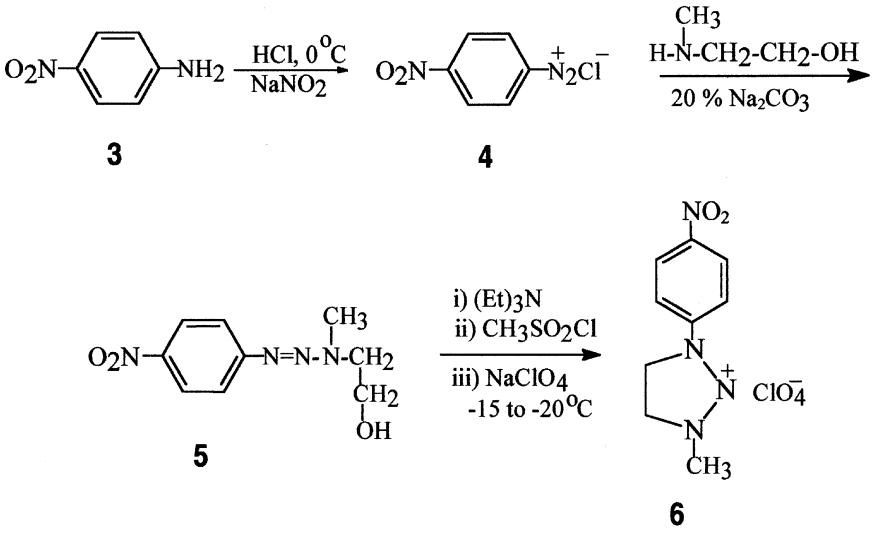
In our previous work, we described the synthesis of some stable nitrenium ions [6] and their comparison study with structurally related carbenes and found that stable nitrenium ions (as their carbene analogues) are electronically different from nonstable ones. To get further insight into their exact nature and role of nitrenium ions, the title compound **6** was synthesised as per Scheme 1 and characterized by X-ray diffraction method.

EXPERIMENTAL

Synthesis and Characterization

3-(2-hydroxyethyl)-3-methyl-1-(4-nitrophenyl)triazene (5)

The preparation of **5** was by diazotization of 4-nitroaniline (10 gm, 0.0724 mol). First, 4-nitroaniline was dissolved in 23 ml of concentrated



SCHEME 1

hydrochloric acid and 23 ml of water and cooled to 0–5°C in an ice bath. Then we added sodium nitrite (7.4 gm, 0.0724 mol) in 16 ml of water to this cold solution. The diazonium salt solution **4** was mixed with a cold solution of 2-(methylamino)ethanol (5.42 gm, 0.0724 mol) in 25 ml of Na_2CO_3 solution (25%). The mixture was stirred for half an hour at 0–5°C, and triazene **5** was extracted with ether and dried with anhydrous sodium sulphate and evaporated the solvent. The product was obtained as red oil to yield (54.4%).

^{1}H NMR ($CDCl_3$, 400 MHz); δ(ppm): 3.38 (s, 4H, N–CH_3 and OH), 3.86–3.93 (m, 4H, CH_2–CH_2), 7.74 (d, 2H, Ar–H), 7.92 (d, 2H, Ar–H); ^{13}C NMR ($CDCl_3$, 100 MHz); δ(ppm): 49.9, 55.8, 62.8, 128.9, 130.8, 136.2, 145.8; IR (Nujol); ν_{max} (cm^{-1}): 3429 (OH), 1548 (C–N). 1619 (C=C), Ana. Calcd. for $C_9H_{12}N_4O_3$: C, 48.21; H, 5.35; N, 25.01. Found: C, 48.32, H. 5.39, N, 25.22.

1-methyl-3-(4-nitrophenyl)-1,2,3 triazolium perchlorate (6)

Triazene **5**(1 gm, 4.46 mmol) was dissolved in dry dichloromethane and cooled to −15 to −10°C. Triethylamine (0.450 gm, 4.46 mmol) was mixed with triazene cold solution. Methyl-sulfonyl chloride (0.364 gm, 4.46 mmol) in 0.9 ml of dry dichloromethane was added to a cold triazene solution without raising the temperature above 5°C. The reaction mixture was stirred for 40–50 min at the same temperature. We distilled out the solvent under reduced pressure up to residueness. The residue was washed with benzene and dissolved in ethanol. To the ethanolic solution aqueous solution of $NaClO_4$ (2 gm of $NaClO_4$ in 30 ml of water) was added. The product

was filtered off and followed by recrystallization with aqueous ethanol(1:1) to yield as yellow crystalline solid (72%). The melting point (mp) of **6** was found to be 159°C.

^{1}H NMR (DMSO-d_6, 400 MHz); δ(ppm): 3.88 (s, 3H, N–CH_3), 4.61 (t, 2H, CH_2–CH_2), 4.83 (t, 2H, CH_2–CH_2), 7.59 (d, 2H, Ar–H), 7.89 (d, 2H, Ar–H); ^{13}C NMR (DMSO-d_6, 100 MHz); δ(ppm): 45.2, 51.5, 56.3, 119.7, 120.9, 132.9, 135.8; IR (KBr); ν_{max}(cm^{-1}): 1489, 1506 (C–N), 1099 (N–N–N). Ana. Calcd. for $C_9H_{11}N_4O_6Cl$: C, 35.24; H, 3.60; N, 18.27. Found: C, 35.62; H, 3.79; N, 18.76.

CRYSTAL STRUCTURE DETERMINATION

Single crystal of dimensions $0.25 \times 0.2 \times 0.25$ mm was chosen for X-ray diffraction studies. The measurements were made on a DIPLabo Imaging

TABLE 1 Crystal Data and Experimental Crystallographic Details of **6**

Empirical formula	$C_9\ H_{11}\ Cl\ N_4\ O_6$
Formula weight	306.67
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinc
Space group	$P2_1/c$
Cell dimensions	$a = 9.704(1)$ Å
	$b = 12.580(2)$ Å
	$c = 13.684(8)$ Å
	$\beta = 129.393(8)°$
Volume	1291.0(3) Å^3
Z	4
Density (calculated)	1.578 Mg/m^3
Absorption coefficient	0.329 mm^{-1}
F_{000}	632
Crystal color	brown
Crystal size	$0.25 \times 0.2 \times 0.25$ mm
Theta range for data collection	2.52° to 24.40°
Index ranges	$-11 \le h \le 11$
	$-14 \le k \le 14$
	$-15 \le l \le 15$
Reflections collected	3676
Independent reflections	2043 [R(int) = 0.0251]
Refinement method	Full-matrix least-squares on F^2
Data/parameters	2043/182
Goodness-of-fit on F^2	1.100
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0854$
R indices (all data)	$R1 = 0.0989$
Extinction coefficient	0.003(4)
Largest diff. peak and hole	0.968 and −0.924 e.Å^{-3}

TABLE 2 Atomic Coordinates and Equivalent Thermal Parameters of the Nonhydrogen Atoms

Atom	x	y	z	U_{eq}
Cl1	0.176(2)	0.2183(1)	0.1880(2)	0.0565(6)
N14	0.8103(5)	0.1273(3)	0.2184(3)	0.0402(10)
C10	0.6008(7)	0.2692(4)	0.0904(5)	0.0498(13)
C11	0.7170(6)	0.2189(4)	0.2066(4)	0.397(11)
N15	0.7553(5)	0.0723(3)	0.1190(4)	0.0441(10)
N7	0.4195(6)	0.4786(4)	0.1727(5)	0.557(12)
N16	0.8568(6)	−0.0065(3)	0.1515(4)	0.0482(11)
C8	0.5296(6)	0.3915(4)	0.1853(5)	0.0448(12)
C13	0.6500(7)	0.3428(4)	0.3021(5)	0.0494(13)
C9	0.5053(7)	0.3567(4)	0.0800(5)	0.0513(13)
C18	0.9652(7)	0.0794(4)	0.3372(5)	0.0481(12)
O6	0.3130(6)	0.5204(3)	0.0690(4)	0.0743(13)
C12	0.7444(7)	0.2570(4)	0.3122(5)	0.0500(13)
C19	0.8317(9)	−0.0784(5)	0.0583(5)	0.0703(18)
C17	1.0107(7)	−0.0099(4)	0.2879(5)	0.0525(13)
O5	0.4384(6)	0.5052(4)	0.2663(4)	0.0745(13)
O1	0.1703(9)	0.2883(6)	0.1052(5)	0.134(3)
O3	0.015(13)	0.185(16)	0.1251(11)	0.364(13)
O4	0.211(2)	0.263(10)	0.2873(8)	0.299(9)
O2	0.288(2)	0.139(10)	0.2327(12)	0.244(7)

TABLE 3 Anisotropic Thermal Parameters of the Nonhydrogen Atoms

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl1	0.060(9)	0.066(10)	0.050(9)	0.004(6)	0.0382(8)	0.0037(6)
N14	0.037(2)	0.045(2)	0.038(2)	0.0021(17)	0.0237(18)	0.0014(17)
C10	0.049(3)	0.062(3)	0.037(3)	0.010(2)	0.027(2)	0.02(2)
C11	0.035(2)	0.041(3)	0.044(3)	−0.0025(19)	0.026(2)	−0.0025(19)
N15	0.045(2)	0.046(2)	0.041(2)	0.0020(18)	0.273(19)	0.0018(17)
N7	0.042(2)	0.054(3)	0.059(3)	0.000(2)	0.026(2)	−0.009(2)
N16	0.054(2)	0.048(2)	0.042(2)	0.008(2)	0.031(2)	0.0040(18)
C8	0.037(2)	0.042(3)	0.050(3)	−0.002(2)	0.025(2)	−0.005(2)
C13	0.049(3)	0.053(3)	0.044(3)	−0.002(2)	0.029(2)	−0.008(2)
C9	0.045(3)	0.057(3)	0.039(3)	0.013(2)	0.020(2)	0.006(2)
C18	0.044(3)	0.054(3)	0.039(3)	0.005(2)	0.023(2)	0.005(2)
O6	0.060(3)	0.070(3)	0.062(3)	0.023(2)	0.025(2)	0.000(2)
C12	0.053(3)	0.050(3)	0.039(3)	0.004(2)	0.025(2)	0.002(2)
C19	0.095(5)	0.056(3)	0.054(4)	0.018(3)	0.044(3)	−0.001(3)
C17	0.049(3)	0.048(3)	0.047(3)	0.005(2)	0.024(2)	0.004(2)
O5	0.073(3)	0.079(3)	0.069(3)	0.013(2)	0.044(2)	−0.016(2)
O1	0.108(5)	0.167(6)	0.079(4)	−0.052(4)	0.037(3)	0.0414(4)
O3	0.116(7)	0.63(3)	0.195(10)	−0.139(12)	0.026(6)	0.211(14)
O4	0.51(2)	0.237(12)	0.099(6)	0.204(13)	0.165(10)	0.031(6)
O2	0.346(16)	0.237(11)	0.266(12)	0.220(12)	0.249(13)	0.154(10)

TABLE 4 Bond Lengths (Å) and Bond Angles (°)

Atoms	Length	Atoms	Length
Cl1-O3	1.280(8)	N15-N16	1.263(6)
Cl1-O4	1.300(7)	N7-O5	1.220(6)
Cl1-O2	1.306(8)	N7-O6	1.222(6)
Cl1-O1	1.370(5)	N7-C8	1.462(7)
N14-N15	1.301(5)	N16-C19	1.453(7)
N14-C11	1.410(6)	N16-C17	1.475(7)
N14-C18	1.471(6)	C8-C9	1.377(7)
C10-C11	1.387(7)	C8-C13	1.387(7)
C10-C9	1.387(7)	C13-C12	1.365(7)
C11-C12	1.379(7)	C18-C17	1.513(7)
Atoms	**Angle**	**Atoms**	**Angle**
O3-Cl1-O4	104.0(2)	O5-N7-O6	123.6(5)
O3-Cl1-O2	111.4(2)	O5-N7-C8	118.0(5)
O4-Cl1-O2	104.7(7)	O6-N7-C8	118.4(5)
O3-Cl1-O1	104.0(5)	N15-N16-C19	121.3(4)
O4-Cl1-O1	116.9(8)	N15-N16-C17	113.9(4)
O2-Cl1-O1	115.4	C19-N16-C17	124.3(4)
N15-N14-C11	120.5(4)	C9-C8-C13	121.6(5)
N15-N14-C18	113.1(4)	C9-C8-N7	119.2(4)
Cl1-N14-C18	126.3(4)	C13-C8-N7	119.1(5)
Cl1-C10-C9	119.0(5)	C12-C13-C8	119.2(5)
C12-C11-C10	121.2(5)	C8-C9-C10	119.1(5)
C12-C11-N14	118.8(4)	N14-C18-C17	101.2(4)
C10-C11-N14	120.0(4)	C13-C12-C11	119.9(5)
N16-N15-N14	109.7(4)	N16-C17-C18	101.2(4)

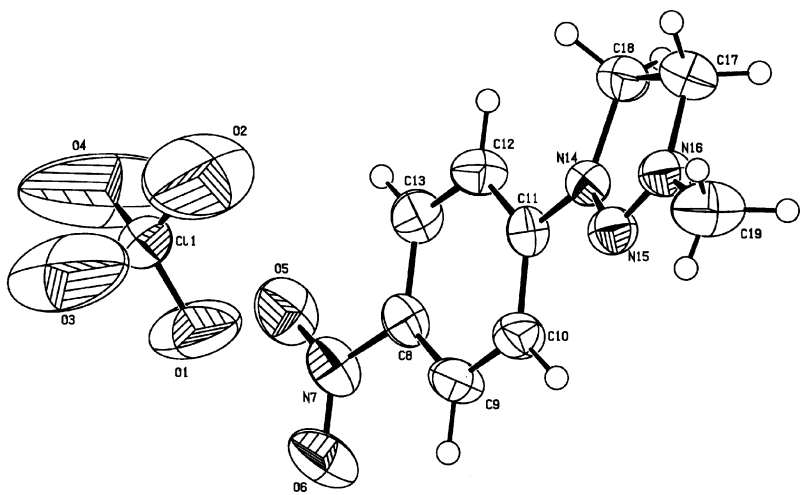


FIGURE 2 ORTEP of the molecule at 50% probability.

Plate system with graphite monochromated MoK_α radiation. Thirty six frames of data were collected using oscillation method. Image processing and data reduction were done by using Denzo [12]. The structure was solved and refined using maXus [10–14] program. All the nonhydrogen atoms were revealed in the first map. Full-matrix least-squares refinement using SHELXL-97 [14] with isotropic temperature factors for all the atoms converged residual to $R = 0.1864$. Refinement of nonhydrogen atoms with anistropic thermal parameters was started at this stage. After eight cycles of refinement the residuals saturated at $R = 0.0854$. The hydrogen atoms were placed at calculated positions and were not refined. Table 1 gives the details of crystal data, data collection, and refinement.

RESULTS AND DISCUSSION

The final positional coordinates with equivalent isotropic temperature factors for all nonhydrogen atoms are given in Table 2. Anisotropic thermal

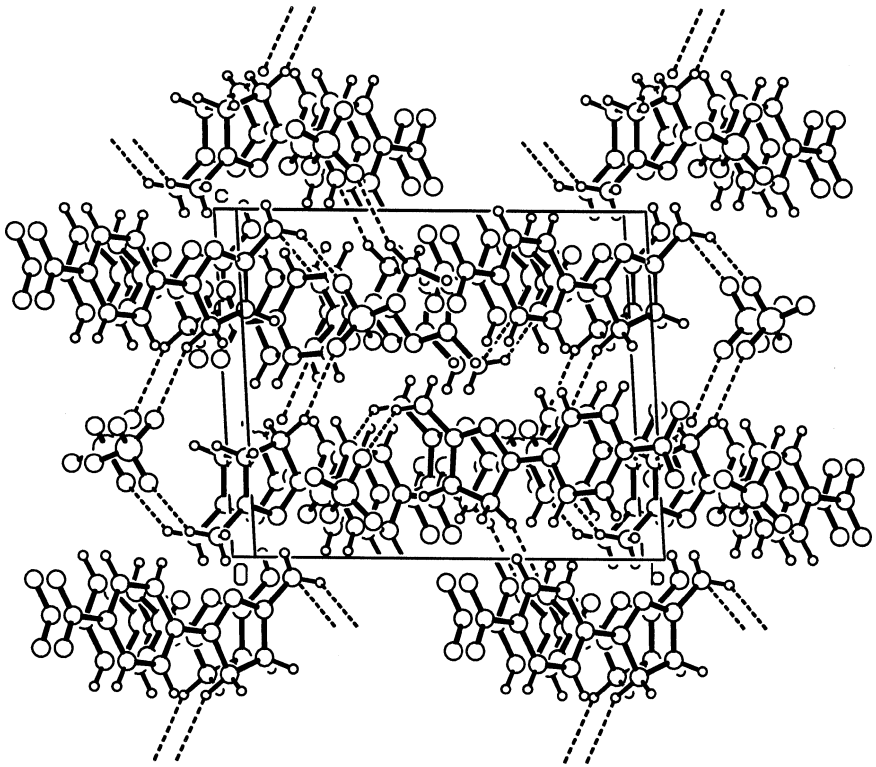


FIGURE 3 Packing of the molecules down *a* axis.

parameter (U_{ij}) for the nonhydrogen atoms are listed in Table 3. Table 4 gives the bond distances and angles of nonhydrogen atoms. The bond distances and bond angles are in good agreement with the standard values.

ORTEP [11] of the molecule at 50% probability is shown in Figure 2. Figure 3 represents the packing of the molecules and dashed lines represent the hydrogen bonds. It shows stacking of molecules in pairs when viewed down a axis. The crystal structure shows that the anion ClO_4^- is not directly connected to the positively charged part of the respective nitrenium ion. ClO_4^- holds cation by means of C–H $\cdots$ ClO_4^- hydrogen bonds [15,16] and their intermolecular interactions appear to be responsible for molecular cohesion in the unit cell. The cationic part of the niternium ion is planar, and phenyl and five-membered rings are independently planar. The intermolecular hydrogen bonds are: C18-H12B . . . O1 (3.336 Å, 127.65°) and C19-H15A . . . O4 (3.119 Å, 131.20°) with symmetry codes $1+x$, $1/2-y$, $1/2+z$ and $1-x$, $-1/2+y$, $1/2-z$, respectively.

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