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Structural and electrochemical characterization of 1,3-bis-(4-methylphenyl)imidazolium chloride

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The structure of 1,3-bis(4-methylphenyl)imidazolium chloride was determined and compared to its related imidazole-based carbene. The important structural difference is the greater N2—C2—N3 angle in the salt (109.6°) than in the carbene (101.2°). An electrochemical investigation of the salt revealed a single reduction at −2.32 V in the forward scan and two oxidations at −0.89 and −0.54 V following scan reversal.

KEY WORDS: Imidazolium, carbenes, sodium hydride.

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Introduction

The recent synthesis of stable carbenes by reduction of imidazolium salts with sodium hydride or potassium *tert*-butoxide constitutes a major breakthrough in this area.[1-5] These carbenes are stable in the absence of oxygen or moisture and offer the possibility of useful synthetic reagents in a variety of chemical systems.[1-5] Although the structures of these carbenes have been reported and discussed in comparison to imidazolium cations, to our knowledge, the only reported comparison of a stable carbene structure to its immediate imidazolium precursor is the di-1-adamantyl derivative.[1] Therefore, we have performed single crystal structural analysis of 1,3-bis(4-methylphenyl)imidazolium chloride, **1**, for comparison to its stable carbene 3-bis(4-methylphenyl)-imidazol-2-ylidene, **2**[5] and to the structurally related salt 1,3-diphenylimidazolium perchlorate, **3**.[6]

For certain synthetic applications of these carbenes, its is easier to form the carbene only as an intermediate, thus, avoiding an isolation step. In these cases, the chemical reduction route may not be desirable because it often requires removal of the reducing agent prior to addition of other reagents. Electrochemical generation of these carbenes would offer an additional rapid and efficient alternative route to these syntheses. Therefore, in addition to the crystal structure, we have also examined the electrochemical reduction of **1** in tetrahydrofuran (THF).

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Experimental section

Synthesis and characterization of 1

The salt **1** was prepared using the method of Arduengo.[7] Paraformaldehyde (1.54 g) was dissolved in 15 ml of 99% anhydrous toluene. To this solution was added dropwise 0.734 g of p-toluidene dissolved in 15 ml of toluene. The mixture was heated in 100°C for 5 min to dissolve all the solids. It was then cooled to room temperature and 8.27 g of 6 M HCl was slowly added. After the addition of the HCl, the solution was stirred for 5 min at room temperature and 7.26 g of 40% glyoxal was added. The mixture was stirred for 2 hr at 100°C. After cooling the volatiles were removed under vacuum. The dark precipitate was washed with acetonitrile and dried. Crystals suitable for crystallographic analysis were obtained by slow evaporation of an acetonitrile water mixture. The salt did not crystallize in the absence of water. The ^{1}H NMR (Varian Gemini 300, TMS internal reference) in CD_3OH (99.99%) of the recrystallized material showed resonances at d 2.18 ppm (s, 6H); 2.45 (s, 6H); 7.46 (d, $^3J_{HH}$ = 8.5 Hz, 4 H, Ar); 7.68 (d, $^3J_{HH}$ = 8.5 Hz, 4 H, Ar); 7.94 (d, $^4J_{HH}$ = 1.6 Hz, 2 H); 9.74 (t, $^4J_{HH}$ = 1.6 Hz, 1 H). The resonance at

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2.18 ppm is assigned to water and corresponds to 2–3 water molecules of hydration. The FT-IR spectrum (Nicolet 510P FT-IR) of the recrystallized product in a KBr pellet revealed a broad absorption at 3400 cm^{-1} consistent with the presence of water.

Crystallography

All crystallographic data were collected with a Siemens R3m/V diffractometer. Data collection parameters and final lattice parameters were determined from the full-matrix least-squares refinement of the angular settings of 50 reflections (20–30°2θ) and are given in Table 1. Data were collected with the 2θ technique, and the intensities were not corrected for absorption. Calculations were carried out with the Siemens SHELXTL (PC version) system of computer programs. Structure solution was accomplished with the aid of a direct methods program included in the SHELXTL system of programs. All nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters. Refinement converged with $R = 0.0451$ for 884 observed reflections and $wR = 0.0597$. The final fractional coordinates for the nonhydrogen atoms are summarized in Table 2. The twofold symmetry equivalents of N1 and C4 are labeled N3 and C5, respectively, in keeping with standard ring numbering nomenclature.

Table 1. Crystal data for 1,3-bis(4-methylphenyl)imidazolium chloride[a]

1,3-Bis(methylphenyl)imidazolium Chloride	Mo Kα radiation
$C_{17}N_2H_{17}Cl \cdot 2H_2O$	$\lambda = 0.71073$ Å
M.W. = 320.65	Cell parameters from 50 reflections
Tetragonal	$\theta = 15$–$30°$
$P4_22_12$	$\mu = 0.233$ mm^{-1}
$a = 17.967(3)$ Å	$T = 296$ K
$c = 5.109(1)$ Å	Plate
$V = 1649.3(5)$ $Å^3$	0.8 × 0.5 × 0.5 mm
$Z = 8$	Orange
$D_x = 1.249$ g/cm^3	
Data collection	
Siemens R3m/V diffractometer	$R_{int} = 2.49\%$
2θ scans	$\theta_{max} = 45°$
Absorption correction: none	$h = 0$–19
measured reflections 2324	$k = 0$–19
independent reflections 1100	$l = -5$–5
observed reflections 884	3 standard reflections monitored
$\lvert F > 4.0\sigma(F)\rvert$	every 100 reflections
Refinement	
Refinement on full-matrix	103 parameters
Least-squares	$w = 1/\lvert\sigma^2(F) + 0.0007F^2\rvert$
Final $R = 0.0451$	$\Delta/\rho_{max} = 0.33$ e $Å^{-3}$
$wR = 0.0597$	$\Delta/\rho_{min} = -0.22$ e $Å^{-3}$
$S = 1.51$	
884 reflections	Atomic scattering factors from SHELXTL/PC (Siemens, 1990)

[a] $wR = [\Sigma\ wt \cdot (F_{obs} - F_{calc})^2/\Sigma\ (wt \cdot F_{obs})^2]^{1/2}$.[10]

Table 2. Final fractional coordinates for nonhydrogen atoms[a]

Atom	x	y	z	U_{eq}
Cl1	0.1346(1)	0.1346(1)	0.0000	0.108(1)
O1	0.2980(2)	0.7020(2)	0.0000	0.116(2)
O2	0.0594(3)	0.0594(3)	0.5000	0.087(3)
N1	0.1749(2)	0.8854(2)	0.1486(7)	0.055(1)
C12	0.3902(2)	0.9587(2)	0.9326(9)	0.072(2)
C11	0.2814(2)	0.8516(2)	0.4225(8)	0.057(1)
C10	0.3329(2)	0.8701(2)	0.6122(8)	0.056(1)
C9	0.3346(2)	0.9388(2)	0.7280(7)	0.056(1)
C8	0.2816(2)	0.9912(2)	0.6442(10)	0.073(2)
C7	0.2298(2)	0.9742(2)	0.4551(9)	0.075(2)
C6	0.2295(2)	0.9036(2)	0.3440(8)	0.054(1)
C4	0.1110(2)	0.9247(3)	0.0936(13)	0.108(2)
C2	0.1746(2)	0.8254(2)	0.0000	0.054(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Electrochemistry

The solvent was Anhydrous Grade THF from Aldrich (<0.005% H_2O) and was dried over 4 Å molecular sieves prior to use. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was vacuum dried overnight at 120°C. The electrolyte for all experiments was 0.1 M $TBAPF_6$ in THF. The salt I decomposed upon heating preventing adequate drying of the salt. Electrochemical studies were performed at 23°C in a Vacuum Atmosphere dry box under a He atmosphere (< 10 ppm O_2 + H_2O).

Voltammetric experiments were performed using an EG&G PARC Model 273 Potentiostat/Galvanostat controlled with the EG&G PARC 270 software package. The electrochemical cell consisted of a glass vessel fitted with a drilled Kel-F cap. The working electrode was a 3 mm glassy carbon (GC) disk electrode from Bioanalytical Systems, and the counter electrode was a 0.5 mm Pt wire. The reference electrode consisted of a 0.5 mm Ag wire immersed in THF containing 0.01 M $AgNO_3$ and 0.1 M $TBAPF_6$. The potential of the ferrocene/ferrocenium couple was −0.012 V versus this Ag/Ag^+ reference electrode. Staircase cyclic voltamograms were collected using a step increment of 5 mV. Positive feedback compensation was used in all experiments to correct for the uncompensated cell resistance, which was approximately 3 kohms.

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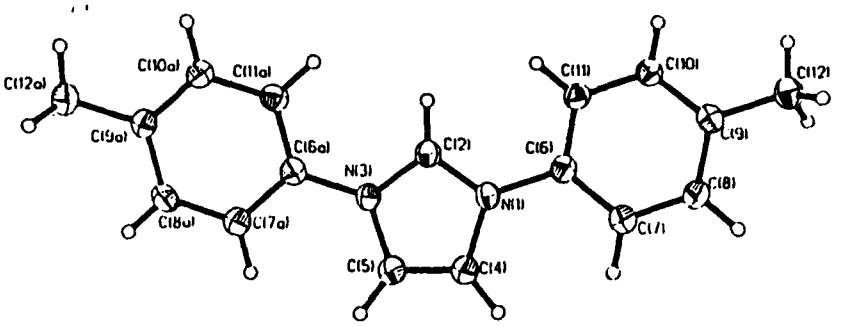

Fig. 1. ORTEP of organic cation of 1.

Results and discussion

Crystal and molecular structure

An ORTEP plot showing the molecular structure and labeling scheme of 1 is provided in Fig. 1 for clarity, the chloride and waters have been omitted. The bond distances and angles for the nonhydrogen atoms are summarized in Table 3. For comparison, the bond distances and angles for the carbene 2[5] and the perchlorate salt 3.[6] are also tabulated. As expected, the molecular bonding parameters for 1 and 3 are similar, while the carbene structure shows important differences (*vide infra*).

The 1,3-bis(4-methylphenyl)imidazolium chloride sits on a cyrstallographic twofold axis. The five member imidazolium ring and the 4-methylphenyl ring exhibit mean deviations from planarity of 0.009 Å and 0.002 Å, respectively. The least-square planes defined by the two rings form an interplanar angle of 12.8°. This compares to an imidazolium-phenyl interplanar angle of 37.1° in 3.[6] The 4-methylphenyl substituents in 2 are not equivalent and form two interplanar angles of 31° and 34° with the imidazolium ring; however, the rings are oriented such that there is a pseudo two-fold rotation axis passing through the C2 in the same manner as the true twofolds seen in 1 and 3.[5,6] The interplanar angle appears to be determined by packing considerations and not by ring to ring electronic interactions.

The two water molecules sit on the twofold rotation axis and are involved in hydrogen bonding. The criterion used to identify a hydrogen bond between O and Cl is the O———Cl distance must be less than the sum of the van der Waals radii, 1.50 and 1.80 Å, respectively.[8] In addition, hydrogen bonds between the imidazolium ring hydrogens and O or Cl are deemed present when the H———X distance is less than the sum of the hydrogen and O or Cl van der Waal radii, respectively.[8] Table 4 summarizes the hydrogen bonds for the structure. Both water molecules participate in hydrogen bonding to the chloride ion with bond distances of 3.076 and 3.189 Å.

A view down the *c*-axis (Fig. 2) shows a packing diagram of the structure. The organic rings form stacks running along the twofold crystallographic axis. The water molecules and chloride ions lie along the channels formed by the organics. The major intermolecular force in the structure appears to be the hydrogen bonding that is occurring between the water molecules and the chloride ions. It is interesting to note that attempts at re-

Table 3. Comparison of bond distances (Å) and angles (°) for 1,3-bistoylimidazolium chloride (1), 3-bis(4-methylphenyl)-imidazol-2-ylidene (2), 1,3-diphenylimidazolium perchlorate (3)

Atoms	1	2	3
C2—N1	1.326(4)	1.371(2)	1.319(4)
C2—N3	1.326(4)	1.375(2)	1.319(4)
C4—C5	1.339(5)	1.334(2)	1.319(1)
N1—C4	1.381(4)	1.392(4)	1.375(5)
N3—C5	1.381(4)	1.394(2)	1.375(5)
N1-substituent	1.432(4)	1.430(2)	1.438(5)
N3-substituent	1.432(4)	1.430(2)	1.438(5)
N1—C2—N3	109.3(3)	101.4(2)	109.6(2)
C5—N1—C2	108.0(3)	112.9(1)	107.4(3)
C4—N3—C2	108.0(3)	113.0(1)	107.4(3)
N1—C5—C4	107.4(3)	106.6(2)	107.7(3)
N3—C4—C5	107.4(3)	106.2(1)	107.7(3)
C2—N1-substituent	126.6(3)	123.1(1)	126.0(3)
C2—N3-substituent	126.6(3)	122.9(1)	126.0(3)

Table 4. Hydrogen bond distances in 1

Atoms	Distance (Å)
O1—Cl1	3.076
O2—Cl1	3.189
O2—H4"	2.389

"Bonded to C4.

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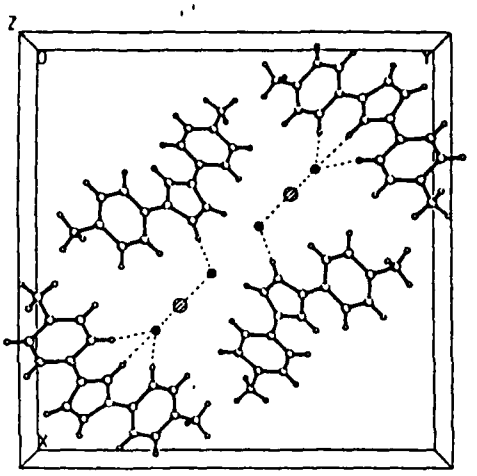

Fig. 2. View of 1 down the c-axis.

crystallizing the salt in the absence of water failed. Previous work has reported the carbene precursors are difficult to dry and that the water can provide a decomposition pathway for the carbene.[5]

The relationship between 1 and the carbene analog are tabulated in Table 3. It has been noted that the angle, N1—C2—N3, is larger in the salt precursors than in the carbene structures.[5] That is indeed the case for both 1 and 2, with N1—C2—N3 angles of 109.6° and 101.2°, respectively. The structural differences can be explained by the tendency of the carbene to stabilize its structure by utilizing both steric and electronic effects.[5] Further evidence of the electronic stabilization of the carbene can be seen in the angle formed by the imidazolium ring and the 4-methylphenyl ring which is smaller in the carbene analog than in 1, 123.1° and 126.6°, respectively.

Electrochemistry

The cyclic staircase voltammagram of (2 mM) 1 in THF is shown in Fig. 3. A single reduction at −2.32 V is observed during the forward scan and two oxidations at −0.89 and −0.54 V appear following scan reversal. A series of staircase cyclic voltammograms were collected at scan rates from 0.5 to 5 V s^{-1} with a 10 s hold at −2.7 V. Currents were normalized by dividing by the square root of the scan rate; for a completely reversible or irreversible diffusion-controlled process, the peak currents for the normalized curves should remain constant.[9] The resulting normalized voltammograms in Fig. 4 display the same peak heights indicating a diffusion-controlled electrochemical process. However, we have not attempted a detailed kinetic (homogeneous or heterogeneous) analysis of the reduction process because of the large correction made for uncompensated resistance which can lead to erroneous interpretations of peak potential shifts and peak shapes.

The two oxidation waves seen during the reverse scan correspond to the generation of one or two electroactive species by the reduction process. Importantly, the peak heights of the normalized oxidation waves increase with increasing scan rate indicating the products are only partially stable during the time of these experiments. At the fastest scan rate, the total oxidation current is approximately 50% of the reduction current. De-

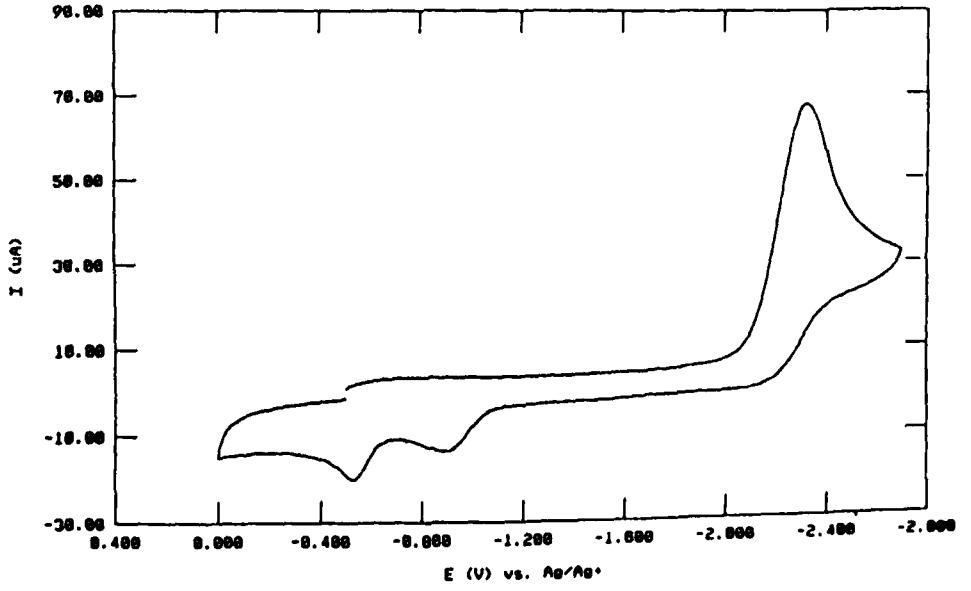

Fig. 3. Staircase cyclic voltammogram of 1 in THF at a glassy carbon electrode.

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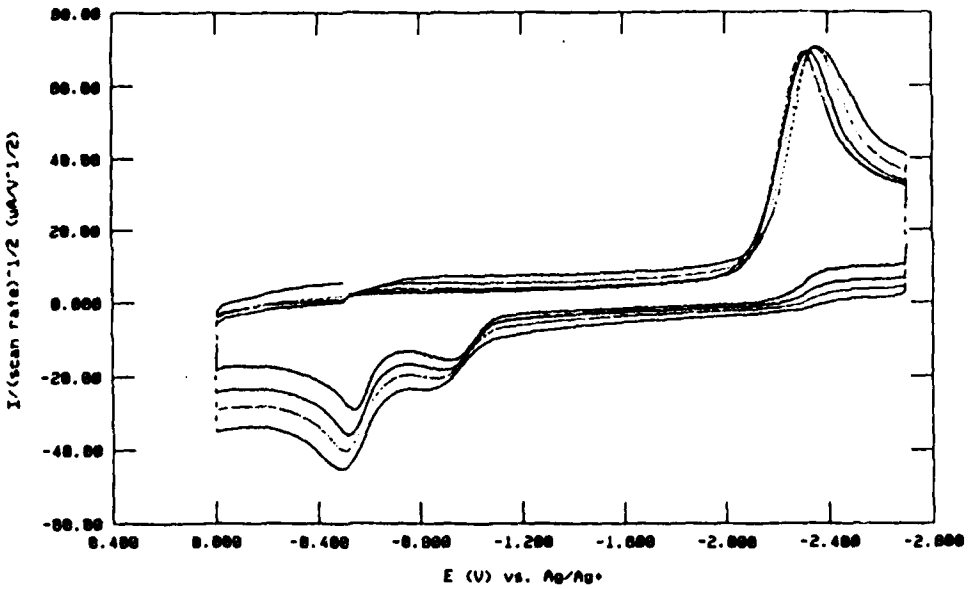

Fig. 4. Staircase cyclic voltammograms for I at scan rates of 0.5, 1, 2, and 5 V s^{-1} with a 10 s hold at −2.7 V. Currents normalized by the square root of the scan rate.

creasing the scan rate to 50 mV s^{-1} and eliminating the 10 s reduction hold (not shown), gives oxidation peaks only 5% of the reduction process. The unstable products of I electrochemical reduction may be the carbene or a carbene reaction by-product. Although the water level in the THF electrolyte is less than 50 ppm (<2 mM), addition of the salt I introduces additional water to a concentration twice that of the imidazolium cation. The carbene is known to be unstable in the presence of trace water. Therefore, future electrochemical investigations will take greater precautions to eliminate water from the system or will employ carbene-complexing reagents such as transition metals to trap the electrochemically generated carbene intermediate.

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