

Electron transfer chemistry of some unusual nitrogen compounds: from stable nitrenium ions to the corresponding nitrogen centered radicals†

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Nitrogen-centered radicals (**1b'**, **2b'**, **3b'**, **4b'**) have been generated upon electron transfer from the corresponding stable nitrenium ions (**1b**⁺, **2b**⁺, **3b**⁺, **4b**⁺) and characterized by electrochemistry and simultaneous spectro-electrochemistry. Reactivity of the radicals is strongly influenced by the substituents attached to the two nitrogen atoms that are directly linked to the ion nitrenium center. While **1b'** and **2b'** are stable on the timescale of the electrochemical experiment, **3b'** and **4b'** have half-lifetimes of *ca.* 1.2–1.25 and 0.9–1 μ s, respectively, in acetonitrile, as determined with ultramicroelectrodes. Redox properties of the nitrenium ion/radical couples and relative stability of the radicals are discussed in light of both experimental results and *ab initio* calculations.

Like carbenes, $R_2C:$, which are the electronic counterparts of nitrenium ions, R_2N^+ , with the latter containing a cationic divalent nitrogen atom,¹ nitrenium ions are involved as highly reactive intermediates in a wide variety of organic reactions.² For example, when substituted with aromatic groups, nitrenium ions are postulated to be the ultimate carcinogens in the carcinogenesis initiated by aromatic amines.³ Recent time-resolved studies allowed the UV and IR spectra of some short-lived aryl nitrenium ions to be measured and provided important results on their structure and reactivity.⁴ Although electronically deficient molecules of the types mentioned above are usually extremely short-lived, Arduengo *et al.*⁵ and others,⁶ following the initial work of Wanzlick *et al.*,⁷ recently isolated and structurally characterized stable crystalline carbenes (Chart 1), opening the route for a rich coordination chemistry.^{6c} Concomitantly, stable crystals of structurally related nitrenium ions or, more precisely, ion pairs of nitreniums (**1b**⁺ I^- , **2b**⁺ ClO_4^- , **3b**⁺ I^- , **4b**⁺ $CF_3SO_3^-$, Chart 2), were synthesized and their X-ray crystal structures obtained.⁸ From experimental data and theoretical calculations it emerges that these molecules are stabilized by electronic delocalization.^{8c} To get further insights into their electronic structures and

properties, we investigated the redox chemistry of these nitrenium ions by means of electrochemical reduction in acetonitrile and simultaneous spectroscopic studies. Transfer of one electron leads to the formation of a nitrogen-centered radical, whose reactivity is a function of the molecular structure. Standard potentials of nitrenium ion/radical redox couples were obtained as well as lifetimes of the radicals and a reduction mechanism is proposed. Stability and reactivity of the nitrogen-centered radicals are discussed and rationalized on the basis of experimental data, and *ab initio* calculations are performed on model compounds (Chart 3).

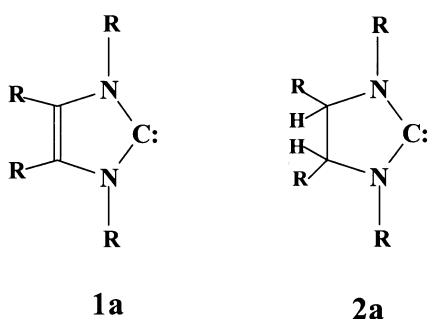


Chart 1 Stable carbenes of the Arduengo (**1a**) and Wanzlick (**2a**) type

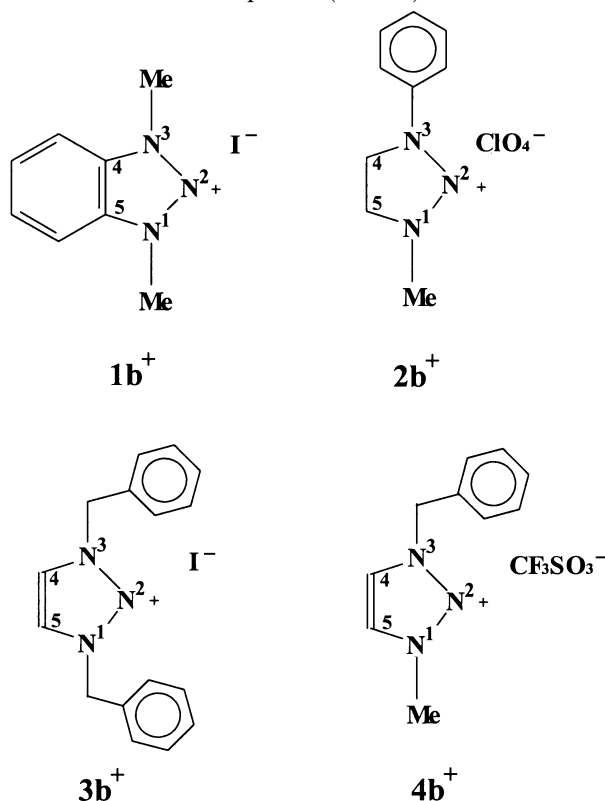


Chart 2 Nitrenium ions investigated in this work

† Non-SI units employed: 1 eV \approx 9.65 J mol⁻¹; 1 kcal \approx 4.18 kJ.

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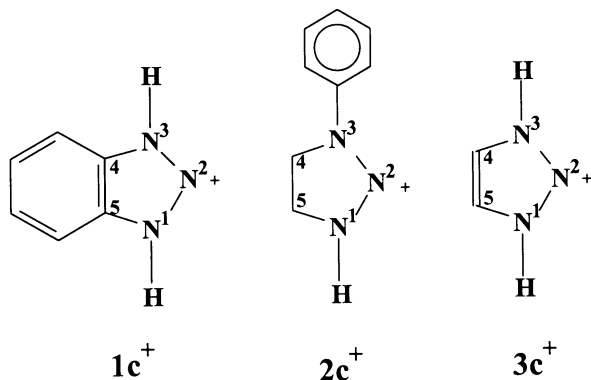


Chart 3 Model compounds investigated (the corresponding radicals $1c^{\cdot}$, $2c^{\cdot}$ and $3c^{\cdot}$ are obtained by addition of one electron)

Results and Discussion

Electrochemical and spectro-electrochemical experiments

Fig. 1 (top) shows a typical voltammogram of the nitrenium ion $1b^+$ at low scan rate. A first reversible one-electron wave⁹ is observed at moderately negative potentials, indicating the formation of a stable radical within the timescale of the experiment, and which could be reoxidized. The cathodic peak width ($E_p - E_{p/2} = 57$ mV at 0.1 V s^{-1}) as well as the peak-to-peak separation ($E_{p, anodic} - E_{p, cathodic} = 62$ mV at 0.2 V s^{-1}) are close to the theoretical values characterizing a fast electron transfer (*i.e.*, a reversible electron transfer)¹⁰ and the standard potential for the corresponding redox couple $1b^+/1b^{\cdot}$, calculated from half of the sum of the anodic and cathodic peak values, is equal to -1.24_5 V *vs.* SCE. The radical $1b^{\cdot}$ could be reduced further as shown by the occurrence of a second mono-electronic and irreversible wave (Fig. 1) at more negative potentials (-2.13 V *vs.* SCE at 0.1 V s^{-1}). The anion $1b^-$, formed by addition of one electron to $1b^{\cdot}$, is used up by a fast and irreversible chemical reaction. One of the various possibilities might be the protonation with residual water.

A rather similar picture emerged from the voltammograms obtained with $2b^+$ (Fig. 1, bottom). The transfer of one electron led to the formation of $2b^{\cdot}$, which appears to be stable enough to return one electron to the electrode upon scan reversal. As indicated by the peak width ($E_p - E_{p/2} = 57$ mV

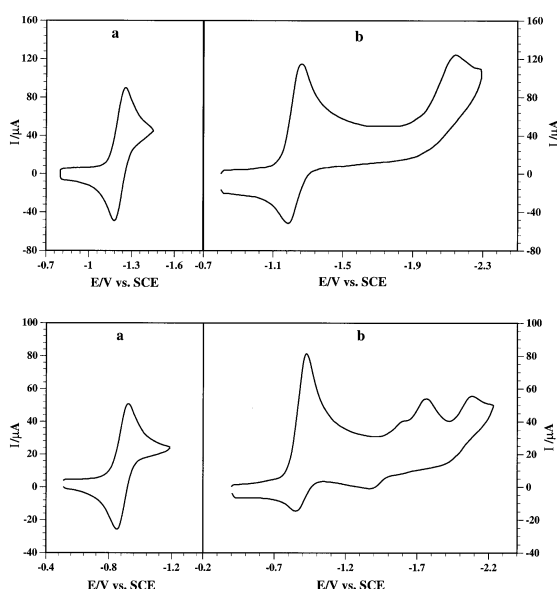


Fig. 1 Cyclic voltammograms of the nitrenium ions $1b^+$ (top: $C = 1.46$ mM; a: $v = 0.5$ V s^{-1} , b: $v = 1$ V s^{-1}) and $2b^+$ (bottom: $C = 1.53$ mM; a: $v = 0.1$ V s^{-1} , b: $v = 0.2$ V s^{-1})

between 0.1 and 1 V s^{-1}) and peak-to-peak separation ($E_{p, anodic} - E_{p, cathodic} = 60$ mV at 0.1 V s^{-1}), the charge transfer process is fast.¹⁰ From the location of the cathodic and anodic peaks, one gets $E^0(2b^+/2b^{\cdot}) = -0.91_5$ V *vs.* SCE. This value is found to be approximately 350 mV more positive than in the case of the $1b^+/1b^{\cdot}$ couple. As shown later, these experimental findings are in agreement with theoretical calculations. Furthermore, two additional reduction waves are observed, which are chemically reversible at low scan rates and which are located at -1.78_5 V and -2.10_5 V *vs.* SCE at 0.2 V s^{-1} . When the scan rate was increased up to a few volts per second, the second wave became chemically irreversible and the third tended to disappear. As shown by the second wave, this indicates that the product formed slowly rearranged to a reducible compound, a process that is prevented on a short timescale (a detailed discussion of the mechanism of this process is beyond the scope of the present work).

Confirmations of these reactions and further insights into the radical structures were obtained by simultaneous spectro-electrochemical experiments. The UV-Vis spectro-cyclovoltammogram of $1b^+$ shows a reversible electrochemical reduction behavior at scan rates of 20 mV s^{-1} (Fig. 2) and 200 mV s^{-1} (Fig. 3) in the case of $2b^+$. Under these conditions, the spectra obtained at the initial and final potentials are identical. Two isobestic points are observed at 251 nm (4.94 eV) and 284 nm (4.37 eV) for $1b^+$ and at 352 nm (3.52 eV) and 463 nm (2.68 eV) for $2b^+$. The corresponding *in situ* voltammetric curves (Fig. 2 and 3), recorded at an Au-LIGA electrode,¹¹ show a current peak ratio of one.¹² It should be noted that the small peak separation and the Gaussian shape of the voltammograms are due to finite diffusion in the capillary slit and inside the hexagon channels of the Au-LIGA structure used as the working electrode. The spectra of the radicals were accurately obtained at the switching potential (*i.e.*, at the potential for which the scan direction is reversed). Because of the fast conversion of the starting cation in the capillary slit of the cell, the radical spectrum is not superimposed by the starting material, even at a scan rate of 200 mV s^{-1} . Normalized UV-Vis spectra of $1b^+$, $1b^{\cdot}$, $2b^+$ and $2b^{\cdot}$ are shown in Fig. 4 and the absorption maxima are listed in Table 1.

While no decay was observed in the UV-Vis spectro-cyclovoltammograms of $1b^{\cdot}$ recorded at low scan rates (indicating a stability of at least a few hundred seconds), some decrease of the 351 nm absorption band of the $2b^{\cdot}$ spectrum was noticed for a scan rate of 20 mV s^{-1} (from 0.480 to 0.370 absorbance units). The fast and complete electrochemical generation of this radical inside the capillary slit of the cell allows us to determine its lifetime. We used the time dependent deconvoluted absorbance, obtained by comparison of the superimposed spectra with the initial spectrum and the spectrum at the switching potential obtained at 200 mV s^{-1} (which is not superimposed by any follow-up product). Both the logarithmic plot and the reciprocal plot of the radical absorbance are linear when plotted against time. Thus, first-order as well as second-order chemical reactions fit with the data (unfortunately we could not distinguish between the two possibilities; 20 mV s^{-1} is in fact the lowest scan rate acces-

Table 1 UV-Vis absorption maxima in nm (eV) of $1b^+$, $1b^{\cdot}$, $2b^+$ and $2b^{\cdot}$

$1b^+$	$1b^{\cdot}$	$2b^+$	$2b^{\cdot}$
275 (4.5)	241 (5.13)	321 (3.86)	269 (4.66)
	296 (4.22)		351 (3.54)
	342 (3.63)		426 (2.91) ^a
	375 (3.29) ^a		
	580 (2.75)		

^a Shoulder.

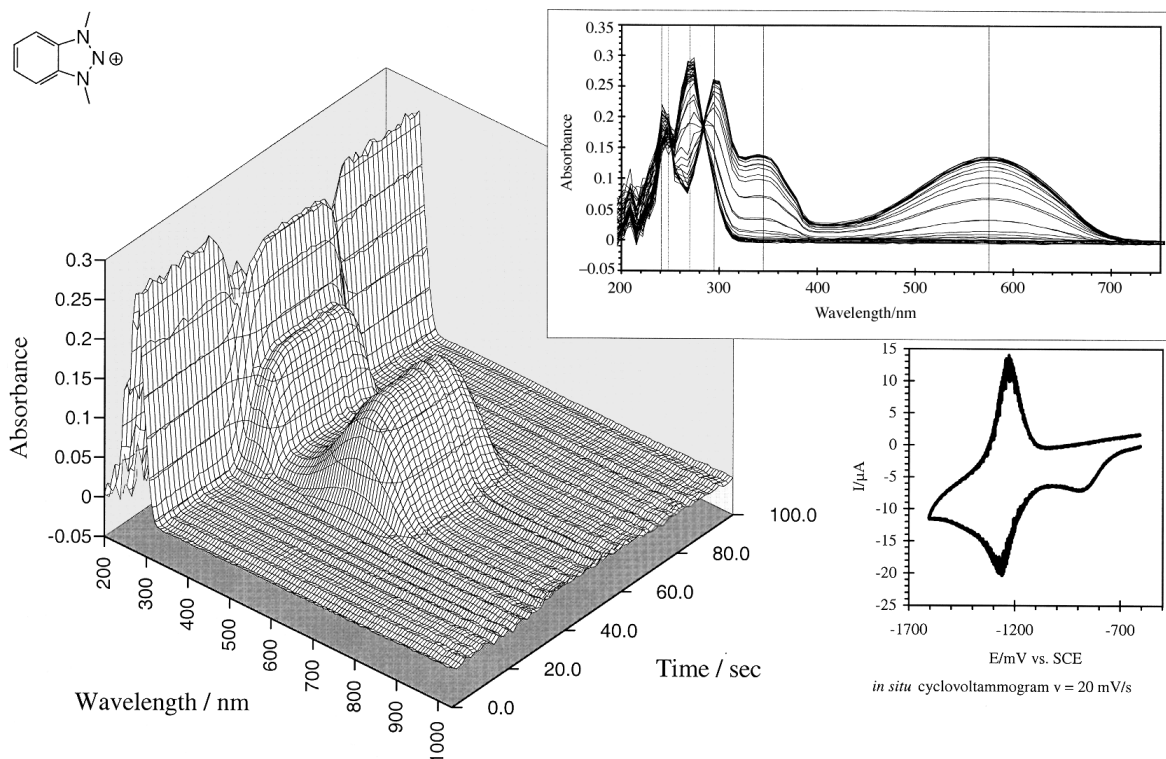


Fig. 2 UV-Vis spectro-cyclovoltammogram of **1b**⁺ (*C* = 3.21 mM) at a scan rate of 20 mV s⁻¹ at a Au-LIGA electrode (see Experimental). The UV-Vis spectra recorded during one scan are plotted *vs.* the time of the experiment (see inset for a 2D plot)

sible since a competition takes place between chemical processes and diffusion of the radical out of the capillary slit at longer times). In the former case, the half-lifetime is calculated to be 110 s ($k = 0.0063 \text{ s}^{-1}$) while the dimerization rate is equal to $1.75 \text{ l mol s}^{-1}$ in the latter case.

The shapes of the voltammograms of **1b**⁺ and **2b**⁺ are drastically different from those of the two nitrenium ions **3b**⁺ and **4b**⁺. With **3b**⁺ and **4b**⁺, a first irreversible and monoelectronic¹³ wave is obtained at potentials much more negative than in the case of **1b**⁺ and **2b**⁺ (see Fig. 5 and Table

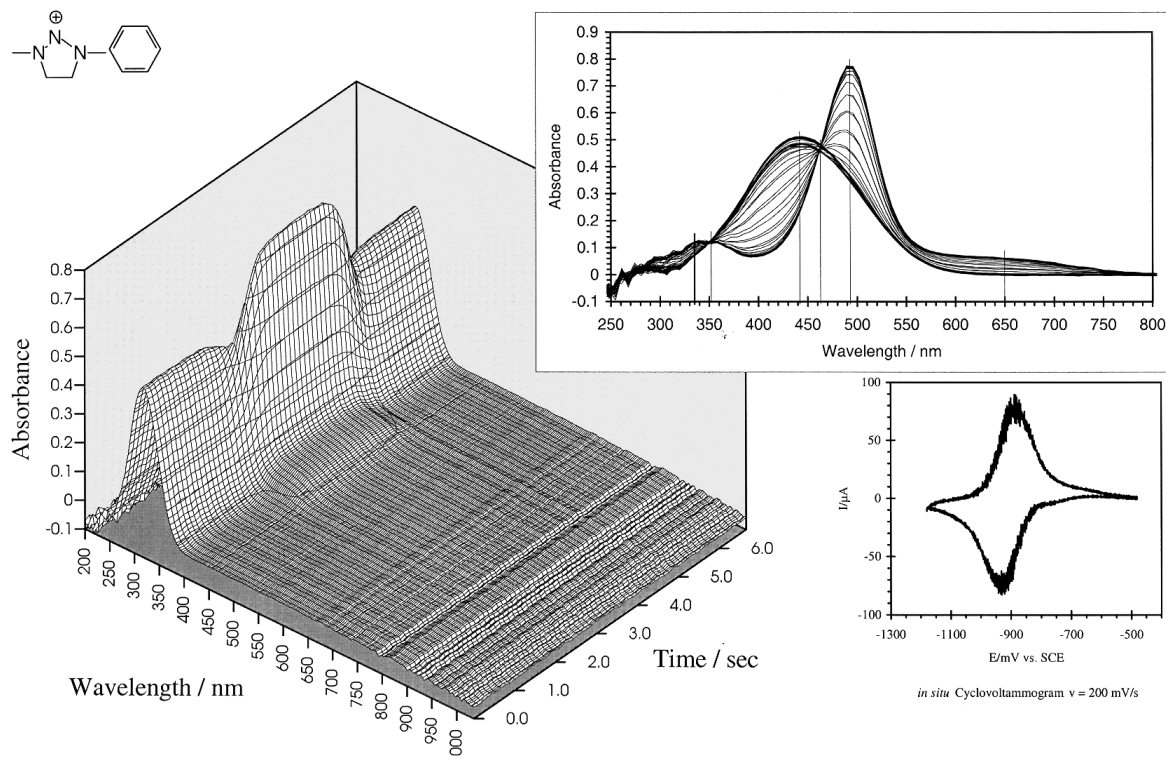


Fig. 3 UV-Vis spectro-cyclovoltammogram of **2b**⁺ (*C* = 4.01 mM) at a scan rate of 200 mV s⁻¹ at a Au-LIGA electrode (see Experimental). The UV-Vis spectra recorded during one scan are plotted *vs.* the time of the experiment (see inset for a 2D plot)

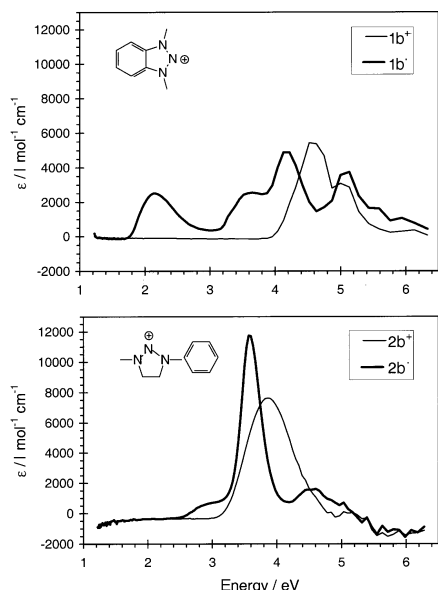


Fig. 4 Normalized UV-Vis spectra of **1b⁺**, **1b[•]**, **2b⁺** and **2b[•]** obtained from the spectro-electrochemical experiments shown in Fig. 2 and 3

2). A second cathodic wave is observed, separated by approximately 0.2 V from the first one. This wave disappears at high scan rates ($v > 50 \text{ V s}^{-1}$). A close examination of the first cathodic wave leads to peak potential values (E_p) and peak widths ($E_p - E_{p/2}$) as a function of the scan rate, as summarized in Table 2. The E_p vs. $\log v$ plot is linear between 0.05 and 1 V s^{-1} with a slope close to 33 mV in both cases.

These characteristics are in agreement with an 'E + C' mechanism,^{10,14} in which the rate determining step is a chemical reaction (C) following a fast electron transfer step (E). Increasing the scan rate led to mixed kinetic control by the two steps, as indicated for example by the progressive increase of the peak width. Since E_p values do not change upon

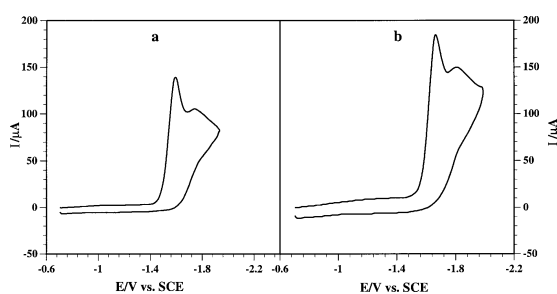


Fig. 5 Cyclic voltammograms of nitrenium ions **3b⁺** (a: $C = 2.92 \text{ mM}$, $v = 0.5 \text{ V s}^{-1}$) and **4b⁺** (b: $C = 2.4 \text{ mM}$, $v = 0.2 \text{ V s}^{-1}$)

Table 2 Cyclic voltammetry of **3b⁺** and **4b⁺** in MeCN: peak width at 0.2 V s^{-1} and variations of the peak potential (between 0.05 and 1 V s^{-1}) with the scan rate

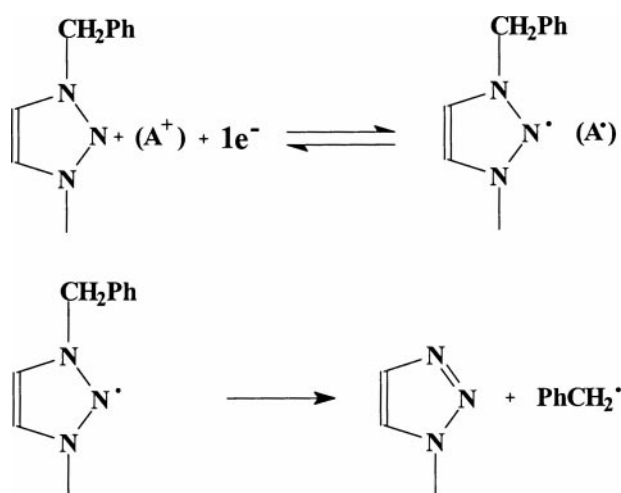
	3b⁺	4b⁺
$E_p/\text{V vs. SCE}$	-1.59_s^a -1.81_s^b	-1.67_o^a -1.86_o^b
$(dE_p/d \log v)/\text{mV}$	34	32
$(E_p - E_{p/2})^a/\text{mV}$	52	50

^a First reduction wave. ^b Second reduction wave.

varying the initial concentration of the substrate, even at very low scan rates at which the charge transfer almost does not interfere in the kinetic control, the 'C' step is a first-order reaction. Moreover, if the radical was consumed by rapid dimerization, then **1b[•]** and **2b[•]** should also dimerize quickly since they are less sterically hindered. This, however, is not observed. Upon adding excess amounts of a weak acid (2,2,2-trifluoroethanol in ten-fold excess) to the solution, peak potentials are negatively shifted by only 10 mV and peak widths are unaffected. The only change is an increase in the height of the peak by a factor of 1.7 and disappearance of the second wave. A possible reduction mechanism for the two nitrenium ions is as follows (see Scheme 1). The initial electron transfer leads to formation of an extremely unstable radical, **3b[•]** (or **4b[•]**). This species is deactivated by the breaking of a N-C_{benzylic} bond, with formation of a benzylic radical (which is well known to be a good leaving group under cathodic conditions)¹⁵ and a stable 1,2,3-triazole. Since PhCH₂[•] is more easily reducible than the starting compound,¹⁶ it is reduced by a second electron and the resulting anion reacts with a starting molecule, leading to an overall one-electron stoichiometry. In the presence of an added acid, the protonation of the benzylic anion competes with the reaction with a nitrenium ion and thus the wave progressively increases in height to two electrons, while the second reduction wave vanishes.

Using an ultramicroelectrode of $10 \mu\text{m}$ diameter (see Experimental), the reduction wave starts to show chemical reversibility above 29000 V s^{-1} with **3b⁺** and above 38000 V s^{-1} with **4b⁺** (Fig. 6). This corresponds to approximate half-lives of 1.2–1.25 μs for **3b[•]** and 0.9–1 μs for **4b[•]**. A rough estimation for the standard potential of the corresponding redox couples gives $E^0(\mathbf{3b}^+/\mathbf{3b}^\bullet) = -1.72 \text{ V vs. SCE}$ and $E^0(\mathbf{4b}^+/\mathbf{4b}^\bullet) = -1.83 \text{ V vs. SCE}$.

Striking differences are thus obtained in the reactivity and stability of the nitrogen-centered radicals as the molecular structure varies. While **1b[•]** and **2b[•]** are stable on the timescale of the electrochemical experiment and redox potentials of the nitrenium ion/radical couple are close to -1 V vs. SCE , **3b[•]** and **4b[•]** are elusive species with half-lives of the order of 1 μs . Moreover, very negative energies are required for their



Scheme 1 Reduction mechanism for **3b⁺** and **4b⁺**

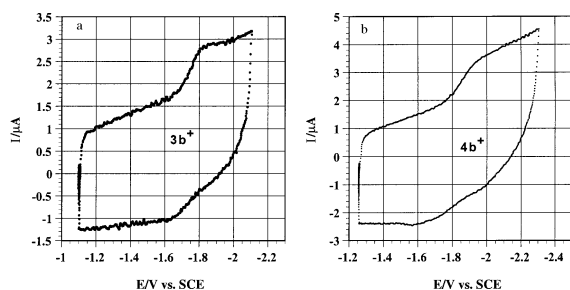


Fig. 6 High scan rate cyclic voltammetry of **3b⁺** (a: $v = 29\,000\text{ V s}^{-1}$) and **4b⁺** (b: $v = 38\,000\text{ V s}^{-1}$)

generation: for example, $E^0(2b^+/2b^\cdot) - E^0(4b^+/4b^\cdot) = 900\text{ mV}$ (see Table 3). It thus seems that removing a phenyl group from a nitrogen atom linked to the nitrenium ion center (as in the **2b⁺**-type structure) and replacing it by a benzyl group (see **4b⁺**) induces fundamental differences both in terms of chemical reactivity and redox properties, despite the presence of a C=C double bond in **4b⁺**. What is the reason for this?

Model calculations

Ab initio calculations have been performed on the model compounds **1c⁺**, **2c⁺** and **3c⁺** (Chart 3) at the UHF/6-31G(d) level of theory, on both the starting nitrenium ions and the radicals **1c[·]**, **2c[·]** and **3c[·]** obtained by reduction with one electron. Like their electronic carbene analogs, nitrenium ions may exist in the ground state as a singlet (with two non-bonding electrons in the same orbital) or as a triplet (with two non-bonding electrons of parallel spin in two different orbitals). Well-converged quantum chemical studies indicate that, while the parent nitrenium ion NH_2^+ has a triplet ground state lying 30 kcal mol^{-1} below the lowest energy singlet, aryl or alkyl substitution as well as substitution by donating atoms like fluorine or nitrogen strongly stabilize and even favor the singlet state over the triplet state.^{8c,17} In the two latter cases, the singlet state mainly benefits from electronic stabilization of the formally empty $p(\pi)$ orbital by the substituents.^{8c} This is similar to what is observed with carbenes, the effect being even more pronounced in the case of the positively charged nitrogen atom of nitrenium ions. The structures of the compounds investigated, as outlined in Tables 4 and 5, thus correspond to those of the most stable singlets of the nitrenium ions and of the most stable radical doublets. Calculations of the structure of **3c⁺** at the MP2/6-31G(d) level of theory, for example, show

Table 3 Standard potentials of nitrenium ion/radical redox couples

	1b⁺/1b[·]	2b⁺/2b[·]	3b⁺/3b[·]	4b⁺/4b[·]
$E^0/\text{V vs. SCE}$	-1.24_s	-0.91_s	-1.72_0	-1.83_0

Table 4 UHF/6-31G(d) bond lengths (pm) and angles (deg) of the nitrenium ions **1c⁺**, **2c⁺** and **3c⁺**

	1c⁺	2c⁺	3c⁺
N(1)—N(2)	127.5	124.7	127.7
N(2)—N(3)	127.5	126.5	127.7
N(3)—C(4)	137.0	146.4	135.3
N(1)—C(5)	137.0	148.0	135.3
C(4)—C(5)	138.1	153.7	135.4
N(1)—N(2)—N(3)	106.6	111.6	104.8
N(2)—N(3)—C(4)	112.7	114.3	113.3
N(2)—N(1)—C(5)	112.7	112.9	113.3
N(3)—C(4)—C(5)	104.0	99.8	104.3
C(4)—C(5)—N(1)	104.0	99.8	104.3

Table 5 UHF/6-31G(d) bond lengths (pm) and angles (deg) of the radicals **1c[·]**, **2c[·]** and **3c[·]**

	1c[·]	2c[·]	3c[·]
N(1)—N(2)	137.7	135.4	137.6
N(2)—N(3)	137.7	138.2	137.6
N(3)—C(4)	139.8	145.4	140.6
N(1)—C(5)	139.8	145.0	140.6
C(4)—C(5)	138.6	151.9	131.8
N(1)—N(2)—N(3)	104.3	105.3	104.0
N(2)—N(3)—C(4)	110.0	109.2	109.2
N(2)—N(1)—C(5)	110.0	112.8	109.2
N(3)—C(4)—C(5)	106.4	100.2	107.6
C(4)—C(5)—N(1)	106.4	100.2	107.6

good agreement with the X-ray crystal structure of **4b⁺ I[−]**. However, it should be emphasized that because of the size of the systems (especially of **1c⁺** and **2c⁺**) as well as the difficulties in handling radical species, geometry optimizations need to be performed at the UHF/6-31G(d) level of theory, for which the agreement between experimental and calculated structures is not as good. Thus, comparisons between the different radicals are meaningful.

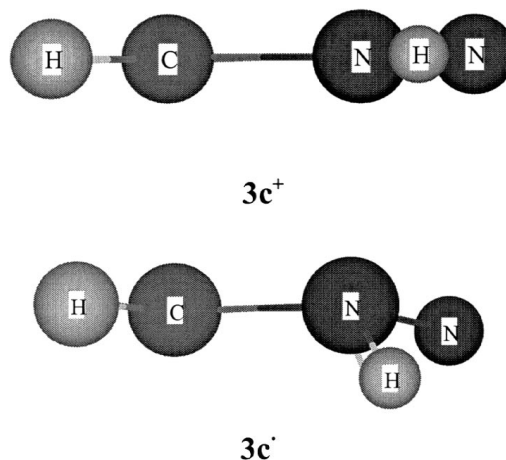


Chart 4 Planar nitrenium ion **3c⁺** and non-planar radical **3c[·]**

Calculated geometries for the cations **1c⁺**, **2c⁺** and **3c⁺** are planar (see Chart 4, showing **3c⁺**, and Table 4). Undoubtedly, electronic stabilization by the amino groups is favorable, as shown by the short N—N bond lengths and by the partial positive charge at the nitrenium ion center, which in all cases is considerably less than one (see Table 6). These charges have been calculated including solvation of the optimized structures in acetonitrile at the UHF/6-31G(d) level of theory, using the isodensity surface polarized continuum model (IPCM) implemented in Gaussian 94.¹⁸ These results are in agreement with recent results, in which X-ray crystal structures clearly show that stable nitrenium ions profit from strong electronic delocalization, at least within the N(1)—N(2)—N(3) framework.^{8c} From Table 7, one can see that on going from the triazole **5¹⁹** to **1b⁺ I[−]**, **2b⁺ ClO₄[−]** and **4b⁺ I[−]**⁸ the N(2)—N(1,3) bonds are shortened. Further calculations and population analyses on

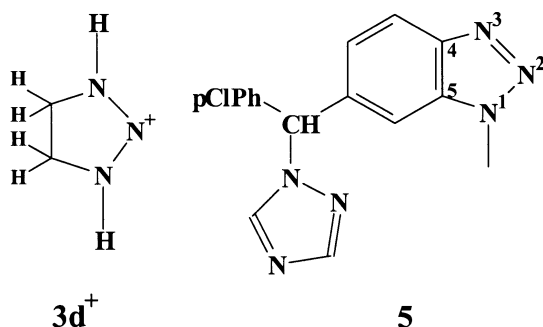
Table 6 Partial atomic charges on nitrogen atoms of the nitrenium ions **1c⁺**, **2c⁺** and **3c⁺**

	N(1)	N(2)	N(3)
1c⁺	-0.553	0.114	-0.553
2c⁺	-0.499	0.202	-0.476
3c⁺	-0.415	0.006	-0.415

Table 7 X-ray crystal structure data (in pm and deg) of the triazolium ions **1b**⁺ I[−], **2b**⁺ ClO₄[−], **4b**⁺ I[−] and triazole **5**

	5	1b ⁺ I [−]	2b ⁺ ClO ₄ [−]	4b ⁺ I [−]
N(1)—N(2)	137.5	130.2	127.1	131.6
N(2)—N(3)	130.2	132.0	129.5	131.9
N(3)—C(4)	138.0	136.8	146.7	134.3
N(1)—C(5)	135.8	136.4	146.6	134.2
C(4)—C(5)	137.9	138.5	150.8	135.5
N(1)—N(2)—N(3)	108.3	106.3	109.7	103.8
N(2)—N(3)—C(4)	108.7	111.4	113.0	112.4
N(2)—N(1)—C(5)	109.4	112.1	114.1	112.7

model compounds (**3c**⁺ and **3d**⁺) also confirmed that nitrenium ions are stabilized by strong p(π) donation of the two adjacent amino groups.^{8c} Finally, it was concluded that unsaturated cations (**3c**⁺-like structure) profit only marginally from the presence of a C=C double bond and that the polarities of the σ_{N–N} bonds are not relevant for the stabilities of these cations.



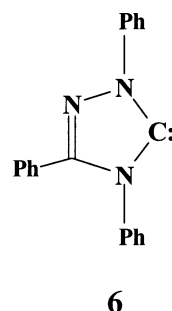
Addition of one electron to nitrenium ions to give the radical species induces important structural changes. Indeed, calculations indicate that for **1c**[•], **2c**[•] and **3c**[•] the geometry around the two nitrogen atoms [N(1) and N(3)] linked to the radical center [N(2)] is pyramidal (see Chart 4 showing **3c**[•]). Furthermore, the N(2)—N(3)—C(4) and N(2)—N(1)—C(5) angles are narrowed: they change from 113.3° in **3c**⁺ to 109.2° in **3c**[•]. Concomitantly, the N(2)—N(1) and N(2)—N(3) bonds are elongated in comparison to those in nitrenium ions, getting close to normal N—N single bonds. Thus, on going from **3c**⁺ to **3c**[•], the N(2)—N(3) bond length increases from 127.7 to 137.6 pm; in the case of **2c**[•] it increases from 126.5 to 138.2 pm. In other terms, hybridization at the atoms N(1) and N(3) in the radicals is closer to ‘normal’ sp³ hybridization with little electronic delocalization over the N(1)—N(2)—N(3) framework. Spin densities on the nitrogen atoms have been calculated after solvation of optimized geometries in acetonitrile (using the IPCM model). The radical charge is found to be mainly localized on the N(2) atom in each radical (80–85%), which is in agreement with the interpretation of N—N bond lengthening.²⁰

Table 8 Experimental and calculated differences between standard potentials of nitrenium ion/radical redox couples

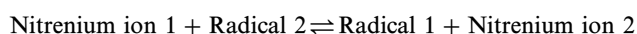
	ΔE ⁰ /mV
E ⁰ (2b ⁺ / 2b [•]) – E ⁰ (1b ⁺ / 1b [•])	330 ^a
E ⁰ (2c ⁺ / 2c [•]) – E ⁰ (1c ⁺ / 1c [•])	640 ^b
E ⁰ (2b ⁺ / 2b [•]) – E ⁰ (4b ⁺ / 4b [•])	915 ^a
E ⁰ (2c ⁺ / 2c [•]) – E ⁰ (3c ⁺ / 3c [•])	1280 ^b
E ⁰ (1b ⁺ / 1b [•]) – E ⁰ (4b ⁺ / 4b [•])	585 ^a
E ⁰ (1c ⁺ / 1c [•]) – E ⁰ (3c ⁺ / 3c [•])	650 ^b

^a Experimental value. ^b Calculated value; the result, obtained in Hartrees, was first converted into Joule and then to mV through the equation: ΔE⁰ = ΔG/F

These results can be compared with recent work by Enders *et al.*²¹ devoted to the electrochemical reduction of a stable carbene, the triazol-5-ylidene **6**, which is structurally close to the nitrenium ions investigated in this work. As already mentioned, carbenes are isoelectronic with nitrenium ions but while the carbene center is rather electron-rich, the nitrenium center is rather electron-deficient, even if donation of the two adjacent nitrogen atoms tends to stabilize the molecule. As a consequence, the radical anion obtained by addition of one electron to carbene **6** is not a ‘true’ carbene radical anion since the extra electron is located on the substituents (mainly on the C—N double bond and the phenyl ring linked to it, as shown by high level *ab initio* calculations) and not on the carbenic carbon.²¹ This leads to a very negative reduction potential, reflecting the electroactivity of the substituents. In contrast to and due to the positive charge borne by the nitrenium center, the extra electron added to the various nitrenium ions upon reduction is essentially located on the N(2) atom and the reduction potentials are found to be substantially more positive than in the case of **6**.



Combination of the results of the frequency calculations and of the solvation of the optimized geometries allows us to obtain the free enthalpy changes associated with the electron exchange reaction between two nitrenium ion/radical redox couples:



The results, shown in Table 8, are compared with the experimental data extracted from the electrochemical experiments pertaining to the corresponding compounds. As one can see there is a good qualitative agreement with the experimental data for the ordering of the redox potentials:

$$E^0(\mathbf{2b}^+/\mathbf{2b}^\bullet) > E^0(\mathbf{1b}^+/\mathbf{1b}^\bullet) \gg E^0(\mathbf{4b}^+/\mathbf{4b}^\bullet)$$

and

$$E^0(\mathbf{2c}^+/\mathbf{2c}^\bullet) > E^0(\mathbf{1c}^+/\mathbf{1c}^\bullet) \gg E^0(\mathbf{3c}^+/\mathbf{3c}^\bullet)$$

Quantitative agreement would require a higher level of calculations. These should take into account salt effects, especially for the nitrenium ions since they exist as ion pairs and since a supporting electrolyte is required in the electrochemical experiment.

Despite a high spin localization at the N(2) atom found by these calculations, we observed experimentally that the radicals **1b**[•], **2b**[•], **3b**[•] and **4b**[•] are stable against dimerization (see electrochemical results), suggesting that such a reaction has very likely a large activation energy. Thus, the difference in reactivity between **1b**[•] and **2b**[•] on one hand, and **3b**[•] and **4b**[•] on the other hand, arises from the presence of a leaving group (the benzyl group) in the two latter compounds. It leads to a fast fragmentation reaction while such a possibility of relaxation does not exist in the case **1b**[•] and **2b**[•].

Conclusions

Nitrenium ions **1b**⁺, **2b**⁺, **3b**⁺ and **4b**⁺ are stable ions that profit from a large stabilization of the positive charge by the

adjacent nitrogen atoms. This makes them electronically distinctly different from the normal ones. Quantum chemical calculations indicate that these ions are planar. They can be used as starting compounds for redox reactions and lead to the corresponding radical species by a one-electron reduction process at carbon or metal electrodes. **1b'** and **2b'** are very stable molecules that survive over a few minutes, despite an important density of spin at the nitrenium center. They have been characterized by their standard redox potentials and in situ UV-Vis spectra. In contrast, substitution of one of the nitrogen atoms adjacent to the nitrenium center by a benzyl group (**3b'** or **4b'** structure) leads to the production of very unstable radicals. Lifetimes of **3b'** and **4b'** are in the range of 1 μ s, the benzyl substituent acting in these cases as a good leaving group.

Experimental

Materials

For the electrochemical and spectro-electrochemical investigations, acetonitrile (Merck Uvasol) and supporting electrolyte, (Et)₄NBF₄ (Fluka, puriss), were used as received. Salt concentration was 0.1 M, except for the ultramicroelectrode experiments, for which it was increased up to 0.6 M. The synthesis of the various pairs of nitrenium ions (**1b**⁺ I[−], **2b**⁺ ClO₄[−], **3b**⁺ I[−], **4b**⁺ CF₃SO₃[−]) has already been described.^{8,22}

Apparatus

Most of the cyclic voltammetric experiments were carried out with a 3 mm diameter glassy carbon disk. In the high scan rate experiments we used a 10 μ m diameter carbon disk (Princeton Applied Research). Experiments were performed in a conventional electrochemical cell designed for use on a vacuum line, the solution volume being 5 mL. Positive currents are cathodic. The electrodes were carefully polished and ultrasonically rinsed with absolute ethanol before each run. The counter electrode was a platinum wire and the reference electrode an aqueous saturated calomel electrode (SCE). The potentiostat, equipped with positive feedback compensation, and current measurer, used at low or moderate scan rates, were the same as previously described.²³ The instrument used with ultramicroelectrodes at high scan rates has been described elsewhere.²³

The spectro-electrochemical cell is equipped with a Au-LIGA electrode ($s_w = 20$ μ m, $s_b = 10$ μ m, $s_h = 110$ μ m) as a working electrode, embedded between two quartz rods (1 mm diameter size). A full description of this cell has been presented elsewhere.¹¹

Calculations

All calculations on geometries and energies were carried out at the UHF/6-31G(d) or MP2/6-31G(d) levels of theory using the program packages Gaussian 94.¹⁸ Frequency calculations were performed for each optimized geometry and no imaginary frequencies were obtained. Care was also taken to avoid spin contamination, which remains below 10% for all radicals.

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