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Mesoionic bora-tetraazapentalenes – fully reversible two step redox systems†

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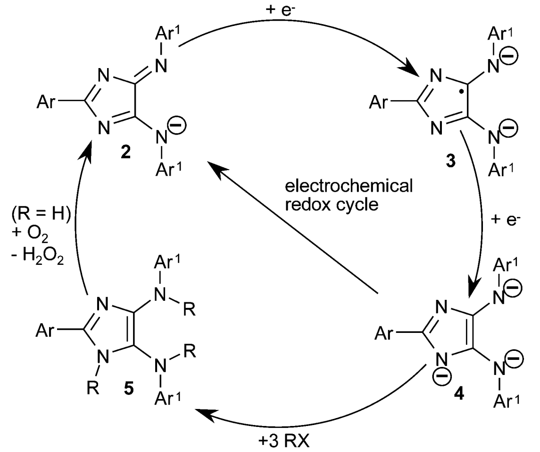
Bora-tetraazapentalenes have been synthesised and characterized; the radical anion shows an unusual thermodynamic stability (semiquinone formation constants K_{SEM} of *ca.* 10^{14}).

New cross-conjugated systems such as 4*H*-imidazoles[1] **1**, tetraazafulvalenes[2a] and tetraazafulvadienes[2b] are easily obtained *via* cyclisation of oxalic acid bis-imidoylchlorides with amidines. These systems are stable, deeply colored crystalline substances. Due to their polyfunctionality, they are suitable building blocks for supramolecular architectures and/or are good ligands for metal complexes.[3]

1

We have demonstrated recently that the 4*H*-imidazoles **1** can be reduced with metallic lithium.[4] Upon deprotonation of **1**, two consecutive single electron transfer steps lead (*via* the radical dianion **3**) to the trianion **4** which possesses an aromatic 6π system. Simple alkylation reactions provided synthetic access to the previously unknown 4,5-diaminoimidazoles **5** which are not only heteroaromatic diamines but also contain an electron-rich tetraaminoethene functionality.[4] The 4*H*-imidazoles **1** can also be reduced with metallic zinc in the presence of acid and water to give the 4,5-diaminoimidazoles **5** (R = H).



These imidazoles **5** are unstable towards air since they are immediately reoxidized to **1** upon contact with oxygen. This redox reaction is quite easily monitored; when the color of **2** has faded away, the reduction is complete (**5** = leuco-form). Exposure to air causes the color (**2**) to be regenerated. In the course of this double single-electron transfer reaction, hydrogen peroxide is formed as an interesting by-product as could be detected by luminometric measurements (chemiluminescence of luminole or lucigenine). This redox-cycle can be repeated several times. Reduction of the 4π-system in **1** to the 6π-system in **5** is an actual example for a reversible, two-electron-redox process.[5]

Cyclovoltammetry was our method of choice for investigating these reversible two-electron transfer processes in **1**. All reduction measurements were carried out in methylene chloride using a mercury drop electrode with tetrabutylammonium perchlorate against Ag/AgCl. In addition, we studied the influence of the substituent R. Derivatives such as **1a–1e** exhibited irreversible potentials between −0.3 and −0.9 V (Table 1). This behaviour is caused by proton abstraction at the exocyclic amino group which leads to a superposition of two peaks. Upon treatment with small amounts of lithium hydride (which primarily forms the anion), we finally succeeded in distinguishing both potentials. Due to the small peak separation the redox steps can only be considered to be quasi-reversible. By employing square-wave techniques, both signals were identified as separate one-electron transfer steps. The absolute shift sufficiently describes the electron density at the 4*H*-imidazole core; the difference between both potentials indicates the stability of the intermediate radical dianion. This difference was observed to be nearly constant (0.10–0.20 V) for all derivatives studied.

We then searched for a way to eliminate the proton abstraction reaction which interferes with the electron transfer process. Unfortunately, the ambidence of anion **2** makes simple alkylations and acylations of 4*H*-imidazoles **1** quite difficult and, when they do succeed, a mixture of regioisomers are obtained. In the course of our search for suitable derivatives, we found that 4*H*-imidazoles **1** react with a series of boranes in the presence of triethylamine to form 1,3,2-diazaborolidines **6**.

Electrochemical investigations of these mesoionic bora-tetraazapentalenes revealed several interesting properties (Table 2). The uv/vis spectra of these intensive red compounds are characterized by a structured absorbtion band between 512 and 614 nm with a relatively high extinction coefficient (log ε = 3.6–4.3).

Table 1 Reduction potentials of the 4*H*-imidazoles (Ar = C_6H_5)

Nr	Derivative	E_1, E_2/V	ΔE/V	K_{SEM}[a]
1a	Ar[1] = 4-CN-C_6H_4	−0.92, −1.05	0.13	160
1b	Ar[1] = 4-F-C_6H_4	−1.15, −1.25	0.10	50
1c	Ar[1] = 4-H-C_6H_4	−1.11, −1.28	0.17	760
1d	Ar[1] = 4-I-C_6H_4	−1.18, −1.31	0.13	160
1e	Ar[1] = 4-CH_3-C_6H_4	−1.26, −1.41	0.15	350

[a] $K_{SEM} = 10^{((E_1 - E_2)/0.059\ V)}$, according to Michaelis.[6]

Table 2 Reduction potentials of the 1,3,2-diazaborolidines (Ar = C_6H_5)

Nr	Derivative	E_1, E_2/V	ΔE/V	K_{SEM}
6a	Ar[1] = 4-CH_3-C_6H_4; R = F	−0.21, −1.07	0.86	$3.8\cdot10^{14}$
6b	Ar[1] = 4-CH_3-C_6H_4; R = C_6H_5	−0.50, −1.28	0.78	$1.7\cdot10^{13}$
6c	Ar[1] = 4-CH_3-C_6H_4; R = C_2H_5	−0.64, −1.39	0.75	$5.2\cdot10^{12}$
6d	Ar[1] = 3,5-CF_3-C_6H_3; R = F	+0.22, −0.61	0.83	$1.2\cdot10^{14}$

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† Electronic supplementary information (ESI) available: The synthesis, characterization and crystallographic data. See http://www.rsc.org/suppdata/cc/b4/b403480e/

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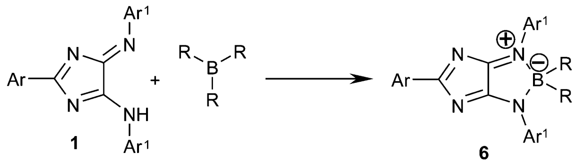

Ar = C_6H_5 R = C_6H_5, C_2H_5, F

6a: Ar¹ = p-CH_3-C_6H_4; R = F
6b: Ar¹ = p-CH_3-C_6H_4; R = C_6H_5
6c: Ar¹ = p-CH_3-C_6H_4; R = C_2H_5
6d: Ar¹ = 3,5-CF_3-C_6H_3; R = F

In contrast to the educts **1**, the bicyclic and thus more rigid derivatives **6** show a strong red fluorescence reaching into the near infrared (576–656 nm). The fluoresence quantum yield (in chloroform; up to 64%) in this spectral region is unusually large.

A single crystal structure analysis of **6a** (illustrated in Fig. 1) shows that compounds of type **6** can be considered to be symmetric mesoionic betaines. The molecule possesses a plane of symmetry (C_{2v}); with all (delocalized) CN-bonds being approximately the same length (*ca.* 1.34 Å) and can thus be interpreted as being a cyanine chromophore. ^{13}C-NMR data correspond to this structure. Delocalisation of the positive charge causes down-field shifts for C5 (*ca.* 13 ppm) and C3a/C6a (*ca.* 4 ppm). Although they are betaines, the boracycles are astonishingly less polar than the parent compounds **1** and are quite soluble in solvents such as toluene.

Cyclovoltammetry (square-wave techniques applied) experiments on these derivatives of **6** showed clearly separated reversible one-electron reductions that are no longer influenced by proton abstractions (Fig. 2). The difference between the single reduction steps is much larger than those observed for the 4*H*-imidazoles **1a–1e**, which suggests that the radicals have been stabilized. The potential shifts can now be tuned. Coarse tuning is achieved by changing the residues on boron (strong influence) whereas a change at amino groups has a smaller 'fine tuning' effect. For example, the shift difference between **6a** and **6c** (fluoro *vs.* ethyl on boron) is 0.72 V; more than double that observed for the 4*H*-imidazoles **1a** and **1e** (0.35 V).

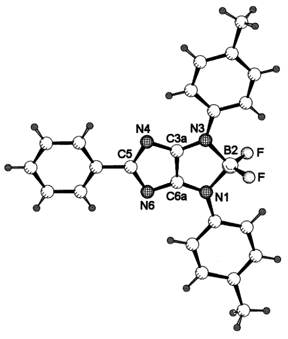

Fig. 1 Crystal structure shows the symmetry of **6a**.‡

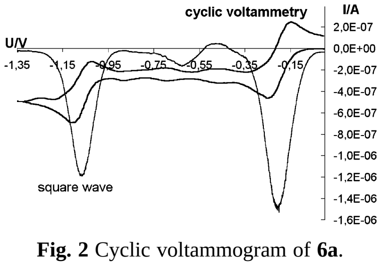

Fig. 2 Cyclic voltammogram of **6a**.

In contrast to the fluorescence of **6a–6f** which shows strong similarity to the difluoroboradiaza-*s*-indacenes[8] ('BODIPY') the electrochemical properties especially the K_{SEM} constants are closer related to boron bridged violenes. For example, the K_{SEM} of distorted *N*,*N*′-dimethyl-2,2′-bipyridylium (10^2) is much lower than that of the ethylene bridged *N*,*N*′-2,2′-bipyridylium[7] (10^8) and the even more rigid *N*,*N*′-2,2′bipyridylboronium cations[9] have K_{SEM} values of up to 10^{12}.

The K_{SEM} values obtained for the 1,3,2-diazaborolidines **6** are even comparable to K_{SEM} of the acceptor part in 'organic metals' derived from tetracyanoquinodimethane (TCNQ) or *N*,*N*′-dicyanochinodiimine[10] (DCNQI) which lie between 10^7 and 10^{11}.

Ultrasonic reduction of compounds **6** with metallic lithium in THF eliminates the boron substructure thus resulting in anions of the starting material **1** and is therefore not suited for isolating intermediates of these single electron transfer reactions.

To summarize, the 1,3,2-diazaborolidines **6** are a new class of substances with an extraordinary combination of properties. They are nonpolar and mesoionic compounds that are stable towards air and light. They melt without decomposition, possess a strong fluorescence at long wavelengths and contain the chromophore of difluoroboradiaza-*s*-indacenes with an odd number of conjugated sp^2-atoms (N3–C3a–N4–C5–N6–C6a–N1). In addition they possess the redox active system of the violenes (N1–C6a–C3a–N3) with an unusually high thermodynamic stability of the resulting radical anion.

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Notes and references

‡ $C_{23}H_{19}B_1F_2N_4$; 400.23 g mol^{-1}; *a* 13.8178(5), *b* 10.3696(4), *c* 13.9651(6) Å; α 90, β 97.692(1), γ 90°; *V* 1982.9(1) Å^3; *P*2(1)/*n*; *T* 183(2) K; *Z* 4; μ 0.094 mm^{-1}; independent reflections 4452 [*R*(int) 0.0454]; final *R* indices [$I > 2\sigma(I)$] R_1 0.0781, wR_2 0.2104. CCDC 232704. See http://www.rsc.org/suppdata/cc/b4/b403480e/ for crystallographic data in .cif or other electronic format.

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