TWO STEP REDOX SYSTEMS LII : 2,2'-BIPYRIDYLBORONIUM SALTS

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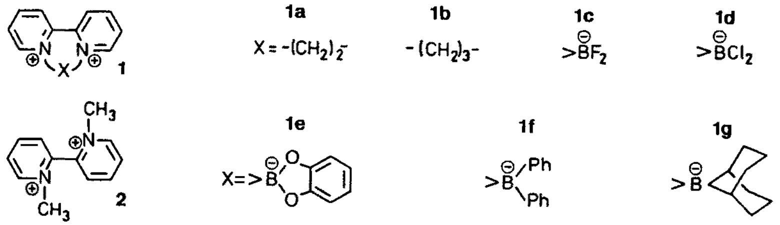
Abstract-Dications 1 derived from 2,2-bipyridine are found to exist as fully reversible two step redox systems with persistent radical ions (SEM) of high thermodynamic stability, if the bridge X forces the two pyridine rings into coplanar positions. The well known derivative 1a (Diquat^R) is now complemented by the boronium ions 1c and 1e -1g, as shown by voltammetry and the uv spectra of the corresponding radicals.

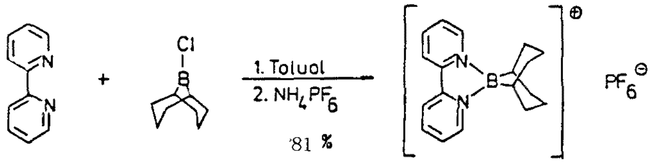
The redox properties of 2,2'-bipyridinium salts in aqueous solution has been thoroughly investigated in connection with their herbicide effects.[2] Although under these conditions reversibility is observed only for the first electron transfer (OX/SEM), reduction of 1a already at -0.57 V (vs. Ag/AgCl) compared to -0.83 V for 1b and -0.88 V for 2 was connected to different geometries[3]: In 1a the two methylene groups force the bipyridine moiety into coplanar positions whereas the larger bridge in 1b and even more so the two methyl groups in 2 create rather distorted systems. Therefore only in 1a-SEM the single electron can be distributed smoothly over the π-systems of both pyridine rings.



In DMF these bipyridinium salts ("Weitz-type"[4]) behave as perfectly reversible two step redox systems, which can be characterized e.g. by the thermodynamic stability of the cation radical (SEM) given as the semiquinone formation constant K_{SEM} for the equilibrium OX + RED $\rightleftharpoons$ 2 SEM.[4]
Indeed K_{SEM} reflects the differences in planarity quite strongly, as can be judged from K_{SEM}'s (DMF) $4 \cdot 10^7$ (1a), $3 \cdot 10^5$ (1b) and ~20 (2).[4,5]
We therefore looked for other bridges X in 1 which will provide a planar π-system. Complexing hetero atoms, especially boron, seemed to be most promising. By this reasoning 1c - 1g were prepared and their redox properties were studied by voltammetric uv/vis spectroscopy.

RESULTS AND DISCUSSION

Boronium ions 1c - 1f have been already described in the literatures,[15,16] although not always fully characterized and partly with different anions. 1g can easily be obtained from bipyridine (3) and 9-BBN chloride (4).



3 4 1g

1g-Cl precipitates from toluene after a slightly exothermic reaction. From its aqueous solution 1g-PF_6 is isolated in 81 % yield after addition of NH_4PF_6.

Since all salts 1c - 1g contain o-substituted pyridine rings, a C-H out of plane vibration[6] is observed at 770 - 730 cm^{-1}.

^{11}B-Nmr resonances are strongly shifted upfield on raising the coordination number from 3 to 4.[7] E.g. the signal of 4 (δ = 82.0 ppm, $CDCl_3$)[8] is shifted in 1g to δ = 8.9 ppm ($\{D_6\}$-DMSO).

The uv-spectra of 1c - 1g (λ_{max} 302 - 322 nm, MeCN) are rather similar to that of 1a (λ_{max} 310 nm, MeCN)[9] with the exception of 1e-PF_6. This salt shows an intense yellow color in the solid state and its slightly yellow solutions are due to a strong band at 371 nm (log ε = 4.29, MeCN).

Solutions of 1a - 1g or 3 in dry DFM turn red to violet by formation of radicals (SEM) on addition of sodium. By the same procedure 1d, however, decomposes as it does by electrochemical reduction. As can be judged from Table 1 absorption maxima of the radicals derived from 1c and 1e - 1g display the same absorption bands as that of the radical ion of 1a[10] containing a bismethylene bridge.

In addition to these, 1c and 1e radicals, carrying the electron attracting oxygen and fluoride ligands, show additional bands at 422/423 nm. On the other hand, aromatic or alicyclic ligands as in 1f and 1g cause additional absorptions at 490 nm and 494 nm, respectively.

Like 1a the boronium salts (1c - 1f) behave as perfectly reversible two step redox systems in DMF. As an example the CV, AC and DC curves of 1g are given in Fig. 1.

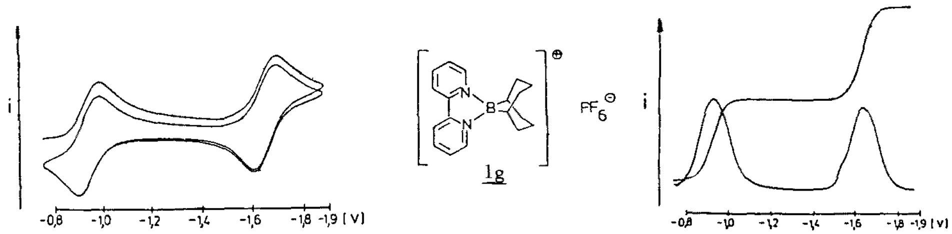


Figure 1. CV (left), DC and AC (right) plots for the boronium salt 1g.

Table 1. Redox potentials E_1 (RED/SEM), E_2 (SEM/OX) and semiquinone formation constants K_{SEM} for 1a, 1c and 1e - 1g[a] together with absorption maxima and molar extinction coefficients for the corresponding radicals (SEM)[b].

	1a	1c	1e	1f	1g
E_1 (mV)[a]	-0.74[11]	-1.20	-1.16	-1.54	-1.62
E_2 (mV)[a]	-0.26[11]	-0.62	-0.62	-0.86	-0.94
K_{SEM}	$1.4\cdot10^{8}$	$7.1\cdot10^{9}$	$1.7\cdot10^{9}$	$3.0\cdot10^{11}$	$3.0\cdot10^{11}$
λ_{max}(nm)[b] (log ε) SEM	377 (4.48)[11]	379 (4.33)	381 (4.67)	377 (3.99)	378 (4.64)
		422 (4.11)	423 (4.50)		
	460 (3.95)[11]	460 (4.02)	458 (4.41)	463 (3.78)	463 (4.14)
				490 (3.76)	494 (4.31)

a) Potentials vers. Ag/AgCl in MeCN, solvent DFM + $n\text{-}Bu_4N^+BF_4^-$ in the presence of neutral Al_2O_3.[12] Potentials derived from CV, DC and AC are identical within ±10 mV. b) 10 ml of the substrate (10^{-3} to 10^{-4} molar) dissolved in dry DMF were treated under N_2 with pieces of sodium in a reaction vessel connected to uv-cell. Uv spectra were recorded when maximal concentration of SEM was reached after 1-2 hours. ε presents minimum value mainly for comparison of different absorption bands in one compound.

One should consider that in contrast to 1a the boronium salts 1c - 1f (OX) carry one positive charge only. Therefore reduction to SEM produces apparently neutral radicals with zwitterionic character. The reduced form RED consequently exists as a mono anion. This difference to the dication 1a probably is responsible for shifting E_1 of the boronium salts to more negative potentials (cf. Table 1). According to high electronegativity of fluoride this shift amounts to only 0.52 V for 1c whereas with alicyclic ligands (1g) already 0.66 V are recorded. The effects of the other ligands arrange 1e and 1f in the expected order.[13]

K_{SEM}'s of 1c and 1e - 1g are even larger than that of 1a, increasing with more negative potentials E_2 as it has been observed as a general rule for Weitz-type redox systems.[4b,11]

CONCLUSIONS

Planar two step redox systems derived from 2,2-bipyridine and including persistent radicals (SEM) of very high thermodynamic stability are not restricted to the dicationic 1a (Diquat[R]) but are also obtained from monocationic boronium salts 1c and 1e - 1g. They may well serve as electron transfer catalysts if potentials more negative than those of 1a by 0.4 - 0.9 V are appropriate.

EXPERIMENTAL

Apparatus. Melting points (corrected): Kofler-microscope. Ir: Perkin-Elmer 157 G. Uv: Cary 17, ~10^{-4} molar solution, 0.1 cm cell. ^{1}H-Nmr: Varian T 60 (60 MHz), EM 360 (60 MHz). ^{13}C- and ^{11}B-Nmr: Bruker WH 90 (22.63 MHz), standardized (^{11}B) against $BF_3 \cdot Et_2O$ extern. Voltammetry: PAR 170 with i.r. compensation, standardized against bis-diphenylchromium iodide.[14]

2,2'-Bipyridyldifluoroboronium hexafluorophosphate (1c$\cdot PF_6$). White crystals[15], mp 180°C, 61 % yield.

2,2'-Bipyridyldichloroboronium hexafluorophosphate (1d$\cdot PF_6$). White crystals[15], mp 254°C, 68 % yield.

2,2'-Bipyridyl-1,2,3-benzodioxaboronium hexafluorophosphate (1e$\cdot PF_6$). Procedure according to l.c.[16], however dichloromethane as solvent instead of benzene. Formation of the PF_6 salt by addition of 1e$\cdot$Cl in water to an aqueous solution of NH_4PF_6 (general procedure). Intense yellow crystals, mp 186°C, 74 % yield.

2,2'-Bipyridyldiphenylboronium bromide (1f$\cdot$Br). Procedure as given for diphenylchloroborane[16], however solvent THF instead of benzene, mp 327°C (dec.), 85 % yield.

2,2'-Bipyridyl(9-boroniumbicyclo{3.3.1}nonane) hexafluorophosphate (1g). 2.19 g (14.1 mmol) of freshly sublimed dry 2,2'-bipyridine (3) in 20 ml of toluene was slowly added to 2.20 g (14.1 mmol) of 9-BBN-Cl[8] in 20 ml of warm water. This solution was added to 2.50 g (15.3 mmol) NH_4PF_6 in 10 ml water; 4.80 g (81 %) white crystals, mp 252°C. Ir (KBr): 3160, 3100, 1960, 1920 (C-H), 1620, 1560, 1460, (arC=C), 1310, 1240, 1160, 1060, 1055 (B-N), 910, 880, 820, 755, 710 cm^{-1} (arC-H). - Uv (CH_3CN): λ_{max} ($\log \varepsilon$) = 239 (4.38), 301 (4.35), 310 (4.32) nm. - ^{1}H-Nmr ({D_6}-DMSO): $\delta = 0.77$ (m; 2H, bridgehead H of 9-BBN), 2.03 (m; 12H, CH_2 groups of 9-BBN), 8.15 (m; 2H, ß-bipy-H), 8.80 (t, J = 7.5 Hz; 2H, γ-bipy-H), 9.22 (d, J = 8 Hz, ß'-bipy-H), 9.49 (d, J = 5 Hz, 2H, α-bipy-H). - ^{11}B-Nmr ({D_6}-DMSO): $\delta = 8.9 \pm 1$ (b).- Anal. calcd for $C_{18}H_{22}BF_6N_2P$ (421.7): C, 52.12; H, 5.22; N, 6.64. Found: C, 51.37; H, 5.18; N, 6.48.

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