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An EPR study of the reaction of tetrabutylammonium borohydride with *N*-Heterocycles

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Abstract

The reactions between tetrabutylammonium borohydride and a series of nitrogen-containing heteroaromatics bases have been investigated by electron paramagnetic resonance (EPR) spectroscopy. The radical anions of the *N*-heterocycles, formed by a single electron-transfer process have been observed with substrates having reduction potentials higher than −1.2 V vs. SCE. With less reducible bases, the radical anions of the adducts formed by complexation by one or two borane units of the nitrogen atoms of the base were observed under photolytic conditions. This is because the complexed *N*-heterocycles have larger electron affinities than the starting base.

Keywords: Boron; Radical anions; Tetrahydroborate; EPR; Electron transfer

1. Introduction

In two previous papers we reported our studies on the spontaneous and photo-induced homolytic reactions of borohydrides with aromatic and aliphatic nitrocompounds [1] and with a number of quinones, ketones, and cyano derivatives [2]. The formation of radical anions resulting from electron transfer (eqn. 1) from the borohydride negative ion, BH_4^-, to the organic substrate was detected in the absence of UV irradiation with compounds having a reduction potential greater than −1.5 V vs. the saturated calomel electrode (SCE). With the less reducible compounds, UV irradiation led to the formation of radical species which, in some cases, were the radical anions produced by photo-induced electron transfer (ET) and, in other cases, the paramagnetic adducts of the borane radical anion, $BH_3^{-\bullet}$ (eqns. 2,3).

$$A + BH_4^- \xrightarrow{(h\nu)} A^{-\bullet} + BH_3 + \tfrac{1}{2}H_2 \qquad (1)$$

$$A \xrightarrow{h\nu} A^* \xrightarrow{BH_4^-} AH^\bullet + BH_3^{-\bullet} \qquad (2)$$

$$A + BH_3^{-\bullet} \rightarrow ABH_3^{-\bullet} \qquad (3)$$

We also allowed the borohydride to react with some nitrogen-containing heteroaromatic bases and found that the more reducible derivatives afforded the corresponding radical anions both in benzene and THF, while with other *N*-heterocycles, very complex EPR spectra were observed which could not be interpreted. However, they were thought to be a result of paramagnetic complexes between the nitrogen base and one or two borane units. Radical species of this kind have been detected by Kaim and coworkers in the reaction of 1,4-diazines and related derivatives with boron and aluminium hydrides [3–6] and with trialkylboranes [6]. In all cases, except with 2,2′-bipyridine, the radical anions of $R_3M(N\text{-}\pi\text{-}N)MR_3$ with M = B or Al were detected and characterised by EPR and ENDOR spectroscopy. The formation of these radicals was explained in terms of electron transfer, although no detailed mechanism was proposed.

In the present paper we report an EPR investigation of the radical species detected during the reactions of Bu_4NBH_4 with the *N*-heterocycles, reported in Table 1. It will be shown that this reaction may follow different routes leading to various radical intermediates, depending on the nature of the heteroaromatic base, such as on the number of ligating sites, its basicity, its reduction potential and on the presence of a complexing agents such as triphenylborane.

2. Results and discussion

According to previous reports [2], nitrogen-containing heteroaromatics with higher reduction potentials

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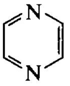
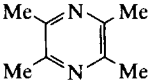
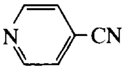
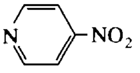
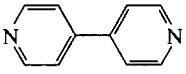
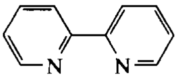
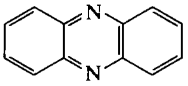
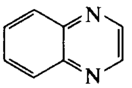
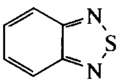
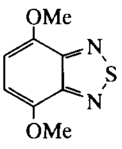
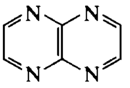
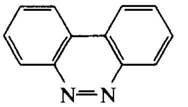
(see Table 1) react spontaneously with Bu_4NBH_4 to afford the corresponding radical anions (eqn. 1), both in benzene and in tetrahydrofuran (THF). This was the case with 4-nitropyridine (**4**), phenazine (**7**) and 1,4,5,8-tetraazanaphthalene (**11**), all having $E_{1/2} \geq -1.20$ V vs. SCE, and also with 4,7-dimethoxybenzo-[2,1,3]thiadiazole (**10**) which is much less reducible ($E_{1/2} = -1.59$ V). The unexpected behaviour of the last compound, as well as that of its parent (**9**), will be discussed below.

Solutions of the remaining substrates with the borohydride did not show any EPR signal in the dark, while upon photolysis benzo[*c*]cinnoline (**12**) afforded its radical anion, and the other compounds gave rise to intense and well-resolved EPR spectra characterised by large overall splittings, both in benzene and in THF. These spectra contained a huge number of lines because of the coupling of the unpaired electron, not only with the nuclei of the organic base but also with those of BH_3 groups, and were thus attributed to paramagnetic complexes between the *N*-heterocycles and the borane. Each spectrum was the superimposition of two or more spectra because of different isotopomers, because the naturally occurring boron consists of the two isotopes. ^{10}B ($I = 3$, 19.8%, $\gamma = 3.03159 \times 10^{27}$ J T^{-1}) and ^{11}B ($I = 3/2$, 80.2%, $\gamma = 9.05322 \times 10^{27}$ J T^{-1}).

Table 1
Reduction potentials of the *N*-heterocycles **1–12** measured in acetonitrile vs. SCE

Compound			$E_{1/2}$ (V)	Ref.
	Pyrazine	**1**	−2.12	[6]
	Tetramethylpyrazine	**2**	−2.51 [a]	[7]
	4-cyanopyridine	**3**	−1.98	[8]
	4-nitropyridine	**4**	> −1.15 [b]	[9]
	4,4′-bipyridinyl	**5**	−1.80	[6]
	2,2′-bipyridinyl	**6**	−2.11 [a]	[10]
	Phenazine	**7**	−1.20	[11]
	Quinoxaline	**8**	−1.61	[10]
	Benzo[2,1,3]thiadiazole	**9**	−1.49	[2]
	4,7-Dimethoxybenzo[2,1,3] thiadiazole	**10**	−1.59	[7]
	1,4,5,8-Tetraazanaphthalene	**11**	−1.06	[2]
	Benzo[c]cinnoline	**12**	−1.50	[2]

[a] In DMF.
[b] See Ref. [9].

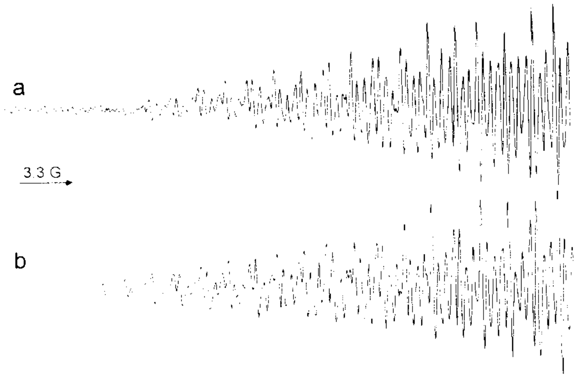
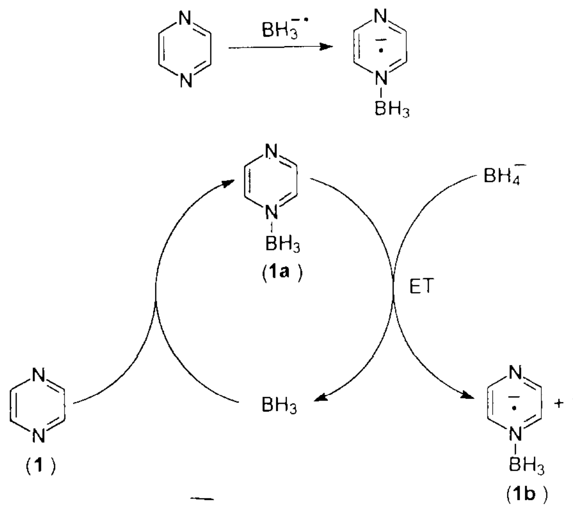


Fig. 1. Experimental (a) and simulated (b) low-field EPR spectrum of radical **1b**, recorded in DME at 80°C.



(4a)

(4b)

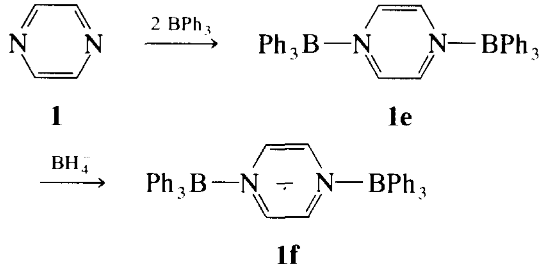
In order to interpret these complex spectra, we made recourse to numerical methods, such as autocorrelation [12] and cepstral [13] techniques. The obtained values of the hyperfine splitting constants were then tested by simulation and refined by an iterative least-squares fitting based on the Monte Carlo method [14] of the simulated to the experimental spectrum. Additional information useful in the spectra interpretation were obtained by generating a given radical by reaction with the deuterated analogue of the borohydride, Bu_4NBD_4.

2.1. *Pyrazine (1) and tetramethylpyrazine (2)*

The EPR spectrum obtained upon photoreaction of pyrazine with Bu_4NBH_4 in deoxygenated DME or benzene solution (see Fig. 1) has been interpreted in terms of coupling of the unpaired electron with two different nitrogens, a boron, three equivalent protons, and two pairs of protons. The number of interacting nuclei and the magnitude of the hyperfine splitting constants (Table 2) are consistent with structure **1b** for the observed paramagnetic species, which formally can be considered the borane-complexed radical anion of pyrazine. In both solvents the radical is quite persistent because, when cutting off the light, the EPR signal disappears only after several hours.

The formation of **1b** might to take place via either of the two different routes exemplified in eqn. 4. One implies direct addition to a nitrogen atom of pyrazine of the borane radical anion, $BH_3^{-\cdot}$, formed by hydrogen abstraction from the BH_4^- ion by a photoexcited state of pyrazine [15,16], and the other implies complexation of **1** by BH_3 followed by electron transfer from the borohydride.

The formation of **1b** via electron transfer from BH_4^- to pyrazine followed by complexation by BH_3 should be disregarded because the reduction potential of **1** is too low (−2.12 V) to permit the ET reaction to take place. However, complexation of the two nitrogen lone pairs by trialkylboranes is known to increase the reduction potential by as much as 1 V [6], as in the bis(triethylborane) adduct of pyrazine, $E_{1/2} = -1.02$ V vs. SCE. If the reaction with Bu_4NBH_4 is carried out in the presence of triphenylborane, the dicomplexed radical **1f**, formed according to eqn. 5, is easily detectable (Fig. 2) even in the dark, both in THF and benzene solution.



(5)

These experiments suggest that if some BH_3 is formed, mono-complexation of **1** occurs in solution, and the resulting diamagnetic adduct **1a** should have a re-

Table 2
EPR spectral parameters of the radical anions of BH_3-complexed *N*-heterocycles, $[H_3B(base)]^{-\cdot}$

Radical	Coupling constants ($1\ G = 10^{-4}$ Tesla)	*g*-factor	*T* (K)
1b	$a(H^{2,6})$ 3.53, $a(H^{3,5})$ 1.64, $a(N^1)$ [a] 7.91, $a(N^4)$ 7.04, $a(^{11}B)$ 3.05, $a(3\ H^{BH_3})$ 6.53	2.0034	353
3b	$a(H^{2,6})$ 2.48, $a(H^{3,5})$ 1.40, $a(N^{CN})$ 2.20, $a(N^1)$ 6.04, $a(^{11}B)$ 2.53, $a(3\ H^{BH_3})$ 5.65	2.0030	342
9b	$a(H)$ 0.77, $a(H)$ 1.50, $a(H)$ 2.68, $a(H)$ 3.94, $a(N^1)$ 5.46, $a(N^3)$ 5.40, $a(^{11}B)$ 1.53, $a(3\ H^{BH_3})$ 3.12	2.0041	298
10b	$a(H)$ 0.28, $a(H)$ 2.01, $a(N^1)$ 6.46, $a(N^3)$ 5.99, $a(^{11}B)$ 1.31, $a(3\ H^{BH_3})$ 3.51	2.0040	298

[a] N_1 is the nitrogen ligated to the boron atom.

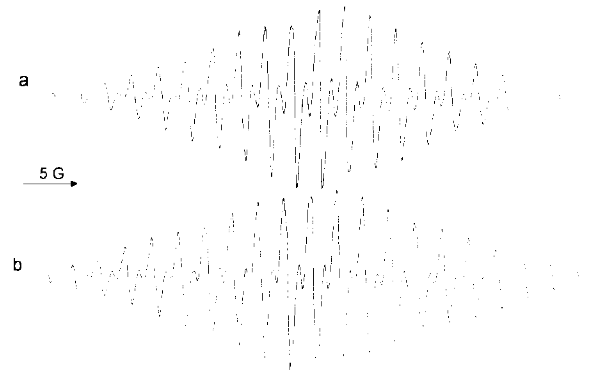


Fig. 2. Experimental (a) and simulated (b) EPR spectrum of radical **1f** recorded in THF at room temperature. Spectrum (b) has been simulated taking into account the presence of the isotopomeric species containing ^{10}B and ^{11}B.

duction potential high enough to be reduced by the borohydride ion (eqn. 4b).

A choice between the two alternative routes which can lead to the formation of **1b** was made on the basis of the following considerations and experimental observations.

Giles and Roberts [17] showed that the addition of $BH_3^{-\bullet}$ to pyridine and four-substituted pyridines takes place either at the carbon atoms in positions four or two, but never at the nitrogen atom. Moreover, when performing the photoreaction of **1** with Bu_4NBH_4 in the presence of di-tert-butylperoxide the intensity of the EPR signal from **1b** remained practically unchanged. Because $Me_3COOCMe_3$ favours the formation of $BH_3^{-\bullet}$, if route 4a is followed a substantial increase of the adduct of the borane radical anion would be expected. This effect was actually observed with nitroalkanes [1]. Further, in the photoreaction of tetramethylpyrazine with Bu_4NBH_4, no EPR signals could be detected in THF, whereas in benzene a very weak spectrum identical to that of the radical anion of the diadduct of BH_3 to tetramethylpyrazine (**2d**) was observed (vide infra). Because the presence of the four methyl groups should not hinder the approach of $BH_3^{-\bullet}$ to one nitrogen atom, similar is observed with the much bulkier $Ph_3Si\bullet$ radical [18], a behaviour identical to that of pyrazine is expected if route 4a is followed. However, this result is much better explained on the basis of the ET mechanism, (route 4b). In fact, it is unlikely that monocomplexation of the less reducible tetramethylpyrazine ($E_{1/2} = -2.51$ V) is sufficient to increase the reduction potential enough to allow electron transfer to take place from BH_4^-, but dicomplexation might make the ET process possible.

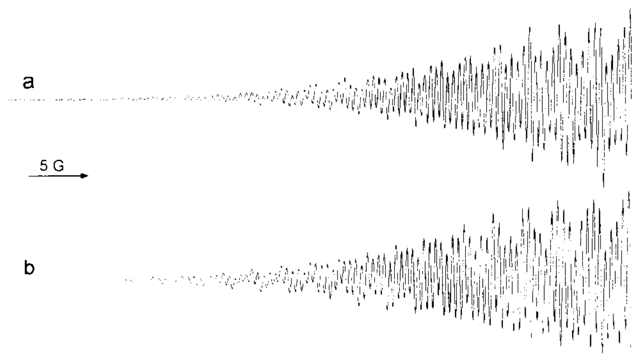
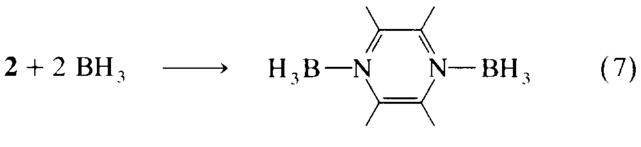
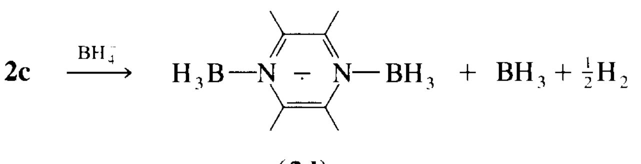


Fig. 3. Experimental (a) and simulated (b) half EPR spectrum of radical **2d**, recorded in benzene at room temperature.

$$BPh_3 + BH_4^- \rightarrow H\bar{B}Ph_3 + BH_3 \qquad (6)$$



(2c)



(2d)

(8)

To check if this was the case, some triphenylborane was added to the solution. We detected immediately a strong EPR spectrum (see Fig. 3) because of a paramagnetic species identified as **2d** rather than of the radical anion of the bis(triphenylborane) adduct **2f**. An explanation can be given in terms of reactions 6–8, which show by way of the developing of a gas believed to be B_2H_6, and by the following proton NMR experiment. We first recorded the NMR spectrum of 2,6-dimethylpyridine (lutidine) in C_6D_6, both in the absence and in the presence of Ph_3B. In both cases the methyl protons showed a single signal with the same chemical shift (2.4 ppm). Because in the BH_3-complexed lutidine the methyl signal is shifted to lower field (2.6 ppm), we infer that triphenylborane is not able to ligate the hindered nitrogen atom of 2,6-dimethylpyridine. In a subsequent experiment some borohydride was added to the solution containing lutidine and BPh_3, and under these conditions two distinct NMR signals from BH_3-complexed and uncomplexed base were clearly detected, confirming the formation of BH_3 by reaction 6.

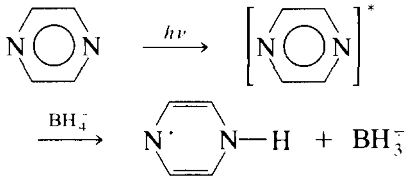
On this basis the results of the experiments performed on **1** and **2** in the presence of Ph_3B can be explained as follows. Pyrazine is complexed by BPh_3 at the two nitrogen atoms and radical **1f** is therefore observed, while the steric crowding because of the methyl groups in tetramethylpyrazine does not allow complexation by BPh_3. Instead, this base can be complexed by the less bulky BH_3, formed in situ. Complexation by two BH_3 (or BD_3 when using Bu_4NBD_4) was

Table 3
EPR spectral parameters of the radical anions of BH_3-dicomplexed *N*-heterocycles, $[H_3B(base)BH_3]^{-\bullet}$.

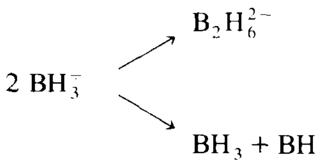
Radical	Coupling constants (1 G = 10^{-4} Tesla)	*g*-factor	*T* (K)
1d	$a(H^{2,3,5,6})$ 2.52, $a(2\ N)$ 8.00, $a(2\ ^{11}B)$ 3.38, $a(6\ H^{BH_3})$ 7.52	2.0034	298
2d	$a(12H)$ 2.40, $a(2\ N)$ 7.25, $a(2\ ^{11}B)$ 2.86, $a(6\ H^{BH_3})$ 8.21	2.0034	323
7d	$a(H^{1,4,5,8})$ 1.01, $a(H^{2,3,6,7})$ 1.45, $a(2\ N)$ 5.98, $a(2\ ^{11}B)$ 2.51, $a(6\ H^{BH_3})$ 6.02	2.0031	298
9d	$a(H^{5,6})$ 1.60, $a(H^{4,7})$ 2.78, $a(2\ N)$ 6.53, $a(2\ ^{11}B)$ 1.88, $a(6\ H^{BH_3})$ 4.32	2.0042	298
10d	$a(H^{5,6})$ 0.95, $a(H^{OCH_3})$ n.r., $a(2\ N)$ 6.16, $a(2\ ^{11}B)$ 1.78, $a(6\ H^{BH_3})$ 4.36	2.0040	298

also detected under the same experimental conditions in other diazines, such as phenazine and 4,7-dimethoxybenzo[2,1,3]thiadiazole (vide infra), where the binding sites are sterically crowded.

One important point about the ET mechanism is the nature of the photoreaction leading to the initial formation of some BH_3. As previously suggested, UV irradiation may give rise to photoexcitation of the *N*-heterocycle and to abstraction of an hydrogen atom from BH_4^- to afford $BH_3^{-\bullet}$, as exemplified in eqn. 9 for pyrazine. The borane radical anion in the absence of any substrate which may react with it, decays at low temperature by second-order kinetics [19], implying either dimerization (eqn. 10) to yield the diborane dianion $(B_2H_6)^{2-}$ or disproportionation to afford BH_3^{2-} and BH_3 (eqn. 11) [20]. It is possible that the initial formation of BH_3 takes place via the latter reaction; and the borane can be regenerated in the electron-transfer step of the chain reaction 4b.



(9)



$$2\,BH_3^{-\bullet} \longrightarrow B_2H_6^{2-} \qquad (10)$$

$$\longrightarrow BH_3 + BH_3^{2-} \qquad (11)$$

Thus, the light should lead to the formation of some BH_3 and not promote electron transfer. Therefore, we should observe **1b** also if the borane radical anion is produced in the absence of UV irradiation. This was done by decomposing tert-butylhyponitrite at 50°C within the EPR tube kept in the dark. Paramagnetic species were also observed in this case, their spectra being identical with those of the borane-complexed radicals detected under UV irradiation, the mono adduct **1b** with pyrazine and the diadduct **2d** with tetramethylpyrazine.

The reaction with the borohydride is affected by the solvent, as shown by the different behaviours observed in benzene and in ethereal solvents (THF, DME). In ethers, no EPR signals were detected with tetramethylpyrazine (**2**), and only a weak spectrum of **1b** was obtained with pyrazine. This can be explained in terms of competition for the complexation of BH_3 by the solvent and the heterocyclic substrate, and of the greater crowding about the nitrogen atoms in **2** with respect to **1**, by assuming that in THF the formation of the complex **1a** is not favoured compared to benzene and that for **2a** is prevented because of the methyl groups adjacent to the ligating site.

We also allowed pyrazine and borohydride to react in THF in the presence of dimethyl sulphate, Me_2SO_4. The reaction of Me_2SO_4 with a borohydride in ether solution (eqn. 12) is known to afford diborane [21], and thus borane.

$$2\ Bu_4NBH_4 + Me_2SO_4 \longrightarrow (Bu_4N)_2SO_4 + 2\ CH_4 + B_2H_6 \qquad (12)$$

Under the above conditions, where borane is produced in large amounts, a strong spectrum because of the radical anion of the dicomplexed pyrazine (**1d**) was observed (see Fig. 4) indicating that the detection of the radical anion either of the monoadduct or of the diadduct of the *N*-heterocycles depends on the amount of borane available in solution.

2.2. Compounds 3, 5, 7–10.

The behaviour of these *N*-heterocycles upon reaction with tetrabutylammonium borohydride, either in the ab-

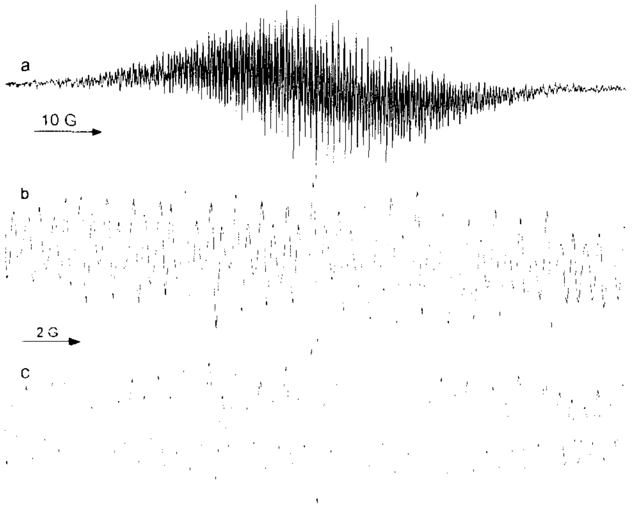


Fig. 4. Room-temperature EPR spectrum (a) of radical **1d** measured in THF. Spectra (b) and (c) represent the expansion of the central part of spectrum (a) and the corresponding simulation, respectively.

Table 4
EPR spectral parameters of the radical anions of BPh_3-complexed *N*-heterocycles, $[Ph_3B(base)BPh_3]^{-\cdot}$.

Radical	Coupling constants (1 G = 10^{-4} Tesla)	*g*-factor	*T* (K)
1f	$a(H^{2,3,5,6})$ 2.65, $a(2\ N)$ 7.99, $a(2\ ^{11}B)$ 2.51	2.0034	298
3f [a]	$a(H^{2,6})$ 2.70, $a(H^{3,5})$ 1.29, $a(N^{CN})$ 2.18, $a(N^{1})$ 6.21, $a(^{11}B)$ 1.94	2.0029	341
5f	$a(H^{2,6,2',6'})$ 0.93, $a(H^{3,5,3',5'})$ 1.84, $a(2\ N)$ 4.05, $a(2\ ^{11}B)$ 1.36	2.0033	298
8f	$a(H^{2,3})$ 3.31, $a(H^{5,8})$ 2.21, $a(H^{6,7})$ 1.11, $a(2\ N)$ 7.35, $a(2\ ^{11}B)$ 2.25	2.0031	335
9f	$a(H^{5,6})$ 1.56, $a(H^{4,7})$ 2.88, $a(2\ N)$ 6.65, $a(2\ ^{11}B)$ 1.42	2.0043	298

[a] Monoadduct of triphenylborane.

sence or the presence of triphenylborane, is analogous to that already discussed for pyrazine (**1**) and tetramethylpyrazine (**2**) and can be interpreted similarly.

4-Cyanopyridine (**3**) afforded the radical anion of the borane adduct **3b** when photoreacted with Bu_4NBH_4, both in benzene and in THF, whereas the BPh_3-complexed radical anion was observed when the reaction was carried out in the presence of triphenylborane (see Tables 2–4). It is remarkable that under the latter conditions the complexed radical species was formed spontaneously in THF, but only under UV irradiation in benzene.

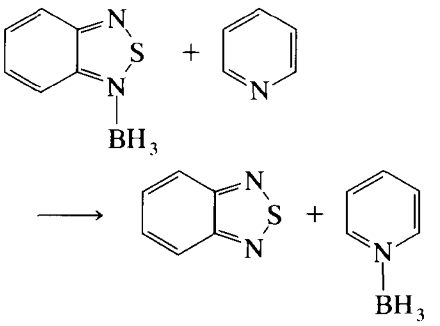
4,4′-Bipyridine (**5**) reacted with Bu_4NBH_4 under photolysis or even thermally on adding some tert-butylhyponitrite to the solution, giving rise to an extremely complex EPR spectrum more than 50 G wide, whose shape changes by using the deuterated borohydride Bu_4NBD_4. In this spectrum the centre does not correspond to the higher line, indicating that the radical must contain only one BH_3 unit. We believe that this spectrum, although not interpreted, is a result of the radical anion of the BH_3 adduct of **5**. In the presence of BPh_3, compound **5** reacted spontaneously with the borohydride affording the corresponding dicomplexed radical anion **5f**.

Phenazine (**7**) afforded the corresponding radical anion when it reacted with Bu_4NBH_4. With time the EPR spectrum started to show additional lines because of a second species which, however, did not completely replace the initial product. The spectrum of this second species, which is much wider than that of the radical detected initially, is presumably a result of the radical anion of the monoadduct of **7** with BH_3. By carrying out the reaction in the presence of BPh_3, a strong EPR spectrum of the radical anion **7d** of the BH_3-dicomplexed phenazine is observed. In this case it also seems that the crowding caused by the *peri* hydrogens prevents the approach of the bulky triphenylborane to the nitrogen atoms. Thus, the role of BPh_3 is that of reacting with BH_4^- to generate BH_3 (eqn. 6), which is ligated by **7**. The same radical, **7d**, is obtained by reaction of **7** with Bu_4NBH_4 in the presence of Me_2SO_4 in THF (eqn. 12).

With quinoxaline (**8**) an uninterpreted EPR spectrum wider than 60 G attributed to the radical anion of the monoadduct **8b**, was again observed in the photoreaction with Bu_4NBH_4. A weak spectrum of the bis(triphenylborane) adduct radical **8f** (see Table 4) was detected in the presence of BPh_3.

Benzo[2,1,3]thiadiazole (**9**) showed very peculiar behaviour. Upon reaction with the borohydride, slow formation of the radical anion of the BH_3 monoadduct **9b** was observed in THF, even in the absence of UV irradiation (see Fig. 5). In benzene this radical was detected only upon photolysis.

The spontaneous formation of **9b** can be explained by assuming an initial slow, reaction of **9** with BH_4^- to give some BH_3, which then undergoes the chain reaction of eqn. (4b). This spontaneous reaction is feasible in the present case because the reduction potential of **9** is higher (−1.49 V vs. SCE) than those of the derivatives previously examined. In the reaction in the presence of pyridine or pyrazine, which are both more basic than **9** (eqn. 13), the radical anion of borohydride was the only detectable species.



(13)

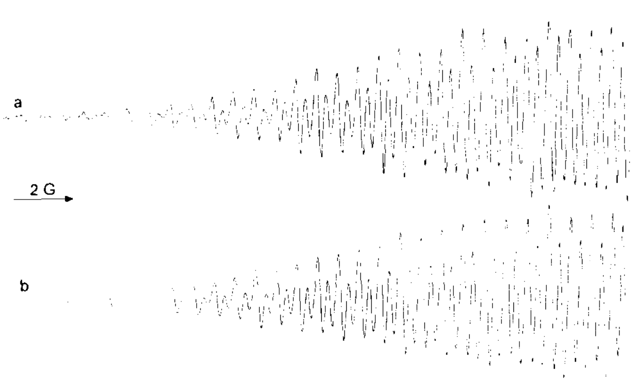


Fig. 5. Experimental (a) and simulated (b) low field half EPR spectrum of radical **9b** obtained by reaction of borohydride with **9** in THF in the absence of light.

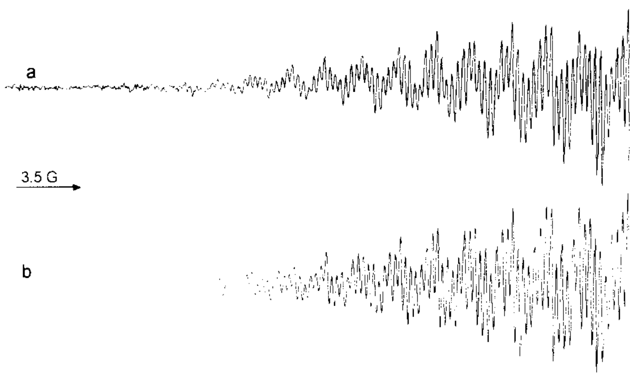


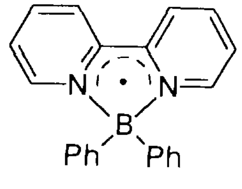
Fig. 6. Experimental (a) and simulated (b) low field half EPR spectrum of radical **9d** recorded in THF at room temperature.

The radical anions of the bis(borane) (see Fig. 6) or bis(triphenylborane) diadduct of **9** were observed when performing the reaction in the presence of either Me_2SO_4 or BPh_3. In the reaction of 4,7-dimethoxybenzo[2,1,3] thiadiazole with the borohydride in the presence of BPh_3, we observed the radical anion of the BH_3 diadduct instead of that of the BPh_3 analogue. This suggest that the crowding caused by the methoxy groups prevents the approach of the bulky triphenylborane to the nitrogen sites. The same spectrum is also obtained when the reaction is carried out in the presence of Me_2SO_4.

Unexpected behaviour was observed on reaction of **10** with the borohydride. In THF the uncomplexed radical anion was the only detectable species, whereas in benzene we observed the growth of a second species after the initial formation of the radical anion. This was identified as the radical anion of the BH_3 monoadduct of **10**.

2.3. 2,2′-Bipyridine

This compound, because of its nature of bidentate ligand, shows a different reactivity from the compounds discussed above. No EPR signal was detected when **6** reacted with Bu_4NBH_4, spontaneously or photolytically. Photolysis of **6** in the presence of BPh_3 gave rise to a strong EPR spectrum attributed to the complex **6g**, on the basis of the measured hyperfine splitting constants. Its formation can be accounted for by a bimolecular homolytic substitution (S_H2) at the boron of triphenylborane, carried out by the excited state of 2,2′-bipyridine [22]. A radical having a similar structure has been observed upon reaction of **6** with AlH_3 [5].



6g

$a(2\ N)=3.08$
$a(4\ H)=0.61$
$a(4\ H)=3.08$
$a(1\ ^{11}B)=3.33$
$g=2.0029$

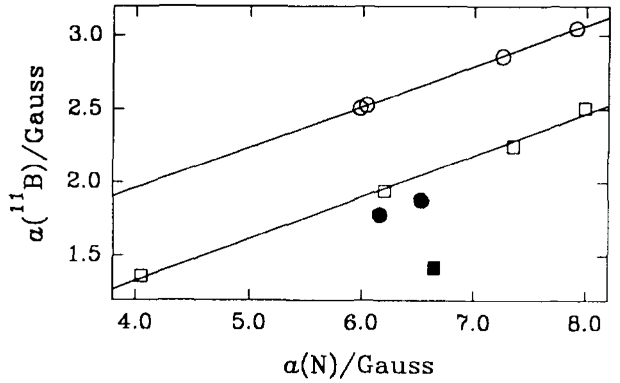


Fig. 7. Dependence of the ^{11}B hyperfine splitting on $a(N)$ in the BH_3 (○) and BPh_3 (□) complexed radical anions of *N*-heterocycles. Radicals derived from species **9** and **10** are indicated by the filled symbol.

2.4. EPR parameters

Values of the hyperfine splitting constants and *g*-factors for the radical anions of the BH_3 or BPh_3-dicomplexed *N*-heterocycles investigated are not too different from those of the uncomplexed radical anions [23]. This suggests either that the spin-density distribution is remarkably similar in the two cases, or that the unpaired electron is only slightly delocalized onto the boron nuclei. This then implies that the nitrogen–boron bond has no π character, and that the important mechanism of spin transfer to boron is spin polarisation. Support for this hypothesis is provided by the linear dependence of the ^{11}B coupling constant on the nitrogen hyperfine splitting as shown in Fig. 7.

Two features emerging from these observations are: the smaller value of the boron coupling in the triphenylborane-complexed radical than in the BH_3-complexed radicals, and the lack of correlation between $a(^{11}B)$ and $a(N)$ in the radical derived from the benzothiadiazoles **9** and **10**. The presence of the sulphur atom in the latter radicals may modify the interaction between the π-system and the boron atom, somewhat.

3. Conclusions

The room-temperature reaction in benzene or ethers of tetrabutylammonium borohydride with 4-nitropyridine, phenazine, and 1,4,5,8-tetraazanaphthalene, all having reduction potentials higher than −1.2 V vs. SCE, gives rise to the corresponding radical anions formed by a single electron-transfer process from the borohydride ion to the *N*-heterocyclic compound. With benzo[*c*]cinnoline ($E_{1/2} = -1.50$ V vs. SCE) the formation of the radical anion was only observed under irradiation with UV light.

All other nitrogen containing heteroaromatics bases investigated, less reducible than the above, afforded the radical anions of the corresponding mono borane or bis(borane) adducts under photolytic conditions.

Because complexation by borane of one or both nitrogen atoms of the *N*-heterocycle makes the base more easily reducible, the number of complexed borane units depends on the reduction potential of the starting compound. Thus with pyrazine ($E_{1/2} = -2.12$ V vs. SCE) monocomplexation is sufficient to induce electron transfer, while with tetramethylpyrazine ($E_{1/2} = -2.51$ V vs. SCE) complexation at both nitrogen atoms is required to make the electron-transfer process possible. The formation of radicals can take place only if some borane is produced initially by a photochemical or thermochemical process.

The detection of paramagnetic species in the reaction of *N*-heterocycles with reducing agents such as borohydrides, generally regarded as nucleophiles, provides an additional examples of the fact that "anionic" reagents can also react homolytically. Although the radical-anion complexes observed in the present investigation may be side-products not involved in the main reduction reaction, which is expected to afford dihydrodiazines [5], their detection provides evidence that borohydrides may behave as single-electron-transfer reagents.

4. Experimental details

4,7-Dimethoxybenzo[2,1,3]thiadiazole [24], 1,4,5,8-tetraazanaphthalene [25], tert-butylhyponitrite [26] and Bu_4NBD_4 [17] were prepared as described in the literature. All other compounds were commercially available and were used after standard purification procedures.

The EPR spectra were recorded on a Bruker ESP 300 spectrometer equipped with an NMR gaussmeter for field calibration and a Hewlett Packard 5350B microwave frequency counter for the determination of the *g*-factors, which were corrected with respect to that of perylene radical cation in concentrated H_2SO_4 ($g = 2.00258$).

Photolysis was carried out by focusing the unfiltered light from a 500 W high-pressure mercury lamp on the EPR cavity. Digitised EPR spectra were transferred to an AT-486 (33 MHz) PC, in order to analyse complex spectra by numerical techniques.

Radical anions $[H_3B(base)]^{-\cdot}$ were generated in benzene, THF or DME solutions of the *N*-heterocycle (ca. 0.1 M) containing Bu_4NBH_4 (ca. 0.4 M) by photolysis with UV light or by thermal decomposition at 50°C of some tert-butyl hyponitrite added to the solution. Radical anions of the bis borane adducts, $[H_3B(base)BH_3]^{-\cdot}$, were obtained by adding Me_2SO_4 (ca. 0.01 M) to the THF solution of the *N*-heterocycle and Bu_4NBH_4.

Radical anions of the bis(triphenyl borane) adducts, $[Ph_3B(base)BPh_3]^{-\cdot}$, were generated in situ by adding a small amount of Bu_4NBH_4 to a deoxygenated THF or benzene solution of the *N*-heterocycle and BPh_3, present in a molar ratio of 1:2. In order to achieve optimum resolution, the concentration of the radicals had sometimes to be lowered by dilution and the spectra were recorded at different temperatures.

The assignment of the ring-proton splitting was made on the basis of HMO/McLachlan spin density calculations [27] performed with standard programs using the following parameters: $h_N = 0.75$, $h_{N(B)} = 1.0$, $k_{CN} = 1.0$, $\lambda = 1.2$.

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