Radical Ions, 41 [1,2]

Durosemiquinone and its BF Analogue — Detection of 1,4-Diborine as an Unexpected Elimination Product

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The photoelectron spectra and the one electron-reduction behaviour of 1,4-difluoro-2,3,5,6-tetra-methyl-1,4-dibora-2,5-cyclohexadiene (1) and of the isoelectronic duroquinone (2) are compared. While duroquinone forms a very stable anion radical, durosemiquinone, the radical anion of the BF analogue was observed only as a short-lived intermediate. In the presence of potassium metal a secondary anion radical is formed, which can be stabilized considerably by complexation of the K^+ cation with dicyclohexyl-18-crown-6. ESR analysis demonstrates that the latter species is the radical anion of 2,3,5,6-tetramethyl-1,4-diborine (3·$^\ominus$), a hitherto unknown benzenoid hetero-cycle.
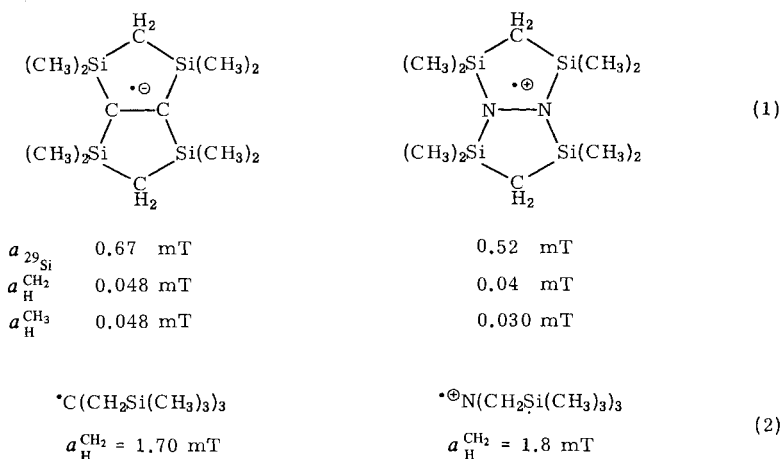
Radikalionen, 41 [1,2]

Durosemichinon und sein BF-Analogon — Nachweis von 1,4-Diborin als unerwartetes Eliminierungsprodukt

Die Photoelektronenspektren und das Einelektronen-Reduktionsverhalten von 1,4-Difluor-2,3,5,6-tetramethyl-1,4-dibora-2,5-cyclohexadien (1) und des isoelektronischen Durochinons (2) werden verglichen. Während Durochinon ein sehr stabiles Anion-Radikal, das Durosemichinon, bildet, ließ sich das Radikalanion des BF-Analogons nur als kurzlebiges Zwischenprodukt nachweisen. In Gegenwart von Kalium bildet sich ein Sekundär-Anionradikal, das durch Komplexierung des K^+-Kations mit Dicyclohexyl-18-krone-6 beträchtlich stabilisiert werden kann; die ESR-Analyse zeigt, daß es sich dabei um das Radikalanion von 2,3,5,6-Tetramethyl-1,4-diborin (3·$^\ominus$) handelt, eines bislang unbekannten benzolischen Heterocyclus.

Radicals and radical ions are valuable systems to study the concept of isoelectronic compounds because the spin distribution due to the unpaired electron is a most sensitive molecular probe: not only small molecules [3] but also isoelectronic polyatomic species [4–7] have been investigated by the method of electron spin resonance (ESR). On comparison of the properties of isoelectronic paramagnetic systems, conspicuous similarities as well as characteristic differences have been observed, e. g. for the anion/cation pair [5,6] in (1) or for the isoelectronic radical vs. radical cation [7] in (2).

Despite comparable methylene proton coupling, only the carbon radical in (2) exhibits a temperature-independent ESR spectrum i. e. free rotation about the $X-CH_2SiR_3$ bond on the ESR time-scale over the whole temperature range[7].

(1)

$a_{29_{Si}}$	0.67 mT	0.52 mT
$a_H^{CH_2}$	0.048 mT	0.04 mT
$a_H^{CH_3}$	0.048 mT	0.030 mT

$$^\bullet C(CH_2Si(CH_3)_3)_3 \qquad\qquad ^{\bullet\oplus}N(CH_2Si(CH_3)_3)_3$$

$$a_H^{CH_2} = 1.70 \text{ mT} \qquad\qquad a_H^{CH_2} = 1.8 \text{ mT}$$

(2)

Among the most prominent paramagnetic organic molecules are the benzosemi-quinones[8], which are easily obtained by one electron-reduction of benzoquinones or by one electron-oxidation of hydroquinone dianions. Many 1,4-benzosemiquinones are persistent at ambient temperatures and, therefore, their ESR hyperfine structure has been first studied in 1955[9].

A class of compounds isoelectronic to 1,4-benzoquinones has become available by the technique of cocondensation of boron monofluoride and acetylenes at low temperatures[10], e. g. **1**.

(3)
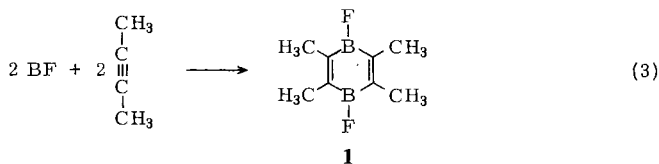
The 1,4-difluoro-1,4-dibora-2,5-cyclohexadienes, like the tetramethyl derivative **1**, show some similarities corresponding to the 1,4-benzoquinones as evidenced by structural[11] and spectroscopic[10] investigations as well as by their complexation chemistry[11]. On the other hand, however, no stable dianion of **1** could by obtained by reduction with sodium amalgam[10]. Advanced methods for radical anion generation[12] now available have led us to attempt the one electron-reduction of **1** to its anion radical **1**$^{\bullet\ominus}$, an isoelectronic counterpart to durosemiquinone. In the following, the one electron-reduction results are presented together with a comparison of the photoelectron spectra of duroquinone and its BF analogue **1**.

A. Photoelectron Spectra and Assignment

The PE spectra of both 1,4-difluoro-2,3,5,6-tetramethyl-1,4-dibora-2,5-cyclohexadiene (**1**) and duroquinone (**2**) display separated bands only in their low-energy region (Fig. 1); the hump above 12 eV is due predominantly to methyl group ionizations.
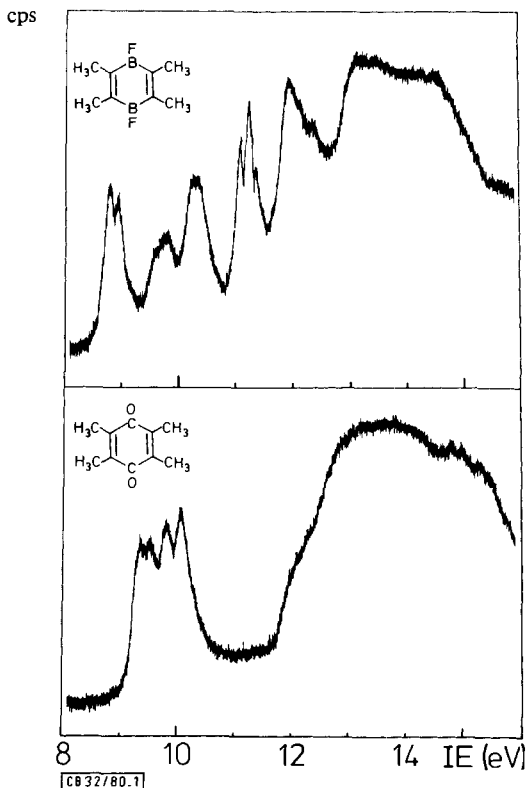

Fig. 1. HeI-Photoelectron spectra (8 to 16 eV) of 1,4-difluoro-2,3,5,6-tetramethyl-1,4-dibora-2,5-cyclohexadiene (**1**) and its isoelectronic analogue duroquinone (**2**)

The assignment of each the four lowest radical cation states will be based via Koopmans correlation $IE_u = -\varepsilon_j^{CNDO/F}$ on calculations using a PE-spectroscopically reparametrized CNDO version F[13], which already has been applied successfully to other boron compounds[13], and which also calculates the correct sequence for benzoquinone[14] (Fig. 2) without any additional configuration interaction[14]. Whereas the CNDO/F orbital sequences differ for the isoelectronic parent compounds, FB(HC = CH)$_2$BF and OC(HC = CH)$_2$CO, on tetramethyl-substitution identical ones result (Fig. 2). This can be traced back to the hyperconjugative effect of the methyl groups on the π orbitals of benzoquinone, shifting both the lone pair combinations $n_O^-(-\sigma_R)$ and $n_O^+(-\sigma_R)$. In spite of the same sequence, the highest occupied orbitals do show considerable difference: CO contributions are much larger than those of the

fluorine lone pairs, which are calculated around 16.6 eV (n_F^π) and 17.7 eV (n_F^σ), respectively.
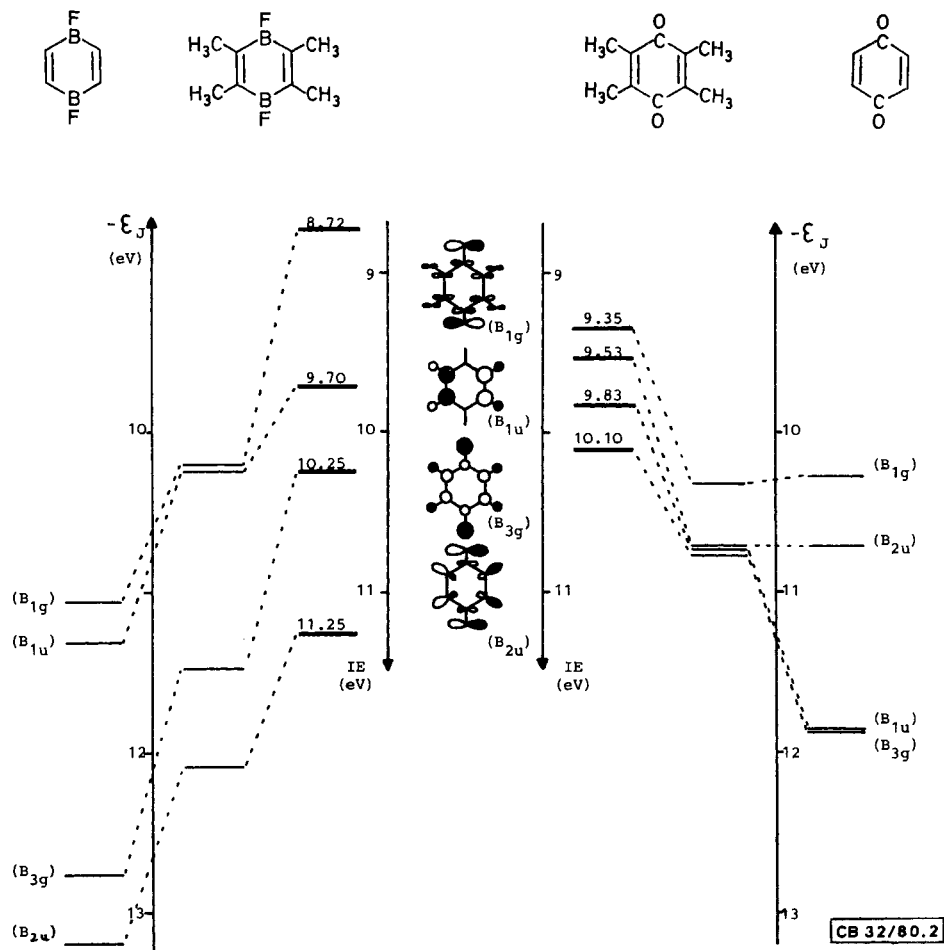

Fig. 2. Assignment of the lowest four radical cation states of the isoelectronic tetramethylated (R = CH$_3$) cyclohexadiene derivatives FB(RC = CR)$_2$BF and OC(RC = CR)$_2$CO based on CNDO/F calculations including the parent compounds (R = H)

The PE spectroscopic ionization patterns (Figs. 1 and 2), however, exhibit distinct differences. To begin with, the center of gravity $\overline{IE_{1-4}}$ is lower for duroquinone (9.70 eV) than for the BF derivative (9.96 eV) in full accord with the mean of the first ionization energies of the respective atoms (C: 11.26 eV; O: 13.16 eV; B: 8.30 eV; F: 17.42 eV)[15]. Most striking is the much larger splitting of 2.43 eV for the BF derivative vs. only 0.75 eV for duroquinone. This observation can be rationalized by the differing radical cation state contributions already mentioned in the discussion of the CNDO/F orbitals (Fig. 2). Thus in duroquinone electrons both from the oxygen lone pairs –

e. g. 2-cyclopenten-1-one exhibits $IE_1(n_O) = 9.34$ eV[16] – and from the ethene π subunits – e. g. 1,2-dimethylethenes ionize at $IE_1(\pi) = 9.14$ eV[17] – make comparable contributions. Due to the perpendicular arrangement of both moieties no direct interaction occurs, and hence ionizations IE_1 to IE_4 crowd within a rather narrow range. On the contrary, the BF derivative displays four lowest $M^{\cdot\oplus}$ states of rather different composition, with the ground state $\tilde{X}(^2B_{1g})$ represented by a ring σ orbital, the next one $\tilde{A}(^2B_{1u})$ and to some extent also $\tilde{B}(^2B_{3g})$ are analogous to the ones of duroquinone (Fig. 2), followed by another and different ring σ cation state, $\tilde{C}(^2B_{2u})$.

Nevertheless, despite of the individual facets displayed by the two isoelectronic molecules, the PE spectroscopic assignment clearly emphasizes an overall chemical relationship. And therefore, since comparable charge distributions were calculated by CNDO/F, given in **A, B**, and durosemiquinone radical anion is known[8], we also tried to reduce the BF derivative.

$$\textbf{A} \quad \overset{+0.42}{\underset{/}{>}}\text{C}\!\!-\!\!-\!\!\overset{-0.42}{\text{O}} \qquad\qquad \textbf{B} \quad \overset{+0.58}{\underset{/}{>}}\text{B}\!\!-\!\!-\!\!\overset{-0.40}{\text{F}}$$

B. One Electron-Reduction and Assignment of the ESR Spectra

The one electron-reduction of tetramethyl-1,4-difluoro-1,4-dibora-2,5-cyclohexadiene **1** with potassium in 1,2-dimethoxyethane (DME) solution at $-60\,°C$ yielded a radical species with an ESR spectrum dominated by a 12 H multiplet and accompanied by some satellite lines[1]. The weak ESR signal decreased rapidly after raising the temperature of the sample above 210 K.

Because of the limited persistence of the radical anion obtained, the reduction has been repeated adding the potassium ion complexing dicyclohexyl-18-crown-6. This advantageous technique[12] allowed to observe the ESR spectra of two different radical anions. The species first generated displays an ESR spectrum with a distinct triplet structure (Fig. 3, A) and a rather large line-width of 0.3 mT. This primary radical $\mathbf{1}^{\cdot\ominus}$ has a limited lifetime of only about 15 minutes even at low temperatures, and on its decay the ESR spectrum described above[1] of the secondary radical anion $\mathbf{3}^{\cdot\ominus}$ appears again, however, this time the complexation of the counterion $K^{\oplus}$ kept the radical species persistent for several hours at room temperature, so that the remarkable temperature dependence of its ESR spectrum (cf. Fig. 4, A) could be observed[1].

The ESR spectrum (Fig. 3, A) of the transient species observed first is assigned to the radical anion of the intact molecule $\mathbf{1}^{\cdot\ominus}$.

Strongest evidence for this assignment is the large triplet most probably due to the two fluorine nuclei (^{19}F: $I = \frac{1}{2}$, 100% nat. abundance), because the ESR coupling constants a_{19F} are generally quite large[8]. As concerns the additional splitting (Fig. 3, A), other nuclei present with non-zero spin are 12 protons and 2 borons. The boron isotope ^{10}B ($I = 3$) occurs in a natural abundance of approximately 20%, whereas the dominating isotope ^{11}B (80%) possesses a nuclear spin of $I = \frac{3}{2}$. Two chemically equivalent boron atoms would give rise to three different isotope combinations with a ratio of the coupling constants a_{11B}/a_{10B} resembling the ratio of the nuclear magnetic moments $\mu_{11B} = 2.6885/\mu_{10B} = 1.8007$. The assumption that the smaller splitting in the ESR spectrum of
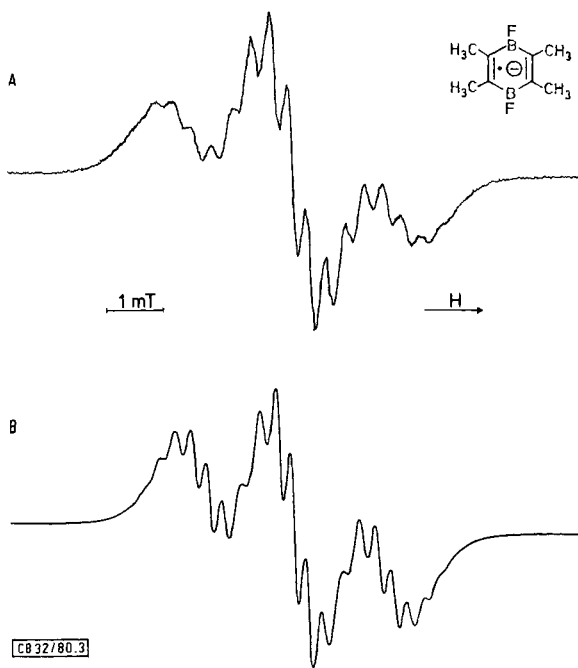
Fig. 3. ESR spectrum of 1,4-difluoro-2,3,5,6-tetramethyl-1,4-dibora-2,5-cyclohexadiene
radical anion ($1^{\cdot\ominus}$) at 210 K (A) and its computer simulation (B)

$1^{\cdot\ominus}$ originates from the 12 methyl protons is based on the following arguments. Coupling constants $a_H^{CH_3}$ are expected to be between 0.1 and 0.5 mT[8], and the resulting ESR lines should be observable. On the contrary, ESR spectra of radical ions containing boron atoms in general[2,4,18-20] display unusual line width effects: lines with group spin quantum numbers $M_B \neq 0$ are severely broadened, and at low temperatures the splitting pattern due to the boron nuclei may disappear almost completely[2,19]. Because the ESR spectrum of $1^{\cdot\ominus}$ (Fig. 3, A) has been recorded at only 210 K, we assign the smaller coupling to the methyl protons. The secondary radical anion $3^{\cdot\ominus}$ gives rise to an ESR spectrum with a comparatively small line width of 0.015 mT and with a marked temperature dependence[1]: At ambient temperature a 12 H multiplet due to the 4 equivalent methyl groups is observed split further by hyperfine interaction with the 2 boron atoms. A computer simulation of the 290 K spectrum (Fig. 4, B) yields correct line positions, although the lines with $M_B \neq 0$ are broadened and, therefore, appear to be somewhat smaller in the experimental spectrum (Fig. 4, A). As outlined above, the line broadening of the $M_B \neq 0$ lines increases at lower temperature: thus at 210 K only the 12 H multiplet keeps up its normal intensity distribution, whereas the remaining lines have almost vanished[1].

The most important feature of the ESR spectrum of the secondary radical anion $3^{\cdot\ominus}$ is, however, the complete absence of any fluorine coupling. Obviously, the excess of potassium metal used in the reduction must have abstracted both fluorine substituents from the the starting molecule 1, thereby producing the 1,4-diborine radical anion $3^{\cdot\ominus}$.

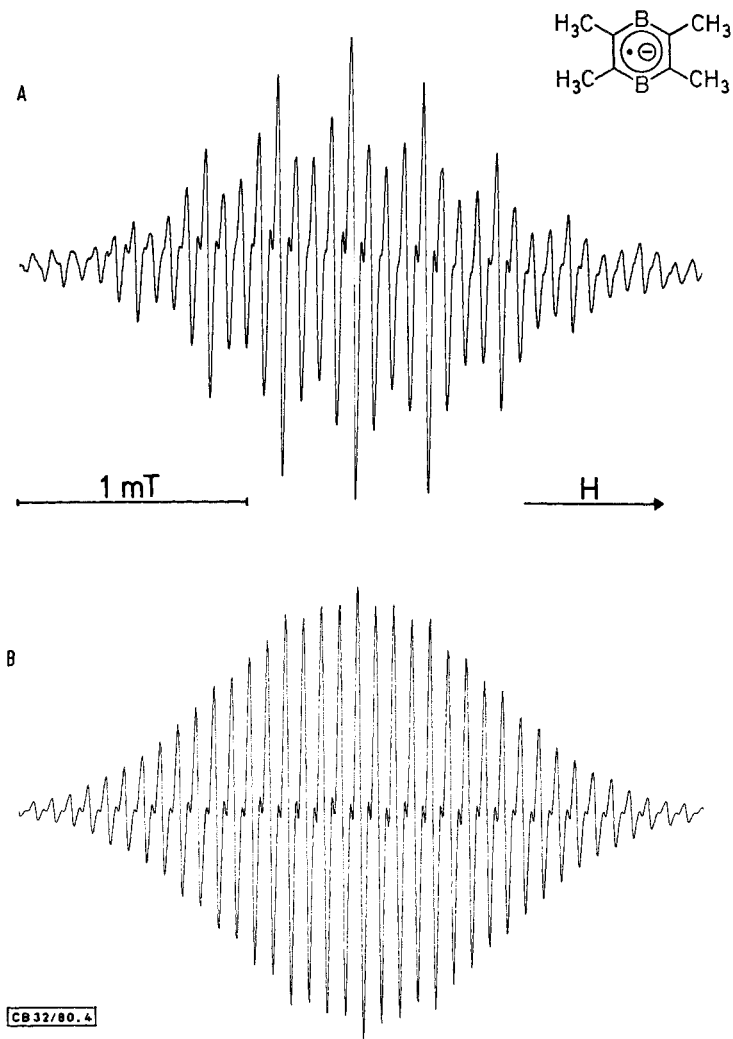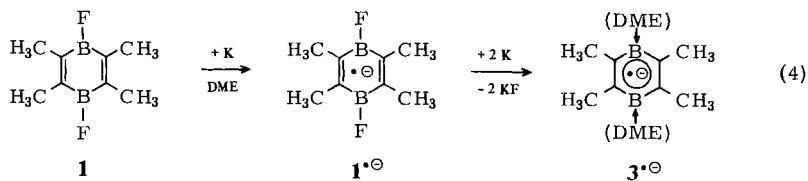$$H_3C\overset{B}{\underset{B}{\bigodot\ominus}}CH_3$$
$$H_3C\qquad\qquad CH_3$$

Fig. 4. Central part of the ESR spectrum of 2,3,5,6-tetramethyl-1,4-diborine radical anion ($3^{\cdot\ominus}$) at 290 K (A) and its computer simulation (B)
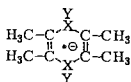
So far, *B*-unsubstituted borabenzenes are not reported in the literature, although anions $C_5H_5BR^{\ominus}$ have been prepared[21] and their complexation chemistry[22,23] studied.

C. Discussion of the Results

The ESR coupling constants of $1^{\cdot\ominus}$ and of $3^{\cdot\ominus}$ as derived by computer simulation of the experimental spectra (Fig. 3 and 4) can be elaborated by comparison with the ESR data of the iso(π)electronic radical anions of durosemiquinone and of 2,3,5,6-tetramethylpyrazine[24], respectively (Tab. 1 and 2). We confirm the methyl proton coupling constant of the former[25] and, in addition, have detected a ^{13}C splitting which is attributed to C-1 and C-4 based on intensity measurements.

Table 1. Coupling constants (mT) of 1,4-difluoro-2,3,5,6-tetramethyl-1,4-dibora-2,5-cyclohexadiene radical anion ($1^{\cdot\ominus}$) and of duroquinone radical anion ($2^{\cdot\ominus}$)

| $M^{\cdot\ominus}$ | | $>XY$ | |
		$>B-F$	$>C=O$
$a_H^{CH_3}$		0.30	0.190
a_X		a)	0.130
a_Y		1.65	0.954 b)

a) Not observable (cf. text). – b) Value for ^{17}O-enriched benzosemiquinone[26].

Table 2. Coupling constants (mT) of 2,3,5,6-tetramethyl-1,4-diborine radical anion ($3^{\cdot\ominus}$) and of 2,3,5,6-tetramethylpyrazine radical anion

| $M^{\cdot\ominus}$ | | X | |
		B	N^{24}
$a_H^{CH_3}$		0.319	0.173
a_X		0.080 a)	0.618 b)

a) Temperature-dependent (210 K: $a_{11_B} = 0.071$ mT). – b) An additional splitting observed[24] has been assigned to the counterion ($a_K = 0.031$ mT).

A comparison of the isoelectronic radical anions, $1^{\cdot\ominus}$ and $2^{\cdot\ominus}$, has to be based on the CH_3 coupling constant as the only ESR parameter available for both of them (Tab. 1). It is significantly larger for $1^{\cdot\ominus}$ than for the duroquinone anion radical, indicating *more* spin density in the 2,3,5,6-positions and *less* spin population in the BF moiety. For the parent radical anion, benzosemiquinone, a spin distribution with approximately $\frac{1}{3}$ of the spin density on the $C=C$ double bonds and $\frac{2}{3}$ residing on the carbonyl groups has been calculated[26].

For the two isoelectronic tetramethyl derivatives investigated, INDO closed shell as well as open shell calculations have been performed under the assumption of comparable and planar structures of the radical anions generated, although especially for the BF derivative $1^{\cdot\ominus}$ some distortion cannot be excluded. The INDO atom charges suggest, that in their ground state both neutral molecules M exhibit comparably polarized groups $C^{\delta+}-X^{\delta-}$. Reduction, however, increases the charges differently: in the quinone mainly at the oxygen center, and in the BF derivative predominantly at boron. In the resulting radical anions, likely the $B-F$ group has less capability to

delocalize an additional unpaired electron than the isoelectronic $C=O$ moiety, although the spin population at the ^{19}F nuclei is quite remarkable as evidenced by the large coupling constant (Tab. 1) and the broadening of the outer triplet lines (Fig. 3, A).

$$(5)$$
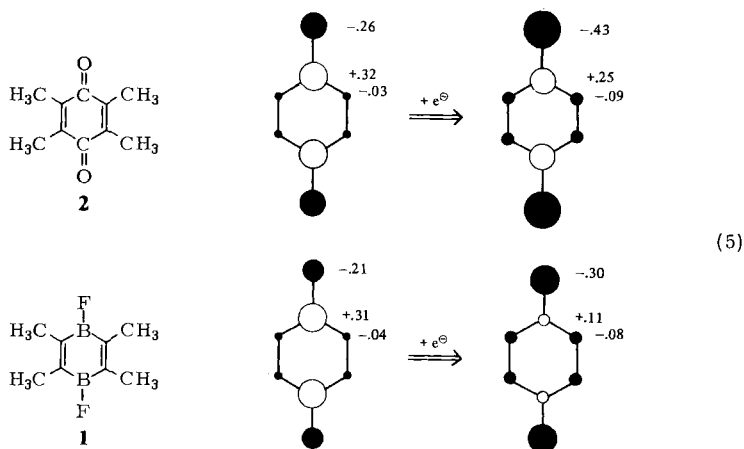
The spin distribution in the secondary radical anion $3^{\cdot\ominus}$; to which we assign the 1,4-diborine structure, is characterized by a comparatively large methyl proton coupling constant and a surprisingly small ^{11}B splitting of only ≈ 0.075 mT; for instance, triphenylboron radical anion $(C_6H_5)_3B^{\cdot\ominus}$ shows $a_{11_B} = 0.784$ mT[4]. To rationalize this observation and to further support the structure proposed for $3^{\cdot\ominus}$, a HMO first order perturbation[27] can be applied for a comparison with the π spin distribution in the isoskeletal, iso(π)electronic 2,3,5,6-tetramethylpyrazine radical anion[24].

$$(6)$$
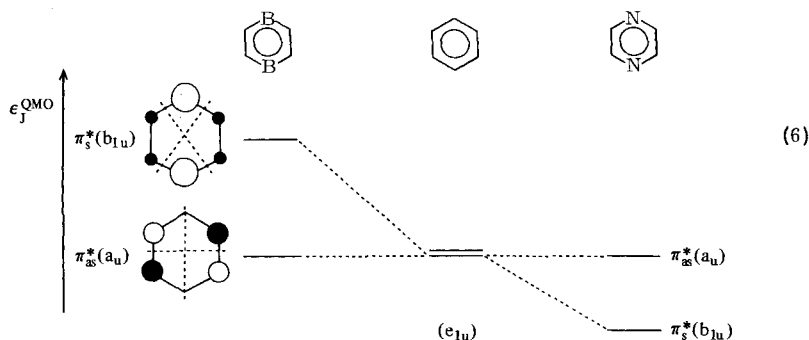
The higher coulomb potential $\alpha_N > \alpha_C$ lowers and the smaller coulomb potential $\alpha_B < \alpha_C$ raises only $\pi_s^*(b_{1u})$ of the antibonding benzene $\pi^*(e_{1u})$ orbitals, while $\pi_{as}^*(a_u)$ due to its nodal plane through both substitution centers should remain unchanged[27]. If the radical anion spin density is represented by the singly-occupied orbital $\pi_s^*(b_{1u})$ as in the pyrazine radical anion, one expects and observes large ^{14}N and comparatively small ^{1}H coupling constants (Tab. 2). In contrast, if the π spin population is represented by

the singly-occupied orbital $\pi^*_{as}(a_u)$ as in the 1,4-diborine radical anion, then a rather large proton and almost zero ^{11}B coupling should result, as indeed found in the ESR measurements (Tab. 2). Small ESR coupling constants are always observed, where symplifying HMO models predict zero spin density[28], whereas e. g. the more refined McLachlan treatment[29] usually produces satisfactory agreement due to small negative spin densities calculated for nuclei in a π nodal plane[28]. Summarizing, the perturbation model (6) allows to generalize the spin distribution in 7π-electron/6-membered ring radical anions and thus adds another facet to the novel benzenoid heterocycle 1,4-diborine.

Concluding Remarks

A rather close chemical relationship between both isoelectronic compounds, 1,4-difluoro-2,3,5,6-tetramethyl-1,4-dibora-2,5-cyclohexadiene (1) and duroquinone (2), is revealed by their photoelectron spectra. On reduction, the molecules yield radical anions of markedly different stability: durosemiquinone is persistent at room temperature, whereas the isoelectronic BF analogue due to a somewhat limited delocalization into the BF groups decomposes at about 200 K.

The counter cation $K^\oplus$ complexation, originally intended to increase the persistence of the reduced BF system, has led to the discovery of a novel benzenoid heterocycle, 2,3,5,6-tetramethyl-1,4-diborine. Its spin distribution as well as the differing one of its 7π-electron analogue, the pyrazine radical anion, can be rationalized by HMO perturbation arguments. It constitutes another[30] and striking example for a molecule M, which is so far unknown, although both its radical cation $M^{\cdot\oplus}$ as well as its radical anion $M^{\cdot\ominus}$ have been detected and characterized spectroscopically either in the gas phase or in solution.

The evident question, whether also the neutral compound 1,4-diborine might be capable of existence, we have tried to approach by a geometry-optimized MNDO calculation[31]. Starting from either hexagonal planar or regular octahedral ensembles, the self-consistent results obtained give a rather gloomy forecast concerning the existence of neutral 1,4-diborine: the planar moiety ($\Delta Hf^{MNDO} \approx 106$ kcal/mol) displays unusual angles CBC $\approx 145°$, and the tetragonal bipyramid ($\Delta Hf^{MNDO} \approx 198$ kcal/mol) should exhibit unlikely bond distances $d_{BC} \approx 180$ pm. Although possibly more stable structures remain to be calculated[31,32], it may well be, that the additional negative charge as well as the reduction mixture which contains DME i. e. a potentially boron complexing ether ligand, both stabilize the 1,4-diborine radical anion as suggested by the ESR evidence. The possibility whether the 1,4-diborine moiety can also be stabilized by complexation with transition metals is actively pursued.

Experimental Part

1,4-Difluoro-2,3,5,6-tetramethyl-1,4-dibora-2,5-cyclohexadiene (**1**) was prepared by cocondensation of BF and 2-butyne at 77 K according to ref.[10]. Duroquinone (**2**) was obtained from Aldrich and was used without further purification.

Radical anion generation has been performed by reacting distilled potassium metal with solutions of the compounds in pure 1,2-dimethoxyethane (DME) on a vacuum line. The persistence of the anion radical **3**$\cdot^{\ominus}$ could be improved considerably by adding dicyclohexyl-18-crown-6: 1 mg of **1** and ca. 5 mg of the crown ether were dissolved in 1 ml of DME, the ESR glass apparatus was sealed off under high vacuum and the solution was brought carefully in contact with a potassium mirror at low temperature. Without the presence of the reducible species the formation of concentrated "solvated electron" solutions is observed; while **1** reacts to give a light green solution.

Photoelectron spectra: Perkin Elmer PS 16, calibration with Xe($^2P_{3/2}$: 12.13 eV), Ar($^2P_{3/2}$: 15.76 eV) or N$_2$(Σ_g: 15.57 eV).

Electron spin resonance spectra: Varian E 9 equipment, frequency 9.5 GHz, magnetic field 330 mT, 100 kHz field modulation; calibration with perylene radical anion in DME[33].

ESR computer simulations have been achieved using the program ESPLOT[34]. The program is designed to handle line-rich spectra with unusual splitting patterns and isotope combinations.

CNDO calculations were carried out with the PE-spectroscopically reparametrized CNDO/F version[13]. For INDO closed and open shell calculations the QCPE program has been used. The ground state geometries of **1** and duroquinone (cf. Fig. 2) were taken from crystallographic data[10,35].

All calculations have been performed at the Hochschulrechenzentrum Frankfurt using its Univac 1108 system and a Calcomp 763 plotter.

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