Inorganic Hybrid Analogues of Thiele's and Chichibabin's Hydrocarbons. Spectroscopy, Electrochemistry, and Structure

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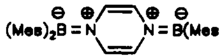
The formal substitution of external C═C bonds in quinonoid hydrocarbons such as 7,7,8,8-tetraaryl-*p*-quinodimethanes and 1,1′-biphenyl-4,4′-diylbis(diarylmethyl) compounds with the isoelectronic B═N function has occurred in 1,4-bis(dimesitylboryl)-1,4-dihydropyrazine (**1**) and 1,1′-bis(dimesitylboryl)-1,1′,4,4′-tetrahydro-4,4′-bipyridylidene (**2**). These new inorganic hybrid analogues of Thiele's and Chichibabin's hydrocarbons are sufficiently electron-rich to allow chemical and electrochemical one-electron oxidation despite the strong π acceptor effect of $BMes_2$ substituents. Unusual small ^{11}B and ^{14}N EPR/ENDOR coupling constants of the cation radicals $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ indicate a considerable degree of π bonding within the B═N units. The crystal structure of **2** as bis(benzene) solvate reveals a significantly higher degree of π electron localization than Chichibabin's hydrocarbon. The B–N distance of 144.4 (3) pm is close to that in borazine or hexagonal boron nitride. Hückel MO calculations were used to interpret EPR/ENDOR, electrochemical, and structural results. Crystal data for $\mathbf{2}{\cdot}2C_6H_6$ at −100 °C: Triclinic $P\bar{1}$, $Z = 1$, $a = 802.7$ (2) pm, $b = 1020.3$ (3) pm, $c = 1499.6$ (5) pm, $\alpha = 97.12$ (1)°, $\beta = 92.85$ (1)°, $\gamma = 98.32$ (1)°.

Introduction

Several aminoboranes,[1] most notably borazine $B_3N_3H_6$ ("inorganic benzene"),[2] have been subject to studies in which the B–N bonds were compared to the isoelectronic C═C bonds in organic analogues. Thus, the borazines were found to exhibit distinctly less π electron delocalization than the "aromatic" benzene analogues.[2b,c] In the following we describe two compounds, **1** and **2**, which—according to the same concept[2b,3]—invite a comparison with *nonaromatic* quinonoid π systems, viz., with tetraaryl-*p*-quinodimethanes of the type of Thiele's hydrocarbon (**3**) and 1,1′-biphenyl-4,4-bis(diarylmethyl) compounds, epitomized by Chichibabin's hydrocarbon (**4**) (Ar = C_6H_5).[4]

In addition to their relation (in the resonance forms **1A** and **2A**) with the all-carbon analogues **3** and **4**, molecules **1** and **2** may be regarded in resonance forms **1B** and **2B** as boryl, i.e. π acceptor-stabilized dihydroheteroaromatics.[5,6] In particular, the 1,4-dihydropyrazine π system underlying **1B** is known to be extremely π electron rich;[5] the cyclic endiamine arrangement and potential 8 π electron conjugation are responsible for the failure so far to observe the parent molecule 1,4-dihydropyrazine, $C_4N_2H_6$.[5] However, π acceptor substituents such as R_3Si, R(O)C, or $R_2(S)P$ are capable of stabilizing this unique structure;[5b,7] the strong π acceptor properties of the dimesitylboryl substituent with its sterical protection of the empty p_z orbital at boron[8,9] were established for carbocyclic π systems.[9]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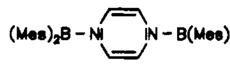
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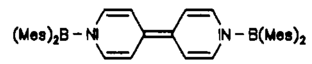
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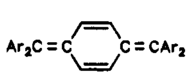
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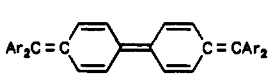
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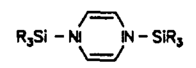
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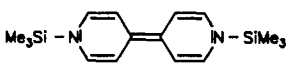
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We have studied the new compounds **1** and **2**[10] spectroscopically and electrochemically; the EPR/ENDOR results of the corresponding cation radicals are also summarized.[11] Since the structures of Thiele's and Chichibabin's hydrocarbons were reported recently,[4c] we have obtained a crystal structure of the

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[1] (a) Niedenzu, K.; Dawson, J. W. *Boron-Nitrogen Compounds*; Springer-Verlag: Berlin, 1965; *Angew. Chem.* **1964**, *76*, 168; *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 86. (b) Meller, A. *Gmelins Handbook of Inorganic Chemistry*: *B 3rd Supplement*; Springer Verlag: Berlin, 1988; Vol. 3, pp 145–158.

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[7] Bessenbacher, C.; Kaim, W.; Stahl, T. *Chem. Ber.* **1989**, *122*, 933.

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[9] Schulz, A.; Kaim, W. *Chem. Ber.* **1989**, *122*, 1863.

[10] The possible formation of compounds such as **2** was discussed in: Hünig, S.; Wehner, I. *Liebigs Ann. Chem.* **1989**, 299.

[11] A report devoted to EPR/ENDOR aspects of boron-containing radical ions including $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ has appeared: Lichtblau, A.; Kaim, W.; Schulz, A.; Stahl, T. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1497.

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analogue **2** for comparison; the larger π system **2** with an internal double bond between the heterocyclic rings should allow a better evaluation of the bonding[12] than compound **1**. Hückel MO calculations were used to interpret EPR/ENDOR results and electrochemical and structural data.

Experimental Section

Procedures. All reactions and manipulations were performed under argon using Schlenk techniques. Solvents were distilled from drying agents as required. Fluorodimesitylborane,[13] 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (**5**),[5a] and 4,4'-bis(trimethylsilyl)-1,1',4,4'-tetrahydro-4,4'-bipyridylidene (**6**)[6b] were prepared according to literature procedures.

1,4-Bis(dimesitylboryl)-1,4-dihydropyrazine (1) was obtained by heating 1.21 g (2.3 mmol) of fluorodimesitylborane and 0.49 g (2.1 mmol) of 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (**5**) under reflux in 50 mL of acetonitrile for 70 h. Removal of the solvent, recrystallization from benzene, and drying under vacuum yielded 0.15 g (12%) of a pale-yellow and moderately air-sensitive powder. Anal. Calcd for $C_{40}H_{48}B_2N_2$ (578.45 g/mol): C, 83.06; H, 8.36; N, 4.84. Found: C, 82.89; H, 8.45; N, 4.39. MS (20 eV): *m/e* 578 [M]$^+$, 249 [Mes_2B]$^+$, 91 [$C_4H_4BN_2$]$^+$. UV/vis (CH_2Cl_2): λ_{max} 357 nm. ^{1}H NMR (C_6D_6): δ 2.15, 2.15 (s, 12H; 4-CH_3), 2.30, 2.30 (s, 24H; 2,6-CH_3), 5.40 (s, 4H; pyrazine CH), 6.75 (s, 8H; 3,5-CH). ^{1}H NMR ($CDCl_3$): δ 2.10 (s, 12H; 4-CH_3), 2.12 (s, 24H; 2,6-CH_3), 5.37 (s, 4H; pyrazine CH), 6.62 (s, 8H; 3,5-CH). ^{13}C NMR (C_6D_6) δ 21.1, 21.2 (4-CH_3), 22.3, 22.6 (2,6-CH_3), 118.8 (pyrazine C), 127.8, 128.3, 128.7 (1,3,5-C), 137.9 (4-C), 141.4 (2,6-C). ^{11}B NMR ($CDCl_3$): δ 42 ppm vs BF_3/C_6D_6 (external). Cyclic voltammetry (CH_2Cl_2/0.1 M Bu_4NClO_4; 1 V/s): $E_{ox1} = +0.61$ V (ΔE_{pp} = 130 mV; i_{pa}/i_{pc} = 1.23), E^{pa}_{ox2} = 1.45 V (irreversible) vs Ag/AgCl.

1,1'-Bis(dimesitylboryl)-1,1',4,4'-tetrahydro-4,4'-bipyridylidene (2) was prepared by adding 0.58 g (1.1 mmol) of fluorodimesitylborane and 0.30 g (1.0 mmol) of 1,1'-bis(trimethylsilyl)-1,1',4,4'-tetrahydro-4,4'-bipyridylidene (**6**) in 50 mL of acetonitrile. The very dark reaction mixture was heated under reflux for 50 h during which the color changed to deep red. The red precipitate formed upon cooling was collected and recrystallized from benzene. Drying under vacuum yielded 0.23 g (35%) of the red, very air-sensitive compound. Anal. Calcd for $C_{46}H_{52}B_2N_2$ (654.55 g/mol): C, 84.41; H, 8.01; N, 4.28. Found: C, 80.27; H, 8.12; N, 4.29. UV/vis (CH_2Cl_2): λ_{max} 473 nm (**2**); 690 nm (**2**·TCNE); 600 sh, 664, 738 nm (**2**$^{\bullet+}$). ^{1}H NMR (C_6D_6): δ 2.19, 2.20 (s, 12H; 4-CH_3), 2.32, 2.33 (s, 24H; 2,6-CH_3), 6.16 (AA'BB'.m, 8H; pyridine CH), 6.78, 6.81 (s, 8H; 3,5-CH). ^{1}H NMR ($CDCl_3$): δ 2.09 (s, 12H; 4-CH_3), 2.18 (s, 24H; 2,6-CH_3), 6.09 (AA'BB'.m, 8H; pyridine CH), 6.70 (s, 8H; 3,5-CH). ^{11}B NMR (C_6D_6): δ 49 ppm vs BF_3/C_6D_6 (external). Cyclic voltammetry (CH_2Cl_2/0.1 M Bu_4NClO_4; 1 V/s): $E_{ox1} = 0.00$ V (ΔE_{pp} = 112 mV; i_{pa}/i_{pc} = 3.6), $E^{pa}_{ox2} = +0.21$ V (irreversible) vs Ag/AgCl.

Radical cations for EPR/ENDOR measurements were obtained by chemical oxidation using $I_2/KClO_4$ (**1**) or $AlCl_3$ in CH_2Cl_2 (**2**) at 295 (**1**) and 235 K (**2**). Perchlorate was used for improvement of EPR resolution by reducing ion-pairing; $AlCl_3$ is a known[16] one-electron oxidant. For UV/vis spectroscopy **2**$^{\bullet+}$ was generated using $AlCl_3$ in CH_2Cl_2 at 295 K, followed by rapid cooling to 213 K. The charge transfer complex of **2** with TCNE was studied using a large excess of TCNE in dichloromethane solution at 295 K.

Crystallography. Compound **2** crystallized from benzene as a red solvate $C_{46}H_{52}B_2N_2 \cdot 2C_6H_6$. Conventional isolation of these crystals for x-ray crystallography was impossible due to their rapid disintegration in the absence of benzene vapor. An unusually large crystal (1.1 × 0.7 × 0.5 mm) was therefore quickly separated from the solution and transferred into a capillary saturated with benzene vapor. Despite these precautions and measurements at −100 °C the diffraction reflections showed rather broad profiles which affected the quality of the structure analysis. All intensity measurements were performed using Mo Kα radiation with a graphite monochromator on a Syntex P2$_1$ diffractometer. Cell constants were obtained from least-squares refinement of optimized values of 2θ, ω, and χ of 32 selected reflections ($20° < 2\theta < 30°$). The intensity data were collected between $3° < 2\theta < 62°$ using a Wyckhoff scan (ω–2θ) ranging in speed from 29 to 2°/min ($-11 \leq h \leq +11$; $-14 \leq k \leq +14$; $-21 \leq l \leq +20$). During the data collection two intensity standards were collected every 98 reflections. No corrections were applied. A number of 7023 unique reflections were observed of which 5247 had $F > 4\sigma(F)$. The structure was solved in the triclinic space group $P\bar{1}$ via direct methods using the package SHELXTL-PLUS.[14] After convergence of the anisotropic refinement of the non-hydrogen centers, the coordinates of all hydrogen atoms were extracted from the difference Fourier map and included into the least-squares refinement with isotropic displacement parameters. Atomic scattering factors were taken from ref 15.

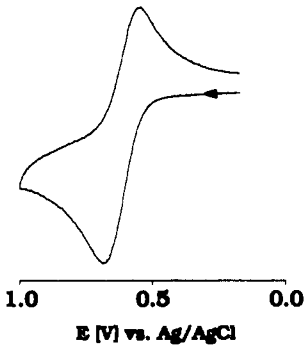

Figure 1. Cyclic voltammogram for the oxidation of **1** in CH_2Cl_2/0.1 M Bu_4NClO_4 (scan rate 1 V/s).

Instrumentation. NMR spectra were taken on Bruker AM 200 (^{11}B) and AC 250 spectrometers. EPR and ENDOR spectra were recorded[11] in the X band on a Bruker System ESP 300 equipped with an ENI A500 RF amplifier, a Bruker ER033 field frequency lock, a Bruker ER035M gaussmeter, and a HP 5350B microwave counter. A Shimadzu spectrophotometer UV160 was used for UV/vis spectroscopy. The mass spectrum of **1** was obtained with a MAT 711 instrument. Cyclic voltammetry was carried out in dichloromethane/0.1 M Bu_4NClO_4 using a three-electrode configuration (glassy carbon working electrode, Pt counter electrode, saturated Ag/AgCl as reference) and a PAR 273/175 potentiostat/function generator. Standard programs[11] were used for EPR simulation and Hückel MO calculations.

Results

1,4-Bis(dimesitylboryl)-1,4-dihydropyrazine (**1**) and 1,1'-bis(dimesitylboryl)-1,1',4,4'-tetrahydro-4,4'-bipyridylidene (**2**) were obtained from reactions between the bis(trimethylsilyl) derivatives **5** or **6** and dimesitylboron fluoride in polar acetonitrile. There was no conversion leading to **1** in less polar solvents such as toluene which suggests a polar character of the substitution reaction (1).

$$Me_3Si\text{-}N(\pi)N\text{-}SiMe_3 + 2Mes_2BF \rightarrow Mes_2B\text{-}N(\pi)N\text{-}BMes_2 + 2FSiMe_3 \quad (1)$$

NMR spectroscopy of **1** (^{1}H/^{13}C) and of **2** (^{1}H) in C_6D_6 revealed *two* resonances of different intensity for each type of mesityl nuclei; no such effect was observed for **2** in $CDCl_3$ solution (cf. Experimental Section). In cyclic voltammetry experiments the smaller system **1** proved to be far more difficult to oxidize than the very air-sensitive compound **2**. The one-electron processes become electrochemically reversible only at high scan rates (>1.0 V/s; Figure 1); the second oxidation steps to the "aromatic" (6 π) dications were always irreversible. Figure 1 shows the cyclovoltammogram of **1**; Table I summarizes redox potentials and ^{1}H NMR shifts of the protons in the heterocycle of **1**, **2**, and related compounds.

The cation radicals formed by electrochemical or—more conveniently—by chemical oxidation using $I_2/KClO_4$ (**1**) or $AlCl_3$ (**2**)[11,16] could be studied using EPR/ENDOR (**1**$^{\bullet+}$, **2**$^{\bullet+}$) and UV/vis spectroscopy (**2**$^{\bullet+}$). Figure 2 shows the EPR and ^{1}H,^{11}B-ENDOR spectrum of **2**$^{\bullet+}$; according to the ENDOR resonance equation $\nu = |\nu_X \pm a_X/2|$ there are ^{11}B and three ^{1}H line pairs centered around $\nu(^{11}B)$ = 4.62 MHz and $\nu(^1H)$ = 14.5 MHz, respectively. The use of ^{1}H- and ^{11}B-ENDOR data allowed us

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(12) Cf.: Goodwin, K. V.; McMillin, D. R.; Robinson, W. R. *Inorg. Chem.* **1986**, *25*, 2033, and literature cited therein.

(13) Pelter, A. Personal communication.

(14) Siemens Analytical X-Ray Instruments, SHELXTL PLUS, Release 3.4, January 1989.

(15) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(16) Bock, H.; Kaim, W. *Acc. Chem. Res.* **1982**, *15*, 9.

Table I. Oxidation Potentials E_{ox1} (V vs SCE) and ^1H NMR Chemical Shifts (ppm vs TMS) of *N*,*N'*-Dihydroheteroaromatics

1,4-Disubstituted 1,4-Dihydropyrazines

substituent	E_{ox1}	E_{ox2}[a]	solvent	$\delta(CH)$[b]	solvent
CH_2Me[c]	−0.67	+0.36	CH_3CN	d	
Si^iPr_3[e]	−0.42	+0.45 (pa)	CH_3CN	4.79	$CDCl_3$
$P(S)Me_2$[c]	+0.26	+0.79 (pa)	CH_3CN	5.46	$CDCl_3$
$BMes_2$[f]	+0.63	+1.47 (pa)	CH_2Cl_2	5.40	C_6D_6
$C(O)Me$[c]	+0.74	+1.12 (pa)	CH_3CN	6.19[g]	$CDCl_3$

1,1′-Disubstituted 1,1′,4,4′-Tetrahydro-4,4′-bipyridylidenes

substituent	E_{ox1}	E_{ox2}[a]	solvent	$\delta(CH)$[b]	solvent
CH_2Me[h]	−0.65	−0.25	CH_3CN	*d*	
$SiMe_3$[h]	−0.65[i]	−0.42[i]	CH_3CN	5.82[j]	$CDCl_3$
$BMes_2$[f]	+0.02	+0.23 (pa)	CH_2Cl_2	6.09	$CDCl_3$

[a] (pa): Anodic peak potential for irreversible process from cyclic voltammetry at 100 mV/s. [b] Protons of the heterocyclic ring. [c] From ref 7. [d] Not available. [e] From ref 24. [f] This work, *E*(SCE) − *E*(Ag/AgCl) = 0.03 V. [g] Average value for the cis/trans isomers.[23] [h] From ref 6; *E*(SCE) − *E*(Ag/AgCl) = 0.03 V. [i] Scan rate 20 V/s. [j] Kaim, W. *J. Am. Chem. Soc.* **1983**, *105*, 707.

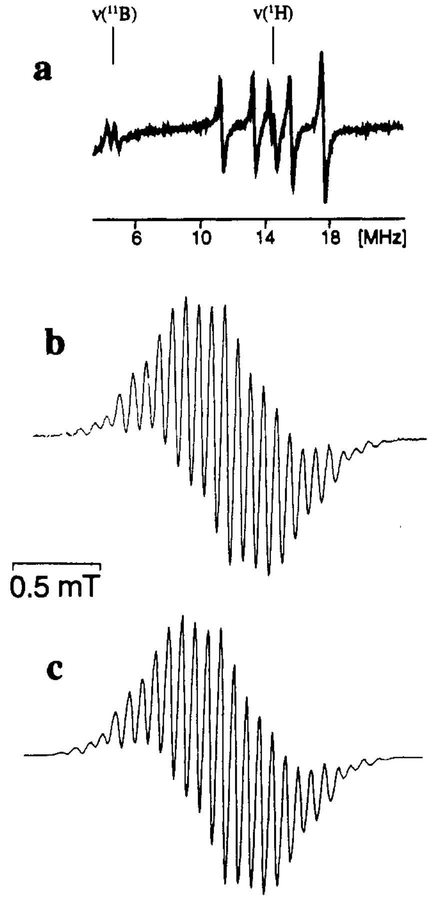

Figure 2. ENDOR (a, 220 K) and EPR spectrum (b, 280 K) of $2^{\bullet+}$, generated from **2** with $AlCl_3$ in CH_2Cl_2. Computer simulation (c) of the EPR spectrum with the data from Table II and 0.020 mT line width.

to determine the ^{14}N EPR coupling constants from simulated EPR spectra (Figure 2b,c). The typical[17] long-wavelength absorption spectrum of the violene-type radical ion $2^{\bullet+}$ is shown together with that of the parent **2** and of its TCNE charge transfer complex in Figure 3. Table II lists the relevant EPR/ENDOR data for some radical cations.

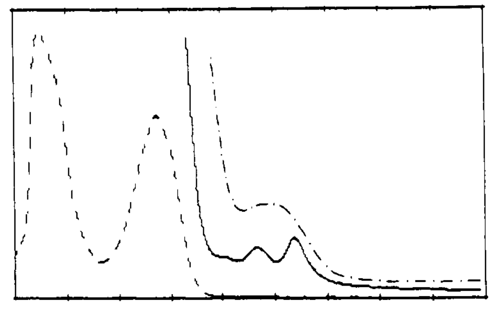

Figure 3. UV/vis absorption spectra of **2** (– –), its charge transfer complex with TCNE (– · · –) and its cation radical $2^{\bullet+}$ (—) in dichloromethane. Absorbance different for each spectrum.

Table II. EPR/ENDOR Data for Radical Cations of Dihydroheteroaromatics[a]

1,4-Disubstituted 1,4-Dihydropyrazines

substituent	*a*(C*H*)	$a(^{14}N)$	*a*(X)	X	*g*	solvent
CH_2Me[b]	0.290	0.850	0.540 0.023	CH_2 CH_3	2.0034	H_2O
$SiMe_3$[b]	0.313	0.668	0.279	^{29}Si	2.0033	CH_2Cl_2
$P(S)Me_2$[b]	0.34	0.68	0.78	^{31}P	2.0031	CH_3CN
$BMes_2$[c]	0.315	0.42	0.081 0.019	^{11}B H_{Mes}	2.0029	
$C(O)Me$[b]	0.29[d]	0.58[d]			2.0027	CH_2Cl_2

1,1′-Disubstituted 1,1′,4,4′-Tetrahydro-4,4′-bipyridylidenes

substituent	*a*(C*H*)	$a(^{14}N)$	*a*(X)	X	*g*	solvent
Me[f]	0.157 (H^2) 0.133 (H^3)	0.423	0.399	CH_3	[g]	MeOH
$SiMe_3$[f]	0.165 (H^2) 0.141 (H^3)	0.319	0.135	^{29}Si	2.0031	CH_2Cl_2
$BMes_2$[c]	0.225 (H^2) 0.083 (H^3)	0.15	0.016 0.011	^{11}B H_{Mes}	2.0030	CH_2Cl_2

[a] Coupling constants in mT (1 T = 10^4 G). [b] From ref 7. [c] This work; see also ref 11. [d] Average values for cis/trans isomers. [e] Protons of the heterocyclic ring. [f] Kaim, W. *J. Organomet. Chem.* **1983**, *241*, 157. [g] Not available.

Table III. Crystallographic Data for $2\cdot2C_6H_6$

chemical formula: $C_{58}H_{64}B_2N_2$	fw = 810.7 g/mol
a = 802.7 (2) pm	space group: triclinic, $P\bar{1}$
b = 1020.3 (3) pm	T = −100 °C
c = 1499.6 (5) pm	λ = 71.073 pm
α = 97.12 (1)°	ρ_{calc} = 1.119 g/cm³
β = 92.85 (1)°	μ = 0.059 mm⁻¹
γ = 98.32 (1)°	R = 0.075[a]
V = 1203.0 (6) pm³ × 10^{-6}	F_{000} = 436[b]
Z = 1	GOF = 0.82

[a] Unit weights; $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] Full matrix, 408 parameters refined.

Crystallization of very sensitive **2** from benzene gave single crystals of moderate quality for X-ray diffraction which were found to contain two benzene molecules per molecule of **2**. Crystallographic information, positional parameters, bond lengths and angles are summarized in Tables III–VI; Figures 4 and 5 show the structure of **2** and its arrangement in the unit cell together with those of two noninteracting benzene molecules.

While the two heterocyclic rings are coplanar within the centrosymmetric unit cell (Z = 1) and show deviations of less than 1 pm from a best plane, the mesityl rings adopt a typically[8] tilted conformation with interplanar angles of 65–70° relative to the plane of the heterocyclic π system. As a consequence of the centrosymmetric arrangement, the molecule **2** with two chiral "propeller" structures at the boron centers[8,9,18] exhibits a meso configuration (C_{2h}).

Hückel MO calculations for the parent heterocyclic π systems (disregarding the mesityl substituents) were carried out using

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[17] Braterman, P. S.; Song, J.-I. *J. Org. Chem.* **1991**, *56*, 4678.

[18] Zettler, F.; Hausen, H.-D.; Hess, H. *J. Organomet. Chem.* **1974**, *72*, 157.

Table IV. Atomic Positional Parameters ($\times 10^4$) and Equivalent Isotropic Displacement Parameters U(eq) (pm^2) and Their Estimated Standard Deviations for **2**·2C_6H_6[a]

	x	y	z	U(eq)
C(1)	4542 (3)	4909 (2)	5375 (1)	221 (6)
C(2)	3706 (3)	5930 (2)	5842 (2)	235 (6)
C(3)	2811 (3)	5726 (2)	6561 (2)	239 (6)
C(4)	3433 (3)	3510 (2)	6495 (2)	262 (6)
C(5)	4317 (3)	3671 (2)	5766 (2)	252 (6)
N(1)	2612 (2)	4515 (2)	6931 (1)	231 (5)
B(1)	1565 (3)	4300 (3)	7671 (2)	225 (6)
C(11)	1779 (3)	3062 (2)	8189 (1)	229 (6)
C(12)	3367 (3)	2955 (2)	8600 (2)	245 (6)
C(13)	3591 (3)	1825 (2)	9004 (2)	279 (7)
C(14)	2267 (3)	788 (2)	9027 (2)	299 (7)
C(15)	694 (3)	919 (2)	8654 (2)	308 (7)
C(16)	416 (3)	2022 (3)	8238 (2)	270 (6)
C(121)	4882 (3)	4044 (3)	8628 (2)	326 (8)
C(141)	2550 (4)	−457 (3)	9427 (3)	437 (10)
C(161)	−1328 (3)	2050 (3)	7816 (2)	401 (9)
C(21)	233 (3)	5280 (2)	7885 (1)	226 (6)
C(22)	186 (3)	6007 (2)	8748 (1)	227 (6)
C(23)	−1067 (3)	6804 (2)	8917 (2)	261 (6)
C(24)	−2291 (3)	6913 (2)	8255 (2)	278 (7)
C(25)	−2257 (3)	6199 (2)	7409 (2)	281 (7)
C(26)	−1019 (3)	5397 (2)	7212 (2)	248 (6)
C(221)	1526 (3)	5975 (3)	9489 (2)	283 (7)
C(241)	−3645 (4)	7775 (3)	8442 (2)	403 (9)
C(261)	−1132 (4)	4636 (3)	6272 (2)	375 (8)
C(01)	9375 (6)	1479 (4)	4979 (3)	746 (17)
C(02)	7768 (7)	743 (5)	4974 (3)	753 (18)
C(03)	6839 (6)	254 (4)	4161 (3)	747 (17)
C(04)	7501 (6)	513 (4)	3356 (3)	717 (16)
C(05)	9110 (6)	1264 (4)	3370 (3)	711 (16)
C(06)	10006 (6)	1741 (4)	4179 (3)	686 (16)

[a] Atom numbering from Figure 4, C(01)–C(06) refer to carbon centers of the benzene molecule.

Table V. Selected Bond Distances (pm) and Their Estimated Standard Deviations for **2**·2C_6H_6[a,b]

C(1)–C(2)	144.7 (3)	C(1)–C(5)	144.9 (3)
C(1)–C(1A)	139.1 (4)	C(2)–C(3)	134.6 (3)
C(3)–N(1)	140.8 (3)	C(4)–C(5)	134.7 (3)
C(4)–N(1)	140.9 (3)	N(1)–B(1)	144.4 (3)
B(1)–C(11)	158.7 (4)	B(1)–C(21)	158.5 (3)
C(11)–C(12)	141.2 (3)	C(11)–C(16)	142.2 (3)
C(12)–C(13)	139.7 (4)	C(12)–C(121)	151.9 (3)
C(13)–C(14)	139.2 (3)	C(14)–C(15)	138.6 (4)
C(14)–C(141)	151.2 (4)	C(15)–C(16)	139.2 (4)
C(16)–C(161)	151.3 (4)	C(21)–C(22)	141.3 (3)
C(21)–C(26)	141.7 (3)	C(22)–C(23)	139.6 (3)
C(22)–C(221)	151.5 (3)	C(23)–C(24)	138.7 (3)
C(24)–C(25)	138.6 (3)	C(24)–C(241)	151.0 (4)
C(25)–C(26)	139.6 (3)	C(26)–C(261)	151.5 (3)
C(01)–C(02)	139.4 (7)	C(01)–C(06)	136.6 (7)
C(02)–C(03)	139.4 (7)	C(03)–C(04)	138.3 (7)
C(04)–C(05)	140.1 (6)	C(05)–C(06)	137.5 (6)

[a] Atom numbering from Figure 4, C(01)–C(06) refer to carbon centers of the benzene molecule. [b] Average C–H bond lengths are 100 pm.

standard heteroatom Coulomb parameters $h_N = 0.5$ and $h_B = -0.5$.[19] For cation radicals, an interaction or "resonance integral" parameter k_{BN} of 1.0 was deduced from an EPR analysis;[11] we used the same parameter here for calculations of π orbital energies and π bond orders (Tables VII and VIII).

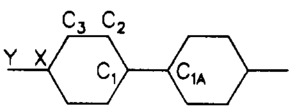

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Table VI. Selected Bond Angles (deg) and Their Estimated Standard Deviations for **2**·2C_6H_6[a,b]

C(2)–C(1)–C(5)	113.0 (2)	C(2)–C(1)–C(1A)	123.7 (3)
C(5)–C(1)–C(1A)	123.3 (3)	C(1)–C(2)–C(3)	122.6 (2)
C(2)–C(3)–N(1)	123.4 (2)	C(5)–C(4)–N(1)	123.2 (2)
C(1)–C(5)–C(4)	122.7 (2)	C(3)–N(1)–C(4)	115.0 (2)
C(3)–N(1)–B(1)	122.2 (2)	C(4)–N(1)–B(1)	122.7 (2)
N(1)–B(1)–C(11)	117.7 (2)	N(1)–B(1)–C(21)	117.8 (2)
C(11)–B(1)–C(21)	124.5 (2)	B(1)–C(11)–C(12)	120.1 (2)
B(1)–C(11)–C(16)	121.9 (2)	C(12)–C(11)–C(16)	118.0 (2)
C(11)–C(12)–C(13)	120.3 (2)	C(11)–C(12)–C(121)	122.2 (2)
C(13)–C(12)–C(121)	117.4 (2)	C(12)–C(13)–C(14)	121.5 (2)
C(13)–C(14)–C(15)	118.0 (2)	C(13)–C(14)–C(141)	120.8 (2)
C(15)–C(14)–C(141)	121.1 (2)	C(14)–C(15)–C(16)	122.4 (2)
C(11)–C(16)–C(15)	119.6 (2)	C(11)–C(16)–C(161)	121.7 (2)
C(15)–C(16)–C(161)	118.6 (2)	B(1)–C(21)–C(22)	122.3 (2)
B(1)–C(21)–C(26)	119.8 (2)	C(22)–C(21)–C(26)	117.8 (2)
C(21)–C(22)–C(23)	120.2 (2)	C(21)–C(22)–C(221)	120.7 (2)
C(23)–C(22)–C(221)	119.0 (2)	C(22)–C(23)–C(24)	121.7 (2)
C(23)–C(24)–C(25)	118.4 (2)	C(23)–C(24)–C(241)	121.5 (2)
C(25)–C(24)–C(241)	120.2 (2)	C(24)–C(25)–C(26)	121.6 (2)
C(21)–C(26)–C(25)	120.3 (2)	C(21)–C(26)–C(261)	122.7 (2)
C(25)–C(26)–C(261)	117.0 (2)	C(02)–C(01)–C(06)	119.2 (4)
C(01)–C(02)–C(03)	120.3 (5)	C(02)–C(03)–C(04)	120.0 (4)
C(03)–C(04)–C(05)	119.2 (4)	C(04)–C(05)–C(06)	120.0 (4)
C(01)–C(06)–C(05)	121.4 (4)		

[a] Atom numbering from Figure 4, C(01)–C(06) refer to carbon centers of the benzene molecule. [b] Average angles involving hydrogen atoms: HCH (CH_3), 106°; CCH (CH_3), 112°; CCH, 119°; NCH, 117°.

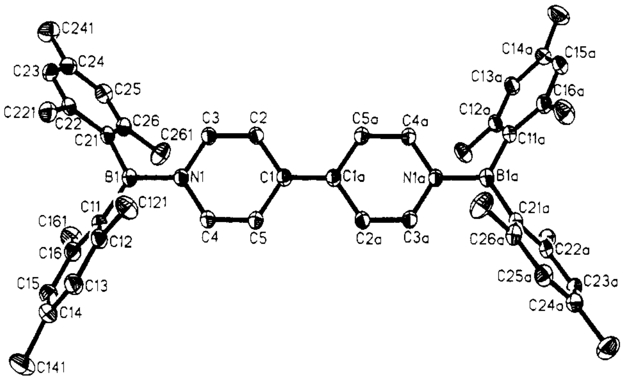

Figure 4. Molecular structure of **2** with the atomic numbering scheme employed. The thermal ellipsoids correspond to 50% probability. Hydrogen atoms are omitted for clarity.

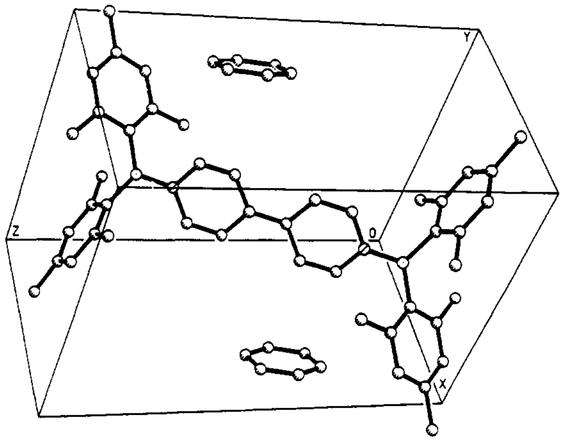

Figure 5. Unit cell of **2**·2C_6H_6.

Discussion

Structure. The kinetic stability and nonassociated nature of **1** and **2**, the former with an "antiaromatic" (8π) resonance form **1B**, can be attributed to the steric protection of the sensitive B–N bonds by mesityl groups. Two such mesityl substituents were previously shown to protect the coordinatively unsaturated boron

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(19) Heilbronner, E.; Bock, H. *The HMO Model and its Applications*; Wiley: London, 1976.

Table VII. Calculated HOMO Energies and HOMO/LUMO Energy Differences[a]

energy	compounds 1	2	3	4
E_j(HOMO)	−1.000	−0.628	−0.311	−0.134
ΔE_j(HOMO/LUMO)	1.000	0.451	0.622	0.268

[a] From Hückel MO calculations excluding aryl substituents. All k = 1.0; h_N = +0.5; h_B = −0.5.

Table VIII. Calculated and Experimental Bond Parameters for Compounds **2** and **4**

bond[a]	calcd π bond orders[b] 2	4	exptl bond lengths (av), pm 2	4
C1–C1a	0.60	0.51	139.1	144.8
C1–C2	0.47	0.53	144.8	142.0
C2–C3	0.81	0.77	134.6	137.1
C3–X	0.40	0.48	140.8	142.6
X–Y	0.59	0.71	144.4	141.5

[a] For numbering see formula I. [b] From Hückel MO calculations excluding aryl substituents at centers Y. All k = 1.0; h_N = +0.5; h_B = −0.5.

atom in a propeller-type conformation, securing a coordination number of three with an empty p_z acceptor orbital.[8] The structure of **2** in the crystal confirms this expectation[9,11] (Figures 4, 5).

The centrosymmetric arrangement in the crystal of $2\cdot 2C_6H_6$ ($Z = 1$) not only is connected to the coplanarity of the two partially reduced but almost planar pyridyl rings of **2**, but also is responsible for the opposite helicity of the two boron propellers (C_{2h} symmetry, meso form). C_{2h} and enantiomeric D_2 forms were also discussed for the all-carbon analogues **3** and **4** in which the phenyl rings are rotated about 43° out of the central plane.[4c]

In contrast to recently reported 1,3,5-tris(dimesitylboryl)benzene which shows a splitting of the 2,6-methyl resonances in the ^{1}H NMR only below 210 K,[8d] compounds **1** and **2** exhibit two slightly different sets of mesityl proton signals in a ratio of about 1:1.5 in C_6D_6 solution at ambient temperature. While solvation with anisotropic benzene as suggested by the solvate structure in Figure 5 should indeed favor the observation of different conformers such as the meso and D/L forms by ^{1}H or ^{13}C NMR, the higher rotation barrier[20] in case of the aminoboranes **1** and **2** is certainly due to a distinctly shorter B–N bond (144.4 pm for **2**) relative to ca. 157 pm for B–C in 1,3,5-tris(dimesitylboryl)benzene.[8d] Additional *electronic* contributions to such a rotational barrier from n(N) → p_z(B) π overlap[20] according to resonance structures **1A** and **2A** may be invoked.

The B–N bond length of 144.4 (3) pm is very similar to that found in borazine $B_3N_3H_6$ (144 pm) and hexagonal boron nitride BN (145 pm).[2b] An electron diffraction study of the nonconjugated and sterically little hindered aminoborane Me_2B–NHMe showed a somewhat shorter B–N bond distance of 139.7 (2) pm.[21] While the value of 144.4 pm suggests a B–N bond order greater than 1.0 in **2**, the presence of a conjugated π system allows a more detailed assessment in conjunction with results from Hückel π MO perturbation calculations on the parent system, i.e. with mesityl substituents neglected. This approach is very useful here since the structure of the carbon analogue **4** is known.[4c] The table of calculated π bond orders and experimental bond lengths (Table VIII) shows a very good reproduction of the changes which occur on going from hydrocarbon **4** to compound **2**: The central bond C(1)–C(1a) and the bonds C(2)–C(3) become shorter (increasing π bond order) whereas the bonds C(1)–C(2) and the exocyclic double bonds (C=C or B=N) lengthen. The discrepancy between the calculated bond orders and observed bond lengths in the case of the C(3)–X bonds (X = C or N) results from a general shortening of C–N bonds relative to C–C bonds. The data from Table VIII thus show a higher degree of π localization in **2** relative to **4**. This result is in agreement with the differences established between benzene and borazine[2c] or between graphite and hexagonal BN (larger band gap for the latter).[2b]

Electrochemistry and Spectroscopy. If the stabilization of the otherwise extremely electron-rich 1,4-dihydropyrazine and 1,1′,4,4′-tetrahydro-1,1′-bipyridylidene π systems can be attributed to some B=N π bonding according to the *p*-quinonoid resonance forms **1A** and **2A**, this effect should also be susceptible to spectroscopic and electrochemical studies. While the corresponding compounds with H or alkyl groups instead of $BMes_2$ substituents at the nitrogen centers are not isolable, well-characterized species were obtained with π acceptors such as trialkylsilyl.[5–7] Table I shows that both the ^{1}H NMR low-field shift of the protons in the heterocycle and the first oxidation potentials confirm the good π accepting properties of the dimesitylboryl substituent, e.g. relative to trialkylsilyl groups. A comparison of ^{13}C resonances of the dihydropyrazine carbon centers adds to this notion: δ 118.8 ppm (**1**) > 115.4 ppm (**5**).[22] Only acyl groups C(O)R are superior to $BMes_2$ in stabilizing the extremely electron rich heterocyclic enamines through π electron delocalization in a carboxamide function.[5b,7,23]

Calculations of Hückel π molecular orbital energies for the parent systems (Table VII) confirm that the smaller compound **1** has a lower lying HOMO than the larger system **2** and is thus harder to oxidize (Table I). Calculated π HOMO/LUMO differences correlate qualitatively with the long-wavelength absorption maxima although the observed intense transitions may involve higher lying unoccupied MOs:[17] Chichibabin's hydrocarbon which absorbs at λ_{max} = 574 nm[4c] has the smallest HOMO/LUMO gap (which fostered the discussion on its biradical character[4c,d]) whereas almost colorless **1** (λ_{max} = 357 nm) is calculated to have the highest such energy difference (Table VII). The red color of **2** (λ_{max} = 473 nm) is typical for the doubly reduced 4,4′-bipyridine chromophor.[6b]

Whereas the second oxidation steps for **1** and **2** are totally irreversible, the radical cations $1^{•+}$ and $2^{•+}$ are stable enough to be studied by EPR/ENDOR (Figure 2) and UV/vis spectroscopy (Figure 3). Despite its rather low oxidation potential of about 0 V (Table I), compound **2** does not undergo complete electron exchange with the acceptor TCNE (E_{red} = +0.24 V vs SCE). Instead, a weak charge transfer complex with a maximum at 690 nm is formed (Figure 3) which indicates substantial steric hindrance to CT complexation.[24]

The established[16] one-electron oxidant $AlCl_3$ in CH_2Cl_2 produces an EPR/ENDOR- and UV/vis-detectable cation radical from **2**. At 213 K $2^{•+}$ exhibits the characteristical, vibrationally structured (ca. 1550 cm^{-1}) absorption band at ca. 600 nm for a violene-type radical ion (Figure 3).[17] Unlike methylviologen and related cation radicals[17,25] the cation $2^{•+}$ has the 0 → 0 component of this $\pi_7 \rightarrow \pi_{10}$ excitation[17] as the most intense feature, suggesting only small geometry changes between ground and excited states and hence substantial π electron delocalization in this oxidation state.

This first conclusion is strongly supported by the result that both the ^{11}B *and* the ^{14}N EPR coupling constants are very small by comparison[11,26] while the general spin distribution is not strongly affected (Table II). In a straightforward interpretation[11,27] the

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(20) Brown, C.; Cragg, H.; Miller, T. J.; O'N Smith, D. *J. Organomet. Chem.* **1985**, *296*, C17.

(21) Almenningen, A.; Grundersen, G.; Mangerud, M.; Seip, R. *Acta Chem. Scand. A* **1981**, *A35*, 341.

(22) Bessenbacher, C.; Kaim, W. *J. Organomet. Chem.* **1989**, *362*, 37.

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(24) Baumgarten, J.; Bessenbacher, C.; Kaim, W.; Stahl, T. *J. Am. Chem. Soc.* **1989**, *111*, 2126 and 5017.

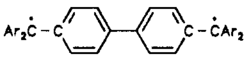
(25) Kaim, W.; Matheis, W. *Chem. Ber.* **1990**, *123*, 1323.

(26) Kaim, W.; Lubitz, W. *Angew. Chem.* **1983**, *95*, 915; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 892; *Angew. Chem., Suppl.* **1983**, 1209.

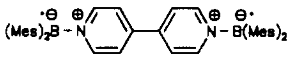
(27) Cf. Rhodes, C. J. *J. Chem. Soc., Perkin Trans. 2* **1992**, 235.

unusually small EPR hyperfine splittings reveal a substantial π component within the B=N groups because the EPR coupling constants are sensitive primarily to contributions from s atomic orbitals (Fermi contact term).[28]

Since the possible contribution from the biradical resonance form **4′** to the ground-state description of Chichibabin's hydrocarbon has attracted some attention,[4c,d] one may formulate a corresponding structure for **2′**.



4′



2′

Although the stabilities of both the triarylmethyl neutral radicals and the triarylborane anion radicals[9] are well established, the resonance form **2′** is not considered to contribute strongly to the ground state of the neutral compound **2**.

Summarizing, the structural, spectroscopic and computational comparisons between the compounds **1**–**4** show how the substitution of the critical external C=C bonds by the dipolar B=N bonds in nonaromatic quinonoid compounds results in substantially decreased bond delocalization *in the neutral state*. On the other hand, the *one-electron oxidized species*, i.e. the radical cations $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ which are formed at rather low potentials exhibit a fairly high degree of π electron delocalization as evident from UV/vis and EPR/ENDOR spectroscopy.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and Volkswagenstiftung for support.

Supplementary Material Available: Crystallographic data (Table S1), atomic coordinates (Table S2), anisotropic thermal parameters of non-H atoms (Table S3), atomic coordinates and isotropic thermal parameters of hydrogen atoms (Table S4), complete bond lengths (Tables S5 and S6) and angles (Tables S5 and S7) including hydrogen atoms, and least-square planes, atomic deviations, and angles between planes (Table S8) for $\mathbf{2}\cdot 2C_6H_6$ (8 pages). Ordering information is given on any current masthead page.

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[28] Gerson, F. *High Resolution E.S.R. Spectroscopy*; Wiley: London, 1970.