Si–B bonds in *commo*-3,3'-Si(3,1,2-SiC₂B₉H₁₁)₂, which contains a single silicon atom bonded within a 12-atom boron-containing cluster: 2.05(1) and 2.14(1) Å.^[7]

The ¹H, ¹³C, ²⁹Si, and ¹¹B NMR spectra of 1 were recorded.^[8] The ¹¹B NMR spectrum (160.367 MHz, [D₆]acetone, 25 °C, external BF₃ · OEt₂) was in agreement with the 1,2disila-closo-dodecaborane(12) cage structure, showing four doublets in 2:2:2:4 intensity ratio at $\delta = -11.2$ (d, J = 147 Hz, B9, 12), -12.6 (d, J = 144 Hz, B8, 10), -13.5(d, J = 152 Hz, B3, 6), and -14.5 (d, J = 147 Hz, B4, 5, 7)11). The assignments are based on a 2D proton-decoupled ${}^{11}B-{}^{11}B$ NMR spectrum. The CH₃ resonance was observed at $\delta = -0.07$ in the ¹H NMR spectrum of 1 in C₆D₆ solution. The proton-decoupled ²⁹SiNMR spectrum of 1 in $C_6 D_6$ solution at 50 °C showed a singlet at $\delta = -37.77$, the proton-decoupled ¹³C NMR spectrum, also in C₆D₆ at 40 °C, a singlet at $\delta = -12.80$. The upfield shifts observed in the ¹³C and ²⁹Si spectra of 1 taken in C₆D₆ solution, as compared with TMS, are consistent with the well-documented electron-deficient nature of boron cages.

Compound 1 is less stable than the *o*-carboranes. It melts at 201–203 °C (sealed capillary) and decomposes with gas evolution above 230 °C. It remains undecomposed when heated at reflux in wet tetrahydrofuran solution for several days. It was unaffected when treated with an excess of CF_3CO_2H in THF at room temperature and remained largely undecomposed when this solution was heated at reflux for 14 hours. It was found to be stable toward AlCl₃ in refluxing benzene. It reacts with and is degraded by alcoholic KOH in THF at room temperature within minutes and it decolorizes a solution of bromine in carbon tetrachloride after several hours at reflux.

Now that the first member of this new class of boron cluster compounds has been isolated, it may be expected that other $1,2-R_2Si_2B_{10}H_{10}$ compounds can be prepared. The development of their chemical reactivity at silicon and at boron will be of some interest as will a comparison of their chemistry with that of the *o*-carboranes.

Experimental Procedure

A 250-mL three-necked flask equipped with a reflux condenser, an addition funnel, and a magnetic stirring bar was flushed with argon and charged with $B_{10}H_{14}$ (6.6 g, 54.0 mmol) and dry toluene (120 mL). To the resulting solution was added dropwise at room temperature 2 (7.1 g, 53.7 mmol)[9]. The reaction mixture was stirred and heated at reflux under argon for 24 h. During this time a white solid precipitated. The reaction mixture was filtered and the filtrate evaporated at reduced pressure. The residue was extracted with two 100-mL portions of hot benzene. Filtration of the extracts and cooling to 3 °C resulted in deposition of 1.45 g of 1 as an amorphous white powder that contained a small amount of white needles. Evaporation of the remaining benzene solution gave 0.6 g of 3, identified on the basis of its ¹H and ¹¹B NMR and mass spectra. The solid that had precipitated during the reaction was sublimed at 90 °C (0.01 Torr) to give an additional 0.15 g of 1. The sublimation residue was 6.0 g of 3. The total yield of the latter was 6.6 g, (58%). The total yield of 1 was 1.60 g, a yield of 15% based on B10H14. Correct C, H, Si elemental analyses; correct high-resolution mass spectrum.

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1, 128270-48-4; 1 \cdot C₆H₆, 128270-49-5; 2, 22705-33-5; 3, 128270-50-8; B $_{10}$ H $_{14},$ 17702-41-9.

for 1 C_6H_6 : orthorhombic, space group *Pccn* (No. 56); a = 10.081(1), b = 10.666(8), c = 16.130(5) Å, V = 1734 Å, Z = 4; $\varrho_{catcd} = 1.052$ g cm⁻³, F(000) = 592, $\mu(Mo_{K_a}) = 1.78$ cm⁻¹, 2291 reflections measured, 2291 unique reflections, 1050 observed $(I > 3\sigma(I))$, 89 variables, r = 0.044, $R_w = 0.058$, Rigaku AFC6R diffractometer, Mo_{K_a} ($\lambda = 0.71069$ Å). Further details of the crystal structure determination may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlichtechnische Information mbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the deposition number CDS-54516, the names of the authors, and the journal citation.

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- [8] NMR spectra, conditions: All measurements at 25 °C unless otherwise specified. ¹¹B, 160.37 and 96.235 MHz, BF₃ OEt₂; ¹H, 300 MHz, TMS; ²⁹Si, 99.34 MHz, TMS; ¹³C, 75.43 MHz, TMS.
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Helicene Dianions: Paratropicity of Twisted Phenanthrene Dianions

By Ron Frim, Albrecht Mannschreck, and Mordecai Rabinovitz*

The smallest polycyclic molecule with an enforced helical structure^[1] is a three-ring system, namely, phenanthrene substituted at the 4,5 positions.^[2] Like the other members of the helicene series, it belongs to the C_2 point group and hence is chiral. Such systems can be resolved into stable enantiomers if the barrier to racemization is sufficiently high. The neutral hydrocarbon species do not show a severe perturbation of the diatropicity according to their ¹H NMR spectra. In the neutral system where the HOMO-LUMO gap is wide, σ_{para} has an insignificant effect on the chemical shift.^[3] Therefore, variations in the helicity do not significantly modify the ¹H NMR parameters.^[4, 5] This phenomenon is illustrated by the chemical shifts of the protons at positions 9 and 10 in phenanthrenes 1-4 (Table 1). Reduction of these hydrocarbons with alkali metals can, in principle, give paratropic dianions.

These $4n\pi$ polycyclic dianions have been studied by NMR spectroscopy^[3] with respect to two major parameters: (1) the electronic structure as related to paratropicity and (2) the detailed mode of electron delocalization. The correlation between the calculated HOMO–LUMO energy gap and the paratropicity as well as the NMR line shape was studied^[5] without taking into account the different paths for delocalization of the various systems.

However, no study has taken into account the effect of the potential nonplanarity of such systems on their spectroscopic parameters. Our approach is to study a series of hydrocarbons and their double negatively charged derivatives, all of which have the same sp^2 skeleton and show a known degree of deviation from planarity^[21] (see above). We assume that

^[1] Gmelin Handbook of Inorganic Chemistry, 8th Edition, Borverbindungen, Vols. 2 (1974), 6 (1975), 11 (1977), 12 (1977), and chapters in the first and second supplements (1980–1983), Springer, Berlin. See also: R. N. Grimes: Carboranes, Academic Press, New York 1970, Chapter 6 and literature cited therein.

^[2] D. Seyferth, W. S. Rees, Jr., unpublished work.

^[3] $1 \cdot C_6H_6$ crystallizes with crystallographic twofold symmetry. One molecule of benzene was found for every molecule of 1 in two sites of equal occupancy; each site has the same crystallographic twofold symmetry. Crystal data

 ^[*] Prof. Dr. M. Rabinovitz, Dipl.-Chem. R. Frim Department of Organic Chemistry, The Hebrew University Jerusalem 91904 (Israel)
 Prof. Dr. A. Mannschreck Institut für Organische Chemie der Universität D-8400 Regensburg (FRG)

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the gross delocalization pattern is the same as long as the sp² carbon skeleton is maintained, and hence the relationship between the nonplanarity of the $4n\pi$ system and the NMR spectroscopic parameters can be studied. A system of choice is the charged $4n\pi$ helicene series in general and 4,5-disubstituted phenanthrenes in particular. The effects of their deviation from planarity should be reflected by both their electronic structure and their NMR spectra. Here we report the influence of the deviations from planarity on the ¹H NMR parameters of a series of dianions of 4,5-disubstituted phenanthrenes.

We chose to concentrate on alkyl-substituted phenanthrenes for two reasons: (1) the ability to modify the twist of the phenanthrene moiety by alkylation; (2) phenanthrene dianion shows a very significant dependence of its ¹H NMR line shapes on the type of reducing metal on the one hand and temperature and solvent on the other.^[5] The $4n\pi$ phenanthrene dianion displays an intermediate HOMO-LUMO energy gap. [3-5] Systems with narrower energy gaps do not show resolved NMR spectra because of the relatively high concentration of a thermally excited or even a groundstate triplet. A wider energy gap will always give wellresolved NMR spectra, since thermal excitation to the triplet state is not possible. For that very reason, we thought that any minor change in the system's geometry and therefore in its energy gap would give rise to a very significant change in the NMR spectra. Indeed, twisted dianions derived from substituted phenanthrenes show a reduced degree of paratropicity and much narrower line shapes (Fig. 1 and Table 1). Our conclusion that these ions are twisted is confirmed by DNMR studies^[6] and by theoretical calculations (MNDO,^[7] MMX^[8a]). The theoretical calculations are in good agreement with X-ray studies.[8b]

On going from the almost planar unsubstituted phenanthrene dianion $(1^{2\Theta})$ to the dianions substituted by bulky alkyl groups, the ¹H NMR line shapes become much narrower and fine structures can be observed (Table 1). Phenanthrene dianion $1^{2\Theta}$ with sodium as countercation shows no ¹H NMR spectrum down to a temperature as low as -70 °C. When lithium is the reducing metal, broad lines emerge at -20 °C. The spectrum is improved in terms of line shape as the temperature is further reduced. At -70 °C one observes a well-resolved, easily interpretable NMR spectrum. The NMR results for 4-*tert*-butylphenanthrene dianion are very similar to those of phenanthrene dianion itself. The reason



Fig. 1. ¹H NMR (200 MHz) chemical shifts of substituted phenanthrene dianions (as dilithium salts) represented by the stick diagram. The effect of helical twisting on the paratropic shift is clearly shown.

for this is the toothed-wheel effect that can take place when phenanthrene bonds become a little longer upon charging of the molecule. A greater degree of twisting can be achieved in 2,4,5,7-tetramethylphenanthrene dianion $(3^{2\Theta})$, for which a significant narrowing in the line shapes is observed. When sodium was used to reduce the parent $(4n + 2)\pi$ system 3, we observed broad lines at -20 °C. At -70 °C a spectrum with rather narrow lines (although without observable spin-spin couplings) is obtained. The lithium salt of this dianion shows a well-resolved spectrum even at room temperature. Conversion of 2,4-di-*tert*-butyl-5,7-dimethylphenanthrene (4) to its dianion resulted in an even more significant effect: $4^{2\Theta}/$ $2Na^{\oplus}$ shows already at -20 °C a resolved spectrum, whereas, as expected, the dilithium salt shows a very well resolved spectrum at room temperature.

Dianions with additional alkyl substituents at positions other than 4 or 5 show line shapes very similar to those of the phenanthrene dianion substituted at positions 4 and 5 only

	δ H9,H10 [a]		Proton line shapes [b]		Calcd twist angle [°]		NMR parameters [a, c]
	Hydrocarbon	Dianion	Na [⊕] counterion	Li [⊕] counterion	Hydrocarbon (MMX/MNDO) [8,7]	Anion (MNDO) [7]	
1	7.83	-1.14	no spectrum	resolved -70°C	0/2	19.87	0.62 (d,2H; H 1,8), <i>J</i> = 6.5 Hz; 0.80 (d,2H; H 4,5), <i>J</i> = 5.7 Hz; 1.69 (t,2H; H 3,6), <i>J</i> = 6.2 Hz; 2.75 (t,2H; H 2,7), <i>J</i> = 6.5 Hz
2	7.57	1.23	L.B. -20° resolved $-70 ^{\circ}$ C	resolved + 20 °C	33.02/36.86	58.82	2.40 (d,2H; H 1,8), $J = 6.3$ Hz; 3.62 (d,2H; H 3,6), $J = 6.3$ Hz; 4.32 (t,2H; H 2,7), $J = 6.3$ Hz
3	7.47	1.65	L.B. -20° resolved $-70 \ ^{\circ}$ C	resolved $+ 20 ^{\circ}\text{C}$	33.15/-	_	2.74 (s,2H; H 1,8); 3.71 (s,2H; H 3,6); 0.65, 0.04 (s,6H; 6H; Me)
4	7.59 d 7.87 d J = 2 Hz	2.49 d 2.28 d J = 2 Hz	resolved - 20 °C	resolved + 20 °C	40.38/42.21	74.04	2.87, 3.07 (s,1 H; 1 H; H 1,8); 4.15, 4.54 (s,1 H; 1 H; H 3,6); 1.23, 0.73 (s,9 H; 9 H TtBu); 1.42, 0.84 (s,3 H; 3 H TMe)

Table 1. The influence of the spatial structure of $4n\pi$ polycyclic helicenes on their ¹H NMR spectra and calculated twist angle.

[a] Lithium salts, Relative to TMS; $[D_8]$ THF line at $\delta = 3.67$ taken as standard. [b] Line broadening of the dianions. resolved = well-resolved spectrum; L.B. = line broadening. [c] δ values and coupling constants of the anions (except for H9, H10).

 $(2^{2\Theta}, \text{Table 1})$. The more twisted the helicene is, the more the paratropicity of the $4n\pi$ system is quenched.^[4]

In order to study this phenomenon, we concentrated on the proton chemical shifts at positions 9 and 10 of the substituted phenanthrenes. The same trend is observed for the protons of the other positions. The 9,10 positions have the largest charge density, as deduced from NMR spectra and $\omega\beta\text{-}HMO$ calculations for a doubly charged phenanthrene $(1^{2\Theta})$. Without exception, the more twisted the phenanthrene moiety is, the less the spectrum is shifted towards higher field (Table 1). For example, in the spectrum of phenanthrene dianion $(1^{2\Theta}/2Li^{\oplus})$ the resonances of protons at positions 9,10 are shifted to $\delta = -1.14$, whereas the resonances of the same protons in 2,4,5,7-tetramethylphenanthrene dianion $(3^{2\Theta}/2Li^{\oplus})$ are shifted to $\delta = +1.65$. Thus, a dramatic chemical shift difference of 2.79 ppm results from the different paratropicities of $1^{2\Theta}$ and $3^{2\Theta}$. In the spectrum of 2,4-di-*tert*-butyl-5,7-dimethylphenanthrene dianion $(4^{2\Theta})$ $2Li^{\oplus}$) those proton resonances appear at $\delta = 2.49$ and 2.28. In all cases studied the same charge distribution pattern has been observed. Changing the countercation, solvent, and temperature did not affect the observed trend of line shape and chemical shift differences.

The paratropicity of $4n\pi$ "antiaromatic" systems and the line shapes of their ¹H NMR signals thus correlate with the degree of twisting. Since antiaromaticity (as well as aromaticity) requires an efficient delocalization, we believe that twisting of the system quenches its antiaromatic properties. Therefore, the paratropic shift and the NMR line shapes can be applied as probes for so-called "antiaromaticity".

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CAS Registry numbers:

1, 85-01-8; 1, dianion, 67382-15-4; 1, $2Li^{\oplus}$, 54667-02-6; 2, 3674-69-9; 2, dianion, 128054-52-4; 2, $2Na^{\oplus}$, 128054-56-8; 2, $2Li^{\oplus}$, 128054-60-4; 3, 7396-38-5; 3, dianion, 128054-53-5; 3, $2Na^{\oplus}$, 128054-58-0; 3, $2Li^{\oplus}$, 128083-45-4; 4, 128054-51-3; 4, dianion, 128054-54-6; 4, $2Na^{\oplus}$, 128083-43-2; 4, $2Li^{\oplus}$, 128054-62-6.

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- [7] MNDO calculations were performed on a CDC Syber 180/855 running under NOS 2.7.1 and NOS/VE 1.4.1. Program: M. J. S. Dewar, W. Thiel, *Molecular Theory Program, Version 2.5.* Hydrogen bonding and lithium parameters included by A. Golblum, Hebrew University of Jerusalem, 1986.
- [8] a) The MMX calculations were performed on an Olivetti M 240 computer with a math coprocessor 18087 applying the PC Model MMX calculations Serena Software, USA. b) X-ray studies: R. Cosmo, T. W. Hambley, S. Sternhell, J. Org. Chem. 52 3119 (1987).
- [9] The NMR spectra were recorded with a Bruker WP-200 SY pulsed-FT spectrometer operating at 200.133 MHz for ¹H NMR, equipped with a ²H lock system and an Aspect-2000 computer (32 K).
- [10] Sample preparation: Lithium or sodium wire was introduced in the upper part of an extended NMR tube containing the polycyclic compound (5-10 mg) dissolved in 0.7 mL of [D₈] THF (Aldrich). The frozen solution was degassed and sealed under vacuum. The solution was then brought into contact with the metal by turning the tube upside down.

Correlations between Magnetism and Structure in Dinuclear Cu^{II}Fe^{III} Complexes with Integer Spin EPR Signals **

By Theodore R. Holman, Kevin A. Andersen, Oren P. Anderson, Michael P. Hendrich, Carlos Juarez-Garcia, Eckard Münck, and Lawrence Que, Jr.*

The relationship between structure and magnetism in coupled dinuclear transition metal complexes has attracted great interest among inorganic and bioinorganic chemists, due to the unique physical properties of these complexes^[1] as well as their relevance to biological systems.^[1, 2] The magnetism of these systems depends on the electronic configurations of the individual metal centers, which, in turn, determine their fundamental spectroscopic properties. Recently, we have developed a systematic method for synthesizing heterobimetallic complexes of the dinucleating ligand 2,6-bis(bis-2-pyridylmethylamino)methyl)-4-methylphenol (Hbpmp),^[3] affording a series of M^{II}Fe^{III} compounds.^[4, 5] Herein, we report the structures of two Cu^{II}Fe^{III} complexes^[6] of bpmp^{Θ} which exhibit integer spin EPR signals that correspond to their markedly different magnetochemistry.^[7]

 $[Cu^{II}Fe^{III}(bpmp)(O_2CC_2H_5)_2](PF_6)_2$ 1 a

 $[Cu^{II}Fe^{III}(bpmp)(O_2CCH_3)(OCH_3)](BPh_4)_2 \cdot 0.22 CH_3CO_2H 2a$

X-ray structure analyses of $1a^{[8, 9]}$ and $2a^{[9, 10]}$ revealed the following features:

In **1a** the cation consists of a discrete, dinuclear $Cu^{II}Fe^{III}$ complex (Fig. 1, top), in which the two metals are bridged by the phenolate oxygen atom of the bpmp^{\ominus} ligand and by two propionate groups. The Fe^{III}...Cu^{II} distance is 3.401(4) Å, consistent with those of similar triply bridged dinuclear cores.^[4] The bpmp^{\ominus} ligand and the propionate groups provide a six-coordinate, roughly octahedral ligand array about each of the metal atoms in **1a**, but the coordination environment about the Cu^{II} atom shows the effects of Jahn-Teller elongation along the N2–Cu–O3 axis.

In **2a** (Fig. 1, bottom), one of the bridging carboxylate groups of **1a** is replaced by a terminal methoxide ligand that is coordinated only to the roughly octahedral Fe^{III} atom, leaving the Cu^{II} atom five-coordinate. One Cu-ligand bond (Cu-O1 = 2.176(4) Å) is elongated considerably relative to the other four in **2a**; this pattern suggests that the bridging phenolate oxygen atom, O1, is best regarded as the apical ligand atom of a square pyramidal coordination array about Cu^{II}. The Fe-O1 bond is also elongated due to the influence of the methoxide ligand, as the strong Fe-OCH₃ interaction affords a short (1.849(4) Å) Fe-O bond and decreases the affinity of the Fe for the phenolate bridge. The lengthening of both M-O1 bonds in **2a**, relative to those in **1a**, is the primary factor in the elongation of the Fe…Cu distance by 0.24 Å, to 3.641(1) Å.

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^[*] Prof. L. Que, Jr., T. R. Holman Department of Chemistry, University of Minnesota Minneapolis, MN 55455 (USA)
Prof. E. Münck, M. P. Hendrich, C. Juarez-Garcia Gray Freshwater Biological Institute, University of Minnesota Navarre, MN 55392 (USA)
Prof. O. P. Anderson, K. A. Andersen Department of Chemistry, Colorado State University Ft. Collins, CO 80523 (USA)

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