

ing an ion which could be assigned to the substituted moiety $C_{13}H_{19}NO_2$ (m/e 221). In addition, ir spectra of complexes **2a** and **2b** exhibited absorptions at 1100 and 1000 cm^{-1} which are characteristic of an unsubstituted cyclopentadienyl ring π bonded to a metal.⁸ Nmr and ir data of a similar nature in support of the structures **3a,b** and **4a,b** were also obtained.

The electrophilic reactivity of the methyl groups of complexes **1a-c** suggested the possibility of realization of base-catalyzed reactions. Complex **1a** was condensed with benzaldehyde in sodium methoxide-ethanol resulting in a mixture of condensation products. These could not be completely separated by chromatography but sufficient fractionation was achieved that nmr analysis (phenyl *vs.* unsubstituted methyl signals) permitted the conclusion that mono, di, tri, and tetra condensation products had been formed. A precise demonstration of the base-catalyzed reactivity of these complexes is provided by the observation that complex **1b** underwent significant deuterium exchange with sodium deuterioxide-methanol-*d*₂ after stirring at room temperature for 12 hr. The deuterium content of the resulting complex was measured by two independent techniques. Assuming that no deuterium exchange had occurred at the cyclopentadienyl ring, comparison by nmr of the integrated intensities of the cyclopentadienyl ring protons and the remainder of the signal for the duroquinone methyl groups indicated that 10.6 atoms of deuterium had been incorporated. Chemical analysis for deuterium content by the falling drop method⁹ indicated that *ca.* 10.9 atoms of deuterium were present in the molecule as a whole. Comparison of these two results permitted the conclusion that no significant deuterium exchange had occurred in the cyclopentadienyl ring and that essentially the total deuterium content resided in the methyl groups of the duroquinone ligand. This is a most provocative conclusion since duroquinone itself does not undergo any exchange under these same conditions.¹⁰

It is appropriate to conclude that π complexation to a transition metal activated the methyl groups of duroquinone toward both acid- and base-catalyzed reactions in an extraordinary manner. This activation promises to be of considerable importance since it demonstrates the potential that complexation of an organic ligand by a transition metal may be useful in the synthesis of previously difficult to obtain or unattainable compounds if the substituted ligand can be removed intact from the metal.^{11,12} Experiments designed to demonstrate this last step in the synthesis of substituted duroquinones are under examination.

Acknowledgment. Support by the Office of Re-

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(11) Four examples of this overall procedure have been reported. Substitution reactions of cyclobutadiene have been described by R. Pettit and coworkers [J. S. Ward and R. Pettit, *J. Amer. Chem. Soc.*, **93**, 262 (1971), and references cited therein] and mesitylene by J. F. Helling and D. M. Braitsch, *J. Amer. Chem. Soc.*, **92**, 7207 (1970); *cf.* also ref 2 and 3.

(12) Mr. R. Marchal has decomposed complex **1a** by use of aqueous ceric ammonium nitrate with recovery of 90% of the duroquinone. In the one instance where a derivatized complex has been decomposed by this technique, **2a** has afforded 2-(*N,N*-dimethylaminoethyl)-3,5,6-trimethyl-1,4-benzoquinone as an oil in 58% yield; nmr τ 7.62 and 7.55 (overlapping singlets), 7.26 (s), and 7.25-6.5 (m) in relative areas of 9:6:4, respectively.

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Cyanoborane Chemistry. I. Preparation of a Novel Series of Macrocyclic Cyanoboranes¹

Sir:

The existence of cyanoborane, BH_2CN , as a stable monomer under ordinary conditions is unlikely. Conceptually, these moieties could undergo association in a number of ways, one being the formation of a coordinate covalent bond by the donation of a nitrogen atom's lone pair of electrons into an empty boron orbital. The result of such a process would be the formation of linear and/or cyclic polymers. Assuming a 180° configuration for difunctional cyanide, four atom BCNB rods would result. Some of the macrocyclic molecules which might be expected are depicted in Figure 1. We wish to report in this communication evidence for a series of macrocyclic oligomers of cyanoborane, $(BH_2CN)_n$, with $n = 4-9$.

A suspension of sodium cyanotrihydroborate, $Na-BH_2CN$,² in dry diethyl ether reacts with hydrogen chloride in a 1:1 ratio at ambient temperatures to yield a quantitative amount of hydrogen, sodium chloride, and, upon removal of the ether, polymeric cyanoborane. Up to 20% of this material is volatile under a vacuum of 10^{-5} Torr at room temperature and can be collected as a white crystalline solid. *Anal.* Calcd for $(BH_2CN)_n$: C, 30.91; H, 5.20; N, 36.06; B, 27.85. Found: C, 30.78; H, 5.25; N, 35.88; B, 27.87.

Analytical glc analysis of the volatile material using OV-17 on acid-washed Chromosorb W resulted in the elution of seven distinct components. Mass spectra obtained on the first five components exhibited sharp cutoffs in the spectra at m/e 156, 195, 234, 273, and 312. These peaks correspond to the molecular ion for $(^{11}BH_2CN)_n$, where $n = 4-8$. All of the fragmentation patterns show the familiar boron isotope and hydrogen loss effects. The mass spectrum for the sixth component was of low intensity due to insufficient sample and the highest peak observed was m/e 348 [*vs.* 351 expected for $(^{11}BH_2CN)_9^+$]. The fragmentation pattern, however, was similar to the others. No mass spectral data were obtained for the seventh component. Relative proportions of the volatile cyanoboranes eluted by glc from a typical run are as follows: 3% $(BH_2CN)_4$, 87% $(BH_2CN)_5$, 8% $(BH_2CN)_6$, 1% $(BH_2CN)_7$, traces of $(BH_2CN)_8$, $(BH_2CN)_9$, and possibly $(BH_2CN)_{10}$.

By means of fractional sublimation, samples containing $(BH_2CN)_5$ in excess of 90% purity as determined by glc analysis could be obtained. The ^{11}B nmr spectrum of this material consists only of a 1:2:1 triplet at +28 ppm ($J = 109$ Hz) relative to $BF_3 \cdot Et_2O$. The appearance of the upfield triplet indicates that all of the

(1) Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971; and at the 163rd National Meeting, Boston, Mass., April 1972.

(2) Available from Ventron Corp., Chemical Division, Beverly, Mass.

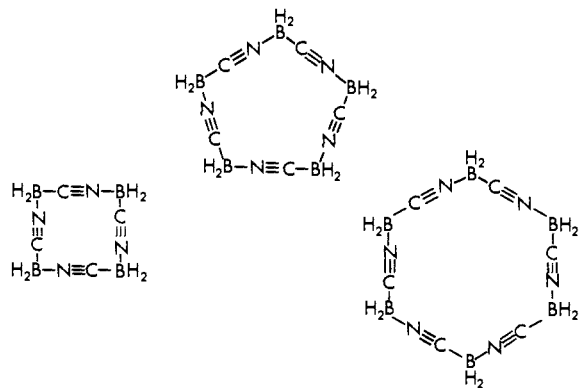


Figure 1. Macrocyclic cyanoboranes.

boron nuclei are in the same four-coordinate environment and have two hydrogens attached to each boron.³ The ambient temperature proton spectrum in DCCl_3 with decoupled boron is a single signal at δ 2.03. These nmr data are consistent only with a cyclic structure. The infrared spectrum includes strong absorption bands at 2469, 2441, and 2429 and at 2295 cm^{-1} (BH_2 and $\text{C}\equiv\text{N}$ stretching, respectively), as well as an intense broad band at 1089 cm^{-1} , and several weaker ones at lower wave numbers. The appearance of only one $\text{C}\equiv\text{N}$ absorption at such a high frequency is consistent with the presence of a single, bridging cyano group⁴ as required in a cyclic oligomer. The number and frequencies of the BH stretching bands fit that expected for a single type of BH_2 with four-coordinate boron.⁵ No absorption characteristic of CH or NH is observed. The preliminary crystal data for $(\text{BH}_2\text{CN})_5$ are as follows⁶: space group $P2_1/c$, monoclinic; $a = 9.46$, $b = 8.88$, $c = 16.04$ Å; $\beta = 106^\circ 5'$; $V = 1295$ Å³; if $Z = 4$, $D_{\text{calcd}} = 0.998$ and $D_{\text{measd}} = 1.00 \pm 0.2$ g/cm^3 . Thus all the data are consistent with a cyclic species as shown in the figure. It is also interesting to note that for $(\text{BH}_2\text{CN})_5$, a planar species would have an NBC bond angle of 108° , close to the normal tetrahedral angle of $109^\circ 28'$.

It is also possible, by means of fractional sublimation techniques, to obtain samples enriched in $(\text{BH}_2\text{CN})_n$ where $n = 6, 7, 8$, with purities (as determined by glc analysis) of 80, 40, and 56%, respectively. All of these samples exhibit ¹¹B nmr and infrared spectra which are very similar to that of $(\text{BH}_2\text{CN})_5$. In view of the very close similarities in the nmr and infrared spectra, as well as very similar mass spectral cracking patterns and intense parent ion envelopes for all of these species, the data are consistent with macrocyclic species rather than linear structures. In addition, on standing in solution, no change in relative concentrations of the various species is noticed. Linear species would be expected to undergo further polymerization.

These compounds are resistant to hydrolysis even in boiling water; in air over long periods, boric acid is deposited. Bases such as trimethylamine cause depolymerization of the cyclic oligomers as well as of the

nonvolatile polymeric mass. An isolable 1:1 amine adduct is formed. We have also identified cyanoborane as a product of the reaction of HCN with THF-borane . The compound $(\text{BH}_2\text{CN})_x$ as "a clear glassy solid" has been reported as one of the products of the thermal decomposition of $\text{H}_3\text{SiCNBH}_3$ or $\text{Me}_3\text{SiCNBH}_3$.⁷ The solid residue was identified by material balance and elemental analysis. However, the infrared spectrum included absorption bands at 3450 and 1630 cm^{-1} , which were assigned to NH stretch and CN or NH bending, respectively. These absorptions are absent from the spectrum of cyanoborane, *vide supra*.

Studies on the purification, X-ray structure determinations, and further chemistry of the macrocyclics are underway. We are also interested in the nature of the nonvolatile polymeric mass.

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Cotton Effects of the Benzene Chromophore in the 300–185-nm Spectral Region

Sir:

The benzene ring today is the most widely studied chromophoric group, but, in spite of the extensive experimental and theoretical work made, several open questions remain unanswered concerning its chiroptical properties.

To date, there has not been published a CD spectrum covering the spectral range in which the three major $\pi \rightarrow \pi^*$ transitions of a single, chirally perturbed benzene chromophore occur. Although many attempts have been made, only the Cotton effect in the 260-nm region has been, until now, characterized in phenylalkanes.^{1–3}

The failure to detect Cotton effects at shorter wavelengths than 240 nm is due to the weak CD with respect to the absorption. Moscowitz has pointed out that the low optical activity in a planar hydrocarbon π system can be associated with the fact that there is no convenient source of magnetic dipole character⁴ for the three transitions in question. Moreover, it also has to be considered that in flexible compounds the observed CD is the average of the CD associated with each conformation.

An examination of models indicated that the chiral 2-phenyl-3,3-dimethylbutane (I) should be a suitable molecule with restricted conformational freedom to investigate the CD of the benzene chromophore.

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