

The electrostatic contribution can be estimated from

$$P_{es} = e^{-Ze\psi/kT} \quad (13)$$

where Z is the ionic charge, e is the electronic charge, and ψ is the surface potential of the micelle.¹¹ The surface potential is sensitive to added salt and has not been determined for our exact experimental conditions, but it does not appear to change substantially once the NaCl concentration exceeds 0.025 M.¹³ Using $\psi = -84$ mV, determined for SDS micelles at [NaCl] = 0.1 M,¹³ we calculate $P_{es} = 27$ and $P_{hy} = 1.5 \times 10^3$ for $\text{Cu}(\text{phen})_2^+$ binding to SDS micelles at 25 °C. Even if P_{es} is only approximate, it is apparent that the strong micellar binding of $\text{Cu}(\text{phen})_2^+$ comes primarily from hydrophobic rather than electrostatic factors.

There is limited data available on how micelles influence metal ion complexation. In systems where there is little reagent association with the micelle, aqueous and micellar ligation rates are similar. For example, the rates of several ligand association and dissociation reactions of cobalamin in SDS solution show little difference from those in water.¹⁴ On the other hand, when the reagents concentrate at the micelle surface, as in the reaction between Ni(II) and PADA (pyridine-2-azo-*p*-dimethylaniline), the micellar rate (SDS) is several orders of magnitude faster than the aqueous rate.¹⁵ However, when corrections are made for the actual micellar concentrations of reagents and hydrogen ion (the association is pH dependent) the calculated second-order rate constant is very close to the value obtained in bulk solution.¹³ Similar results have recently been reported for Ni(II) complexation with 2,2'-bipyridyl and 4,4'-dimethyl-2,2'-bipyridyl.¹⁶

There is strong binding between SDS micelles and $\text{Cu}(\text{phen})_2^+$ (and presumably $\text{Cu}(\text{phen})^+$ as well), but the 5-fold inhibition of the phenanthroline association rates is in marked contrast to the rate enhancement seen for the Ni(II)-chelate reactions.^{13,15,16} If the actual micellar concentration of phenanthroline were known, the inhibition would be even more substantial. Micelles are known to inhibit the association reaction of a ligand with a dissociable proton by increasing the concentration of hydrogen ion at the micelle surface.¹³ Although previous electron-transfer studies with $\text{Cu}(\text{phen})_2^+$ have shown that (1) is independent of pH over the range $6 \leq \text{pH} \leq 8$,¹ we are currently investigating the reaction over a wider pH range.

We have previously suggested the possibility of ion-pair complex formation between the copper species and the detergent head groups.¹ The stability of such a complex, $\text{Cu}(\text{L})^*$, would be enhanced by strong hydrophobic interactions between phenanthroline and the detergent tails. The rate constant for any subsequent reaction of $\text{Cu}(\text{phen})_2^+$ or $\text{Cu}(\text{phen})^+$, whether it is electron transfer, ligand association, or water exchange, would be modified by the ion-pair equilibrium constant, K^* :



Thus, SDS micelles may inhibit the reactions of $\text{Cu}(\text{phen})_2^+$ and $\text{Cu}(\text{phen})^+$ by forming nonreactive complexes. Since aquonickel(II) has no ligands for strong hydrophobic interactions, the association reaction would not be similarly inhibited. A possible explanation for why the ligand dissociation of $\text{Cu}(\text{phen})_2^+$ is strongly inhibited by SDS micelles while that

for the similar NiPADA^{2+} complex is unaffected is that the latter complex is only loosely bound to the micelle surface. Studies now in progress over a wider range of detergent concentration and with a nonionic detergent should help resolve some of these questions.

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Registry No. $\text{Cu}(\text{phen})_2^+$, 17378-82-4.

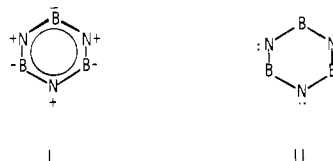
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π -Donor Complexes of Heteroaromatic Boron-Nitrogen Compounds with Iodine

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Borazine, $\text{B}_3\text{N}_3\text{H}_6$, is isoelectronic and isostructural with benzene; for this reason it is expected to behave as an aromatic system with the planar ring structure I. Although its physical properties and spectra are consistent with such an interpretation, its chemical reactivity for the most part is that expected for a cyclic aminoborane with the puckered ring structure II.¹



Evidence for aromatic chemical behavior in borazine derivatives comes from the study of weak electron donor-acceptor complexes. Champion et al.² report a π -donor complex between hexamethylborazine and tetracyanoethylene with an absorption maximum at 461 nm and a stability constant of 0.7 L/mol. Mellon and Lagowski,³ however, report an absorption maximum at 320 nm for the same complex, leaving the evidence for the characteristics of the complex in doubt. Muszkat and Kirson⁴ present evidence of π -complex formation between several triphenylborazines and tetracyanoethylene without making it clear whether the bonding interaction involves the borazine ring or the attached phenyl groups. Dewar and Rogers⁵ present spectral evidence for π -complex formation between tetracyanoethylene and several heteroaromatic compounds containing B-N bonds but report no stability constant values.

The objective of this work is to obtain chemical evidence for π -complex formation involving B-N aromatic systems from stability constant values. Our method is similar to that of Eubanks and Lagowski,⁶ who sought to determine whether substituted aminoboranes behave as lone-pair, or n, donors

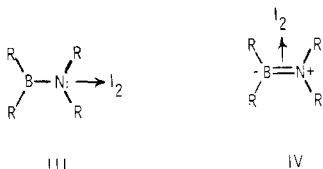
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Table I. Data for HMB-I₂

| 10 ³ C _{I₂} , M | 10 ³ C _{HMB} , M | A(280 nm) |
|--|--------------------------------------|-----------|
| 1.05 | 9.1 | 0.089 |
| 1.05 | 17.9 | 0.156 |
| 1.05 | 26.4 | 0.260 |
| 1.05 | 44.0 | 0.411 |

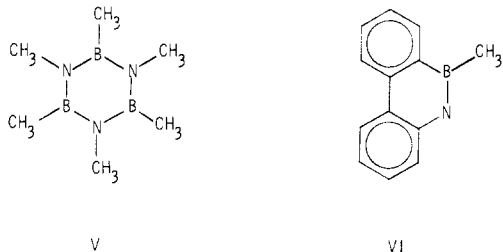
(III) or π donors (IV) when they form complexes with iodine. They show that stability constants of several aminoborane derivatives with iodine have values similar to those of amino-iodine ($K > 10^2$) rather than olefin-iodine complexes ($1 < K < 4$).



III

IV

In this study we report data obtained for the complexes of hexamethylborazine (V) and 10-methyl-10,9-borazarophenanthrene (VI) with iodine. These compounds are referred to hereafter as HMB and MBAP. In each compound the boron atoms are bonded to a methyl group since B-H bonds are subject to rapid oxidation by iodine.



V

VI

Experimental Section

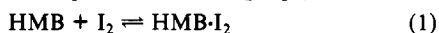
Reagents. Hexamethylborazine was prepared according to the method of Haworth and Hohnstedt,⁷ purified by vacuum sublimation, and characterized by its melting point, 98–99 °C (lit.⁸ mp 97 °C), and by its infrared spectrum.

10-Methyl-10,9-borazarophenanthrene was prepared by the method of Dewar et al.⁹ and purified by vacuum sublimation; its identity was confirmed by its melting point, 101–103 °C (lit.¹⁰ mp 103–104 °C), and ultraviolet and infrared spectra.

Analytical reagent iodine (Mallinckrodt AR) and spectral grade carbon tetrachloride (Mallinckrodt SpectrAR) were used without further purification. Stock solutions were prepared fresh and used on the same day.

Spectral Measurements. Spectra were recorded on a Beckman Acta III spectrophotometer with 1-cm quartz cells.

Hexamethylborazine-Iodine Complex. HMB solutions in CCl₄ absorb strongly in the ultraviolet region with a sharp cutoff at 265 nm. Spectra of HMB-I₂ mixtures in CCl₄ exhibit a peak at 280 nm, which appears as a shoulder on the HMB absorbance curve. This peak is attributed to a 1:1 complex of HMB and I₂ (eq 1). In addition,



iodine has a weak absorbance maximum ($\epsilon = 50$) at 280 nm. Interference from the HMB is removed by using HMB-CCl₄ solutions of the appropriate concentration in the reference cell. The iodine concentration is kept constant at 1×10^{-3} M so that the same absorbance blank may be used for all samples. The data are given in Table I.

Fresh solutions of HMB and iodine have the magenta color typical of iodine dissolved in nonpolar solvents. However, these solutions turn orange on standing overnight and deposit a white solid. It appears

Table II. Data for MBAP-I₂

| 10 ³ C _{I₂} , M | 10 ³ C _{MBAP} , M | A(358 nm) |
|--|---------------------------------------|-----------|
| 1.04 | 57.8 | 0.175 |
| 3.01 | 47.2 | 0.435 |
| 5.03 | 35.0 | 0.551 |
| 8.04 | 23.7 | 0.619 |
| 9.05 | 12.0 | 0.380 |

Table III. Values of K and ϵ for I₂ Complexes in CCl₄

| donor | λ_{max} , nm | ϵ | K , L/mol |
|--|-----------------------------|-------------|-------------|
| HMB ^a | 280 | 4000 ± 2500 | 2.3 ± 1.5 |
| MBAP ^a | 358 | 960 ± 50 | 3.7 ± 0.2 |
| hexamethylbenzene ¹⁴ | 375 | 8200 | 1.35 |
| phenanthrene ¹⁵ | 364 | 7100 ± 1200 | 0.45 ± 0.06 |
| (dimethylamino)dimethylborane ⁶ | 388 | | 190 ± 12 |
| piperidinodimethylborane ⁶ | 390 | | 1350 ± 70 |

^a Determined at 21 °C.

that HMB and iodine equilibrate rapidly to form a weak complex and also to react slowly and irreversibly to form solid materials. Consequently, all spectra were taken within a few minutes after sample preparation.

10-Methyl-10,9-borazarophenanthrene-Iodine Complex. MBAP solutions in CCl₄ absorb strongly in the ultraviolet region with a cutoff at 330 nm. Solutions of MBAP and iodine in CCl₄ exhibit a peak at 358 nm, which appears as a shoulder on the MBAP absorbance curve. This peak is attributed to a 1:1 complex of MBAP and I₂ (eq 2). Iodine absorbance at 358 nm is small and is compensated by



subtracting the absorbance value for a blank iodine solution. Interference from MBAP was eliminated by using MBAP-CCl₄ solutions of appropriate concentration in the reference cell. The spectra appear as well-defined peaks. Data are given in Table II.

Results and Discussion

The absorbance values for HMB-I₂ complexes at 280 nm for each solution, when plotted against HMB concentration, yield a straight line; the intercept of this line at zero HMB concentration (calculated by the least-squares method) yields a value for the blank at that wavelength. This procedure is repeated for absorbance values at 285, 290, 295, and 300 nm, and the array of corrected absorbance values is analyzed according to the method described by Briegleb.¹¹ Mean absorbance values so obtained are substituted into the Benesi-Hildebrand equation (eq 3),¹² which yields values of the in-

$$C_A/A = 1/\epsilon + (1/K\epsilon)(1/C_D) \quad (3)$$

tercept ($1/\epsilon$) and slope ($1/K\epsilon$) by least-squares analysis. The symbols C_A and C_D are the molar concentrations of the acceptor (I₂) and donor (HMB). The excellent fit of the data to the line (the correlation coefficient is 0.996) indicates that little appreciable irreversible reaction had taken place at the time the data were recorded. Calculated values of ϵ_{280} and K , with uncertainties tabulated at 50% confidence limits, are shown in Table III.

The absorbance data for the MBAP-I₂ complex are taken at 354, 358, 362, 366, 370, and 374 nm and processed according to the procedure described by Briegleb.¹¹ The mean absorbance values are fit to the Scott equation (eq 4)¹³ by the

$$C_A C_D / A = (1/K\epsilon) + (1/\epsilon)C_D \quad (4)$$

least-squares procedures with a correlation coefficient of 0.964. The values of ϵ_{358} and K , calculated from the intercept ($1/K\epsilon$) and slope ($1/\epsilon$) are shown in Table III.

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Comparison of our results with those of Andrews and Keefer¹⁴ on the hexamethylbenzene-I₂ complex and of Peters and Person¹⁵ on the phenanthrene-I₂ complex (Table III) show that our values are within 1 order of magnitude of the corresponding values for these π -donor systems. In contrast, stability constant values for aminoborane-I₂ complexes reported by Eubanks and Lagowski⁶ (Table III) are 2 or 3 orders of magnitude larger than our values.

We conclude that aromatic compounds incorporating B-N bonds prefer to complex with iodine by means of the π -donor interaction, rather than the stronger n-donor interaction. This suggests that the energy required to transform a planar aromatic ring to a puckered ring is too large to be offset by the formation of an n-donor bond between the nitrogen atom and I₂.

Acknowledgment. The authors are grateful for support from a Northern Michigan University Faculty Research Grant and thank Dr. Leo F. Hohnstedt, Dr. E. K. Mellon, Dr. Jerome A. Roth, Dr. David W. Kingston, and Dr. Philip I. Pavlik for valuable discussions and correspondence.

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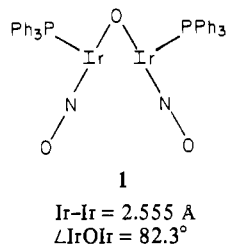
Presence of a Substantially Bent Ir-Ir Bond in Ir₂O(PPh₃)₂(NO)₂

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There has been much discussion of the possible existence of "bent" metal-metal bonds.¹ Calculations have confirmed the presence of metal-metal interactions in Fe₂S₂(CO)₆² and Rh₂Cl₂(CO)₄³ which represent compromises between the "bent-bond" and "straight-bond" extremes, that is, between metal-orbital hybridization optimized for metal-ligand and metal-metal overlap, respectively. It has been asserted that Co₂(CO)₈ contains no metal-metal bond, bent or straight; the pairing of electrons leading to diamagnetism is predicted to occur in an orbital that is Co-Co antibonding (though Co-Co_{br} bonding.⁴

Among such molecules, Ir₂O(PPh₃)₂(NO)₂ (1) has long



appeared the likeliest candidate for a strong, considerably bent bond.⁵ The Ir-Ir distance is shorter relative to the metal-atom

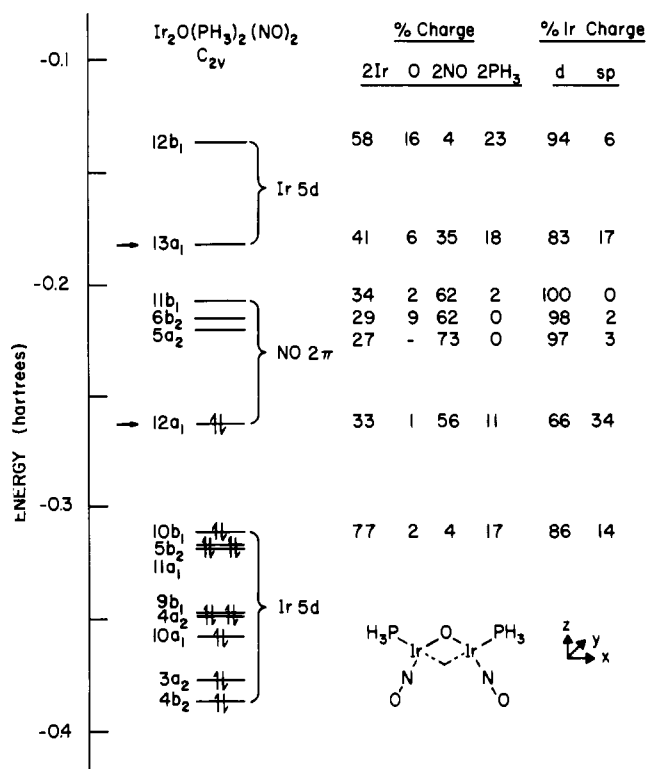
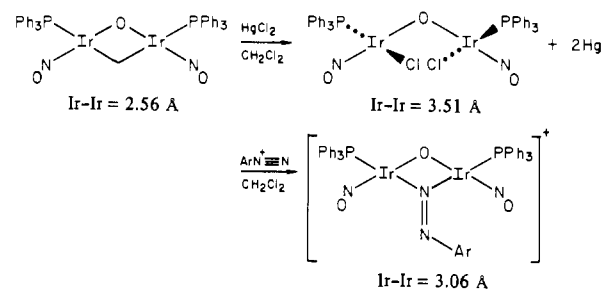


Figure 1. SCF-X α -SW energy levels for Ir₂O(PH₃)₂(NO)₂ above -0.42 hartree, labeled as Ir 5d or NO 2 π according to their predominant character. The exact charge distributions are given for some of the levels; that for 10b₁ is fairly typical of the occupied 5d band. The two levels marked by arrows are those important for consideration of the nature of Ir-Ir bonding in the molecule.

Scheme I



radius than in those in the other complexes mentioned above. Moreover, the molecule behaves chemically as a powerful reducing agent, with accompanying structural changes interpretable as oxidative cleavage of the Ir-Ir bond. Two representative examples are shown in Scheme I.⁶⁻⁸ Particularly fascinating is the unusual reduction of the N \equiv N- linkage in diazonium salts to an Ir₂N=NO- moiety, suggestive of the first step of N₂ reduction by the proposed sulfur-bridged Mo-Fe site in nitrogenase.⁹ It is tempting to speculate that the outward projection of Ir-Ir bonding electrons by bond bending lowers activation energies for these reactions.

We undertook SCF-X α -SW calculations¹⁰ of Ir₂O(PH₃)₂(NO)₂ to clarify the nature of the Ir-Ir bonding.

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