of 2, although the ligand field strength of water is certainly less than that of pyridine, and the rate of aquation[19c] of the aquo complex is equal to or faster than that of the pyridino complex.

The hypothesis we put forth above is supported by the data. Ammonia and the series of substituted pyridines have roughly the same ligand field strength,[18] although that of Clpy may be slightly lower. However, the value of the σ bonding strength of the ligands, as measured by the acidity of the conjugate acids,[20] decreases along the series $NH_3 > 3,5\text{-}(CH_3)_2py > 3\text{-}(CH_3)py > py > 3\text{-}Clpy$. These data indicate that the rate constant increases in direct response to the lower σ-bonding power of the variable nonbridging ligand.

The factors that influence the change in rate constant as nonbridging ligands are varied are numerous; it is clear that our hypothesis is not sufficient to account for all of the effects,[21] but we believe that there are many systems where the determining factor will be the σ-bonding strength of the nonbridging ligands. We are currently expanding the scope of these studies to include other cases in order to test more rigorously the hypothesis.

(20) That the σ bonding strength of the ligand is proportional to the pK of the corresponding conjugate acid of the ligand can be supported. There are some electronic configurations that can yield values of the relative σ bonding strength of ligands by McClure's treatment. One of these involves high-spin complexes of Fe(II). Data taken from a study of the spectra of such complexes indicate a roughly linear correlation between the relative σ bonding power of the substituted pyridine and the acidity of its conjugate acid: D. M. L. Goodgame, M. Goodgame, M. A. Hitchman, and M. J. Weeks, *Inorg. Chem.*, **5**, 635 (1966).
(21) The rate of reduction of *cis*-Co(en)$_2$H$_2$OCl^{2+} compared to *cis* Co(en)$_2$pyCl^{2+} is a special case. By using the pK as a measure of σ-bonding strength, we predict that the aquo complex should be reduced about 100 times faster than the pyridino complex. However, it is not to be expected that the pK–σ bonding correlation will hold for such different species.
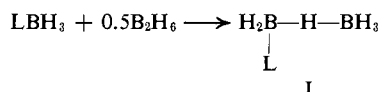
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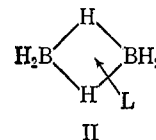
Further Studies and Comments on $B_2H_6 \cdot NR_3$

Sir:

Recently[1] we discussed the properties of singly hydrogen-bridged boranes (I), prepared through reactions of amine boranes with diborane

$$LBH_3 + 0.5B_2H_6 \longrightarrow H_2B\text{---}H\text{---}BH_3$$
$$|$$
$$L$$
$$I$$

where L is an amine base. Eastham[2] has reinterpreted our nmr data,[1] concluding that the material we studied was effectively an intact diborane molecule with the

(1) S. G. Shore and C. L. Hall, *J. Am. Chem. Soc.*, **88**, 5346 (1966).
(2) J. F. Eastham, *ibid.*, **89**, 2237 (1967).

ligand symmetrically attached through a π bond between an nonbonding orbital of diborane and the lone pair of the amine to give II.[3] Experimental work described below is consistent with structure I. Furthermore, this new information plus available thermodynamic data militate strongly against the structure proposed by Eastham.[2]

II

For the systems we have studied,[1] structure II would have to be formed through a reaction in which *a σ boron–nitrogen bond is broken*. In a tracer study, we added $B^{10}_2H_6$ to $(CH_3)_3NBH_3$ which contained a normal distribution of boron isotopes. In principle, this gave rise to one of the two structures in eq 1.

$$(1)$$
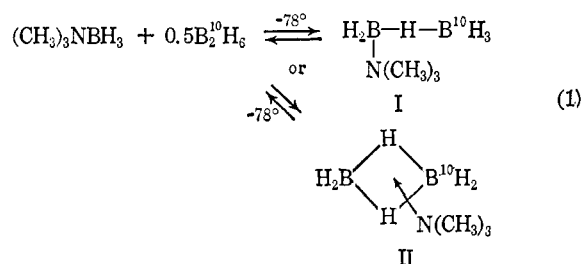
This reaction is reversible; diborane added to the amine borane can be quantitatively pumped away and recovered. Results presented in Table I below clearly show that there is essentially no enrichment of boron-11 in the recovered diborane. This result is consistent

Table I. Mass Spectra of Recovered Diborane

| | | Relative intensities | | |
| | | | Diborane Recovered | |
e/m	$B_2H_6{}^a$	$B^{10}_2H_6{}^a$	A^b	B^c
20	...	2.5	2.0	2.6
21	...	6.4	5.2	6.7
22	2.6	68.7	62.3	68.5
23	32.9	29.4	35.1	41.4
24	88.2	49.0	50.5	54.8
25	52.6	100	100	100
26	100	7.4	19.0	15.9
27	100	2.5	9.7	2.0
28	...	...	...	...

^{a} Relative intensities observed from samples used in this study. ^{b} In A, $B^{10}_2H_6$ was added to $(CH_3)_3NBH_3$ in CH_2Cl_2, and the system was continuously stirred for 48 hr at $-78°$ before recovery of diborane. ^{c} In B, $B^{10}_2H_6$ was added to $(CH_3)_3NBH_3$ in glyme, and the system was continuously stirred for 10 hr at $-78°$ before recovery of diborane.

with structure I and refutes the presence of structure II. For structure II, the symmetrical attachment of the amine to diborane requires that a statistical distribution of boron isotopes be present in the recovered diborane.

(3) Structure II is considered to be analogous to that suggested for butyllithium dimer coordinated to ether;[2] Z. K. Cheema, G. W. Gibson, and J. F. Eastham, *ibid.*, **85**, 3517 (1963). However, since the coordinate bond between lithium and ether is an ordinary σ bond, we believe that it should not be cited as an analog of structure II, which involves an unusual type of coordinate π bond.

Thermodynamic data available for a number of years also speak against structure II. Consider the reaction

$$(CH_3)_3NBH_3 + 0.5B_2H_6 \longrightarrow H_2B\diagup\diagdown BH_2$$
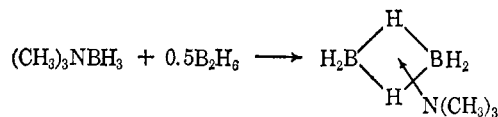
The heat of formation of $(CH_3)_3NBH_3$ in solution from diborane and trimethylamine is about -22 kcal/mole.[4] From a thermochemical cycle it can be seen that for the reaction to be exothermic, the heat of formation of structure II would have to exceed that of $(CH_3)_3NBH_3$. We doubt that such an amount of energy is available from interaction of a vacant nonbonding orbital with an electron donor as Eastham[2] envisions.

Even the direct reaction of diborane with an amine offers little hope of preparing and identifying structure II. It is well known that such a reaction will produce either a simple adduct, LBH_3, or an analog of the diammoniate of diborane, $BH_2L_2^+BH_4^-$, at temperatures as low as $-78°$. Only on rare occasions, under extremely mild conditions of reaction, has a metastable intermediate species been suggested.[5] Such conditions were used by Rathjens and Pitzer to study, calorimetrically, solutions of diborane in ammonia.[6] Freezing point depression studies showed it to be molecular containing two boron atoms per mole. It was not $H_2B(NH_3)_2^+BH_4^-$, but it must have been the precursor to this compound.[7] While there is no direct information to distinguish the material studied by Rathjens and Pitzer[6] as either structure I or structure II, we believe that the measured heat of reaction between diborane and ammonia to form this two boron atom species (-16 kcal/mole) suggests that structure I was formed.

The principal experimental argument on which structure II is based rests in the claim[2] that the boron-11 nmr spectrum assigned to structure I[1] is "virtually superimposable on the first boron-11 nmr spectrum published 12 years ago by Ogg."[8] It should be recognized, however, that Ogg's spectrum was taken at 6 Mc while our spectrum was taken at 19.25 Mc. There is in fact a marked difference between the spectra in methylene chloride at 19.25 Mc.[1] The diborane spectrum consists of nine well-resolved lines (a triplet of triplets), in contrast to the relatively poorly resolved septet assigned to structure I.

Eastham[2] has generalized structure II, suggesting that all compounds which were formerly considered to be singly bridged analogs of structure I are in fact intact diborane molecules with the ligand attached symmetrically. In the case of $B_2H_7^-$, the boron-11 nmr spectrum is not ambiguous; the only reasonable interpretation favors a single hydrogen bridge, $H_3B-H-BH_3^-$.[9] If there is a problem with the boron-11 spectrum assigned to structure I,[1] it probably arises from a complicating exchange process; we are looking into this possibility.

(4) A. C. Boyd, Jr., *Dissertation Abstr.*, 17, 1908 (1957).
(5) R. W. Parry and S. G. Shore, *J. Am. Chem. Soc.*, 80, 15 (1958).
(6) G. W. Rathjens, Jr., and K. S. Pitzer, *ibid.*, 71, 2783 (1949); private communication.
(7) B. Z. Egan and S. G. Shore, *ibid.*, 83, 4717 (1961).
(8) R. A. Ogg, *J. Chem. Phys.*, 22, 1933 (1954).
(9) D. F. Gaines, *Inorg. Chem.*, 2, 523 (1963).

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Preferred "Symmetrical" Cyclopropyl Conformations in Hydrocarbon Anion Radicals

Sir:

Much interest has recently focused on the conformations of cyclopropyl rings joined to potentially conjugating centers. "Bisected" cyclopropyl conformations (1) appear to have been established as absolute conformational energy minima for the dimethylcyclopropylcarbinyl cation,[1] cyclopropylcarboxaldehyde,[2] cyclopropyl methyl ketone,[3] cyclopropylcarbinyl chloride,[4] phenylcyclopropane,[5] vinylcyclopropane,[6] and cyclopropylsemidiones.[7] It therefore seems desirable to call attention to two species, both hydrocarbon anion radicals, in which the "symmetrical" conformation (2) of cyclopropyl is preferred over the "bisected" conformation.

$$a_\beta \approx 0 \qquad a_\beta = a_{max}$$

1   **2**
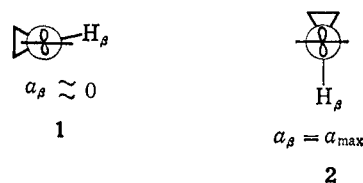
Equation 1 is generally accepted as approximating the conformational dependence of the hyperfine splitting constant, a_β, of a hydrogen β to a carbon 2p orbital having spin density ρ_i; θ represents the angle between the β C–H bond and the relevant p orbital.[8]

$$a_\beta = \rho_i a_{max} \cos^2 \theta \qquad (1)$$

Thus **1** should be characterized by $a_\beta \approx 0$ and **2** by $a_\beta = a_{max}$. Although a_{max} is not directly measurable, $a_\beta(CH_3) = 0.5 a_{max}$ by application of (1). Thus, $C(R) = a_\beta(R)/a_\beta(CH_3)$ is a measure of the predominance of form **1** or **2**; specifically, if $C(R) < 1$, **1** is preferred; if $C(R) > 1$, **2** is preferred. The range of $C(R)$ is $0 < C(R) < 2$.[9] Table I gives values of $C(R)$ for various 9-substituted anthracene and 1,4-disubstituted naphthalene anion radicals. *In both cases the symmetrical cyclopropyl form is favored.* These appear to be the first reported instances of preferred symmetrical cyclopropyl conformations. In all other cases previously studied, q_i, the excess *charge* density present in the relevant p orbital, is zero or positive.[10] Thus it is reasonable to assume that the change in the conformational preference

(1) C. U. Pittman, Jr., and G. A. Olah, *J. Am. Chem. Soc.*, 87, 2998 (1965).
(2) L. S. Bartell and J. P. Guillory, *J. Chem. Phys.*, 43, 647 (1965).
(3) L. S. Bartell and J. P. Guillory, *ibid.*, 43, 654 (1965).
(4) L. S. Bartell, J. P. Guillory, and A. P. Parks, *J. Phys. Chem.*, 69, 3043 (1965).
(5) G. L. Closs and B. Klinger, *J. Am. Chem. Soc.*, 87, 3265 (1965).
(6) G. R. DeMare and J. S. Martin, *ibid.*, 88, 5033 (1966).
(7) G. A. Russell and H. Malkus, *ibid.*, 89, 160 (1967).
(8) C. Heller and H. M. McConnell, *J. Chem. Phys.*, 32, 1535 (1860).
(9) The approximation is made that all β C–H bonds have approximately equal a_{max}.
(10) Even in the semidione anion radical systems q_i is calculated (HMO) to be positive ($\sim +0.10$).