divided by the number of π electrons that fill the levels resulting from the difference of the HMO energy levels and the levels resulting from the matching (acyclic) polynomial of a molecular graph. Thus, the index TRE(PE) is obtained by measuring the aromaticity that results from the $4n + 2$ rule with respect to the number of π electrons. The TRE method is straightforwardly applied to closed-shell charged and to open-shell neutral and charged conjugated compounds. In almost all cases the TRE method classifies species according to their chemical characteristics. Used with no refinements, the TRE method is generally applicable to any conjugated ion, radical, or ion radical. In some cases the agreement between the predictions based upon the calculated TRE values and the actual experimental properties is not properly quantified; an in-depth analysis reveals as main causes of the disagreement an incomplete conjugation, a time-dependent nonplanarity, and medium effects. Simple refinements are easily applicable to the TRE method and result in a simple, complete method generally applicable to conjugated species be they neutral closed shell, neutral open shell, or charged, both closed and open shell.

Acknowledgment. We thank Professors B. A. Hess, Jr. (Nashville), I. Murata (Osaka), and M. Rabinovitz (Jerusalem) for helpful discussions, and Professor M. Randić (Ames) for correspondence about the aromatic stability of conjugated ions, radicals, and ion radicals.

Registry No. **1**, 26810-74-2; **2**, 60512-06-3; **3**, 20829-57-6; **4**, 12240-33-4; **5**, 34531-09-4; **6**, 34561-57-4; **7**, 59963-50-7; **8**, 29661-18-5; **9**, 62744-94-9; **10**, 12127-83-2; **11**, 34504-50-2; **12**, 34562-85-1; **13**, 26811-28-9; **14**, 3551-27-7; **15**, 34464-18-1; **16**, 34568-48-4; **17**, 64113-53-7; **18**, 37306-59-5; **19**, 34484-44-1; **20**, 34510-85-5; **21**, 34510-09-3; **22**, 45730-23-2; **23**, 62668-20-6; **24**, 2154-56-5; **25**, 7419-60-5; **26**, 7419-61-6; **27**, 4471-17-4; **28**, 2216-49-1; **29**, 13948-08-8; **30**, 60644-50-0; **31**, 72844-22-5; **32**, 36510-10-8; **33**, 72866-10-5; **34**, 62697-82-9; **35**, 62673-28-3; **36**, 12107-28-7; **37**, 72866-13-8; **38**, 72844-18-9; **39**, 72881-39-1; **40**, 72866-14-9; **41**, 64062-09-5; **42**, 34527-68-9; **43**, 72881-24-4; **44**, 64062-12-0; **45**, 12203-21-3; **46**, 12128-54-0; **47**, 34512-27-1; **48**, 34509-91-6; **49**, 29432-93-7; **50**, 12203-30-4; **51**, 72791-66-3; **52**, 72844-19-0; **53**, 72866-11-6; **54**, 72844-14-5; **55**, 72852-80-3; **56**, 72881-23-3; **57**, 51053-95-3; **58**, 54447-98-2; **59**, 72844-15-6; **60**, 72844-05-4; **61**, 72852-81-4; **62**, 72881-22-2; **63**, 56843-00-6; **64**, 62684-05-3; **65**, 63397-57-9; **66**, 42299-42-3; **67**, 34471-83-5; **68**, 64492-53-1; **69**, 72852-79-0; **70**, 72866-21-8; **71**, 72843-94-8; **72**, 72843-95-9; **73**, 62157-22-6; **74**, 34533-10-3; **75**, 34478-97-2; **76**, 72843-96-0; **77**, 59926-11-3; **78**, 72844-02-1; **79**, 72844-03-2; **80**, 72844-04-3; **81**, 72866-22-9; **82**, 2299-68-5; **83**, 12257-35-1; **84**, 72852-82-5; **85**, 72844-01-0; **86**, 72881-21-1; **87**, 72844-16-7; **88**, 72866-16-1; **89**, 72881-19-7; **90**, 72881-20-0; **91**, 72844-17-8; **92**, 72866-17-2; **93**, 72866-19-4; **94**, 62684-07-5; **95**, 35612-78-3; **96**, 34493-60-2; **97**, 62684-08-6; **98**, 12147-01-2; **99**, 3924-44-5; **100**, 42464-32-4; **101**, 12564-47-5; **102**, 72881-18-6; **103**, 34539-26-9; **104**, 12564-35-1; **105**, 72844-11-2; **106**, 57891-91-5; **107**, 72866-15-0; **108**, 69742-87-6; **109**, 62684-01-9; **110**, 72844-12-3; **111**, 60016-22-0; **112**, 72844-13-4; **113**, 55563-45-6; **114**, 69717-97-1; **115**, 72866-20-7; **116**, 63882-11-1; **117**, 59659-00-6; **118**, 64045-03-0; **119**, 26811-00-7; **120**, 12319-46-9; **121**, 12190-17-9; **122**, 72881-40-4; **123**, 49598-08-5; **124**, 72843-98-2; **125**, 72866-18-3; **126**, 72843-99-3; **127**, 61189-58-0; **128**, 72866-09-2; **129**, 72866-07-0; **130**, 72866-08-1; **131**, 28084-93-7; **132**, 72844-23-6; **133**, 72866-06-9; **134**, 72844-24-7; **135**, 72844-00-9; **136**, 72881-17-5; **137**, 72844-25-8; **138**, 64317-43-7; **139**, 12312-62-8; **140**, 34468-12-7; **141**, 34468-13-8; **142**, 72866-23-0; **143**, 72844-20-3; **144**, 26811-02-9; **145**, 72844-21-4; **146**, 72905-11-4; **147**, 31468-22-1; **148**, 40807-34-9; **149**, 34480-04-1; **150**, 72866-12-7.

Chemical Effects of Steric Strains. 24. ^{13}C NMR Study of the Interaction of 9-Borabicyclo[3.3.1]nonane with Amines of Increasing Steric Requirements

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The ^{13}C NMR spectra of the interaction of 9-borabicyclo[3.3.1]nonane (9-BBN) with two series of amines, involving regularly increasing steric requirements, were used to study the role of steric strains as a factor in the stability of addition compounds formed and their exchange with the amine. A set of pyridine bases, including pyridine and 2-methyl-, 2-ethyl-, 2-isopropyl-, and 2-*tert*-butylpyridines, and a set of aliphatic amines, including *n*-propylamine, isopropylamine, diethylamine, diisopropylamine, and triethylamine, with increasing steric requirements were selected for examination. Quinuclidine was also selected, as a base of relatively low steric requirements, for comparison with triethylamine, a base with very large steric requirements. The results reveal four types of behavior: formation of stable complexes with no observable exchange with excess amine; formation of stable complexes with rapid exchange of amine; formation of partially dissociated complexes with rapid exchange; and no detectable interaction of 9-BBN and amines of large steric requirements. In general, there is a regular progression along these four types of behavior with increasing steric requirements in both series of amines. Thus, triethylamine fails to show any interaction with 9-BBN, whereas quinuclidine forms a stable adduct which does not exchange with excess amine. ^{13}C NMR provides a valuable tool for exploring the role of such steric effects in the formation and stability of molecular addition compounds.

It was previously observed that the complex of pyridine (Py) with 9-borabicyclo[3.3.1]nonane (9-BBN), Py-9-BBN, exhibits an unusual ^{13}C NMR spectrum.[2] The two halves of the cyclooctyl ring of 9-BBN are different. Also, rapid exchange with excess free pyridine does not occur. Therefore, it was of interest to examine how these spectral characteristics would change with increasing steric requirements of the base.[3,4] Two series of bases with in-

(1) Graduate research assistant on Grant CHE 76-20846 of the National Science Foundation.

(2) Brown, H. C.; Soderquist, J. A. *J. Org. Chem.* **1980**, *45*, 846.

(3) For a summary of the data and conclusions see: Brown, H. C. "Boranes in Organic Chemistry"; Cornell University Press: Ithaca, NY, 1972; Chapters 5-8.

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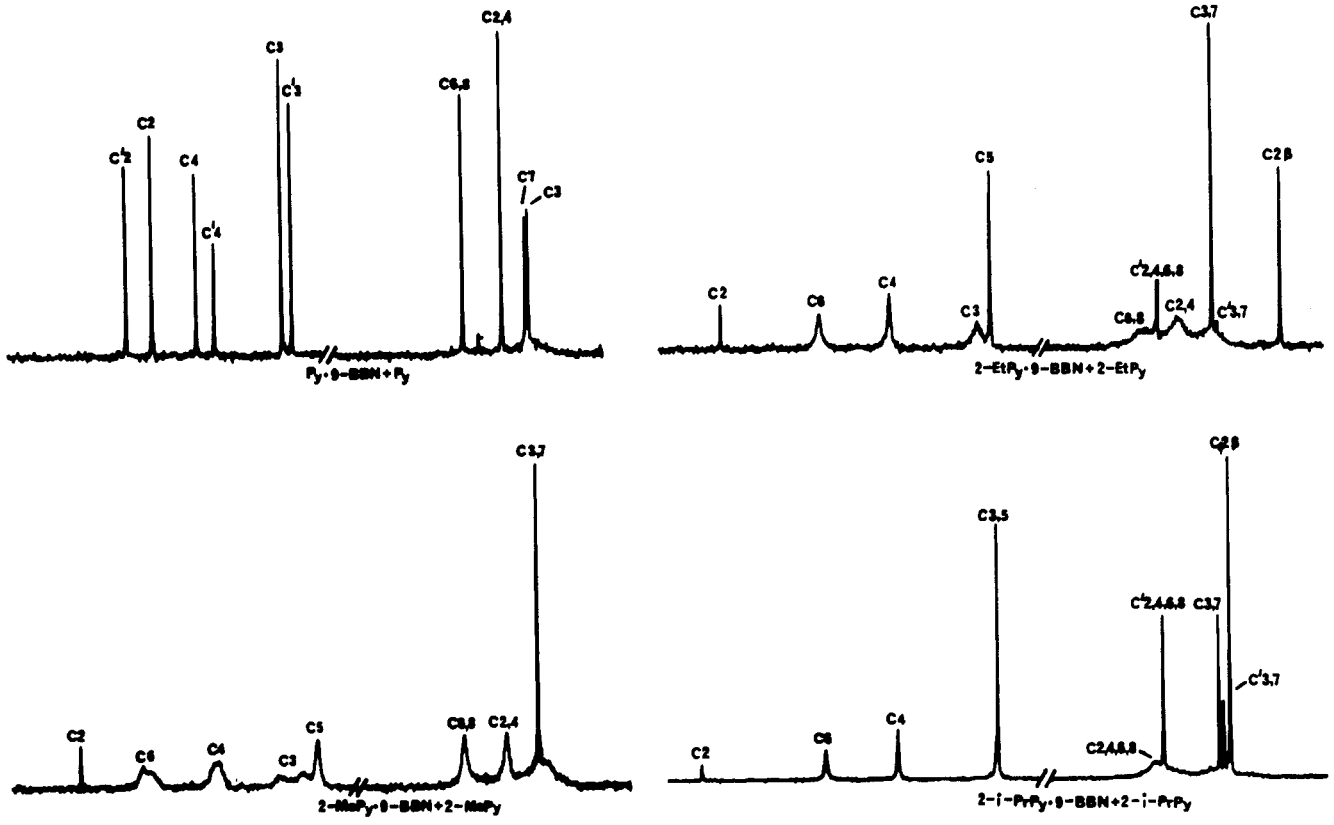


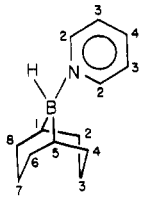
Figure 1. ^{13}C NMR spectra of solutions of 9-BBN with 100% excess pyridines in $CDCl_3$. Carbons bearing a "prime" notation refer to uncomplexed pyridine base and 9-BBN dimer.

creasing steric requirements were selected for study: (a) pyridine bases, including pyridine and 2-methyl- (2-MePy), 2-ethyl- (2-EtPy), 2-isopropyl- (2-*i*-PrPy), and 2-*tert*-butylpyridines (2-*t*-BuPy); and (b) aliphatic amines, including *n*-propylamine (*n*-$PrNH_2$), isopropylamine (*i*-$PrNH_2$), diethylamine (Et_2NH), diisopropylamine (*i*-Pr_2NH), and triethylamine (Et_3N). Quinuclidine (QN), a base with relatively low steric requirements,[5] was also selected for comparison with triethylamine.

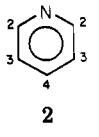
Results and Discussion

The ^{13}C NMR samples were prepared by adding 4.0 mmol of each amine (100% excess) to a 2.0-mL solution of 9-BBN dimer $(9\text{-BBN})_2$[6] (0.50 M, 1.0 mmol) in $CDCl_3$. Thus, in cases where the formation of the complex proceeds to completion, the solution contains equimolar quantitites of the complex and the free amine. After the equilibrium between $(9\text{-BBN})_2$ and the amine had been established, the proton-decoupled ^{13}C NMR spectra were recorded.

In the case of less sterically hindered amines, such as pyridine and *n*-$PrNH_2$, the ^{13}C NMR spectra for the reaction mixtures Py·9-BBN + Py and *n*-$PrNH_2$·9-BBN + *n*-$PrNH_2$ cleanly establish that there are ten different carbons in the solution (Figure 1) for each of these two amines. This can be accounted for on the basis that the rate of exchange between the amine coordinated with 9-BBN and the free amine is slower than the ^{13}C NMR time scale.[7] Therefore, in the solution of Py·9-BBN + Py, three different carbon atoms are observed for the pyridine coordinated with 9-BBN (1) and three for the free pyridine (2).



1



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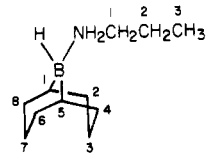
In addition, there are four different carbon atoms (C-2,4, C-6,8, C-3, C-7) (1) on the cyclooctyl ring of 9-BBN. Signals for C-1 and C-5 are too broad to be seen due to the quadrupole effect of the adjacent boron atom. Consequently, the spectrum reveals ten distinct peaks for ten different carbon atoms.

If there were a rapid exchange between the Py·9-BBN and the free pyridine base, only five distinct peaks for five types of carbon atoms would be observed, three from the averaged pyridine carbon atoms and two from the cyclooctyl ring (C-2,4,6,8 and C-3,7) of 9-BBN.

The existence of ten different carbons in the solution of *n*-$PrNH_2$·9-BBN + *n*-$PrNH_2$ can be accounted for similarly (3 and 4). Here also, rapid exchange between the



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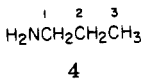

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free *n*-$PrNH_2$ and *n*-$PrNH_2$·9-BBN would simplify the observed spectrum to show only five peaks, three for the

(4) Brown, H. C.; Wang, K. K. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 117.
(5) Brown, H. C.; Sujishi, S. *J. Am. Chem. Soc.* **1948**, *70*, 2878.
(6) Brown, H. C.; Knights, E. F.; Scouten, C. G. *J. Am. Chem. Soc.* **1974**, *96*, 7765.
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averaged absorption for n-$PrNH_2$ and two for the "symmetrical" 9-BBN ring moiety.

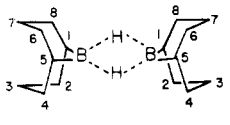
Increasing steric requirements in the pyridine base series and the aliphatic amine series result in a progressive change of the ^{13}C NMR spectra observed for the related complexes with 9-BBN. This phenomenon is closely related to the early studies of the stability of molecular addition compounds of borane, boron trifluoride, and trimethylborane with the present selected pyridine base series and the aliphatic amine series which first provided clear evidence for the importance of the steric requirements of the amine on such stability.[3] More recent studies of the extent of dissociation of molecular addition compounds of 9-BBN with these two series of amines utilizing IR spectroscopy have paralleled closely earlier results.[4]

With 2-MePy, 9% dissociation was observed at equilibrium for the addition compound, 2-MePy·9-BBN (0.13 M in cyclohexane solvent at 25 °C).[4] In the present case, the formation of the addition compound of 9-BBN with 2-MePy is essentially complete (eq 1) due to the presence

$$\underset{100\%\text{ excess}}{4(\text{2-MePy}) + (\text{9-BBN})_2} \rightarrow \underset{100\%\text{ at equilibrium}}{2(\text{2-MePy·9-BBN}) + 2(\text{2-MePy})} \quad (1)$$

of 100% excess 2-MePy and the higher concentration. ^{13}C NMR peaks of the 9-BBN dimer are completely absent from the spectrum of the 2-MePy·9-BBN + 2-MePy solution (Figure 1). However, unlike the solution of Py·9-BBN + Py, which also forms a completely associated adduct, the ^{13}C NMR spectrum of 2-MePy·9-BBN + 2-MePy exhibits very different characteristics. The ^{13}C NMR signals of the aromatic carbons on the pyridine rings are broadened, and coalescence of the 2-MePy coordinated with 9-BBN and the free 2-MePy is observed (Figure 1). C-2,4 and C-6,8 on the cyclooctyl ring of 9-BBN are also broadened, whereas C-3 and C-7 coalesce.

As the 2-alkyl group is changed from Me to Et to i-Pr, the earlier study showed that the extent of dissociation increases to 41% with 2-EtPy and to 74% with 2-i-PrPy.[4] These enhanced dissociations are reflected in the present ^{13}C NMR spectra. Two additional peaks in the solution of 2-EtPy·9-BBN + 2-EtPy and 2-i-PrPy·9-BBN + 2-i-PrPy are observed (Figure 1). These peaks appear at the precise absorptions shown by free 9-BBN dimer (C-2,4,6,8 and C-3,7) (5) in the solvent. Consequently, in the case



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of these two compounds, in contrast to the behavior of the corresponding system of 2-MePy·9-BBN + 2-MePy, there is considerable dissociation of the addition compound, even in the presence of excess 2-EtPy and 2-i-PrPy. Moreover, the spectrum establishes that any exchange of such free 9-BBN dimer with the addition compounds must be slow on the NMR time scale.

In spite of the presence of uncoordinated 9-BBN dimer, the spectra of the solutions of 2-EtPy·9-BBN + 2-EtPy and 2-i-PrPy·9-BBN + 2-i-PrPy resemble closely that of the solution of 2-MePy·9-BBN + 2-MePy. The aromatic carbons on the pyridine rings of 2-EtPy and 2-i-PrPy coordinated with 9-BBN and free 2-EtPy and 2-i-PrPy not only coalesce but also are increasingly sharpened (Figure 1). The peaks attributed to C-2,4 and C-6,8 of the cyclooctyl ring of 9-BBN are further broadened in the solution

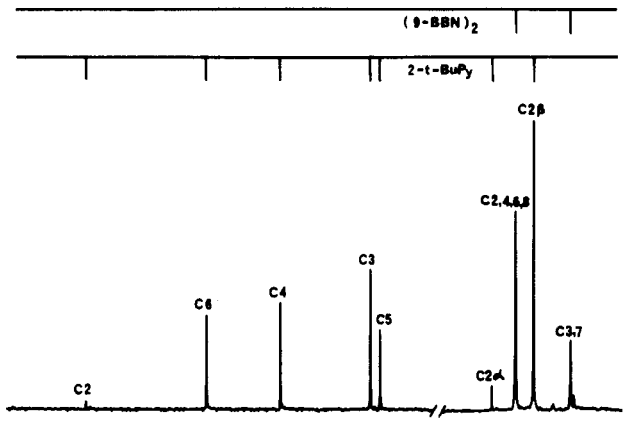

Figure 2. ^{13}C NMR spectrum for the solution of $(9\text{-BBN})_2$ + 2-t-BuPy (100% excess) for formation of complex in $CDCl_3$. Chemical shifts for isolated pure 2-t-BuPy and $(9\text{-BBN})_2$ are given at the top of the diagram.

of 2-EtPy·9-BBN + 2-EtPy and finally coalesce in the solution of 2-i-PrPy·9-BBN + 2-i-PrPy.

Finally, in the solution of 2-t-BuPy·9-BBN + 2-t-BuPy only free 2-t-BuPy and uncoordinated 9-BBN dimer are observed (Figure 2). The ^{13}C NMR chemical shifts for both 2-t-BuPy and the 9-BBN dimer in the solution appear virtually unaffected from those for the isolated components. This is also consistent with our previous observation that 2-t-BuPy (0.13 M) does not exhibit any association with 9-BBN dimer (0.065 M) in cyclohexane solvent at 25 °C.[4]

The progressive change of the ^{13}C NMR spectra of the pyridine series can be accounted for simply in terms of the increasing steric requirements for these bases from pyridine through 2-t-BuPy.[3] Pyridine forms a highly stable addition compound with 9-BBN, attributed to its relatively small steric requirements. Therefore, the rate of dissociation (eq 2) is slower than the ^{13}C NMR time scale and it exhibits no exchange phenomena.

$$\text{9-BBN·amine} \rightleftharpoons \text{9-BBN} + \text{amine} \quad (2)$$

In the solution of 2-MePy·9-BBN + 2-MePy, the presence of excess 2-MePy shifts the equilibrium toward the right side of eq 1 and the formation of addition compound is essentially complete. However, the steric strains arising from the interaction of the 2-Me substituent with the 9-BBN moiety results in a small amount of rapid dissociation of the 2-MePy·9-BBN complex (eq 2), sufficient to permit exchange with the excess amine. Therefore, only averaged ^{13}C NMR signals are observed for the 2-MePy coordinated with 9-BBN and the free 2-MePy. The unsymmetrical nature of the cyclooctyl ring of 9-BBN also starts to vanish.

The rate of exchange increases as the 2-alkyl group is changed from Me to Et to i-Pr, attributed to even larger steric strains in the latter two derivatives. Consequently, sharpened pyridine ring carbons from the averaged signals of the pyridine derivative coordinated with 9-BBN and the free amine are observed. The cyclooctyl ring carbons of 9-BBN are further broadened. In addition, the steric strains in these two cases are sufficiently large so that there occurs sufficient dissociation at equilibrium so as to be detectable, even in the presence of the excess base (eq 3).

$$2\text{amine} + (\text{9-BBN})_2 \rightleftharpoons 2(\text{amine·9-BBN}) \quad (3)$$

This results in the presence in the spectra of two additional peaks from the free 9-BBN dimer. It is consistent with this interpretation that the peaks for the 9-BBN dimer are larger in the solution of 2-i-PrPy·9-BBN + 2-i-PrPy than

in the 2-EtPy system (Figure 1).

As was pointed out earlier, the spectra of the solutions of 2-EtPy·9-BBN + 2-EtPy and 2-*i*-PrPy·9-BBN + 2-*i*-PrPy establish that the 9-BBN dimer does not undergo rapid exchange with the pyridine adducts. On the basis of our kinetic studies,[8,9] this is not unexpected. Just as the reaction of olefins with $(9\text{-BBN})_2$ proceeds through a prior dissociation to monomer, we have observed that the reaction of 2-EtPy and 2-*i*-PrPy with $(9\text{-BBN})_2$ proceeds through a similar prior dissociation of the dimer, followed by reaction of the monomer with the amine[9] (eq 4 and 5).

$$(9\text{-BBN})_2 \rightleftharpoons 2(9\text{-BBN}) \quad (4)$$

$$\text{amine} + 9\text{-BBN} \rightarrow \text{amine·9-BBN} \quad (5)$$

The rate of dissociation of 9-BBN dimer (eq 4) is far slower than the ^{13}C NMR time scale measured here.

It was previously pointed out that the steric requirements of 2-EtPy and 2-*i*-PrPy are only modestly larger than those for 2-MePy.[10] The 2-Et and 2-*i*-Pr groups can rotate in such a way as to reduce their steric interactions with the group adding to the nitrogen atom. However, the 2-*t*-Bu group is spherically symmetrical. It cannot reduce the steric interactions by mere rotation. Consequently, it exhibits far larger steric effects than do the corresponding 2-Et and 2-*i*-Pr derivatives.[10] This large steric interaction is again observed in the present study. The ^{13}C NMR spectrum for the solution of 2-*t*-BuPy·9-BBN + 2-*t*-BuPy exhibits only free 9-BBN dimer and free 2-*t*-BuPy (Figure 2). Presumably, the steric strain is now so large that essentially no complexation occurs.[4]

In the series of aliphatic amines, similar progressive changes in the ^{13}C NMR spectra are observed. *i*-$PrNH_2$ is a base of considerably larger steric requirements than *n*-$PrNH_2$.[11] However, in the present case we observe similar behavior for both *n*-$PrNH_2$·9-BBN + *n*-$PrNH_2$ and *i*-$PrNH_2$·9-BBN + *i*-$PrNH_2$. The latter solution exhibits both fully coordinated 9-BBN adduct and the free amine. The two halves of the cyclooctyl ring of 9-BBN are different. Consequently, there is no NMR evidence for exchange. Presumably, the steric strains in the *i*-$PrNH_2$·9-BBN complex are not large enough to cause significant dissociation.

In the case of Et_2NH, complete association was previously observed for the addition compound Et_2NH·9-BBN (0.13 M in cyclohexane solvent at 25 °C).[4] In the present case, the formation of the addition compound of 9-BBN with Et_2NH is also essentially complete. ^{13}C NMR peaks for the 9-BBN dimer are completely absent. Moreover, the two halves of the cyclooctane ring system are distinct and there is no evidence for exchange in the system. On the other hand, exchange phenomena are observed in the solution of *i*-Pr_2NH·9-BBN + *i*-Pr_2NH. In addition, the spectrum reveals two additional peaks attributed to the presence of uncoordinated 9-BBN dimer, as in the case of 2-EtPy and 2-*i*-PrPy. Clearly, the large steric strain in the *i*-Pr_2NH·9-BBN complex results in a faster rate of dissociation, even with excess amine present.[4]

It would have been interesting to observe a case in the aliphatic system comparable to the behavior of the 2-MePy·9-BBN + 2-MePy system, namely, 100% association with rapid exchange. Presumably, such behavior would be achieved by an amine with steric requirements lying between those for Et_2NH and *i*-Pr_2NH. A possible candidate would be Et-*i*-PrNH. However, we did not test this possibility.

Table I. Summary of ^{13}C NMR Observations on the Interaction of 9-Borabicyclo[3.3.1]nonane with Representative Amines

100% associated, no exchange	100% associated, rapid exchange	partially associated, rapid exchange	not associated
Py	2-MePy	2-EtPy 2-*i*-PrPy	2-*t*-BuPy
n-$PrNH_2$ *i*-$PrNH_2$ Et_2NH QN		*i*-Pr_2NH	Et_3N

Finally, with the large steric requirements of Et_3N,[12] only free 9-BBN dimer and free Et_3N are observed in the solution. Presumably, like 2-*t*-BuPy, the steric strains are too large to permit detectable complexation.[4]

It was earlier pointed out that the instability of the addition compound of Et_3N with trimethylborane (Me_3B) must be the result of very large steric requirements of the Et_3N molecule,[5] with the three groups competing for the space required by the Me_3B moiety. By tying the three ethyl groups back to a common carbon atom in the cage structure of quinuclidine, the stability of the Me_3B adduct is greatly increased.[5] The same phenomenon is observed here, with the QN·9-BBN complex exhibiting the same spectroscopic characteristics of the stable Py·9-BBN and *n*-$PrNH_2$·9-BBN adducts. QN·9-BBN is a stable complex which shows no NMR evidence for any exchange with the excess amine. Thus, the simple change in structure from Et_3N to QN, reducing the steric requirements, brings about a major change in the nature of the interaction with 9-BBN, clearly revealed by the ^{13}C NMR spectra.

Conclusion

The present study of the interaction of 9-borabicyclo[3.3.1]nonane with the two families of amines reveals four types of behavior: (a) formation of stable complexes with no observable exchange with excess amine (Py, *n*-$PrNH_2$, *i*-$PrNH_2$, Et_2NH, QN); (b) formation of stable complexes with rapid exchange of amine (2-MePy); (c) formation of partially dissociated complexes with rapid exchange (2-EtPy, 2-*i*-PrPy, *i*-Pr_2NH); and (d) no detectable interaction of the 9-BBN with the amine (2-*t*-BuPy, Et_3N). These results are summarized in Table I.

It is evident that in both families there is observed with increasing steric requirements of the amine a regular progression from (a) to (b) to (c) to (d).

These results confirm the earlier studies of the stabilities of these addition compounds by the IR spectroscopic method previously utilized to establish the degree of association.[4] However, they provide considerable additional information about the exchange or lack of exchange in addition compounds that are completely associated under the experimental conditions. Consequently, the ^{13}C NMR method separates these compounds into two separate classes, (a) and (b), providing a more sensitive probe into the effects of steric strains, even in systems whose association is essentially complete.

Although we did not explore temperature effects in the present study, it is evident that such studies would permit the determination of the coalescence temperature and

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(11) Brown, H. C.; Barbaras, G. K. *J. Am. Chem. Soc.* **1953**, *75*, 6.
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Table II. ^{13}C NMR Chemical Shift Data (ppm) for the Complexation of Representative Pyridine Bases with 9-BBN

amine[e]		9-BBN[a] C-2,4,6,8	9-BBN[a] C-3,7	complexed or free amine[b]	amine C-2	amine C-3	amine C-4	amine C-5	amine C-6	amine C-2α	amine C-2β
pyridine	syn	29.0	24.9	CA	145.7	125.3	138.8				
	anti	35.1	25.3	FA	149.8	123.7	135.9				
				IA	149.8	123.6	135.7				
2-MePy	syn	29.6	24.6	CA }	158.4	127.4	137.3	121.3	147.9	c	
	anti	36.3		FA }							
				IA	158.6	123.0	135.9	120.6	149.4	24.3	
2-EtPy	syn	30.3	24.6	CA }	163.6	123.3	137.1	121.2	148.1	c	13.9
	anti	34.9		FA }							
	$(9\text{-BBN})_2$[d]	33.3	23.8	IA	163.4	121.8	136.1	120.7	149.1	31.4	13.8
2-*i*-PrPy	syn } anti }	34.9	24.5	CA } FA }	167.7	121.2	136.9	121.2	148.2	c	22.8
	$(9\text{-BBN})_2$	33.3	23.8	IA	167.4	121.0	136.3	120.6	149.1	36.4	22.6
2-*t*-BuPy	syn			CA							
	anti			FA	169.4	120.5	135.9	118.9	148.6	37.4	30.2
	$(9\text{-BBN})_2$	33.3	23.9	IA	169.4	120.5	136.0	119.0	148.6	37.4	30.2

[a] See ref 2 for the assignments of the peaks. [b] The complexed amine, the free amine, and the isolated amine without the presence of 9-BBN are abbreviated CA, FA, and IA, respectively. CA and FA in braces when rapid exchange occurs. [c] Too broad to be seen. [d] The isolated $(9\text{-BBN})_2$ exhibits chemical shifts at 33.4 ppm for C-2,4,6,8 and at 23.9 ppm for C-3,7. [e] Amine in amine·9-BBN or amine + 9-BBN.

Table III. ^{13}C NMR Chemical Shift Data (ppm) for the Complexation of Representative Aliphatic Amines with 9-BBN

amine[e]		9-BBN[a] C-2,4,6,8	9-BBN[a] C-3,7	complexed or free amine[b]	amine C-1	amine C-2	amine C-3
n-$PrNH_2$	syn	30.2	24.8	CA	45.7	23.3	11.3
	anti	34.5	25.9	FA	44.2	27.0	11.3
				IA	44.3	27.0	11.3
i-$PrNH_2$	syn	30.3	24.8	CA	46.0	23.0	
	anti	34.5	25.8	FA	42.9	26.1	
				IA	42.8	26.2	
Et_2NH	syn	30.4	24.8	CA	41.3	11.1	
	anti	34.8	25.7	FA	44.0	15.4	
				IA	44.1	15.4	
i-Pr_2NH	syn	30.3	25.2	CA }	45.7	22.6	
	anti	34.9		FA }			
	$(9\text{-BBN})_2$[d]	33.4	23.9	IA	45.4	23.5	
Et_3N	syn			CA			
	anti	33.4	24.0	FA	46.6	11.9	
	$(9\text{-BBN})_2$[d]	33.4	23.9	IA	46.7	12.0	
QN	syn	30.2	24.4	CA	51.3	25.1	20.6
	anti	38.1	26.0	FA	47.9	26.7	20.8
				IA	47.9	26.9	20.9

[a-e] See Table II for footnotes.

would greatly expand the utility of ^{13}C NMR spectroscopy in exploring the behavior of such addition compounds.

Expermental Section

Materials. All amines except QN were distilled from calcium hydride prior to use. QN, chloroform-*d*, and the crystalline 9-BBN dimer obtained from Aldrich were used directly.

Methods. A typical example for obtaining the ^{13}C NMR spectrum is as follows: a 10-mm NMR tube was dried in an oven (140 °C, 4 h), capped with a rubber septum, and cooled to room temperature under a stream of dry nitrogen. A 2.0-mL aliquot of a 0.50 M solution of $(9\text{-BBN})_2$ in $CDCl_3$ (2.0 mmol of 9-BBN) was added to the tube via a syringe,[13] followed by 0.32 mL of pyridine (4.0 mmol). Tetramethylsilane (0.30 mL) was then injected into the tube as an internal reference.

The complete disappearance of 9-BBN dimer or the establishment of the equilibrium with a more hindered amine was determined from the ^{11}B NMR spectra obtained with a Varian FT-80A spectrometer. The proton-decoupled ^{13}C NMR spectrum at the probe temperature was then recorded on the same Varian FT-80A spectrometer equipped with a broad-band probe.[14] The probe temperature was closely monitored and kept constant throughout the entire study. A sweep width of 5000 Hz and 8000 data points were used. Pulses of 8-μs width were applied at about 1-s intervals. At the concentrations used, 1000–2000 pulses resulted in satisfactory signal intensity.

The ^{13}C NMR chemical shifts of all systems studied are summarized in Tables II and III. The ^{13}C NMR chemical shifts of C-2,6 in the pyridine derivatives are usually displaced to higher fields in the complexes. The ^{13}C NMR signals for all other carbon atoms in these pyridine rings are usually displaced to lower fields. This is similar to that observed in the case of the pyridinium ion.[15] However, in contrast, the ^{13}C NMR chemical shifts at the α carbon (C-1) of aliphatic amines are usually displaced to lower fields. All other carbons are displaced to higher fields. This behavior is analogous to that observed in the case of the boron trihalide complexes with ethers.[16]

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research. We also thank Drs. J. B. Grutzner and J. A. Soderquist for helpful discussions regarding this work.

Registry No. 1, 64045-95-0; 2, 110-86-1; 3, 70338-02-2; 4, 107-10-8; 9-BBN·*i*-PrNH$_2$, 70338-03-3; 9-BBN·Et$_2$NH, 70338-05-5; 9-BBN·QN, 73178-72-0; 9-BBN·2-EtPy, 70338-11-3; 9-BBN·2-*i*-PrPy, 70338-12-4; 9-BBN·*i*-Pr$_2$NH, 70338-06-6; 9-BBN·2-MePy, 70338-10-2; *i*-PrNH$_2$, 75-31-0; Et$_2$NH, 109-89-7; QN, 91-22-5; 2-MePy, 109-06-8; 2-EtPy, 100-71-0; 2-*i*-PrPy, 644-98-4; *i*-Pr$_2$NH, 108-18-9; 2-*t*-BuPy, 5944-41-2; Et$_3$N, 121-44-8; (9-BBN)$_2$, 70658-61-6.

Mechanistic Aspects of Gas-Phase Photodecarbonylation Reactions of Bicyclo[3.1.0]hexanones[1]

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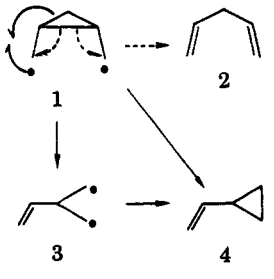
The gas-phase photodecarbonylation and photofragmentation reactions of substituted bicyclo[3.1.0]hexan-3-ones have been studied in detail. Photolysis of these ketones yields 1,3-dienes, vinylcyclopropanes, and 1,4-dienes as detectable products. The possible mechanisms for these reactions are discussed in light of the regiochemical and stereochemical results obtained. In addition, methyl substitution at C-6 and C-2 of these ketones has been shown to have a pronounced effect on both product ratios and overall reaction efficiency. These effects are discussed in terms of stereoelectronic and electronic controls of rates of cyclopropane ring opening of intermediate acylcyclopropylcarbinyl diradicals.

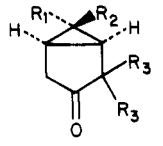
Introduction

Cyclopropyldicarbinyl diradicals (1) have been invoked



and discussed as short-lived intermediates in transformations of ground[4] and excited[5] states of polycyclic azoalkanes as well as in the familiar di-π-methane rearrangements of singlet and triplet excited 1,4-dienes.[6] These studies have demonstrated that this diradical species can participate in one of two characteristic reaction pathways, Grob fragmentation producing 1,4-dienes (1 → 2)[7] and di-π-methane-type reactivity resulting in generation of vinylcyclopropanes through a one- (1 → 4) or two-step (1 → 3 → 4) process. Similar types of diradical species having oxygen in place of a carbinyl center have been discussed as reactive intermediates in oxa-di-π-methane rearrangements.[8]

Several years ago Hess and Pitts[9] noted that the major gas-phase photodecarbonylation reactions of bicyclo[3.1.0]hexanone (5) generating 1,4-pentadiene and vinylcyclopropane could be rationalized by invoking the intermediacy of the parent cyclopropyldicarbinyl diradical (1). Although this mechanistic postulate remains speculative, it suggests that the gas-phase photochemistry of bicyclo[3.1.0]hexan-3-ones could potentially serve as a particularly useful method for generation of these diradicals. Our interest in this feature was stimulated by earlier studies[10] which suggested that the stereochemical and regiochemical outcomes of nonconcerted di-π-methane rearrangements might be controlled by factors influencing the pathways chosen for conversion of 1 to vinylcyclopropanes. As a result, we have embarked on an exploratory effort designed to gain information about both the mechanism for photodecarbonylation of bicyclo[3.1.0]hexanones and perhaps the nature of pathways converting cyclopropyldicarbinyl and related diradicals to 1,4-dienes and vinylcyclopropanes. Specifically, we have prepared and



5, R_1 = H; R_2 = H; R_3 = H
6en, R_1 = H; R_2 = CH_3; R_3 = H
6ex, R_1 = CH_3; R_2 = H; R_3 = H
7, R_1 = CH_3; R_2 = CH_3; R_3 = H
8, R_1 = H; R_2 = H; R_3 = CH_3

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