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Molecular Orbital Study of Cyanide Complexes of BX_3 and AlX_3 (X = H, CH_3, F, and Cl)

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Abstract: Ab initio molecular orbital calculations are employed to study the binding preferences of $C{\equiv}N^-$ for BX_3 and AlX_3 (X = H, CH_3, Cl, and F). Electronegative substituents are shown to favor binding through nitrogen. The unimolecular rearrangement of $CNBH_3^-$ to $NCBH_3^-$ is studied. The calculated transition state is very similar to that obtained previously for the $CNCH_3 \rightarrow NCCH_3$ system (ref 13), while the barrier to interconversion is significantly smaller.

The cyanotrihydroborate ion, $NCBH_3^-$, was first synthesized as the lithium salt by Wittig and Raff in 1951.[1] Later, the sodium salt was prepared by the reaction of sodium borohydride and HCN in THF.[2] In addition to being a useful synthetic reagent,[3] this ion is of interest because it is isoelectronic to the well-known methyl isocyanide–methyl cyanide system. In fact, both isocyano- and cyanotrihydroborate ions have been characterized, and an isocyano–cyano rearrangement has been observed:[2]

$$CNBH_3^- \rightarrow NCBH_3^- \qquad (1)$$

This rearrangement occurs in THF at 60 °C in the presence of HCN. The formal similarity of the above reaction to the very well studied methyl isocyanide rearrangement has led us to investigate the energetics of cyanide and isocyanide binding to BH_3 and other related molecules by ab initio SCF and SCF–CI techniques. Specifically, we present here an ab initio SCF–CI study of the ΔE and unimolecular activation energy for reaction 1. In addition, we present calculated ΔE's at the SCF level for the analogous isomerizations of isocyanide complexes of several different derivatives of the cyanotrihydroborate ion, in order to investigate the substituent effects on the isomerization energy produced by various isoelectronic substitutions. Similar calculations are presented for the isoelectronic system obtained by substituting aluminum for boron. Our results will be compared in detail to previous ab initio studies on the hydrogen isocyanide and methyl isocyanide systems.

In order to facilitate comparisons to CNH and $CNCH_3$, we will first briefly discuss the relevant experimental and theoretical work on these systems. Using a polarized double-ζ basis set and ab initio molecular orbital theory, Schaefer and co-workers[4] have calculated ΔE for the reaction:

$$HNC \rightarrow HCN \qquad (2)$$

They found a ΔE of −9.5 kcal/mol at the SCF level and −14.6 kcal/mol including correlation corrections via a full single–double CI treatment. In addition, they showed that the barrier to interconversion of the two isomers is 40.2 kcal/mol (SCF), or 34.9 kcal/mol (SCF-CI), and that the transition state lies closer to the product (HCN) than the reactant (HNC), in violation of Hammond's postulate, which states that the transition state should resemble the reactant geometry if the reaction is exothermic. More recently, Redmon, Purvis, and Bartlett[5] studied the ΔE for reaction 1 with very large basis set ab initio calculations and extensive treatment of correlation energy via many-body perturbation theory. They find a ΔE of −15 kcal/mol, in good agreement with Schaefer et al.[4] Both values are significantly different than a recent experimental determination of ca.−10 kcal/mol.[6]

The alkali metal cyanides have also been studied in some detail, although direct comparison to the boron and aluminum systems dealt with here is difficult because of the presumed highly ionic character of the alkali metal–cyanide interaction. A number of studies on the lithium cyanide system have been published, the most recent of which includes a study of correlation effects.[5] Binding through nitrogen in this system is energetically favored by ~4 kcal/mol. Recent spectroscopic evidence[7] suggests that NaCN and KCN are T-shaped molecules, rather than the linear structures assumed by HCN and LiNC.

A recent experimental determination[8] of the enthalpy of isomerization of methyl isocyanide yielded −23.7 kcal/mol. This value compares remarkably well with a calculated result[9] of −24.1

(1) Wittig, G.; Raff, P. *Z. Naturforsch.*, B., **1951**, *6*, 225.
(2) Wade, R. C.; Sullivan, E. A.; Berschied, J. R.; Purcell, K. F. *J. Am. Chem. Soc.* **1970**, *92*, 2146.
(3) Borch, R. F.; Durst, H. D. *J. Am. Chem. Soc.* **1969**, *91*, 3996.
(4) Pearson, P. K.; Schaefer, H. F.; Wahlgren, V. *J. Chem. Phys.* **1975**, *62*, 350.
(5) Redmon, L. T.; Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1980**, *72*, 986.
(6) Blackman, G. L.; Brown, R. D.; Godfrey, P. D.; Gunn, H. I. *Chem. Phys. Lett.* **1975**, *34*, 241. Also see footnote 19 of ref 5.
(7) Törring, T.; Bekoog, J. P.; Meerts, W. L.; Hoeft, J.; Tiemann, F.; Dymanus, A. *J. Chem. Phys.* **1980**, *73*, 4875.
(8) Baghal-Vayjooee, M. H.; Collister, J. L.; Pritchard, H. O. *Can. J. Chem.* **1977**, *55*, 2634.
(9) Moffat, J. B. *Chem. Phys. Lett.* **1978**, *55*, 125.

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Table I. Optimized Geometries[a]

molecule	basis	CN	NB(Al)	CB(Al)	C-B(Al)-X
$CNBH_3^-$	3G	1.164	1.562		108.2
	4-31G	1.161	1.542		108.5
$NCBH_3^-$	3G	1.157		1.610	108.3
	4-31G	1.154		1.613	108.7
$CNB(CH_3)_3^-$	3G	1.164[b]	1.592		106.4
$NCB(CH_3)_3^-$	3G	1.157[b]		1.643	106.8
$CNBCl_3^-$	3G	1.168	1.552		107.3
$NCBCl_3^-$	3G	1.156		1.626	107.3
$CNBF_3^-$	3G	1.165	1.677		105.9
$NCBF_3^-$	3G	1.156		1.771	106.3
$CNAlH_3^-$	3G	1.166	1.855		106.8
$NCAlH_3^-$	3G	1.156		1.954	107.0
$CNAl(CH_3)_3^-$	3G	1.166[b]	1.843		107.1
$NCAl(CH_3)_3^-$	3G	1.156[b]		1.947	107.4
$CNAlCl_3^-$	3G	1.166[b]	1.786		109.1
$NCAlCl_3^-$	3G	1.156[b]		1.900	109.3
$CNAlF_3^-$	3G	1.166[b]	1.840		107.8
$NCAlF_3^-$	3G	1.156[b]		1.953	108.3

[a] Angstroms and degrees. [b] Not optimized.

kcal/mol at the STO-3G level. Earlier,[10] Schaefer's group obtained a value of −17.4 kcal/mol, using a double-ζ basis. A polarized double-ζ basis set yields −19.2 kcal/mol,[11] and extensive treatment of correlation energy differences by many-body perturbation theory resulted[11] in a correlation correction of −3.5 kcal/mol and a predicted ΔE of −22.7 kcal/mol. Thus, the excellent agreement of the STO-3G results[9] and experiment[8] is in part fortuitous, but the qualitative results are similar at all levels of ab initio theory.

Little theoretical work has appeared on substituted systems; however, Moffat[9] has calculated ΔE for the rearrangement of $CNCF_3$ at the STO-3G level and finds a value of −11.5 kcal/mol, a full 12.6 kcal/mol higher than was found for $CNCH_3$ with the same basis.

The transition state for the methyl isocyanide rearrangement has also been well studied. The experimental activation energy is 38.4 kcal/mol.[12] Theoretical values are 87.8 kcal/mol[9] (STO-3G), 60.4 kcal/mol[10] (double-ζ), and 45.4 kcal/mol[13] (polarized double-ζ). The elegant vibrational analysis of Schaefer et al.[13] yields a zero-point correction of −1.8 kcal/mol, and by combining this with an earlier correlation correction of −2.8 kcal/mol,[11] a theoretical estimate of 40.8 kcal/mol is obtained, in excellent agreement with the experimental value. The theoretical values for this system also support a transition-state geometry which lies closer to the product than the reactant, again violating Hammond's postulate.

In summary then, calculated ΔE's for isomerization of CNH and $CNCH_3$ are moderately insensitive to basis set variations, but accurate calculation of the relative transition-state energy requires a moderately large basis set, including polarization functions. Correlation corrections to both the isomerization energy and the barrier appear to be small (3–5 kcal/mol), as are vibrational effects on the barrier.

In this paper, we present a theoretical study of the $CNBH_3^-$–$NCBH_3^-$ rearrangement. We show that, in agreement with the earlier work on CNH and $CNCH_3$, the transition state lies closer to the products than the reactants. We have calculate 4-31G optimized geometries for several points along the reaction surface including the transition state. Using the STO 4-31G geometries, we have also calculated energies for the reactant, transition state, and product with a Slater orbital basis set of approximately polarized double-ζ quality with limited configuration interaction. Our best estimate for the isomerization energy is −17 kcal/mol,

Table II. Isomerization Energies

molecule	basis	ΔE[a]	molecule	basis	ΔE[a]
$CNBH_3^-$	3G	−11.4	$CNBCl_3^-$	3G	−6.9
	4-31G	−11.6	$CNBF_3^-$	3G	−0.6
$CNB(CH_3)H_2^-$	3G	−9.8		4-31G	−1.2
	4-31G	−9.3	$CNAlH_3^-$	3G	−2.7
$CNB(CH_3)_2H^-$	3G	−8.2	$CNAl(CH_3)_3^-$	3G	−1.7
	4-31G	−7.2	$CNAlCl_3^-$	3G	−1.3
$CNB(CH_3)_3^-$	3G	−6.9	$CNAlF_3^-$	3G	−0.1

[a] kcal/mol.

Table III. Standard Bond Lengths

bond	length, Å	bond	length, Å
C≡N	1.160	C–Al	1.954
C–B	1.691	N–Al	1.848
N–B	1.620		

Table IV. Isomerization Energies Using Standard Geometries[a]

molecule	ΔE, kcal/mol	molecule	ΔE, kcal/mol
$NCBH_3^-$	−10.7	$NCAlH_3^-$	−2.7
$NCB(CH_3)_3^-$	−6.6	$NCAl(CH_3)_3^-$	−1.8
$NCBCl_3^-$	−7.3	$NCAlCl_3^-$	−1.7
$NCBF_3^-$	−0.1	$NCAlF_3^-$	−0.1

[a] STO-3G basis.

while the activation energy is estimated to be 29 kcal/mol. We have also computed ΔEs for the isomerization of $CNB(CH_3)_3^-$, $CNB(CH_3)H_2^-$, $CNB(CH_3)_2H^-$, $CNBF_3^-$, $CNBCl_3^-$, $CNAlH_3^-$, $CNAl(CH_3)_3^-$, $CNAlF_3^-$, and $CNAlCl_3^-$ using STO-3G basis sets with geometry optimization and single point STO 4-31G calculations for some of the above species. We show that substitution of F for H in $CNBH_3^-$ raises the calculated isomerization energy by ~12 kcal/mol, in complete accord with earlier results for $CNCF_3$.[6] Substitution of CH_3 or Cl for H has a similar, but smaller effect, and qualitatively similar effects are seen for the corresponding aluminum systems.

Calculations

Both isomers of the cyanotrihydroborate ion were completely optimized at the STO-3G and STO 4-31G level,[14] except for the B–H distance which was held constant at 1.19 Å. Similar optimizations were performed at the STO-3G level only for all other molecules studied here. Assumed distances which were not optimized include B–F = 1.32 Å, B–Cl = 1.72 Å, $B-C_{Me}$ = 1.60 Å, Al–H = 1.65 Å, Al–F = 1.63 Å, Al–Cl = 2.14 Å, $Al-C_{Me}$ = 2.06 Å, and C_{Me}–H = 1.09 Å. All other parameters were fully optimized except as noted in Table I. For $CNBH_3^-$, $CNBF_3^-$, $CNB(CH_3)H_2^-$, and $CNB(CH_3)_2H^-$, single point STO 4-31G calculations were carried out at the STO-3G optimized geometries (the mono- and dimethyl derivatives were constructed from the optimized STO-3G parameters by replacing one or two methyl groups with hydrogen and leaving all bond angles unaltered). STO 4-31G calculations on the trimethyl and trichloro derivatives were not performed because of program limitations. The excellent agreement between the 3G and 4-31G values for the isomerization energy (Table II) provide a strong indication that the STO-3G basis set is adequate for at least a qualitative description of the substituent effects in this system. This is somewhat surprising, since in general minimal basis sets are *not* adequate for anions; however, a population analysis indicates that the negative charge is highly delocalized, with no atom being more negative than −0.40 e, and a delocalized charge distribution may not require diffuse function for a reasonably accurate description. In order to test the effects of geometry variations on the calculated isomerization energies a set of standard bond lengths and angles was obtained by averaging all chemically similar parameters (Table III). The

(10) Liskow, D. H.; Bender, C. F.; Schaefer, H. F. *J. Am. Chem. Soc.* **1972**, *94*, 5178.
(11) Redmon, L. T.; Purvis, G. D.; Barlett, R. J. *J. Chem. Phys.* **1978**, *69*, 5386.
(12) Bunker, D. L.; Hase, W. L. *J. Chem. Phys.* **1973**, *59*, 4621.
(13) Saxe, P.; Yamaguchi, Y.; Pulay, P.; Schaefer, H. F. *J. Am. Chem. Soc.* **1980**, *102*, 3718.
(14) Hehre, W. J.; Latham, W. A.; Ditchfield, R.; Newton, M. D.; Pople, J. A., Quantum Chemistry Program Exchange, Indiana University, GAUSSIANN 70, No. 236.

Table V. Total Energies[a,b]

molecule	basis	energy	molecule	basis	energy
$NCBH_3^-$	3G	−117.1771	$NCBCl_3^-$	3G	−1479.3480
$NCBH_3^-$	4-31G	−118.5853	$CNBCl_3^-$	3G	−1479.3369
$CNBH_3^-$	3G	−117.1590	$NCBF_3^-$	3G	−409.6949
$CNBH_3^-$	4-31G	−118.5668	$NCBF_3^-$	4-31G	−415.0240
$NCB(CH_3)_3^-$	3G	−232.9144	$CNBF_3^-$	3G	−409.6940
$CNB(CH_3)_3^-$	3G	−232.9034	$CNBF_3^-$	4-31G	−415.0221
$NCB(CH_3)H_2^-$	3G	−155.7564	$NCAlH_3^-$	3G	−331.7883
$NCB(CH_3)H_2^-$	4-31G	−157.5635	$CNAlH_3^-$	3G	−331.7840
$CNB(CH_3)H_2^-$	3G	−155.7408	$NCAl(CH_3)_3^-$	3G	−447.6089
$CNB(CH_3)H_2^-$	4-31G	−157.5487	$CNAl(CH_3)_3^-$	3G	−447.6062
$NCB(CH_3)_2H^-$	3G	−194.3359	$NCAlCl_3^-$	3G	−1694.2073
$NCB(CH_3)_2H^-$	4-31G	−196.5427	$CNAlCl_3^-$	3G	−1694.2053
$CNB(CH_3)_2H^-$	3G	−194.3228	$NCAlF_3^-$	3G	−624.3496
$CNB(CH_3)_2H^-$	4-31G	−196.5313	$CNAlF_3^-$	3G	−624.3495

[a] Atomic units. [b] Optimized geometries.

Table VI. Slater Orbital Basis Sets

	S1	S2		S1	S2
B 1s	4.67934	7.33800	B 2p	2.21734	4.55800
1s′		3.99600	2p′	1.00551	1.75300
2s	1.41314	1.72400	2p″		0.93100
2s′	0.87564	1.11000	3d	1.49000	1.49000
3s		4.79600			
C 1s	5.67263	9.05500	C 2p	2.73045	4.79600
1s′		5.02500	2p′	1.25656	1.98900
2s	1.83068	1.40600	2p″		1.12200
2s′	1.15282	1.91000	3d	1.72000	1.72000
3s		6.06700			
N 1s	6.66507	10.55800	N 2p	3.24933	5.57300
1s′		6.03700	2p′	1.49924	2.55500
2s	2.26086	2.53900	2p″		1.35200
2s′	1.42457	1.58800	3d	1.91000	1.91000
3s		7.33400			
H 1s	1.44900	1.44900	H 2s	1.02050	1.02050

calculated isomerization energies at the STO-3G level (Table IV) are in excellent agreement with the corresponding values in Table II, even though the optimized bond distances, particularly the B–C, B–N, Al–C, and Al–N distances, vary considerably with the substituent. Total energies for all STO-3G and 4-31G calculations are given in Table V.

In order to further test the effects of basis set on the calculated isomerization energies, larger basis set calculations were carried out on the cyanotrihydroborate ion with the STO 4-31G optimized geometries. The first basis set, denoted S1, is essentially a double-ζ basis with a minimum basis description of inner shells and a set of polarization functions (3d's) on carbon, boron, and nitrogen. Exponents for the s and p functions were taken from Clementi and Roetti,[15] while the d orbital exponents were obtained from optimized values for smaller molecules.[16] This basis set yielded an isomerization energy of −7.0 kcal/mol, slightly smaller than STO-3G or 4-31G results. A partial CI (denoted CI1) correction including all single and double excitations into the virtual orbitals which would be present in a minimum basis set calculation yielded a value of −10.3 kcal/mol. Finally, a large basis set (S2), which is essentially polarized triple-ζ on boron, carbon, and nitrogen[16] and double-ζ on hydrogen, yielded an isomerization energy of −11.7 kcal/mol at the SCF level and -17.1 kcal/mol with CI corrections to the SCF energy. The latter CI (denoted CI2) consisted of all excitations defined by a "first-order" CI[17] but without pseudo-natural-orbital iterations and included 2978 determinates in C_{3v} symmetry. The Slater orbital basis sets are given in Table VI.

(15) Clementi, E.; Roetti, C. *At. Data Nucl. Data Tables* **1974**, *14*, 3, 4.
(16) Hall, J. H.; Marynick, D. S.; Lipscomb, W. N. *Inorg. Chem.* **1972**, *11*, 3126. Marynick, D. S.; Dixon, D. A. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 410. Stevens, R. M. *J. Chem. Phys.* **1971**, *55*, 1725.
(17) Schaefer, H. F.; Klemm, R. A.; Harris, F. E. *Phys. Rev.* **1969**, *181*, 137.

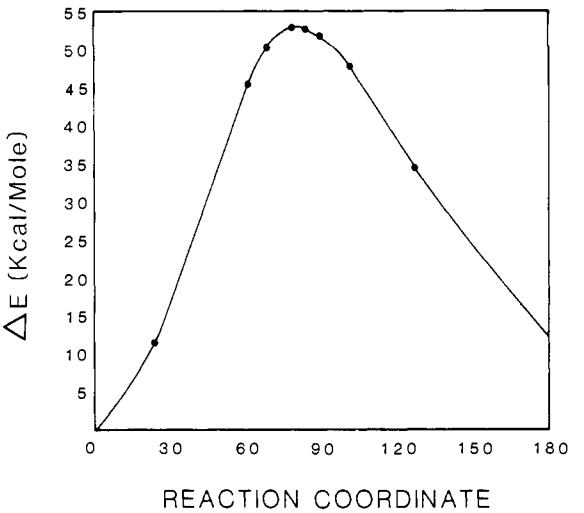

Figure 1. Potential surface at the 4-31G level for the rearrangement of $CNBH_3^-$ (see text).

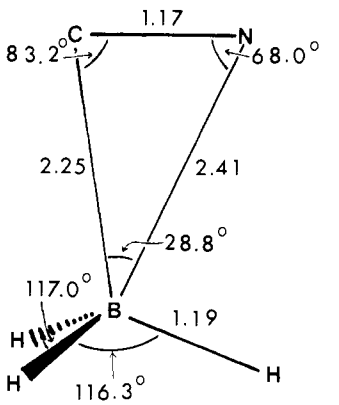

Figure 2. Optimized geometrical parameters for the $CNBH_3^- \rightarrow NCBH_3^-$ transition state at the 4-31G level.

For the cyanotrihydroborate ion a potential surface for the isomerization reaction was calculated at the 4-31G level by the following procedure. Following earlier work[10] on methyl cyanide, the reaction coordinate was taken as the angle between the cyanide carbon, the center of mass of the cyanide group, and the boron. C_s symmetry was assumed to be preserved along the reaction path, since Schaefer et al.[13] find that the methyl cyanide system has a transition state of this symmetry. Within these constraints, all geometrical parameters were optimized, except the B–H bond distance. The transition state was then taken as highest energy point along the reaction coordinate, which was estimated by a quadratic fit to the nearest three points. Two different structures are consistent with the above geometrical constraints, corre-

Table VII. Isomerization Energies for $CNBH_3^-$ Using Slater Basis Sets

basis/calculation	ΔE^a	basis/calculation	ΔE^a
S1/SCF	−7.0	S2/SCF	−11.7
S1/SCF-CI1	−10.3	S2/SCF-CI2	−17.1

[a] kcal/mol.

Table VIII. Overlap Populations[a]

$CNBH_3^-$	0.272	$CNAlH_3^-$	0.191
$CNB(CH_3)_3^-$	0.272	$CNAl(CH_3)_3^-$	0.195
$CNBCl_3^-$	0.303	$CNAlCl_3^-$	0.228
$CNBF_3^-$	0.207	$CNAlF_3^-$	0.160
$NCBH_3^-$	0.311	$NCAlH_3^-$	0.219
$NCB(CH_3)_3^-$	0.312	$NCAl(CH_3)_3^-$	0.222
$NCBCl_3^-$	0.343	$NCAlCl_3^-$	0.257
$NCBF_3^-$	0.239	$NCAlF_3^-$	0.184

[a] B-N, B-C, Al-N, and Al-C bonds only.

sponding to the in-plane hydrogen atom being closer to carbon or nitrogen. Optimization of both possible transition states showed that the structure with the in-plane hydrogen closer to nitrogen is favored by ~3 kcal/mol, in agreement with earlier[13] work on the CH_3NC rearrangements. The potential surface at the 4-31G level is shown in Figure 1, where the transition-state energy is seen to lie 34.6 kcal/mol above $CNBH_3^-$. The bond lengths and angles at the calculated transition state are shown in Figure 2. The corresponding STO-3G value for this barrier is ~46 kcal/mol. In order to investigate the effects of polarization functions and correlation energy on the calculated transition-state energy, basis set S1 was employed with the 4-31G optimized geometry and a CI equivalent to CI1 was performed. These calculations produced energy barriers of 28.9 kcal/mol (SCF) and 28.7 kcal/mol (SCF–CI). The results of the calculations with basis sets S1 and S2 are given in Table VII.

Discussion

Qualitatively similar trends in isomerization energies are seen for the boron and aluminum systems. In both cases, substitution of CH_3, Cl, or F for hydrogen results in a lowering of the energy differences between the two isomers, with the trifluoro derivatives showing little preference for binding through carbon or nitrogen. Roughly speaking, the more electronegative the substituent the greater is the preference for bonding through nitrogen. Moffat[9] finds a similar effect for fluorine in $NCCF_3$, where fluorine substitution reduces the energy difference between the two isomers by 12.6 kcal/mol. There is no apparent correlation between donor–acceptor atom overlap populations (Table VIII) or optimized bond lengths (Table I) and the substituent effects seen here. The substitution of methyl for hydrogen in both systems has little effect on the overlap populations or optimized bond lengths of the B–C, B–N, Al–C, and Al–N bonds (root mean square difference, 0.02 Å) although the substituent effect on the isomerization energy is a significant 7 kcal/mol. Chlorine uniformly increases the overlap populations and decreases the bond lengths of the corresponding bonds, while fluorine has the opposite effect (except in the aluminum system where fluorine substitution has little effect on the bond lengths). While a correlation between the substituent effect on the isomerization energy and overlap population cannot be made, a rough correlation between the charge on the central atom of the Lewis acid monomer (Table IX) and the isomerization energy is possible. The general trend is consistent with the simple electrostatic argument that a large positive charge on the central atom of the receptor molecule should favor binding through the more highly negative nitrogen. This trend is illustrated graphically in Figure 3, where a plot of ΔE vs. Mulliken charge is seen to be nearly linear for the boron-containing system studied here. A similar plot holds for the aluminum system, except that the $AlCl_3$ point deviates substantially from linearity. However, the range of ΔE's calculated for the aluminum system (−2.7 to −0.1 kcal/mol) is substantially smaller than that of the corresponding boron systems (−11.4 to −0.6 kcal/mol), making detailed correlations of this type difficult.

Table IX. Monomer Charges[a]

BH_3	0.189	AlH_3	0.832
$B(CH_3)_3$	0.406	$Al(CH_3)_3$	0.956
BCl_3	0.445	$AlCl_3$	1.250
BF_3	0.645	AlF_3	1.150

[a] Central atom, planar geometry, STO-3G basis.

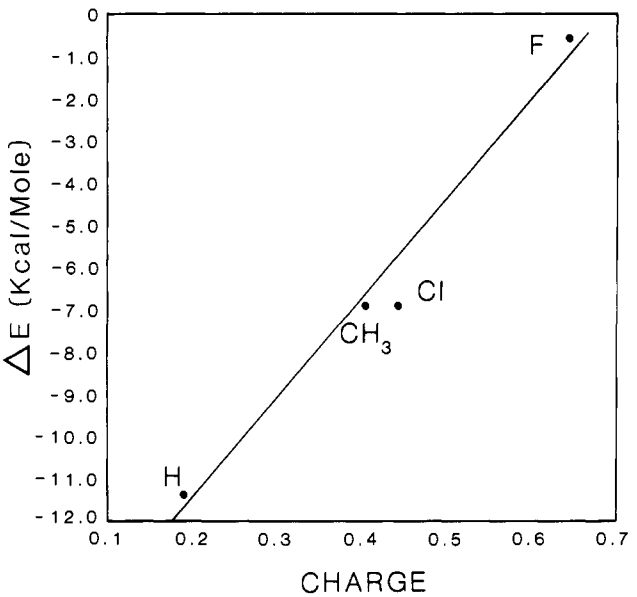

Figure 3. Plot of isomerization energy vs. Mulliken charges for the boron-containing species.

The isomerization energy of $CNBH_3^-$ is fairly insensitive to basis set at the SCF level, with only the S1 basis producing an anomalously low value. Similarly, the CI1 correction to the S1 SCF energy difference is small compared to the more complete CI treatment employed with the S2 basis (Table VII). The S2/CI2 results presented here are similar to previous results for HCN[4] and CH_3CN[11] both in the magnitude of the isomerization energy at the SCF level (~11.7 kcal/mol) and in the CI correction (−5.4 kcal/mol). The CI corrections favor binding through carbon, in agreement with previous results for HCN,[4,5] LiCN,[5] and CH_3CN.[11] An energy decomposition analysis of correlation effects in HCN and LiCN[5] suggests that this preference is due to π orbital effects, probably associated with a smaller HOMO–LUMO gap in the cyanide isomers. However, the HOMO–LUMO gap is actually larger in $NCBH_3^-$ (0.6433 au) than in $CNBH_3^-$ (0.6271 au). Nevertheless, our calculated CI correction to the isomerization energy is completely consistent with previous work.

The calculated transition state for the unimolecular isomerization of $CNBH_3^-$ at the 4-31G level agrees remarkably well with that of the corresponding carbon system. The transition state is found to lie closer to the product than the reactant, in violation of Hammond's postulate for an exothermic reaction. The angle between the cyanide carbon, the center of mass of the CN group, and the boron is 80.7°, very close to previously reported values for the methyl system (79.2° with a double-ζ basis[10] and 80.4° with a polarized doubleζ basis[13]). Other similarities between the two systems include short C≡N distances in the transition state, indicating that the carbon–nitrogen triple bond is preserved in the transition state, the large H–B–H angles, indicating that the BH_3 group has a tendency to flatten out in the transition state. One clear difference between the two systems is the actual magnitude of the barrier. Our best estimate of the $CNBH_3^-$ isomerization barrier is ~29 kcal/mol at the SCF level, while the corresponding value for $CNCH_3$ is 45.5 kcal/mol.[14] Our limited CI calculations produced no significant change in the barrier, but we would expect that a more complete CI would further lower the barrier a few kilocalories per mole, as would

inclusion of vibrational zero-point energies. Our results, of course, refer only to the gas-phase process, and the experimentally observed rearrangement can (and probably does) proceed by a significantly different path.

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Registry No. $CNBH_3^-$, 35798-27-7; $NCBH_3^-$, 33195-00-5; $CNB(CH_3)_3^-$, 79735-17-4; $NCB(CH_3)_3^-$, 44248-05-7; $CNBCl_3^-$, 79735-18-5; $NCBCl_3^-$, 79735-19-6; $CNBF_3^-$, 68830-29-5; $NCBF_3^-$, 79735-04-9; $CNAlH_3^-$, 79735-05-0; $NCAlH_3^-$, 79735-06-1; $CNAl(CH_3)_3^-$, 79735-07-2; $NCAl(CH_3)_3^-$, 79735-08-3; $CNAlCl_3^-$, 79735-09-4; $NCAlCl_3^-$, 79735-10-7; $CNAlF_3^-$, 79735-11-8; $NCAlF_3^-$, 79735-12-9; $CNB(CH_3)H_2^-$, 79735-13-0; $CNB(CH_3)_2H^-$, 79735-14-1; $NCB(CH_3)H_2^-$, 79735-15-2; $NCB(CH_3)_2H^-$, 79735-16-3; BH_3, 13283-31-3; $B(CH_3)_3$, 593-90-8; BCl_3, 10294-34-5; BF_3, 7637-07-2; AlH_3, 7784-21-6; $Al(CH_3)_3$, 75-24-1; $AlCl_3$, 7446-70-0; AlF_3, 7784-18-1.

Carbon–Hydrogen Bond Dissociation Energies in Alkylbenzenes. Proton Affinities of the Radicals and the Absolute Proton Affinity Scale

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Abstract: Rate constants (k) were measured for proton-transfer reactions from alkylbenzene ions RH^+ to a series of reference bases B, i.e., $RH^+ + B \rightarrow BH^+ + R\cdot$. For exothermic reactions ($\Delta H \leq -1$) k is large, but as weaker bases are used and the reaction becomes thermoneutral the collision efficiency decreases sharply. The variation of k with ΔH determines the proton affinity (PA) of the radical R· relative to a set of reference bases to within ±0.5 kcal mol^{-1}. For example, the reaction $C_6H_5CH_3^+ + B \rightarrow BH^+ + C_6H_5CH_2\cdot$ is fast (reaction efficiency = $k/k_{col} \geq 0.5$) when B = MeO-t-Bu or stronger bases, but k/k_{col} is significantly smaller when B is n-Pr_2O or weaker bases. From the falloff curve of reaction efficiency vs. PA(B), we find PA(n-Pr_2O) = PA($C_6H_5CH_2\cdot$) + 0.8 kcal mol^{-1} = 200.0 kcal mol^{-1}. Since PA($C_6H_5CH_2\cdot$) is obtained from known thermochemical data, this relation defines the absolute PA of n-Pr_2O. Through a ladder of known PA, we then obtain PA(i-C_4H_8) = 186.8 kcal mol^{-1}; we also obtain the absolute PAs of other oxygen bases. Falloff curves of reaction efficiencies of 3-$FC_6H_4CH_3^+$, $C_6H_5C_2H_5^+$, C_6H_5-n-$C_3H_7^+$, and C_6H_5-i-$C_3H_7^+$ with these reference bases give then the following PAs of R· and R–H bond dissociation energies ($D°$) (all in kcal mol^{-1}) as R·, PA(R·), $D°$(R–H): 3-$FC_6H_4CH_2\cdot$, 197.2, 89.4; $C_6H_5\dot{C}HCH_3$, 197.9, 86.2; $C_6H_5\dot{C}HC_2H_5$, 199.1, 86.1; $C_6H_5(CH_3)_2$, 199.6, 86.1. In a similar manner, rate constants for H^+ transfer from $C_6H_5NH_2^+$ to reference pyridines and amines yield PA($C_6H_5NH\cdot$) = 221.5 and $D°$(C_6H_5NH–H) = 85.1 kcal mol^{-1} (1 kcal mol^{-1} = 4.18 kJ mol^{-1}).

I. Introduction

It has been assumed for some time that the occurrence or nonoccurrence of proton-transfer reactions such as

$$RH^+ + B \rightarrow BH^+ + R\cdot \qquad (1)$$

can be used to distinguish between exothermic and endothermic processes, respectively. Using this principle, the proton affinity (PA) of R· can be bracketed by two references bases such that PA(B_1) < PA(R·) < PA(B_2). This relation can be used for the following: (1) if PA(R·) is known independently, the absolute PAs of B_1 and/or B_2 can be estimated; or (2) conversely, if PA(B_1) or PA(B_2) is known, PA(R·) can be bracketed. In conjunction with ionization potential data (see below), these measurements also yield the bond dissociation energy $D°$(R–H) and the heat of forrmation $\Delta H_f°$ (R·). Recently, DeFrees et al.[1] used this bracketing method to measure the PA and $\Delta H_f°$ of several hydrocarbon radicals including $C_6H_5CH_2\cdot$.

One limitation to the accuracy by which this bracketing technique defines thermochemical values is that the transition from fast kinetics to "nonoccurrence" in a set of reactions is, in fact, gradual, rather than abrupt. While strongly exothermic reactions are usually fast, reactions closer to thermoneutral are usually slower,[2] and, on the other hand, slightly endothermic reactions may still proceed at detectable rates. This fact usually limits the accuracy of the *bracketing* measurements to within ±2 kcal mol^{-1}. In the present work we set out to measure rate constants for reactions of RH^+ with a set of bases B whose PAs are closely spaced. This way we can better quantify the transition from fast to slow kinetics, and therefore we can define with better accuracy the thermoneutral point in such a set of reactions. This should yield improved accuracy in relating the PAs of alkylbenzene radicals R· to the PAs of the reference bases B.

We shall use this method to: (a) relate the PAs of some reference bases to the absolute PA of $C_6H_5CH_2\cdot$ which in turn can be calculated from available data (thereby we can obtain the absolute PAs of the reference bases), and (b) we will then measure PAs of several other alkylbenzene radicals and calculate from these data R-H bond dissociation energies. We shall show that differences as small as 0.5 kcal mol^{-1} between the PAs of alkylbenzene radicals can be clearly measured by this kinetic technique.

II. Experimental Section

The measurements were performed on the NBS pulsed ion cyclotron resonance (ICR) mass spectrometer, using standard techniques.[3,4] In most experiments the gases RH and B were admitted in two separate inlets; in a few kinetic experiments and most equilibrium measurements premixed mixtures were used. Every rate constant was measured in at least three different mixtures with different RH:B ratios. These ratios usually ranged from 10:1 to 1:2. Total source pressures were 1 to 4 × 10^{-6} Torr.

(1) DeFrees, D. G.; McIver, R. T.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 3334.
(2) Lias, S. G.; Shold, D. M.; Ausloos, P. *J. Am. Chem. Soc.* **1980**, *102*, 2540, and ref 5, 8, and 9 therein.
(3) Lias, S. G.; Euler, J. R.; Ausloos, P. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *19*, 219.
(4) Lias, S. G.; Ausloos, P.; Horvath, Z. *Int. J. Chem. Kinet.* **1976**, *8*, 719.

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