J|A|C|S
A R T I C L E S

An Infrared νNH Scale for Weakly Basic Anions. Implications for Single-Molecule Acidity and Superacidity

Evgenii S. Stoyanov,* Kee-Chan Kim, and Christopher A. Reed*

Contribution from the Department of Chemistry, University of California, Riverside, California 92521

Received January 30, 2006; E-mail: chris.reed@ucr.edu

Abstract: The N−H stretching frequencies of tri-*n*-octylammonium salts are reported for a series of weakly basic anions (A⁻), many of which are the conjugate bases of known strong acids and superacids. Data have been collected primarily in carbon tetrachloride, where Oct_3N^+−H···A⁻ contact ion pairs are formed. In the more polar solvent 1,2-dichloroethane, some salts form both contact and solvent-separated ion pairs. Salts have also been studied in crystalline form or as oils. In general, the νNH frequencies decrease in the order fluoroanions > carboranes > oxyanions, reflecting the relative basicities of the anions. By inference, the data reflect differences in the acidity of the corresponding conjugate acids (HA). This qualitative indicator of acid strength is useful because it reflects acidity on an individual molecule basis rather than in bulk. In this respect, it provides a condensed-phase analogy to gas-phase ("intrinsic") acidity and gives insight into the aggregation phenomena that determine bulk acidity. The data also reveal the importance of the chemical stability of conjugate base anions in attaining high acidity and suggest where acids stronger than those presently known may be discovered.

Introduction

In this paper we report N−H stretching frequencies for trialkylammonium salts with a series of weakly basic anions (A⁻). The idea behind the study is that νNH data contain information about the relative acidities of the conjugate acids (HA). In H-bonded contact ion pairs of type **I**, the lower the

$$R_3N^+\text{—}H\cdots A^-$$
I
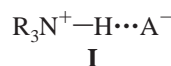
basicity of A⁻, the weaker will be the NH···A⁻ hydrogen bond strength and the higher the νNH frequency. For weak bases, νNH (>2800 cm⁻¹) is energetically well separated from $\nu(H\cdots A^-)$ (<400 cm⁻¹), and νNH will be a highly characteristic stretching vibration. Anharmonicity will be unimportant, and νNH will be a sensitive indicator of NH···A⁻ hydrogen bond strength. Since H-bonding is a largely electrostatic phenomenon and since acidity is an ionization phenomenon, it follows that νNH will be related to the acidity of HA.

The correlation of NH···A⁻ hydrogen bond strength and HA acidity will be most direct when A⁻ is a weakly basic, low-polarizability anion, i.e., when H-bonding is weak and covalence is minimal. For more highly basic anions, which form stronger H-bonds with increasing covalence, the νNH frequency shifts below 2800 cm⁻¹ and is expected to begin losing its utility. This is because anharmonicity of the NH vibrations becomes increasingly significant as the proton potential becomes increasingly double-well shaped. When the proton is more or less equally shared between the two bases, ultimately forming very strong, low-barrier, double-well H-bonds,[1-3] the method will lose its meaning entirely. This is why, in the present work, we

evaluate the basicity of only the least basic anions, mostly those whose conjugate acids are stronger than sulfuric acid, i.e., superacids.

It has been shown that the strength of H-bonds formed by acid HA′ with small, strongly basic anions (e.g., RO⁻, RCC⁻) does not correlate with gas-phase acidity in A′H···A⁻ complexes.[4-6] This is because electrostatic charge effects dominate the energetics of gas-phase species, and the electrostatic requirements of an anion and its conjugate acid can be very different. With weakly basic, low-polarizability anions, however, the difference in the electrostatic requirements of the acid and anion are small, and H-bonding can be expected to be a much better reporter of anion basicity.

Indications of relative HA acidity from changes in νNH in **I** are of interest for a number of reasons. Like gas-phase acidity, a νNH scale of acidity would reflect acidity on an individual molecule basis rather than a bulk (or neat) acid basis. Acidity is typically measured as a bulk property from the thermodynamics of the reaction of an acid with a base (ΔH, pK_a, etc.), and such measurements are highly valued because they are quantitative. Nevertheless, a bulk thermodynamic measurement gives little insight into the chemical factors that determine acid strength. Condensed-phase acidity is especially dependent on

(1) Bratos, S.; Ratajczak, H. J. *J. Chem. Phys.* **1982**, *76*, 77−85.
(2) Sokolov, N. D.; Vener, M. V.; Savel'ev, V. A. *J. Mol. Struct.* **1988**, *177*, 93−110.
(3) Zundel, G.; Fritsch, J. *The Chemical Physics of Solvation*; Dogonadze, R. R., Kálmán, E., Kornyshev, A. A., Ulstrup, J., Eds.; Elsevier: Amsterdam, 1986; Vol. 2, Chapter 2, pp 21−96.
(4) Chabinyc, M. L.; Brauman, J. I. *J. Phys. Chem. A* **1999**, *103*, 9163−9166.
(5) Chabinyc, M. L.; Brauman, J. I. *J. Am. Chem. Soc.* **2000**, *122*, 5371−5378.
(6) Chabinyc, M. L.; Brauman, J. I. *J. Am. Chem. Soc.* **2000**, *122*, 8739−8745.

intermolecular H-bonding in aggregates and extended structures whose complexity can be difficult to unravel.[7] The best-known example is the formation of strongly H-bonded acid dimers of carboxylic, phosphoric, and phosphinic acids.[8] Their dimerization may be considered as the result of an acid−base neutralization which decreases bulk acidity, leaving the intrinsic acidity of the monomer unknown. For example, di(2-ethylhexyl)-phosphoric acid, whose acid strength in the monomeric state we will show is close to that of nitric acid, loses its acidic properties upon dimerization. In hydrates of these dimers, water acts as the H-bond donor, not the acceptor, indicating that the dimeric acid is acting as a base, not an acid.[9] Thus, an independent indicator of the acidity of a monomer is useful in providing information about intrinsic acidity. Typically, intrinsic acidities have only been available in the gas phase, where extensive experimental data[10−12] and generally reliable calculational estimates[13,14] of the proton affinities of individual molecules have been determined. These would appear to be the logical point of departure for discussing acidity in bulk, but little progress has been made in correlating gas-phase acidities with condensed-phase acidities. There is a clear need for a measure of intrinsic acidity in condensed phases.

Our interest in collecting data for a wide range of weakly basic anions arose from the desire to compare the strengths of their conjugate acids across diverse structural classes and phases. We have recently prepared a new class of acids, called carborane acids,[15,16] which are the strongest isolable protic acids presently known.[17] Their conjugate bases are the exceptionally inert and weakly basic icosahedral carborane anions of the type CHB_{11}-$R_5X_6{}^-$ (R = H, Me, Cl; X = Cl, Br, I). On the Hammett acidity scale, most oxyacids are superacids, defined as having $H_0 < -12$. Of these, fluorosulfuric acid ($HFSO_3$, $H_0 = -15.1$) has long been considered the strongest pure acid.[18] The observation that carborane acids readily protonate benzene whereas $HFSO_3$ does not led us to conclude that carborane acids are stronger acids than oxyacids.[19] This was confirmed for dilute acids in liquid SO_2 solution using the $\Delta\delta$ ^{13}C NMR method with mesityl oxide as indicator.[17] Nevertheless, since the acidity of carborane acids is leveled in SO_2 solution, it was not possible to fully quantify relative acidities or make extrapolations to project H_0 values.

The problem is more fundamental. H_0 values are measured in the liquid state, but carborane acids are solids. How does one go about quantifying the acidity of a solid acid and comparing it to that of a liquid? This is a classical problem of surface chemistry and has been approached by a variety of methods, most of which probe the thermodynamics of binding of a base to an acidic surface.[20] Surface acidity has been probed via IR stretching frequencies of acidic X−H bonds, but the relationship to thermodynamic acidity has been questioned.[20−22] Nevertheless, acidity rankings based on IR data have been shown to have validity within certain boundaries.[23−27] For example, the O−H stretching frequency of phenols shows a linear correlation with the enthalpy of reaction with 33 different O and N atom bases,[24] but linear correlations with pK_a values hold only for bases segregated into structurally similar groups.[28] With less polarizable anions, such as carboranes, IR methods are expected to be even more reliable. Based on these observations, we published preliminary data on the νNH frequencies for a series of 10 tri-*n*-octylammonium carborane salts and concluded that the carborane acid with 11 chlorine substituents, $H(CHB_{11}Cl_{11})$, was the strongest acid within the carborane class.[17] Calculations of the molecular electrostatic potentials of carborane anions are consistent with $CHB_{11}Cl_{11}{}^-$ having the lowest basicity.[29]

n-Octyl substituents are chosen for the trialkylammonium ion to provide solubility of salts in carbon tetrachloride, a low-dielectric solvent which promotes the formation of contact ion pairs. In the present paper, we report data for a diverse range of weakly basic anions to explore the potential wider utility of the scale. We include fluoroanions such as $BF_4{}^-$, $PF_6{}^-$, etc., the familiar oxyanions from common strong acids and super-acids, some new carboranes, and a variety of other anions whose conjugate acid strength is of current interest, including $C_5(CN)_5{}^-$, $B(C_6F_5)_4{}^-$, $N(SO_2CF_3)_2{}^-$, and chlorometalates.

Experimental Section

General. Tri-*n*-octylamine (98%) and fuming sulfuric acid (20% SO_3) were purchased from ACROS and used as received. Fluorosulfuric acid (FSO_3H), trifluoromethanesulfonic acid (CF_3SO_3H, 99%), and silver salts of $AsF_6{}^-$, $PF_6{}^-$, $SbF_6{}^-$, $BF_4{}^-$, $CF_3SO_3{}^-$, $ReO_4{}^-$, and $NO_3{}^-$ (98−99% purity) were purchased from Aldrich and used without further purification. The bistrifluoromethanesulfonimide acid, $HN(SO_2CF_3)_2$, and its lithium salt were obtained from Fluka and used as received. Chlorinated cobalt bis-dicarbollide $[Co^{III}(C_2B_9H_8Cl_3)_2]^-$ (90% in H form and 10% in Na form) was obtained from Katchem (Czech Republic). High-purity dichloromethane (Omnisolv) and *n*-hexane were purchased from EM Science, and benzene (Spectranalyzed) was obtained from Fisher and purified and dried by standard methods.[30] Carbon tetrachloride (HPLC grade from Aldrich) and 1,2-dichloroethane (spectrophotometric grade from EM Science) were dried with activated molecular sieves before preparation of the solutions for IR spectroscopy. Elemental analyses were performed by Desert Analytics (Tucson, AZ).

(7) McLain, S. E.; Benmore, C. J.; Turner, J. F. C. *J. Chem. Phys.* **2002**, *117*, 3816−3821.

(8) Stoyanov, E. S.; Popov, V. M.; Mikhailov, V. A. *Zh. Prikl. Spectrosk.* **1984**, *40*, 77−84.

(9) Stoyanov, E. S.; Mikhailov, V. A.; Popov, V. M. *Zh. Neorg. Khim.* **1985**, *30*, 3066−3070.

(10) Lias, S. G.; Bartmess, L. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data, Suppl. 1* **1988**, *17*, 1−861.

(11) Viggiano, A. A.; Henchman, M. J.; Dale, F.; Deakyne, C. A.; Paulson J. F. *J. Am. Chem. Soc.* **1992**, *114*, 4299−4306.

(12) Koppel, I. A.; Taft, R. W.; Anvia, F.; Zhu, S.-Z.; Hu, L.-Q.; Sung, K.-S.; DesMarteau, D. D.; Yagupolskii, L. M.; Yagupolskii, Y. L.; Ignat'ev, N. V.; Kondratenko, N. V.; Volkonskii, A. Y.; Vlasov, V. M.; Notario, R.; Maria, P.-C. *J. Am. Chem. Soc.* **1994**, *116*, 3047−3057.

(13) Koppel, I. A.; Burk, P.; Koppel, I.; Leito, I.; Sonoda, T.; Mishima, M. *J. Am. Chem. Soc.* **2000**, *122*, 5114−5124.

(14) Burk, P.; Koppel, I. A.; Koppel, I.; Yagupolski, L. M.; Taft, R. W. *J. Comput. Chem.* **1996**, *17*, 30−41.

(15) Reed, C. A.; Kim, K.-C.; Bolskar, R. D.; Mueller, L. *Science* **2000**, *289*, 101−104.

(16) Reed, C. A. *Chem. Commun.* **2005**, 1669−1677.

(17) Juhasz, M.; Hoffmann, S. P.; Stoyanov, E. S.; Kim, K.-C.; Reed, C. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5352−5355.

(18) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; John Wiley & Sons: New York, 1985.

(19) Reed, C. A.; Kim, K.-C.; Stoyanov, E. S.; Stasko, D.; Tham, F. S.; Mueller, L. J.; Boyd, P. D. W. *J. Am. Chem. Soc.* **2003**, *125*, 1796−1804.

(20) Farneth, W. E.; Gorte, R. J. *Chem. Rev.* **1995**, *95*, 615−635.

(21) van Santen, R. A.; Kramer, G. J. *Chem. Rev.* **1995**, *95*, 637−660.

(22) Fărcaşiu, D.; Hâncu, D *Catal. Lett.* **1998**, *53*, 3−6.

(23) Iogansen, A. V. In *The Hydrogen Bond*; Sokolov, N. D., Ed.; Nakau: Moscow, 1981; pp 112−155.

(24) Joesten, M. D.; Drago, R. S. *J. Am. Chem. Soc.* **1962**, *62*, 3817−3821.

(25) Arnett, E. M.; Joris, L.; Mitchell, E.; Murty, T. S. S. R.; Gorrie, T. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2365−2377.

(26) Drago, R. S.; O'Bryan, N.; Vogel, G. C. *J. Am. Chem. Soc.* **1970**, *92*, 3924−3929.

(27) Sherry, A. D.; Purcell, K. F. *J. Am. Chem. Soc.* **1972**, *94*, 1853−1857.

(28) Gordon, J. E. *J. Org. Chem.* **1961**, *26*, 738−745.

(29) Balanarayan, P.; Gadre, S. R. *Inorg. Chem.* **2005**, *44*, 9613−9615.

(30) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press Ltd.: Sydney, 1980.

Tri-*n*-octylammonium chloride, [(*n*-C$_8$H$_{17}$)$_3$NH]Cl, was prepared by the literature method.[31] The cesium salts of the parent carborane, CHB$_{11}$H$_{11}^-$, and the halogenated and methylated derivatives were prepared according to the literature methods,[17,32–38] and the corresponding silver salts were obtained by metathesis with silver nitrate in water or mixed solvent of water and ethanol. In a glovebox (H$_2$O, O$_2$ < 0.5 ppm), Et$_3$Si(B(C$_6$F$_5$)$_4$)[39] was prepared from its trityl salt, [(C$_6$H$_5$)$_3$C]-[B(C$_6$F$_5$)$_4$], with dry triethylsilane in dry benzene. The silver salt of pentacyanocyclopentadienide, Ag[C$_5$(CN)$_5$], was obtained via an improvement[40] of a literature method.[41] The silver salt of the tetra-cyanocyclopentadienide ion was obtained from trimethylammonium tetracyanocyclopentadienide,[40] which was purified by dissolving in deionized water, filtering off any insoluble material, and treating with sodium carbonate (1 equiv) with stirring for 20 min. Silver nitrate (1.3 equiv) was added to the solution with stirring. The silver salt was collected on a medium-porosity glass frit, washed three times with small portions of water, and dried under vacuum.

Preparation of Tri-*n*-octylammonium Salts. For the preparation of the tri-*n*-octylammonium salts of AsF$_6^-$, PF$_6^-$, SbF$_6^-$, BF$_4^-$, CHB$_{11}$H$_{11}^-$, CHB$_{11}$Cl$_{11}^-$, CHB$_{11}$H$_5$Cl$_6^-$, CHB$_{11}$(CH$_3$)$_5$Cl$_6^-$, CHB$_{11}$H$_5$Br$_6^-$, CHB$_{11}$(CH$_3$)$_5$Br$_6^-$, CHB$_{11}$H$_5$I$_6^-$, CHB$_{11}$(CH$_3$)$_5$I$_6^-$, C$_5$(CN)$_5^-$, C$_5$H(CN)$_4^-$, CF$_3$SO$_3^-$, ReO$_4^-$, and NO$_3^-$ anions, the silver salts were used in metathesis reactions with tri-*n*-octylammonium chloride in dichloromethane. In a typical preparation, tri-*n*-octylammonium chloride (0.3 g) was dissolved in dichloromethane (50 mL), and the silver salt of the anion (1 equiv) was added to the solution with magnetic stirring. The mixture was stirred for 30 min at room temperature. The AgCl$_{(s)}$ byproduct was removed by filtration with a fine-porosity glass frit, and the dichloromethane filtrate was evaporated under reduced pressure. In the case of AsF$_6^-$ and PF$_6^-$, the dichloromethane was allowed to evaporate naturally in order to prevent decomposition of the trioctyl-ammonium salts to HF and volatile AsF$_5$ and PF$_5$ under reduced pressure. Analysis of the tri-*n*-octylammonium salt of perrhenate, ReO$_4^-$, was consistent with the formula [(C$_8$H$_{17}$)$_3$NH$^+$][ReO$_4^-$]. Anal. Calcd for C$_{24}$H$_{52}$NReO$_4$: C, 47.66; H, 8.67; N, 2.32. Found: C, 47.36; H, 8.71; N, 2.41.

The tri-*n*-octylammonium salt of hydrogen sulfate, HSO$_4^-$, was prepared by the following method. Under an argon atmosphere, trioctylamine (3 mL) was dissolved in dry *n*-hexane (50 mL), and 1 equiv of H$_2$SO$_4$ in the form of fuming sulfuric acid (20% SO$_3$) was added dropwise from a Pasteur pipet (38 drops were added; weight of 1 drop was measured to be 0.0216 g) with vigorous stirring. After completion of the addition, the solution was stirred for 20 min, and the solvent was completely removed under reduced pressure. This gave a light brown oily product. Analysis of the product was consistent with the formula [(C$_8$H$_{17}$)$_3$NH$^+$][HSO$_4^-$]. Anal. Calcd for C$_{24}$H$_{53}$NSO$_4$: C, 63.81; H, 11.82; N, 3.10; S, 7.10. Found: C, 64.02; H, 11.76; N, 3.19; S, 6.72. Tri-*n*-octylammonium salts containing excess sulfuric acid, with average formula (C$_8$H$_{17}$)$_3$NH$^+$[HSO$_4^-$·(H$_2$SO$_4$)$_{4.4}$], were obtained by extraction from fuming sulfuric acid with a benzene solution of tri-*n*-octylamine. The volatiles were evaporated under reduced pressure. Anal. Calcd for C$_{24}$H$_{61.8}$NS$_{5.4}$O$_{21.6}$: C, 32.63; H, 7.05; N, 1.59; S, 19.60. Found: C, 32.74; H, 7.08; N, 1.74; S, 19.38.

The tri-*n*-octylammonium salts of Cl$^-$, ClHCl$^-$, and Cl$^-$(HCl)$_2$ were prepared by extraction from aqueous HCl with CCl$_4$ solutions of tri-*n*-octylammonium. The number of excess HCl molecules was deter-mined by titration.

For the preparation of the ammonium salt of the B(C$_6$F$_5$)$_4^-$ anion, the triethylsilyl compound (C$_2$H$_5$)$_3$Si[B(C$_6$F$_5$)$_4$] was used for a meta-thesis reaction with trioctylammonium chloride in benzene, in a manner similar to that used for the silver salts. The triethylchlorosilane byproduct and benzene were removed under reduced pressure to give solid product.

The hydrated acid salt of cobalt dicarbollide, H(H$_2$O)$_n^+$[Co^{III}(C$_2$B$_9$-H$_8$Cl$_3$)$_2^-$], was obtained from the commercially available acid form of cobalt dicarbollide, which was composed of 90% acid form and 10% Na form, by shaking a 0.1 M solution in 1,2-dichloroethane with 2 M sulfuric acid in 1:1 volume ratio for 5 min. The 1,2-dichloroethane layer was then separated from the aqueous sulfuric acid layer. Tri-*n*-octylamine (1 equiv) was added to the 1,2-dichloroethane solution, and after the solution was stirred for 10 min, the solvent was evaporated under reduced pressure to give [octyl$_3$NH$^+$][Co^{III}(C$_2$B$_9$H$_8$Cl$_3$)$_2^-$].

For the preparation of the perchlorate salt, tri-*n*-octylamine (1 mL) was dissolved in dichloromethane (50 mL), and excess perchloric acid (70%) (5 mL) was added to the solution. The immiscible layers were mixed with vigorous stirring for 20 min. The dichloromethane layer was separated, and the solvent was evaporated under reduced pressure to give product. ***Caution: Perchlorate salts can be explosive! While no problems were observed in the present studies, proper precautions are advised.***

The tri-*n*-octylammonium salts of FSO$_3^-$ and TeOF$_5^-$ were prepared by addition of tri-*n*-octylamine into the acids with 1:1 molar ratio under inert conditions to give oily products.

For the preparation of the tri-*n*-octylammonium salt of the bistri-fluoromethanesulfonimide ion, N(SO$_2$CF$_3$)$_2^-$, Li[N(SO$_2$CF$_3$)$_2$] (10.5 mmol) and AgNO$_3$ (10.5 mmol) were dissolved in 30 mL of deionized water. Tri-*n*-octylammmonium chloride (10.5 mmol) in 40 mL of dichloromethane was then added. The two layers were vigorously mixed with magnetic stirring for 20 min. The dichloromethane layer was separated and the solvent removed under reduced pressure to give an oily product.

Preparation of N-Deuterated Tri-*n*-octylammonium, [(*n*-C$_8$H$_{17}$)$_3$-ND]$^+$, Salts. Each tri-*n*-octylammonium salt was dissolved in 5 mL of dichloromethane. The solution was transferred to a separatory funnel. Deuterium oxide (4 mL; 99.9% D) was added to the funnel and shaken for 5 min. When the two layers were clearly separated, the dichlo-romethane layer (bottom layer) was separated off, the solvent was completely removed under vacuum, and the product was transferred into a glovebox under vacuum without exposure to air.

Infrared Spectroscopy. Spectra were recorded on a BOMEM M-102 FTIR spectrometer or a Shimadzu-8300 FTIR spectrometer in the 4000–500 cm^{-1} range. IR spectra of 0.005–0.01 M solutions of tri-*n*-octylammonium salts in carbon tetrachloride or in 1,2-dichloroethane were obtained using cells with CaF$_2$ or silicon windows. The silicon windows were wedged to prevent interference. IR spectra of the tri-*n*-octylammonium salts were obtained as KBr disks for the solid samples or using CaF$_2$ windows for oily samples. IR spectra of deuterated tri-*n*-octylammonium, [(*n*-C$_8$H$_{17}$)$_3$ND]$^+$, salts were obtained on a spec-trometer installed within an inert atmosphere glovebox (H$_2$O, O$_2$ level < 1 ppm). When the N–H stretching frequency was lower than 3000 cm^{-1}, the νNH band became overlapped with νCH bands of the tri-*n*-octylammonium ion. In these cases, the νNH band was isolated by digital subtraction of the νCH bands using GRAMS software. The spectrum of [(*n*-C$_8$H$_{17}$)$_3$NH][C(CH$_3$)B$_{11}$F$_{11}$] in CCl$_4$ was kindly supplied by Yoshihiro Kobayashi and Prof. Steven S. Strauss of Colorado State University.

X-ray Crystallography. Single crystals of butyl$_3$NH$^+$[CHB$_{11}$I$_{11}$]$^-$ were grown from benzene solution by slow evaporation. Details of the structure determination are available as Supporting Information.

(31) Stoyanov, E. S.; Popandopulo Yu, I.; Bagreev, V. V. *Coord. Chem. (Translation of Koord. Khim.)* **1980**, *6*, 1809–1814.
(32) Knoth, W. H. *J. Am. Chem. Soc.* **1967**, *89*, 1274–1275.
(33) Plešek, J.; Jelínek, T.; Drdáková, E.; Heřmánek, S.; Štíbr, B. *Collect. Czech. Chem. Commun.* **1984**, *49*, 1559–1562.
(34) Jelínek, T.; Baldwin, P.; Scheidt, W. R.; Reed, C. A. *Inorg. Chem.* **1993**, *32*, 1982–1990.
(35) Xie, Z.; Jelínek, J. T.; Bau, R.; Reed, C. A. *J. Am. Chem. Soc.* **1994**, *116*, 1907–1913.
(36) Xie, Z.; Manning, J.; Reed, R. W.; Mathur, R.; Boyd, P. D. W.; Benesi, A.; Reed, C. A. *J. Am. Chem. Soc.* **1996**, *118*, 2922–2928.
(37) Xie, Z.; Tsang, C.-W.; Sze, E. T.-P.; Yang, Q.; Chan, D. T. W.; Mak, T. C. W. *Inorg. Chem.* **1998**, *37*, 6444–6451.
(38) Stasko, D.; Reed C. A. *J. Am. Chem. Soc.* **2002**, *124*, 1148–1149.
(39) Lambert J. B.; Zhang, S. *J. Chem. Soc., Chem. Commun.* **1993**, 383–384.
(40) Richardson, C.; Reed, C. A. *Chem. Commun.* **2004**, 706–707.
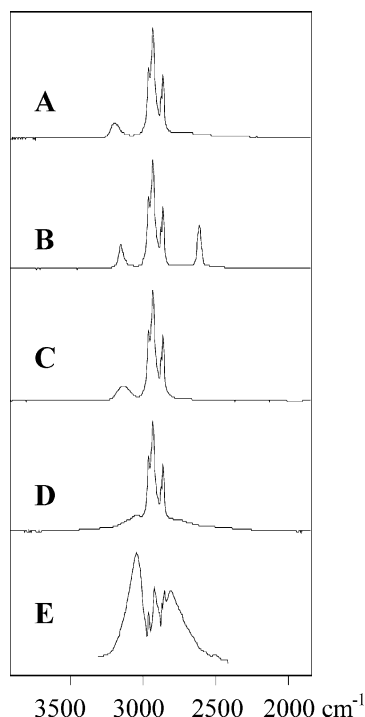(41) Webster, O. W. *J. Am. Chem. Soc.* **1966**, *88*, 3046–3050.

Figure 1. Infrared spectra in the νNH (>3000 cm^{-1}) and νCH regions (<3000 cm^{-1}) for trioctylammonium salts with (A) PF$_6^-$, (B) CB$_{11}$H$_6$Cl$_6^-$, (C) BF$_4^-$, (D, E) FSO$_3^-$ in CCl$_4$. Spectrum E was isolated after computer subtraction of most of the νCH bands.

Results

Octyl$_3$NH$^+$A$^-$ salts for a series of uninegative anions A$^-$ were sufficiently soluble in CCl$_4$ solution to obtain infrared spectra. Typical data are illustrated in Figure 1. The νNH frequencies are listed in Table 1. The strong dependence of νNH on the nature of the anion indicates that contact ion pairs are formed. With the exception of the acidic bisulfate ion, HSO$_4^-$, which forms dimers because of strong H-bonding, all anions lack additional ionizable H atoms and are monomeric. Data were taken in dilute solution (0.005–0.01 M) where there was no concentration dependence, indicating that discrete, monomeric ion pairs are formed. There are only two exceptions: The first is octyl$_3$NH$^+$Cl$^-$, which forms a monomer with νNH 2330 cm^{-1} at low concentration and a dimer (2440 cm^{-1}) with increasing concentration.[42] The second is the salt with the bistrifluoromethanesulfonimide ion, N(SO$_2$CF$_3$)$_2^-$, which showed a νNH band at 3086 cm^{-1} at low concentration and a new one at 3141 cm^{-1} at increasing concentration up to the pure state. As discussed below, they are assigned to monomer and dimer, respectively.

The CMeB$_{11}$F$_{11}^-$ salt showed two νNH bands at 3219 and 3263 cm^{-1}, the latter frequency being higher than that observed for any anion. These are assigned to a contact ion pair and a solvent-separated ion pair (SSIP), respectively. In the more polar solvent 1,2-dichloroethane (DCE), a number of salts showed a second νNH band with constant frequency at 3179 ± 1 cm^{-1}, independent of the nature of the anion. This indicates that the 3179 cm^{-1} band belongs to ion pairs separated by DCE, and the subset of νNH data showing this phenomenon is given in Table 2. The νNH frequency of an SSIP is determined by the

H-bond-accepting ability of the solvent, and predictably, the value is higher in carbon tetrachloride than in the more basic DCE. The value in carbon tetrachloride is taken as the appropriate point to anchor the νNH scale, and differences between 3263 cm^{-1} and the value for any particular contact ion pair in CCl$_4$ are expressed as Δ values in Table 1. The νNH frequencies for contact ion pairs in DCE maintain the same ordering as those in CCl$_4$, although the values for carboranes are typically somewhat higher (1–17 cm^{-1}) and those for BF$_4^-$ and C$_5$(CN)$_5^-$ are ca. 20 cm^{-1} lower.

The direct determination of the Δ values for salts with νNH below 3054 cm^{-1} is difficult because the νNH band is distorted into broad overlapping components by Fermi resonance with overtones of lower frequency vibrations (see, for example, Figure 1D, E). The true νNH frequency would typically be determined from the center of gravity of the distorted band, but overlap with the intense absorptions from CH$_2$ and CH$_3$ groups of the octyl groups prevents its accurate assessment. However, deuteration of the trioctylammonium salts readily circumvents this problem. The observation of single νND bands for ClO$_4^-$ through ReO$_4^-$ salts gives a precise ordering and confirms that their νNH values are subject to Fermi resonance (see Table 1). The νNH/νND ratio is 1.340 ± 0.004 over the entire range of compounds, so anharmonicity considerations are unimportant. The νNH frequencies for the distorted bands were calculated as 1.340 × νND.

Infrared spectra were also obtained for octyl$_3$NH$^+$A$^-$ salts in the solid state (or as viscous oils). The νNH frequencies are listed in Table 1, along with the differences between values in CCl$_4$ solution. In all cases, the values in the solid state are higher than those in solution. They are 8–20 cm^{-1} higher for carboranes and are highest for fluoro ions PF$_6^-$, AsF$_6^-$, and SbF$_6^-$ (26–29 cm^{-1}).

As mentioned above, the bistrifluoromethanesulfonimide anion, N(SO$_2$CF$_3$)$_2^-$, has a specific distinction from all others. Its trioctylammonium salt in CCl$_4$ solutions developed νNH frequencies at 3086 and 3141 cm^{-1} at low and high concentrations, respectively, and the latter frequency coincides exactly with that for the solid state (Table 1). This can be explained by dimerization of ion pairs in the solid state and with increasing its concentration in CCl$_4$. The N(SO$_2$CF$_3$)$_2^-$ anion is readily polarizable, and its conjugate acid may behave as a strong or weak acid, depending on conditions.[43] Pairwise dipole–dipole dimerization will decrease the Oct$_3$N$^+$- - -A$^-$ electrostatic interaction and increase the NH frequency. Evidence in favor of a redistribution of electron density from the N atom to the S=O bonds[44] is found in the increased frequencies of the ν$_{as}$SO$_2$ and ν$_s$SO$_2$ stretching vibrations by 2–4 cm^{-1} and decreased frequency of the SNS bend by 2 cm^{-1} on passing from monomer to dimer.

Discussion

The νN–H Scale and Anion Basicity. On the νNH scale, fluoroanions such as BF$_4^-$, SbF$_6^-$, etc. all rank higher than oxyanions such as ClO$_4^-$, FSO$_3^-$ etc. This is in keeping with the observation that oxyanions can be protonated to give their well-known conjugate acids (HClO$_4$, HFSO$_3$, etc.), but there is

(42) Stoyanov, E. S.; Popandopulo Yu, I.; Bagreev, V. V. *Koord. Khim.* **1980**, *6*, 1815–1821.

(43) Stoyanov, E. S.; Kim, K.-C.; Reed, C. A. *J. Phys. Chem. A* **2004**, *108*, 9310–9315.

(44) Rey, I.; Johansson, P.; Lindgren, J.; Lassègues, J. C.; Grondin, J.; Servant, L. *J. Phys. Chem. A* **1998**, *102*, 3249–3258.

Table 1. νNH Frequencies for Octyl$_3$NH$^+$A$^-$ Salts in CCl$_4$ and Solid State

	νNH in CCl$_4$					νNH	Δ solid
anion	expt	calc^e	$\Delta\nu$NH	νND	νNH/νND	solid or wax	relative to CCl$_4$
none^a	3263		0				
B(C$_6$F$_5$)$_4^-$	3233		30	2405	1.344	3241	8
CMeB$_{11}$F$_{11}^-$	3219		44				
PF$_6^-$	3191		72	2375	1.343	3219	28
AsF$_6^-$	3190		73	2376	1.343	3219	29
SbF$_6^-$	3175		88	2364	1.343	3201	26
CHB$_{11}$Cl$_{11}^{-\ b}$	3163		100	2362	1.339	3180	17
CHB$_{11}$Me$_{11}^-$	3155		108			3175	20
CHB$_{11}$H$_5$Cl$_6^{-\ b}$	3148		115	2350	1.340	3158	10
Co^{III}(C$_2$B$_9$H$_8$Cl$_3$)$_2^-$	3145		118	2342	1.343	3162	17
CHB$_{11}$Me$_5$Cl$_6^{-\ b}$	3143		120	2346	1.340	3150	7
CHB$_{11}$(2-F)H$_{10}^-$	3143		120			3152	9
[N(SO$_2$CF$_3$)$_2$]$_2^{-\ b}$	3141		122			3141	0
CHB$_{11}$Br$_{11}^-$	3140		123			3150	10
CFB$_{11}$H$_{11}^-$	3136		127			3148	12
BF$_4^-$	3133		130	2340	1.339	3156	23
CHB$_{11}$H$_{11}^-$	3129		134	2336	1.339	3149	20
GaCl$_4^-$	3126		137				
CHB$_{11}$H$_5$Br$_6^{-\ b}$	3125		138	2332	1.340	3135	10
CHB$_{11}$Me$_5$Br$_6^{-\ b}$	3120		143	2329	1.340	3128	8
CHB$_{11}$I$_{11}^{-\ b}$	3118^d		145^d			3113	-5^d
FeCl$_4^-$	3117		146				
CHB$_{11}$H$_5$I$_6^{-\ b}$	3097		166	2316	1.337	3106	9
C$_5$(CN)$_5^{-\ b}$	3097		166	2307	1.342	3105	8
CHB$_{11}$Me$_5$I$_6^{-\ b}$	3091		172	2313	1.336	3100	9
N(SO$_2$CF$_3$)$_2^{-\ b}$	3086		177	2306	1.338		f
C$_5$H(CN)$_4^-$	3054		209	2288	1.335	3070	16
ClO$_4^{-\ b}$	3050, 2801	3049	214^e	2282		3098	48
FSO$_3^{-\ b}$	3040, 2806	2953	310^e	2211		3045	92
(HSO$_4$)$_2^{2-\ b}$	3021, 2660	2942 $\pm$ 7	321^e	2202 $\pm$ 5		3080	138
CF$_3$SO$_3^{-\ b}$	3031, 2801	2939	324^e	2200		3056, 2815	14$-$25
ReO$_4^{-\ b}$	2984, 2730	2863	400^e	2143		3007, 2760	23$-$30
NO$_3^{-\ b}$	2451		812			2571	120
(C$_8$H$_{17}$O)$_2$PO$_2^{-\ c}$	2427		836				
Cl$^{-\ b}$	2330		933			2452 asym	122

^{a} Value in solvent-separated ion pair with CMeB$_{11}$F$_{11}^-$. ^{b} Anions whose conjugate acids are known. ^{c} Data from: Stoyanov, E. S.; Popov, V. M.; Mikhailov, V. A. *Zh. Prikl. Spectrosk.* **1984**, *40*, 235$-$238. ^{d} Because of low solubility in CCl$_4$, the data are given for CH$_2$Cl$_2$ solutions. ^{e} Calculated from νND frequencies. ^{f} Monomer value unavailable because solid phase is aggregated.

Table 2. νNH Frequencies (cm^{-1} $\pm$ 1) for Those Octyl$_3$NH$^+$A$^-$ Salts That Form Solvent-Separated Ion Pairs in 1,2-Dichloroethane at 0.01$-$0.005 M

	CCl$_4$	1,2-dichloroethane^b	
	νNH contact ion pair	νNH contact ion pair	νNH solvent-separated ion pair
anion			
B(C$_6$F$_5$)$_4^-$	3233	3233 w	3178 s
AsF$_6^-$	3190		3184 asym
CHB$_{11}$Cl$_{11}^-$	3163		3178 asym
CHB$_{11}$H$_5$Cl$_6^-$	3148		3180
Co^{III}(C$_2$B$_9$H$_8$Cl$_3$)$_2^-$	3145	3161	3180
CHB$_{11}$H$_{11}^-$	3129	3135	3178 vw
CHB$_{11}$H$_5$Br$_6^-$	3125	3130	3179
CHB$_{11}$Me$_5$Br$_6^-$	3120	3121	3179
CHB$_{11}$I$_{11}^-$	3118^a	3113 vw	3177
CHB$_{11}$H$_5$I$_6^-$	3097	3105	3178
C$_5$(CN)$_5^-$	3097	3076	3178 w

^{a} In dichloromethane. ^{b} asym = asymmetric; s = strong; w = weak; vw = very weak.

almost no evidence that fluoroanions can be protonated.[45] Although HBF$_4$, HPF$_6$, etc. are commonly written in their acid forms, their actual formulation involves protonated HF or aqueous acid. Anhydrous "HBF$_4$" is a mixture of [H(HF)$_x$]$^+$-[BF$_4\cdot n$BF$_3$]$^-$ ions because HBF$_4$ is unstable with respect to HF

(45) Culmann, J. C.; Fauconet, M.; Jost, R.; Sommer, J. *New J. Chem.* **1999**, *23*, 863$-$867.

and BF$_3$. As a class, carborane acids all rank higher on the νNH scale than oxyanions. This is consistent with the finding that carborane acids protonate benzene in dilute solution, whereas oxyacids (dilute or neat) do not.[19] These general observations suggest that the νNH scale largely reflects intrinsic anion basicity.

To understand trends in the νNH scale in more detail, it is useful to consider the factors that affect anion basicity, primarily electrostatics and polarizability. All other effects being equal, the larger the anion, the lower will be its basicity. This is fundamentally an electrostatic argument. On the other hand, the more polarizable the anion, the higher will be its basicity. Thus, fluoroanions are generally weaker bases than oxyanions because F is less polarizable than O. The interplay of these factors can be seen in a number of trends in Table 1. The B(C$_6$F$_5$)$_4^-$ anion ranks highest on the νNH scale because it combines large size with very low polarizability. Neither the overall negative charge (formally localized at the B atom) nor the F atoms in the C$-$F bonds (the likely H-bond donor atoms) are particularly polarizable.

Within isostructural series of halogenated carborane anions, the νNH order is always F > Cl > Br > I. This indicates that the polarizability of the anion donor atom is more important than the overall size of the anion. For example, among the hexahalo anions of type CHB$_{11}$H$_5$X$_6^-$ (X = Cl, Br, I), the hexachloro anion is highest on the scale and the $\Delta\nu$NH interval

to the hexabromo is 23 cm^{-1}. That between the hexabromo and hexaiodo anions is 28 cm^{-1}. The same ordering is true for the undecahalo anions CHB$_{11}$X$_{11}^-$ (X = Cl, Br, I), and the analogous intervals are 23 and 22 cm^{-1}, respectively. Data are available for the nearly homologous undecafluoro anion having a methyl group at the 1-position, and its νNH value is 56 cm^{-1} higher than that of the undecachloro derivative. The effect of the methyl group relative to an H atom at the 1-position (i.e., the C atom) is expected to be no more than a few wavenumbers. The 1-monofluoro CFB$_{11}$H$_{11}^-$ anion has νNH 7 cm^{-1} higher than the all-hydrido CHB$_{11}$H$_{11}^-$ anion. Placing five methyl groups in the 2−6-positions of the hexahalo carboranes, giving CHB$_{11}$Me$_5$X$_6^-$ (X = Cl, Br, I), decreases Δν values relative to those of CHB$_{11}$H$_5$X$_6^-$ by 5 or 6 cm^{-1} in each case. This consistency illustrates that the scale is sensitive to small changes in anion structure within a structural class. Contrary to conventional organic chemistry, methyl groups are believed to be electron withdrawing in carboranes, at least in the neutral C$_2$B$_{10}$R$_{12}$ system.[46] Nevertheless, the νNH scale suggests that replacement of B−H bonds by B−Me bonds in the anionic CHB$_{11}$H$_5$X$_6^-$ system makes the anion surface more electron rich.

The low basicity of carborane anions has recently been treated theoretically in an attempt to rationalize the superacidity of their conjugate acids.[29] In general, the lowest basicity correlates with the minimum molecular electrostatic potential (MESP) calculated on the zero-flux surface. This indicator of surface charge density suggests an increasing basicity order CHB$_{11}$Cl$_{11}^-$ < CHB$_{11}$H$_5$Br$_6^-$ < CHB$_{11}$H$_5$Cl$_6^-$ < CHB$_{11}$Me$_5$Cl$_6^-$ < CHB$_{11}$F$_{11}^-$ that differs from that of the νNH scale: CMeB$_{11}$F$_{11}^-$ < CHB$_{11}$Cl$_{11}^-$ < CHB$_{11}$H$_5$Cl$_6^-$ < CHB$_{11}$Me$_5$Cl$_6^-$ < CHB$_{11}$H$_5$Br$_6^-$. The differences arise from the interplay of surface charge density, size, and polarizability, whose interrelationships are not presently understood. Interestingly, the νNH scale predicts that H(CMeB$_{11}$F$_{11}$) will be a stronger acid than H(CHB$_{11}$Cl$_{11}$), whereas the MESP method suggests the reverse. Fluorinated carborane acids have yet to be synthesized. The νNH scale is presently the only experimental indicator of basicity of carborane anions, because the acidity of their conjugate acids is leveled in SO$_2$ solution, the lowest basicity solvent suitable for such measurements.[17]

In the case of more traditional complex fluoroanions, the tradeoff between electrostatics and polarizability is more subtle. If size were the only factor and the F atoms forming the H-bonds all had the same polarizability, one would expect basicities to increase with decreasing size: SbF$_6^-$ < AsF$_6^-$ < PF$_6^-$ < BF$_4^-$. Experimentally, the νNH order is PF$_6^-$ ≈ AsF$_6^-$ < SbF$_6^-$ < BF$_4^-$, although the differences between the three octahedral ions are small. Subtleties in the nature of the element−fluorine bonding apparently act to counter the effect of size, making the F atoms attached to Sb slightly better H-bond acceptors than F atoms attached to P or As. In the corresponding bulk acids, so-called HSbF$_6$ is the strongest of the fluoroacids, suggesting subtle differences in the H-bonding of monomer versus bulk.

Polarizability effects can be local or global. The influence of charge polarizability within an anion is visible in the νNH rankings. For example, easily polarizable anions such as C$_5$(CN)$_5^-$ and C$_5$H(CN)$_4^-$ are quite strong H-bond acceptors.

(46) Teixidor, F.; Barberà, G.; Vaca, A.; Kivekäs, R.; Sillanpää, R.; Oliva, J.; Viñas, C. *J. Am. Chem. Soc.* **2005**, *127*, 10158−10159.

The easily polarizable N(SO$_2$CF$_3$)$_2^-$ anion is informative because of the dimerization which decreases its acceptor strength (Δν = 55 cm^{-1} between monomer and dimer). Dipole/dipole compensation within the larger anion leads to lower basicity. The HSO$_4^-$ ion exists only in dimeric form. The monomeric anion, unobtainable under the present conditions, is expected to have a higher basicity and a lower νNH value.

Solvent-separated ion pairs formed only with large anions having low overall charge polarizability. This is consistent with SSIP formation being dependent on two main factors: the solvation energy and the surface charge density of the anion. In the nonpolar "inert" CCl$_4$ solvent, only one salt showed an SSIP, namely CMeB$_{11}$F$_{11}^-$, the carborane having the weakest H-bonding interaction with the cation. In DCE, however, the ability of the solvent to separate ion pairs was observed with all carborane anions. The largest carborane anion, CHB$_{11}$I$_{11}^-$, formed almost entirely SSIPs in DCE with an insignificant portion of the contact ion pair. The CHB$_{11}$Br$_{11}^-$ ion formed only SSIPs, even though the νNH scale in CCl$_4$ indicates it forms one of the stronger H-bonds. This shows that cation/anion binding strengths do not correlate with H-bond strengths. Other anions that develop SSIPs include the large-volume anions B(C$_6$F$_5$)$_4^-$ and C$_5$(CN)$_5^-$. Solvent separation depends more on the volume and dimensions of the anion than on its ability to form an H-bond because of the importance of solvation energies to the stability of contact ion pairs. These observations show that the degree of ion separation in an "active" solvent such as DCE cannot serve as an indicator of anion basicity.

It is significant that the rank order of anions is essentially the same in solution as in the solid state (Table 1, last column). Despite the opportunity for crystal packing effects to reorient or distort the H-bonding interaction of NH groups with the anions, the same qualitative H-bond-accepting ability of anions is reported in the νNH frequencies. This indicates that νNH is reporting an intrinsic property of the anion, i.e., the local basicity of the anion as sought by the cationic N−H moiety.

The νNH values in the solid state are always higher than those in solution. This must reflect differences in the relative importance of the field effect (i.e., solvent dielectric) versus specific solvation effects of the ion pair in solution. The field effect is a decrease in the internal electrostatic interaction in the octyl$_3$NH$^+$- - -A$^-$ contact ion pairs when they are surrounded by similar polar ion pairs in the solid state. Compared to CCl$_4$ solution, they are in a more polar environment. A similar positive shift in νNH frequencies is seen when data obtained in CCl$_4$ are compared to those obtained in the more polar solvent DCE.

A possible concern in determining νNH rankings is the presence of the octyl groups in the cation. In theory, they are long enough to wrap around the cation and influence the binding of the anion to the N−H group. To check this possibility experimentally, the IR spectra of octyl side chains were compared to those of shorter butyl side chains in the octyl$_3$-NH$^+$ and butyl$_3$NH$^+$ salts of the CHB$_{11}$I$_{11}^-$ ion, which, possibly because it is so large, appeared to be the most sensitive to this substitution compared to other anions. The IR spectra of DCE solutions of both salts coincide and show two νNH bands: one intense band at 3173 cm^{-1} due to the SSIP and a second very weak band at 3118 cm^{-1} due to the contact ion pair (Figure 2). This indicates that the length of the side chain is not a factor
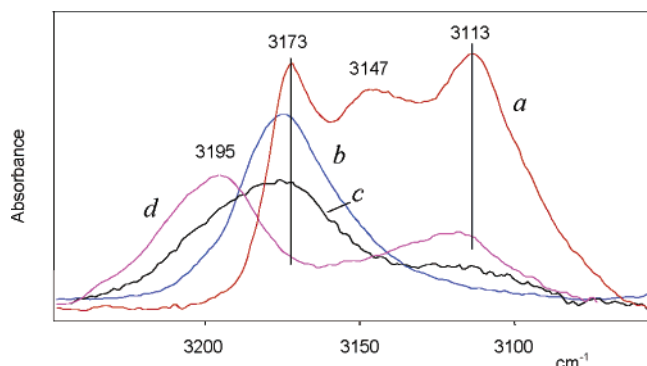
Figure 2. IR spectra of Bu₃NH[CHB₁₁I₁₁]: (a) solid amorphous, (b) solid crystal, (c) DCE solution, and (d) dichloromethane solution.
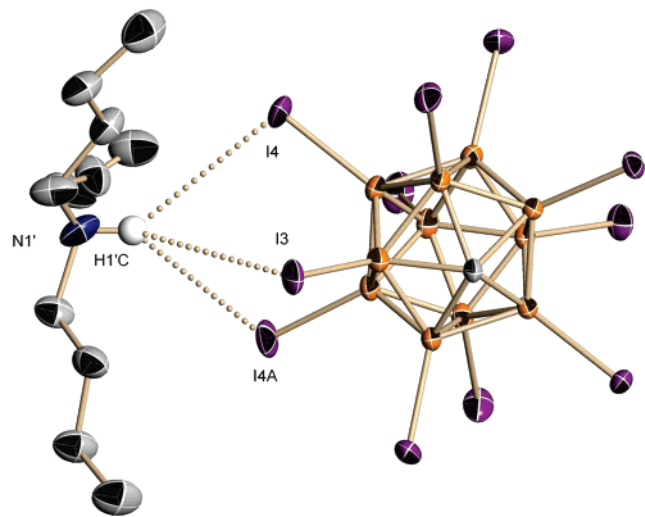
Figure 3. Perspective view of the cation−anion interaction in the X-ray structure of Butyl₃NH⁺[CHB₁₁I₁₁]⁻. Thermal ellipsoids are shown at the 50% probability level.

Figure 4. Plot of available experimental gas-phase acidity data ($\Delta G°$) versus $\Delta\nu$NH ($y = 0.0472x + 282$; $R = 0.961$). Points: 1, $(CF_3SO_2)_2NH$; 2, $HClO_4$; 3, FSO_3H; 4, H_2SO_4; 5, CF_3SO_3H; 6, HNO_3; and 7, HCl.

that influences the νNH scale. Nevertheless, we explored the sensitivity of νNH in the solid state to gain a deeper insight.

In the spectrum of the amorphous solid butyl₃NH⁺[CHB₁₁I₁₁]⁻ salt, obtained by rapid evaporation of DCE solution, the band of the contact ion pair increased as expected. Surprisingly, however, since the solvent had been removed, some of the νNH band at 3173 cm⁻¹ ascribed to a SSIP remained present. In addition, a third band with intermediate frequency at 3147 cm⁻¹ appeared (Figure 2). For *crystalline* butyl₃NH⁺[CHB₁₁I₁₁]⁻ salt, obtained by *slow* solvent evaporation, the IR spectrum showed only one band at 3173 cm⁻¹, i.e., at the same frequency as the SSIP in DCE (Figure 2). X-ray analysis of the crystal phase showed the absence of solvent and only weak association of cation and anion. The N−H bond of the cation is directed toward the center of a triangle of three iodine atoms from the CHB₁₁I₁₁⁻ anion (Figure 3), and the long H···I distances (3.469, 3.704, and 3.383 Å) preclude the possibility of significant H-bonding. This "trifurcated" interaction is electrostatic in nature, and its strength is coincidentally the same as in the SSIP in DCE, giving rise to accidentally identical νNH stretching frequencies at 3173 cm⁻¹. This is confirmed by the spectrum of butyl₃NH⁺-[CHB₁₁I₁₁]⁻ in dichloromethane solution (Figure 2). Two νNH bands are observed: one from the contact ion pair with unchanged frequency at 3118 cm⁻¹ and the second from an SSIP with blue-shifted frequency at 3195 cm⁻¹. The higher frequency of the SSIP in dichloromethane relative to that in DCE reflects
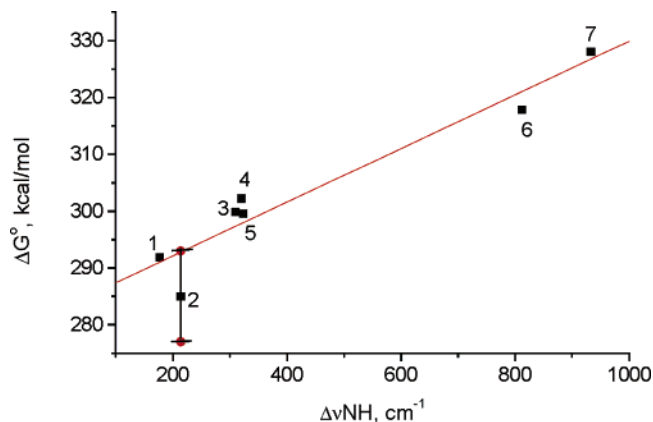
the lower solvent basicity of this solvent. The appearance of the third, intermediate frequency band at 3147 cm⁻¹ in amorphous solid butyl₃NH⁺[CHB₁₁I₁₁]⁻ is ascribed to a weak, possibly bifurcated, contact ion pair with a structure intermediate between that of the dominant contact ion pair and the trifurcated electrostatic interaction. In the longer side chain octyl analogue, only the electrostatic interaction is observed in the amorphous solid state (νNH 3173 cm⁻¹). Thus, chain lengthening in R₃-NH⁺ from butyl to octyl favors the formation of electrostatic ion pairs in the amorphous solid state but *not* in solution. νNH frequencies for contact ion pairs are indistinguishable between phases, and hence, the length of the aliphatic chain does not influence the νNH measurement.

Individual Molecule Acidity. Inasmuch as νNH reflects anion basicity, the νNH scale reflects the acidity of the conjugate acid. This acid strength indicator differs from traditional measures of acidity in that it reflects the acidity of an individual molecule of acid rather than an H-bonded aggregate typical of bulk acids. From this point of view, it is conceptually closer to gas-phase acidity, since gas-phase acidities are determined on an individual molecule basis.

Nevertheless, the νNH scale and gas-phase acidity are conceptually distinct. In the condensed-phase R₃NH⁺···A⁻ ion pair, the interaction of the proton with the anion is weak, causing only a small change in the charge distribution and symmetry of the anion. Thus, the νNH frequency reports the basicity of an anion only slightly perturbed by the proton electric field. By contrast, the binding of a naked proton to an anion in the gas phase causes a much larger change in the charge distribution and symmetry of the anion. As a result, correlations between the νNH scale and gas-phase acidity may be expected for a series of anions having similar polarizability. For "hard" low-polarizable anions such as halogenated carboranes, the slope of the plot of $\Delta G°$ as a function of $\Delta\nu$NH should be small. Since $\Delta G°$ is more dependent on the "softness" and polarizability of anions, the slope should increase as polarizability increases.

As shown in Figure 4, there is a reasonably good linear correlation ($R = 0.961$) of gas-phase acidity data ($\Delta G°$)[14] with $\Delta\nu$NH for available experimental data (mostly oxyanions). Error limits for the $\Delta G°$ data are small (a few tenths of a kilocalorie per mole), except for $HClO_4$ (285 ± 8 kcal/mol), which happens to be the most outlying datum point (2). The H_2SO_4 datum point (no. 4) uses $\Delta\nu$NH for the dimerized anion, $(HSO_4)_2{}^{2-}$, because

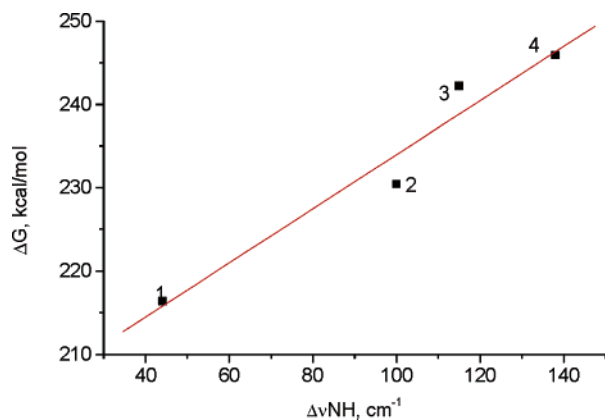**Figure 5.** Plot of calculated gas-phase acidity data ($\Delta G°$) versus $\Delta\nu$NH ($y = 0.325x + 201.5$; R = 0.977). Points: **1**, $CRB_{11}F_{11}^{-}$ (R = Me for $\Delta\nu$NH, H for ΔG); **2**, $CHB_{11}Cl_{11}^{-}$; **3**, $CHB_{11}H_5Cl_6^{-}$; **4**, $CHB_{11}H_5Br_6^{-}$.

Table 3. νNH Frequencies for $Oct_3NH^+A^-(HA)_n$ Salts with Complex Anions in 0.1 M CCl_4 Solutions

anion	νNH	$\Delta\nu$
Cl^-	2330	933
$ClHCl^-$	2632	631
$Cl^-(HCl)_2$	2740	523
$(HSO_4)_2^-$	2942	321
$HSO_4^-(H_2SO_4)_{4.5}$	3174	89

the value for monomeric HSO_4^- is unobtainable. Any reasonable estimate for HSO_4^- (e.g., compare other oxyanions in Table 1) would increase $\Delta\nu$NH by 50–100 cm^{-1}, moving point no. 4 closer to the linear regression line.

Because carborane acids are poorly volatile, air-sensitive solids, their experimental gas-phase acidities have not yet been measured. However, since calculated gas-phase acidities are generally reliable, we can plot calculated $\Delta G°$ data versus $\Delta\nu$NH for carborane anions. To give greater confidence, calculated $\Delta G°$ values were obtained at a higher level of theory than previously available.[13] At the B3LYP/6-311+G(d,p) level, DFT-calculated $\Delta G°$ values for four halogenated carborane acids show a good correlation with $\Delta\nu$NH (Figure 5). The R factor is 0.977 and, as expected for anions less polarizable than oxyanions, the slope is much smaller than in Figure 4.

The correlations in Figures 4 and 5 support the notion that the νNH scale reflects individual molecule or "intrinsic" condensed-phase acidity. When a strong acid is solvated in the solution phase, the stronger the Solv$\cdots$H$-$A interaction, the further HA is removed from the gas-phase state. When the solvation is strong enough to cause proton transfer to the solvent molecule with contact ion pair formation (i.e., the acid ionizes), the acid approaches a state like that in the $R_3NH^+\cdots A^-$ ion pair used in the νNH scale. This is why the νNH scale better matches the expression of strong acidity of solvated acids in condensed media. From this point of view, the νNH scale has higher practical importance for solution chemistry than the gas-phase acidity scale.

Acid Strength Trends and Self-Association. A plot of νNH versus Hammett acidity function values (H_0) for bulk acids produces no correlation (R = 0.54). These data included only fluoroacids and oxyacids since, at present, there is no reliable way to measure H_0 values for solid carborane acids. The reason behind this lack of correlation is aggregation. In bulk (and even dilute) acids, HA molecules bind consecutively with anions, forming linear associates $A(HA)_n^-$ of increasing size and decreasing basicity with increasing n. The formation of these complex anions may be the origin of superacidity in certain acids. Reflecting the decreasing basicity of anions with increasing HA complexation, the νNH shift for Cl^- at 2330 cm^{-1} increases dramatically to 2632 cm^{-1} for the $ClHCl^-$ ion, and then to 2740 cm^{-1} for the $Cl(HCl)_2^-$ ion. Thus, the strength of

their conjugate acids (if they exist) is expected to increase HA < H(AHA) < H[A(HA)$_n$] ($n \geq 2$).

Another example of the complexation of an acid to its conjugate base is nitric acid. Attaching a HNO_3 molecule to a NO_3^- anion strongly decreases its basicity: the resulting $(NO_3HNO_3)^-$ anion has a base strength comparable with that of $CF_3SO_3^-$.[11] The formation of $H_3O^+[NO_3\cdot(HNO_3)_3]$ species in highly concentrated nitric acid was determined by Raman spectroscopy.[47] Species with similar structure are retained in tributyl phosphate extracts. Along with the H-bonded TBP- - -HNO_3 monosolvate, ionized acid in the form $TBP\cdot H_3O^+$-$(H_2O)_2[NO_3\cdot(HNO_3)_n]^-$, where $n = 1$–3, is produced.[48] The $\nu(P{=}O)_{TBP}$ frequency decreases with increasing n in a manner conceptually similar to the decrease in νNH with decreasing anion basicity. Thus, acidity strongly increases with increasing values of n in complex acid/anion aggregates. By contrast, the protons actually involved in $[A(HA)_n]^-$ complex anion formation have lowered acidity relative to individual HA molecules, as shown below with examples of cyclic dimerization.

Similarly behavior is observed with H_2SO_4. At a 1:1 molar ratio with trioctylamine, the $(Oct_3NH^+)_2(HSO_4)_2$ salt is formed, having strongly H-bonded dimers of the bisulfate ion. The
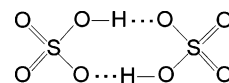

protons in this anion are so weakly acidic that the interaction with excess trioctylamine is insignificant. Nevertheless, when equilibrated with 100% sulfuric acid in benzene solution, the dimeric anion binds additional H_2SO_4 molecules, forming an acid of average formula $(Oct_3NH^+)[HSO_4(H_2SO_4)_n]^-$, with $n = 4.5$. The νNH frequency of this salt is much higher than that with the bisulfate ion (Table 3) and corresponds to dramatically increased acidity in the conjugate acid, which exceeds those for all carborane acids (Table 1). Thus, the superacidity of neat sulfuric acid, in which molecules are self-associated, can be understood in terms of a small fraction of the protons possessing a high acidity at the expense of most of the others. This peculiarity of neat liquid H_2SO_4 excludes its use as a reference point for evaluation of superacidity strength on an individual molecule basis.

In the case of self-association of liquid-phase acids, where only cyclic dimers form, such as with carboxylic and dialkyl phosphoric/phosphinic acids,[8] there is no increase in acidity due to aggregation. The fraction of free, ionizable OH groups becomes insignificant, and practically all protons are trapped at lower acidity relative to the monomer. Even in pure

(47) Pham, T. M.; Herzog-Cance, M.; Potier, A.; Potier, J. *J. Raman Spectrosc.* **1981**, *11*, 96–107.
(48) Stoyanov, E. S.; Mikhailov, V. A.; Chekmarev, A. M.; Chizhevskaya, S. V. *Zh. Neorg. Khim.* **1990**, *35*, 1451–1459; *Chem. Abstr.* **1990**, *113*, 104213q.

trioctylamine solution, we find that acetic acid shows IR spectra mainly due to (AcOH)$_2$ dimers. Dialkyl phosphoric acids, whose monomers are even stronger than acetic acid monomers and comparable to nitric acid on the νNH scale, form such strong dimers that they act as bases, not acids, toward water molecules. Water is the H-bond donor to the acid rather than vice versa.[9]
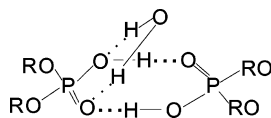
This insight into the effect of aggregation in acids allows us to understand why the conjugate acid of the C$_5$(CN)$_5^-$ anion is not a condensed-phase superacid. Gas-phase acidity,[49,50] the νNH scale, and the observation that this anion cannot be protonated by perchloric acid[51] all suggested that H(C$_5$(CN)$_5$) could be a superacid. However, once this acid was finally prepared,[40] it was deduced to have an insoluble polymeric (or possibly dimeric[50]) structure (in arenes, diethyl ether) which for all practical purposes does have not have a free, ionizable CN$-$H group. This annuls potential superacidity of the monomeric acid. Only bases of moderate strength, such as acetonitrile or tetrahydrofuran, dissolve the acid but, in doing so, form proton disolvates and level the acidity down to values well below those of a superacid.

Like H(C$_5$(CN)$_5$), carborane acids are polymeric in the solid state.[52] Nevertheless, they express superacidity by protonating solvents as weakly basic as benzene.[19] This illustrates just how strong they are as acids. They are presumably even stronger acids in the gas phase because they have a monomeric structure.[52]

Conjugate Base Stability. Table 1 suggests that the conjugate acid of the perfluorinated tetraphenylborate ion, H[B(C$_6$F$_5$)$_4$], could be a very strong acid. However, it is unattainable. The anion is unstable with respect to B$-$phenyl bond cleavage under strongly Brønsted acid conditions.[19] According to the νNH scale, the next strongest acids should be HPF$_6$, HAsF$_6$, and HSbF$_6$, derived from fluoroanions, but again, except for recent evidence for the formation of some HSbF$_6$ in HF/SbF$_5$ mixtures,[45] these too are nonexistent acids. Indeed, all fluoroanion-based acids are unstable with respect to HF and the corresponding neutral Lewis acid (PF$_5$, SbF$_5$, BF$_3$, etc.).

Of the anions whose conjugate acids are isolable (designated with the letter *b* in Table 1), the carborane-based acids are the strongest on the νNH scale, and on the mesityl oxide scale in

dilute solution.[17] They outrank the well-known superacidic oxyacids such as H$_2$SO$_4$, HClO$_4$, CF$_3$SO$_3$H, and FSO$_3$H, as well as the strong imido-based acid HN(SO$_2$CF$_3$)$_2$. These observations indicate that the present upper bound of Brønsted acid strength (in the absence of added Lewis acids) depends as much on chemical stability of the anion as on low basicity. Many anions appear to have the requisite low basicity to form conjugate acids of extremely high acidity but lack the intrinsic chemical stability to sustain it. Carborane anions not only have low basicity because of their large size, delocalized charge, low polarizability, and weakly basic halogen substituents, but they also have exceptional chemical inertness.[53] This arises from a unique feature of boron chemistry: σ aromaticity in the delocalized bonding of the CB$_{11}$ icosahedral cage, making it extraordinarily resistant to disruption.

Conclusion

The νNH scale for weakly basic anions is a useful guide to conjugate acid strength on an individual molecule or "intrinsic" basis in condensed media, providing a better point of departure than gas-phase acidities for discussing acidity in bulk. By focusing attention on the relative acidity of individual molecules in condensed media, the effects of aggregation and H-bonding on acid strength become more apparent and interpretable. The scale correctly shows that carborane acids are stronger than oxyacids or fluoroacids and predicts that fluorinated carboranes will give rise to even stronger acids than those presently known.

While the present ideas have been developed for weak anionic bases, there are indications that similar IR scales can be developed for weak neutral bases. For example, νOH stretching of dissolved hydronium ions, [H$_3$O·3Solvent]$^+$, reflect the solvent basicity order: CCl$_4$ < dichloromethane < benzene $\sim$ 1,2-dichloroethane $\ll$ H$_2$O.[43,54]

Supporting Information Available: Details of theX-ray crystal structure determination of [C$_{12}$H$_{28}$N]$^+$[CHB$_{11}$I$_{11}$]$^-$·2C$_6$H$_6$ and atomic coordinates of the DFT-calculated structures of carborane acids and anions used in Figure 5. This material is available free of charge via the Internet at http://pubs.acs.org.

JA060714V

(49) Vianello, R.; Liebman, J. F.; Maksic, Z. B. *Chem.-Eur. J.* **2004**, *10*, 5751–5760.
(50) Lord, R. L.; Wheeler, S. E.; Schaefer, H. F., III. *J. Phys. Chem. A* **2005**, *109*, 10084–10091.
(51) Webster, O. W. *J. Am. Chem. Soc.* **1966**, *88*, 4055–4060.
(52) Stoyanov, E. S.; Hoffmann, S. P.; Juhasz, M.; Reed C. A. *J. Am. Chem. Soc.* **2006**, *128*, 3160–3161.

(53) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 133–139.
(54) Stoyanov, E. S.; Kim K.-C.; Reed C. A. *J. Am. Chem. Soc.* **2006**, *128*, 1948–1958.