Can Changes in One-bond Spin−spin Coupling Constants in Acids Be Related to Gas-Phase Proton Affinities of Bases?

Janet E. Del Bene*,† **and José Elguero**‡

Department of Chemistry, Youngstown State University, Youngstown, Ohio 44555, and Instituto de Química Médica, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain

Received: March 17, 2007; In Final Form: May 2, 2007

Ab initio EOM-CCSD calculations have been carried out in search of acids with one-bond spin−spin coupling constants which could serve as probes of molecular basicity upon complex formation. Only ^{1}J(F−H) and ^{1}J(B−Li) in complexes F−H···Y and H_2B−Li···Y, respectively, are able to differentiate among the protonation energies of bases containing Y. Changes in ^{1}J(F−H) upon complex formation are related to the protonation energies of bases, but only when these energies are about 200 kcal/mol or greater. On the other hand, changes in ^{1}J(B−Li) upon complexation are related to base protonation energies in the range between 100 and about 190 kcal/mol. Thus, these two one-bond coupling constants ^{1}J(F−H) and ^{1}J(B−Li) are complementary probes. For the first time, the computed NMR property of a gas-phase one-bond spin−spin coupling constant has been related to the experimental gas-phase thermodynamic property of proton affinity.

Introduction

The overhelming majority of NMR studies of molecules have been conducted in condensed phases, usually in solution, but recently also in the solid state. Gas-phase NMR studies have been limited for the most part to simple, isolated, volatile molecules.[1,2] Very few gas-phase NMR studies of hydrogen-bonded complexes have been reported,[3] in contrast to the numerous studies based on microwave spectroscopy.[4] On the other hand, studies of the dependence of NMR parameters, both chemical shifts and coupling constants, on solvent bulk properties are very common.[5−7]

In two recent papers,[8,9] we noted apparent discrepancies between experimental B−Li coupling constants, B−Li bond distances, and B chemical shifts for a boryllithium molecule and the computed values of these properties for models of this molecule. We attributed these differences to an underestimation of the ion-pair character of the B−Li bond in the gas-phase molecule relative to that bond in the crystal with DME or in solution with THF. We were able to demonstrate the dramatic effect of the solvent on these properties as a function of the degree of solvation of Li and the basicity of the solvent.

The results of these two studies led us to ask whether a one-bond coupling constant could be generally useful as a probe of molecular basicity, as measured by protonation energy or proton affinity. To answer that question, we examined one-bond coupling constants for a large number of possible acid probes interacting with a set of bases. In the present paper, we present the criteria used to evaluate the suitability of acid probes, and we identify those probes that exhibit changes in one-bond spin−spin coupling constants, which might be indicators of molecular basicity.

Methods

The structures of all complexes in which the acid is an X−H donor for hydrogen bond formation were optimized at second-order Møller−Plesset perturbation theory (MP2)[10−13] with the 6-31+G(d,p) basis set,[14−17] under the constraint that the X−H···Y hydrogen bond be linear. Although the equilibrium structures of the majority of these complexes are stabilized by linear hydrogen bonds, hydrogen bonds in some of the remaining complexes deviate slightly (within 10°) from linearity. The impact of the linearity constraint on coupling constants will be assessed below.

Since our previous studies of ^{11}B−^{7}Li coupling constants had been carried out using optimized MP2/6-311++G(d,p)[18] geometries, we optimized additional complexes in which H_2B−Li is the Lewis acid at that same level of theory. These optimizations were done under the constraint of a linear B−Li···Y arrangement, where *Y* is the atom which is the interaction site in the base. A second optimization constraint required the Li atom to sit along the dipole moment vector of the base. Although some of the complexes optimized under these two constraints are equilibrium structures, some are not. These constraints do not unduly bias the computed results, as will be demonstrated below.

One-bond spin−spin coupling constants for complexes in which the acid probe is an X-^{1}H donor ($X = {}^{13}$C, ^{15}N, ^{17}O, ^{19}F, ^{31}P) or a ^{11}B−^{7}Li donor, were computed using the equation-of-motion coupled cluster singles and doubles (EOM-CCSD) method in the CI(configuration interaction)-like approximation[19−22] with all electrons correlated. The Ahlrichs[23] qzp basis set was placed on C, N, O, and F atoms and the qz2p basis on P and the hydrogen-bonded H atom. The Dunning cc-pVDZ basis[24,25] was placed on all other hydrogens. The recently developed hybrid basis sets were used for B and Li.[8,9,26] In the nonrelativistic approximation, the total coupling constant (*J*) is a sum of four contributions: the paramagnetic spin−orbit (PSO), diamagnetic spin−orbit (DSO), Fermi-contact (FC), and spin-dipole (SD).[27] For hydrogen-bonded complexes with F−H as the donor, the calculation of all terms is not feasible for some of the complexes, so the sum of the FC and PSO terms for ^{19}F−^{1}H coupling has been used to approximate ^{1}J(F−H). For complexes with ^{11}B−^{7}Li as the acid probe, the FC term has

---

* Corresponding author. E-mail: jedelbene@ysu.edu.

† Department of Chemistry, Youngstown State University.

‡ Instituto de Química Médica, CSIC.

10.1021/jp072145z CCC: $37.00

been used to approximate ^1J(B−Li). The validity of these approximations will be examined below. Geometry optimizations were carried out using the *Gaussian 03* suite of programs,[28] and coupling constants were evaluated using *ACES II*.[29] All calculations were performed on the Cray X1 or the Itanium Cluster at the Ohio Supercomputer Center.

Results and Discussion

Identification of Suitable Acid Probes. What characteristics of a one-bond coupling constant of an acid would make it a good probe of molecular basicity? It is reasonable to suggest that a useful acid probe should have the following properties.

1. The acid must act as a relatively strong neutral donor. Although cations can be strong X−H donors, these have not been considered because of the possibility of proton transfer.

2. The coupling constant probe must be able to differentiate base strength over a significant range of protonation energies (proton affinities).

3. The acid must be a simple molecule so that coupling constant calculations are feasible for a relatively large set of complexes with a variety of bases.

Finally, it is desirable that the coupling constant which serves as the acid probe is one which, at least in principle, could be easily measured experimentally.

Hydrogen cyanide, N≡C−H, as a C−H donor has been examined as a possible acid probe, but it was eliminated because changes in ^1J(C−H) do not adequately differentiate base strength. For example, the difference between the C−H coupling constant in N≡C−H···NCH and N≡C−H..pyridine is only 2.5 Hz,[30] although the difference in the protonation energies of the two bases is 55 kcal/mol. Similarly acetylene, H−C≡C−H, has been eliminated because of lack of sensitivity to base strength. For example, ^1J(C−H) for H−C≡C−H is 242.5 Hz, and increases only slightly to 248.6 Hz for the complex H−C≡C−H···NH_3. However, it is important to note that this small increase in ^1J(C−H) upon interaction with NH_3 is consistent with experimental values of ^1J(C−H) in the gas-phase (242.69 Hz) and in acetone at 300 K (248.3 Hz), as reported by Jackowski.[2]

Other acids that are C−H donors have been eliminated on the basis of criteria 2 and 3 together. Acids that are O−H and Cl−H donors were not considered because of quadrupole broadening of the corresponding NMR signals needed to measure ^1J. When a molecule such at phosphine, PH_3, acts as a P−H donor, ^1J(P−H) often increases significantly relative to the isolated monomer, but differences in ^1J(P−H) do not discriminate among protonation energies. Thus, the difference in ^1J(P−H) in complexes with PH_3 as the proton donor to the bases NCH and NH_3 is only 6 Hz, although the protonation energies of these two bases differ by 40 kcal/mol. Hence, P−H donor molecules have been eliminated. Only acids that are N−H or F−H donors for hydrogen bond formation, or a Lewis acid that is a B−Li donor, remain.

The simplest and a relatively good N−H donor for hydrogen bonding is hydrogen isocyanide, C≡N−H, which has an N−H coupling constant that should be experimentally measurable. Moreover, ^1J(N−H) can be approximated by the FC term, which is very appealing from a computational viewpoint since this significantly reduces the computational task. To evaluate the suitability of this acid, spin−spin coupling constants were computed for isolated C≡N−H and two of its complexes, C≡N−H···NH_3 and C≡N−H···pyridine. The FC term and ^1J(N−H) for C≡N−H are −114.4 and −115.8 Hz,[30] respectively, further evidence that the FC term can be used to estimate ^1J(N−H). However, the computed FC terms for C≡N−H···NH_3 and C≡N−H···pyridine are −109.2 and −107.4 Hz, respectively.[30] The corresponding protonation energies of these two bases are 214.7 and 229.6 kcal/mol (the experimental proton affinities are 204 and 222 kcal/mol[31]) respectively. Thus, when C≡N−H is the proton donor, ^1J(N−H) changes by less than 2 Hz when the difference between the protonation energies of two bases is 15 kcal/mol. Moreover, when C≡N−H is the donor to a weaker base such as HCN (C≡N−H···N≡C−H), the FC term is −114.9 Hz,[30] a slight increase relative to the monomer. Thus, ^1J(N−H) for a molecule such as C≡N−H is not a useful probe because it fails to satisfy criterion 2. Simple acids with sp^2 or sp^3 N atoms as N−H donors are usually weak donors for hydrogen bonding; stronger donors are often more complex molecules. Therefore, ^1J(N−H) has been eliminated as a suitable probe of molecular basicity.

TABLE 1: Computed MP2/6-31+G(d,p) Protonation Energies ($-\Delta E_e$) and Experimental Proton Affinities ($-\Delta H^{298}$) (kcal/mol), and the Sum of the PSO and FC Terms (PSO + FC) and ^1J(F−H) (Hz) for Complexes with F−H as the Proton Donor[a]

base	$-\Delta E_e$	$-\Delta H^{298\ b}$	(PSO + FC)	^1J(F−H)
N≡N	121.6	118.	493.3	494.9
HC≡N	174.3	170.4	492.5	492.2
H_3C−C≡N	189.8	186.2	489.4	488.6
1,3,5-triazine	204.9	202.9	454.5	
H_2C=NH	216.3	203.8	445.2	442.8
1,4-diazine	216.5	209.6	436.9	
pyridine	229.6	222.	423.9	
4-Li−pyridine	254.1		398.5	
NH_3	214.7	204.	434.3	431.4
$NH_2(CH_3)$	225.2	214.9	405.0	402.0
$NH(CH_3)_2$	232.9	222.2	376.4	373.3
$N(CH_3)_3$	236.4	226.8	353.6	
CO (at O)	104.0	101.9	495.8	497.6
H_2O	172.7	165.	484.1	483.0
H_2CO	175.8	170.4	481.0	480.3
$(CH_3)_2O$	196.8	189.3	457.4	480.3
FH	119.5	116.	497.5	498.1

[a] F−H monomer: (PSO + FC) = 492.7 Hz; ^1J(F−H) = 494.8 Hz. [b] Reference 31.

If the acid probe is to be one that is an X−H donor for hydrogen bond formation, the only remaining candidate is hydrogen fluoride, F−H. Unfortunately, the FC term for F−H coupling (308.8 Hz) is not a good approximation to ^1J(F−H) (494.8 Hz), but the sum of the PSO and FC terms (492.7 Hz) does approximate ^1J(F−H) quite well. The ability of (PSO + FC) to approximate ^1J(F−H) has been further established by computing these terms and total ^1J(F−H) for 12 complexes stabilized by F−H···Y hydrogen bonds. As is evident from Table 1, the largest difference between the sum of these terms and total ^1J(F−H) is 3.1 Hz when ^1J(F−H) is 373.3 Hz. This is an important result, since it renders unnecessary the evaluation of the computationally most expensive SD term. (The ratio of computer times FC:SO:SD is about 1:3:6, which reflects the ratio of the number of perturbations required to evaluate each term). What now remains is to examine whether or not ^1J(F−H) can discriminate among the protonation energies of a set of bases.

^1J(B−Li) has also been considered as a possible Lewis acid for complexes stabilized by B−Li···Y interactions. Boryllithium, H_2B−Li has been found to be a useful model for such a probe, even though it might be experimentally difficult to find suitable B−Li donor molecules for complex formation. Nevertheless, since ^1J(B−Li) was found to be sensitive to base strength in ref 9, we further examined changes in ^1J(B−Li) upon complex formation with a much larger set of bases. From a computational

TABLE 2: FC Term and ^1J(B−Li) (Hz) for Selected Complexes with H_2B−Li[a]

base	FC	^1J(B−Li)
N≡N	88.6	89.3
HC≡N	79.2	80.0
H_3C−C≡N	76.9	
1,3,5-triazine	80.0	
1,4-diazine	79.1	
pyridine	77.3	
NH_3	77.0	
$NH_2(CH_3)$	76.9	
$NH(CH_3)_2$	77.2	
$N(CH_3)_3$	77.8	
CO (at O)	90.0	90.8
H_2O	82.1	82.8
H_2CO	80.5	
$(CH_3)_2O$	80.5	
FH	88.3	89.0

[a] H_2B−Li monomer: FC = 113.7; ^1J(B−Li) = 114.4 Hz.

viewpoint, ^1J(B−Li) is an attractive probe because the FC term is a good approximation to the total coupling constant, as can be seen from the data of Table 2.

The Effect of Geometrical Constraints on Coupling Constants. Before examining F−H and B−Li coupling constants as possible probes of basicity, it is necessary to first examine the effect on coupling constants of the structural constraints imposed when these complexes were optimized. For complexes formed with F−H as the donor, the F−H···Y hydrogen bond was constrained to be linear. To assess the effect of this constraint, coupling constants have been evaluated for the complex FH···OCH_2, which has a hydrogen bond which shows the largest deviation from linearity. (The H−F···O angle is 8.2°.) ^1J(F−H) values, approximated as the sum of the PSO and FC terms, for the fully optimized and constrained complexes are similar at 477.6 and 481.0 Hz, respectively. The deviation from linearity of the hydrogen bonds in the remaining complexes is much less. For example, in the optimized FH···OH_2 complex the deviation is only 1.6°, with the result that the difference between ^1J(F−H) for the equilibrium structure and for the structure with a linear F−H···O hydrogen bond is only 0.1 Hz. Thus, the hydrogen bond linearity constraint imposed for complexes FH:$NH_2(CH_3)$, FH:$NH(CH_3)_2$, FH:N(H)CH_2, FH:OH_2, FH:OCH_2, FH:$O(CH_3)_2$, and FH:FH does not appear to unduly influence ^1J(F−H).

The complexes of H_2BLi with bases were optimized under the constraints that the B−Li···Y arrangement is linear and the Li atom sits on the dipole moment vector of the molecule which acts as the base. The equilibrium structures of some of these complexes are consistent with both of these constraints. For others, however, the first constraint is necessary to prevent interaction of acidic groups bonded to Y with the B−Li group, as exemplified when H_2O or FH is the base.[9] The second constraint simply reflects the tendency of Li^+ to sit at the negative end of the dipole moment vector of a base, which is helpful from a computational viewpoint since it leads to complexes with higher symmetry. To assess the effect of this constraint, ^1J(B−Li) was computed for the optimized C_{2v} structure of H_2BLi···FH and for a second C_s structure in which the Li···F−H angle was also optimized. The impact of this constraint is minimal, since corresponding FC terms and ^1J(B−Li) differ by only 0.4 Hz.

^1J(F—H) as a Probe of Basicity. Table 1 lists MP2/6-31+G(d,p) protonation energies and the available experimental proton affinities[31] for the bases investigated in this study. Although proton affinities need to be evaluated at a higher level of theory if quantitative agreement with experimental data are to be obtained, MP2/6-31+G(d,p) protonation energies are linearly related to experimental proton affinities, with a correlation coefficient of about 0.99. The range of protonation energies for the bases included in this study is large, from 104 kcal/mol for CO (protonated at O), to 254 kcal/mol for 4-Li−pyridine. Of the 17 bases, 12 have sp, sp^2, or sp^3 nitrogens as the proton acceptor atom. The four oxygen bases include CO, H_2CO, H_2O, and $(CH_3)_2O$, with sp, sp^2, and sp^3 hybridized O atoms. The remaining base is FH.

Table 1 lists the sum of the PSO and SD terms for F−H coupling for the FH monomer and the 17 complexes having F−H as the proton donor for hydrogen bond formation. In the discussion that follows, the sum of the PSO and FC terms for F−H coupling will be designated as ^1J(F−H). Except for complexes formed with the three weakest bases (CO, FH, and N_2), ^1J(F−H) decreases upon complex formation. How sensitive is ^1J(F−H) to the strength of the proton-acceptor base, as measured by its protonation energy? Figure 1 provides a plot of ^1J(F−H) vs the protonation energies of the 17 bases. The quadratic curve shown is the best fit ($y = -0.0094x^2 + 2.466x + 338.8$; $r^2 = 0.84$), although the curvature of this parabola is incorrect at the lower end of the protonation energy scale.

It is apparent from Figure 1 that ^1J(F−H) does not discriminate well among bases with protonation energies less than about 200 kcal/mol, since in the protonation energy range from 100 to 195 kcal/mol, ^1J(F−H) varies by less than 17 Hz. Hydrogen bonding with the three weakest bases CO, FH, and N_2 which have protonation energies of 104, 120, and 122 kcal/mol, respectively, leads to an increase in ^1J(F−H) of 3.1, 4.8, and 0.6 Hz, respectively. Hydrogen bonding with the three sp-hybridized nitrogen bases, N_2, HCN, and H_3CCN with protonation energies of 122, 174, and 190 kcal/mol, respectively, changes ^1J(F−H) by only +0.6, −0.2, and −3.3 Hz, respectively. It is also interesting to note that for these same bases, the sum (PSO + FC) decreases by 6 Hz in the order N_2 > HCN > H_3CCH. The PSO term also decreases by 31 Hz in the same order, while the FC term increases by 27 Hz in the reverse order N_2 < HCN < H_3CCH, and this results in only small changes in ^1J(F−H). However, for the sp^2 and sp^3 nitrogen bases, the PSO and FC terms appear to vary together, and changes in these terms are directly reflected in the variation of the sum of the PSO and FC terms.

From Figure 1 it can be seen that for protonation energies greater than 200 kcal/mol, the best-fit curve splits the points into two sets, with five points lying above this curve and four below. Points lying above this curve belong to complexes with sp^2 hybridized nitrogen bases; those below belong to complexes with sp^3 nitrogen bases. Figure 2 presents one curve which relates ^1J(F−H) to the protonation energies of the amine bases NH_3, $NH_2(CH_3)$, $NH(CH_3)_2$, and $N(CH_3)_3$ involved in complex formation, and a second curve which relates these two variables for the complexes formed with the sp^2 aromatic bases pyridine, 1,4-diazine (pyrazine), 1,3,5-triazine, and 4-Li−pyridine, and one nonaromatic sp^2 base, H_2C=NH (methylenimine). The trendlines are given by the equations ($y = -0.0027x^2 + 1.418x + 536.09$) and ($y = -0.00623x^2 + 24.158x - 192.2$), respectively, with $r^2 = 0.979$ and 0.997, respectively. The trendlines intersect just above 200 kcal/mol, very close to the point for the complex of FH with $O(CH_3)_2$ at a protonation energy of 197 kcal/mol. Thus, the magnitude of the change in the one-bond F−H coupling constant upon hydrogen bond formation is a measure of basicity, provided that the proton affinities are above about 200 kcal/mol, and the nitrogen bases are grouped

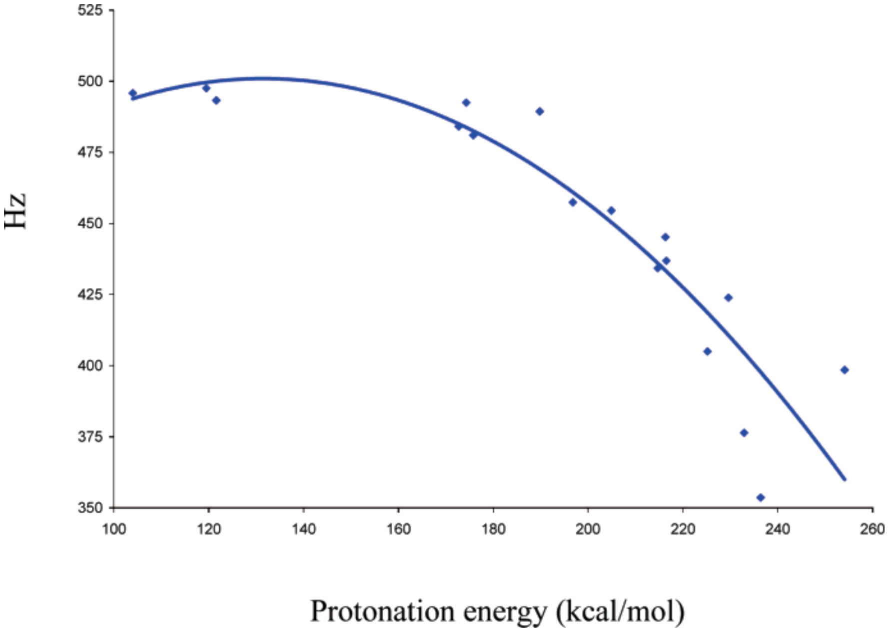

Figure 1. ^1J(F−H) vs the protonation energies of the 17 bases.

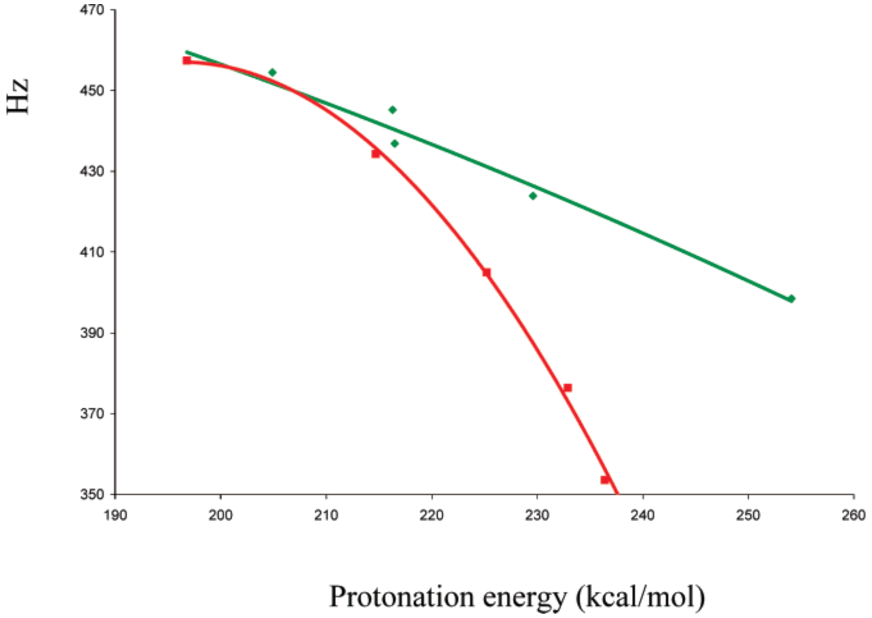

Figure 2. ^1J(F−H) vs the protonation energies of nitrogen bases that are sp^2 (◆) and sp^3 (■) hybridized. The point at a protonation energy slightly less than 200 kcal/mol belongs to FH···O(CH_3)$_2$.

according to the hybridization of the proton-acceptor atom. Although not shown in Figure 2, the values of ^1J(F−H) for complexes FH···PH_3 and FH···$PH_2(CH_3)$ do not fit on either curve since changes in ^1J(F−H) upon complexation are too small relative to the protonation energies of the P bases.

^1J(B—Li) as a Probe of Basicity. Table 2 lists the FC terms for B−Li coupling in H_2B−Li and its complexes with 15 bases. Total B−Li coupling constants ^1J(B−Li) for H_2B−Li and five of its complexes are also listed, and support the use of the FC term as an approximation to ^1J(B−Li) since the difference between them is less than 1 Hz. Figure 3 presents a plot of these data over a protonation energy range from 100 to 240 kcal/mol. It is apparent from this plot that ^1J(B−Li) decreases as the protonation energy of the base increases. Despite a relatively good correlation over the entire range of protonation energies ($y = -0.0008x^2 - 0.3669x + 120.87$; $r^2 = 0.91$), closer examination indicates that ^1J(B−Li) does not differentiate among base protonation energies when these are about 190 kcal/mol or greater. Thus, the protonation energies of the three aromatic nitrogen bases and the four amine bases span a range of 31.5 kcal/mol. Over that range, ^1J(B−Li) varies by only 3.1 Hz. Hence, ^1J(B−Li) is not a suitable probe of basicity in this region.

If, however, the bases are restricted to those with protonation energies less than 190 kcal/mol, then ^1J(B−Li) is a probe of molecular basicity. Figure 4 presents a plot of ^1J(B−Li) vs the protonation energies of bases ranging between 100 and 190 kcal/mol. The best-fit quadratic curve ($y = -0.0011x^2 + 0.1748x + 83.558$) has a correlation coefficient of 0.978. The point for $(CH_3)_2O$, which would appear at a protonation energy of 197 kcal/mol, is not a good fit to this line and has not been included.

^1J(F—H) and ^1J(B—Li) as Basicity Probes. In this study, it has been demonstrated for the first time that the computed gas-phase NMR property of a one-bond spin−spin coupling

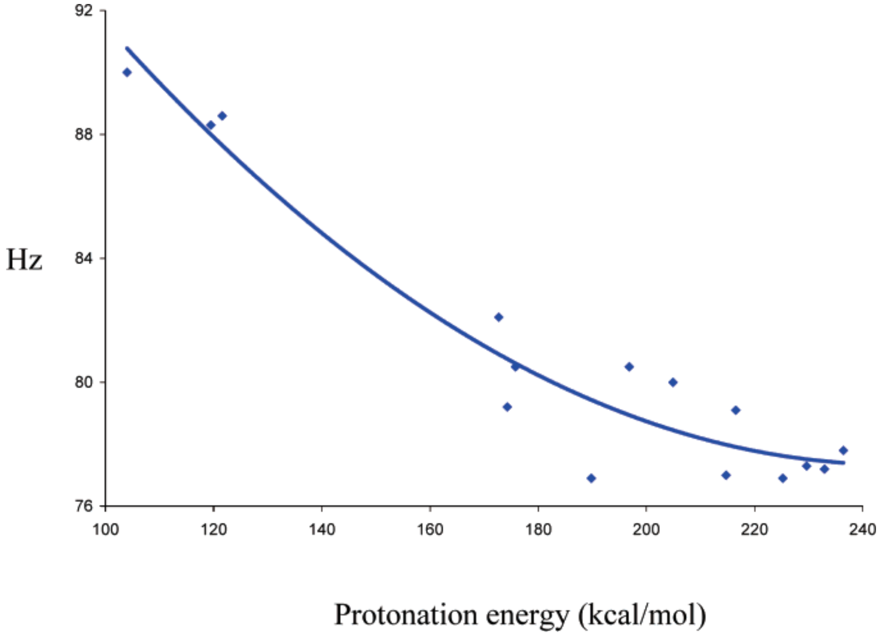

Figure 3. ^1J(B−Li) vs the protonation energies of 15 bases.

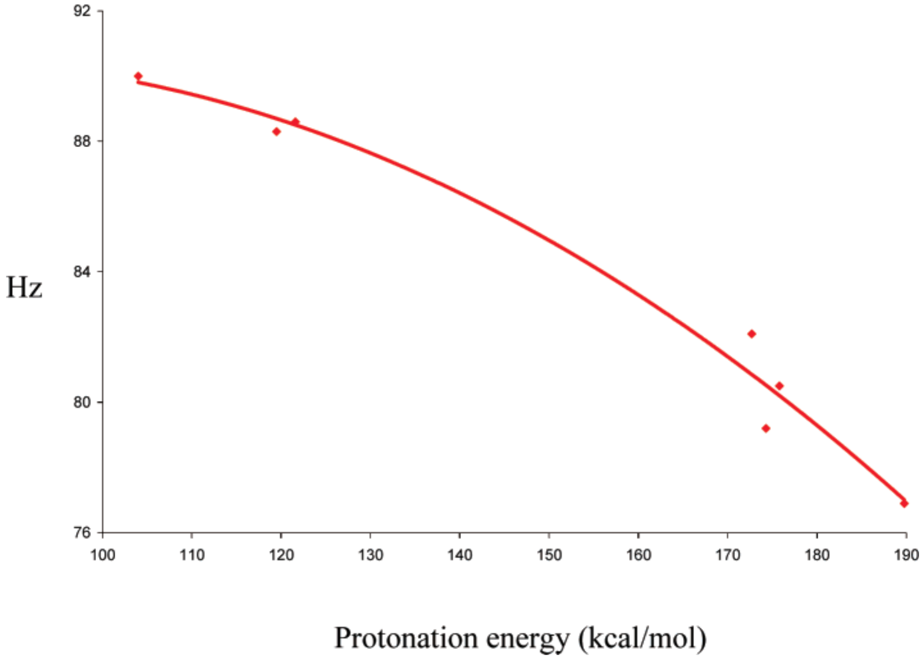

Figure 4. ^1J(B−Li) vs the protonation energies of bases in the range 100 − 190 kcal/mol.

constant can be related to the thermodynamic gas-phase property of the proton affinity of a base, which is clearly different from the bulk property of that base as a solvent.[5] There are two questions which still need to be addressed. How are changes in ^1J(F−H) and ^1J(B−Li) upon complexation related to the protonation energies of bases? An obvious first-response is that for a given proton donor, the stronger the proton acceptor the shorter the intermolecular distance, and the longer the F−H or B−Li distance. Moreover, as base strength increases, the proton-shared character of the F−H···Y hydrogen bond and the ion-pair character of the B−Li bond increase, thereby reducing ^1J(F−H) and ^1J(B−Li). While this response has some validity, it is overly simplistic. Changes in coupling constants should not be viewed as a direct consequence of distance changes, as recently demonstrated for ^1J(B−Li) in ref 9. Rather, since these coupling constants are second-order properties, they must reflect differences in F−H and B−Li electron densities in ground and excited states upon complex formation.

The second question which remains is whether or not these coupling constants could be used experimentally to probe proton affinities. The difficulties of working with FH are well-known, and many experimentalists are reluctant to use FH in their experimental setups because it can damage the instrument or destroy the reaction vessels, including most NMR tubes. Despite this difficulty, Limbach et al. have used FH extensively in a series of fundamental NMR studies of complexes involving FH as a proton donor.[32−38] Compounds with boron−lithium bonds are for the moment unsuitable as experimental probes. (H_2B−Li has never been isolated, and lithiated boranes R_2B−Li were unknown until recently.[39−41]) Both ^{11}B (80%, $I = {}^3/_2$) and ^7Li (92%, $I = {}^3/_2$) are quadrupolar nuclei. Consequently $^1J(^{11}B-{}^7Li)$ is almost impossible to measure even as an isolated species, and measuring its variation upon complexation would be an extremely difficult task.

Conclusions

In this study, three criteria were proposed to identify acids with one-bond spin−spin coupling constants that could be potentially useful as probes of the protonation energies (proton affinities) of bases. On the basis of these criteria, two probes were selected for detailed investigation. The first is F−H, acting as a proton donor in hydrogen-bonded complexes; the second is B−Li acting as a Lewis B−Li donor. EOM-CCSD calculations indicate that changes in ^1J(F−H) upon complex formation are related to the protonation energies of bases, but only when these energies are about 200 kcal/mol or greater. On the other hand, while changes in ^1J(B−Li) upon complex formation do not discriminate among protonation energies if these are above 200 kcal/mol, a correlation does exist in the protonation energy range between 100 and about 190 kcal/mol. Thus, these two one-bond coupling constants ^1J(F−H) and ^1J(B−Li) are complementary. For the first time, the computed NMR property of a gas-phase one-bond spin−spin coupling constant has been related to the experimental gas-phase thermodynamic property of proton affinity.

Acknowledgment. This work was supported by the Ohio Supercomputer Center and by the Spanish Ministry of Health (Project No. SAF-2006-13391-C03-C02). The authors gratefully acknowledge this continuing support.

References and Notes

(1) True, N. S. Gas phase NMR studies of chemical exchange processes. In *Encyclopedia of NMR*; Grant, D. M., Harris, R. K., Eds.; John Wiley and Sons: New York, 1996; pp 2173−2178. True, N. S.; Suarez. C. Gas phase NMR studies of conformational processes. In *Advances in Molecular Structure Research*; JAI Press, Inc.: Greenwich, CT, 1995; Vol. 1, pp 115−155.

(2) Jackowski, K. *Int. J. Mol. Sci.* **2003**, *4*, 135, and references therein.

(3) Chidek, J. A.; Foster, R.; Jorgensen, N. J. *Chem. Soc. Faraday Trans. 1* **1981**, *77*, 3081.

(4) Legon, A. C. In *Atomic, Molecular Beam Methods*; Scoles, G., Ed. Oxford University: Oxford, U.K., 1992, Vol. 2, Chapter 9, pp 289−308; López, J. C.; Alonso, J. L.; Lorenzo, F. J.; Rayón, V. M.; Sordo, J. A. *J. Chem. Phys.* **1999**, *111*, 6363.

(5) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed.; Wiley-VCH: Weinheim, Germany, 2003.

(6) Barfield, M.; Johnston, M. D. *Chem. Rev.* **1973**, *73*, 53.

(7) Hansen, P. E. *Prog. NMR Spectrosc.* **1982**, *14*, 175.

(8) Del Bene, J. E.; Elguero, J.; Alkorta, I.; Yáñez, M.; Mó, O. *J. Phys. Chem. A* **2007**, *111*, 419.

(9) Del Bene, J. E.; Elguero, J. *Magn. Reson. Chem.* **2007**, *45*, 484.

(10) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1976**, *10*, 1.

(11) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91.

(12) Bartlett, R. J.; Silver. D. M. *J. Chem. Phys.* **1975**, *62*, 3258.

(13) Bartlett, R. J.; Purvis, G. D. *Int. J. Quantum Chem.* **1978**, *14*, 561.

(14) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1982**, *56*, 2257.

(15) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta.* **1973**, *238*, 213.

(16) Spitznagel, G. W.; Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comput. Chem.* **1982**, *3*, 3633.

(17) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

(18) Krishnan, R. R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(19) Perera, S. A.; Sekino, H.; Bartlett, R. J. *J. Chem. Phys.* **1994**, *101*, 2186.

(20) Perera, S. A.; Nooijen, M.; Bartlett, R. J. *J. Chem. Phys.* **1996**, *104*, 3290.

(21) Perera, S. A.; Bartlett, R. J. *J. Am. Chem. Soc.* **1995**, *117*, 8476.

(22) Perera, S. A.; Bartlett, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 7849.

(23) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.

(24) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(25) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1995**, *103*, 4572.

(26) Del Bene, J. E.; Elguero, J.; Alkorta, I.; Yáñez, M.; Mó, O. *J. Phys. Chem. A* **2006**, *10*, 9959.

(27) Kirpekar, S.; Jensen, H. J. Aa; Oddershede, J. *Chem. Phys.* **1994**, *188*, 171.

(28) Frisch, M. J.; et al. Gaussian 03, Gaussian, Inc.: Wallingford CT, 2004.

(29) Stanton, J. F.; et al. ACES II a program product of the Quantum Theory Project, University of Florida.

(30) Del Bene, J. E.; Elguero, J. *J. Am. Chem. Soc.* **2004**, *126*, 15624.

(31) Linstrom, P. J., Mallard, W. G., Eds. *NIST Chemistry Webbook*; NIST Standard Reference Database No. 69; National Institute of Standards and Technology: Gaithersburg, MD, 20899, March 2003; http://webbook.nist.gov.

(32) Shenderovich, I. G.; Smirnov, S. N.; Denisov, G. S.; Gindin, V. A.; Golubev, N. S.; Dunger, A.; Reibke, R.; Kirpekar, S.; Malkina, O. L.; Limbach, H.-H. *Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 422.

(33) Golubev, N. S.; Shenderovich, I. G.; Smirnov, S. N.; Denisov, G. S.; Limbach, H.-H. *Chem. Eur. J.* **1999**, *5*, 492.

(34) Benedict, H.; Shenderovich, I. G.; Malkina, O. L.; Malkin, V. G.; Denisov, G. S.; Golubev, N. S.; Limbach, H.-H. *J. Am. Chem. Soc.* **2000**, *122*, 1979.

(35) Shenderovich, I. G.; Burtsev, A. P.; Denisov, G. S.; Golubev, N. S.; Limbach, H.-H. *Magn. Reson. Chem.* **2001**, *39*, S91.

(36) Shenderovich, I. G.; Limbach, H.-H.; Smirnov, S. N.; Tolstoy, P. M.; Denisov, G. S.; Golubev, N. S *Phys. Chem. Chem. Phys.* **2002**, *4*, 5488.

(37) Shenderovich, I. G.; Tolstoy, P. M.; Golubev, N. S.; Smirnov, S. N.; Denisov, G. S.; Limbach, H.-H. *J. Am. Chem. Soc.* **2003**, *125*, 11710.

(38) Golubev, N. S.; Tolstoy, P. M.; Smirnov, S. N.; Denisov, G. S.; Limbach, H.-H. *J. Mol. Struct.* **2004**, *700*, 3.

(39) Wagner, M.; Eikema Hommes, N. J. R. v; Nöth, H.; Schleyer, P. v. R. *Inorg, Chem.* **1995**, *34*, 607.

(40) Segawa, Y.; Yamashita, M.; Nozaki, K. *Science* **2006**, *134*, 113.

(41) Braunschweig, H. *Angew. Chem., Int. Ed.* **2007**, *46*, 1946.