Gas-Phase Basicities of *N*-Methyl Substituted 1,8-Diaminonaphthalenes and Related Compounds

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Abstract: The gas-phase basicities of *N*-methyl substituted 1,8-diaminonaphthalenes and several related compounds were determined by measurement of proton transfer equilibria (1), $B_1H^+ + B_2 = B_1 + B_2H^+$, with a high-pressure mass spectrometer. The gas-phase basicity ladder obtained through continuous equilibria (1) extends over a 30 kcal/mol interval from methylamine to 1,8-bis(dimethylamino)naphthalene. The results indicated that ring protonation in *m*-phenylenediamine and 1-aminonaphthalene leads to a more stable ion than with N-protonation. The 1,8-diaminonaphthalenes are N-protonated. The gas-phase basicity results are in agreement with the previously postulated reason for the unusually high basicity of 1,8-bis(dimethylamino)naphthalene, namely, that steric strain in the neutral base is relieved by protonation. It is found that the methyl substituent effects on the basicity of the 1,8-diaminonaphthalenes are strongly attenuated in solution, as expected since N-methylated ions are less well solvated. The proton-induced relief of strain in the fully methylated base produces nearly the same energy change in the gas phase and in solution, as expected since this change should not affect the solvation of the ion. The neutral base 1,2-bis(dimethylamino)benzene is not strained and therefore is of considerably lower basicity.

Introduction

The remarkably high basicity of 1,8-bis(dimethylamino)-naphthalene in aqueous solution was reported some time ago.[2a] The present work presents measurements of the gas-phase basicities of *N*-methyl substituted 1,8-diaminonaphthalenes including the tetramethyl substituted compound. Comparison of the gas-phase and aqueous basicities allows one to assess the effect of the solvent.

The gas-phase determinations of basicities are obtained by measuring the equilibrium constants for the proton transfer reactions

$$B_1H^+ + B_2 = B_1 + B_2H^+ \qquad (1)$$
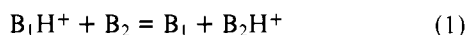
The equilibrium constants K_1 are then used to obtain ΔG°_1 from the equation $-RT \ln K_1 = \Delta G^\circ_1$. Since the diaminonaphthalenes have very high basicities, several bases B of gradually diminishing strength had to be used in equilibrium reactions 1 in order to connect the diaminonaphthalenes to standard bases of known gas-phase basicity. In this manner a continuous ladder of ΔG°_1 determinations was obtained covering the range from methylamine to the 1,8-diaminonaphthalenes. This ladder also should be of general usefulness to readers interested in gas-phase basicities.

In order to compare the basicities of the 1,8-diaminonaphthalenes with monosubstituted 1-aminonaphthalene, the proton affinities of the latter compound and of naphthalene were also determined. In aqueous solution anilines and naphthylamines are N-protonated since the resulting ammonium ions are stabilized by efficient hydrogen bonding to the solvent. In the gas phase ring protonation sometimes can lead to ions of lower energy. Therefore an examination of the possible sites of protonation of the naphthylamines had to be included in the discussion.

Experimental Section

The measurements of the proton transfer equilibria 1 were carried out with a pulsed electron beam, high ion source pressure mass spectrometer whose general design and features have been described previously.[2b] The instrument used in the present work utilizes a quadrupole mass filter. This instrument has been used in previous proton affinity determinations[3,4] from this laboratory. Information specifically related to the present measurements and particularly the diaminonaphthalenes is given below. In our general procedure a gas mixture of a major gas and the two bases B_1 and B_2 is prepared in a

storage bulb. The mixture is then bled through an all-metal valve into tubing leading in and out of the ion source. The resulting gas flow through the ion source ($\sim$50 cm^3 s^{-1} at 4 Torr) is viscous so that no fractionation of the mixture occurs. In the present work the known pressure of the major gas was varied between 1 and 4 Torr while the bases B were between 0.1 and 10 mTorr. The gas mixtures were generally prepared by injecting a CHCl$_3$ solution of B_1 and B_2 into a 5-L storage bulb which contained 120 Torr of the major gas. The gas handling plant containing the storage bulb was kept at 170 °C.

The aminonaphthalenes are relatively nonvolatile and their vapor pressures are not known. Since in some of the runs the partial pressures of given bases in the bulb could be as high as 0.3 Torr, tests were made to make certain that the aminonaphthalene sample was completely evaporated. This was done by admitting solid aminonaphthalene into the bulb and observing whether complete evaporation occurred.

In previous measurements[3,4] methane was most often used as carrier gas. The final ions obtained on electron bombardment of pure methane are CH$_5^+$ and C$_2$H$_5^+$ in a ratio of 6:5. Both CH$_5^+$ and C$_2$H$_5^+$ are strong acids that can protonate most bases B. However, for the diaminonaphthalenes, methane proved unsuited as the major gas. With methane, in addition to BH$^+$ also the formation of B$^+$ was observed. The concentration of B$^+$ was somewhat smaller but nearly equal to that of BH$^+$. This suggests that C$_2$H$_5^+$, instead of engaging in proton transfer 2, was mostly engaging in the charge transfer reaction 3.

$$C_2H_5^+ + B = C_2H_4 + BH^+ \qquad (2)$$

$$C_2H_5^+ + B = C_2H_5 + B^+ \qquad (3)$$
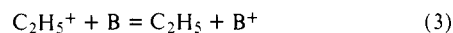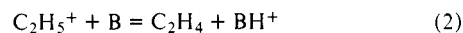
The ionization potential of the ethyl radical is 8.38 eV.[5] The ionization potentials of the diaminonaphthalenes are not known; however, IP-(aniline) = 7.69 eV.[6] The aminonaphthalenes may be expected to have even lower ionization potentials. Therefore, the charge transfer reaction 3 will be strongly exothermic, and its occurrence very probable. Since both BH$^+$ and B$^+$ are of high mass, where the resolution of our quadrupole was not quite sufficient to separate the two ions completely, the presence of B$^+$ was undesirable. The BH$^+$ could be cleanly produced by using *t*-C$_4$H$_9^+$ as reactant. The ionization potential IP(*t*-C$_4$H$_9$) = 6.9 eV.[5] This is probably lower than IP(B) so that charge transfer is not possible. The *tert*-butyl cation is essentially the only final ion in electron irradiated isobutane.[7] We have found that isobutene also produces *tert*-butyl as major ion, the only other ion being C$_4$H$_9$·C$_4$H$_8^+$. Therefore, equilibrium 1 measurements with isobutane or isobutene as major gas were performed. The results were, as expected, identical.

Results and Discussion

A. Results. General. The gas-phase measurements based on determinations of the equilibrium constants for the proton transfer reactions 1 are summarized in Figure 1, which gives
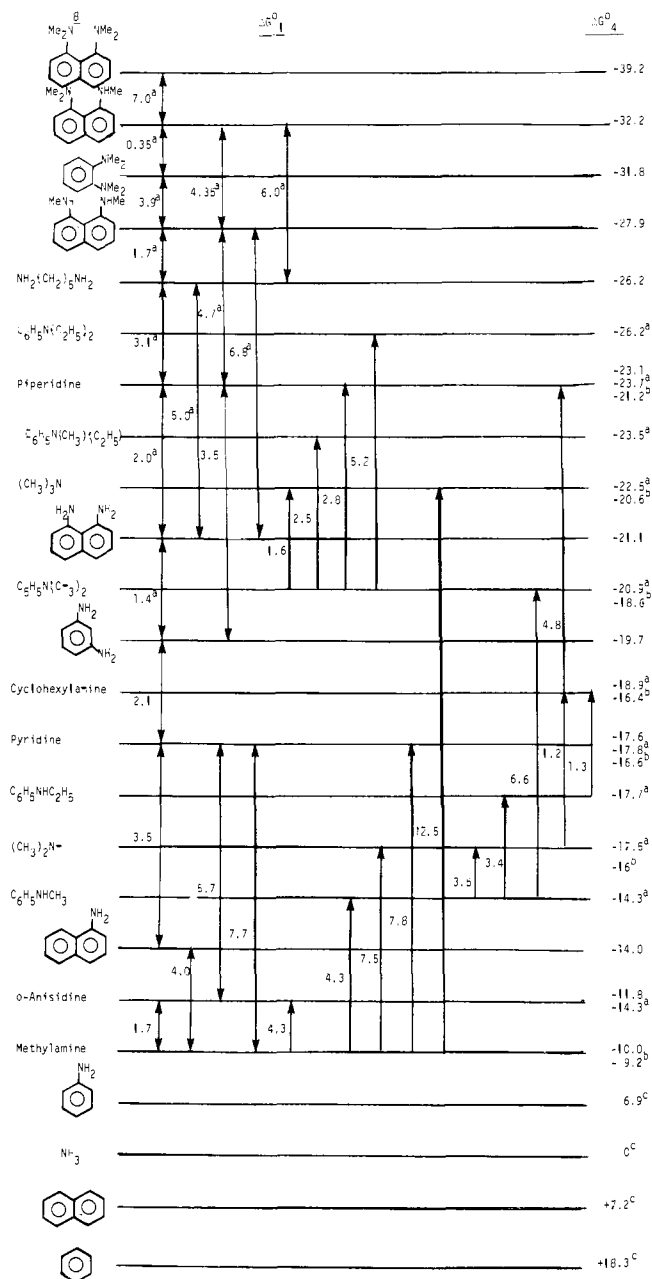
Figure 1. Gas-phase basicity ladder based on measurements of equilibrium constants K_1 for equilibria 1, $B_1H^+ + B_2 = B_1 + B_2H^+$, in gas phase. Values given beside double arrows connecting bases B_1 and B_2 correspond to $\Delta G^\circ_1 = -RT \ln K_1$. All values in kcal/mol. All ΔG°_1 values with superscript (a) were done at 460 K, the rest at 600 K. Values beside single arrows on the right side correspond to results obtained from earlier determinations from this laboratory.[9,10] ΔG°_4 relates to proton transfer involving NH_3 as standard base 4: $NH_4^+ + B = NH_3 + BH^+$. ΔG°_4 values with superscript (a) are previous results from this laboratory; those with superscript (b) are from Taft[11] and relate to 300 K; those with superscript (c) are based on gas basicity ladder given in ref 8.

a continuous free-energy ladder of $\Delta G^\circ_1 = -RT \ln K_1$ values extending from methylamine to 1,8-bis(dimethylamino)-naphthalene and covering a span of some 30 kcal/mol basicity difference. The partial pressures of B_1 and B_2 were varied in order to examine whether the equilibrium constant is independent of the concentrations. Results from such runs are shown in Figure 2.

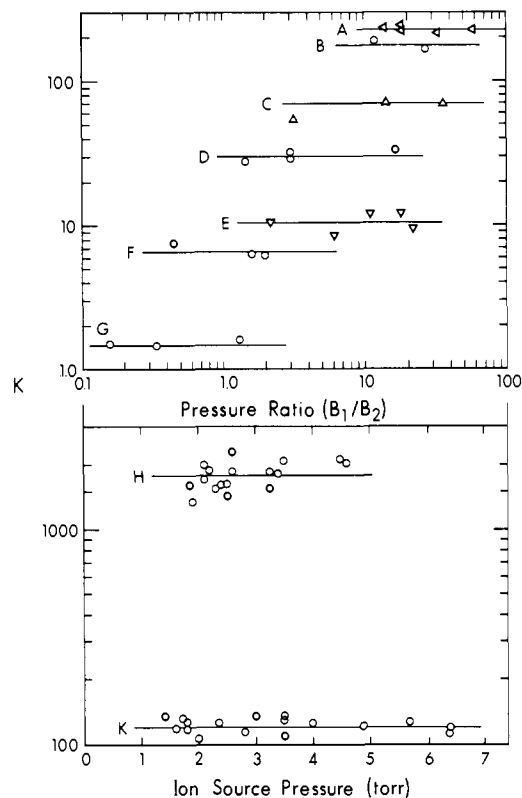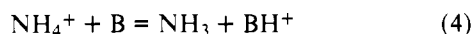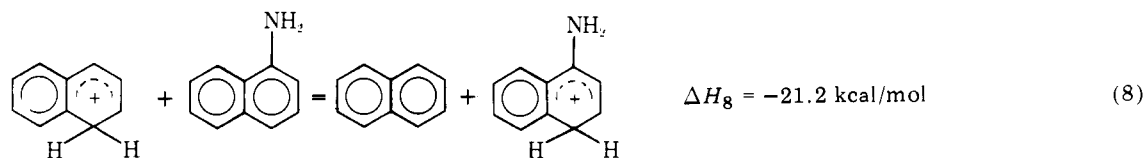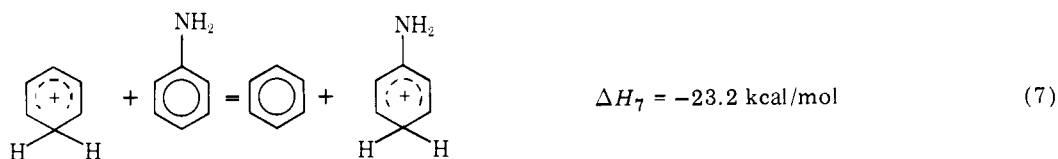The ΔG°_4 values given in Figure 1 relate to proton transfer from ammonia, i.e.,
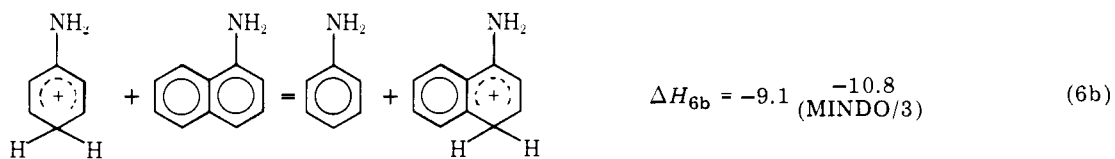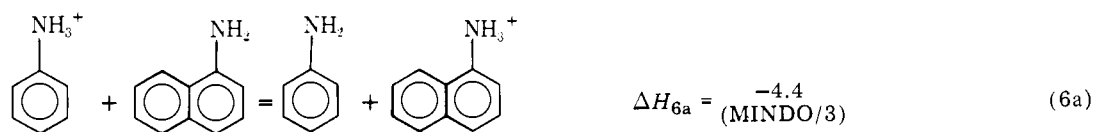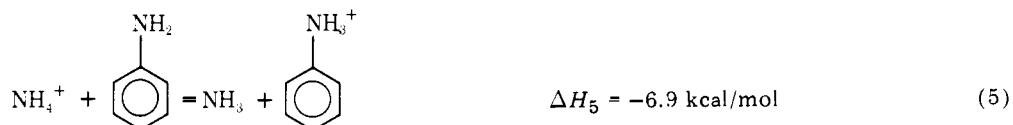
$$NH_4^+ + B = NH_3 + BH^+ \qquad (4)$$

Figure 2. Results showing that equilibrium constant K_1 for reaction 1, $B_1H^+ + B_2 = B_1 + B_2H^+$, does not change with total ion source pressure and with B_1/B_2 ratio. Upper figure: (B_1,B_2): A, (1,8-diaminonaphthalene, 1,5-diaminopentane); B, (piperidine, 1,8-bis(methylamino)naphthalene); C, (1,8-bis(methylamino)naphthalene, 1,2-bis(dimethylamino)benzene); D, (piperidine, 1,5-diaminopentane); E, (1,8-diaminonaphthalene, piperidine); F, (1,5-diaminopentane, 1,8-bis(methylamino)naphthalene); G, (1,2-bis(dimethylamino)benzene, 1-dimethylamino-8-methylamino-naphthalene). Lower figure: (B_1,B_2); H, (1,8-diaminonaphthalene, 1,8-bis(methylamino)naphthalene); K, (1,8-bis(methylamino)naphthalene, 1-dimethylamino-8-methylaminonaphthalene).

For bases stronger than ammonia, ΔG°_4 is negative. $\Delta G^\circ_4(CH_3NH_2) = -10.0$ kcal/mol was obtained from a basicity ladder involving a large number of bases and covering the range from isobutene to ammonia to methylamine.[8] These results were obtained recently in our laboratory.[8] An earlier result, $\Delta G^\circ_4(CH_3NH_2) = -10.8$ kcal/mol, obtained in this laboratory[9] is considered less accurate. Therefore all the ΔG°_4 shown in Figure 1 are based on $\Delta G^\circ_4(CH_3NH_2) = 10.0$ kcal/mol (600 K). Previous basicity determinations for pyridine and piperidine from this laboratory[10] are also shown in Figure 1. The agreement with the present results is within 0.2 kcal/mol for pyridine and 0.6 kcal/mol for piperidine. Included in Figure 1 are also determinations from Beauchamp's and Taft's[11] laboratories whenever available. On the whole these ΔG°_4 are about 1-2 kcal/mol lower. Part of the difference must be due to the different temperatures used. Taft's determinations are at 300 K while the results from this laboratory are for 460 K and more often 600 K. For example, considering symmetry number changes only, ΔS°_4 for pyridine is $R \ln 4$ = 2.7 cal/deg, which for a ΔT of 300 K leads to $\Delta G^\circ_4(600)$ = -0.8 kcal/mol. Thus the present ΔG°_4(pyridine) = -17.6 kcal/mol at 600 K, when corrected to 300 K, becomes -16.8 kcal/mol, which is very close to the -16.6 kcal/mol obtained by Taft.

Approximate proton affinities can be obtained from the ΔG°_4 given in Figure 1 by neglecting $T\Delta S^\circ_4$, which is probably in the 1 kcal/mol range. Using $PA(NH_3) = 207$ kcal/mol[12] one obtains $PA(B)$ by adding $-\Delta G^\circ_4$ to 207 kcal/mol. Thus PA(bistetramethyldiaminonaphthalene) $\approx 39.2 + 207$

$$\Delta H_5 = -6.9 \text{ kcal/mol} \tag{5}$$

$$\Delta H_{6a} = \begin{matrix} -4.4 \\ (\text{MINDO}/3) \end{matrix} \tag{6a}$$

$$\Delta H_{6b} = -9.1 \begin{matrix} -10.8 \\ (\text{MINDO}/3) \end{matrix} \tag{6b}$$

$$\Delta H_7 = -23.2 \text{ kcal/mol} \tag{7}$$

$$\Delta H_8 = -21.2 \text{ kcal/mol} \tag{8}$$

= 246.2 kcal/mol. This is the highest proton affinity for a neutral organic base measured so far.

B. Basicities of Diaminonaphthalenes and Sites of Protonation of Some Amino-Substituted Aromatic Compounds. Before discussing the relative gas-phase basicities of the diaminonaphthalenes we need to consider the sites of protonation in the gas phase. In earlier work from this laboratory[4] a comparison of the relative proton affinities of para-substituted benzenes with the corresponding σ^+ substituent constants, based on solution experiments, showed that the proton affinity of aniline for ring protonation (para to NH_2) must be very similar to that for protonation on the nitrogen. Since aniline is known to be a nitrogen base in solution of hydrogen-bonding solvents, it was evident[4] that the greater stability of the N-protonated structure in solution must be due to better hydrogen bonding of the solvent molecules to the acidic hydrogens of the $-NH_3^+$ group. Subsequent examination of protonated aniline by Taft, Hehre, et al.,[13] showed that the proton affinities for nitrogen or ring protonation were the same within the error of the estimate. These results were obtained by STO-3G calculation of the energy change ΔE in isodesmic proton transfer reactions involving aniline. Additional considerations involving a second substituent led these authors[13] to conclude that the proton affinity for nitrogen protonation is 1–3 kcal/mol higher than that for ring protonation.

In a related paper Taft, Hehre, et al.,[14] discussed sites of protonation of substituted anilines and compared the gas-phase and aqueous basicities. This work showed that in the gas phase ring protonation is favored over N-protonation when electron-donating substituents like CH_3, CH_3O, and NH_2 are introduced in position meta to the amino group. A particularly vivid example was *m*-phenylenediamine, for which the authors[14] estimated (from STO-3G calculated ΔE for isodesmic proton transfer reactions) that the proton affinity for ring protonation is 17 kcal/mol higher than that for N-protonation. Since, in aqueous solution, *m*-phenylenediamine is N-protonated, this illustrates, as pointed out by the authors,[14] the very much poorer solvation of the charge-delocalized benzenium ion as compared to the hydrogen-bonding anilinium ion. Attempts to determine the proton affinity of *m*-phenyl-

enediamine by ICR measured proton transfer equilibria had been unsuccessful.[14]

In the present measurements, the basicity of *o*-phenylenediamine was considered of interest for the purpose of comparing it with the basicity of 1,8-diaminonaphthalene. Therefore basicity determinations of *o*-, *m*-, and *p*-phenylenediamine were attempted. The result obtained for *m*-diaminonaphthalene is given in Figure 1. According to the results of Hehre and Taft[14] this value should be assigned to the ring-protonated species. Unfortunately Hehre and Taft did not give the actual STO-3G deduced proton affinity for ring and N-protonation of *m*-phenylenediamine but only the difference between those two affinities. Therefore the present result cannot be directly compared with their data. However, the present result can be used for an independent estimate of the proton affinity difference for ring and substituent protonation. Using the linear correlation between aqueous basicities and the proton affinities of N-protonated anilines (see Figure 1, ref 14) and the known aqueous basicity of aniline and *m*-phenylenediamine one obtains[15] a predicted proton affinity for N-protonated phenylenediamine which is ∼2.1 kcal/mol higher than that of aniline. Since the present proton affinity of *m*-phenylenediamine is 12.8 kcal/mol higher than that of aniline (see Figure 1), the estimated difference between the proton affinities for ring and N-protonation in *m*-phenylenediamine is 12.8 − 2.1 = 10.7 kcal/mol. This is somewhat smaller than the STO-3G calculated difference of 17 kcal/mol[14] but still of similar magnitude.

Unfortunately the measurements of proton equilibria involving *o*- and *p*-phenylenediamine were not successful. The protonated amines were found to rapidly decompose to an ion of molecular weight lower by two mass units.

The values of the proton affinities of naphthalene and 1-aminonaphthalene are given in Figure 1. The aminonaphthalene could be ring or substituent protonated. The following arguments lead to the conclusion that the more stable ion is the ring-protonated species. The substitution of a phenyl group for hydrogen in reaction 5 increases the proton affinity by 6.9 kcal/mol. This increase is due to stabilization of the ion by the polarizability provided by the phenyl group. Further expansion

of the aromatic system as in reaction 6a should have no larger effect; i.e, we expect an exothermicity for reaction 6a which is considerably smaller than that for reaction 5. If the experimental PA of α-naphthylamine is used (assuming that N-protonation is favored) one obtains a $\Delta H_{6a} = -7.1$ kcal/mol, an exothermicity that is higher than that for reaction 5. This discrepancy indicates that the N-protonation is not the favored process. Evaluation[17] of ΔH_{6a} using MINDO/3 calculated heats of formations for all reactants[17] leads to ΔH_{6a}(MINDO/3) $= -4.4$ kcal/mol, which is of expected magnitude.

The MINDO/3 calculated enthalpy change[17] for reaction 6b, ΔH_{6b}(MINDO/3) $= -10.8$ kcal/mol, is in agreement with a $\Delta H_{6b} = -9.1$ kcal/mol obtained by using the experimental PA of 1-aminonaphthalene and PA(ring-protonated aniline) = PA(N-protonated aniline) $-$ 2 kcal/mol (see preceding discussion and Hehre and Taft[14]). This agreement also supports the premise that the ring-protonated aminonaphthalene is the more stable form. Using the ΔH_{6a}(MINDO/3) $= -4.4$ kcal/mol and PA(aniline) = 209.2 kcal/mol one obtains the estimate PA(1-aminonaphthalene, N-protonation) ≈ 213.6 kcal/mol. This is about 3 kcal/mol lower than the experimental proton affinity of 1-aminonaphthalene (216.3 kcal/mol), which, according to the preceding discussion, relates to ring protonation. Reactions 7 and 8 give the amino group substituent effect for ring protonation in benzene and naphthalene. The exothermicity of reaction 8 is similar but slightly smaller than that for reaction 7, a result that could have been expected.

The more stable protonated 1-aminonaphthalene being the ring-protonated structure one may ask oneself whether the 1,8-diaminonaphthalene is ring protonated or N-protonated. The two amino groups in the naphthalene are at a distance which is fairly suitable for an $N-H^+\cdots N$ hydrogen bond involving the proton and the two nitrogen lone pairs (see structure I). The distance between the N–N centers in 1,8-diaminonaphthalene should be about 2.5 Å (Einsphar et al.[18]). This distance can be compared with 2.7 Å for the distance between the nitrogens in the N–H—N bond in $H_3NHNH_3^+$ obtained from SCF–MO calculations by Peyerimhoff et al.[19] The bond energy $D(NH_4^+ - NH_3) = 25$ kcal/mol was measured some time ago in this laboratory.[20] The lone pairs on the amino groups in 1,8-diaminonaphthalene are not properly oriented. Therefore the N-H---N bond in the protonated species cannot be linear but will be bent and therefore weaker. Assuming that this strain reduces the bond energy to 50-70% of the energy of a linear bond, and taking $D(NH_4^+ - NH_3) = 25$ kcal/mol as a representative for such a linear bond; one obtains 10-17 kcal/mol H-bonding inducement for the formation of structure I. To roughly estimate ΔG°_{9a} we must include also the 3-4
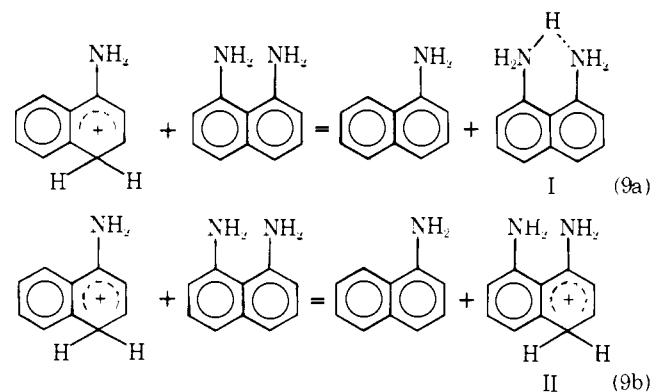
mole. Therefore $-\Delta G_{9a}$ should probably amount to less than 10 kcal/mol. The experimental result for proton transfer from naphthylamine to 1,8-diaminonaphthalene is -7.1 kcal/mol (see Figure 1) and thus of the expected magnitude for process 9a. The energy change in reaction 9b depends on the substituent effect of a second amino group in position 8. Reaction 9b should be exothermic, but much less than reaction 8 in which the first amino group in the 1 position was introduced (ΔG°_8 = -21.2 kcal/mol). This follows from general observations of substituent effects in naphthalenes. When a π interacting substituent goes on the ring not containing the functional group its effect is very small. Dewar and Grisdale[21] in a study of the acidities of 1-naphthoic acids determined the Hammett substituent constant values, $\sigma_4 = -0.72$ and $\sigma_5 = -0.13$, for the effect of an amino group in the 4 or 5 position. These σ values should have some validity also for the gas phase since for systems of this type a linear relationship between gas-phase and aqueous properties is obtained.[4,14,22] Using the $\Delta G^{\circ 8} = -21.2$ kcal/mol and assuming that the σ's are additive for double substitution one obtains an estimate for $\Delta G^\circ_{9b} = -21.2 \times \sigma_5/\sigma_4 = -3.8$ kcal/mol. This exothermicity is much smaller than the experimentally observed proton affinity difference between 1-naphthylamine and 1,8-diaminonaphthalene of 7.1 kcal/mol. We conclude that 1,8-diaminonaphthalene is nitrogen protonated and has the hydrogen bond bridged structure I. From the -7.1 kcal/mol experimental proton affinity difference between 1-naphthylamine and 1,8-diaminonaphthalene, which relates to reaction 9a, and the above estimate of -3.8 kcal/mol for reaction 9b, one obtains 3.3 kcal/mol as an estimate for the difference between the protonated diaminonaphthalene structures I and II.

Since the 1,8-diaminonaphthalene is nitrogen protonated, the other N-methylated diaminonaphthalenes will be also nitrogen protonated, since the effect of the N-methyl substituents will be bigger on the nitrogen basicity than on the aromatic ring basicity.

C. Gas-Phase and Aqueous Basicities of N-Methyl Substituted 1,8-Diaminonaphthalenes. The gas-phase and aqueous basicities of the methylated diaminonaphthalenes are best discussed in comparison with the methyl substituent effects in ammonia and aniline. The observed free-energy changes for proton transfer in the gas phase and in aqueous solution for the three series are given below.

$$NH_3 \xrightarrow[-1.9]{-10} NH_2Me \xrightarrow[0]{-7.6} NHMe_2 \xrightarrow[+1.1]{-4.9} NMe_3 \qquad (10)$$
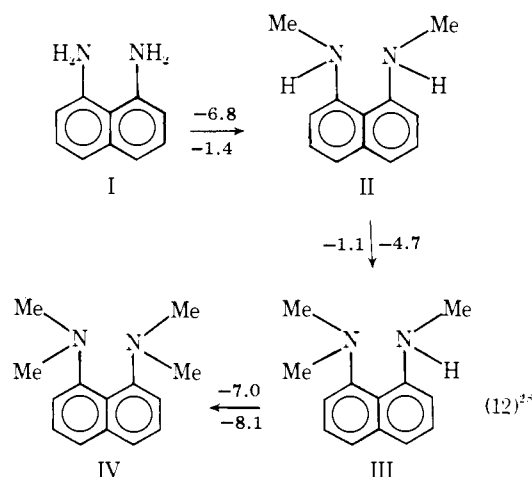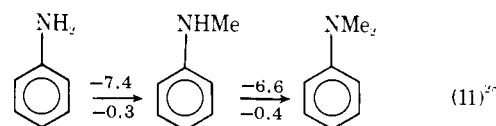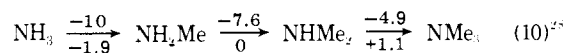

kcal/mol energy required to move the proton from the ring to the N-protonated position and some adverse $T\Delta S$ change because of loss of freedom in the freezing of the (restricted) rotation of the amino groups which will occur on protonation. This $T\Delta S$ loss may be expected to be a few kilocalories per

In the ammonia series methyl substitution increases substantially the gas-phase basicity. One observes an attenuation of the substituent effect since each new methyl substitution gives a progressively smaller basicity increase.[23] The methyl substituent effect in aqueous solution is very much smaller and becomes reversed with progressive substitution. This is the well-known amine anomaly which is mainly due to the progressively worsening solvation of the ammonium ions with methyl substitution.[23] The methyl substituents decrease the solvation of the ammonium ion by removing hydrogen-bonding positions and simultaneously decreasing the hydrogen-bonding interactions with water for the remaining hydrogen-bonding positions.[23-25]

In aniline, methyl substitution substantially increases the gas-phase basicity (see eq 11). The effect of the second methyl is much less attenuated than was the case for the aliphatic amines. The methyl substituent effect on the anilines in solution is extremely attenuated compared with the gas phase, but no reversal is observed.

For the diaminonaphthalenes, unfortunately, an experimental result for single methyl substitution is not available (see eq 12). The 6.8 kcal/mol difference between the nonsubstituted and the 1,8-bis(methylamino)—substituted naphthalene probably should be split unevenly, say 5 and 1.8 kcal/mol, between the first and second methyl substitution. The second methyl does not go to the same nitrogen. The potential energy for proton motion between the two nitrogens in protonated 1,8-diaminonaphthalene may be expected to have a double minimum as is the case for $H_3NH^+NH_3$ according to the calculations of Peyerimhoff.[19] The barrier for the proton motion, when the nitrogens are kept fixed to the equilibrium position, was calculated[19] to be about 3.5 kcal/mol. Assuming a similar or even larger barrier to occur for the bent hydrogen bond in the protonated 1,8-diaminonaphthalene (see preceding section) one expects the second methyl (which is on the second nitrogen) not to interact as a direct substituent but only as a substituent increasing the H bond interaction. This view is supported by the observed proton affinity change of 4.7 kcal/mol between 1,8-bis(methylamino)naphthalene and 1-dimethylamino-8-methylaminonaphthalene, i.e., II and III in eq 12. For this case the new methyl substituent is on the nitrogen with which the proton is associated. The observed 4.7 kcal/mol energy change for an increase by a single methyl is, as expected, rather large.

Since the last methyl group for the change from trimethyl- to tetramethyldiaminonaphthalene, i.e., III to IV in eq 12, is to be associated with the nitrogen opposite to that holding the proton one might have expected a very small proton affinity change of some 1–2 kcal/mol. The observed change of 7 kcal/mol is very much larger. However, this experimental result is fully in accord with the explanation by Alder et al.[2a] of the unusually high basicity of the 1,8-bis(dimethylamino)-naphthalene. This work attributes[2a] the high basicity to steric strain in the neutral base. Because of repulsion between the four methyl groups and the two lone pairs on the N atoms, the neutral base IV is highly strained. The nitrogens are not in the plane of the naphthalene rings; in fact, the naphthalene plane is twisted at carbons 9 and 10 allowing in this manner an increase of distance between the two methylamino groups.[2a,18] Protonation allows the two nitrogen lone pairs to align and the naphthalene moiety to become planar. The relieved strain energy shows up as an increase of proton affinity.

The basicity changes with methylation of the naphthalene-diamines in solution are seen to be strongly attenuated when compared to the gas-phase basicity changes. The attenuation should have the same causes as that for the methylamines and methylanilines, i.e., while methyl substitution stabilizes the protonated ion it also decreases the solvation of the ion. Significantly the aqueous change of basicity between the tri-

methyldiamine III and tetramethyldiamine IV is as large as (actually larger than) the corresponding gaseous change (see eq 12). Since the major driving force for increased basicity in this case is the relief of strain energy and this relief does not affect the solvation of the protonated ion, the gas-phase and aqueous basicity changes should be very similar. Since the protonated trimethyl compound III has one hydrogen bonding position its solvation should be more favorable than that for the protonated tetramethyl ion IV. Therefore one might have expected that the gas-phase basicity change should have been slightly larger than the aqueous change. It is not clear why the measurements give the reverse result. However, the observed difference is small and the cause for the difference probably unimportant.

The hydration of the protonated III and IV in which there is steric hindrance for hydrogen bonding may be expected to resemble that of other similarly sterically hindered and relatively bulky systems and also of cations that are with delocalized charge such that there is not an exposed strong cationic site. All these systems will experience only physical solvation and if they are of roughly similar size their hydration energies should be roughly the same. Taft et al.[26] have measured the free-energy changes for proton transfer from the ammonium ion to bases B, i.e., reaction 4, which on protonation lead to BH^+ ions to the above type. A comparison of $\Delta G_4°(g)$ with $\Delta G_4°(aq)$ for these systems has shown that the difference $\Delta = \Delta G_4°(aq) - \Delta G_4°(g)$ is approximately constant and equal to $\Delta = 35 \pm 1$ kcal/mol. Since the ion hydration is generally the dominant term in Δ, a near-constant Δ indicates a very similar solvation of the BH^+ ions while the large positive value of Δ reflects the much better solvation of NH_4^+ as compared to that of BH^+. Examples of B that fit the relationship are α-methylstyrene ($\Delta = 34$), 1,1-diphenylethylene (34.7), hexamethylbenzene (35.2), 2,6-di-*tert*-butylpyridine (34.1) (see Table I, ref 26). The first three BH^+ are charge delocalized while the pyridine has a sterically hindered hydrogen bonding site.

The calculated Δ for the diaminonaphthalenes III and IV are 36.0 and 35 kcal/mol.[27] Thus these compounds also fit the relationship. This means that their ionic hydration energies are very similar to those of the above quoted BH^+, a result that is interesting and obeys the considerations given above.

The gas-phase basicity for *o*-dimethylaminobenzene (V) was also determined and is shown in Figure 1. The basicity of

V

VI
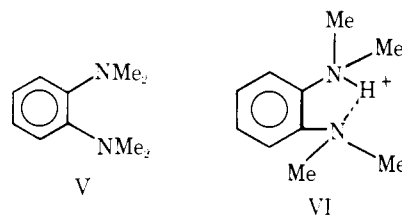
this compound is found to be 7.4 kcal/mol lower than that for the tetramethylated diaminonaphthalene IV. Steric models show that the two amino groups are very much less constrained in V than in IV. One may expect that the protonated base will have the hydrogen bond bridged structure VI. Since one does not expect a relief of steric strain on protonation of V, the gas-phase basicity of V should be lower than that of IV by (approximately) the amount of the relieved strain energy in the protonation of IV, i.e., 6–7 kcal/mol. The experimental result of 7.4 kcal/mol. is in line with this reasoning. The fact that the decrease of 7.4 kcal/mol is slightly higher than the expected 6–7 kcal/mol probably reflects also a decreased stability in VI (relative to the protonated IV) because of the more strongly bent hydrogen bond in VI.

performing the MINDO/3 calculation. Financial support by the Canadian National Research Council is gratefully acknowledged.

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(28) $\Delta G°$ for proton transfer given above arrow for gas phase and below arrow for aqueous solution.

The Use of Chlorine Kinetic Isotope Effects for Evaluating Ion Pairing in Nucleophilic Displacements at Saturated Carbon

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Abstract: Use of the Winstein scheme to describe ion pairing leads to the conclusion that chlorine kinetic isotope effects (KIE) are primarily responsive to processes involving the covalently bound chlorine and less indicative of reactions which occur after the formation of the initial ion pair. This conclusion has been tested by showing that the calculated equilibrium isotope effect (1.0057) and observed (1.0059₆ ± 0.0001₁) KIE are nearly identical when the solvolysis of *p*-methylbenzyl chloride is forced toward a limiting case with 97% trifluoroethanol as solvent. The reaction of *p*-phenoxybenzyl chloride showed similar behavior with an equilibrium KIE value of 1.0058₄ ± 0.0001₁. These results suggest that competing ion-pair and S$_N$2 processes may be one factor contributing to Hammett plot curvature for these nucleophilic displacement reactions. Chloride KIE values for the reaction of *n*-butyl chloride with thiophenoxide anion, where ion pairing does not occur, show little variation with a wide variety of solvents.

Introduction

Evidence has been accumulating which demonstrates that several reversibly formed ion pair intermediates must be considered to interpret the mechanisms of solvolytic displacement reactions at saturated carbon.[4,5] Shiner and co-workers[6] have shown that ion pair intervention influences the magnitude of the secondary deuterium isotope effects observed for solvolytic displacement reactions, and an imaginative study by Murr and Donnelly[7,8] has demonstrated the feasibility of interpreting the observed, overall isotope effect by considering the isotope effects on each individual process and the overall rate constant for the reaction. Maximum α-deuterium isotope effects occur[6] when the dissociation of one of the ion pair intermediates (k_2 or k_3 in Winstein's[4] Scheme I) is rate determining.