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The Basicity of Unsaturated Hydrocarbons as Probed by Hydrogen-Bond-Acceptor Ability: Bifurcated N−H$^+$···π Hydrogen Bonding

Evgenii S. Stoyanov,* Irina V. Stoyanova, and Christopher A. Reed*[a]

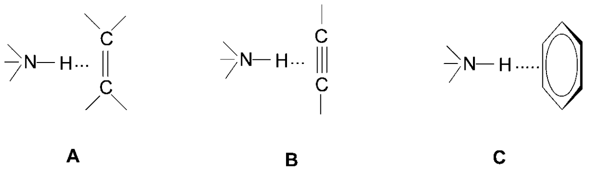
Abstract: The competitive substitution of the anion (A^-) in contact ion pairs of the type $[Oct_3NH^+]B(C_6F_5)_4^-$ by unsaturated hydrocarbons (L) in accordance with the equilibrium $Oct_3NH^+\cdots A^- + nL \rightleftarrows [Oct_3NH^+\cdots L_n]A^-$ has been studied in CCl_4. On the basis of equilibrium constants, K, and shifts of νNH to low frequency, it has been established that complexed $Oct_3NH^+\cdots L_n$ cations with $n=1$ and 2 are formed and have unidentate and bifurcated N−H$^+$···π hydrogen bonds, respectively. Bifurcated hydrogen bonds to unsaturated hydrocarbons have not been observed previously. The unsaturated hydrocarbons studied include benzene and methylbenzenes, fused-ring aromatics, alkenes, conjugated dienes, and alkynes. From the magnitude of the redshifts in the N−H stretching frequencies, $\Delta\nu$NH, a new scale for ranking the π basicity of unsaturated hydrocarbons is proposed: fused-ring aromatics ≤ benzene < toluene < xylene < mesitylene < durene < conjugated dienes ≈ 1-alkynes < pentamethylbenzene < hexamethylbenzene < internal alkynes ≈ cycloalkenes < 1-methylcycloalkenes. This scale is relevant to the discussion of π complexes for incipient protonation reactions and to understanding N−H$^+$···π hydrogen bonding in proteins and molecular crystals.

Keywords: basicity · bifurcated hydrogen bonds · IR spectroscopy · hydrogen bonds · unsaturated hydrocarbons

Introduction

X−H···π hydrogen-bonding interactions have been studied for a long time. Following the suggestion by Dewar in 1946 that π complexes might be involved in the mechanism of electrophilic aromatic substitution,[1] Brown and Brady showed in 1952 that HCl formed complexes with aromatic compounds and alkenes in hydrocarbon solutions.[2] Information on the molecular structures of these complexes was not available, but equilibrium binding constants were determined and, within families of structurally similar compounds, a rough correlation with other measures of basicity was found. When exceptions were noted, they were attributed to differences in π versus σ basicity. Stability constants became the primary method of studying π complexes,[3] but a more specific measure of π basicity in condensed phases did not develop.

In the gas phase, weak X−H···π hydrogen-bonding interactions were identified in 1981 in complexes of HCl with alkynes, alkenes, and arenes.[4–6] T-shaped structures were deduced for the alkene and alkyne complexes (**A** and **B**) with the X−H bond at approximately 90° and directed to the center of the multiple C−C bond. Recent atomic deformation calculations indicate that maximum electron density lies at the mid-point of the double and triple bonds.[7] With benzene, the X−H bond is preferentially directed near the center of the aromatic ring in a π-face manner (Scheme 1, structure **C**).



Scheme 1. Structures of hydrogen-bonded alkenes (**A**), alkynes (**B**), and benzene (**C**).

Stronger interactions with unsaturated hydrocarbons occur when the complex involves positively charged proton donors, such as the N$^+$−H bond of the ammonium ion.[8]

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The addition of this electrostatic effect increases the binding enthalpy of the complex by several kcal mol^{-1} such that ΔH for the gas phase $NH_4^+\cdots C_6H_6$ complex is 19.3 kcal mol^{-1}.[9] Calculations indicate that the energetics are dominated by the charge/quadrupole interaction[10] and do not significantly distort the π-electron distribution.

The T-shaped structure of the 2-butyne•HCl complex (Scheme 1 structure **B**)[11] and the π-face structure of $NH_4^+\cdots C_6H_6$ (Scheme 1 structure **C**)[12] have been confirmed in the solid state by X-ray crystallography. In the $H_3O^+\cdot 3\,C_6H_6$ cation,[13] the O–H bonds are directed more closely to carbon atoms than to the centroid of benzene. More generally, the X–H···π hydrogen-bonding interaction has become widely recognized as a weak but prevalent intermolecular interaction in small molecule crystallography.[14–19] The range of acceptors now includes nitrogen heterocycles[20] and π-ligand transition-metal complexes[18] and these types of interactions are beginning to be utilized in crystal engineering.[21] X–H···π interactions have also been identified in proteins[19,22,23] and N–H···π interactions can be sufficiently strong to affect secondary (folding) structure.[24]

Estimations of the strengths of X–H···π interactions have typically relied on the determination of the thermodynamics of complexation. This can be informative in the gas phase, but in condensed phases the difficulty of separating the intrinsic strength of the hydrogen-bonding interaction from the contribution of solvation energies to the stability constant has thwarted the development of useful scales of π basicity. Mayr and co-workers have recently developed a nucleophilicity scale for π bases based on extensive kinetic data for reactions with electrophiles.[25,26] In favorable cases, distance information from crystallography might be utilized in a comparative manner,[27] but without the precise location of the hydrogen atom, typically achieved only in neutron diffraction studies, this method is limited.

In the present work, with the idea of developing a ranking system of interaction strength, we use IR spectroscopy to explore the N–H···π interaction of the trioctylammonium ion with alkynes, alkenes, and arenes upon reaction with ion pairs (IPs) of the type $[Oct_3NH^+]\{B(C_6F_5)_4^-\}$ in CCl_4. Carbon tetrachloride is a weakly solvating, low dielectric solvent that favors contact IP formation. Of commercially available anions, the perfluorinated tetraphenylborate ion, $B(C_6F_5)_4^-$ (abbreviated to $\{F_{20}^-\}$), is the least interacting towards the Oct_3NH^+ ion, as judged by νNH stretching frequencies in contact IPs.[28] This allows weak acceptors (L), such as unsaturated hydrocarbons, to compete with the $\{F_{20}^-\}$ anion and bind to the NH^+ group of the cation, forming solvated IPs of the type $[Oct_3NH^+\cdot L]\{F_{20}^-\}$. In these complexes, the extent of the $Oct_3NH^+\cdots L$ interaction can be measured by two methods: equilibrium binding constants (*K*) and changes in νNH in the IR spectrum. Equilibrium binding constants can be compared across different classes of π bases when *K* values for 1:1 or potentially 1:*n* complexation are determined from equilibria [Eq. (1)].

$$\underset{\text{Contact IP}}{Oct_3NH^+\cdots\{F_{20}^-\}} + nL \rightleftharpoons \underset{\text{Solvated IP}}{[Oct_3NH^+\cdots nL]\{F_{20}^-\}} \qquad (1)$$

We have recently shown that νNH bands in the IR spectra of the Oct_3NH^+ cation in contact IPs of the type $[Oct_3NH^+]A^-$ (A^- = anion) decrease in frequency as a function of increasing hydrogen-bond-acceptor strength of the anion, leading to a sensitive basicity scale for anions.[28] The same concept is now applied to neutral molecules. In addition to changes in the frequency of the νNH band, its intensity, band width, and shape give further information about hydrogen bonding in the $Oct_3NH^+\cdots L$ interaction.

We anticipated that these two measures of the basicity of L would give somewhat different rankings. They measure different properties: νNH frequencies give a measure of the $NH^+\cdots L$ interaction strength, whereas stability constants are a composite of the interaction strength and the differences in solvation energies of all reactants and products. Nevertheless, we did tend to choose mostly six-membered ring compounds for this study so that solvation energy differences between different compounds (or classes of compounds) were minimized. We also anticipated that these rankings would not correlate with existing measures of the basicity of unsaturated hydrocarbons, for example, gas-phase ionization energies, complexation enthalpies, and proton affinities[29,30] or condensed-phase equilibrium constants[3] and nucleophilicities.[25] These scales are based on different thermodynamic quantities or physical phenomena that do not readily lend themselves to quantitative connections between gas- and condensed-phase data. The X–H···π interaction under study is a weak, localized effect, whereas the energetics of complete protonation (σ basicity) involve larger, more global molecular phenomena.

A specific point of interest is the possible existence of bifurcated π hydrogen bonds of the type $X\text{–}H^+\cdots 2\,L$, which are formed by a positively charged cation with two unsaturated hydrocarbons (L). The formation of bi- and even trifurcated hydrogen bonds has occasionally been observed by X-ray crystallography for trialkylammonium cations, when they interact with O or N-heteroatoms, such as the $(C_2H_5)_3NH^+$ cation with three hydroxyl oxygen atoms.[31,32] Sometimes one of the acceptors of a bifurcated hydrogen bond is an oxygen atom, the other an alkyne[19,33,34] or arene.[24,35] Bi- or multifurcated hydrogen bonds are frequently deduced from protein crystallography.[36] The solution-phase existence of compounds with bifurcated π hydrogen bonds involving only unsaturated hydrocarbons has not been reported.

Further interest in X–H···π interactions arises from the long-held belief that hydrogen-bonded complexes are incipient proton-transfer reactions, that is, models for the early stages of π systems reacting with strong acids.[37] Indeed, in the 1970s there was an intense debate on whether π complexation of electrophiles could be rate-determining in the mechanism of electrophilic aromatic substitution.[38] Current consensus holds that σ (rather than π) complexes and Ar^+E^- charge-transfer IPs[39] are more important in the transition state, nevertheless weak π complexation is widely believed to precede formation of these activated complexes. Our interest in models for incipient proton transfer is piqued by the recent isolation and X-ray structural characterization of a fully protonated alkene (e.g., *tert*-butyl cation),[40] the equivalent of a protonated alkyne (i.e., a vinyl cation),[41] and protonated benzene ($C_6H_7^+$).[42] More information is needed on pre-protonation complexes if they are to become widely accepted as early intermediates in protonation reactions.

Results

IR spectra of 0.04 M solutions of $[Oct_3NH^+]\{F_{20}^-\}$ in CCl_4 show a narrow νNH band at 3233 cm^{-1}. From studies with other anions, we know this corresponds to a contact IP rather than a solvent-separated IP.[28] The band frequency is independent of concentration between 0.005 and 0.04 M.[28] When unsaturated hydrocarbons (L) are added to these solutions, the intensity of this band decreases with increasing concentration of L (c_L). At the same time a new, lower frequency νNH band arising from complexed ion pairs (CIP) of $[Oct_3NH^+\cdot nL]\{F_{20}^-\}$ appear. The intensity of the new νNH band grows with increasing c_L. An example is shown in Figure 1 for L = benzene. Representative spectra for other arenes, normalized to unit intensity of νNH of the uncomplexed contact IP (3323 cm^{-1}), are shown in Figure 2.

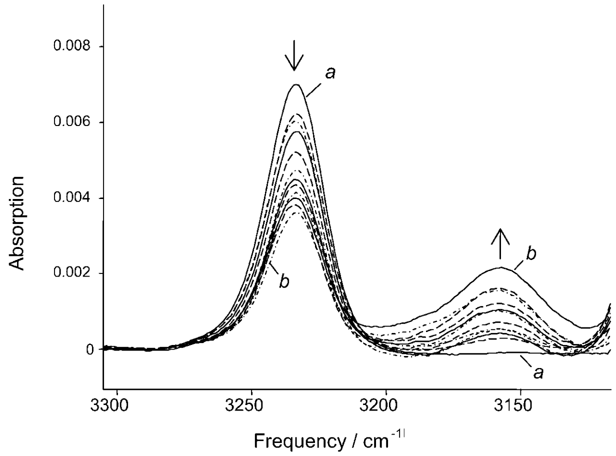


Figure 1. Evolution of the IR spectrum in the νNH region of 0.4 M $[Oct_3NH^+]\{F_{20}^-\}$ in CCl_4 as benzene is added. Benzene concentrations increase from zero (*a*) to 100% (*b*).

The concentration of the $[Oct_3NH^+]\{F_{20}^-\}$ contact IP (c_{IP}) was determined from the decreasing intensity of its νNH band at 3233 cm^{-1} as $c_{IP} = 0.04f$, in which f is the scaling factor with which the νNH band is fully subtracted from the spectrum of the 0.04 M solution of $[Oct_3NH^+]\{F_{20}^-\}$. The concentration of the $[Oct_3NH^+\cdots nL]\{F_{20}^-\}$ π-CIP (c_{CIP}) is defined by $c_{CIP} = 0.04 - c_{IP}$. These concentrations allow the equilibrium constant of the reaction (K) to be determined from Equation (2):

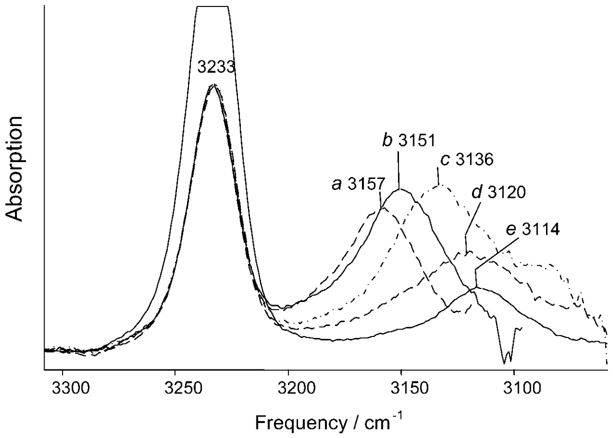


Figure 2. Representative IR spectra showing the formation of $[Oct_3NH^+\cdots nL]\{F_{20}^-\}$ CIPs with their νNH frequencies for arenes L = benzene (*a*), toluene (*b*), mesitylene (*c*), pentamethylbenzene (*d*), hexamethylbenzene (*e*). Spectra, with the exception of *a*, are normalized to νNH of the uncomplexed contact IP at 3323 cm^{-1}.

$$K = c_{CIP}/(c_L)^n c_{IP} \tag{2}$$

in which c_L is equilibrium concentration of free L. Because complexation of the π base is weak and c_{CIP} is small compared with the total concentration of L (c_L^o), the approximation $c_L \approx c_L^o$ is valid and Equation (2) becomes Equation (3):

$$c_{CIP}/c_{IP} = K(c_L^o)^n \tag{3}$$

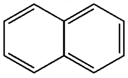
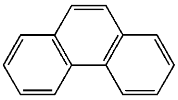
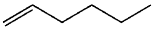
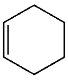
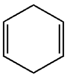
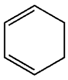
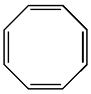
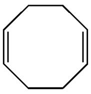
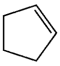
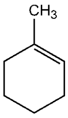
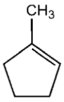
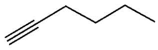
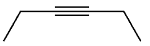
Taking logarithms of Equation (3) gives Equation (4),

$$\log(c_{CIP}/c_{IP}) = \log K + n \log c_L^o \tag{4}$$

in which the slope of the function $\log(c_{CIP}/c_{IP}) = f(\log c_L^o)$ gives the number, n, of molecules L that are directly bound to NH group. The equilibrium constant K, that is, the stability constant for L-CIP, $[Oct_3NH^+\cdots nL]\{F_{20}^-\}$, can be determined from the slope of Equation (3) for a fixed value of n.

Aromatic hydrocarbons: As illustrated for benzene and hexamethylbenzene in Figure 3, the slope of Equation (4) is equal to one for all aromatic hydrocarbons studied (L = benzene; toluene; *o*- and *p*-xylene; 2,4,6-mesitylene; tetra-, penta- and hexamethylbenzenes; naphthalene, and phenanthrene; see Table 1). In other words, only 1:1 adducts with the NH$^+$ group are formed. The frequencies of the νNH band for all compounds are practically independent of the concentration of L, although the width of this band ($S_{1/2}$) shows mild concentration dependence in the case of benzene and the methylbenzenes. As illustrated in Figure 4 for the representative case of benzene, $S_{1/2}$ increases with increasing c_L. There is a break at approximately 6 M benzene and $S_{1/2}$ increases more rapidly with increasing concentra-

Table 1. Characteristics of $[Oct_3NH^+\cdots nL]\{F_{20}^-\}$ complexes in CCl_4.

L	K	n	νNH[a] [cm^{-1}]	$\Delta\nu NH$[b] [cm^{-1}]	$S_{1/2}$[d] [cm^{-1}]
C_6H_6	0.085	0.99	3156.5	75	27
$C_6H_5CH_3$	0.114	1.05	3151	82–83[c]	34
$C_6H_4(CH_3)_2$	0.139	1.06	3144	88–91[c]	36
$C_6H_3(CH_3)_3$	0.142	0.97	3140	94.5–98[c]	38
$C_6H_3(CH_3)_4$	0.148		3130	103.5–104.5	46
$C_6H(CH_3)_5$	0.160	0.997	3120	113	39
$C_6(CH_3)_6$	0.154	1.09	3114	118–119[c]	35
	0.260	1.06	3136	70	30
	0.458	1.04	3166	67	39
	< 0.002	0.99	≈3075	≈158	155 ± 5
	0.084	0.99	≈3075	≈158	155 ± 5
	0.0725	1.04	≈3072[g]	≈160[g]	[f]
	0.41 0.257	1.14 1.97	3125 3084	108 149	76
	0.216 0.722	0.496 0.98	3125 3084	108 149	49 131
	0.025	[f]	[f]	[f]	[f]
	0.094	0.998	3100 ± 5	133 ± 5	150 ± 10
	0.215	1.00	3063	170	150
	1.15	1.04	3048, ≈2880[e]	185	[f]
	0.254 [f]	1.01 (2)[f]	3123 3086	109–117 147	150 ± 5 115
	2.02 3.65	1.08 1.94	3094 3072, ≈2880[c]	139 161	163 [f]
water	174	0.94	3090	143	61

[a] For 1:1 arene complexes at low concentrations of L. [b] The scale is anchored to the contact IP ($\Delta\nu NH = 0$ at 3233 cm^{-1}), for 1:1 complexes data are given for low concentrations of L (except for arenes). [c] Frequency interval for solutions of arenes from low to high concentrations. [d] For 1:1 complexes at low concentration of L. [e] νNH band is distorted by Fermi resonance; the true νNH frequency cannot be obtained because both components are partially overlapped with intense absorptions from the octyl chains of the cation and CH vibrations from the unsaturated hydrocarbon. [f] Cannot be determined. [g] Calculated from νND frequency (see Table 2).

tion. With the methylbenzenes, the break is shifted to lower concentrations of L as the number of methyl groups increases, and is approximately 0.32 M for hexamethylbenzene. This indicates some change in the character of the $[Oct_3NH^+\cdots L]$ group at high c_L concentrations, presumably due to outer-sphere solvation of the cation by additionally associated L [Eq. (5)], that is, the formation of solvent separated complexed ion pairs (SSCIPS) that nevertheless remain specified as 1:1 hydrogen-bonded complexes.

$$\underset{\text{CIP}}{[Oct_3NH^+\cdots L]\{F_{20}^-\}}+mL \rightleftharpoons \underset{\text{SSCIP}}{[Oct_3NH^+\cdots L]L_m\{F_{20}^-\}} \quad (5)$$

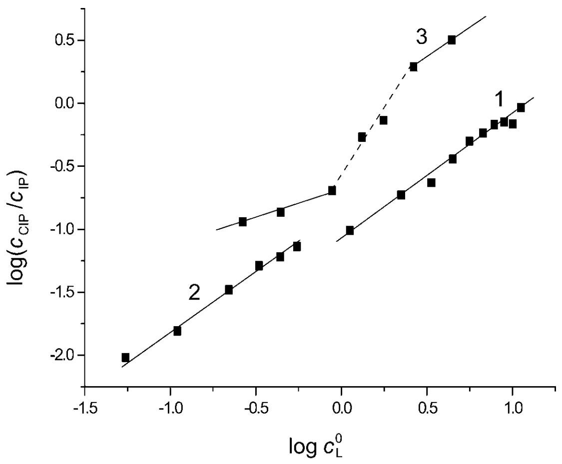


Figure 3. Slopes of Equation (4) for benzene (1, $n=0.99$), hexamethylbenzene (2, $n=0.98$), and 1,3,5,7-cyclooctatetraene (3, $n=0.50$ and 0.98).

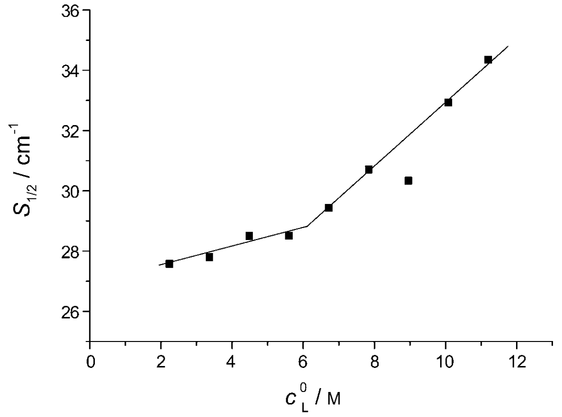


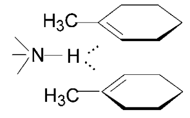
Figure 4. Plot of band width at half height ($S_{1/2}$) for νNH of $[\text{Oct}_3\text{NH}^+\cdots\text{C}_6\text{H}_6]\{\text{F}_{20}^-\}$ with increasing concentration of benzene (2.24–11.2 M).

Later we provide evidence to support this proposal. As indicated by the essential constancy of the νNH frequency, outer-sphere solvation of the CIP by aromatic hydrocarbons does not change the strength of the $\text{NH}^+\cdots\text{L}$ interaction. Thus, outer-sphere solvation does not affect the determination of n or K. In the case of condensed aromatics, naphthalene and phenanthrene, there is no concentration dependence of $S_{1/2}$ of the νNH band, presumably because outer-sphere association is absent or it is present to a similar extent over the entire concentration range studied.

For the methylbenzenes, $\text{C}_6\text{H}_{6-y}(\text{CH}_3)_y$, the νNH frequency decreases regularly with increasing number of methyl groups (y), which indicates that the strength of $\text{N-H}^+\cdots\text{L}$ hydrogen bonding increases with increasing arene basicity (Figure 2, Table 1). K values increase in a roughly parallel manner.

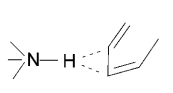
Alkenes: From the lack of changes in the IR spectrum, 1-hexene is unable to displace the $\{\text{F}_{20}^-\}$ anion in the $[\text{Oct}_3\text{NH}^+]\{\text{F}_{20}^-\}$ contact IP, even when used instead of CCl_4 as a solvent. On the other hand, cyclohexene and cyclopentene, and two cyclic dienes (1,4-cyclohexadiene and 1,5-cyclooctadiene) with isolated (nonconjugated) C=C bonds, are able to displace the $\{\text{F}_{20}^-\}$ ion and bind to the NH^+ group. The slope of Equation (3) indicates that these complexes have a 1:1 composition with common T-shaped π hydrogen bonds of type **A** (Scheme 1). The K values are given in Table 1. Because the K value for 1,5-cyclooctadiene is small, it was only possible to evaluate a 50 vol % solution. The νNH bands of all of these complexes have low intensity, are strongly broadened, and are redshifted (Table 1).

Methylcycloalkenes with the unsymmetrical $-\text{C(CH}_3\text{)=CH}-$ chromophore (1-methyl-1-cyclopentene and 1-methyl-1-cyclohexene) in the concentration range below 1 M form 1:1 compounds with larger K values, especially for 1-methyl-1-cyclopentene. Similar to symmetrical cycloalkenes, their νNH bands show large redshifts and very strong broadening (Table 1). The redshift of νNH for unsymmetrical alkenes is even greater than that for symmetrical alkenes. At concentrations higher than 1 M, the slope of Equation (4) starts to exceed one and, as the intensity of νNH of the 1:1 compounds decreases, a new, very broad, and greatly redshifted νNH band with maximum at approximately 2880 cm^{-1} appears, increasing in intensity with increasing alkene concentration. The higher stoichiometry (presumably 1:2), and the very low νNH value, suggests the formation of bifurcated π hydrogen bond (**D**).

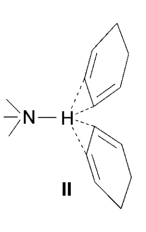


D

Cycloalkenes with conjugated double bonds, 1,3-cyclohexadiene and 1,3,5,7-cyclooctatetraene, show an improved ability to solvate the NH^+ group than alkenes with symmetrical isolated C=C bonds. For 1,3-cyclohexadiene, the slope of Equation (4) is close to one at low alkene concentrations ($C_L < 1$ M), but at higher concentrations is close to two (Figure 5). Thus, 1,3-cyclohexadiene forms both 1:1 and 1:2 compounds. In the ranges of c_L concentrations at which only one compound is formed, the dependence of Equation (3) increases proportionally with concentration, allowing both K values to be determined (Table 1). The complexes differ significantly in their νNH frequencies, 3125 cm^{-1} for the 1:1 complex and 3084 cm^{-1} for 1:2, indicating distinctly different types of π hydrogen bonding. If the 1:1 complex has a normal π hydrogen bond (**I**), then the 1:2 complex (with the much lower νNH frequency) must have a bifurcated hydrogen bond (**II**).

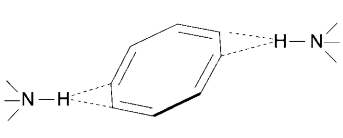


I

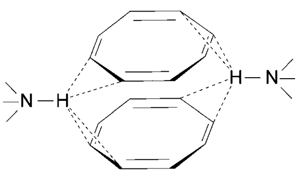


II

For 1,3,5,7-cyclooctatetraene, the value of n was $^1\!/_2$ at low c_L and transitioned to one at higher c_L (Figure 3). This indicates that at low c_L, 1,3,5,7-cyclooctatetraene acts as two separate diene units bonded to two Oct_3NH^+ cations, resulting in the formation of 2:1 complex **III**.



III



IV

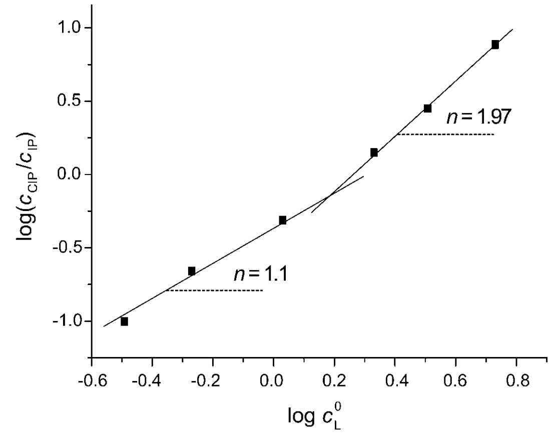


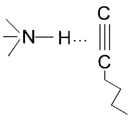
Figure 5. The slope of Equation (4) with 1,3-cyclohexadiene concentration.

Indeed, the exact coincidence of the νNH frequencies of complexes **I** and **III** (3125 cm^{-1}) indicates that both C=C–C=C chromophores in 1,3,5,7-cyclooctatetraene are acting independently, uninfluenced by each another. On the other hand, the 1,3,5,7-cyclooctatetraene complex with $n=1$ has the same νNH frequency (3084 cm^{-1}) as complex **II** (that is, 1:2 with 1,3-cyclohexadiene). This indicates a 2:2 composition with two bifurcated hydrogen bonds (**IV**).

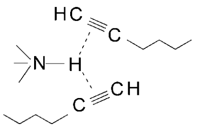
The K values of all compounds are given in Table 1.

Alkynes: Whereas linear alkenes, such as 1-hexene, do not complex the NH^+ group, linear alkynes do. IR spectra of the complexes formed by 1- and 3-hexynes are concentration dependent. In the case of 1-hexyne in the range of $c_L=$ 0.26–1.73 M, the maximum of the νNH band varies somewhat from 3124 to 3116 cm^{-1}. This is probably due to a greater role for alkynes in outer-sphere solvation of the Oct_3NH^+L cation, that is, the formation of the solvent-separated IPs $Oct_3NH^+{\cdots}L{\bullet}(L_m)\{F_{20}^-\}$ with variable m. In this concentration region, Equation (4) has a linear dependence on c_L with slope $n=1$ and Equation (3) leads to $K=0.254$. Therefore, this complex has a 1:1 composition with common π hydrogen bonding (**V**).

At higher c_L (50–100 vol % of 1-hexyne), a new νNH band from a second complex appears at 3087 cm^{-1} and the slope (n) of Equation (4) increases, indicating formation of a 1:2 complex with a bifurcated π hydrogen bond (**VI**).



V



VI

In the case of 3-hexyne, the νNH frequencies are more strongly redshifted than for 1-hexyne and the transition from a 1:1 to a 1:2 complex begins to take place at a lower alkyne concentration ($c_L\approx0.88$) (Figure 6). In the range of 1:1 complex formation, the slope of function $c_{CIP}/c_{CIP}=f(c_L)$ gives a value of $K=2.02$ (Figure 7) and in the range of 1:2 complex formation, the slope of the function $c_{CIP}/c_{CIP}=f(c_L)^2$ gives a value of $K=3.65$ (Figure 8).

Outer-sphere solvation: The existence of outer-sphere solvation of the complexed $Oct_3NH{\cdots}L^+$ cation by L for arenes and dienes is indicated by broadening of the νNH band at

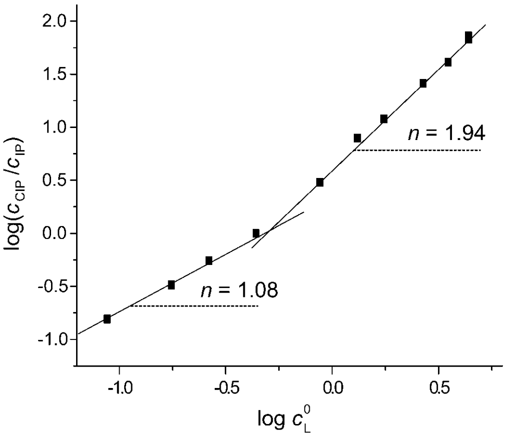


Figure 6. The slope of Equation (4) with 3-hexyne concentration.

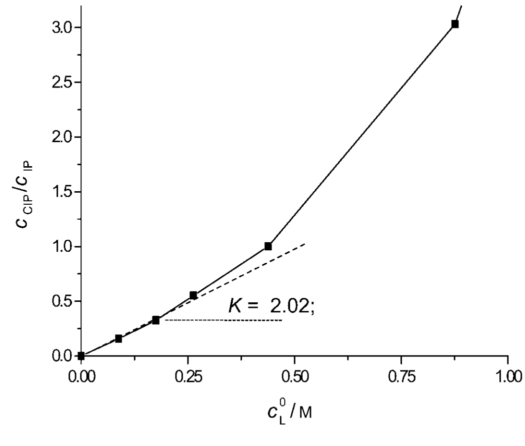


Figure 7. The slope of Equation (3) with $n=1$ for 3-hexyne.

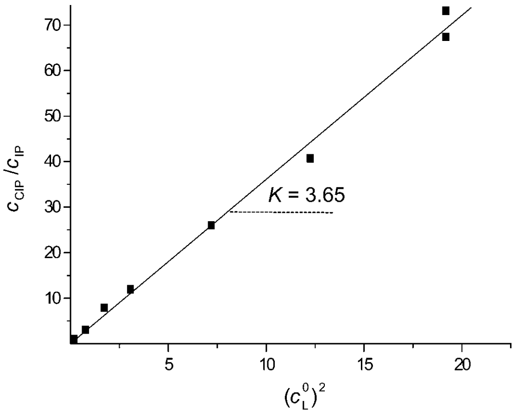


Figure 8. The slope of Equation (3) with $n=2$ for 3-hexyne.

high c_L. In the case of 1- and 3-alkynes there is also a gradual shift in the νNH frequency (≈8 cm^{-1}). In general, we find no evidence that the IR spectra of the unsaturated hydrocarbon molecules forming outer-sphere solvation shells are altered. Indeed, even those directly π hydrogen bonded to the NH^+ group are practically unchanged. However, 3-hexyne is an exception. Even though the frequencies and intensities of the fundamental vibrations of 3-hexyne are scarcely changed, the frequency of one of its combination bands at 1680 cm^{-1} decreases significantly (by 25 cm^{-1}) to 1655 cm^{-1} (Figure 9). This combination band may include one of the skeletal bending vibrations in the 200–550 cm^{-1} region that are conformationally dependent.[43] Most probably, the formation of an outer-sphere shell causes the 3-hexyne molecules to change their conformation. The relative band intensities at 1680 and 1655 cm^{-1} may therefore be used to investigate outer-sphere solvation of the Oct_3NH^+ cation by 3-hexyne.

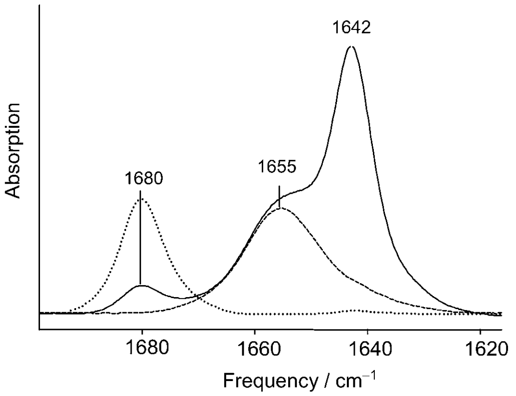


Figure 9. IR spectra of a solution of 0.04 M $Oct_3NH^+\{F_{20}\}$ in CCl_4 with 10 vol % of 3-hexyne (——) and a solution of 10 vol % 3-hexyne in CCl_4 (•••••). The dashed spectrum shows the band at 1655 cm^{-1}, which was isolated by sequential subtraction of the spectrum of free hexyne and the band at 1642 cm of $\{F_{20}\}^-$.

From the intensity of the band of free 3-hexyne at 1680 cm^{-1}, the equilibrium concentration in solution was determined as $c_L^{free}=f\times c_L^{st}$, in which f is the coefficient with which the band at 1680 cm^{-1} in the spectrum of the studied solution is fully subtracted by using the spectrum of standard 3-hexyne solution, and c_L^{st} is the concentration of L in the standard solution (in Figure 9 $f=0.755$, $c_L^{st}=0.876$ M or 10 vol %). The concentration of 3-hexyne molecules experiencing the conformation change in the solvation shell of the NH^+ group was determined from $c_L^{solv}=c_L^{o}-c_L^{free}$. Figure 10 shows the dependence of the number of conformationally affected 3-hexyne molecules per NH^+ group (m) as a function of c_L^o. The composition of the solvating shell is unexpectedly large. At $c_L^o=0.088$ M (1 vol %), 92.5 % of the alkyne is absorbed into the solvation shell, bringing the value of m to approximately 13. At $c_L^o=4.38$ M (50 vol %), this increases to about 30. Thus, substantial clustering of the alkyne occurs around the CIP. Most of the alkyne is not randomly mixed in the solution in CCl_4.

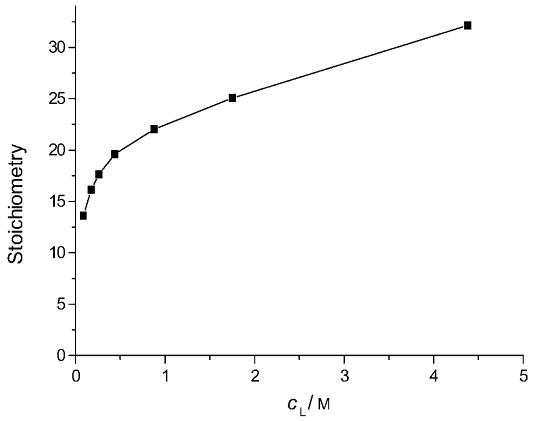


Figure 10. Dependence of m on 3-hexyne concentration.

To rule out the possibility that this alkyne solvation might originate from solvation of the $B(C_6F_5)_4^-$ anion or the octyl chains of cation, as opposed to that from the N−H···alkyne interaction, the solvation of the tetraoctylammonium salt of $B(C_6F_5)_4^-$ in 3-hexyne was studied under identical conditions. In the IR spectra of these solutions, the intensity of the band at 1680 cm^{-1} did not significantly decrease as 3-hexyne was added. A weak band grew in at 1671 cm^{-1} and the small redshift of this band relative to free 3-hexyne (1680 cm^{-1}, $\Delta=9$ cm^{-1}) suggests a minor association with the IP. The stoichiometric ratio determined as c_L^{solv}/c^o is around 2.4 for 10 vol % of 3-hexyne and increases to around 3.1 for 20 vol % solution.

Finally, for the purposes of comparison of unsaturated hydrocarbons to a traditional hydrogen-bond acceptor, we have investigated the interaction of H_2O with the $[Oct_3NH^+][F_{20}^-]$ IP. The IR spectrum of a 0.0156 M solution of $(Oct)_3NH^+\{F_{20}^-\}$ prepared in water-saturated CCl_4 (0.0055 M H_2O) shows νOH bands from water bound to the N−H group at 3674 and 3596 cm^{-1} and a new νNH band at 3090 cm^{-1} (Figure 11). From the concentrations of the complexed water and the Oct_3NH^+ cation, it was determined

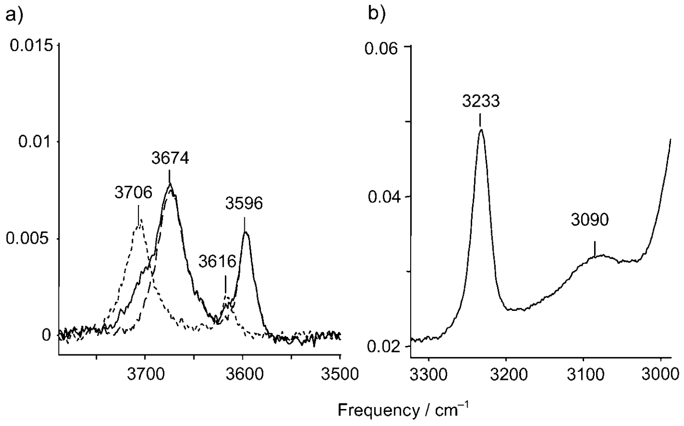


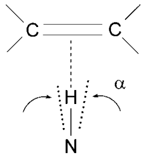
Figure 11. IR spectrum of 0.0156 M $(Oct)_3NH^+\{F_{20}^-\}$ in CCl_4 with 0.0055 M water in the frequency region of νOH (a) and νNH (b). ——: measured spectrum. -----: spectrum of 0.0055 M of water in CCl_4. ———: spectrum of $[(Oct)_3NH^+\cdots OH_2]\{F_{20}^-\}$ IP obtained by subtraction of ----- from ——.

that the molar ratio was close to one. The K value is given in Table 1.

Discussion

In the solutions under study, three types of IPs are formed that differ in the character of the solvation of the NH^+ group: 1) 1:1 mono-CIP, $[Oct_3NH^+\cdots L]\{F_{20}^-\}$, with the cation and anion separated by one unsaturated hydrocarbon molecule L, 2) SSCIPs with some intervening unsaturated hydrocarbon molecules L_m, $[Oct_3NH^+\cdots L]\cdot L_m\{F_{20}^-\}$, in which the cation retains the essential character of mono-CIPs, and 3) 1:2 di-SSCIPs $[Oct_3NH^+\cdots 2L]\cdot L_m\{F_{20}^-\}$, with two molecules of L directly bonded to the NH^+ group, that is, with bifurcated hydrogen bonds. The transition from CIP to SSCIP, caused by outer-sphere solvation of the NH^+ group by excess L, has practically no effect on the experimentally determined values of n and K. Therefore, both CIP and SSCIP formulations are attributed to 1:1 compounds.

π Hydrogen bonding: The νNH band is exceedingly broad ($\approx 150\,cm^{-1}$) for both alkene and alkyne complexes (Table 1). For example, comparing the 1-hexyne complex with the 1,3-cyclohexadiene, 1,3,5,7-cyclooctatetraene, and tetra- and pentabenzene complexes, all with similar νNH frequencies, the νNH band width ($S_{1/2}$) is two to four times higher. Some contribution to the broadness that develops in the νNH band in all complexes may arise from outer-sphere solvation effects. Another, perhaps larger, effect may be because the π hydrogen bond directed towards the center of the C=C or C≡C bond is not fixed, but fluctuates in the limits of some angle (α) because the maximum of the π-electron density centered between two carbon atoms is very flat (**E**). This phenomenon, in varying degrees, may explain the change in the νNH band width as a function of progressive methylation of benzene. As shown in Figure 12, the band width reaches a maximum at durene. It is smallest for symmetrical benzene and hexamethylbenzene. Possibly, in the most symmetrical arenes, the proton is directed at the exact center of the aromatic ring and this minimizes the angular fluctuation of the NH bond. This is in line with neutron diffraction data in which N−H vectors of the N$^+$−H···phenyl interactions between an NH_4^+ ion and phenyl groups are time-averaged towards the centroid of the phenyl rings, whereas the 50 % probability ellipsoids of the N−H vector samples the entire face of the aromatic ring.[12]



E

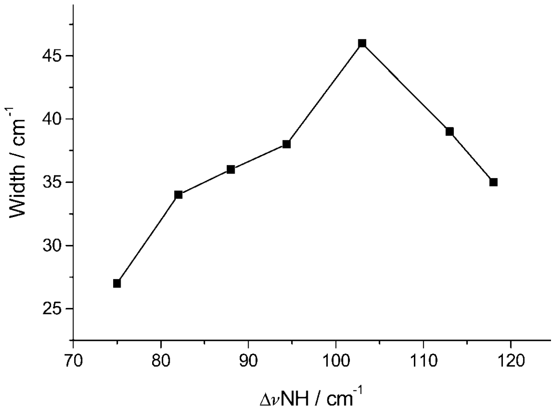
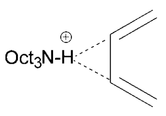


Figure 12. Dependence of the width of the νNH band on the $\Delta\nu$NH frequency for a set of arenes $C_6H_{6-y}(CH_3)y$ in which $y=0$–6.

In the 1:1 complexes formed by cyclic molecules with a pair of conjugated C=C bonds, the functionality acts as a single C=C−C=C chromophore. The absorption of this chromophore for the free (noncomplexed) molecule of L has two νC=C bands (1603 and 1578 cm^{-1}) of medium to low intensity. Upon complex formation in **I** and **III** the νC=C absorption does not change, which indicates that this type of interaction is symmetrical (**F**).



F

The four conjugated C=C groups of 1,3,5,7-cyclooctatetraene in complex **II** act as two independent C=C−C=C chromophores that do not influence one another. This case is distinguished from 1:1 complexes formed by arenes with formally three conjugated C=C bonds. These act as a single aromatic chromophore with an interaction strength lower than that of the C=C−C=C chromophore (Table 1).

Conjugated dienes and alkynes show an unexpectedly high capacity for the formation of 1:2 complexes with bifurcated π hydrogen bonds (such as in complexes **II**, **IV**, and **VI**). The bonding of the second base is indicated by greater $\Delta\nu$NH shifts. This phenomenon may be much more prevalent than previously realized and may play important role in synthetic organic chemistry and biochemistry.

Trends in νNH and *K*: Application of the νNH frequency as an IR probe of the relative interaction strength of N$^+$–H with unsaturated hydrocarbons can be made for all 1:1 compounds. This indicates that π basicity increases phenanthracene < naphthalene < benzene < toluene < xylene < mesitylene < durene < conjugated dienes ≈ 1-alkynes < pentamethylbenzene < hexamethylbenzene < internal alkynes ≈ cycloalkenes < 1-methylcycloalkenes. By this measure, fused ring aromatics show slightly lower π basicities than single ring benzenes. This is a reversal from that observed in gas-phase proton affinities[29] and can be understood in terms of the importance of large size in stabilizing gas-phase cations. The ranking for increasingly methylated benzenes correlates with expectations based on traditional measures of basicity, showing that the inductive effects of methyl groups do affect π basicity. Alkenes, especially 1-methylcycloalkenes, register more basic than alkynes. This is a counterintuitive result inasmuch as alkynes might be considered more π-electron rich than alkenes.

The IR spectra of the 1:2 complexes with bifurcated hydrogen bonds are less suitable for ranking interaction strength because they are formed more rarely than 1:1 complexes and their νNH frequencies cannot be determined with the same accuracy as for 1:1 complexes.

When the νNH frequency is less than 3054 cm^{-1}, this band becomes subject to Fermi resonance interactions with overtones of low frequency vibrations.[28] If this takes place, the band becomes distorted and a broad asymmetric component appears in the low frequency region (2700–2950 cm^{-1}). The best way to determine the presence of the Fermi resonance is to study deuterated analogues because the νND band of $Oct_3ND^+\{F_{20}\}^-$ lies in a frequency range that is not coupled with overtones of low-frequency vibrations.[28] However, these experiments can be thwarted by H/D exchange reactions. For example, the D atom of the Oct_3ND^+ cation readily exchanges with H atoms of alkynes, such that the IR spectra of $[Oct_3ND^+\cdots L]\{F_{20}\}$ IPs with L = 1-hexyne or 3-hexyne developed only the νNH band. Similar fast H/D exchange was observed in the $D_3O^+\cdot(C_6H_6)_3$ cation in solution in benzene, the spectrum of which showed only bands due to the H_3O^+ cation and C_6H_5D.[44] H/D exchange is much slower between the Oct_3ND^+ cation and cyclohexene and cyclohexadienes. Thus, IR spectra of these showed a single symmetric νND band with νNH/νND isotope ratios close to the ideal harmonic oscillator value of 1.34 (Table 2). This means that their νNH bands are not disturbed by Fermi resonance. Using this isotope ratio, it is possible to calculate νNH for the 1,4-cyclohexadiene complex from its νND value (Table 2). The νND frequencies for other hydrocarbons with higher *K* values and faster H/D exchange could not be determined with reliable accuracy.

Table 2. The νNH/D [cm^{-1}] frequencies of $[Oct_3NH^+\cdots nL]\{F_{20}^-\}$ complexes.

L	Complex	νNH	νND	νNH/νND
1-cyclohexene	1:1	≈3075	2260	≈1.36
1,4-cyclohexadiene	1:1	≈3072[a]	2301	-
1,3-cyclohexadiene	1:2	3084	2321	1.33
noncomplexed $Oct_3NH/D^+\{F_{20}\}$		3233	2407	1.34

[a] Calculated from νND. Unavailable experimentally due to overlap with strong νCH bands from the CH=CH group.

Only two complexes show definite distortion of the νNH band from Fermi resonance, the 1:1 complex with 1-methyl-1-cyclopentene and the 1:2 complex with 3-hexyne. An additional broad component appears at around 2880 cm^{-1}. The true νNH frequency is the center of gravity of the whole absorption, but this cannot be determined because both components are partially overlapped with intense absorptions from the octyl chains of the cation and CH vibrations from the unsaturated hydrocarbon.

Application of the *K* value as a probe of the complexing ability of unsaturated hydrocarbons in 1:1 compounds with the Oct_3NH^+ cation leads to the following order: 1-alkenes ≪ cycloalkenes < benzene < methylbenzenes < 1-alkynes ≤ conjugated dienes ≤ 1-methylcycloaklenes < internal alkynes < condensed aromatics. While there is some correlation with the νNH scale ordering, a close correspondence is not expected because *K* values are influenced not only by hydrogen-bonding strength, but also by solvation energy changes of both reactants and products. It is not possible to extract the N–H···L interaction strength from the composite of enthalpic and entropic terms that make up the observed *K* value. Nevertheless, for a family of structurally very similar compounds, such as methylbenzenes or, with more caution, hexacyclic mono- and dienes, the solvation energy effects may be approximately leveled and *K* may reflect hydrogen-bond interaction strengths.

To illustrate this point, consider the correlation between K and $\Delta\nu$NH for progressively methylated benzenes. For 1:1 $[Oct_3NH^+\cdots L]\{F_{20}^-\}$ CIPs with $C_6H_{6-y}(CH_3)_y$, the low frequency shift relative to the uncomplexed contact IP, $\Delta\nu$NH, increases proportionally with increasing number of CH_3 groups *y* (Figure 13). This mirrors the well known increasing σ basicity of progressively methylated benzenes towards protonation[45] and suggests that π basicity follows the same qualitative trend. Each additional CH_3 group increases $\Delta\nu$NH an average increment of 7.2 cm^{-1}. The increment is

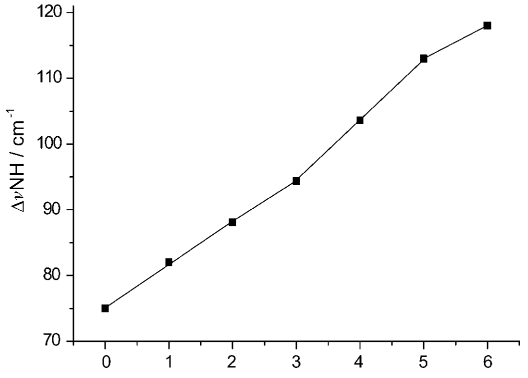


Figure 13. Dependence of $\Delta\nu$NH shifts on the number of CH_3 groups in methylbenzenes.

very similar for the first three methyl groups (≈6.5 cm^{-1}), larger for the fourth (9.2 cm^{-1}) and fifth (9.4 cm^{-1}), and lower for the sixth (5 cm^{-1}). This may reflect a steric effect and changes in the π-electron density as a function of the location of the N–H···π bond, that is, being closer to a CH rather than $C(CH_3)$ carbon atom of the aromatic ring, inasmuch as the smallest increment occurs at hexamethylbenzene in which no unmethylated C atoms remain. For *ortho*- and *para*-xylenes ($y=2$), no difference in their π basicities was discernable by the νNH probe (Table 1).

The *K* values for progressively methylated benzenes also increase with an increasing number of methyl groups (Figure 14), but the trend is not as smooth as with νNH and there is a reversal at hexamethylbenzene. For toluene and xylenes, the increase from benzene is significant, but for the higher methylated benzenes the incremental increase is less. The origins of the discontinuities presumably lie in the subtleties of the solvation energy contributions to *K*, suggesting that νNH is a better probe of the π basicity of arenes.

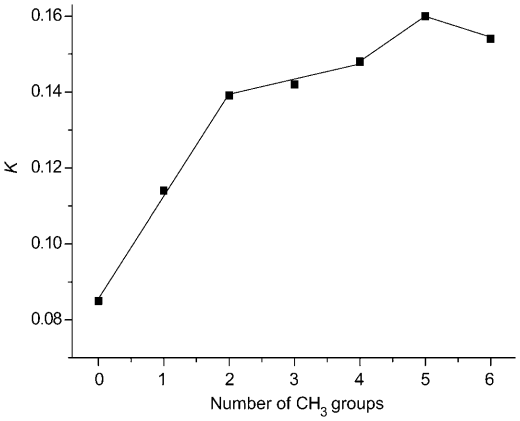


Figure 14. Dependence of *K* on the number of CH_3 groups in methylbenzenes.

Proceeding to the condensed aromatics, naphthalene and phenanthrene, the lack of a correlation between νNH and *K* becomes more obvious. Relative to benzene, the ΔνNH values actually decrease: 5 cm^{-1} for naphthalene and a few more cm^{-1} for phenanthrene (Table 1) even though the *K* values increase significantly. Therefore, by the νNH measure of arene π basicity, condensed aromatics are somewhat weaker π bases as the number of fused rings increases. The *K* values, however, increase significantly as the number of fused rings increases.

The role of solvation energy is well illustrated by the observation that linear alkenes, such as 1-hexene, are unable to compete with the anion in the $Oct_3NH^+\{F_{20}^-\}$ IP, whereas cycloalkenes can. There is no reason to believe that the intrinsic basicity of these C=C bonds towards hydrogen bonding are very different and yet the binding constants differ significantly. On the other hand, the *K* values for 1:1 complexes of cyclohexene, 1,4-cyclohexadiene and benzene are all similar despite the different functionality of the hydrogen-bonding acceptor. Their νNH frequencies are similar as well. Probably because these π donors are all unsubstituted six-membered rings, the solvation energy differences are leveled and their comparable binding constants are in line with their comparable basicity on the NH scale.

Some comments can be made about the π basicity of the conjugated diene C=C–C=C chromophore. The νNH frequencies of complexes formed by both 1,3-cyclohexadiene and 1,3,5,7-cyclooctatetraene coincide when they have unidentate π hydrogen bonds (structures **I** and **III** respectively) or bifurcated π hydrogen bonds (structures **II** and **IV**) (Table 1). Therefore, the basicity of the C=C–C=C chromophore apparently does not depend on the size of the cycle or on joining two of the same chromophores. Coincidentally, the NH scale indicates similar basicity for conjugated dienes with 1-hexyne (ΔνNH≈109 cm^{-1}). Movement of the C=C bond to an internal part of the hydrocarbon chain in 3-hexyne results in a significant increase in π basicity (ΔνNH = 139 cm^{-1}), reflecting the stronger electron donation of an alkyl substituent versus H.

The lack of a broad correlation between νNH and *K*, except perhaps in a closely related family of compounds, is also illustrated by the comparison of unsaturated hydrocarbons with a common hydrogen-bonding base, water. The νNH shift for $[Oct_3NH^+\cdots OH_2]\{F_{20}^-\}$ is about the same as for an internal alkyne, but the *K* value is about two orders of magnitude higher. This very large difference in complex ability can be understood in terms of solvation energy differences between the polar water molecule and the less-polar alkyne. The NH$^+$···L interaction strength may be very similar, but complexed water will not be as well solvated as the alkyne in nonpolar CCl_4, thereby driving the equilibrium towards product formation.

The most π-basic chromophores, that is, internal alkynes, conjugated dienes, and the asymmetric cyclic $-C(CH_3)=CH-$ group, can bind to the NH$^+$ moiety in a bifurcated manner forming 1:2 and 2:2 complexes (structures **IV**, **VI** and **VIII**). To the best of our knowledge, the existence of this type of bifurcated π hydrogen bond has not been predicted theoretically nor determined experimentally before.

Relative strength of the N$^+$–H Proton Donor: To get an indication of the strength of the Oct_3NH^+ ion as a hydrogen-bond donor, it is instructive to compare the NH$^+$ interaction with those of the hydrated proton. Such an evaluation can be made by comparing the values of the redshift of the νP=O band in tributylphosphate (TBP) in $Oct_3NH^+\cdots TBP$ complex with those in the complexes with $H^+(H_2O)_nTBP_m$. As shown in Table 3, the proton-donor ability of Oct_3NH^+ cation on the νPO scale is roughly comparable to that of the tetra-solvated $H_5O_2^+$ cation. It is considerably weaker than that of the H_3O^+ ion, but much stronger than that of a free H_2O molecule. The basicity of the TBP molecule and that of self-associated water molecule are practically the same. Thus, the interaction of the hydrated proton, $H^+(H_2O)_n$ ($n>2$), with unsaturated hydrocarbons is expected to be very similar to those found for $(Oct)_3NH^+$ cation.

Table 3. Comparison of proton-donor abilities of the Oct_3NH^+ cation and proton hydrates through low frequency shifts of the νP=O band in TBP.

Compound	νP=O [cm^{-1}]	ΔνP=O [cm^{-1}]	Reference
$H_3O^+(TBP)_3$	1187	74	[46]
$H_5O_2^+(TBP)_4$	1222	39	[46]
$H_5O_2^+(TBP)_2(H_2O)_2$	1222	39	[46]
$Oct_3NH^+\cdots TBP$	1228	33	present work
$TBP\cdots H_2O$	1248	13	[47]
TBP_{free}	1261	0	present work

Conclusion

We have developed a νNH scale for ranking the localized basicity of unsaturated hydrocarbons in their interactions with hydrogen-bond donors. The scale indicates that π basicity increases in the following order: fused-ring aromatics ≤ benzene < toluene < xylene < mesitylene < durene < conjugated dienes ≈ 1-alkynes < pentamethylbenzene < hexamethylbenzene < internal alkynes ≈ cycloalkenes < 1-methylcycloalkenes. Alkenes are unexpectedly strong π bases. As expected for a localized weak interaction, there is no overall correlation with molecular basicity as measured by gas-phase proton affinities. The utility of the scale is that it offers one of the first ways to gauge the relative strength of the N–H···π interactions in crystals, proteins, and pre-protonation complexes.

Stability constants (K) have been measured for the binding of unsaturated hydrocarbons to the $[Oct_3NH^+]\{F_{20}^-\}$ IP and these have led to the discovery of the first examples of bifurcated hydrogen bonding to unsaturated hydrocarbons in solution. Bifurcated hydrogen bonds occur only with the more strongly complexing substrates. This structural motif is likely to be found in proteins and small-molecule crystals.

Finally, this work has revealed how solutions containing ion-pair solutes can be quite nonideal. For example, with 3-hexyne in <0.1 M solution, >90 % of the alkyne is absorbed into the second solvation shell of the IP, bringing the number of molecules associated with it to around 13.

Experimental Section

All manipulations were carried out under dry conditions in an inert atmosphere in a glove box (H_2O, $O_2 < 0.5$ ppm). Solvents and Et_3SiH (Aldrich, 99 % purity) were dried by using standard methods.[48] $[Ph_3C][B(C_6F_5)_4]$ was a gift from Albemarle Corporation. $Et_3Si\{B(C_6F_5)_4\}$[49] was prepared by adding Et_3SiH (1.5 mL) to $[Ph_3C][B(C_6F_5)_4]$ (1 g) in benzene (10 mL). The mixture was stirred for 1–2 d until the solid changed completely from yellow to colorless. The volatile compounds (benzene and Et_3SiCl) were removed under reduced pressure and the solid was washed with several aliquots of hexane. $[Oct_3NH]Cl$ was prepared by passing gaseous anhydrous HCl through a solution of Oct_3N in hexane at 0 °C. The white crystalline product was collected by filtration. $[Oct_3NH][B(C_6F_5)_4]$ was prepared from 1:1 molar ratios of $[Oct_3NH]Cl$ and $Et_3Si(B(C_6F_5)_4)$ in benzene. The solution was stirred for 30 min. and the volatile compounds (benzene and Et_3SiCl) were removed under reduced pressure. The light-yellow oil product crystallized over time.

All unsaturated hydrocarbons were purchased from Acros and used without additional purification. Solutions were prepared by dissolving a weighed quantity of $[Ph_3C][B(C_6F_5)_4]$ and the solid hydrocarbon or a measured volume of the liquid hydrocarbon in CCl_4. The $[Oct_3NH][B(C_6F_5)_4]$ concentration in all solutions under study was constant at 0.04 M. IR spectra were recorded by using a Shimadzu-8300 FTIR spectrometer in the $\tilde{\nu} = 4000–450\ cm^{-1}$ range. A cell with Si windows with a 0.036 mm separation at the beam transmission point was used. To avoid interference effects, the cell configuration was slightly wedge-shaped. IR data were manipulated using GRAMS/AI software (Galactic Industries, Salem, NH).

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