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The Basicity of Unsaturated Hydrocarbons as probed by H-Bond Acceptor Ability. Bifurcated N–H⁺... π Hydrogen Bonding

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Abstract

The competitive substitution of the anion in contact ion pairs of the type $[\text{Oct}_3\text{NH}^+]\text{B}(\text{C}_6\text{F}_5)_4^-$ by unsaturated hydrocarbons L in accordance with the equilibrium $\text{Oct}_3\text{NH}^+\cdots\text{Anion}^- + n\text{L} \leftrightarrow [\text{Oct}_3\text{NH}^+\cdots\text{L}_n]\text{Anion}^-$ has been studied in CCl_4 solution. On the basis of equilibrium constants K and shifts of ν_{NH} to low frequency, it is established that complexed $\text{Oct}_3\text{NH}^+\cdots\text{L}_n$ cations with $n = 1$ and 2 are formed, having unidentate and bifurcated N–H⁺... π hydrogen bonds, respectively. Bifurcated H-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 red shifts in N–H stretching frequencies, $\Delta\nu_{\text{NH}}$, a new scale for ranking the π -basicity of unsaturated hydrocarbons is proposed: fused-ring aromatics \leq benzene < toluene < xylene < mesitylene < durene < conjugated dienes \sim 1-alkynes < pentamethylbenzene < hexamethylbenzene < internal alkynes \sim cyclo-alkenes < 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

Bifurcated H-bonding; IR spectroscopy; π -basicity; unsaturated hydrocarbons

Introduction

X–H... π H-bonding interactions have been studied for a long time. Following the 1946 suggestion by Dewar that π complexes might be involved in the mechanism of electrophilic aromatic substitution,[1] Brown in 1952 showed 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**) having the X–H bond at ca. 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

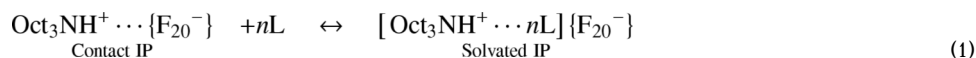
benzene, the X–H bond is preferentially directed near the center of the aromatic ring in a π -face manner (structure **C**, Scheme 1).

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] 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 $19.3 \text{ kcal.mole}^{-1}$. [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 (**B**) [11] and the π -face structure of $NH_4^+ \cdots C_6H_6$ (**C**) [12] have been confirmed in the solid state by X-ray crystallography although, in the $H_3O^+ \cdot 3C_6H_6$ cation, [13] the O–H bonds are directed more closely to carbon atoms than to the centroid of benzene. More generally, the $X-H \cdots \pi$ 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] $X-H \cdots \pi$ interactions have also been identified in proteins [19,22,23] and $N-H \cdots \pi$ interactions can be sufficiently strong to affect secondary (folding) structure. [24]

Estimations of the strengths of $X-H \cdots \pi$ 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 H-bonding interaction from the contribution of solvation energies to the stability constant has thwarted the development of useful scales of π basicity. Mayr has 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 H 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 $N-H \cdots \pi$ interaction of the trioctylammonium ion with alkynes, alkenes and arenes upon reaction with ion pairs of the type $[Oct_3NH^+][B(C_6F_5)_4^-]$ in CCl_4 solution. Carbon tetrachloride is a weakly solvating, low dielectric solvent that favors contact ion pair formation. Of commercially available anions, the perfluorinated tetraphenylborate ion, $B(C_6F_5)_4^-$ (abbrev. $\{F_{20}^-\}$), is the least interacting towards the Oct_3NH^+ ion, as judged by ν_{NH} stretching frequencies in contact ion pairs. [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 ion pairs of the type $[Oct_3NH^+ \cdots L][F_{20}^-]$. 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 ν_{NH} 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).



We have recently shown that ν_{NH} bands in the IR spectra of the Oct_3NH^+ cation in contact ion pairs of the type $[Oct_3NH^+][Anion^-]$ decrease in frequency as a function of increasing H-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 H-bonding in the $\text{Oct}_3\text{NH}^+\cdots\text{L}$ interaction.

We anticipated that these two measures of the basicity of L would give somewhat different rankings. They measure different things. νNH frequencies give a measure of the $\text{NH}^+\cdots\text{L}$ 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 e.g., 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 phase and condensed phase data. The $\text{X-H}\cdots\pi$ interaction under study is a weak, localized effect whereas the energetics of complete protonation (σ basicity) involves larger, more global molecular phenomena.

A specific interest is the possible existence of bifurcated π -H-bonding of the type $\text{X-H}^+\cdots 2\text{L}$, formed by a positively charged cation with two unsaturated hydrocarbons (L). The formation of bi- and even tri-furcated H-bonds has occasionally been observed by X-ray crystallography for trialkylammonium cations, when they interact with O or N-heteroatoms, such as the $(\text{C}_2\text{H}_5)_3\text{NH}^+$ cation with three hydroxyl O-atoms.[31,32] Sometimes one of the acceptors of a bifurcated H-bond is an O-atom, the other an alkyne[19,33,34] or arene.[24,35] Bi- or multi-furcated H-bonds are frequently deduced from protein crystallography.[36] The solution phase existence of compounds with bifurcated π -H bonds involving only unsaturated hydrocarbons has not been reported.

Further interest in $\text{X-H}\cdots\pi$ interactions arises from the long held belief that H-bonded complexes are incipient proton transfer reactions, i.e. models for the early stages of π systems reacting with strong acids.[37] Indeed, the 1970s witnessed 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 complexes (rather than π) and Ar^+E^- charge-transfer ion pairs[39] are more important in the transition state but, 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. t-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 $[\text{Oct}_3\text{NH}^+][\text{F}_{20}^-]$ solutions in CCl_4 show a narrow νNH band at 3233 cm^{-1} . From studies with other anions, we know this corresponds to a contact ion pair (IP) rather than a solvent separated ion pair.[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 L concentration (C_L). At the same time a new, lower frequency νNH band arising from complexed ion pairs (CIP) of formulation $[\text{Oct}_3\text{NH}^+ \cdot n\text{L}][\text{F}_{20}^-]$ appears. 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 ion pair (3233 cm^{-1}), are shown in Figure 2.

The concentration of the $[\text{Oct}_3\text{NH}^+]\{\text{F}_{20}^-\}$ contact ion pair (C_{IP}) was determined from the decreasing intensity of its νNH band at 3233 cm^{-1} as $C_{\text{IP}} = 0.04 \cdot f$, where f is the scaling factor with which the νNH band is fully subtracted against the spectrum of 0.04 M $[\text{Oct}_3\text{NH}^+]\{\text{F}_{20}^-\}$ solution. The concentration of the $[\text{Oct}_3\text{NH}^+ \cdots n\text{L}]\{\text{F}_{20}^-\}$ π -complexed ion pair (C_{CIP}) is defined by the difference: $C_{\text{CIP}} = 0.04 - C_{\text{IP}}$. These concentrations allow the equilibrium constant of the reaction (K) to be determined from Eq. 2

$$K = C_{\text{CIP}} / (C_{\text{L}})^n \cdot C_{\text{IP}}, \quad (2)$$

where C_{L} is equilibrium concentration of free L. Because complexation of the π base is weak and C_{CIP} is small compared to the total L concentration (C_{L}^0), the approximation $C_{\text{L}} \approx C_{\text{L}}^0$ is valid and Eq. 2 becomes Eq. 3.

$$C_{\text{CIP}} / C_{\text{IP}} = K \cdot (C_{\text{L}}^0)^n \quad (3)$$

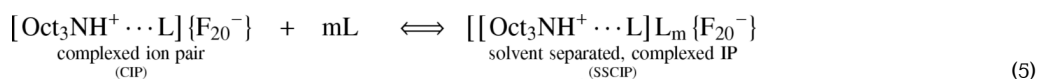
Taking logarithms,

$$\log(C_{\text{CIP}} / C_{\text{IP}}) = \log K_{\text{eq}} + n \log C_{\text{L}}^0, \quad (4)$$

the slope of the function $\log(C_{\text{CIP}} / C_{\text{IP}}) = f(\log C_{\text{L}}^0)$ gives the number n of molecules L which are directly bound to NH group. The equilibrium constant K, i.e. the stability constant for L-complexed ion pair, $[\text{Oct}_3\text{NH}^+ \cdots n\text{L}]\{\text{F}_{20}^-\}$, 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 function (4) is equal to 1 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 on 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 ca. 6 M benzene and $S_{1/2}$ increases more rapidly with increasing concentration. With the methylbenzenes, the break is shifted to lower L concentrations as the number of methyl groups increases, being ca. 0.32 M for hexamethylbenzene. This indicates some change of character of the $[\text{Oct}_3\text{NH}^+ \cdots \text{L}]$ group at high C_{L} concentrations, presumably due to outer sphere solvation of the cation by additionally associated L (Eq. 5), i.e. the formation of solvent separated ion pairs that nevertheless remain specified as 1:1 H-bonded complexes.



Later we provide evidence to support this proposal. As indicated by the essential constancy of the νNH frequency, outer sphere solvation of the complexed ion pair by aromatic hydrocarbons does not change the strength of the $\text{NH}^+ \cdots \text{L}$ interaction. Thus, outer sphere solvation does not effect 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

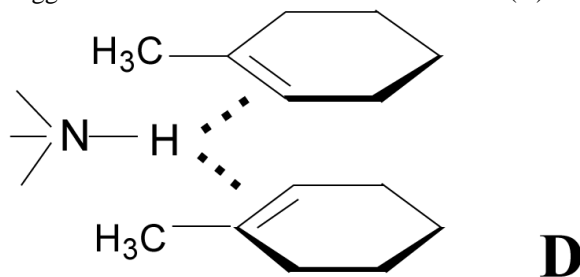
because outer sphere association is absence or it is present to similar effect over the entire concentration range studied.

For the methylbenzenes, $C_6H_{6-m}(CH_3)_m$, the ν_{NH} frequency decreases regularly with increasing number of methyl groups (m) indicating that the strength of $N-H^+ \cdots L$ hydrogen bonding increases with increasing arene basicity (Figure 2, Table 1). K values increase in a roughly parallel manner.

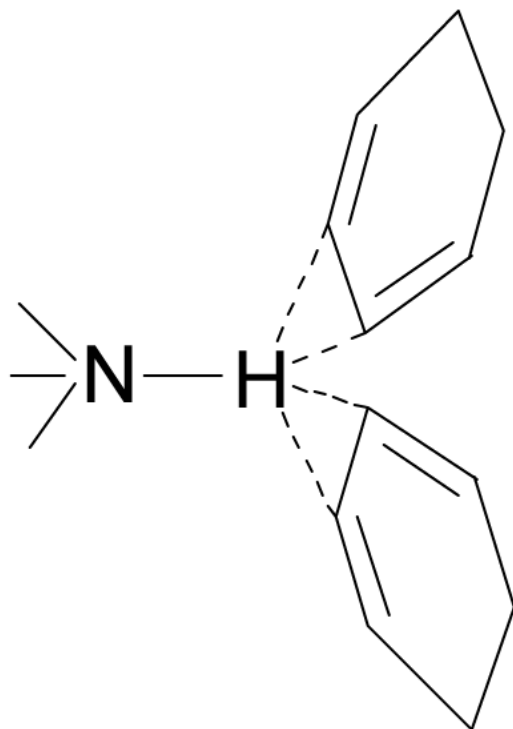
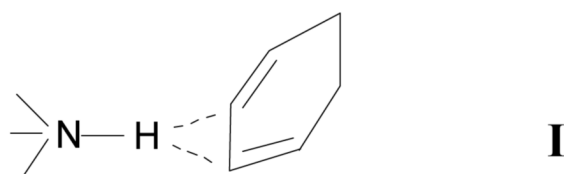
Alkenes

From the lack of changes in the IR spectrum, 1-hexene is unable to displace the $\{F_{20}^-\}$ anion in the $[Oct_3NH^+]\{F_{20}^-\}$ contact ion pair, even when used in place of CCl_4 as solvent. On the other hand, cyclohexene and cyclopentene, and two cyclic dienes (1,4-cyclo-hexadiene and 1,5-cyclo-octadiene) having isolated (non-conjugated) $C=C$ bonds, are able to displace the $\{F_{20}^-\}$ ion and bind to the NH^+ group. The slope of equation (3) indicates that these complexes have 1:1 composition with common T-shaped π -H bond of **A** type (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 at 50 vol. % solution. The ν_{NH} bands of all of these complexes have low intensity, are strongly broadened and red shifted (Table 1).

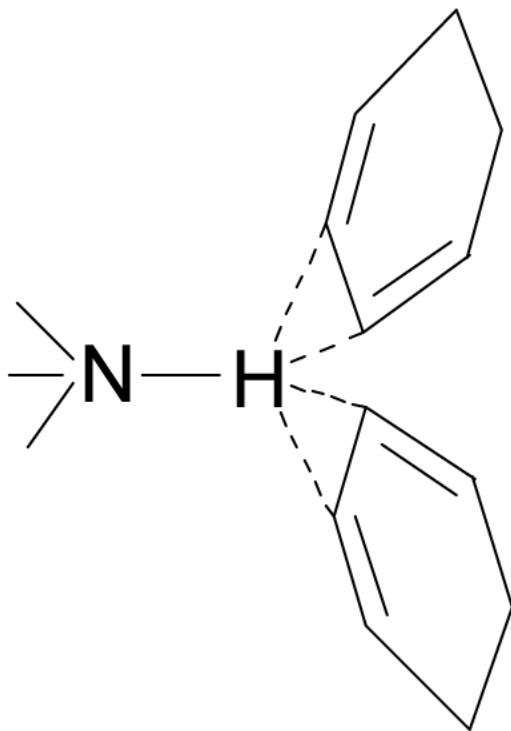
Methyl-cyclo-alkenes having the unsymmetrical $-C(CH_3)=CH-$ chromophore (1-methyl-1-cyclopentene and 1-methyl-1-cyclohexene) in the concentration range below 1 M form 1:1 compounds with larger K values, especially for 1-methyl-1-cyclopentene. Like symmetrical cycloalkenes, their ν_{NH} bands show large red shifts and very strong broadening (Table 1). The red shift of ν_{NH} for unsymmetrical alkenes is even greater than that for symmetrical alkenes. At concentrations higher than 1 M, the slope of Eq. 4 starts to exceed 1 and, as the intensity of ν_{NH} of the 1:1 compounds decreases, a new, very broad and greatly red-shifted ν_{NH} band with maximum at $\sim 2880\text{ cm}^{-1}$ appears, increasing in intensity with increasing alkene concentration. The higher stoichiometry (presumably 1:2), and the very low ν_{NH} value, suggests the formation of bifurcated π -H bond (**D**):



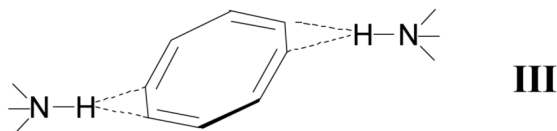
Cycloalkenes having conjugated double bonds, 1,3-cyclo-hexadiene and 1,3,5,7-cyclo-octatetraene, relatively to alkenes with symmetrical isolated $C=C$ bonds, show higher ability to solvate the NH^+ group. For 1,3-cyclohexadiene, the slope of function (4) is close to 1 at low alkene concentration ($C_L < 1\text{ M}$), but at higher concentrations is close to 2 (Figure 5). Thus, 1,3-cyclohexadiene forms both 1:1 and 1:2 compounds. In the ranges of C_L concentrations where only one compound is formed, the dependence of function (3) increases proportionally with concentration, allowing both K values to be determined (Table 1). The complexes differ significantly in their ν_{NH} frequencies, 3125 cm^{-1} for the 1:1 complex and 3084 cm^{-1} for 1:2, indicating distinctly different types of π -H bonding. If the 1:1 complex has a normal π -H bond (**I**),



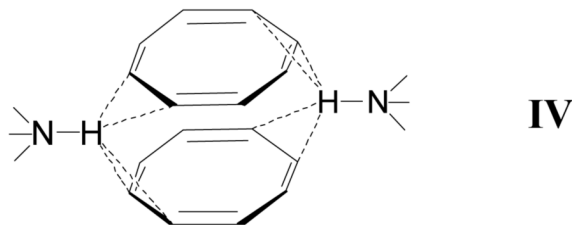
then the 1:2 complex (with the much lower ν_{NH} frequency) must have a bifurcated H-bond (**II**):

**II**

For 1,3,5,7-cyclooctatetraene, the value of n was $\frac{1}{2}$ at low C_L and transitioned to 1 at higher C_L (Figure 3). This indicates that at low C_L , 1,3,5,7-cyclooctatetraene is acting as two separate diene units bonded to two Oct_3NH^+ cations, resulting to formation of 2:1 complex **III**:

**III**

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

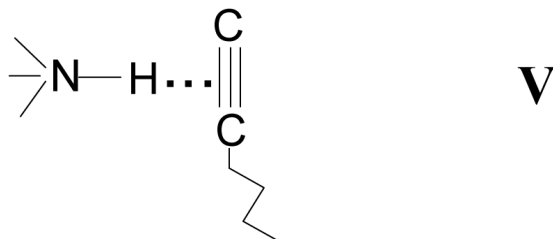
**IV**

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

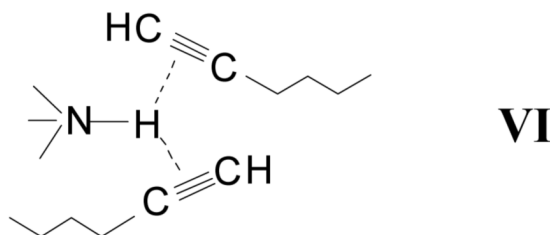
Alkynes

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 $C_L = 0.26\text{--}1.73\text{ M}$, 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 $\text{Oct}_3\text{NH}^+\text{L}$ cation, i.e. the formation of the solvent-separated ion pairs $\text{Oct}_3\text{NH}^+\cdots\text{L}\cdot(\text{L}_m)\{\text{F}_{20}^-\}$ with variable m . In this concentration region, function (4) has a linear dependence on C_L with slope $n=1$ and function (3) leads to $K = 0.254$. So, this complex has a 1:1 composition with common $\pi\text{--H}$ 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 function (4) increases, indicating formation of a 1:2 complex with a bifurcated $\pi\text{--H}$ bond (VI):



In the case of 3-hexyne, the νNH frequencies are more strongly red shifted 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 ($C_L \sim 0.88$) (Figure 6). In the range of 1:1 complex formation, the slope of function $C_{\text{CIP}}/C_{\text{CIP}} = f(C_L)$ gives the value of $K = 2.02$ (Figure 7) and in the range of 1:2 complex formation, the slope of the function $C_{\text{CIP}}/C_{\text{CIP}} = f(C_L)^2$ gives a value of $K = 3.65$ (Figure 8).

Outer sphere solvation

The existence of outer sphere solvation of the complexed $\text{Oct}_3\text{NH}\cdots\text{L}^+$ cation by L for arenes and dienes is indicated by broadening of the νNH band at high C_L . In the case of 1- and 3-alkynes there is also a gradual shift in the νNH frequency (ca. 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 H-bonded to 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 from $200\text{--}550\text{ cm}^{-1}$ 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.

From the intensity of the band of free 3-hexyne at 1680 cm^{-1} , the equilibrium concentration in solution was determined as $C_L^{\text{free}} = f \times C_L^{\text{st}}$, where f is the coefficient with which the band 1680 cm^{-1} is fully subtracted with the spectrum of standard 3-hexyne solution, and C_L^{st} is the

L concentration 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 NH^+ group was determined from the difference $C_L^{solv} = C_L^o - C_L^{free}$. Figure 10 shows the dependence of the number of conformationally affected 3-hexyne molecules as a function of C_L^o . The composition of the solvating shell is unexpectedly large. At low $C_L^o = 0.088$ M (1 vol%), 92.5% of the alkyne is absorbed into the solvation shell, bringing to ca. 13 the number of molecules per NH^+ group. At higher $C_L^o = 4.38$ M (50 vol%), this increases to about 30. Thus, substantial clustering of the alkyne occurs around the complexed ion pair. Most of the alkyne is not randomly mixed in the CCl_4 solution.

In order 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 $N-H \cdots$ alkyne interaction, the solvation of the *tetraoctylammonium* salt of $B(C_6F_5)_4^-$ with 3-hexyne solutions 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 red shift of this band relative to free 3-hexyne (1680 cm^{-1}) ($\Delta = 9\text{ cm}^{-1}$) suggests a minor association with the ion pair. The stoichiometric ratio determined as C_L^{solv}/C^o is ~ 2.4 for 10 vol% of 3-hexyne and increases to ~ 3.1 for 20 vol% solution.

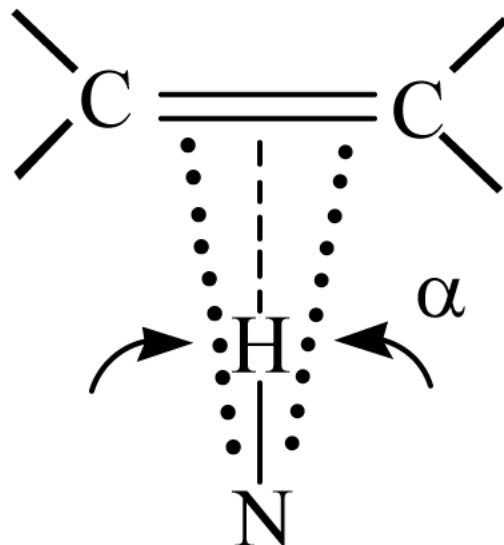
Finally, for the purposes of comparison of unsaturated hydrocarbons to a traditional H-bond acceptor, we have investigated the interaction of H_2O with the $[Oct_3NH^+]\{F_{20}^-\}$ ion pair. The IR spectrum of 0.0156 M solution of $(Oct)_3NH^+\{F_{20}^-\}$ prepared in water-saturated CCl_4 (0.0055 M 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 complexed water and Oct_3NH^+ cation it was determined that the molar ratio was close to 1. The K value is given in Table 1.

Discussion

In the solutions under study, three types of ion pairs are formed, differing in the character of the solvation of the NH^+ group: (a) 1:1 *mono*-complexed ion pairs (CIP), $[Oct_3NH^+ \cdots L]\{F_{20}^-\}$, with the cation and anion separated by one unsaturated hydrocarbon molecule L, (b) solvent-separated complexed ion pairs (SSCIP) having some number of intervening unsaturated hydrocarbon molecules L_m , $[Oct_3NH^+ \cdots L] \cdot L_m \{F_{20}^-\}$, where the cation retains the essential character of mono-complexed ion pairs, and (c) 1:2 *di*-complexed, solvent-separated ion pairs $[Oct_3NH^+ \cdots 2L] \cdot L_m \{F_{20}^-\}$, with two molecules of L directly bonded to the NH^+ group i.e., having bifurcated H-bonds. The transition from complexed ion pair to solvent-separated ion pair (CIP to SSCIP), caused by outer sphere solvation of 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.

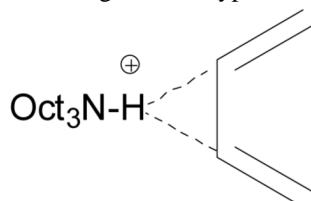
π -Hydrogen bonding

The νNH band is exceedingly broad ($\sim 150\text{ cm}^{-1}$) 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 penta-benzene complexes, all having similar νNH frequencies, the νNH band width ($S_{1/2}$) is 2 - 4 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 -H-bond directed toward the center of the $C=C$ or $C\equiv C$ bond is not fixed but fluctuates in the limits of some angle α because the maximum of π -electron density centered between two carbon atoms is very flat (**E**).

**E**

This phenomenon, in varying degrees, may explain the change in the ν_{NH} 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 where N–H vectors of the $\text{N}^+ \cdots \text{H} \cdots \text{phenyl}$ interaction between an NH_4^+ ion and phenyl groups are time-averaged orientation is 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]

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 (non-complexed) L molecule has two $\nu_{\text{C}=\text{C}}$ bands (1603 and 1578 cm^{-1}) of medium to low intensity. Upon complex formation in **I** and **III** the $\nu_{\text{C}=\text{C}}$ absorption does not change indicating that this type of interaction is symmetrical (**F**):

**F**

The four conjugated C=C groups of 1,3,5,7-cyclo-octatetraene in complex **II** act as two independent C=C–C=C chromophores, not influencing one another. This case is distinguished from 1:1 complexes formed by arenes having formally three conjugated C=C bonds. These act as a single aromatic chromophore with an interaction strength lower than that of 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 -H bonds (such as in complexes **II**, **IV**, **VI**). The bonding of the second base causes is indicated by greater $\Delta\nu_{\text{NH}}$ shifts. This phenomenon may be much more prevalent than previously realized and may play important role in synthetic organic chemistry and in biochemistry.

Trends in νNH and K

Application of the νNH frequency as an IR probe of the relative interaction strength of $\text{N}^+\text{-H}$ 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 \sim 1-alkynes < pentamethylbenzene < hexamethylbenzene < internal alkynes \sim 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 H 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 ($2700\text{-}2950\text{ cm}^{-1}$). The best way to determine the presence of Fermi-resonance is to study deuterated analogues because the νND band of $\text{Oct}_3\text{ND}^+\{\text{F}_{20}\}^-$ lies in a frequency range that is not coupling 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 $[\text{Oct}_3\text{ND}^+\cdots\text{L}]\{\text{F}_{20}\}^-$ ion pairs with $\text{L} = 1\text{-hexyne}$ or 3-hexyne developed only the νNH band. Similar fast H/D exchange was observed in the $\text{D}_3\text{O}^+(\text{C}_6\text{H}_6)_3$ cation in benzene solutions, resulting in the appearance the spectrum of H_3O^+ cation only along with bands from $\text{C}_6\text{H}_5\text{D}$. [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 $\nu\text{NH}/\nu\text{ND}$ isotope ratios close to 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.

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 ca. 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 Oct_3NH^+ cation leads to the following order: 1-alkenes \ll cycloalkenes < benzene < methylbenzenes < 1-alkynes \leq conjugated dienes \leq 1-methylcycloalkenes < 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 H-bonding strength but also by solvation energy changes of both reactants and products. It is not possible to extract the $\text{N-H}\cdots\text{L}$ 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, as methylbenzenes or, with more caution, hexacyclic mono- and

dienes, the solvation energy effects may be approximately leveled and K may reflect H-bond interaction strengths.

To illustrate this point, consider the correlation between K and $\Delta\nu\text{NH}$ for progressively methylated benzenes. For 1:1 $[\text{Oct}_3\text{NH}^+\cdots\text{L}]\cdots\{\text{F}_{20}^-\}$ complexed ion pairs with $\text{C}_6\text{H}_{6-m}(\text{CH}_3)_m$, the low frequency shift relative to the uncomplexed contact ion pair, $\Delta\nu\text{NH}$, increases proportionally with increasing number of CH_3 groups m (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 $\Delta\nu\text{NH}$ an average increment of 7.2 cm^{-1} . The increment is very similar for the first three methyl groups ($\sim 6.5\text{ cm}^{-1}$), 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 $\text{N}-\text{H}\cdots\pi$ bond, i.e. being closer to a CH rather than $\text{C}(\text{CH}_3)$ carbon atom of the aromatic ring, inasmuch as the smallest increment occurs at hexamethyl-benzene where no unmethylated C atoms remain. For ortho- and para-xylenes ($m = 2$), no difference in their π -basicities was discernable by the νNH probe (Table 1).

The K values for progressively methylated benzenes also increase with 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 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.

Proceeding to the condensed aromatics, naphthalene and phenanthrene, the lack of a correlation between νNH and K becomes more obvious. Relative to benzene, the $\Delta\nu\text{NH}$ 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. So, 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 $\text{Oct}_3\text{NH}^+\{\text{F}_{20}^-\}$ ion pair whereas cycloalkenes can. There is no reason to believe that the intrinsic basicity of these $\text{C}=\text{C}$ bonds towards H-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 H-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 $\text{C}=\text{C}-\text{C}=\text{C}$ chromophore. The νNH frequencies of complexes formed by both 1,3-cyclohexadiene and 1,3,5,7-cyclo-octatetraene coincide when they have unidentate π -H bonds (structures **I** and **III** respectively) or bifurcated π -H bonds (structures **II** and **IV**) (Table 1). Therefore, the basicity of the $\text{C}=\text{C}-\text{C}=\text{C}$ chromophore apparently does not depend on the size of the cycle or on joining of two the same chromophore. Coincidentally, the NH scale indicates similar basicity of conjugated dienes with 1-hexyne ($\Delta\nu\text{NH} \sim 109\text{ cm}^{-1}$). Movement of the $\text{C}\equiv\text{C}$ bond to an internal part of the hydrocarbon chain in 3-hexyne results in a significant increase in π -basicity ($\Delta\nu\text{NH} = 139\text{ cm}^{-1}$) 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 closed related family of compounds, is also illustrated by the comparison of unsaturated hydrocarbons with a common H-bonding base, water. The νNH shift for $[\text{Oct}_3\text{NH}^+\cdots\text{OH}_2]\{\text{F}_{20}^-\}$ is about the same as for an internal alkyne but the K value is about an 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 $\text{NH}^+\cdots\text{L}$ interaction strength may be very similar but complexed water will not be as well solvated as alkyne in the non-polar CCl_4 , thereby driving the equilibrium towards product formation.

The most π -basic chromophores, i.e. internal alkynes, conjugated dienes, and the asymmetric cyclic $-\text{C}(\text{CH}_3)=\text{CH}-$ group, can bind to the NH^+ moiety in a bifurcated manner forming 1:2 and 2:2 complexes (structures **IV**, **VI** and **VIII**). To our knowledge, the existence of this type of bifurcated π -H-bond has not been predicted theoretically nor determined experimentally before.

Relative strength of the $\text{N}^+\text{-H}$ Proton Donor

In order to get an indication of the strength of the Oct_3NH^+ ion as an H-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 red shift of the $\nu\text{P=O}$ band in tributylphosphate (TBP) in $\text{Oct}_3\text{NH}^+\cdots\text{TBP}$ complex with those in the complexes with $\text{H}^+(\text{H}_2\text{O})_n\text{TBP}_m$. 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 hydrated proton, $\text{H}^+(\text{H}_2\text{O})_n$ ($n > 2$), with unsaturated hydrocarbons is expected to be very similar to those found for $(\text{Oct})_3\text{NH}^+$ cation.

Conclusion

We have developed a νNH scale for ranking the localized basicity of unsaturated hydrocarbons in their interactions with H-bond donors. The scale indicates that π -basicity increases: fused-ring aromatics \leq benzene $<$ toluene $<$ xylene $<$ mesitylene $<$ durene $<$ conjugated dienes \sim 1-alkynes $<$ pentamethylbenzene $<$ hexamethylbenzene $<$ internal alkynes \sim 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 $\text{N-H}\cdots\pi$ interactions in crystals, proteins and pre-protonation complexes.

Stability constants (K) have been measured for the binding of unsaturated hydrocarbons to the $[\text{Oct}_3\text{NH}^+]\{\text{F}_{20}^-\}$ ion pair and these have led to the discovery of the first examples of bifurcated H-bonding to unsaturated hydrocarbons in solution. Bifurcated H-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 non-ideal. For example, with 3-hexyne in < 0.1 M solution, $> 90\%$ of the alkyne is absorbed into the second solvation shell of the ion pair, bringing to ca. 13 the number of molecules associated with it.

Experimental Section

All manipulations were carried out under dry conditions in an inert atmosphere glovebox (H_2O , $\text{O}_2 < 0.5$ ppm). Solvents and Et_3SiH (Aldrich, 99% purity) were dried by standard methods.[48] $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ was a gift from Albemarle Corporation. $\text{Et}_3\text{Si}\{\text{B}(\text{C}_6\text{F}_5)_4\}$ [49] was prepared by adding Et_3SiH (1.5 mL) to $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (1 g) of in benzene (10 mL). The mixture was stirred for 1-2 days until the solids change completely from yellow to colorless. The volatiles (benzene and Et_3SiCl) were removed under reduced pressure and the solid was washed with several aliquots of hexane. $[\text{Oct}_3\text{NH}]\text{Cl}$ was prepared by passing gaseous anhydrous HCl through a hexane solution of Oct_3N at 0°C . The white crystalline product was collected by filtration. $[\text{Oct}_3\text{NH}][\text{B}(\text{C}_6\text{F}_5)_4]$ was prepared from 1:1 molar ratios of $[\text{Oct}_3\text{NH}]\text{Cl}$ and $\text{Et}_3\text{Si}(\text{B}(\text{C}_6\text{F}_5)_4)$ in benzene solution. The solution was stirred for 30 min. and the volatiles (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 $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ and the solid hydrocarbon or a measured volume of the liquid hydrocarbon in CCl_4 . The $[\text{Oct}_3\text{NH}][\text{B}(\text{C}_6\text{F}_5)_4]$ concentration in all solutions under study was constant at 0.04 M. IR spectra were run on a Shimadzu-8300 FT-IR spectrometer in the $4000\text{--}450\text{ cm}^{-1}$ range. A cell with Si windows having 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 GRAMMS software.

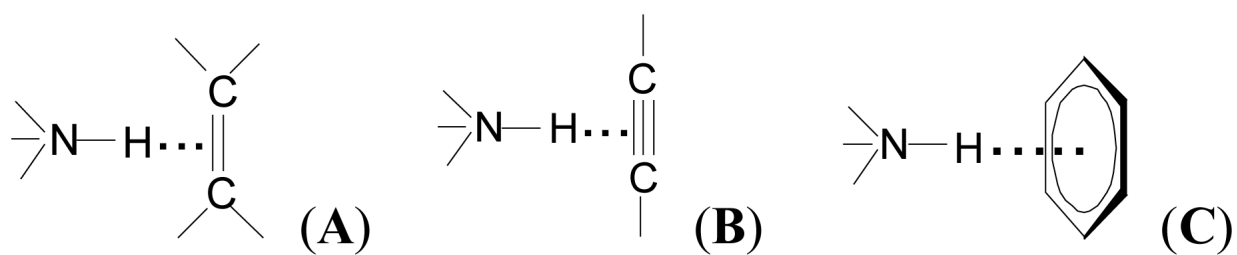
Acknowledgements

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**Scheme 1.**

Structures of H-bonded alkenes (A), alkynes (B) and benzene (C).

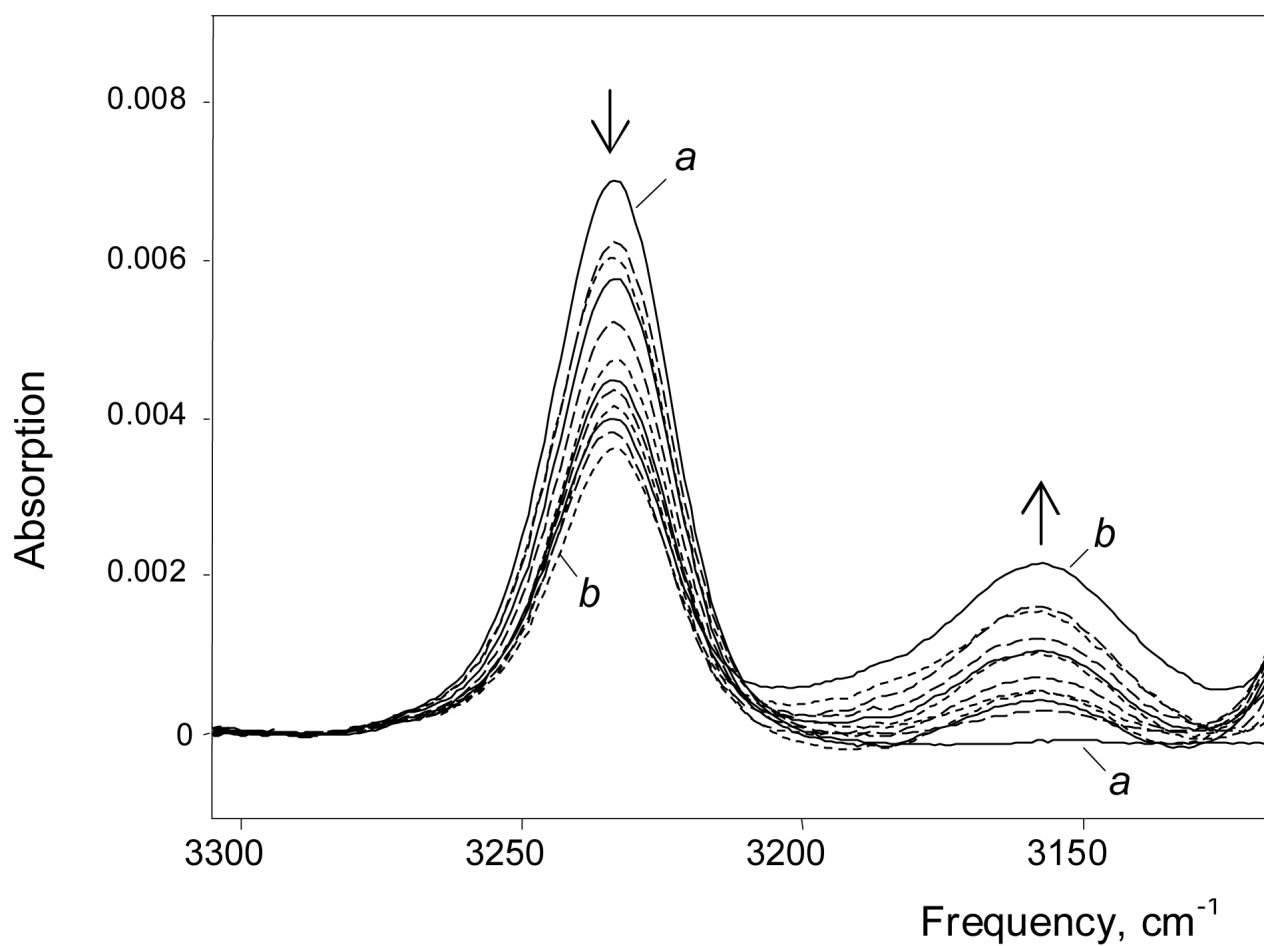


Figure 1. Evolution of the IR spectrum in the ν_{NH} region of 0.4 M $[\text{Oct}_3\text{NH}^+]\{\text{F}_{20}^-\}$ in CCl_4 as benzene is added. Benzene concentrations increase from zero (*a*) to 100% (*b*).

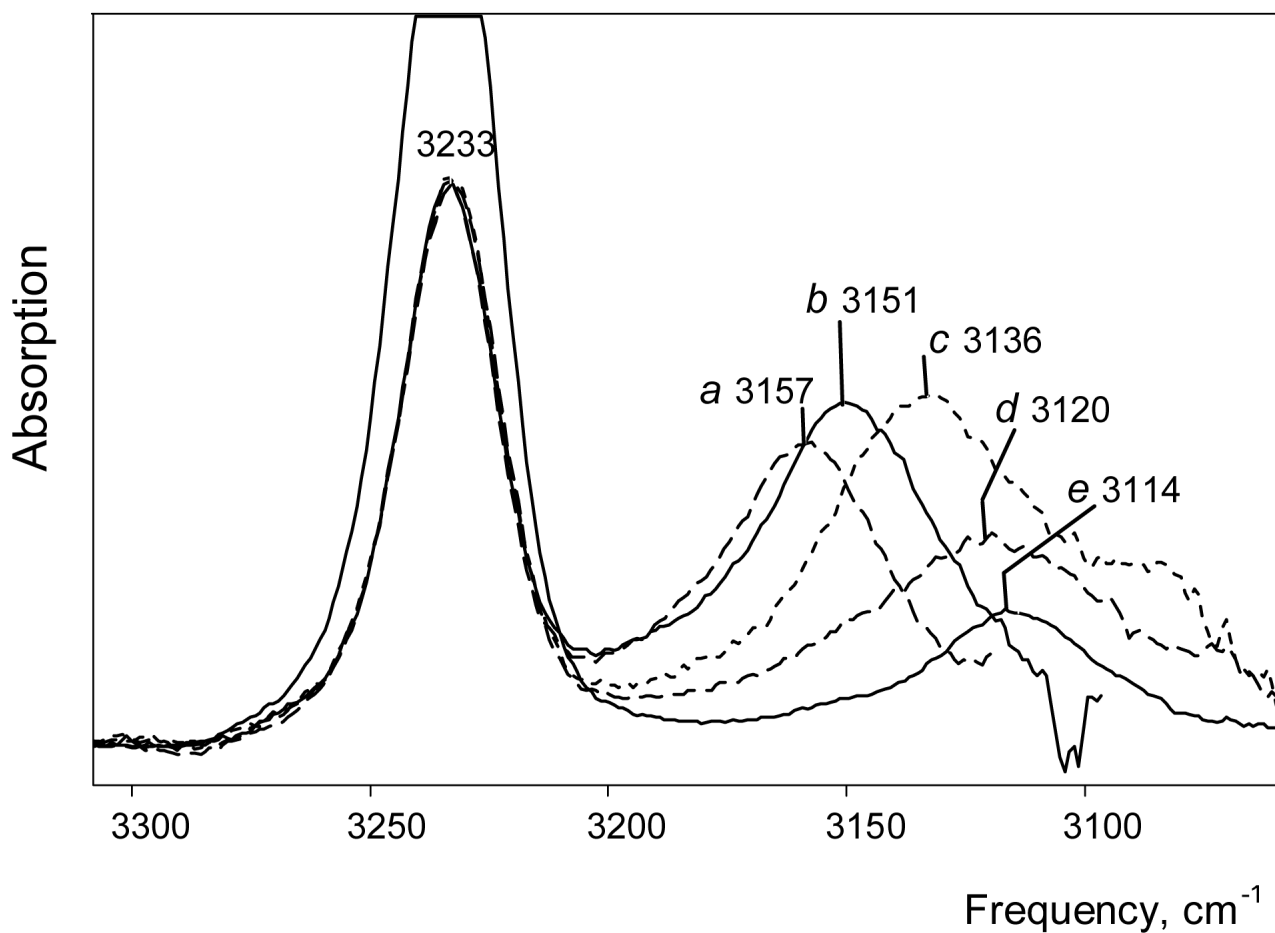


Figure 2.

Representative IR spectra showing the formation of $[\text{Oct}_3\text{NH}^+\cdots n\text{L}]\{\text{F}_{20}^-\}$ complexed ion pairs with their νNH frequencies for arenes L = benzene (*a*), toluene (*b*), mesitylene (*c*), pentamethyl-benzene (*d*), hexamethylbenzene (*e*). Spectra, with the exception of (*a*), are normalized to νNH of the uncomplexed contact ion pair at 3233 cm^{-1} .

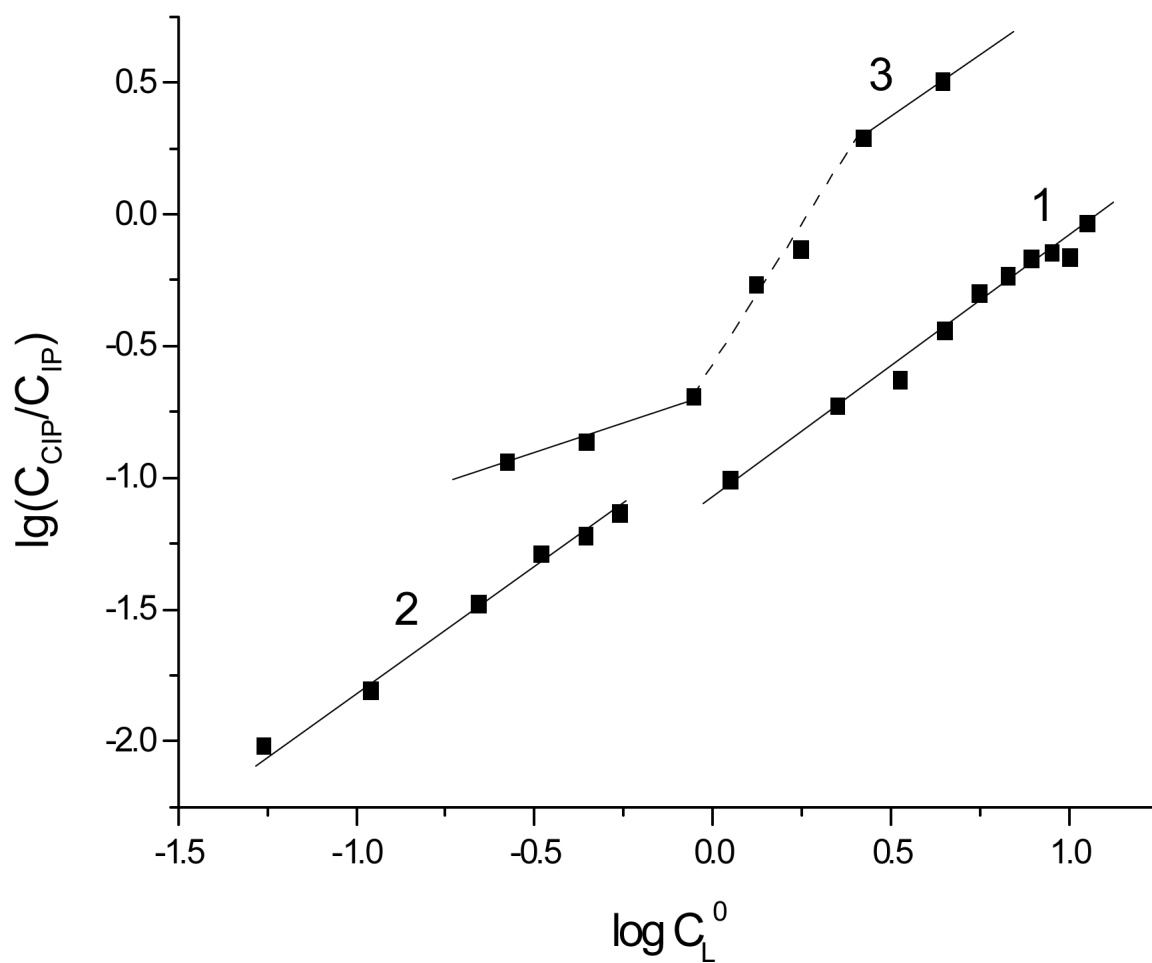


Figure 3. Slopes of function (4) for benzene (1, $n = 0.99$), hexamethyl-benzene (2, $n = 0.98$) and 1,3,5,7-cyclooctatetraene (3, $n = 0.50$ and 0.98).

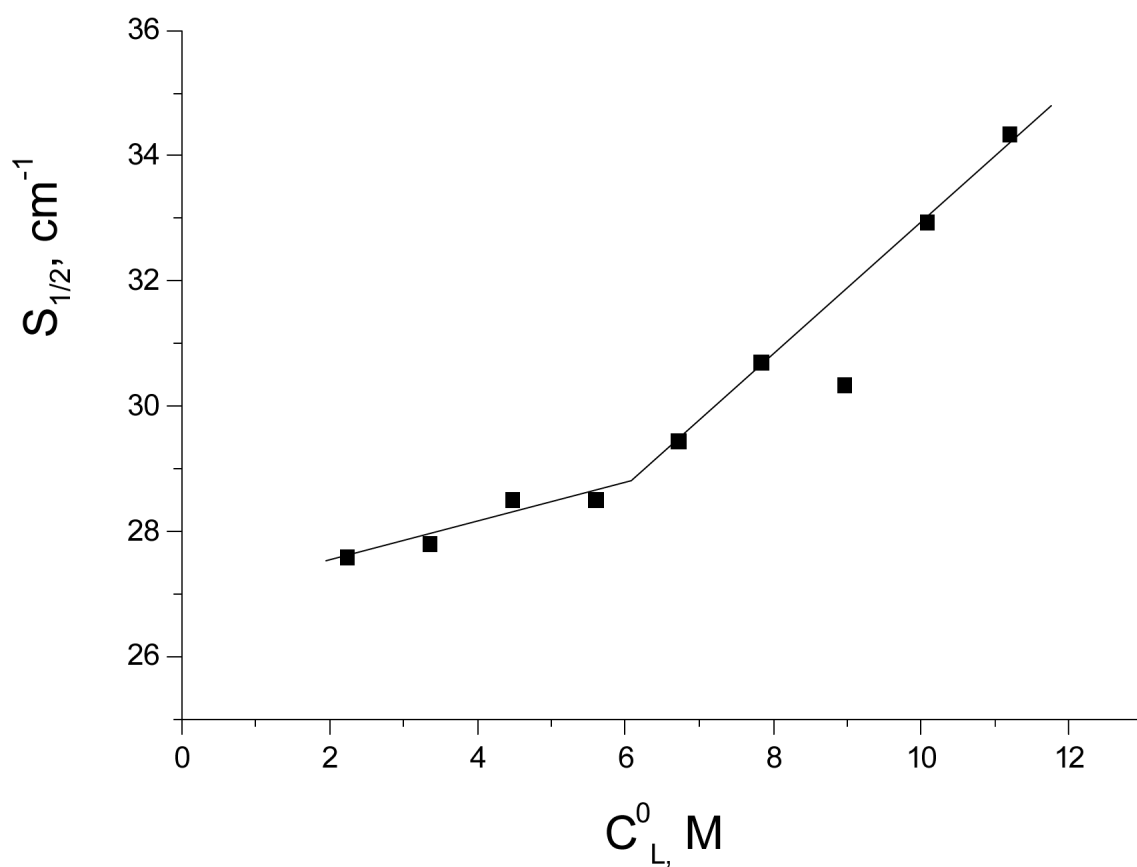


Figure 4. Plot of band width at half height ($S_{1/2}$) for νNH of $[\text{Oct}_3\text{NH}^+\cdots\text{C}_6\text{H}_6][\text{F}_{20}^-]$ with increasing concentration of benzene (2.24-11.2 M).

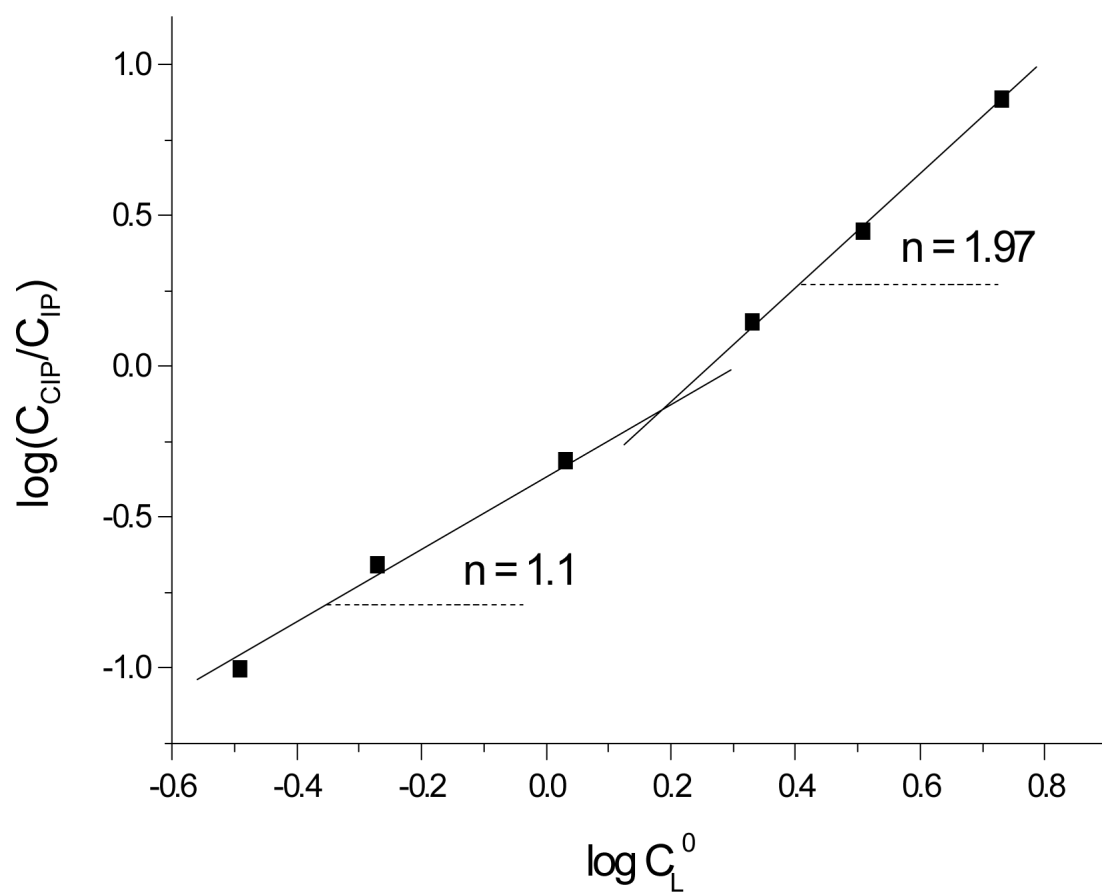


Figure 5.
The slope of function (4) with 1,3-cyclohexadiene concentration.

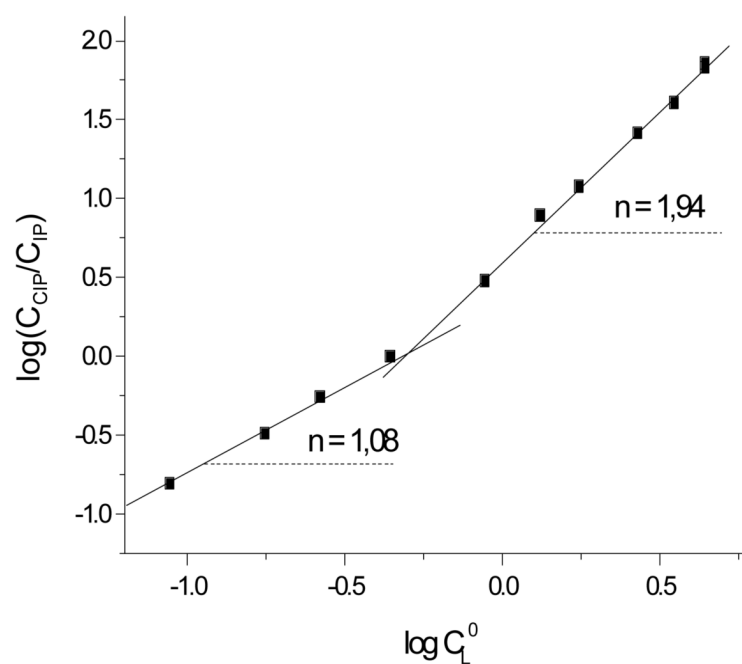


Figure 6.
The slope of function (4) with 3-hexyne concentration.

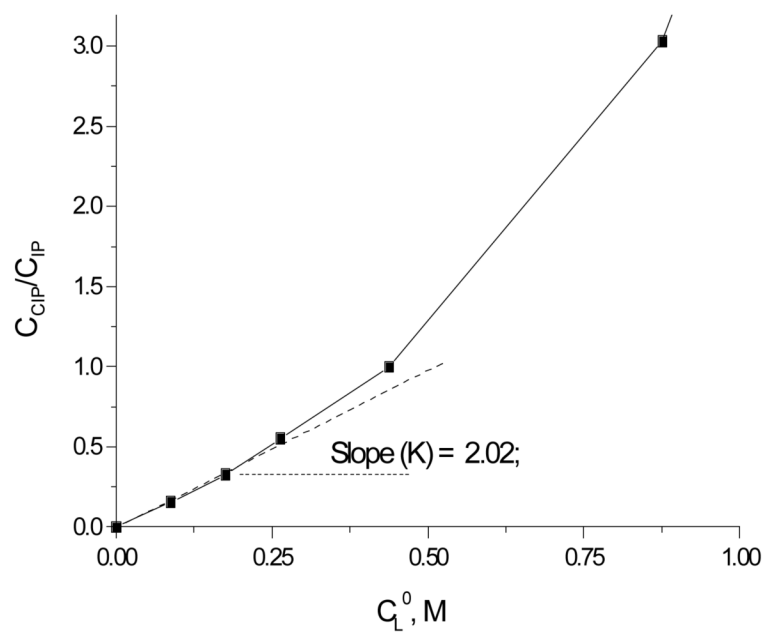


Figure 7.
The slope of function (3) with $n = 1$ for 3-hexyne.

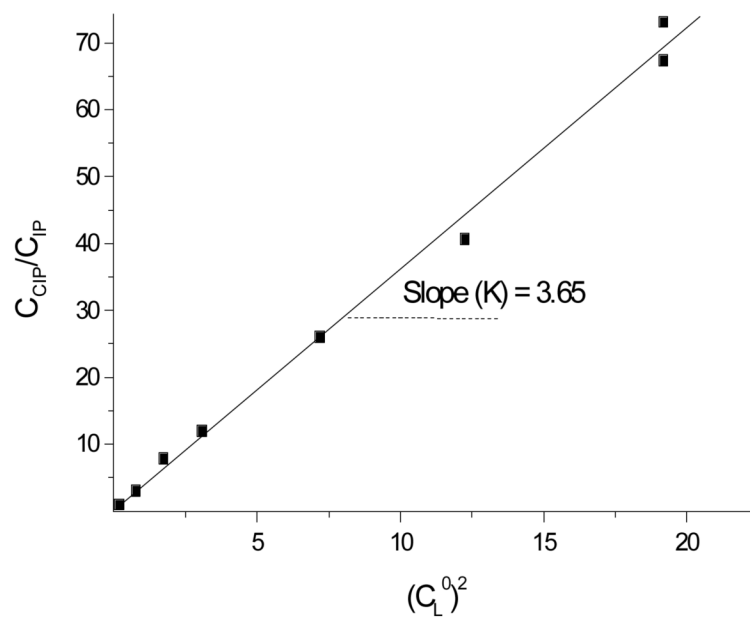


Figure 8.
The slope of the function (3) with $n = 2$ for 3-hexyne.

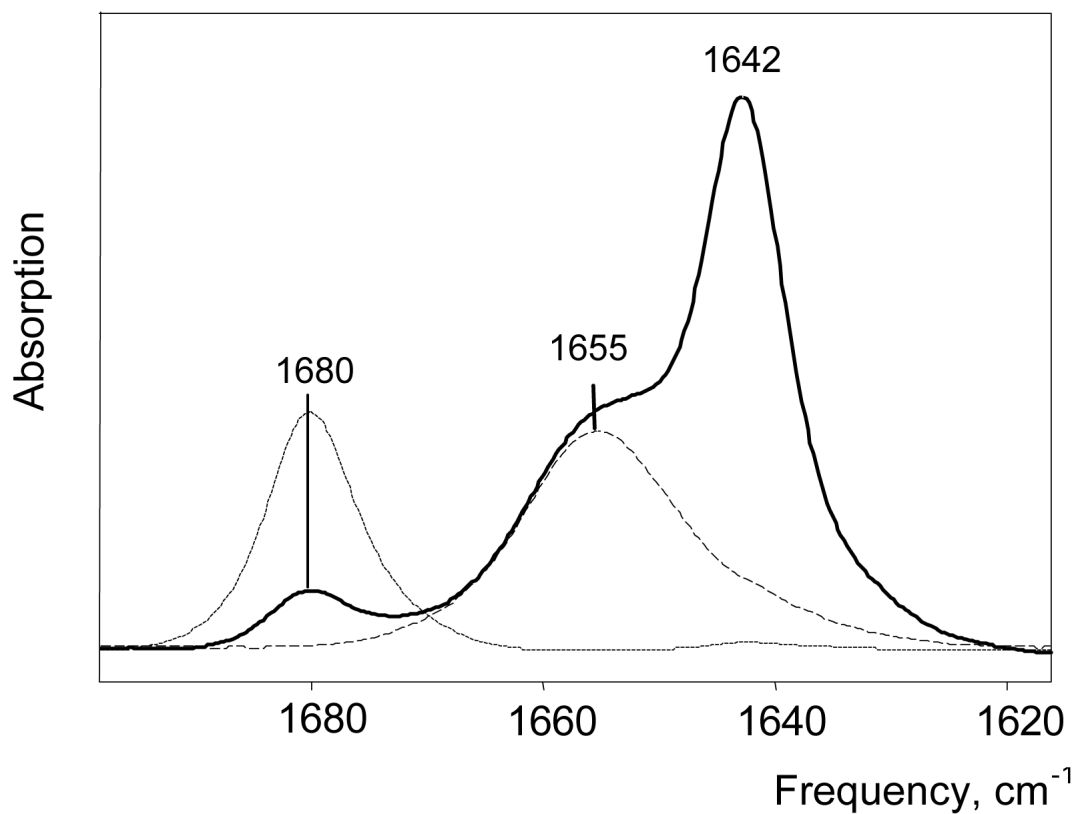


Figure 9.

IR spectra of (a) CCl₄ solution of 0.04 M Oct₃NH⁺{F₂₀} with 10 vol% of 3-hexyne (solid) and (b) CCl₄ solution of 10 vol% 3-hexyne (dotted). The dashed spectrum shows the band at 1655 cm⁻¹ that was isolated by sequential subtraction of the spectrum of free hexyne and the band at 1642 cm⁻¹ of {F₂₀}⁻.

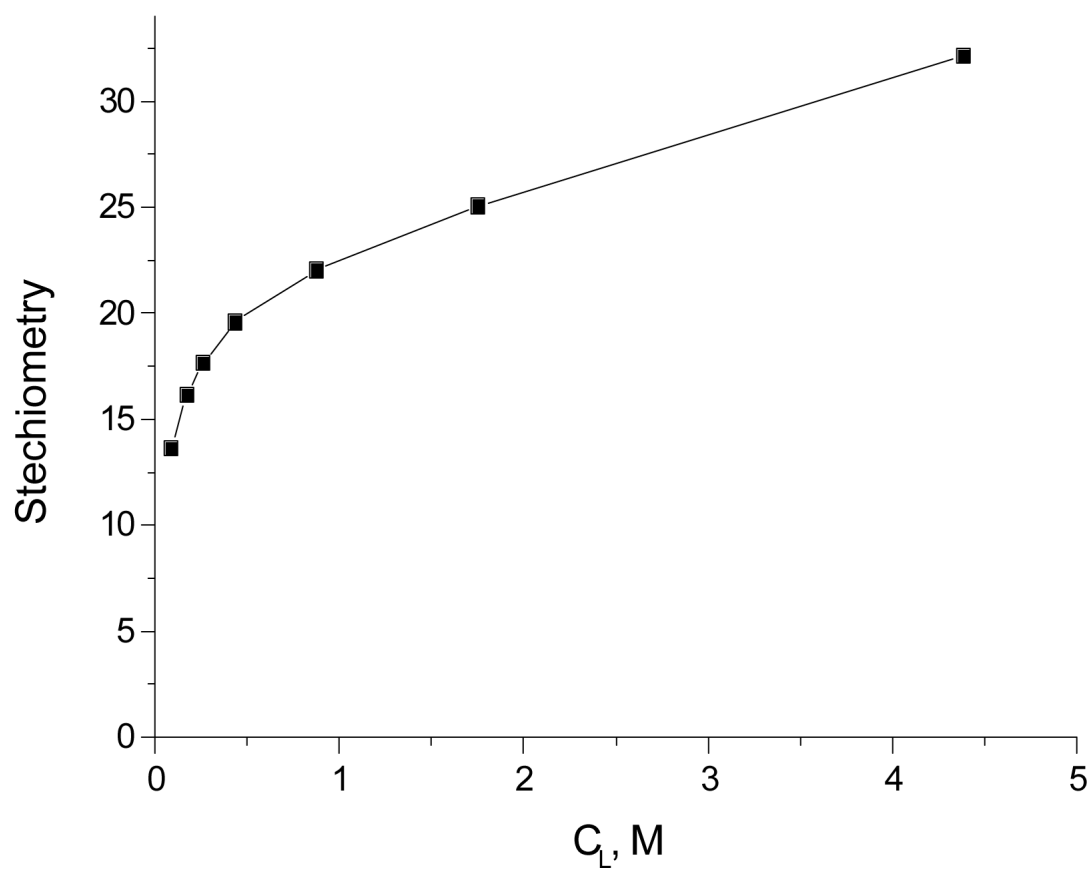
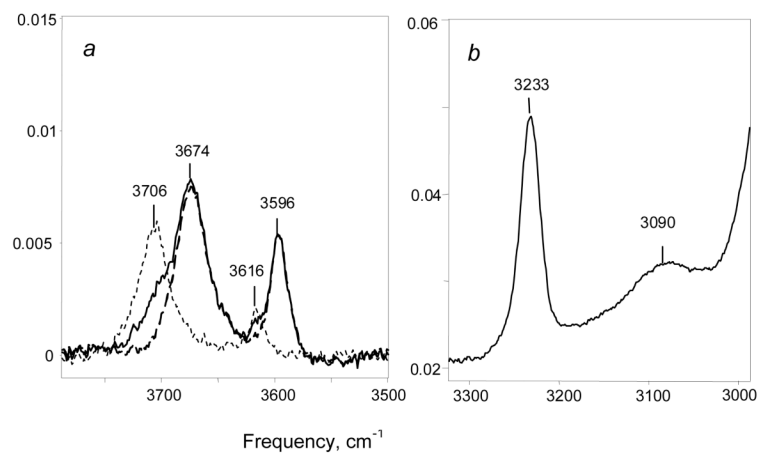


Figure 10.
Dependence of m on 3-hexyne concentration.

**Figure 11.**

IR spectrum of 0.0156 M $(\text{Oct})_3\text{NH}^+\{\text{F}_{20}^-\}$ in CCl_4 with 0.0055 M water in the frequency region of νOH (a) and νNH (b). Solid line: measured spectrum. Dotted: spectrum of 0.0055 M of water in CCl_4 . Dashed: spectrum of $[(\text{Oct})_3\text{NH}^+\cdots\text{OH}_2]\{\text{F}_{20}^-\}$ ion pair obtained by subtraction of dotted from solid.

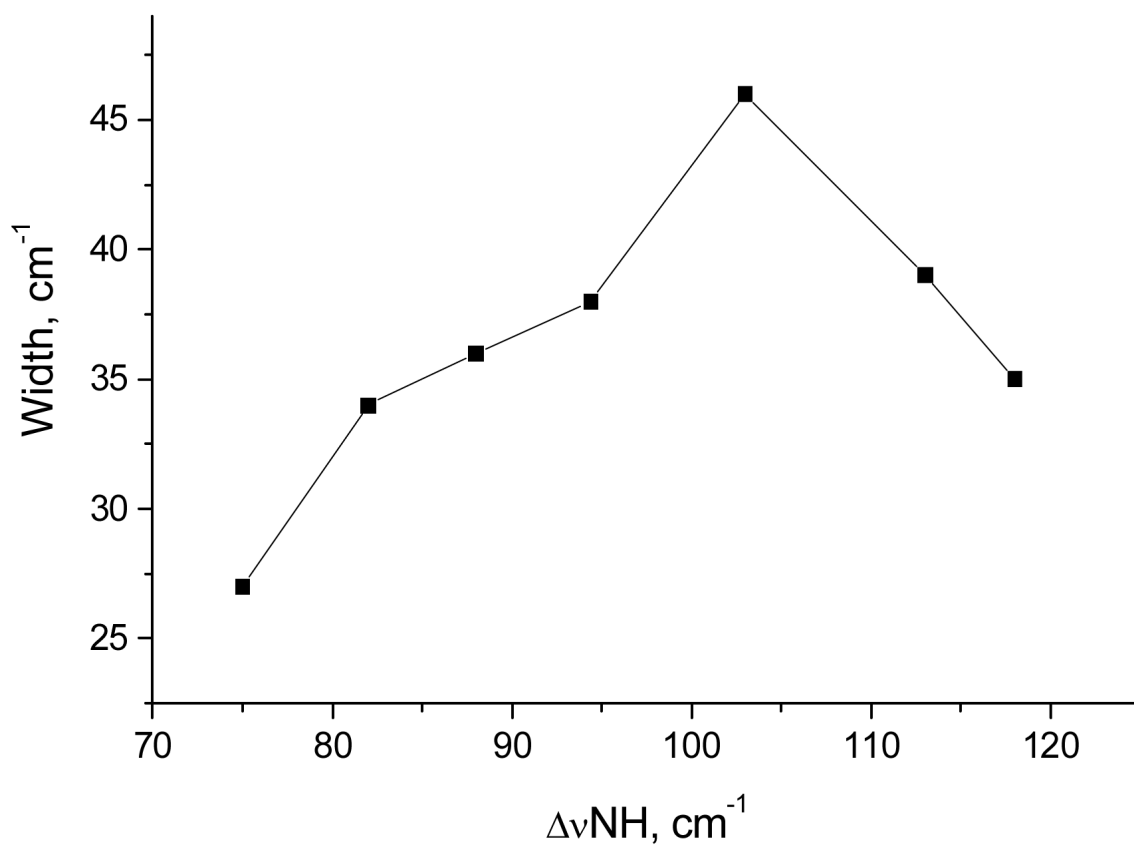


Figure 12.

Dependence of the width of the νNH band on the $\Delta\nu\text{NH}$ frequency for set of arenes

$\text{C}_6\text{H}_{6-n}(\text{CH}_3)_n$ with $n = 0-6$.

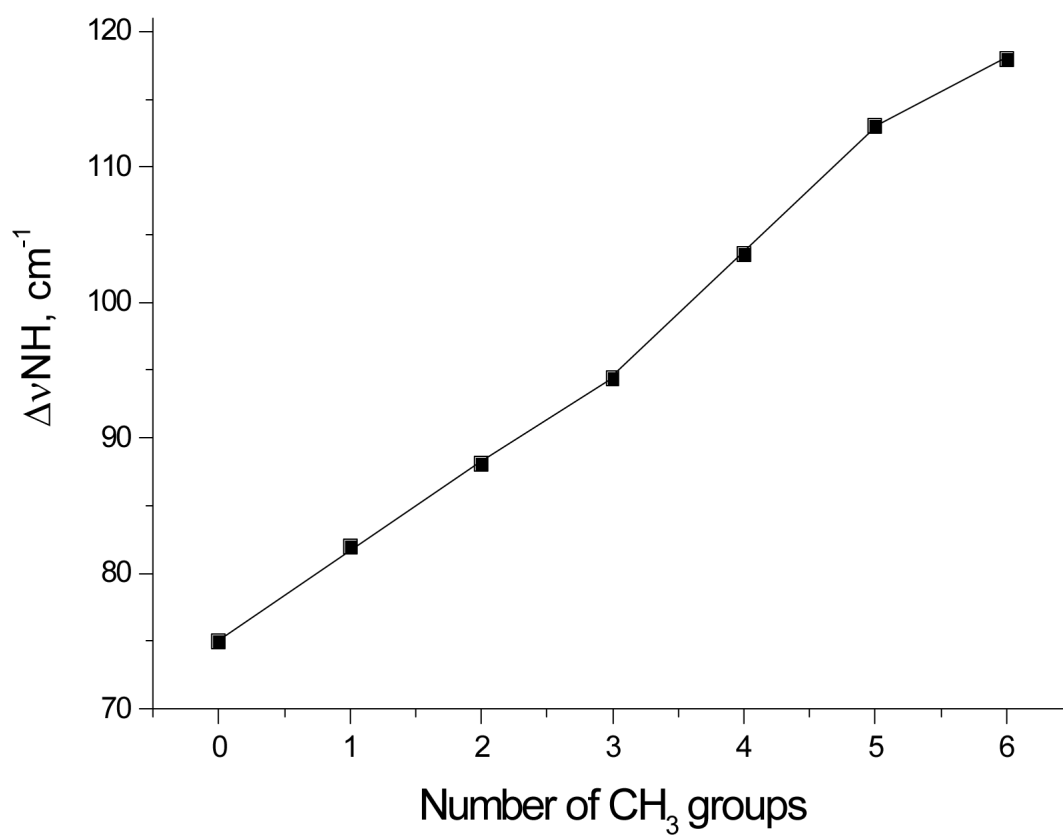


Figure 13.
Dependence of $\Delta\nu_{\text{NH}}$ shifts on the number of CH_3 groups in methylbenzenes.

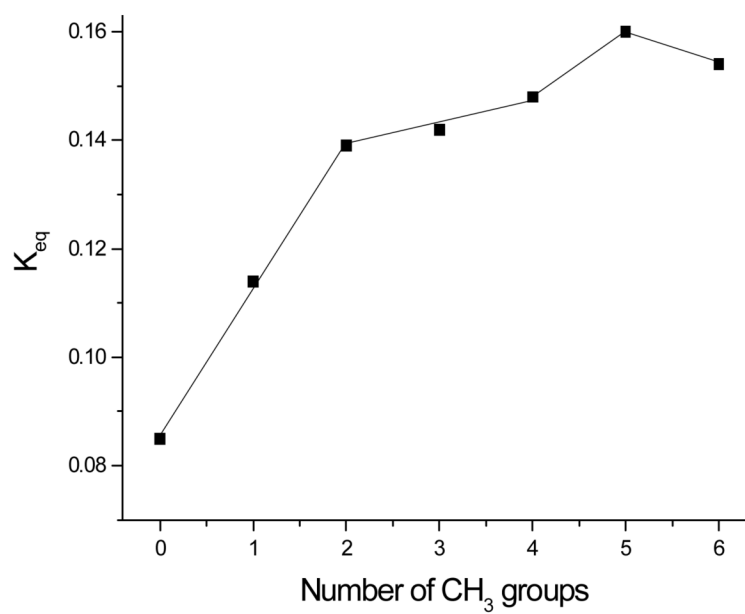
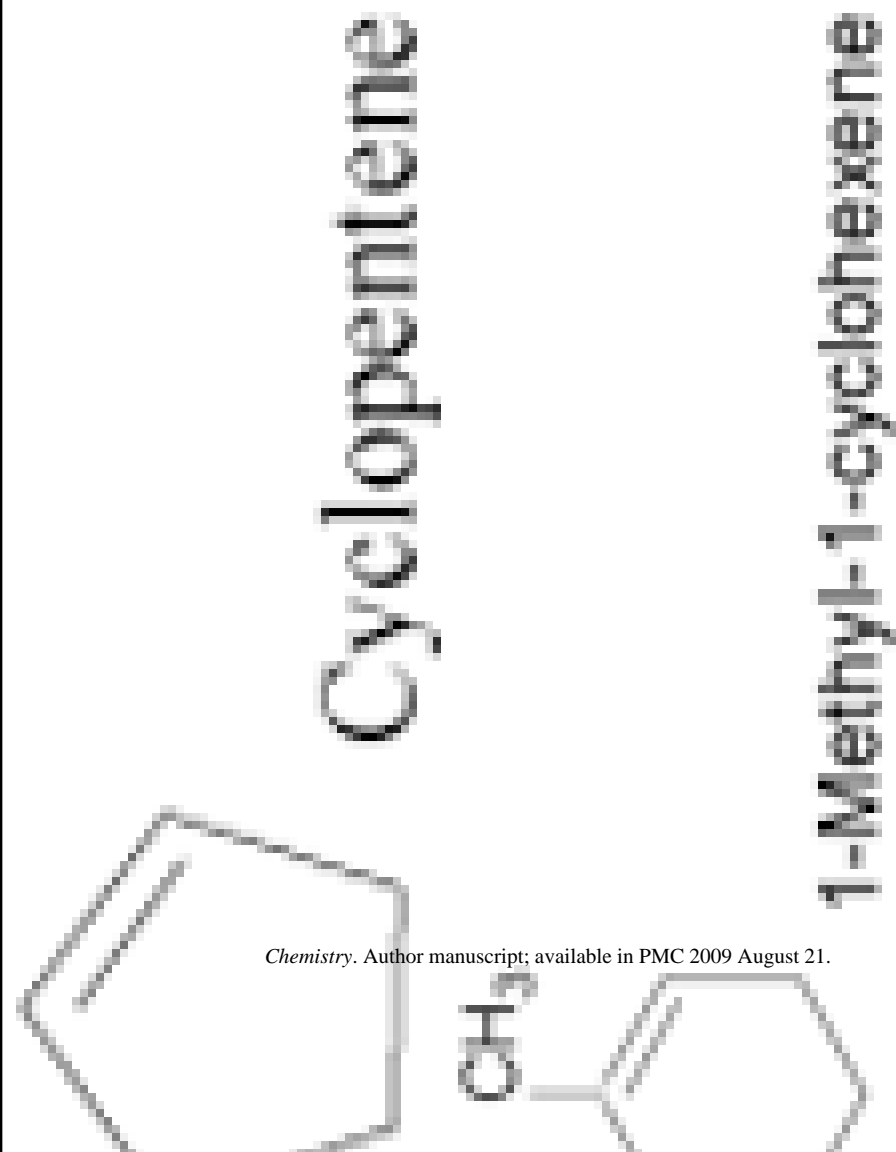


Figure 14.
Dependence of K_{eq} on the number of CH_3 groups in methylbenzenes.

Characteristics of [Oct₃NH⁺...nL] $\{F_{20}^{-}\}$ complexes in CCl₄ solutions.

base, L	K _{eq}	n	ν_{NH} [a] (cm ⁻¹)	$\Delta\nu_{NH}$ [b] (cm ⁻¹)	S _{1/2} [d] (cm ⁻¹)
H ₃	0.085	0.99	3156.5	75	27
H ₃ /2	0.114	1.05	3151	82-83 [c]	34
H ₃ /3	0.139	1.06	3144	88-91 [c]	36
H ₃ /4	0.142	0.97	3140	94.5-98 [c]	38
H ₃ /5	0.148		3130	103.5-104.5	46
H ₃ /6	0.160	0.997	3120	113	39
	0.154	1.09	3114	118-119 [c]	35
	0.260	1.06	3136	70	30
Naphthalene	0.458	1.04	3166	67	39
Phenanthrene	<0.002	0.99	~3075	~158	155 ± 5
1-hexene	0.084	0.99	~3075	~158	155 ± 5
cyclohexene					

se, L	K_{eq}	n	$\nu_{NH} [a] \text{ (cm}^{-1}\text{)}$	$\Delta\nu_{NH} [b] \text{ (cm}^{-1}\text{)}$	$S_{1/2} [d] \text{ (cm}^{-1}\text{)}$
	0.0725	1.04	$\sim 3072 [g]$	$\sim 160 [g]$	[f]
1,4-cyclohexadiene	0.41 0.257	1.14 1.97	3125 3084	108 149	76
1,3-cyclohexadiene	0.216 0.722	0.496 0.98	3125 3084	108 149	49 131
1,3,5,7-cyclooctatetraene	0.025	[f]	[f]	[f]	[f]
1,5-cyclooctadiene					



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K_{eq}	n	$\nu_{NH} [a] \text{ (cm}^{-1}\text{)}$	$\Delta \nu_{NH} [b] \text{ (cm}^{-1}\text{)}$	$S_{1/2} [d] \text{ (cm}^{-1}\text{)}$
0.094	0.998	3100±5	133±5	150±10
0.215	1.00	3063	170	150

se, L	K_{eq}	n	$\nu_{NH} [a] \text{ (cm}^{-1}\text{)}$	$\Delta\nu_{NH} [b] \text{ (cm}^{-1}\text{)}$	$S_{1/2} [d] \text{ (cm}^{-1}\text{)}$
1-Methyl-1-cyclopentene	1.15	1.04	3048 ~2880 [e]	185	[f]
1-hexyne	0.254 [f]	1.01 (2)	3123 3086	109–117 147	150±5 115
3-hexyne	2.02 3.65	1.08 1.94	3094 3072 ~2880 [c]	139 161	163 [f]
	174	0.94	3090	143	61

:1 arene complexes at low L concentration

scale is anchored to the contact ion pair ($\Delta\nu_{NH} = 0$ at 3233 cm^{-1}), for 1:1 complexes data are given for low L concentration (except for arenes)

frequency interval for arenes solutions from low to high concentration

:1 complexes at low L concentration

band is distorted by Fermi-resonance, the true ν_{NH} frequency cannot be obtained since both components are partially overlapped with intense absorptions from the octyl chains of the cation and anions from the unsaturated hydrocarbon

l7] Cannot be determined

l8] Calculated from vND frequency (see Table 2).

Table 2The $\nu\text{NH}/\text{D}$ frequencies of $[\text{Oct}_3\text{NH}^+\cdots n\text{L}]\{\text{F}_{20}^-\}$ complexes.

L	Complex	νNH	νND	$\nu\text{NH}/\nu\text{ND}$
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
Non complexed		3233	2407	1.34
Oct ₃ NH/D ⁺ {F ₂₀ } ion pair				

^[a] Calculated from νND . Unavailable experimentally due to overlap with strong νCH bands from the $\text{CH}=\text{CH}$ group

Table 3

Comparison of proton-donor abilities of Oct₃NH⁺ cation and proton hydrates via low frequency shift of the νP=O band in TBP.

Compound	νP=O	ΔνP=O	Ref
H ₃ O ⁺ (TBP) ₃	1187	74	[46]
H ₅ O ₂ ⁺ (TBP) ₄	1222	39	[46]
H ₅ O ₂ ⁺ (TBP) ₂ (H ₂ O) ₂	1222	39	[46]
Oct ₃ NH ⁺ ...TBP	1228	33	Present work
TBP...H ₂ O	1248	13	[47]
TBP _{free}	1261	0	Present work