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I am submitting herewith a thesis written by Robert R. Todd, Jr. entitled "Nuclear Magnetic Resonance Studies of 1,3,5-Trinitrobenzene Complexes." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

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NUCLEAR MAGNETIC RESONANCE STUDIES OF 1,3,5-TRINITROBENZENE COMPLEXES

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Robert R. Todd, Jr.

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ABSTRACT

NMR studies of molecular complexes of 1,3,5-trinitrobenzene in 1,2-dichloroethane have been done, employing both ^{13}C-NMR and ^{1}H-NMR. Association constants and shifts of the pure complexes were obtained. Whereas the results could largely be interpreted in terms of a ring current model that has been previously proposed this was not entirely successful. There was evidence that electron transfer is taking place in some of the systems presented.

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CHAPTER I

INTRODUCTION

A. The Nature of Weak Complexes

A weak complex can be defined as a complex in which there is a preferred orientation between two molecules, but there is no covalent bond that holds the molecules together in a fixed conformation.[1] There appears to be an attraction of one molecule for another to the extent that the attraction is to a specific site.[2] It has been suggested that for weak complexes, there may be no true complex, but only molecular contact in a preferred manner.[3]

Complex formation has been suggested to occur when the complexing molecules interact with each other in a preferred orientation such that it would allow appropriate orbitals to overlap.[1] If the complexing molecules do not behave in this manner, the resultant phenomenon has been called solvation, and not complexation. Recently, it has been suggested[4] that for previously reported weak complexes, solvation rather than complexation occurs.

There is still controversy concerning the factors responsible for the changes in the observed nmr spectra of nuclei upon complexation,[5,6,7,8] and the purpose of this work, in part, is an attempt to investigate the nature of the effects responsible for the shifts. Both ^{1}H and ^{13}C nmr spectroscopies are employed. The chemical shifts due to the anisotropic ring current of the complexing molecules should be of the same order of magnitude for both the ^{1}H and ^{13}C nuclei.[9] If the observed chemical shifts are due primarily

to charge transfer effects, it is expected that the shifts would be very much larger in ^{13}C nmr spectroscopy than in ^{1}H.[10] This is due to the fact that ^{13}C nuclei are more sensitive to changes in electron density, as is borne out by both experimental data and theoretical calculations. For example, Fraenkel[11,12] and Spiesecke and Schneider[13,14] have developed expressions relating changes in chemical shifts, $\Delta\sigma$, to change in charge density, Δq. They arrived at the expressions $\Delta\sigma = -10\Delta q$ for ^{1}H nmr, and $\Delta\sigma = -160\Delta q$ for ^{13}C nmr, in p.p.m. Therefore, ^{13}C chemical shifts should be about sixteen times more sensitive to charge density changes than the shifts of the protons attached to those carbons.

The nmr signal of the complexed species and the uncomplexed species appear as a time averaged signal of the two species.[15] This is because the thermal motion of the solution lowers the lifetime of the complex so that it is shorter than the nmr time scale. In theory, as the temperature of the solution is lowered, the signal of the complexed and uncomplexed species should separate into two respective peaks because the thermal motion would be less.[15,16] Then if the temperature is lowered to a greater extent, only one signal would be obtained for the acceptor or donor molecule, whichever is not in excess, because lowering the temperature favors the most stable species which is the complex.[17]

Complexes between donor and acceptor molecules have been suggested as occurring in a 1:1 ratio, although exceptions are known.[4] If either the acceptor or donor is in large excess, 1:2 ratios of molecules have been discovered to exist.[18,19]

Models to describe the physical occurrence of complexation in solution have been proposed by several authors.[1,4,20,21,22] For example, Carter, et al.[1] has suggested that the donor, acceptor, and also the complexed molecules are surrounded by a well-defined solvation shell, with each species having a specific solvation number. The idea of a change in the solvation shell number upon complexation has been developed further to explain the anomaly of non-integral ratios of molecules that have been found to exist in some complexes.[20] Nagy and co-workers[20,21] supported the idea that what is occurring is not true complexation, but rather solvation and that this is competitive with regard to a particular type of preferred solvating molecule. A similar theory has been developed by Homer, et al.[4] It has also been suggested by Engler and Laszlo[22] that for very weak complexes, (0.5 L/mol or less) the idea of a 1:1 ratio of molecules is not valid. They propose that for such complexes, a time averaged cluster of solvent molecules is a much better physical interpretation of the complexation than that of a 1:1 ratio of donor and acceptor molecules.

Several authors have noted that the value of the association constant is very dependent upon the nature of the solvent.[23,24] For example, when 1,3,5-trinitrobenzene is complexed with naphthalene, the value of the association constant decreases in the following order of solvents: pentane > cyclopentane > hexane > carbon tetrachloride > carbon disulfide > chloroform.[24] In other studies,[25] it has been found that the effect of specific solvation is especially significant for systems in which the value of the association constant is 1.0 L/mol or less.

There have been a large number of discussions concerning why the complexes should form.[8,26,27] One author has suggested that the basis for stabilization is dipole - induced dipole interactions.[27] This idea has also been supported by Foster,[28] who has claimed that the stabilization of complexes between 1,3,5-trinitrobenzene and various donor molecules is due to the electrostatic interaction of the positively charged nitrogen of the NO_2 group and negative centers in the donor molecules.

Other authors[29,30] have proposed that other factors could be responsible for complex formation. Wilson,[29] in a proton nmr study of dichlorodiphenyltrichloroethane (D.D.T.) complexed with benzene and naphthalene, definitely concluded that electron charge density donation by aromatic donors occurs, however, she completely ignored ring current effects. Van der Waals dispersion forces have also been invoked to explain the complex formation.[30] These authors, however, could not completely separate the dipole attraction effects from the Van der Waals dispersion forces.

B. Experimental Treatment of Complexation Using NMR

The HAFF equation, derived by Hanna, Ashbaugh, Foster, and Fyfe, is one of the earliest means for theoretically treating the equilibrium condition studied by nmr.[31] It is an extension of the equation known as the Benesi-Hildebrand equation which had been previously employed to study the equilibrium of weak complexes using ultraviolet and visible spectroscopy. Whereas the molar extinction coefficient of the pure complex is obtained using the Benesi-Hildebrand equation, the nmr chemical shift of the pure complex is obtained when the HAFF equation is employed.[32]

The experimental technique for using the HAFF equation is as follows: (1) either the donor or acceptor molecule is in large excess; (2) the smaller constituent concentration is then kept constant from sample to sample, while the larger constituent concentration is varied; (3) the chemical shift of the smaller constituent is monitored as the concentration of the larger constituent is changed.[33]

For the purpose of deriving the HAFF equation, the specific case of donor concentration in large excess will be employed. It is noted, however, the case of acceptor molecule in large excess is equally valid.

Key for HAFF equation derivation:

d = observed chemical shift of acceptor

d_a = chemical shift of uncomplexed acceptor molecule

d_{ad} = chemical shift of fully complexed acceptor molecule

Δ = observed chemical shift of acceptor molecule relative to uncomplexed $(d-d_a)$

Δ_o = shift of fully complexed acceptor molecule relative to uncomplexed acceptor $(d_{ad}-d_a)$

P_a = relative population of uncomplexed acceptor molecule

P_{ad} = relative population of complexed acceptor molecule

(A_o) = initial concentration of acceptor molecule

(D_o) = initial concentration of donor molecule

(AD) = concentration of complexed species

k = association constant of the complexation

$$d = P_a d_a + P_{ad} d_{ad} \qquad (1)$$

The preceding equation (1) was derived by Gutowsky, et al.[15] in their work on rapid exchange in nmr. Therefore, the following equation is valid.

$$P_{ad} = \frac{(AD)}{(A)_o} = \frac{\Delta}{\Delta_o} \qquad (2)$$

$$k = \frac{(AD)}{[(D)_o - (AD)][(A)_o - (AD)]} \qquad (3)$$

because $(D)_o >> (A)_o$, $[(D)_o - (AD)] \simeq (D)_o$.

therefore, $k = \frac{(AD)}{(D)_o[(A)_o - (AD)]}$. Substituting in for $(A)_o$ and subsequent rearrangement yields: $\frac{1}{\Delta} = \frac{1}{k} \cdot \frac{1}{\Delta_o} \cdot \frac{1}{(D)_o} + \frac{1}{\Delta_o}$. Further rearrangement yields $\frac{\Delta}{(D)_o} = -\Delta k + \Delta_o k$, which is the HAFF equation.[33]

If $\Delta/(D)_o$ versus Δ is plotted, the slope of the graph will be equal to negative k, and the "y" intercept will be $k\Delta_o$. For simplicity, if the abscissa and ordinate axis both begin at zero, the "x" intercept will give Δ_o directly.

A further equation has been developed that takes into account the possibility of AD_2 formation.[34] It has been suggested that AD_2 at the most would only be 5% of AD formed if k_{AD} was approximately equal to 10.0 L/mol.[35] The possibility of AD_3 complexes being formed is probably remote, since the acceptor will be between two donor molecules already, and the third donor molecule would be hindered because of steric factors.[36]

C. The Validity of the Association Constants and Chemical Shifts Obtained from the HAFF Equation

Because of the necessity of studying one of the species in high excess of the other species, the reliability of the results

have been questioned. Several factors effecting the validity of the method have been discussed, notably, deviations from ideality,[37] formation of higher-order species,[18,19] and possible changes in solvent coordination number.[20]

It is intuitively evident that the true chemical shift of the pure complex should be the same regardless of the concentration scale used to obtain it with the HAFF equation. Although this was indeed found to be true by several authors,[37] an exception was found upon complexing caffeine with benzene in carbon tetrachloride.[38] Δ_o values of 53.0 Hz and 106.0 Hz, using the molality and mole fraction units, respectively, were obtained. It was suggested that the two different Δ_o values obtained were probably due to the small association constants, which are 1.0 or less on either scale.

The question of which concentration scale to use is not as intuitively obvious compared to the fact that Δ_o should be independent of the concentration scale. Trotter and Hanna have demonstrated that the solution can be ideal only on one concentration scale.[17] Thus, the problem of choosing the correct concentration scale is very important.

Several investigators have attacked this problem.[39,40] For example, experiments have been done using so called "inert solvents," differing only in their molar volumes.[40] The concentration scale that gave a consistent association constant was found to be the molarity scale. Association constants have also been obtained by using infrared spectroscopy.[41,42] Again, it was found that the molarity scale worked successfully.

For the association constants obtained to be true thermodynamic constants, wide variations in concentration should have no effect upon the association constants obtained from the HAFF equation. There are several reports that this has not always been found to occur.[18]

Scott showed that, even if a straight line is obtained with a Benesi-Hildebrand type of equation, the association constants and readily obtainable ΔG, ΔH, and ΔS values need not be true thermodynamic constants.[39] Proof that the association constants are not true thermodynamic constants is shown by examples in which negative intercepts were obtained, with the resultant negative association constants definitely not being true thermodynamic functions.[4,31] In other work in which negative intercepts were found, they were rationalized by stating that the solvent, dioxane, was not serving as an inert solvent, but was competing in the complex formation.[6]

It has been proposed that the discrepancies found in experiments were due to termolecular complex formation.[18] Homer, et al.[43] suggested that a good test for the formation of 1:1 complexes is to compare the obtained association constants under the extreme conditions of (A)>>(D) and (D)>>(A). Similar association constants from both extremes would not support the possibility of termolecular formation. Ultraviolet spectroscopy studies on systems in which it was suspected that termolecular species were present failed to confirm their presence.[18] Other examples are available where the resultant association constants from the two extremes were not similar to each other,[44] while there are also numerous examples where they were similar.[45]

More recently, several attempts have been made to interpret nmr measurements of weak complexes by models other than 1:1 formation.[20,21] In these models attention has been given to the role of the solvent. For example, Nagy and co-workers[20] proposed that the experimental anomalies discussed above could be interpreted in terms of a "competitive preferential solvent theory." According to this theory, the "inert solvent" is really not inert, but is competing with either the donor or acceptor molecule in solvating the other molecular species. Nagy, et al.[20] continued by defining the equation $t = C_{AD}/C_A$, where C_{AD} is equal to the population of the acceptor molecules in the complexed state and C_A is equal to the total population of the acceptor molecule, under the conditions that the donor concentration is very much greater than the acceptor concentration. The author concluded that the Benesi-Hildebrand type equations could only be valid under the conditions $0.2 \leq t \leq 0.8$.

D. Previous ^{1}H NMR Work with 1,3,5-Trinitrobenzene (TNB) as a Complexing Agent

Published work that dealt with ^{1}H nmr studies of TNB in complexes, before 1972, is thoroughly reviewed in the theses of Cole[32] and Chen.[36] Since then a number of papers reporting proton nmr data of TNB complexes has been published,[46,47,48,49,50,51,52,53] but since they contain no new concepts, nor do they settle any of the controversy concerning the nature of the complexes, they will not be discussed further.

In Cole's work various indoles were complexed with TNB.[32] It was found that the chemical shift of the indole hydrogens were all

shifted to higher field. This was proposed as evidence that the ring current of TNB had a major effect on the shifts, rather than the supposed charge transfer from the indole to TNB. The latter effect would be expected to shift the peaks of indole downfield.[36]

Cole also discussed,[32] as does Foster,[54] the situation in which the association constants and the chemical shifts, obtained from the HAFF equation, are not the result of one geometrical configuration, but rather the mean of several dynamic complexes, that occur with different geometrical arrangements between the molecules. Both authors report equations relating the experimental association constants to the individual association constants for each individual complex.

A very extensive study, which is very relevant to the work of this thesis, is the proton work of Chen.[36] 2-Methylnaphthalene and 2-methylquinoline were complexed with TNB, and their respective association constants compared. It was discovered that the hetero-atom has a significant effect on the value of the association constants. The naphthalene association constants were significantly larger than the quinoline values.

The major conclusion of Chen[36] however, was that in TNB complexes of aromatic azines, there was a dynamic situation in which the observed association constants were linear combinations of a number of equilibrium constants representing several 1:1 complexes, each with its own geometry. The observed chemical shifts were then interpreted as a weighted average of the shifts for each individual complex. Chen assumed that the observed shifts in the azines were primarily due to the ring current of the TNB,

and that the effect of the latter could be calculated for a given geometry by the use of the well known Johnson and Bovey tables.[55] This enabled Chen to calculate average geometries for the complexes. For example, for the azine pyridine complex, it was concluded that the geometry of major importance is that in which the nitrogen lone pair (n electrons) points towards the middle of the TNB ring and the molecular plane of the latter is not quite perpendicular to the pyridine ring plane. This geometry is very different from the face to face, π-π, overlap usually assumed for aromatic hydrocarbon complexes. Chen also showed that for the quinoline-TNB complex, there is a dynamic equilibrium between at least two complexes of different geometry, one in which the n electrons interact with the π electrons of TNB in a similar way to that proposed for the pyridine-TNB complex, and one in which the π orbitals of quinoline overlap with the π orbitals of TNB, just as they do in the naphthalene-TNB complex.

As will be discussed in Chapter IV, the ^{13}C chemical shift studies on the TNB complexes of naphthalene and quinoline were initiated in the hope of clarifying in more detail the difference between the n-π and π-π type of complexes proposed by Chen.

It should be pointed out that although errors were found to exist[56] in the sample calculations given by Chen (Appendix C of reference 36), because of the apparent reversal of the Bovey parameters z and p, the actual calculations, upon which Chen's conclusions were based, have been thoroughly checked[56] and found to be correct.

E. Previous Work with Nuclei Other Than ^{1}H

There have been relatively few investigations on donor-acceptor complexes in which the chemical shifts of nuclei other than ^{1}H were used. However, the little work that has been done, was encouraging enough to inspire the ^{13}C chemical shift work described in Chapters III and IV. Most of the previous work has been by Foster's research group[23] using fluoranil as an acceptor molecule and monitoring the ^{19}F chemical shifts, but a few sets of experiments have also been done with ^{13}C nuclei.[7,13,52,57,58,59,60]

Brown, et al.[23] have complexed various donor molecules with fluoranil, observing shifts of the order 1-2 p.p.m. for the ^{19}F nuclei. It was observed that, as methylation of the donor molecules increased, the value of the obtained association constants increases The k value with hexamethylbenzene as donor is 15.4kg./mole, while with benzene the much smaller value of 0.70kg./mole was obtained. These values were obtained with carbon tetrachloride as the solvent. When the work was repeated in other solvents, it was found that the value of the association constants decreases tremendously as the solvent became chloroform, dichloroethane, or dichloromethane.

The same authors,[23] it should be noted, used TNB as the acceptor molecule and monitored the chemical shifts of the TNB hydrogens. The association constants obtained were comparable to those of the fluoranil systems.

The second study is very important with respect to the work described in this thesis. Griffith, et al.[57] complexed naphthalene, benzene, mesitylene, and anthracene with a slight excess of TNB, and monitored the shifts of the donor carbon atoms. The solvent was

9:1 by volume dichloroethane and chloroform. They found similar values of association constants to those in the literature, for the same systems, studied by ultraviolet spectroscopy. The Δ_o values obtained for the naphthalene C_9, C_1, and C_2 carbons are 20.2 Hz (1.34 p.p.m.), 10.3 Hz (0.682 p.p.m.), and -5.9 Hz (-0.39 p.p.m.), respectively. The positive shifts correspond to shifts of higher field. The authors concluded that because the shift of C_2 is negative, "charge transfer must occur from the extremities of the molecule".

Complex formation of o-chloranil with mesitylene, naphthalene, and anthracene has been recently studied by monitoring the ^1H and ^{13}C chemical shifts of the donors.[5] The association constants were obtained from the ^1H shifts using the HAFF equation, and were then used, with one ^{13}C chemical shift measurement per donor, to estimate shifts for the pure complex. This was necessary because the actual ^{13}C chemical shifts observed (0.1-0.2 p.p.m.) were too small to use the HAFF equation directly. The smallness of the shifts was due to solubility problems, similar to those encountered in the work described in Chapter III. Whereas all the proton shifts are upfield (shielded), some of the ^{13}C Δ_o values were downfield (deshielded), which were interpreted as demonstrating that charge transfer from the hydrocarbon to the chloranil occurred. However, the local magnetic anistropy of the C=C and C=O bonds in the chloranil was neglected, which could, depending on the geometry, results in small upfield or downfield shifts.

Larkindale and Simkin[58] have complexed pyridine with iodine, and have measured the shifts so induced, by both ^1H and ^{13}C nmr

spectroscopy. The authors discovered that the ^{13}C chemical shifts were significantly larger, several p.p.m., compared to ^{1}H chemical shifts, which were no greater than 0.1 p.p.m. Because of the much larger shifts, the authors claim that significant charge transfer is occurring, because the ^{13}C nuclei are well known to be much more sensitive to electron charge changes than ^{1}H nuclei as discussed previously.

Bright, et al,[59] also used ^{13}C and ^{1}H nmr spectroscopy in a study in which D.D.T. was complexed with acetone, in dilute chloroform-cyclohexane mixture. It was discovered that comparable association constants were obtained from both nuclei, the values are 0.84 L/mole and 0.74 L/mol, respectively. Δ_o values of 2.00 p.p.m. and 0.93 p.p.m. were obtained for the respective nuelei.

One interesting study[7] was on the ^{13}C chemical shifts of nitro 2.2 cyclophanes in which two benzene rings are held face to face (in the ideal position for π-π overlap). The distance between the center of the two rings being approximately 3.0 $\mathring{A}$.[60] The small ^{13}C chemical shifts obtained were interpreted as indicating no significant charge transfer occurs in the ground state.

The only other ^{13}C study in the literature was a study in which ^{13}C spin lattice relaxation times were used to obtain values for association constants.[61] 2-Methylindole was complexed with TNB in 1,2-dichloroethane and the relaxation times measured with addition of TNB. A value of 1.90 kg solvent/mole for the association constant was obtained for the donor-acceptor equilibrium, compared to a value of approximately 2.16 kg/mole when the system was studied by ^{1}H nmr spectrocopy in chloroform.[62]

CHAPTER II

EXPERIMENTAL TECHNIQUES

A. Sample Purification and Preparation

All reagents were used without further purification unless specifically noted. 1,2-Dichloroethane, carbon tetrachloride, and benzene were obtained from Fisher Scientific Company. Pyridine was purchased from Baker and Adamson. Naphthalene was obtained from Cardinal Products. para-Chloranil, para-benzoquinone, pyrrole, furan, thiophene, and hexamethylbenzene were obtained from Eastman Chemical Company. N-methyl pyrrole was obtained from Columbia Organic Chemical Company and was distilled for further purification.

TNB was obtained from three different sources. That obtained from Eastman Chemical was dried in a vacuum oven at 60°C. Another source of the chemical was from a bottle that did not have a manufacturers label. This was purified by vacuum distillation at 150°C onto a cold finger.

Finally since TNB is no longer commerically available, it was made from meta-dinitrobenzene.[63] Eight grams of meta-dinitrobenzene was placed in a five hundred milliliter reagent bottle with twenty seven milliliters of concentrated nitric acid and fifty three milliliters of thirty percent fuming sulfuric acid. The bottle was capped and kept in an oven at 80°C for one day, and then for three days at 135°C. The contents were then poured into a beaker of cold water, which precipitated the TNB. This was filtered and recrystallized in ethanol. The product was then dried in a vacuum oven at 60°C, with a yield of about twenty percent based on meta-dinitrobenzene. Although this experiment is easy to carry out,

the quantities which could be prepared were limited by unexpected difficulties in procuring fuming sulfuric acid.

The purity of all the reagents was checked by both ^{1}H-nmr and ^{13}C-nmr. No contaminants were detected in any of the reagents.

All sample solutions were prepared on the molarity scale. The ^{1}H-nmr solutes were weighed with an accuracy of a milligram on an Oertling balance, and then placed in five milliliter volumetric flasks. Solvent was then added to the appropriate level. The ^{13}C-nmr samples were made in similar manner, but the solutions were made up to twenty five milliliters in appropriate volumetric flasks.

The solvent used in the majority of experiments was 1,2-dichloroethane. In a few experiments, carbon tetrachloride was used to check the inertness of the 1,2-dichloroethane. Those experiments where carbon tetrachloride was used are specifically noted in the tables in Chapter III.

B. Instrumental Techniques

1. ^{1}H-NMR

The measurements were made on a Varian HA-100 spectrometer. The sweep width used was one thousand hertz, with a two hundred and fifty second sweep time. The lock signal was provided by the solvent, and all reported shifts in Chapter III are given relative to the lock signal. The samples were run in a five millimeter tube at a temperature of 28.5°C.

The calibration of the chart paper was found to disagree with the reference oscillator frequency counter. The expanded

following procedure was employed to obtain accurate values of the shifts: (1) the spectrum was obtained; (2) the radio frequency oscillator was turned off and the sweep time changed to one thousand seconds; (3) the field was swept to the point of signal occurrence, and stopped at precisely this point; (4) the value of the signal frequency was obtained from the reference frequency oscillator. The values obtained were reproducible to within 0.5 Hz (0.005 p.p.m.).

2. ^{13}C-NMR

The ^{13}C measurements were made on a Nicolet TT-14 Fourier Transform spectrometer operating at 15.088 megahertz, with the spectrum being fully hydrogen decoupled. The effective probe temperature with proton decoupling was approximately 30°C. The sweep width was four thousand hertz, which encompassed the resonance frequency of all constituent molecules. All acquired shifts are relative to the solvent chemical shift. The memory allocation for the free induction decay signal was 16K, although 8K was used if the signal to noise level was not satisfactory. The reduction of memory allocation reduced the resolution, but was sometimes necessary to obtain shifts of carbons with extremely long-lived excited states.

The tip angle and delay time between acquisitions were adjusted to give the optimum signal/noise/time ratio. The values of P2 = 30 μ-seconds and D5 = 5 seconds were found to give the best results. A typical run with a twenty millimeter sample tube and the above conditions would require the acquisitions to be approximately fifteen thousand, corresponding to twenty four hours of operating time.

The instrument lock signal used was external deuterium oxide located within the probe in a glass capillary. Tuning the instrument for field homogeneity about the sample must be done with internal locking. The samples contained no source of deuterium. Since this is necessary for internal locking, the field homogeneity was tuned with a sample of ethylbenzene (90%) and deuterated chloroform (10%).

An experiment was done to measure the effects of phasing on the position of the resonances. It was found that although the shape and symmetry of the peaks could be drastically altered by misphasing the spectrum, the position of the crest of the peak was not altered by more than a few hundreths of a hertz. This eliminated the possibility of phasing being a source of significant experimental error. No specific accuracy can be attributed to the measured ^{13}C chemical shifts. The accuracy is very dependent upon the signal to noise value of each independent peak. Experiments indicated that peaks of average intensity were reproducible to less than 0.5 Hz.

C. Analytical Treatment of Data

All data were treated analytically by employing the HAFF equation. A standard least squares linear regression analysis was utilized on a Wang programmable calculator.

CHAPTER III

EXPERIMENTAL DATA

Tables I-XXV (pp. 20-46) of this chapter list the raw data as taken directly from the nmr instruments. It has not been treated by any analytical tool. Only the chemical shift values at the various concentrations of the constituent in excess are tabulated. The data were all measured at the temperature of the probe, as described in Chapter II.

TABLE I

NAPHTHALENE COMPLEXED WITH EXCESS TNB, CHLOROFORM AS SOLVENT[a,b]

Molarity of Excess TNB	Observed Shifts (Hz) Relative to Solvent Shift			Shifts Relative to Uncomplexed Shifts[c]		
	C_9	C_1	C_2	C_9	C_1	C_2
0.00	852.88	767.68	736.35	0.00	0.00	0.00
SATURATED TNB	842.70	761.75	738.46	10.18	5.87	-2.11

[a]Measurement made on TT-14.

[b]Solvent was $CDCl_3$.

[c]Positive shifts correspond to higher field.

TABLE II

NAPHTHALENE COMPLEXED WITH EXCESS TNB, CHLOROFORM AND DICHLOROETHANE 1/1 BY VOLUME, AS SOLVENT[a,b]

Molarity of Excess TNB	Observed Shifts (Hz) Relative to Solvent Shift			Shifts Relative to Uncomplexed Shifts[c]		
	C_9	C_1	C_2	C_9	C_1	C_2
0.00	847.71	762.59	732.42	0.00	0.00	0.00
0.13	844.39	760.15	732.09	3.32	2.44	0.33

[a]Measurement made on TT-14.

[b]Solvent was 1/1 $CDCl_3$: CH_2ClCH_2Cl by volume.

[c]Positive shifts correspond to higher field.

TABLE III

NAPHTHALENE COMPLEXED WITH EXCESS TNB, CHLOROFORM AND DICHLOROETHANE 1/9 BY VOLUME, AS SOLVENT[a,b]

Molarity of Excess TNB	Observed Shifts (Hz) Relative to Solvent Shift			Shifts Relative to Uncomplexed Shifts[c]		
	C_9	C_1	C_2	C_9	C_1	C_2
0.000	1350.51	1265.00	1235.45	0.00	0.00	0.00
0.667	1342.66	1260.25	1235.91	7.85	4.75	-0.46
1.000	1340.67	1258.90	1235.95	9.84	6.10	-0.50

[a]Measurement made on TT-14.

[b]Solvent was 9/1 CH_2ClCH_2Cl: $CDCl_3$ by volume.

[c]Positive shifts correspond to higher field.

TABLE IV

NAPHTHALENE COMPLEXED WITH EXCESS TNB, ^{13}C CHEMICAL SHIFTS[a,b]

Molarity of Excess TNB	Observed Shifts (Hz) Relative to Solvent Shift			Shifts Relative to[c] Uncomplexed Shifts		
	C_9	C_1	C_2	C_9	C_1	C_2
0.00	1348.77	1263.49	1234.31	0.00	0.00	0.00
0.40	1344.00	1260.72	1234.73	4.77	2.77	-0.42
0.60	1342.32	1259.72	1235.08	6.45	3.77	-0.77
0.80	1337.65	1258.25	1235.03	11.12	5.24	-0.72
1.00	1338.75	1257.54	1234.04	10.02	5.95	0.27
1.50	1335.70	1255.53	1234.80	13.07	7.96	-0.47
1.75	1333.95	1254.90	1234.36	14.82	8.59	-0.05
2.00	1333.82	1254.37	1234.73	14.95	9.12	-0.42

[a]Measurement made on TT-14.

[b]Solvent was CH_2ClCH_2Cl.

[c]Positive shifts correspond to higher field.

TABLE V

TNB COMPLEXED WITH EXCESS NAPHTHALENE, ^{13}C CHEMICAL SHIFTS[a,b]

Molarity of Excess Naphthalene	Observed Shifts (Hz) relative to Solvent Shift		Shifts relative to Uncomplexed Shifts[c]	
	C_{NO_2}	C_H	C_{NO_2}	C_H
0.00	1579.34	1200.47	0.00	0.00
1.00	1566.62	1189.39	12.72	11.08
2.00	1558.06	1182.94	21.28	17.53
2.75	1553.09	1178.80	26.25	21.67
3.50	1548.94	1176.12	30.40	24.35

[a]Measurement made on TT-14.

[b]Solvent was CH_2ClCH_2Cl.

[c]Positive shifts correspond to higher field.

TABLE VI

TNB COMPLEXED WITH EXCESS NAPHTHALENE, ^{1}H CHEMICAL SHIFTS[a,b]

Molarity of Excess Naphthalene	Observed Shifts (Hz) Relative to Solvent Shift $H_{2,4,6}$	Shifts Relative to Uncomplexed Shifts[c] $H_{2,4,6}$
0.00	558.5	0.0
1.00	509.9	48.6
2.00	489.0	69.5
2.75	480.0	78.5
3.50	478.0	80.5

[a]Measurement made on HA-100.

[b]Solvent was CH_2ClCH_2Cl.

[c]Positive shifts correspond to higher field.

TABLE VII

QUINOLINE COMPLEXED WITH EXCESS TNB, ^{13}C CHEMICAL SHIFTS[a,b]

Molarity of Excess TNB	Observed Shifts (Hz) Relative to Solvent Shift			Shifts Relative to Uncomplexed Shifts[c]		
	C_2	C_3	C_4	C_2	C_3	C_4
0.00	1605.30	1163.47	1382.72	0.00	0.00	0.00
0.40	1603.70	1163.22	1380.98	1.60	0.25	1.74
0.60	1602.89	1163.16	1380.53	2.41	0.31	2.19
1.00	1602.42	1162.77	1378.90	2.88	0.70	3.82
1.50	1601.48	1162.61	1377.98	3.82	0.86	4.74
1.75	1601.05	1162.71	1377.66	4.25	0.76	5.06
2.00	1600.39	1162.27	1377.00	4.91	1.20	5.72

TABLE VII (continued)

Molarity of Excess TNB	Observed Shifts (Hz) Relative to Solvent Shift			Shifts Relative to Uncomplexed Shifts[c]		
	C_5	C_6	C_7	C_5	C_6	C_7
0.00	1264.26	1243.24	1286.07	0.00	0.00	0.00
0.40	1262.68	1242.89	1285.53	1.58	0.35	0.54
0.60	1262.03	1243.01	1284.86	2.23	0.23	1.21
1.00	1260.83	1242.42	1283.66	3.43	0.82	2.41
1.50	1260.27	1242.08	1283.70	3.99	1.16	2.37
1.75	1259.53	1241.97	1283.82	4.73	1.27	2.25
2.00	1259.07	1241.89	1283.01	5.19	1.35	3.06

TABLE VII (continued)

Molarity of Excess TNB	Observed Shifts (Hz) Relative to Solvent Shift			Shifts Relative to Uncomplexed Shifts[c]		
	C_8	C_9[d]	C_{10}	C_8	C_9	C_{10}
0.00	1289.74	1576.33	1271.35	0.00	0.00	0.00
0.40	1285.53		1267.84	4.21		3.51
0.60	1284.86		1267.14	4.88		4.21
1.00	1283.66		1260.83	6.08		10.52
1.50	1280.44		1260.27	9.03		11.08
1.75	1279.18		1259.53	10.56		11.82
2.00	1278.07		1259.07	11.67		12.28

[a]Measurement made on TT-14.

[b]Solvent was CH_2ClCH_2Cl.

[c]Positive shifts correspond to higher field.

[d]TNB obscures signal.

TABLE VIII

TNB COMPLEXED WITH EXCESS QUINOLINE, ^{13}C CHEMICAL SHIFTS[a,b]

Molarity of Excess Quinoline	Observed Shifts (Hz) Relative to Solvent Shift		Shifts Relative to Uncomplexed Shifts[c]	
	C_{NO_2}	C_H	C_{NO_2}	C_H
0.00	1579.34	1200.47	0.00	0.00
1.00	[d]	1196.44		4.03
2.00		1191.29		4.59
2.75		1188.39		4.39
3.50		1187.33		3.75

[a] Measurement made on TT-14.

[b] Solvent was CH_2ClCH_2Cl.

[c] Positive shifts correspond to higher field.

[d] Quinoline obscures signal.

TABLE IX

HEXAMETHYLBENZENE COMPLEXED WITH EXCESS TNB, ^{13}C CHEMICAL SHIFTS[a,b]

Molarity of Excess TNB	Observed Shifts (Hz) Relative to Solvent Shift		Shifts Relative to Uncomplexed Shifts[c]	
	C-ring	C-meth	C-ring	C-meth
0.00	1321.58	-415.808	0.00	0.00
2.00	1319.79	-423.418	1.79	7.61

[a]Measurement made on TT-14.

[b]Solvent was CH_2ClCH_2Cl.

[c]Positive shifts correspond to higher field.

TABLE X

HEXAMETHYLBENZENE COMPLEXED WITH EXCESS p-CHLORANIL, ^{13}C CHEMICAL SHIFTS[a,b]

Molarity of Excess p-Chloranil	Observed Shifts (Hz) Relative to Solvent Shift		Shifts Relative to Uncomplexed Shifts[c]	
	C-ring	C-meth	C-ring	C-meth
0.00	1321.58	-514.808	0.00	0.000
saturated/then filtered	1321.97	-415.820	-0.39	0.012

[a]Measurement made on TT-14.

[b]Solvent was CH_2ClCH_2Cl.

[c]Positive shifts correspond to higher field.

TABLE XI

p-BENZOQUINONE COMPLEXED WITH EXCESS NAPHTHALENE, ^{13}C CHEMICAL SHIFTS WITH DICHLOROETHANE AS SOLVENT[a,b]

Molarity of Excess Naphthalene	Observed Shifts (Hz) Relative to Solvent Shift		Shifts Relative to Uncomplexed Shifts[c]	
	C=O	C-H	C=O	C-H
0.00	2157.73	1393.46	0.00	0.00
3.50	2154.53	1386.20	2.76	7.26

[a]Measurement made on TT-14

[b]Solvent was CH_2ClCH_2Cl.

[c]Positive shifts correspond to higher field.

TABLE XII

p-BENZOQUINONE COMPLEXED WITH EXCESS NAPHTHALENE, ^{13}C CHEMICAL SHIFTS WITH CARBON TETRACHLORIDE AS SOLVENT[a,b]

Molarity of Excess Naphthalene	Observed Shifts (Hz) Relative to Solvent Shift		Shifts Relative to Uncomplexed Shifts[c]	
	C_{NO_2}	C_H	C_{NO_2}	C_H
0.00	1349.51	603.482	0.00	0.000
3.50	1350.40	589.936	-0.89	13.546

[a]Measurement made on TT-14.

[b]Solvent was CCl_4.

[c]Positive shifts correspond to higher field.

TABLE XIII

TNB COMPLEXED WITH EXCESS PYRIDINE, ^{13}C CHEMICAL SHIFTS[a,b]

Molarity of Excess Pyridine	Observed Shifts (Hz) Relative to Solvent Shift		Shifts Relative to Uncomplexed Shifts[c]	
	C_{NO_2}[d]	C_H	C_{NO_2}	C_H
0.00	1579.34	1200.47	0.00	0.00
3.50				

[a]Measurement made on TT-14.

[b]Solvent was CH_2ClCH_2Cl.

[c]Positive shifts correspond to higher field.

[d]Pyridine obscures signal.

TABLE XIV

TNB COMPLEXED WITH EXCESS N-METHYL PYRROLE, ^{13}C CHEMICAL SHIFTS[a,b]

Molarity of Excess N-Methyl Pyrrole	Observed Shifts (Hz) Relative to Solvent Shift		Shifts Relative to Uncomplexed Shifts[c]	
	C_{NO_2}	C_H	C_{NO_2}	C_H
0.00	1579.34	1200.47	0.00	0.00
1.00	1577.03	1200.24	2.31	0.23
2.00	1578.19	1198.24	1.15	2.23
2.75	1573.06	1198.53	1.28	1.94
3.50	1575.03	1196.40	4.31	4.07

[a]Measurement made on TT-14.

[b]Solvent was CH_2ClCH_2Cl.

[c]Positive shifts correspond to higher field.

TABLE XV

TNB COMPLEXED WITH EXCESS THIOPHENE, ^{13}C CHEMICAL SHIFTS[a,b]

Molarity of Excess Thiophene	Observed Shifts (Hz) Relative to Solvent Shift		Shifts Relative to Uncomplexed Shifts[c]	
	C_{NO_2}	C_H	C_{NO_2}	C_H
0.00	1579.34	1200.47	0.00	0.00
3.50	1578.64	1198.64	0.70	1.83

[a]Measurement made on TT-14.

[b]Solvent was CH_2ClCH_2Cl.

[c]Positive shifts correspond to higher field.

TABLE XVI

TNB COMPLEXED WITH EXCESS FURAN, ^{13}C CHEMICAL SHIFTS[a,b]

Molarity of Excess Furan	Observed Shifts (Hz) Relative to Solvent Shift		Shifts Relative to Uncomplexed Shifts	
	C_{NO_2}	C_H	C_{NO_2}	C_H
0.00	1579.34	1200.47	0.00	0.00
3.50	1580.21	1201.71	-0.87	-1.24

[a]Measurement made on TT-14.

[b]Solvent was CH_2ClCH_2Cl.

[c]Positive shifts correspond to higher field.

TABLE XVII

TNB COMPLEXED WITH EXCESS BENZENE, ^{13}C CHEMICAL SHIFTS[a,b]

Molarity of Excess Benzene	Observed Shifts (Hz) Relative to Solvent Shift[d]		Shifts Relative to Uncomplexed Shifts[c]	
	C_{NO_2}	C_H	C_{NO_2}	C_H
0.00	1579.34	1200.47	0.00	0.00
3.50	1578.119		1.22	

[a]Measurement made on TT-14.

[b]Solvent was CH_2ClCH_2Cl.

[c]Positive shifts correspond to higher field.

[d]Benzene obscures signal.

TABLE XVIII

TNB COMPLEXED WITH EXCESS PYRIDINE, ^{1}H CHEMICAL SHIFTS[a,b]

Molarity of Excess Pyridine	Observed Shifts (Hz) Relative to Solvent Shift $H_{2,4,6}$	Shifts Relative to Uncomplexed Shifts[c] $H_{2,4,6}$
0.00	558.5	0.00
1.00	556.5	2.00
2.00	557.0	1.50
2.75	557.0	1.50
3.50	557.0	1.50

[a]Measurement made on HA-100.

[b]Solvent was CH_2ClCH_2Cl.

[c]Positive shifts correspond to higher field.

TABLE XIX

TNB COMPLEXED WITH EXCESS N-METHYL PYRROLE, ^{1}H CHEMICAL SHIFTS[a,b]

Molarity of Excess N-Methyl Pyrrole	Observed Shifts (Hz) Relative to Solvent Shift $H_{2,4,6}$	Shifts Relative to Uncomplexed Shifts[c] $H_{2,4,6}$
0.00	558.5	0.0
1.00	548.5	10.0
2.00	544.5	14.0
2.75	541.0	17.5
3.50	539.5	19.0

[a]Measurement made on HA-100.

[b]Solvent was CH_2ClCH_2Cl.

[c]Positive shifts correspond to higher field.

TABLE XX

TNB COMPLEXED WITH EXCESS PYRROLE, ^1H CHEMICAL SHIFTS[a,b]

Molarity of Excess Pyrrole	Observed Shifts (Hz) Relative to Solvent Shift $H_{2,4,6}$	Shifts Relative to Uncomplexed Shifts[c] $H_{2,4,6}$
0.00	558.5	0.0
1.00	550.0	8.5
2.00	545.5	13.0
2.75	543.0	14.5
3.50	541.5	17.0

[a]Measurement made on HA-100.

[b]Solvent was CH_2ClCH_2Cl.

[c]Positive shifts correspond to higher field.

TABLE XXI

TNB COMPLEXED WITH EXCESS FURAN, ^1H CHEMICAL SHIFTS[a,b]

Molarity of Excess Furan	Observed Shifts (Hz) Relative to Solvent Shift $H_{2,4,6}$	Shifts Relative to Uncomplexed Shifts[c] $H_{2,4,6}$
0.00	558.5	0.0
1.00	555.5	3.0
2.00	555.5	3.0
2.75	554.0	4.5
3.50	554.0	4.5

[a]Measurement made on HA-100.

[b]Solvent was CH_2ClCH_2Cl.

[c]Positive shifts correspond to higher field.

TABLE XXII

TNB COMPLEXED WITH EXCESS THIOPHENE, ^{1}H CHEMICAL SHIFTS[a,b]

Molarity of Excess Thiophene	Observed Shifts (Hz) Relative to Solvent Shift $H_{2,4,6}$	Shifts Relative to Uncomplexed Shifts[c] $H_{2,4,6}$
0.00	558.5	0.0
1.00	553.0	5.5
2.00	550.0	8.5
2.75	548.0	10.5
3.50	546.5	12.0

[a]Measurement made on HA-100.

[b]Solvent was CH_2ClCH_2Cl.

[c]Positive shifts correspond to higher field.

TABLE XXIII

TNB COMPLEXED WITH EXCESS BENZENE, ^1H CHEMICAL SHIFTS[a,b]

Molarity of Excess Benzene	Observed Shifts (Hz) Relative to Solvent Shift $H_{2,4,6}$	Shifts Relative to Uncomplexed Shifts[c] $H_{2,4,6}$
0.00	558.5	0.0
1.00	551.0	7.5
2.00	545.0	13.5
2.75	542.0	16.5
3.50	540.8	17.8

[a]Measurement made on HA-100.

[b]Solvent was CH_2ClCH_2Cl.

[c]Positive shifts correspond to higher field.

TABLE XXIV

N-METHYL PYRROLE COMPLEXED WITH EXCESS TNB, ^{1}H CHEMICAL SHIFTS[a,b]

Molarity of Excess TNB	Observed Shifts (Hz) Relative to Solvent Shift		Shifts Relative to Uncomplexed Shifts[c]	
	$H_{2,5}$	$H_{3,4}$	$H_{2,5}$	$H_{3,4}$
0.00	280.5	227.5	0.0	0.0
1.00	268.5	207.5	12.0	20.0

[a]Measurement made on HA-100.

[b]Solvent was CH_2ClCH_2Cl.

[c]Positive shifts correspond to higher field.

TABLE XXV

THIOPHENE COMPLEXED WITH EXCESS TNB, ^{1}H CHEMICAL SHIFTS[a,b]

Molarity of Excess TNB	Observed Shifts (Hz) Relative to Solvent Shift		Shifts Relative to Uncomplexed Shifts[c]	
	$H_{2,5}$	$H_{3,4}$	$H_{2,5}$	$H_{3,4}$
0.00	360.0	336.0	0.0	0.0
1.00	352.0	328.0	8.0	8.0

[a]Measurement made on HA-100.

[b]Solvent was CH_2ClCH_2Cl.

[c]Positive shifts correspond to higher field.

CHAPTER IV

RESULTS AND DISCUSSION

A. Attempts to Reproduce Previous Work

Attempts have been made (Table III (p. 22)) to reproduce the ^{13}C work of Griffith, Grant, and Roberts[33] on complexing naphthalene with excess TNB using 1,2-dichloroethane and chloroform in a 9:1 ratio by volume, respectively, as solvent. It is believed that the concentrations reported by the authors were not correct in some way.

Griffith, et al.[33] reported results which they claimed were obtained from solutions containing 0.33M naphthalene and concentrations of TNB of 1.00M and greater. In this author's work, all attempts to obtain solutions of this concentration were unsuccessful. The mixture of naphthalene and TNB corresponding to 0.33M donor and 1.0M TNB would not go completely into solution, even when heated to the point of boiling while stirring. The ^{13}C-NMR spectrum was obtained, even though solid existed in the solvent. The shifts for the C_9, C_1, and C_2 carbons were 9.8 Hz, 6.1 Hz, and -0.50 Hz, respectively, whereas Griffith, et al,[33] report shifts of 8.3 Hz, 4.2 Hz, and -2.5 Hz, respectively, for a solution of this concentration. Since nmr results of mixtures with solids floating in the sample tube are not valid, no further work was done on this system. This author has no explanation of how Griffith, et al.[33] were able to work at the concentrations claimed in their published work.

B. New Work on Naphthalene and Quinoline TNB Complexes

Naphthalene (0.05M) was complexed with excess TNB (Table XXVI (p. 49)). It was found that the HAFF equation worked well for both the C_9 and C_1 carbons, and the association constants obtained for them were similar to those of Griffith, et al.[33] The C_2 carbons, however, were found to exhibit downfield shifts upon addition of TNB. The downfield shifts were small and scattered. It is interesting that the C_9 and C_1 carbon shifts were upfield, while the C_2 shifts are downfield. In previous work,[33] when downfield shifts were obtained, it was suggested that they were due to opposing factors affecting the shift at the C_2 position, namely the ring current of the TNB causing an upfield shift and charge transfer from the naphthalene to the TNB causing a downfield shift.

A subsequent study was done in which the naphthalene was in excess, and the shifts of the TNB carbons were measured. Obviously, the association constants obtained from the two extremes should be similar, if they are to be considered as valid thermodynamic association constants. 0.05M TNB was complexed with excess naphthalene up to 3.5M (Table XXVII (p. 50)). The linearity of the HAFF plots was very good, but the association constant as determined by the chemical shifts of the C_H carbon was shightly greater than that based on the C_{NO_2} carbon. The association constants were found to agree closely with those found in the previous experiments.

In view of the proton nmr results obtained by Chen[36] on quinoline, the next logical step was to look at the complexes of this molecule with TNB by ^{13}C-NMR spectroscopy. It would be interesting to compare

TABLE XXVI

^{13}C DATA[a] OF NAPHTHALENE COMPLEXED WITH EXCESS TNB

	C_9	C_1	C_2[b]
k(L/mol)	0.32	0.32	
Δ_o (p.p.m.)	2.73	1.58	
correlation	0.92	0.98	
k(L/mol)[c]	0.71	0.765	0.51

[a]Obtained from experimental results of Table IV (p. 23).

[b]Shifts too small to use in HAFF equation.

[c]Griffith values, reference 33.

TABLE XXVII

^{13}C DATA[a] OF TNB COMPLEXED WITH EXCESS NAPHTHALENE

	C_{NO_2}	C_H
k(L/mol)	0.20	0.30
Δ_o (p.p.m.)	4.51	3.05
correlation	0.999	0.995

[a]Obtained from experimental results of Table V (p. 24).

TABLE XXVIII

^{1}H DATA[a] OF TNB COMPLEXED WITH EXCESS NAPHTHALENE

	$H_{2,4,6}$
k(L/mol)	0.74
Δ_o (p.p.m.)	1.13
correlation	0.986

[a]Obtained from experimental results of Table VI (p. 25).

these to the naphthalene experiments, in order to observe the effects that the heteroatom has upon the association constants and the chemical shifts. 0.05M quinoline was complexed with excess TNB (Table XXIX (p. 52); the TNB concentrations were the same as those in the naphthalene experiments. The association constants appear larger when obtained from C_2, C_4 C_5 and C_8 than in the naphthalene experiments. However, the C_3, C_6, C_7, and C_{10} carbons exhibited very small shifts upon complexation, which leads to large correlation errors in the plots, and negative association constants for C_3, C_6, and C_7.

^{13}C experiments were also done in which the quinoline was in excess, and the shifts of the TNB carbons measured. 0.05M TNB was complexed with excess quinoline to 3.5M, (Table XXX (p. 52)) i.e. the same concentrations as were used in the naphthalene experiments. The largest shift obtained was 0.304 p.p.m. compared to 1.612 p.p.m. in the naphthalene experiments.

In order to use the experimental results described above to investigate the geometry of complexes, several assumptions were made. It was assumed that the ring current effects are the same for both ^{13}C and ^{1}H nuclei, as has been previously claimed.[9] It was also assumed that the observed shifts in naphthalene and quinoline are almost entirely due to aromatic ring currents. Finally, it was assumed that the Johnson and Bovey tables[55] give realistic values for the ring current. It was found that the data obtained when naphthalene (0.05M) was complexed with excess TNB for both the ^{13}C Δ_o values (Table XXVI (p. 49)) and Chen's[30] ^{1}H Δ_o values for 2-methylnaphthalene could be explained by assuming a distance of 2.5 $\mathring{A}$ between parallel planes in the π-π complex. In the model adopted

TABLE XXIX

^{13}C DATA[a] OF QUINOLINE COMPLEXED WITH EXCESS TNB

	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_{10}
k(L/mol)	0.55	-0.00	0.33	0.40	-0.10	-0.05	0.46	0.08
Δ_o (p.p.m.)	0.52	0.04	0.82	0.71	0.02	0.10	1.13	0.85
correlation	0.902	0.023	0.904	0.953	0.300	0.111	0.777	0.211

[a]Obtained from experimental results of Table VII (pp. 26-28).

TABLE XXX

^{13}C DATA[a] OF TNB COMPLEXED WITH EXCESS QUINOLINE

	C_H
k(L/mol)	0.006
Δ_o (p.p.m.)	0.87
correlation	0.74

[a]Obtained from experimental results of Table VIII (p. 29).

it was assumed that the center of the TNB aromatic ring is undergoing motion about the mid-point of the 9-10 bond in naphthalene to the extent that, at least for part of the time, the center of the TNB is above carbons 9 and 10. The most important features introduced were the restriction of the TNB to the center of the ring in order to explain the small shift of carbon two, and the necessity of moving the TNB about the center of the 9-10 bond in order to explain the large C_9 shift.

According the Chen,[36] the predominant type of complexing for the quinoline-TNB system is of n-π type, so that part of the total chemical shift attributed to the π-π type of complex should be small. This explains the small shifts observed for the C_4, C_5, and C_{10} carbons (Table VII (p. 26)), compared to the corresponding carbons in naphthalene. For the C_2 and C_8 carbons, the n-π model predicts very large shifts for any reasonable geometry, which is required to simultaneously explain the large proton shifts. In order to interpret the observed small carbon shifts, there seems to be no alternative but to invoke charge transfer. According to the equation relating charge density to ^{13}C chemical shifts (p. 2), a small charge loss on C_2 or C_8 of 0.025 is more than adequate (+4 p.p.m.) to explain the observed data. This should be regarded as a very speculative conclusion.

In order to clarify the above findings, the experiments in which the naphthalene and quinoline were in excess of TNB were performed (Table V and VIII p. 24 and p. 29)). The observed chemical shifts for the quinoline - TNB complex were very peculiar, in that as the quinoline concentration was increased, the ^{13}C chemical shifts

diminished. This phenomenon has not been observed in any other system, and no explanation can be offered. Unfortunately, the large block of instrument time (120 hours) necessary to repeat these results has not become available, and will not be available in the forseeable future.[64]

The data for the naphthalene - TNB system were very good. (Table XXVI (p. 49)). The k values obtained for the two positions were very similar to each other and to the values observed when TNB was in excess. The Δ_o values of TNB were larger than those of naphthalene. A similar situation prevails for the proton shifts also (Table XXVIII (p. 50)). In using the ring current tables to calculate these shifts, it is reasonable that the TNB shifts are due to the presence of the two aromatic rings of the naphthalene contributing additively to the total ring current. Using the same geometry previously discussed to explain the naphthalene shifts, a Δ_o value of 3.4 ± 0.5 p.p.m. is obtained. This is in good agreement with the Δ_o value for the carbon to which the hydrogen is attached. No reasonable geometry is capable of producing a ring current effect as large as the Δ_o value obtained for C_{NO_2}. Again, there seems to be no alternative but to consider that a small amount of electron transfer has occurred. If it is assumed that the difference of 1.46 p.p.m. observed for the two carbon atoms in TNB is due to preferential electron donation from the naphthalene to the very positively charged carbon atoms in TNB, then an amount of only 0.009 of electronic charge on the appropriate carbon atom is required to explain the shift. The large Δ_o value of 1.13 p.p.m. observed for the ^1H in TNB (Table XXVIII (p. 50)) can also be explained

by the same range of geometry parameters used in the Johnson - Bovey tables as were successful in explaining the carbon shifts.

C. Complexes of Five Membered Cyclic Compounds and TNB

As an extension of Chen's[36] work on the proton nmr of azine-TNB, the complexing power of benzene and a number of five membered ring complexes was examined using ^{13}C and ^{1}H nmr. The chemical shifts for the ^{13}C nuclei were too small (Tables XIV, XV, XVI, XVII (p. 35-38)) to treat with the HAFF equation. The proton shifts, with the exception of furan, were much larger and gave an excellent linear correlation using the HAFF plots (Table XXXI (p. 56)). The k values were all in the usual range. However, the proton Δ_o values showed interesting differences. The Δ_o value of TNB compared to benzene is small and can be well accounted for by the ring current effect. It is surprisingly smaller than the value obtained for the naphthalene complex, signifying that the rings do not come into as close contact in the benzene complex as in the latter. The benzene molecule appears to have adopted a different geometry in which the benzene is seeking out the positively charged nitrogen atoms in such a way that the TNB protons never experience the full effect of the benzene ring current.

The Δ_o values due to pyrrole, N-methyl pyrrole, and thiophene are about two thirds of that of benzene, which is in agreement with the idea that the ring current in these molecules is about 60 - 80 % that of benzene.[65]

It is also generally accepted that furan is not aromatic enough to support a ring current.[65] Thus, the small shifts observed for the

TABLE XXXI

^{1}H DATA[a] OF TNB COMPLEXED WITH EXCESS FIVE MEMBERED CYCLIC COMPOUNDS

	k(L/mol)	Δ_o (p.p.m.)	correlation
N-methyl pyrrole	0.48	0.292	0.967
Pyrrole	0.45	0.267	0.982
Furan[b]			
Thiophene	0.32	0.223	0.989
Benzene	0.21	0.399	0.938
Pyridine[b]			
Naphthalene	0.74	1.133	0.986

[a]Obtained from experimental results of Tables VI (p. 25) and XVIII, XIX, XX, XXI, XXII, XXIII (pp. 39-44).

[b]Shifts too small to use in HAFF equation.

TNB - furan system are in full agreement with the ring current hypothesis.

The pyridine results support Chen's conclusions[36] that this molecule assumes an n-π complex type of configuration, in which the TNB experiences very little of the ring current of pyridine.

The measurements on the ^{13}C shifts of TNB in the presence of excess of the five membered ring compounds were performed because initially, results on the pyridine - TNB system were thought to have very large chemical shifts. These could only be explained by the existence of considerable charge transfer, and it was thought that these molecules would show this, coupled with a varying degree of ring current. However, the small shifts obtained for the series led to a more careful examination of the pyridine data. It was discovered that they had been erroneously interpreted. The actual shifts of the TNB were obscured by the signals of pyridine.

In (Tables XIV, XV, XVI, XVII (p. 35-38)), the observed chemical shifts for 0.05M TNB in the presence of 3.5M donor are reported. Unlike the case of the proton nmr (Table XXXI (p. 56)), the shifts for N-methyl pyrrole are larger than for benzene. It can be concluded that electron transfer from the N-methyl pyrrole, which has, apart from naphthalene, the lowest ionization potential of all the molecules investigated, is significantly larger.

The furan results are not the first negative shifts reported for TNB complexes.[33] Previously, small negative shifts have been found for the donor carbons and attributed to charge transfer. This cannot be the case for the TNB carbons, and although no explanation for these measurements is available, it clearly invalidates the previously used hypothesis that negative shifts were due to loss of electron charge.[5,33]

D. Miscellaneous Experiments

A number of exploratory experiments were carried out on other donor and acceptor systems, in an attempt to find systems other than the naphthalene - TNB system which would provide large enough chemical shifts to be treated analytically. Many systems were found unsuitable, because of solubility problems. For example, previous work by Foster[66] indicated that hexamethylbenzene should be an extremely good donor compared to benzene, by at least an order of magnitude. However, ^{13}C experiments (Table IX (p. 30) using this donor and excess TNB gave disappointingly small shifts and were not encouraging enough to pursue further, considering the limited instrument time available.

The best organic acceptors in terms of the electron affinity of acceptors are the benzoquinones.[67] Also, these are non-aromatic, so any shifts observed in the donors, using these acceptors, could be ascribed to factors other than aromatic ring currents. p-Chloranil has an electron affinity of 2.50eV whereas TNB has a value of 1.89eV.[67] Unfortunately, with naphthalene as a donor, no nmr signals could be obtained in a twenty four hour period of data acquisition and the system was quickly abandoned.

The next attempt was to try the combination of one of the best donors with one of the best acceptors theory, namely the hexamethylbenzene-p-chloranil system. The system again turned out to be impractical, because, even though nmr signals were seen, the shifts (Table X (p. 31)) were very small due to the small amount of complex in solution.

Since p-benzoquinone has an electron affinity value about the same as TNB,[67] its complexation with naphthalene was investigated

(Table XI (p. 30)). The results for the 3.5M naphthalene did not warrant a full association constant determination. The shifts were less than 30% of the shifts measured for a TNB - naphthalene system (Table V (p. 24)) of the same concentration.

Since complexes are usually stronger in CCl_4 than in dichloroethane, the effect of 3.5M naphthalene on 0.05M p-benzoquinone in CCl_4 was studied (Table XII (p. 33)). The shift for the C_H was larger in CCl_4 than in the more polar solvent, but the carbonyl carbon exhibited a slight downfield shift. Again, no plausible explanation for this is offered. Finally, it should be pointed out that attempts to use p-benzoquinone in excess and to study the shifts of the donor molecules failed because of solubility difficulties.

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