Carbon-13 Nuclear Magnetic Resonance Spectroscopy. Charge-Transfer Complexes[1a]

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High-resolution ^{13}C pulse Fourier transform nuclear magnetic resonance has been used to study the effects of charge-transfer complexation between trinitrobenzene (1) and aromatic donor molecules: benzene (2), mesitylene (3), naphthalene (4), and anthracene (5). Plots of the chemical shifts of the donor carbons as a function of acceptor concentration allows the ready determination of the association constants, K_{AD}, and the bound shifts of the donor carbons in the pure 1:1 complexes, Δ_0. The Δ_0 values so obtained indicate that diamagnetic ring anisotropy and transfer of charge are as phenomenologically important to ^{13}C as to ^1H NMR for aromatic molecules.

There has been an upsurge of interest in molecular complexes of the donor–acceptor type during the last two decades,[2] because of the pronounced electronic changes induced in both donor and acceptor moieties, their unusual physical properties, and the possible importance of charge-transfer complexation to the interactions of biological systems. Whereas the geometries of a substantial number of complexes in the solid state are known from X-ray diffraction data, relatively little is known about their structures in solution. ^1H and ^{19}F nuclear magnetic resonance have been demonstrated to be important methods for the study of molecular complexation in solution,[3] because these techniques provide a simple way for obtaining information on complex composition and thermodynamic data on complex formation equilibria by using the Hanna–Ashbaugh–Foster–Fyfe (HAFF) equation or modification thereof.[4] Much important information has been obtained by these techniques, but they are, for the most part, applicable to simple symmetric systems, and not to the study of larger unsymmetrical donors and acceptors, because of the inherent complexity of the ^1H and ^{19}F NMR absorptions. It has long been recognized that ^{13}C NMR investigations could be important in this connection, as the chemical shifts at all unique positions of a complex donor or acceptor molecule could be determined simultaneously; however, the low sensitivity of carbon magnetic resonance signals and the difficulty in obtaining accurate measurements of small chemical-shift changes has thus far made such studies difficult. The recent advent of pulsed Fourier transform NMR spectrometers has helped to alleviate these difficulties and permitted a study of the 1:1 charge-transfer complexes of the strong acceptor 1,3,5-trinitrobenzene (1) with benzene (2), mesitylene (3), naphthalene (4), and anthracene (5) acting as donor molecules. All of these complexes have been previously well characterized by investigations utilizing other techniques.[2]

Experimental Section

The carbon-13 spectra were taken with our Brukarian[5] DFS-60 pulse Fourier transform modified spectrometer operating at 15.09 MHz with field stabilization via internal deuterium lock, and with full proton noise decoupling. The temperature was maintained at 28.5° with a Bruker B-ST 100/700 temperature controller.

The solvents, ethylene dichloride and chloroform, were MCB "spectroquality", as was the benzene and mesitylene, and were used without further purification. The naphthalene (MCB), anthracene (MCB), and 1,3,5-trinitrobenzene (Eastman) were recrystallized to constant melting point each of which was in accord with literature values.

The sample concentrations were prepared to four-digit accuracy in a 10-mm tube fitted with a vortex plug and a 3-mm coaxial insert filled with D_2O to establish the deuterium lock.

The carbon-13 chemical shifts in each case were measured in hertz relative to the major constituent of the solvent which was demonstrated to be affected less than ±0.1 Hz over the entire concentration range of added trinitrobenzene. This procedure was superior to the use of a small amount of an internal reference such as tetramethylsilane, $CHCl_3$, or CCl_4, as the induced shifts of the reference were quite large (0.4–0.8 Hz).

Results and Discussion

There are several detailed accounts of how to relate nuclear magnetic resonance chemical shifts under conditions of fast exchange to the thermodynamic properties of complexation, the most common treatment utilizing the so-called HAFF equation,[2,3,4] and these will be given only very limited attention here. Because in ^{13}C studies we are primarily interested in the variation of chemical shifts of the donor species with increased acceptor concentration, the opposite situation of nearly all the reported ^1H or ^{19}F NMR studies, we have utilized the inverse of the derived HAFF expression. Thus, for a 1:1 molecular complex AD

$$K_{AD} = \frac{[AD]}{[A][D]} \text{ and } \frac{\Delta}{[A]} + \Delta K_{AD} = \Delta_0 K_{AD}$$

where Δ is the donor chemical shift observed (δ_{obsd}) minus the chemical shift of the uncomplexed donor (δ_0), and Δ_0 is the chemical shift of the donor in the pure 1:1 complex relative to δ_0. Thus, a plot of Δ vs. $\Delta/[A]$ for a given resonance will be a straight line with $-K_{AD}$ as the slope, and Δ_0 (the chemical shift of the resonance in the pure 1:1 complex) as the intercept under the condition that $[A] \gg [D]$.

The advantage of the ^{13}C technique over ^1H and ^{19}F lies in the ability to determine multiple resonances in symmetrical or unsymmetrical donors simultaneously so that we could obtain multiple equiparallel data sets. To analyze these data mathematically, we have set up equations for determining the best fit of the slope (m) and intercepts (b_j) for $j = 1$ to n in a series of n parallel sets of data. If the measured values of the ordinate and coordinate are $y_i^{(j)}$ and $x_i^{(j)}$, respectively, and the best predicted value of the ordinate is $\bar{y}_i^{(j)}$, then we may write

$$\bar{y}_i^{(j)} = m x_i^{(j)} + b_j$$

where the parallel slopes are all given by a single value for m, and the various intercepts by b_j. If k_j is the number of data points in each subsets j, and n is the number of subsets, then the best values for m and b_j may be obtained using standard least-squares techniques. Defining the sum of squares of the deviations from perfect fit as

$$\delta = \sum_{j}^{n} \sum_{i}^{k_j} (y_i^{(j)} - \bar{y}_i^{(j)})^2$$

and minimizing with respect to $m, b_1, b_2, \ldots, b_n$ yields $n + 1$ simultaneous equations of the following form.

Table I
Δ ^{13}C Chemical Shift Values for 0.333 *M* Benzene, Mesitylene, and Naphthalene as a Function of 1,3,5-Trinitrobenzene Concentration

Trinitrobenzene, mol l.$^{-1}$	Benzene,[a],[b] Δ, Hz	Mesitylene,[a],[b] Δ, Hz	Naphthalene,[b],[c] Δ, Hz
0.667	C_1 +2.0	C_1 +1.0	C_9 +6.3
		C_2 +2.5	C_1 +3.1
		CH_3 +3.5	C_2 −2.1
1.000	C_1 +2.8	C_1 +1.5	C_9 +8.3
		C_2 +3.5	C_1 +4.1
		CH_3 +4.5	C_2 −2.5
1.333	C_1 +3.6	C_1 +2.0	C_9 +9.4
		C_2 +4.3	C_1 +4.8
		CH_3 +5.5	C_2 −2.9
1.667	C_1 +4.4	C_1 +2.5	C_9 +10.5
		C_2 +5.0	C_1 +5.6
		CH_3 +6.5	C_2 −3.2
2.000	C_1 +4.8	C_1 +3.0	C_9 +12.0
		C_2 +5.5	C_1 +6.0
		CH_3 +7.5	C_2 −3.2
2.333	C_1 +5.3	C_1 +3.4	C_9 +12.6
		C_2 +6.0	C_1 +6.6
		CH_3 +8.0	C_2 −3.2

[a] In CH_2ClCH_2Cl at 28.5°. [b] Positive shifts are to higher field. [c] In 9:1 $CHClCH_2Cl$-$CHCl_3$ at 28.5°.

$$\frac{\partial\delta}{\partial m} = 0 = \sum_j^n \sum_i^{k_j} x_i^{(j)} \left(y_i^{(j)} - m x_i^{(j)} - b_j\right)$$

$$\frac{\partial\delta}{\partial b_1} = 0 = \sum_i^{k_1} \left(y_i^{(1)} - m x_i^{(1)} - b_1\right)$$

$$\frac{\partial\delta}{\partial b_2} = 0 = \sum_i^{k_2} \left(y_i^{(2)} - m x_i^{(2)} - b_2\right)$$

$$\vdots \qquad \vdots$$

$$\frac{\partial\delta}{\partial b_n} = 0 = \sum_i^{k_n} \left(y_i^{(n)} - m x_i^{(n)} - b_n\right)$$

Solving for m, and the n different b_j's yields

$$m = \frac{\sum_j^n \sum_i^{k_j} \left(x_i^{(j)} y_i^{(j)}\right) - \sum_j^n \left(\sum_i^{k_j} y_i^{(j)}\right)\left(\sum_i^{k_j} x_i^{(j)}\right) \Big/ k_j}{\sum_j^n \sum_i^{k_j} \left(x_i^{(j)}\right)^2 - \sum_j^n \left(\sum_i^{k_j} x_i^{(j)}\right)^2 \Big/ k_j}$$

$$b_j = \frac{\left(\sum_i^{k_j} y_i^{(j)}\right) - m\left(\sum_i^{k_j} x_i^{(j)}\right)}{k_j}$$

for each j set of data. The standard deviation (σ) of the fit is given for

$$N = \sum_j n_j$$

total pieces of data is:

$$\sigma = \frac{\delta}{N - n - 1}$$

where ($N - n - 1$) is the number of degrees of freedom not used to set the $n + 1$ parameters ($m, b_1, b_2, \ldots, b_n$). These equations have been incorporated in a computer program for rapid analysis of the ^{13}C chemical shift data.

The ability to utilize this type of analysis is crucial for the carbon resonances exhibiting relatively small shifts as the parallelization procedure can give reasonably accurate b_j values for a given subset, even though the error for that subset is much larger than in the other subsets, and in addition, the error in K_{AD} is clearly lower than what is achievable from measurement of a single resonance.

Table II
Δ ^{13}C Chemical Shifts and Δ/[A] Values for 0.167 *M* Anthracene as a Function of 1,3,5-Trinitrobenzene Concentration

TNB[A], mol l.$^{-1}$	Δ, Hz	Δ/[A], Hz l. mol^{-1}
0.333	C_{11} +6.2	18.60
	C_1 +5.3	15.90
	C_9 +3.9	11.70
	C_2 −4.5	−13.50
0.500	C_{11} +7.9	15.80
	C_1 +6.5	13.00
	C_9 +5.1	10.20
	C_2 −5.4	−10.80
0.667	C_{11} +9.2	13.80
	C_1 +7.5	11.25
	C_9 +5.8	8.70
	C_2 −6.4	−9.60
0.833	C_{11} +10.1	12.12
	C_1 +8.4	10.08
	C_9 +6.4	7.68
	C_2 −6.8	−8.16
1.000	C_{11} +11.1	11.10
	C_1 +9.2	9.20
	C_9 +7.0	7.00
	C_2 −7.4	−7.40
1.167	C_{11} +11.8	10.11
	C_1 +9.8	8.40
	C_9 +7.3	6.26
	C_2 −7.8	−6.69
1.333	C_{11} +12.4	9.30
	C_1 +10.0	7.58
	C_9 +7.6	5.70
	C_2 −8.4	−6.30

The chemical-shift assignments are well documented for these molecules.[6] A discrepancy with the early values reported[7] for anthracene was discovered, but this has subsequently been corrected in the literature.[8]

Table I contains the carbon-13 chemical-shift differences (Δ) for 0.333 *M* solutions of the donor molecules, benzene (**2**), mesitylene (**3**), and naphthalene (**4**), as a function of the acceptor concentration [A] of 1,3,5-trinitrobenzene (**1**), relative to the chemical-shift values of 0.333 *M* solutions in the absence of **1**, at 28.5°. Because of the relative insolubility of anthracene (**5**), similar experiments were performed at 0.167 *M* anthracene concentration and in a 2:1 mixture of $CHCl_3$-CH_2ClCH_2Cl at 28.5°. The results of these experiments are recorded in Table II. Positive values of Δ refer to shifts to higher field (shielding) and negative values refer to shifts to lower field (deshielding).

A typical plot of Δ, the observed ^{13}C chemical shifts vs. Δ/[A] is given in Figure 1 for 0.167 *M* solutions of 1,3,5-trinitrobenzene concentration [A]. The lines have the slopes (m) and intercepts (b_j) obtained from the least-squares computer analysis of the data. It is apparent from Figure 1 that the K_{AD} values are extremely well determined from the slope of the ^{13}C data, and the extrapolations from the data points to intercepts yield very reliable values for Δ_0.

The first thing to be noted from Tables I and II is that the induced chemical shifts due to charge-transfer complexation are reasonably large, even for the weak complex between benzene and trinitrobenzene. A second, and perhaps more important, observation is that for donors with

Table III
Maximum Observed Shifts, Δ_{max}, Calculated Shifts for the Pure Complexes, Δ_0, and Association Constants, K_{AD}, for 1,3,5-Trinitrobenzene Donor Complexes at 28.5°

Donor	Solvent	Δ_{max}, Hz	Δ_0, Hz	K_{AD}, l. mol^{-1}
Benzene	CH_2ClCH_2Cl	C_1 +5.3	+15.9	0.22
Mesitylene	CH_2ClCH_2Cl	C_1 +3.4	+6.3	0.37
		C_2 +6.0	+13.0	
		CH_3 +8.0	+17.0	
Naphthalene	9:1 CH_2ClCH_2Cl–$CHCl_3$	C_9 +12.6	+20.2	0.69
		C_1 +6.6	+10.3	
		C_2 −3.2	−5.9	
Anthracene	2:1 $CHCl_3$–CH_2ClCH_2Cl	C_{11} +12.4	+17.7	1.64
		C_1 +10.1	+14.7	
		C_9 +7.6	+11.1	
		C_2 −8.4	−12.1	

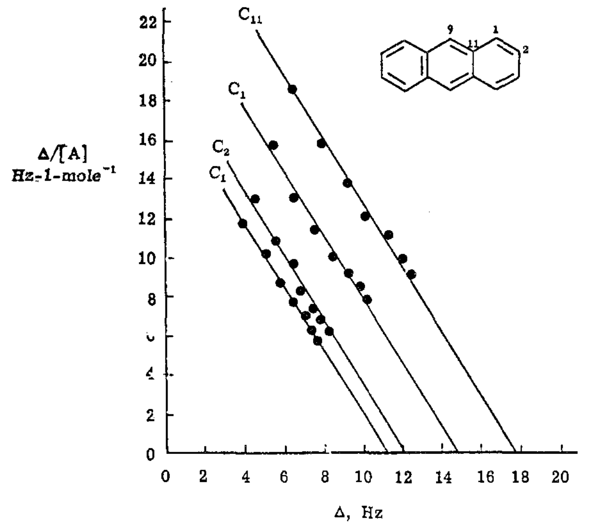

Figure 1. A plot of Δ vs. Δ/[A] for 0.167 *M* anthracene as a function of 1,3,5-trinitrobenzene concentration. The *negative* Δ shifts for C_2 have been reflected into the *positive* quadrant.

magnetically different carbons, the corresponding resonances gave distinct differential shifts, which opens up possibilities for obtaining information on the magnitude of aromatic shieldings and charge-transfer effects, the preferred sites of interaction, and spacings between donor–acceptor pairs.

For **2** and **3**, positive shifts (shielding) are observed at all carbon resonances, as is the case in the proton NMR of all known simple benzenoid complexes,[2b] and commonly attributed to the predominance of ring-current induced diamagnetic shielding effects from the opposing benzene ring in the favored equiplanar geometry. With the polycyclics, **4** and **5**, similar effects are observed, except for the peripheral C-2 carbons, which display negative shifts. A similar feature had been noted previously for ^1H NMR studies of **4** and **5** in which the α H's were shifted upfield to a greater extent than the β H's at high trinitrobenzene concentrations.[2b]

The maximum observed shifts, Δ_{max}, the mean values of the association constant, K_{AD}, and the chemical shifts of the carbons in the pure 1:1 complexes, Δ_0, computed from the data in Tables I and II by the least-squares procedure, are summarized in Table III. The association constants obtained in the present study are in accord with those obtained by optical[9] and ^1H NMR[3b,10,11] measurements when the effects of solvent and temperature are considered. For example, K_{AD} for the complex of **1** and **3** in CH_2ClCH_2Cl at 33.5° from ^1H NMR[11] is 0.26 l. mol^{-1} compared to our 0.37 l. mol^{-1} at 28.5°. The magnitude of the association constants K_{AD} is **5** > **4** > **3** > **2** with trinitrobenzene, as expected on the basis of donor strength,[2b] and this series correlates directly with the HMO energies of the highest filled molecular orbitals.

The large differential chemical shifts Δ_0 obtained for a particular donor species suggests considerable sensitivity of ^{13}C NMR to the effect of charge transfer as well as diamagnetic anisotropy which, judging from the small variations in acceptor Δ_0 values obtained, is presumably the predominant effect in ^1H NMR.[2b] The negative shifts observed at C-2 of **4** and **5** are not well explained by the shielding arguments previously proposed,[2b] as these positions are well within the shielding cone of the acceptor molecule at the distances and geometries involved in complexation.[12,13,14] This phenomenon may be best ascribed to the predominance of the opposing charge-transfer effect at these positions and the apparent tendency to transfer charge more effectively from the extremities of the donor molecules.

The ability to completely describe the shielding parameters for 1,3,5-trinitrobenzene should allow for separation and quantitization of these two opposing effects.

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References and Notes

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Nuclear Magnetic Resonance Spectroscopy. Carbon-13 Chemical and Carbon-13 Proton Couplings in Some Esters and Ethers.[1]

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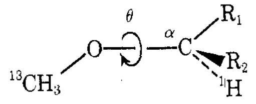
Carbon-13 chemical shifts and three- (or more) bond ^{13}C–proton couplings have been obtained for a variety of alkyl ethers and esters. The results have been interpreted on the basis of preferred rotational conformations.

The current availability of commercial spectrometers has made the measurement of carbon chemical shifts relatively routine. Thus, in unpublished work, we have compiled from the literature carbon chemical-shift data for nearly 2000 compounds on molecular fragments, and the current explosion of published ^{13}C data appears to make the task of continually updating this compilation quite impossible.

Despite the interest in carbon-13 nuclear magnetic resonance (^{13}C NMR) spectroscopy, the complete assignment of resonances remains one of the most difficult problems faced by the users of this method, and the application of carbon chemical-shift information to problems of structure elucidation and conformational analysis has, as a result, been relatively limited.

The measurement of relaxation times (T_1) for carbon nuclei is now becoming quite common, even for rather large molecules.[2] The unique information regarding molecular motions which can be derived from such measurements promises to give increasing importance to T_1 measurements in the future. Other techniques, notably the measurement of nuclear Overhauser enhancements,[3] will doubtless also provide much valuable information to organic chemists who seek to understand the structure and conformations of molecules.

In the present paper, we report some preliminary results regarding the measurement of geminal and vicinal carbon–proton couplings, and the application of such coupling data to problems in acyclic conformational analysis. A review[4] of the literature shows that a surprising number of measurements of these coupling constants have been made. Although their counterparts in proton–proton coupling commonly provide extensive and useful information about structure and conformation, few systematic investigations of vicinal and geminal carbon–proton couplings in other than aromatic systems[5] have appeared.[6] Frequently, these couplings are described as "long-range", thereby implying that they are small. In fact, their magnitudes are commonly comparable to those of the analogous proton–proton couplings and are easily measured with modern ^{13}C NMR spectrometers. In view of this, we have begun an extensive investigation of the measurement of carbon–proton couplings and report here some aspects of vicinal carbon–proton coupling, leaving the geminal cases for a later, more general, discussion. Our primary interest was the investigation of the earlier report[7] of a dihedral dependence of this coupling. More recently, the dihedral dependence of vicinal carbon–proton coupling has been verified in other laboratories, and the variation has been described as being similar in form to that of the analogous proton–proton coupling.[8] Our approach has been to study systems in which geminal coupling would be absent, thus facilitating the measurement of vicinal coupling. We therefore initiated our study with a survey of *O*-methyl ethers. Examination of 1 suggests that the dihedral angle θ should be, to at least some extent, dependent on the character and bulk of R_1 and R_2. By studying the vicinal coupling between the *O*-methyl carbon and the α proton as a function of R_1 and R_2, we sought to understand its dependence upon dihedral and substituent effects. During the course of this work it became clear that it was frequently possible to measure the vicinal coupling between the α carbon and the *O*-methyl protons, even though this situation was complicated by the presence of geminal and, in some cases, other vicinal couplings. This finding allowed the extension of this research to include a number of related compounds, including a selection of esters and cyclic ethers.



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The measurement of splittings in proton-coupled spectra are rather more difficult than taking carbon spectra with full proton decoupling. For this reason, we have made some attempts to correlate carbon chemical-shift changes with conformational effects which influence the couplings. An earlier effort to correlate carbon chemical shifts of *O*-methyl ethers with conformation has been described for somewhat more complicated systems.[9]

Experimental Section

Carbon chemical shifts were measured in 1,4-dioxane or cyclohexane solutions under conditions of full proton decoupling with a digital frequency-sweep spectrometer described previously.[10] Chemical shifts were subsequently referred to external carbon disulfide on the basis of the chemical shifts of 1,4-dioxane and cyclohexane relative to that reference (126.2 and 166.2 ppm, respectively). They can be reasonably accurately converted to the Me_4Si scale by subtracting them from 192.8 ppm.

Proton-coupled carbon-13 spectra were measured with the same spectrometer, using neat solutions and internal proton lock. Several experiments using varied internal lock power had no effect on the spacings in the obtained spectra.