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High-Resolution ^{13}C NMR Study of Solid π–π Molecular Complexes Using "Magic Angle" Spinning Techniques

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Abstract: With the use of cross-polarization, high-power decoupling, and "magic-angle" spinning techniques, high-resolution ^{13}C NMR spectra have been obtained for the solid crystalline π–π molecular complexes of the donor molecule hexamethylbenzene with a series of acceptor molecules. Small shifts were found for the aromatic carbon resonance of the hexamethylbenzene moiety in the complexes compared to that for solid hexamethylbenzene itself. The shifts were roughly proportional to the electron affinities of the acceptor molecules, indicating a small degree of electron transfer *in the ground state* for these compounds. With the use of chemical shift^{1}charge density relationships determined from solution NMR studies, the degree of electron transfer was estimated at $\leq$10% for the complexes studied.

"Charge-transfer" or "molecular" complexes[1] are formed, usually in a 1:1 ratio, from an electron-rich (donor) molecule and an electron-deficient (acceptor) molecule. The difference in electron density between the two components is in many cases the driving force behind the association and often the complexes are characterizied by a new optical absorption band in the visible region of the spectrum, referred to as the "charge-transfer" band.

The interaciton between the components forming the complex is commonly described in the valence-bond formulation first advanced by Mulliken.[2] Thus, the ground state is characterized by a wave function ψ_N as in eq 1 where $\psi_0(D,A)$ represents the

$$\psi_N = a\psi_{0(D,A)} + b\psi_{1(D^+A^-)} \tag{1}$$

$$\psi_E = a\psi_{1(D^+A^-)} - b\psi_{0(D,A)} \tag{2}$$

contribution from all other bonding interacitons at the correct intermolecular distance and $\psi_{1(D^+,A^-)}$ the contribution from the form where there has been complete transfer of one electronic charge from the donor to the acceptor molecule. For weak molecular complexes, $a \gg b$ in the ground state. Correspondingly, there is an excited state ψ_E of the complex (eq 2 with again $a \gg b$) where the main contributing form is ψ_1. The origin of the charge-transfer absorption band is thought to be due to an electronic transition between these two levels. Because the complexes are colored, the main thrust of early work was the description and understanding of their optical spectra, but more recently, attention has focused on the geometry of the complex and the stabilizing contributions to the ground state, particularly the extent to which the charge-transfer interaction represented by ψ_1 in eq 1 contributes to the ground-state stabilization. The possible importance of other types of weak bonding interaction which would be included in the term $\psi_{0(D,A)}$ to the stability and structure of the ground state has been stressed.[3] Unfortunately, the interactions are weak (typically $\Delta G \simeq 6$ kcal mol^{-1}, $\Delta H \simeq 4$ kcal mol^{-1}, and $\Delta S \simeq 12$ cal mol^{-1} deg^{-1} [1b,c]) and in solution the complex is mainly dissociated into its components in a fast exchange equilibrium. Unambiguous information regarding the ground state is thus very difficult to obtain directly from solution studies. The structures of the complexes are, however, well described in the solid state:[4] These typically consist of alternating planes of donor and acceptor species with the molecules oriented so that there is considerable π–π molecular overlap between adjacent donor and acceptor molecules within a -D-A-D-A-D-A- stack. Although the solid-state structures are thus well described, it has not been possible to use this information with that from spectroscopic techniques to investigate the degree of electron transfer in the ground state because of the nondiagnostic low-resolution nature of these techniques when applied to solid systems.

It had recently been shown[5] that a combination of high-power proton decoupling, cross-polarization,[6] and "magic-angle" spinning[7] techniques yields ^{13}C NMR spectra of solid samples with line widths of the order of 10–30 Hz for crystalline materials. These techniques have already been applied to a variety of organic systems.[8] The purpose of the present work is to apply these techniques to the investigation of a series of π–π molecular complexes to see if changes occur in the isotropic chemical shift values of the aromatic carbons of the components of the complex which could be ascribed to the complex fromation and perhaps then be related to the degree of electron transfer in the ground state via chemical shift–charge density relationships developed from solution ^{13}C NMR studies of isolated charged species.

A series of complexes with hexamethylbenzene (**1**) as a common donor were chosen. There were several reasons for this choice: First, hexamethylbenzene is a typical and reasonably strong donor molecule. Second, the six ring carbon atoms of hexamethylbenzene are chemically equivalent, and measurements should directly yield the average change in electron density in the ring from the single absorption peak. Third, from solid-state ^{1}H NMR studies[9] it is anticipated that the hexamethylbenzene in the complexes will be

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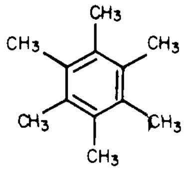
moving rapidly on the NMR time scale in its molecular plane at room temperature by successive sixfold jumps. (This feature is of particular importance as it gives an actual magnetic equivalence to the six ring carbons in the solid complex on the NMR time scale, which again makes it possible to obtain average data for the interaction without any recourse to molecular orbital calculations on the complex or consideration of the detailed geometry of the complex in the solid state.) Finally, crystal structure data are available for a number of hexamethylbenzene complexes[10] so that the spectra and results obtained will be, in some cases at least, for systems of well-defined geometry, which may be useful for future comparisons with data from other solid-state techniques.

The acceptor molecules used were tetracyanoethylene (TCNE) (**2**), 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (**3**), tetracyanoquinodimethane (TCNQ) (**4**), chloroanil (CHL) (**5**), pyromellitic dianhydride (PMDA) **6**); 3,5-dinitrocyanobenzene (DNCB) (**7**), and 1,2,4,5-tetracyanobenzene (TCNB) (**8**). They cover a wide range of acceptor strengths as judged from their electron affinities[11] from very strong (TCNE, DDQ, TCNQ) to relatively weak (TCNB) and were chosen so that any ^{13}C chemical shifts observed could be checked for consistency with the expected trend with acceptor strength before being considered as induced by the charge-transfer interaction between the two component molecules.



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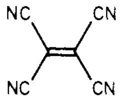

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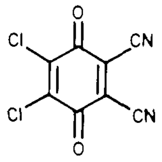

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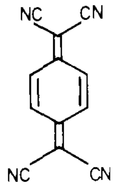

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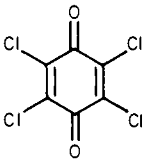

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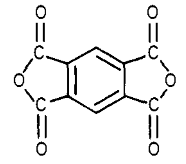

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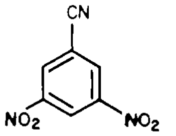

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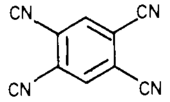

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Experimental Section

The high-power, high-resolution ^{13}C NMR experiments were performed at a proton frequency of 90 MHz, using a Bruker CXP 100 spectrometer with a horizontal probe insert. The proton spin-locking and decoupling fields were approximately 9 to 10 G. The fast spinning at the magic angle of polycrystalline samples loaded into hollow Kel-F rotors (~70 μL volume) was achieved with the spinning apparatus previously described.[12]

The complexes were prepared by literature techniques and had melting points (sealed tubes) in agreement with reported values and NMR spectra and chamical analyses consistent with their formulation as 1:1 complexes.

Results and Discussion

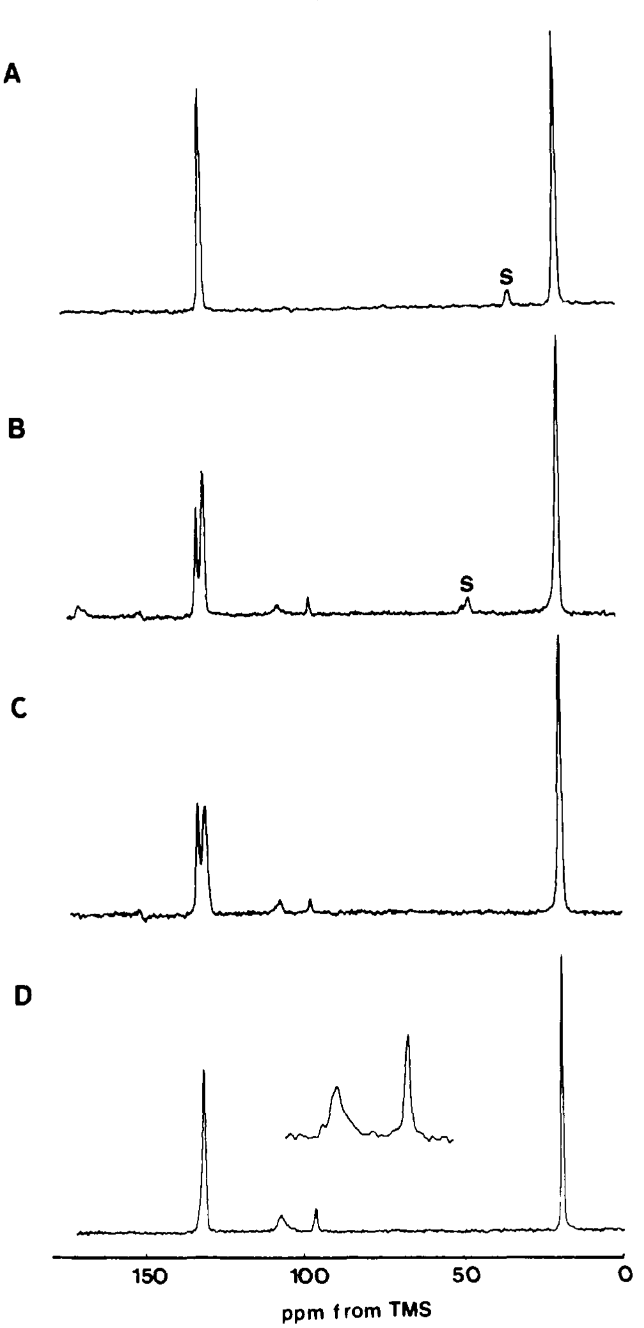

Figure 1. ^{13}C/MAS spectra at 22.6 MHz of polycrstalline HMB and the HMB/TCNE complex. Powdered samples (~65 mg) of HMB, the HMB/TCNE complex, and fresh mixtures of the two powders were spun in hollow Kel-F containers at the magic angle. Cross-polarization times were 10 ms and recycle times 2 s. Chemical shifts were calibrated indirectly through external methanol (δ_{MeOH} 49.1 relative to Me_4Si). (A) HMB (2000 scans), the aromatic carbons resonate at 134 ppm and the methyl carbons at 19 ppm downfield from Me_4Si, (B) a mixture of equal parts (by wieght) of the complex and HMB (9100 scans), (C) a mixture of 1 part HMB and 2 parts complex (5000 scans), and (D) TCNE:HMB in a 1:1 complex (2000 scans) showing the aromatic peak at δ 136, methyl carbons at δ 19, the TCNE cyano carbons at δ 109 and the TCNE ethylene carbons at δ 99. The inset in (D) shows an expansion of the TCNE peak region. The small peaks marked "s" denote spinning sidebands.

Spectra were obtained by using high-power proton decoupling to eliminate the ^{13}C H dipolar broadening and high-speed "magic-angle" spinning (MAS) to eliminate broadening from the carbon chemical shift anisotropy. In addition, matched spin-lock cross-polarization (CP) was used to enhance the sensitivity. In this latter experiment, the carbon and proton spins are spin-locked simultaneously with the spin-locking fields H_{1H} and H_{1C} satisfying the relationship

$$\gamma_H H_{1H} = \gamma_C H_{1C} \qquad (3)$$

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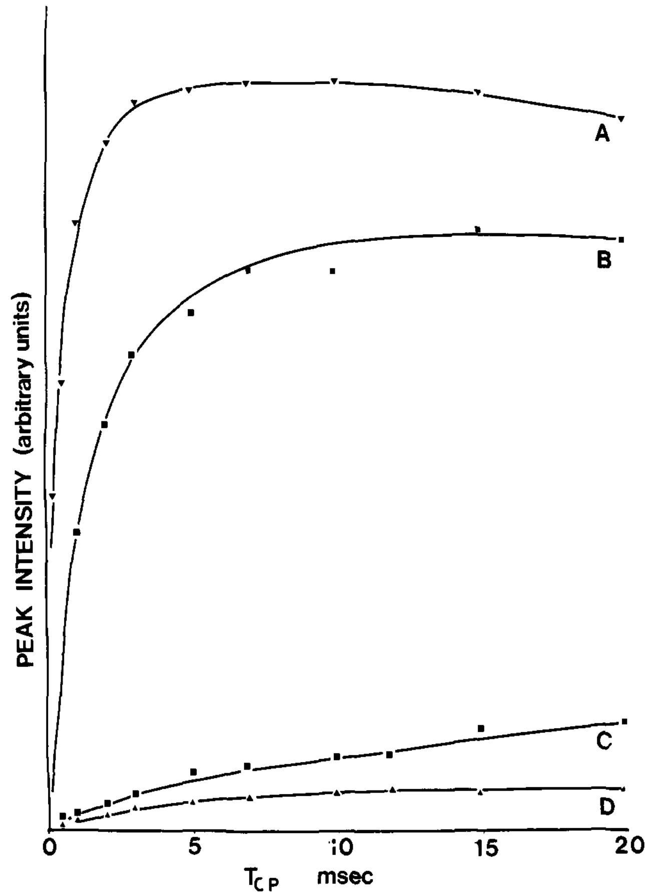

Figure 2. The change with increasing cross-polarization time of peak intensities for the ^{13}C signals of the TCNE:HMB complex: for the signal due to (A) the methyl carbons, (B) the aromatic carbons, (C) the ethylene carbons, and (D) the cyano group carbons. The recycle time was 2 s, cross-polarization times from 0.2–20 ms, line broadening 10 Hz, and number of scans in each case 1000.

The buildup of magnetization for a particular carbon is governed by the cross-relaxation time in the rotating frame which, in turn, is related to the strengths of the static dipolar interactions between the carbons and protons.[6] Single contacts were taken during each spin-lock period. The experimental variables are the cross-polarization time, the recycle time for the pulse sequence, and the number of free induction decays averaged.

Figure 1A shows the high-resolution ^{13}C NMR spectrum of solid hexamethylbenzene obtained by using CP/MAS techniques under the conditions indicated in the figure caption. Two sharp ($\Delta\nu_{1/2} \simeq 25$ Hz) signals are observed for the aromatic and methyl carbons (133.9 and 18.9 ppm, respectively, with respect to external Me_4Si). Figure 1D shows the corresponding spectrum of the solid hexamethylbenzene–tetracyanoethylene complex. There has been a downfield shift of the aromatic carbons of the hexamethylbenzene moiety (Table I) which, although small, is reproducible. The shift is further evidenced in Figures 1B and 1C which are the corresponding spectra of *mixtures* of discrete crystals of *solid* hexamethylbenzene and the *solid* complex in the same spinner. The difference in chemical shift of the hexamethylbenzene ring carbons between the free and complexed states of the molecule (Table I) was measured directly from the spectra of mixtures such as those shown in Figures 1B and 1C. The accuracy of this measurement was determined by the digital resolution (±11 Hz) used in the experiment. Within the accuracy of the measurement, no shift in the HMB methyl carbons was observed.

The crystal structure of the HMB–TCNE complex[11a] indicates that the two molecules are stacked with their centers above each other and indicates a disorder in the TCNE molecules. Since the component molecules do not have the same symmetry, the methyl and ring carbons of the HMB will not be equivalent if the molecule is static. This is confirmed by spectra obtained at −190 °C which show a definite broadening of the ring carbon resonance.

Table I. The Change in the Chemical Shift ($\Delta\delta$) of the Ring Carbon Absorption of HMB in the Solid π–π Molecular Complexes Formed with the Acceptor Molecules Indicated in the Table Compared to That of Solid Hexamethylbenzene Itself[a]

acceptor molecule	electron affinity, eV[12]	$\Delta\delta$
TCNE, 2	2.2	2.2 ± 0.5
DDQ, 3	1.95	2.1 ± 0.6
TCNQ, 4	1.7	2.1 ± 0.6
CHL, 5	1.37	1.2 ± 0.6
PMDA, 6	0.8	unresolved (<1)
DNCB, 7	0.7	unresolved (<1)
TCNB, 8	0.4	unresolved (<1)

[a] The difference was measured directly from spectra recorded from mixtures of solid polycrystalline HMB and the appropriate solid polycrystalline complex.

It is of interest that the spectrum of the complex also shows clearly resonances due to the cyano and alkene carbons of the tetracyanoethylene. It might be thought that, since this molecule contains no hydrogen atoms, it might be "transparent" in a CP experiment. Figure 2 shows the growth of the individual signals in the spectrum of the complex as a function of contact time. It can be seen that the signals of the tetracyanoethylene are polarized *intermolecularly* by the protons of the hexamethylbenzene methyl groups.

The shift anisotropy pattern of the HMB aromatic carbons was investigated to see if the small change observed in the isotropic chemical shift value in the MAS experiment might be due to a cancellation of larger changes in the principal values of the shift tensor. Due to the rotation of the HMB in its molecular plane, the shift anisotropy pattern at room temperature will be axially symmetric as shown previously for HMB itself by Waugh and co-workers.[13] The presence of the TCNE is a complicating feature as these carbons would also be expected to have large shift anisotropies which would overlap with those of the HMB aromatic carbons; with the use of the data in Figure 2, contact times were chosen for the CP experiments which minimized the contribution from the TCNE carbons. A further complication is that the shift anisotropy of the hexamethylbenzene ring carbons is such that the pattern extends to the base of the methyl signal and accurate shift anisotropy parameters are difficult to measure directly from a static powder sample. For this reason they were evaluated by running the spectra as a function of spinning angle with respect to the magnetic field direction.[14] One spectrum for the HMB/TCNE complex is shown in Figure 3 and the results are tabulated in Table II. The HMB shift tensor values are relatively unchanged in the complex, indicating that only a small perturbation of the hexamethylbenzene π system has occurred in the complex formation and that the change in the isotropic shift might be a measure of this perturbation.

Similar results are obtained for other complexes. Figure 4 shows the data obtained for the HMB/TCNQ complex. Again, the use of mixtures of HMB and the HMB/TCNQ complex (Figure 4) shows that a small shift to lower field occurs on complexing (Table I), and again the shift anisotropy pattern indicates that there is little overall perturbation of the π system of the HMB on complexation. The crystal structure of the HMB/TCNQ complex shows that the components are oriented with the center of the HMB over the end of the TCNQ[11b] again making the HMB ring carbons nonequivalent when the molecule is stationary. This is confirmed in spectra obtained at −190 °C which show a definite

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(14) Anisotropy parameters $\sigma_{\perp}$ and $\sigma_{\parallel}$ refer respectively to principle elements of the anisotropic chemical shift perpendicular to and parallel to the axis of molecular rotation through the benzene ring of HMB. Boundaries $\sigma'_{\perp}$ and $\sigma'_{\parallel}$ are measured upfield (+) and downfield (−) from the isotropic chemical shift $\bar{\sigma}$; principal elements $\sigma_{\perp}$ and $\sigma_{\parallel}$ are calculated by using the relationship $\sigma = 2\sigma/(3\cos^2\theta - 1)$, and the calculated isotropic shift $\bar{\sigma}$ gives a measure of the accuracy of choice of the less easily discernable parameter $\sigma'_{\parallel}$ relative to $\sigma'_{\perp}$. All measurements are in ppm.

Table II. The Ring Carbon Shift Anisotropy Parameters for Free Hexamethylbenzene and Hexamethylbenzene in Its Charge-Transfer Complex with Tetracyanoethylene Obtained from Variable Angle Spinning Experiments with Respect to the Applied Magnetic Field[14]

spinning angle with respect to field	pure HMB		TCNE:HMB (1:1)			pure HMB: static sample (ref 13)
	71 ± 3°	90 ± 3°	65 ± 1°	74 ± 3°	90 ± 3°	
obsd $\sigma'_\perp$	21 ± 0.5	29 ± 0.7	14 ± 0.5	24 ± 0.7	30 ± 1.5	
obsd $\sigma'_\parallel$	−42 ± 0.5	−56 ± 0.5	−27 ± 0.5	−45 ± 0.5	−58 ± 0.5	
calcd $\sigma_\perp$	−62 ± 9	−58 ± 2	−58 ± 3	−62 ± 10	−60 ± 10	−56 ± 6
calcd $\sigma_\parallel$	122 ± 15	111 ± 4	112 ± 7	111 ± 18	116 ± 3	112 ± 14
calcd $\bar{\sigma}$	−0.6 ± 8	−1.3 ± 2	−4.0 ± 8	−2.6 ± 8	1.3 ± 3	−5 ± 9

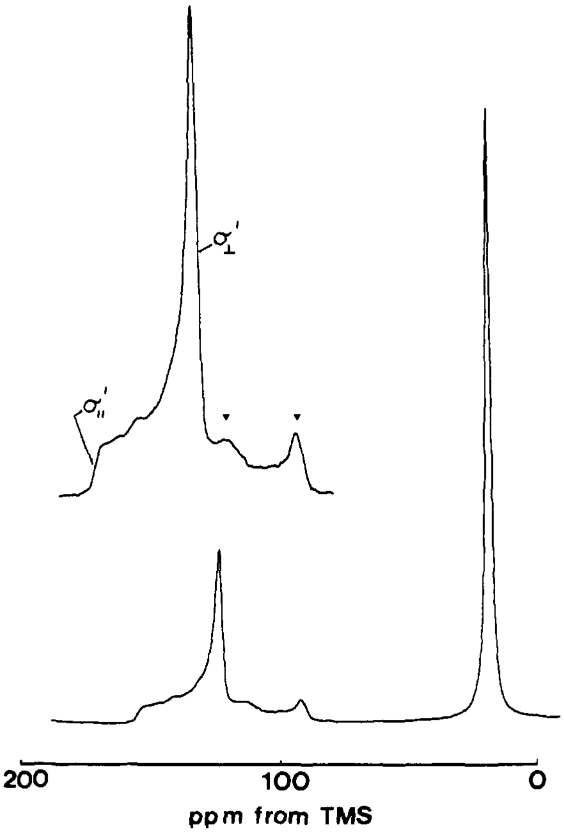

Figure 3. The ^{13}C spectrum at 22.6 MHz of the HMB:TCNE (1:1) complex, spinning about an axis of 65 ± 1° to the direction of the static magnetic field with a cross-polarization time 1 ms, recycle time 2 s. $\sigma'_\parallel$ and $\sigma'_\perp$ indicate the shift values limiting the anisotropic ring-carbon peak, from which the elements of the motionally averaged shift tensor were calculated (Table II). The small peaks marked by filled triangles are due to the TCNE carbons.

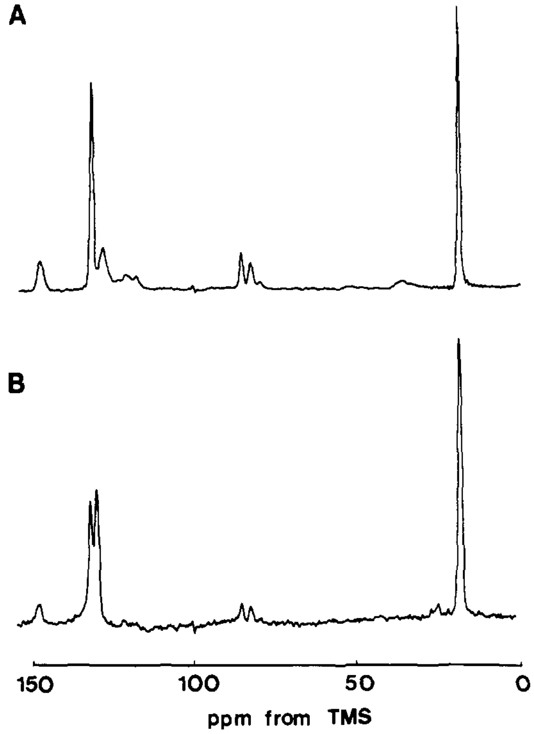

Figure 4. ^{13}C CP/MAS spectra at 22.6 MHz of the solid 1:1 HMB/TCNQ charge-transfer complex obtained by using a cross-polarization time of 10 ms and recycle time of 2 s. (A) HMB/TCNQ complex alone (9041 scans): the small peaks in the spectrum are due to the TCNQ moeity. (B) Polycrystalline complex mixed in a 2:1 ratio with polycrystalline HMB.

broadening of the HMB ring carbon absorption.

The results for the whole series of complexes (Table I) show the existence of small, low-field shifts. This is the general direction (lower electron density, lower field) that the shifts should be in if they are due to the charge-transfer interaction in the ground state where the direction of electron transfer is from the HMB to the acceptor. Further, as the electron affinity of the acceptor molecules becomes lower and the strength of the complexes less (Table I), the shift becomes smaller. It is possible to estimate the degree of charge transfer in the ground state more quantitatively from the charge density/chemical shift relationship developed from high-resolution ^{13}C NMR studies of charged species in solution.[15] This is given in eq 4 where $\Delta\sigma$ is the shift in ppm and P is the fractional charge on that carbon. (Thus, a unit positive charge localized on a single carbon would induce a shift of approximately 160 ppm to low field.)

$$\Delta\sigma = -(160 \pm 20)P \qquad (4)$$

with the use of this relationship, the percentages of electron transfer in the ground states of the complexes of HMB with TCNE, DDQ, TCNQ, CHL, and TCNB are 8.1, 7.9, 7.9, 4.8, and ≤2%, respectively (Table I).

The results of this study thus indicate clearly that there is little perturbation of the aromatic π systems in the formation of these complexes but that there are small changes in the spectra which can be attributed to complex formation and which indicate, based on charge density–^{13}C shift relationships, that the percentage contribution of the electron transfer form $\psi_{1(D^+A^-)}$ to the ground state is less than 10% for the complexes studied. Since these complexes are reasonably typical of π–π molecular complexes in general, it may be concluded that the contribution of the charge-transfer interaction itself to the ground state stabilization of these species is small.

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