evidence for orientational transitions was completely suppressed.

The absence of a packing density (orientational) transition when $C_{\rm HO}^{0}$ exceeded 0.1 mM was not unexpected since, at $C_{\rm HQ}^{0} = 2$ mM and in the absence of competing surface-active material, HQ spontaneously forms a *closed-packed* η^2 -oriented adlayer.^{1c,d} Hence, any NHQ adsorption when $C_{\rm NHO}^0 < 0.1$ mM and $C_{\rm HO}^0$ = 2.0 mM can occur only in the η^2 -orientation due to molecular area limitations. Direct evidence for this postulate appears in Figure 7 which shows the individual and total packing densities as a function of NHQ concentration when HQ was fixed at 2.0 mM. (i) As expected, Γ_{HO} decreased and Γ_{NHO} increased as C_{NHO}^0 was increased; since $\Gamma_{HQ} = \Gamma_{NHQ}$ at $C^0_{NHQ} \sim 1$ mM (lower than $C^0_{HQ} = 2$ mM), preferential adsorption of NHQ relative to HQ is indicated.^{1w} (ii) The total packing density was virtually unchanged (~ 0.58 nmol cm⁻²) at all NHQ concentrations studied; that is, the sum $\Gamma_{\rm NHQ} + \Gamma_{\rm HQ}$ was a constant regardless of the $\Gamma_{\rm NHQ}/\Gamma_{\rm HQ}$ ratio in the mixed adlayer. This result is understandable only if NHQ and HQ were each chemisorbed in vertical orientations in which their respective molecular area requirements were very similar, a requirement which is fulfilled only by the 2.3-n² orientation.^{1a,d}

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Registry No. NHQ, 571-60-8; NQ, 123-31-9; HClO₄, 7601-90-3; Pt. 7440-06-4; benzene, 71-43-2; benzoic acid, 65-85-0.

Optical and Resonance Raman Studies of the 1:1 and 2:1 Complexes of Hexamethylbenzene with Tetracyanoethylene

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The electron donor-acceptor (EDA) complexes of hexamethylbenzene (HMB) and tetracyanoethylene (TCNE) have been studied by optical and resonance Raman spectroscopy in a variety of solvents. The visible absorption spectra of the 1:1 and the 2:1 complexes in cyclohexane have been resolved by multiwavelength linear regression of concentration-dependent absorbance data. The resonance Raman spectra of CCl₄, CH₂Cl₂, and cyclohexane solutions of HMB and TCNE have been obtained with 5145-Å excitation. A low-frequency mode at 163-169 cm⁻¹ is assigned to the first overtone of the donor-acceptor stretch, ν_{DA} . In cyclohexane, the second overtone of ν_{DA} is also observed, but is overlapped by an a_{2u} out-of-plane bending vibration of the methyl groups of HMB, which becomes allowed in the 2:1 complex due to vibronic coupling. A simple molecular orbital picture of the bonding in the 1:1 and 2:1 complexes is proposed which explains the resolved visible spectra as well as the low-frequency Raman data. It is concluded that the second donor molecule is not bound by "charge-transfer" forces, and that, although the ground state 2:1 complex has D_{2h} symmetry, the two D-A bonds are of unequal strength.

I. Introduction

The existence of electron donor-acceptor (EDA) complexes of the type D_2A in solutions of high donor concentration is wellestablished.^{1,2} The intense "charge-transfer" electronic transition has frequently been exploited to determine the equilibrium constants for the formation of 1:1 and 2:1 complexes from the concentration dependence of the optical absorbance at the wavelength of maximum absorbance.³ Although including ternary complexes in the model has avoided some of the wavelength- and concentration-dependent discrepancies which were found in the early work, the question of the nature of the binding of the second donor molecule has not really been addressed. Is the structure of the 2:1 complex D-D-A or D-A-D? Is the second donor molecule bound by charge-transfer forces, or are other interactions (van der Waals, electrostatic, etc.) at work? How does the excited state of the 2:1 complex differ from that of the 1:1 complex? In this paper, we use optical and resonance Raman spectroscopy to address these questions for the EDA complexes of hexamethylbenzene (HMB) and tetracyanoethylene (TCNE) in cyclohexane, CH₂Cl₂, and CCl₄ solutions.

HMB and TCNE form a fairly strongly bound $\pi - \pi^*$ EDA complex. ΔH° for the 1:1 complex has been reported to be -8.44 kcal/mol in CH₂Cl₂⁴ and -7.75 kcal/mol in CCl₄.⁵ Previously

TABLE I: Fauilibrium Constants of HMR-TCNE Complexes

	quinorium conorm		contraction of the second
solvent	K_1 , L mol ⁻¹	K_2 , L mol ⁻¹	ref
cyclohexane	339-280 ^g	30	a
•	293 ± 20	24 ± 4	b (at 533 nm, 33.5 °C)
	280 ± 20	20 ± 4	b (at 580 nm, 33.5 °C)
CH ₂ Cl ₂	11.988 ± 0.008		с
	16.8		d
	17 ± 2		e
	19.6	4	а
CCl₄	180	6.1	b
,	149		f
	173	14	a

^a Mouchet, J.-P.; Rousset, Y. J. Chim. Phys. 1980, 77, 529. ^b Reference 12. ^c Herndon, W. C.; Feuer, J.; Mitchell, R. E. J. Chem. Soc., Chem. Commun. 1971, 435. d'Merrifield, R. E.; Phillips, W. D. J. Am. Chem. Soc. 1958, 80, 2778. [•] Michaelian, K. H.; Rieckoff, K. E.; Voigt, E.-M. J. Phys. Chem. 1977, 81, 1489. [•] Briegleb, G.; Czekalla, J.; Reuss, G. Z. Phys. Chem. (Frankfurt am Main) 1961, 30, 333. ^gCalculated K_1 was found to depend on the formal concentration of donor.

determined formation constants (K_1 and K_2) for the 1:1 and 2:1 complexes are given in Table I for the three solvents of interest in this work. Resonance Raman spectra of CH_2Cl_2 solutions of HMB/TCNE have also been reported.^{6,7} An X-ray study⁸ of

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⁽³⁾ Foster, R. "Molecular Complexes", Vol. 2, Foster, R., Ed.; Crane, Russak and Co., Inc.: New York, 1974; Chapter 3.

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Sci. U.S.A. 1975, 72, 4196. (b) Chem. Phys. Lett. 1973, 23, 5. (c) Chem.</sup> Phys. Lett. 1976, 39, 521.

the crystal structure of the 1:1 complex has confirmed that the local symmetry of the D-A unit is approximately C_{2v} , as expected on the basis of orbital overlap considerations.⁹ The infrared spectra of the 1:1 and the 2:1 complexes have been measured in the crystalline phase¹⁰ and in Ar and N_2 matrices.¹¹ The dipole moment of the ground state of the 2:1 complex has been determined to be zero.¹² Although the excited state of the 2:1 complex has also been found to have a center of symmetry, the dipole moment in the upper state has been found to be significantly different from zero.¹³ This will turn out to be an important factor in our conclusions concerning the bonding in the complex. Also of particular interest in this work is the reported far-infrared absorption spectra of the crystalline complexes,¹⁴ in which a strong band at 89 cm⁻¹ has been assigned to an "intra-charge-transfer" mode, ν_{DA} .

In section III of this paper, we report the results of a numerical resolution of the optical spectra of HMB:TCNE in cyclohexane into contributions from 1:1 and 2:1 EDA complexes. As shown in Table I, traditional approaches for calculating equilibrium constants of this system have been fraught with discrepancies. We have recently reported a multiwavelength reiterative least-squares method for calculating equilibrium constants and optical spectra.¹⁵ When applied to cyclohexane solutions of HMB:TCNE, however, the line shapes and positions of the spectra of the 1:1 and 2:1 complexes were found to be very similar. Although this feature renders impossible the unambiguous resolution of the observed spectra, and thus determination of K_1 and K_2 , the similarity of the line shapes and peak frequencies provides an interesting structural clue concerning the 2:1 complex. Our conclusions in this paper also depend strongly on the related work of Liptay et al.,¹³ who combined multiwavelength linear regression analysis with density, permittivity, and electrooptical measurements in a study of HMB:TCNE in CCl₄. They too found the resolved spectra of the 1:1 and 2:1 complexes to be very similar, although the molar absorptivity of the 2:1 complex was found to be nearly a factor of two higher. In addition, their determination of the symmetry and dipole moment of the HMB:TCNE complexes provides us with additional support for the molecular orbital picture of the bonding to be presented in this paper.

In section IV we present low-frequency resonance Raman data for HMB:TCNE dissolved in CH₂Cl₂, CCl₄, and cyclohexane. By comparing our Raman data to the reported far-IR absorption spectra¹⁴ of crystalline HMB:TCNE and (HMB)₂:TCNE, we conclude that the weak Raman band at 165 cm⁻¹ is the first overtone of a totally symmetric donor-acceptor stretching vibration, ν_{DA} . Contrary to expectations for a symmetrically bound D-A-D complex, the frequency of the intermolecular vibration does not appear to split into symmetric and antisymmetric vibrational modes. This observation, combined with the optical absorbance data of section III, lead us to the molecular orbital picture of the bonding presented in section V. The conclusion of the MO approach is that the second donor molecule is not bound by a charge-transfer interaction, and that, therefore, the bond strengths in the D_{2h} 2:1 complex are not equal. Alternatively, a VB wave function can be constructed to represent the resonance structures $D^+A^-D \rightleftharpoons DA^-D^+$. Poor overlap of the donor orbitals results in a resonance frequency so slow that charge transfer can be considered to involve one donor only. The optical and low-

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frequency Raman data are then readily interpreted if the second donor molecule is pictured as strongly solvating the 1:1 complex. In addition, the symmetries of the ground and excited states are consistent with our interpretation of the appearance at 223 cm⁻¹ of an a_{2u} out-of-plane methyl deformation in the Raman spectrum of (HMB)2:TCNE in cyclohexane. The resonance Raman activity of this normally forbidden vibration is interpreted in terms of vibronic coupling of the ground and charge-transfer electronic states.

II. Experimental Section

Hexamethylbenzene and tetracyanoethylene were both purchased from Aldrich and purified by repeated recrystallization and vacuum sublimation. Spectrograde solvents were freshly dried over molecular sieves to prevent reaction of TCNE with water. For the determination of K_1 and K_2 in cyclohexane, four different mixtures containing 1.288×10^{-3} M TCNE and HMB in the range 3.081×10^{-2} to 9.243×10^{-2} M were prepared. A fifth solution contained 1.849×10^{-2} M HMB and 7.027×10^{-4} M TCNE. The absorbance of each solution at 25 different wavelength in the range 440-660 nm was recorded in 2-mm cells on a Beckman Acta MVII spectrophotometer. In order to establish values of the standard deviation of each absorbance data point (see eq 15 of ref 15), each of the five solutions was prepared four times and the spectra were recorded. The temperature was held constant at 25 °C.

Raman spectra were recorded on a Spex Ramalog spectrometer with a 14018 double monochromator and argon ion laser excitation at 5145 Å. A rotating quartz cell was used as a sample holder, and 90° scattering was employed. Laser power at the sample was typically kept low (<100 mW) to avoid sample heating and dissociation of the complex. The digital output of the photometer was collected on a Hewlett Packard 9825 A computer via a home-built 16-bit interface. The weak low-frequency bands were recorded as averages of at least ten scans, using an integration interval of 1 cm^{-1} and an integration time of 1 s. Slits were typically set at 360 μ m, corresponding to a resolution of about 4 cm⁻¹. It was empiricially determined that a sample absorbance of about 5 or 6 per 1 cm path length resulted in good Raman data without excessive reabsorption of incident or scattered radiation.

III. Determination of K_1 and K_2 and Resolved Visible Absorbance Spectra

In order to interpret the resonance Raman spectra of HMB/TCNE solutions, it is necessary to know not only the amount of 2:1 and 1:1 complexes, but also the contribution of each component to the total absorbance at the wavelength used to excite the Raman spectrum. It was decided, therefore, to employ the previously mentioned least-squares approach for resolving the optical spectra of the 1:1 and 2:1 complexes and determining the formation constants K_1 and K_2 . The details of the mathematical manipulations are given in ref 15 and will not be repeated here. However, a brief discussion of our earlier results for chloroform solutions of *p*-xylene and *p*-bromanil will serve to introduce the technique and to explain why our results for HMB/TCNE were surprising.

As reported in ref 15, the electronic transition of the 2:1 complex of p-xylene with p-bromanil was found to be red-shifted with respect to that of the 1:1 complex. The spectrum of the 2:1 complex also has lareger intensity and line width. These results are easily understood if the structure of the 2:1 complex is D-D-A, since in this case resonance stabilization, $D^+-D^-A^- \leftrightarrow D^-D^+-A^-$, will lower the energy of the excited state relative to that of the 1:1 complex. In fact, the observed red shift is the same order of magnitude as, but somewhat less than, the binding energy of the gas-phase *p*-xylene dimer cation.¹⁶ The increased oscillator strength of the D-D-A complex is also reasonable, since the intensity of a charge-transfer transition has been shown to depend on the distance through which the charge is transferred.⁹ Finally,

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TABLE II: Equilibrium Constants and Molar Absorptivities for HMB-TCNE and (HMB)2-TCNE from Multiwavelength Linear Regression

solvent	K_1 , L mol ⁻¹	K_2 , L mol ⁻¹	ϵ_1 , L mol ⁻¹ cm ⁻¹	ϵ_2 , L mol ⁻¹ cm ⁻¹	ref	
CCl ₄ cyclohexane	151 ± 0.03 300 ± 100	7.3 ± 0.07 40 ± 10	4613 ± 10 , at 526 nm 3813 ± 500 , at 522 nm	6770 ± 70 , at 526 nm 5835 \pm 50, at 530 nm	13 this work	



Figure 1. Resolved visible spectra of HMB-TCNE and (HMB)2-TCNE in cyclohexane.

the low-frequency intermolecular vibrational modes have been determined to contribute significantly to the line width,¹⁷ so it is not surprising that the 2:1 complex has a broader spectrum than the 1:1 complex. Using the criterion that χ^2 error values less than or equal to 1 be considered valid, we determined K_1 and K_2 in this system to be 3.696 ± 0.052 and 1.095 ± 0.006 M⁻¹, respectively.

In this work, optical absorbance data for HMB/TCNE in cyclohexane and CH₂Cl₂ were submitted to linear regression analysis, but it was found that a wide range of K_1 and K_2 values yield acceptable results for the χ^2 error function. The reason for the "looseness" of the fitting procedure is easily understood upon inspection of Figure 1, where it is shown that the resolved spectra of the two complexes are similar in shape and have nearly coincident absorbance maxima. Thus any arbitrary linear combination of the spectra of the two complexes can be made to reproduce the total unresolved spectrum by suitable adjustment of the equilibrium constants and molar absorptivities. In Figure 1, calculated with $K_1 = 300 \text{ M}^{-1}$ and $K_2 = 40 \text{ M}^{-1}$, the difference between the experimental and calculated unresolved spectra cannot be discerned on the scale of the plot used.

For the CH₂Cl₂ solutions, it was not possible to find a minimum in the χ^2 error plot. χ^2 was found to be less than 1 for a wide range of K_1 and K_2 values, encompassing those reported in Table I and obtained by analysis of single wavelength data. In cyclohexane solution, a shallow minimum at $\chi^2 = 3.2$ was obtained for $K_1 = 300 \text{ M}^{-1}$ and $K_2 = 40 \text{ M}^{-1}$. The corresponding molar absorptivities at λ_{max} were found to be 3813 and 5835 $\tilde{L}~mol^{-1}$ cm⁻¹ for the 1:1 and 2:1 complexes, respectively. The uncertainties reported in Table II were established, somewhat arbitrarily, by using the values of K_1 and K_2 that yield χ^2 less than or equal to 4.0. It was not possible to make a reasonable fit to the data with a model which neglects the formation of 2:1 complexes.

Although our uncertainties are large due to the shallowness of the χ^2 function, the values of K_1 and K_2 which minimize χ^2 are in good agreement with those of earlier workers who analyzed absorbance data at a single wavelength. The calculated molar absorptivities at λ_{max} are also in line with those of ref 1. Furthermore, the line shapes of the resolved spectra are in good qualitative agreement with those of Liptay et al.¹³ for HMB/ TCNE in CCl₄. Their data for CCl₄ are also shown in Table II for comparison. Using a variety of physical measurements, Liptay et al. have concluded that a model which includes just 1:1 and 2:1 complexes is sufficient to account for all the data in CCl_4

TABLE III: Resonance Enhanced Raman Lines of HMB-TCNE

solvent	<i>ν</i> , cm ^{−1}	$\begin{array}{c}\Delta\nu_{1/2},\\\mathrm{cm}^{-1}\end{array}$	depolarzn ratio	assignment
cyclohexane	163	12	0.33	2v _{DA}
	223	18	0.28	$3\nu_{\rm DA}$ + $\Gamma(\rm C-CH_3)$
	1555	9		ν _{C=C}
	2223	5		ν _{C=N}
CCl₄	166			$2\nu_{DA}$
	1554			ν _{C=C}
	2223			^µ C≡N
CH_2Cl_2	169			$2\nu_{\rm DA}$
	1550			ν _{C=C}
	2223			^ν C≡N

solution. Liptay et al. found the absorption maxima of the two complexes in CCl₄ to be nearly coincident, and the molar absorptivity was found to be nearly twice as great for the 2:1 complex. From electrooptical measurements, the investigators in ref 13 concluded that the 1:1 and 2:1 complexes have C_{2v} and D_{2h} symmetry, respectively. The dipole moment of the excited electronic state of the 2:1 complex was found to be perpendicular to the planes of the three molecules and nearly equal in magnitude to the transition dipole moment of the 1:1 complex.

Given the size of K_2 (~40 M⁻¹), it is hard to see how the second donor molecule could be bound so strongly without greatly changing the width and λ_{max} of the charge-transfer spectrum. Is the nearly twofold increase in molar absorptivity significant? Before addressing these questions, we turn next to a discussion of the low-frequency vibrational modes of EDA complexes, and present our Raman data for HMB/TCNE solutions.

IV. Resonance Raman Spectra of HMB/TCNE in CCl₄, CH₂Cl₂, and Cyclohexane

The resonance Raman spectra of methylene chloride solutions of HMB/TCNE have been previously obtained at several argon ion laser wavelengths.^{6,7} In addition to the resonance enhanced totally symmetric C=C and C=N stretches of TCNE, a new mode near 160 cm⁻¹ has been observed and assigned by Voigt et al. to a totally symmetric scissoring vibration, ν_5 of TCNE.^{6c} Since this conclusion contradicts the previously published normal co-ordinate calculations for TCNE,^{18,19} we considered the possibility that the 160-cm⁻¹ line observed by Voigt et al. is actually the first overtone of the totally symmetric donor-acceptor stretching mode ν_{DA} observed in the far-IR at 89 cm^{-1.14} The increased frequency of this mode as the strength of the donor increases, as reported in ref 6c, makes this assignment reasonable. In addition, the donor-acceptor distance is quite likely to be shorter in the excited state than in the ground state, so that the donor-acceptor stretch, $\nu_{\rm DA}$, is a good candidate for both resonance enhancement and overtone progression.²⁰ The depolarization ratio of the peak in question is 1/3, suggesting that the mode is totally symmetric and derives intensity from a single nondegenerate electronic state.²¹

Our original plan was to gather the low-frequency Raman spectra of HMB/TCNE in different solvents to see if the peak frequency increased with the strength of the complex. The problem with such an approach is that there is also an ordinary solvent effect on the peak frequency which is difficult to account for quantitatively. The D-A stretch has a large dipole moment derivative and should therefore be red-shifted by the attractive part of the intermolecular potential.²² Indeed, as shown in Table

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Figure 2. Raman spectrum of cyclohexane solution of HMB and TCNE.

TABLE IV: Concentration Dependence of Intensity Ratio I 223/I 163

HMB-TCNE concn, $C_1 \times 10^4$, M	$(HMB)_2$ -TCNE concn, $C_2 \times 10^4$, M	I_{223}/I_{163}	C_{2}/C_{1}
8.71	9.75	0.14 ± 0.03	1.1
5.75	13.4	0.20 ± 0.04	2.3
4.24	15.0	0.38 ± 0.08	3.6

III, the peak frequency of 2 ν_{DA} is highest (169 cm⁻¹) in CH₂Cl₂. Of the three solvents used, CH₂Cl₂ has the lowest packing fraction (0.53) and molar polarization (16 cm³).

In CCl_4 and CH_2Cl_2 , the formal concentrations of donor and acceptor were such that the concentration of 2:1 complex was negligible. In cyclohexane, however, the limited solubility of TCNE required excess donor concentrations in order to obtain solutions dark enough to give good Raman data. Thus the concentration of 2:1 complexes was always significant in cyclohexane. If the DAD complexes were symmetrically bound, the DA stretch would be split into a lower frequency symmetric stretch and a higher frequency asymmetric stretch. In Raman spectra of cyclohexane solutions of HMB/TCNE, the peak at 163 cm⁻¹ does not shift or split as the concentration of 2:1 complexes increases; however, a weak broad feature of 223 cm⁻¹, not observed in CCl₄, or CH_2Cl_2 , begins to appear (Figure 2). The depolarization ratio of the 223-cm⁻¹ band was found to be about 0.28, which is close to the value of 0.33 found for the 163-cm⁻¹ line. The half-width of the 223-cm⁻¹ peak is 3/2 that of the band at 163 cm⁻¹, so it is reasonable to speculate on the possibility that the two modes are first and second overtones of the same fundamental.²³ In fact, if such an assumption is made, the equation for the energy levels of an anharmonic oscillator can be used to calculate v_e and $x_e v_e$:

$$E_{\rm v} = (v + 1/2)h\nu_{\rm e} - (v + \frac{1}{2})^2 x_{\rm e} h\nu_{\rm e} \tag{1}$$

The result is $v_e = 103 \text{ cm}^{-1}$ and $x_e v_e = 7.2 \text{ cm}^{-1}$. With these values the fundamental frequency is predicted to be 89 cm⁻¹, in perfect agreement with the frequency of the intracharge-transfer mode reported by Rossi and Haselbach.¹⁴ Although these arguments for assigning the peaks in Figure 1 to the first and second overtones of ν_{DA} appear quite strong, it was found that the ratio of their intensities did not remain constant as the relative concentrations of DA and D_2A were varied. As shown in Table IV, the ratio of intensities I_{223}/I_{167} increases as the ratio of the concentration of the 2:1 complex to that of the 1:1 complex increases, but the increase in intensity is not as great as would be expected if the peak at 223 cm⁻¹ were entirely due to the 2:1 complex. Note that although the calculation of concentrations and their ratios are subject to errors in K_1 and K_2 , the ratio of the ratios, which is of interest here, is determined largely by the formal donor concentration and is therefore quite accurately known. An out-ofplane methyl deformation $\Gamma(C-CH_3)$ of a_{2u} symmetry has been observed at 220 cm⁻¹ in the IR spectrum of HMB.²⁴ As will be



Figure 3. Overlap of π orbitals in HMB-TCNE.

shown in the next section, this normally Raman forbidden vibration could be activated in the 2:1 complex by vibronic coupling of the ground and excited states. We suggest, therefore, that the 223cm⁻¹ band contains contributions from $3\nu_{DA}$ as well as the $\Gamma(C-$ CH₃) mode of HMB. The lack of splitting of the D-A stretch in the 2:1 complex is an indication that the second donor molecule is not as strongly bound as the first. This conclusion is also in agreement with the data presented in ref 14. There, ν_{DA} was shown to be proportional to the inverse square root of the reduced mass, $(1/M_{\rm D} + 1/M_{\rm A})^{1/2}$, for a series of donors complexes with TCNE, including the 2:1 crystalline complex of HMB with TCNE. In the next section is presented a molecular orbital picture of the bonding in (HMB)₂TCNE which explains how the complex can have D_{2h} symmetry yet unequal D-A bond strengths.

V. Molecular Orbital and Valence Bond Pictures of Bonding in EDA Complexes of HMB with TCNE

Although other intermolecular forces besides charge transfer can influence the geometry of a complex,²⁵ the "overlap and orientation" principle of Mulliken²⁶ has successfully predicted the structures of many EDA complexes as determined by X-ray crystallography. In the case of a HMB-TCNE 1:1 complex, Mulliken's theory of maximum overlap of the donor HOMO with the acceptor LUMO can be used to explain the local symmetry of the crystalline complex as determined by the X-ray analysis of Saheki et al.8 A recent LCAO-SCF calculation has determined the symmetry of the TCNE LUMO to be b_{3g} .²⁷ Favorable overlap of this orbital with one of the degenerate e_{1g} HOMO's of HMB is possible in either of two geometries. Each of these geometries has C_{2v} symmetry and a stacked parallel configuration of the two planar molecules. They differ by a 90° rotation of the TCNE about an axis parallel to the planes of the molecules. The X-ray analysis of ref 8 has confirmed the existence of two such structures, in a ratio of 3:1, in the 1:1 crystalline adduct of HMB with TCNE. The predominant geometry is the one which optimizes the HOMO-LUMO overlap as shown in Figure 3. In either structure, an electronic transition polarized perpendicular to the direction of the molecular planes is predicted, consistent with what is expected for a charge-transfer transition. In what follows, we will employ the predominant geometry in our analysis. None of our symmetry based conclusions would be altered if the other configuration were considered.

An X-ray study of the crystalline 2:1 complex has apparently not been reported, but solution-phase dielectric¹² and electrooptical¹³ data are consistent with the assumption of D_{2h} symmetry, at least in the ground electronic state. Thus, either a symmetric or antisymmetric combination of the two HMB e_{1g} orbitals could act as the donor orbital in a charge-transfer transition. The in-phase combination of the two HMB HOMO's, shown in Figure 4a, has the same symmetry as the TCNE LUMO, which is b_{3g} in the D_{2h} point group. An excited state that derives from the

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⁽²³⁾ The half-width of an overtone of order n varies as n to n^2 . See Madden, P. A.; Battaglia, M. R. Mol. Phys. 1978, 36, 1601.

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Figure 4. (a, b) Overlap of π orbitals in $(HMB)_2$ -TCNE.

configuration in which the in-phase HMB HOMO and the TCNE LUMO are each singly occupied is therefore dipole forbidden and cannot be responsible for the observed optical absorption. If, on the other hand, an out-of-phase combination of HMB orbitals is considered as the donor orbital, as shown in Figure 4b, then the charge-transfer excited state is of $b_{2u} \times b_{3g} = B_{1u}$ symmetry. A z-polarized electronic transition is predicted, in agreement with the conclusions of Liptay et al.¹³ In the usual Mulliken⁹ picture, however, this dipole-allowed charge-transfer state cannot contribute to the stabilization of the ground state of the complex via mixing with the totally symmetric "no-bond" wave function representing the interaction of the closed-shell molecules. The conclusion is that the two D-A bonds in a symmetric D₂A complex cannot *both* be stabilized by charge-transfer interaction.

To elaborate further, we review the Mulliken picture for the bonding in a 1:1 EDA complex. For an ordinary weakly bound complex, the ground-state wave function contains a large contribution from a hypothetical no-bond wave function $\psi_0(D,A)$ and a small contribution from an ionic wave function $\psi_1(D^+,A^-)$:

$$\psi_{g} = a\psi_{0}(D,A) + b\psi_{1}(D^{+},A^{-}); \quad a \gg b$$
 (2)

The configuration ψ_1 differs from that of ψ_0 by the promotion of an electron from the donor HOMO ϕ_D to the acceptor LUMO ϕ_A . In order for ψ_1 to mix with ψ_0 , ϕ_D and ϕ_A must belong to the same symmetry species in the point group of the complex. This is the basis for the overlap and orientation principle of Mulliken. The ground-state energy W_g , obtained by linear variation theory, is well-known:

$$W_{\rm g} = W_0 - \frac{(H_{01} - SW_0)^2}{W_1 - W_0} \tag{3}$$

where W_0 and W_1 are the energies of the no-bond and ionic states, respectively, H_{01} is the resonance integral connecting these states, and S is their overlap integral. Thus mixing in the ionic wave function stabilizes the complex with respect to the hypothetical no-bond state. The other root of the secular equation gives the excited state energy, which is destabilized relative to the hypothetical ionic state. Since the corresponding excited state wave function ψ_e contains a large contribution from ψ_1 , the transition $\psi_g \rightarrow \psi_e$ is appropriately referred to as a charge-transfer transition.

Now consider a similar approach for a symmetric D_2A complex. The ground state wave function is

$$\psi_{g} = a\psi_{0}(DAD) + b\psi_{1}(D^{+}A^{-}D) + c\psi_{2}(DA^{-}D^{+})$$
(4)

Symmetry considerations dictate that $b = \pm c$, but for a totally symmetric ψ_g only the choice b = c can contribute. For the system of interest here, the choice b = c corresponds to the interaction of a HOMO and LUMO of the same symmetry, as shown in Figure 4a. As described previously, this symmetric charge-transfer state may contribute to the ground-state stabilization of the complex, but cannot contribute to the final state of a dipole-allowed electronic transition. The choice a = 0, b = -c, on the other hand, seems to be a good representation of the excited-state wave function. Unfortunately, this leads to two predictions which are at odds with experimental results. That is, if either donor molecule can transfer charge, the dipole moment of the excited state should be zero and the electronic absorption spectrum of the 2:1 complex should be red-shifted due to resonance stabilization of the excited state. Liptay and et al.¹³ have found the dipole moment of (HMB)₂TCNE to be about 4 D in the excited state and zero in the ground state. This increase in dipole moment was also found to be approximately the same as that of the 1:1 complex, which has a dipole moment of about 6 D in the excited state and about 2 D in the ground state.¹³ The fact that no red shift is observed and that the excited-state dipole moment is not zero is good evidence for one-way charge transfer in the 2:1 complex.

We turn now to a valence bond approach for a better interpretation of the experimental results. The excited-state wave function ψ_e is taken to be a linear combination of wave functions ψ_1 and ψ_2 , representing bonds to the first and second donor molecules, respectively:

$$\psi_{\rm e} = \psi_1 - \psi_2 \tag{5}$$

The minus sign is chosen so that ψ_e will have B_{1u} symmetry. ψ_1 represents charge transfer from donor HOMO ϕ_D to the TCNE LUMO ϕ_A :

$$\psi_1 = |\phi_A(1)\alpha(1) \ \phi_{D1}(2)\beta(2)| - |\phi_A(1)\beta(1) \ \phi_{D1}(2)\alpha(2)| \tag{6}$$

and ψ_2 is a similar valence bond wave function for charge transfer from the same HOMO on the second donor molecule, ϕ_{D2} , to the TCNE LUMO ϕ_A :

$$\psi_2 = |\phi_A(1)\alpha(1)| \phi_{D2}(2)\beta(2)| - |\phi_A(1)\beta(1)| \phi_{D2}(2)\alpha(2)|$$
(7)

The frequency with which the positive charge may be considered to resonate between the two donor molecules is

$$\nu = \frac{1}{h} \langle \psi_1 | \hat{H} | \psi_2 \rangle \sim \frac{1}{h} \langle \phi_A \phi_{D1} | \hat{H} | \phi_A \phi_{D2} \rangle \tag{8}$$

Now the two donor molecules in a stacked π -complex D-A-D are probably about 7 Å apart; hence the orbital overlap of ϕ_{D1} and ϕ_{D2} is expected to be very small. The matrix element of the Hamiltonian in eq 8 is correspondingly very small. Experimental data confirm the prediction that the resonance frequency ν is quite small compared to the time scales of the spectroscopic transitions. Thus, it is again concluded that the charge transfer is essentially only from one donor molecule at a time. Of course, either of the two HMB molecules could act as the donor, so it is easy to understand why the oscillator strength of the 2:1 complex is nearly twice that of the 1:1 complex.

In summary then, since charge-transfer stabilization is not simultaneously possible for both D-A bonds, the bond strengths are not equal in the ground state of the 2:1 complex. The binding of the first donor molecule can be considered in the conventional Mulliken approach, but the binding of the second donor molecule is best interpreted in terms of weaker van der Waals interactions. Since the second donor molecule just solvates the 1:1 EDA complex, it is not surprising that the intermolecular mode ν_{DA} does not split into symmetric and antisymmetric combinations. The idea of unequal bond strengths may seem to conflict with the assumption of D_{2h} symmetry, but it should be pointed out that intermolecular distances in weakly bound solution phase EDA complexes are largely dictated by the van der Waals radii. In the excited state, however, the two bonds are expected to differ in length and in strength due to the contribution of the ionic wave function.

Finally, the orbital picture presented above is used to interpret the appearance of the a_{2u} methyl deformation in solutions containing significant quantities of 2:1 complex. It has been previously established in Raman studies of benzene derivatives that perturbations in the direction perpendicular to the plane of the ring can lead to enhanced intensity of out-of-plane modes.²⁸ We do not, however, observe a Raman band at 223 cm⁻¹ in solutions which contain the complex predominantly in 1:1 form. Unfortunately, solubility limitations in CCl₄ render the observation of such a weak mode very difficult, and in CH₂Cl₂ there is a strong solvent line at 284 cm⁻¹. In the 2:1 complex, the Γ (C-CH₃) mode is of b_{1u} symmetry. Since the charge-transfer state is also of B_{1u} symmetry, the out-of-plane mode could derive intensity from vibronic coupling of the ground (A_g) and excited (B_{1u}) electronic states via the normal coordinate for $\Gamma(C-CH_3)$. In the 1:1 complex, however, the $\Gamma(C-CH_3)$ mode is totally symmetric, and

(28) Ito, M.; Abe, H.; Murakami, J. J. Chem. Phys. 1978, 69, 606.

totally symmetric vibrations normally derive intensity from the Franck-Condon factors (Albrecht's "A" term²⁹). Thus, unless the methyl groups are distorted out of the plane in the excited state, one does not expect to see resonance enhancement of Γ -(C-CH₃) in the 1:1 complex.

VI. Conclusions

We have presented optical and resonance Raman data for the HMB-TCNE complexes which support a molecular orbital picture of unsymmetrical bonding in the D-A-D complex. Although the precision with which the values of the equilibrium constants for the two complexes can be determined is limited by the similarity in their optical spectra, the similarity itself provides insight into the structure of the 2:1 species. The optical and Raman data both lead to a model, supported by molecular orbital or valence bond considerations, in which the second donor molecule serves to strongly solvate the 1:1 complex. In cyclohexane solution the first and second overtones of the donor-acceptor stretch are observed in the resonance Raman spectrum; the latter is overlapped by an out-of-plane methyl deformation which becomes active in the 2:1 complex by vibronic coupling. The observation of a low-frequency intermolecular vibration of a weakly bound complex is an exciting result which should stimulate further studies of the solution phase structure of EDA complexes. Further Raman studies of the low-frequency modes with tunable laser excitation are currently in progress and will provide more information about the excited states of these complexes.

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An Approximate Three-Dimensional Quantum Mechanical Calculation of Reactive Scattering Cross Sections for the H + $Cl_2(\nu) \rightarrow HCl(\nu')$ + Cl Reaction

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An approximate three-dimensional quantum mechanical method has been used to calculate reactive scattering cross sections for the $H + Cl_2(v) \rightarrow HCl(v') + Cl$ reaction. Both integral and differential cross sections are presented as a function of energy and of initial reactant and final product vibrational quantum states. The method used to perform the calculations is the bending corrected rotating linear model recently introduced by Walker and Hayes. We compare our calculated results with those of collinear quantum mechanical and of classical trajectory calculations. The product vibrational state distribution is found to be bimodal at high collision energies for reaction from both the first and second excited vibrational states of Cl_2 . This is in qualitative agreement with results of all the recent collinear quantum mechanical calculations. The calculated differential cross sections are, as expected, backward peaked, the width of the distribution increasing with increasing energy. The calculated cross sections are used to compute detailed rate constants as a function of temperature.

I. Introduction

The elucidation of the details of elementary chemical reactions is a centrally important step toward gaining a broader understanding of chemical processes. The technical advances of the past 20 years have opened wide the door to the experimental study of these processes,¹⁻⁴ and the body of experimental results which is now available calls out for precise theoretical interpretation.

⁽¹⁾ C. T. Rettner and J. P. Simons, *Faraday Discuss. Chem. Soc.*, 67, 329 (1979); see also other paper in this volume.