factors involved. The large increases in shielding on direct protonation of butterfly interstitials show that an important component of their low shielding is due to low-energy circulations of quasi-lone-pair electrons (weakly bonding to the metal), and a contribution of this type is likely in square-pyramidal clusters also.

It is likely that the significant factors in the patterns of interstitial shieldings include not only the ones that determine the local paramagnetic circulation but also those determining the diamagnetic and paramagnetic circulations on the cluster metal, which are not negligible within the cluster. The sizable increase in shielding down the group of the metal (for a given symmetry) shows the importance of the diamagnetic contribution most clearly.

This parallels the increase in shielding with the coordination number of oxygen in polyoxometalates (cf. Table II and Figure 4) and the increases in shielding observed for non-metals and metals with heavy substituents, such as the heavier halogens. It is likely that relativistic contributions to the shielding of the interstitial will be important with the heaviest metals, Au in particular, and that the effects of heavy neighbors will be particularly marked in the shielding of the lightest interstitial, hydride.[20]

Effects of Positions of Donor and Acceptor Type Substituents on Ground- and Excited-State Charge Transfer: Electrochromism of Some Benzene Derivatives

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Abstract: 4-NO_2, 3-NO_2, and 3,5-di-NO_2 substituents as acceptors (A) relative to 1-NH_2, 1-OMe, and 1-C≡CH as donors (D) on the benzene ring have been examined in order to understand the relation between position of D and A moieties relative to each other and the charge distribution in the ground and excited states. Ground-state dipole moments (μ_g) [obtained from dielectric measurements] in each case follow the order 4-NO_2 > 3,5-di-NO_2 > 3-NO_2. On the other hand, the excited-state dipole moments (μ_e) and the change in dipole moment ($\Delta\mu$) [obtained from electrooptic measurements] show a different trend, i.e., 4-NO_2 > 3-NO_2 > 3,5-di-NO_2. In the excited state the charge migration from the donor site to the acceptor site in the meta isomer has been found to be comparable to that in the para isomer, and this supports the unusual meta effect found in various photochemical reactions. The observed changes have been interpreted with simple molecular orbital calculations, and a regular trend has been found in each case studied.

Introduction

Intramolecular charge transfer (ICT) in organic molecules containing donor (D) and acceptor (A) groups has relevance to many aspects of physics and chemistry. For example, organic materials having strong charge-transfer characteristics are attractive for applications in nonlinear optics, such as frequency doubling of semiconductor lasers, electrooptic modulation of light, etc.[1,2] Charge transfer in the excited state can bring about very interesting chemical phenomena, such as twisting of the molecular skeleton,[3] intermolecular interactions,[4] unusual chemical reactivity, etc.[5] To understand such physical and chemical phenomena of excited states, it is essential to have a clear picture of the electrical properties of the molecule in its ground and electronically excited state. Experimentally, one step in this direction would be to

examine how variations in the position of the same substituents effect the resultant charge distribution in both the ground and excited states, which has been attempted in this paper.

The most simple systems for which ICT has been well-recognized in the ground state are substituted benzenes containing donor and acceptor moieties.[6] The effect of the relative position of D and A type substituents on the electronic spectral characteristics have been elegantly discussed by McGlynn et al.[6] However, similar reports describing excited-state charge-transfer properties are scarce in the literature. In most reported experiments, the electronic spectral shift method (more commonly known as the solvatochromic method) has been used to determine the excited-state dipole moment, which reflects the charge-transfer character in the excited state.[7] This method has been considered to be a highly approximate procedure, particularly when the chromophores are strongly interacting in nature (termed specific interaction), due to the assumptions in the derivation and practical application of the formulas required for the calculations.

On the other hand, electrochromism permits the determination of dipole moment and polarizability of a nonequilibrium (Frank–Condon) state with relatively high precision, although even

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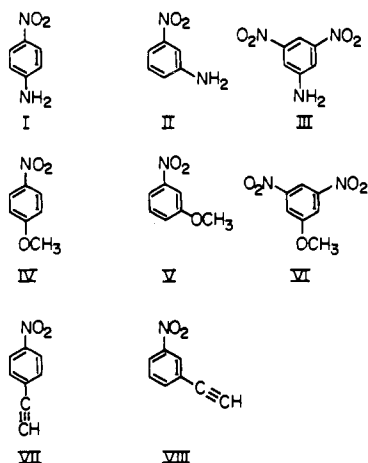
Figure 1. Molecular structure of the compounds selected for the electric field study.

in this case the final formulas used are appreciably simplified by various assumptions.[8] Initially developed by Czekalla, Labhart, and Liptay,[9] this method has been successfully used to derive information regarding excited-state electronic properties, such as dipole moments and polarizabilities of both polar as well as nonpolar molecules.[10,11] This method has been employed here to obtain the excited-state dipole moment of several substituted benzene derivatives. Both the nature and position of the substituents have been systematically varied (see Figure 1) to shed light on the possible correlation between positional variation of the substituents and the ground- and excited-state charge-transfer processes. Theoretical justification for the observed trends has been provided to supplement the experimental results.

Theory of Electric Field Perturbation

An intense electric field affects the intensity of both absorption and fluorescence, and such electric field effects were first quantitatively interpreted by Labhart, Czekalla, and Liptay independently.[9] The basic principles of electrochromic measurements with appropriate theoretical reasoning have been reviewed by Liptay.[8] In addition, our previous papers also present a complete experimental and physical description of electrooptical measurements on macroscopic systems.[11] Hence this will not be repeated, but the basic principles will be summarized here.

For dipolar molecules in solution the perturbation due to the presence of a strong external electric field on the electronic absorption intensity is mainly due to two factors: (i) anisotropic molecular distribution and (ii) change in the electronic transition energy if the ground-state dipole moment (μ_g) is different from the excited-state dipole moment (μ_e). The theoretical expression relating the change in the extinction coefficient $(\Delta\epsilon)$ to the frequency (ν) of the incident light, the internal field strength (F_{int}), and the angle (χ) between the direction of the applied field and the polarization direction of the incident light, according to Liptay,[8] is

$$\Delta\epsilon = F_{int}^2\epsilon\left[A\chi + \frac{B_\chi}{15h}\frac{\partial/\partial\nu(\epsilon/\nu)}{\epsilon/\nu} + \frac{C_\chi}{30h^2}\frac{\partial^2/\partial\nu^2(\epsilon/\nu)}{\epsilon/\nu}\right] \quad (1)$$

If the contributions of the polarizability terms are considered to be small, which is a valid assumption for molecules having sufficiently large permanent dipole moment, the A_χ, B_χ, and C_χ terms in eq 1 are related to the dipole moment parameters in the following way:

$$A_\chi = (1/30)E(3\cos^2\chi - 1) \quad (2)$$

$$B_\chi = 5F + G(3\cos^2\chi - 1) \quad (3)$$

$$C_\chi = 5H + I(3\cos^2\chi - 1) \quad (4)$$

where

$$E = \beta^2[3(\hat{p}\cdot\mu_g)^2 - \mu_g^2] \quad (5)$$

$$F = \beta(\Delta\mu\cdot\mu_g) \quad (6)$$

$$(F + G)/3 = \beta(\hat{p}\cdot\Delta\mu)(\hat{p}\cdot\mu_g) \quad (7)$$

$$H = (\Delta\mu)^2 \quad (8)$$

$$(H + I)/3 = (\hat{p}\cdot\Delta\mu)^2 \quad (9)$$

In these equations, $\hat{p}$ is a unit vector in the direction of the molecular transition moment, μ_g and $\Delta\mu$ are the ground-state dipole moment and the change in dipole moment upon electronic excitation, and $\beta = (kT)^{-1}$, where k is Boltzmann's constant and T is the temperature.

Methods

The detailed description of the electronic field apparatus used for the determination of μ_e has been presented in previous papers.[11] Since the field induced changes in the extinction coefficient are very small, the required sensitivity was achieved by simultaneously applying a 20-kV dc potential and a 12-kV (root mean square) 500-Hz ac potential and detecting $\Delta\epsilon$ with a phase and frequency sensitive amplifier (PAR 128). The value of the effective external field F_{ext} is in the range of 3×10^4–6×10^4 V/cm, depending on the signal strength. The externally applied field was converted to an internal field by using spherical cavity approximation, given by

$$F_{int} = F_{ext}\frac{3\xi}{2\xi + 1} \quad (10)$$

where ξ is the dielectric constant of the solvent. Since dioxane ($\xi = 2.209$) was used as solvent $F_{int} = 1.224F_{ext}$.

The absorption spectrum in the absence of the electric field was measured, and its first and second derivatives with respect to frequency were computed numerically. For each molecule the electric field signals were collected at three different values of χ and for several wavelengths λ within the absorption band of interest. The $\Delta\epsilon$ at different wavelengths was obtained from the equation

$$\Delta\epsilon = -\frac{1}{2.303cl}\frac{\Delta I}{I} \quad (11)$$

where ΔI is the difference in the transmitted light intensity in the presence and absence of the field, I is the transmitted light intensity in the absence of the field, c is the concentration, and l is the path length of the electric field cell. The values of A_χ, B_χ, and C_χ were then obtained by making a least-squares fit of the observed $\Delta\epsilon$ spectrum to a sum of the absorption spectrum and its first and second derivatives (see eq 1). The contribution from the second derivative term (see eq 1) to the electric field signal was found to be very small, as observed for several other similar polar molecules.[11,12] Therefore this term has been neglected in the regression analysis. Finally, the molecular parameters were calculated from the slopes and intercepts of least-square plots of A_χ and B_χ versus $(3\cos^2\chi - 1)$.

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Table I. Values of the Coulomb and Bond Integrals Used in HMO Calculations

H_{ii}	h_N (NO$_2$) (1.5)	h_O (NO$_2$) (1.66)	h_N (NH$_2$) (1.5)	h_C (C≡C) (0.4)	h_O (OMe) (2.0)
H_{ij}	K_{CN} (0.8)	K_{NO} (1.65)	$K_{C≡C}$ (1.65)	K_{CO} (0.8)	

Table II. Molecular Parameters Obtained from Electrooptical Measurements on Systems I–VIII[a]

compd	$10^{20}E$ (m^2 V^{-2})	$10^{38}F$ (C m^2 V^{-1})	$10^{38}G$ (C m^2 V^{-1})	$(F + G)/3$	θ[b]
I	137.8	13.5	22.8	12.2	≈0
II	−9.9	9.0	−4.2	1.6	
III	−26.8	4.0	−7.2	−1.1	≈90
IV	69.2	12.1	18.5	10.2	≈0
V	5.7	4.8	3.2	2.7	
VI	−13.8	2.5	−4.2	−0.6	≈90
VII	17.7	9.9	16.7	8.9	≈0
VIII	1.6	5.9	6.3	4.1	

[a] The average estimated error in the values reported is within 10%. [b] θ is the angle between the dipole moment (μ_g) and transition moment (p) vectors. For meta-substituted compounds this angle is $0 < \theta < 90$.

No correction has been made either for the effect of dipole reaction field or for the contribution of molecular polarizability to the electric field signal. The magnitude of these effects is expected to be small for these types of highly dipolar molecules. In fact, recent electric field measurements, comparing gas-phase and solution-phase results on similar molecules, show that the combined error due to the lack of the above corrections amounts to less than 10%.[13]

Theoretical Calculations

The empirical modification of the basic Hückel molecular orbital method, applied here, has been described in detail elsewhere.[11b,c] The coulomb integral terms H_{ii} for the heteroatoms of the aromatic side chain were obtained with the approximate linear relationship between E_{HOMO} and I_p reported by Streitwieser for a series of aromatic hydrocarbons.[14] The bond integrals H_{ij} were obtained from the curved relationship between K_{XY} and the experimental XY bond length, also reported by Streitwieser.[14] The values of H_{ii} and H_{ij} obtained in this way for various atomic centers and bonds are given in Table I. For the aromatic ring carbons, standard values of H_{ii} and H_{ij} were used unmodified. Overall, the combination of these empirically derived H_{ii} and H_{ij} terms led to the calculated electron density distributions from which dipole moments were calculated. Excited-state dipole moments were calculated by promoting one electron from the HOMO to the LUMO and recalculating the q_i terms. In addition, symmetries of the calculated HOMO and the LUMO could be used to predict the directions of transition moments with respect to the dipole moment.

Experimental Results

For the sake of convenience in discussion the compounds will be grouped together in the following way: compounds I, IV, and VII (all para disubstituted) will be indicated as p-A-ph-D systems, compounds II, V, and VIII (all meta disubstituted) as m-A-ph-D systems, and compounds III and VI (all 1,3,5-trisubstituted) as 3,5-A$_2$-ph-D systems. The absorption spectral features of all three series of compounds reveal a regular trend. For example, in each series the long wavelength absorption maxima follow the trend $\lambda(p$-A-ph-D$) < \lambda(m$-A-ph-D$) < \lambda(3,5$-A$_2$-ph-D$)$, whereas the corresponding intensities are in the reverse order.

The molecular parameters for each series, obtained from electric field experiments, are shown in Table II. The excellent fit between the calculated and observed electric field spectra (see Figure 2 for a typical example) shows that eq 1 adequately describes the field-induced changes in the absorption spectrum. Since the contribution of the second derivative term (see eq 1) to the electric
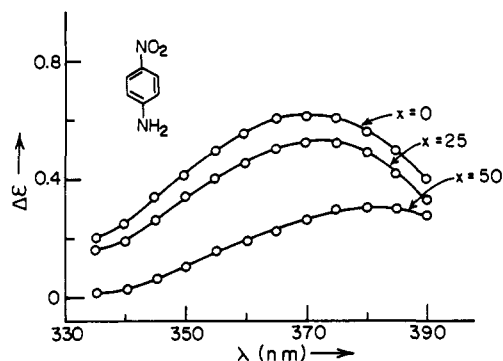
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Figure 2. Electric field spectrum of p-nitroaniline at three different χ values in dioxane solution at 298 K. The circles indicate mean experimental data points, and the solid line is the calculated curve estimated by multiple linear regression.
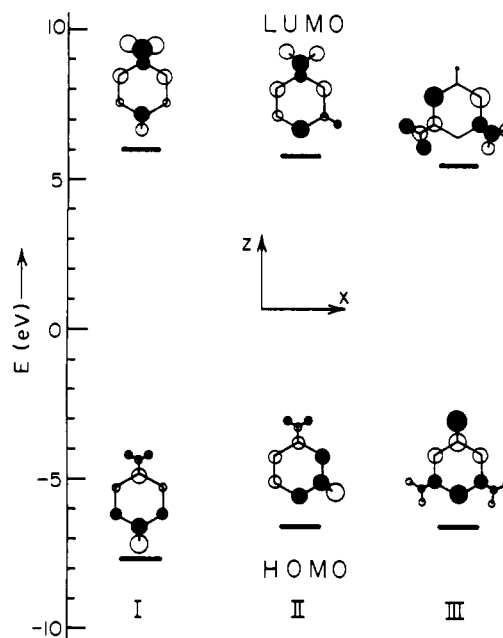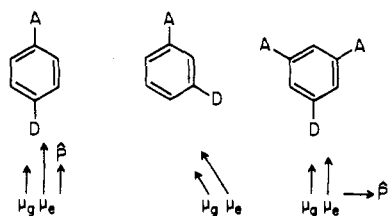

Figure 3. Energy levels and molecular orbital coefficients of the HOMO and LUMO of compounds I, II, and III calculated by modified HMO method.

field signal was very small, the values of H and I (see eq 4) cannot be obtained accurately. Similar observations have been made for other polar molecules in solution as well.[11b,c,12] Therefore, this term has been neglected in the regression analysis.

With the coefficients E–G, determination of individual electronic parameters, such as μ_g, μ_e, $\Delta\mu$, etc., is possible for molecules possessing suitable symmetry. For example, in molecules having C_{2v} symmetry, since the dipole moment and the transition moment vectors must be either perpendicular or parallel to each other, i.e., $\hat{p} \cdot \mu_g$ must be either zero or equal to μ_g. Thus eqs 5–7 can be reduced to simple form allowing the determination of individual parameters with reasonable accuracy. In the present case, although the above simplification can be applied to p-A-ph-D and 3,5-A$_2$-ph-D systems, similar simplification in case of the m-D-ph-A system should be treated with caution due to its low symmetry. However, composite parameters, as shown in Table II, can be used to analyze the relative directions of the dipole moment and transition moment vectors.

For p-A-ph-D type compounds the magnitude of E is large and positive, and F is nearly equal to $(F + G)/3$. This indicates for these molecules $\hat{p}$, μ_g, and $\Delta\mu$ are all in the same direction. On the other hand, in 3,5-A$_2$-ph-D type compounds the negative values of E and nearly zero magnitude of $(F + G)/3$ indicate $\hat{p}$ is perpendicular to the direction of μ_g and $\Delta\mu$. However, positive F indicates μ_g and $\Delta\mu$ are in the same direction. For m-D-ph-A type compounds, where the above simplifications cannot be applied,

Figure 4. Relative orientation of the transition moment, μ_g and μ_e, in p-A-ph-D, m-A-ph-D, and 3,5-A$_2$-ph-D systems. In m-A-ph-D systems the angle between $\hat{p}$ and μ_g varies from 0° to 90° depending on the substituents.

Table III. Experimental and Theoretical Values of Dipole Moments of Compounds I–VIII[a,b]

compd	experimental			theoretical		
	μ_g	μ_e	$\Delta\mu$	μ_g	μ_e	$\Delta\mu$
I	6.2	13.5	7.2	6.0	19.1	13.1
II	4.9	11.6	6.7	5.1	17.0	11.9
III	5.7	8.2	2.5	5.6	12.9	7.3
IV	4.7	12.9	8.2	5.6	17.1	11.5
V	3.9	9.4	5.5	4.5	14.9	10.4
VI	4.2	6.3	2.4	5.3	11.0	5.7
VII	3.6	12.9	9.3	3.8	11.2	7.4
VIII	3.0	10.1	7.1	3.8	13.7	9.9

[a] Dipole moments are in Debye unit. [b] The average estimated error in the dipole moment values is within 10%.

it is evident that the magnitude and signs of the parameters [E, F, $(F + G)/3$] are dependent on the nature of the substituents, and direct comparison of the parameters, as done above, indicates that the angle between μ_g or μ_e and $\hat{p}$ lies between 0° and 90° depending on the nature of the substituents (i.e., $0 < \theta < 90$).

The experimental values of μ_g, μ_e, and $\Delta\mu$ for each molecule are summarized in Table III. μ_g's are either taken from reported values or determined by the dielectric method.[15] For m-A-ph-D systems the $\Delta\mu$ values were obtained from eq 6, by assuming that μ_g and $\Delta\mu$ are parallel. This assumption is supported by theoretical calculations (see theoretical results and Figure 4), which show that the angle between μ_g and $\Delta\mu$ does not exceed 5° for the three m-A-ph-D systems studied here.[16] Taking this into account, the percentage error in the evaluation of $\Delta\mu$ from eq 6 should be less than 5% for these molecules. Furthermore, the relative magnitudes of $\Delta\mu$'s of I and II (see Table III) match those reported by solvatochromic shift methods ($\Delta\mu$(I) = 10.1D, $\Delta\mu$(II) = 7.5D).[17] Analysis of the data in Table III reveals several general features concerning the charge migration in the ground and excited states of substituted benzenes. In p-A-Ph-D systems both μ_g and $\Delta\mu$ have higher magnitude due to the extensive conjugation present in the ground state, which is enhanced further upon electronic excitation. In m-A-Ph-D systems, even though μ_g's are decreased considerably due to reduced conjugation in the ground state, μ_e's are substantially higher, indicating extensive charge migration in the excited state from D to A orbitals, even though the substituents are meta to each other. However upon introducing a second meta substituent in the m-A-ph-D system, as in 3,5-A$_2$-ph-D systems, the resultant charge distribution is modified considerably. In fact, the $\Delta\mu$'s have minimum values in comparison to meta- and para-substituted ones, reflecting inefficient charge migration in such systems on electronic excitation.

Theoretical Results

Modified HMO calculations were carried out to obtain a theoretical explanation for the observed changes in dipole moment.

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(16) The directions of μ_g and μ_e were found by obtaining the position of the centers of gravity of positive and negative charges both in the ground and excited states. Such calculations indicated that even though the centers of gravity of positive and negative charges are shifted considerably in the excited state in comparison to the ground state, the directions of μ_g and μ_e are parallel in compounds II and V and nearly 7° apart in compound VIII.

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In spite of its simplicity, this method has been shown to predict satisfactorily the charge-transfer properties of excited states of nitroaromatics in particular, as compared to other sophisticated semiempirical SCF methods, such as MNDO, MINDO/3, and AM1. This has been correctly pointed out in our previous papers and also by other authors.[11b,18]

The energies of the HOMO and LUMO of I, II, and III are shown in Figure 3. The regularity of the change in energy on variation of substituent position is apparent from the above figure. In the meta isomer the HOMO in each case is destabilized in comparison to that in the corresponding para isomer, as expected. This can be explained in valence bond terms as due to a lower contribution of dipolar resonance structures to the total molecular wave function in the case of meta-substituted species. Substitution of an additional meta substituent, as in 3,5-A$_2$-ph-D systems, hardly affects the energy of the HOMO. However, the effect of the substituent position on the relative energy of LUMO is worth noticing. Interestingly, the LUMO of the m-D-ph-A system and the 3,5-A$_2$-ph-D system is stabilized with respect to that of the p-D-ph-A system. Similar variations in energy were also noticed in the case of other two series, i.e., nitroanisoles and nitrophenylacetylenes. This is clearly in line with the red shift observed in the absorption spectrum, pointed out earlier.

The contributions of the molecular orbital coefficients to the HOMO and LUMO of compounds I, II, and III are also shown in Figure 3. The MOs of the other two series (nitroanisoles and nitrophenylacetylenes) show very similar characteristics. Significant contributions from intramolecular charge-transfer structures to the molecular wave function, particularly involving the LUMO, are apparent in p-A-ph-D systems. This is obvious from the large values in μ_g's and μ_e's calculated for such systems (see Table III). In m-A-ph-D systems, even though the μ_g's reflect reduced contributions of ionic structures in the ground state, which is expected due to the meta positions of the substituents, the large $\Delta\mu$ values calculated, which are comparable to those of the corresponding para isomer, indicate significant charge transfer from D to A orbitals upon electronic excitation.

In 3,5-A$_2$-ph-D systems the additive nature of the dipole moment vectors in the ground state is very evident, since μ_g increases relative to that of m-A-ph-D system and approaches the value of the p-A-ph-D system. In contrast, μ_e of 3,5-A$_2$-ph-D drops significantly with the appearance of a nodal plane along the symmetry axis of the molecule. The decrease in $\Delta\mu$ of this system in comparison to that in the para and meta systems can be assigned to a large decrease in the distance between the centers of gravity of the positive and negative charges due to the fact that the negative charge is shared by the two symmetrically positioned –NO$_2$ groups in the excited state. Furthermore, this is also accompanied by a relatively small degree of charge transfer from donor to the acceptors. The calculated and observed dipole moments follow the same trend, even though their magnitudes differ significantly.

Symmetry properties of the HOMO and LUMO can be used to assign the polarization direction of the transition in each case, except for the m-D-ph-A system, due to its lower symmetry. In p-A-ph-D systems the HOMO(b$_2$) to LUMO(b$_2$) transition is A$_1$ type, which is M$_z$ polarized and hence parallel to the dipole moment direction (see Figure 3 for molecular coordinate axes). On the other hand, in the 3,5-A$_2$-ph-D systems the HOMO is b$_2$ type, whereas LUMO changes to a a$_2$ type orbital. Therefore the resulting transition is M$_x$ polarized and should be perpendicular to the direction of the dipole moment vector. Experimentally, the direction of the transition moment vector with respect to the dipole moment can be determined reasonably accurately from eq 5, i.e., a positive slope of the plot of A_x vs ($3 \cos^2 \chi - 1$) indicates two vectors are nearly parallel and a negative slope is an indication that the vectors are nearly perpendicular. As shown in Table II, the theoretical predictions for transition polarization agree very

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well with the experimental results.

Discussion

Both physical and chemical properties of molecules are modified considerably upon electronic excitation and are often in complete contrast to ground-state properties. Ground- and excited-state dipole moments, being intrinsic properties of a molecule, reflect directly the magnitude of the difference in the electronic charge distribution in the ground and excited states. Therefore, measurement of such quantities should help to rationalize various unusual observations that seem to depend on the electronic charge distribution. The change in dipole moment ($\Delta\mu$) upon electronic excitation is particularly important in this respect.

The three different series of molecules studied here have, in each case, a common acceptor group $-NO_2$, whereas the nature of the donor groups is variable. For example, the $-NH_2$ group is considered to be the strongest donor and the $-C\equiv CH$ group the weakest, according to ground-state properties. However, in each series the members differ from one another by the position of the substituents on the ring. These have been chosen to arrive at a possible correlation between excited charge-transfer properties and the position of the substituents.

In p-A-ph-D systems, where D is $-NH_2$ or $-OMe$ or $-C\equiv CH$ and A is a $-NO_2$ group (compounds I, IV, and VII), extensive charge transfer from D to A can be seen from the large $\Delta\mu$ values observed both experimentally and theoretically (see Table III and Figure 3). The HOMO to LUMO transitions in these cases have been found to be ^1L_a type, which is essentially a CT transition, polarized along the long molecular axis (symmetry axis) of the molecule. Similar observations have also been reported by McGlynn et al. from their systematic investigation of electronic spectra of disubstituted benzenes.[6] One observation worth pointing out is that in the p-A-ph-D systems μ_g decreases in the following order, i.e., D = $-NH_2$ > $-OMe$ > $-C\equiv CH$, as expected since the relative conjugative power of these donor groups varies in the same order. However, a careful examination of $\Delta\mu$ values indicates that the above trend is no longer true in the excited state, and, in fact, $\Delta\mu$ increases in reverse order as compared to μ_g, suggesting that the contributions of ionic structures to the molecular wave function can be substantially different in the excited state. This observation clearly demonstrates that the excited-state substituent effect must be quite different from the ground-state substituent effect, which has also been predicted by other workers from their studies of various photochemical reactions.[19] However, theoretically calculated $\Delta\mu$ values do not reflect the trend observed experimentally since both μ_g and $\Delta\mu$ values decrease with the conjugative power of the donor group. As reported earlier, since excited-state charge transfer is not only dependent on the nature of the substituents but also on the nature of the HOMO and LUMO involved in the electronic transition, this reverse order of $\Delta\mu$ could be due to the combination of both effects.[11b,c] It has been found that in nitrobenzene the LUMO is predominantly localized on the antibonding nitro group orbital.[11b] However, substitution of a strong electron-donating substituent, such as $-NH_2$ at the para position, results in more mixed character of both HOMO and LUMO. Therefore, since both HOMO and LUMO are less localized, but delocalized over the whole molecular skeleton, the overall shift in the electron density may be relatively small, resulting in small or moderate $\Delta\mu$. On the other hand, in the case of a weak donor, such as $-C\equiv CH$, where the localization of LUMO could be still effective due to weak interaction of the donor, the net shift in the electron density may be quite large reflecting a larger $\Delta\mu$. The larger $\Delta\mu$ in the case of compound VII (D = $-C\equiv CH$) in comparison to compound I (D = $-NH_2$) could also be partly due to larger effective distance of separation of the centers of gravity of positive and negative charges because in VII the LUMO will be mainly localized on the nitro group.

The study of m-D-ph-A systems is particularly important in rationalizing the meta-activating effect found in many photochemical reactions.[19] It has been observed that many substituents, which are ortho- and para-directing in the ground state, are strongly meta-directing in the excited state. Zimmerman et al. from their experimental and theoretical work[19c] suggested that effective transmission of electron density exclusively from or to the meta position depending on the nature of the substituent is the primary reason for such unusual photochemistry in the excited state. On the basis of these observations non-Kekulé valence bond structures have been proposed to explain the photochemical behavior. Therefore, since the meta effect is primarily the enhancement or reduction of electron density upon electron excitation at the meta position, the experimental $\Delta\mu$ values should provide direct evidence for such electron shifts. Both theoretical and experimental $\Delta\mu$ values (see Table III) of m-A-ph-D systems have been found to be quite large and comparable to those of corresponding para isomers, indicating significant charge redistribution in the excited state. Assuming that the charge transfer takes place from the D to the A group and taking the distance between the centers of positive and negative charges into account, it can be shown that the percentage of charge transfer in both p-A-ph-D and m-A-ph-D systems is nearly equal in magnitude. Since the usual valence bond structures, as in p-A-ph-D systems, cannot be used to account for the large dipole moment change in meta systems, resonance forms of non-Kekulé type may be the contributing structures in excited states of m-A-ph-D systems which control the photochemical reactivity, as correctly pointed out by Zimmerman et al.[19c] Furthermore, it is apparent from the data of Table II (from E and $(F + G)/3$ values) that the angle between the dipole moment and transition moment vectors is dependent on the nature of the substituents. For example, for strong A and weak D, as in compound VIII, this angle is small, whereas in compound III, where both D and A are strongly interacting in nature, the vectors are nearly perpendicular to each other.

Substitution of a second meta substituent, as in 3,5-A_2-ph-D systems, has a profound effect not only on the resultant charge distribution upon electronic excitation but also on the direction of the polarization of transition. For such systems the dipole moment and transition moment vectors are perpendicular to each other (see E and $(F + G)/3$ values of compounds III and VI) suggesting that the longest wavelength transition is ^1L_b type, polarized perpendicular to the principal symmetry axis of the molecule. This is in contrast to the p-A-ph-D systems, where the transition is ^1L_a type and parallel to the principal symmetry axis. Theoretical predictions, which show that the HOMO-to-LUMO transition changes from A_1 type in the case of p-D-ph-A systems to B_1 type in 3,5-A_2-ph-D systems, are in accord with the experimental results. A theoretical prediction for the transition polarization direction of (3,5-dinotrophenyl)acetylene, which is the analogue of compounds III and VI, is virtually identical with the 3,5-A_2-ph-D systems studied here (see Discussion later).

As pointed out earlier, the change in dipole moment ($\Delta\mu$) for 3,5-A_2-ph-D systems is found to be very small when compared with those of other two systems. Theoretically, the appearance of a nodal plane along the principal axis of the molecule in the LUMO (see Figure 3) can be used to explain the small degree of charge transfer in the excited state. In fact, the calculated $\Delta\mu$ for such systems are found to be smaller (see Table III) in comparison to those of the other two systems, if the node is present in the LUMO. The presence of a nodal plane through the reaction center in the excited state can have a large impact on photochemical reactions which are known to follow ionic mechanisms. Recently, this has been found to be true for photooxidation of nitrobenzyl alcohols.[20] For example the order of reactivity of photooxidation has been found to be (m-nitrophenyl)benzyl alcohol > (p-nitrophenyl)benzyl alcohol $\gg$ (3,5-dinitrophenyl)benzyl alcohol.[20b] In fact, the latter compound is essentially unreactive under conditions where both the meta- and para-substituted

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compounds react readily photolytically. Such an unusual order of reactivity of nitrobenzyl alcohols can be nicely interpreted in terms of the results presented in this paper. Furthermore, from the point of view of the appearance of nodal planes and less significant charge transfer in the excited state of 3,5-A$_2$-ph-D systems, one would predict that (3,5-dinitrophenyl)acetylene should undergo no or inefficient photohydration reaction.[21] The photophysics and photochemistry of such systems are currently under investigation in our laboratory.

Finally, Figure 4 summarizes the relative directions of $\bar{p}$, μ_g, and μ_e for all three different substituted benzene systems studied here. Even though these directions are definitively assigned for *p*-A-ph-D and 3,5-A$_2$-ph-D systems, similar assignment is less clear in the case of corresponding meta isomers. However, the experimental values in Table II suggest that depending on the nature of the substituents the angle θ varies between 0° and 90° (0° < θ < 90°).

Both (*p*- and (*m*-nitrophenyl)acetylene (compounds VII and VIII) are known to undergo fast and efficient photohydration from the first excited triplet state.[21] The enhancement of reactivity in both singlet and triplet state photohydrations has been explained as due to a high degree of charge transfer in the respective states, which facilitates the protonation step. $\Delta\mu$ values of (*p*- and (*m*-nitrophenyl)acetylene, which are quite large, provide direct evidence for extensive charge transfer in the excited state of such systems. Though the $\Delta\mu$ values represent the charge transfer in the excited singlet π,π^* state, there is no reason to invalidate a similar magnitude of charge transfer in the triplet $\pi\pi^*$ state of VII and VIII, from which the reaction proceeds in the above systems. In fact, semiempirical MO calculations on simple nitro compounds show very little difference in the calculated dipole moments of corresponding singlet and triplet states, which supports the above argument.[22]

Experimental Section

Conclusion

Variation of nature or position of substituents on the benzene ring has a profound effect on the charge-transfer characteristics of the molecule, particularly in the excited state. The simple additive nature of group moments, which is true for the ground state, is found to be inapplicable in explaining the observed dipole moment of the excited state. This indicates quite different substituent effects in the excited state. Depending on the position of the substituents, the direction of the transition moment varies between 0° and 90° with respect to the direction of μ_g, rendering the HOMO-to-LUMO transition either ^1L_a or ^1L_b type in the extreme cases. Occurrence of extensive charge transfer in the excited states and the presence of a nodal plane through the reaction center are found to be the key factors in many photochemical reactions.

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Kinetics of Static and Diffusive Electron Transfer between Zinc-Substituted Cytochrome *c* and Plastocyanin. Indications of Nonelectrostatic Interactions between Highly Charged Metalloproteins

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Abstract: Cupriplastocyanin, pc(II), quenches the triplet state of zinc cytochrome *c*, ^{3}Zn(cyt), by electron transfer as shown in Scheme I. All the experiments are done at pH 7.0. Nonredox modes of quenching are ruled out by detection of the cation radical Zn(cyt)$^+$ and by experiments in which redox quenching is precluded. At the ionic strengths of 0.100 M and higher, the electron-transfer reaction occurs bimolecularly, via the encounter complex ^{3}Zn(cyt)/pc(II); $k_f = (2.8 \pm 0.6) \times 10^5$ s^{-1}, and the equilibrium constant K_a depends on ionic strength. At the ionic strengths of 10 mM and lower, the reaction can be made to occur predominantly unimolecularly, within the preformed complex ^{3}Zn(cyt)/pc(II); $k_F = (2.5 \pm 0.4) \times 10^5$ s^{-1} within ^{3}Zn(cyt)/pc(II), and $k_B = (1.1 \pm 0.5) \times 10^6$ s^{-1} within Zn(cyt)$^+$/pc(I). The rate constant k_f is independent of ionic strength (in the range from 10 to 100 mM) and so is the rate constant k_F (below 20 mM). The equality of k_f and k_F shows either that the encounter complex and the preformed complex have structures with equal electronic couplings and activation energies for electron transfer or that both complexes can reach such structures by fast rearrangement before the electron-transfer step. The estimated association constant K_a for zinc cytochrome *c* and cupriplastocyanin at zero ionic strength is $(2 \pm 1) \times 10^7$ M^{-1}. Cytochrome *c* interacts similarly with various anionic metalloproteins, and replacement of iron with zinc does not noticeably alter these docking interactions. As the ionic strength increases, the efficiency of charge separation in the bimolecular reaction first increases and then decreases. At high ionic strength, even these charged proteins perhaps attract each other by hydrophobic or other nonelectrostatic forces.

I. Introduction

Metalloproteins participate in various biological oxidoreduction processes, and it is important to understand kinetics and mech- anisms of their electron-transfer reactions. Many studies have dealt with bimolecular reactions between proteins and, lately, also with unimolecular reactions within modified proteins[1-12] and within