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Hole Transfer Equilibrium in Rigidly Linked Bichromophoric Molecules

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Two bichromophoric molecules consisting of anthracene and diphenylpolyene moieties linked by two fused norbornyl bridges undergo photoionization upon ultraviolet (UV) pulsed laser irradiation. The simultaneous observation of the cation radicals of both anthracene and polyene groups points to a rapid (nanosecond or faster) intramolecular hole transfer equilibrium between the two chromophores. The existence of an equilibrium is supported by the results of one- and two-laser transient absorption and electrochemical experiments. Equilibrium constants (293 K) were determined by both transient absorption and cyclic voltammetry measurements and were independent of the method used within experimental error. For A-sp-VB, which contains anthracene and vinyldiphenylbutadiene chromophores, $K_{eq} = 4.0 \pm 2$ (transient absorption) and 3.2 ± 2 (electrochemical), favoring the anthracene cation radical. For A-sp-VS, containing anthracene and vinylstilbene groups, $K_{eq} = 70 \pm 30$ (transient absorption) and 105 ± 50 (electrochemical), favoring the anthracene cation radical.

Introduction

The synthesis of polychromophoric molecules that can perform the same tasks as devices manufactured with bulk materials has recently received considerable attention. Thus, molecules have been designed to carry out the functions of a variety of electronic devices including wires, switches, gates, rectifiers, and diodes.[1] The common feature of these molecules is their ability to undergo rapid and/or controlled intramolecular charge and energy transfer. Many intramolecular charge-transfer studies have focused on photoinduced electron transfer in charge-neutral ground-state molecules, but in some studies hole transfer has also been reported. Thus, the intramolecular migration of charge has been reported for bi- and polychromophoric molecules in which the ground-state molecule is charged or where charge is created following photoexcitation or pulse radiolysis.[2] Closs reported intramolecular hole transfer in bichromophores consisting of naphthalene and a variety of aromatic charge acceptors bridged by cyclohexane, androstane, and *trans*-decalin structures.[2a,b] Transfer lifetimes in these molecules were related to the number of intervening bonds in the bridges and the stereochemistry of the chromophores relative to the bridge (axial or equatorial) and were generally on the order of a few nanoseconds or less. A through-bond mechanism was suggested. Paddon-Row et al.[2f] also observed rapid (subnanosecond) through-bond hole transfer following pulse radiolysis of a naphthalene−dimethoxynaphthalene bichromophore that utilizes norbornyl spacers. A similarly fast rate was also observed for intramolecular anion transfer in molecules containing the same norbornyl bridges.[3] Lindsey recently reported energy transfer and electron/hole hopping in homo- and heterodimers consisting of zinc tetraphenylporphyrin and free base porphyrin moieties linked by phenylene or diarylethyne groups.[2c] In the zinc homodimers, hole hopping was suggested by an analysis of electron paramagnetic resonance (EPR) line widths, and estimates of the hole transfer rates were made based on the time resolution of the EPR technique, with the rate constants ranging from $<4 \times 10^5$ to $>2 \times 10^7$ s^{-1} depending on fluorine substitution of the phenyl rings. A through-bond mechanism was suggested based on the distance of separation between chromophores.

Hole transfer has also been observed in tri- and tetrachromophores following photoinduced charge separation. Osuka et al.[2d] investigated hole transfer in a trichromophore consisting of zinc tetraphenylporphyrin, a free base porphyrin, and pyromellitimide groups linked by a variety of aryl spacers. Excitation of this molecule initially results in charge separation between the free base porphyrin and the pyromellitimide, followed by hole transfer to the zinc tetraphenylporphyrin, with a rate constant governed by the linker. Rate constants (measured by picosecond absorption) ranged from 5×10^{10} s^{-1} for a simple phenylene linker to $<10^8$ s^{-1} for a phenylene−bicyclooctyl−phenylene spacer. Gust and co-workers[2e] have reported a hole transfer process in a carotenoid − free base porphyrin − quinone − quinone tetrachromophore that is also initiated by photoinduced charge separation. No kinetics were reported for this system.

Our studies of intramolecular transfer to date have been focused on singlet−singlet and triplet−triplet energy transfer (SSET and TTET, respectively) in bi- and trichromophores incorporating rigid norbornyl spacers[4] as well as flexible

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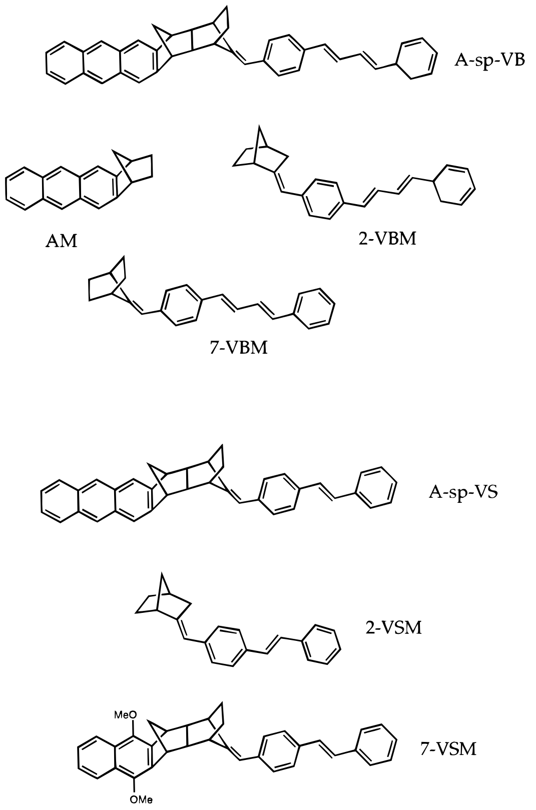

methylester[5] and peptide[6] bridging groups. We recently reported rapid intramolecular TTET from upper excited triplet states in a series of molecules, each of which contained an anthracene triplet energy donor linked by way of two norbornyl spacer groups to alkene, diene, and styryl energy acceptors.[4] In addition to TTET, a common photochemical feature of these compounds was the efficient photoionization of the anthracene chromophore, as evidenced by the intense cation radical absorption at λ_{max} 730 nm.[7] Production of cation radicals in these compounds provided the opportunity to study hole transfer behavior in these systems. To this end, we have synthesized the bichromophores A-sp-VB and A-sp-VS shown with a variety of model compounds in Chart 1. Each of these bichromophores incorporates the anthracene group joined via two norbornyl spacer groups to a diphenylpolyene chromophore. The latter are known to photoionize readily and in the process form strongly absorbing cation radicals,[8] thereby providing a potential spectroscopic probe for the hole transfer process. We report here our observations for these molecules. In addition to forming triplet states, photoexcitation of A-sp-VB and A-sp-VM causes the production of both the anthracene and polyene cation radicals. Evidence was obtained illustrating an intramolecular hole transfer equilibrium between the two chromophores.

Experimental Section

Materials and Methods. All synthetic starting materials and solvents for spectroscopic studies (spectrophotometric grade) were used as received from Aldrich.

Syntheses: General Methods. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on either a Bruker ACE 200 (200 MHz) NMR spectrometer or a Bruker Avance 400 (400 MHz) NMR spectrometer. Chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) at 0.00 ppm. ^{13}C NMR spectra were recorded using a Bruker Avance-400 spectrometer at 100.66 MHz. Infrared (IR) spectra were obtained with a Perkin-Elmer 683 spectrometer or a Perkin-Elmer 1600 Series Fourier transform infrared (FT-IR) spectrometer. The ultraviolet (UV) spectra were recorded with a Hitachi U2000 UV−vis spectrometer. Melting points are uncorrected.

Analytical thin-layer chromatography (TLC) was performed with precoated silica gel plates (0.25 mm, Merck 60F254) with 254 nm fluorescence indicator and were visualized under a UV lamp. Flash chromatography was performed on J. T. Baker 40 μm diameter silica gel under a positive pressure of air. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone just prior to use. Toluene, ethanol, and dichloromethane were distilled under nitrogen from calcium hydride immediately prior to use.

All reactions were carried out under nitrogen, and all extracts were dried over anhydrous Na_2SO_4 or $MgSO_4$.

Syntheses of the compounds used in this study are provided in Supporting Information.

Absorption Spectroscopy. Ground-state absorption spectra and extinction coefficients for the compounds studied were obtained with a Shimadzu 2100U absorption spectrometer.

Laser Flash Photolysis. The laser flash photolysis system has been described in detail elsewhere.[4,9] Briefly, for kinetic studies and transient absorption spectra, solutions were prepared at concentrations sufficiently large to give absorbances in the range 0.6−0.8 at the excitation wavelength. Unless otherwise noted, the solutions, contained in a reservoir, were continuously purged with a stream of nitrogen and were caused to flow through a specially constructed quartz cell (7 × 7 mm) with a peristaltic pump. This procedure ensured that a fresh volume of solution was exposed to each laser pulse, thereby avoiding accumulation of any photoproducts. Samples were irradiated with the pulses of a Lumonics EX 510 excimer laser (308 nm; ∼ 20 mJ/pulse; 8-ns pulse duration) or the frequency-tripled output of a Continuum Nd:YAG laser (355 nm, ∼30 mJ/pulse, 5 ns). In the two-laser studies, the 308 (or 355)-nm pulse was followed, after a period of 1−2 μs, by the pulse from a flashlamp-pumped dye laser (590 nm; <120 mJ; ∼400 ns). All experiments were carried out at 293 K.

Electrochemistry. Cyclic voltammetry was performed with a PAR model 273A Potentiostat/Galvanostat interfaced to a personal computer (PC) using the EG&G model 270 software package. The cell was a standard three electrode setup using a 3-mm diameter glassy carbon or 1-mm diameter gold working electrode, a platinum coil counter electrode, and a reference electrode consisting of a silver wire in a glass tube with a cracked glass seal containing a 0.1 M solution of tetrabutylammonium perchlorate (TBAP) in acetonitrile. All measurements were internally referenced to the ferrocene/ferrocenium couple that has a potential of 0.440 V versus saturated calomel electrode (SCE). Acetonitrile was distilled from CaH_2 under 1 atm of argon prior to use. The supporting electrolyte, TBAP, was recrystallized three times from 10% hexane in ethyl acetate and dried in a vacuum oven (40 °C, 10 Torr).

Results and Discussion

Transient Behavior. Figure 1 shows the transient absorption spectra for the model compounds AM and 2-VBM obtained 1 μs after 355-nm pulsed laser photolysis of nitrogen-saturated cyclohexane solutions. The spectrum for AM is similar to the T−T absorption spectrum reported for anthracene[10] and, on this basis as well as the decreased lifetime observed in the presence of air, is assigned to the triplet state. The spectrum obtained for 2-VBM is similar to those of the triplet states of both 1,4-

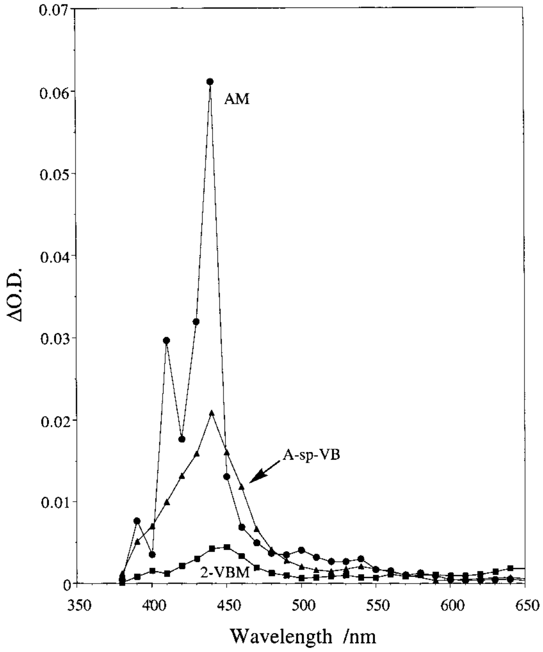

Figure 1. Transient absorption spectra for AM, 2-VBM, and A-sp-VB obtained 1 μs following 355-nm pulsed laser irradiation in nitrogen-saturated cyclohexane.

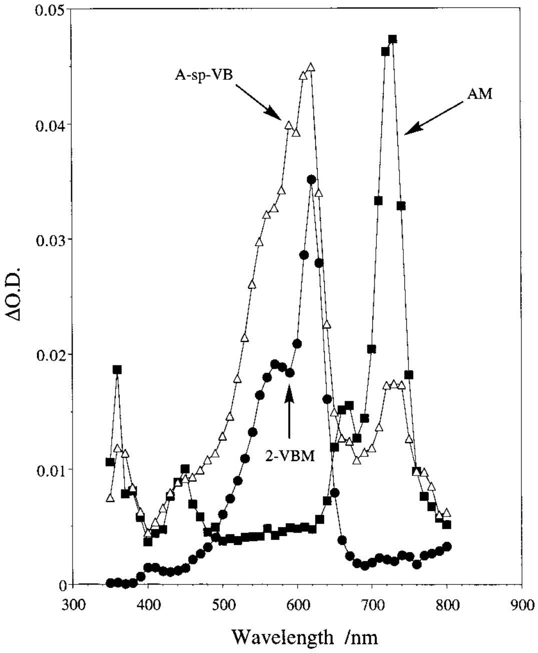

Figure 2. Transient absorption spectra for AM, 2-VBM, and A-sp-VB (open triangles) obtained 1 μs following 355-nm pulsed laser irradiation in air-saturated MeCN.

diphenyl-1,3-butadiene (DPB) and 1,6-diphenyl-1,3,5-hexatriene (DPH) reported previously[11] and repeated in this work. Its assignment as a triplet state is further supported by its sensitivity to air and its relatively weak absorption, reflecting the low Intersystem Crossing (ISC) quantum yield characteristic of α,ω-diphenylpolyenes. The T−T wavelength maximum for 2-VBM is nearly identical to triplet DPH (i.e., red-shifted 45 nm relative to DPB), indicating that the position of the phenyl rings relative to the double bonds in the polyene chain does not have a major impact on the triplet state spectroscopy. This lack of effect of phenyl ring position was also observed in the cation radical spectra, as described later. Although the decay of triplet AM follows monoexponential kinetics and is quite similar to that observed for anthracene, that of triplet 2-VBM exhibits nonexponential behavior, having both short and long components with the short-lived component increasing in importance at wavelengths lower than ~420 nm. This behavior was observed for both DPB and DPH and could be due to the excitation of a variety of ground-state polyene isomers or conformers, the triplet states of which possess different lifetimes.

Figure 1 also shows the transient absorption spectrum obtained for the bichromophore A-sp-VB under conditions similar to those used for AM and 2-VBM. The air-sensitive spectrum obtained was nearly identical to those of both AM and 2-VBM, although the shoulder seen in AM is absent. Thus, although the transient absorption is likely due to a triplet state, it is not clear from the spectrum alone whether it is an anthracene or polyene triplet or a mixture of both (the ground states of both chromophores absorb at the laser wavelength). However, the kinetic behavior of A-sp-VB parallels that of 2-VBM in that both slow and long components with roughly the same rate constants and relative contributions as those in 2-VBM were observed in the decay. From this observation we conclude that the polyene triplet is a major contributor to the spectrum of A-sp-VB. An important difference between the spectra of A-sp-VB and 2-VBM is the magnitude of the absorption at the maximum; that is, the absorbance for A-sp-VB is about four times that of 2-VBM for samples with matched ground state absorbance at the laser wavelength. Assuming that the incorporation of these two chromophores into the same molecule does not significantly increase the intersystem crossing yield for the polyene, the observed enhancement points to a possible intramolecular TTET process from the anthracene chromophore to the polyene chromophore. This suggestion is supported by the observation made previously of intermolecular TTET from anthracene to DPH.[11b] Our recent study of intramolecular TTET in rigidly linked bichromophores consisting of an anthracene donor and alkene and diene acceptors also supports this conclusion.[4] Experiments are underway to further characterize this process.

Figure 2 shows the transient absorption spectra obtained in air-saturated acetonitrile (MeCN) 1 μs following 355-nm pulsed laser photolysis of AM and 2-VBM. The band positions and shapes are nearly identical to those reported for the anthracene and DPH cation radicals, respectively,[7,8] produced by photoionization and on this basis are assigned as the cation radicals, $AM^{+\cdot}$ and $2\text{-}VBM^{+\cdot}$. The similarity of the $2\text{-}VBM^{+\cdot}$ and DPH $^{+\cdot}$ spectra is consistent with the similarity of the T−T absorption spectra of the two compounds as already described. Although observation of a solvated electron would have provided further confirmation of this photoionization process, the electron is known to react rapidly and irreversibly with the solvent, MeCN. Also, poor solubility prevented the use of water as solvent and although the solubility in methanol of these compounds was good, the spectral position of the solvated electron absorption in methanol lies in the same region as the strong cation radical absorptions.

Figure 2 also shows the transient spectrum obtained for A-sp-VB under similar conditions. This spectrum exhibits two major features with band shapes and positions similar to the cation radical absorptions observed in the model compounds. The anion radicals of these chromophores absorb in the same general spectral region as the cation radicals, but the observation of these transient absorptions under both nitrogen- and air-saturated conditions confirms their positively charged character. Thus, we assign the spectrum to the cation radicals of the anthracene and polyene chromophores. Because the ground states of both chromophores absorb appreciably at the laser wavelength (the ratio of ground-state extinction coefficients for the two model

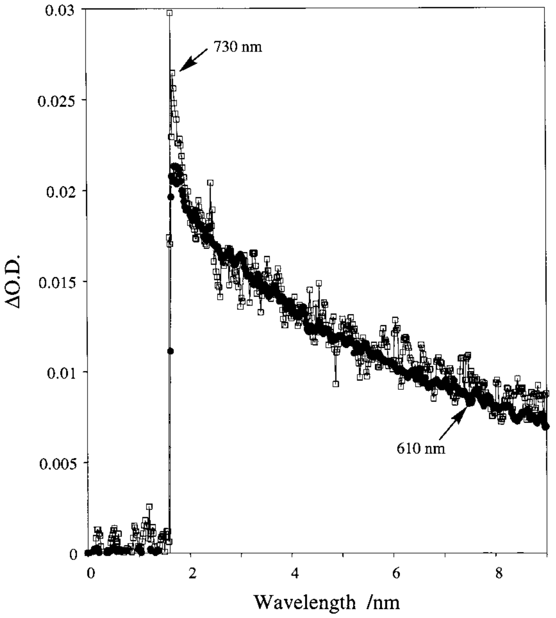

Figure 3. Transient decay monitored at 730 and 610 nm following 355-nm pulsed laser irradiation of A-sp-VB in air-saturated MeCN. The 730-nm profile is normalized to the 610-nm decay.

compounds at 355 nm in MeCN is $\epsilon_{2-\mathrm{VBM}}/\epsilon_{\mathrm{AM}} \approx 2$), it would seem likely that a fraction of each cation radical absorption is produced by direct photoionization (i.e., the two chromophores partition the excitation photons with the result that some molecules are initially photoionized in the polyene and others in the anthracene group). The photoionization mechanisms are discussed below.

Given the well-established ability of rigid spacers and in particular, norbornyl structures, to facilitate rapid intramolecular charge separation and hole transfer in bichromophores,[2f,12] the concurrent observation of both cation radicals suggests the possibility of an intramolecular hole transfer equilibrium between the chromophores. In addition to this observation, a rapidly established intramolecular hole transfer equilibrium was also supported by the following observations.

(i) The decay kinetics of the two cation radical absorptions in A-sp-VB were the same. This behavior is illustrated in Figure 3, which shows the decay profiles obtained at 610 and 730 nm (normalized to 610 nm). It is clear that with the exception of very short times after the laser pulse, the decays at both wavelengths are identical, whereas the decay kinetics for the cation radicals generated from the two model compounds were significantly different. In fact, the rapid decay at the beginning of the anthracene cation radical profile in A-sp-VB may reflect the rate at which the equilibrium is established; that is, the initial nonequilibrium concentration of the anthracene cation radical is larger than the equilibrium value. The fact that the only difference between the decay kinetics at these two wavelengths is observed at very short times after the laser pulse rules out the possibility of intermolecular interaction between chromophores. (The concentration of A-sp-VB used was $\sim 3 \times 10^{-5}$ M).

(ii) The dependence of the cation radical absorbances on laser intensity for the model compounds differed from that observed for the bichromophore. Figure 4 shows the intensity dependences for AM measured at 730 nm, 2-VBM measured at 610 nm, and A-sp-VB measured at 730 and 610 nm. For AM, the dependence appears to be monophotonic, although the downward curvature of the plot at higher intensities indicates either saturation of the ground state or interfering absorption due to another transient. For 2-VBM, the plot is curved upward, indicating a biphotonic ionization mechanism. These mono- and biphotonic behaviors have been reported previously for anthracene and DPH, respectively.[7,8a,13,14] In the bichromophore, A-sp-VB, however, the dependences at both monitoring wavelengths were the same and resembled that of AM. This result suggests that significant amounts of the anthracene and polyene cation radicals in A-sp-VB are produced by a common mechanism. Furthermore, the similarity between the behavior of AM and A-sp-VB suggests that ionization occurs primarily at the anthracene chromophore and is followed by production of the polyene chromophore by hole transfer. It is reasonable to suggest that monophotonic ionization of this chromophore is more efficient than biphotonic ionization of the polyene unless the two-photon cross section of the polyene is unusually large.

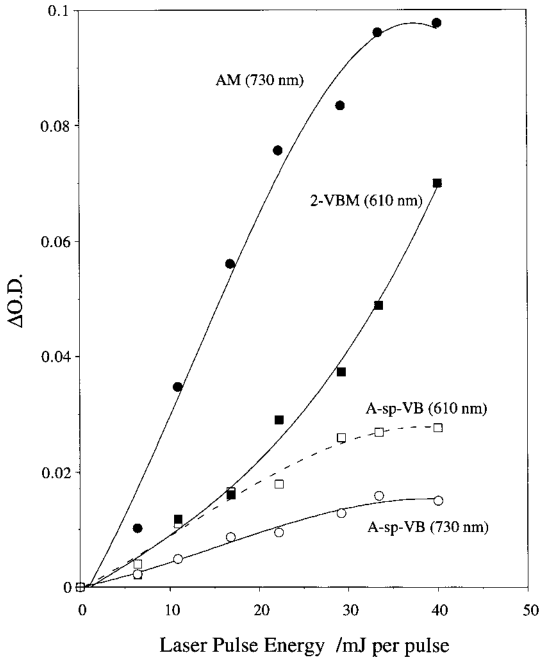

Figure 4. Dependence of transient absorption on 355-nm laser pulse energy for AM, 2-VBM, and A-sp-VB in air-saturated MeCN.

(iii) The ratio of cation radical absorbances in A-sp-VB is independent of laser excitation wavelength. Both 308 and 355 nm excitations lead to the same ratio even though the ground-state extinction coefficients of AM and 2-VBM (and therefore the anthracene and polyene chromophores in A-sp-VB) are significantly different at these two wavelengths. (At 355 nm, $\epsilon_{2-\mathrm{VBM}}/\epsilon_{\mathrm{AM}} \approx 2$; at 308 nm, $\epsilon_{2-\mathrm{VBM}}/\epsilon_{\mathrm{AM}} \approx 1.3$.)

(iv) The transient behavior of A-sp-VS differs from that of A-sp-VB. Electrochemical measurements (described in detail later) indicate that the oxidation potential of the vinylstilbene moiety in A-sp-VS is considerably more positive than that of the vinylbutadiene group in A-sp-VB and, as a result, the equilibrium should be shifted substantially in the direction of the anthracene cation radical in A-sp-VS. Figure 5 shows the transient absorption spectrum obtained following 355-nm photolysis of 2-VSM, AM (for comparison), and A-sp-VS in air-saturated MeCN. The spectrum of 2-VSM is similar to that obtained for 2-VBM, although the maximum is blue-shifted by ~60 nm. The spectrum is also nearly identical to that obtained for $\mathrm{DPB}^{+\cdot}$ reported previously and repeated in the present study and, on this basis, it is assigned as the 2-VS cation radical, $2\text{-VS}^{+\cdot}$. The spectrum of A-sp-VS differs from that of A-sp-VB in that the anthracene cation radical absorption is now considerably larger than that of the vinylstilbene cation radical. Although it is not possible to obtain cation radical extinction

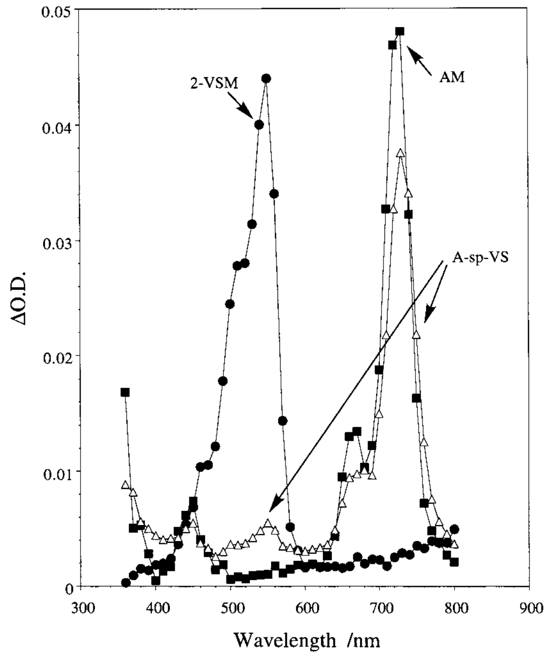

Figure 5. Transient absorption spectra for AM, 2-VSM, and A-sp-VS (open triangles) obtained 1 μs following 355-nm pulsed laser irradiation in air-saturated MeCN.

coefficients from this work, previous studies have reported the DPB and DPH cation radical extinction coefficients to be large ($\sim 10^5$ $M^{-1}cm^{-1}$) and comparable to each other.[8] If this relationship holds for the vinylpolyene groups in the present study, then the spectrum obtained for A-sp-VS suggests a considerably smaller vinylstilbene cation radical concentration and an equilibrium that more strongly favors the anthracene cation radical than in A-sp-VB. A complete discussion of equilibrium constants obtained from the spectral and electrochemical measurements is given later.

(v) Two-laser (two-color) excitation of A-sp-VB leads to transient changes that are consistent with disruption and reestablishment of an equilibrium. Figure 6 shows the kinetic decay profiles obtained following 355-nm + 590-nm photolysis of A-sp-VB in air-saturated acetonitrile. In this experiment, 355-nm excitation is used to produce the cation radicals. A 590-nm dye laser pulse fires ~ 1 μs after the first pulse and causes excitation of the polyene cation radical. This second excitation pulse results in a temporary depletion of the polyene cation radical absorption as monitored at 610 nm and concurrent enhancement of the anthracene cation radical absorption monitored at 730 nm. We interpret this result as a photoinduced transient disruption of the anthracene−polyene cation radical equilibrium followed by reestablishment of the equilibrium after the 590-nm pulse ends. We have demonstrated previously that photoexcitation of cation radicals (including DPH) and other positively charged species increases their ability to oxidize added substrates.[15] For example, the ground-state $DPH^{+\cdot}$ is unreactive toward 1,2-dimethoxybenzene (veratrole). However, the cation radical excited state produced following 590-nm excitation is efficiently quenched by this electron donor.

The depletion/enhancement caused by the 590-nm pulse in A-sp-VB follows the dye laser pulse profile (400-ns pulse duration), That is, both effects ‘track’ the dye laser pulse profile rather than exhibiting exponential behavior. This result indicates that the kinetics of the equilibrium are on the nanosecond time scale or shorter, in agreement with the nanosecond and subnanoscond hole transfer observed previously.[2f]

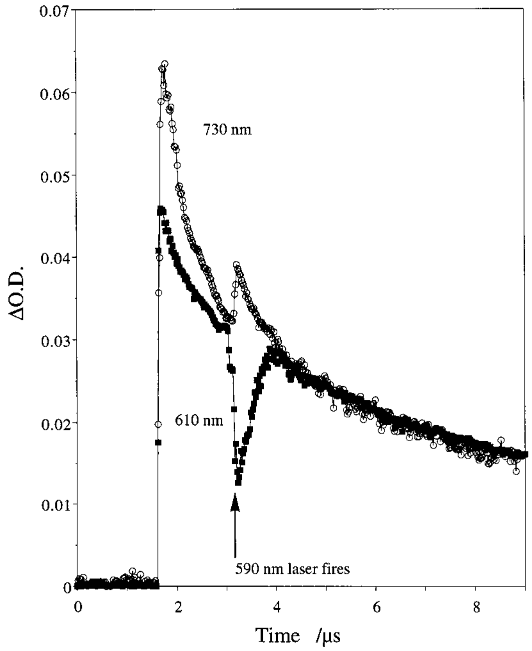

Figure 6. Transient decay monitored at 730 and 610 nm following 355-nm + 590-nm two-laser irradiation of A-sp-VB in air-saturated MeCN. The 590-nm laser fires ~ 1.5 μs following the 355-nm pulse. The 730-nm profile is normalized to the 610-nm decay.

Spectroscopic and Electrochemical Estimates of the Intramolecular Hole Transfer Equilibrium Constant. From the transient spectra for A-sp-VB and A-sp-VS and estimates of the cation radical extinction coefficients for the anthracene and polyene chromophores it is possible to calculate the hole transfer equilibrium constants for these compounds. Although the extinction coefficients for AM and the vinylpolyene models are not available, values have been reported for the anthracene cation radical ($\epsilon_{730} = 1.16 \times 10^4$ $M^{-1}cm^{-1}$),[16] and for the polyenes that are closest in spectroscopic behavior to the vinylstilbene and vinylbutadiene cation radicals; $DPB^{+\cdot}$ ($\epsilon_{540} = 1.2 \times 10^5$ $M^{-1}cm^{-1}$) and $DPH^{+\cdot}$ ($\epsilon_{610} = 1{-}2 \times 10^5$ $M^{-1}cm^{-1}$).[8] Given the range of values reported for $DPH^{+\cdot}$, we have chosen, somewhat arbitrarily, the same extinction coefficient, 1.2×10^5 $M^{-1}cm^{-1}$, for both vinylstilbene and vinylbutadiene cation radicals. These values and the transient absorbances yield K_{eq}(A-sp-VB) ≈ 4 and K_{eq}(A-sp-VS) ≈ 70, favoring the anthracene cation radical.

In principle, it should also be possible to determine the equilibrium concentration of the anthracene and polyene cation radicals from their respective standard potentials ($\Delta G_{ET} = -F(E^\circ_{+\bullet A-sp-VB(S)} - E^\circ_{A-sp-VB(S)+\bullet})$. Unfortunately, direct electrochemical measurements of A-sp-VB did not allow unequivocal assignment of the standard potentials for oxidation of the two electroactive species. Two one-electron, reversible reduction peaks were observed corresponding to the formation of $^{-\bullet}$A-sp-VB and $^{-\bullet}$A-sp-VB$^{-\bullet}$, respectively. However, only one irreversible two-electron oxidation wave is observed (Table 1). The absence of a second oxidation wave can be rationalized in terms of the fast intramolecular hole transfer outlined in eqs 1−4. As the anthracene cation radical is formed, the hole transfer equilibrium is established (eqs 1 and 2). An irreversible chemical reaction of the vinylbutadiene cation radical (on the time scale of the electrochemistry, $\sim$seconds) will then drive the equilibrium toward the product, A-sp-P (eq 3), and allow the anthracene to donate a second electron (eq 4). This mechanism assumes that the moiety, P, is sufficiently difficult to oxidize that the hole transfer equilbrium lies entirely on the anthracene cation

TABLE 1: Electrochemical Data for the Oxidation and Reduction of A-sp-VB and Some Model Compounds[a]

compound	E^{p}_{ox}	E°_{red}
A-sp-VB	0.83	$-2.45,^{b}$ -2.55^{c}
AM	0.80	-2.50
2-VSM	0.82	-2.58
DMN-sp-VS	$0.78,^{d}$ 0.92^{e}	$-2.54,^{e}$ -2.71^{d}
2-VBM	0.73	-2.45
7-VBM	0.83^{f}	-2.41^{f}

[a] In acetonitrile containing 0.1 M tetrabutylammonium perchlorate. The values are the average of four independent measurements, two using a glassy carbon working electrode and two using a gold working electrode. The precision in the determination of the peak potential is ±10 mV. Unless otherwise indicated, the oxidation peaks are chemically irreversible and the reduction peaks are chemically reversible. [b] In volts versus the ferrocenium/ferrocene couple (internal standard), which has a potential of 0.440 V SCE. [b] Reversible potential assigned to the vinylbutadiene moiety. [c] Reversible potential assigned to the anthracene moiety. [d] Reversible potential assigned to the 1,4-dimethoxylnaphthalene moiety. [e] Assigned to the vinylstilbene moiety. [f] Estimated value assuming that $E^{\circ}_{2-VSM} - E^{\circ}_{DMN-sp-VS} = E^{\circ}_{2-VBM} - E^{\circ}_{7-VBM}$.

TABLE 2: Equilibrium Constants from Spectroscopic and Electrochemical Data (293 K)

equilibrium	method	K
K_{eq}(A-sp-VB)	spect[a]	4.0 ± 2
	elec[b]	3.2 ± 2
K_{eq}(A-sp-VS)	spect[a]	71 ± 30
	elec[c]	105 ± 50
K_{eq}(A-sp-VS)/K_{eq}(A-sp-VB)	spect	18 ± 10
	elec	33 ± 20

[a] From the transient spectra assuming $\epsilon_A = 1.16 \times 10^4$ M^{-1}cm^{-1},[16] $\epsilon_{VB} = \epsilon_{VS} = 1.2 \times 10^5$ M^{-1}cm^{-1}. [b] Using the data for model compounds in Table 1: $\Delta G_{ET} = -F(E^{\circ}_{AM} - E^{\circ}_{7-VBM})$. [c] Using the data for model compounds in Table 1: $\Delta G_{ET} = -F(E^{\circ}_{AM} - E^{\circ}_{7-VBM})$.

radical side.

$$\text{A-sp-VB} \rightarrow {}^{+\bullet}\text{A-sp-VB} + e \qquad (1)$$

$$ {}^{+\bullet}\text{A-sp-VB} \rightleftarrows \text{A-sp-VB}^{+\bullet} \qquad (2)$$

$$\text{A-sp-VB}^{+\bullet} \rightarrow \text{A-sp-P} \qquad (3)$$

$$\text{A-sp-P} \rightarrow {}^{+\bullet}\text{A-sp-P} + e \qquad (4)$$

As a result, it was necessary to use model compounds to obtain an electrochemical estimate of the standard potentials for oxidation of the anthracene and polyene moieties. For the anthracene component, the model compound was AM. Both the oxidation and reduction were within 50 mV of the corresponding potentials for A-sp-VB (the actual assignments of the reduction waves are based on comparisons with the model compounds, see below and Table 1). Initially, the 2-methylene norbornyl derivatives were used to model the 7-methylene bichromophores (chosen for synthetic convenience). The oxidation and reduction data for these models are also given in Table 1. To assess the difference between the redox properties of the 2-methylene norbornane model compounds (2-VBM and 2-VSM) and the 7-methylene substituted bichromophore (A-sp-VB) one other, more synthetically challenging model compound, was prepared (DMN-sp-VS). In this case, the 1,4-dimethoxynaphthalene group was chosen to closely mimic the structure of the bichromophores while at the same time separating the standard potentials of the fused aromatic ring from those of the polyenes. It is clear from the model compounds that there is a significant difference (~100 mV) between the oxidation potentials of 2-VSM and DMN-sp-VS. This difference, although not as large, is also observed in the reduction potentials.

These data can be used to provide estimates of the equilibrium constants for intramolecular hole transfer (eq 5). The spectroscopic values (determined at 293 K), K_{eq}(A-sp-VB) ≈ 4 and K_{eq}(A-sp-VS) ≈ 70, yield a ratio K_{eq}(A-sp-VS)/K_{eq}(A-sp-VB) ≈ 18. Using the electrochemical data (also obtained at 293 K) for AM, 2-VSM, and 2-VBM, the ratio of the equilibrium constants agrees to within a factor of 2 with the spectroscopic ratio (Table 2), but the individual equilibrium constants calculated from the potentials of the 2-substituted models are underestimated by a factor of ~50. However, if the potential for DMN-sp-VS is used instead, the estimate of K_{eq}(A-sp-VS) is within 50% of the spectroscopic value. This result emphasizes the importance of using model compounds that resemble the compounds of interest as closely as possible. A small shift of 100 mV (2.3 kcal/mol) in the potential leads to a large error in the equilibrium constant because the potentials are used in an exponential term.

$$\text{A-sp-R}^{+\bullet} \rightleftarrows {}^{+\bullet}\text{A-sp-R} \qquad (\text{R} = \text{VS or VB}) \qquad (5)$$

Synthetic difficulties prevented the preparation of 7-VBM. However, given that the data using 2-VSM and 2-VBM provide a reasonable (within experimental error) estimate of K_{eq}(A-sp-VS)/K_{eq}(A-sp-VB), it is reasonable to assume that the change in potential from 2-VSM to DMN-sp-VS will be the same for 2-VBM compared with 7-VBM. Making this assumption yields a value for K_{eq}(A-sp-VB) that is within 30% of the value obtained from the spectroscopic results. Although both techniques are known to be prone to error (in the estimate of extinction coefficients or in standard potentials), the agreement between these two estimates is satisfying and provides further evidence in support of rapid (on the laser flash time scale) hole transfer equilibration in the rigidly linked bichromophores. Certainly, the electrochemical measurements must pertain only to the electronic ground states.

Summary

The UV laser irradiation of A-sp-VB and A-sp-VS leads to photoionization of both the anthracene and polyene chromophores and simultaneous observation by transient absorption of the cation radicals of each group. The polyene cation radical spectra of A-sp-VB and A-sp-VS are nearly identical to those of 1,6-diphenyl-1,3,5-hexatriene and 1,4-diphenyl-1,3-butadiene, respectively, indicating that the positions of the phenyl rings and double bonds is unimportant to the spectroscopy of the cation radicals. The simultaneous observation of the cation radicals in A-sp-VB coupled with the known ability of norbornyl spacers to promote rapid charge separation and hole transfer indicates that a hole transfer equilibrium exists between the chromophores. Supporting this conclusion are the following observations: (i) the decay rates of the two cation radical absorptions are identical; (ii) the ratio of the absorbances of the two cation radicals is independent of excitation wavelength; (iii) the absorbance/energy dose profiles for the cation radicals are similar in the bichromophore but different for the individual model compounds; (iv) the ratio of the cation radical absorbances changes dramatically for a new bichromophore (A-sp-VS) containing a polyene with a higher oxidation potential (vinylstilbene); (v) two-laser irradiation of A-sp-VB involving the specific excitation of the polyene cation radical causes a transient depletion of the polyene cation radical absorption and concurrent enhancement of the anthracene cation radical absorption. This observation is consistent with the temporary disruption of the equilibrium followed by a return to an equilibrium

condition. The fact that this behavior follows the 400-ns laser pulse indicates that the hole transfer occurs on a nanosecond time scale or faster.

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Supporting Information Available: Synthetic details are available (10 pages). Ordering information is given on any current masthead page.

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