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Excimer and Exciplex Formation in van der Waals Dimers of Toluene and Benzene

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Structural isomerization dynamics of photoexcited van der Waals dimers of toluene and benzene have been investigated by means of fluorescence and mass spectroscopic methods. Two isomeric forms of the heterodimer complex formed between toluene and benzene, assigned to parallel displaced and T-shaped configurations, are found to rearrange into exciplexes when excited in the S_1 state with a small amount of vibrational energy. The toluene homodimer also reveals similar excess energy dependence on excimer formation. The excited-state dynamics are contrasted with those of the T-shaped benzene homodimer where no vibrational energy is required for structural isomerization. The excess energy dependence observed for the toluene complexes is attributed to a steric requirement of sandwich-type excimer geometry. Dissociation behavior of these exciplex/excimer complexes has been measured by photodepletion spectroscopy and compared with that of the benzene excimer. These excited-state complexes are found to strongly absorb in the wavelength range between 440 and 560 nm. The absorption band is representative of the excimer/exciplex and is assigned to a transition into a charge-transfer state.

Introduction

Noncovalent interactions between aromatic moieties play a key role in the conformational stabilization of various chemical systems. For example, these interactions are suggested to affect the binding properties of nucleic acids and the stabilization of proteins.[1] Although the nature of aromatic−aromatic interactions has been the subject of extensive studies over the years, little information is currently available on their interaction behavior in electronically excited states.

In a series of papers,[2−5] we demonstrated that most van der Waals (vdW) dimers of aromatic molecules rearrange into parallel stacked structures upon electronic excitation. The structural isomerization process is termed as excimer formation because it resembles that observed in concentrated solutions of these molecules. A typical example is the homodimer of benzene (Bz_2).[5] While it is T-shaped in the ground electronic state, it undergoes rapid structural isomerization into an excimer from the zero-point level of the S_1 state. The observation unequivocally demonstrated that the parallel stacked arrangement of the excimer is preferred over the initially excited T-shaped structure. Moreover, none of the larger clusters of benzene, e.g., trimer and tetramer, are found to exhibit excimer behavior, presumably because of geometrical constraint. Photodissociation experiments on the excimer showed that it absorbs strongly at about 500 nm where no significant absorption occurs from the initially excited T-shaped state. The characteristic excimer absorption band was accounted for by invoking charge-transfer (CT) interaction between the two benzene molecules.

This paper is concerned with excimer formed from a homodimer of toluene (Tol_2) and exciplex formed from a mixed dimer of toluene and benzene (Tol−Bz). The objectives of this study were threefold. The first objective was to further elucidate the nature and stabilization forces of the excimer state and its formation dynamics in Bz_2. The methyl group of toluene will increase dipole−dipole interaction and dispersion effects, which favors a face-to-face configuration over a T-shaped configuration. Consistent with this expectation, Law et al.[6] found that there exist two isomeric forms for the Tol−Bz dimer. The apparent structural similarity of the parallel isomer with a sandwich-type geometry assumed for the exciplex predicts that structural rearrangement would be preferred for this isomer over the T-shaped one. The second objective was to learn about a driving force of the excimer stabilization in Bz_2. Excimers of large aromatic hydrocarbons are believed to be bound largely by exciton-resonance (ER) interaction between the two identical constituents. This implies that exciplexes formed between different constituent molecules should be less stable than excimers. For the case of dimers involving toluene, we also need to consider a steric factor for the stabilization of excimer/exciplex. Previous solution results[7−10] suggested that the Bz_2 excimer is more stable by 0.05 eV than the Tol_2 excimer, which was taken as a manifestation of such steric effects. The third objective was to identify the origin of the excimer characteristic absorption band observed for Bz_2. Although a similar absorption band was observed for the Bz_2 excimer formed in solution, no rigorous assignment was given to this band.

Experimental Section

The experimental apparatus used to record fluorescence excitation and dispersed fluorescence spectra were described in a previous paper.[5] In brief, vdW dimers generated by a pulsed valve (General Valve) were interacted at 10 mm downstream with the doubled output (7 ns) of a YAG-pumped dye laser

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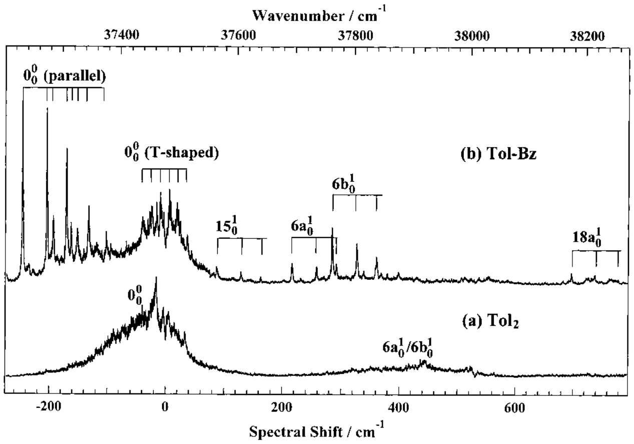

Figure 1. R2PI spectra of (a) Tol$_2$ and (b) Tol−Bz. The spectral shift is relative to the S_1 origin of the Tol monomer at 37 477 cm^{-1}. Both spectra were measured at a sample liquid temperature of 0 °C and a He backing pressure of 3 atm.

(Continuum PL8000/ND6000/UVT-1). The resulting fluorescence was collected either by a glass filter or by a 0.32-m monochromator (Jobin-Yvon HR320) with a low resolution of 10 nm and detected with a photomultiplier tube (PMT) to obtain fluorescence excitation spectra. For recording dispersed fluorescence spectra, the monochromator was used with better spectral resolutions. The PMT output was averaged with a boxcar integrator or time-resolved with a fast oscilloscope and then sent to a computer for analysis.

In photodepletion experiments, part of the frequency-tripled output of the YAG laser was used to pump a second dye laser (Molectron DL-14). The visible beam was time-delayed by ≈7 ns with respect to the pump beam and was used to deplete the fluorescence generated by the pump laser. Photodepletion spectra were obtained by recording the depletion cross section $\ln(I_{\mathrm{off}}/I_{\mathrm{on}})$, where I_{on} and I_{off} are the integrated fluorescence intensities with the depletion laser turned on and off, respectively, as a function of the depletion laser frequency.

Resonance-enhanced two-photon ionization (R2PI) experiments were employed to identify dimer transitions appearing in the fluorescence excitation spectra. In this study, the free-jet expansion was skimmed with a 2-mm skimmer and ionized with the dye laser. The resulting photoions were analyzed by a Wiley−McLaren type time-of-flight mass spectrometer. Background pressure in the ionization region of the spectrometer was kept at 3×10^{-7} Torr during the nozzle operation while that in the flight tube was maintained below 2×10^{-7} Torr. Mass-selected R2PI spectra were obtained by detecting the ion intensity of a particular dimer mass as a function of the ionization laser frequency.

The fluorescence and R2PI measurements were carried out for Tol−Bz and Tol$_2$. The homodimer was generated by passing helium at a pressure of 3 atm over Tol liquid. A 1:1 volume ratio of Tol and Bz liquids, corresponding to a vapor concentration ratio of 1:4, was used to produce predominantly the Tol−Bz heterodimer with the interfering Tol$_2$ homodimer less abundant. The liquid samples were held at 0 °C to prevent the formation of larger clusters.

Results

A. R2PI Spectra. The R2PI spectra of Tol−Bz and Tol$_2$ are shown in Figure 1. These spectra are in qualitative agreement with those reported by Law et al.[6] The vibrational mode numbers of these dimers are those used by Varsanyi[11] for the Tol monomer. The heterodimer spectrum in Figure 1b reveals two sets of features corresponding to the S_1 origin: one set is red-shifted with respect to that of the Tol monomer by 250−100 cm^{-1} and the other located near the origin region of the monomer gives rise to a progression. They were assigned as arising from different structural isomers on the basis of the different behavior in two-color photoionization.[6] The former corresponds to a parallel-displaced structure of Tol−Bz, while the latter set is assigned to a T-shaped structure. The homodimer spectrum is characterized by broad and less structured absorption bands. The red shift is analogous to the higher energy set of the heterodimer, suggesting a T-shaped structure for Tol$_2$.

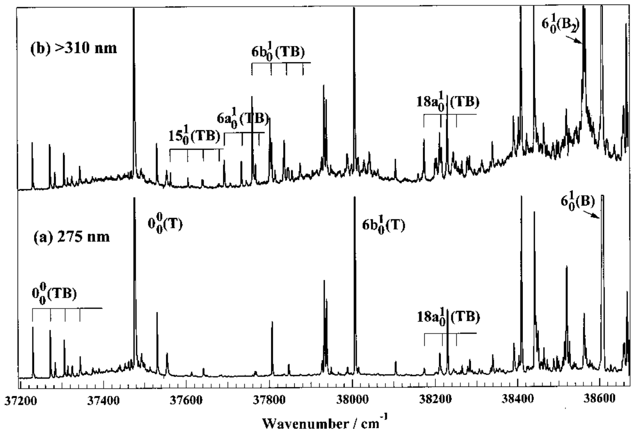

Figure 2. Fluorescence excitation spectra encompassing the S_1 regions of Tol and Bz, obtained by detecting fluorescence (a) at 275 ± 5 nm and (b) at >310 nm. A 1:1 volume mixture of Tol and Bz liquids held at 0 °C was used to record both spectra. The vibrational assignments for dimers of Tol$_2$ (T$_2$) and Tol−Bz (TB) are based on the R2PI spectra in Figure 1. The truncated spectral features marked by B and B$_2$ are assigned to the 6_0^1 transitions of benzene and its dimer, respectively

The excitation spectra also include vibronic transitions with excess energies up to 1000 cm^{-1}. The Tol−Bz spectrum displays sharp features which can be assigned to 15_0^1, $6a_0^1$, $6b_0^1$, and $18a_0^1$ transitions of the parallel-displaced isomer. Analogous to the origin band region, each transition displays fine structure due to intermolecular vibrations. Spectral features of the T-shaped isomer in this region are apparently too weak to be measured. The homodimer spectrum exhibits broad bands in the $6a_0^1/6b_0^1$ regions, which cannot be resolved clearly because of their overlap.

B. Fluorescence Excitation Spectra. The fluorescence excitation scans for the 1:1 mixture of Tol and Bz liquids were performed by recording fluorescence either at 275 ± 5 nm or at >310 nm. The result is shown in Figure 2. When the fluorescence is detected at 275 nm, spectral features associated with the 0_0^0 transition of the parallel isomer of Tol−Bz are observed in the energy range of 37230−37400 cm^{-1}. However, those corresponding to the vibronic transitions, 15_0^1, $6a_0^1$, and $6b_0^1$, are nearly suppressed in the spectrum. As the excess energy is increased further, one can see a set of weak peaks assignable to the $18a_0^1$ transition at around 38 200 cm^{-1}. The excitation spectrum obtained by detecting red-shifted fluorescence (Figure 2b) displays essentially all vibronic transitions appearing in the R2PI scan. More importantly, the set of the $6b_0^1$ vibronic transition appears to be stronger than that of the origin when the fluorescence is filtered at >310 nm. This observation indicates that the heterodimer emission is considerably shifted to the red of the excitation, an implication of exciplex formation. Note also that a broad background feature is seen near 38 000 cm^{-1} in the spectrum. It can be assigned to

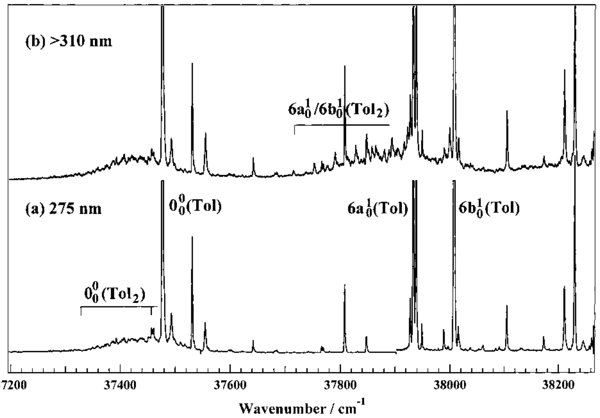

Figure 3. Fluorescence excitation spectra for the pure Tol sample obtained by detecting fluorescence (a) at 275 ± 5 nm and (b) at >310 nm.

the $6a_0^1/6b_0^1$ transitions of the T-shaped isomer of Tol−Bz. It is therefore concluded that both isomers give rise to similar excess energy dependence on exciplex formation. The >310-nm spectrum also reveals a doublet structure assigned to the 6_0^1 transition of Bz$_2$ at around 38 560 cm^{-1}.[5] Since the Bz$_2$ dimer excited at this level rearranges into the excimer, its fluorescence is considerably red-shifted and thus isolated under the detection condition. Although the spectral features of the Tol−Bz dimer are also seen in the origin band region of the >310-nm spectrum, the excitation is found to produce no exciplex emission on the basis of the dispersed fluorescence result shown below.

The fluorescence excitation spectra recorded for the neat toluene sample are shown in Figure 3. The bottom spectrum obtained by detecting a monomer-like emission at 275 nm gives rise to broad structure to the red of the monomer origin denoted by 0_0^0(Tol). The general feature of the broad spectrum matches well the origin band region of Tol$_2$ in Figure 1a. Given this assignment, it is important to note that such broad structure is absent in the $6a_0^1/6b_0^1$ band regions. In contrast, the top spectrum obtained at >310 nm displays complicated bands which are not seen in the 275-nm spectrum. This excess energy-dependent behavior is similar to that of the Tol−Bz dimer and assigned as arising from excimer formation. The spectral congestion observed for Tol$_2$ may be associated with excitation of the ground-state dimer into its S$_1$ state of very different equilibrium geometry. Thus, the broadening can be assigned to unresolved spectral features of low-frequency intermolecular vibrations that are coupled to the electronic transition. Consistent with this assigment, the R2PI spectrum of the T-shaped isomer of Tol−Bz structure shown in Figure 1b is characterized by a vibrational progression of a low-frequency mode. Most homodimers of large aromatic hydrocarbons such as naphthalene[3] and dibenzofuran[12] also give rise to apparently unresolved $S_1 \leftarrow S_0$ excitation spectra because of coupling with intermolecular vibrations.

Figure 4 compares the $6a_0^1/6b_0^1$ band region of the >310-nm fluorescence excitation spectrum (Figure 3b) and the same region of the R2PI spectrum of Tol$_2$ (Figure 1a) with an expanded scale to see the details. In Figure 4b, a set of resolved peaks is observed which is superimposed on the broad structure assigned to the T-shaped isomer of Tol$_2$. The peaks are likely to constitute a progression with an interval of 40 cm^{-1}. The frequency is similar to the stretching vibrational frequency of the parallel structure of Tol−Bz (42 cm^{-1}), which suggests the possibility of a parallel isomer for Tol$_2$. These peaks are also discernible in the R2PI spectrum of Figure 4a. However, no corresponding features are apparently seen in the origin band region of the fluorescence excitation spectra (Figure 3). This observation could be rationalized on the basis of an assumption that the parallel isomer rearranges into an excimer with higher efficiency than the T-shaped isomer and thus emits strongly at >310 nm.

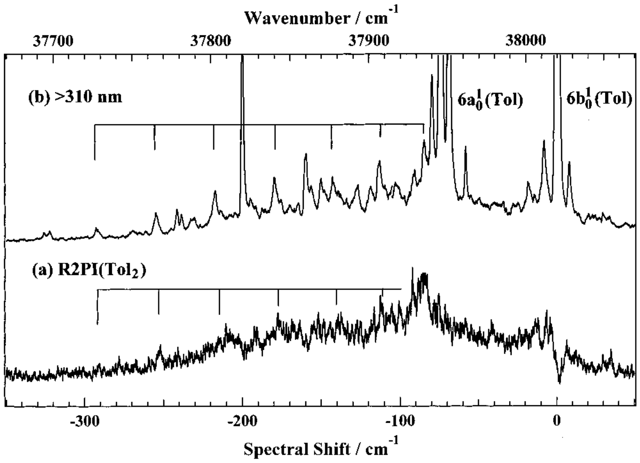

Figure 4. (a) An expanded view of the $6a_0^1/6b_0^1$ band region of the R2PI spectrum of Tol$_2$ in Figure 1a and (b) an expanded view of the same region of the fluorescence excitation spectrum in Figure 3b. The spectral shift is relative to the monomer $6b_0^1$ transition at 38 020 cm^{-1}.

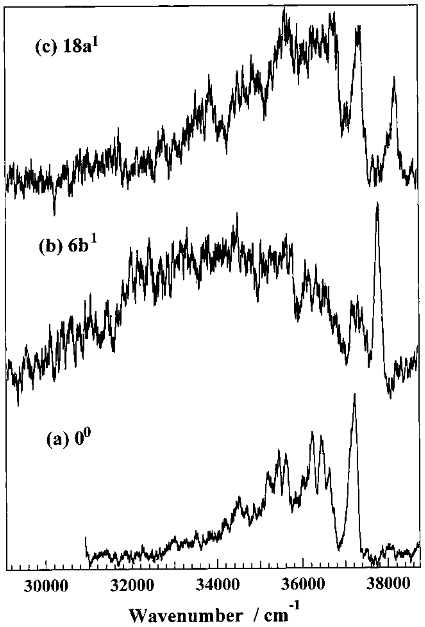

Figure 5. Dispersed fluorescence spectra of Tol−Bz excited at (a) 0_0^0 (37 230 cm^{-1}), (b) $6b_0^1$ (37 760 cm^{-1}), and (c) $18a_0^1$ (38 170 cm^{-1}) transitions. The respective spectral resolutions were 160, 320, and 80 cm^{-1}. The highest energy features of the spectra in parts b and c are due to scattered laser light.

C. Dispersed Fluorescence Spectra. The dispersed fluorescence spectra of the parallel isomer of Tol−Bz excited at the 0_0^0 (37 230 cm^{-1}), $6b_0^1$ (37 760 cm^{-1}), and $18a_0^1$ (38 170 cm^{-1}) transitions are displayed in Figure 5. While the origin spectrum shows resolved bands which resemble those of the Tol monomer spectrum,[13] the 6b^1 spectrum is characterized by a broad and red-shifted feature centered around 300 nm. The dramatic change in the emission spectra is attributed to the exciplex formation between Tol and Bz, consistent with the fluorescence excitation result. Excitations of the dimer at the lower energy transitions of $15a_0^1$ and $6a_0^1$ are also found to produce exclu-

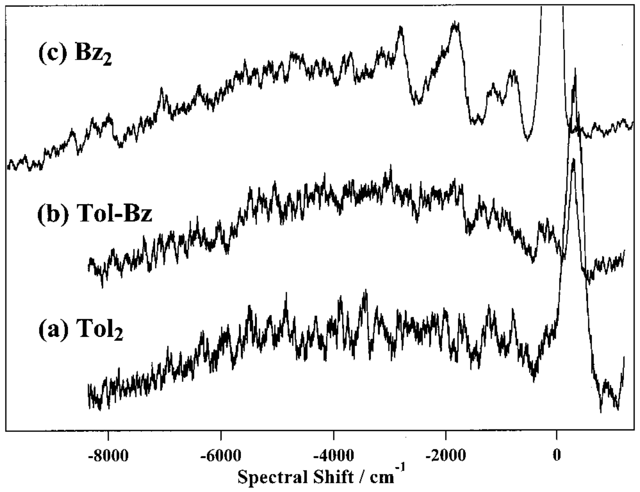

Figure 6. Dispersed fluorescence spectra of (a) Tol$_2$, (b) Tol−Bz, and (c) Bz$_2$. In each case, the spectral shift is relative to the S_1 origin of the corresponding monomer, i.e., 37 477 cm^{-1} for Tol and 38 086 cm^{-1} for Bz. All spectra were recorded with a resolution of 320 cm^{-1}. The spectrum in part a was obtained through excitation of a prominent feature at 37 803 cm^{-1} shown in Figure 4b, which is assigned to a member of the $6b^1_0$ transitions of the parallel isomer. The spectrum in part b is reproduced from Figure 5b. The spectrum in part c was obtained by exciting the T-shaped dimer of Bz through the 0^0_0 transition. The sharp peaks appearing with spectral shifts of <3000 cm^{-1} in the Bz$_2$ spectrum (part c) are those from excitation of underlying larger cluster features. The highest energy feature in each spectrum is due to scattered laser light, indicative of no resonance fluorescence.

sively the exciplex fluorescence, which suggests that the vibrational energy required for the exciplex formation is lower than 230 cm^{-1}, i.e., the frequency of ν_{15} vibration in S_1. The $18a^1$ spectrum in Figure 5c is analogous to the origin spectrum except that it extends below 32 000 cm^{-1}. On the basis of the fact that the spectral features corresponding to the $18a^1_0$ transition are seen in the excitation spectrum of the red-shifted fluorescence in Figure 2b, the lower energy portion of the emission is assigned to exciplex fluorescence. The structured emission which resembles the origin spectrum is assigned as originating from vibrational predissociation of the dimer at its vdW potential well. Dissociation of the Tol−Bz dimer will lead to the formation of an electronically excited Tol fragment and thus produce fluorescence in the monomer energy region. The observation of the dual fluorescence suggests that both exciplex formation and dimer dissociation take place at this level of excess energy.

The dispersed fluorescence spectrum from the $6a^1_0/6b^1_0$ band region of Tol$_2$ is shown in Figure 6. Also shown for comparison are the excimer/exciplex fluorescence spectra from the Bz$_2$ and Tol−Bz dimers. The spectra of Tol$_2$ and Tol−Bz show similar red shifts of ~4000 cm^{-1} with respect to the S_1 energy of Tol, which are noticeably smaller than the corresponding shift of the Bz$_2$ spectrum. The difference predicts the Bz$_2$ excimer to be more stable than the excimer/exciplex of Tol$_2$ and Tol−Bz and will be discussed later. When the Tol$_2$ dimer is excited at the origin band region, its fluorescence appears to be nearly identical to that of the Tol−Bz dimer, i.e., no indication of excimer formation.

D. Fluorescence Lifetimes. The fluorescence lifetimes of the Tol−Bz and Tol$_2$ dimers are listed in Table 1. They are apparently in agreement with the lifetime data obtained by Law et al.[6] using a two-color photoionization technique. Their contention was that the decrease in the lifetimes with increasing the excess energy is due to excimer/exciplex formation. However, our results indicate unambiguously that the lifetimes they measured are actually those of the excimer/exciplex and the structural isomerization is occurring on a much faster time scale. As indicated above, the excitation of the Tol−Bz dimer at $18a^1_0$ shows two fluorescence emissions. Their lifetimes are measured to be different, 48 ns for the structured fluorescence and 37 ns for the exciplex fluorescence.

TABLE 1: Fluorescence Lifetimes (ns) of Tol and Its Dimers

	Tol−Bz	Tol$_2$	Tol
0^0	70	60	86
$6b^1$	38	38	72
$18a^1$	48,[a] 37[b]		76

[a] The value for the Tol fragment fluorescence. [b] The value for the exciplex fluorescence.

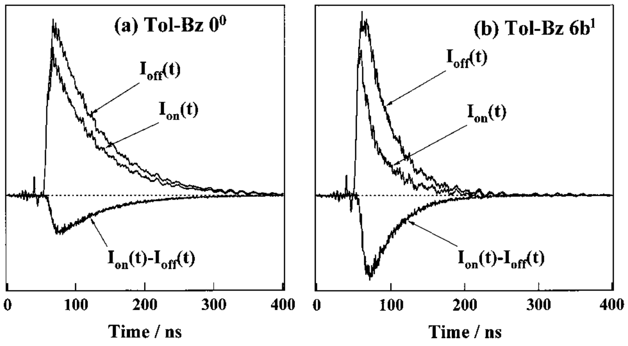

Figure 7. Photodepletion signals recorded for the (a) 0^0_0 and (b) $6b^1_0$ fluorescence of Tol−Bz. The visible beam at 0.4 mJ/pulse was delayed by 7 ns with respect to the pump beam. The difference signals, $I_{on} - I_{off}$, are produced by subtracting the signal with the depletion laser turned off (I_{off}) from that with the laser turned on (I_{on}). The depletion cross section, $\ln(I_{off}/I_{on})$, in part b is estimated to be larger by a factor of 3 than that in part a.

E. Photodepletion Spectra. Photodepletion experiments on the Tol$_2$ and Tol−Bz dimers have been carried out in the wavelength range between 590 and 430 nm using several different laser dyes. Figure 7 shows an example of the results obtained for the Tol−Bz dimer. When the exciplex fluorescence is probed and the visible beam is irradiated at 500 nm, substantial depletion of the fluorescence is observed as shown in Figure 7b. The depletion cross section, $\ln(I_{off}/I_{on})$, is 0.87 in this case. Under the same irradiation condition, the origin band fluorescence from the dimer shows a depletion cross section of 0.29 (Figure 7a). This observation demonstrates that the exciplex absorbs strongly at this wavelength to dissociate. Analogous photodepletion behavior is observed for the excimers of Tol$_2$ and Bz$_2$, but their depletion maxima differ considerably from that of the exciplex. Figure 8 compares the depletion yield spectra for Bz$_2$, Tol−Bz, and Tol$_2$. The depletion maximum for Tol−Bz is 480 nm, which is located between the maxima of Bz$_2$ (455 nm) and Tol$_2$ (515 nm). Relative intensities of these maxima are found to be nearly equal. In all cases, no fragment fluorescence was observed after photodissociation. This differs from the case of dimers of naphthalene and fluorene in which dissociation of their excimers leads to the formation of a fluorescent monomer fragment. One possible explanation for the difference is that the upper state reached by the excimer transition in Tol$_2$ and Bz$_2$ is of CT character, as discussed below, which may render internal conversion from this state less efficient.

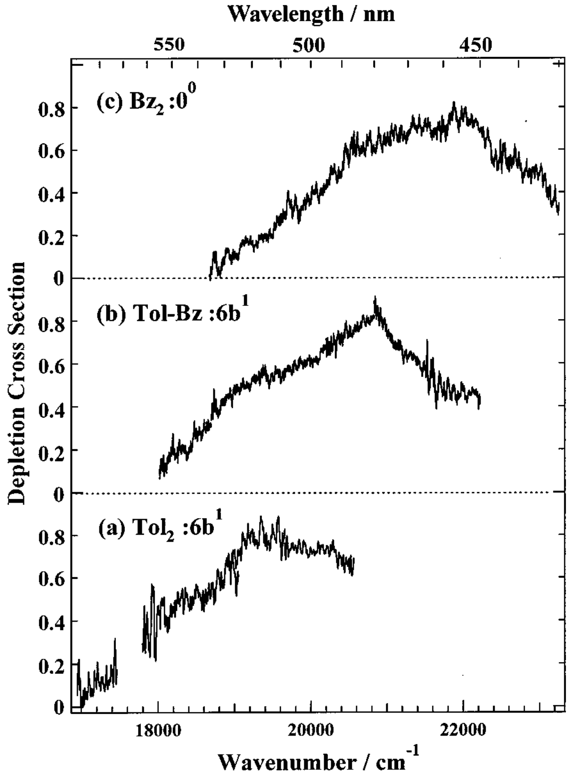

Figure 8. Photodepletion spectra of (a) Tol$_2$, (b) Tol−Bz, and (c) Bz$_2$. The ordinate scales represent the depletion cross section, ln(I_{off}/I_{on}), where I_{on} and I_{off} are the integrated fluorescence intensity with the depletion laser turned on and off, respectively. Each curve was recorded by monitoring the respective fluorescence shown in Figure 6 using a red pass (>310-nm) filter. The cross section of Tol$_2$ relative to that of Tol−Bz is 1.8 at 530 nm while the cross section of Tol−Bz relative to that of Bz$_2$ is 1.6 at 500 nm. In part a, no measurement was carried out in the range between 572 and 560 nm.

Discussion

The most important factor that governs the ability to form excimers/exciplexes in vdW dimers is the relative stability of the initially excited vdW state. It has been generally accepted that excimer stabilization of aromatic molecules is due to configuration interaction between the exciton-resonance states $\varphi\varphi^* \pm \varphi^*\varphi$ and the charge-resonance states $\varphi^+\varphi^- \pm \varphi^-\varphi^+$, where φ and φ^* are the ground- and excited-state wave functions of an aromatic molecule, respectively, and φ^+ and φ^- denote the ionic state wave functions.[14] For the case of large aromatic molecules (e.g., naphthalene and fluorene), the excimer stabilization has been explained satisfactorily on the basis of the dominance of exciton-resonance interaction.[2−4] A recent INDO/S calculation on naphthalene dimer[15] has also supported this interpretation.

The stabilization force of the Bz$_2$ excimer has been a source of controversy. Unlike other dimers, the S$_1$ parentage of the dimer will not split by exciton-resonance interaction in the D_{6h} symmetry. Thus, Vala et al.[16] suggested by their semiempirical study that it is stabilized primarily by interaction with the charge-resonance state. In the present investigation, both the excimer formation in Tol$_2$ and the exciplex formation in Tol−Bz are found to occur at similar excess energies. The exciplex is formed between Tol and Bz regardless of the energy mismatch of 608 cm^{-1} between the respective S$_1$ origins. The energy gap should result in the reduction of the exciton-resonance interaction in the heterodimer. Analogous behavior was observed for heterodimer complexes of fluorene and of dibenzofuran. For example, a complex of fluorene with 1,2,4,5-tetrachlorobenzene, in which the energy gap of their S$_1$ states is 451 cm^{-1}, is found to form an exciplex with an excess vibrational energy of <204 cm^{-1}.[17] Yip and Levy[18] also showed that heterodimers of fluorene (or dibenzofuran) with 2,3-benzofuran can rearrange into exciplexes, irrespective of the S$_1$ energy gaps of more than 2000 cm^{-1}. From their results, the authors pointed out the possibility of CT interaction as a source of the excimer/exciplex stabilization. Although high-level computation on these excimers and exciplexes is yet to be performed, these observations suggest that the exciton-resonance interaction may not be the dominant factor for the exciplex/excimer stabilization. Here, we consider other factors which are likely to contribute the exciplex/excimer stability of the Tol dimer systems. Among several possible sources, vdW geometry, steric effects, and CT interaction will be discussed below.

A. van der Waals Geometry. Our previous investigations on naphthalene clusters[3,4] demonstrated that initial vdW geometry is an important driving force for promoting structural isomerization into excimers. A typical example is the trimer in which excimer formation is severely restricted due to its triangular geometry and thus requires a substantial vibrational energy to form a strongly bound dimeric core. In striking contrast, the tetramer which presumably possesses a nearly parallel molecular pair inside the cluster can rearrange into excimer geometry with less excess energy. In terms of the geometrical restriction motif, vdW dimers may be considered as less restricted systems so that initial geometry could be less critical for excimer formation. Indeed, the T-shaped vdW dimer of Bz$_2$ was found to form an excimer with a unit quantum yield even at the S$_1$ electronic origin.[5]

While the dominant isomer of Bz$_2$ is T-shaped, two structural isomers, parallel-displaced and T-shaped, coexist in Tol−Bz and Tol$_2$. Theoretical calculations[19,20] also strongly indicate that both vdW isomers have similar binding energies. The increased stability of the parallel isomer is interpreted by the presence of methyl groups which is expected to increase the dispersion force. This brings up an important question of whether excimer/exciplex formation is dependent on the structural isomers. If the geometrical restriction prevails, structural rearrangement would be more favorable for the parallel dimer than for the T-shaped one. However, the present results show that both isomers reveal similar excimer/exciplex behavior. If the two isomers were substantially isolated from each other by an energy barrier which is higher than those into the excimer/exciplex state, isomer-dependent behavior would be observed. Thus, the present result is rationalized by invoking low-energy barriers between the isomers such that a small amount of excess energy can induce interchange prior to structural rearrangement. This situation is apparently very different from the case of the anthracene dimer where its two structural isomers are found to lead to different excimers.[21]

B. Steric Effects. Toluene excimer is observed in highly concentrated solutions. Birks et al.[7] reported that its binding energy (0.17 eV) is less than that of Bz$_2$ (0.22 eV) and suggested steric hindrance as an explanation for excimer stability. The value for Tol$_2$ was reevaluated by Greenleaf et al.[8] to be 0.29 eV. Subsequently, Cundall and Robinson[9] pointed out that the Birks' data for Bz$_2$ were calculated on the basis of an inadequate assumption that the decay rate constants of monomer and excimer are independent of temperature. They claimed the binding energy of Bz$_2$ excimer to be 0.34 eV. Hirayama and Lipsky[10] reported a binding energy of >0.36 eV for Bz$_2$. These solution results established that Bz$_2$ excimer is more stable by

0.05 eV than Tol_2, which is consistent with the steric requirements of sandwich-type excimer geometry.

As shown in Figure 6, the red shifts of the dispersed fluorescence in Tol−Bz and Tol_2 ($\approx$4000 cm^{-1}) are apparently smaller than that for Bz_2 ($\approx$5000 cm^{-1}). From the fluorescence red shift, which is the sum of the excimer binding energy and the repulsive energy of the dimeric ground state, we obtain the latter energy to be 0.28 eV for Bz_2 and 0.21 eV for Tol_2. The larger value for Bz_2 implies that its interplanar separation is smaller than that of Tol_2, which is in qualitative agreement with the trends in the excimer stabilization. Thus, a steric effect is invoked. Although no binding energy value is reported for the Tol−Bz exciplex, it may be deduced to be similar to that of Tol_2 on the basis of the fluorescence red shift and the excess energy-dependent behavior. The exciplex stabilization could be explained if near-resonance interaction between the S_1 states of Tol and Bz prevails over steric effects.

Binding energy calculations[20] indicate that the minimum energy isomer of Tol_2 corresponds to that of parallel-displaced antiparallel structure where the two aromatic rings are in a face-to-face configuration but the two methyl groups are located in opposite directions. This is a structure that minimizes repulsion due to the methyl groups. Its excimer is expected to have a similar stacked structure, but with a shorter intermolecular separation. The reduced face-to-face distance presumably places the two rings in a more displaced configuration, thus resulting in the less stable excimer than that of Bz_2. Although the above considerations suggest steric effects on the excimer/exciplex stabilization in Tol−Bz and Tol_2, it is evident that more rigorous computational study on these excited-state species is needed to rationalize the present results.

C. Charge-Transfer Interaction. Next, we consider CT interaction as a source for the excimer/exciplex stability. This prediction is borne out by the essentially identical behavior of the exciplex formation in Tol−Bz and the excimer formation in Tol_2. However, there is little information on the CT interaction in these neutral dimers. The CT state energy of a dimer may be estimated from $IP - EA - C(r)$, where IP and EA are the ionization potential and electron affinity of the component molecules and $C(r)$ is the Coulombic interaction between positive and negative ions. Using the known values IP(Tol) = 8.83 eV,[22] EA(Tol) = −1.11 eV,[23] IP(Bz) = 9.24 eV,[24] and EA(Bz) = −1.15 eV,[23] IP − EA values are calculated to be 9.94 eV for Tol and 10.39 eV for Bz. This predicts that the CT state of Tol_2 is lower by 0.45 eV than that of Bz_2 at infinite separation. Because the CT state energies will decrease because of $C(r)$ as the interplanar separation is decreased, the lowest exciton-resonance state that correlates to $S_1 + S_0$ may also be stabilized as a result of configuration interaction. The excimer stabilization of Tol_2 and Bz_2 could be rationalized by this interpretation. If the CT stabilization dominates, the excimer state of Tol_2 would be more stable than that of Bz_2. On the other hand, if steric hindrance in Tol_2 renders the Coulombic interaction less significant, its CT state could be located higher than that of Bz_2.

In light of the preceding paragraph, it is pertinent to consider the possibility that the visible absorption bands observed for the excimer/exciplex originate in the CT state. The excimer of Bz formed in neat liquid reveals a strong absorption band centered at around 500 nm.[25−27] It shifts to 540−550 nm in toluene liquid.[25,27] Exactly parallel behavior is observed for the excimers produced from their vdW precursors. In going from Bz_2 to Tol_2, the excimer absorption band shifts from 455 to 515 nm. The origin of this absorption has not been unequivocally understood. Our previous results for excimers of larger aromatic molecules (e.g., fluorene and naphthalene)[4] suggested that their excimer transitions are likely to occur between a pair of the exciton-resonance states, both of which are being stabilized by interaction with the charge-resonance states. However, the semiempirical result on Bz_2[16] indicated that the observed visible absorption band cannot be explained by the energy level splitting calculated from this assumption. Thus, Cooper and Thomas[25] assigned the 515-nm absorption in benzene liquid to a transition from the lowest excimer state, B_{1g}, correlating to the monomer S_1 state, to an upper state that correlates to the monomer E_{1u} state. It should be pointed out that their assignment is based on the transition energy observed in solution (2.4 eV). Katoh et al.[28] suggested that excimers of benzene and other aromatic molecules are primarily of CT character and their absorption bands can be understood as transitions into CT states. Furthermore, a recent INDO/S computation by East and Lim[15] reinforced that the near-IR absorption of the naphthalene dimer should be assigned to a CT band.

The assumption of CT transition as the origin of the excimer/exciplex absorption bands allows us to calculate vertical CT state energies above the ground state. The absorption maximum occurs at 19 400 cm^{-1} (2.41 eV) for Tol_2 and at 21 500 cm^{-1} (2.72 eV) for Bz_2. The excimer absorption is expected to arise after energy relaxation in the bound excimer potential. This relaxation effect may be evaluated roughly by subtracting the excimer binding energy from the monomer S_1 energy. On the basis of the binding energy values reported for Tol_2 (0.29 eV) and Bz_2 (0.34 eV), the respective vertical CT state energies are calculated to be 6.79 and 7.10 eV above their ground states. The difference in the CT state energy between Tol_2 and Bz_2 (0.31 eV) is smaller by 0.14 eV than the difference at infinite separation. This behavior could be associated with a steric effect on the Coulombic interaction $C(r)$ in Tol_2. The larger CT interaction in Bz_2 is consistent with the larger excimer stability. The general features of the energy diagram pertinent to the above considerations are summarized in Figure 9. The estimated CT state energy in Bz_2 also agrees well with a semiempirical result obtained for a D_{6h} excimer with a ring separation of 3.3 Å.[16] In neat Bz liquid, a broad absorption at >6.3 eV was assigned to a CT state formed by a pair of Bz molecules,[29] which is lower by <0.9 eV than the present gas-phase value.

Finally, it is interesting to see whether the CT interpretation is consistent with the exciplex stability in Tol−Bz. If the binding energy of the Tol−Bz exciplex is assumed to be similar to that of the Tol_2 excimer, the energy of the CT state representative of Tol^+Bz^- can be estimated from the exciplex absorption band of 20 700 cm^{-1} (2.56 eV) to be 6.91 eV. This energy is somewhat closer to the value of Tol_2 and lower by 3 eV than that at infinite intermolecular separation. As shown in Figure 9, the trend in the CT stabilization is in qualitative agreement with that of the excimer/exciplex stablization. Another interesting point is that analogous stabilization behavior is observed for corresponding dimer cations, i.e., Tol_2^+, $(Tol-Bz)^+$, and Bz_2^+. Their energies from the respective neutral ground states can be calculated on the basis of binding energy values reported by Ernstberger et al.[30] The results are also shown in Figure 9.

Conclusions

The main results of the present study are summarized as follows. It has been shown that the Tol−Bz heterodimer and the Tol_2 homodimer reveal similar excess energy-dependent behavior in exciplex/excimer formation in the S_1 state. The dynamics are nearly identical for the two structural isomers of

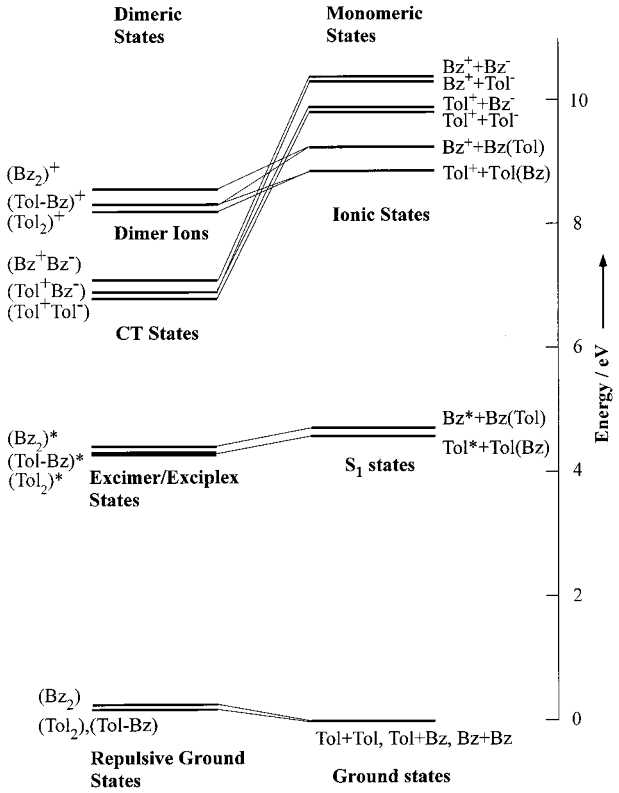

Figure 9. Schematic energy diagram illustrating the excimer/exciplex states, the CT states, and the dimer cation states of the Tol_2, Tol−Bz, and Bz_2 dimers. The energy is scaled relative to the neutral pair limits, Tol + Tol, Tol + Bz, and Bz + Bz. The dimer ground states are repulsive in excimer geometry. The vdW states of these dimers are not shown.

each dimer but differ significantly from that of the T-shaped dimer of Bz where no excess energy is required for excimer formation. Therefore, it is concluded that unlike dimers and clusters of large aromatic molecules, vdW geometry is not a determining factor for the excimer/exciplex formation in these systems. The stabilization of these excited-state species is explained as arising largely from interaction of the dimer state of S_1 parentage with an upper CT state. The observation of the visible absorption bands of the excimer/exciplex is explained as a manifestation of the CT interaction. It is also likely that the excimer/exciplex state of Tol is less stable than that of Bz_2 excimer because of steric requirements.

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