Spectroscopy and Photochemistry of a Derivative of an Anthracene–Naphthalene Phane

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Abstract: The effects of interchromophore interaction on the energy levels of two different polyacene chromophores (anthracene and naphthalene) have been determined. Two new coupled-chromophore compounds were used for the study, 1,2,3,4-tetra-hydro-[2.3](9,10)-anthracenophane (V) and 1-(9-anthryl)-3-(1',2',3',4'-tetrahydro-9'-anthryl)propane (III). Polarized absorption spectra of V and III, the latter obtained in a face-to-face conformation by photocleavage of its photoisomer, were observed as guests in the single crystal host material 1,3-di(9-anthryl)propane photoisomer (cycloadduct, DAPC). V was also studied by fluorescence polarization methods in a rigid hydrocarbon glass. These measurements have unambiguously detected the presence of two interchromophore charge-transfer bands at 33 000 and 37 000 cm^{-1}, the lower of which is likely to be from anthracene to naphthalene. The ^1L_a and ^1L_b states of each chromophore are appreciably shifted to low energy by the face-to-face interaction between the two π-electron systems, but the two ^1B states are merged into one state in the phane. The spectrum of V does not require consideration of "through-bond" interactions between the two chromophores, and the important interactions are "through-space" in nature. Fluorescence is observed from V at low temperatures, but this is quenched at room temperature with the formation of the photoisomer. Ultraviolet irradiation of the latter gives rise to electronically excited product fluorescence identical with that from V. Fluorescence from V has been assigned to a mixture of localized ^1L_a and ^1L_b states of the anthracene chromophore.

There is an increasing interest in phane compounds, and a recent review has summarized the information that has been derived from photoelectron studies of a large number of cyclophanes.[1] The photoelectron data provide convincing evidence for the concepts of "through-space" and "through-bond" interactions between the two chromophores comprising the cyclophanes, ideas which were introduced by Gleiter[2] and Hoffman.[3] However, the photoelectron spectra of larger phanes, such as the naphthalenophanes, are not so easily rationalized.[1] On the other hand, the higher phanes offer much from examination of their electronic spectroscopy because of their lower energy states and the possibility of isolating particular conformations, so that the effects of interchromophore interaction can be delineated. Studies of some anthracenophanes have been reported[4–7] and work in this area is continuing. However, because of the degeneracy of the energy levels of the isolated chromophores, symmetrical phanes have electronic structures which are more complicated to unravel than hetero-phanes. We are therefore examining the spectroscopy of heter-ophanes, and the present paper deals with a phane comprising anthracene and naphthalene chromophores, derived from [2.3](9,10)anthracenophane by hydrogenation of the 1–4 positions of one of the anthracene chromophores, i.e., 1,2,3,4-tetrahydro-[2.3](9,10)anthracenophane (V).

The first report of interacting anthracene and naphthalene chromophores was given by Chandross and Schiebel,[8] who studied the coupled chromophore 1-(9-anthryl)-3-(1-naphthyl)propane (ANP) and its photoisomer (ANPC). Further investigations of this compound have been given,[9,10] and a detailed analysis of the

reversible photochemistry involving ANP and ANPC has been completed recently.[11] In the present paper we concentrate on changes in the electronic spectra of the component chromophores (anthracene and naphthalene) that result from π-electron inter-action in a face-to-face or sandwich conformation. V, through the constraints of the two chemical bridges, provides the closest approach between these two chromophores that we have so far been able to realize.

We have also prepared the closely related compound 1-(9-anthryl)-3-(1',2',3',4'-tetrahydro-9'-anthryl)propane (III) and its photoisomer IIIc. Photochemical cleavage of the latter gives III, and by carrying this out in a rigid glass or a crystal-host medium (the photoisomer of 1,3-di(9-anthryl)propane (DAPC)), various sandwich conformations of III can be trapped, so that the cor-relation between the absorption spectrum of V and the spectra of anthracene and naphthalene can be followed. Of particular interest is the observation of two absorption bands in the spectrum of V which are absent in the spectrum of the open form of III. These are shown to involve electronic transitions between the two chromophores, i.e., intramolecular charge-transfer transitions.

Experimental Section

General. ^1H NMR spectra were recorded on a Bruker CXP-200 spectrometer (200 MHz) in deuteriochloroform with tetramethylsilane as an internal reference. Mass spectra were measured on a VG Micro-mass 7070F mass spectrometer. Absorption and luminescence spectra were measured by using techniques and equipment described previous-ly,[5–7,9,10] except that spectrometer scanning and data collection were under computer control. Spectroscopic grade methylcyclohexane (MCH), de-calin (D), and 2-methylbutane (IP) were used to obtain glassy solvent media.

Materials (Scheme I). **1-(9-Anthroyl)-2-(1',2',3',4'-tetrahydro-9'-anthryl)ethane (II).** Finely pulverized chalcone 1-(9-anthroyl)-2-(9'-anthryl)ethylene (I) (3.5 g) in THF (600 mL) was hydrogenated in the presence of Pd/C (10%) (0.7 g) at room temperature and atmospheric pressure for 48 h or longer, and the progress of the hydrogenation was checked on TLC silica gel and benzene/*n*-hexane (1:1). After filtration and evaporation of the solvent, the remnant was extracted with hot petroleum ether (60–80 °C), the solvent was evaporated, and the rest was chromatographed on an Al$_2$O$_3$ neutral column using benzene/*n*-hexane (1:1). The first pale yellow fraction was collected, evaporated, and crystallized first from ether and then from hot petroleum ether (100–130 °C), giving 430 mg (12%) of slightly yellow prisms, mp 195–198 °C: ^1H NMR (CDCl$_3$) δ (ppm) 1.61–2.04 (m, 2 H, hydroaromatic), 2.8–3.1 (m,

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Scheme I
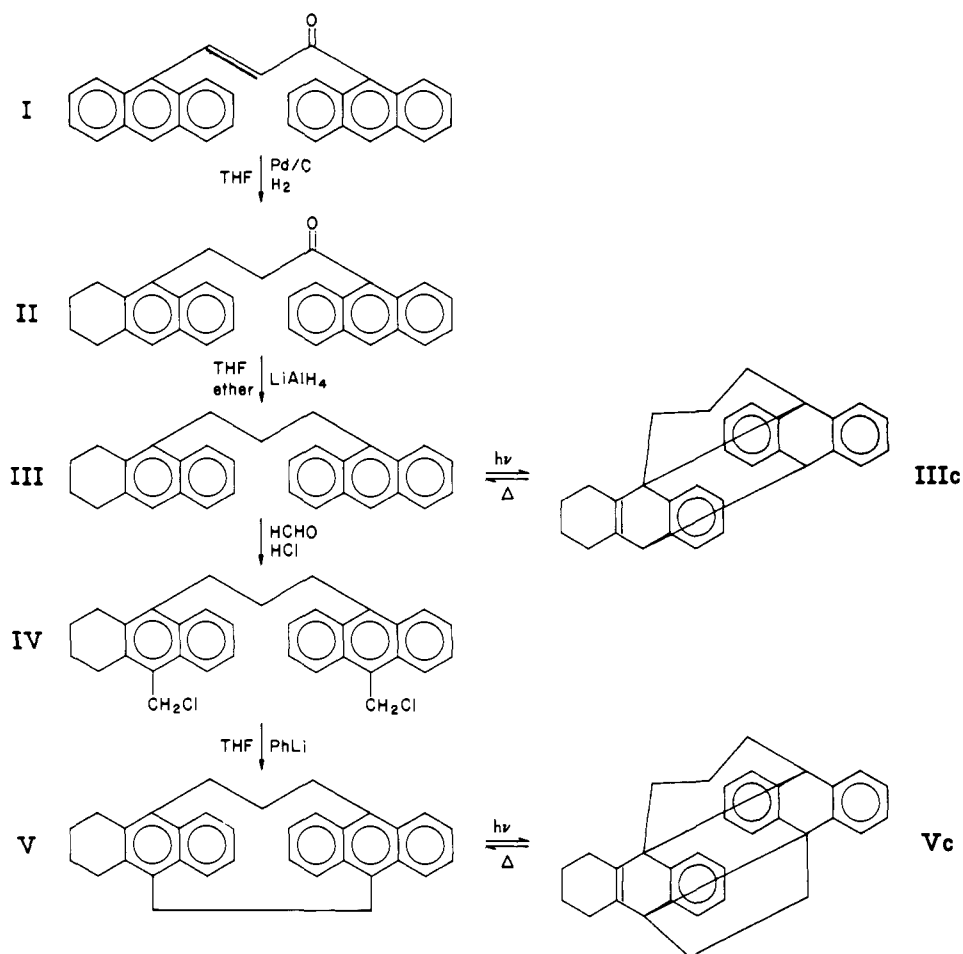
2 H, hydroaromatic), 3.15–3.8 (m, 4 H, hydroaromatic), 3.36–3.59 (t, 2 H, ethylene bridge), 4.1–4.35 (t, 2 H, ethylene bridge); mass spectrum, m/e 414, 194 ($C_{14}H_{13}CH$), 204.9 ($C_{14}H_9CO$), 209 ($C_{14}H_{13}CH_2CH$). The main byproduct was 1-(9-anthroyl)-2-(9'-anthryl)ethane, mp 214–216 °C.

1-(9-Anthryl)-3-(1',2',3',4'-tetrahydro-9'-anthryl)propane (III). The ketone II (100 mg) in THF (2 mL) was slowly added to a suspension of LiAlH$_4$ (100 mg) in ether (2 mL), and the mixture was stirred and refluxed for about 30 min, until dark green. After cooling and decomposition with cold ethyl acetate and dilute HCl, the solvents were evaporated on steam, and the deposit was collected, washed with water, dried, dissolved in a little CHCl$_3$, and chromatographed on preparative TLC silica gel using n-heptane as the solvent. The byproduct anthracene was faster, and the byproduct 1,3-di(9-anthryl)propane (DAP) was slightly slower. The spot with III was extracted with ether and the product crystallized from hot petroleum ether (100–130 °C), forming 30 mg (21%) of light yellow needles: mp 165–166 °C; ^{1}H NMR (CDCl$_3$) δ (ppm) 1.64–1.94 (m, 4 H, tetrahydroanthracene H$_{2,3}$), 2.80–3.00 (m, 4 H, tetrahydroanthracene H$_{1,4}$), 2.05–2.26 (m, 2 H, internal CH$_2$ of propene bridge), 3.18–3.37 (quartet, 2 H, $J \approx 7$ Hz, external CH$_2$ of propene bridge), 3.72–3.95 (quartet, 2 H, $J \approx 7$ Hz, external CH$_2$ of propene bridge), 7.24–7.37, 7.90–8.03 (m, 4 H, anthracene H$_{1',4',5',6'}$), 7.37–7.49 (m, 4 H, anthracene H$_{2',3',6',7'}$), 8.32 (s, 1 H, anthracene H$_{10'}$), 7.62–7.90 (m, 2 H, tetrahydroanthracene H$_{6,7}$), 8.10–8.25 (m, 2 H, tetrahydroanthracene H$_{5,8}$), 8.17 (s, 1 H, tetrahydroanthracene H$_{10}$); mass spectrum, m/e 400 and 396, indicating presence of very small quantity of DAP.

1-(10-(Chloromethyl)-9-anthryl)-3-(1',2',3',4'-tetrahydro-10'-(chloromethyl)-9'-anthryl)propane (IV). Pulverized paraformaldehyde (50 mg) and III (50 mg) were suspended in dioxane (1 mL) and concentrated HCl (0.4 mL). The mixture was stirred and refluxed for 1 h while bubbling a fine stream of HCl gas through the mixture. The reaction mixture was left at room temperature overnight, and the precipitate was filtered off and washed with ethyl alcohol. The yield was 44 mg (72%) of yellow crystalline powder: mp > 200 °C dec; mass spectrum, m/e (496). The product was used for cyclization without further purification.

1,2,3,4-Tetrahydro-[2.3](9,10)-anthracenophane (V). IV (44 mg) was suspended in THF (5 mL) and a 0.6 M ether solution of PhLi (1.25 mL)

added. The mixture was stirred and gently heated until it became clear and golden-yellow in color (about 10 min), and then the reaction was stopped by addition of excess icy water. HCl (dilute) was added and the product extracted with ether. The ether solution was dried with Na$_2$SO$_4$ (anhydrous) and evaporated and the residue heated on an oil bath (180 °C) for 30 min under vacuum. The solid was then dissolved in a minimum amount of benzene and chromatographed on SiO$_2$ column using a benzene/petroleum ether (60–80 °C) (1:6) mixture as the solvent. The main byproducts, i.e., polymers, diphenyl, dimethyl, and dibenzyl derivatives of 1-(9-anthryl)-3-(1',2',3',4'-tetrahydro-9'-anthryl)propane, were separated, and the product, still containing traces of a slightly slower moving [2.3](9,10)-anthracenophane (mass 422), was purified on preparative SiO$_2$ TLC, using n-heptane as the solvent. The yellow spot was extracted with ether, the ether evaporated, and the product crystallized from hot petroleum ether (100–130 °C), forming 2 mg (4%) of yellow prisms: mp > 300 °C dec; ^{1}H NMR (CDCl$_3$) δ (ppm) 1.05–1.30 (m, 4 H, tetrahydroanthracene H$_{2,3}$), 2.28–2.53 (m, 4 H, tetrahydroanthracene H$_{1,4}$), 2.10–2.28, 2.63–2.82 (m, 2 H, internal CH$_2$ of propene bridge), 2.87–3.25 (m, 2 H, external CH$_2$ of propene bridge), 3.43–3.57, 3.70–3.84 (m, 2 H, external CH$_2$ of propene bridge), 3.61–3.73 (quartet, 2 H, $J \approx 7$ Hz, ethylene bridge CH$_2$), 4.08–4.20 (quartet, 2 H, $J \approx 7$ Hz, ethylene bridge CH$_2$), 6.75–6.93 (m, 4 H, anthracene H$_{1',4',5',8'}$), 7.26–7.57 (m, 4 H, anthracene H$_{2',3',6',7'}$), 7.58–7.85 (m, 2 H, tetrahydroanthracene H$_{6,7}$), 8.11–8.25 (m, 2 H, tetrahydroanthracene H$_{5,8}$): mass spectrum, m/e 426.

Elementary analyses of all compounds described were consistent with their molecular structures.

Crystal Structures. The necessary polarization information relating to the transition moment directions in V and cleaved IIIc was obtained by including these compounds in single crystals of the host material DAPC. This compound crystallizes the rectangular prisms having well-developed 010 and 100 faces. The crystal structure of DAPC has been determined,[12] and the extremely useful property this material has as a host for phane molecules has been demonstrated.[6] The structure

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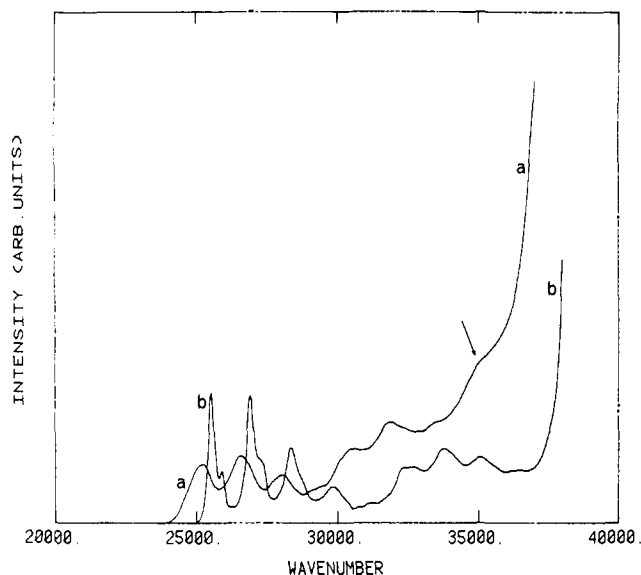
Figure 1. Corrected excitation spectra at 90 K of III after photocleavage of IIIc in MCH:D (a) and after softening of the glass and return to 90 K (b).

Figure 2. Polarized absorption spectra of III in DAPC at 10 K after photocleavage of IIIc. The light was incident normal to the 010 face and the X and Y refer to polarization directions defined in ref 12.

contains two different sites in the unit cell, one is an ordered site while the other is disordered with respect to the orientation of the molecule. It is this latter site which is preferred by guest molecules because of the greater volume available. The two well-developed faces of the crystal provide clear polarization differences for all three molecular axes. For light propagating normal to the 010 face, the long molecular axis polarization appears completely in one extinction direction while the 100 face allows a discrimination between the short axis and interchromophore polarization, the former making a larger projection (*b*) and the latter a larger projection (*c*). The detailed considerations are given elsewhere.[12]

Results and Analysis

Ultraviolet irradiation of the photoisomer of III (IIIc) in MCH:D at about 90 K quickly produces III in which a "sandwich" arrangement of the two chromophores is maintained by the constraints of the rigid glass. Subsequent increase of temperature leads to softening of the glass and relaxation of the chromophores to an open conformation. Figure 1 shows the relevant spectra. The effect of the interchromophore interaction produces a red shift of about 300 cm^{-1} in the anthracene chromophore absorption band and a shift of about 2000 cm^{-1} in the naphthalene chromophore absorption band. These results are analogous to those obtained earlier for ANP, obtained by photodissociation of ANPC in a very rigid glass of MCH:IP at 45 K.[9] There is another band in Figure 1, a shoulder at about 35000 cm^{-1} (indicated by the arrow) which has no counterpart in the spectrum of either chromophore.

The absorption spectrum of IIIc has its lowest band about 2 nm longer than the wavelength of that of DAPC. Inclusion of the former as the guest in the latter allows the selective monochromatic photodissociation of IIIc at about 10 K. The resultant absorption spectrum, for incident light normal to the 010 face of DAPC is shown in Figure 2 for the two polarization directions X and Y.[12] The crystal spectra provide information about the polarizations of the bands. Earlier work[6] has established that guest molecules prefer the disordered site in the DAPC crystal and the 010 face allows discrimination between long and short molecular axis polarization. The absorption between 29000 and 33000 cm^{-1} in Figure 2 is strongly polarized (X) consistent with a ^1L_a assignment of the excited state of the naphthalene chromophore. On the other hand, the anthracene chromophore shows mixed polarization, indicating both long and short axis polarization. The relative intensities are, however, not given by Figure 2 because of the small projection which a short axis moment of a cleaved molecule would make on the 010 face. This point has been considered previously, and with the assumption that the guest molecule has the same orientation as the host molecule and on cleavage, it opens symmetrically; then the correction factor should be about 3[12] so that the absorption (X) (Figure 2) should be
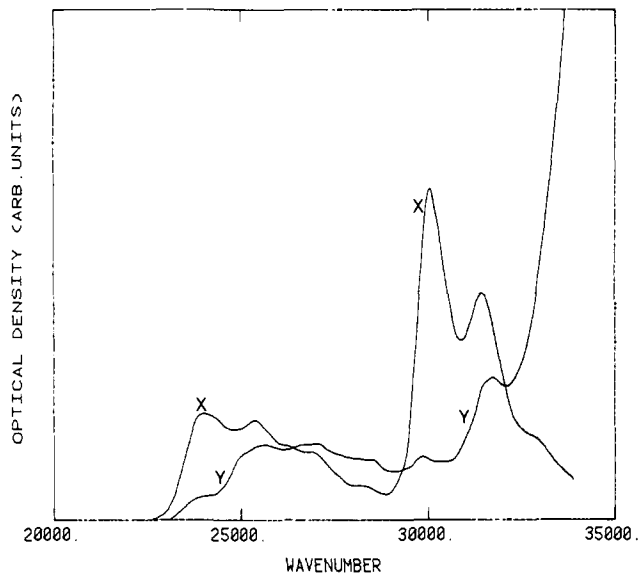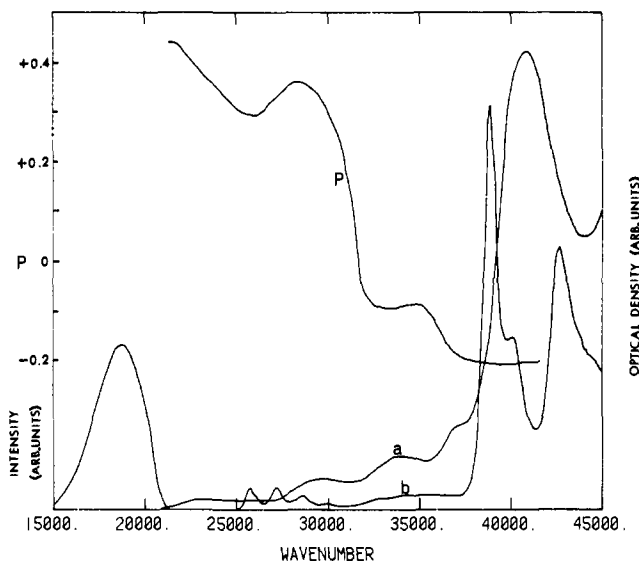
Figure 3. Absorption spectra of V (a) and III (b) in MCH at room temperature. The fluorescence spectrum (100 K) of V is included along with the polarization ratio (P) of the fluorescence (100 K).

increased by this factor. There remains a substantial absorption intensity (Y), and it has been shown recently[7] that this intensity correponds to a transition to the ^1L_b excited state of anthracene, which carries about 20% of the overall intensity observed in the solution spectrum.[7] The significant feature of the spectrum in Figure 2 is the appearance of long axis intensity in the lowest energy band (pure electronic transition) at 24000 cm^{-1}, in contrast to the naphthalene chromophore absorption which has no corresponding long axis polarization intensity. This suggests a significant shift of the anthracene ^1L_b state to lower energy as a result of the interchromophore interaction.

Next we consider V. Here, the chemical bridges maintain specific conformational relationships between the two chromophores. If we neglect the internal conformations of the tetrahydrogenated ring, there will be four configurations of V for each of the two conformations of [2.3](9,10)-anthracenophane, dependent on the position of the tetrahydrogenated ring, a total of eight conformations. Whereas features of the two conformations of [2.3](9,10)-anthracenophane could be identified in its absorption spectrum in different media,[6] the absorption spectrum of V comprises a set of broad bands either in rigid glasses or in the single-crystal host DAPC.
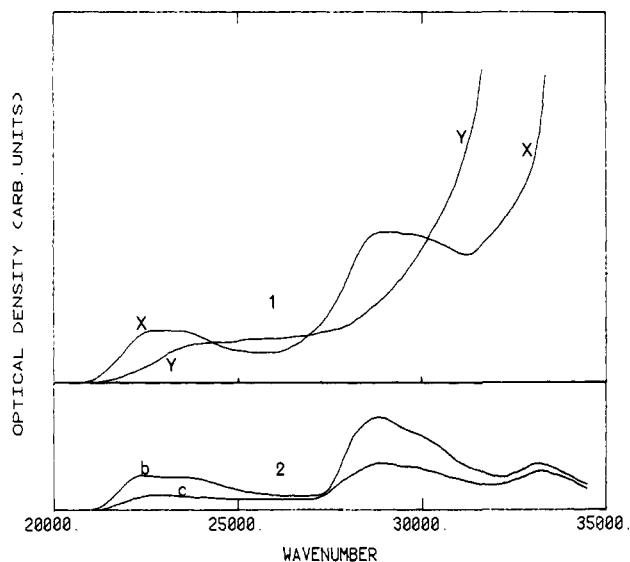
Figure 4. (1) Room temperature polarized absorption spectra of V in DAPC for light incident on the 010 face. X and Y polarization directions are defined in ref 12. (2) Polarized absorption spectrum of V at 10 K for light incident normal to the 100 face of the host crystal DAPC.

The solution spectrum of V is given in Figure 3 as well as that of III for comparison. The latter shows four main absorption bands, corresponding to the two ^1L_a and the two ^1B states of each chromophore. Previous work[9,10] and the spectra in Figures 1 and 2 identify the two lowest absorption bands, at 23 000 and 29 000 cm^{-1}, as transitions to the ^1L_a states of anthracene and naphthalene, respectively. The two ^1B bands have coalesced into one band which appears close to the center of gravity of the individual chromophore bands. There remain two bands at 33 000 and 38 000 cm^{-1} which have no obvious counterparts in the spectra of either component chromophore.

V is nonfluorescent at room temperature and exposure to visible light quickly forms the photoisomer. However, cooling of solutions leads to the appearance of fluorescence and a quenching of photoisomerization. The fluorescence band observed at 100 K in MCH:IP is shown in Figure 3, and the polarization ratio of the corresponding excitation spectrum at 100 K is also included in Figure 3. We see that the onset of the absorption spectrum, near 21 000 cm^{-1}, has high positive polarization which then drops steadily across the lowest energy band. The ratio then increases for the second band and then drops rapidly as the third band near 33 000 cm^{-1} is approached, becoming negative. A further negative drop is seen for the fourth band at 37 000 cm^{-1}, and the ratio remains negative into the intense band near 41 000 cm^{-1}. Interpretation of these results requires a consideration of the polarization properties of the crystal absorption spectra before a definitive assignment of all the absorption bands can be made.

The absorption spectrum given in Figure 4a (a = X and Y) shows that the lowest energy absorption band has mixed long and short molecular axis polarizations, in contrast to the second band, between about 27 500 and 32 000 cm^{-1}, which is nearly completely polarized along the short molecular axis. These conclusions come from the crystal structure of DAPC and the projections of the molecules on the (010) face,[12] used to obtain the polarized spectra in Figure 4a. The similarity between the dichroism of the spectrum of V (Figure 4a) and that of III (Figure 2) is obvious.

Returning to Figure 3, we see that the decrease of the polarization ratio across the lowest energy absorption band is due to the long molecular axis component associated with the ^1L_b state of anthracene. The subsequent increase, between 26 000 and 28 000 cm^{-1}, is due to the transition to the ^1L_a state of naphthalene, which will have its polarization direction at a small angle to the corresponding direction in the anthracene chromophore. The sharp change of sign in the polarization ratio for excitation in the remainder of the absorption spectrum to higher energy indicates absorption polarization directions which are orthogonal to the

fluorescence polarization direction. These can be either along the long molecular axis or from one chromophore to the other. The former case must apply to the broad band near 40 000 cm^{-1}, but the latter case applies to the band near 33 000 cm^{-1} for certain. This conclusion comes from the crystal spectrum observed for light incident normal to the 100 face, given in Figure 4b. For this face, long molecular axis polarization makes essentially zero projection,[12] and yet the 33 000-cm^{-1} band is clearly evident. Its absorption intensity, relative to the bands at lower energy, is somewhat less than in the solution spectrum (Figure 3), which is consistent with the molecular projections onto the 100 face because a moment from one chromophore to the other will make a smaller projection than will a short chromophore moment which lies completely in the 100 face.

The combination of fluorescence polarization and single-crystal dichroism establishes, therefore, that the absorption band near 33 000 cm^{-1} is a charge-transfer band, corresponding to the transfer of an electron from one chromophore to the other. The direction of electron transfer is more likely from anthracene to naphthalene as the photoelectron ionization energy of [2](2,5)-furano-[2]-(9,10)-anthracenophane is lower (6.87 eV) than that of the similar phane *anti*-[2](2,5)-furano-[2](1,4)-naphthalenophane (7.46 eV).[13] Another band, slightly higher in energy at 37 000 cm^{-1}, is also likely to be a charge-transfer band because of its negative polarization, but it is hidden in the crystal absorption spectrum by transitions of the host, so that similar confirmation cannot be obtained. It might, perhaps, correspond to a transfer in the reverse direction, but the more negative polarization ratio (Figure 3) suggests that different orbitals are involved. The lowest energy absorption band, however, is localized in the anthracene chromophore and the mixed polarization arises from overlapping contributions from transitions to the analogues of the anthracene transitions $^1A_1 \rightarrow {}^1L_a$, ^1L_b, not from (out-of-plane) charge-transfer transitions.

The latter conclusion is at variance with the theoretical ideas developed by Beens and Weller[14] for the description of exciplexes. From their model we would expect that the states of the molecular complex could be described by an admixture of localized and charge-transfer basis functions which would be reflected in the polarizations associated with absorption of light. Turning to Figure 4b, which contains absorption intensity polarized along the short chromophore axes and between the chromophores, we see that the bands corresponding to transitions to the ^1L_a states of each chromophore (between 21 000 and 32 000 cm^{-1}) are both polarized more strongly parallel to b, and the ratio b/c is the same for both (2:1). The observed ratio is consistent with short axis polarization, at least a dominant short axis polarization, and it might be argued that the admixture of charge-transfer character into the localized states is relatively small and does not provide a significant change in the dipole strengths of the transitions of the isolated chromophores. While the determination of absolute dipole strengths of the bands of the interacting chromophore systems is out of the question, we are able to compare the relative dipole strengths of the two transitions associated with the ^1L_a state of each chromophore as the interaction is "urned on" experimentally.

In the open form of III, the integrated absorption intensities of the two regions corresponding to the two ^1L_a states are approximately equal. For cleaved IIIc in DAPC (Figure 4a), the dipole strength of the naphthalene band is 1.15 times that of the anthracene band. For V in DAPC (Figure 4b), the ratio is 1.5:1. There is, therefore, a very significant change in the relative dipole strengths of the transitions associated with the ^1L_a states of each chromophore as a result of a face-to-face sandwich interaction between the two chromophores. These changes, present in the absorption spectra of both guests in the same host crystal, are not seen in the absorption spectrum of photocleaved IIIc in MCH:D at 90 K (Figure 1).

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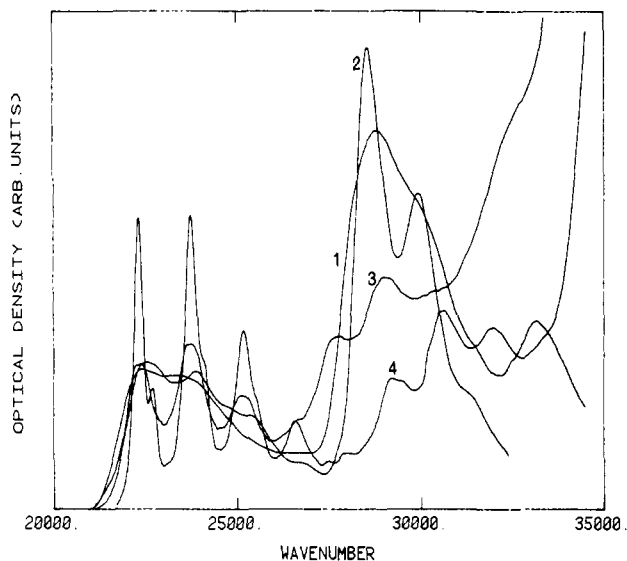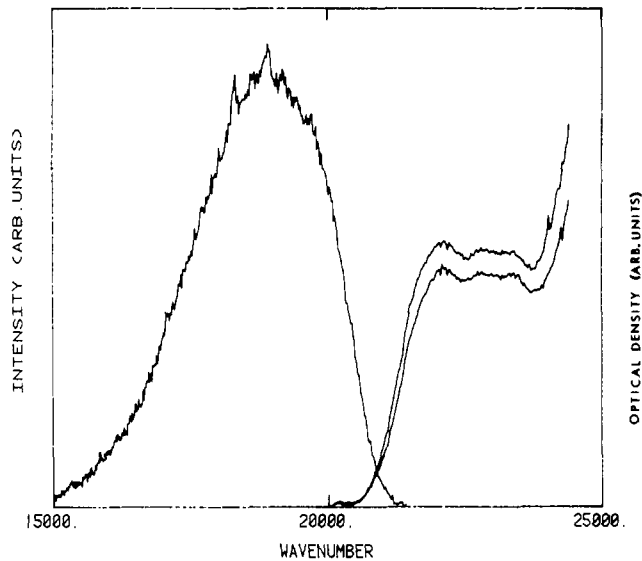
Figure 5. Absorption spectra of (1) V, *b* from Figure 4b, (2) III, *X* from Figure 2, (3) face-to-face form of III in MCH from Figure 1, (4) open form of III from Figure 1. (2), (3), and (4) have been displaced by 1500, 2900, and 3200 cm^{-1}, respectively, to lower energy, and the integrated absorption intensities from 21 000 to 26 000 cm^{-1} have been made equal.

Figure 6. Absorption (polarized) and fluorescence of V in a single-host crystal of the photoisomer of [2.3](9,10)-anthracenophane at 10 K. The light was incident on the unknown well-developed face of the crystal for the absorption spectra.

It is useful to compare the various spectra in a more quantitative way to illustrate the effects of the interchromophore interaction. Here again, only relative comparisons can be made, and we choose to compare four sets of spectra in such a way that the integrated absorption intensity of the ^1L_a band of anthracene is made equal for four spectra, the two given in Figure 1 together with the *c* polarized spectra of Figures 2 and 4b. The four spectra are shown in Figure 5, in which the three spectra of III have been displaced so that their vibrational structure, in the ^1L_a anthracene chromophore region, overlap the corresponding structure in the spectrum of V. It can be seen that the phane interaction leads to a greater lowering of the energy of the naphthalene ^1L_a state compared to the spectrum of the open form of III. The centers of gravity of the anthracene and naphthalene ^1L_a chromophore bands are lowered by 2900 and 5000 cm^{-1}, respectively, from the values of the open form. The corresponding values for III cleaved in DAPC are 1400 and 3500 cm^{-1}.

The difference between the shifts of the two spectra from the spectrum of the open form is 1500 cm^{-1}, of which about half could be given by the increased red shift associated with disubstitution in both chromophores. The remainder, about 750 cm^{-1}, is all that can possibly be ascribed to "through-bond" interaction in the phane, via the dimethylene bridge. Even this could possibly be due to a stronger "through-space" interaction because of the tighter constraints provided by the chemical bridges compared with the constraints of the lattice cage holding the cleaved III in a face-to-face conformation.

Closer comparison of the spectra of III in DAPC and in MCH:D shows quite a different intensity distribution in the ^1L_a band of the naphthalene chromophore in the two spectra, the latter being very similar to that of the open form (see Figure 5). There is also a distinct difference in the higher energy region of the spectrum of III in MCH:D (face-to-face conformation) and that of V in MCH. The former shows the ^1B band of the anthracene chromophore shifted to lower energy (see also the analogous result for ANP in MCH:IP[9]), while for V, the B states of anthracene and naphthalene are coalesced into one band lying between the bands of the individual chromophores (see also analogous results for ANP[9]).

The fluorescence properties were studied in crystalline host media as well as in glassy solutions, but there are no essential differences between the two types of medium. The fluorescence and absorption (polarized) spectra of V as a guest in the [2.3](9,10)-anthracenophane photoisomer are given in Figure 6. The structureless fluorescence band is considerably broader than the (structured) absorption band. This lack of good mirror-image symmetry indicates a decrease of interchromophore spacing in the fluorescent state, typical of excimers and exciplexes, but there is only a relatively small shift of the fluorescence band from the absorption band and there is a small region of overlap.

The fluorescence spectra of V in various media and those of III and ANP, photocleaved in rigid glasses or host crystals, all show reasonable overlap with the corresponding absorption spectra, so it seems likely that the emitting state are closely related to those reached by absorption from the ground states. This means that the fluorescent states, in each case, are best described in similar, qualitative terms. The emitting state of the anthracene–chromophore exciplex appears to be localized on the anthracene chromophore and has both ^1L_a and ^1L_b character. The lengthening of the decay time[9] then comes from the ^1L_b state and is not a consequence of the mixing of charge-transfer character into the ^1L_a state. We therefore made some attempts to determine the effect of temperature on the polarization of the fluorescence of V in DAPC.

Quantitative measurements of the polarization of luminescence from crystals are always difficult to make because of internal reflections and sample inhomogenities, particularly in solution-grown crystals. For the present work, crystals were mounted over 200 μm diameter apertures in thin Al foil, and the exciting light was focused, by means of a reflecting objective, onto the aperture. The exciting radiation fell on the 100 face, and the emission was collected, at 90°, from the 010 face. Spectra were determined for polarizations parallel and perpendicular to the *c* axis. At about 8 K the intensities of the two polarizations were nearly equal with *c*. Increase of temperature leads to an increase of this ratio; i.e., the emission becomes more short axis polarized (from ^1L_a). The low-temperature result then indicates that about 30% of the emission comes from the ^1L_b component.

It would appear likely that the quenching of the fluorescence, involving temperature-dependent factors, would be different for each state (^1L_a and ^1L_b). Attempts were made to determine the temperature dependence of the fluorescence intensity of V in DAPC single crystals. Here again, the quantitative characterization of the observations was imprecise due to variations from crystal to crystal. However, the qualitative observations were similar in each case. Between about 8 and 100 K, the fluorescence intensity drops by about 20–30% of its low-temperature value. The remainder of the intensity is quenched over the range 100–250 K. Further progress in this area will have to await the availability of other anthracene–naphthalene phanes currently being synthesized.

Irradiation of the photoisomer of V (Vc) with ultraviolet light leads to the production of V, and, as with ANPC and IIIc, part of the product is fluorescent, the emission being identical with the exciplex fluorescence obtained by excitation of V. The quantum yield of this electronically excited product is about 10% of the corresponding value observed from irradiation of ANPC

at about 100 K in glassy solvents.[11]

Photophysical Studies on 1-(*p*-Aminophenyl)pyrene. Characterization of an Intramolecular Charge-Transfer State with Application to Proton-Transfer Dynamics

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Abstract: A photophysical study on 1-(*p*-aminophenyl)pyrene (I) reveals two principal fluorescences arising from π,π^* (locally excited in pyrene ring) and charge-transfer (CT) (aniline as donor, pyrene as acceptor) states. The latter dominates in organic solvents and aqueous media at pH ≥ 7. The estimated energy of the CT state in highly polar solvents (near 500 nm, ~ 2.5 eV) agrees well with the measured redox energetics (2.7 eV) while the dependence of the transition energy on solvent dielectric constant indicates an excited state dipole moment of ~ 14 D. The photophysics of I is pH dependent in aqueous media because of a conjugate acid/base equilibrium with ground- and excited-state constants of $pK_a = 4.05$, $pK_a^* = 3.3$ (Forster cycle), respectively, in ethanol–water (50:50). The rather similar acidities of the ground and excited states of I indicate little or no CT contribution to the deprotonation step in the excited state. Deprotonation of the locally excited π,π^* state of I (conjugate acid form) is thought to initially yield the locally excited free base form of I which rapidly relaxes to the CT state. The latter is subject to proton-transfer quenching (most likely involving the pyrene radical anion moiety of the CT state), $k_q = (7.38 \pm 1.5) \times 10^8$ M^{-1} s^{-1} (corrected for changing proton activity coefficients in ethanol–water). A study of the rate of deprotonation of the conjugate acid of I* from room temperature through the liquid/solid phase transition (near ~ 50 °C) to –196 °C allows an estimate of the enthalpy and entropy of activation in several different regions. As the temperature is lowered from 295 to 160 K, the enthalpy term decreases from 5360 to 780 cal/mol while the entropy term changes from –6.1 to –24.3 cal/(K·mol).

Charge-transfer (CT) interaction is an important contributor to the electronic excited states of molecules.[1] The almost ubiquitous nature of CT in photochemistry arises from the relatively favorable energetics of redox reactions when one of the reactants is photoexcited. Both inter-[2] and intramolecular[3] excited-state CT complexes are known with varying degrees of CT character. One common structural arrangement of these complexes has the interacting π-systems in parallel planes 3 or 4 Å apart.[4] Recently, another type of CT complex has been identified in systems where π-electron donor and acceptor groups, directly connected by a single bond, reside in mutually orthogonal planes. These complexes have been named twisted intramolecular charge-transfer (TICT) complexes.[5] Examples of compounds forming excited-state TICT complexes are *p*-(dimethylamino)benzonitrile[6] (the classical case) and *p*-(9-anthryl)-*N,N*-dimethylaniline and derivatives.[7] Dual fluorescences are often observed from these systems arising from a locally excited π,π^* state (which is rather solvent independent)

and the TICT state (which is very solvent dependent because of a large dipole moment).

This paper describes the photophysics of 1-(*p*-aminophenyl)-pyrene (I),[8] which is dominated by a low-energy TICT state. The dual fluorescences observed in this system, which arise from locally excited, π,π^* (conjugate acid) and TICT (free base) states, may be readily modulated by pH. An important observation is the apparent uncoupling of deprotonation of the locally excited conjugate acid from transformation of the π,π^* into the TICT state. Finally, we demonstrate the usefulness of I as a probe of proton-transfer dynamics over a wide temperature range.
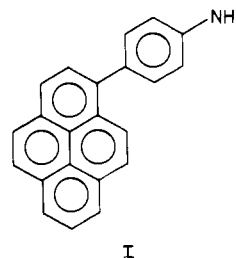
I

Results and Discussion

Synthesis and Structure of 1-(*p*-Aminophenyl)pyrene. Compound I was synthesized by conventional procedures starting with coupling of *p*-nitrophenyldiazonium chloride with pyrene. Careful column chromatography led to isolation of both 1-(*p*-nitrophenyl)- and 2-(*p*-nitrophenyl)pyrene. Both compounds were reduced to the corresponding amines (Sn/HCl). Mass spectral analysis confirmed the formulas of both the nitro and amino compounds while the structures of the 1- and 2-isomers were elucidated by

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