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Symmetry Breaking in the Relaxed S_1 Excited State of Bianthryl Derivatives in Weakly Polar Solvents

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Abstract: The flash-photolysis time-resolved microwave conductivity technique (**FP-TRMC**) has been used to investigate the nature of the relaxed S_1 state of 9,9′-bianthryl (**AA**), 10-cyano-9,9′-bianthryl (**CAA**), and 10,10′-dicyano-9,9′-bianthryl (**CAAC**). Changes in both the real, $\Delta\epsilon'$ (dielectric constant), and imaginary, $\Delta\epsilon''$ (dielectric loss), components of the complex permittivity have been measured. The dielectric loss transients conclusively demonstrate the dipolar nature of S_1 for all three compounds in the pseudopolar solvents benzene and 1,4-dioxane, and even in the nonpolar solvents *n*-hexane and cyclohexane. The required symmetry breaking is considered to result from density and structural fluctuations in the solvent environment. The dipole relaxation times for AA (CAAC) are ca. 2 ps for the alkanes and 7.9 (5.3) and 14 (14) ps for benzene and dioxane, respectively. The time scale of dipole relaxation for the symmetrical compounds is much shorter than that for rotational diffusion and is attributed to intramolecular, flip-flop dipole reversal via a neutral excitonic state. The dipole moment of the transient dipolar state is estimated to be ca. 8 D, that is much lower than the value of ca. 20 D determined from the solvatochromic shifts in the fluorescence in intermediate to highly polar solvents which corresponds to close to complete charge separation. For the asymmetric compound, CAA, a dipole moment close to 20 D is found in all solvents, including *n*-hexane. Dipole relaxation in this case occurs on a time scale of several hundred picoseconds and is controlled mainly by diffusional rotation of the molecules. The mechanism and kinetics of formation of the dipolar excited states are discussed in the light of these results.

Introduction

9,9′-Bianthryl (AA), with its D_{2d} symmetry in the ground state, has become the classic example of the occurrence of symmetry breaking on photoexcitation. The initial evidence that the relaxed S_1 state of bianthryl could be highly dipolar was presented in 1968 by Schneider and Lippert[1,2] in the form of the pronounced bathochromic shift of its fluorescence in polar solvents. The photophysical processes leading to charge separation after photoexcitation were described in considerable detail by the original authors. The absolute value of the dipole moment of the S_1 state of AA in polar solvents of close to 20 D estimated in the initial study from the solvatochromic shift has been reproduced in subsequent studies.[3−6] Most of the discussion and the large body of experiments carried out in more recent years have focused on the precise mechanism and the dynamics of the conversion from the initially formed, locally excited state, A*A, to the eventual charge-separated state, A^+A^-. A full understanding is complicated by the fact that both torsional motion around the central σ-bond and solvent reorganization can be invoked as reaction coordinates.[7]

While there is reasonable agreement at present concerning the photophysics of bianthryl in polar solvents for which solvation is considered to play the major role, the processes occurring in nonpolar (saturated hydrocarbon) and weakly polar solvents (e.g., benzene, dioxane, dialkyl ethers) remain contentious. In the region of effective dielectric constant less than ca. 6, Schneider and Lippert, and subsequent workers, found only a very weak dependence of the fluorescence on the solvent polarity (as defined for example by the $E_T(30)$ value).[1−6] Liptay et al.[8,9] showed that the temperature-dependent fluorescence spectra of bianthryl in an alkane solvent and benzene could be adequately explained in terms of a single, neutral excitonic state whose potential energy surface has a shallow double minimum at torsional angles of ca. 60° and 120° in contrast to the ground state whose potential energy surface has only a single minimum at a torsional angle of 90° between the anthracene units. While this excitonic state is considered to contain an admixture of charge resonance states at the torsional minima, the degeneracy of these states, resulting from the D_2 symmetry, should result in no net dipole moment of the molecule. Further evidence for the lack of charge transfer character in weakly polar solvents has been provided by transient optical absorption measurements which display no spectral features characteristic of the known

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(1) Schneider, F.; Lippert, E. *Ber. Bunsen-Ges. Phys. Chem.* **1968**, *72*, 1155−1160.

(2) Schneider, F.; Lippert, E. *Ber. Bunsen-Ges. Phys. Chem.* **1970**, *74*, 624−630.

(3) Zander, M.; Rettig, W. *Chem. Phys. Lett.* **1984**, *110*, 602−610.

(4) Müller, S.; Heinze, J. *Chem. Phys.* **1991**, *157*, 231−242.

(5) Fritz, R.; Rettig, W.; Nishiyama, K.; Okada, T.; Müller, U.; Müllen, K. *J. Phys. Chem. A* **1997**, *101*, 2796−2802.

(6) Nishiyama, K.; Honda, T.; Reis, H.; Müller, U.; Müllen, K.; Baumann, W.; Okada, T. *J. Phys. Chem. A* **1998**, *102*, 2934−2943.

(7) Honma, K.; Arita, K.; Yamasaki, K.; Kajimoto, O. *J. Chem. Phys.* **1991**, *94*, 3496−3503.

(8) Wortmann, R.; Elich, K.; Lebus, S.; Liptay, W. *J. Chem. Phys.* **1991**, *95*, 6371−6381.

(9) Wortmann, R.; Lebus, S.; Elich, K.; Assar, S.; Detzer, N.; Liptay, W. *Chem. Phys. Lett.* **1992**, *198*, 220−228.

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radical ion spectra of anthracene; features which are, however, observed for bianthryl in polar solvents such as acetonitrile.[5,6]

Despite the above evidence to the contrary, time-resolved microwave conductivity (TRMC)[10,11] and electrooptical emission (EOEM)[12] measurements have clearly demonstrated that the relaxed S_1 state of AA does have an appreciable dipole moment within the low polarity regime, even in saturated hydrocarbon solvents. In addition, several groups[4,5,13−18] have suggested that the spectral form and picosecond-time scale relaxation of the fluorescence of AA in weakly polar media can best be explained in terms of an equilibrium between a neutral, excitonic state, E (frequently denoted as LE), and a zwitterionic, charge transfer state, CT. From spectral and kinetic analysis of the experimental data values of the equilibrium constant, $K_{ECT} = [CT]_{eq}/[E]_{eq}$, have been derived.

Evidence for an equilibrium between a neutral and a dipolar state in weakly polar solvents was also provided by the TRMC study of Fessenden et al.[11] who measured the change in both the real (dielectric constant) and imaginary (dielectric loss) components of the permittivity of AA solutions on photoexcitation. From these measurements the dipole relaxation time could be measured and was found to be ca. 10 ps in benzene and dioxane. Since this was too fast to be explained by rotational diffusion of the molecules, it was attributed to intramolecular dipole reversal, possibly via an intermediate, neutral excitonic state. The dipole moments of the individual dipolar states calculated from the TRMC data using the equilibrium constants determined in the fluorescence measurements were, however, much lower than the ca. 20 D found in polar solvents: a value which is close to that expected for full charge separation over the center-to-center distance of 4.3 Å between the anthryl units.

It is apparent from the above that considerable uncertainty still exists as to the nature of the relaxed S_1 state of AA in weakly polar media. The possibility that the molecular symmetry could be broken even in completely nonpolar hydrocarbon solvents is of particular relevance for a full understanding of the mechanism of intramolecular charge separation in general, not just for bianthryl itself. Since, in our opinion, TRMC experiments should provide the most clear-cut evidence for a dipolar character of the relaxed S_1 state, we have repeated the measurements of Visser et al.[10] and Fessenden et al.[11] using a somewhat different approach to measure the photoinduced changes in the real and imaginary components of the permittivity. In addition to solutions of AA in benzene and dioxane, we have carried out measurements on the symmetric 10,10′-dicyano-substituted derivative (CAAC) and the asymmetric 10-cyano derivative (CAA). Measurements have also been made on alkane solutions which could not be studied by Fessenden et al.[11] The results confirm the dipolar nature of the S_1 states of the symmetrical molecules even in alkane solvents and show that flip-flop dipole reversal occurs on a time scale of ca. 10 ps in benzene and dioxane, and ca. 2 ps in the alkanes. The TRMC results are complemented by optical absorption and emission measurements in a variety of solvents.

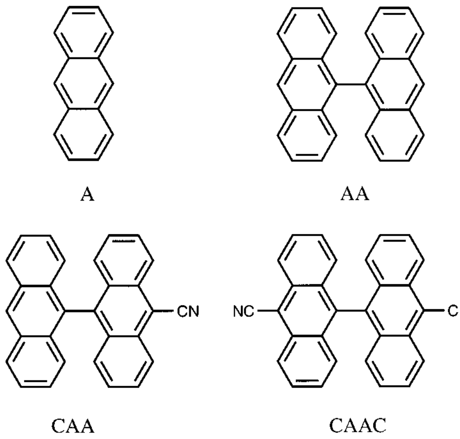

Figure 1. The molecular structures of the compounds studied, together with their pseudonyms used in the text.

Experimental Methods

The molecular structures of the four solute molecules investigated together with their pseudonyms used throughout the text are shown in Figure 1. The solvents *n*-hexane (NHX; Merck Uvasol), cyclohexane (CHX; Merck Uvasol), benzene (BEN; Fluka, for spectroscopy), tetrahydrofuran (THF; Aldrich, spectrograde), ethyl acetate (Fluka, for spectroscopy), *N*,*N*-dimethylformamide (DMF; Aldrich, spectrograde), and acetonitrile (Aldrich, spectrograde) were used without further purification. The ethers dibutyl ether (Aldrich, anhydrous), diisopropyl ether (Aldrich, anhydrous), and diethyl ether (Aldrich, spectrograde) were dried on potassium hydroxide pellets, while 1,4-dioxane (DOX; Fluka, for spectroscopy) was dried over activated silica gel prior to use.

The optical densities of the solutions at 308 (TRMC) or 337 nm (fluorescence) were monitored using a Kontron Uvikon 940 UV−vis spectrophotometer. For TRMC measurements an optical density of close to unity is usually preferred, but due to an extremely low extinction coefficient at 308 nm for all bianthryls investigated the optical density was less than 0.3 in all cases. All solutions used for fluorescence measurements had an optical density between 0.05 and 0.15 at 337 nm.

Steady-state emission spectra were measured on a PTI quantamaster II spectrofluorimeter equipped with a double excitation and a single emission monochromator. All solutions were degassed by bubbling for at least 15 min with Ar prior to use and excited at 337 nm. One slit setting was used for all samples investigated. All spectra were corrected for any spurious emission originating from impurities in the solvent. The quantum yield of the observed emission, ϕ_{fl}, was calculated from the integrated intensity under the emission band, *A*, using:[19]

$$\phi_{fl} = \frac{OD_{ref}\, A_{fl}\, n_{fl}^2}{OD_{fl}\, A_{ref}\, n_{ref}^2}\phi_{ref} \tag{1}$$

In eq 1 OD is the optical density of the solution at the excitation wavelength, and *n* is the refractive index of the solvent. 9,10-Diphenylanthracene (DPA) in cyclohexane was used as reference ($\phi_{ref} = 0.90$).[19]

The fluorescence decay transients were measured after photoexcitation of the Ar degassed solutions using a 0.8 ns pulse of 337 nm light from a PRA LN1000 N_2 laser. The light emitted from the sample perpendicular to the laser beam is passed through a Jobin-Yvon monochromator and was detected using a Photek PMT-113-UHF channel-plate photomultiplier with a rise time of 150 ps. Lifetimes were

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[10] Visser, R.-J.; Weisenborn, P. C. M.; van Kan, P. J. M.; Huizer, B. H.; Varma, C. A. G. O.; Warman, J. M.; de Haas, M. P. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 689−704.

[11] Toublanc, D. B.; Fessenden, R. W.; Hitachi, A. *J. Phys. Chem.* **1989**, *93*, 2893−2896.

[12] Baumann, W.; Spohr, E.; Bischof, H.; Liptay, W. *J. Lumin.* **1987**, *37*, 227−233.

[13] Rettig, W.; Zander, M. *Ber. Bunsen-Ges. Phys. Chem.* **1983**, *87*, 1143−1149.

[14] Kahlow, M. A.; Kang, T. J.; Barbara, P. F. *J. Phys. Chem.* **1987**, *91*, 6452−6455.

[15] Kang, T. J.; Kahlow, M. A.; Giser, D.; Swallen, S.; Nagarajan, V.; Jarzeba, W.; Barbara, P. F. *J. Phys. Chem.* **1988**, *92*, 6800−6807.

[16] Kang, T. J.; Jarzeba, W.; Barbara, P. F.; Fonseca, T. *Chem. Phys.* **1990**, *149*, 81−95.

[17] von der Haar, T.; Hebecker, A.; Il'ichev, Y.; Jiang, Y.-B., Kühnle, W.; Zachariasse, K. A. *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 430−442.

[18] Schütz, M.; Schmidt, R. *J. Phys. Chem.* **1996**, *100*, 2012−2018.

[19] Eaton, D. F. *Pure Appl. Chem.* **1988**, *60*, 107−1114.

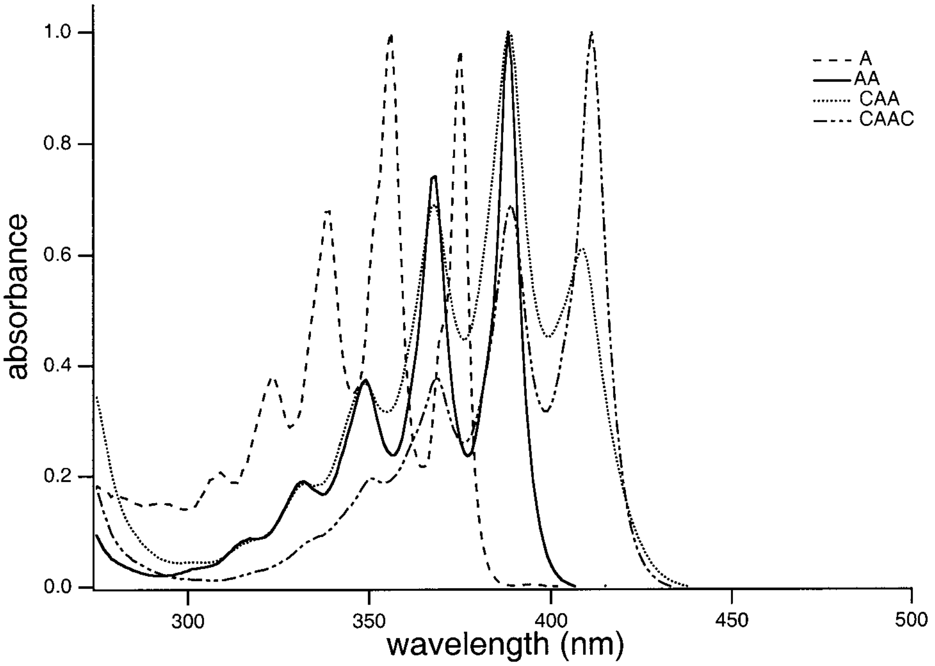

Figure 2. The absorption spectra of *n*-hexane solutions of anthracene (A), 9,9′-bianthryl (AA), 10-cyano-9,9′-bianthryl (CAA), and 10,10′-dicyano-9,9′-bianthryl (CAAC).

obtained from convolution fits to the transients, taking into account the separately recorded shape of the laser pulse.

The TRMC solutions were contained in a resonant cavity and irradiated with the 7 ns pulse of a Lumonics HyperEx 400 excimer laser (XeCl: 308 nm). Oxygen was removed from the solutions by bubbling with CO_2, which is also a good scavenger for mobile electrons that might be formed in low-yield multiphoton ionization events. The power output of the laser was monitored routinely using a Scientec 365 power meter, and the actual fraction of photons entering the TRMC-cell was determined using a solution of 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene (DMANS) in benzene as an internal actinometer. Averaging up to 64 single-shot transients was used to improve the signal-to-noise ratio. A full description of the microwave circuitry has been given elsewhere.[20,21]

The transient change in the reflected microwave power, ΔR, was not only monitored at the resonance frequency, f_0, but also at both half power frequencies, f_- and f_+. In contrast to measurements at f_0, which allow only the determination of the changes in the dielectric loss of the solution, $\Delta\epsilon''$, measurements at f_- and f_+ allow the determination of both $\Delta\epsilon''$ and the change in the dielectric constant of the solution, $\Delta\epsilon'$. By addition and subtraction of a pair of f_- and f_+ transients, separate transients can be obtained which are related to changes in $\Delta\epsilon''$ and $\Delta\epsilon'$ respectively:

$$\Sigma_\pm = (\Delta R_- + \Delta R_+) = B\Delta\epsilon'' \qquad (2)$$

$$\Delta_\pm = (\Delta R_- - \Delta R_+) = C\Delta\epsilon' + D\frac{\mathrm{d}\Delta\epsilon'}{\mathrm{d}t} \qquad (3)$$

The values of B and C in eqs 2 and 3 can be calculated from the characteristics of the resonant cavity.[21] The differential term in eq 3 results from a nondissipative change in the energy stored within the cavity as a result of the fluctuation in ϵ'. This leads to an oscillatory component in the $\Delta_\pm$ transients. The value of D was determined by fitting transients for the formation of the highly polarizable triplet state of Michler's ketone.[22] Knowing B, C, and D the absolute magnitude of $\Delta\epsilon'$ and $\Delta\epsilon''$ on flash photolysis can be determined.

A slight difference in the sensitivity for $\Delta\epsilon''$ at f_+ and f_- will result in a contribution to the $\Delta_\pm$ transient. This "cross-talk" contribution will become appreciable when $\Delta\epsilon''$ is large. The proportionality between the "cross-talk" contribution and the magnitude of $\Delta\epsilon''$ has been determined experimentally. This allows the correction of all $\Delta_\pm$ transients for the apparent change in ϵ' resulting from "cross-talk".

Results and Discussion

The optical absorption and emission spectra of bianthryl and its derivatives have been studied extensively.[1−6,8,9] However, no single report has appeared in which data are provided on all of the solute/solvent combinations studied in the present TRMC investigation. We have therefore carried out a comprehensive study of the solvatochromic properties of AA, CAAC, and CAA to have a consistent set of optical data which can be related to the microwave results.

Optical Measurements. The absorption spectra of the present bianthryl derivatives are almost independent of solvent polarity from saturated hydrocarbons to acetonitrile, in agreement with previous studies. Only the spectra in *n*-hexane are therefore shown in Figure 2. All of the solutes display equally sharp, vibrationally structured absorption bands. A red-shift of the 0,0 band of 13 nm (0.11 eV) occurs in going from monomeric anthracene to bianthryl, and a further red-shift of 22 nm (0.18 eV) occurs on going from AA to CAAC. The great similarity of the form of the spectra of the dimeric compounds to that of anthracene alone indicates that absorption of a photon results initially in the excitation of a single anthryl unit and the formation of a locally excited state, A*A. The absorption spectrum of CAA is seen to be close to an equally weighted sum of the spectra for AA and CAAC, indicating that photoexcitation of this asymmetric compound also involves initially the separate, vertical excitation of the individual A and CA chromophoric units, with the ratio CAA*/CA*A being dependent on the excitation wavelength. Therefore, in the initial state formed for all three bianthryl derivatives in all solvents the excitation energy resides on a single anthryl moiety and the two anthryl units are almost completely electronically decoupled as a result of their mutual orthogonal orientation.

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(20) de Haas, M. P.; Warman, J. M. *Chem. Phys.* **1982**, *73*, 35−53

(21) Schuddeboom, W. *Photophysical Properties of Opto-Electric Molecules studied by Time-Resolved Microwave Conductivity,* Ph.D. Thesis; Delft 1994, ISBN 90-73861-21-7.

(22) Warman, J. M.; Schuddeboom, W.; Jonker, S. A.; de Haas, M. P.; Paddon-Row: M. N.; Zachariasse, K. A.; Launay, J.-P. *Chem. Phys. Lett.* **1993**, *210*, 397−404.

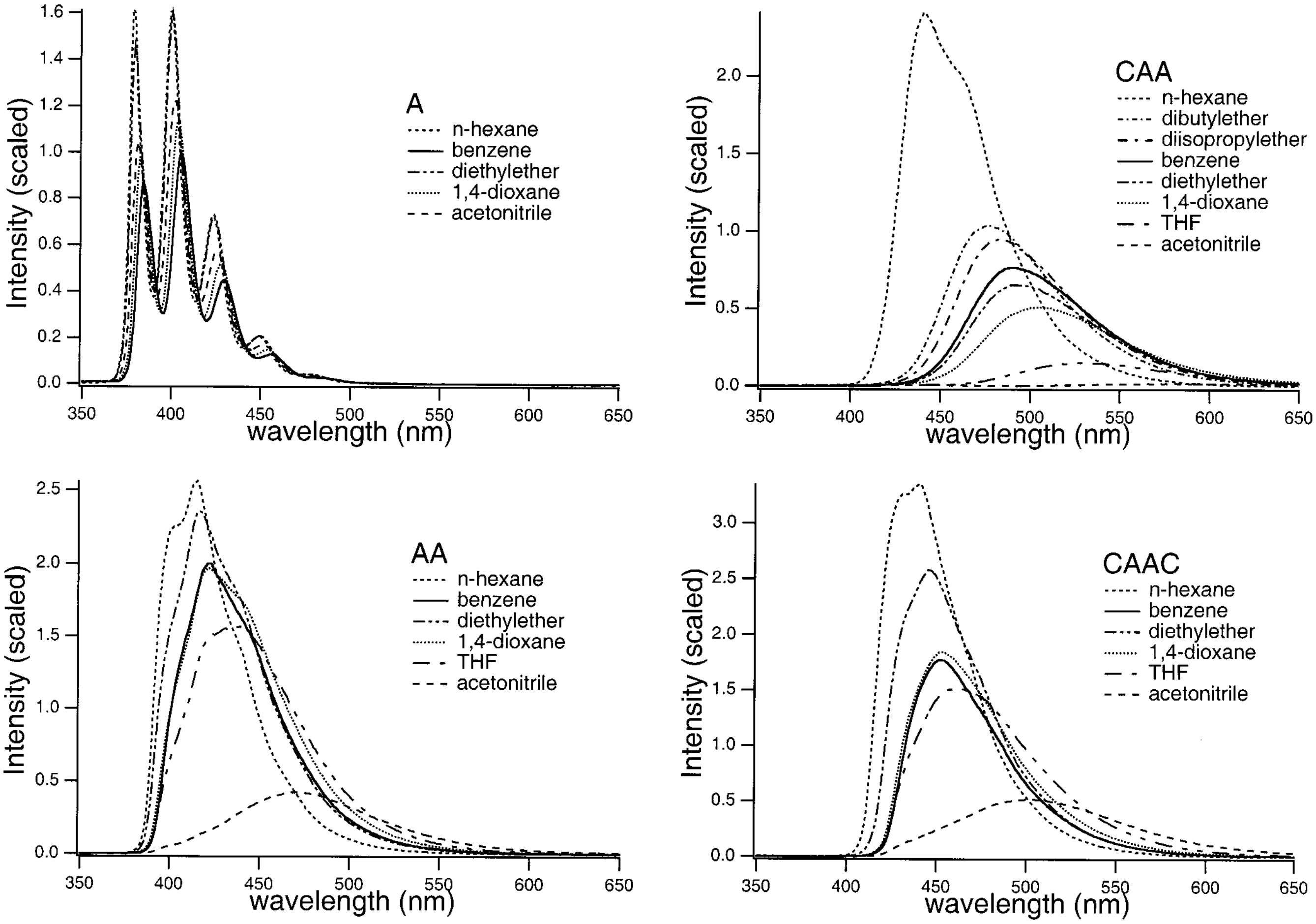

Figure 3. The fluorescence spectra of A, AA, CAA, and CAAC in selected solvents. For a complete compilation of fluorescence maxima, decay times, and quantum yields see Table 1.

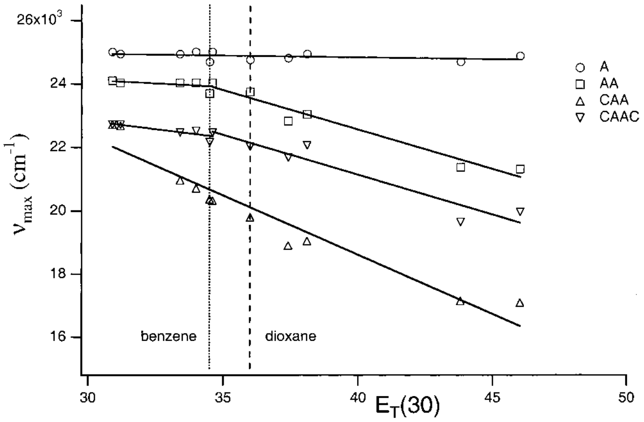

Figure 4. The dependence of the fluorescence maxima on the solvent polarity parameter $E_T(30)$.

The emission spectra in selected solvents are shown in Figure 3. They illustrate the dramatic difference between the relaxed S_1 state of all three bianthryl derivatives and that of anthracene alone. The sharply structured, almost solvent-independent anthracene fluorescence is replaced by spectra which are much broader, less structured and which display pronounced bathochromic shifts with increasing polarity of the solvent. Even the emission spectra in *n*-hexane are significantly different to that found for anthracene itself.

Also illustrated by the data in Figure 3 is the difference between the symmetrical compounds, AA and CAAC, and the asymmetric derivative, CAA. Thus, while the latter displays a continuous red-shift in emission maximum with increasing solvent polarity, even for low-polarity solvents, the former show a substantial shift only for solvents of intermediate to high polarity. This difference is illustrated more clearly in Figure 4 where the emission maxima, $h\nu_{fl}$, are plotted against the solvent polarity parameter $E_T(30)$ for all of the solute/solvent combinations studied. The very weak initial dependence of $h\nu_{fl}$ on increasing polarity for AA and CAAC gives way to a pronounced, close-to-linear dependence for $E_T(30)$ values in excess of ca. 35, as was found in the initial work of Schneider and Lippert.[1,2] The CAA compound, on the other hand, shows a continuous, close-to-linear decrease from the lowest-polarity (alkane) solvents. In the intermediate- to high-polarity regime the solvent dependence is seen to be quite similar for all three solutes. A complete compilation of the data obtained from the fluorescence measurements is given in Table 1.

Plots of the $h\nu_{fl}$ data have also been made against the polarity parameter Δf which should obey the linear relationship:[24-26]

$$h\nu_{fl} = h\nu_{fl}^{0} - \frac{2\mu(S_1)^2}{3\epsilon_0 c V_c}\Delta f \tag{4}$$

with:

$$\Delta f = \frac{(\epsilon_s - 1)}{(2\epsilon_s + 1)} - \frac{1}{2}\frac{(n^2 - 1)}{(2n^2 + 1)} \tag{5}$$

In eqs 4 and 5, $\mu(S_1)$ is the dipole moment of the relaxed S_1 state, ϵ_0 is the permittivity of vacuum, c is the velocity of light in vacuum, V_c is the cavity volume of the solute, and ϵ_s and

Table 1. Fluorescence Maximum, λ_{max}, Quantum Yield, ϕ_f, and Decay Time, τ_f, for Compounds Investigated in the Solvents Shown

			A			AA			CAA			CAAC		
solvent	$E_T(30)$[a]	Δf[b]	λ_{max} (nm)	ϕ_f	τ_f (ns)	λ_{max} (nm)	ϕ_f	τ_f (ns)	λ_{max} (nm)	ϕ_f	τ_f (ns)	λ_{max} (nm)	ϕ_f	τ_f (ns)
cyclohexane	30.9	0.100	401	0.35	5.9	416	0.84	8.0	441	0.83	14.5	440	*c*	7.3
n-hexane	31.0	0.093	400	0.40	5.9	415	0.94	7.3	440	0.89	13.8	440	*c*	8.0
dibutyl ether	33.0	0.192	401	0.38	5.9	416	0.94	10.3	477	0.43	29.7	445	0.98	9.3
diisopropyl ether	34.1	0.237	400	0.40	5.9	416	0.84	9.9	483	0.40	33.0	444	0.94	9.8
benzene	34.3	0.116	405	0.27	4.3	422	0.82	11.7	491	0.32	33.8	451	0.65	9.2
diethyl ether	34.5	0.256	400	0.40	6.2	416	0.96	12.2	492	0.28	31.7	445	0.97	11.4
1,4-dioxane	36.0	0.122	404	0.30	5.1	421	0.88	16.5	505	0.23	30.1	454	0.73	12.3
THF	37.4	0.309	403	0.33	5.5	438	0.78	21.3	529	0.07	15.8	461	0.70	17.0
ethyl acetate	38.1	0.292	401	0.35	5.9	434	0.78	20.0	525	0.07	15.6	453	0.78	17.5
DMF	43.2	0.377	405	0.26	4.1	468	0.38	37.8	583	0.01	6.2	509	0.30	28.0
acetonitrile	45.6	0.392	402	0.33	5.4	469	0.22	25.8	585	0.01	5.6	501	0.29	24.2

[a] Solvent polarity parameter from ref 23. [b] Solvent polarity parameter calculated using eq 5. [c] Solubility to low.

n are the static dielectric constant and refractive index of the solvent, respectively. Excited-state dipole moments were calculated from best linear fits to the data in the intermediate to high-polarity regime using cavity volumes calculated on the basis of a sphere with a radius of 6 Å for AA (as used in the original work of Schneider and Lippert[2]) and increased in proportion to the molecular weight for CAA and CAAC. The values of $\mu(S_1)$ found are 21, 23, and 21 D for AA, CAAC, and CAA, respectively. These values are in good agreement with previously determined estimates.

In connection with the subsequent TRMC measurements we emphasize that the red-shift in the fluorescence maxima of AA and CAAC on going from *n*-hexane to benzene or dioxane is considerably less than 0.1 eV and is similar for both of the latter solvents. This is to be compared with shifts for CAA of 0.29 eV for benzene and 0.36 eV for dioxane; values which approach those of 0.40 and 0.55 eV, respectively, which have been determined for the completely charge-separated state (dipole moment ca. 25 D) of the 4 σ-bond-bridged donor−acceptor compound Fluoroprobe.[27] The fluorescence results therefore clearly show that the dipolar character of S_1 and the accompanying solvent reorganization energy are very much smaller for AA and CAAC in benzene and dioxane than for CAA. The question is whether S_1 has in fact any net dipolar character at all in weakly polar solvents. As pointed out in the Introduction, the answer derived from the fluorescence measurements depends on the model used to interpret the spectral data.

As mentioned above, while the emission maxima of AA and CAAC are not strongly red-shifted in weakly polar media, the spectral shapes do differ considerably from that of the monomer and display a pronounced temperature dependence even in alkane solvents.[10] Liptay et al.[8,9] have shown that the fluorescence spectra of AA and CAAC in alkanes and benzene can be described very well in terms of a single, neutral excitonic S_1 state by taking into account the large amplitude torsional motion about the central bond. From their analysis of the fluorescence data, it was concluded that the double-minimum potential of the S_1 state of AA occurs at angles of 62°/118° and 58°/122° in isopentane and benzene with barriers to rotation at the orthogonal conformation of 0.035 and 0.058 eV, respectively. These values are to be compared with energy minima at 71°/109° and a barrier height of 0.015 eV determined for AA in the gas phase.[28−30] The position of the minima and the central barrier height were found to be very similar for AA and CAAC in isopentane.[31] For CAA in isopentane a considerably higher barrier of 0.084 eV was estimated compared with 0.036 eV for CAAC. Even in the case of the asymmetric compound, however, it was concluded that there was no evidence in the spectral data for a charge-transfer nature of S_1.

A completely different explanation of the fluorescence spectra and picosecond time-scale spectral relaxation in weakly polar solvents has been favored by other groups,[4,5,13−18] who propose a model in which an equilibrium is established after photoexcitation between a neutral, excitonic state, E, and a dipolar, charge transfer state, CT. The fluorescence spectra are then deconvoluted into two (or more) components on the basis of comparative solvent studies or the early-time relaxation kinetics, and equilibrium contributions of the E and CT states are then estimated. The CT state is often taken to resemble the highly dipolar state formed in polar solvents, that is with a dipole moment of ca. 20 D. To date, however, no mechanism has been proposed which can adequately explain the symmetry breaking required for the formation of the CT state, particularly in alkane solvents.

Microwave Measurements. As mentioned in the Experimental Section, the sum of the TRMC transients monitored at the half-power frequencies, $\Sigma_\pm$, is proportional to the change in the dielectric loss of the solution on flash photolysis, $\Delta\epsilon''$. The observation of a transient change in ϵ'' is indicative of the formation of a dipolar excited state for which the time scale for dipole relaxation (i.e., randomization of the net dipole moment), $\Theta*$, is comparable to the reciprocal radian frequency, $1/\omega$, of the microwaves used; corresponding to ca. 15 ps for X-band microwaves.

Dielectric loss transients are shown in Figure 5 for bianthryl solutions in *n*-hexane, cyclohexane, benzene, and dioxane. For comparison, transients are also shown for solutions of monomeric anthracene in *n*-hexane and dioxane. For the monomer solutions, signals close to the noise level are observed, indicating, as expected, a very small, if any, dipole moment of the S_1 state of anthracene alone. In contrast, all of the bianthryl solutions display a $\Delta\epsilon''$ transient which is outside of the noise limits. While the signals for the alkane solvents are much lower than those for benzene and dioxane, they are nevertheless readily

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(23) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319−2358.

(24) Lippert, E. *Z. Naturforsch.* **1955**, *10a*, 541−545.

(25) Mataga, N.; Kaifu, Y.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1955**, *28*, 690−691.

(26) Beens, H.; Weller, A. *Chem. Phys. Lett.* **1969**, *3*, 666−668.

(27) Mes, G. F.; de Jong, B.; van Ramesdonk, H. J.; Verhoeven, J. W.; Warman, J. M.; de Haas, M. P.; Horsman-van den Dool, L. E. W. *J. Am. Chem. Soc.* **1984**, *106*, 6524−6528.

(28) Yamasaki, K.; Arita, K.; Kajimoto, O.; Hara, K. *Chem. Phys. Lett.* **1986**, *123*, 277−281.

(29) Kajimoto, O.; Yamasaki, K.; Arita, K.; Hara, K. *Chem. Phys. Lett.* **1986**, *125*, 184−188.

(30) Khundkar, L. R.; Zewail, A. H. *J. Chem. Phys.* **1986**, *84*, 1302−1311.

(31) Elich, K.; Lebus, S.; Wortmann, R.; Petzke, F.; Detzer, N.; Liptay, W. *J. Phys. Chem.* **1993**, *97*, 9947−9955.

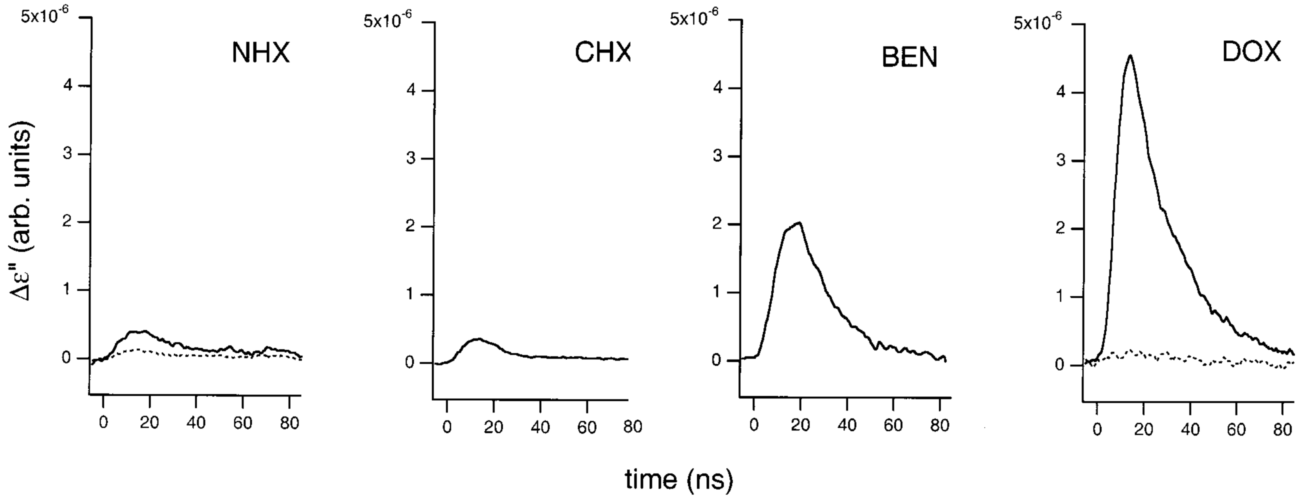

Figure 5. Transient changes in the dielectric loss, $\Delta\epsilon''$, on flash photolysis of solutions of 9,9′-bianthryl in (from left to right) *n*-hexane, cyclohexane, benzene, and dioxane (solid line). The $\Delta\epsilon''$ transients for anthracene solutions measured under similar conditions in *n*-hexane and dioxane are shown by the dashed lines.

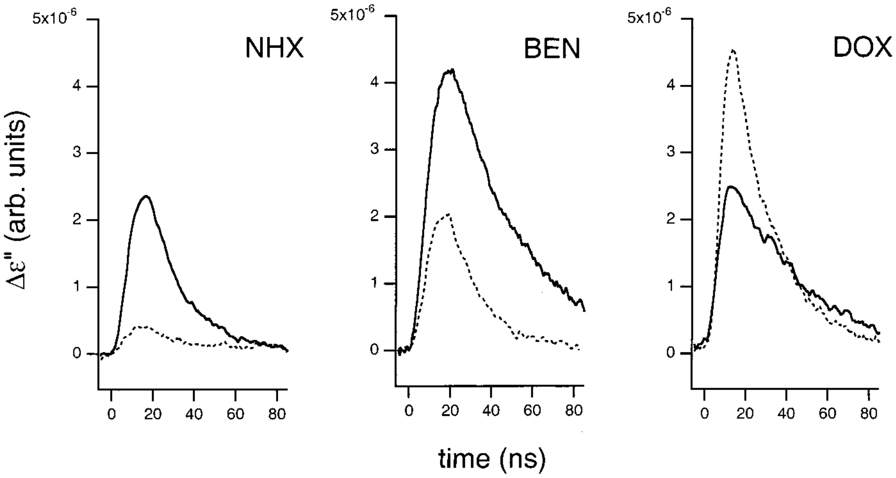

Figure 6. Transient changes in the dielectric loss on flash photolysis of solutions of 10-cyano-9,9′-bianthryl in (from left to right) *n*-hexane, benzene, and dioxane (solid lines). For comparison the transients of 9,9′-bianthryl are also included (dashed lines).

measurable. The present results therefore confirm those in a previous TRMC[10] study in which it was concluded that the relaxed S_1 state of AA has a dipolar character with a relaxation time on the order of at least picoseconds, even in completely nonpolar solvents.

The dicyano derivative, CAAC, was insufficiently soluble in the alkane solvents to carry out meaningful experiments. The $\Delta\epsilon''$ transients for this compound in benzene and dioxane were, however, similar in magnitude to those for AA, indicating also a dipolar character of the relaxed S_1 state for this symmetrical derivative.

It is of interest to compare the $\Delta\epsilon''$ transients for AA with those for the asymmetric compound CAA which are shown for *n*-hexane, benzene, and dioxane solutions in Figure 6. Two aspects of such a qualitative comparison are worthy of comment. First, the transient for CAA in *n*-hexane is more than an order of magnitude larger than that for AA. A much larger dielectric loss transient for CAA is, however, not particularly surprising since a larger excited-state dipole moment might have been expected intuitively for the asymmetric derivative. In the case of dioxane, however, the $\Delta\epsilon''$ transient for CAA is seen to be substantially *smaller* than that for AA. An explanation for this, intuitively unexpected, result in terms of a larger dipole moment of the S_1 state of the symmetrical compound is considered to be extremely unlikely. Such an explanation would also be in contradiction with the fluorescence data, presented in the previous section and shown in Figures 3 and 4, which indicate a much larger dipolar character for CAA than for AA in benzene and dioxane. An explanation for this apparent anomaly can be found in the role that the dipole relaxation time plays in determining the magnitude of the dielectric loss transients. This is discussed below.

The formation of a concentration $N*$ of excited molecules with dipole moment $\mu*$, will result in a change in the dielectric loss given by eq 6:

$$\Delta\epsilon'' = KN*\left[\frac{\omega\Theta*}{1+(\omega\Theta*)^2}\mu_*^2 - \frac{\omega\Theta_0}{1+(\omega\Theta_0)^2}\mu_0^2\right] = KN*[\Delta Im] \tag{6}$$

with:

$$K = \frac{[\epsilon(\infty)+2]^2}{27\epsilon_0 k_B T} \tag{7}$$

In eq 6, μ_0 and Θ_0 are the dipole moment and dipole relaxation time, respectively, of the ground-state molecule. For AA and CAAC, $\mu_0 = 0$. For CAA μ_0 is expected to be close to the value

Table 2. Values of the Parameters ΔIm (see Eq 6) and ΔRe (see Eq 9) Derived from the Transient Change in the Imaginary (Dielectric Loss) and Real (Dielectric Constant) Component of the Complex Permittivity of Solutions of AA, CAA, and CAAC in the Solvents Shown

	ΔIm (10^{-60} C^2 m^2)			ΔRe (10^{-60} C^2 m^2)		
solvent	AA	CAA	CAAC	AA	CAA	CAAC
n-hexane	30.5	369	*a*	261	144	*a*
cyclohexane	32.1	*a*	*a*	269	*a*	*a*
benzene	202	264	165	429	99.2	526
1,4-dioxane	309	170	393	378	43.4	458

[a] Not measured.

of 4 D determined for 9-cyanoanthracene[32] so that the condition $\mu_0{}^2 \ll \mu\ast^2$ will therefore be fulfilled for this compound if $\mu\ast$ is as large as indicated by the solvatochromic shift measurements, that is, 21 D. A good approximation for ΔIm for all of the solutes investigated is therefore:

$$\Delta Im = \frac{\omega\Theta\ast}{1 + (\omega\Theta\ast)^2}\mu_\ast^2 \qquad (8)$$

The values of ΔIm derived from fitting the $\Delta\epsilon''$ transients, using the known S_1 state lifetimes, are listed in Table 2 for all of the solute/solvent combinations studied.

As can be seen from eq 8, if $\omega\Theta\ast$ is much larger than unity for CAA but is close to unity for AA and CAAC, then a much smaller $\Delta\epsilon''$ transient would be obtained for the former compound even if the dipole moments were equal. We conclude therefore that the most probable explanation of the above-mentioned anomaly is that dipole relaxation occurs much more rapidly for the relaxed S_1 state of the symmetrical compounds than for that of CAA.

A consequence of the occurrence of dipole relaxation on a time scale similar to or shorter than $1/\omega$ is that a substantial change in the real (dielectric constant) component of the complex permittivity, $\Delta\epsilon'$, should also be observed. The dipolar contribution to $\Delta\epsilon'$ is given by:

$$\Delta\epsilon' = KN\ast[\Delta Re] \qquad (9)$$

with:

$$\Delta Re = \frac{1}{1 + (\omega\Theta\ast)^2}\mu_\ast^2 \qquad (10)$$

For the condition that $\omega\Theta\ast$ is much larger than unity, the change in ϵ' should be relatively small. Therefore, if the above explanation of the anomalously high dielectric loss transients is correct, a much smaller $\Delta\epsilon'$ transient should be observed for CAA than for AA or CAAC.

Changes in ϵ' are reflected in the difference transients, $\Delta_\pm$, obtained by subtraction of the two TRMC transients monitored at the half-power frequencies. In Figure 7 both the sum, $\Delta\epsilon''$, and difference, $\Delta\epsilon'$, transients are shown for solutions of AA, CAA, and CAAC in benzene. The change in dielectric constant is in fact seen to be very much smaller for CAA than for AA or CAAC. As discussed above, this is an immediate, qualitative indication that the dipole relaxation time for the S_1 state of CAA is in fact considerably longer than for the symmetrical compounds. The values of ΔRe determined by fitting the $\Delta\epsilon'$ transients are listed for all of the solute/solvent combinations studied in Table 2.

As can be seen by comparing eqs 8 and 10, the absolute value of the dipole relaxation time can be obtained from the relationship:

$$\Theta\ast = \frac{1}{\omega}\frac{\Delta Im}{\Delta Re} \qquad (11)$$

The values of $\Theta\ast$ derived from the present experimental values of ΔIm and ΔRe are listed in Table 3.

In using eq 11 to determine $\Theta\ast$ the implicit assumption is made that the only contribution to ΔRe arises from out-of-phase dipolar motion. An additional contribution could, however, arise if the electronic polarizability of the molecules, α_e, increased substantially on photoexcitation. The change in ϵ' can in fact be discussed in terms of an overall change in the polarizability of the molecule, $\Delta\alpha$, consisting of electronic and dipolar contributions, that is, $\Delta\alpha = \Delta\alpha_e + \Delta\alpha_D$:

$$\Delta\epsilon' = KN\ast[3k_B T\Delta\alpha] \qquad (12)$$

From eqs 9 and 12 the value of $\Delta\alpha$ is seen to be related to the measured value of ΔRe simply by:

$$\Delta\alpha = \frac{\Delta Re}{3k_B T} \qquad (13)$$

The values of the overall change in the polarizability obtained for AA and CAAC using eq 13 and the measured values of ΔRe are listed as the polarizability volumes, $\Delta\alpha' = \Delta\alpha/4\pi\epsilon_0$, in Table 3.

The values of $\Delta\alpha'$ of ca. 200 Å^3 or more for the relaxed S_1 state of the symmetrical compounds are an order of magnitude larger than the value of 17 Å^3 found for the vertical transition to the Franck–Condon state in electrooptical absorption measurements on anthracene or bianthryl.[33,34] They do, however, agree with the value of 220 Å^3 reported by Baumann et al. for the relaxed S_1 state of bianthryl in an electrooptical emission study.[6,12] On the basis of the much smaller values of $\Delta\alpha'$ found for anthracene alone and for CAA, we conclude that the major contribution to the excess polarizabilities found for the symmetrical dimers arises from dipole relaxation and hence that eq 11 can therefore be used to provide a reasonably good estimate of the dipole relaxation time. Any correction for an electronic contribution to the polarizability would tend to increase the value of $\Theta\ast$ calculated. A further discussion of this aspect of the results will be given in the next section.

The values of $\Theta\ast$ obtained for bianthryl in benzene and dioxane of 7.9 and 14 ps are similar to the values found for CAAC and are in reasonably good agreement with the values of 9.2 and 11.7 ps determined by Fessenden et al.[11] In that work the authors directly measured the phase shift resulting from the change in dielectric constant using an experimental approach different from that used in the present work. They did, however, also make the assumption that the change in dielectric constant could be attributed entirely to dipole relaxation. For the nonpolar alkanes, which could not be measured by Fessenden et al., a considerably shorter relaxation time of ca. 2 ps is found.

The $\Delta\epsilon'$ transients measured for CAA solutions are, in general, very small. Since, the $\Delta\epsilon''$ transients measured for the same solutions are large, the observed amplitude of these $\Delta\epsilon'$ transients will be determined to a large extend by the cross-talk contribution. The value of ΔRe of CAA given in Table 2, which are derived from the cross-talk corrected $\Delta\epsilon'$ transients,

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(32) McClellan, A. L. *Tables of Experimantal Dipole Moments*; Rahara Enterprises: El Cerrito, 1989; Vol. 2, p 598.

(33) Liptay, W.; Walz, G.; Baumann, W.; Schlosser, H.-J.; Deckers, H.; Detzer, N. *Z. Naturforsch.* **1971**, *26a*, 2020–2038.

(34) Mathies, R.; Albrecht, A. C. *J. Chem. Phys.* **1974**, *60*, 2500–2508.

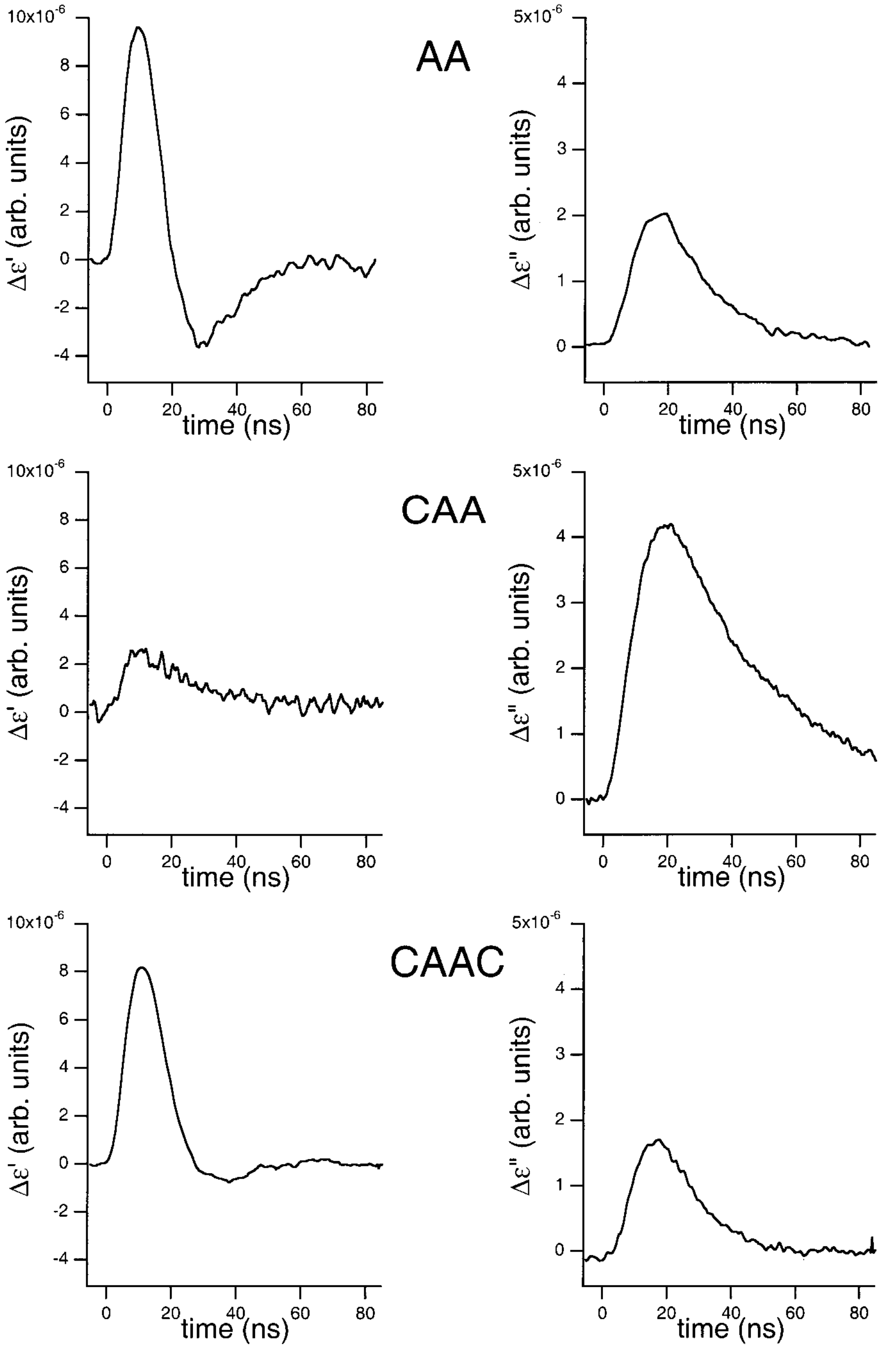

Figure 7. Transient changes in the real (dielectric constant, left) and imaginary (dielectric loss, right) components of the permittivity on flash photolysis of benzene solutions of 9,9′-bianthryl (top), 10-cyano-9,9′-bianthryl (middle), and 10,10′-dicyano-9,9′-bianthryl (bottom).

Table 3. Dipole Relaxation Time, Θ∗, Effective Dipole Moment, μ∗, and Excess Polarizability Volume, Δα′, of the Relaxed S_1 State of AA, CAA, and CAAC for the Solvents Shown

			Θ∗^{c} (ps)			μ∗ (ps)			Δα′ (Å^3)	
solvent	η^a (cP)	$\Theta_D{}^b$ (ps)	AA	CAAC	CAA	AA	CAAC	CAA	AA	CAAC
NHX	0.31	66	1.8	-	(151)^d	4.9	-	18	190	-
CHX	1.02	225	1.9	-	-	4.9	-	-	196	-
BEN	0.65	139	7.9	5.3	316	6.9	7.2	(21)	313	383
DOX	1.41	312	14	14	485	7.5	8.4	(21)	276	334

[a] Solvent viscosity. [b] Diffusional rotation time calculated from eq 14 assuming the molecule to occupy a compact sphere with a radius of 6 Å. [c] Determined for AA and CAAC from the ratio between ΔIm and Δ*Re* (eq 11), and for CAA in benzene and dioxane from ΔIm assuming a dipole moment of 21 D (eq 8). [d] Estimate based on the value of Θ∗ for benzene and the ratio between the solvent viscosities.

are therefore prone to a much larger error than the values determined for the symmetric compounds. As a result from this larger error in the values of Δ*Re* of CAA, the values of Θ∗ calculated using eq 11 have to be considered as no more than very crude estimates. For this compound we have therefore used a different approach to estimate Θ∗. This is based on the observation that the bathochromic shifts of the fluorescence for CAA in benzene and dioxane are large and lie on the straight line drawn through all solvents in Figure 4. We make the reasonable assumption therefore that the value of $\mu*$ for the S_1 state of CAA in these solvents is close to the value of 21 D determined from the combined fluorescence data. This value of $\mu*$ has then been substituted in eq 9 together with the experimental ΔIm values for the benzene and dioxane solutions to determine the corresponding values of $\Theta*$ which are listed in Table 3.

The experimental values of $\Theta*$ are compared in Table 3 with estimated values of the rotational relaxation time, Θ_D, of the solute molecules in the different solvents. These values were calculated using the Stokes–Einstein relationship for a spherical molecular geometry with a molecular radius of 6 Å:

$$\Theta_D = \eta \frac{4\pi R^3}{3k_B T} \tag{14}$$

In eq 14, η is the microscopic coefficient of friction toward molecular rotation (taken to a first approximation to be equal to the viscosity), and R is the molecular radius.

For the symmetrical solutes, $\Theta*$ is much shorter than Θ_D and displays no correlation with the solvent viscosity. Dipole relaxation must therefore be occurring mainly via an intramolecular process of flip-flop dipole reversal as was suggested by Fessenden et al.[11] To obtain the intramolecular relaxation time, Θ_I, from the measured $\Theta*$ values a correction should be applied for the contribution of Θ_D to the overall value of $\Theta*$:

$$\Theta_I = \frac{\Theta*}{\left(1 - \frac{\Theta*}{\Theta_D}\right)} \tag{15}$$

However, since the rotational relaxation times are in general more than an order of magnitude longer than the overall measured relaxation times for AA and CAAC, the correction will be small, and Θ_I will in fact be close to the measured value of $\Theta*$.

The value of $\Theta*$ determined from the $\Delta Im/\Delta Re$ ratio can be used together with the absolute values of ΔIm to determine the effective dipole moment of the dipolar state undergoing the intramolecular flip-flop process. These values are listed in Table 3. Beginning with a value of approximately 5 D for the alkane solvents, $\Theta*$ increases slightly to approximately 7 D in benzene and 8 D in dioxane. These values are somewhat larger than the values determined by Fessenden et al. (3.9 D for benzene and 4.5 D for dioxane[11]) and by electrooptical emission measurements (ca. 3 D for *n*-hexane and cyclohexane, and ca. 7 D for dioxane[12]). There is general agreement, however, that the effective dipole moment of the relaxed S_1 state in nonpolar and weakly polar solvents is considerably lower than the ca. 20 D determined from fluorescence measurements for AA and CAAC in medium to highly polar solvents.

The values of $\Theta*$ for CAA are seen to be larger than the values of Θ_D. This can be readily explained by the fact that the CAA molecules are in reality not perfect compact spheres. In fact taking the geometry to be closer to that of a prolate ellipsoid results in estimates of Θ_D which are approximately a factor of 2 larger than the values for a sphere and in quite good agreement with the values of $\Theta*$ determined. The results for CAA in benzene and dioxane are therefore in accord with the formation of a relaxed S_1 state with a dipole moment close to 20 D for which dipole relaxation is controlled mainly by rotational diffusion of the molecules.

For CAA in *n*-hexane we have taken the rotational diffusion time to be approximately half of that for benzene on the basis of the difference in viscosity of the solvents, that is $\Theta_D \approx 151$ ps. Combining this value with the value of ΔIm determined results in an estimate of 18 D for $\mu*$. Thus, even in this completely nonpolar solvent, CAA appears to form a highly dipolar state on photoexcitation with a dipole relaxation time which is controlled mainly by rotational diffusion of the solute molecules. There is, however, evidence from the $\Delta\epsilon'$ transients for CAA that, at least in *n*-hexane, dipole relaxation may be occurring to a certain extent via a flip-flop mechanism involving an equilibrium between the fully charge-separated and locally excited states.

General Discussion

The present results demonstrate conclusively that the relaxed S_1 states of the symmetrical compounds AA and CAAC have a net dipolar character with flip-flop dipole reversal occurring on a time scale of picoseconds even in alkane solvents, in agreement with previous studies on AA using either microwave dielectric loss[10,11] or electrooptical emission[12] techniques. Since both the initial, locally excited state, LE, and the torsionally relaxed excitonic state, E, should be electrostatically neutral as a result of their underlying D_2 symmetry, a mechanism must exist whereby the molecular symmetry of the combined solute/solvent system is in some way broken in the excited state.

In the case of CAA the asymmetry of the molecule can clearly provide an energetic driving force for charge separation since the electron affinity of the CA moiety is larger by ca. 0.3 eV than that of unsubstituted anthracene.[17] In addition, the fact that CAA has a dipole moment in the ground state ensures that the surrounding solvent molecules have a prearranged orientation favorable for initiating full solvation of the zwitterionic state. That the energetic driving force is the major factor in ensuring complete charge separation for CAA is indicated by the very large dipole moment found for the S_1 state of this solute even in the apolar solvent *n*-hexane. It is worth noting that this result is in contradiction with the conclusion by Liptay et al. that “Neither the analysis of the fluorescence spectra nor the evaluation of the fluorescence lifetime and quantum yield measurements yields any indication of a fluorescence from a CT state for CAAC and CAA in isopentane”.[31]

Returning to the symmetric compounds: The optical absorption spectra leave no doubt that photoexcitation results initially in the formation of a locally excited anthryl moiety which is orthogonally oriented with respect to its ground-state partner. This has been further substantiated by electroabsorption (Stark effect) measurements[33] which show that the increase in polarizability of AA on vertical photoexcitation is relatively small (ca. 20 Å^3) and close to that for excitation of anthracene alone. Since the anthryl moieties are electronically decoupled in their initial orthogonal conformation, the direct formation of a charge-transfer state from the locally excited state, LE, is not possible even in a polar solvent.

The LE state can, however, subsequently undergo torsional relaxation and, for angular configurations other than 90°, electronic coupling between the two anthryl moieties becomes allowed. This results in the formation of a fully delocalized excitonic state, E, which is derived from a combination of the local ^1L_a type states of the aromatic moieties and charge resonance states, CR.[3,13] Because of the D_2 symmetry, the two mirror-image CR states are degenerate and do not therefore result in a net dipole moment of E. The intermixing of states is, however, expected to result in a large molecular polarizability. A slight asymmetry in the (di)electric environment of the molecule will then be sufficient to remove the degeneracy of the CR states and result in a net dipole moment.[7]

The electronic coupling between two aromatic moieties, and hence the degree of stabilization of the excitonic state, should be maximum for a coplanar, that is zero degree, configuration. For bianthryl, however, there is a strong repulsive interaction between the hydrogen atoms at the 1,1′ and 8,8′ positions. The net result of the opposing electronic and steric interactions is the occurrence of potential minima for the excitonic state at angles of approximately 60° and 120°.[4,8,9,13,31,35] The resulting central barrier to torsional relaxation is estimated to be only on the order of k_BT for AA and CAAC so that rapid equilibration of the angular distribution with maxima at the angles corresponding to the potential minima is expected to occur within a time scale on the order of a picosecond.[8,9,31,35] Within the ensemble of excited molecules at any given time there will therefore be those which are highly polarizable with torsional angles close to that corresponding to a potential minimum and those which are only weakly polarizable for angles close to 90°.

Ab initio calculations on the excited state of ethylene have shown that for this molecule a large increase in polarizability occurs at a torsional configuration between the planar and orthogonal geometries.[36] The calculations showed furthermore that in this configuration even density (refractive index) fluctuations in an enviroment of nonpolar molecules was capable of breaking the symmetry, thus removing the degeneracy of the CR states, and inducing a net dipole moment. The lifetime of such a density-fluctuation-induced dipolar state, CT, is expected to be of the same order as the time taken for an acoustic wave to propagate over the dimensions of the solute/solvent system, that is, ca. 1 nm. Since the velocity of sound in organic liquids is on the order of 1000 m.s^{-1} this time scale will be on the order of a picosecond. The CT lifetime will, of course, also be influenced by the residence time of an excited molecule in the optimal, highly polarizable angular configuration. This is also expected to be on the order of picoseconds. In view of this we conclude that the transient dipolar state of AA and CAAC found in alkane solvents with a dipole relaxation time of ca. 2 ps results from solvent density fluctuations in the vicinity of those excited solute molecules which have a conformation close to that corresponding to a potential minimum.

In the case of polar solvents density fluctuations will be accompanied by stochastic orientational fluctuations of the solvent dipoles (or quadrupoles) which can even more effectively break the symmetry of the overall solute/solvent system and induce a larger net dipole moment. This has also been shown by the theoretical calculations on ethylene.[36] The temporary induction of even a small, net dipole moment can, in this case, be followed by a snowball effect in which further dipole-induced solvent relaxation drives charge separation to completion resulting in a fully charge-separated state, CS. The tens of picoseconds fluorescence relaxation times found for AA in polar solvents do in fact agree quite well with the values expected for such a solvent relaxation mechanism.[14−16,37,38] The CS state can be further stabilized by torsional relaxation to an orthogonal configuration of the anthryl moieties. The lack of electronic coupling in this configuration would then retard intramolecular electron transfer and considerably slow the return to the neutral excitonic state.

It is worth pointing out that to observe the full solvatochromic effect of a solvent on the fluorescence spectrum it is sufficient that dipole reversal occurs on a time scale considerably longer than the solvent relaxation time. Evidence that dipole reversal, via an intermediate neutral excitonic state, does in fact still take place in the case of AA and CAAC even in highly polar solvents is provided by the small, but readily observable shoulder in the fluorescence in the short wavelength region. This can be seen in Figure 2 even for acetonitrile. In addition, the transient optical absorptions observed on flash photolysis of solutions of bianthryl in acetonitrile could not be explained completely in terms of the radical anion and radical cation spectra alone but required admixing of the spectrum of the nonpolar excitonic state as found in *n*-hexane.[39]

In weakly polar solvents the strength of the dipolar or quadrupolar (in the cases of benzene and dioxane) solvent interactions are apparently insufficient to drive charge separation to completion and prevent the rapid return to the neutral excitonic state on a time scale shorter than the time required for full solvent relaxation. The fact that a somewhat larger degree of stabilization of the charge-transfer state occurs due to the quadrupolar nature of benzene and dioxane is, however, indicated by the slower intramolecular dipole relaxation times and the somewhat higher transient dipole moments found in the present work for these solvents compared with alkanes.

Since the relaxed S_1 states in a molecular ensemble will contain some molecules with close to an orthogonal configuration and hence zero dipole moment and some with a configuration close to a potential minimum with an appreciable dipole moment, the question arises as to what the actual dipole moment of the "charge transfer" state is. This question is not easily answered since it requires a knowledge of the equilibrium angular distribution and the corresponding molecular polarizabilities. A provisional answer can, however, be obtained on the basis of a frequently used, much simplified model in which the two possible CT states of dipole moment μ_{CT} are in thermal equilibrium with a nondipolar excitonic state.

$$\mathrm{CT}_{+/-} \underset{k_{\mathrm{CTE}}}{\overset{k_{\mathrm{ECT}}}{\rightleftarrows}} \mathrm{E} \underset{k_{\mathrm{CTE}}}{\overset{k_{\mathrm{ECT}}}{\rightleftarrows}} \mathrm{CT}_{-/+} \tag{A}$$

In terms of the processes represented in Scheme A the intramolecular dipole relaxation time is given by:

$$\Theta_I = \frac{1}{(k_{\mathrm{CTE}} + 2k_{\mathrm{ECT}})} \tag{16}$$

Since the values of Θ_I for AA and CAAC in weakly polar solvents are much shorter than the eventual S_1 decay times of several nanoseconds, the processes in Scheme A can be taken to be fully equilibrated in the present experiments. This being the case, the equilibrium fraction of excited molecules in a CT state, *F*(CT), will be:

$$F(\mathrm{CT}) = \frac{[\mathrm{CT}]_{\mathrm{eq}}}{[\mathrm{CT}]_{\mathrm{eq}} + [\mathrm{E}]_{\mathrm{eq}}} \tag{17}$$

$$= \frac{2k_{\mathrm{ECT}}}{(k_{\mathrm{CTE}} + 2k_{\mathrm{ECT}})} \tag{18}$$

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(35) Smith, M. J.; Krogh-Jespersen, K.; Levy, R. M. *Chem. Phys.* **1993**, *171*, 97−106.

(36) Zijlstra, R. W. J.; Grozema, F. C.; Swart, M.; Feringa, B. L.; van Duijnen, P. Th. *J. Phys. Chem. A* **2001**, *105*, 3583−3590.

(37) Jurczok, M.; Plaza, P.; Rettig W.; Martin, M. M. *Chem. Phys.* **2000**, *256*, 137−148.

(38) Nagarajan, V.; Brearley, A. M.; Kang, T.-J.; Barbara, P. F. *J. Chem. Phys.* **1987**, *86*, 3183−3196.

(39) Mataga, N.; Yao, H.; Okada, T.; Rettig, W. *J. Phys. Chem.* **1989**, *93*, 3383−3386.

$$= 2k_{\mathrm{ECT}}\Theta_{\mathrm{I}} \quad (19)$$

For equilibrium conditions, the value of the CT state dipole moment can be derived from the measured effective dipole moment, $\mu*$, if F(CT) is known from:

$$\mu_{\mathrm{CT}} = \frac{\mu*}{\sqrt{F(\mathrm{CT})}} \quad (20)$$

Estimates of F(CT) of 0.35, 0.70, and 0.74 for AA in the solvents *n*-hexane, benzene, and dioxane, respectively, have been made by Barbara et al.[15] and Schütz and Schmidt[18] by analyzing the fluorescence spectra on the basis of an equilibrium model. Using these values of F(CT) together with our measured $\mu*$ values results in estimates of 8.3, 7.8, and 8.7 D, respectively, for μ_{CT}. The values of the dipole moment of the CT state in weakly polar solvents obtained in this way are seen to be independent of solvent and less than half the value of the dipole moment of the CS state. If the dipole moment of the CT state was in fact as large as 20 D, then this would require the CT content of S_1 to be only approximately 10%, which is much lower than the estimates based on the analysis of the fluorescence spectra. Those estimates have, however, been supported by an analysis of the picosecond fluorescence relaxation kinetics which also leads to an F(CT) value of approximately 0.7 for AA in toluene.[17] We emphasize that the two-state, equilibrium model used above to derive μ_{CT} values is much simplified, and a fuller theoretical treatment is obviously required.

Support for a dipolar character of the CT state in weakly polar solvents much smaller than the CS state formed in polar solvents is provided by transient optical absorption measurements.[39] Thus, in alkane solvents no trace is found of absorptions characteristic of the radical anion and cation of anthracene. Such absorptions would have been expected to be observable if CT was in fact a fully charge-separated state present at a fractional concentration as high as 35% as derived from the fluorescence experiments.

A further aspect of the present results which can be related to fluorescence measurements is the relaxation time. According to Scheme A the mean time to relax to the equilibrium situation starting from the neutral excitonic state should be equal to the value of $\Theta*$ measured in the present work. Zachariasse et al.[17] have monitored the spectral relaxation of the fluorescence from solutions of AA and CAAC in toluene and found initial relaxation times of 23 and 16 ps, respectively. These values are to be compared with the $\Theta*$ values of 7.9 and 5.3 ps for AA and CAAC measured in the present work in benzene. The ratios of the relaxation times for the two solutes are seen to be closely similar. The fact that the relaxation times are longer in the fluorescence study can be ascribed to the lower temperature used in that work (−45 °C). In fact if the values of $\Theta*$ for AA in benzene determined at 9°, 22°, and 58° by Fessenden et al.[11] are plotted in an Arrhenius fashion together with the value of Zachariasse et al.,[17] a reasonably good linear relationship is found with a corresponding activation energy of 0.068 eV. Interestingly, this activation energy is quite close to the value of 0.058 eV estimated for the potential energy barrier for torsional motion for AA in benzene,[9] indicating that torsional motions are probably the controlling factor in the rate of dipole reversal.

Summary

We have confirmed that the relaxed S_1 state of bianthryl has a transient dipolar character in the weakly polar solvents benzene and dioxane and also in the nonpolar solvents *n*-hexane and cyclohexane. Dipole relaxation, however, occurs on a picosecond time scale via an intramolecular, flip-flop mechanism involving an intermediate neutral, excitonic state. The relaxation times determined are 14, 7.9, and ca. 2 ps for 1,4-dioxane, benzene, and the alkanes, respectively. Similar relaxation times are found for the symmetrical 10,10′-dicyano derivative in 1,4-dioxane and benzene. The dipole moment of the charge transfer state is estimated to be ca. 8 D, that is much lower than the ca. 20 D found from the bathochromic shifts in the fluorescence in medium-to-high polarity solvents.

The results are in accordance with the following photophysical processes:

(a) initial formation of a locally excited anthryl moiety in an orthogonal conformation with respect to its partner; (b) torsional relaxation to the neutral excitonic state which has potential minima for angles of ca. 60° and 120. This state can be considered to contain contributions from charge resonance states and local excited states; (c) a large increase in the exciton polarizability for conformations close to the potential minima; (d) solvent-density-fluctuation-induced removal of the degeneracy of the charge resonance states and the development of a net dipole moment in the solute; (e) rapid dipole relaxation due to fluctuations in the solvent environment and torsional motion about the central bond.

In the case of the asymmetrically substituted 10-cyano derivative the TRMC and fluorescence results show that a highly dipolar, ca. 20 D, charge separated state is formed even in *n*-hexane. In this case dipole relaxation occurs on a time scale of hundreds of picoseconds and is attributed to rotational diffusion of the solute molecules. Symmetry breaking for CAA is driven mainly by the ca. 0.3 eV difference in the electron affinities of the anthryl and cyano-anthryl moieties which results in close to complete charge separation in all solvents and probably the ultimate adoption of an electronically decoupled, orthogonal charge-separated state.

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