Photoinduced Electron Transfer in Bianthryl and Cyanobianthryl in Solution: The Case for a High-Frequency Intramolecular Reaction Coordinate

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Received: August 20, 2002; In Final Form: August 15, 2003

Photoinduced intramolecular electron transfer (ET) in symmetric 9,9′-bianthryl (BA) was studied by femtosecond pump-supercontinuum-probe spectroscopy in solvents covering the whole polarity scale. Results are compared with those obtained for the nonsymmetric 10-cyano derivative (CBA). The behavior exhibited by both compounds is qualitatively the same, which suggests that symmetry plays no essential role. Our measurements provide novel aspects: (i) electron-transfer proceeds in CBA within a time on the order of 10 fs and therefore along a high-frequency coordinate, (ii) the observation of both educt and product bands allows an estimate of the ET equilibrium, which shifts through solvent relaxation. We find no evidence of dynamics along the intramolecular twist coordinate before ET.

I. Introduction

Symmetric 9,9′-bianthryl (BA), which consists of two equal anthracene units, has received considerable attention due to its extraordinary solvatochromic behavior.[1−12] Absorption spectra of BA are nearly independent of solvent polarity, in agreement with the zero ground- and first-excited singlet state dipole moments required by molecular symmetry.[1,10] Besides, the spectra are similar to those of nondipolar anthracene but shifted to the red, leading to the conclusion that the locally excited (LE) state of BA is nonpolar. However, stationary fluorescence emission of BA shows a pronounced red shift in solvents of increasing polarity,[1] which indicates a dipolar character of the relaxed S_1 state and therefore symmetry reduction.[2,3] Interestingly, asymmetric and polar[4] 10-cyano-9,9′-bianthryl (CBA) shows similar solvatochromic behavior: its absorption spectra are independent of solvent polarity whereas the fluorescence spectra show strong solvatochromism.

Earlier transient fluorescence experiments[5,6] on BA suggested that in polar solvents ET is governed mainly by solvation whereas intramolecular torsion around the central σ-bond is of secondary importance. In nonpolar and moderately polar solvents, to the contrary, the intramolecular coordinate was considered to be the only relaxation path for the nondipolar excitonic state.[7,8] More recently a three-state model was proposed to explain pump−probe[9,10] and fluorescence upconversion[11] measurements of BA and of nonsymmetric derivatives in linear alcohols and dimethyl ether. A first process (state 1 → state 2) on the subpicosecond time scale was assigned to torsional motion of the two anthracenic units and a second process (state 2 → state 3) corresponds to solvation-controlled ET.

The goal of our work was to measure the photoinduced ET process undergone by BA and CBA in polar and nonpolar solvents and to resolve the initial process. The results suggest that an ET equilibrium for both compounds is reached already on a time scale of 10 fs after optical excitation. Subsequent solvent relaxation shifts the equilibrium toward the CT state. We assess quantitatively the electron-transfer equilibrium, which depends on the solvent coordinate. The dynamics does not show any indication of intramolecular twist before ET. The twist may happen, but it is not seen in the dynamics. It appears that a new picture of ET in BA and CBA is needed, which involves a high-frequency reaction coordinate and dissipative solvent dynamics.

II. Experimental Section

BA and CBA were of the same samples used in previous studies.[9−11] The femtosecond setup has been described in detail elsewhere.[13] BA and CBA were excited by 60 fs pulses centered at different wavelengths in the first vibronic band of BA. Parallel pump−probe polarization was used in the experiments here. The pump-induced transient absorption signal was monitored with a supercontinuum probe in the range 280−650 nm. The sample net thickness was 0.5 mm. No photodegradation was observed except with CCl_4 as solvent. The optical density of the sample was around 1 at the absorption maximum corresponding to a concentration of 6×10^{-3} M. After the sample was probed, the supercontinuum was registered on a photodiode array (512 pixels) with a spectral resolution of 1.5 nm. The recorded transient spectra $\Delta OD(t,\lambda)$ are time corrected for the chirp of the supercontinuum.[13] The pump−probe cross-correlation time τ_{cc} was 130−210 fs, being shorter for 400−600 nm and deteriorating in the UV. The temporal resolution after time correction and deconvolution from the pump pulse is estimated to be ∼50 fs over the entire probe range.

III. Results

Figure 1 shows transient spectra of BA and CBA in highly polar acetonitrile and in nonpolar cyclohexane with excitation at 397 nm. We start with BA in acetonitrile (a). The UV range is dominated by two prominent excited-state absorption (ESA) bands at 363 and 315 nm, which were already assigned to the LE[9,10] and CT[14] state, respectively. The spectral vibronic structure between 330 and 400 nm originates from the bleach contribution. Stimulated emission (SE) is recognized in the 400−500 nm region. At the earliest delay shown (0.15 ps) the SE band shows the same vibronic structure as the bleach band. With increasing time the structure disappears and the band decays and shifts to the red reflecting intramolecular ET.[5,6,9−11]

10.1021/jp026802t CCC: $25.00

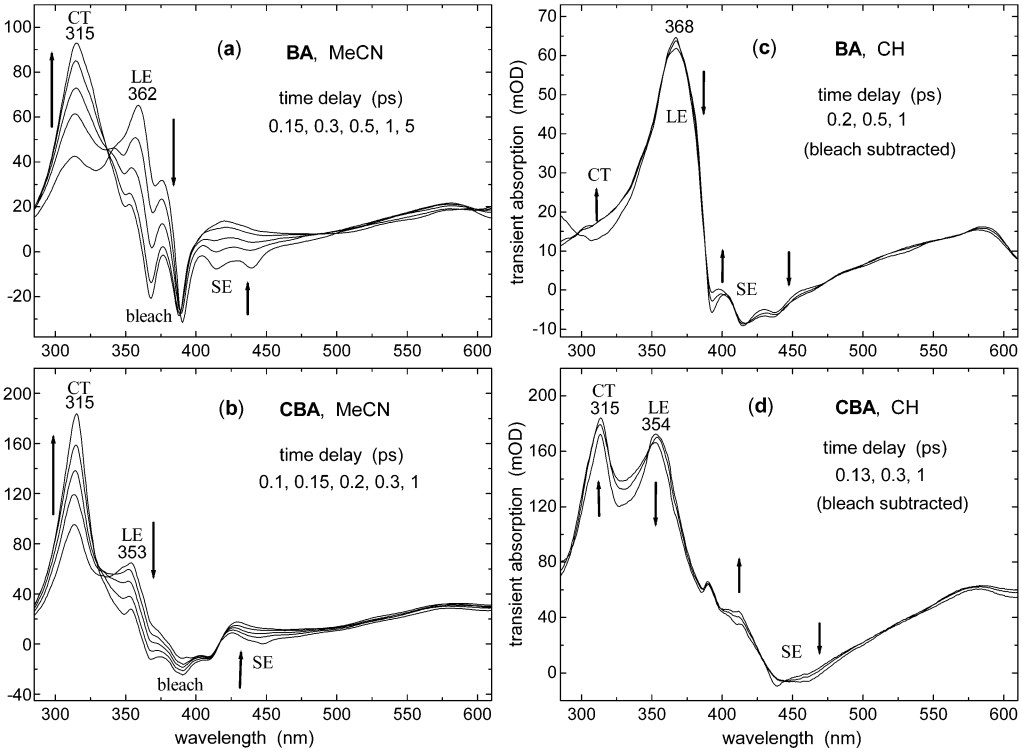

Figure 1. Transient absorption spectra of BA and CBA in acetonitrile and cyclohexane (CH) after excitation at 397 nm. Time delays are indicated. The negative signal corresponds to bleach or stimulated emission (SE), and the positive, to excited-state absorption (ESA). Arrows indicate signal evolution. In acetonitrile (a, b) ET is recognized from the decay of the LE band at 363 nm with concomitant growth of the CT band at 315 nm, and from the decay and red shift of SE. For CH (c, d) the bleach spectrum has been subtracted.

The same ET process is seen more prominently in the UV range as decay of the LE band and concomitant growth of the charge transfer (CT) band, the characteristic time τ being $\approx$0.4 ps. For CBA in acetonitrile (b) the spectral evolution is similar to that for BA but proceeds much faster, with $\tau = 0.15$ ps. The CT band peaks again at 315 nm as for BA.

Let us now consider the cyclohexane solutions (c, d). For this case the bleach contribution has been subtracted[9,10] from the transient spectra to expose the relative amplitudes of the ESA bands. For BA the CT band is seen to be much weaker than the LE band whereas for CBA the two bands are of equal intensity. We come to this point further below. The evolution in cyclohexane appears weak both for BA (c) and CBA (d), in the sense that the time-zero spectra (at $t = 0$) are not much different from those at late time. Comparison of the earliest spectrum of BA in acetonitrile with the spectra in cyclohexane shows close similarity between them, especially in the SE region. When the evolution is traced back to $t = 0$, one expects the same similarity in the ESA region as well, implying that the spectra measured at $t = 0$ are in fact independent from solvent and identical to the spectrum at $t = 0$ in cyclohexane. Thus for acetonitrile at $t = 0$, the CT band must be weak for BA (a) but relatively intense for CBA (b). Apparent deviations from this prediction seen in the experimental spectra are due to a finite pulse duration.

Experimental data for other solvents are qualitative the same and are not shown for the sake of brevity.

IV. Discussion

First we look for a signature of torsion. Figure 2 displays transient spectra of BA in acetonitrile after excitation at 393 nm (a, solid lines). The spectra between 60 fs and 1 ps are shown on an energy scale to expose vibronic structure. The evolution was analyzed by singular-value decomposition (SVD) which provides the independent spectral components and their associated dynamics. A coherent contribution is always present during pump−probe overlap and it can be uniquely identified.[15,16] The evolution other than the coherence requires for its description only two independent spectra and single exponential kinetics. This allows only for a precursor−successor kinetic model. The experimental spectra are well fitted (dashed lines in Figure 2a) by the coherent spectrum, the precursor and the successor spectrum shown in Figure 2b. The successor spectrum is identified with that of the CT state. The fitted time constant $\tau = 330$ fs is on the order of the solvation correlation time $\tau_{\mathrm{solv}} = \int_0^\infty C(t)\,\mathrm{d}t = 203$ fs in acetonitrile, as determined from dielectric data.[17] Note that the loss of structure in the SE region is due to the disappearance of the precursor spectrum, which has to be the LE state.[18] There is no signature of separate dynamics along a low-frequency coordinate (and particularly the torsional coordinate) before the ET reaction, as was suggested for BA.[9−11]

Now we focus on the relative amplitudes of the CT and LE ESA bands of CBA in acetonitrile and cyclohexane at $t = 0$, Figure 1 (b and c). The following reasoning will lead to the time scale of elementary ET in CBA. We observe equal amplitudes for the LE and CT bands of CBA at $t = 0$ in polar and nonpolar solvents. As we will show below, the relative amplitudes of the LE and CT ESA bands reflect directly the relative populations of both states because the oscillator strength is roughly the same for both. Therefore, a substantial amount of molecules populates the CT state already at time zero. Now imagine that the substantial CT population observed at zero delay comes about by direct excitation (the optical transition to the CT state may in fact be weakly allowed even though it has A_2 electronic symmetry). As CBA has a nonvanishing dipole moment in the ground state,[4] from the theory of solvatochromism it then follows that the position and shape of the CBA

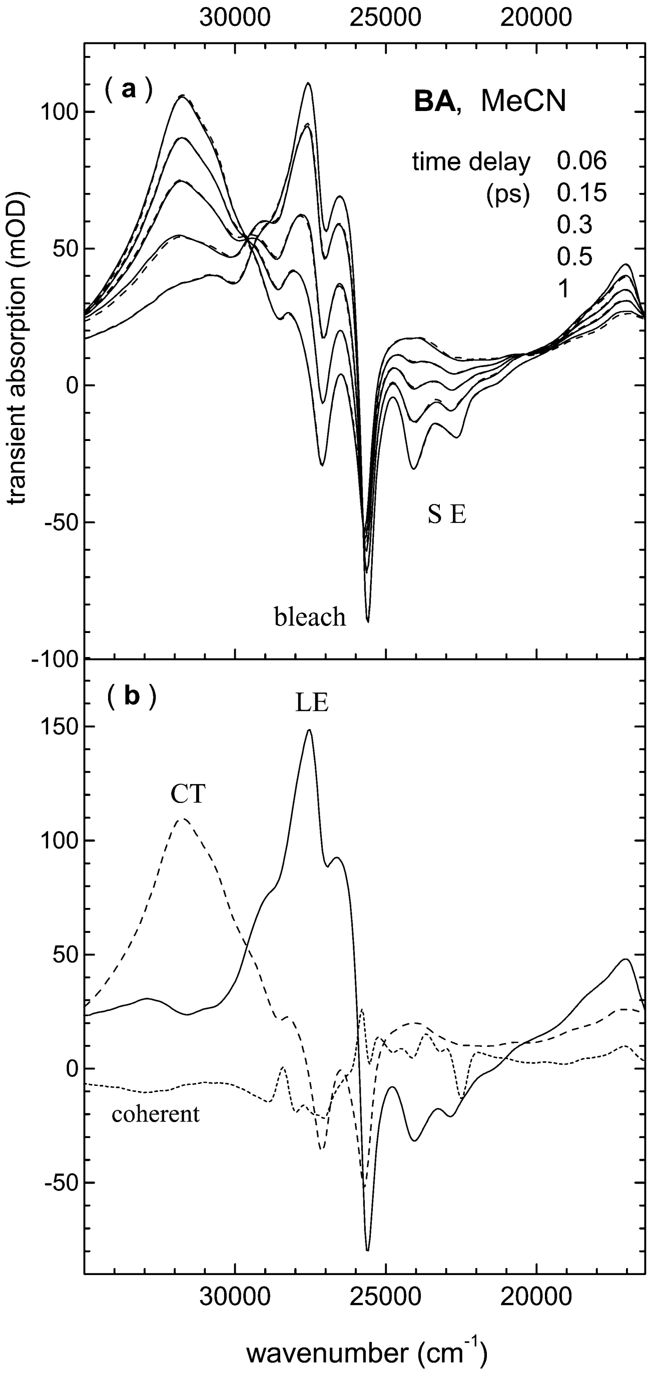

Figure 2. (a) Transient spectra of BA in acetonitrile after excitation at 393 nm (solid lines). The fit spectra (dashed) obtained with singular value decomposition (SVD) are the sum of a coherent spectrum, precursor spectrum, and successor spectrum. The precursor (LE) and successor (CT) evolution is modeled by the same single-exponential behavior with 330 fs time constant. Time delays are indicated. (b) Species-associated spectra for the pulse (coherence), a precursor (LE), and a successor (CT).

absorption should depend on solvent polarity. The solvatochromism should be observable because the first two vibronic bands are narrow so that relative shifts on the order of 10 cm^{-1} can be detected. But the stationary absorption spectrum of CBA shows no measurable polarity dependence in the first absorption band, which means that the contribution of a hypothetical optical transition to the CT state is negligible. Another possible argument for optical coupling between the ground and CT states of CBA may be given by the fact that its absorption spectrum is broadened compared to that of anthracene or BA. This argument is, however, not conclusive because relative broadening of the CBA absorption spectrum is primarily introduced by the loss of symmetry as compared to BA. Transitions to the noncoupled ^1L_b states of the 10-cyanoanthracene and anthracene moieties are overlapped with the optical transition to the excitonic ^1L_a. Broadening is introduced because the former are not degenerate. Furthermore, in the case of CBA the optical transition to the symmetric excitonic ^1L_a state is weakly allowed and overlapped with the other transitions, thus introducing additional broadening. Therefore we conclude that the CT state of CBA is not directly excited in our experiments. In that case ET must proceed extremely fast after optical excitation. We estimate that the characteristic time of intrinsic ET, τ_{ET}, is between 1 and 10 fs. Optical decoupling between the ground and CT state gives the lower estimate whereas our time resolution suggests the upper one.

A characteristic time on the order of 10 fs suggests that the reaction coordinate of ET is not classical. For CBA in cyclohexane the CT and LE states have comparable populations already at $t = 0$ so that the two states must be nearly degenerate.[19] The subsequent "slow" evolution of the quasi-equilibrium nuclear distribution in CBA reflects the change of the energy gap between the LE and CT states. Because the dynamics is governed by the solvation process, a strong correlation between solvation and shift of the LE $\rightleftarrows$ CT distribution is expected, as suggested by previous workers.[5,6,9−11] We extend the same view of ET to bianthryl as well: *ultrafast* ($\sim$ 10 fs) attainment of a quasi-stationary LE $\rightleftarrows$ CT distribution and subsequent slower population dynamics.

Now that the model is outlined we turn for the remainder to the ET kinetics. It can be obtained from SVD, as was shown in Figure 2. Another method that may be more precise for a narrow spectral region involves the band integrals[20] $\mathrm{BI}(\lambda_1,\lambda_2) = \int_{\lambda_1}^{\lambda_2}\Delta\mathrm{OD}(t,\lambda)\,\mathrm{d}\lambda/\lambda$. In our case the integrals are taken over the LE or CT bands. An example is displayed in Figure 3 for BA and CBA in acetonitrile and cyclohexane. Also shown is the integral over the two bands together, BI(290,390), which is used to extract the pump−probe cross-correlation time τ_{cc} and to demonstrate that the ET reaction takes place with negligible change of oscillator strength. In most solvents this band integral is close to a step-function, with a small decay reflecting slightly nonequal oscillator strengths of the bands. Usually, the decay of the LE band is in reasonable agreement with the growth of the CT band. Small discrepancies between the rise of the CT band and the decay of the LE band, such as seen in Figure 3, are mainly due to loss of time resolution inherent to the UV. For higher precision in the final kinetic analysis we therefore used only the LE band. Multiexponential fits of the experimental kinetics are collected in Table 1. Here rows marked S represent the solvation correlation function $C(t)$[20−22] and those marked B and C correspond to the ET kinetics for BA and CBA, respectively. Numbers in parentheses are the amplitudes a_i (%) of the corresponding components. The inverse rate τ_0, and the correlation time τ in the third column characterize the fast and slow component of solvation or ET, respectively.[22]

A general conclusion drawn from Table 1 is a strong correlation between the solvation and intermoiety ET dynamics, noted already before[5,6,9−11] and extended here to nonpolar solvents. For BA this correlation is best expressed by the slow component τ (in alcohols $\tau_S \approx \tau_{ET}$ within 10%). For CBA instead, the fast component τ_0 of ET is in better agreement with the solvation time τ_0 (methanol, dioxane). We already noted that the observed population kinetics reflect the solvation-induced dynamic shift of the LE $\rightleftarrows$ CT equilibrium, the actual

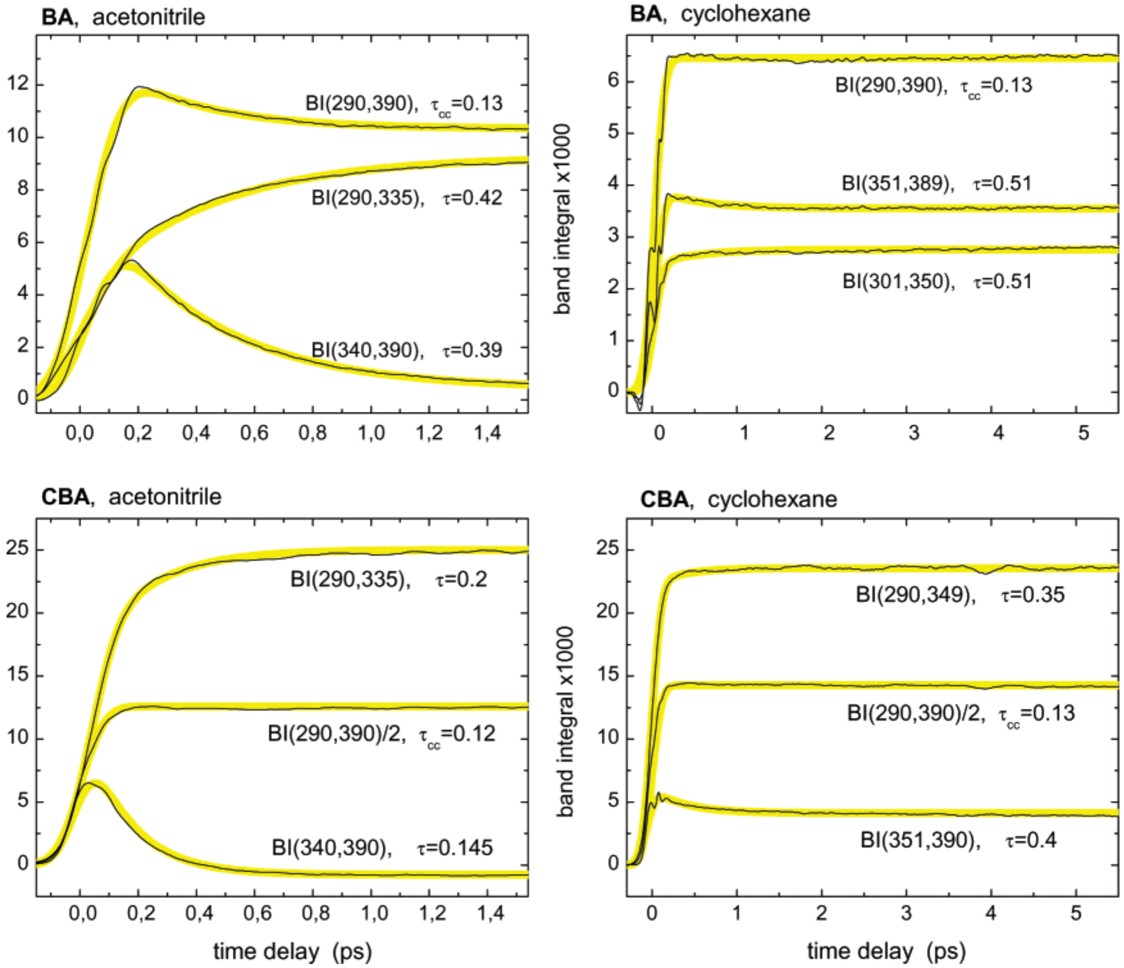

Figure 3. ET kinetics (black lines) for the LE and CT state for BA and CBA in acetonitrile and cyclohexane from the corresponding band integrals BI(λ_1,λ_2) together with the behavior of the sum of two bands, BI(290,390). Yellow lines are one-exponential fits as given in Table 1. τ_{cc} is pump−probe cross-correlation, τ is the time for ET.

microscopic ET is ultrafast (unresolved). A substantial contribution to the observed different kinetics for BA and CBA comes from different starting conditions of ET for the two chromophors. For CBA the LE and CT states are nearly degenarate already at $t = 0$. Solvation by polar solvents substantially lowers the energy of the CT state resulting in a strong shift of the LE $\rightleftarrows$ CT equilibrium and the shift correlates with the fast solvation component. For BA instead, the CT state at $t = 0$ lies higher in energy, by $\geq$500 cm^{-1} (see Table 1 for cyclohexane), than the LE state. Therefore a measurable increase of the CT population is delayed until the solvated CT state becomes comparable in energy to that of the LE state. As a result, the apparent rate of ET in the case of BA correlates better with the slow component of solvation.

The last column in Table 1 represents the quasi-equilibrium population [CT]$_{eq}$ derived from late spectra as of Figure 1 and the Gibbs energy difference $\Delta G°$ between the two states, as obtained from the relation $K = [CT]_{eq}/[LE]_{eq} = \exp(-\Delta G°/kT)$. Up to now direct experimental values are not available so that we may only compare our estimates with results from approximate models and semiempirical quantum mechanical calculations.[5,14] Kang et al.[5] used a model that involves dramatic simplifications—compared with our experimental results, the difference amounts to between 1 and 2 orders of magnitude. Grabner et al.[14] performed semiempirical quantum mechanical calculations of BA in the gas phase; they reported that the CT state lies above the LE state by 2300 cm^{-1}. We repeated their work with the same methodology and kept, as they did, the D_{2d} symmetry of BA. We corroborate their electronic spectrum but find that the assignment of these calculations is as follows (energies relative to the ground state in the gas phase): 25 800 cm^{-1} (anti-symmetric excitonic ^1L_a state), 27 600 cm^{-1} (degenerate, noncoupled, pair of anthracenic ^1L_b states), 28 170 cm^{-1} (symmetric excitonic ^1L_a state), 33 300 cm^{-1} (degenerate, noncoupled, pair of CT states). Therefore the correct value for the LE-CT splitting of BA from these semiempirical calculations is 7530 cm^{-1} whereas 2300 cm^{-1} in fact refers to the ^1L_a excitonic coupling. Despite the good agreement between the calculated electronic spectrum and the experimental one, the obtained $\Delta G° = E_{CT} - E_{LE}$ seems to be too large in value compared with our experimental values: $\Delta G° \geq 500$ cm^{-1} in cyclohexane and $\Delta G° \approx -180$ cm^{-1} in acetonitrile, Table 1. The reason for this difference is probably associated with the restricted symmetry of the calculations and the lack of vibronic coupling. Jahn−Teller[23] interaction breaks the molecular symmetry and destroys the degeneracy of the two CT configurations allowing for the existence of polar states. Such effects cannot be taken into account within the Born−Oppenheimer approximation. Interaction of the polar states with the solvent pushes them down in energy and thereby reduces the LE-CT energy gap. Local solvent fluctuations could also contribute to break the molecular symmetry even before optical excitation to the S_1 surface. Once symmetry is broken by any of these mechanisms, the case of BA reduces to the nonsymmetric case of CBA but with different starting conditions: the $\Delta G°$ at $t = 0$ is positive for BA whereas in CBA it is roughly zero.

TABLE 1: Fit Results for Intermoiety ET in BA and CBA[a]

		C(t) or [LE], multiexp. fit					$[CT]_{eq}$	$-\Delta G^0$
solvent		τ_1 (a_1)	τ_2 (a_2)	τ_3 (a_3)	τ_0	τ	%	cm^{-1}
MeCN	Solv	0.07 (67)	0.60 (33)		0.10	0.24		
	BA	0.39 (100)			0.39	0.39	70	180
	CBA	0.15 (100)			0.15	0.15	79	280
MeOH	Solv	0.10 (30)	0.97 (34)	11 (36)	0.30	4.4		
	BA	0.34 (42)	2.4 (33)	15 (25)	0.72	4.7	70	180
	CBA	0.14 (84)	1.0 (16)		0.16	0.28	83	330
EtOH	Solv	0.11 (26)	1.4 (23)	25 (51)	0.40	8.1		
	BA	0.41 (34)	2.4 (28)	18 (38)	1.03	7.7	60	85
	CBA	0.17 (73)	1.5 (27)		0.22	0.53	79	280
BuOH	Solv	0.13 (22)	8.2 (26)	93 (52)	0.60	51		
	BA	0.41 (24)	7.7 (22)	99.7 (54)	1.6	56	60	85
	CBA	0.18 (63)	2.7 (21)	12 (16)	0.28	2.6	79	280
Diox	Solv	0.30 (62)	1.6 (38)		0.43	0.8		
	BA	0.59 (43)	3.5 (57)		1.1	2.1	52	17
	CBA	0.35 (67)	1.7 (33)		0.47	0.8	76	240
Benz	Solv	0.19 (66)	2.4 (34)		0.28	0.94		
	BA	0.50 (38)	4.0 (62)		1.1	2.7	41	−76
	CBA	0.30 (32)	2.2 (68)		0.73	1.6	70	180
CH	Solv							
	BA	0.51 (100)			0.51	0.51	5−10	−500[b]
	CBA	0.40 (100)			0.40	0.40	55	50

[a] All times are in picoseconds. For each solvent the first row Solv represents the solvation correlation function $C(t)$,[20−22] the rows marked BA and CBA correspond to the ET kinetics of the two compounds. Numbers in parentheses are the amplitudes a_i (%) of a fit $a_1 \exp(-\tau/\tau_1) + a_2 \exp(-t/\tau_2) + a_2 \exp(-t/\tau_3)$. $1/\tau_0 = a_1/\tau_1 + a_2/\tau_2 + a_3/\tau_3$, $\tau = a_1\tau_1 + a_2\tau_2 + a_3\tau_3$. The last column gives the CT population at late time and the energy difference $\Delta G° = -kT \ln [CT]/[LE]$ between the LE and the CT state. [b] Due to the small evolution observed in this solvent, the value of $\Delta G°$ is highly imprecise and must be understood as a minimum limiting value.

We summarize the main points of our communication. The elementary ET reaction takes place along a high-frequency coordinate with a characteristic time of about 10 fs for CBA. The ET equilibrium is rapidly established. Subsequent solvent relaxation shifts the equilibrium toward the CT state. On the basis of the similarities exhibited by BA and CBA, we propose the same mechanism of ET for the two compounds. An appropriate model for these systems must incorporate dynamics along a high-frequency mode and dissipative solvent effects. This will be the issue of a forthcoming paper.

Acknowledgment. The Volkswagen Stiftung, the Deutsche Forschungsgemeinschaft, and the Fonds der Chemischen Industrie are gratefully acknowledged for financial support.

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(18) A range 250 ≤ τ ≤ 450 fs is certain from our data. Note that $\tau \leq$ 450 fs by itself does not rule out torsion as the underlying process. For example when an initial S_0 torsional distribution is propagated on the S_1 potential under diffusive conditions (damping constant $\gamma = 8$ ps^{-1}) and the relative population with angle $\alpha \leq 71°$ or $\alpha \geq 109°$ is calculated, then a monoexponential 430 fs rise is found. But if the observed kinetics is assigned to torsion, then this implies that there is no dynamics due to solvation, contrary to previous analyses.[5,6,9−11]

(19) An approximate degeneracy of the LE and CT states for CBA in solution is supported by our semiempirical calculations, which reveal two CT states, C^-A^+ and C^+A^- (where A and C represent the anthryl and the cyanoanthryl unit, respectively). The first one is indeed close in energy to the LE state, and the second one lies higher in energy and is not accessible even in strongly polar solvents. Semiempirical quantum mechanical calculations were done with the AM1 Hamiltonian, as implemented in VAMP 7.5a. Electron correlation was included with the PECI method taking into account 364 configurations. Solvent effects were modeled with the SCRF method, (*VAMP 7.5a*, T. Clark, A. Alex, B. Beck, J. Chandrasekhar, P. Gedeck, A. Horn, M. Hutter, B. Martin, G. Rauhut, W. Sauer, T. Schindler, and T. Steinke, Erlangen, 2001).

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