J. Phys. Chem. A **2006,** *110,* 13145−13150 **13145**

Ultrafast Intersystem Crossing in 9,10-Anthraquinones and Intramolecular Charge Separation in an Anthraquinone-Based Dyad

Hendrik J. van Ramesdonk,[†] Bartholomeus H. Bakker,[†] Michiel M. Groeneveld,[†]
Jan W. Verhoeven,*,[†] Ben D. Allen,[‡] James P. Rostron,[‡] and Anthony Harriman*,[‡]

Chemistry Department, HIMS, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands, and the Molecular Photonics Laboratory, School of Natural Sciences, University of Newcastle, Newcastle upon Tyne, NE1 7RU, United Kingdom

Received: September 26, 2006

Femtosecond transient absorption spectroscopy was employed to determine quantitatively the ultrafast S_1-T_1 intersystem crossing in a 2-substituted 9,10-anthraquinone derivative (**3**), $k_{isc} = 2.5 \times 10^{12}$ s^{-1}. Notwithstanding this rapid process, photoexcitation of dyad **1** is followed by competition between intersystem crossing and intramolecular charge separation, the latter leading to a short-lived (2 ps) singlet charge-transfer (CT) state. The local triplet state itself undergoes slower charge separation to populate a relatively long-lived (130 ns) triplet CT state. An earlier report about the formation of an extremely long-lived CT state (>900 μs) in **1** was found to be erroneous and was related to the sacrificial photo-oxidation of the dimethylsulfoxide solvent used in that study. Finally, some important criteria have been formulated for future experimental validation of “unusually long-lived” CT states.

Introduction

Quinones are widely employed as electron and hydrogen atom acceptors in thermal and photochemical processes by nature as well as in man-made systems. In recent studies, Armitage et al. and Schuster, for example, showed that, in particular, 9,10-anthraquinones (AQ) constitute very suitable and recyclable photoinitiators (“photonucleases”) for oxidative DNA cleavage.[1,2] In this process, as well as in most other photodriven reactions of quinones, their very rapid and virtually complete S_1-T_1 intersystem crossing is the primary step after photoexcitation. The long-lived triplet (T_1) state thus populated is, in general, the reactive species mainly responsible for the strong electron and hydrogen atom abstracting properties of quinones under photochemical conditions,[3] although as shown by Hubig et al., the short-lived S_1 state may also enter into electron-transfer processes.[4] Such electron abstraction by singlet excited quinones leads to singlet radical ion pairs that are very short-lived and typically decay by charge recombination within a few picoseconds.[4] As pointed out by both Schuster[2] and Hubig et al.,[4] electron or hydrogen atom abstraction by the triplet state of a quinone primarily creates a radical (ion) pair with triplet spin configuration. This slows down its eventual recombination to the singlet reactants and thereby provides for more efficient dissociation and consecutive reactions, such as charge migration along the DNA chain.

Formation of a tight, triplet radical ion pair in the form of a triplet charge-transfer state (^{3}CT) has also been observed in several compact electron donor−acceptor dyads and has, for the same reason, been found to allow such ^{3}CT states to survive much longer than the corresponding ^{1}CT states.[5,6] Typically, ^{3}CT lifetimes in compact dyads range from tens of nanoseconds to several microseconds whereas the ^{1}CT lifetimes are usually subnanosecond. Because of the small energy gap between ^{1}CT and ^{3}CT states, the upper limit for the ^{3}CT lifetime is, in general, determined by the rate of thermal equilibration between these two states. This, in turn, is governed by the spin relaxation time which is typically in the microsecond domain in solution at ambient temperature provided the energy gap between ^{1}CT and ^{3}CT significantly exceeds the hyperfine interaction (hfi) energy. As discussed elsewhere,[6] the latter requirement is usually fulfilled in compact dyads where the electron spin−spin exchange interaction tends to be much larger than the hfi energy.

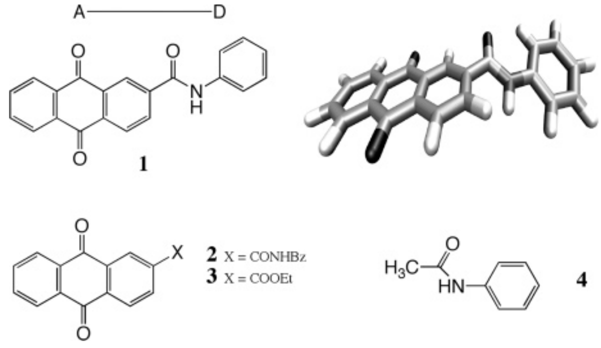

Figure 1. Molecular formulas of the compounds studied and an energy-minimized perspective of the dyad **1**.

We were much surprised therefore by the recent report that, in the compact and tightly coupled donor−acceptor dyad **1** (see Figure 1), photoexcitation leads to an intramolecular CT state that undergoes negligible intramolecular charge recombination. Indeed, in liquid solution, the CT state is reported to decay solely by intermolecular charge exchange extending over more than 900 μs.[7] On the basis of time-resolved spectroscopic data, it was concluded that, after initial S_0-S_1 excitation of the 9,10-anthraquinone (AQ) chromophore in **1**, very rapid (~0.4 ps) intersystem crossing occurs to form the T_1 state of this

---

* To whom correspondence should be addressed. E-mail: jwv@science.uva.nl, Anthony.Harriman@newcastle.ac.uk.

[†] University of Amsterdam.

[‡] University of Newcastle.

10.1021/jp0663098 CCC: $33.50

chromophore. This step was reported to be followed by intramolecular charge separation within ~1.7 ps to populate the extremely long-lived CT state. Although this was not mentioned explicitly, the CT state thus formed should clearly be ^{3}CT in nature, but even so a lifetime exceeding a few microseconds appears unprecedented. In the original report, the lack of intramolecular charge recombination was attributed to a pronounced "inverted region" effect.[7] Remarkably enough, an earlier investigation of **1** by flash photolysis is in fact available, but this study by Hamanoue et al. makes no mention of a particularly long-lived transient.[8] In view of the importance of quinone-mediated electron-transfer processes, and because of the challenges and problems generally encountered during efforts to create long-lived CT states in simple dyads, we have reinvestigated the photophysics and redox behavior of **1** and a few simpler systems intended to model the acceptor (**2** and **3**) and the donor (**4**) functionalities inherent to the target compound (see Figure 1).

Experimental Section

Synthesis and Photostability. The dyad **1**, together with the model AQ derivatives **2** and **3**, was synthesized, see Supporting Information for more details, via amidation or esterification of 9,10-anthraquinone-2-carboxylic acid (Aldrich) and was purified by repeated recrystallization from acetonitrile. While the crude compounds show weak fluorescence in the near UV region, the purified materials that we obtained are devoid of detectable fluorescence. We conclude therefore that the weak fluorescence reported earlier for **1**, and related AQ derivatives, arises from the presence of trace impurities.[9] It has been reported previously that although **3** and a series of related *n*-alkyl 9,10-anthraquinone-2-carboxylates are nonfluorescent when pure, they undergo photoinduced breakdown leading to the formation of highly fluorescent products.[3] In this context, we note that in fluid solution not only **3** but also compounds **1** and **2** show varying degrees of photolability leading to the formation of fluorescent products. For **2** and **3**, photodegradation is especially pronounced in solvents such as tetrahydrofuran that contain readily abstractable hydrogen atoms. Under such conditions, **1** is less photolabile, but even so, prolonged photolysis in solvents with little hydrogen-donating capability, such as acetonitrile, leads to decomposition of the solute. The donor model acetanilide (**4**) was available from stock.

Results and Discussion

Nanosecond Flash Photolysis, Solvent Dependence. In view of the observed solvent-dependent photolability of the AQ derivatives **1**−**3**, acetonitrile was selected as solvent for the initial photophysical studies. This solvent combines low hydrogen atom donating ability and large oxidative resistance with good solvating power. Furthermore, solutions for flash photolysis were stirred during the measurement or, in certain cases (see below), a flow cell was employed to replenish the solution after each laser shot. A full description of the nanosecond laser flash photolysis setup is given elsewhere.[10]

As expected on the basis of earlier reports about 9,10-anthraquinone and its derivatives, laser flash photolysis (λ = 355 nm) of the simple AQ derivatives **2** and **3** creates within the laser pulse duration (fwhm 2 ns) a transient with a lifetime of ca. 30 μs. This species has its main absorption maximum below 400 nm and some much weaker absorption in the visible region (see Figure 2). Similar transient spectral records have been reported before and can be considered as a typical signature of the T_1−T_n absorption of the (2-substituted) AQ chromophore.[3,8,11] The lowest-energy triplet state associated with such compounds is of *n*,π* character.[3,11]

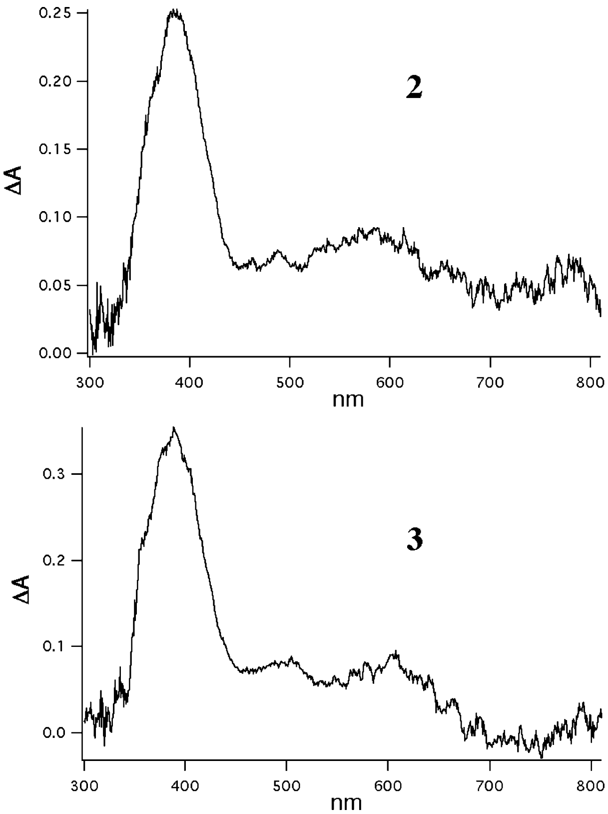

Figure 2. Transient absorption spectra of **2** and **3** in deoxygenated acetonitrile, showing formation of the anthraquinone triplet with λ_{max} ~ 390 nm and lifetime of ca. 30 μs.

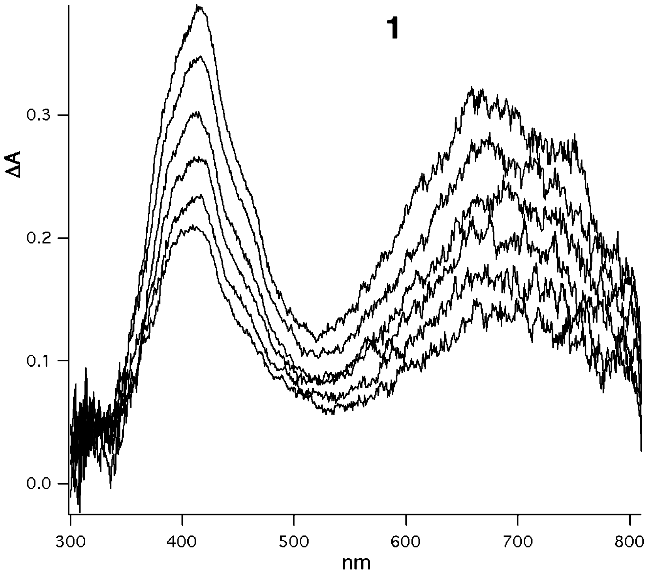

Figure 3. Transient absorption spectra of **1** in deoxygenated acetonitrile, increments 20 ns, lifetime 130 ns.

The behavior of **1** is markedly different to that of the simpler derivatives. As shown in Figure 3, the transient spectrum (again formed on a subnanosecond time scale) now shows two broad absorption bands. One maximum is around 410 nm while the second band, being of almost equal intensity, covers a large domain in the red-to-near IR region and is centered at around 700 nm. This spectrum decays with a wavelength-independent time constant of 130 ns in carefully deoxygenated acetonitrile, but this is reduced to 63 ns in aerated solution. Initially, and in

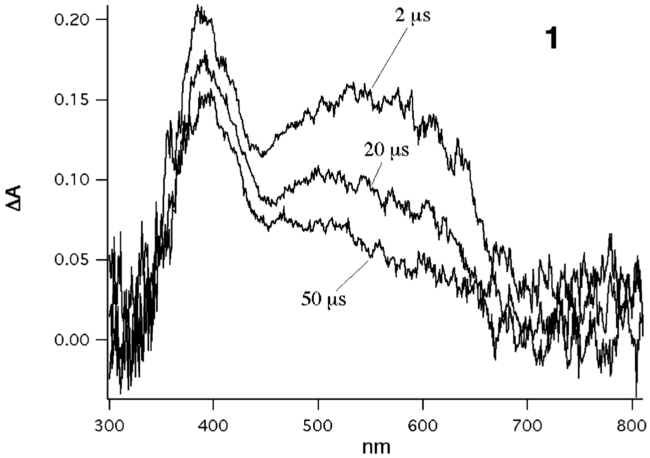

Figure 4. Transient absorption spectra of **1** in deoxygenated DMSO at three delay times. Note the change in spectral shape at delay times beyond 20 μs where the 550-nm band attributed to the anthraquinone radical anion becomes less pronounced.

agreement with the observations of Hamanoue et al.,[8] a much weaker and longer-lived (ca. 10 μs) transient was observed having a spectrum similar to that of the T_1-T_n spectra of **2** and **3** around 390 nm. However, variation of the laser power suggested that this latter species was due to minor decomposition during photolysis. Indeed, when employing a flow cell, the spectrum shown in Figure 3 decays cleanly to the prepulse baseline with no indication of a longer-lived species.

The observations described above support the proposed[7] occurrence of intramolecular charge separation in **1**. The feasibility of this process is confirmed by both thermodynamic considerations and density functional theory (DFT) calculations, which place the CT state below the T_1 state of the AQ chromophore in polar solvents (see below). Nevertheless, there is a dramatic difference in lifetime of the CT state as observed here ($\sim$130 ns) and as reported by Okamoto et al.[7] (>900 μs). It is also clear that the transient absorption spectrum observed here in acetonitrile solution (see Figure 3) does not at all match that reported by Okamoto et al. for the same compound in dimethylsulfoxide (DMSO). In the latter case, only a limited spectral range was studied (420−750 nm) in which a broad absorption maximum was found around 550 nm. This was attributed to the radical anion of the AQ chromophore and perhaps to some minor contribution from the formanilido radical cation. Simple addition of the individual spectra of the constituent radical ions is unlikely to be adequate to describe the spectrum of the CT state given the close proximity enforced in **1**.

Under our conditions, replacing the acetonitrile solvent with benzonitrile or tetrahydrofuran had little effect, except for a significant increase in the extent of photodecomposition in tetrahydrofuran, as explained earlier. This situation changed dramatically, however, when DMSO was used as a solvent. In this specific case, transient spectra (see Figure 4) with an extremely long persistence were observed following laser excitation at 355 nm. These spectral features fully reproduce those reported earlier at 2- and 20-μs delay times by Okamoto et al.[7] However, the wider spectral range and the extension to longer delay times (see Figure 4) used in the present work reveal an evolution in spectral shape over time. Such behavior clearly indicates the involvement of more than one species.

On the basis of these observations, and from the well-documented facile electrochemical[12,13] oxidation of DMSO, we infer that this solvent acts as a sacrificial electron donor to the excited AQ chromophore present in **1**. Such a reaction would lead to intermolecular electron transfer from DMSO to produce the anion radical of **1**. This hypothesis was confirmed by the observation that illumination not only of **1** but also of **2** and **3**, and even AQ itself, in DMSO produces persistent transient spectra dominated by an absorption in the 550−620 nm region (see Figure 5) which is typical for their radical anions[14,15] as we also verified by spectro-electrochemistry (see Supporting Information).

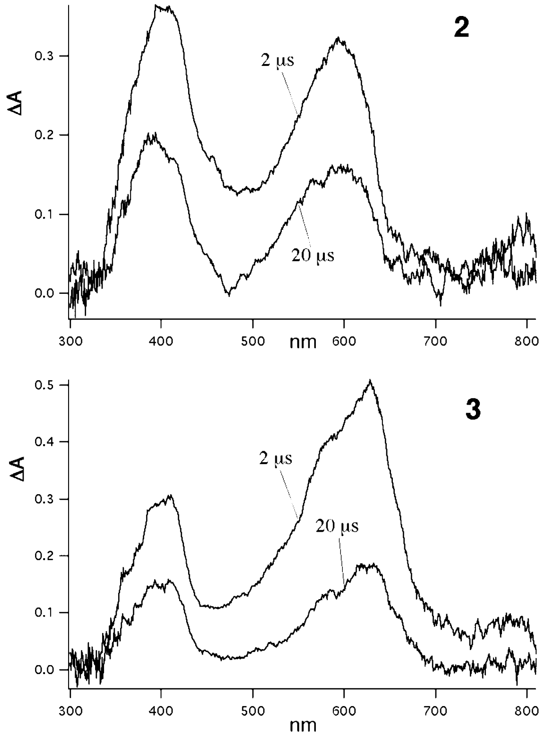

Figure 5. Transient absorption of **2** and **3** in deoxygenated DMSO showing the formation of the corresponding radical anions characterized by a broad absorption around 600 nm.

Photoinduced[16] and thermal[17,18] anion radical formation is known to occur with other strong electron acceptors dissolved in DMSO. Such radical anions were found to be quite persistent because the DMSO radical cation undergoes decomposition reactions, which are also responsible for the irreversible electrochemical oxidation of DMSO, that compete with charge recombination. In the case of **1**, the anion band seems to be significantly broader than in the case of **2** and **3**. Our spectro-electrochemical results (see Supporting Information) suggest that this is could be caused by formation of not only the monoanion but to some extent also the dianion of the anthraquinone moiety, perhaps because of electron abstraction from DMSO not only by the local triplet state but also by the intramolecular CT state of **1**, which contains the very labile (see Supporting Information) radical cation of the formanilide donor moiety.

We are forced, therefore, to conclude that the very long lived transients reported[7] to arise upon photolysis of **1** in DMSO are due to sacrificial photo-oxidation of this solvent by **1**. In less easily oxidized solvents, like acetonitrile, **1** undergoes photoinduced intramolecular charge transfer, but the lifetime of the charge-separated state is limited to $\sim$130 ns.

Femtosecond Transient Absorption (TA) Spectroscopy. The nanosecond flash photolysis study described in the preceding section reveals the formation of an intramolecular CT state for **1** with a lifetime ($\sim$130 ns in acetonitrile) compatible with a triplet spin configuration (^{3}CT) that slows down charge recombination in spite of the short donor−acceptor distance. Also, the significant shortening of the CT lifetime (i.e., from

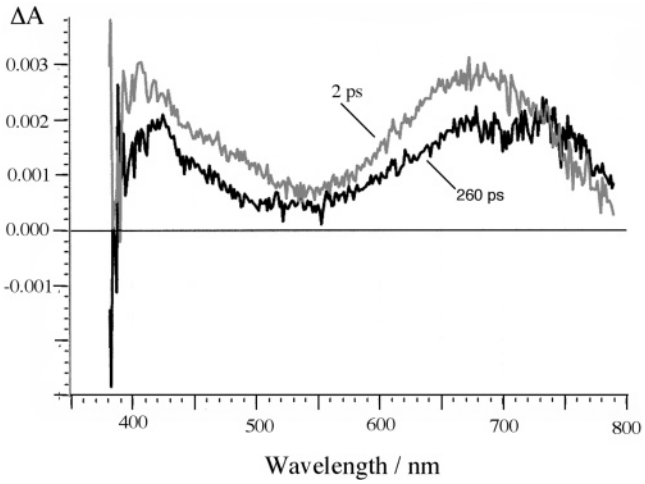

Figure 6. Transient absorption of **1** in acetonitrile recorded at two delay times after femtosecond laser excitation at 340 nm.

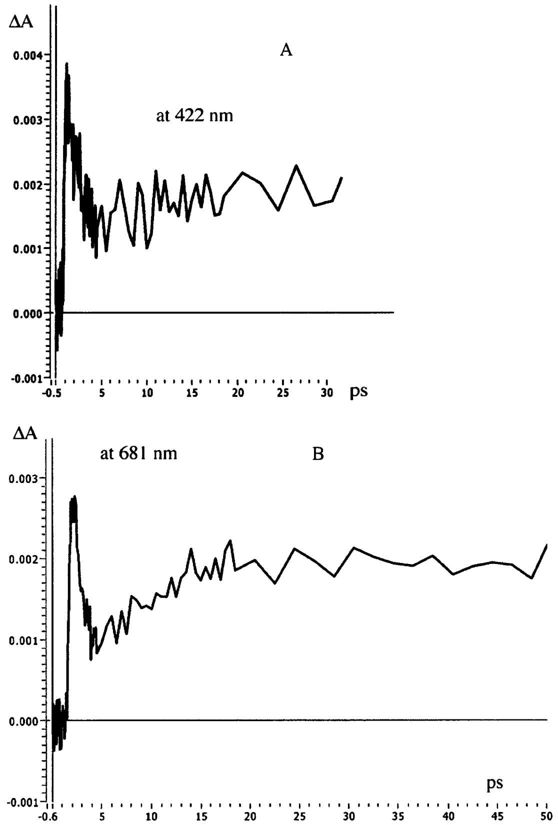

Figure 7. Kinetic traces at two wavelengths of the transient absorption for **1** in acetonitrile following femtosecond laser excitation at 340 nm.

130 to 60 ns) observed upon aeration is fully consistent with the triplet character of the CT state. Without adequate time resolution, however, it is not possible to comment on the rate of any intersystem crossing step that precedes formation of ^{3}CT nor about the possible role of a shorter-lived ^{1}CT state, such as has been observed during certain intermolecular electron-transfer reactions with quinones.[4] We therefore subjected both the dyad **1** and the acceptor model **3** to femtosecond transient absorption spectroscopy. To avoid sacrificial photoreactions, acetonitrile was used as solvent rather than DMSO. It is also important to stress that our samples show insufficient absorbance at 420 nm, the excitation wavelength used in the fs studies of Okamoto et al., to facilitate recording transient absorption spectra and, therefore, the excitation wavelength was moved to 340 nm. A full description of the instrumental setup used has been published elsewhere.[19]

Femtosecond TA spectra (not shown) of **3** are straightforward. With a single risetime of ~0.4 ps, a spectrum develops which is identical to that already observed in the nanosecond experiments (see Figure 2) and which is identified as being due to T_1-T_n absorption by the AQ chromophore. These results thus confirm, and quantify, the ultrafast intersystem crossing inherent to the AQ chromophore, as proposed before.[1,7] The subpicosecond behavior of **1** is much more complex, however, and is also very different from that described earlier with DMSO as solvent.[7] Here, a spectrum similar, but not identical, to that observed on nanosecond time scales develops with a risetime of ~0.2 ps (see Figure 6). This species (denoted as X) decays with a time constant of ~2 ps (see Figure 7A) to be replaced by a species (denoted as Y) having a spectrum identical to that observed on nanosecond time scales. The risetime of Y is ~15 ps, as monitored (see Figure 7B) at long wavelength where Y absorbs more strongly than X. Because of the spectral similarity between X and Y, we propose that both are intramolecular CT states but with different spin configuration, X being of singlet (^{1}CT) character and Y being of triplet (^{3}CT) character. Extensive DFT calculations confirmed (see below) that in a polar solvent both the lowest singlet and the lowest triplet states of **1** indeed have strong CT character, and the calculated absorption spectrum of the ^{3}CT state coincides very well with that of Y.

The fact that decay of ^{1}CT is more rapid than the growth of ^{3}CT implies that ^{1}CT is not the only precursor of ^{3}CT. Instead, it appears that **1** follows the more usual scheme whereby excitation initially populates the local AQ singlet state, which undergoes internal conversion to ^{1}CT in competition with intersystem crossing to ^{3}AQ. While ^{1}CT (=X) decays by way of charge recombination within ~2 ps, ^{3}AQ undergoes relatively slow (~15 ps) charge separation to populate ^{3}CT (=Y). That the latter charge separation is slower is simply because there is less driving force, that is, because of the small energy gap between ^{3}AQ and ^{3}CT (see below). Charge recombination from ^{3}CT to the ground state is spin forbidden, thereby explaining the relatively long lifetime (~130 ns) of this state. This value lies in the range (0.1−2 μs) considered to be typical for ^{3}CT states in compact dyads.[5,6]

Energetics of Charge Separation in 1, Time Dependent DFT (TD-DFT) Calculations. The lowest locally excited singlet and triplet states associated with **1** are clearly resident on the AQ chromophore, which is known to have S_1 and T_1 energies of 2.94 and 2.72 eV, respectively.[20] Phosphorescence spectra (see Supporting Information) recorded for **1** and **2** in an ethanol glass at 77 K indicate that, under these conditions, the anthraquinone-based n,π^* state is the lowest-energy triplet species in both **1** and **2**. Both compounds show strong and structured phosphorescence from an n,π^* T_1 state with a zero−zero transition at 2.74 eV and with a lifetime of about 2.5 ms. These observations agree fully with earlier reports of Hamanoue et al.[8] concerning the phosphorescence of **1** and of Tanimoto et al.[3] concerning the phosphorescence of **3**. We can conclude, therefore, that charge separation from T_1 does not take place for **1** in a glassy matrix at low temperature.

It was proposed earlier by Okamoto et al. that in a polar solvent at room temperature the lowest excited state of **1** is of CT character and should be some 2.24 eV above the ground state.[7] This estimate was, however, based upon electrochemical data that we have been unable to reproduce. Thus, cyclic voltammetry (see Supporting Information) shows that the reduction potential for the AQ unit in **1** of −0.88 V (vs SCE)

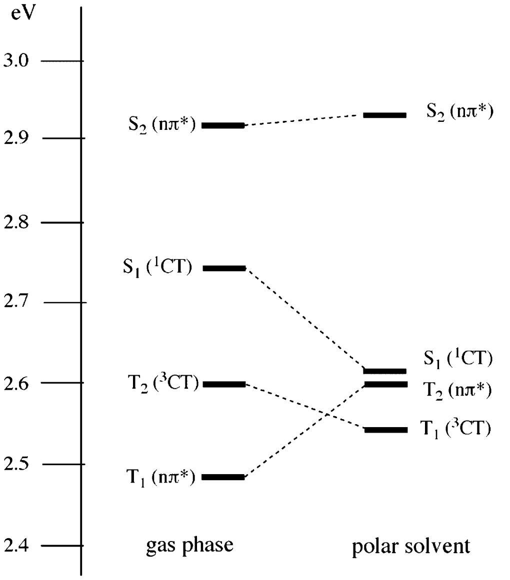

Figure 8. State energy diagram for the lowest two excited singlet and triplet states of **1** as calculated via TD−DFT (PCM).

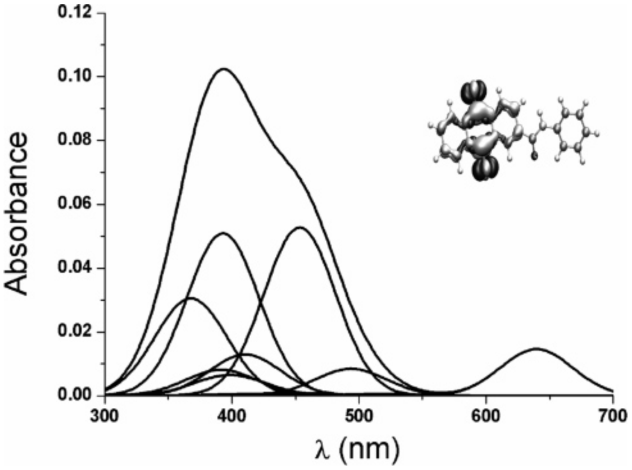

Figure 9. Computed (transient) absorption spectrum for the local *n*,*π** triplet state of **1** together with the difference charge-density map of this state. The spectrum has been compiled by summation of the individual transitions, scaled according to their computed oscillator strength, and assigned an arbitrary bandwidth of 50 nm. The dark areas shaded on the density map refer to negative regions and the lighter areas represent positive regions.

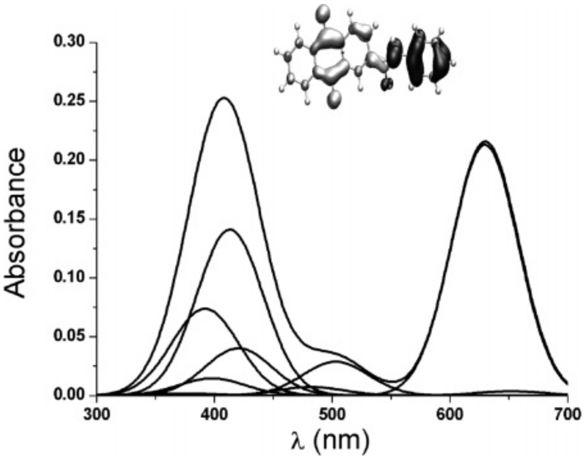

Figure 10. Computed (transient) absorption spectrum for the triplet charge-transfer (^{3}CT) state of **1** together with the difference charge-density map of this state. See Figure 9 for details.

is in full agreement with the data of Okamoto et al. However, there was no indication for oxidation of the formanilido donor group at or near the claimed potential of 1.37 V (vs SCE). Instead, a fully irreversible oxidation process was found to set in at much higher potentials. In fact, the complete irreversibility of the electrochemical oxidation of the donor group in **1** might be expected on the basis of the behavior reported for similar functionalities.[21] A crude estimate of the donating ability of the formanilido group was obtained from the observation that complexation of **4** (acetanilide) with tetracyanoethylene (TCNE) in dichloromethane leads to a CT complex with $\lambda_{\max} = 480$ nm, which is close to that of the TCNE/anisole complex (510 nm).[22] The oxidation potential of anisole[23] is 1.76 V (vs SCE) and thus that of the formanilido donor in **1** must also be around 1.8 V (vs SCE). If correct, this derived oxidation potential can be used to argue that a pure CT state in **1** should be situated at ca. 2.68 eV, which is barely below the AQ triplet state known from low-temperature phosphorescence spectra to reside at 2.74 eV. The small energy gaps between local and CT states in **1**, and the likelihood of the resultant configuration interaction, make it desirable to obtain a more sophisticated estimate of the relative state energies needed for construction of an energy diagram for **1**. For this purpose, we have performed extensive TD−DFT calculations[24] employing the B3LYP functional[25] in which the influence of a solvent was modeled via the polarizable continuum model (PCM) method.[26] Figure 8 shows the resultant state energy diagram.

These calculations confirm that in polar solution both the T$_1$ and S$_1$ states of **1** possess pronounced CT character. However, in nonsolvating environments, only the S$_1$ state is of CT character and the T$_1$ state has the appearance of a local *n*,*π** state. These results nicely explain why in a low-temperature glassy matrix **1** shows the phosphorescence typical of the AQ chromophore while in polar solvents at room temperature both ^{1}CT and ^{3}CT states are populated. The much larger energy gap between the local singlet state and the ^{1}CT state, as compared to the rather small energy gap between the local triplet state and the ^{3}CT state, provides the rationale for the significantly faster rate of charge separation observed in the singlet manifold. Furthermore, systematic variation of the solvent dielectric constant in the PCM model indicates that, at the intended level crossing, the minimum energy gap between the lowest triplet states is 16 cm^{-1} (see Supporting Information). This latter finding implies an electronic coupling matrix element between the local triplet and ^{3}CT states of 8 cm$^{-1.}$

Absorption spectra were computed both for the local triplet state and for the triplet CT state of **1**, in a solvent reservoir using a common bandwidth of 50 nm for the various Gaussian components and using the computed oscillator strengths for each projected band. These spectra are shown in Figures 9 and 10, respectively, together with the difference charge density maps for these states relative to the ground state. While the computed T$_1$−T$_n$ absorption spectrum of the *n*,*π** triplet state (Figure 9) corresponds very well with the transient absorption spectrum of this state as observed for **2** and **3** (see Figure 2), the computed absorption spectrum of the CT state (see Figure 10) clearly agrees much better with the experimental transient absorption spectra observed for **1** in nonreactive polar solvents on both nanosecond and picosecond time scales (see Figures 3 and 6). Such behavior confirms our assignment of these spectra to an internal CT state of **1**. On the other hand, the experimental transient absorption spectrum of **1** in DMSO (see Figure 4) cannot be reconciled with that of either the local triplet or the CT state and, as already explained above, must be attributed to species resulting from irreversible photo-oxidation of this solvent. The most likely product is the anthraquinone radical anion or species derived from it, such as the also stable dianion (see Supporting Information).

Concluding Remarks. We have determined the rate constant for S_1-T_1 intersystem crossing in a 9,10-anthraquinone derivative (**3**), $k_{isc} = 2.5 \times 10^{12}$ s^{-1}. Notwithstanding this ultrafast process, photoexcitation of the dyad **1** is followed by competition between intersystem crossing and intramolecular charge separation to give a short-lived (2 ps) singlet CT state. The local triplet state itself undergoes slower charge separation to populate a relatively long-lived (130 ns) triplet CT state. An earlier report[7] about the formation of an extremely long-lived CT state (>900 μs) in **1** was found to be erroneous and was related to the sacrificial photo-oxidation of the DMSO solvent used in that study. An interesting feature of the dyad **1** concerns the high density of local and CT excited states within a fairly narrow energy region. These various states interconvert on fast time scales and, in reality, it is by no means certain that the lowest two triplet states are not in thermal equilibrium at ambient temperature. Thus, the assignment of the lowest-energy triplet as being of CT character might be somewhat misleading.

At this point, we would like to comment on the general concept of claiming unusually long-lived CT states from compact molecular dyads; the term “unusually long-lived” might be taken to refer to any CT state where the ratio of rates of charge separation and subsequent charge recombination exceeds a factor of ca. 5000-fold, regardless of the actual rates involved. There have been several such claims in recent years[6] and, in fact, the subject will probably become more topical with the inevitable resurgence of interest in solar energy conversion. Some of these systems have been re-examined[27−29] and have been found to be seriously flawed while potential problems have been highlighted in respect to other systems.[5,6] Clearly, it is not useful to repeat all such claims, and a few obvious ground rules need to be imposed before any new claims are made. With this in mind, we suggest that the following criteria must be fulfilled before describing any more long-lived CT states. The proposed “rules” can be summarized as follows:

(1) The excitation step must correspond to a well-defined absorption transition localized on either donor or acceptor.

(2) The full photon balance must be given.

(3) All intermediate species, starting with the initial locally excited singlet state, must be identified unambiguously and their decay followed over a wide spectral and temporal range.

(4) There must be no gaps in the temporal window.

(5) Triplet excited states, both local and CT, must be fully accommodated in the overall scheme.

(6) Both oxidized and reduced species in the final CT state must be recognizable by spectroscopic analysis and their stoichiometry should be established.

(7) Both radical ions comprising the CT state must be fully reversible in an electrochemical sense.

(8) The solvent must be resistant to both oxidation and reduction and must be subjected to rigorous purification by well-tested methods.

The main problems to emerge thus far have involved dyads where one of the radical ions comprising the CT state is an intrinsically unstable species dissolved in inappropriate solvents. Furthermore, claims for a long-lived CT state have been based on detection of only one of the radical ions, thus leaving open the question of sacrificial photochemistry. A particular problem emerges when trying to invoke the Marcus inverted region as a means by which to inhibit fast charge recombination since high potential donors often undergo irreversible (e.g., deprotonation) electrochemistry. The same stringent conditions should be applied to long-lived CT states formed from triads, tetrads, pentads, and so forth. We would like to go so far as to discount all claims for long-lived CT states that do not abide by the above rules.

Acknowledgment. We thank the University of Amsterdam, the University of Newcastle, and EPSRC (GR/S00088/01) for financial support.

Supporting Information Available: Synthetic details and structural identification for compounds **1**−**3**, cyclic voltammetry and spectro-electrochemistry of **1**, phosphorescence spectra, and details for the quantum chemical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Armitage, B.; Yu, C.; Devadoss, C.; Schuster, G. B. *J. Am. Chem. Soc.* **1994**, *116*, 9847.

(2) Schuster, G. B. *Acc. Chem. Res.* **2000**, *33*, 253.

(3) Tanimoto, Y.; Uehara, M.; Takashima, M.; Itoh, M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3121.

(4) Hubig, S. M.; Bockman, T. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 2926.

(5) Verhoeven, J. W.; Ramesdonk, H. J. v.; Groeneveld, M. M.; Benniston, A. C.; Harriman, A. *Chem. Phys. Chem.* **2005**, 2251.

(6) Verhoeven, J. W. *J. Photochem. Photobiol., C: Photochem. Rev.* **2006**, *7*, 40.

(7) Okamoto, K.; Hasobe, T.; Tkachenko, N. V.; Lemmetyinen, H.; Kamat, P. V.; Fukuzumi, S. *J. Phys. Chem. A* **2005**, *109*, 4662.

(8) Hamanoue, K.; Nakayama, T.; Nanshow, H.; Hanada, T.; Naruta, Y.; Kodo, T.; Maruyama, K. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3243.

(9) Allen, N. S.; Pullen, G.; Shah, M.; Edge, M.; Holdsworth, D.; Weddell, I.; Swart, R.; Catalina, F. *J. Photochem. Photobiol, A: Chem.* **1995**, *91*, 73.

(10) Oosterbaan, W. D.; Koeberg, M.; Piris, J.; Havenith, R. W. A.; Walree, C. A. v.; Wegewijs, B. R.; Jenneskens, L. W.; Verhoeven, J. W. *J. Phys. Chem. A* **2001**, *105*, 5984.

(11) Hamanoue, K.; Nakayama, T.; Kajiwara, Y.; Yamaguchi, T.; Teranishi, H. *J. Chem. Phys.* **1987**, *86*, 6654.

(12) Koncka, M.; Stojek, Z. *Electroanalysis* **1995**, *7*, 1010.

(13) Courtot-Coupez, J.; Demezet, M. L. *Bull. Soc. Chim. France* **1967**, *12*, 4744.

(14) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1988; Vol. 34.

(15) Brodard, P.; Sarbach, A.; Gumy, J. C.; Bally, T.; Vauthey, E. *J. Phys. Chem. A* **2001**, *105*, 6594.

(16) Brezova, A.; Gügel, A.; Rapta, P.; Stasko, A. *J. Phys. Chem.* **1996**, *100*, 16232.

(17) Stewart, F. E.; Eisner, M.; Carper, W. R. *J. Chem. Phys.* **1966**, *44*, 2866.

(18) Kushibiki, N.; Yoshida, H. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 349.

(19) Vergeer, F. W.; Kleverlaan, C. J.; Stufkens, D. J. *Inorg. Chim. Acta* **2002**, *327*, 126.

(20) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker Inc.: New York, 1993.

(21) Garrido, E. M.; Lima, J. L. F. C.; Delerue-Matos, C.; Borges, F.; Silva, A. M. S.; Brett, A. M. O. *Anal. Chim. Acta* **2001**, *434*, 35.

(22) Voigt, E. M.; Reid, C. *J. Am. Chem. Soc.* **1964**, *86*, 3930.

(23) Zweig, A.; Hodgson, W. G.; Jura, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 4124.

(24) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(25) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(26) (a) Cossi, M.; Barone, V.; Robb, M. A. *J. Chem. Phys.* **1999**, *111*, 5295. (b) Cossi, M.; Barone, V. *J. Chem. Phys.* **2000**, *112*, 2427. (c) Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *106*, 5151. (d) Cammi, R.; Mennucci, B.; Tomasi, J. *J. Phys. Chem. A* **1999**, *103*, 9100.

(27) Benniston, A. C.; Harriman, A.; Li, P.; Rostron, J. P.; Ramesdonk, H. J. v.; Groeneveld, M. M.; Zhang, H.; Verhoeven, J. W. *J. Am. Chem. Soc.* **2005**, *127*, 16054.

(28) Benniston, A. C.; Harriman, A.; Li, P.; Rostron, J. P.; Verhoeven, J. W. *Chem. Commun.* **2005**, 2701.

(29) Verhoeven, J. W.; Ramesdonk, H. J. v.; Zhang, H.; Groeneveld, M. M.; Benniston, A. C.; Harriman, A. *Int. J. Photoenergy* **2005**, *7*, 103.