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Photoisomerization of a Capped Azobenzene in Solution Probed by Ultrafast Time-Resolved Electronic Absorption Spectroscopy

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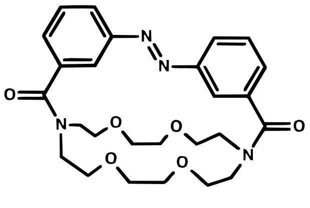
Ultrafast time-resolved electronic absorption spectroscopy has been used to study the photochemistry of *trans*-azobenzene and *trans*-**1**, a derivative in which azobenzene is capped by an azacrown ether, on UV excitation to the $S_2(\pi\pi^*)$ state. Excitation of *trans*-**1** results in transient absorption which decays with a dominant component of lifetime ca. 2.6 ps and in bleaching of the ground-state UV absorption band which recovers on a similar time scale. In contrast, excitation of *trans*-azobenzene results in transient absorption which decays with a dominant component with a shorter lifetime of ca. 1 ps, and in bleaching which recovers on a much longer time scale of ca. 18 ps. The recovery of the ground-state UV absorption band is not complete in either case, and the ultrafast data indicate that the quantum yield of trans-to-cis photoisomerization of **1** is approximately twice that of azobenzene. These observations demonstrate that the restricted rotational freedom of the phenyl groups in *trans*-**1** has a significant effect on the excited-state dynamics and decay mechanism. The differences in lifetime and quantum yield of photoisomerization are attributed to rapid internal conversion from the S_2 to S_1 excited states of *trans*-**1**, which results in photoisomerization by an inversion mechanism in the S_1 state, whereas fast rotation in the S_2 state of *trans*-azobenzene populates a "bottleneck" state which delays the recovery of the ground state and which reduces the yield of photoisomerization; this "bottleneck" state is not accessible by *trans*-**1**. The results support the proposal that rotation is the dominant pathway for decay of the first-formed S_2 state of *trans*-azobenzene but that inversion is the dominant pathway for decay of the S_1 state.

Introduction

The photoisomerization of azobenzene and its derivatives has been the subject of many studies.[1] These studies often have been aimed at developing molecules in which the isomerization of the azobenzene chromophore can be used as a light-controlled switch to change a molecular structure and thereby to induce a particular reaction.[2−5] The fundamental aspects of azobenzene photochemistry also have been considered[1] and are crucial in developing a full understanding of the light-induced reactions and their applications. The mechanism of azobenzene photoisomerization has been debated for many years, mainly on the basis of steady-state studies of its photochemistry,[1,6−10] because direct, time-resolved studies of this ultrafast reaction have been inaccessible until recently. Nevertheless, the earlier experimental and theoretical[11] studies have led to the proposal of a dual mechanism in which the photoisomerization pathway is dependent on excitation wavelength.[1] Visible excitation to the $S_1(n\pi^*)$ state is proposed to lead to photoisomerization by an inversion mechanism, in which there is in-plane motion of a phenyl group. UV excitation to the $S_2(\pi\pi^*)$ state is proposed to lead to photoisomerization by a rotation mechanism in which there is large-scale twisting of a phenyl group around the −N=N− bond, similar to that which occurs in the photoisomerization of stilbene.[12] Particularly important among the studies that led to these proposals for the dual photoisomerization mechanism were those on derivatives in which the two phenyl groups of azobenzene were linked by an aliphatic chain[8,9] or rendered bulky by derivatization.[10] These derivatives provided model compounds with which the photochemistry of azobenzene could be studied when the rotation pathway was blocked but the inversion pathway remained available.

We recently reported the first direct study of azobenzene photoisomerization, using ultrafast time-resolved UV−visible absorption spectroscopy to observe the photochemistry on UV excitation to the $S_2(\pi\pi^*)$ state.[13] These observations have been extended more recently by studies of visible excitation to the $S_1(n\pi^*)$ state by ourselves[14] and others.[15] Together, these direct studies have provided important new information on both the dynamics and the mechanism of the photoisomerization reactions.

In this paper, we report ultrafast studies of the "capped" azobenzene derivative, *trans*-**1**, in which large-scale motion of the phenyl groups is restricted by their linkage to a bridging azacrown ether. This compound has been the subject of extensive steady-state studies,[9,16−18] including those which provided important evidence to substantiate the dual mechanism for photoisomerization of azobenzene. This compound enables us to extend our studies of azobenzene photochemistry to a



trans-**1**

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model in which rotation is blocked, and in particular, it provides us with an ideal opportunity to test our interpretation of the ultrafast spectroscopic results from azobenzene itself.

Experimental Section

trans-**1** was a gift from Professor S. Shinkai; its synthesis and characterization have been described.[16,17] *trans*-**1**, *trans*-azobenzene (Aldrich), and chloroform (Aldrich, HPLC grade) were used as received. *trans*-**1** was found to have insufficient solubility in alkane, acetonitrile, or benzene solvents but to have sufficient solubility in chloroform for the ultrafast laser studies.

Sample solutions (ca. 4×10^{-4} mol dm^{-3}, 30 cm^3 reservoir volume) under air were circulated at a flow rate of >100 cm s^{-1} through a 1 mm path length quartz cell, using a gear-pump-driven flow system. Measurements were made on solutions at room temperature (ca. 18 °C). UV−visible absorption spectra of the solutions were measured, with a Hitachi U-3000 spectrometer, before and after the laser experiments. Small differences in absorbance (<15%) were observed after several hours of study using the ultrafast laser apparatus. These changes indicated that irreversible photoreactions were occurring in addition to partial trans-to-cis photoisomerization, and they are attributed to the side reactions that have been reported to occur on photolysis in halogenated solvents.[17] Fresh sample solutions were used for each set of ultrafast measurements.

The ultrafast laser apparatus used for this study is described in detail elsewhere.[13,19] Briefly, a portion of the output from an amplified dye laser system was frequency doubled to generate photolysis pulses (303 nm, 1.4−1.8 μJ, 1050 Hz), while the remainder was directed round an optical delay line and used to generate a white-light continuum for use as the probe beam. The pump and probe beams were focused to diameters of ca. 250 and 200 μm, respectively, in the sample cell. The emerging probe beam was analyzed using 10 nm band-pass interference filters and a photodiode. The pump beam was synchronously chopped at 525 Hz, and two lock-in amplifiers were used to recover the differential and average transmitted intensities from which changes in absorbance (ΔA) were calculated. In some experiments, a probe beam at 303 nm (attenuated to ca. 1 nJ/pulse) was obtained from a portion of the pump beam instead of generating a white-light continuum. In all cases, the relative polarization of the pump and probe beams was set at the “magic angle” of 54.7°. Kinetics were fitted by a sum of exponentials convoluted with the instrument response function of ca. 0.5 ps; the uncertainties in lifetimes that are quoted indicate the range in which satisfactory fits were obtained from several data sets.

Results and Discussion

Steady-State Spectra. The steady-state UV−visible absorption spectra of *trans*-azobenzene in chloroform and of *trans*-**1** in chloroform are shown in Figure 1. These spectra are similar, comprising a weak band at ca. 445 nm assigned to the $S_1(n\pi^*)$ transition and a strong band at ca. 320 nm assigned to the $S_2(\pi\pi^*)$ transition. This similarity indicates that the electronic structures of *trans*-azobenzene and *trans*-**1** are similar and that the derivatization of azobenzene by capping with an azacrown ether to form compound **1** does not perturb the molecule significantly in its ground-state geometry.

Ultrafast Studies of *trans*-Azobenzene. Excitation of *trans*-azobenzene at 303 nm resulted in transient absorption which was probed at 390−420 nm and in transient bleaching which was probed at 303 nm. The decay of the transient absorption at 390−405 nm was found to fit to a dual-exponential function, giving lifetimes of $\tau_1 = 1.2 \pm 0.3$ ps and $\tau_2 = 16 \pm 8$ ps. The short-lived component was dominant, with >85% of the ΔA amplitude at a probe wavelength of 405 nm. The recovery of the bleaching at 303 nm was fitted adequately by a single-exponential function, giving a lifetime of $\tau_3 = 18 \pm 4$ ps. Examples of fits to the data are shown in Figures 2 and 3a. Figure 2 shows data plotted on a time scale that enables direct comparison of transient absorption and bleaching kinetics and of the data from *trans*-**1** presented below in Figure 4; Figure 3a gives an expanded plot of the transient absorption data which illustrates the kinetics at the earliest delay times more clearly.

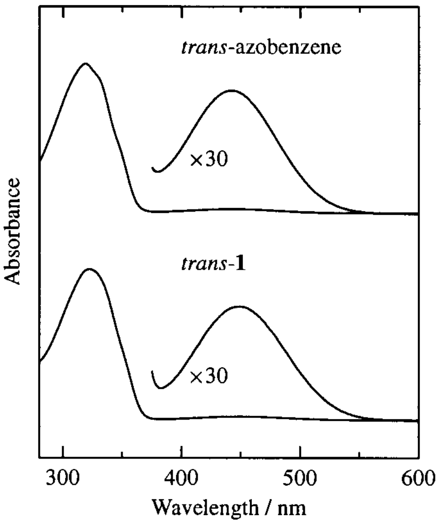

Figure 1. Steady-state UV−visible absorption spectra of *trans*-azobenzene and *trans*-**1** in chloroform.

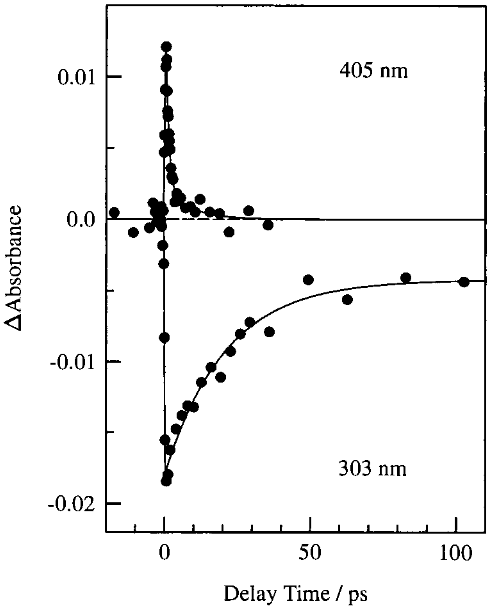

Figure 2. TRVIS kinetics obtained on 303 nm excitation of *trans*-azobenzene in chloroform probed at 405 nm, fitted to $\tau_1 = 1.0$ ps (87% amplitude) and $\tau_2 = 9$ ps (13% amplitude), and probed at 303 nm, fitted to $\tau_3 = 21$ ps (77% amplitude) and a long-time offset (23% amplitude).

The recovery of the ground-state absorption of *trans*-azobenzene at 303 nm was not complete, and the extent of bleaching at >100 ps can be quantified from these data as $\Delta A_\infty/\Delta A_0 = 0.23$, where ΔA_0 and ΔA_∞ are the initial and final ΔA values obtained from the kinetic analysis. This partial recovery is attributed to photoisomerization because *cis*-azobenzene has

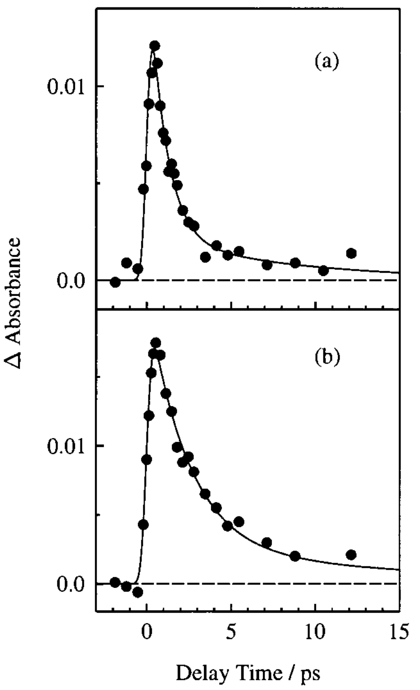

Figure 3. TRVIS kinetics obtained on 303 nm excitation of (a) *trans*-azobenzene in chloroform probed at 405 nm, fitted to $\tau_1 = 1.0$ ps (87% amplitude) and $\tau_2 = 9$ ps (13% amplitude), and (b) *trans*-**1** in chloroform probed at 405 nm, fitted to $\tau_1 = 2.4$ ps (88% amplitude) and $\tau_2 = 16$ ps (12% amplitude).

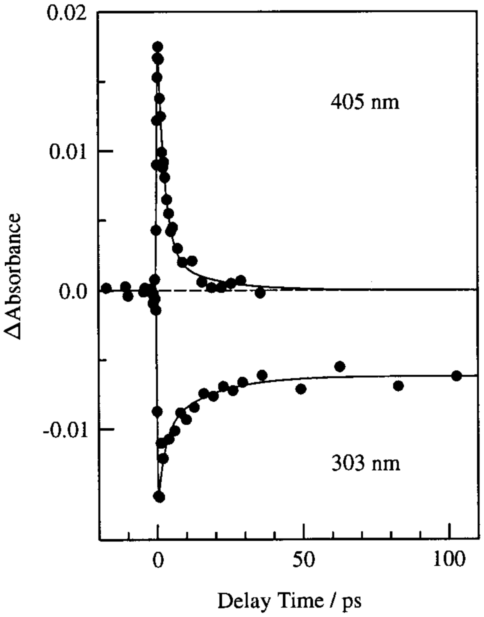

Figure 4. TRVIS kinetics obtained on 303 nm excitation of *trans*-**1** in chloroform probed at 405 nm, fitted to $\tau_1 = 2.4$ ps (88% amplitude) and $\tau_2 = 16$ ps (12% amplitude), and probed at 303 nm, fitted to $\tau_3 = 2.4$ ps (36% amplitude), $\tau_4 = 16$ ps (24% amplitude), and a long-time offset (40% amplitude).

a smaller absorption coefficient (ϵ_c) than *trans*-azobenzene (ϵ_t) at this wavelength. If the only contributions to the ΔA signal at 303 nm arise from ground-state absorption, then the yield of trans−cis photoisomerization can be estimated as $\Phi_{t\rightarrow c} = (\Delta A_\infty/\Delta A_0)\{\epsilon_t/(\epsilon_t - \epsilon_c)\}$; for azobenzene, this gives an estimate of $\Phi_{t\rightarrow c} = 0.26$ for excitation to the $S_2(\pi\pi^*)$ state. This expression is based on the assumption that no overlying transient absorption contributes to the value of ΔA_0, and thus it may overestimate the yield of photoisomerization;[13] literature values from steady-state studies of azobenzene lie in the range $\Phi_{t\rightarrow c} = 0.1-0.2$ for excitation to the $S_2(\pi\pi^*)$ state.[1,6−10]

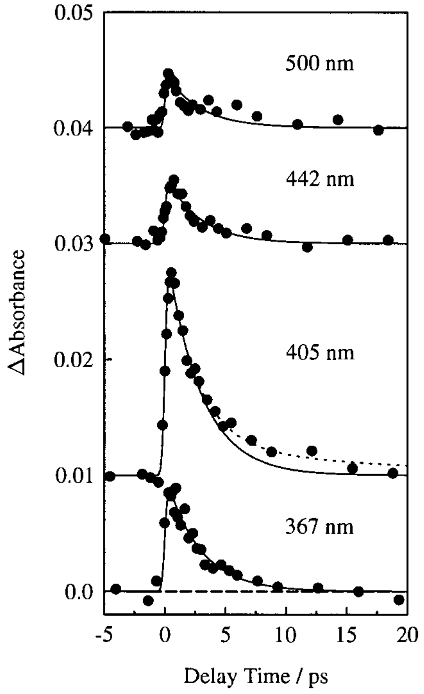

Figure 5. TRVIS kinetics obtained on 303 nm excitation of *trans*-**1** in chloroform probed at 500, 442, 405, and 367 nm: the solid lines show fits to a single-exponential decay of $\tau_1 = 2.8$ ps; the dashed line shows the small improvement obtained on fitting the data at 405 nm to a dual-exponential decay of $\tau_1 = 2.4$ ps and $\tau_2 = 16$ ps.

The results and analysis reported here for *trans*-azobenzene in chloroform at 18 °C are consistent with those of our earlier studies of *trans*-azobenzene in alkane and in acetonitrile solutions at 30 °C, where we observed the following: transient absorption at 370−450 nm which decayed according to a dual-exponential function which gave lifetimes of $\tau_1 \approx 1$ ps and $\tau_2 \approx 15$ ps, with the short-lived component dominant; transient bleaching at 303 nm which recovered according to a single-exponential decay which gave a lifetime of $\tau_3 \approx 15$ ps; a value of $\Delta A_\infty/\Delta A_0 = 0.25$ for the long-time bleaching which gave an estimate for the yield of trans−cis photoisomerization of $\Phi_{t\rightarrow c} = 0.28$ for azobenzene in cyclohexane. The results we reported previously for *trans*-azobenzene showed only a small dependence on solvent;[13] the results we report here, for *trans*-azobenzene in a different solvent and at a different temperature, are similar to and thus confirm these earlier results.

Ultrafast Studies of *trans*-1. Excitation of *trans*-**1** at 303 nm resulted in transient absorption which was probed at 367−500 nm and in transient bleaching which was probed at 303 nm, as shown in Figures 4 and 5. The transient absorption was strongest at 405 nm and ca. 4 times weaker at 500 nm, and its decay throughout the region 367−500 nm was fitted adequately by a single-exponential function, giving a lifetime of $\tau_1 = 2.8 \pm 0.4$ ps (Figure 5); a small improvement in the fit was obtained in some cases by the addition of a second, longer-lived component of small amplitude (<20% of total ΔA), which resulted in a fit to $\tau_1 \approx 2.4$ ps and $\tau_2 \approx 16$ ps (illustrated in Figure 5 for 405 nm probing). The recovery of the bleaching at 303 nm could be fitted adequately by a single-exponential function, giving a lifetime of $\tau_3 \approx 6$ ps, although a better fit again was obtained by the addition of a second, longer-lived component of small amplitude (15−25%), which resulted in a

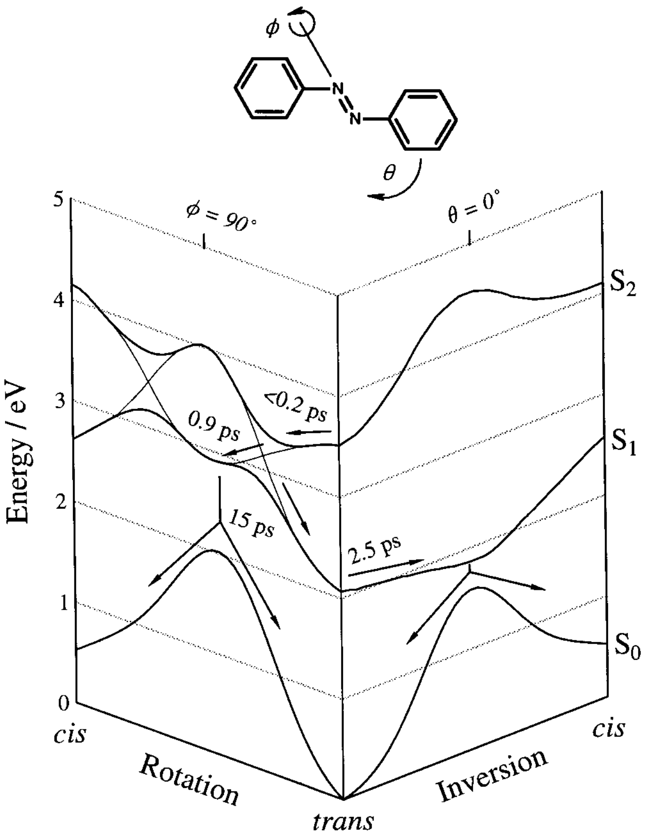

Figure 6. Schematic representation of the potential energy curves of azobenzene and possible decay routes following excitation of *trans*-azobenzene. The curves are derived from the results of calculations on azobenzene reported in ref 11. The arrows on the molecular structure indicate the coordinates for rotation (ϕ), by twisting of a phenyl group around the N−N bond, and inversion (θ), by in-plane motion of a phenyl group through a linear N−N−phenyl structure.

fit to lifetimes of $\tau_3 = 2.7 \pm 0.5$ ps and $\tau_4 = 16 \pm 8$ ps. The examples of fits to experimental data shown in Figure 4 illustrate cases in which transient absorption and bleaching data were fitted with a dual-exponential function corresponding to lifetimes of 2.4 and 16 ps in both cases; Figure 3b shows an expanded plot of the transient absorption data which illustrates the kinetics at the earliest delay times more clearly.

The recovery of the ground-state absorption of *trans*-**1** at 303 nm was not complete, and the extent of bleaching at >100 ps is measured from the kinetic data to be $\Delta A_\infty/\Delta A_0 = 0.40$. As for *trans*-azobenzene, this partial recovery of *trans*-**1** is attributed to trans−cis photoisomerization, and the quantum yield is estimated similarly to be $\Phi_{t\rightarrow c} = 0.44$.

Excited-State Decay Mechanisms. Our present interpretation of the photochemistry of *trans*-azobenzene has been developed in two recent reports,[13,14] and it may be summarized conveniently by the simple potential energy curves given in Figure 6, which are based on the results of ab initio calculations reported in the literature.[11] UV excitation promotes the molecule to the $S_2(\pi\pi^*)$ state, and our most recent results indicate that the initial process in this state is rotation on a time scale of <200 fs.[14] Interaction between the S_1 and S_2 states gives a barrier that restricts the extent of rotation to form a partially twisted structure, $S_2^\dagger$; the molecule then undergoes internal conversion in ca. 900 fs to reside in a “bottleneck” state, $S_1^\dagger$, from which the yield of photoisomerization is relatively low and from which its decay to repopulate the ground state is relatively slow, taking ca. 15 ps. This interpretation is consistent with most of the experimental data published to date on this system: it is applicable, similarly, to the results we report here for *trans*-azobenzene in chloroform although the <200 fs process is too fast to be resolved in the present study.

It is clearly evident, from both the appearance of the experimental data and their more detailed analysis, that the transient absorption dynamics on UV excitation of *trans*-**1** (Figures 4 and 3b) are different from those on UV excitation of *trans*-azobenzene (Figures 2 and 3a). Three pieces of evidence may be considered in turn: the transient absorption data, the transient bleaching data, and the quantum yields of photoisomerization.

First, the transient absorption observed here at 367−500 nm on UV excitation of *trans*-**1** decays with a lifetime of $\tau_1 \approx 2.6$ ps. This is different from the decay of the transient absorption observed at 390−405 nm on UV excitation of *trans*-azobenzene, the fit of which requires a dual-exponential function with a dominant component that is 2−3 times faster, with $\tau_1 \approx 1$ ps. In addition, we do not observe significant transient absorption at >450 nm for azobenzene at delay times >0.5 ps following UV excitation, whereas we do observe a significant signal for *trans*-**1**. Although these results obtained on UV excitation of *trans*-**1** to the $S_2(\pi\pi^*)$ state are different from those obtained on UV excitation of *trans*-azobenzene to the $S_2(\pi\pi^*)$ state, they are notably similar to those we have reported for visible excitation of *trans*-azobenzene: the $S_1(n\pi^*)$ state of *trans*-azobenzene displays a transient absorption spectrum in the region 360−620 nm, with a wavelength dependence similar to that observed here for *trans*-**1**, and it decays with a lifetime of $\tau_1 = 2.5$ ps.[14]

Second, the recovery of the transient bleaching observed here at 303 nm on UV excitation of *trans*-**1** is fitted adequately by a single-exponential function with $\tau_3 \approx 6$ ps and better by a dual-exponential function with a dominant component of $\tau_3 \approx 2.7$ ps and a smaller component of $\tau_4 \approx 16$ ps. Again, this is different from the recovery of the transient bleaching observed at 303 nm on UV excitation of *trans*-azobenzene, which we have observed here and reported previously[13] to fit well to a single-exponential function with a lifetime, of $\tau_3 \approx 15$ ps, which is significantly slower. In this case, there are no results on the bleaching recovery following visible excitation of *trans*-azobenzene to the $S_1(n\pi^*)$ state available for comparison: the much higher (ca. 40 times) absorption coefficients in the UV than those in the visible region (illustrated in Figure 1) preclude the observation of bleaching of the ground-state band at ca. 320 nm because of the high absorbance of samples prepared at a concentration appropriate for efficient visible excitation; bleaching of the ground-state band at ca. 450 nm cannot be observed because of overlying excited-state absorption in this region.[14]

Third, the value of $\Delta A_\infty/\Delta A_0 = 0.40$ observed for bleaching of *trans*-**1** on UV excitation is significantly higher than that of 0.23 observed for *trans*-azobenzene on UV excitation. Although these values may lead to an overestimate of the quantum yield of trans−cis photoisomerization, as discussed above, they suggest that this quantum yield is approximately halved on going from *trans*-**1** to *trans*-azobenzene when using UV excitation. This observation is consistent with steady-state studies in which this quantum yield was reported to reduce from 0.29 for **1** to 0.12 for azobenzene in ethanol at room temperature.[9]

The general aspects of the similarities and differences described above are clearly evident from the raw data presented in Figures 2 and 4; we note that the actual values obtained from the analysis may depend, in part, on the fitting procedures used. However, taken together, the results of these ultrafast studies indicate clearly that the excited-state decay mechanism which operates on UV excitation of *trans*-**1** is different from that which operates on UV excitation of *trans*-azobenzene to the $S_2(\pi\pi^*)$ state but that it is similar to the mechanism which operates on visible excitation of *trans*-azobenzene to the $S_1(n\pi^*)$ state. Consequently, the data provide direct, real-time evidence that supports several proposals about the mechanism.

First, the data indicate that photoisomerization of azobenzene proceeds from the $S_1(n\pi^*)$ state when rotation is blocked because of the similarity of the results for UV excitation of *trans*-**1** presented here and those reported previously for visible excitation of *trans*-azobenzene directly to the $S_1(n\pi^*)$ state.[14] This interpretation also is consistent with the similar quantum yields of $\Phi_{t\rightarrow c} = 0.29$, 0.29, and 0.24, which have been reported for **1** on UV excitation, **1** on visible excitation, and azobenzene on visible excitation, respectively;[9] in each case, photoisomerization proceeds from the $S_1(n\pi^*)$ state and results in a similar quantum yield. Furthermore, the ultrafast data suggest that internal conversion from the S_2 to S_1 states is fast (<0.5 ps) in the absence of a rotational mechanism for decay; a rise time was not resolved in the signal attributed to the S_1 state of *trans*-**1**, although absorption from the first-formed S_2 state also may contribute to the observed signal.

Second, the data indicate that rotation occurs on UV excitation of *trans*-azobenzene to the $S_2(\pi\pi^*)$ state because the excited-state dynamics are significantly different from those obtained on UV excitation of *trans*-**1**, for which rotation is blocked. If rotation were not a significant decay route following UV excitation of *trans*-azobenzene, then this difference would not be expected. Consequently, the data also suggest that photoisomerization occurs by an inversion mechanism in the $S_1(n\pi^*)$ state. However, they do not enable us to draw any conclusion as to whether the relatively small quantum yield of photoisomerization on UV excitation of *trans*-azobenzene occurs by rotation, by inversion, or by both routes, because the results provide no information on the route of decay from $S_1^\dagger$ to S_0.

Third, the data indicate that a "bottleneck" state is accessed by rotation on UV excitation of *trans*-azobenzene to the $S_2(\pi\pi^*)$ state because the recovery of the ground-state bleaching occurs much faster for *trans*-**1**, for which rotation is blocked and, therefore, such a state is rendered inaccessible. A recent study by ultrafast time-resolved infrared spectroscopy revealed that vibrational cooling of azobenzene occurs on a time scale of ca. 20 ps following photoisomerization.[20] The contribution of vibrational relaxation was discussed in our earlier interpretation of the slow recovery of the ground-state bleaching on UV excitation of *trans*-azobenzene, but it was considered unlikely that this alone could account for the observations; the presence of a "bottleneck" state was considered to be a more plausible interpretation.[13] The data obtained here on UV excitation of *trans*-**1** support this interpretation; although the same photon energy is deposited into the *trans*-**1** and *trans*-azobenzene molecules on UV excitation, it is only *trans*-azobenzene which gives a time scale for bleaching recovery that is significantly (at least 10 times) longer than that for the decay of the excited state we assign as $S_2^\dagger$. The photon energy that is deposited in the azobenzene chromophore must flow to the solvent in each case, and the derivatization by capping with an azacrown ether is unlikely to result in such a dramatic difference in the time scale for vibrational relaxation. Therefore, the results strongly support the presence of a "bottleneck" state which is accessed by rotational motion on the S_2 potential energy surface of *trans*-azobenzene and which is inaccessible to *trans*-**1**. The small-amplitude, ca. 16 ps time scale contribution to the kinetics that we observe for *trans*-**1** is likely to arise from vibrational relaxation. Vibrational excitation in the ground state will result in a relatively small increase in absorbance at the long-wavelength edge of the ground-state UV absorption band and in a relatively small decrease in absorbance at its peak: thus, the small components in the absorption decay at ca. 405 nm, and the bleaching recovery at 303 nm, both with a lifetime of ca. 16 ps, may be assigned to the changes arising from vibrational relaxation in the ground state of *trans*-**1**.

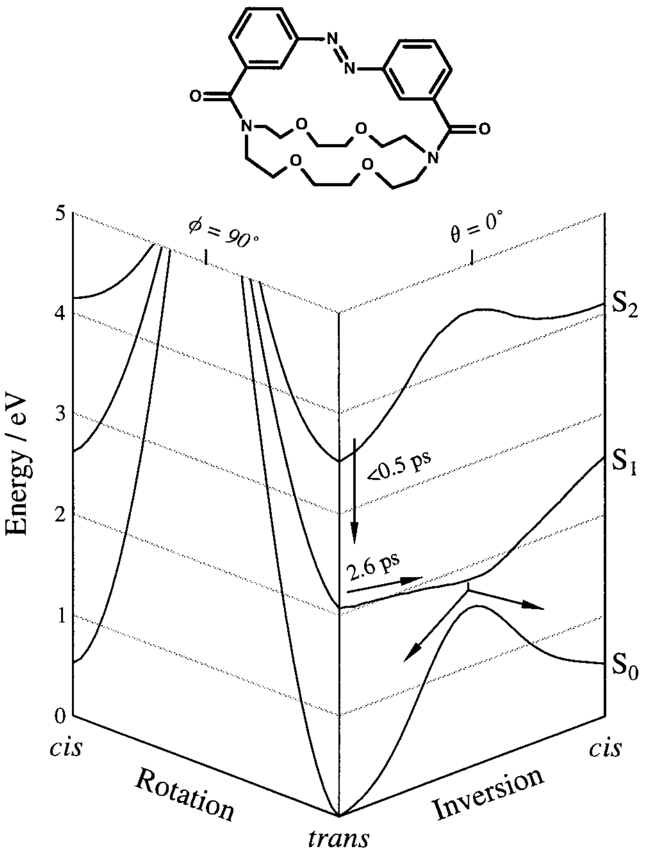

Figure 7. Schematic representation of the potential energy curves of **1** and possible decay routes following UV excitation to the S_2 state of *trans*-**1**. The curves are derived, in part, from the results of calculations on azobenzene reported in ref 11.

Fourth, the data from *trans*-**1** indicate that any barrier along the reaction pathway on the $S_1(n\pi^*)$ potential energy surface is small, i.e., that there is not a significant "bottleneck" state, because the time scale for ground-state recovery is relatively fast and is close to the time scale of ca. 2.6 ps for the decay of the S_1 excited state. In addition, the observation that the S_1 state of *trans*-**1** decays with a lifetime of ca. 2.6 ps on 303 nm excitation provides an interesting contrast with our recent results on visible excitation of *trans*-azobenzene to the S_1 state. The S_1 state of *trans*-azobenzene has been found to decay according to a monoexponential function of lifetime 2.5 ps on excitation at 503 nm, close to the origin, but in a nonmonoexponential way on excitation at 390−420 nm, well above this origin; the decay on excitation at 390−420 nm has been fitted with a dual-exponential function of lifetimes 2.6 and 0.6 ps, with the faster component dominant.[14] In the present study, despite exciting *trans*-**1** with a high-energy photon at 303 nm and rapidly forming its S_1 state, presumably with an even higher excess energy above the origin than that of *trans*-azobenzene excited at 390−420 nm, we do not observe a significant <2 ps component in the decay of the S_1 state of *trans*-**1**; rather, the dynamics we observe from *trans*-**1** excited at 303 nm are similar to those from *trans*-azobenzene excited at 503 nm, close to the

S_1 origin. The absence of the fast decay component in the data from *trans*-**1** suggests that its presence requires not only that the excited state is formed with excess energy but also that the phenyl groups are free to rotate. Consequently, this suggests that the faster decay of the S_1 state of *trans*-azobenzene on excitation well above the origin arises from placing the molecule at a point on the S_1 potential energy surface where the slope is quite different from that near the origin and from which motion along rotational coordinates can occur in the absence of the constraining azacrown "cap" of *trans*-**1**. This suggestion is supported also by detailed studies of the resonance excitation profile of the *trans*-azobenzene Raman spectrum, which have revealed that there is strong interaction between the S_1 and S_2 states in this region at <500 nm.[21]

The evidence in support of these proposals concerning the mechanism enables us to construct a schematic potential energy curve diagram for **1** (Figure 7) which is based on that for azobenzene (Figure 6)[11] and with which it provides an interesting contrast. Although these diagrams are undoubtedly oversimplified representations[14] which more detailed studies may cause to be revised, together they provide a useful schematic summary that is consistent with our current interpretation of azobenzene photochemistry.

Conclusions

Ultrafast electronic absorption spectroscopy has been used to study the excited-state decay dynamics and photoisomerization mechanisms of *trans*-azobenzene in "free" and "capped" forms on UV excitation to the $S_2(\pi\pi^*)$ state. These studies have provided direct, real-time evidence that restricting the rotational freedom of the phenyl groups has a significant effect on both the ultrafast dynamics and the photoisomerization mechanism. The data indicate that photoisomerization proceeds by an inversion mechanism in the $S_1(n\pi^*)$ state when rotation is blocked, that a long-lived "bottleneck" state is accessed by rotation on UV excitation of *trans*-azobenzene to the S_2 state, and that there is no "bottleneck" state along the photoisomerization pathway in the S_1 state. The results have been interpreted in terms of the existing model for azobenzene photoisomerization in which both rotation and inversion routes may contribute to the excited-state decay mechanism.

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