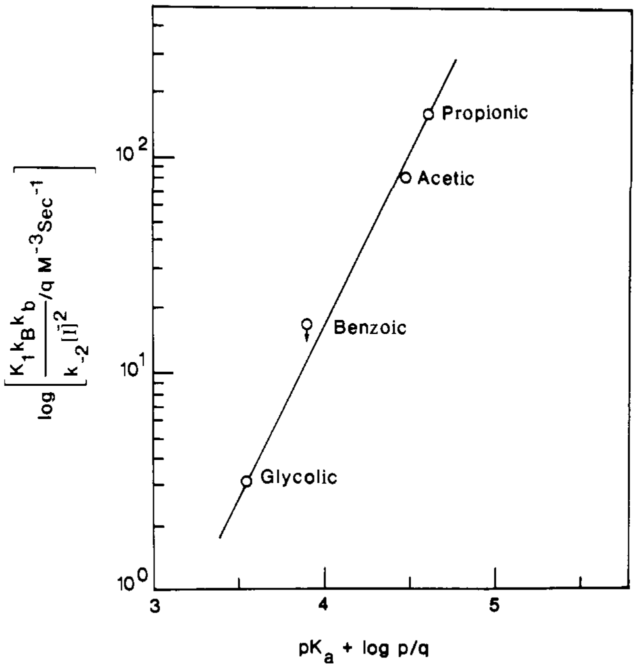
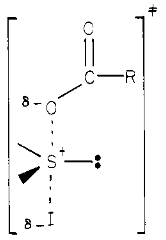
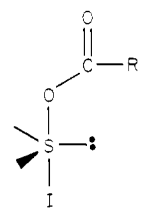


Figure 6. Brønsted plot of the catalytic constants obtained from the linear portion of curves such as those in Figure 2; see eq 5. The point for benzoic acid is an upper limit.

of the attacking carboxylate will roughly parallel the substituent effect on the reactivity of the *O*-acylsulfoxide, regardless of the exact nature of the transition state, as long as no serious charge imbalance is present.[14] If β_{nuc} for the k_b step is indeed small, then β_S for k_{-2} is about $1.0 - 1.5 = -0.5$ and the equilibrium β for *O*-acylsulfoxide formation is 1.5. It should be pointed out that the k_{-2} step is the attack of iodide anion on the sulfur of an *O*-acylsulfoxide. Since *O*-acylsulfoxides are typically unstable compounds at room temperature, usually undergoing Pummer-er-type rearrangements,[13] the reactivity of these compounds toward substitution at sulfur can only be studied under conditions such as these they are present only as short-lived reaction intermediates. The present data suggest that it will be possible to systematically study the reactivity of these compounds through the continued study of the catalyzed iodine oxidation reaction.

If β_{eq} for the formation of the *O*-acylsulfoxide intermediate is about 1.5, then it appears "as if" the carboxylate anion has had a change in effective charge from −1 to 0 in the rate-limiting transition state.[14] A possible transition state that is consistent with the experimental Brønsted coefficient is shown below (III).


III


IV

This transition state represents a simple S_N2 reaction in which bond formation to the sulfur is about 66% complete and the iodide anion has about 0.66 negative charge. Since complete formation of the oxygen-sulfur bond results in a change in effective charge of about 1.5, the carboxylate would appear as if it were neutral, consistent with the observed β_{nuc} of 1.0.

A second transition state that is consistent with the data is one involving, or closely resembling, a tetracoordinate sulfurane such as IV. Since the central sulfur in IV is neutral, the β_{eq} for sulfurane formation would be expected to be about 1. Since the observed value of β_{nuc} is 1.0, a transition state involving essentially complete sulfurane formation is consistent with the experimental data. It is also interesting to speculate that the rate-limiting step may involve a conformational change, perhaps pseudorotation[15,16] of a fully formed sulfurane intermediate. In order for pseudorotation to be a necesary process, the initially formed sulfurane must have entering and leaving groups positioned axial-equatorial. Such a geometry is certainly possible in these types of compounds since the electronegativities of carbon and iodine are approximately the same.

Acknowledgment. This work was supported by a grant from the National Science Foundation, CHE 80-00054.

Registry No. *N*-Acetylmethionine methyl ester, 35671-83-1; propionic acid, 79-09-4; acetic acid, 64-19-7; benzoic acid, 65-85-0; glycolic acid, 79-14-1; I_2, 7553-56-2.

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On the Rotation–Inversion Controversy on Photoisomerization of Azobenzenes. Experimental Proof of Inversion

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Abstract: We report on the direct cis–trans photoisomerization reaction of two azobenzenophanes for which inversion is the only possible isomerization pathway. Thermal cis–trans relaxation is also observed. For one of the azobenzenophanes we can determine trans–cis isomerization quantum yields which are wavelength independent in contrast to those of the parent azobenzene. On the basis of our results we suggest different isomerization mechanisms in different excited states for normal azobenzenes.

Ethylenes and diazenes (azo compounds) are textbook representatives for the phenomenon of cis–trans isomerism demonstrating the rotoresistant property of the π double bond. Cis and trans compounds are normally well-defined molecules which, however, can be interconverted either by heat or by light. There is no doubt that the weakening of the double bond by excitation

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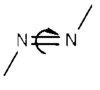
of high-amplitude torsional vibrations or by exciting an electron from a π-bonding to a π^*-antibonding orbital enables the ethylenes to isomerize by rotation. However, in diazenes one of the elements determining the trans or cis configuration is not a σ bond but a lone electron pair whose excitation energy is much lower than the one of bonding σ electrons and is even lower than that of the π electrons. From simple energy considerations a difference in the mechanism of isomerization cannot be rejected.

In fact, a number of theoretical papers[1-14] indicate an intense interest in the isomerization mechanism of diazenes. Isomerization along two reaction coordinates is discussed: (a) twisting around the central N=N double bond (rotation mechanism) and (b) planar variation of one or (c) both C–N–N angles (inversion mechanism).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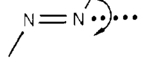
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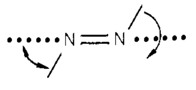
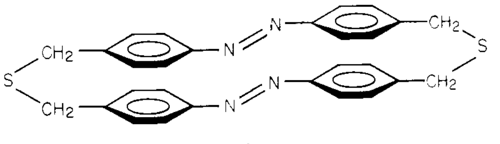

c

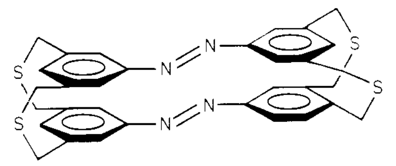
Ab initio calculations of excited state potential energy surfaces have up to now been restricted to diimine[1-5] and azomethane[5-7] (dimethyldiazene) as representatives of the essentially unperturbed azo grouping. The results of these calculations follow: exclusion of inversion mechanism c via a linear transition state (energetically too expensive) and rotation a being more favorable than inversion b in the $^1(n,\pi^*)$ state. Accordingly we can eliminate mechanism c from our further considerations.

In this paper our interest is concentrated on the isomerization of the simplest aromatic azo compound, azobenzene (diphenyldiazene). Unfortunately there is no calculation yet that would be comparable to the ab initio work mentioned. A first ab initio calculation for four representative points, i.e., the trans,cis, 90° twist, and the semilinear geometries of azobenzene by Orlandi et al.[14] seems to indicate qualitatively different results for the $^1(n,\pi^*)$ state: the 90°-twisted transition state is much higher in energy than both trans and cis whereas the semilinear configuration is between them.

Of course, spectroscopists and photochemists have been aware of the inversion–rotation problem for a long time[15] and many experimental papers[16-30] deal with this subject. It is, however, difficult to review them briefly as substituted azobenzenes require careful consideration of the positions and the mixing of $^1(n,\pi^*)$ and $^1(\pi,\pi^*)$ states. There is evidence provided for the rotation[16-19] and inversion[20-25] mechanisms of the thermal cis → trans isomerization in the ground state and there are photoisomerization results supporting the idea of inversion.[26-30] However, at close inspection it becomes obvious that for simple azo compounds no really conclusive experimental evidence for either of the two mechanisms of photoisomerization has been presented thus far. The lack of conclusive data may be due to the problem of neutralizing the gradient of the potential energy surfaces in the direction of one reaction coordinate and not in the direction of the other. We have reached this goal by using the azobenzenophanes[31] 2,19-dithia[3.3](4,4′)-*trans*-diphenyldiazeno(2)phane (**1**) and 2,19,36,39-tetrathia[3.3.3.3](3,3′,5,5′)-*trans*-diphenyldiazeno(4)phane (**2**). In these molecules planar inversion should be possible, rotation, however, should be blocked.[32] The results of this work prove for the first time the existence of the inversion mechanism.



1



2

We believe that our results justify further thought about the photoisomerization of the parent azobenzene molecule. We suggest different isomerization mechanisms in different excited states.

Experimental Section

Materials. **1** was prepared according to literature procedures[33] by condensation of 4,4′-bis(bromomethyl)azobenzene with Na_2S in high dilution. Because of poor solubility, purification and identification of **1** are somewhat complicated. Small amounts sufficient for spectroscopic work can be purified by consecutive chromatography on Sephadex-LH 20 and SiO_2 columns operated at elevated temperature (40 °C with DMF and benzene as eluents, respectively). The compound is characterized by elemental analysis, NMR, mass spectroscopy,[31] and X-ray analysis.[34] This reveals centrosymmetry of the molecule, a distance of the parallel trans azo groups of 386 pm and of the benzene ring centers of 357 pm. The crystal structure shows close packing of the molecules with inter- and intramolecular distances of the azobenzene units being nearly equal. We assume that this is the reason for the poor solubility.

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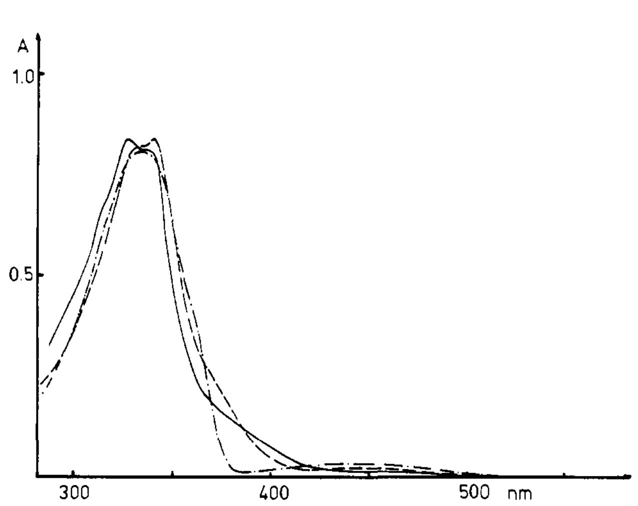

Figure 1. Absorption spectra of (–·–) 4,4′-dimethylazobenzene ($c = 3.8 \times 10^{-5}$ M), (– – –) **1** ($c = 1.65 \times 10^{-5}$ M), and **2** (c unknown) in benzene solution.

2 was prepared according to literature procedures[33] by alkaline condensation of 3,3′,5,5′-tetrakis(bromomethyl)azobenzene and 3,3′,5,5′-tetrakis(mercaptomethyl)azobenzene in extreme dilution. Although it is virtually insoluble,[31] if the reaction mixtures are never brought to dryness supersaturated solutions can be chromatographed on SiO_2 columns with chloroalkanes or toluene as eluents. **2** was characterized by mass spectroscopy, NMR ($CDCl_3$, supersaturated), high-resolution mass spectroscopy,[31] and UV (vide infra). Rapid filtration of the fraction of **2** through membrane filters gave solutions suitable for spectroscopic investigation which were stable for irreproducible lengths of time. No absorption coefficients could be determined.

Solvents were MERCK Uvasol benzene, toluene and dichloromethane distilled twice, and EtOH of Uvasol quality.

Irradiation and Kinetic Evaluation. Stirred solutions of **1** and **2** in benzene prepared to an optical density of 1 to 1.5 near 330 nm were irradiated at room temperature (except for activation energy determinations) in a 1-cm square cell by a HPK 125 W Hg-irradiation source (Phillips) with 313, 365, and 436 nm UV-PIL-filters (Schott). The UV spectra were recorded with a ZEISS DMR 10 spectrometer.

The photoisomerization of **1** showed features that demanded higher accuracy of photometric and time measurements. Professor Mauser, Tübingen, made his specialized UV and data processing equipment[35] available to us. His ZEISS DMR 21 spectrophotometer with integrated Hg-irradiation source (HPK 125 W with UV-PIL-filters) requires 1 s of interruption of irradiation for determining the absorbance at preselectable wavelengths. We took about 100 data points per irradiation to the photostationary state; the digitized time and OD values are punched on tape and evaluated by means of computer programs KINAL[36] and KINALYSE.[37] The spectra of solutions of **1** were measured immediately after irradiation (14 s dark for the transport from the irradiation setup to the spectrophotometer) and their time development was taken on the ZEISS DMR 10 with the fastest wavelength transport. Lamp output was determined by Parker's[38] and Gauglitz's[39] actinometers.

Results

Absorption Spectra. Figure 1 shows the absorption spectra of the trans isomers of 4,4′-dimethylazobenzene (**3**), **1**, and **2**. Generally speaking **1** and **2** have typical *trans*-azobenzene spectra. The two azobenzene units of **1** seem to absorb nearly independently: $\epsilon_{340} = 50\,500$ L mol^{-1} cm^{-1} and $\epsilon_{436} = 1400$ L mol^{-1} cm^{-1} of **1** in benzene are roughly twice as high as the corresponding ϵ of **3**. Because of poor solubility of **1** we consider ϵ to be accurate to ±5%. We could not determine a value of ϵ for **2** (see Experimental Section).

There are distinct features of the cyclophane structure in the spectra of **1** and **2**: (a) the oscillator strengths of the structureless n → π* transitions decrease relative to those of the π → π* bands the more the azobenzene units are forced to planarity, (b) vibrational structure of the π → π* band emerges due to increased rigidity of the phanes, (c) an additional band at the long wavelength side of the π → π* band is observed, and (d) the intense π → π* band is blue shifted in the sequence **3** → **1** → **2**. Features c and d may suggest increased exciton interaction by increasingly better card pack arrangement of the azobenzene units. Conventional exciton theory, however, seems to be insufficient for the understanding of the transannular interaction in cyclophanes.[40,41]

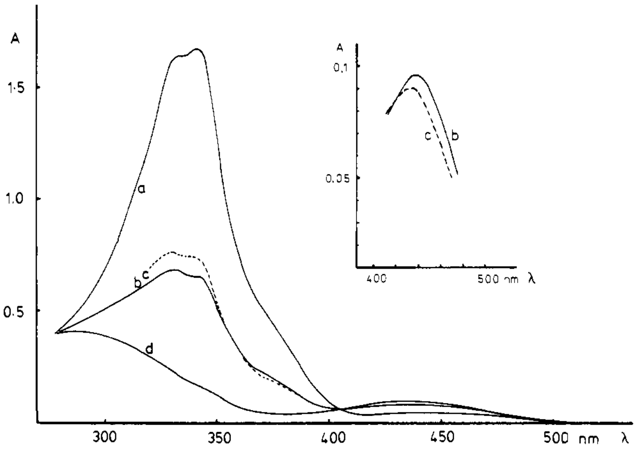

Figure 2. Reaction spectra of the photoisomerization of **1**. See text.

No emission of **1** or of **2** has been found, neither in the solid nor in solution. The sensitivity of low-temperature measurements, however, was low as neither **1** nor **2** is soluble in glass-forming solvents.

Isomerization of 1. Irradiation of **1** leads to reaction spectra very similar to those of the parent azobenzene. But a detailed analysis reveals that the reaction of **1** is more complicated than just trans ⇄ cis.

Figure 2 contains some selected spectra of the photoreaction induced by 366-nm quanta: (a) the spectrum before irradiation—this spectrum is of the *trans*-azobenzene type; (b) a transient spectrum at an arbitrary extent of the 366-nm photoreaction taken immediately after switching off the irradiation source; (c) the spectrum of the same solution 10 min after the end of the irradiation, i.e., after the termination of a fast dark reaction—this dark reaction leads back toward the trans form; and (d) the spectrum of the photostationary state of 366-nm irradiation—this spectrum is of the *cis*-azobenzene type, characterized by high n → π* and low π → π* bands.

The reaction whose spectra are shown in Figure 2 can be reversed by 436-nm irradiation to a stationary state with a spectrum near that of the initial spectrum a. Subsequent irradiation with 366 and 436 nm moves the system between the two stationary states repeatedly, but always the stationary state spectra are reached within photometric accuracy. These data exclude a mechanism of isomerization by opening the CH_2–S–CH_2 bridge as has been found by Reich and Cram[42] and Wassermann and Keehn.[43] In such a mechanism the reformation of the phane never is quantitative. An irreversible change is, however, effected by prolonged 313-nm irradiation.

Finally, spectrum a of Figure 2 is always reached by a very slow dark reaction at room temperature or by boiling the solution in the dark regardless of how far the photoisomerization reaction has been pushed.

We have analyzed this reaction system by the powerful means of Mauser diagrams.[44] We find that the reaction spectra of

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Table I. Isomerization of Azobenzene and Azobenzeno-2-phane (1)

Photoreaction

	$\Phi_{t\rightarrow c}$	$\Phi_{t,t\rightarrow t,c}$
(n,π^*)	0.23	0.24
(π,π^*)	0.10	0.21

Dark reaction

	c → t	t,c → t,t	c,c → t,c
τ_{298}	3.5 d	6.25 min	~5 d
E_a	23	19.8	~40 kcal mol^{-1}
A	1.95 10^{11} s^{-1}	6.9 10^{11} s^{-1}	
$\Delta S^{\ddagger}_{298}$	-8.8 cal K^{-1}	-6.4 cal K^{-1}	

436-nm irradiation contain two independent reactions. There is hidden a third one in the 366-nm spectra which is, however, really unimportant and is given no further consideration in this paper. From this analysis we infer that the reaction sequence of isomerization of **1** is

$$t,t \underset{\Delta,\,k_1}{\overset{h\nu}{\rightleftharpoons}} t,c \underset{\Delta,\,k_2}{\overset{h\nu}{\rightleftharpoons}} c,c \qquad (1)$$

with $k_1 >> k_2$, where c and t represent the trans and cis configuration of one azo group of **1**.

The photoisomerization quantum yields can be calculated from the time development of the absorption if the absorption coefficients of the reacting molecules are known. We could not determine the exact value of ϵ of (c,c)-**1** by isolation of the reaction product. However, from the Mauser diagrams of reaction 1 it becomes obvious that the photoconversion in the 366-nm stationary state (Figure 2d) is at least 95%. On this basis we determined $\epsilon_{340} = 2500$ L mol^{-1} cm^{-1} and $\epsilon_{436} = 2900$ L mol^{-1} cm^{-1} for (c,c)-**1** from solutions kept carefully away from any daylight. The spectrum of the short-lived (t,c)-**1** cannot be computed from the photoreaction spectra nor do we know the concentrations of (t,c)-**1**. Thus we cannot obtain a value for its ϵ. The assumption, however, that the azobenzene units absorb nearly independently is also a sound one for t,c. At 340 nm $\epsilon = (\epsilon_{t,t} + \epsilon_{c,c})/2 = 26\,500$ L mol^{-1} cm^{-1} for (t,c)-**1**. This and the values of $\epsilon_{366} = 17\,100$ and $\epsilon_{436} = 1400$ L mol^{-1} cm^{-1} for (t,t)-**1** were used to evaluate the t,t → t,c quantum yields from the initial portions of the A_{340} vs. t plots. These plots were linear for about 12 s or 6% extent of reaction at $\pi \rightarrow \pi^*$ excitation and for about 40 s or 3.5% extent of reaction for the $n \rightarrow \pi^*$ excitation. We used the formula

$$\left.\frac{dA_{340}}{dt}\right|_0 = -1000 I_0 \frac{1 - 10^{-A'}}{A'} \epsilon_{t,t}' \phi_{t,t} C_{0;t,t} (\epsilon_{t,t;340} - \epsilon_{t,c;340}) \qquad (2)$$

A is the absorbance, I_0 is the light intensity, $\phi_{t,t}$ is the quantum yield of disappearance of t,t, $C_{0;t,t}$ is the initial concentration of t,t, and the primed quantities are those at the irradiation wavelength. It was found that the factor $(1 - 10^{-A'})/A'$ did not vary more than 4% during this initial irradiation phase. The quantum yields are 0.21 for high energy and 0.24 for low energy excitation (Table I). From the errors in the absorption coefficients of 5% and in the intensity of 10% we estimate that the yields are precise to ±20%.

For the determination of the other quantum yields in the reaction system we should need more precise values of the absorption coefficients, especially of those at the irradiation wavelength, to obtain reasonable error margins.

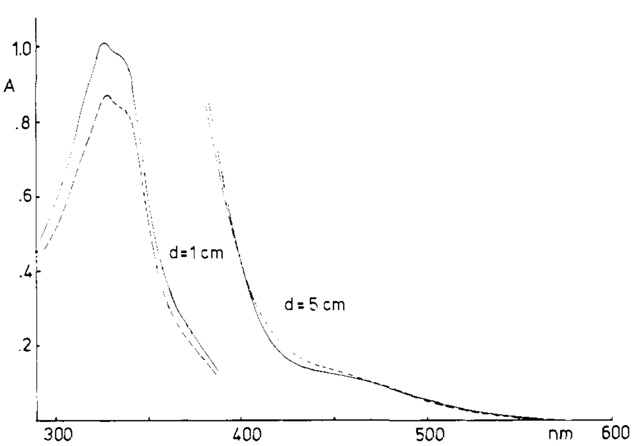

Figure 3. Initial spectrum (—) and spectrum of 366 nm photostationary state (- - -) of a solution of **2**. d is the length of the absorption cell.

In Table I the t,t → t,c quantum yields of **1** are compared to the trans → cis isomerization quantum yields of azobenzene.[15,45-50] We see that in **1** ϕ(t,t → t,c) after excitation to the $(n \rightarrow \pi^*)$ state has the same value as the (n,π^*) state isomerization yield in azobenzene. Moreover, in **1** the (n,π^*) and (π,π^*) state isomerization yields are equal which is significantly different from the azobenzene case.

The slow and fast dark reactions can be investigated separately. The data of the first order reactions are collected in Table I together with those of azobenzene taken from the literature or calculated therefrom.[15] The activation energy of **1** is only 3 kcal mol^{-1} lower than that of cis → trans relaxation of azobenzene. This reflects the steric strain in the structure of (t,c)-**1**. Talaty and Fargo[24] report activation energies between 21.1 and 23.8 kcal mol^{-1} for various substituted azobenzenes.

We may also induce photoisomerization of **1** with use of triplet sensitizers. When benzil (E_T = 54 kcal mol^{-1}) is the sensitizer we observe the same steady state of cis and trans units, regardless of whether we start from the t,t or c,c side of the isomerization system. Eosine (E_T = 45 kcal mol^{-1}) and Rose Bengale (E_T = 43 kcal mol^{-1}) induce cis → trans but not trans → cis isomerization. This is exactly like the reaction of azobenzene proper.[51] Azulene does not sensitize the isomerization and it does not change the trans/cis ratio of the photostationary state of the benzil sensitized isomerization. Azulene either does not quench the isomerization at all or it quenches the t,t and the c,c triplets at the same rate.

In summary, **1** can be isomerized reversibly by successive isomerization of the two units in photoreactions and dark reactions. On direct excitation the quantum yields of trans → cis isomerization of the (t,t) molecule are identical for $n \rightarrow \pi^*$ excitation and $\pi \rightarrow \pi^*$ excitation, and they are equal to that of $n \rightarrow \pi^*$ excitation of azobenzene. The (t,c)-**1** molecule is thermally unstable, that is its activation energy of cis → trans isomerization is lower than that of azobenzene presumably because of steric strain. The (c,c) molecule on the other hand is kinetically much more stable than *cis*-azobenzene.

Isomerization of 2. Irradiation of **2** also leads to a reversible photoreaction. In Figure 3 the initial spectrum and the spectrum of the 366-nm photostationary state are presented: photoconversion with 366-nm quanta is much less efficient for **2** than for **1**. Irradiation at 436 nm leads back to a steady state whose spectrum is nearly coincident with the initial spectrum. An

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isosbestic point is observed at 405 nm—Mauser's A diagrams[44] are linear. The stationary state spectra persist (until precipitation occurs), and a dark reaction is not perceptible.

Compared to the spectrum before irradiation the 366-nm stationary state spectrum shows the features that are expected if a cis molecule should be formed: decrease of absorption in the wavelength region of the $\pi \rightarrow \pi^*$ band and increase in that of the $n \rightarrow \pi^*$ band. The conversion is small and, moreover, it is dependent on irradiation intensity. Low light intensity shifts the stationary state spectrum toward the one of the starting material. This indicates the participation of a thermal back reaction too fast to be detected by our apparatus. The experimental evidence is in agreement with the same reaction scheme that we have suggested for **1** (vide supra). The steric strain in (t,c)-**2** is very high as molecular models show so that a fast thermal relaxation t, c → t,t would be anticipated.

We cannot determine the t,t → t,c quantum yields of **2** for $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitation as we do not know the values of the absorption coefficients. In addition the thermal t,c → t,t rate constant is so high that the t,t spectrum and the 436-nm photostationary state spectrum are barely different. Thus the isomerization experiments with **2** show qualitative agreement with the behavior of **1**, and for **2** rotation is clearly impossible.

Discussion

For a long time azobenzene isomerization has been considered to differ in some way from stilbene isomerization.[15] The low activation energy of thermal cis → trans conversion was a hint, but for photoisomerization there was little hard evidence. Viscosity and substituent effects on the isomerization quantum yields were the only experimental clues and were interpreted by Fischer et al.[26,29] in favor of the inversion mechanism in an excited state. Recently we have induced isomerization of optically active azo steroids in a solid methyl methacrylate matrix at room temperature with 366- and 436-nm irradiation. We ascertained that no rotation occurred either around the C–N or around the N=N bond by analysis of the CD spectra.[27] This is strong evidence that isomerization proceeds via inversion. Unfortunately the solid matrix is not suitable for normal kinetic evaluation.

The reversible photoisomerization of **1** and **2** finally provides unequivocal proof that trans–cis isomerization of azo compounds can proceed via inversion.

Our results, conclusive as they are for **1** and **2**, do not prove that inversion is the only mechanism active in all azo compounds. In *trans*-azobenzene,[15,29,45–50] substituted *trans*-azobenzenes[29] and *trans*-azonaphthalenes[46] trans–cis photoisomerization quantum yields have been found to differ at room temperature for excitation in the $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ bands up to a factor of 2. The yields for high-energy excitation are always smaller than those for low-energy excitation. This means that azobenzene molecules excited to the $^1(\pi,\pi^*)$ state cannot or only partly reach the state populated by direct $n \rightarrow \pi^*$ excitation. This is a violation of Kasha's rule. However, photochemistry from higher excited states is not really uncommon.[52]

On the other hand, in cyclophane **1** we observe equal quantum yields on $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitation indicating that all the $\pi \rightarrow \pi^*$ excited molecules end up in the same (n,π^*) state which is populated on direct $n \rightarrow \pi^*$ excitation. This isomerization behavior differing from the normal azobenzenes stems from the reluctance of **1** to rotate. Moreover, the quantum yield of photoisomerization in **1** is equal to the yield of (n,π^*) isomerization in azobenzene suggesting isomerization by the same mechanism in azobenzene and in **1**.

We recall another feature of the spectra of azobenzene and the azobenzenophanes that is important in this context: The shapes of the absorption bands of azobenzene and **1** and **2** are virtually identical for the $n \rightarrow \pi^*$ transitions but are in contrast for the $\pi \rightarrow \pi^*$ transitions.[53–55] These band contours give information about the shapes of the potential energy surfaces of the excited states. Obviously these shapes are similar in the (n,π^*) states but different in the (π,π^*) states of the molecule which can rotate and of those which do not rotate.

These results allow us to suggest that normal azobenzenes might isomerize via inversion in the (n,π^*) state but that on $\pi \rightarrow \pi^*$ excitation a rotational feature should become important.

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