Triplet-State Cis-Trans Isomerizations of a Bisstyrylcyclooctatetraene. Inefficient Processes Facilitating Observation of the Intrinsic T_1-T_n Absorption Spectra of the Z,Z, E,Z, and E,E Isomers

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The mechanism for triplet-sensitized Z-E isomerizations of Z,Z-, E,Z-, and E,E-1,5-bisstyryl-3,7-dimethylcyclooctatetraene (**ZZ**, **EZ**, and **EE**) has been studied by quantum yield measurements and laser flash photolyses. **ZZ** isomerizes via **EZ** as a ground-state intermediate to **EE** with small quantum yields. At the photostationary state the isomer mixture consists of more than 99% **EE**. The three E,Z isomers have different T_1-T_n absorption spectra. These results can be explained with a triplet energy surface, with local minima at geometries, in which the noncyclic double bonds are planar. The dominating decay process of ${}^{3}ZZ^{*}$, ${}^{3}EZ^{*}$, and ${}^{3}EE^{*}$, is intersystem crossing to the corresponding ground states. Their triplet energies were estimated to be between 40 and 43 kcal mol⁻¹.

Introduction

The shape of the energy surface of the excited state is an important factor determining whether the Z-E photoisomerization will proceed by a diabatic or an adiabatic mechanism. An excited-state energy surface with a minimum located at a reaction coordinate corresponding to a 90° twisted double bond, will give the classical diabatic isomerization mechanism.¹ On the other hand, an adiabatic mechanism is favored if the excited state has the important decay funnels at the planar double-bond geometries. If the excited-state energy surface has pronounced maxima for the twisted double-bond geometries, the Z-E photoisomerization will be hindered.

During the past 10 years, several examples of molecules undergoing adiabatic Z-E photoisomerization have been presented.² In a previous investigation we showed that the ZZ isomers of a set of bisstyrylarenes isomerized adiabatically on triplet-sensitized excitation in a single- and 2-fold manner to an EZ and an EE configuration, respectively.³ The ratio of 2-fold to single isomerizations increased with increasing size and decreasing triplet energy of the central aromatic unit. The best explanation to these observations is that the triplet energy levels of the planar species are significantly lowered by increasing size and decreasing triplet energy of the central aromatic unit. The triplet energy levels of the twisted species, however, are not affected to the same extent by the properties of the central aromatic unit.

To explore the scope and limitations of 2-fold adiabatic photoisomerizations, we have turned our attention to a set of bisstyryl compounds with a central cyclooctatetraene (COT) unit; Z,Z-, E,Z-, and E,E-1,5-bisstyryl-3,7-dimethylcyclooctatetraene. COT is a nonplanar nonaromatic hydrocarbon with alternating single and double bonds in the ground state. Recently, COT has been shown to be a "nonvertical" acceptor of triplet energy with an unusually large range for nonvertical energy transfer approaching 20 kcal mol^{-1,4,5}

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Experimental Section

Materials. ZZ, EZ, and EE were prepared as described in ref 6. We further purified the isomers by preparative HPLC, using hexane as eluent and a medium-polar column packed with Sperisorb S10 CN, which gave ZZ, EZ, and EE with isomeric purities >99.5%. The photochemical measurements were performed in cyclohexane of spectroscopic grade. The solutions were freed from oxygen by flushing them with nitrogen or, in the case of quenching of the anthracene triplet, by four freezepump-thaw cycles. Biacetyl (99%, GC, Aldrich) and anthracene (test substance for elemental analysis, Merck) were used as received. Azulene was purified by sublimation.

Isomerization Measurements. Samples of ZZ, EZ, and EE $((2.1-2.7) \times 10^{-4} \text{ M})$ with biacetyl as a triplet sensitizer were irradiated with light of 436 ± 8 nm, in an optical bench arrangement (Applied Photophysics), with a 150 W xenon arc lamp and a monochromator. The isomerizations were followed by analytical HPLC, using hexane as eluent and a mediumpolar column; Sperisorb S5 CN. Quantum yields were determined by using ferrioxalate actinometry.⁷

Laser Flash Photolyses. Solutions of ZZ, EZ, and EE in concentrations similar to those in the isomerization measurements and biacetyl (added in such amounts as to give the samples an absorbance at 425 nm of about 0.6) were irradiated with light pulses of 425 nm from a dye laser (SL 4000 B, Spectron Laser Systems, stilbene 420 in ethanol), pumped with 355 nm light from a tripled Nd:YAG laser (SL 803 G, Spectron Laser Systems). The absorptions of the triplet transients were measured by a laser photolysis spectrometer (Applied Photophysics). The spectrometer comprised a pulsed xenon arc lamp

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Figure 1. Minimized structures of ZZ, EZ, and EE according to MM2 calculations.



Figure 2. UV absorption spectra of ZZ, EZ, and EE.

SCHEME 1: Triplet-State Isomerization Pathways and Quantum Yields of 1,5-Bisstyryl-3,7-dimethylcyclooctatetraene



and a photomultiplier connected to a digital oscilloscope (Phillips PM 3323/401). A computer (Acorn Archimedes 440/ 1, software by Applied Photophysics) was used to control the laser flash photolysis system, as well as to store and analyze data.

The quenching of ${}^{3}ZZ^{*}$, ${}^{3}EZ^{*}$, and ${}^{3}EE^{*}$ (0.9–1.0 mM) by azulene (0.85–1.3 mM) was studied by measuring the decay of the triplets. Biacetyl (absorbance at 425 nm of about 0.6) was used as a sensitizer. The measurements were done using the same equipment and experimental conditions as mentioned above.

Solutions of ZZ, EZ, and EE ($(1.3-2.0) \times 10^{-4}$ M) and anthracene (total absorbance at 355 nm of about 0.8) were irradiated with light pulses of 355 nm from the tripled Nd:YAG laser and analyzed with the equipment mentioned above. The quenching of triplet excited anthracene by ZZ, EZ, and EE was thus studied by measuring the decay of the anthracene triplet.

Results and Discussion

COT is a nonplanar compound with relatively high barriers to inversion and bond shift, ca. 20 and 25 kcal mol⁻¹, respectively.⁸ The bisstyryl derivatives should be no exceptions. Molecular mechanics calculations with Allingers MM2 force field gave the minimized geometries shown in Figure 1. The UV spectra in Figure 2 show red shifts with increasing number of *E* double bonds. The absorption spectrum of *EZ* is not the average of those of *ZZ* and *EE*, indicating that the two styryl groups are not electronically independent.

On triplet sensitized excitation, ZZ isomerized, via EZ as a ground-state intermediate, to EE with low quantum yields (Scheme 1). The experimental errors in quantum yields were estimated to be within $\pm 10\%$. This shows that decay to the corresponding ground states is the dominating process of ${}^{3}ZZ^{*}$, ${}^{3}EZ^{*}$, and ${}^{3}EE^{*}$. At photostationary state the isomer mixture consists of more than 99% EE.

Consistent with the low isomerization quantum yields, sensitized excitation of ZZ, EZ, and EE produced three different



Figure 3. T_1-T_n absorption spectra and triplet lifetimes of the three *E*,*Z* isomers.

 T_1-T_n absorption spectra (Figure 3). The transient produced by sensitization of ZZ is further distinguished from the two others by its different lifetime (Figure 3). The triplet sensitizer, biacetyl, could not have a affected the shape of the transient absorption spectra to any significant extent, since we observed no time dependencies in the shapes of the spectra. The three different spectra should thus originate from three different excited species produced from triplet-sensitized excitation of ZZ, EZ, and EE. We believe that the three triplet species have similar geometry at the styryl double bonds as ZZ, EZ, and EE respectively.

For most one-way isomerizing olefins only one common T_1 - T_n absorption spectrum is observed regardless of which E,Z isomer is excited. **ZZ**, **EZ**, and **EE** are different since triplet sensitization of the different isomers produce different T_1-T_n absorption spectra.^{3,9} The three isomers are also different from most one-way isomerizing olefins by the low isomerization quantum yields and by their remarkably short triplet lifetimes (0.71, 0.53, and 0.53 μ s, respectively).^{3,9} The shortness of the lifetimes should not be due to any decay processes connected with the isomerizations since the quantum yields are very low.

Although the lifetimes of ${}^{3}ZZ^{*}$, ${}^{3}EZ^{*}$, and ${}^{3}EE^{*}$ are short, the isomerizations would still be efficient unless they were inhibited by high-energy barriers and/or low preexponential factors for double-bond torsion.

Most likely the isomerizations proceed by an adiabatic mechanism, although the low quantum yields make it impossible to rule out a diabatic contribution to the mechanism. If there is a diabatic contribution, arrival at the diabatic decay funnels should still be inhibited by high-energy barriers and/or low preexponential factors for double-bond torsion.

To get further details on the nature of ${}^{3}\mathbf{Z}\mathbf{Z}^{*}$, ${}^{3}\mathbf{E}\mathbf{Z}$, and ${}^{3}\mathbf{E}\mathbf{E}^{*}$ a series of quenching experiments were done. The triplet excited state of anthracene $(E_{\rm T} = 43 \text{ kcal mol}^{-1})^{10}$ was quenched by $\mathbf{Z}\mathbf{Z}$ with a rate constant determined to be $0.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.¹¹ The corresponding values for $\mathbf{E}\mathbf{Z}$ and $\mathbf{E}\mathbf{E}$ are 1.4×10^9 and $2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively.¹¹ ${}^{3}\mathbf{Z}\mathbf{Z}^{*}$ was quenched by azulene $(E_{\rm T} = 40 \text{ kcal mol}^{-1}).^{12}$ The experimental rate constant is $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and the corresponding values for ${}^{3}\mathbf{E}\mathbf{Z}^{*}$ and ${}^{3}\mathbf{E}\mathbf{E}^{*}$ are both $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. In Figure 4, an example of a decay curve fitted with a triple-exponential function is shown. Thus, the quenching with azulene is clearly reversible. The experimental rate constants for back energy transfer to the isomers were roughly estimated to have the common value 2 $\times 10^9 \text{ M}^{-1} \text{ s}^{-1}.^{13}$ The triplet energies of $\mathbf{Z}\mathbf{Z}, \mathbf{E}\mathbf{Z}$, and $\mathbf{E}\mathbf{E}$ can be estimated to $40-43 \text{ kcal mol}^{-1}.^{13}$

Conclusions

Of all the bisstyryl compounds we have studied, these are the first for which we have observed different T_1-T_n absorption spectra on sensitized excitation of the different *E*,*Z* isomers. These results indicate that stabilization of the triplet species with



Figure 4. T_1-T_n absorption transient detected at 410 nm, obtained on laser excitation of a cyclohexane solution of biacetyl, *EE*, and azulene. A triple-exponential curve has been fitted to the transient with a least-squares method. The first exponential corresponds to the buildup phase of the transient, and the two others correspond to the decay.

planar styryl double bonds, with respect to those with twisted styryl double bonds, can be obtained in bisstyryl compounds with nonaromatic cyclic olefins as central units, even when the styryl groups are cross-conjugated.

The most likely mechanism for the stepwise isomerizations in the triplet state is an adiabatic one. However, it is not possible to exclude a diabatic contribution to the mechanism. It is clear, however, that decay to the corresponding ground states is the most efficient process of ${}^{3}ZZ^{*}$, ${}^{3}EZ^{*}$, and ${}^{3}EE^{*}$.

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References and Notes

(1) Saltiel, J.; Charlton, J. L. *Rearrangement in ground and excited states*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, and references therein.

(2) (a) Arai, T.; Tokumaru, K. Chem. Rev. 1993, 93, 23. (b) Sundahl,
M.; Wennerström, O.; Sandros, K.; Arai, T.; Tokumaru, K. J. Phys. Chem.
1990, 94, 6731. (c) Sandros, K.; Sundahl, M.; Wennerström, O.; Norinder,
U. J. Am. Chem. Soc. 1990, 94, 3082. (d) Saltiel, J.; Waller, A. S.; Sears,
D. F., Jr. J. Am. Chem. Soc. 1990, 112, 4580. (e) Sandros, K.; Becker,
H.-D. J. Photochem. 1987, 39, 301. (f) Sundahl, M.; Wennerström, O.;
Sandros, K.; Arai, T.; Okamoto, H.; Tokumaru, K. Chem. Phys. Lett. 1990,
168, 395. (g) Sandros, K.; Sundahl, M.; Wennerström O. J. Phys. Chem.
1993, 97, 5291.

(3) Anger, I.; Sundahl, M.; Wennerström, O.; Sandros, K.; Arai T.; Tokumaru, K. J. Phys. Chem. **1992**, *96*, 7027.

(4) The term nonvertical energy transfer is not a proper one, since the nonvertical behavior stems from the fact that there are populations of ground states with nonminimum energy, but it is retained for historical reasons.

(5) Forward, P. J.; Gorman, A. A.; Hamblett, I. J. Chem. Soc., Chem. Commun. 1993, 250.

(6) Auchter-Krummel, P.; Müllen, K., Angew. Chem., Int. Ed. Engl. 1991, 30, 1003.

(7) Hatchard, C. G.; Parker, C. A. Proc. R. Soc. London, Ser. A 1956, 235, 518.

(8) See, e. g.: Paquette, L. A., Acc. Chem. Res. 1993, 26, 57-62.

(9) Arai, T.; Karatsu, T.; Misawa, H.; Kuriyama, Y.; Okamoto, H.; Hiresaki, T.; Furuuchi, H.; Zeng H.; Sakuragi, H.; Tokumaru, K. Pure Appl. Chem. 1988, 60, 989.

(10) Murov, S. L., Handbook of photochemistry; Marcel Dekker: New York, 1973.

(11) Not corrected for back energy transfer.

(12) Gorman, A. A.; Hamblett, I.; Harrison, R. J. J. Am. Chem. Soc. 1984, 106, 6952.

(13) Sandros, K. Acta Chem. Scand. 1964, 18, 2355.

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