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Single and twofold *cis–trans* isomerization of *Z,Z*-1,4-bis(1-propenyl)benzene on triplet-sensitized excitation

Helene Jonson, Mikael Sundahl

Department of Organic Chemistry, Chalmers University of Technology, S-412 96 Göteborg, Sweden

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Abstract

The mechanism for triplet-sensitized *cis–trans* photoisomerization of the isomers of 1,4-bis(1-propenyl)benzene, denoted by **ZZ**, **EZ** and **EE**, has been studied by quantum yield measurements and laser flash photolyses. The triplet lifetime is long enough to give an isomerization pattern that is essentially determined by the thermodynamics of the triplet excited state surface, that is, equilibration processes are faster than decay processes. Decay from the triplet excited state surface occurs predominantly from ^3E,p*, but there is also a minor decay from ^3Z,p*. Thus, on sensitized excitation of **ZZ** there are about equal amounts of single and twofold isomerization to **EZ** and **EE** respectively. The photostationary state composition **ZZ**:**EZ**:**EE** is 1.5:49:49.5. Addition of azulene as a quencher to the reaction mixture increased the amount of twofold isomerization from **ZZ** to **EE** as well as the amount of **EE** at the photostationary state. The T_1–T_n absorption spectra ($\lambda_{max} = 390$ nm) for all three isomers are identical (more than 100 ns after the excitation pulse) as is the triplet lifetime ($\tau = 290$ ns). Probably ^3E,p* and ^{3}**EE*** are close to isoenergetic (about 1 kcal mol^{-1} difference). The triplet energies of the isomers were estimated by measuring the energy transfer rates from ^{3}biacetyl* to the isomers. Taken in the order **ZZ**, **EZ** and **EE**, the experimental values of the triplet energies were 56.4, 56.2 and 55.4 kcal mol^{-1}.

Keywords: *Cis–trans* photoisomerization; Triplet state; T_1–T_n absorption spectra; Quenching; Triplet state energies; Reaction mechanism; Adiabatic; Diabatic

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1. Introduction

Cis–trans photoisomerizations are extensively studied processes and particularly stilbene has been thoroughly investigated [1]. Despite this fact, new details of stilbene photoisomerization are continuously discovered. An important recent discovery by Saltiel et al. was the adiabatic (in a photochemical context the term "adiabatic reaction" refers to a reaction proceeding on a single electronic state surface, which means that an excited-state product is formed) contribution to the singlet state isomerization of *cis*-stilbene [2]. Preceding work by Sandros and Becker showed that a series of *cis*-9-styrylanthracenes underwent adiabatic singlet state isomerization on excitation [3]. Singlet state adiabatic *cis–trans* isomerization was also demonstrated by Mazzucato et al. [4]. We have previously shown that adiabatic isomerization in the singlet state of molecules with two double bonds can give twofold isomerizations [5].

Triplet state adiabatic isomerizations have been extensively studied by Tokumaru and coworkers and they established the "one-way" isomerization concept [6]. We have studied the triplet state *cis–trans* isomerizations in molecules having two or more conjugated double bonds [7]. The reaction pattern of such isomerizations is often determined by the thermodynamics of the triplet state, the major reason being that deactivation of a triplet excited state to the ground state is a spin-forbidden process and excited state energy barriers of isomerizations are often not high. This implies that multiple isomerizations should be facile and common processes in the triplet state of molecules having two or more conjugated double bonds. We have investigated a series of molecules with double bonds and aromatic rings. Triplet state isomerizations ranging from single to sixfold have been found [7]. The size of the conjugated π system is important for the reaction mode [7f]. Molecules with large conjugated π systems having low triplet energy tend to undergo multiple isomerizations in favour of single isomerizations [7e,7f]. In this paper, we present our results on the triplet state isomerizations of the 1,4-bis(1-propenyl)benzene isomers, denoted by **ZZ**, **EZ** and **EE**. It is important to investigate the triplet state isomerizations of these isomers since the molecules constitute some of the

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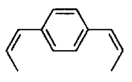
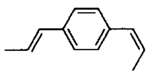
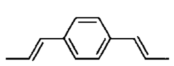
structurally simplest molecules containing a benzene ring and two double bonds.



ZZ



EZ



EE

2. Experimental details

2.1. Materials

1,4-bis(1-propenyl)benzenes were synthesized by a twofold Wittig reaction from terephthaldialdehyde and ethyltriphenylphosphonium bromide. The phosphonium salt (3.99 g, 10.7 mmol) and the dialdehyde (0.85 g, 5.4 mmol) were dissolved in dry dimethylformamide (25 ml) and the flask was flushed with nitrogen (a slow stream was kept during the reaction). Lithium ethoxide in ethanol, made by adding Li (0.30 g, 43 mmol) to ethanol (99.5%, 30 ml), was added slowly to the reaction mixture to allow the coloured ylide formed to react between successive additions. When all the base was added, the reaction was allowed to proceed for 3 h. The reaction was then quenched with HCl (aqueous, 2 M, 40 ml) and the mixture was extracted with diethylether (3 × 30 ml). The combined ether fractions were washed with water (40 ml) and then dried with magnesium sulphate. The solvent was evaporated and the residual was subjected to flash chromatography on silica gel with methylene chloride as the eluent. The first band contained a mixture (0.5 g, 50%) of **ZZ**, **EZ** and **EE** (35:44:21). The isomers were separated by preparative high performance liquid chromatography (HPLC) (Jones Chromatography, C_{18}, internal diameter 20.0 mm, length 25 cm, eluent ethanol–water (75:25, 5.0 ml min^{-1})). The purities thus obtained were above 98%.

(*Z*,*Z*)-1,4-bis(1-propenyl)benzene (**ZZ**). ^1H nuclear magnetic resonance (NMR) (400 MHz, $CDCl_3$), $\delta = 7.26$ (s, 4H), 6.42 (dq, $J = 11.8$ Hz, $J = 1.8$ Hz, 2H), 5.79 (dq, $J = 11.8$ Hz, $J = 7.2$ Hz, 2H), 1.93 (dd, $J = 7.2$ Hz, $J = 1.8$ Hz, 6H); mass spectrometry (MS), m/z (relative intensity) = 158 (100, M^+), 143 (14), 129 (35), 116 (38), 91 (21), 77 (13); UV (EtOH-H_2O, 75:25), $\lambda_{max} = 269$ nm, $\epsilon_{max} = 19\,500$ M^{-1} cm^{-1}; IR, 854 cm^{-1} (s), 676 cm^{-1} (s).

(*E*,*Z*)-1,4-bis(1-propenyl)benzene (**EZ**): ^1H NMR (400 MHz, $CDCl_3$), $\delta = 7.30$ (d, $J = 8.4$ Hz, 2H), 7.23 (d, $J = 8.4$ Hz, 2H), 6.39 (m, 2H) (two overlapping doublets of quartets), 6.24 (dq, $J = 15.8$ Hz, $J = 6.5$ Hz, 1H), 5.8 (dq, $J = 11.7$ Hz, $J = 7.2$ Hz, 1H), 1.91 (dd, $J = 7.2$ Hz, $J = 1.8$ Hz, 3H), 1.89 (dd, $J = 6.5$ Hz, $J = 1.6$ Hz, 3H); MS, m/z (relative intensity) = 158 (47, M^+), 143 (30), 128 (100), 116 (64), 91 (30), 77 (16); UV (EtOH-H_2O, 75:25), $\lambda_{max} = 275$ nm, $\epsilon_{max} = 41\,200$ M^{-1} cm^{-1}; IR, 963 cm^{-1} (s), 854 cm^{-1} (s), 667 cm^{-1} (s).

(*E*,*E*)-1,4-bis(1-propenyl)benzene (**EE**): ^1H NMR (400 MHz, $CDCl_3$), $\delta = 7.26$ (s, 4H), 6.37 (dq, $J = 15.8$ Hz, $J = 1.6$ Hz, 2H), 6.21 (dq, $J = 15.8$ Hz, $J = 6.5$ Hz, 2H), 1.88 (dd, $J = 6.5$ Hz, $J = 1.6$ Hz, 6H); MS, m/z (relative intensity) = 158 (100, M^+), 143 (20), 129 (58), 116 (70), 91 (38), 77 (25); UV (EtOH-H_2O, 75:25), $\lambda_{max} = 284$ nm, $\epsilon_{max} = 50\,400$ M^{-1} cm^{-1}; IR, 962 cm^{-1} (s), 855 cm^{-1} (s); melting point 50–56 °C.

Isomerizations and laser flash photolyses were conducted in either argon- or nitrogen-flushed solutions with spectroscopic grade benzene as solvent. Benzophenone (Aldrich) was recrystallized from ethanol prior to use. Biacetyl was used as received (Aldrich, better than 99% by gas chromatography) and azulene was purified by sublimation.

2.2. Isomerizations

Irradiations of samples of **ZZ**, **EZ** and **EE** (1.8–2.0 mM) with benzophenone (17–21 mM) as a sensitizer were performed in an optical bench arrangement using a 150 W xenon arc lamp and a monochromator (334 or 355 nm). (The excitation wavelength was 334 nm when the solution contained no quencher and 355 nm when azulene was added as quencher. Azulene has a strong molar absorptivity at 334 nm and almost none at 355 nm.) Photon fluxes were determined by azobenzene actinometry [8] and quantum yields were determined by plotting the concentrations against the irradiation time and extrapolating to 0% conversion. The analyses of the composition at different irradiation times were done by HPLC (Varian MCH-10, C_{18}, internal diameter 8.0 mm, length 30 cm, eluent ethanol–water (75:25, 3.0 ml min^{-1})).

2.3. Laser flash photolyses

Benzophenone was excited with a frequency-tripled Nd:YAG laser (Spectron Laser Systems, SL803G, 355 nm, 7 ns full width at half-maximum). Biacetyl was excited with a dye laser (Spectron Laser Systems, SL4000B, 425 nm, stilbene 420) pumped with the above frequency-tripled Nd:YAG laser. A commercially available system from Applied Photophysics was used for the transient absorption measurements. A pulsed xenon arc lamp was used for the detection light. The excitation and detection beams were at right angles to each other. A monochromator for the detection light was used in front of the R928 photomultiplier tube. The signal from the photomultiplier tube was fed into a digital oscilloscope (Philips PM3323). The timing sequences of the laser and the detection systems were controlled through an Acorn Archimedes 440/1 computer. The same computer was used for the collection and the kinetic treatment of data.

3. Results and discussion

3.1. Isomerizations

In all isomerizations, benzophenone was used as a sensitizer ($E_T = 69$ kcal mol^{-1}) [9]. In order not to obtain too

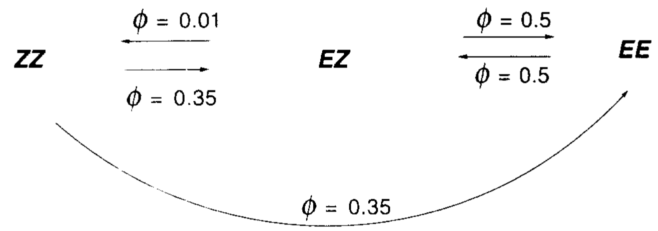


Fig. 1. Isomerization pathways and the corresponding quantum yields. The quantum yield for isomerization of **ZE** to **ZZ** was estimated from the photostationary state composition.

many hydrogen abstraction reactions of triplet excited benzophenone, benzene was used as solvent [10]. In Fig. 1, the isomerizations and the corresponding quantum yields are summarized. The triplet-sensitized isomerizations can be summarized as follows: (1) **ZZ** undergoes single and twofold isomerization to **EZ** and **EE** respectively; (2) **EZ** isomerizes mainly to **EE** but a minor part also to **ZZ**; (3) **EE** isomerizes predominantly to **EZ**.

On sensitized excitation of any one of the three isomers, a photostationary state mixture is approached with the composition **ZZ**:**EZ**:**EE** = 1.5:49:49.5. Addition of a quencher, azulene (2.0×10^{-3} M), increases the amount of **EE** at the photostationary state and the composition **EZ**:**EE** is 9.8:90.2 (no **ZZ** could be detected). Starting with **ZZ** under similar experimental conditions, an initial isomer ratio **EZ**:**EE** (determined at 20% conversion) of 1:9 was determined.

3.2. *Laser flash photolyses*

The T_1–T_n absorption spectra were observed on benzophenone sensitization with pulsed (7 ns) excitation at 355 nm. All three isomers exhibit, within error limits, an identical T_1–T_n absorption spectrum (Fig. 2) and the same triplet lifetime ($\tau = 290$ ns) (Fig. 3). The T_1–T_n absorption spectra were observed by slicing traces at different wavelengths 100 ns after the laser pulse. (The benzophenone contribution to the difference absorption spectrum is negligible when slicing at 100 ns after the laser pulse at these wavelengths.) Thus we conclude that, regardless of starting isomer, the same equilibrated triplet is reached in less than 100 ns (most likely much less than 100 ns).

A series of experiments with biacetyl as a sensitizer ($E_T = 55$ kcal mol^{-1}) and excitation at 425 nm (dye laser, stilbene 420) were conducted. Energy transfer rates from ^{3}biacetyl* to the isomers were measured. In a classical paper, Sandros has shown how to extract energy transfer rate constants from biexponential decay curves in systems with reversible energy transfer and also how to use the obtained rate constants to calculate energy differences between the triplets involved [11]. In Table 1, experimental values of the biexponentials k' and k'' are shown. The rate constants k_{et} calculated from these biexponentials and the ground state concentration of the isomers, from ^{3}biacetyl* to the isomers, in the order **ZZ**, **EZ** and **EE** are 5.9×10^8, 8.9×10^8 and 25.3×10^8 M^{-1} s^{-1}. The triplet energies of the isomers can be calculated from these energy transfer rate constants if a value of the diffusional rate constant is known. The diffusional rate constant was determined in the experiments where benzophenone was used as a sensitizer (Fig. 3). Benzophenone has a triplet energy considerably higher (more than 6 kcal mol^{-1} higher) than the isomers and thus the rate constant for energy transfer from ^{3}benzophenone* to the isomers should be diffusion controlled. The experimental value k_{diff} is 7.2×10^9 M^{-1} s^{-1}. Sandros' equation [11] then gives the differences between the biacetyl triplet and the isomer triplet:

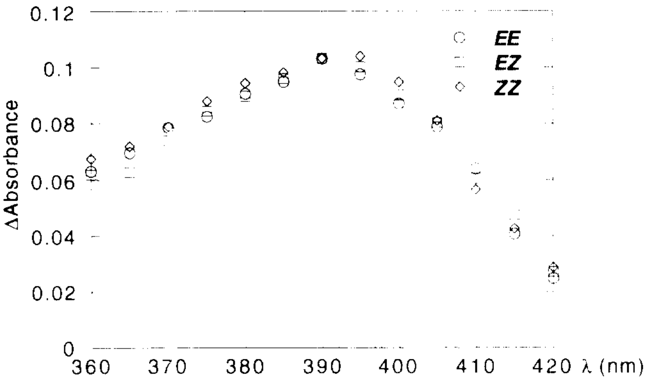


Fig. 2. T_1–T_n absorption spectra of **ZZ**, **EZ** and **EE**.

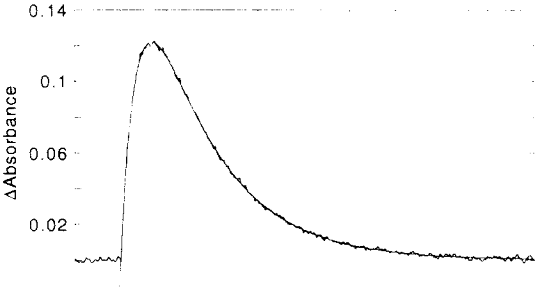


Fig. 3. T_1–T_n absorption transient of **ZZ** at 390 nm with biexponential curve fitted. The build-up corresponds to sensitization with benzophenone and the decay to the triplet lifetime.

$$k_{et} = k_{diff}/(1 + e^{-\Delta G/RT}) \qquad (1)$$

The calculated triplet energies $E_{T,ZZ} = 56.4$ kcal mol^{-1}, $E_{T,EZ} = 56.2$ kcal mol^{-1} and $E_{T,EE} = 55.4$ kcal mol^{-1}. Also, the transfer rates of the reverse process from the equilibrated

Table 1
Experimentally obtained exponentials k' and k'' obtained by fitting two exponential curves to the absorption transients at 390 nm

Isomer	$k' \times 10^{-6}$ (s^{-1})	$k'' \times 10^{-6}$ (s^{-1})
ZZ	5.18	1.95
EZ	5.94	2.65
EE	13.1	3.31

The absorption transients were obtained by laser excitation at 425 nm of mixtures of biacetyl (0.025 M) and the isomers **ZZ** (4.9 mM), **EZ** (5.1 mM), **EE** (5.0 mM).

triplet of the isomers to biacetyl were calculated. The values of k_{et} for the different isomers as starting materials are, in the order **ZZ**, **EZ** and **EE**, 30×10^6, 23×10^6 and 16×10^6 M^{-1} s^{-1}. These rate constants should be identical if the same equilibrated triplet is reached regardless of starting isomer and they are within error limits. Since cancellation problems occur as these rate constants are derived from the difference between the two experimentally obtained exponentials for each isomer (Table 1), it is difficult to obtain precise values of these rate constants. The rather low value of the reverse energy transfer rate constant implies that there is not a large amount of energy available in the equilibrated triplet (about 3 kcal mol^{-1} less than the triplet energy of biacetyl) (calculated from Eq. (1) by using the reverse energy transfer rate constant and the diffusional rate constant) to explain why the energy minimum or equilibrium position of the excited triplet should be displaced from that of ground state **EE**.

3.3. Reaction model

A reaction model which explains the experimental observations is shown in Fig. 4. There are some important features to note. Similar amounts of **EZ** and **EE** are formed on decay from the triplet state and the decay occurs predominantly from ^3E,p*. A minor decay path is via ^{3}Z,p* as there is 1.5% **ZZ** at the photostationary state. Assuming a 50:50 partitioning between **ZZ** and **EZ**, 3% of the decay should occur by this path. Furthermore, if the decay rate constants for decay from ^3E,p* and ^{3}Z,p* are assumed to be equal, then the energy difference ΔG between ^3E,p* and ^{3}Z,p* can be calculated and the value is 2.1 kcal mol^{-1} at 298 K ($\Delta G = RT \ln K$). The value of the difference in energy between planar ^{3}**EE***and ^3E,p* can only be estimated with the present data. If we assume that the value of the decay rate constant from ^3E,p* is the same as the corresponding value of 1-propenylbenzene ($k_{\mathrm{p}} = 3.8 \times 10^7$ s^{-1}) [12], then the difference ΔG is 1.4 kcal mol^{-1} at 298 K ($\Delta G = RT \ln K$, $K = k_{\mathrm{Ep}}\tau - 1$). The relative ground state energies were obtained by a molecular mechanics calculation using Allinger's MM2 force field. (Energies for different rotamers were calculated and the lowest energy rotamer was chosen. The differences were small, however (less than 0.35 kcal mol^{-1}).) Triplet state *cis–trans* isomerizations often proceed by quantum chain processes [6]. In this system very high concentrations would be needed to obtain a significant effect of a quantum chain process, since the lifetime of the triplet is short and there is not much energy available in the excited triplet. For compounds having two double bonds, in principle it would be possible to have both double bonds twisted, that is a ^{3}p,p* state (see, for example, Ref. [13]). Such an intermediate is at least unlikely since only a small amount of **ZZ** is present in the photostationary state mixture. It is most likely that the **ZZ** is formed via decay from a ^{3}Z,p* intermediate. Although some of the energies in Fig. 4 are only estimates, a clear and rather detailed picture of the triplet state isomerizations has emerged from the experimental work presented in this paper.

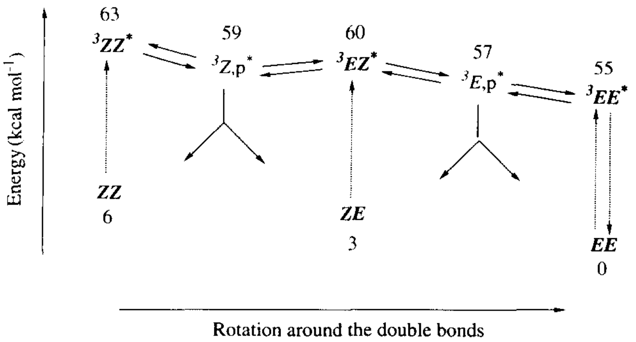


Fig. 4. Reaction model for sensitized isomerizations of **ZZ**, **EZ** and **EE**.

3.4. Comparison with sensitized isomerization of bis(3,3-dimethyl-1-butenyl)durenes

Liu and Kini [14] have shown that bis(3,3-dimethyl-1-butenyl)durene reacts differently from our 1,4-bis(1-propenyl)benzene. That is, on benzophenone-sensitized excitation a photostationary state mixture (*Z,Z*:*E,Z*, 86:14) containing no *E,E* isomer is approached. Furthermore, starting with pure *E,E* isomer they showed that the ratio between *E,Z* and *Z,Z* changes during the course of the reaction. Thus, the triplet is not thermalized, which means that decay processes from triplets to ground states have to be faster than equilibration on the triplet surface. Most likely, the triplet energies as well as rate constants are affected by the steric crowding in these isomers to give the observed reaction pattern.

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