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Cis–Trans Photoisomerization of Bis-stilbenes with Ethylene Bridges

Ingjald Anger,[†] **Kjell Sandros,**[‡] **Mikael Sundahl,**[*,†] **and Olof Wennerström**[†]

Departments of Organic and Physical Chemistry, Chalmers University of Technology,
S-412 96 Göteborg, Sweden

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The mechanisms for *Z*–*E* photoisomerization of two bisstilbenes, 4,4′-bis(3,5-di-*tert*-butylstyryl)bibenzyl, **1**, and [2.2]-4,4′-stilbenophane, **2**, have been studied. The isomerizations of ***ZZ*-1** and ***EE*-1** are similar to those of *Z*- and *E*-stilbene, respectively. On excitation of ***ZE*-1** there is a competition between an energy transfer process from the *E*- to the *Z*-chromophore and isomerization. This results in a small quantum yield (<0.01) for isomerization of ***ZE*-1** to ***ZZ*-1**, whereas that of ***ZE*-1** to ***EE*-1** is 0.19. The *Z*–*E* isomerizations of the stilbenophane, **2**, are clearly different from those of **1**. ***EE*-2** is, to our knowledge, the first example of two stilbene units forming an excimer. In ***EZ*-2** there is neither efficient energy transfer from **EZ^*-2** nor from **E^*Z-2** while for a higher excited state **EZ^{**}-2** efficient energy transfer yielding **E^*Z-2** takes place. The *Z*–*E* isomerization of ***ZZ*-2** is again more similar to that of *Z*-stilbene.

Introduction

It is generally accepted that *Z*–*E* photoisomerization of stilbene occurs via a diabatic process from a twisted excited state to a twisted ground state species which relaxes to the *Z*- or *E*-isomer of stilbene.[1] However, Saltiel has recently found an alternative adiabatic pathway which is a minor process in the direct photoisomerization of stilbene.[2] This can be explained by assuming that the energy surfaces of the singlet excited state is flatter than was previously assumed in most textbooks on photochemistry. This means that relatively small changes of the energy for the planar and twisted geometries on the excited state energy surfaces can lead to significant changes of the reaction paths. A series of such cases has already been found for various styrylarenes by Tokumaru and co-workers[3] as well as by Becker and Sandros.[4] We have observed that a simple extension of the conjugated system of stilbene to styrylstilbene has the same effect on both the first excited singlet and triplet energy surfaces.[5] We were able to prove that adiabatic processes occur for the *Z*–*E* photoisomerization resulting in two-fold reactions which means that one photon triggers the isomerization at two double bonds. Intermolecular chain processes are also possible for adiabatic, sensitized, *Z*–*E* photoisomerizations of styrylstilbenes. We have also shown that adiabatic *Z*–*E* photoisomerizations occur on sensitized irradiation of 1,4-bisstyrylnaphthalene and 9,10-bisstyrylanthracene.[6] Now, we have prepared and studied two series of bis-stilbenes, the 1,2-bis(stilbene)ethanes, **1**, and the stilbenophanes, **2**. In these two series of molecules we have no π conjugation between the stilbene units. Previously, we have suggested that the size of the π system is important for the mode of isomerization and now we confirm this as we could see no multiple *Z*–*E* isomerizations for these molecules. Instead the *Z*–*E* isomerizations are determined by an intriguing balance between intramolecular energy transfer and other processes. For the stilbenophane we also report on the formation of an excimer.

Experimental Section

Materials. 4,4′-Bis(3,5-di-*tert*-butylstyryl)bibenzyls (**1**) were synthesized in a twofold Wittig reaction from 3,5-di-*tert*-butylbenzyltriphenylphosphonium bromide and 4,4′-bibenzyldialdehyde. The phosphonium salt (2.74 g, 5.02 mmol) and the aldehyde (0.47 g, 2.0 mmol) were dissolved in dry DMF (50 mL). The mixture was cooled to –40 °C and the flask was flushed with nitrogen. Lithium ethoxide in ethanol (0.55 M) was added slowly to allow the coloured ylide formed to react with aldehyde groups between successive additions. When no change of colour was observed on addition of lithium ethoxide the reaction mixture was stirred for another 12 h. After the reaction was completed the mixture was allowed to reach room temperature and then diluted with water (50 mL).

The reaction mixture was extracted with ether (3 × 50 mL). The combined ether fractions were washed with water several times and dried over magnesium sulfate, and then the solvent was evaporated. The crude product was purified by flash chromatography on silica gel with CH_2Cl_2 as eluent. The first band contained a mixture of the *Z*/*E* isomers which most efficiently were separated by preparative HPLC (hexane as eluent and a medium polar column, Spherisorbe nitril). After the HPLC separation the compounds were recrystallized from ethanol.

***ZZ*-1**: yield 16%; mp 141 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.22 (t, J = 1.8 Hz, 2 H), 7.20 (d, J = 8.0 Hz, 4 H), 7.11 (d, J = 2.0 Hz, 4 H), 7.04 (d, J = 8.0 Hz, 4 H), 6.56 (s, 4 H), 2.82 (s, 4 H), 1.22 (s, 36 H); UV (cyclohexane) λ_{max} = 232 nm, ϵ = 44 100 M^{-1} cm^{-1}.

***EZ*-1**: yield 26%; mp 84 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.45 (d, J = 8.0 Hz, 2 H), 7.36 (d, J = 2.0 Hz, 2 H), 7.34 (t, J = 1.6 Hz, 1 H), 7.23 (t, J = 1.8 Hz, 1 H), 7.22 (d, J = 8.0 Hz, 2 H), 7.17 (d, J = 8.0 Hz, 2 H), 7.123 (d, J = 16.3 Hz, 2 H), 7.120 (d, J = 2.0 Hz, 2 H), 7.07 (d, J = 15.6 Hz, 2 H), 7.06 (d, J = 8.0 Hz, 2 H), 6.56 (s, 2 H), 2.88 (s 4 H), 1.36 (s, 18 H), 1.22 (s, 18 H); UV (cyclohexane) λ_{max} = 302 nm, ϵ = 42 000 M^{-1} cm^{-1}.

***EE*-1**: yield 11%; mp 190–192 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.0 Hz, 4 H), 7.36 (d, J = 1.6 Hz, 4 H), 7.34 (t, J = 1.6 Hz, 2 H), 7.18 (d, J = 8.4 Hz, 2 H), 7.13 (d, J = 16.0 Hz, 2 H), 7.07 (d, J = 16.0 Hz, 2 H), 2.94 (s, 4 H), 1.36 (s, 36 H); UV (cyclohexane) λ_{max} = 317 nm, ϵ = 66 000 M^{-1} cm^{-1}.

The stilbenophanes, ***ZZ*-2** and ***EE*-2** were prepared and characterized as previously reported.[7] *E*,*Z*-Stilbenophane (***EZ*-2**) was prepared photochemically from ***EE*-2**. A nitrogen purged solution of ***EE*-2** (27 mg, 4 mL of CH_2Cl_2) was irradiated with light of 340 ± 20 nm. The equipment used was an optical bench arrangement with a xenon arc lamp and a monochromator, Applied Photophysics Model 4060 and 7300 respectively. The reaction was followed by analytical HPLC, using a column (15 cm length, 4.6 mm inner diameter) packed with spherisorbe S5CN, and hexane/dichloromethane (95/5, flow rate 1 ml/min) as eluent.

[†] Department of Organic Chemistry.

[‡] Department of Physical Chemistry.

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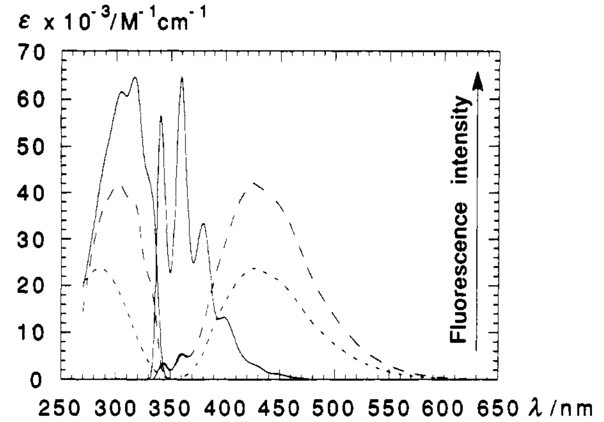


Figure 1. Absorption spectra at 298 K and emission spectra at 77 K of ***ZZ*-1** (- - -), ***EZ*-1** (– – –), and ***EE*-1** (—).

The isomerization was stopped after 8.5 hr when the reaction mixture contained 25, 38, and 37%, of the *Z,Z*-, *E,Z*-, and *E,E*-isomer, respectively. The solvent was evaporated from the reaction mixture, which was then dried under vacuum. ***EE*-2** was separated from the crude product by recrystallization from hexane. The mother liquor was concentrated by evaporation and subjected to preparative HPLC (hexane/dichloromethane, 97/3, as eluent and a medium polar column spherisorbe nitril, S10CN). About 10 mg of ***EZ*-2**, recrystallized from ethanol/water, was obtained.

***EZ*-2**: mp 166–168 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.20 (d, J = 8.2 Hz, 4 H), 7.07 (d, J = 8.2 Hz, 4 H), 6.87 (d, J = 8.4 Hz), 6.67 (s, 4 H), 6.31 (d, J = 8.4 Hz, 4 H), 6.18 (s, 4 H), 2.91 (A,A′,B,B′, 4 H), 2.77 (A,A′,B,B′, 4 H); UV (cyclohexane) λ_{max} = 293 nm, ϵ = 43 200 M^{-1} cm^{-1}.

All measurements were performed in argon flushed spectroscopic grade methylcyclohexane.

Fluorescence Measurements. Fluorescence spectra were obtained with an Aminco SPF 500 (corrected spectra) instrument. Fluorescence quantum yields are based on that of 9,10-diphenylanthracene in cyclohexane (ϕ_f = 0.90).[8] Fluorescence lifetimes were determined with a single-photon counting (SPC) equipment described previously.[9] The data were deconvoluted by the global-reference method[10] with subsequent calculation of the species associated spectra.[11] A liquid-nitrogen cryostat (Oxford Instruments DN 1704 with temperature controller DTC2) was used for the measurements at lower temperatures.

Isomerization Measurements. Irradiations were performed in an optical bench arrangement from Applied Photophysics, using a 150-W xenon arc lamp and a monochromator. Quantum yields were determined with ferrioxalate actinometry.[12] The isomerizations were followed by analytical HPLC (Spherisorbe nitril, hexane/methylene chloride 95/5 as eluent).

Results and Discussion

4,4′-Bis(3,5-di-*tert*-butylstyryl)bibenzyl, 1. *Absorption and Emission Spectra.* The absorption spectra at 298 K and the emission spectra at 77 K are shown in Figure 1. The molar absorptivity of ***EZ*-1** is the average of that of ***ZZ*-1** and ***EE*-1**. Thus, we conclude that the two chromophores in ***EZ*-1** are independent. This is also assumed to be the case for ***ZZ*-1** and ***EE*-1**. The emission spectrum of ***EZ*-1** resembles that of ***ZZ*-1** except for a small part which is due to emission from the *E*-chromophore. This spectrum can be explained in terms of intramolecular energy transfer from ***E*Z*-1**, where the *E*-chromophore is excited, to ***EZ**-1**, where the *Z*-chromophore is excited. On excitation of ***EZ*-1** at 316 nm, where 85% of the light is absorbed by the *E*-chromophore, the emission arising from ***E**** is only 2.0% of the total. We conclude that the excitation energy of the *Z*-chromophore is lower than that of the *E*-chromophore.

Isomerization and Fluorescence Quantum Yields. The isomerization quantum yields as well as the fluorescence quantum yields are shown in Figure 2. In agreement with the energy transfer model discussed above, the quantum yield for isomerization of ***EZ*-1** to ***ZZ*-1** is very low. The fluorescence of ***EZ*-1**, can be divided in two parts, one emission from ***E*Z*-1** and the other emission from ***EZ**-1** with quantum yields 0.0044 and 0.0015, respectively. The latter figure is identical with the fluorescence quantum yield of ***ZZ*-1** as expected if the intramolecular energy transfer from ***E*Z*-1** is efficient. The fluorescence quantum yields of ***ZZ*-1** and ***EE*-1** are higher than those of *Z*- and *E*-stilbene,[12] respectively. This might be due to the *tert*-butyl groups and the linkage of two units giving larger groups to rotate and thus a higher friction along the isomerization coordinate. The fluorescence quantum yields at 77 K are within limits of error equal to unity for all three isomers.

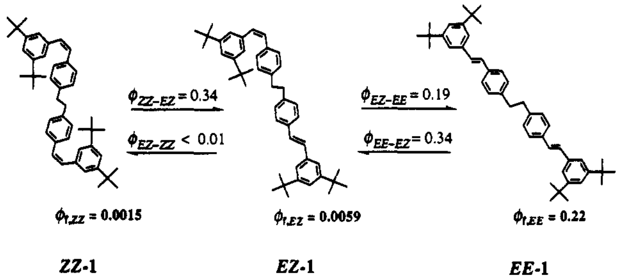


Figure 2. Isomerization and fluorescence quantum yields of ***ZZ*-**, ***EZ*-**, and ***EE*-1** on excitation with 297-nm light at 298 K.

TABLE I: Experimental and Calculated Radiative Rate Constants at 77 K

	k_f (calculated), s^{-1}	k_f (experimental), s^{-1}
***ZZ**-1**	2.0×10^8	2.2×10^8
***EZ**-1**	2.0×10^8	2.2×10^8
***E*Z*-1**	7.9×10^8	7.5×10^8
***EE**-1**	7.9×10^8	7.4×10^8

Fluorescence Decay Measurements. At 298 K only ***EE**-1** has a fluorescence lifetime measurable by our system, τ_{EE^*-1} = 0.33 ns. The fluorescence lifetimes of the other isomers are <0.01 ns. At 77 K the lifetimes are 4.6 ns and 1.35 ns for ***ZZ**-1** and ***EE**-1**, respectively. In support of our energy transfer model ***EZ*-1** shows a biexponential decay with lifetimes 0.032 ns and 4.6 ns for ***E*Z*-1** and ***EZ**-1**, respectively. Important to note is that the lifetimes of ***EZ**-1** and of ***ZZ**-1** are identical. The lifetime ratio, $\tau_{E^*Z-1}/\tau_{EE^*-1}$ = 0.024, is in perfect agreement with the fluorescence quantum yield ratio $\phi_{E^*Z-1}/\phi_{EE^*-1}$ = 0.020/0.85 = 0.024, obtained by correction for the fact that not all light is adsorbed by the *E*-chromophore in ***EZ*-1**.

Kinetics Parameters and Reaction Model. As a test of the independent functioning of the chromophores the experimentally determined fluorescence rate constants are compared with those calculated from absorption and emission spectra using the Strickler–Berg equation[13] (Table I). The molar absorptivities used are those of the individual chromophores. The agreement is remarkably good.

At 77 K, the rate constant for energy transfer, k_{et}, from ***E*Z*-1** to ***EZ**-1** is calculated from the energy transfer quantum yield, ϕ_{et}, and the lifetime of ***E*Z*-1**, $k_{et} = \phi_{et}/\tau_{E^*Z-1} = 0.976/0.032 \times 10^{-9} = 3.1 \times 10^{10}\ s^{-1}$. At 298 K, we calculate the energy transfer rate constant as $k_{et} = k_{f,EE^*} \times 0.85/\phi_{f,E^*Z-1} = 6.7 \times 10^8 \times 0.85/0.0044 = 1.3 \times 10^{11}\ s^{-1}$ (0.85 is a correction term to get ϕ_{f,E^*Z-1} based on the part of ***EZ*-1** that got the *E*-chromophore excited).

All our results are consistent with a diabatic isomerization model where decay from the singlet excited state surface, giving rise to isomerization, occurs from a perpendicular state with the double bond twisted close to 90°. We assume that 50% of the molecules that reach this perpendicular state isomerize and the other 50% return to their original configuration (α = 0.5).

Furthermore, for an excited *Z*-chromophore the decay rate constant at 298 K, k_{tot,Z^*}, is calculated from the radiative rate

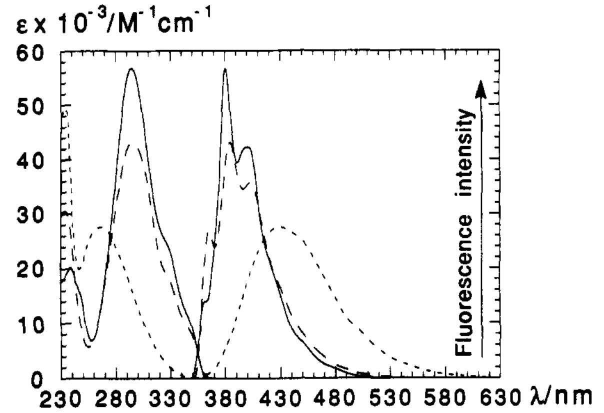
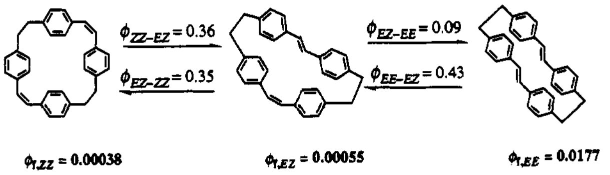


Figure 3. Absorption spectra at 298 K and emission spectra at 77 K of ***ZZ*-2** (- - -), ***EZ*-2** (– – –), and ***EE*-2** (—).

constant, obtained from the Strickler-Berg equation, and the fluorescence quantum yield, $k_{\mathrm{tot},Z^*} = k_{\mathrm{f,ZZ^*}}/\phi_{\mathrm{f,ZZ}} = 1.7 \times 10^8/0.0015 = 1.1 \times 10^{11}\ \mathrm{s}^{-1}$. The rate constant for isomerization from ***ZZ**-1** $k_{\mathrm{iso}} = \phi_{\mathrm{iso}} \times k_{\mathrm{tot},Z^*}/\alpha = 0.34 \times 1.1 \times 10^{11}/0.5 = 7 \times 10^{10}\ \mathrm{s}^{-1}$. We note that part of the ***ZZ**-1** neither isomerizes nor fluoresces, but undergoes a nonradiative deactivation process other than the isomerization. The rate constant for this internal conversion process $k_{\mathrm{ic}} = 4 \times 10^{10}\ \mathrm{s}^{-1}$. For ***EZ**-1** $k_{\mathrm{iso}} = 4 \times 10^{10}\ \mathrm{s}^{-1}$ and $k_{\mathrm{ic}} = 7 \times 10^{10}\ \mathrm{s}^{-1}$ are calculated. A maximum value of the rate constant for isomerization from ***E**Z-1** $k_{\mathrm{iso}} = \phi_{\mathrm{iso}} \times k_{\mathrm{et}}/\alpha < 0.01 \times 1.3 \times 10^{11}/0.5 = 2.6 \times 10^9\ \mathrm{s}^{-1}$. For ***EE**-1** the isomerization rate constant is given by $k_{\mathrm{iso}} = \phi_{\mathrm{iso}}/(\tau_{\mathrm{EE^*}} \times \alpha) = 0.34/(0.33 \times 10^{-9} \times 0.5) = 2 \times 10^9\ \mathrm{s}^{-1}$. The internal conversion rate constant is calculated as $k_{\mathrm{ic}} = 1/\tau_{\mathrm{EE}}{}^* - k_{\mathrm{iso}} - k_{\mathrm{f,EE^*}} = 3 \times 10^9 - 2 \times 10^9 - 0.67 \times 10^9 = 3 \times 10^8\ \mathrm{s}^{-1}$.

Energy Transfer Mechanism. If we assume that the energy transfer, from ***E**Z-1** to ***EZ**-1**, occurs by a dipole–dipole interaction we can then calculate a distance, *R*, between the two chromophores.[14] We calculate the spectral overlap integral, between the emission of excited *E*-chromophore and the absorption of *Z*-chromophore, $J_{\mathrm{DA}} = 5 \times 10^{-27}\ \mathrm{M}^{-1}\ \mathrm{cm}^3$. We also need an orientation factor, κ^2, which from geometry considerations we decided to vary from 2/3 to 4. From the rate constants, for energy transfer, k_{et}, and intrinsic decay of the donor, $k_{\mathrm{EE^*}}$, using the equation; $R^6 = 8.8 \times 10^{17} \times \kappa^2 \times \phi_{\mathrm{f}} \times J_{\mathrm{DA}} \times k_{\mathrm{EE^*}}/(k_{\mathrm{et}} \times n^4)$ we get $R = 0.96$ Å and 0.71 Å for $\kappa^2 = 4$ and $^2/_3$, respectively. Even for the case of perfect orientation, $\kappa^2 = 4$, we get a distance shorter than a C–C bond. Thus, the energy transfer is not (or not exclusively) occurring by a dipole–dipole mechanism but more likely by an electron exchange mechanism, either through the σ-bond or through space.

Stilbenophane, 2. *Absorption and Emission Spectra.* The absorption and emission spectra are shown in Figure 3. The molar absorptivity for ***EZ*-2** is not the average of that of ***ZZ*-2** and ***EE*-2**. This is not to be expected even if the chromophores are electronically independent, because there is different steric congestion in the different isomers. We note that the absorptivity of the *Z*-chromophore is suppressed and that of the *E*-chromophore is enhanced. We prefer explaining this in terms of Franck–Condon factors and changed geometries rather than in terms of an exciton coupling. The emission spectrum of ***EZ*-2** is similar to that of ***EE*-2**. This might either be due to an efficient energy transfer from the *Z* to the *E* chromophore or to a large difference in molar absorptivity of the *Z* and *E* chromophores, the molar absorptivity of *E* being higher, combined with incomplete or no energy transfer. Later we will see that the energy transfer is inefficient from the *Z*-chromophore in its lowest excited state while from higher excited states there is an efficient energy transfer. As the species associated emission spectra of neither the *Z* nor the *E* chromophores in the different isomers are the same it is not possible to calculate the different contributions to the emission spectrum for ***EZ*-2**.



***ZZ*-2** ***EZ*-2** ***EE*-2**

Figure 4. Isomerization and fluorescence quantum yields of ***ZZ*-**, ***EZ*-**, and ***EE*-2** on excitation with 297-nm light at 298 K.

Isomerization and Fluorescence Quantum Yields. The isomerizations and the corresponding quantum yields as well as the fluorescence quantum yields are shown in Figure 4. The excitation wavelength for the isomerization quantum yields given was 297 nm. For ***EZ*-2** the wavelength was changed in order to look for a wavelength dependence. At 265 nm the ratio between the quantum yields $\phi_{\mathrm{EZ\text{-}ZZ}}/\phi_{\mathrm{EZ\text{-}EE}}$ was 1.6 and at 340 nm it was 11. We conclude that there is neither efficient energy transfer from ***E**Z-2** nor from ***EZ**-2**. Surprisingly, at 234 nm where the *Z*-chromophore is assumed to absorb most of the light the ratio $\phi_{\mathrm{EZ\text{-}ZZ}}/\phi_{\mathrm{EZ\text{-}EE}}$ was 4.0. We explain this in terms of an energy transfer from a higher excited state, ***EZ***-2**, giving ***E**Z-2**.

Emission Measurements. In Table II, the fluorescence lifetimes and the corresponding fluorescence quantum yields at a series of temperatures are summarized. The fluorescence of ***ZZ*-2** is structureless and the fluorescence decay is monoexponential.

The fluorescence of ***EZ*-2** shows a more complicated behavior. In a methylcyclohexane glass at 100 K, the fluorescence decay was biexponential. The fluorescence spectrum was deconvoluted and the longer lifetime component corresponds to a structureless emission assigned as emission from the *Z*-chromophore. Two different excitation wavelengths were used in the SPC measurements, 297 nm and 337 nm. At 297 nm the quantum yield for the fluorescence corresponding to the long lived component is twice as high as when the excitation wavelength was 337 nm, where the *Z*-chromophore should absorb a smaller part of the excitation light. Furthermore, for an emission spectrum of ***EZ*-2** with excitation at 239 nm, the structureless emission is further reduced. These findings are in accordance with the wavelength dependence found for the formation of isomerization products.

The emission behavior of ***EE*-2** is even more complicated. We explain the decay in solution as involving the formation of an excimer of the two stilbene units. The excimer formation will be treated separately below. In the glass where there is no possibility for formation of an excimer there is still a biexponential behavior of the fluorescence decay. This is most easily explained in terms of two confomers of ***EE*-2**, with parallel and crossed double bonds, respectively. In the glass there should be no possibility for conversion between the two conformers while in solution this might take place. The fluorescence component with the shorter lifetime has its emission "center of gravity" at a shorter wavelength than the other one. It is therefore not surprising that the quantum yield of this component is relatively decreased when going from glass to fluid solution at 153 K.

Excimer Formation. This is to our knowledge the first example of an excimer between two stilbene units. From an Arrhenius plot of the excimer formation we get an activation energy of 3.7 kcal mol^{-1} with a frequency factor $4.5 \times 10^{11}\ \mathrm{s}^{-1}$ (Figure 5). The contribution from the component with the shorter lifetime is small at 153 K and higher temperatures. Therefore, the existence of more than one excimer forming conformer was neglected. We note that the shape of the emission spectrum as well as the radiative lifetime of the longlived component is clearly consistent with the expected properties of an excimer (Figure 6). The activation energy for the non radiative decay of the excimer was calculated to be 5.0 kcal mol^{-1} with a frequency factor of $2.9 \times 10^{12}\ \mathrm{s}^{-1}$.

Kinetic Parameters. A calculation of the rate constants for

TABLE II: Fluorescence Lifetimes and the Corresponding Species Associated Fluorescence Quantum Yields in Percent

	***ZZ*-2**[a]		***EZ*-2**[a]				***EE*-2**[a]					
T (K)	τ (ns)	ϕ	τ_1 (ns)	ϕ_1	τ_2 (ns)	ϕ_2	τ_1 (ns)	ϕ_1	τ_2 (ns)	ϕ_2	τ_3 (ns)	ϕ_3
298		0.038		0.055					0.17	1.24	1.43	0.53
250									0.55	4.2	7.87	2.55
200									1.95	16.2	29.1	3.98
153	1.00	8.7	0.10				1.78	3.2	3.78	28.5	39.4	0.91
100	5.30	46	1.05	24	2.88	8	2.96	27	6.43	12		
			1.05[b]	31[b]	2.88[b]	4[b]						

[a] The excitation wavelength was 297 nm in all experiments except for *b*. [b] The excitation wavelength was 337 nm.

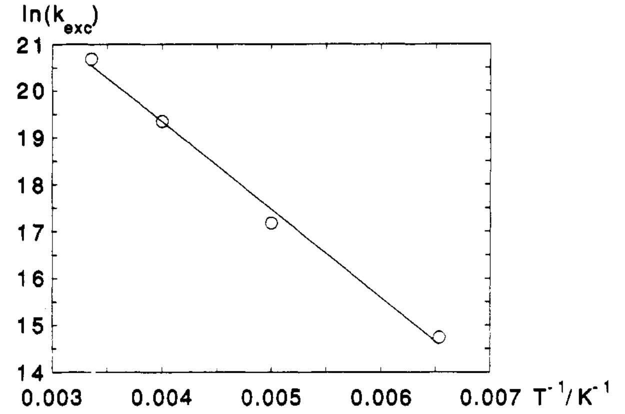


Figure 5. Arrhenius plot of the rate constant for excimer formation of ***EE*-2**.

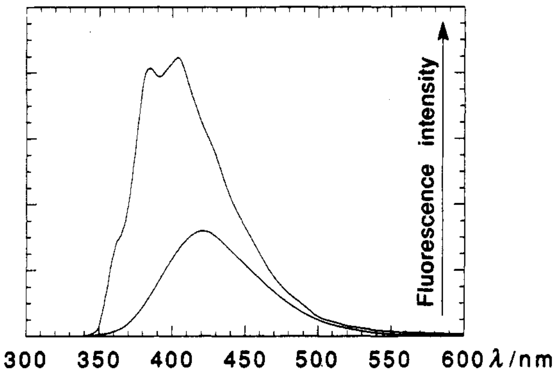


Figure 6. Spectra of the total and excimer emission of ***EE*-2** at 250 K.

***E**Z*-2** and ***EZ**-2** is not possible as the individual absorptivities of the chromophores are unknown. Assuming that the radiative rate constants are proportional to the square of the refractive index of the solvent and that on isomerization the partition ratio $\alpha = 0.5$ the following rate constants at 298 K are obtained for the other isomers: ***ZZ*-2**; $k_f = 7.8 \times 10^7$ s^{-1}, $k_{iso} = 1.5 \times 10^{11}$ s^{-1}, $k_{ic} = 0.6 \times 10^{11}$ s^{-1}, ***EE*-2**; $k_f = 7.3 \times 10^7$ s^{-1}, $k_{iso} = 5.1 \times 10^9$ s^{-1}, $k_{exc} = 9.6 \times 10^8$ s^{-1} (excimer formation).

The large Stokes shifts indicate big geometrical differences between ground and excited states with concomitant small Franck–Condon factors. It is therefore expected that the radiative rate constants are much smaller than those calculated by the Strickler–Berg equation[13] 1.8×10^8 s^{-1} and 4.1×10^8 s^{-1} for ***ZZ**-2** and ***EE**-2**, respectively.

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