ethanol to give 2,3-dimethyl-2,3-diphenylbutane (**63**) (2.4 g, 47%): ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.32 (s, 12 H, $4CH_3$), 7.15 (s, 5 H, arom); MS m/z (rel intensity) 119 (100), 118 (26), 117 (18), 103 (16), 91 (50), 78 (12), 77 (16).

2-[4-(Trifluoromethyl)phenyl]-2-propanol. This alcohol was prepared by the addition of methylmagnesium iodide to 4-(trifluoromethyl)-acetophenone according to the procedure described for the preparation of 2-(4-methylphenyl)-2-propanol. 2-[4-(Trifluoromethyl)phenyl]-2-propanol (81%) was isolated by distillation: bp 84 °C/1.1 Torr; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.57 (s, 6 H, $2CH_3$), 2.48 (brd q, 1 H, OH), 7.57 (s, 4 H, arom); MS m/z (rel intensity) 204 (M^+, 1), 189 (49), 186 (47), 151 (20), 145 (12), 117 (48), 115 (23), 43 (100).

2-(4-Cyanophenyl)-2-propanol. A solution of methylmagnesium iodide prepared from methyl iodide (3.8 mL, 60 mmol), magnesium (1.45 g, 0.060 g atom), and dry diethyl ether (20 mL) was added dropwise to an ether solution of 4-cyanoacetophenone (7.3 g, 50 mmol). The mixture was stirred for 0.5 h and was then poured into aqueous saturated NH_4Cl solution (200 mL). The product was extracted with dichloromethane (2 × 100 mL) and dried with $MgSO_4$, and the solvent was evaporated. Analysis (GC/MS) of the extract indicated that the conversion of 4-cyanoacetophenone to the alcohol was not complete. A significant amount of 4-cyanoacetophenone remained; however, no addition to the cyano group was observed under these conditions. The 2-(4-cyanophenyl)-2-propanol was partially separated by flash chromatography by using dichloromethane as eluent. The enriched fractions were combined, and the product was distilled under vacuum (bp 115–118 °C/0.2 Torr) to give 2-(4-cyanophenyl)-2-propanol (5.0 g, >96% purity) still contaminated with the starting ketone: MS m/z (rel intensity) 161 (M^+, 1), 146 (51), 43 (100).

2-(4-(Trifluoromethyl)phenyl)propene. A sodium hydride dispersion (3.8 g, 80 mmol, 50% NaH) in mineral oil was washed with n-hexane (3 × 20 mL), and the clean NaH residue was added to a solution of methyl triphenylphosphonium bromide (25.7 g, 72 mmol) in anhydrous diethyl ether (100 mL). The mixture was refluxed under argon for 3 h, then 4-(trifluoromethyl)acetophenone (9.4 g, 50 mmol) in diethyl ether (25 mL) was added, and the solution was refluxed overnight. The reaction mixture was poured into water (200 mL), extracted with dichloromethane (2 × 75 mL), and dried with magnesium sulfate, and the solvent was evaporated. The crude mixture was vacuum distilled at 53 °C/0.8 Torr to afford pure 2-(4-trifluoromethylphenyl)propene (6.3 g, 68%): ^{1}H NMR (60 MHz, $CDCl_3$) δ 2.18 (d, 3 H, CH_3), 5.22 (m, 1 H, $=CH_A$), 5.45 (m, 1 H, $=CH_B$), 7.58 (s, 4 H, arom); MS m/z (rel intensity) 186 (M^+, 100), 171 (24), 167 (21), 151 (47), 146 (17), 117 (100), 115 (50).

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Cis–Trans Photoisomerization of a *p*-Styrylstilbene, a One- and Twofold Adiabatic Process

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Abstract: The mechanism of the Z/E photoisomerization of a p-styrylstilbene has been studied by steady state and time-resolved fluorescence measurements combined with isomerization quantum yield determinations. It was found that on excitation of the Z,Z isomer both the isomers, Z,E and E,E, are produced initially, mainly by adiabatic processes on the singlet excited surface. Quantum mechanical calculations give surface profiles supporting the adopted mechanism.

The mechanism of photoisomerization of stilbenes has been discussed for more than 50 years.[2] Until a few years ago Z/E photoisomerization of olefinic compounds was assumed always to be a diabatic process. In this model the isomerization proceeds via a minimum on the lowest excited singlet or triplet surface where the double bond is twisted 90°. A radiationless transition to the ground-state surface, which has a maximum at this geometry, is followed by a relaxation to either the Z or the E configuration.

However, in 1983, Tokumaru and co-workers presented strong evidence for an adiabatic Z/E isomerization[3] on the triplet state surface of a 1-(2-anthryl)-1-butene.[4] Later, three 9-styrylanthracenes were shown to isomerize adiabatically on both the excited singlet and triplet state surfaces.[5]

For molecules having a number of double bonds, an adiabatic mechanism allows for more than one isomerization per absorbed photon. Recently, a number of m-styrylstilbenes have been studied and the results are stated to be in accordance with a diabatic mechanism.[6] In contrast, the triplet-sensitized 6-fold Z/E isomerization of (*all-Z*)-(2_6)orthoparacyclophene directly to the *all-E* isomer, which we found to occur with a quantum yield of 0.62 in oxygen free benzene, is considered to be an adiabatic process.[7,8] Extended conjugation seems to be an important factor and we have thus turned our attention first to the photoisomerization of a p-styrylstilbene, **1–3**. Somewhat surprisingly, its behavior is very different from that of stilbenes and m-styrylstilbenes. This p-styrylstilbene is, to our knowledge, the first example of a molecule showing twofold adiabatic isomerization on its lowest excited singlet state surface.

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[1] (a) Department of Physical Chemistry. (b) Department of Organic Chemistry. (c) Astra Research Centre.

[2] For a review, see: Saltiel, J.; et al. *Org. Photochem.* **1973**, *3*, 1–113.

[3] In photochemical context the term "adiabatic reaction" refers to a process proceeding on a single electronic state surface, which means that an excited state product is formed.

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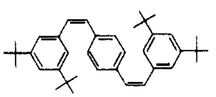

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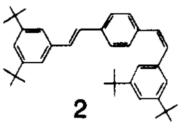

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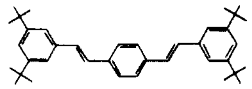

3

Experimental Section

Materials. 3,3″,5,5″-tetra-*tert*-butyl-4′-styrylstilbenes were prepared by a 2-fold Wittig reaction from 3,5-di-*tert*-butylbenzyltriphenylphosphonium bromide and terephthalic aldehyde. The phosphonium salt (28.4 mmol) and the aldehyde (14.2 mmol) were dissolved in dry DMF (250 mL). The mixture was cooled to −40 °C and the flask was flushed with nitrogen. Lithium ethoxide in ethanol was added slowly to allow the colored ylide formed to react with aldehyde groups between successive additions. When no color was observed upon addition of base, the mixture was stirred for another 12 h. After the reaction was completed the reaction mixture was allowed to reach room temperature and then diluted with water (250 mL). The mixture was extracted with diethyl ether (4 × 100 mL). The combined ether fractions were washed with water several times and dried over magnesium sulfate, and then the solvent was evaporated. The residue was subjected to flash chromatography on silica gel with dichloromethane as eluent. The first band contained a mixture (4.76 g, 66%) of the *Z,Z*, *Z,E*, and *E,E* isomers (29:51:20) of the styrylstilbene. The isomers were most efficiently separated by preparative HPLC (hexane as eluent and a medium polar column, Spherisorbe nitril). After the HPLC separation the compounds were recrystallized from ethanol. The purity thus obtained was >99.8%.[9]

(*Z*,*Z*)-3,3″,5,5″-Tetra-*tert*-butyl-4′-styrylstilbene (1): mp 79–81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, J = 1.8 Hz, 2 H), 7.15 (s, 4 H), 7.14 (d, J = 1.8 Hz, 4 H), 6.55 (d, J = 12 Hz, 2 H) 6.49 (d, J = 12 Hz, 2 H), 1.23 (s, 36 H); MS m/z (rel intensity) 506 (6, M^+), 238 (14), 57 (100); UV (methylcyclohexane) λ_{max} = 320 nm, ϵ = 17400 M^{-1} cm^{-1}.

(*Z*,*E*)-3,3″,5,5″-Tetra-*tert*-butyl-4′-styrylstilbene (2): mp 112–114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8 Hz, 2 H), 7.35 (s, 3 H), 7.28 (d, J = 8 Hz, 2 H), 7.25 (t, J = 1.8 Hz, 1 H), 7.15 (d, J = 1.8 Hz, 2 H), 7.11 (d, J = 16 Hz, 1 H), 7.04 (d, J = 16 Hz, 1 H), 6.63 (d, J = 12 Hz, 1 H), 6.56 (d, J = 12 Hz, 1 H), 1.37 (s, 18 H), 1.24 (s, 18 H); MS m/z (rel intensity) 506 (4, M^+), 238 (8), 57 (100); UV (methylcyclohexane) λ_{max} = 337 nm, ϵ = 35500 M^{-1} cm^{-1}.

(*E*,*E*)-3,3″,5,5″-Tetra-*tert*-butyl-4′-styrylstilbene (3): mp 230–232 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 4 H), 7.38 (d, J = 1.8 Hz, 4 H), 7.36 (t, J = 1.8 Hz, 2 H), 7.18 (d, J = 16 Hz, 2 H), 7.10 (d, J = 16 Hz, 2 H), 1.37 (s, 36 H); MS m/z (rel intensity) 506 (9, M^+) 238 (8), 57 (100); UV (methylcyclohexane) λ_{max} = 357 nm, ϵ = 57600 M^{-1} cm^{-1}.

All measurements were performed in argon-flushed solutions with spectroscopic grade methylcyclohexane as solvent.

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).[10] Fluorescence lifetimes were determined with single-photon counting (SPC) equipment described previously.[11] The data were deconvoluted with the global-reference method[12] with subsequent calculation of the species-associated spectra.[13] The excitation wavelength 337 nm was used in all the emission measurements. A liquid-nitrogen cryostate (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 (313 ± 5 nm). Quantum yields were determined with ferrioxalate actinometry.[14] The isomerizations were followed both by UV spectroscopy and analytical HPLC.

Method of Quantum Mechanical Calculations. The AM1 calculations were performed with the MOPAC program (V.4.0) with inclusion of 400 singly excited configuration interactions.[15] All computations were performed with complete geometry optimization. Chem-X was used for display purposes.[16] A complete list of optimized geometries is available from one of the authors (U. Norinder).

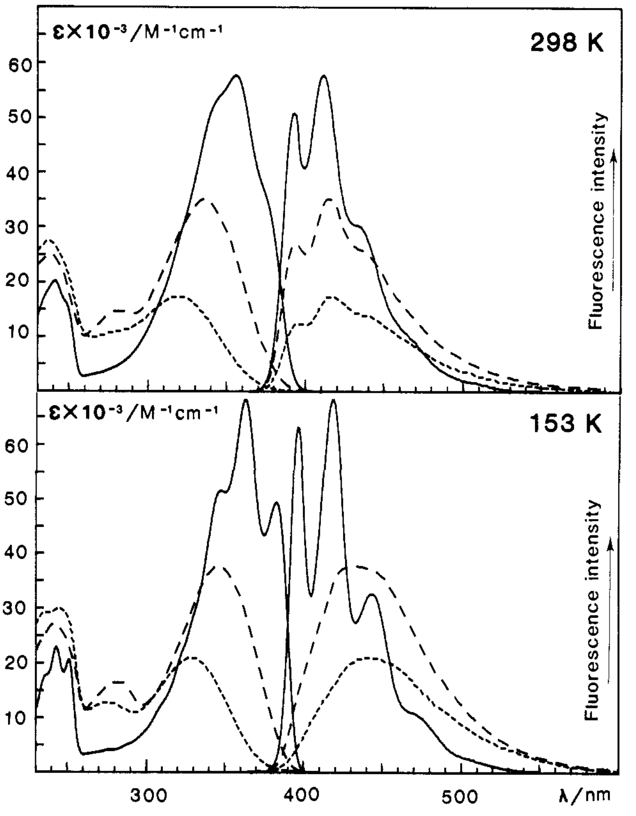

Figure 1. Absorption and emission spectra of **1** (---), **2** (——), and **3** (—) in methylcyclohexane solutions at 298 and 153 K.

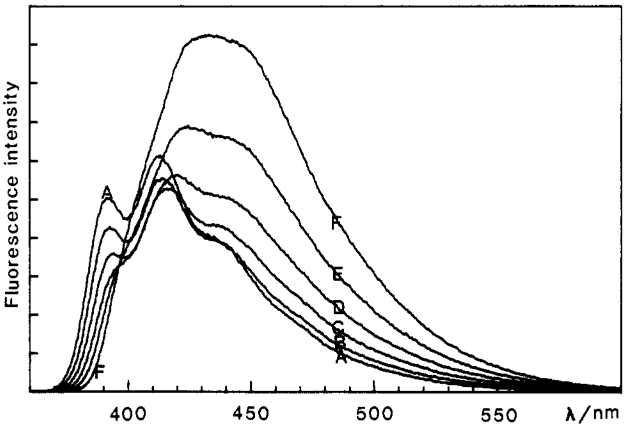

Figure 2. Temperature dependence of the dual emission from a methylcyclohexane solution of **2**. The spectra A–F are recorded at the following temperatures of the solution: 323, 298, 273, 248, 212, and 153 K, respectively.

Results and Discussion

Absorption and Emission Spectra. The absorption and emission spectra of **1**–**3** show some remarkable features (see Figure 1).[17] The long wavelength absorption bands of **1** and **2** are structureless

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[9] The *E,E* isomer has been prepared earlier in a Wittig reaction at ambient temperature, see: Heinze, J.; Mortensen, J.; Müllen, K.; Schenk, R. *J. Chem. Soc., Chem. Commun.* **1987**, 701–703.

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[15] (a) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909. (b) MOPAC V4.0 is available from the QCPE.

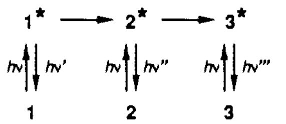
[16] Chem-X, developed and distributed by Chemical Design Ltd, Oxford, England.

[17] No excitation wavelength dependence of the emission spectra was observed. Possible effects of selective photoexcitation of rotamers are expected to be small for the studied compounds in low-viscosity solvents. Cf.: Fischer, E. *J. Mol. Struct.* **1982**, *84*, 219–226. Castel, N.; Fischer, E.; Bartocci, G.; Masetti, F.; Mazzucato, U. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1969–1975.

Table I. Temperature Dependence of Time-Resolved Fluorescence Properties of **1**–**3** in Methylcyclohexane

	T, K	τ_1, ns	τ_2, ns	τ_3, ns
1	323	0.18	0.42	1.28
	298	0.19	0.65	1.25
	153	0.33		
2	323		0.46	1.28
	298		0.68	1.24
	153		1.99	
3	323			1.26
	298			1.24
	153			1.12

Scheme I



even at low temperature while that of **3** shows a vibrational structure which, as expected, is more marked at low temperature. The emission of **3** has a normal temperature dependence in contrast to the fluorescence of **1** and **2**. Surprisingly, these isomers have structured emission spectra at 298 K and structureless spectra at 153 K. The gradual change of the emission spectrum of **2** at a series of temperatures is shown in Figure 2. Time-resolved fluorescence measurements will explain the puzzling steady state emission behavior of **1** and **2**. It will be demonstrated that the fluorescence from these isomers is composite as a result of adiabatic isomerization processes. There is a single emission from the primarily excited isomer only at low temperatures.

As seen from the spectra at 153 K the Stokes shifts for **1** and **2** are 8000 and 5800 cm^{-1}, respectively, indicating major differences between ground- and excited-state geometries. The shift for **3** is only 800 cm^{-1}.

Fluorescence Decay Measurements. The results of the SPC measurements are summarized in Table I. At low temperature all three isomers have monoexponential fluorescence decays. Isomer **3** shows the same behavior also at higher temperatures, the lifetime increasing somewhat with temperature. In contrast, the emission decays of **1** and **2** at higher temperatures are triexponential and biexponential, respectively. It should also be noted that at both 323 and 298 K the time constants correspond within limits of error.

These results and the temperature dependence of the emission spectra can be accounted for by assuming the following scheme involving adiabatic isomerizations on the excited singlet state surface.

As the emission quantum yield of **1** is small compared to those of **2** and **3** the possibility that the solutions of **1** were contaminated with **2** and/or **3** had to be carefully examined. The low-temperature results, steady state and time resolved, rule out impurity concentrations in the original solution of **1** high enough to affect the measurements. In the high-temperature spectral measurements small excitation intensities were used in order to avoid appreciable photochemical isomerization. (The SPC measurements involve very small amounts of absorbed quanta.) Furthermore, repeated spectral recordings were found to be identical as were the excitation and absorption spectra.

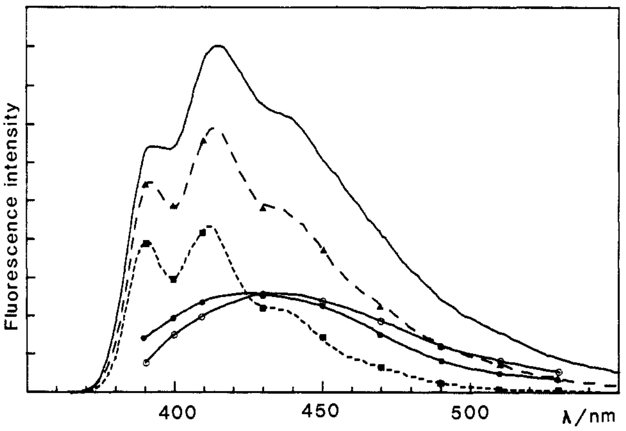


Figure 3. Deconvolution of the triple emission (—) from a methylcyclohexane solution of **1** at 298 K by means of SPC data. The calculated fluorescence contributions from **1*** and **2*** are denoted as open and solid circles, respectively. The intensities after subtraction of the **1*** and **1*** + **2*** contributions from the total emission are marked by ▲ and ■. The emissions from solutions of **2** (— — —) and **3** (- - -), normalized at 390 nm, are shown for comparison.

Table II. Fluorescence Quantum Yields of **1**–**3** in Methylcyclohexane Obtained by Combination of Steady State and Time-Resolved Emission Measurements

	T, K	$\Phi_{f,tot}$	$\Phi_{f,1^*}$	$\Phi_{f,2^*}$	$\Phi_{f,3^*}$
1	323	0.0204	0.0043	0.0050	0.0111
	298	0.0138	0.0046	0.0047	0.0045
	153	0.0094	0.0094		
2	323	0.289		0.094	0.195
	298	0.280		0.144	0.136
	153	0.52		0.52	
3	323	0.87			0.87
	298	0.87			0.87
	153	0.86			0.86

Deconvolution of Fluorescence Spectra. From a series of SPC measurements at different emission wavelengths treated by global analysis the species-associated spectra can be calculated from the total emission spectrum. Figure 3 shows the result of a deconvolution of the triple emission from a solution of **1** at 298 K. As seen the calculated emission spectra of **1*** and **2*** are both structureless in accordance with the spectra from solutions of **1** and **2** at 153 K, a temperature low enough to make adiabatic isomerization negligible. The wavelengths of the emission maxima, 435 and 425 nm, are the expected ones as those at 153 K are 445 and 435 nm. There is a general red shift of about 10 nm in both the absorption and emission spectra of the three isomers when the temperature is changed from 298 to 153 K. As a further test of the adopted reaction scheme the emission intensities after subtraction of the **1*** and **1*** + **2*** contributions from the total fluorescence are compared with the emissions from solutions of **2** and **3**, normalized at 390 nm. As seen the agreement is good. It should also be noted that deconvolution of the total emission from **2** at 323 and 298 K gave **2*** and **3*** emission spectra (not shown) which are, within limits of error, identical with those shown in Figure 3.

Fluorescence Quantum Yields. The total and the excited species associated emission quantum yields are presented in Table II. The low fluorescence yield of **1** is expected as *cis*-stilbene is almost nonfluorescent in normal solution.[18] The total emission yield of **1** decreases significantly with decreasing temperature. The intrinsic emission yield of **1*** is low even at 153 K, and the isomerization to **2*** and **3*** is effectively inhibited at that temperature. For **2** the yield is somewhat lower at 298 K than at 323 K because of less efficient isomerization, but it is almost doubled in going to 153 K where the rate of internal conversion is much lower. The fluorescence yield of **3** is very high and therefore almost independent of temperature. If Scheme I is correct and complete the ratio $\Phi_{f,2^*}/\Phi_{f,3^*}$ should be the same independently of whether **1** or **2** is primarily excited. At 298 K the values of the ratio are 1.04 and 1.06, respectively. The corresponding values at 323 K are 0.45 and 0.48.

The quantum yields of adiabatic isomerization on the singlet excited surface can be calculated from the fluorescence yields. Thus the yield of isomerization of **1** to **2** and **3** at 298 K is $(\Phi_{f,2^*} + \Phi_{f,3^*})/\Phi_{f,tot,2} = (0.0047 + 0.0045)/0.28 = 0.033$ and that of **2** to **3** is $\Phi_{f,3^*}/\Phi_{f,tot,3} = 0.136/0.87 = 0.16$. The corresponding total isomerization yields are 0.057 and 0.26 (see below). The adiabatic path on the excited singlet surface is thus dominating in both cases.

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[18] Sharafy, S.; Muszkat, K. A. *J. Am. Chem. Soc.* **1971**, *93*, 4119–4125.

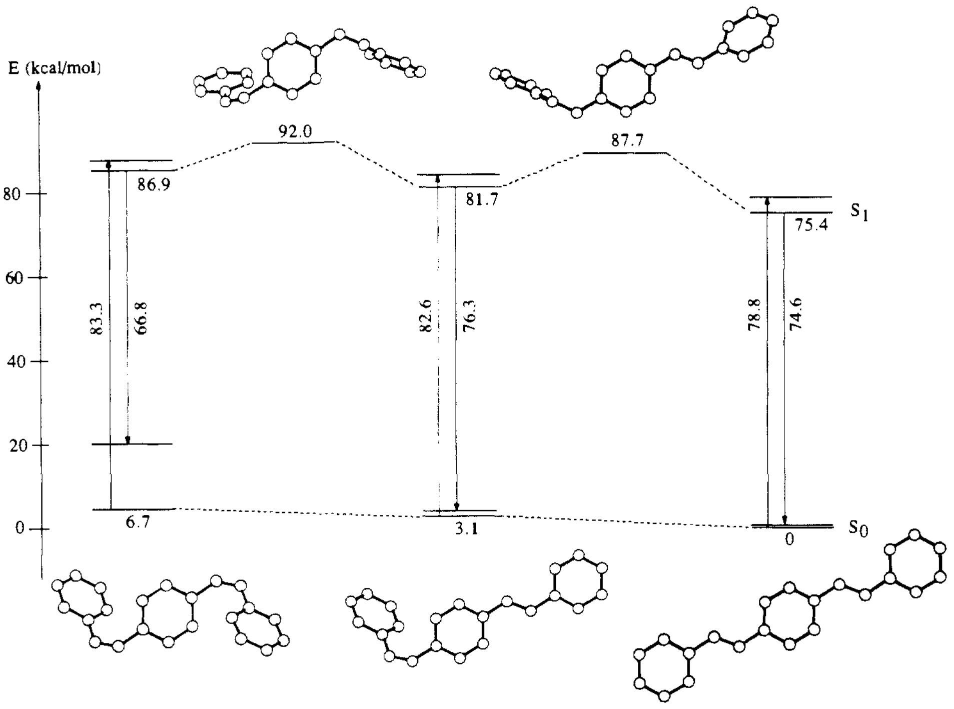

Figure 4. Calculated relative energies of ground and singlet excited states of *p*-styrylstilbene. The Franck–Condon transitions are indicated by arrows. Calculated geometries for the isomers in their ground states and for the singlet excited states with one of the double bonds twisted ($^1Z,p^*$ and $^1E,p^*$) are shown with the hydrogen atoms omitted.

Table III. Fluorescence Rate Constants from Measurements in Methylcyclohexane Solutions Compared with Values Calculated from Absorption and Emission Spectra[a]

	T, K	Φ_f	τ_f, ns	$k_f \times 10^{-8}$, s^{-1}	$k_{f,calc} \times 10^{-8}$, s^{-1}
1	298	0.0046	0.19	0.25	1.6
	153	0.0094	0.33	0.28	2.0
2	298	0.144	0.67	2.2	3.7
	153	0.52	1.99	2.6	4.1
3	298	0.87	1.24	7.0	7.4
	153	0.86	1.12	7.7	8.0

[a] The emission yields given are species associated obtained by deconvolution of the total emissions.

Kinetic Parameters. A comparison between the experimentally determined fluorescence rate constants and those calculated from absorption and emission spectra[19] may serve as a further test of the adiabatic model and emission identification. The results are summarized in Table III. The rate constants, experimental and calculated, increase with decreasing temperature. This is mainly a refraction index effect, the ratio of n^2 for methylcyclohexane at 153 K and at 298 K being 1.10. Thus the temperature dependence of the experimentally determined emission rate constants supports the adopted emission identification. The ratio $k_f/k_{f,calc}$ is close to unity (0.95) for **3** but only 0.60 and 0.15 for **2** and **1**, respectively. The values of the Stokes shift give a clue of the reason. Isomer **3** with a shift of only 800 cm^{-1} can be expected to be well-behaved while the shifts of **2** and **1** (5800 and 8000 cm^{-1}) suggest great geometrical differences between ground and excited states with concomitant small Franck–Condon factors.

The isomerization rate constants can be calculated as $k_{1^\bullet \to 2^\bullet} = (\Phi_{f,2^\bullet} + \Phi_{f,3^\bullet})/\Phi_{f,tot,2}\tau_1$ and $k_{2^\bullet \to 3^\bullet} = \Phi_{f,3^\bullet}/\Phi_{f,tot,3}\tau_2$. The values of $k_{1^\bullet \to 2^\bullet}$ are 1.7×10^8 s^{-1} and 3.1×10^8 s^{-1} at 298 and 323 K. The corresponding values of $k_{2^\bullet \to 3^\bullet}$ are 2.3×10^8 s^{-1} and 4.2×10^8 s^{-1}. Both the activation energies may thus be estimated at 4.6 kcal/mol.

It should be noted that the main deactivation path of **1*** is an internal conversion process with low activation energy. The sum of the rate constants of internal conversion and intersystem crossing has the values 5.1×10^9 and 5.2×10^9 s^{-1} at 298 and 323 K, respectively, and the triplet formation yield is low.

Isomerization Quantum Yields. On irradiation of the *Z,Z* isomer **1** both **2** and **3** are formed initially. The quantum yields at 298 K are $\Phi_{12} = 0.038$ and $\Phi_{13} = 0.019$, respectively, as compared to the quantum yield, 0.033, for the adiabatic singlet state isomerization from **1** to **2** and **3** obtained from the fluorescence measurements. The difference indicates a contribution of triplet state isomerization. Irradiation of **2** gives **3** ($\Phi_{23} = 0.26$) with a small back reaction (photostationary state >99:1), which most probably is due to a triplet state process.

From the temperature dependence of the isomerization quantum yields the energy barriers for **1** → **2** and **2** → **3** are estimated at 3.1 and 3.5 kcal mol^{-1}, respectively. These values are lower than those obtained for the adiabatic singlet state isomerizations (4.6 kcal mol^{-1} for both), supporting the idea that part of the isomerizations on direct excitation are triplet-state processes with lower energy barriers. In a later publication, together with Tokumaru and Arai, we will show that the triplet energy surface shows two decay funnels, one for the planar *E,E* isomer and one for a conformation where one double bond has a planar *E* structure and the other is twisted. This triplet energy surface is similar to that reported for 1,4-diphenylbutadiene,[20] while the excited singlet state surfaces are completely different.

Quantum Mechanical Calculations. The AM1 calculations were performed on the three configurational isomers of *p*-styrylstilbene omitting the *tert*-butyl groups. The geometry of the *E,E* isomer, the most stable one, is almost completely planar. The *E,Z* and *Z,Z* isomers have slightly higher ground-state energies, 3.1 and 6.7 kcal mol^{-1}, respectively. A similar result was obtained by molecular mechanics calculations (MM2 85) which give 3.0 and 5.3 kcal mol^{-1}, respectively, for the *E,Z* and *Z,Z* isomer. These isomers are not planar. The *E,Z* isomer has calculated central torsion angles of 2.1° and 35.8° and outer torsion angles of 1.7° and 45.2°. The *Z,Z* isomer has almost the same larger torsional angles. Several rotamers exist for the three isomers. The difference in energy between them is typically less than 0.5 kcal/mol. We have thus chosen the rotamer with the lowest ground-state energy for each isomer for the calculation of excited-state geometries and energies. Inclusion of a relatively large number of

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configuration interactions is necessary to obtain a solution where the energies of the different geometries of the singlet excited state are stable. As the CI number was increased the energies of the perpendicular geometries were less affected (lowered) compared with the *E* and *Z* ones.

The results are summarized in Figure 4. As regards the Franck–Condon transition energies the agreement with experimental data is fair. The structureless absorption and emission spectra of **1** and **2** make the energy evaluations somewhat ambiguous. The longest wavelength absorption maxima at 153 K (where the vibronic structures in the spectra of **3** are resolved) correspond to the energies 86, 83, and 75 kcal mol^{-1} for **1**, **2**, and **3**, respectively. The Franck–Condon energies similarly estimated from the emission spectra are 64, 66, and 72 kcal mol^{-1}.

A prerequisite for an adiabatic mechanism is that there are no energy minima on the excited-state energy surface in the regions of 90° double bond twists. The calculated energy difference between $^1Zp^*$ and $^1ZZ^*$ (5.1 kcal mol^{-1}) and that between $^1ZE^*$ and $^1Ep^*$ (6.0 kcal mol^{-1}) are remarkably close to the experimentally determined energy barriers for the adiabatic isomerizations of **1** and **2** (4.6 kcal mol^{-1} for both).

For comparison the method of calculation applied to stilbene gives a distinct global minimum for a twisted structure starting from either *cis*- or *trans*-stilbene.

Outlook. The simple extension of the conjugated π-system of stilbene to a *p*-styrylstilbene changes the mechanism for the photoinduced *Z*/*E* isomerization from diabatic to mainly adiabatic processes. This together with previous findings by us and others of adiabatic singlet and triplet *Z*/*E* photoisomerizations encourage us to try to explore the scope and limitations as well as applications of this conceptually new photoreaction in molecules with extended linear or cyclic π-systems.

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Phthalocyaninato Polysiloxanes Substituted with Crown Ether Moieties

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Abstract: We describe the synthesis and characterization of phthalocyaninato polysiloxanes substituted with 15-crown-5, 18-crown-6, and 21-crown-7 rings. The degree of polymerization of the polymer samples depends on the size of the crown ether rings and varies between 6 and 18 units. NMR spectroscopy reveals that the polysiloxanes have a rigid structure with staggered phthalocyaninato (Pc) units. The binding of alkali-metal ions to the plymers and their monomers is reported and discussed. Upon polymerization of the phthalocyaninato dihydroxysilanes the electronic conductivity increases from $<10^{-9}$ to 10^{-7} S/m. The polymer substituted with 21-crown-7 rings conducts sodium ions.

Phthalocyanines (Pc's) substituted with crown ether rings are currently receiving great interest.[1,6] Recently, we reported that these molecules can be aggregated by addition of alkali-metal salts, which become complexed to the crown ether rings.[1b,c] Electrical measurements of the aggregated species revealed an increase in electrical conductivity that is 2–3 powers of 10 higher than that of the nonaggregated ones.

In this paper we report another method of aggregating phthalocyanines.[2] This method, first described by Joyner and Kenney,[3a] involves the polycondensation of a phthalocyaninato dihydroxysilane containing four crown ether rings. In this way a stacked quasi-one-dimensional arrangement of crowned Pc's is achieved in which the central silicon atoms are bridged through O^{2-} ligands (Figure 1). These stacks are expected to transport electrons and ions in the stacking direction: electrons via the central Pc macrocycles and cations via the crown ether moieties. Such compounds when incorporated in vesicle bilayers could be used as synthetic models to mimic both electron and ion channels of natural transport systems.

Substituted and unsubstituted phthalocyaninato polysiloxanes, $[PcSiO]_m$, have been studied by many scientists.[3] Unsubstituted polysiloxanes are formed by the uncatalyzed polycondensation of phthalocyaninato dihydroxysilane for 1–12 h at 440 °C under

Table I. ^{13}C Chemical Shifts of **5c** in Solution and in the Solid State[a]

	C_1,$C_{1'}$	C_4,$C_{4'}$	C_2,$C_{2'}$	C_3,$C_{3'}$	crown ether
solution[b]	151.3	155.0	132.3	108.1	72.4
solid state	151.8	151	129.5	102.5	70.9

[a] In ppm relative to tetramethylsilane. [b] Solvent CD_3OD.

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