

**PHOTOCHEMISTRY OF PHENYLFULGIDES
XX: ABSENCE OF ACTIVATION BARRIERS FOR PHOTO-
ISOMERIZATION REACTIONS IN THE EXCITED SINGLET
STATE OF EXTREMELY STERICALLY HINDERED α,δ -DI-
(4-ALKOXYPHENYL)-FULGIDE ISOMERS[†]**

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Summary

The partial quantum yields of the singlet photoisomerization reactions $EE \xrightleftharpoons[h\nu]{h\nu} EZ \xrightarrow{h\nu} ZZ$ are nearly independent of the solvent polarity and of the temperature in the investigated range down to 110 K. At low temperatures, a barrier to the $ZZ \xrightarrow{h\nu} EZ$ reactions and fluorescence of the ZZ isomers which competes with the isomerization step are observed. Increasing the viscosity of the solutions has no influence on the $EE \xrightarrow{h\nu} EZ$ reaction. Only in rigid polymer matrices is the rate of the reaction $EZ \xrightarrow{h\nu} ZZ$ slightly decreased.

We conclude that the rotation of the 4-alkoxyphenyl groups about the exocyclic double bonds of the investigated *s-cis*-fixed 1,4-di(4-alkoxyphenyl)butadiene systems proceeds without any activation barriers for the isomerization sequence $EE \xrightarrow{h\nu} EZ \xrightarrow{h\nu} ZZ$, this effect being caused by the extreme steric hindrance in the EE and EZ isomers. A potential curve model for the isomerization reactions is given.

1. Introduction

The deactivation behaviour of sterically hindered and similar but sterically non-hindered molecules differs considerably. Probably the most investigated example is stilbene and its derivatives. Thus, no internal activation barrier exists in the excited state of *cis*-stilbene, following the sequence $S_1^{cis} \rightarrow S_{exc}^{perp} \rightarrow S_0^{cis}/S_0^{trans}$ (*cf.* ref. 2). However, there is a barrier of 3.3 kcal mol⁻¹ between S_1^{trans} and S_{exc}^{perp} under collision-free conditions and a barrier of 2 - 4 kcal mol⁻¹ in solution (*cf.* refs. 3 and 4).

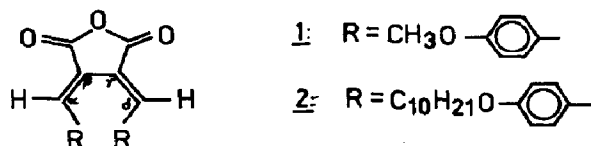
Generally, the introduction of steric hindrance into a phenyl polyene-like molecule produces the following changes. Firstly, the absorption and

[†]For part XIX see ref. 1; this series was started by the late Professor Dr. R. Paetzold.

fluorescence spectra [5] and their temperature dependence [6] can be markedly altered. Secondly, the potentials of the torsional vibration modes in the excited singlet state, which are responsible for the extent of twisting towards the S_{exc}^{perp} state, are expected to be different [2]. This effect is connected with a change in the shape of the excited state potential curves (*i.e.* a reduction or disappearance of activation barriers) for sterically hindered compounds (*cf.* refs. 4 and 7). Moreover, sterically non-hindered molecules have smaller molecular volumes than sterically hindered molecules (*cf.* ref. 4). According to the free volume concept, in the case of sterically hindered molecules the solvent should introduce a smaller external viscosity-dependent activation barrier for the intramolecular torsion in a critical free volume (*cf.* ref. 8).

The quantitative microscopic theories for the internal motion of the bulky parts of a molecule involve a consideration of the frictional forces exerted by the solvents [8 - 12]. Velsko *et al.* [11], by comparing data for several molecules, showed that the effective friction during the rotation process is strongly dependent on the shape of the potential barrier. Therefore, using these microscopic theories, strong differences ought to be found between the isomerization rates of sterically non-hindered and sterically hindered molecules.

The aim of this work is to investigate the activation barriers that exist in the course of the photoisomerization, starting with the EE isomers of compounds 1 and 2.



It is expected that extreme steric hindrance, particularly in the EE isomers and to a smaller extent in the EZ isomers (*cf.* Fig. 1), causes considerably altered photochemical and photophysical properties in comparison with sterically less hindered molecules such as, for instance, the ZZ fulgide isomers or *cis*-stilbene and α -methylstilbenes (*cf.* refs. 4 and 13). Furthermore, a larger free volume is necessary in the course of the rotation processes of the 4-decyloxyphenyl substituents (compound 2) than with the 4-methoxyphenyl substituents (compound 1). Therefore we expect different rotation rates about the exocyclic double bonds for 1 and 2. In this paper the experimental results under steady irradiation will be discussed. Another paper is concerned with the time-resolved absorption measurements on the picosecond time scale [14].

The thermal and photochemical reaction mechanisms of phenylfulgides are complicated [15 - 18] and are strongly influenced by the nature of the phenyl substituents [19]. Figure 1 shows the mechanism accepted for 4-alkoxy-substituted compounds. The EE isomers are prepared as pure substances by means of the Stobbe condensation according to ref. 15. Electrocyclic ring closure is suppressed by the electronic influence of the 4-alkoxy

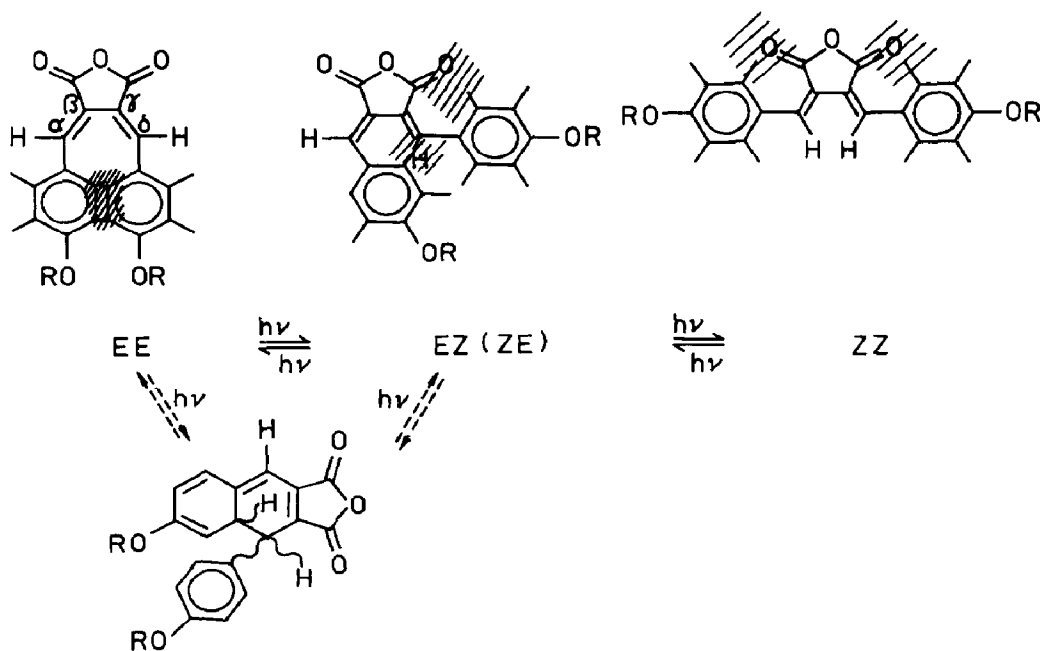


Fig. 1. Isomerization mechanism and regions of steric hindrance in 4-alkoxyphenyl fulgides 1 and 2 (1, R \equiv CH₃; 2, R \equiv C₁₀H₂₁).

substituents ($\phi_{\text{cyc}} < 10^{-5}$) [18, 20]. Furthermore, we could not detect dimerization reactions (concentrations up to 10^{-1} mol l⁻¹) of either compound in isotropic solvents [21]. Because of this simplified reaction mechanism compounds 1 and 2 were selected for investigation. To date, however, there have been no results concerning the dependence of the partial quantum yields of these compounds on irradiation wavelength, solvent polarity, viscosity or temperature.

2. Experimental details

The compounds under study were prepared and purified as described elsewhere [15, 22]. As solvents we used Uvasol quality (Merck, Darmstadt) cyclohexane and benzene. Toluene, 2-methyltetrahydrofuran (2-MTHF) and acetonitrile were purified by following standard procedures [23]. The triplet sensitizers and quenchers were recrystallized four or five times or were commercial samples. The solutions for the sensitization and quenching experiments were degassed by bubbling argon through them for 20 min. The sensitizer absorbed more than 99% of the irradiation light in the sensitization experiments. Polystyrene films containing 1 and 2 were prepared from liquid polymer solutions in toluene. The film thicknesses were about 100 μm and therefore concentrations of 10^{-3} mol l⁻¹ of 1 and 2 were used. The films were air dried or in some cases were dried at 310 K for 5 h *in vacuo*.

For the UV-visible absorption measurements a Cary 17 spectrometer (Varian) and a microprocessor-controlled M 40 (VEB, Carl Zeiss, Jena) were employed. The low temperature equipment has been described previously [24]. The irradiations were performed using stabilized high pressure mercury lamps (HBO 200, Narva, Berlin) in combination with a high intensity monochromator (Bausch & Lomb). The light intensities were determined using a stirred homogeneously irradiated sample cuvette by means of a Parker actinometer [25].

The methods generally employed for the calculation of molar absorption coefficients and isomer concentrations are described in ref. 26. For 1 and 2, the spectra of the EE and EZ isomers were calculated using the concentration ratios of the isomer mixtures determined using proton nuclear magnetic resonance spectroscopy (*cf.* ref. 1). Fractional crystallization (described in ref. 15) was not performed. The molar absorption coefficients of the EE, EZ and ZZ isomers at different temperatures were calculated using the spectra of cooled solutions of photostationary mixtures formed at 293 K and the isomer concentration ratios which are known. The spectra were corrected with respect to volume contraction and in some cases for changes in the refractive index.

The fluorescence spectra were recorded by means of a correcting FICA 55 spectrofluorometer-phosphorometer (ARL, France). Using a liquid-nitrogen filled quartz Dewar, the fluorescence quantum yields were determined relative to Rhodamine B ($\phi_F^{77} \approx 1$) as the internal standard (solvent, 2-MTHF).

3. Results

3.1. Temperature dependence of the absorption spectra

It is known that the intensities of the long wavelength absorption bands increase in the EE, EZ and ZZ series of fulgide isomers [15, 17, 19].

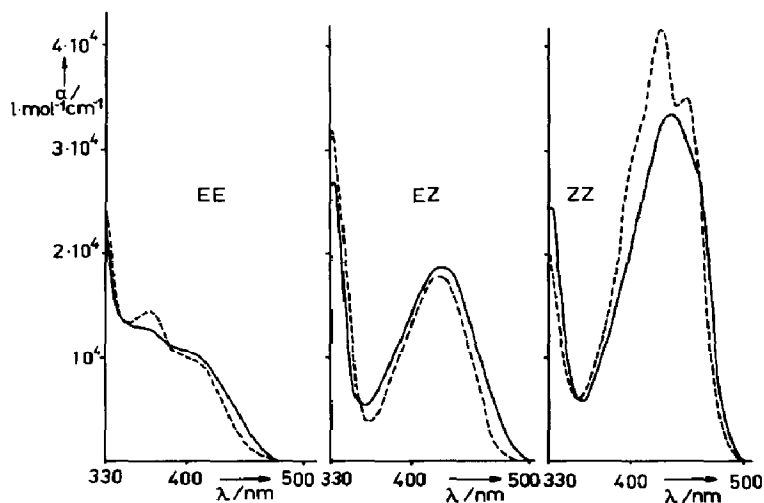


Fig. 2. Isomer absorption spectra of 1 in 2-MTHF at 293 K (—) and 110 K (---).

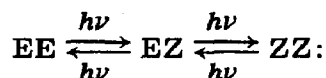
The nature of the electronic transitions has recently been investigated [27]. To determine the temperature dependence of the quantum yields we calculated the isomer absorption coefficients at different temperatures. Furthermore, from these values we can determine the relative extent of steric hindrance in the series of isomers (*cf.* ref. 6).

Figure 2 shows the absorption spectra of the EE, EZ and ZZ isomers of compound 2 in 2-MTHF solution at 293 K and 110 K. The spectra of 1 and 2 are nearly identical. On lowering the temperature, vibrational structure appears in the ZZ spectrum of both 1 and 2 and the absorption coefficients increase. However, the EZ absorption coefficients of 1 and 2 remain nearly constant. In the case of the EE isomers the $S_1 \leftarrow S_0$ long wavelength intensity decreases and the $S_2 \leftarrow S_0$ absorption intensity increases.

3.2. Photoisomerization under direct irradiation

3.2.1. Solvent polarity and temperature dependence of the partial quantum yields

For a stirred and homogeneously and monochromatically irradiated cuvette, the following equations [28] describe the dependence on the irradiation time of the concentrations of the components of the system



$$\frac{dc_{EE}}{dt} = (-\alpha'_{EE}c_{EE}\phi_{EZ}^{EE} + \alpha'_{EZ}c_{EZ}\phi_{EE}^{EZ})F' \quad (1)$$

$$\frac{dc_{EZ}}{dt} = \{\alpha'_{EE}c_{EE}\phi_{EZ}^{EE} - \alpha'_{EZ}c_{EZ}(\phi_{EE}^{EZ} + \phi_{ZZ}^{EZ}) + \alpha'_{ZZ}c_{ZZ}\phi_{EZ}^{ZZ}\}F' \quad (2)$$

$$\frac{dc_{ZZ}}{dt} = (\alpha'_{EZ}c_{EZ}\phi_{ZZ}^{EZ} - \alpha'_{ZZ}c_{ZZ}\phi_{EZ}^{ZZ})F' \quad (3)$$

where α'_i is the absorption coefficient at the irradiation wavelength of the *i*th component and $F' = I_0(1 - 10^{-A_{\lambda'}})/A_{\lambda'}$ ($A_{\lambda'}$ is the absorbance at the irradiation wavelength and I_0 (einstein $\text{cm}^{-2} \text{s}^{-1}$) is the irradiation intensity). Equations (1) - (3) cannot be integrated analytically. Therefore the partial quantum yields ϕ'_i were calculated by the formal integration method developed by Mauser [28]. The results of the so-called forward integration ($t_0 \rightarrow t_n$) are collected in Table 1 for different solvents and irradiation wavelengths. The solvent polarity shows no systematic influence, but for longer irradiation wavelengths the values ϕ_{EE}^{EZ} of compound 1 and ϕ_{ZZ}^{EZ} and ϕ_{EZ}^{ZZ} of both 1 and 2 become significantly lower on increasing the solvent polarity. It should also be noted that for compound 2 the ϕ_{EE}^{EZ} increase and the ϕ_{ZZ}^{EZ} decrease on changing the irradiation wavelength from 313 nm to 436 nm.

As a first step the temperature dependence of the photoisomerization reactions can be demonstrated qualitatively. A comparison between the

TABLE 1

Partial quantum yields of direct isomerization of 1 and 2 ($T = 293$ K; estimated error, $\pm 15\%$)

Compound (solvent)	λ' (nm)	ϕ_{EE}^{EE}	ϕ_{EE}^{EZ}	ϕ_{EZ}^{EZ}	ϕ_{ZZ}^{ZZ}
1 (toluene)	313	0.29	0.18	0.12	0.56
	333	0.30	0.18	0.10	0.46
	365	0.25	0.21	0.20	0.47
	405	0.26	0.09	0.23	0.50
	436	0.26	0.06	0.14	0.36
1 (acetonitrile)	313	0.30	0.22	0.16	0.43
	333	0.30	0.13	0.10	0.16
	366	0.31	0.13	0.08	0.21
	405	0.30	0.09	0.08	0.18
	436	0.29	0.07	0.07	0.16
2 (cyclohexane)	365	0.30	0.04	0.07	0.21
2 (toluene)	313	0.30	0.010	0.10	0.38
	333	0.28	0.015	0.10	0.43
	365	0.27	0.024	0.07	0.22
	405	0.27	0.045	0.03	0.14
	436	0.30	0.056	0.02	0.11
2 (acetonitrile)	313	0.28	0.006	0.14	0.32
	365	0.29	0.06	0.10	0.28

reaction spectra at 293 K (*cf.* Fig. 3(a)) and at 110 K (*cf.* Fig. 3(b)) shows that long wavelength irradiation ($\lambda' = 436$ nm) at low temperatures also leads to photostationary states (PSS) with high ZZ concentrations. The spectra of the PSS reached under irradiation at different wavelengths are very similar at 110 K. This behaviour is observed for both 1 and 2.

The exact determination of the partial quantum yields presents some difficulty for the EE-EZ-ZZ three-component system at low temperatures (*cf.* ref. 29). Because it is impossible to stir the solutions, one important condition for the validity of eqns. (1) - (3) is not fulfilled. However, it is possible to calculate the partial quantum yields with the necessary accuracy using sample solutions of low concentration ($A_{\lambda} \leq 0.2$). In this manner, marked concentration gradients can be avoided. We also calculated the quantum yields ϕ_{EZ}^{EE} by the initial slope method. For the reaction $EE \xrightarrow{h\nu} EZ$ the following equation holds:

$$\left. \frac{dA_{\lambda}}{dt} \right|_{t=0} \approx - \frac{dc_{EE}}{dt} \alpha_{\lambda EE} + \frac{dc_{EZ}}{dt} \alpha_{\lambda EZ}$$

$$\approx (\alpha_{\lambda EZ} - \alpha_{\lambda EE}) F' \alpha'_{EE} c_0 \phi_{EZ}^{EE} \quad (4)$$

The quantum yields calculated by means of eqns. (1) - (4) are collected in Table 2 for different temperatures in 2-MTHF solution. No (or negligible)

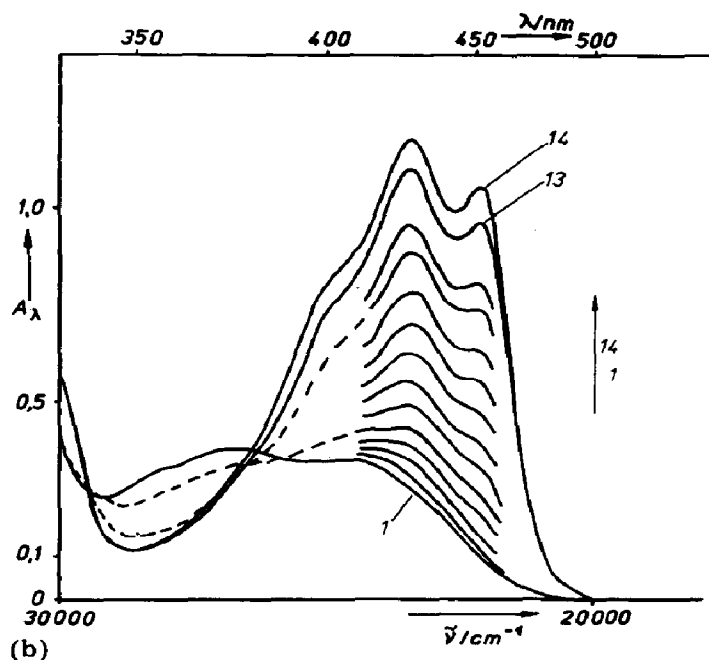
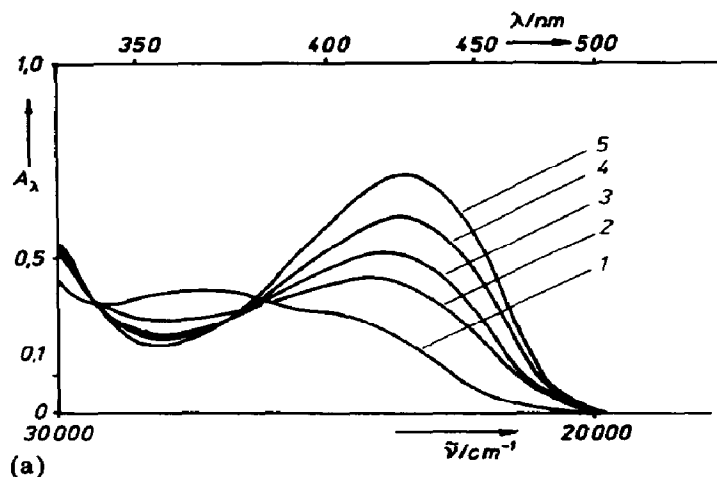


Fig. 3. (a) Spectra of photostationary states of 1 in 2-MTHF at 293 K (curve 1, EE isomers; curve 2, $\lambda' = 436$ nm; curve 3, $\lambda' = 405$ nm; curve 4, $\lambda' = 366$ nm; curve 5, $\lambda' = 313$ nm). (b) Change in the spectra of 1 under direct irradiation at 110 K (curve 1, EE isomers; curves 2 - 13, prolonged irradiation at $\lambda' = 436$ nm; curve 13, PSS; curve 14, PSS with $\lambda' = 313$ nm).

temperature dependence of the ϕ_{EE}^{EE} , ϕ_{EE}^{EZ} and ϕ_{ZZ}^{EZ} values is observed. However, the quantum yields ϕ_{ZZ}^{ZZ} clearly decrease at low temperatures.

3.2.2. Qualitative investigation of the viscosity dependence

The influence of polymer matrices on the photoisomerizations was investigated in the following manner. Polystyrene films and toluene solutions in sample cells of path length 0.5 mm were irradiated with the same

TABLE 2

Temperature dependence of the partial quantum yields (2-MTHF solution; $\lambda = 365$ nm; estimated error, $\pm 15\%$)

Compound	T (K)	Equations (1) - (3)				Equation (4)
		ϕ_{EE}^{EE}	ϕ_{EE}^{EZ}	ϕ_{ZZ}^{EZ}	ϕ_{ZZ}^{ZZ}	ϕ_{EE}^{EZ}
1	293	0.3 ₀	0.1 ₀	0.07 ₀	0.2 ₁	0.3 ₅
	233	0.2 ₉	0.2 ₉	0.07 ₁	0.1 ₉	0.3 ₀
	211	0.2 ₉	0.3 ₀	0.06 ₂	0.1 ₇	0.3 ₂
	198	0.2 ₈	0.3 ₅	0.06 ₈	0.1 ₇	0.3 ₁
	161	0.3 ₁	0.1 ₉	0.06 ₉	0.1 ₃	0.3 ₅
	110	0.3 ₀	0.1 ₉	0.06 ₀	0.0 ₆	0.3 ₅
2	293	0.3 ₀	0.1 ₀	0.08 ₀	0.1 ₈	0.3 ₃
	218	0.2 ₉	0.1 ₀	0.07 ₈	0.1 ₂	0.3 ₂
	193	0.2 ₈	0.09 ₆	0.07 ₈	0.08 ₇	0.2 ₉
	173	0.2 ₉	0.1 ₀	0.08 ₁	0.06 ₈	0.2 ₉
	153	0.2 ₉	0.09 ₃	0.07 ₈	0.05 ₂	0.3 ₂
	112	0.2 ₅	0.05 ₀	0.07 ₀	0.00 ₉	0.3 ₃

light intensity. The absorbance at the irradiation wavelength was adjusted so as to be equal for all samples. Under these conditions we obtained comparable absorbance time curves $A_\lambda = f(I_0 t)$ for the liquid solution and the polymer matrix. Figure 4 shows these plots for different samples of 2. It is observed that the initial slope ($EE \xrightarrow{h\nu} EZ$ isomerization step) is identical for all the viscosities. In the solid polymer matrix only the ZZ concentration is lowered in the PSS (cf. Fig. 4, curves 2 - 4).

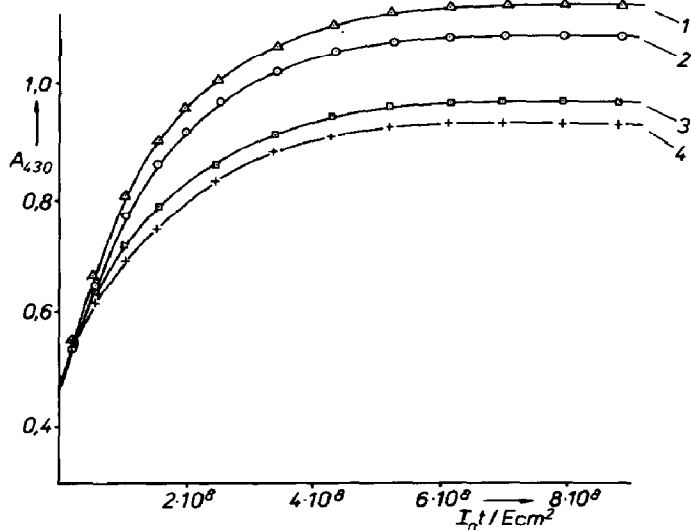


Fig. 4. Absorbance plots $A_{430} = f(I_0 t)$ of 2 starting with pure EE isomers ($\lambda = 366$ nm): curve 1, toluene solution; curve 2, toluene-50wt.% polystyrene; curve 3, air-dried polystyrene film; curve 4, vacuum-dried polystyrene film.

3.3. Quenching and sensitization experiments

Degassing the solutions or adding the triplet quencher ferrocene at both 293 K and 77 K has no significant effect on the partial quantum yields of the direct isomerization reactions. Moreover, no dependence on the total concentration is observed in the investigated range of 10^{-6} - 10^{-1} mol l⁻¹.

The reaction $EE \rightleftharpoons ZZ$ can be induced by triplet sensitizers at 293 K. This reaction does not pass through the EZ isomers, as is shown by the reaction spectra in Fig. 5 (e.g. compound 1). In the case of naphthalene-sensitized isomerization (Fig. 5(a)) an isosbestic point appears at 381.1 nm (i.e. the EE-ZZ-spectra cross-over). In contrast to this the cross-overs of the reaction spectra induced by direct irradiation range from 383.5 nm (the cross-over of the EE-EZ spectra) to 382.2 nm (cf. Fig. 5(b)). This behaviour is caused by the three-component reaction sequence $EE \xrightleftharpoons{h\nu} EZ \xrightleftharpoons{h\nu} ZZ$.

To determine the energy of the common triplet state of the EE and ZZ isomers we have utilized the Saltiel plot (Fig. 6, e.g. 2). A triplet energy

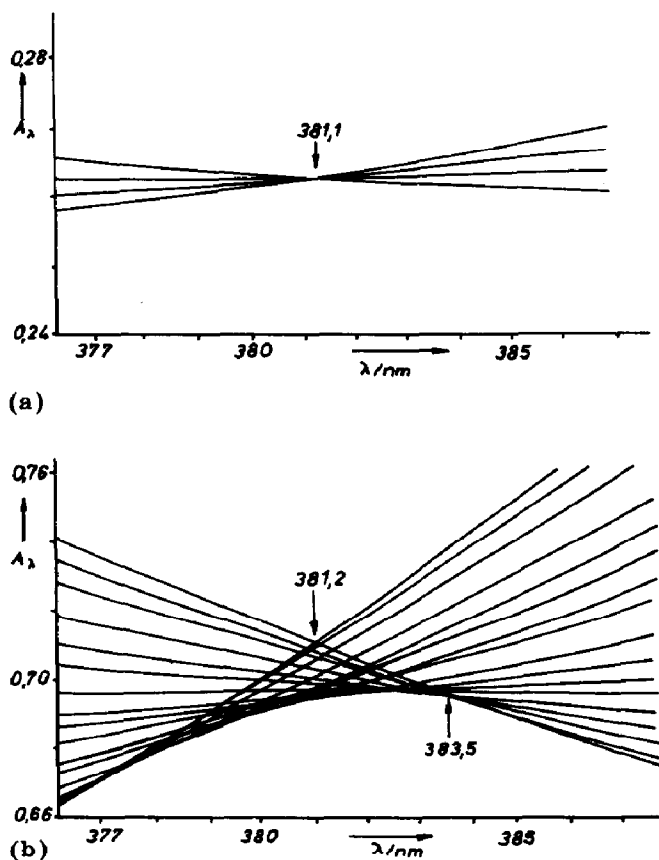


Fig. 5. Expanded ranges of isomerization spectra of 1 in degassed toluene solution starting with pure EE isomers at 293 K: (a) naphthalene-sensitized reaction ($\lambda' = 313$ nm; $c_{\text{naphth}} = 10^{-2}$ mol l⁻¹); (b) direct irradiation ($\lambda' = 366$ nm).

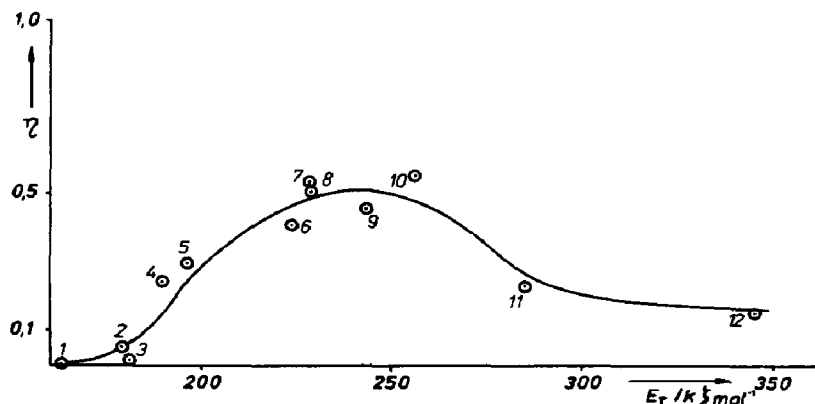


Fig. 6. Saltiel plot $\eta = c_{ZZ}/c_0 = f(E_T)$ of **2** (starting with pure EE isomers in degassed cyclohexane solution). Sensitizers: 1, azulene; 2, perylene; 3, ferrocene; 4, anthracene; 5, acridine; 6, fluorenone; 7, benzil; 8, coronene; 9, chrysene; 10, naphthalene; 11, fluorene; 12, toluene.

of nearly 240 kJ mol^{-1} ($57.3 \text{ kcal mol}^{-1}$) is observed for both 1 and 2, and this lies in the range of triplet energies for other phenylfulgides [18].

3.4. Luminescence behaviour

The EE and EZ isomers do not show any luminescence in the temperature range 293 - 77 K. Only the ZZ isomers fluoresce weakly at 77 K, with $\phi_F^{1-ZZ} \approx 2 \times 10^{-4}$ and $\phi_F^{2-ZZ} \approx 10^{-4}$. In Fig. 7 the normalized fluorescence and fluorescence excitation spectra, which are in agreement with the ZZ absorption spectra, are shown. The ZZ fluorescence disappears at temperatures above 130 K.

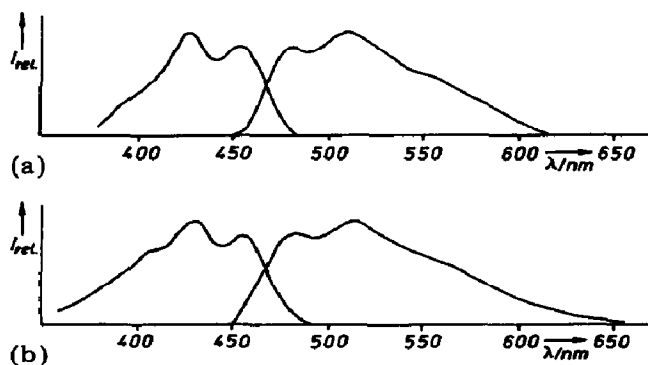


Fig. 7. Normalized fluorescence and fluorescence excitation spectra of (a) 1-ZZ and (b) 2-ZZ, both in 2-MTFH at 77 K.

3.5. Electron spin resonance investigations

We could not observe any triplet or radical signal under stationary irradiation at 77 K using the electron spin resonance equipment described previously [30].

4. Discussion

The direct photoisomerizations $EE \xrightleftharpoons[h\nu]{h\nu} EZ \xrightleftharpoons[h\nu]{h\nu} ZZ$ are singlet state reactions as shown by their independence of O_2 concentration and added triplet quenchers. The isomerization step $EE \rightleftharpoons ZZ$ can be induced only by triplet sensitizers. The isomerization steps $EE \rightleftharpoons EZ \rightleftharpoons ZZ$ are impossible in the triplet state, as was also shown for other diene systems [31].

The quantum yields ϕ_{EZ}^{EE} are independent of the solvent polarity and irradiation wavelength. In contrast, the quantum yields ϕ_{EE}^{EZ} , ϕ_{ZZ}^{EZ} and ϕ_{EZ}^{ZZ} show a marked irradiation-wavelength dependence. We assume that EZ and ZZ species, with different phenyl torsion angles, possess different absorption spectra and that therefore it is this that causes the observed irradiation-wavelength dependence of the quantum yields (*cf.* ref. 32). The irradiation-wavelength independence of the ϕ_{EZ}^{EE} values is in agreement with the restricted 4-methoxyphenyl rotation in the S_0 state of the 1-EE isomers [33].

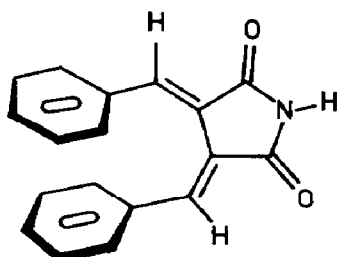
Furthermore, we know that the isomerization rates of the $EE \xrightarrow{h\nu} EZ$ and $EZ \xrightarrow{h\nu} ZZ$ steps are ultrafast [14]. Therefore isomerization steps starting within the S_2 state may also be possible. In this case the rotation process must compete with $S_2 \rightarrow S_1$ internal conversion (*cf.* ref. 32 and examples cited therein). The quantum yields for compound 2 indicate that the reaction step $EZ \xrightarrow{h\nu} EE$ occurs to a greater extent on excitation to S_1 whereas the $EZ \xrightarrow{h\nu} ZZ$ step proceeds to a greater extent on excitation to S_2 or higher states. Whether a reaction from an upper excited singlet state is possible or not will be discussed in detail later.

Within the limit of experimental error the quantum yields ϕ_{EZ}^{EE} , ϕ_{EE}^{EZ} and ϕ_{ZZ}^{EZ} are temperature independent. Therefore no activation barrier due to internal or external (*i.e.* induced by the environment) causes exists in the excited state for these processes. In contrast, there must be a barrier for the excited state process $S_1^{ZZ} \rightarrow S_{exc}^{pexp}$ because of the clear temperature dependence of the ϕ_{EZ}^{ZZ} and because of the temperature dependence of the competing ZZ fluorescence. The high ZZ concentrations in the PSS mixtures at low temperatures (*cf.* Fig. 3) are the result of decreased quantum yields ϕ_{EZ}^{ZZ} . No indications could be found for intersystem crossing processes at low temperatures. In rigid polymer matrices the concentration of ZZ isomers in the PSS is reduced whereas the reaction $EE \xrightarrow{h\nu} EZ$ remains unaffected (*cf.* Fig. 4). Obviously the free volume of the matrix is sufficient for EZ isomers of both 1 and 2 to be formed. Only for the $EZ \xrightarrow{h\nu} ZZ$ reaction does a matrix-induced barrier arise because of the necessarily greater critical volume for this isomerization step.

To date there are neither experimental nor theoretical data on the shape of the potential curves for the torsion angles of $\alpha-\beta$ and $\gamma-\delta$ bonds in both the ground and the excited singlet states. Therefore only a first qualitative isomerization model can be given in terms of the stilbene isomerization model (*cf.* refs. 3, 34 and 35).

The ground state enthalpy difference between EE, EZ and ZZ isomers could not be determined exactly by direct measurements [21] but the

temperature dependence of the isomer absorption spectra gives a direct indication of the different extents of steric hindrance. In the case of ZZ isomers the reduction in the distortion of 4-alkoxyphenyl groups, because of less steric hindrance, results in a higher absorption intensity at low temperatures (*cf.* Fig. 2). For the EZ isomers and especially for the EE isomers such a reduction in the phenyl torsion angles is impossible because of the higher steric hindrance. It can be concluded that the ground state energy increases in the order $ZZ < EZ < EE$. Furthermore, utilizing the QCFF/PI procedure [36], the equilibrium geometries and the corresponding energies of the EE, EZ and ZZ isomers of the hypothetical molecule 3



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in the electronic ground state were calculated by Sühnel *et al.* [37]. It was calculated that the ZZ isomer is the most stable, followed by the EZ and EE isomers. The energy differences are $U_{EE}^0 - U_{EZ}^0 = 7.2 \text{ kcal mol}^{-1}$ and $U_{EZ}^0 - U_{ZZ}^0 = 3.4 \text{ kcal mol}^{-1}$.

Provided that the ground state energy differences of the isomers are identical for 1, 2 and 3 the corresponding energy differences in the S_1 state can be easily calculated on considering the $S_1 \leftarrow S_0$ transition energies, which are known experimentally (*cf.* Table 3). The results for 1 and 2 are similar and for 1 we get $U_{EE}^1 = U_{EZ}^1 + 9.5 \text{ kcal mol}^{-1} = U_{ZZ}^1 + 18.1 \text{ kcal mol}^{-1}$.

In principle the isomerization behaviour of 1 and 2 is the same as that of a "two-bond four-component" system (*cf.* ref. 31). Of course, the isomers EZ and ZE are identical for 1 and 2. But for the sake of completeness we

TABLE 3

$S_1 \leftarrow S_0$ transition energies of isomers of 1 and 2 at 110 K

Isomer	$U(S_1 \leftarrow S_0)$ (nm)	Remark
1-EE	408	Absorption maxima of separated S_1-S_0 transitions assuming a gaussian band shape
2-EE	409	
1-EZ	422	Long wavelength absorption maxima
2-EZ	424	
1-ZZ	455	0,0 transitions
2-ZZ	457	

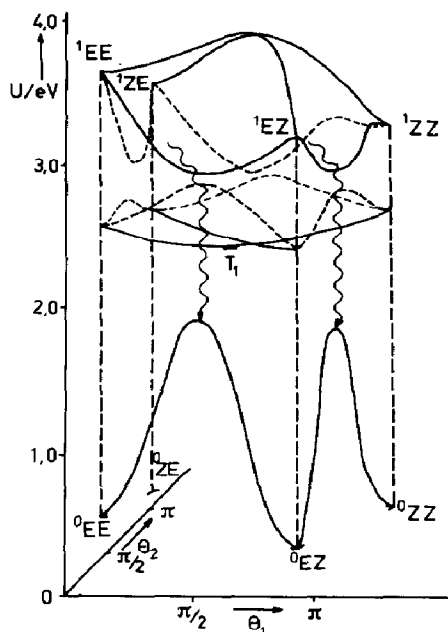


Fig. 8. Assumed potential curves $U = f(\Theta_1, \Theta_2)$ for the EE-EZ-ZE-ZZ two-bond four-component system (Θ_1 and Θ_2 , torsion angles about the α - β and γ - δ bonds).

shall take into account both isomers. Figure 8 shows the assumed potential curves. The three-dimensional plot involves the torsion angles Θ_1 and Θ_2 about the exocyclic α - β and γ - δ bonds as reaction coordinates. The heights of the ground state torsion barriers were assumed to be 25 - 30 kcal mol⁻¹. An energy gap between the $S_{\text{exp}}^{\text{erp}}$ and S_0^{erp} states of about 1 eV was assumed.

For the triplet manifold we have only determined the energy of a triplet state along the EE \rightleftharpoons ZZ isomerization reaction coordinate. The precise isomer triplet energies are as yet unknown. The triplet isomerization step EZ \rightleftharpoons ZE cannot be observed spectroscopically and it appears to only be a deactivation channel.

In summary, it is worth noting that the heights of the activation barriers for the isomerization reactions in the excited singlet state of phenyl polyenes can be decreased by three effects: (i) introducing steric hindrance into the molecule (*cf.* ref. 7), (ii) increasing the conjugation within the molecule (*cf.* ref. 3) and (iii) alteration of the solvent polarity because A_g and B_u states differ in their polarity (*cf.* ref. 38). The fact that crossing of these states is avoided introduces the activation barriers on the potential curves, *e.g.* for stilbene and 1,4-diphenylbutadiene [3, 34].

Our experimental finding that in the case of compounds 1 and 2 no internal activation barriers exist for the singlet reactions $\text{EE} \xrightleftharpoons[h\nu]{} \text{EZ} \xrightarrow{h\nu} \text{ZZ}$

can be understood in terms of (i) and (ii). For (iii) we have no clear indication. Moreover, the rotation of the EE and EZ 4-alkoxyphenyl groups

(motion following the arrows in Fig. 8) should proceed on excited state potential curves with a marked curvature $dU/d\Theta_{1(2)} < 0$. It is thought that this curvature is more marked than in the case of *cis*-stilbene because of the larger steric hindrance. The consequences of this supposed potential-curve shape will be discussed in a following paper [14] in which we shall report on the direct determination of the isomerization rate constant.

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