PHOTOCHEMISTRY OF PHENYLFULGIDES[†]
XXI: ULTRAFAST PHOTOISOMERIZATION AND RADIATIONLESS DEACTIVATION PROCESSES IN α,δ-DI-(4-ALKOXYPHENYL)-FULGIDES AND α,δ-BIFLUORENYLFULGIDES

H.-D. ILGE

Sektion Chemie, Friedrich-Schiller-Universität, 6900 Jena (G.D.R.)

M. KASCHKE and D. KHECHINASHVILI

Sektion Physik, Friedrich-Schiller-Universität, 6900 Jena (G.D.R.)

Summary

The photoisomerization processes of two α,δ-di-(4-alkoxyphenyl)-fulgides **1** and **2** and the radiationless deactivation processes of an α,δ-bifluorenylfulgide **3** were investigated by means of a picosecond excite-and-probe beam spectrometer. For **1** and **2** an ultrafast formation of EZ and ZZ isomers in the reaction sequence EE $\xrightarrow{h\nu}$ EZ $\xrightarrow{h\nu}$ ZZ was observed for $\tau \leqslant 5$ ps. These reactions due to the rotation of the bulky molecular parts may be the fastest which have been observed up to date. Compound **3** exhibits ground state bleaching in the spectral range of the $S_1 \leftarrow S_0$ transition with a recovery time of 12 ps. The observed $(S_n, n \geqslant 3) \leftarrow S_1$ excited state absorption disappears with the same decay time. The results are discussed in terms of the photoisomerization model used previously in the case of stilbene. Because of the large degree of steric hindrance in the EE and EZ isomers of **1** and **2** and in compound **3**, the torsion about the ethylenic bonds to give perpendicular states which interact strongly and non-adiabatically with the ground state is considered to occur with a strong intramolecular driving force in the excited state, for which no activation barriers could be observed.

1. Introduction

The rate of photoisomerization about polyenic and polymethinic double bonds is sensitive to the shape of the excited state intramolecular potential curve for the isomerization reaction. In sterically non-hindered molecules such as, for example, *trans*-stilbene, the model of isomerization [2] assumes an initial barrier crossing followed by a motion into a "funnel"
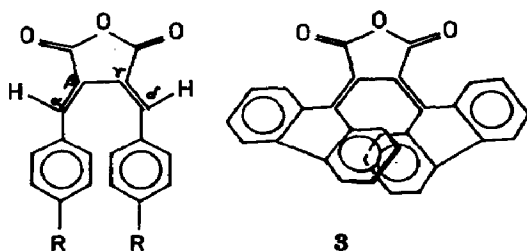

[†]For part XX see ref. 1.

of the one-dimensional or multidimensional excited state surface (see ref. 3 and references cited therein), from which, because of strong non-adiabatic interaction, very rapid radiationless deactivation to the ground state is very likely to take place. In terms of this model it is generally assumed that the crossing of the intramolecular barrier is the rate-limiting step for the deactivation of such molecules.

Both the introduction of steric hindrance into a molecule [4] and an increase in conjugation of the system [5] lead to a decrease in or even the disappearance of the excited state rotational barrier. These effects can be understood because the height of the barrier on the excited state potential surface depends on the relative energy of the excited B_u and A_g states (cf. ref. 5 and references cited therein). The fact that crossing of these states is avoided causes the appearance of the activation barrier, as, for example, in the case of trans-stilbene [2]. Comparing the potential curves for the reaction sequences (excited trans-stilbene → perpendicular state) and (excited cis-stilbene → perpendicular state) it can be seen (cf. refs. 2 and 5) that on starting with the sterically crowded cis-stilbene the activation barrier disappears. A similar effect has been found in the case of sterically hindered trans-α-methylstilbene and its derivatives, for which reduced fluorescence quantum yields (with respect to sterically non-hindered trans-stilbene) and temperature-independent isomerization quantum yields have been obtained [4].

Furthermore, the increase in the conjugation of the polyene-like molecules (e.g. styrene, trans-stilbene and diphenylbutadiene) causes a decrease in the relative energy of the B_u and A_g states and therefore the barrier height is reduced [5, 6].

The purpose of this paper is the investigation of the rates of rotation about ethylenic bonds in the extremely sterically hindered arylfulgides 1 - 3 (cf. Fig. 1). It has been shown [1, 7] that isomerization reactions (cf. Fig. 2) possess the highest efficiency within the fulgide system. Thus, the EE and EZ isomers of 1 and 2, and the compound 3, do not fluoresce in the temperature range 293 - 77 K, whereas the ZZ isomers exhibit weak

1: R = CH₃O

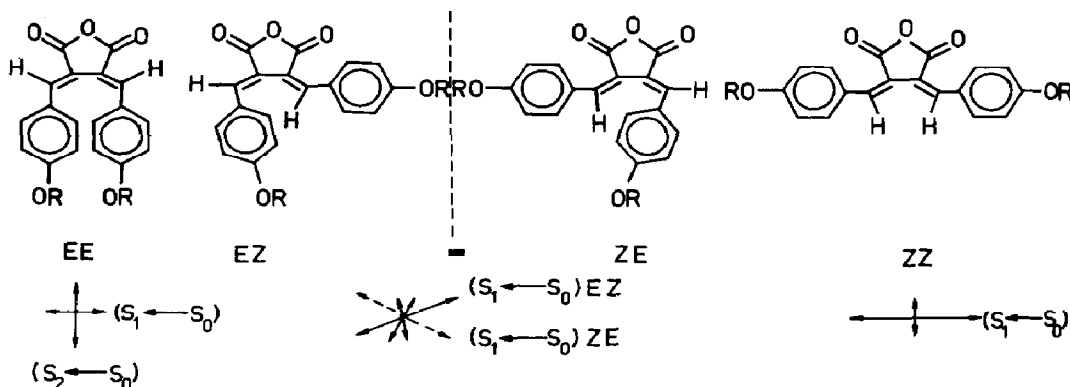2: R = C₁₀H₂₁O

Fig. 1. Structure of compounds studied.

Fig. 2. Polarization directions of $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ electronic transitions of orientational unrelaxed isomers of 1 and 2 (the length of the arrows is proportional to the magnitude of the Pariser–Parr–Pople-calculated transition moments [8]).

fluorescence at 77 K. Furthermore, no intersystem crossing processes could be observed for 1 - 3. For compound 3 no isomers with s-cis-fixed butadiene structure are possible. The compound undergoes a weak photolytic reaction (an electrocyclic ring-closure reaction [7], quantum yield $\phi_{\text{photol}} < 10^{-4}$) which is, however, negligible for our investigations.

Because of the extreme steric hindrance in the EE and EZ isomers there is no activation barrier in the excited singlet state of 1 and 2 for the reaction sequence EE $\xrightarrow{h\nu}$ EZ $\xrightarrow{h\nu}$ ZZ (cf. ref. 1) and we expect a very rapid rotation to take place in the excited states of these isomers. We have therefore studied the isomer formation of these compounds on intense picosecond excitation by means of a picosecond excite-and-probe beam spectrometer. The spectral changes observed on picosecond excitation were compared with UV–visible absorption measurements under stationary irradiation.

2. Experimental details

The compounds under study were prepared as described in a previous paper [7]. The solvent toluene was of Uvasol quality. The picosecond excite-and-probe beam spectrometer, which is driven by a neodymium phosphate glass laser, is depicted schematically in Fig. 3 [9]. From the pulse train of a passively mode-locked neodymium phosphate glass oscillator (1) a single pulse ($\tau_p \approx 5$ ps) is selected by means of a Pockels cell. After passing through a two-stage amplifier (3) the main part (90%) of the amplified single pulse ($\lambda = 1054$ nm, $E = 20$ mJ) is frequency-converted to the second harmonic ($\lambda = 527$ nm, $E = 5$ mJ) and to the third harmonic ($\lambda = 351$ nm, $E = 0.6$ mJ). These light pulses of the portion split from the fundamental pulse (4) serve as excitation beams. The remaining part, after further amplification (9) of the split fundamental wave pulse (4), generates the picosecond broad band continuum in a 10 cm cuvette containing D_2O
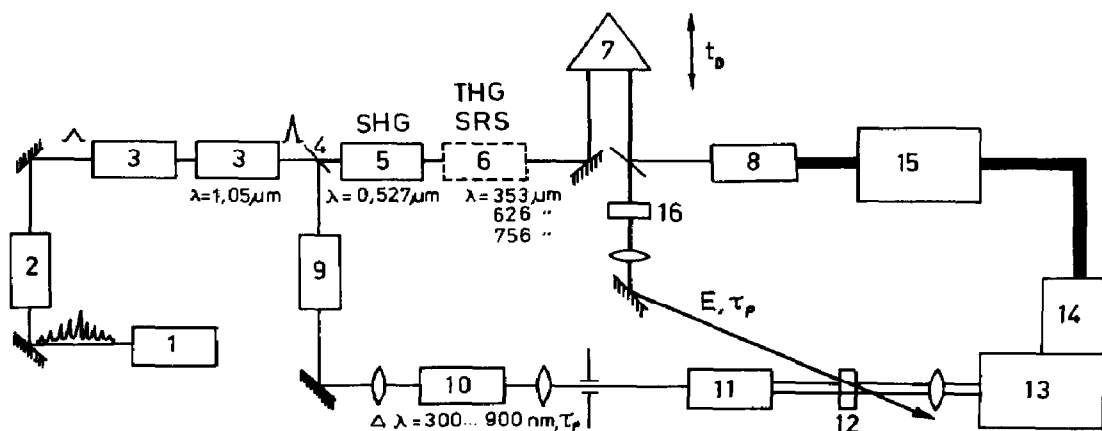
Fig. 3. Picosecond excite-and-probe beam spectrometer: 1, passively mode-locked neodymium phosphate glass oscillator; 2, Pockels cell; 3 and 9, amplifiers; 4 and 11, beam splitters; 5 and 6, frequency converters; 7, delay distance, prism; 8, detector; 10, D_2O cuvette; 12, sample; 13, spectrograph; 14, vidicon; 15, OMA II; 16, polarizer.

(10). The picosecond continuum covers a wavelength range of 300 - 900 nm and is used as an interrogation beam after having been split into a probe beam and a reference beam (11) which probe the transmission of the excited and unexcited sample volume (12). Both light pulses are focused onto the entrance slit of a spectrograph (13) and detected by using a vidicon (14; range of sensitivity, 400 - 1100 nm) of an optical multichannel analyser (15) (PAR OMA II). The spectral resolution of this arrangement amounts to 2 nm in an overall spectral range of 250 nm. The probe beam can be delayed (7) and altered in polarization (16). Throughout the measurements parallel polarization of the continuum with respect to the excitation is used. The automatic registration by the optical multichannel analyser contains a special procedure for the discrimination of the excitation pulse energy (8) and the pulse duration. The time resolution of this equipment is better than 6 ps. A registration accuracy of 2% for the changes in transmission is obtained by accumulation of 15 laser shots. To ensure that each shot finds the sample in its original state and to exclude any effects arising from irreversibly formed photoproducts a flow-through cuvette was used.

3. Results

The EE and ZZ isomers of 1 and 2 and compound 3 possess C_{2v} symmetry (within the nuclear magnetic resonance time scale, cf. ref. 10). Therefore an alternating orientation (perpendicular, parallel, perpendicular etc.) of the transition moments results ($S_1 \leftarrow S_0$, $S_2 \leftarrow S_0$, $S_3 \leftarrow S_0$ etc.) with respect to the molecular coordinate system [11]. Thus, the polarization of the continuum with respect to the excitation was chosen according to the spectral range and the polarization of the transitions to be followed.

Compound **3** was excited by the second harmonic, ($\lambda_{exc} = 527$ nm) which only allows $S_1 \leftarrow S_0$ transitions as seen in Fig. 4(a). To observe the ground state bleaching, parallel polarization of the continuum and the excitation light was used. Figure 5(a) shows the time-dependent spectra of the changes in the optical density (ΔD spectra). In addition to the ground state bleaching in the spectral range of the $S_1 \leftarrow S_0$ absorption band (440 - 500 nm) a transient absorption at longer wavelengths (575 - 700 nm) is observable. This absorption is mainly due to the transition $S_n \leftarrow S_1$ ($n \geqslant 3$) as can be deduced from the absorption spectrum in Fig. 5(b). The ground state recovery and the decay of excited state absorption are governed by the same time constant $\tau_R \approx 12$ ps. This time was determined by an evaluation of the kinetic curves (ΔD values at fixed wavelength *versus* delay time t_D, *cf.* Fig. 5(c)) in which the pulse duration was taken into account.

The EE isomers of **1** and **2** were excited by the third harmonic ($\lambda_{exc} = 351$ nm). According to Fig. 4(b) the main contribution to the absorption
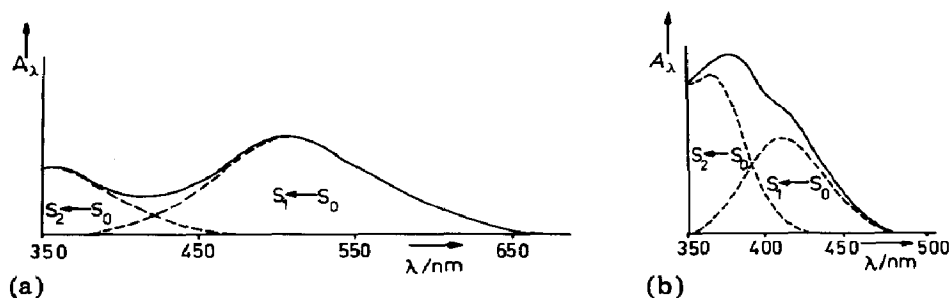

Fig. 4. Separated $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions (utilizing absorption polarization measurements in orientated nematic solutions (*cf.* ref. 11). (a) Compound **3**; (b) EE isomers of **2**.
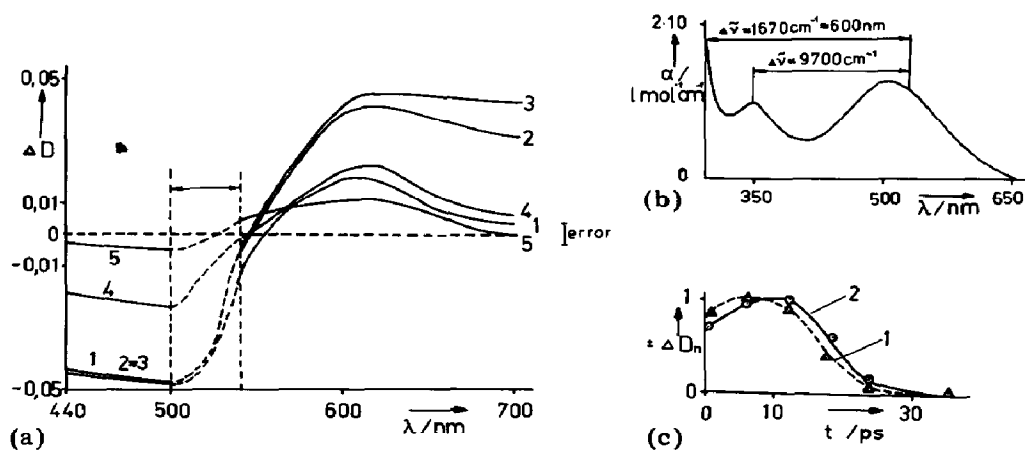

Fig. 5. (a) ΔD spectra of **3** at different delay times t_D between the excitation and the probe beam (curve 1, $t_D = 0$ ps; curve 2, $t_D = 6$ ps; curve 3, $t_D = 12$ ps; curve 4, $t_D = 18$ ps; curve 5, $t_D = 24$ ps. ($\Delta\lambda_{exc}$, scattered light of the excitation pulse.) (b) Stationary absorption spectrum of **3** in toluene and wavelengths of $S_2 \leftarrow S_1$ and $S_3 \leftarrow S_1$ electronic transitions. (c) Normalized ΔD values *vs.* delay time of $S_1 \leftarrow S_0$ bleaching ($\lambda = 473.5$ nm) and excited state absorption ($\lambda = 617.5$ nm): compound **3** in toluene.

at this wavelength is brought about by the $S_2 \leftarrow S_0$ transition. The absorption behaviour of 1-EE is similar to that of 2-EE. Observation of time-dependent spectra was only possible at wavelengths above 400 nm because of the range of sensitivity of the optical multichannel analyser vidicon. To observe the formation of EZ and ZZ isomers the polarization of the excitation and interrogation light pulse could again be chosen to be parallel because the absorption changes due to ground state bleaching in the $S_1 \leftarrow S_0$ absorption band for this polarization can be neglected. Since orientational effects of EE isomers can be excluded ($\tau_{or} > 100$ ps) changes in optical density should only be caused by the formation of EZ (and ZZ) isomers (see below).

Figure 6(a) shows the ΔD spectra for compound 1 under excitation of pure EE isomers for different delay times. We observed an absorption band which rose following the excitation pulse and then remained of constant intensity after the build-up by the excitation pulse. An analysis of the form and position of this absorption band reveals that it originates from a mixture of EZ and ZZ isomers (cf. Fig. 6(b)). The build-up of the absorption band is illustrated in Fig. 7 in which, in addition to the ΔD values from the appearance of EZ and ZZ isomer absorption, the ground state bleaching for third-harmonic-excited Rhodamine 6G is depicted and follows the excitation pulse without delay. The rise of the absorbance change of 1 (Fig. 7, curve 1) follows the excitation pulse (Fig. 7, curve 3) with a small delay.
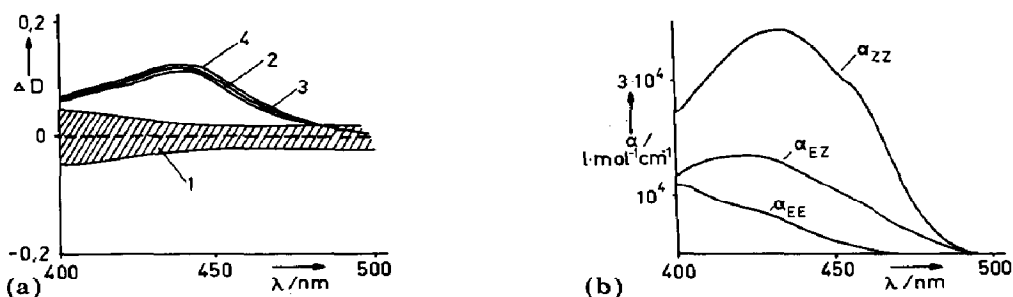

Fig. 6. (a) ΔD spectra after excitation of EE isomers of 1 in toluene at different delay times t_D of -30, 0, 6 and 126 ps (curves 1 - 4), with parallel polarization of the exciting third harmonic pulse-and-probe beam. (b) Stationary absorption spectra of 1 isomers in toluene solution.
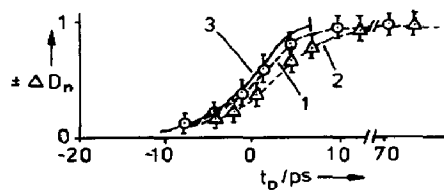

Fig. 7. Dependence of normalized ΔD values on the delay time for 1 (curve 1, at $\lambda = 445$ nm) and 2 (curve 2, at $\lambda = 450$ nm) in comparison with the $S_1 \leftarrow S_0$ ground state bleaching of third-harmonic-excited Rhodamine 6G (curve 3).
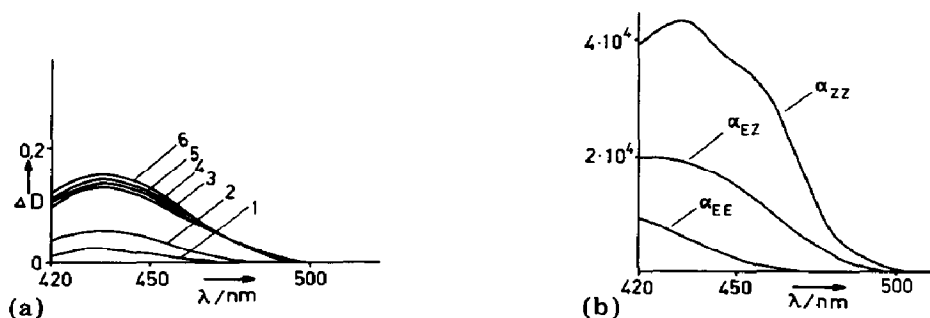
Fig. 8. (a) ΔD spectra after excitation of EE isomers of 2 in toluene at different delay times t_D of -18, -12, -6, 0, 6 and 66 ps (curves 1 - 6), with parallel polarization of the exciting third harmonic pulse-and-probe beam. (b) Stationary absorption spectra of 2 isomers in toluene solution.

When the EE isomers of **2** are excited, analogously to **1**, one can observe the formation of an absorption band corresponding in form and location to an absorption band of an EZ–ZZ mixture (*cf.* Figs. 8(a) and 8(b)). In the case of compound **2**, the build-up of this absorption band is somewhat more delayed with respect to the excitation pulse. This is illustrated in Fig. 7, curve 2.

4. Discussion

The ultrafast relaxation processes on picosecond excitation observed for compounds 1 - 3 will be discussed in terms of a model which assumes a one-dimensional torsional motion along a reaction coordinate. The results obtained from UV–visible absorption measurements under stationary irradiation revealed that the torsional angles about the α—β and γ—δ bonds (*cf.* Fig. 1) can be assigned as the relevant reaction coordinates for the fulgide system [1]. Torsion about one of these bonds may be regarded as the special case of the stilbene (or 1,4-diphenylbutadiene) isomerization, allowing us to relate our discussions of the fulgide isomerization to the thoroughly investigated stilbene isomerization.

Figure 9 shows an approximate scheme of the dependence of the energy levels (*cf.* ref. 1) of the isomers of compound 1 on the reaction coordinates (torsional angles about the α—β and γ—δ bonds). In accordance with the experimental results given in ref. 1, from which no indications of potential barriers in the excited state were found for the EE $\rightarrow$ EZ and EZ $\rightarrow$ ZZ (following the arrows in Fig. 9) isomerization steps, a possible dependence of the energy on the reaction coordinates is depicted (broken lines). A similar scheme is valid for compound 2. The ultrafast rise of the observed absorption in the wavelength region 400 - 500 nm can be understood by assuming the formation of EZ and ZZ isomers within time intervals that are short compared with the pulse duration of the excitation pulse. That
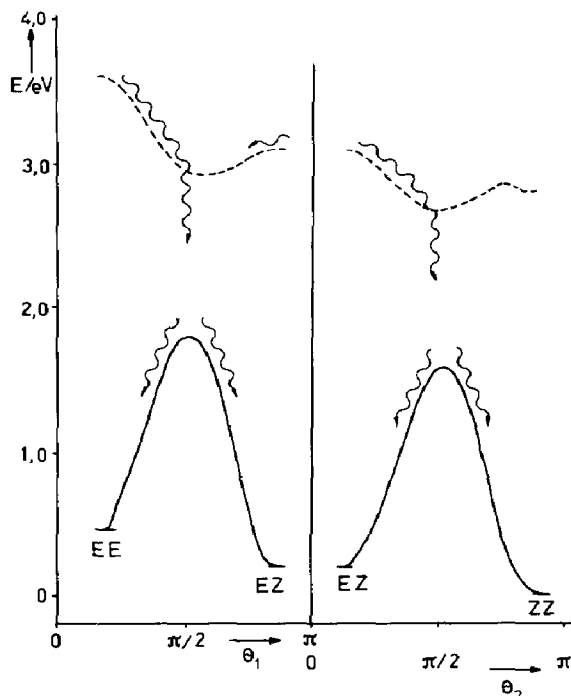
Fig. 9. Assumed potential curves $U = f(\Theta_{1,2})$; $\Theta_{1,2}$, torsion angle about $\alpha-\beta$ and $\gamma-\delta$ bonds (cf. Fig. 1).

the formation of both isomers follows the sequence EE $\xrightarrow{h\nu}$ EZ and EZ $\xrightarrow{h\nu}$ ZZ within a time of about 5 ps is indicated by the shape of the absorption band on picosecond excitation (see the ΔD spectra, Figs. 6 and 8). It should be noted that because of the asymmetry of the structure of the EZ (and the ZE) isomers, their absorption is quite depolarized (cf. Fig. 2) and therefore it can be observed by means of a parallel-polarized probe-and-excite beam. The intense $S_1 \leftarrow S_0$ transition of the ZZ isomers is in the same direction within the molecular coordinate system as that of the initial EE isomers [11] (cf. Fig. 2). However, it is likely that the ZZ isomers formed in the sequence EE $\xrightarrow{h\nu}$ EZ and EZ $\xrightarrow{h\nu}$ ZZ lose the original orientation of the EE isomers during the torsion processes. Therefore the ZZ absorption also becomes distinctly depolarized, and this is also observable in the case of a parallel excite-and-probe beam.

Assuming that the relevant motion of the 4-alkoxyphenyl groups is more likely to be diffusional than inertial, the somewhat more delayed rise of the EZ and ZZ isomer absorption (with respect to the excitation pulse) in the case of compound 2 is obviously caused by the diffusion coefficient of the 4-decyloxyphenyl groups being lower than that of the 4-methoxyphenyl group in compound 1 for which the absorption rise following excitation by the pulse is only slightly delayed.

Compound 3 can only be deactivated by rotation about one of the exocyclic double bonds. The bond order of the exocyclic double bonds in

the S_1 state of 3 is higher than that for 1 and 2 [8]. Thus, it can be assumed that the rotation of the aryl group in 3 is slower than in 1 and 2, which is confirmed by the measured recovery time and the decay time of the excited state absorption (both about 12 ps).

The question arises of why the rotations of the phenyl and fluorenyl groups in the excited state should proceed so very rapidly. We suggest that a strong intramolecular driving force (*i.e.* $dU/d\Theta < 0$) exists in the excited states of both the EE and the EZ isomers. This assumption is very likely to be correct because of the absence of intramolecular barriers on the excited state potential curves. If one considers that after 20 fs the α—α' bond of the excited *cis*-stilbene molecule is already twisted by 25° [12] and that the complete cis–trans isomerization of the stilbene molecule takes place within 20 ps [13] of the picosecond excitation, one should expect an even more rapid internal rotation in the case of the much more sterically hindered (*cf.* ref. 1) EE and EZ fulgide isomers. The steric hindrance might be responsible for the strong intramolecular driving force and, consequently, for the very rapid rotational motion.

5. Conclusions

On the basis of UV–visible spectroscopic analysis of compounds 1 - 3 under stationary irradiation the absorption changes induced on picosecond excitation can be related to the primary reaction steps of the photoisomerization. The steric hindrance in the α,δ-phenylfulgide system is responsible for the ultrafast internal rotation about the exocyclic α—β and γ—δ bonds. As revealed by our measurements, radiationless deactivation of excited molecules mediated by intramolecular rotation of bulky molecular moieties subject to strong steric hindrance can proceed in a time scale of a few picoseconds or even less. Thus, a more detailed investigation of the ultrafast isomerization in fulgide molecules requires spectroscopic techniques with femtosecond time resolution. An analysis of the rapid internal rotation of the systems under study in terms of a Fokker–Planck model [14] will be given in a subsequent paper. Furthermore, we shall turn to the question of whether the simple one-dimensional model is applicable in the case of isomerization processes proceeding on a femtosecond time scale.

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