

PHOTOCHEMISTRY OF PHENYLFULGIDES XXII: COMPETING ULTRAFAST RADIATIONLESS DEACTIVATION, E-Z ISOMERIZATION AND ELECTROCYCLIC RING-CLOSURE REACTIONS[†]

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Summary

The photoisomerization about the α - β and γ - δ double bonds and the electrocyclic ring-closure reaction are competing processes within the excited singlet state of the phenylfulgides. Both processes are induced by the torsion of bulky molecular parts. Because of the extreme steric hindrance the torsion processes occur on potential curves without any activation barrier and consequently the photoisomerization, the photocyclization and the radiationless deactivation of the phenylfulgides are ultrafast processes proceeding within a few picoseconds, or even less, as the absorption measurements performed on a picosecond excite-and-probe beam spectrometer reveal. The competition between the E-Z isomerization and the cyclization is expressed by means of the partial quantum yields of these processes. The experimental results are interpreted in terms of the π -bond orders and the sums of free-valence indices for the bond-forming atoms in the S_1 state calculated by the Pariser-Parr-People method.

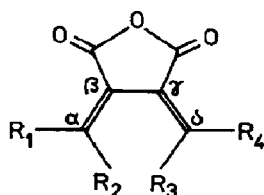
1. Introduction

Intramolecular rotations of bulky molecular parts are of increasing interest (see refs. 2 - 9 and references cited therein). Hitherto most experimental work has been focused on stilbene and 1,4-diphenylbutadiene. Both compounds were used as test models for microscopic theories of the photoisomerization in the excited singlet state.

[†]For Part XXI see ref. 1.

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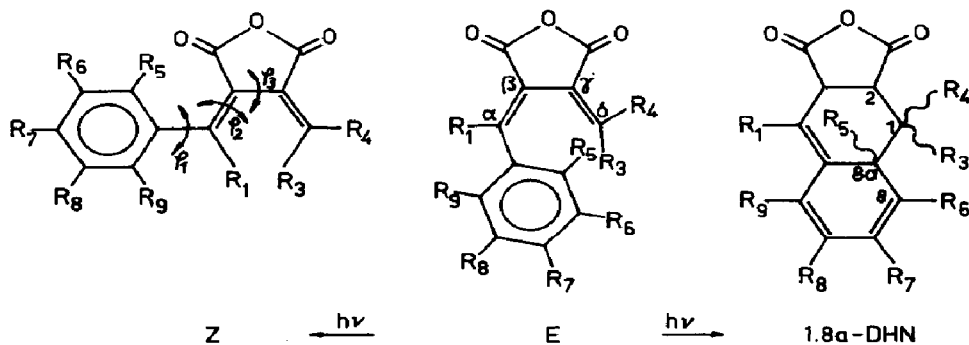
We have investigated the rotation of styryl and fluorenyl groups of the phenylfulgides (see Formula 1 and Table 1) [1, 10 - 12]. The fulgides are *s-cis*-fixed butadienes (*s-cis*-But) showing extreme steric hindrance within the molecular framework [13 - 16]. Thus, the excited state torsional processes about the α - β and γ - δ bonds occur without any activation barrier within a few picoseconds [1]. The introduction of more bulky substituents does not significantly reduce the rate of torsion (see Table 1, for example, compounds 5d and 5dD).



Formula 1.

The E-Z isomerization about the α - β and γ - δ bonds in the excited singlet state of the fulgides competes with the electronic ring-closure reaction (see Scheme 1; cf. refs. 11, 17, 18 and references cited therein). In the case of phenylfulgides the cyclic 1.8*a*-dihydronaphthalene (1.8*a*-DHN) isomers are formed after light excitation and they can be converted reversibly into the *s-cis*-But, E and EE isomers, respectively. These two kinds of isomers, the non-cyclized and the cyclized, exhibit different absorption spectra [19, 20] and therefore the isomerization reactions are open to UV-visible spectroscopic investigations.

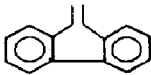
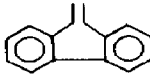
In the course of the cyclization reaction the hybridization of the δ carbon atom (C_5) and of the *o*-phenyl carbon atom (equivalent to C_{8a} in Scheme 1) is changed from sp^2 to sp^3 . Together with this change, the torsion of the groups R_3 , R_4 and R_5 in the excited state proceeds conrotatorily according to the Woodward-Hoffmann rules [21]. This rotation and the formation of the C_1 - C_{8a} σ bond are synchronous processes as is evident from the stereochemical properties of the ring-closure products [22, 23].



Scheme 1.

TABLE 1

Investigated compounds (see Formula 1) and isomers important for this work (the notation of the compounds is chosen as in previous papers [11, 13 - 16])

Compound	R ₁	R ₂	R ₃	R ₄	Isomers
1c	CH ₃	CH ₃	CH ₃	CH ₃	
2b	H	C ₆ H ₅	CH ₃	CH ₃	E, Z, 1.8a-DHN
2c	CH ₃	C ₆ H ₅	CH ₃	CH ₃	E, Z, 1.8a-DHN
3b	C ₆ H ₅	C ₆ H ₅	CH ₃	CH ₃	<i>s-cis</i> -But, 1.8a-DHN
4a	H	C ₆ H ₅	C ₆ H ₅	H	EE, EZ, ZZ, 1.8a-DHN
5d	H	4-CH ₃ OC ₆ H ₄	4-CH ₃ OC ₆ H ₄	H	EE, EZ, ZZ
5dD	H	4-C ₁₀ H ₂₁ OC ₆ H ₄	4-C ₁₀ H ₂₁ C ₆ H ₄	H	EE, EZ, ZZ
6a	H	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	E, Z, 1.8a-DHN-α(δ)
6b	CH ₃	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	E, Z, 1.8a-DHN-α(δ)
7a	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	<i>s-cis</i> -But, 1.8a-DHN
7m					<i>s-cis</i> -But, cyclic isomer ^a

^a2,3-Dihydrofluoranthene-3-spiro-9'-fluorene-1,2-dicarboxylic anhydride.

Both the photochemical E-Z isomerization and the photocyclization are related to the torsion about one ethylenic bond. The primary rate constants for both reactions must be of the same order of magnitude because both reactions can be observed by stationary measurements.

To determine more directly the rate constants for E-Z isomerization, photocyclization and radiationless deactivation, we have investigated the isomerization processes and the S₁ lifetimes by picosecond excite-and-probe beam spectroscopy. For a quantitative description of the competing isomerization processes the partial quantum yields were determined by real-time photokinetic measurements.

A deeper insight into the excited state reactions requires knowledge of the excited state potential curves along the relevant reaction coordinates. These data are not yet available for the phenylfulgides. Only for model heterocyclic fulgides have the cyclization potential curves in the S₀ and S₁ states been calculated using the method of MINDO-3 [24]. However, it should be possible to obtain some qualitative information about excited state torsion and ring closure from π-bond orders and free-valence indices. These theoretical values are calculated by means of the Pariser-Parr-Pople (PPP)-configuration interaction (CI) method (see Section 2). Furthermore, in this work we have studied the influence of the number of non-substituted phenyl rings in a molecule on the deactivation behaviour. The effects of replacing the α-hydrogen atoms by α-CH₃ groups (see Table 1, the pairs of compounds 2b, 2c and 6a, 6b) and of connecting the phenyl rings (see Table 1, compounds 7a, 7m) were also investigated.

The isomers of the investigated compounds which are important for this work are collected in Table 1. The 1.8 α -DHN isomers formed by the cyclization of an α -phenyl ring and a δ -phenyl ring are assigned as the 1.8 α -DHN- α isomer and the 1.8 α -DHN- δ isomer respectively.

2. Experimental details and methods

The compounds studied were prepared as reported previously [25]. Toluene (Uvasol quality) was used as solvent. The measurements performed in this work were carried out at 293 K.

The determination of the partial quantum yields of the E-Z isomerization and cyclization reactions is described in ref. 26. A home-built photokinetic spectrometer [27] was used. The picosecond excite-and-probe beam spectrometer is described in ref. 1. The applied videcon was sensitive above 420 nm.

Transition energies, charge distribution and reactivity indices were calculated by the PPP method [28, 29]. The molecules under study were assumed to have standard geometry (see ref. 19) except for the torsional angles ϕ_1 , ϕ_2 and ϕ_3 (see Scheme 1) which were adjusted so that the calculated transition energies fitted the experimental absorption spectra. For the CI calculation, 36 singly excited configurations were taken into account. The dependence of the resonance integrals $\beta_{\mu\nu}(\phi_1)$ on the torsional angles was calculated according to

$$\beta_{\mu\nu}(\phi_1) = \beta_{\mu\nu}(0) \cos \phi_1$$

Further details of the PPP calculations are described in refs. 19 and 28.

3. Results

3.1. Partial quantum yields

The partial quantum yields of the E-Z isomerization and cyclization reactions starting with the *s-cis*-But isomers (compounds 3b, 7a, 7m), with the E isomers (compounds 2, 6) and with the EE isomers (compounds 4, 5) respectively, are collected in Table 2. Both monophenylfulgides of series 2 exhibit similar quantum yields ϕ_Z^E . However, by introducing the α -CH₃ group the cyclization tendency is increased (Table 2, compounds 2b, 2c). The same effect can be observed for 6a and 6b (*cf.* $\phi_{(1.8\alpha\text{-DHN})}^E$ values in Table 2).

The sums of the cyclization and E-Z isomerization quantum yields are smaller in the series of the triphenylfulgides than in the series of the monophenylfulgides and diphenylfulgides. The compounds 6a-E and 6b-E exhibit direct photoisomerization $E \xrightarrow{h\nu} Z$ to a very small extent only.

The dependence of the partial quantum yields of the isomerization steps $E(\text{EE}) \xrightarrow{h\nu} Z(\text{EZ})$ and $E(\text{EE}) \xrightarrow{h\nu} 1.8\alpha\text{-DHN}$ on the nature of the

TABLE 2

Partial quantum yields of E-Z isomerization and cyclization ($T = 293$ K, toluene solution, stationary irradiation at $\lambda' = 366$ nm)

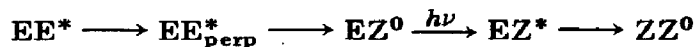
Compound	E-Z isomerization	Cyclization
2b	$\phi_{Z}^E = 0.26$	$\phi_{(1.8a\text{-DHN})}^E < 10^{-3}$
2c	$\phi_{Z}^E = 0.18$	$\phi_{(1.8a\text{-DHN})}^E = 0.084$
3b ^a	—	$\phi_{(1.8a\text{-DHN})}^{(s\text{-cis-But})} = 0.060$
4a	$\phi_{EZ}^{EE} = 0.40$	$\phi_{(1.8a\text{-DHN})}^{EE} = 0.046$
5d	$\phi_{EZ}^{EE} = 0.25$	$\phi_{(1.8a\text{-DHN})}^{EE} < 10^{-5}$
5dD	$\phi_{EZ}^{EE} = 0.23$	$\phi_{(1.8a\text{-DHN})}^{EE} < 10^{-5}$
6a	$\phi_{Z}^E < 10^{-3}$	$\phi_{(1.8a\text{-DHN-}\alpha)}^E < 10^{-3}$ $\phi_{(1.8a\text{-DHN-}\delta)}^E = 0.015$
6b	$\phi_{Z}^E < 10^{-3}$	$\phi_{(1.8a\text{-DHN-}\alpha)}^E = 0.010$ $\phi_{(1.8a\text{-DHN-}\delta)}^E = 0.012$
7a ^a	—	$\phi_{(1.8a\text{-DHN})}^{(s\text{-cis-But})} = 0.001$
7m ^a	—	$\phi_{\text{cyclic isomer}}^{(s\text{-cis-But})} < 10^{-5}$

^aNo E-Z isomers are possible.

substituents R₅ to R₉ (Scheme 1) has been discussed previously [11]. Thus, the electronic influence of the 4-alkoxy groups (e.g. compounds 5d, 5dD) suppresses the cyclization reaction nearly completely. Furthermore, neither the partial quantum yields of the isomerization steps $E \xrightarrow{h\nu} Z$, $EE \xrightarrow{h\nu} EZ$, $EZ \xrightarrow{h\nu} ZZ$ nor of the cyclization step exhibit a marked temperature dependence within the range 110 - 293 K [10, 12].

3.2. Picosecond absorption measurements

The time-dependent spectra of the changes in the optical density (ΔD spectra) after intense picosecond pulse excitation ($\tau_p < 5$ ps) were measured for compounds 3b, 5d-EE, 5dD-EE, 7a and 7m. The results for compounds 5d-EE, 5dD-EE and 7m have been described previously [1] in more detail. It can be summarized that, on excitation of the EE isomers, the EZ and ZZ isomers are actually formed during the pulse duration. Therefore, the complete process

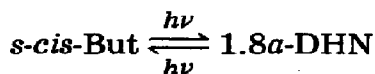


should be terminated within 3 - 4 ps. In the case of compound 7m both the decay of an excited state absorption $S_n \longleftarrow S_1$ ($n \geq 3$) and the S_0 recovery time are in the time range of about 12 ps.

To complete the studies on the ultrafast deactivation of fulgides we investigated the deactivation behaviour of the compounds 3b and 7a. The two compounds do not exhibit different E-Z isomers, and therefore the

isomerization mechanism is simplified in comparison with compounds 4a, 6a and 6b [11].

The stationary irradiation of 3b leads to the reversible isomerization [11] (see Fig. 1(a))



The compound 7a also forms the 1.8 α -DHN isomers, but with a very small quantum yield (see below, and Table 2).

The time behaviour of the ΔD spectra of 3b after intense picosecond pulse excitation is shown in Fig. 1(b). The formation of an excited state absorption at the long wavelength edge of the *s-cis*-But isomers is seen. This absorption rise follows the excitation pulse and decays within a time of about 6 ps (Fig. 2). Within the same time of about 6 ps the absorption of the 1.8 α -DHN isomers is formed. This absorption remains constant over a rather long time ($t > 500$ ps).

In the case of compound 7a, neither an excited state absorption $S_n \leftarrow S_1$ nor the $S_1 \leftarrow S_0$ bleaching could be observed. Furthermore, the formation of the 1.8 α -DHN isomers cannot be detected by means of the excite-and-probe beam spectrometer. Obviously, the lifetime of the S_1 state of 7a is very short and we cannot observe any ΔD change by means

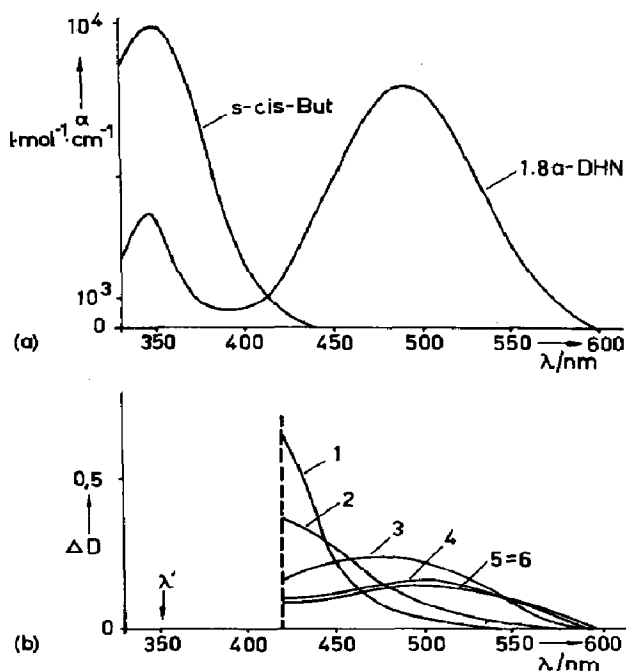


Fig. 1. (a) Stationary absorption spectra of 3b isomers in toluene. (b) ΔD spectra after intense picosecond excitation of *s-cis*-But isomers of 3b in toluene at various delay times t_D between the excitation and the probe beam: curve 1, $t_D = 0$ ps; curve 2, $t_D = 3$ ps; curve 3, $t_D = 6$ ps; curve 4, $t_D = 12$ ps; curve 5, $t_D = 60$ ps; curve 6, $t_D = 500$ ps.

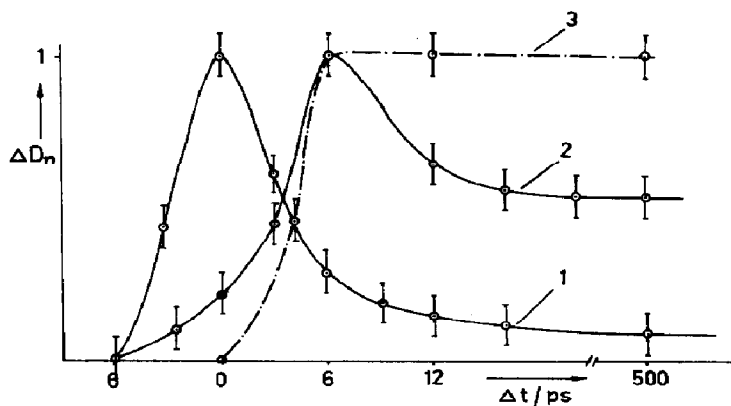


Fig. 2. Dependence of normalized ΔD values on the delay time starting with pure **3b**-*s-cis*-But isomers at various wavelengths: curve 1, $\lambda = 430$ nm; curve 2, $\lambda = 470$ nm; curve 3, $\lambda = 540$ nm.

TABLE 3

Time duration of investigated ultrafast processes

Compound	Reference	Investigated process	Time duration (ps)
3b	This work	Decay of excited state absorption, rise of 1.8a-DHN	About 6 About 6
5d-EE	1	Rise of EZ and ZZ isomers	Less than or equal to 3
5dD-EE	1	Rise of EZ and ZZ isomers	Less than or equal to 4
7a	This work	Neither $S_1 \leftarrow S_0$ bleaching nor excited state absorption could be observed	($\tau_{S_1} < 3$)
7m	1	S_0 recovery time, decay of excited state absorption	About 12 About 12

of the picosecond absorption technique. The results of the picosecond absorption measurements are collected in Table 3.

3.3. Bond orders and indices of free values in the S_1 state

Our aim was to relate the bond orders and indices of free valences to the structure and reactivity characteristics of the compounds under study.

The torsional angles ϕ_1 , ϕ_2 and ϕ_3 (see Scheme 1) were adjusted so as to fit the experimental spectrum [19, 29]. For the molecular geometries obtained in this way the S_1 bond orders for the α - β and the γ - δ bonds are presented in Table 4.

It can be seen that for an asymmetric compound of series 2 and 6 the α - β and γ - δ π -bond orders in the S_1 state are different. The dependence

TABLE 4

Calculated S_1 π -bond orders ρ^{S_1} of α - β and γ - δ bonds (see Formula 1, Table 1) and sums of indices of free valence ΣFr^* of non-cyclized isomers

Compound	$\rho^{S_1}_{(\alpha-\beta)}$	$\rho^{S_1}_{(\gamma-\delta)}$	ΣFr^*	Cyclization product
1c	0.506	0.506		
2b-E	0.471	0.714	1.53	1.8 α -DHN
2c-E	0.522	0.710	1.55	1.8 α -DHN
3b	0.800	0.439	1.41	1.8 α -DHN
4a-EE	0.577	0.577	1.20	1.8 α -DHN
5d-EE	0.591	0.591	1.14	1.8 α -DHN
5dD-EE	0.591	0.591	1.14	1.8 α -DHN
6a-E	0.605	0.517	0.790	1.8 α -DHN- α
			0.987	1.8 α -DHN- δ
6b-E	0.490	0.630	0.870	1.8 α -DHN- α
			1.170	1.8 α -DHN- δ
7a	0.519	0.519	0.860	1.8 α -DHN
7m	0.529	0.529	0.790	Cyclic isomer

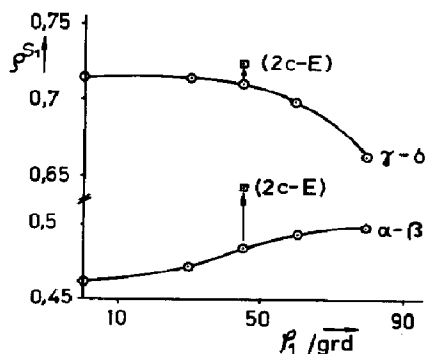


Fig. 3. Dependence of S_1 π -bond orders ρ^{S_1} on the torsion angle ϕ_1 of the phenyl rings: \circ , 2b-E, $\phi_2 = \phi_3 = 0$; \square , 2c-E, $\phi_3 = 20^\circ$

of the bond orders on the torsional angle ϕ_1 is shown for compound 2b-E in Fig. 3. In the case of $\phi_2 = 0$ and $\phi_3 = 0$ an increasing value of ϕ_1 results in an increasing α - β bond order but in a decreasing γ - δ bond order. An increasing value of ϕ_3 , (this phenomenon is relevant to the H-CH₃ exchange between 2b-E and 2c-E [13]) gives mainly an increasing α - β bond order.

The influence of the electronic and geometric structure on cyclization can be described by the sum of free valences ΣFr^* for the atoms which form the new σ bond [28, 30]. ($Fr^* = 1.732 - \sum_s \rho_{rs}^*$ where ρ_{rs}^* is the bond order in the S_1 state when atom r is bonded to atom s .)

The ΣFr^* values correlate with the cyclization quantum yields within the series of mono-, di-, tri- or tetra-phenylfulgides [28, 30]. As is well known for reactivity indices the corresponding values for different reaction series cannot be correlated. The data of Table 4 show increasing ΣFr^* values

with increasing torsional angles ϕ_1 of the phenyl rings (see the pairs of compounds 2b and 2c, 6a and 6b, 7m and 7a; the second compound is more twisted than the first). For the compounds 6a and 6b the ΣFr^* values are larger for the formation of 1.8a-DHN- δ than for 1.8a-DHN- α . For 4a-EE and 5d-EE there is a difference in the ΣFr^* values, already discussed in refs. 11, 28 and 30.

4. Discussion

The picosecond absorption measurements for the compound 3b reveal that the S_1 lifetime of the *s-cis*-But isomers is about 6 ps because the observed $S_n \leftarrow S_1$ absorption decays in this time (Figs. 1 and 2). The rise time of the 1.8a-DHN is also nearly 6 ps, and was measured by the growth of the ($S_1 \leftarrow S_0$)-1.8a-DHN absorption. Therefore, the excited *s-cis*-But isomers must be the direct precursors of the 1.8a-DHN isomers. This result is in agreement with the stationary absorption measurements which are utilized by means of matrix rank analysis [31].

The rise time of the 1.8a-DHN isomers may be expected within the duration of a valence vibration ($10^{-14} - 10^{-12}$ s) because the formation of a σ bond should require this time. The rate-determining step of the cyclization reaction is obviously the torsion about the γ - δ bond in the case of 3b and we observe a 1.8a-DHN rise time which is in accord with γ - δ (or α - β) bond torsion.

We can conclude from the results summarized in Table 3 that both the E-Z isomerization and the cyclization reaction of the extremely sterically hindered *s-cis*-But, E and EE isomers are ultrafast processes. Both reaction steps are connected with the torsion of bulky molecular parts about the α - β and γ - δ bonds of the fulgide system.

In the excited singlet state no activation barriers exist for the torsional processes of the E(EE) $\xrightarrow{h\nu}$ Z(EZ) $\xrightarrow{h\nu}$ ZZ reaction series. Thus, the computer simulations of the torsional process $EE^* \longrightarrow EE_{\text{perp}}^* \longrightarrow EZ^0$ in 5d and 5dD on the basis of a Fokker-Planck model [32, 33] reveal that the motion of the bulky molecular parts following the barrierless potential curve in the excited state may proceed within the femtosecond time range. As our investigations on the temperature dependence of the cyclization quantum yields [10] reveal, the cyclization reaction in the excited singlet state also proceeds on a barrierless potential curve.

It was shown [7-9, 34] that in the case of radiationless processes involving large amplitude motion in the absence of an internal barrier the solvent friction provides the only "resistance" to motion on the excited state surface and that the decay of the excited state depends strongly on the shape of the excited state potential curve. Furthermore, a barrierless potential curve leads to excitation-wavelength-dependent torsional rate constants [9]. From this point of view a further explanation for the found wavelength dependence of the partial quantum yields ϕ_{ZZ}^{EZ} and ϕ_{EE}^{EZ} of compounds 5d and 5dD [12] can be given [29].

In our case of fulgide deactivation in toluene solution at 293 K we wished to compare qualitatively the possibilities of torsion about α - β and γ - δ bonds following the barrierless potential curves. It is known (for example, ref. 35) that in the excited singlet state of the butadiene system, only one of the ethylenic bonds can twist but not both bonds simultaneously. The phenylfulgides show the same behaviour [12]. Thus, for the phenylfulgides of series 2, 3 and 6 substituted unsymmetrically the type of bond twisted determines the competition between E-Z isomerization and cyclization. For instance, in the case of the α - β bond torsion in 2b-E, 2c-E and 3b-*s-cis*-But no cyclization is possible because the distance between the relevant *o*-phenyl carbon atom and the C_8 atom increases following the twist process. However, the γ - δ bond torsion (connected with the formal change in hybridization $sp^2 \rightarrow sp^3$ of the C_8 atom) can induce the cyclization reaction.

The torsion about the α - β and γ - δ bonds in the excited singlet state is determined by the interplay of steric hindrance and electronic effects. In comparison with stilbene, where the barrier of the excited singlet state conversion (excited trans state) \rightarrow (excited perpendicular state) is caused by the avoided crossing of a B_u and a doubly excited A_g state [36], the barriers in the singlet state of fulgides can disappear because of the extreme steric hindrance and the increased electronic π system (see refs. 37 and 38 for other examples). The relative extent of the torsion about the α - β and γ - δ bonds is determined by the bond strengths of these bonds in the excited state. We assume that the calculated π -bond orders are a convenient measure of the bond strength. Consequently, it can be assumed that the

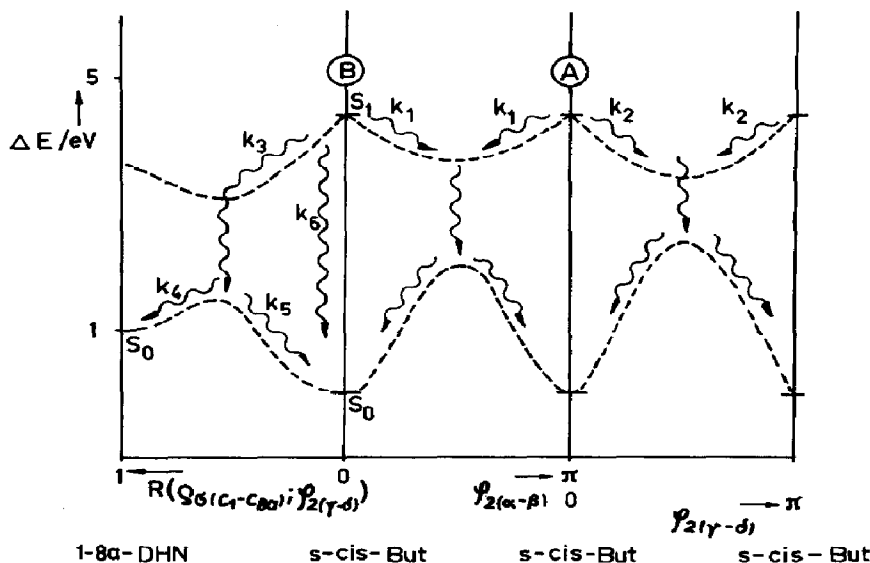
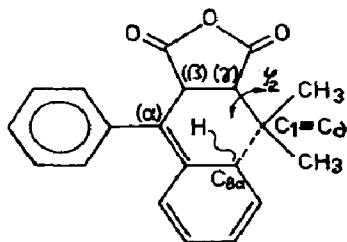


Fig. 4. Assumed potential curves ΔE as a function of R , $\phi_{2(\alpha-\beta)}$ and $\phi_{2(\gamma-\delta)}$: R , cyclization reaction coordinate, dependent on the strength $\rho_{\alpha(C_1-C_{8a})}$ of the σ bond between the C_1 and C_{8a} atoms as well as on the torsion angle about the γ - δ bond; $\phi_{2(\alpha-\beta)}$; $\phi_{2(\gamma-\delta)}$, torsion angle about α - β and γ - δ bonds (see Formula 2).

bond with the smaller π -bond order can be more easily twisted than the bond with a higher π -bond order.

As yet, exact theoretical molecular orbital calculations of the torsional potential curves of fulgides are not at hand. Therefore, in Fig. 4 only a hypothetical potential curve model for the isomerization and deactivation reactions of the selected compound 3b can be given.

In the case of the twisting reactions occurring without cyclization the torsion angles ϕ_2 of the α - β and γ - δ bonds are the reaction coordinates. In the case of cyclization the reaction coordinate is determined both by the distance of the bond-forming atoms C_1 (equivalent to C_δ) and C_{8a} and by the torsional angle $\phi_{2(\gamma-\delta)}$ (see Formula 2).



Formula 2.

The following qualitative conclusions can be drawn about the shape of the ground and excited state potential curves of compound 3b.

(i) The S_0 π -bond order of the α - β bond is smaller than that of the γ - δ bond [29]. Therefore, a smaller barrier should exist for the torsion about the α - β bond in the ground state than about the γ - δ bond. The ground state barrier height is expected to be between 20 and 30 kcal mol⁻¹ in accordance with other polyenic bonds.

(ii) The ground state energy of 1.8a-DHN must be greater than the energy of the *s-cis*-But isomers because the thermal ring-opening reaction (activation energy, about 12 kcal mol⁻¹) occurs with a decrease in free energy as a result of the rearomatization of a phenyl ring [23]. We assume an energy difference ($E_{S_0-1.8a-DHN} - E_{S_0-s-cis-But}$) of about 1 eV. The energy of the S_1 state of the isomer can be estimated easily by means of the $S_1 \leftarrow S_0$ transition energies ($\lambda_{\max(s-cis-But)} = 350$ nm; $\lambda_{\max(1.8a-DHN)} = 490$ nm).

(iii) For the excited singlet state, the relative extent of the S_1 π -bond orders of the α - β and γ - δ bonds (Table 3) allows us to conclude that in the case of γ - δ bond torsion occurring without cyclization the barrierless $\phi_{2(\gamma-\delta)}$ potential curve should be steeper, at least in the initial range, than the $\phi_{2(\alpha-\beta)}$ potential curve (see situation at the point A in Fig. 4).

The competition between α - β bond torsion and cyclization is illustrated in Fig. 4, point B. Provided that the α - β bond torsion is faster than γ - δ bond torsion (*i.e.* $k_1 \gg k_2$ (Fig. 4)) cyclization cannot occur. As cyclization can be observed, it can be concluded that γ - δ bond torsion is faster than α - β bond torsion and this is in agreement with the relative ordering of S_1 π bond orders (Table 4). The influence of doubly excited

singlet states on the shape of the true potential curves and the effects of non-adiabatic interaction of the twisted excited states with the ground state are neglected in our simple model.

The relatively low isomerization quantum yield $\phi_{cyc} = 0.06$ of 3b, and of other compounds can be caused by an unfavourable decay ratio $DR = k_4/(k_4 + k_5)$ (Fig. 4) of the S_0 transition state as well as by further radiationless deactivation channels, for instance, by a rate constant k_6 (Fig. 4). Such a process could be the torsional motion of the phenyl rings about the phenyl- C_α and/or phenyl- C_δ single bond varying the angles ϕ_1 (Scheme 1). The phenyl ring torsion can also lead to a "funnel" on the multidimensional true excited state potential curve, and the deactivation can occur without isomerization following the ϕ_1 torsional coordinate.

Summarizing the results shown in Tables 2-4 the following conclusions about the deactivation behaviour of the phenylfulgides can be drawn.

(i) Substituting the α -hydrogen atom by the CH_3 group, as in the case of compounds 2b-E and 2c-E, the cyclization quantum yields and the α - β S_1 π -bond order increase (*cf.* Fig. 3 and Tables 2 and 4). Assuming a nearly equal S_0^{exp} -decay ratio DR for the H- and CH_3 -substituted compounds, the reason for the increase in ϕ_{cyc} of 2c-E should be a reduced tendency to undergo α - β bond torsion because the γ - δ bond order and the ΣFr^* values, which describe the electronic influence on the cyclization tendency, vary only slightly.

Comparing the S_1 π -bond orders of 2b-E and 3b (see Table 4) it can be concluded that the α - β bond torsion in 2b-E should be faster than the γ - δ bond torsion whereas in 3b the γ - δ bond torsion is faster than the α - β bond torsion. Therefore, the very small cyclization quantum yield shown by 2b-E can be understood.

(ii) The differences in the quantum yields $\phi_{(1.8\alpha-DHN-\alpha)}^E$ and $\phi_{(1.8\alpha-DHN-\delta)}^E$ of the compounds 6a-E and 6b-E as well as those between the cyclization quantum yields of 7a and 7m are obviously caused electronically as the ΣFr^* values verify (see Table 4).

The very small quantum yields ϕ_Z^E of the triphenylfulgides 6 cannot be explained exactly by the ordering of the α - β and γ - δ S_1 π -bond orders. Obviously, the radiationless phenyl torsional processes contribute to a larger extent to the deactivation than in the case of 2b-E and 2c-E (see below).

(iii) We conclude that the additional deactivation pathway by phenyl ring torsion is very likely for the phenylfulgides. First, the increase in the number of phenyl rings in the molecules (*e.g.* in the series of compounds 2b-E, 3b-*s-cis*-But, 4a-EE, 6a-E, 7a-*s-cis*-But) leads to the decrease in the sums of E-Z and cyclization quantum yields except for the statistically enlarged ϕ_{EZ}^{EE} values of compounds 4 and 5 [11] where both the α - β and the γ - δ bond torsion results in $EE \xrightarrow{h\nu} EZ/ZE$ isomerization. The more phenyl rings there are in a fulgide molecule the larger should be the probability of thermal deactivation following the phenyl ring torsion coordinate ϕ_1 .

Secondly, the influence of phenyl torsional processes on deactivation becomes obvious when comparing the S_1 lifetimes. From Table 3 the relation $\tau_{7m} > \tau_{3b} > \tau_{5d-EE} \approx \tau_{5dD-EE} > \tau_{7a}$ can be derived. For the interpretation of the lifetime ordering the α - β and γ - δ S_1 π -bond orders are not significant. The steric driving forces for the α - β and γ - δ bond torsion are as yet unknown but they should be comparable for these five compounds. Therefore, we conclude that steric hindrance does not cause large differences in the torsional rates about the ethylenic bonds. Consequently, the extent of the torsion about these bonds should not provide the main contribution to the lifetime ordering observed. Furthermore, the cyclization reaction should only slightly influence the ordering of deactivation rates because the cyclization quantum yields are low and their ordering $\phi_{cyc}^{3b} > \phi_{cyc}^{7a} > \phi_{cyc}^{7m} > \phi_{cyc}^{5dD-EE}$ is different to that of the lifetimes.

We conclude that the flexibility of the phenyl rings in 3b and 7a in comparison with the fixed rings in 7m is the essential reason for the longer lifetime of the excited state of 7m. Our first suggestion [1] that the α - β and γ - δ S_1 π -bond orders of 7m should be higher than those of 7a could not, however, be supported by PPP calculations [29].

The larger excited state lifetime of 7m as compared with that of 7a is in accordance with the recently found lifetime ordering [39] at low temperature between *trans*-stilbene and its structurally rigid derivatives, the substituted tetrahydrochrysenes, which show increased fluorescence lifetimes in comparison with *trans*-stilbene. The same behaviour can be expected when comparing the low-temperature fluorescence quantum yields of *trans*-stilbene and *trans*-1,1'-bi-indanylidene ("stiff stilbene") [40].

The rate of isomerization and radiationless deactivation processes of compounds 1c, 2b-E, 2c-E, 4a-EE, 6a-E and 6b-E, not yet investigated by means of the picosecond excite-and-probe beam technique, is also expected to lie within the picosecond-femtosecond time scale, because the partial quantum yields, the S_1 π -bond orders and the extent of steric hindrance are comparable with the corresponding values for compounds 3b, 5d-EE, 5dD-EE, 7a and 7m.

5. Conclusions

The ultrafast deactivation behaviour of phenylfulgides belongs to the barrierless case according to the microscopic theories of photochemical isomerization dynamics.

We have interpreted the competition between the principal deactivation processes of different phenylfulgides, *i.e.* the E-Z isomerization, electrocyclic ring-closure reaction and radiationless deactivation, by means of a simple model utilizing the PPP-calculated S_1 π -bond orders and sums of indices of free valence.

Increasing the number of phenyl rings within the molecules the torsional motions of the rings become an important radiationless deactivation

channel. However, in the case of the excited bifluorenylfulgide (7m) with fixed phenyl rings and which exhibits a very small cyclization tendency, the torsion about one exocyclic double bond of the *s-cis*-fixed butadiene system is the only important deactivation pathway. Therefore, this compound can serve as model for the deactivation behaviour on a barrierless, one-dimensional potential curve and we shall present our results on picosecond excite-and-probe beam investigations of the viscosity and temperature dependence of the deactivation rate in a subsequent paper.

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Note added in proof

After submission of the manuscript we learned of a paper by Lenoble and Becker which had just been published [41]. This paper is concerned with the investigation of the fulgide isomerization reactions on the nanosecond time scale. The finding of these workers, that the isomerization processes of the fulgides are completed in less than 1 ns, is in agreement with our picosecond investigations.

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