

EMISSION SPECTRA OF PHOTOCHROMIC SPIRO[1,8-*a*]DIHYDRO-INDOLIZINES AND MECHANISM OF THE ELECTROCYCLIC RING OPENING REACTION[†]

HUBERT GROSS and HEINZ DÜRR

Fachrichtung 14.1 Organische Chemie, Universität des Saarlandes, D-6600 Saarbrücken 11 (F.R.G.)

WOLFGANG RETTIG

I.N. Stranski Institut für Physikalische und Theoretische Chemie, Technische Universität Berlin, D-1000 Berlin 12 (F.R.G.)

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Summary

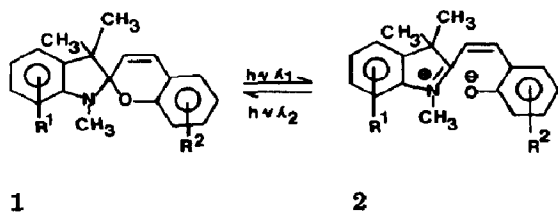
The photochemical pericyclic ring opening of the new photochromic system of spiro[1,8-*a*]dihydroindolizines (DHIs) was studied. From absorption and emission spectra the singlet energy $E(S_1)$ of the DHIs was calculated to be of the order of 60 - 70 kcal mol⁻¹. Measurements of the fluorescence quantum yields ϕ_F and the singlet lifetimes τ_s of the DHIs (at room temperature and 77 K) as well as quenching experiments gave radiative lifetimes τ_{rs} which are two orders of magnitude larger than the τ_{rs} values calculated by the Strickler-Berg equation, suggesting that the two excited singlets involved in absorption and emission are not the same. From negative reaction quenching and negative chemiexcitation by dioxetane the excited state of the DHIs was concluded to be a singlet. The pericyclic ring opening may therefore be regarded as a fast singlet reaction.

1. Introduction

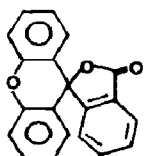
The development of new silver-free photochemical imaging systems is currently a field of much interest [1]. In this context, new photochromic systems are of great importance for silver-free imaging systems, data storage (computer, video disc), data display systems or the development of light filters and photoprint and photoresistance systems [1]. Furthermore, photochromic systems are of great potential interest as far as solar energy conversion is concerned [2]. A photochromic system can be based on various reversible reactions. According to the mechanism involved six different classes are conceivable [3]: (1) *cis-trans* isomerization; (2) electrocyclic

[†]Eighth paper on photochromic systems (for seventh paper see H. Dürr, H. Gross and G. Hauck, *Chem. Ber.*, 116 (1983) 856).

reactions; (3) tautomerization; (4) dissociation; (5) electron transfer; (6) triplet-triplet absorption. The most common systems involve electrocyclic reactions, *i.e.* class 2. Systems of this type are, for example, the spiropyrans 1 [1, 4] which have been studied extensively

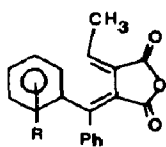


the rhodamine derivatives 3 [5]



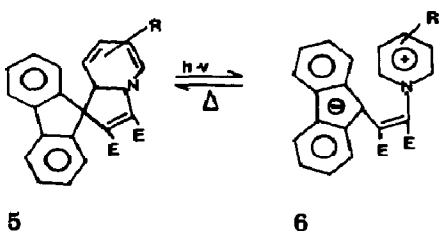
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the triarylmethanes [1], the indenoxides [1], the nitrones [1] and the fulgides 4 [6, 7]:

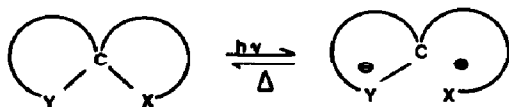


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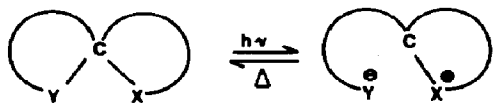
We have described a new system which is based on the photochemical ring opening of spiro[1,8-*a*]dihydroindolizines (DHIs) 5 [8] ($E \equiv CO_2CH_3$):



System 5 seems to be related to the spiropyrans 1. A detailed analysis, however, shows that the photochromism of 5 demonstrates characteristic differences with regard to the spiropyrans 1, *i.e.* 5 is a new photochromic system:



i.e. 5 \rightleftharpoons 6, with the ring negatively charged and



i.e. 1 \rightleftharpoons 2, with the ring positively charged.

Photochromism in 5 is due to a pericyclic reaction. The photochemical ring opening 5 \rightarrow 6, as well as the thermal 1,5-cyclization, is an electrocyclic reaction. Therefore the photodissociation should be conrotatory whereas the thermal back reaction should be disrotatory [8].

In this paper we report on (1) the fluorescence spectra of DHIs 5 at room temperature and at 77 K, (2) the fluorescence quantum yields of 5 at room temperature, (3) the lifetime τ_f measurements with 5 obtained via time-resolved spectroscopy and fluorescence quenching and (4) the determination of the product quantum yields and reaction rates for the conversion 5 \rightarrow 6.

2. Results

2.1. Fluorescence measurements and determination of the singlet energy $E(S_1)$ of the spiro[1,8-a]dihydroindolizines 5

The emission spectra of DHIs 5 (Table 1) show a large difference between the excitation and the emission maximum (up to 100 nm). This large Stokes shift (about 5300 cm^{-1}), however, is independent of the solvent polarity (Fig. 1, which shows the polar solvent effect on the fluorescence spectra of 5g).

In Table 1 the maxima of the fluorescence and excitation are given together with the singlet energy $E(S_1)$. The singlet energies were calculated from

$$E(S_1) = \frac{hc}{\lambda \text{ (nm)}} = \frac{28600}{\lambda} \text{ kcal mol}^{-1} \quad (1)$$

using the wavelength of the 0-0 transition of the fluorescence. These energies were obtained from the wavelengths where the maximum intensity had dropped to a value of $1/e$. A second value was calculated from the intersection of the UV [4] and the emission spectra (see Fig. 1).

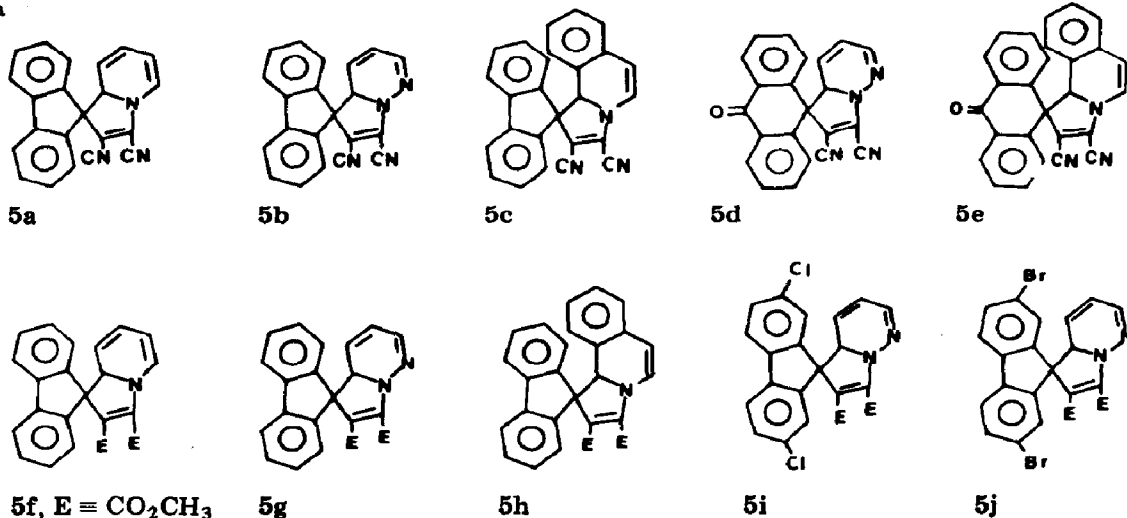
The emission spectra were recorded for 5 at room temperature and the 0-0 transition was determined as reported [9]. However, this gives only an

TABLE 1

Emission maxima and singlet energies of 5

DHI ^a	$\lambda_f(\text{max})^b$ (nm)	$\lambda_{ex}(\text{max})^c$ (nm)	$E(S_1)^d$ (kcal mol ⁻¹)	$E(S_1)^e$ (kcal mol ⁻¹)
5a	495	360	67.6	62.2
5b	454	370	66.6	67.1
5c	460	410	65.0	64.0
5d	508	400	63.6	60.6
5e	520	450	58.9	59.3
5f	460	335	68.2	67.6
5g	493	340	66.5 (65.7) ^f 65.8	67.6
5h	450	330	65.8	70.2
5i	462	395	66.5	66.5
5j	497	390	66.1	66.5

a

^b $\lambda_f(\text{max})$, fluorescence maxima at 25 °C in CH₂Cl₂.^c $\lambda_{ex}(\text{max})$, excitation maxima of emission.^dFrom emission spectra.^eFrom the intersection of absorption and emission spectra

$$E(S_1) = \frac{hc}{\lambda(\text{nm})} = \frac{28600}{\lambda} \text{ kcal mol}^{-1}$$

^fAt 77 K.

approximation of the correct 0-0 transition. For 5b, 5f and 5g the emission spectra were recorded at room temperature as well as at 77 K.

In Fig. 2 the fluorescence spectra of 5g in ether-pentane-alcohol (EPA) at room temperature and 77 K are compared with the UV spectrum at room temperature. The large Stokes shift can be seen from these data.

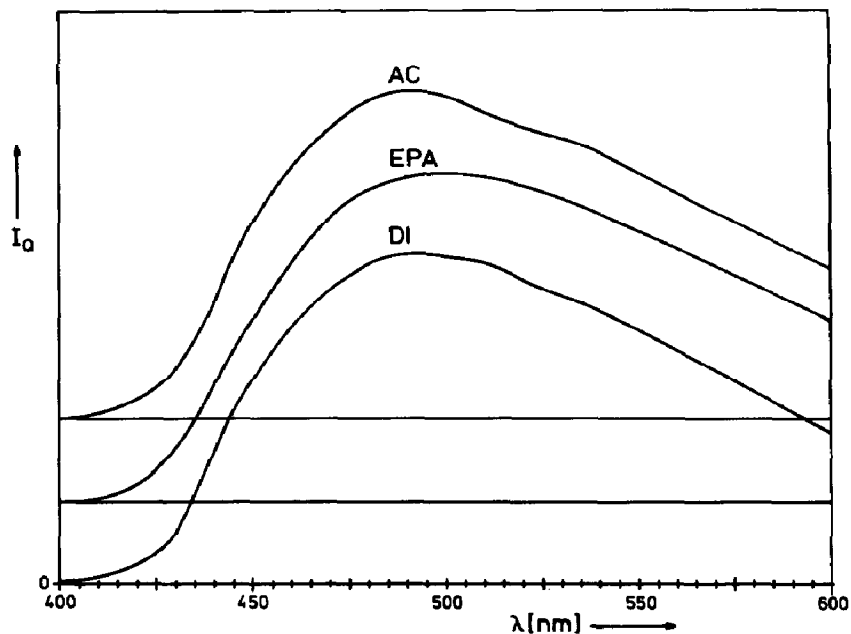


Fig. 1. Quantum-corrected fluorescence spectra of 5g in 2,3-dimethylbutane:isopentane (DI) (8:3), ether:pentane:alcohol (EPA) (5:5:2) and acetonitrile (AC) ($\lambda_{\text{ex}} = 395 \text{ nm}$).

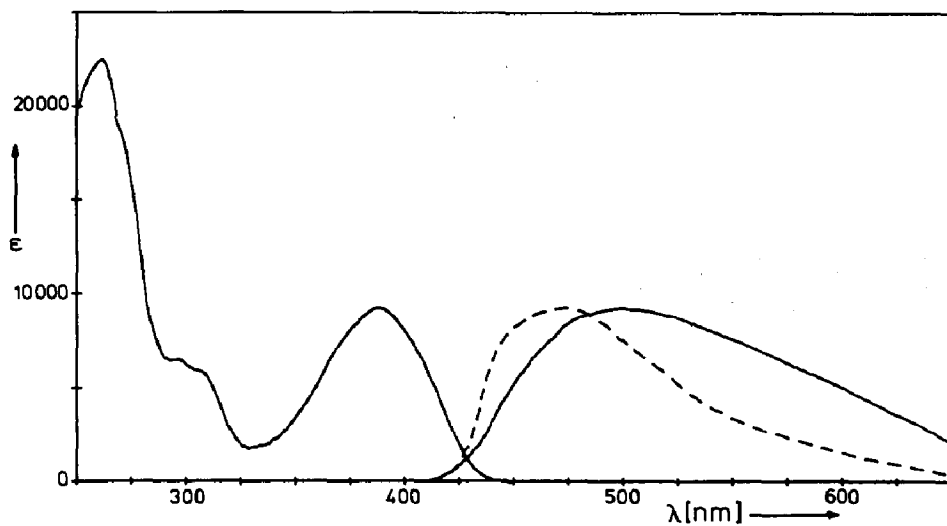


Fig. 2. UV and fluorescence spectra of 5g in EPA ($\lambda_{\text{ex}} = 395 \text{ nm}$): —, room temperature; ---, 77 K.

2.2. Fluorescence quantum yield and fluorescence lifetime

2.2.1. Measurements at room temperature

The fluorescence quantum yields ϕ_f were determined with biacetyl ($\phi_f = 0.003$) and anthracene ($\phi_f = 0.27$) standards [10, 11]. Biacetyl was especially well suited, since it absorbs in the same region as 5 and emits with a similar quantum yield. The measured values for ϕ_f are given in Table 2

TABLE 2
 ϕ_f and lifetime of S₁ states (in CH₂Cl₂ at room temperature)

DHI	λ_{\max} (nm)	$\epsilon_{\max} \times 10^{-3}$ (cm ² mol ⁻¹)	ϕ_f^a	$\tau_{rs}^b \times 10^9$ (s)	$\tau_s^c \times 10^{11}$ (s)	$\tau_s^d \times 10^{10}$ (s)	$\tau_s^e \times 10^{10}$ (s)	$\tau_s^f \times 10^{10}$ (s)
5a	410	6.7	0.0063	14.36	9.00			
5b	395	9.9	0.0035	9.01	3.15	2.57	2.25	1.5
5c	415	15	0.0032	6.56	2.10			
5d	392	8.5	0.0022	10.38	2.27	2.08	2.02	
5e	420	6.8	0.0029	14.43	4.18			
5f	384	10.4	0.0024	8.11	1.93			
5g	390	12	0.0038	7.27	2.76	3.40	8.51	2.3
5h	360	15.4	0.0052	4.83	2.51			
5i	338	11.1	0.0029	5.58	1.70			
5j	388	7.6	0.0038	11.33	4.30			

^a ϕ_f from $F_x/F_{st} = E_x \phi_f(x)/E_{st} \phi_f(st)$, where F_x is the integrated fluorescence intensity of 5, E_x is the optical density of 5, F_{st} is the integrated fluorescence intensity of the standard and E_{st} is the optical density of the standard.

^b $1/\tau_{rs} = 2.9 \times 10^{-9} n^2 \nu_{\max}^2 \epsilon_{\max} \Delta\nu^{1/2}$, where $\Delta\nu^{1/2} = 3000 \text{ cm}^{-1}$ and $n^2 = 2.01$.

^c From $\tau_s = \phi_f \tau_{rs}$.

^d Biacetyl as quencher.

^e Azulene as quencher.

^f $\tau_s(RT) = \tau_s(77 \text{ K}) \phi_f(RT)/\phi_f(77 \text{ K})$ (where RT denotes room temperature).

together with the natural fluorescence lifetimes τ_{rs} determined from the absorption spectra. τ_{rs} was calculated in terms of the halfwidth $\Delta\nu_{1/2}$ (cm^{-1}) of the longest wavelength absorption band from

$$\frac{1}{\tau_{rs}} = 2.9 \times 10^{-9} n^2 \nu_{\max}^2 \epsilon_{\max} \Delta\nu_{1/2} \quad (2)$$

(This relation is valid only in simple cases where the excited singlet reached by absorption and the fluorescent singlet are identical. No difference in geometry or solvent cage should occur during excitation.) Equation (2) is a simplification of the Strickler-Berg equation [12, 13] which describes the relation between light absorption and the fluorescence rate constant $1/\tau_{rs}$ [14] in simple cases. The natural lifetime τ_{rs} , e.g. the lifetime of the S_1 state in the absence of radiationless deactivation processes, is related to the fluorescence quantum yield ϕ_f and the experimentally measurable fluorescence lifetime τ_s via

$$\tau_{rs} \phi_f = \tau_s \quad (3)$$

Since the natural lifetime τ_{rs} can be calculated by eqn. (2) the singlet lifetime τ_s can be obtained by measuring ϕ_f and using eqn. (3) (see Table 2).

2.2.2. Direct measurement of the natural lifetime τ_{rs} at 77 K

After τ_s and ϕ_f have been determined, eqn. (3) can also be used to calculate the natural lifetime τ_{rs} . τ_s is given by

$$\frac{1}{\tau_s} = k_f + k_d + k_r(T) \quad (4)$$

by taking into account the rate constants for fluorescence $k_f (= 1/\tau_{rs})$ together with the rate constants for radiationless decay k_d (temperature independent) and $k_r(T)$ (temperature dependent). The low fluorescence quantum yield (see Table 2) did not allow a direct determination of τ_s at room temperature with the laser apparatus. Cooling to 77 K, however, decreases $k_r(T)$ to such an extent that the fluorescence quantum yield ϕ_f is increased, thus allowing a direct measurement of τ_s . The values for τ_s and ϕ_f at 77 K for 5b and 5g are given in Table 3 together with the τ_{rs} values derived from these data.

TABLE 3

Fluorescence lifetime τ_s and fluorescence quantum yield ϕ_f at 77 K in ether-pentane-alcohol and natural lifetime τ_{rs}

DHI	$\tau_s \times 10^9$ (s)	ϕ_f	$\tau_{rs} \times 10^9$ (s)
5b	2 ± 0.3	$(4.5 \pm 2) \times 10^{-3}$	444
5g	11 ± 2.0	$(2.2 \pm 1) \times 10^{-2}$	500

3. Fluorescence quenching of spiro [1,8-*a*]dihydroindolizine emission (5b, 5d and 5g)

Fluorescence quenching can be evaluated from the τ_s values given by

$$\frac{\phi_{f_0}}{\phi_{f(Q)}} = 1 + k_q \tau_s [Q] \quad (5)$$

where ϕ_{f_0} is the fluorescence quantum yield in the absence of a quencher, $\phi_{f(Q)}$ is the fluorescence quantum yield in the presence of a quencher and the quenching constants k_q are approximately equal to the rate of diffusion.

Equation (5) is a Stern-Volmer relation [15]. At very low concentrations the quenching constant can be approximated by the rate of diffusion k_{diff} , when the energy difference between the singlet state of the donor and that of the acceptor is $\Delta E(S_1) \geq 3 \text{ kcal mol}^{-1}$.

Biacetyl and azulene were employed as quenchers of the fluorescence of 5b, 5d and 5g. Since the experiments were carried out in ethanol $k_{diff} = 0.9 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$ was used. This is valid only if diffusion control is assumed. The Stern-Volmer plots are given in Fig. 3 and the resulting values of τ_s are collected in Table 2.

Quenching of the fluorescence (degassed or air-saturated solutions) of 5b and 5g in acetonitrile at room temperature with oxygen led to an upper limit of 1 ns for τ_s .

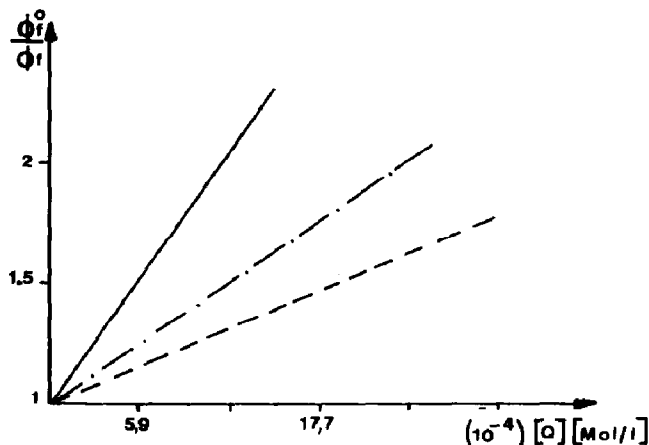


Fig. 3. Stern-Volmer plot of fluorescence quenching for 5b (---), 5d (- · -) and 5g (—) with azulene as quencher.

4. Discussion of absorption and emission studies

4.1. Interpretation of spectroscopic data

The data obtained for 5 can be divided into three groups as follows: dihydroindolizines 5 having (i) a spirobridge containing six carbon atoms, (ii) a spirobridge with five carbon atoms and ester substituents in the double bond and (iii) a spirobridge with five carbon atoms and cyanosubstituents

in the double bond. The data of these three groups show the following trend: by enlarging the five-membered spirobridge to a six-membered spirobridge the fluorescence, as well as the absorption maxima, is shifted bathochromically. The fluorescence quantum yields ϕ_f are very small (10^{-3}) and change only slightly in going from a five-membered to a six-membered spirobridge.

The singlet energies $E(S_1)$ in the spirocycles 5 containing five rings show values between 65 and 68 kcal mol⁻¹, whereas the spirocompounds having a six-membered ring (5d, 5e) have $E(S_1)$ values of 59 - 63 kcal mol⁻¹. An additional nitrogen atom in the heterocyclic ring of 5 as well as annellation of a benzene nucleus lead to a decrease in the singlet energy in both the ester-substituted and the cyano-substituted series of compounds 5.

As far as the absorption spectra are concerned an important question is as follows: which chromophore is responsible for the longest wavelength band? A comparison of the spectra of biphenyl, fluorene and benzophenone shows that this band cannot be attributed to one of these chromophores and it is thus assigned to the amino part of the molecule. Pariser-Parr-Pople calculations support this assignment. For the compounds 5a, 5b, 5d, 5f, 5g, 5i and 5j this molecular part is related to sterically fixed butadienyl vinyl amines. Very little is known on the absorption data of such compounds. These compounds, however, are isoelectronic with octatetraene and are related to the visual pigments [16]. The red-shifted fluorescence in 5 shows no measurable solvatochromy (see Fig. 1). Thus, the ground and the excited state of 5 probably have similar dipole moments. A twisted intramolecular charge transfer state which has been observed in many bichromophoric systems [17 - 19] can thus be excluded. However, the larger τ_{fs} value at 77 K seems to suggest that the emitting state may not be identical with the singlet state reached by absorption. As seen from eqn. (2) and Table 2, the lifetimes calculated for 5b and 5g from the absorption band are too short. From this fact it may be concluded that the emitting state is a ¹A_g state which cannot be seen in absorption [16, 20]. This state can be described by including doubly excited configurations [21]. The other alternative is that the Strickler-Berg equation does not hold any more for 5 since structural changes are significant in 5*.

4.2. Kinetics

The experimentally determined (77 K) low fluorescence quantum yields demonstrate that k_d is larger than k_f (eqn. (4)). If it is assumed that $k_r(T)$ at 77 K can be neglected, then the k_d values are 5×10^8 s⁻¹ for 5b and 9×10^7 s⁻¹ for 5g. The increase in k_d by a factor of 5 in going from 5g to 5b can be attributed to the effect of the cyano substituents.

Using the same assumption $k_r(T)$ can be estimated at room temperature, being mainly due to the ring opening $5^* \rightarrow 6$. $k_f + k_d$ (from the low temperature study) in connection with $k_f + k_d + k_r = 1/\tau_s$ (from the quenching experiments) gives $k_r \approx 3.3 \times 10^9$ s⁻¹ for 5b and $k_r \approx 3.1 \times 10^9$ s⁻¹ for 5g. Ring opening $5 \rightarrow 6$ is therefore larger by a factor of $10^{10} - 10^{12}$ than the thermal back reaction (see refs. 8 and 13).

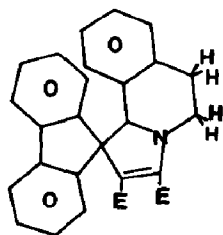
4.3. Quantum yields of reaction and independent rate determination

4.3.1. Determination of ϕ_r

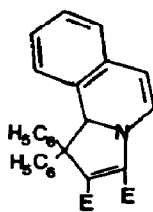
The quantum yields ϕ_{r1} for the electrocyclic ring opening $5 \rightarrow 6$ were measured for compounds **5a**, **5b**, **5f** and **5g**, and for **5a** and **5b** the quantum yields ϕ_{r2} for cycloreversion were measured as well. The UV absorption of **5** and **6** was used as an analytical tool.

The number of light quanta absorbed was determined with iron oxalate actinometry [22]. An automatic quantum counter according to Schaffner and coworkers [23] was employed and the quantum yields were extrapolated to zero conversion to exclude light absorption by the betaine **6** (see also ref. 24). ϕ_r decreases with increasing time (Fig. 4).

This effect must be attributed to a filter effect of the coloured betaine **6**. However, DHI systems **5** with long half-life times of cycloreversion had to be investigated to obtain reasonable precision in ϕ_r . From a comparison of the different systems it can be seen that the cyanosubstituted DHIs **5a** and **5b** possess much larger quantum yields than **5f** and **5g** (ester). The simple DHI **8** having no spiro bridge shows a rather low ϕ_{r1} value. The decreasing efficiency of the DHI systems **5a**, **5b**, **5f** and



7



8

is evident from the following sequence for ϕ_{r1} : $5a > 5b > 7 > 5f > 8$.

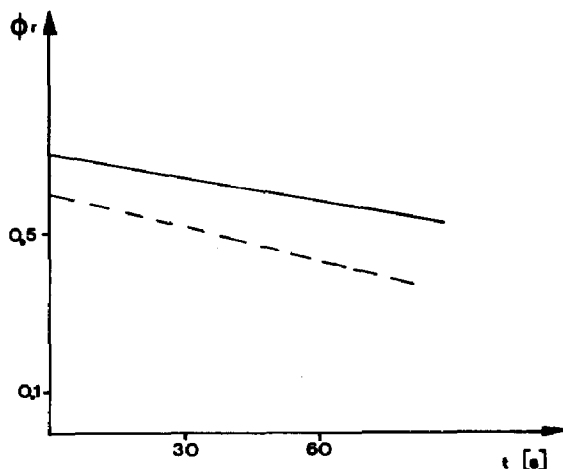


Fig. 4. Dependence of quantum yield for the photoreaction of **5f** (—) and **5g** (---) on conversion time.

5. Multiplicity studies with 5

Quenching studies were used to evaluate the multiplicity of the photo-reaction $5 \rightarrow 6$. Since the triplet energy of 5 was unknown, 5a was embedded in a polymer matrix ((vinylidene chloride)-acrylonitrile copolymer) (SARAN) and the phosphorescence emission was checked. Room temperature measurements of SARAN films containing 5 as well as EPA matrices of 5 (77 K) showed no phosphorescence. Therefore E_T for 5 was assumed to be of the order of 60 kcal mol^{-1} . Biacetyl ($E_T = 56.3 \text{ kcal mol}^{-1}$) and anthracene ($E_T = 42 \text{ kcal mol}^{-1}$) were therefore employed as quenchers.

The quenching experiments $5a \rightarrow 6a$ and $5b \rightarrow 6b$ with both quenchers showed no effect whatsoever. Hence 5 reacts either (a) via an *excited singlet state* or (b) via a bimolecularly *non-quenchable triplet state*.

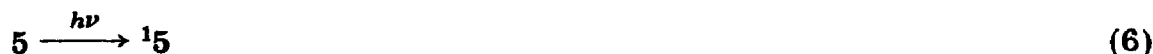
5.1. Sensitization by chemiexcitation

A very elegant method to induce triplet reactions is the application of chemiexcitation or in other words "photochemistry without light" [25]. An ideal substrate is tetramethyldioxetane (TMD) which in solution decomposes quantitatively to acetone by a first-order reaction [26]. Thus 30% T_1 acetone, 0.5% S_1 acetone and ground state acetone are produced [25 - 27] ($E_T(\text{acetone}) = 78 \text{ kcal mol}^{-1}$). Chemiexcitation with TMD for 5 was used in the following way: 5a was dissolved in cyclohexane and TMD was added. The degassed solution of 5 and TMD was then thermolysed at 70°C . After this process the UV spectrum showed the decrease in 5 (the products were not identified in this reaction); however, no betaine 6 was produced (control experiment: 5 plus TMD; room temperature; no decomposition of 5). Thus 6 is certainly not generated by triplet excited 5.

The sensitization and the chemiexcitation experiments therefore show very clearly that the photorearrangement $5 \rightarrow 6$ does occur via a *singlet excited state*. The 35 obviously leads to other products.

6. Calculation of rate constants

The excited state of DHI 5 has the following possibilities for deactivation:





Reactions (7) - (10) are the deactivation modes of singlet 5 whereas (11) - (13) are those of triplet 5. Since the photorearrangement $5 \rightarrow 6$ involves 15 , routes (11) - (13) can be neglected. The rate constants can therefore be calculated from

$$\phi_f + \phi_r + \phi_{ic} + \phi_{isc} = 1 \quad (14)$$

For some DHIs 5 τ_s , ϕ_f and ϕ_r could be determined, thus allowing the evaluation of k_f , k_r and $k_d (= k_{ic} + k_{isc})$. Table 4 shows the rate constants calculated that way. It can be seen that k_r decreases in the order $5b > 5f > 5a$, showing that 5b is the fastest reacting molecule in this series.

TABLE 4

Rate data k_f , k_r and k_{ic} of spiro[1,8-*a*]dihydroindolizines 5a, 5b, 5d, 5f and 5g

DHI	τ_s (s)	ϕ_f	ϕ_{ic}	k_r (s^{-1})	k_{ic} (s^{-1})
5a ^a	9.04×10^{-11} ^a	0.70		$0.03_5 \times 10^9$ ^a	
5b ¹ ^a	2.80×10^{-11}	0.63	0.37		
5b ² ^b	2.57×10^{-10}	0.63		2.45×10^9	1.42×10^9
5b ³ ^b	2.25×10^{-10}	0.63		2.80×10^9	1.63×10^9
5b ⁴ ^c	1.50×10^{-10}	0.63		3.30×10^9	1.83×10^8
5d	2.02×10^{-10}	0.6 ^d		2.97×10^9	
5f ^a	1.93×10^{-10}	0.43	0.56	0.46×10^9 ^a	2.30×10^8
5g ^c	2.30×10^{-10}	0.4 ^d		1.73×10^9	

^a a, b¹ and f are calculated from τ_{rs} in Table 2.

^b b² and b³ are calculated from quenching experiments with biacetyl and azulene respectively.

^c Experimental value.

^d Estimated value.

7. Experimental part

7.1. Spectrometers

The following equipment was used: Cary 14 (Varian) and DU-8 (Beckman) UV spectrometers; an MPF 44a (Perkin-Elmer) or a 650-60 (Perkin-Elmer) fluorometer (for the room temperature spectra of Figs. 1 and 2); an MAT 311 (Varian) (70 eV) mass spectrometer. The UV spectra (Table 1) were measured in CH_2Cl_2 .

7.2. Actinometry

The number I of quanta emitted by the lamp (Osram HBO 200) in a Bausch and Lomb monochromator was measured with an iron oxalate actinometer (Hatchard and Parker).

7.3. Quantum yields

The quantum yield ϕ_x for the reaction $5 \rightarrow 6$ was measured in a quantum counter according to Schaffner and coworkers [23] (room temperature). Concentrations of $E = 2$ were chosen for 5; five runs were evaluated using the equation

$$\phi_x = \frac{\Delta C}{It}$$

7.4. Fluorescence spectra

The fluorescence spectra at 77 K were recorded on an FICA 55 MK II spectrofluorometer, and ϕ_f (77 K) was determined as described [28]. Anthracene and biacetyl were used as standards for ϕ_f determinations at room temperature. 10^{-5} M solutions of 5 were employed. Fluorescence lifetime measurements were carried out with a neodymium-glass laser system [29] using the third harmonic ($\lambda_{ex} = 353$ nm).

7.5. Quenching experiments

Quenching experiments of the reaction $5a \rightarrow 6a$ and $5b \rightarrow 6b$ were run with anthracene and biacetyl as quenchers.

7.5.1. Anthracene

Six cells containing 2 ml of a 2.93×10^{-4} M solution of 5a or a 1.75×10^{-4} M solution of 5b in CH_2Cl_2 were diluted with increasing amounts of a 1×10^{-2} M solution of anthracene in CH_2Cl_2 to 3 ml. Five runs were taken and the quantum yields remained constant: $\phi = 0.59 \pm 0.04$ for 5a and $\phi = 0.39 \pm 0.04$ for 5b.

7.5.2. Biacetyl

Under the same conditions an 8.28×10^{-3} M solution of biacetyl in CH_2Cl_2 was used: $\phi = 0.59 \pm 0.005$ for 5a and $\phi = 0.43 \pm 0.01$ for 5b with no change at increasing quencher concentration.

7.6. Fluorescence quenching: with 5b, 5d and 5g

7.6.1. Biacetyl

Five runs were made using 10^{-4} M solutions of 5b, 5d and 5g in ethanol. Increasing amounts of a 0.482 M biacetyl solution in ethanol were added to a constant volume of 3 ml. Fluorescence spectra were measured and corrected for biacetyl absorption.

7.6.2. Azulene

Similarly azulene was employed as a fluorescence quencher. k_D for ethanol of $0.9 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$ was taken for the τ_F calculations.

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