

THE DEACTIVATION BEHAVIOUR OF PHOTOEXCITED 2,6-DIPHENYL-4-(*p*-DIMETHYLAMINOPHENYL)-BENZOYLIMINO- PYRIDINIUM YLIDE

WERNER ABRAHAM, ANDRE HENRION and DIETER KREYSIG

Sektion Chemie, Humboldt-Universität zu Berlin, DDR-1040 Berlin (G.D.R.)

(Received 27 June, 1985; in revised form April 4, 1986)

Summary

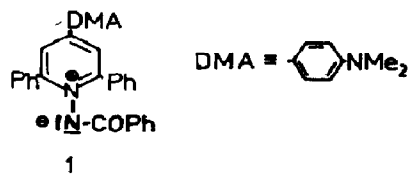
The photophysical and photochemical deactivation behaviour of 2,6-diphenyl-4-(*p*-dimethylaminophenyl)-benzoyliminopyridinium ylide as a model compound of *N*-ylides has been studied. The solvent has a marked influence on its absorption and fluorescence spectra and also on its photophysical and photochemical deactivation behaviour.

A deactivation scheme is discussed in the light of fluorescence lifetime and quantum yield measurements. The main radiationless deactivation process in protic solvents involves torsional relaxation and is viscosity dependent. In solvents of moderate polarity it is postulated that the formation of a valence isomer diminishes the population of the fluorescing state. The influence of the solvent can be described by means of the multiparameter model of Kamlet and Taft.

The photochemical N—N bond cleavage originates from the triplet state but the intramolecular rearrangement to the 1,2-diazepine occurs in the singlet state. The properties of the solvent determine which of the two photoreactions predominates.

1. Introduction

The photochemistry of pyridinium ylides such as 1



is characterized by competition between ring enlargement leading to 1,2-diazepines and conversion to 2-aminopyridines [1]. In contrast to other heterocyclic *N*-imines, N—N bond rupture in the electronically excited state does not play an important role. This reaction, which leads to nitrenes and pyridines, is the main reaction of the ground state [2, 3].

The photoreactions of pyridinium ylides have been investigated extensively [1], but there has been a lack of investigation concerning the properties of excited states and their role in photochemistry. Therefore the aim of this paper is to report on investigations regarding the photophysical and photochemical deactivation behaviour of the model compound **1**, the first pyridinium ylide found to exhibit fluorescence. The conditions under which N—N bond cleavage is the main reaction were explored to enable the photochemical production of acylnitrenes to be carried out with high efficiency.

2. Results

2.1. Absorption spectrum

A source of information on the nature and properties of excited states is the dependence of absorption and fluorescence spectra on the properties of the solvent. Therefore, it is important to analyse the influence of the solvent on absorption and luminescence energies, quantum yields, fluorescence lifetimes etc. Exact procedures for the characterization of this influence are not yet available. An accepted model for the description of the effect of the solvent is the multiparameter model of Kamlet *et al.* [4], and this is also suitable for the interpretation of the influence of the solvent on the transition energies and photophysical deactivation parameters of the ylide **1**.

The maximum of the longest wavelength absorption band is correlated with the solvent parameter π^* (the polarity) and the parameter α for the hydrogen-bonding capacity of the solvent:

$$\tilde{\nu}_A (\times 10^5 \text{ m}^{-1}) = 26.03(\pm 0.32) - 1.95(\pm 0.52)\pi^* - 1.27(\pm 0.32)\alpha \quad (1)$$

where the multiple correlation coefficient $R = 0.954$, the standard deviation SD of the regression fit is 0.244 and the number N of solvents used is 18 [5].

The absorption energy is not affected by the properties of the solvent alone but is also dependent on the temperature. From Fig. 1 it can be seen that the absorption band is shifted bathochromically on decreasing the temperature in alcoholic solvents.

2.2. Fluorescence spectrum

Whilst absorption spectra provide information about the Franck-Condon excited state, one can also obtain some insight into the nature of the relaxed excited state from the dependence of the fluorescence energies on the solvent properties.

To obtain a good correlation between the fluorescence energies and the properties of the solvent it is necessary to include a solvent-viscosity parameter $\hat{\eta}$ [5]:

$$\tilde{\nu}_F (\times 10^5 \text{ m}^{-1}) = 21.98(\pm 0.47) - 3.91(\pm 0.68)\pi^* - 1.54(\pm 0.46)\alpha + 0.55(\pm 0.36)\hat{\eta} \quad (2)$$

($R = 0.982$; SD = 0.191; $N = 12$). Also, in the case of fluorescence, the temperature affects the energy, but in contrast to the absorption maximum

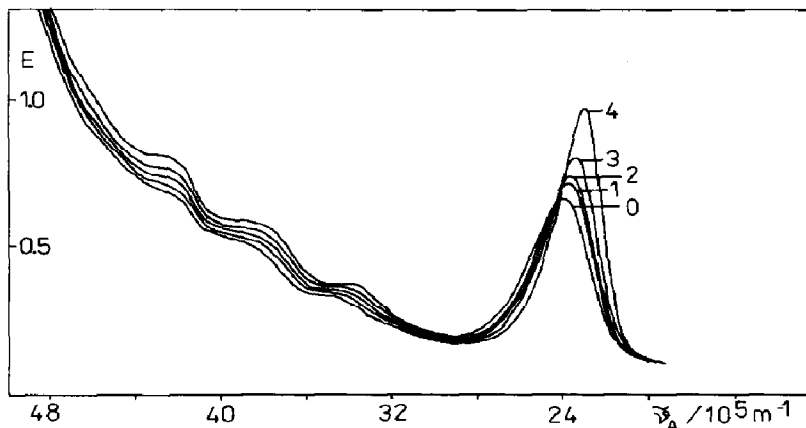


Fig. 1. Absorption spectrum of compound 1 in ethanolic solution at different temperatures: curve 0, 0 - 290 K; curve 1, 238 K; curve 2, 219 K; curve 3, 163 K; curve 4, 92 K.

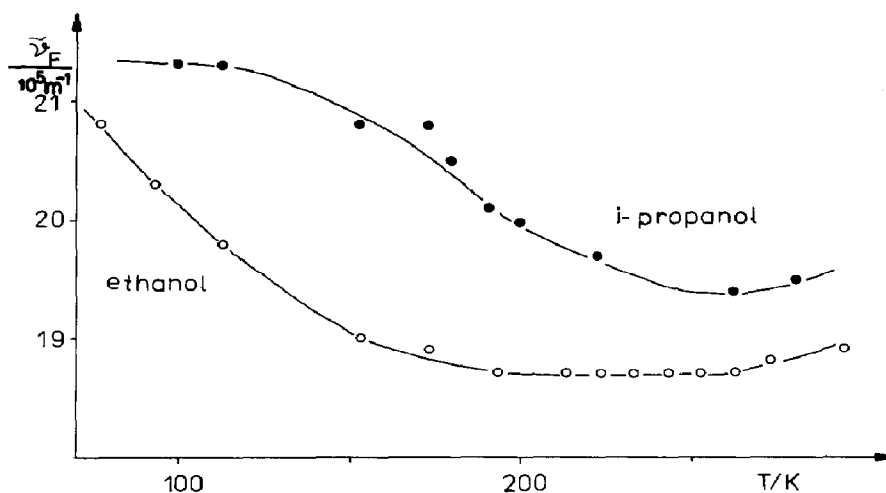


Fig. 2. Dependence of the fluorescence maximum of 1 in ethanol and *i*-propanol on the temperature.

the fluorescence maximum is shifted hypsochromically on decreasing the temperature (Fig. 2). As with the fluorescence energy, the fluorescence quantum yield and the fluorescence lifetime are also strongly dependent on the properties of the solvent (Table 1).

Varying the temperature is useful in the detection of thermally activated processes in the excited states and to prevent radiationless deactivation processes at low temperatures. In this way it is possible to measure the fluorescence quantum yield and fluorescence lifetime in the absence of thermally activated radiationless processes (Table 2).

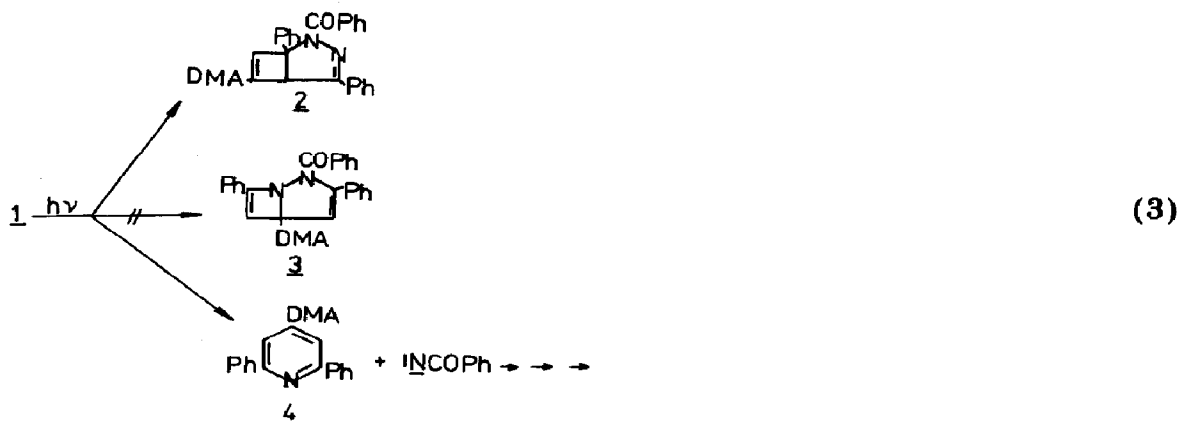
TABLE 1

Fluorescence maxima $\tilde{\nu}_F$, quantum yields ϕ_F and lifetimes τ_F of 1 in different solvents

| Solvent | $\tilde{\nu}_F(\times 10^5 \text{ m}^{-1})$ | ϕ_F | $\tau_F(\text{ns})$ | $\phi_F/\tau_F(\times 10^8 \text{ s}^{-1})$ |
|---------------------|---|----------|---------------------|---|
| Methanol | 18.52 | 0.02 | 0.1 | 1.9 |
| Ethanol | 19.05 | 0.07 | 0.4 | 1.8 |
| <i>n</i> -Propanol | 19.61 | 0.20 | 1.3 | 1.5 |
| <i>i</i> -Propanol | 19.61 | 0.27 | 1.8 | 1.5 |
| <i>n</i> -Butanol | 19.42 | 0.29 | 1.5 | 1.9 |
| <i>n</i> -Pentanol | 19.23 | 0.36 | 1.9 | 1.9 |
| <i>i</i> -Pentanol | 19.23 | 0.42 | 2.2 | 1.9 |
| Heptanol | 19.23 | 0.37 | 1.9 | 1.9 |
| Octanol | 20.00 | 0.31 | 2.5 | 1.2 |
| 1,2-Ethanediol | 18.35 | 0.06 | 0.4 | 1.3 |
| Dimethyl sulphoxide | 18.52 | 0.05 | 0.3 | 1.6 |
| Dimethylformamide | 18.69 | 0.03 | 0.3 | 1.2 |
| Acetonitrile | 19.05 | 0.01 | 0.1 | 1.1 |
| Ethyl acetate | 20.62 | 0.002 | 0.6 | 0.05 |
| Tetrahydrofuran | 20.20 | 0.002 | 0.2 | 0.1 |
| Diethyl ether | 21.28 | 0.006 | 1.2 | 0.05 |
| Toluene | 21.20 | 0.002 | 1.2 | 0.02 |
| Methylene chloride | 20.40 | 0.008 | 1.7 | 0.05 |

2.3. Photochemical reactivity

Two completely different reactions could be detected.



In the solvent diethyl ether the bicyclic compound 2 was the only detectable product of the photoreaction. In *n*-butanol, only the product of the N—N bond cleavage, the 2,6-diphenyl-4-(*p*-dimethylaminophenyl)-pyridine 4, was isolated. These results are different from those obtained with other pyridinium ylides [6]. Using the known absorption spectra of the photoproducts 4 and 2, it was possible to calculate the proportions of 4 or 2 by comparison with the absorption spectrum of the solution in other solvents after the photoreaction

TABLE 2

Fluorescence quantum yields, lifetimes and fluorescence maxima of compound 1 in alcoholic solvents at different temperatures

| T (K) | $\tilde{\nu}_F$ ($\times 10^5$ m^{-1}) | ϕ_F | τ_F (ns) |
|-------------------|--|----------|---------------|
| <i>Ethanol</i> | | | |
| 298 | 18.9 | 0.07 | 0.4 |
| 273 | 18.8 | 0.08 | 0.84 |
| 263 | 18.7 | 0.09 | 1.1 |
| 253 | 18.7 | 0.1 | 1.2 |
| 243 | 18.7 | 0.12 | 1.3 |
| 233 | 18.7 | 0.15 | 1.4 |
| 223 | 18.7 | 0.17 | 1.5 |
| 213 | 18.7 | 0.2 | 1.6 |
| 190 | 18.7 | 0.3 | 1.8 |
| 173 | 18.9 | 0.5 | 2.1 |
| 163 | — | — | 2.5 |
| 153 | 19.0 | 0.6 | 2.6 |
| 133 | — | 0.6 | 3.0 |
| 113 | — | 0.6 | 2.9 |
| 77 | 20.8 | 0.6 | 3.1 |
| <i>i-Propanol</i> | | | |
| 292 | 19.6 | 0.27 | 2.1 |
| 281 | 19.5 | 0.28 | — |
| 240 | 19.5 | 0.42 | 2.7 |
| 223 | 19.7 | 0.46 | 2.7 |
| 203 | 20.0 | 0.54 | 2.9 |
| 191 | 20.1 | 0.57 | 3.1 |
| 180 | 20.5 | 0.61 | 3.1 |
| 172 | 20.8 | 0.66 | 3.2 |
| 153 | 20.8 | 0.6 | 2.9 |
| 143 | — | 0.6 | 2.9 |
| 133 | — | 0.6 | 2.8 |
| 113 | 21.3 | 0.5 | 2.7 |
| 93 | 21.3 | 0.7 | 2.7 |

was complete. Therefore the photoreactions were followed by monitoring the absorption spectra (Fig. 3). From Fig. 3 it can be seen that the two kinds of photoreactions can be discriminated easily by the UV absorption spectra.

The intramolecular cyclization leads to 2 exclusively. The other possible product 3 could not be detected. The formation of 2 is preferred in less polar and non-polar solvents such as diethyl ether and cyclohexane (yield of 2, above 90%). The N—N bond cleavage with the formation of 4 is dominant in more polar solvents, such as acetonitrile, and in alcohols. In solvents of moderate polarity, such as tetrahydrofuran, the products 2 and 4 are obtained in nearly equal proportions.

The formation of the bicyclic compound 2 involves a sequence of photochemical reactions. The non-linear *E*—*E* diagram obtained by following the photoreaction spectroscopically (Fig. 3(a)) shows that there must be an

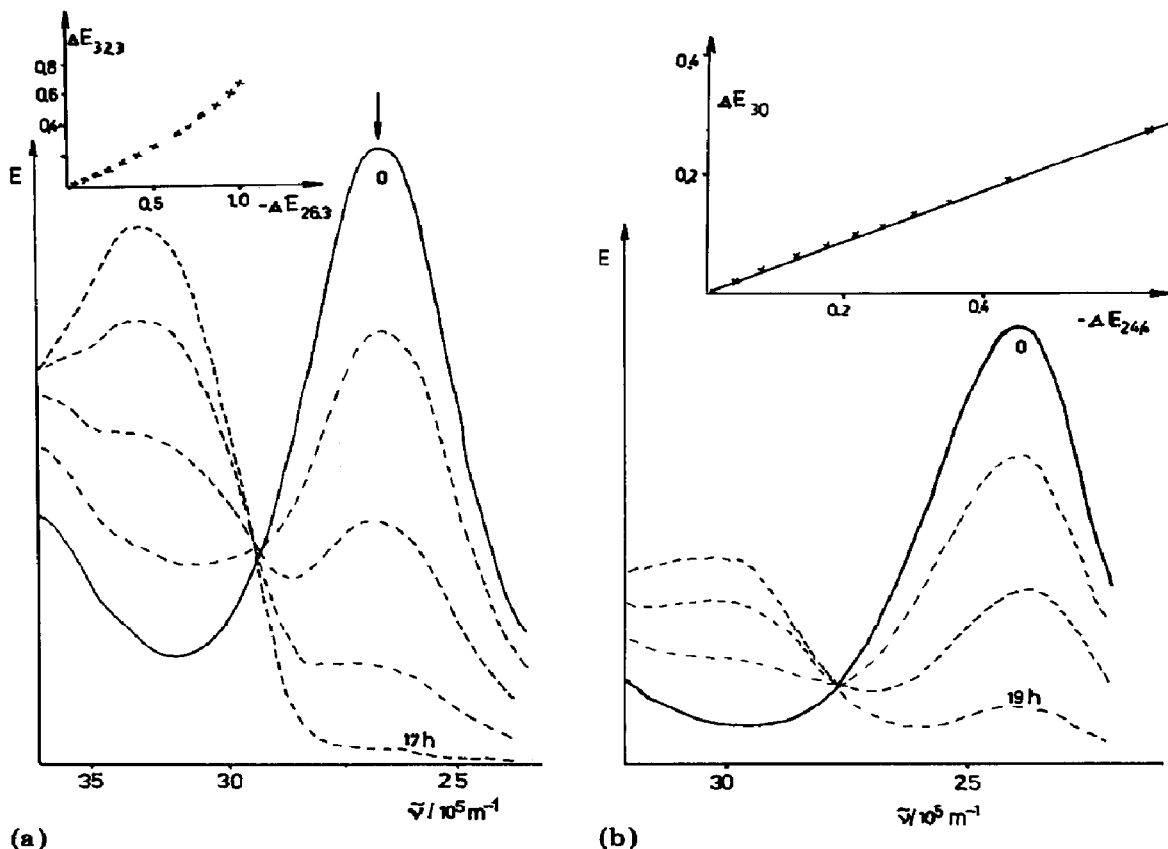


Fig. 3. UV spectra of the solution of 1 at various exposure times ($\lambda_{\text{exc}} = 405 \text{ nm}$): (a) cyclohexane; (b) *n*-butanol.

intermediate product [7] (this could not be isolated as a photoproduct). The bond rupture is a uniform reaction (Fig. 3(b)), and the rate of bond cleavage is dependent on the viscosity of the solvent. Therefore the reaction rates are in the sequence *n*-butanol \gg ethanol $>$ methanol. The rate of the reaction is also influenced by oxygen. The rate of the bond cleavage is three times greater in solutions without oxygen than in air-saturated solutions. Furthermore, this photoreaction can be sensitized in acetonitrile by biacetyl. The phosphorescence of biacetyl is quenched by adding 1.

The efficiency of the formation of the bicyclic compound 2 is generally much larger than that of the bond rupture without sensitization. Oxygen does not influence the rate of the cyclization reaction.

3. Discussion

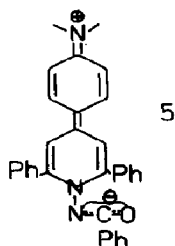
3.1. Absorption spectra

The double-bond character of the N—N bond in heterocyclic *N*-ylides is commonly increased in the excited state compared with the ground state

because of the charge transfer to the heterocyclic ring which results on light absorption [8]. The dipole moment of such compounds is smaller in the excited state than in the ground state, causing the negative solvatochromism of the longest wavelength absorption band.

On introducing the dimethylaminophenyl substituent (a strong electron donor) in a pyridinium ylide such as 1, the direction of the charge transfer in the excited state is changed. The dipole moment is now increased in the excited state compared with the ground state.

The positive solvatochromism associated with the direction of the charge transfer is expressed in eqn. (1) by the sign of the regression coefficient for the polarity parameter π^* . Hydrogen bonding between the solvent and the exocyclic nitrogen atom of the ylide fragment in 1 in the ground state is increased in the excited state because of the increased negative charge at this nitrogen atom (see resonance structure 5).



The progressive red shift of the UV absorption band of 1 in ethanol as a result of cooling (Fig. 1) can be explained by the assumption of torsional motions of the single bond between the donor and the acceptor moiety of the molecule, which are expected to be appreciably excited at room temperature. Upon cooling the torsional motions are reduced, resulting in nearly planar geometries with more efficient conjugation. An increase in intensity can be expected in systems which include conjugative interactions between two chromophores because the oscillator strength depends on the twisting angle. Similar effects have been observed in other non-rigid molecules, such as tetraphenylbutadiene [9] or arylcycloheptatrienes [10].

According to this explanation of the effect of temperature on the absorption spectrum it can be assumed that the structure of the molecule 1 is altered only slightly at low temperatures.

3.2. Fluorescence spectra

From eqns. (1) and (2) a moderate Stokes shift can be derived. As usually observed, the influence of polarity and hydrogen-bonding capacity of the solvent is greater for the fluorescence energy than for the absorption energy (see the regression coefficients). The inclusion of the viscosity in eqn. (2) leads to a significant improvement in the correlation for the fluorescence energy [5]. This means that the relaxation from the Franck-Condon state to the equilibrium excited state configuration involves torsional motions

which are limited by the solvent viscosity. The incomplete twisting relaxation causes a blue shift of the fluorescence maximum [9], which is expressed by the positive regression coefficient in eqn. (2) for the parameter $\tilde{\eta}$.

Also, the large blue shift of $2.3 \times 10^5 \text{ m}^{-1}$ on going from the fluid solvent ethanol to a rigid glass at 77 K may be explained by the viscosity dependence of the fluorescence energy. This explanation is supported by the different dependence of the fluorescence maximum on the temperature in two alcohols which have a different dependence of the viscosity on the temperature (Fig. 2). The increase in $\tilde{\nu}_F$ over the temperature range from 260 K to room temperature in Fig. 2 may be due to temperature-induced selective quenching by population of the upper torsional modes which undergo more efficient internal conversion (selective red quenching [11]).

The torsional modes may be identified with twisting motions of the donor fragment (dimethylaminophenyl ring) and the acceptor moiety (pyridinium ylide). This means that the molecule in the fluorescing state is more coplanar than in the ground state.

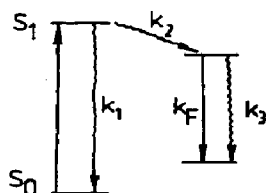
3.3. Photophysical deactivation

The measured values of the fluorescence quantum yields together with the fluorescence lifetimes in several solvents are given in Table 1. The formally calculated fluorescence rate constants $k_F = \phi_F/\tau_F$ differ considerably in different solvents. Only for alcoholic solvents do the fluorescence rate constants, which can be evaluated from the absorption spectrum [12], agree with the experimentally measured k_F ($k_F(\text{calc}) = 1.8 \times 10^8 \text{ s}^{-1}$ for butanol). According to the absorption spectra such large deviations of k_F in moderately polar and non-polar solvents cannot be expected because the extinction coefficients are of a similar order of magnitude in all solvents. Two different reasons for the differences are possible.

(1) The fluorescent state in the moderately polar and non-polar solvents is not identical with the singlet state reached by absorption.

(2) Both states are adequate but the quantum yield of the population of the fluorescent state from the Franck-Condon excited state is smaller than unity.

Two arguments support the assumption of case (2): (i) those solvents in which 1 exhibits the anomalous k_F values are described by correlations (1) and (2); (ii) neither from the excitation spectra nor from the behaviour of the fluorescence spectra can any reference to a special excited state in moderately polar and non-polar solvents be seen. Therefore, two competing processes in the Franck-Condon excited state must be assumed.



(4)

The experimental natural fluorescence lifetime is given by

$$\frac{1}{\tau_{\text{exp}}^0} = \frac{\phi_{\text{F}}}{\tau_{\text{exp}}} = \frac{k_2}{k_1 + k_2} \frac{1}{\tau_{\text{calc}}^0} \quad (5)$$

In highly polar solvents $k_1 \ll k_2$ is valid but in moderately polar and non-polar solvents $k_2 < k_1$.

The radiationless process characterized by k_3 in process (4) must be related to the viscosity of the solvent because both the fluorescence quantum yield and the lifetime are quite different in different alcohols (Table 1). Taking into account the different ratios of k_1 to k_2 in several solvents, the rate constants k_3 cannot be evaluated from ϕ_{F} and τ_{F} but must be evaluated from the lifetime alone according to

$$\frac{1}{\tau_{\text{F}}} = k_{\text{F}} + k_3 + k_4 \quad (6)$$

The rate constant k_4 is introduced as an additional radiationless process from the fluorescent state because the measured fluorescence lifetime does not reach the calculated value of 5.6 ns (from the absorption spectrum) in either highly viscous solvents or at 77 K. Thus a viscosity- and temperature-independent fourth deactivation pathway must be assumed. According to the lifetime at 77 K in ethanol or in EPA a limiting lifetime $\tau_0 = 3.2$ ns was derived and used in eqn. (6) leading to the relation

$$k_3 = \frac{1}{\tau_{\text{F}}} - \frac{1}{\tau_0} \quad (7)$$

with $k_0 = k_{\text{F}} + k_4 = 1/\tau_0$.

The influence of the solvent viscosity on the deactivation rate constant k_3 is obvious from the data in Table 1. We believe that this influence results from the control by the viscosity of a torsional relaxation process in 1 which is associated with large amplitude motion. Such effects of solvents on the radiationless decay of excited molecules which are thought to undergo large amplitude structural changes have been the subject of both early [13, 14] and recent [15, 16] studies. The rate constants can be expressed generally as a function $f(\eta)$ of the viscosity and the internal barrier height E_0 of the radiationless process. Courtney and Fleming [15] found at higher viscosities that their data were fitted by an equation of the form

$$k = \frac{B}{\eta^a} \exp\left(-\frac{E_0}{RT}\right) \quad (8)$$

Solvents may affect both terms of eqn. (8), the separation of which should be possible by using similar solvents for the correlation between the deactivation rate constant and the viscosity of the solvent. Indeed, from Fig. 4, a rather good linear function of $\ln k_3$ from the solvent viscosity in alcoholic solutions can be seen. The larger deviations of the less polar alcohols lead to the assumption that, besides the viscosity, polarity parameters may also be involved. Indeed a correlation of the radiationless rate constant k_3 with

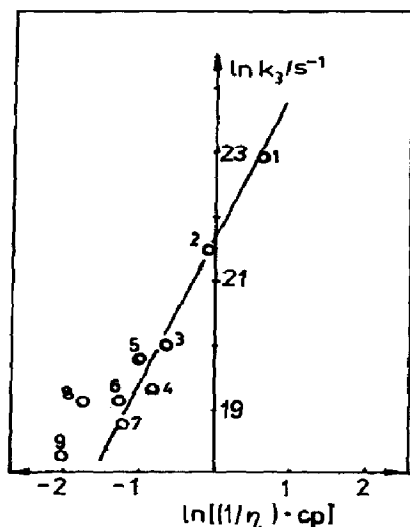


Fig. 4. Plot of the radiationless deactivation rate constant k_3 on the solvent viscosity in alcoholic solutions: 1, methanol; 2, ethanol; 3, *n*-propanol; 4, *i*-propanol; 5, *n*-butanol; 6, *n*-pentanol; 7, *i*-pentanol; 8, heptanol; 9, *n*-octanol.

solvent parameters for the viscosity ($\hat{\eta}$), polarity (π^*) and hydrogen-bonding capacity (α) can describe the influence of the solvent on k_3 for all solvents used [17]:

$$\ln k_3 = 19.72(\pm 1.06) + 6.00(\pm 1.56)\pi^* + 2.02(\pm 1.37)\alpha - 2.69(\pm 1.17)\hat{\eta} \quad (9)$$

($R = 0.937$; $SD = 0.670$; $N = 14$). Equation (9) shows the complex character of the influence of the solvent on the deactivation of the fluorescent S_1 state in the ylide 1. The polarity and hydrogen-bonding capacity of the solvent both influence the shape and the height of the intrinsic energy barrier along a twisting coordinate. Such effects were also found for other cases [18].

Considering eqn. (9), it can be seen that an increase in solvent polarity (π^* and α) favours barrier crossing (increased k_3). This may be due to the stabilization of a twisted state which is more polar than the initial state. This will also lower the crossing point of the two states [18].

Increasing the solvent viscosity $\hat{\eta}$ lowers the rate of barrier crossing; this is associated with the structural changes of the molecule during barrier crossing.

We believe that the radiationless deactivation channel corresponds to a twisted intramolecular charge transfer state (TICT) (this is known to exist for other donor-acceptor-substituted molecules [19]). The radiationless deactivation of the postulated TICT state is so fast that fluorescence from this state cannot be observed. The formation of the TICT state is irreversible. This can be concluded from the temperature dependence of the fluorescence lifetime, which does not correspond to a back reaction as in other cases [19] (Fig. 5). An activation energy of 7 kJ mol^{-1} results in the low temperature region in which the fluorescence maximum does not depend on

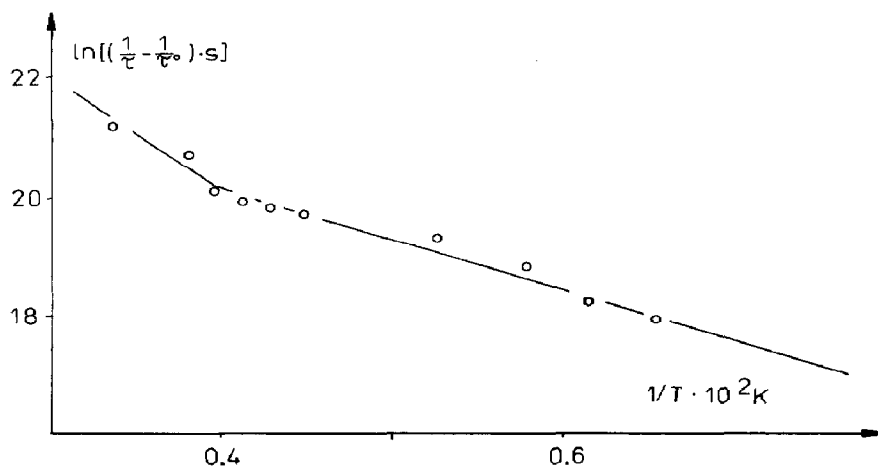


Fig. 5. Dependence of k_3 on the temperature in ethanolic solution.

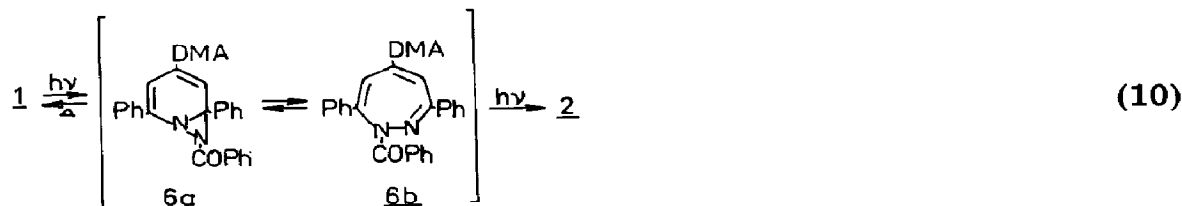
the temperature. This activation energy of the corresponding twisting process is significantly lower than the apparent activation energy of the ethanol viscosity (15 kJ mol^{-1}). This indicates that there must be a low internal barrier for relaxation in alcoholic solvents.

The third deactivation channel which is independent of temperature and limits the lifetime of the fluorescence to about 3 ns can be associated with an intersystem crossing process ($k_4 \approx 3 \times 10^8 \text{ s}^{-1}$). Indeed, phosphorescence can be observed in ethanol at 77 K with a maximum at 600 nm.

3.4. Photochemical deactivation

3.4.1. Intramolecular cyclization

According to studies with other pyridinium ylides [1, 20] the reaction $1 \rightarrow 2$ should proceed via the singlet state with the known sequence (10) [1].



Therefore the $E-E$ diagrams must be non-linear. The postulated singlet reaction is confirmed by the failure to observe any influence of oxygen on the reaction rate. In contrast to the other examples photochemical enrichment of the intermediate 1,2-diazepine **6b** is not possible, and there are two reasons for this.

(1) The absorption spectra of compounds **1** and **6b** are superimposed, as can be seen from a comparison of the thermally prepared 1,2-diazepine **6b** with the ylide **1** (Fig. 6).

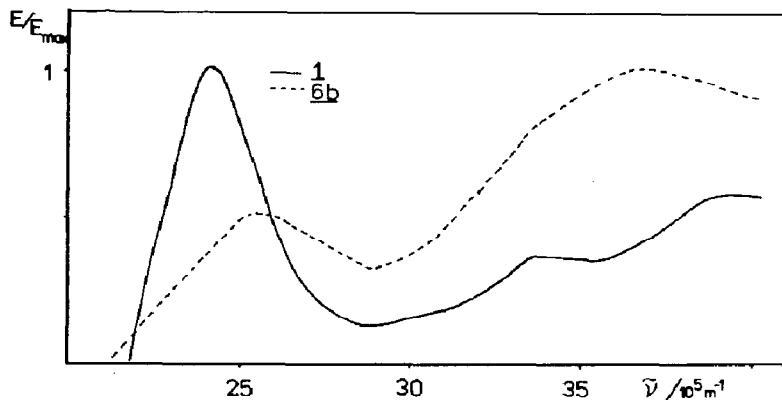


Fig. 6. UV spectra of compounds **1** and **6b** in *n*-butanol.

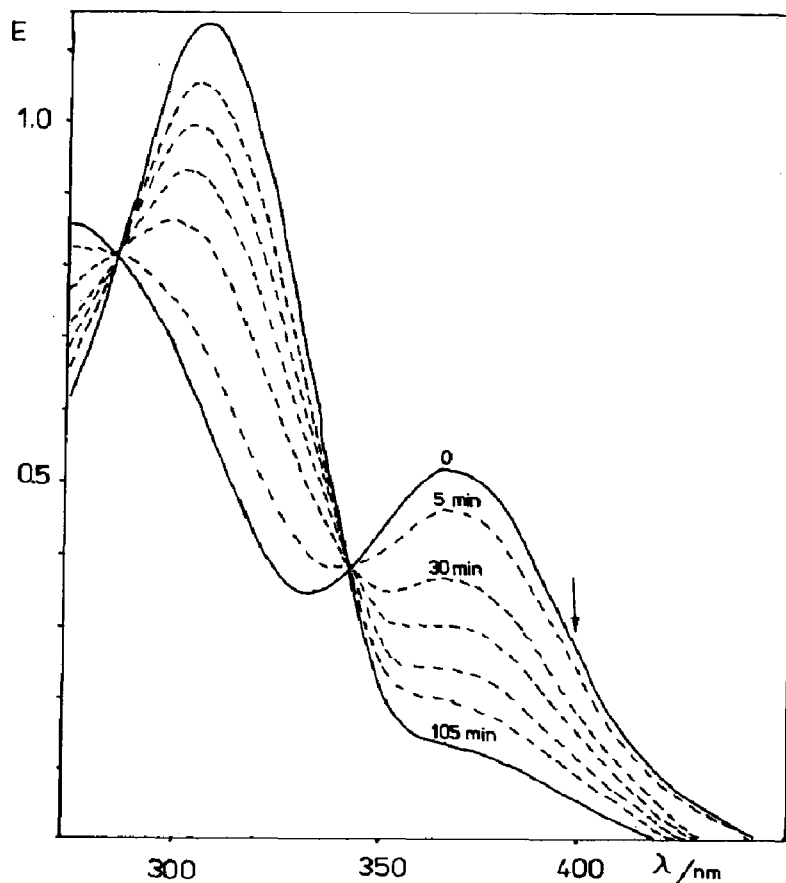


Fig. 7. UV spectra of the solution of **6b** in cyclohexane at various exposure times ($\lambda_{\text{exc}} = 405 \text{ nm}$).

(2) The quantum yield of the cyclization $6b \rightarrow 2$ is significantly higher than that of the ring enlargement $1 \rightarrow 6b$ as can be seen from a comparison of the exposure times of reaction $1 \rightarrow 2$ (Fig. 3(a)) with those of $6b \rightarrow 2$ (Fig. 7).

The intramolecular bond formation leading to 2 is regiospecific under the influence of the donor substituent in the seven-membered ring [21]. The formation of the bicyclic compound 2 is observed exclusively in those solvents in which an additional deactivation channel from the Franck-Condon excited state was postulated (k_1). Therefore it may be concluded from these results that the ring enlargement reaction represents this deactivation channel k_1 . This means that this photoreaction does not proceed via the fluorescing singlet state but is a competing process of the population of the fluorescing state provided that the fluorescence observed in moderately polar or non-polar solvents really belongs to compound 1. This question was discussed in Section 3.3. An alternative explanation would be the classification as the fluorescence of the compound 6b formed in an adiabatic photoreaction. But this interpretation would be in contradiction with the generally low fluorescence quantum yields of such 1,2-diazepines [22]. Indeed compound 6b does not fluoresce in solvents such as hexane, ethyl acetate, ethers or toluene. Taking into account the low efficiencies of fluorescence and formation of 2 it is necessary to postulate additionally an intermediate product which is able to react thermally to 1 to dissipate the excitation energy in this way. The recent studies by Kwart *et al.* [23] support the postulated mechanism of the photorearrangement of pyridine *N*-acylimines via the 1,7-diazanorcaradienes. Therefore it is obvious that the bicyclic compound 6a is the first intermediate which reacts mainly back to the ylide 1 and to a smaller extent to the seven-membered ring. In polar solvents 6a is not formed ($k_2 \gg k_1$). This is the reason why the reaction $1 \rightarrow 2$ does not occur in these solvents. The experiment shows that the 1,2-diazepine 6b also reacts to the bicyclic compound 2 in polar solvents, with a quantum yield which is comparable with that in non-polar solvents.

3.4.2. *N*—*N* bond cleavage

Both the influence of oxygen and the possible sensitization of the photoreaction by the triplet generator biacetyl indicates that this photoreaction takes place via the excited triplet state. The population of the triplet state occurs from the fluorescing state in competition with the radiationless deactivation via the torsional motion. Increasing the solvent viscosity diminishes the radiationless deactivation rate and favours, therefore, the transition to the triplet state. Therefore the *N*—*N* bond cleavage

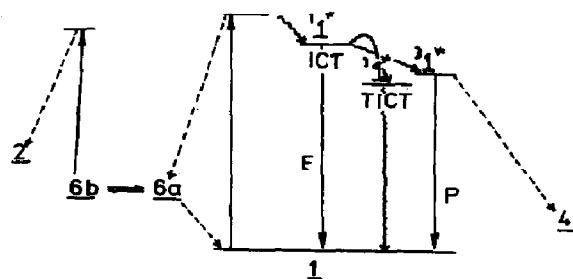


Fig. 8. Deactivation scheme for photoexcited 1.

can be observed in butanol but can be neglected in ethanol or methanol. The quantum yield of the N—N bond scission rises considerably by direct population of the triplet state with a sensitizer.

The deactivation possibilities of photoexcited **1** are summarized in Fig. 8. ICT denotes the planar intramolecular charge transfer state from which the fluorescence originates. As described above, which of the different deactivation channels is selected is mainly controlled by the solvent.

4. Experimental details

4.1. Materials

2,6-diphenyl-4-(*p*-dimethylaminophenyl)-benzoyliminopyridinium ylide (**1**) was prepared as described in ref. 24 and purified by recrystallization (with acetonitrile) and column chromatography.

1,4-diphenyl-2-benzoyl-6-(*p*-dimethylaminophenyl)-2,3-diaza-bicyclo-[3.2.0]hepta-3,7-diene (**2**) was prepared by irradiation of a solution of 0.2 g **1** in 0.5 l diethyl ether for 4 h using a photoreactor with a mercury lamp (VEB NARVA) and a filter solution of sodium nitrite in water. After evaporating, the precipitate obtained was extracted with boiling ethanol. The insoluble residue was recrystallized from acetonitrile to give 0.18 g **2** (purity, 90%; melting point, 270 °C; λ_{\max} (diethyl ether) = 308 nm ($\lg \epsilon = 3.2$); $\tilde{\nu}_{\max}$ (C=O) = 1630 cm^{-1} ; $m/e = 469$ (13%) M^+ , 145 (100%)). Because of the poor solubility of compound **2** in all solvents the identification of **2** cannot be carried out by nuclear magnetic resonance spectroscopy, but the absorption spectrum excludes the alternative formation of the other possible bicyclic compound **3**. The mass spectrum of **2** agrees with the spectra of other similar bicyclic compounds [21], especially regarding the formation of the fragment *p*-dimethylaminophenylacetylene (M^{++} , 145). The obtained carbon, hydrogen and nitrogen contents agree within the error limit with the calculated values.

In similar manner the irradiation of **1** was carried out in butanol. After evaporation of the reaction solution the 2,6-diphenyl-4-(*p*-dimethylaminophenyl)-pyridine (**4**) was isolated and recrystallized from ethanol. The identification was carried out by comparison with an authentic sample. Solvents (Uvasol and Merck) were used as received.

4.2. Spectrometers

Absorption and fluorescence measurements were performed using a Perkin-Elmer 556 spectrometer and an MPF 2A spectrofluorometer respectively. Fluorescence quantum yields were determined using quinine sulphate in 1 N H_2SO_4 as the standard ($\phi_{\text{F}} = 0.56$). Air-saturated solutions of **1** with an optical density of about 0.05 were used. Oxygen does not influence the fluorescence quantum yield.

Fluorescence lifetimes were measured using an LIF 200 laser impulse fluorometer (ZWG, Academy of Sciences of G.D.R.) with a nitrogen laser as

the excitation source and ORTEC single-photon-counting apparatus (excitation wavelength, 405 nm). The lifetimes were calculated by deconvolution of the fluorescence decay [25]. The error can be estimated to be $\pm 10\%$.

The low temperature measurements were performed using an Oxford Instruments cuvette. Removal of oxygen was achieved by the freeze-thaw technique. The multiple regression computations were carried out with a least-squares program.

4.3. Photochemical investigations

The spectroscopic investigations of the photoreactions were performed using dilute solutions ($(1 - 3) \times 10^{-5}$ mol l^{-1}). A mercury high pressure lamp (HBO 500, VEB NARVA) combined with metal interference filters was the excitation source. The relative rates of the photoreactions were estimated from the extinction-time functions using the tangent method for comparative measurements.

Sensitization experiments for the reaction $1 \rightarrow 4$ were run with biacetyl as the sensitizer. The optical density of 1 and biacetyl amounts to 1.5. Oxygen was removed by the freeze-thaw technique. The formation of the substituted pyridine 4 ($\lambda_{\max} = 330$ nm) could be followed by UV spectroscopy because an optical window exists at 330 nm in the reaction mixture. Using the excitation wavelength 436 nm, all 1 was transformed into 4 within 6 min. The irradiation of 1 alone with 436 nm light does not yield any reaction within this time period. After evaporation of the solution of the sensitization experiment the residue was dissolved in methylene chloride. The reaction product 4 was identified by thin-layer chromatography and by its known fluorescence.

Acknowledgments

E. Rehak is gratefully acknowledged for providing compound 6b, and we thank Professor Dr. M. G. Kuzmin of Moscow for his support.

References

- 1 Y. Tamura and M. Ikeda, *Adv. Heterocycl. Chem.*, **29** (1981) 71.
- 2 V. Snieckus, *J. Chem. Soc., Chem. Commun.*, (1969) 831.
- 3 A. R. Katritzky, J. Lewis and P.-L. Nie, *J. Chem. Soc., Perkin Trans. I*, (1979) 446.
- 4 M. J. Kamlet, J. L. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.*, **48** (1983) 2877.
- 5 M. Kupfer and W. Abraham, *J. prakt. Chem.*, **325** (1983) 95.
- 6 H. Fritz, R. Gleiter, M. Nastasi, J. L. Schuppiser and J. Streith, *Helv. Chim. Acta*, **61** (1978) 2887.
- 7 H. Mauser, *Z. Naturforsch., Teil B*, **23** (1968) 1025.
- 8 H. J. Timpe and H. G. O. Becker, *Chimia*, **26** (1972) 473.
- 9 A. El-Bayoumi, *J. Phys. Chem.*, **80** (1976) 2259.
- 10 W. Abraham, H. Otto and D. Kreysig, *J. Photochem.*, **16** (1981) 261.

- 11 J. Kordas and A. El-Bayoumi, *J. Am. Chem. Soc.*, 96 (1974) 3043.
- 12 S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, 37 (1962) 814.
- 13 Th. Förster and G. Hoffmann, *Z. Phys. Chem. N. F.*, 75 (1971) 63.
- 14 G. Oster and Y. Nishijima, *J. Am. Chem. Soc.*, 78 (1956) 1581.
- 15 S. H. Courtney and G. R. Fleming, *Chem. Phys. Lett.*, 103 (1984) 443.
- 16 S. Rentsch and B. Wilhelmi, *J. Mol. Struct.*, 114 (1984) 1.
- 17 M. Kupfer, A. Henrion and W. Abraham, *Z. Phys. Chem.*, 267 (1986) 705.
- 18 S. P. Velsko and G. R. Fleming, *J. Chem. Phys.*, 76 (1982) 3553.
- 19 Z. R. Grabowski, K. Rotkiewicz, A. Siemiarczuk, D. J. Cowley and W. Baumann, *Nouv. J. Chim.*, 3 (1979) 443.
- 20 J. Streith, *Pure Appl. Chem.*, 49 (1977) 305.
- 21 W. Abraham, K. Buck and D. Kreysig, *Z. Chem.*, 22 (1982) 57.
- 22 W. Abraham, M. Kupfer, K. Buck and D. Kreysig, *Z. Naturforsch., Teil A*, 36 (1981) 1213.
- 23 H. Kwart, D. A. Benkő, J. Streith and J. L. Schuppiser, *J. Am. Chem. Soc.*, 100 (1978) 6502.
- 24 E. Rehak, *Thesis*, Humboldt University, Berlin, 1986.
- 25 W. Abraham, M. Kupfer and D. Kreysig, *J. prakt. Chem.*, 327 (1985) 505.