

PHOTOCHEMISTRY OF 2,2'-DIHYDROXY-1-NAPHTHALDAZINE

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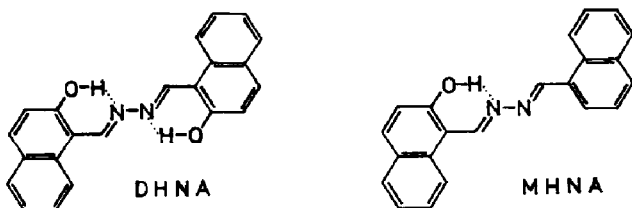
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Summary

2,2'-Dihydroxy-1-naphthaldazine (EE isomer) undergoes reversible photoisomerization to form the EZ and ZZ isomers. Flash spectroscopy reveals a short-lived phototautomer. It follows from the temperature dependence of the fluorescence quantum yield, and the relative yields of the phototautomer and the EZ isomer, that after adiabatic proton transfer internal conversion and EZ isomerization start from a higher vibronic level than do fluorescence and formation of the phototautomer. In the presence of acids in toluene a long-lived transient is observed which is formed in consecutive thermal reactions from one of the photoproducts. It is assigned to a doubly tautomerized isomer. There is no indication of a cooperative double proton transfer in the excited state.

1. Introduction

In our group's investigations on photochromic acyclic aromatic azines we were also interested in the photochemical behaviour of the *ortho*-hydroxy-substituted compounds



(DHNA, 2,2'-dihydroxy-1-naphthaldazine; MHNA, 2-monohydroxy-1-naphthaldazine). Strong O—H...N hydrogen bonds are observed with these types of compounds [2] which favour a coplanar arrangement for the whole molecule [3]. This in turn produces a bathochromic shift in the absorption band, a resolvable vibrational structure and an enhanced fluorescence quantum yield. As concluded from fluorescence investigations [4] and by analogy with the extensively investigated photochemistry of salicylidene-

aniline and related compounds (*e.g.* see ref. 5) a rapid proton transfer occurs in the excited state of DHNA [6]. Therefore, the photochromic properties of the 2-hydroxy-substituted azines were expected to differ markedly from those of the other acyclic azines hitherto investigated. However, DHNA and related compounds might be possible candidates for a double proton transfer, a process which has recently been of considerable interest (see ref. 7). We intend to discover whether or not a double proton transfer can occur either in a concerted reaction or in successive steps.

2. Experimental details

2.1. Materials

The synthesis of acyclic aromatic azines is described in ref. 8 and papers cited therein. DHNA was purified by repeated recrystallization from glacial acetic acid and finally from dry toluene. Sublimation *in vacuo* did not change its spectral properties. The unsymmetric MHNA was prepared from equimolar amounts of 2-hydroxy-1-naphthanol and 1-naphthaldehyde hydrazone in absolute ethanol. The compound was identified using mass spectroscopy (JEOL JMS-D100; $M_{\text{exp}} = 324.1253$, $M_{\text{calc}} = 324.1263$) and thin-layer chromatography, and these also showed the symmetric azines to be absent.

2.2. Apparatus and procedures

Cary 17 (Varian) and Specord M40 (Carl Zeiss Jena) spectrophotometers were used for the spectral measurements in the long time scale. The quantum yields $\varphi_{\text{EE} \rightarrow \text{EZ}}$ and $\varphi_{\text{EZ} \rightarrow \text{EE}}$ were determined using a home-made photokinetic spectrometer [9] by applying the procedure described in ref. 10. Conversion was kept sufficiently low to allow the $\text{EZ} \xrightarrow{h\nu} \text{ZZ}$ isomerization to be neglected. Fluorescence spectra were recorded using a FICA 55 spectrofluorometer with quinine sulphate as a standard for the quantum yield determination. To localize the 0-0 transitions for the calculation of the Stokes shift, three gaussian curves were fitted to the absorption band and two gaussian curves were fitted to the fluorescence band.

The fluorescence lifetime was determined using a picosecond fluorometer [11]; excitation was performed with the third harmonic of a selected single pulse of a mode-locked neodymium glass laser and emission was recorded by means of a streak camera. The flash photolysis equipment was the same as that briefly described in ref. 12. Freshly prepared solutions (non-deaerated) were flashed only once. The exposure of the samples to the analysing light was minimized to not more than one second before measurement in order to exclude the EZ and ZZ isomers. To produce the transient spectra (see Figs. 4 and 6 below) by point-by-point recording of the kinetic curves (10 nm steps) the same solution was flashed repeatedly after it had been verified that the time lag between two shots allowed the complete recovery of the original spectrum. The relative yields of the irreversible

bleaching (within the time scale of flash spectroscopy) due to the $EE \rightarrow EZ$ isomerization and the transient absorbance were measured simultaneously in two channels using a beam splitter in the analysing beam and two separate detecting systems. Any additions to the azine solutions left the ordinary absorption spectrum unchanged unless stated otherwise.

3. Results and discussion

3.1. Long time scale isomerizations

The spectral changes of DHNA under continuous irradiation (see Fig. 1) closely resemble those observed with the unsubstituted acyclic azines [13]. Upon prolonged irradiation there are significant deviations from the isosbestic behaviour observed in the initial period of irradiation. The spectral changes are both photochemically and thermally reversible. It follows unequivocally from the extinction difference (ED) diagrams and the extinction difference quotient (EDQ) diagrams (insets in Fig. 1) that two photoisomers are formed in addition to the most stable isomer. They are formed in consecutive reactions and are assigned to the EZ and ZZ isomers of the parent EE isomer. This assignment is strongly supported by the spectral analogy with the unsubstituted azines [13] and by the fact that the tautomers are known to absorb at longer wavelengths. However, neither the photochemical forward isomerizations $EE \xrightarrow{h\nu} EZ \xrightarrow{h\nu} ZZ$ nor the thermal back reactions can be expected to follow the known rotation-inversion mechanism because

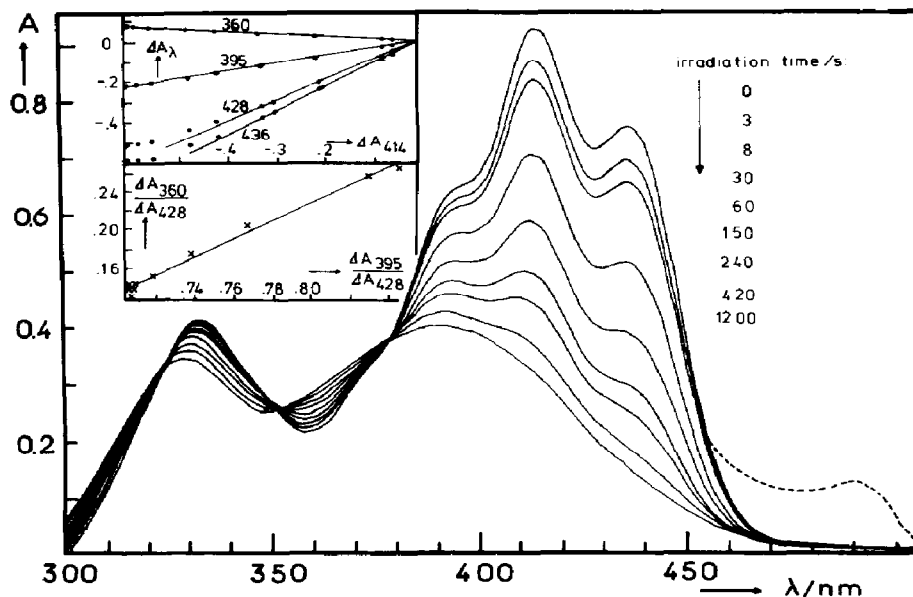


Fig. 1. Set of absorption spectra demonstrating the photoisomerization of 3.0×10^{-5} M DHNA in toluene under irradiation with $\lambda' = 436$ nm (HBO 200, interference filter): broken line, absorption spectrum in the presence of 0.22 M dichloroacetic acid; insets, ED and EDQ diagrams.

of the completely different primary photoreactions (*cf.* Sections 3.2 and 3.3) and the different kinetics of the back reaction. Though small deviations from simple first-order kinetics were observed for the thermal reaction $EZ \rightarrow EE$, first-order rate constants were evaluated to examine the temperature dependence. The Arrhenius plot (Fig. 2) shows small but significant deviations from linearity. Since it is rather unusual to observe curvature in such a narrow temperature region (though of course it is possible) for a single elementary reaction, this might possibly indicate a more complex mechanism. According to Schmid and Sapunov [14] a "concave down" curvature in the Arrhenius plot as observed here is typical for consecutive reactions with a change in the rate determining step. Linear regression of the data in Fig. 2 yields $\lg A = 6.9 \pm 0.9$ and $E_A = 49 \pm 5 \text{ kJ mol}^{-1}$. Together with the observed sensitivity of the isomerization rate to contamination of the solvent by acid or base these findings are consistent with the assumption of a back reaction mediated by tautomeric species.

The quantum yields for the photoisomerizations are $\varphi_{EE \rightarrow EZ} = 0.14$ and $\varphi_{EZ \rightarrow EE} \approx 0.3$ at room temperature.

3.2. Fluorescence behaviour

Figure 3 shows a set of fluorescence spectra recorded in the temperature range 20 - 80 °C in toluene. The quantum yield at 20 °C is $\varphi_f = 0.034$. There is no H/D isotope effect either on the quantum yields or on the shape of the fluorescence spectra. The wavelengths of the fluorescence and absorption maxima are essentially independent of the solvent polarity as demon-

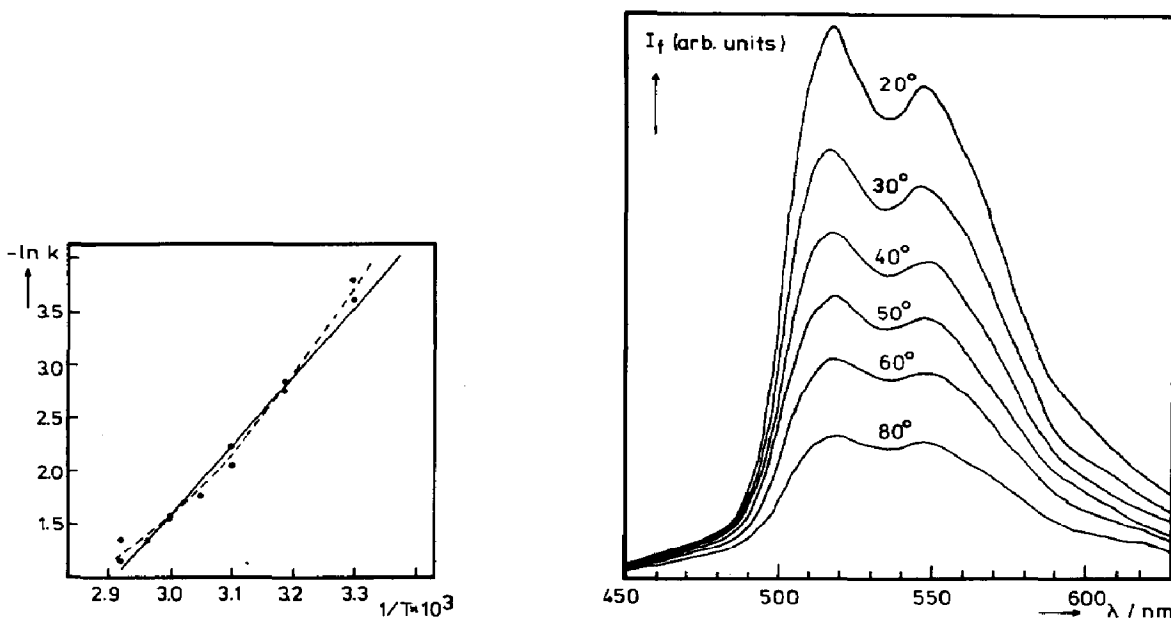


Fig. 2. Arrhenius plot of the thermal back reaction $EZ \rightarrow EE$.

Fig. 3. Set of corrected fluorescence spectra of $7.3 \times 10^{-6} \text{ M}$ DHNA in toluene recorded at the temperatures indicated.

TABLE 1

Wavenumbers of the 0-0 transitions of DHNA and MHNA for absorption and emission in various solvents and Stokes shifts of the fluorescence

Solvent	MHNA			DHNA		
	$\nu_{00}(\text{abs})$ (cm^{-1})	$\nu_{00}(\text{fl})$ (cm^{-1})	Stokes shift (fluorescence) (cm^{-1})	$\nu_{00}(\text{abs})$ (cm^{-1})	$\nu_{00}(\text{fl})$ (cm^{-1})	Stokes shift (fluorescence) (cm^{-1})
Hexane	24168	20008	4160	23038	19646	3392
Dioxane	24035	19977	4058	23077	19610	3467
Toluene				22796	19268	3528
Chloroform	23911	20039	3872	22889	19417	3472
Ethanol	24166	20139	4027	22945	19206	3739
Acetonitrile	24337	19410	4927	23286	19724	3562

strated by the data in Table 1. The same is true for MHNA. This means that the dipole moment change induced by electronic excitation is completely compensated by the adiabatic proton transfer from O to N. Consequently, it cannot be decided by changing the solvent polarity whether or not a double proton transfer occurs in the excited state as was possible with 2,2'-bipyridyl-3,3'-diol [15]. Owing to the lack of unrelaxed fluorescence and because the rate constant of excited state proton transfer has been found to be very rapid with related compounds ($k_{\text{H}^+} > 2 \times 10^{11} \text{ s}^{-1}$ [16]) it seems reasonable to assume that there is no effective process competitive to the proton transfer. If we further assume that only one thermally activated process exists which competes with the fluorescence it follows for the reciprocal fluorescence quantum yield

$$\varphi_f^{-1} = 1 + \frac{k_d}{k_f} + \frac{A}{k_f} \exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

where Σk_d would give the sum of all non-activated decay processes with the exception of the radiative decay constant k_f . With $\varphi_f = k_f \tau_f$ and $\tau_f = 147 \text{ ps}$, $k_f = 2.3 \times 10^8 \text{ s}^{-1}$. Parameter fitting using eqn. (1) yields the values $\Sigma k_d = 4.2 \times 10^9 \text{ s}^{-1}$, $A = 1.8 \times 10^{14} \text{ s}^{-1}$ and $E_a = 27 \pm 2 \text{ kJ mol}^{-1}$. From these data the quantum yield φ_{act} for the activated process at 20 °C is calculated to be 0.4.

On addition of acids to solutions of DHNA the ground state tautomeric equilibrium becomes spectroscopically observable (see the broken line in Fig. 1). This behaviour is closely analogous to that of many other substances with related structures (*cf.* ref. 17). Exciting the ground-state tautomer at 490 nm yields exactly the same fluorescence spectrum, and the new band is also observed in the excitation spectrum. This tautomer will be assigned to the *cis*-quinoid (Q_c).

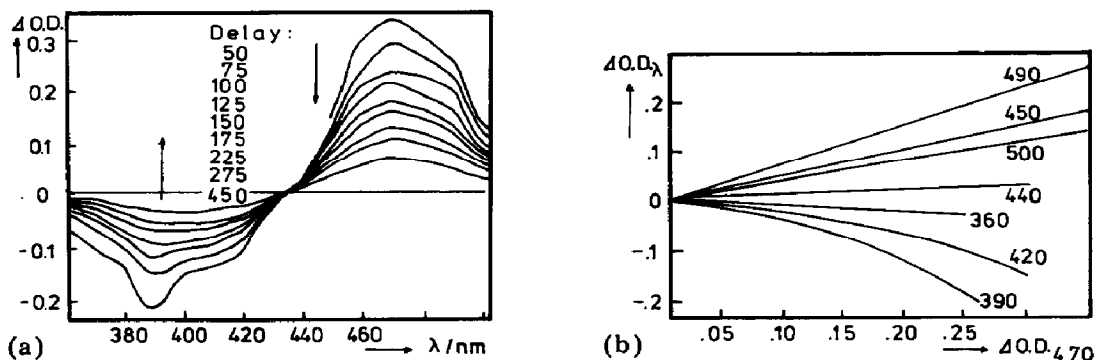


Fig. 4. (a) Set of transient difference spectra obtained by conventional flash photolysis of 8×10^{-6} M DHNA in toluene at 60°C . The delay times are given in microseconds. (b) ED diagram derived from the transient spectra shown in Fig. 4(a). (At the shorter wavelengths a transient overload of the detector-amplifier system owing to intense scattered light from the flash did not allow the density change at the shortest delay times to be recorded.)

3.3. Flash spectroscopy

Figure 4(a) shows a set of difference spectra obtained on flashing DHNA in toluene. The optical-density differences are defined by

$$\Delta\text{OD}_{(t)} = \text{OD}_{(t)} - \text{OD}_{(t \rightarrow \infty)}$$

where ∞ refers to $t > 5$ ms. Using this equation the difference spectra do not contain the persistent spectral change due to the EZ isomerization. It follows from the linear ED diagrams for $\lambda \geq 440$ nm (Fig. 4(b)) that only one transient is responsible for the short-lived absorption band. The curvature in the depletion region $\lambda < 440$ nm indicates the participation of an additional species with an absorption spectrum similar to the most stable EE form. (Possibly single cis-trans isomers are involved. The temperature dependence of the IR and UV-visible absorption spectra strongly support this assumption.)

The decay of the 480 nm transient does not obey a simple rate law. It can be described by two competitive first-order and second-order reactions

$$\Delta\text{OD}_{(t)} = \frac{k_2 \Delta\text{OD}_{(0)}}{e^{k_1 t} (k_1 + k_2 \Delta\text{OD}_{(0)}/\epsilon d) - k_2 \Delta\text{OD}_{(t)}/\epsilon d} \quad (2)$$

where k_1 and k_2 are the first- and second-order rate constants, ϵ is the molar absorption coefficient and d is the cell thickness. Fitting of the kinetic data to eqn. (2) gave the parameters $k_1 = 540 \pm 40 \text{ s}^{-1}$ and $k_2/\epsilon = 1.8 \times 10^5 \text{ cm s}^{-1}$. The decay rate depends only weakly on temperature. The Arrhenius parameters were determined as $\lg A = 3.4 \pm 0.5$, $E_A = 3.6 \pm 3.1 \text{ kJ mol}^{-1}$ and $\lg A = 6.8 \pm 0.2$, $E_A = 8.6 \pm 0.9 \text{ kJ mol}^{-1}$ for k_1 and k_2 respectively. The very small temperature dependence is indicative of a multistep mechanism including reversible reactions, whether or not eqn. (2) is the absolutely correct kinetic model.

This phototransient must not be identified with Q_c because of its comparatively long lifetime. Some geometric isomerization must have taken place during the phototautomerization[†] removing the intramolecular hydrogen bond.

It has been a long-standing controversy with the salicylideneanilines whether this isomerization is essentially a rotation around the $C_{\text{ring}}-C_{\text{chain}}$ bond or the C—NH bond. In a recent paper [5] dealing with the effect of the substituent and the acid–base catalysis on the thermal re-tautomerization of flashed salicylideneanilines we have concluded that in fluid solutions at room temperature the geometric isomerization consists essentially of a rotation around the $C_{\text{ring}}-C_{\text{chain}}$ bond.

Acids and bases catalyse the decay of the DHNA phototransient and cause pseudo-first-order kinetics if applied in sufficiently high concentrations. Both protonation of the oxygen atom and deprotonation of the nitrogen atom of the tautomer, which are considered as the primary steps of the catalysed reactions, should weaken the $C_{\text{ring}}-C_{\text{chain}}$ bond at the expense of the adjacent C—N bond. This becomes obvious from a consideration of the corresponding mesomeric formulas. Therefore, we assign a *trans*-quinoid structure to the phototransient and denote it Q_t .

Since essentially the same results were obtained from flash spectroscopy with MHNA we conclude that only one half of the bichromophoric molecule is involved in the phototautomerization. As first proposed by Ottolenghi and coworkers [18] and later proved by picosecond spectroscopy [16, 19] phototautomerization of salicylideneanilines starts from a higher vibronic level of the emitting state. In order to examine whether phototautomerization is the process which causes the marked decrease of the fluorescence quantum yield with increasing temperature we measured the relative yields of the phototautomer and of the EZ isomer as a function of temperature. The results are shown in Fig. 5. Unexpectedly the yield of Q_t

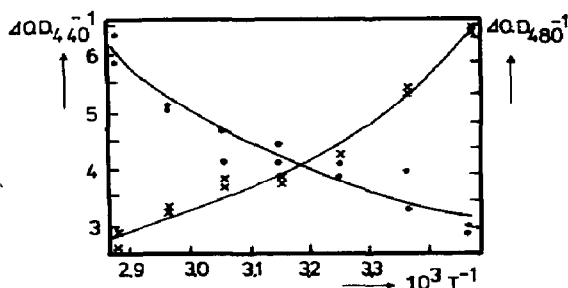
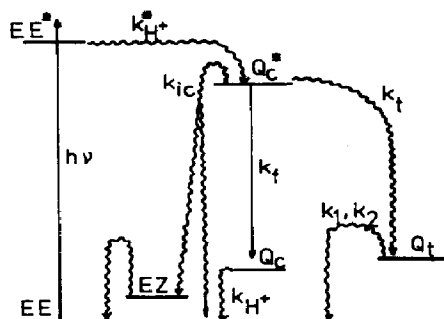


Fig. 5. Temperature dependence of the relative yields of the EZ isomer (x) and of the phototautomer Q_t (●).

[†]Throughout this paper the photogeneration of the flash transient Q_t (see below) will be denoted as phototautomerization, even though it involves proton transfer and an isomerization, in order to distinguish this process from the formation of the EZ isomer denoted as photoisomerization which needs no net proton transfer.

also decreases with increasing temperature. Parameter fitting using the expression analogous to eqn. (1) yields an activation energy $E_a = 32 \pm 7$ kJ mol⁻¹ which agrees with that obtained from the fluorescence quantum yields. Therefore it must be concluded that phototautomerization requires only a negligible activation energy and that there exists an activated process which competes with both fluorescence and phototautomerization. As can be seen from Fig. 5, curve 2, the yield of the EZ isomer increases with temperature. An activation energy $E_A = 22 \pm 7$ kJ mol⁻¹ is obtained which again agrees within experimental error with both the values given above. The following reaction mechanism explains the experimental findings most simply.



$k_{H^+}^*$; k_{H^+} very fast

$$k_t = 2.3 \times 10^8$$

$$k_{ic} = 2.8 \times 10^9$$

$$k_t = 4.2 \times 10^9$$

It has been questioned by the referees why the fluorescence does not originate from Q_t . We rule out this possibility because this would require adiabaticity for both the proton transfer and the geometric isomerization which seems to be highly improbable. However, all attempts to measure the fluorescence of Q_t failed. We were unable to detect Q_t on irradiation of DHNA in methyltetrahydrofuran in the whole temperature range down to 77 K by ordinary absorption spectroscopy. The decay kinetics of Q_t including the very small temperature dependence in methyltetrahydrofuran observed by flash spectroscopy in the range 15 - 65 °C are comparable with those measured in toluene. We do not know whether the lifetime of Q_t at 77 K is still too short for detection by non-time-resolved spectroscopy or whether its formation is at all inhibited by the high viscosity of the solvent.

In the presence of acids in a concentration high enough to generate detectable amounts of Q_c the lifetime of Q_t is too short for the detection of its decay owing to acid catalysis even with our laser flash photolysis apparatus (time resolution, 20 ns). During the photoisomerization $EE \xrightarrow{h\nu} EZ$ the proton must be transferred back to the oxygen atom before an appreciable change in the geometry of the molecular framework takes place.

Rapid back transfer of the proton should only occur in the ground state. Therefore it seems reasonable to attribute the activated step to an internal conversion and to think of the photoisomerization as being a hot ground-state reaction. Because $\varphi_{EE \rightarrow EZ} < \varphi_{ic}$ it is assumed that internal conversion leads to both the EE and the EZ isomers. Obviously Σk_d in eqn. (1) has to be identified with the rate constant k_t of the phototautomerization in the above mechanism.

3.4. Double tautomerization

There are no arguments in favour of a double proton transfer in the excited state of DHNA. A comparison of the photochemical behaviour of DHNA with that of MHNA which has only one transferable proton does not reveal any qualitative difference. In particular, the Stokes shift of the DHNA fluorescence is no greater than that of MHNA (*cf.* Table 1). The coupling of the two halves of the molecule seems to be very weak, which means that excitation should be localized on one half of the molecule only and a cooperative double proton transfer is unlikely.

However, if solutions of DHNA are flashed in the presence of a certain critical acid concentration a new transient is observed which we assign to a doubly quinoid tautomer (DQ). Figure 6 shows such an example. From the similarity of the transient spectra of DQ and Q_t it must be concluded that DQ is also a tautomeric species, in particular because the EZ and ZZ isomers are known to absorb at shorter wavelengths than the most stable EE isomer. Since the long-lived transient DQ is not observed with MHNA or 2-hydroxy-1-naphthanil we conclude that both OH...N linkages are involved in the tautomerization. Decay of DQ leads to complete recovery of the original absorption spectrum. The long lifetime $\tau_{DQ} = 10.2$ s (with $C_{HAc} = 0.22$ M) as compared with $\tau_{Q_t} = 13.4$ ns (calculated from the acid catalysis constant determined by laser flash photolysis, $k_{HAc} = 3.4 \times 10^8$ M⁻¹ s⁻¹) indicates some effective stabilization of DQ. The temperature dependence of the

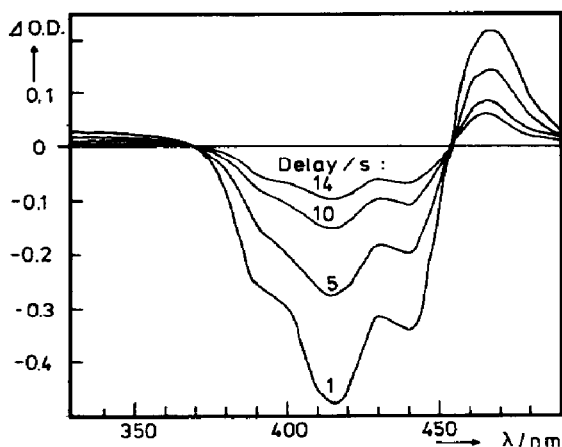
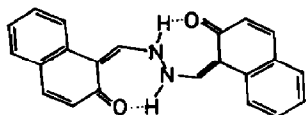


Fig. 6. Transient difference spectra obtained from flashing 8×10^{-6} M DHNA in toluene in the presence of 0.22 M acetic acid.

decay rate obeys the Arrhenius law: $\lg A = 9.8 \pm 0.4$ and $E_A = 61.0 \pm 2.6$ kJ mol⁻¹ ($C_{\text{Hac}} = 0.24$ M). As proved by the linear dependence of the signal height on the flash intensity, this transient is formed in a monophotonic reaction. The transient is also generated when the ground-state tautomer Q_c is excited. There is no fluorescence quenching up to a concentration of acetic acid of 1 M. This means the transient DQ is formed in a ground-state reaction from one of the photoproducts described above.

The lifetime of DQ decreases slowly with increasing acid concentration; however, the acid catalysis constants are considerably smaller ($k_{\text{Hac}} = 0.20 \pm 0.01$ M⁻¹ s⁻¹) than those for the decay of Q_t . Together with the absence of the long-lived transient in proton acceptor or donor solvents like ethanol or dioxane this may lead to the conclusion that hydrogen bonds are responsible for the stabilization of DQ. A twofold tautomer of the following structure



with two seven-membered hydrogen-bridged rings might tentatively explain the experimental findings. The stabilization of a phototautomer by the formation of a new hydrogen bond has also been observed with azomethines derived from 7-hydroxy-quinolin-8-aldehyde [20].

An alternative explanation by an intermediate acylation can be ruled out because with acetic anhydride the long-lived absorption is negligibly small, and furthermore it can also be observed with hydrochloric acid as catalyst.

With salicylaldazine we were unable to detect a long-lived transient under comparable conditions, but with 4,4'-bis(dimethylamino)salicylaldazine it was again observable. These differences may be explained in terms of different resonance energies of the various aromatic centres.

Acknowledgments

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References

- 1 K. Appenroth, M. Reichenbacher and R. Paetzold, *J. Photochem.*, **24** (1984) 65.
- 2 E. Mendelez and J. L. Serrano, *Mol. Cryst. Liq. Cryst.*, **91** (1983) 173.

- 3 J. Fayos, M. Martinez-Ripoll, M. Garcia Mina, J. Gonzalez Martinez and F. Arrese, *Acta Crystallogr., Sect. B*, **36** (1980) 1952.
- 4 A. Weller and H. Wolf, *Ann. Chem.*, **657** (1962) 64.
- 5 U.-W. Grummt, *J. Prakt. Chem.*, **327** (1985) 227.
- 6 D. Fassler, V. I. Ivanov and M. G. Kuzmin, *Khim. Vys. Energ.*, **10** (1967) 187.
- 7 J. Waluk, A. Grabowska, B. Pakula and J. Sepiol, *J. Phys. Chem.*, **88** (1984) 1160.
- 8 M. Reichenbacher, R. Paetzold and K. Appenroth, *Z. Chem.*, **24** (1984) 21.
- 9 A. Jacobi, H.-D. Ilge and D. Fassler, *Mitteilungsbl. — Chem. Ges. Dtsch. Demokr. Repub.*, **68** (1983) 224.
- 10 H.-D. Ilge and R. Paetzold, *Z. Phys. Chem. (Leipzig)*, **264** (1983) 849.
- 11 V. Brückner, D. Fassler, K. H. Feller and R. Gase, *Exp. Tech. Phys.*, **31** (1983) 511.
- 12 U.-W. Grummt, H. Langbein, R. Nöske and G. Röbbisch, *J. Photochem.*, **24** (1984) 53.
- 13 R. Paetzold, M. Reichenbacher and K. Appenroth, *Z. Chem.*, **21** (1981) 421.
- 14 R. Schmid and V. N. Sapunov, Non Formal Kinetics, in H. F. Ebel (ed.), *Monographs in Modern Chemistry*, Verlag Chemie, Weinheim, 1982, p. 107.
- 15 H. Bulska, *Chem. Phys. Lett.*, **98** (1983) 398.
- 16 P. F. Barbara, P. M. Rentzepis and L. E. Brus, *J. Am. Chem. Soc.*, **102** (1980) 2786.
- 17 R. S. Becker and W. F. Richey, *J. Am. Chem. Soc.*, **89** (1967) 1298.
- 18 T. Rosenfeld, M. Ottolenghi and A. Y. Meyer, *Mol. Photochem.*, **5** (1973) 39.
- 19 R. Nakagaki, T. Kobayashi, J. Nakamura and D. Nagakura, *Bull. Chem. Soc. Jpn.*, **50** (1977) 1909.
- 20 C. Franke, W. Richter and G. Tomaschewski, *Khim. Vys. Energ.*, **13** (1979) 442.