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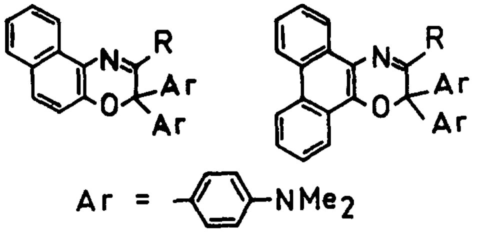
NEW PHOTOCHROMIC 2H-1.4-OXAZINES AND SPIRO-2H-1.4-OXAZINES

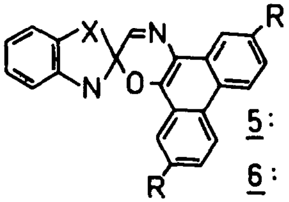
Ulrich-W. Grummt, Manfred Reichenbacher and Roland Paetzold*
Sektion Chemie der Friedrich-Schiller-Universität
DDR-6900 Jena

Abstract: The synthesis and the photochemical behaviour of 4 new 2H-1.4-oxazines and 3 new spiro-2H-1.4-oxazines is described.

Photochromic spirocompounds, especially spiropyranes and spirobipyranes have been of interest for many years.[1] In this communication we wish to present preliminary results on the synthesis and the photochemical behaviour of the following 2H-1.4-oxazines, indolino- and benzothiazolino-spiro-phenanthro-2H-1.4-oxazines:

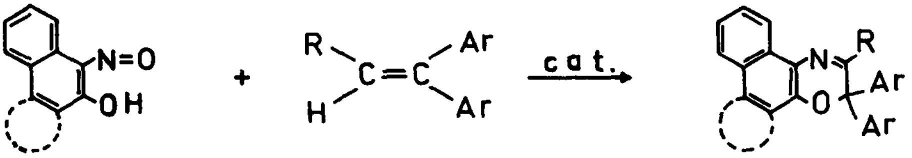


1: R = H ; 2: R=Me; 3: R=H; 4: R=Me



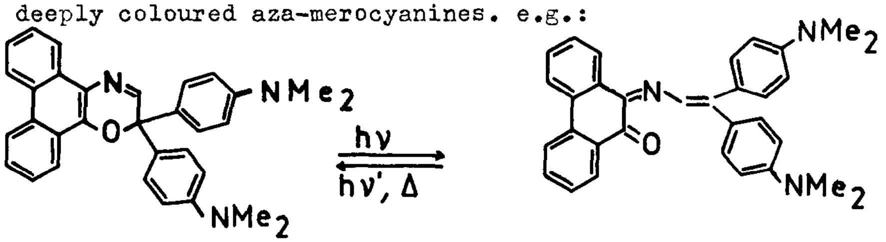
5: X = CMe_2, R = H
6: X = CMe_2, R = NO_2
7: X = S , R = H

The 2H-1.4-oxazines, 1-4, were obtained in good yields by the reaction of 1-nitroso-2-naphthol or phenanthrenequinone-monoxime with 1.1-bis[p-(dimethylamino)phenyl]-ethylene and 1.1-bis[p-(dimethylamino)phenyl]-2-methyl-ethylene, resp., in absolute ethanol in the presence of catalytic amounts of glacial acetic acid (20 h refluxing) according to the equation:



The spiro-compounds were analogously prepared from phenanthrenequinone-monoxime or its 2.7-dinitro-derivative and 2-methylene-1.3.3-trimethylindoline (Fischer's base)or 2.3-benzothiazolium iodide in the presence of piperidine. Compounds 6 and 7 were separated from unidentified byproducts by preparative TLC (silicagel, benzene elution), all other compounds were found to be chromatographically pure after recrystallization. All compounds are blue in the adsorbed state on silicagel. The structures of 1 - 7 were confirmed by elemental analysis, mass spectra[2] and UV/VIS spectra. The photochemical behaviour of the compounds was investigated by flash spectroscopy, flash kinetic spectroscopy, and by UV/VIS spectroscopy in the temperature range of -40 to -10° C.

Compounds 1 - 6 exhibit photochromism due to reversible ring opening forming deeply coloured aza-merocyanines. e.g.:



The most important spectroscopic and kinetic data of the reverse reaction are listed in the following table:

Compd.	Form A		Form B					
	$\tilde{\nu}_{max}$ /cm^{-1}	ε_{max} /cm^{-1}M^{-1}	$\tilde{\nu}_{max}$ /cm^{-1}	τ/s			E_A/kJM^{-1} 5)	
				EtOH	Diox.	Bzn.	EtOH	Bzn.$^{1)}$
1	37,700	34,800	16,400	7.8×10^{-3}	0.21	0.32	45.4	53.8
2	27,500	13,000	16,400	0.47	-	-	39.1	-
3	38,500	38,800	16,400	5.5×10^{-3}	2.3	5.5	39.1	58.1
4	35,700	42,400	16,900	0.56	-	-	39.8	-
5	38,200	24,000	16,900	0.2	3.0	4.7	72.0	38.5
6	32,300	11,250	16,200	19.3	27.2	53.3	66.1	74.9
7$^{2)}$			16,300	0.09	-	0.4	72.3	70.6
8$^{3)}$	30,000	6,400	24,000$^{4)}$	2.4×10^{-4}	n.d.	n.d.	24.7	n.d.
9$^{3)}$	32,000	5,300	15,200	2.2	n.d.	n.d.	96.6	n.d.

1) toluene for 6 and 7

2) inverse photochromism; kinetic data refer to the thermal recovery of the dye after photochemical bleaching

3) 8 = 3-phenyl-2H-1.4-benzoxazine, 9 = 2.2-bis[p-(dimethylamino)phenyl]-2H-chromene; included for comparison[6]

4) no distinct maximum, broad shoulder

5) from 12 measurements in the temperature range 15-70°C

Compounds 5, 6 and 7 are in thermal equilibrium with their corresponding coloured forms in all solvents used. Attempts to shift these equilibria quantitatively to either side by variing the solvent polarity or by adding small amounts of acids or bases failed. The main constituent in the solutions of 5 and 6 are the closed forms A. The ε_{max} values of the open forms are in the order of magnitude of 10^5 $M^{-1}cm^{-1}$ (e.g. 86000 $M^{-1}cm^{-1}$ for 5 B)[3]. Upon flash photolysis about 1 % of the absorption produced per flash persists. These solutions, as well as the unflashed ones, can be completely bleached by irradiation with red light at a temperature of -40° C. Obviously, there exists an isomer of the merocyanine being more stable than the primarily formed one. These isomers are interconvertible by red light.[4]

By contrast with all other compounds 7 crystallises in the merocyanine form B. It shows negative photochromism; note that the kinetic data for this compound refer to the thermal recolouration reaction after photochemical bleaching by the flash. Side reactions leading to decomposition of the dye proceed to a considerable extent. Solutions in dioxane are thermally unstable. The thermal relaxation of the photocoloured forms of 1 - 3 and 8 cannot be described by a single first order reaction alone; the kinetic curves were fitted to a biexponential decay, $A_{(t)} = a_1 \cdot \exp(-k_1 t) + a_2 \cdot \exp(-k_2 t)$, (A = absorbance). The kinetic data in the table refer to the main term (this one with the greatest pre-factor a). This is the faster one for 1, 3 and 8 ($a_1 > a_2$; $k_1 \gg k_2$) and the slower one for 2 ($a_1 < a_2$; $k_1 \gg k_2$). This kinetic behaviour may be a consequence of EZ isomerizations of the open form. Thus, care should be taken in comparing these data because they need not describe the same reaction step nor do they necessarily refer to an elementary reaction at all. Irreversible side reactions also contribute to the decay kinetics.

The 3-substituted oxazines 2 and 4 do not show photochromism in aprotic solvents. The influence of the 3-methyl group has not yet been well understood: In the case of the spiropyranes the lifetime of the coloured forms is drastically shortened by substitution in 3-position.[5] The photoinduced ring opening of 3-methylchromene and its thia- and selena-derivative could not be detected at all neither by µs flash photolysis nor by irradiation at 77 K.[6] 2 and 4 show considerable photodegradation; the methyl group seems to favour irreversible side reactions, though one should expect a much better reversibility due to the shorter lifetime as compared to 1 and 3, resp.. Further synthetic and mechanistic photochemical work is in progress to clarify this problem, especially with 3-substituted benzothiazolino-2H-oxazines.[7]

The outstanding property of the indolino-phenanthroxazines is its extraordinary stability against thermal and photochemical degradation.[8]

Interestingly the lifetime of the merocyanine form of all compounds described in this paper decreases with increasing solvent polarity. This unexpected behaviour may be explained by the solvent influence on the kinetics of a possible syn-anti-isomerization around the C=N - bond of the open form prior to ring closure.

Compounds 3, 5 and 6 have also been studied in solutions of higher viscosity, e.g. glycerol η = 1141 cP) and paraffin oil (η = 117 cP). The lifetimes of the blue forms are increased by a factor of 3 if glycerol is compared to ethanol and paraffin oil to benzene. In polymer matrices the lifetime can be further increased up to minutes depending on the polymer and the amount of placticizer added.

The data given in the table demonstrate well the principles that should be taken into consideration if new photochromic compounds were designed:

- The open form B should exhibit a cyanine like chromophor to produce a long wavelength absorption with a large molar absorptivity.
- Benzoannelation in 5.6- and 7.8-position of the benzoxazine moiety stabilizes the open form.
- The aza-substituent lowers the lifetime of the coloured form.
- A methyl group in 3-position drastically affects the lifetime of the open form, and it favours side reactions.

References

1 G.H. Brown, Techniques of Chemistry Vol. III, Photochromism, Wiley-Interscience, New York (1971).

2 Mass spectral data (JEOL, JMS-D 100; experimental m/e values (peak matching) and calculated masses in parenthesis): 1:421.2144 (421.2154; $C_{28}H_{27}N_3O$); 2: 435.2309 (435.2310; $C_{29}H_{29}N_3O$); 3: 471.2304 (471.2311; $C_{32}H_{29}N_3O$); 4: 485.2459 (485.2467; $C_{33}H_{31}N_3O$); 5: 378.1753 (378.1732; $C_{26}H_{22}N_2O$); 6: 468.1449 (468.1434; $C_{26}H_{20}N_4O_5$); 7: 368 (no peak matching because of too low intensity). We are indepted to Dr. Schade, Zentr.Inst. für Mikrobiologie und Exp. Therapie der AdW der DDR, for the measurements.

3 The absorption spectra of the pure forms A and B of 5 will be published as an example in a paper concerned with a new method for the calculation of the individual spectra in a system $A \underset{h\nu,\Delta}{\overset{h\nu,\Delta}{\rightleftharpoons}} B$ in H.D. Ilge, R. Paetzold, J. Photochem. (1981) (submitted for publication).

4 See for comparison Y. Hirschberg, E. Fischer, J. Chem. Soc., 3129 (1954).

5 R. Gautron, Bull. Soc. Chim. France, 3190 (1968).

6 U.W. Grummt, unpublished results; compare also R. S. Becker, J. Kolc, J. Phys. Chem., 72,997 (1968), J. Am. Chem. Soc., 86,6513 (1964).

7 In the case of benzothiazolino-spiropyranes the 3-methylgroup has been reported to shift the relative thermodynamic stability of the open and the closed form; cf. R. Guglielmetti, J. Photogr. Science 22, (1974) 77

8 M. Reichenbächer, U.-W. Grummt, R. Paetzold, WPC 09K/227 607/7

9 Table computer EMG 666, we thank Drs. S. H. Schütz and E. Stutter, Zentralinstitut für Mikrobiologie und Experimentelle Therapie der AdW der DDR for their programm "ALAU SB".

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