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Photodecomposition of Rhodamine 6G in Chlorinated Solvents**

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Abstract: Rhodamine 6G (Rh6G) dissolved in trichloromethane or 1,2-dichloroethane undergoes a spectral change when exposed to light. The resulting new molecule «Rh-N» is shown by NMR spectra and mass spectrometry to be deficient in two ethyl groups adjacent to the amino groups (cf. Fig. 3).

Rhodamine 6G (Rh6G) in ethanol is used widely as the active medium in dye lasers. Its fundamental properties have been studied a great deal and reported in a large number of publications[1] and references therein.

Recently an extensive study of the dynamical behaviour of various rhodamine dyes has been carried out by continuous and time-resolved spectroscopy and some of the pathways of the activation were attributed to formation of charge transfer complexes[2].

In a preceding investigation[1] we detected a peculiar behaviour of Rh6G when dissolved in chloroform and 1,2-dichloroethane and since these solvents are used for preparation of polymers incorporating Rh6G for luminescent solar concentrators[3] an additional study of the behaviour was needed.

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Experimental

The following materials were used: rhodamine 6G chloride (Eastman Kodak Co.) and analytical grade methanol, ethanol, chloroform and 1,2-dichloroethane (Frutarom).

A series of solutions of Rh6G of concentrations varying from 10^{-6} to 10^{-4} M were prepared in the above solvents.

The absorption spectra were measured using a Perkin-Elmer Lambda 5 double beam spectrometer. The measurements were performed at room temperature.

The fluorescence spectra were measured on a commercial SLM 4800C spectrofluorimeter which provides corrected emission spectra. The fluorescence lifetimes were obtained using the same apparatus with a phase-shift attachment. This attachment only allows measurement of lifetimes exhibiting exponential behaviour.

The ^{1}H- and ^{13}C-NMR spectra were recorded on Bruker WP-200 and WP-300 instruments. Mass spectrometry was performed using a Varian MAT-311 instrument.

The crystals formed when a saturated solution of Rh6G in 1,2-dichloroethane was exposed to light indoors for one month were redissolved in methanol and in chloroform. We refer to those crystals as Rh-N: ***m.p.*** 264–265 °C; 200 MHz ^{1}H-NMR (CD_3OD): δ 0.871 (3 H, t, $J = 7.1$ Hz), 2.024 (3 H, s), 3.890 (2 H, 9, $J = 7.1$

Hz), 6.738 (2 H, s), 6.748 (2 H, m), 7.337 (1 H, dd, $J = 2.0$, 3.3 Hz), 7.732 (2 H, m), 8.202 (1 H, dd, $J = 2.0$, 3.3 Hz); 50.32 MHz $^{13}C\{H\}$-NMR (CD_3OD): δ 14, 17.3, 62.6, 98.4, 115.3, 126.3, 131.3, 131.8, 132.1, 132.5, 134.1, 135.3, 158.6, 160.3, 167; MS (70 eV): *m/z*. 422 (M^+), 387 $(C_{24}H_{23}N_2O_3)^{\cdot+}$, 359 $(C_{22}H_{19}N_2O_3)^+$, 327 $(C_{22}H_{15}O_3)^{\cdot+}$, 315 $(C_{21}H_{19}N_2O)^{\cdot+}$, 300 $(C_{20}H_{16}N_2O)^+$, 298 $(C_{20}H_{14}N_2O)^{\cdot+}$, 194 $(C_{13}H_8NO)^+$, 156 $(C_{10}H_6NO)^{\cdot+}$, rest of fragments: 149, 64, 44, 38, 36, 29, 28.

Fig. 1 presents the absorption spectra of Rh6G and its photodecomposition product «Rh-N», respectively: curve 1 is the normal absorption spectrum of Rh6G in methanol, curve 2 is the absorption spectrum of Rh-N in methanol and curve 3 of Rh-N in chloroform. The main maxima of curves 2 and 3 coincide, however, an additional peak is observed around $\lambda = 470$ nm due to aggregates in $CHCl_3$ solution ($c \approx 10^{-6}$ M)[4]. Fig. 2 shows the corresponding emission spectra.

The absorption spectra of Rh-N are similar to those observed previously[2] for Rh-A which is similar in structure to Rh6G without ethyl on the two amino groups and without the two methyl groups in the 3,7-positions (see Fig. 3 for the corresponding formulae). The hypsochromic effect can be attributed to the disappearance of the two *N*-ethyl substituents. There is no change in the absorption spectra due to the methyl groups at the aromatic rings.

Comparing the absorption and emission spectra of Rh-N with the spectra of Rh-A[2] brought us to the conclusion that the *N,N'*-ethyl groups of the secondary bisamine are replaced by hydrogen as a result of a photochemical process the mechanism of which is still to be clarified. These results are different from those obtained by *Davie* et al.[5] where thermal degradation of rhodamine 6G hydrochloride resulted first in the loss of the ethyl group from the ethyl carboxylate constituent whereas in our case the ethyl group from the ethyl amino constituent is lost first.

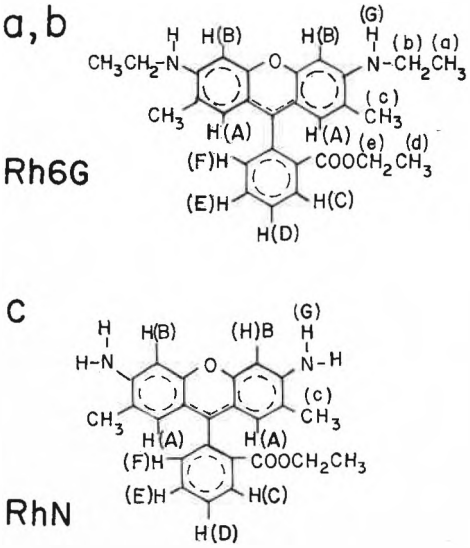

Fig. 3. Structure of Rh6G (a,b) and Rh-N (c). See also Fig. 4.

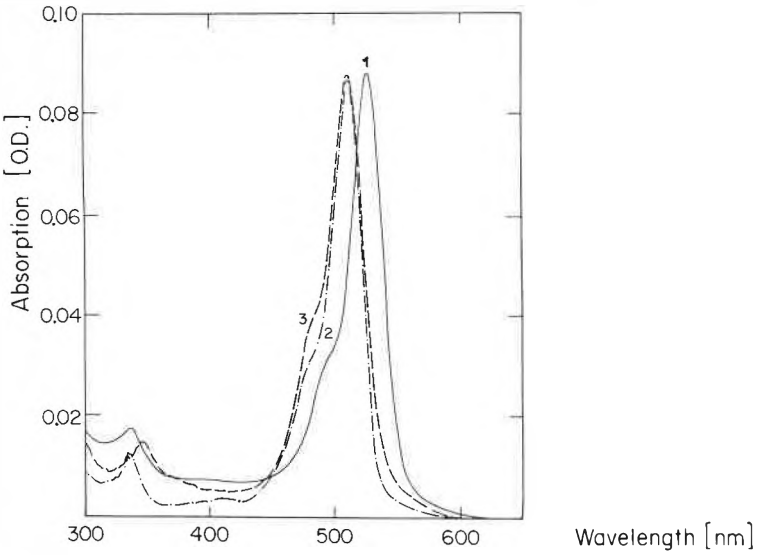

Fig. 1. Absorption spectra. Curve 1: Rh6G in methanol; curve 2: Rh-N in methanol; curve 3: Rh-N in chloroform.

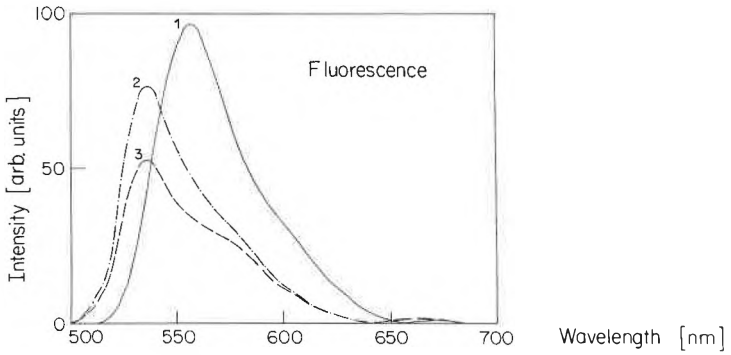

Fig. 2. Emission spectra. Curve 1: Rh6G in methanol; curve 2: Rh-N in methanol; curve 3: Rh-N in chloroform.

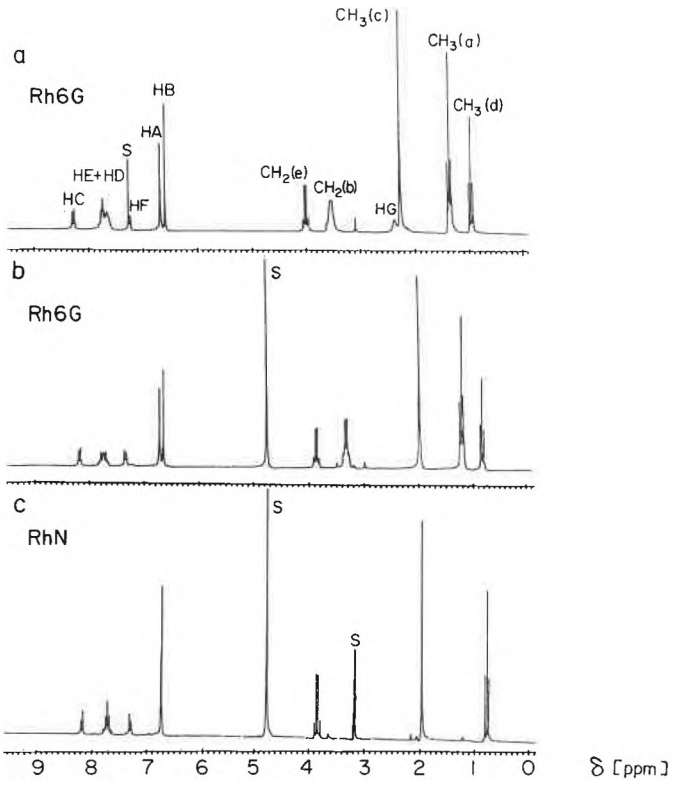

Fig. 4. ^{1}H-NMR spectra. (a) Rh6G deuterated chloroform; (b) Rh6G in deuterated methanol; (c) Rh-N in deuterated methanol.

Fig. 4 presents (a) the ^{1}H-NMR spectrum of Rh6G in deuterated chloroform (for assignment see Fig. 3) which is consistent with the spectrum reported previously by *Abramov* et al.[6]. Comparison of the NMR spectra of Rh6G and Rh-N in deuterated methanol (b and c) shows the absence of the two ethyl groups attached to nitrogen and a displacement of the chemical shift of proton H_B which comes very close to the proton H_A by a very small difference due to the missing ethyl groups making the new rhodamine more electrophilic as compared to the original Rh6G. In the last two spectra almost all the amino protons have been exchanged by the deuterium of the solvent in contrast to the first spectrum which was measured in $CDCl_3$. The amino protons appear as a multiplet at $\delta = 2.1$ and also the N–CH_2 signal is a multiplet at $\delta = 3.4$ due to the existence of *cis* and *trans* configurations in Rh6G[6].

The ^{13}C-NMR spectrum of the product is in good agreement with the proton spectrum where the signals corresponding to the *N*-ethyl groups in Rh6G are absent (in rhodamine they are found at 17 and 40 ppm for the CH_3 and CH_2 groups, respectively). The rest of the spectrum is the same as for Rh6G but again with the discrepancy of the chemical shifts which here are downfield due to the ethyl effect (see discussion above on absorption spectra).

Table 1. Absorption and emission maxima, lifetimes and quantum efficiencies of Rh6G and Rh-N ($c \approx 10^{-6}$ M).

Dye	Solvent	Absorption λ [nm]	Emission λ [nm]	Lifetime [s]	Quantum Efficiency [%]
Rh6G	MeOH	527	557	3.95	98
	$CHCl_3$	530	557	3.40	95
RhEA	MeOH	530 ± 10	580 ± 20	3.96	≈ 100
Rh-N	MeOH	512	536	3.90	75
	$CHCl_3$	511	536	3.40	45
Rh-A	EtOH	510 ± 10	560 ± 20	3.85	

Table 1 presents the absorption and emission maxima, lifetimes and quantum efficiencies of Rh6G and Rh-N at concentration $\approx 10^{-6}$ M as compared to RhEA and Rh-A[2].

The photodecomposition of Rh6G in chlorinated solvents is energetically favourable since the steric hindrance is prevented in the new material[7].

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[1] R. Reisfeld, R. Zusman, Y. Cohen, M. Eyal, *Chem. Phys. Lett. 147* (1988) 142.
[2] M. Vogel, W. Rettig, R. Sens, K.H. Drexhage, *Chem. Phys. Lett. 147* (1988) 452.
[3] R. Reisfeld, M. Eyal, V. Chernyak, R. Zusman, *Sol. Energy Mater. 17* (1988) 439.
[4] L.V. Levshin, A.M. Saletskii, V.I. Yuzhakov, *Zh. Strukt. Khim. 26* (1985) 95; translation to English: *J. Struct. Chem. USSR 26* (1986) 913.
[5] E. Davie, J.H. Morris, W.E. Smith, *Org. Mass Spectrom. 9* (1974) 763.
[6] A.F. Abramov, S.S. Anufrik, G.R. Gineviz, W.A. Mostovnikov, A.N. Rubin, *Zh. Prikl. Spektrosk. 26* (1977) 1017.
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