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108. Photochromism and Triplet states in the Dianthrone System[1]

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(7. III. 73)

When we obtained our first flash results indicating the involvement of triplet states of dianthrone molecules in their photocoloration, we were well aware that these results contradict the excellent work of *Huber, Wild & Gunthard* [1]. We there-

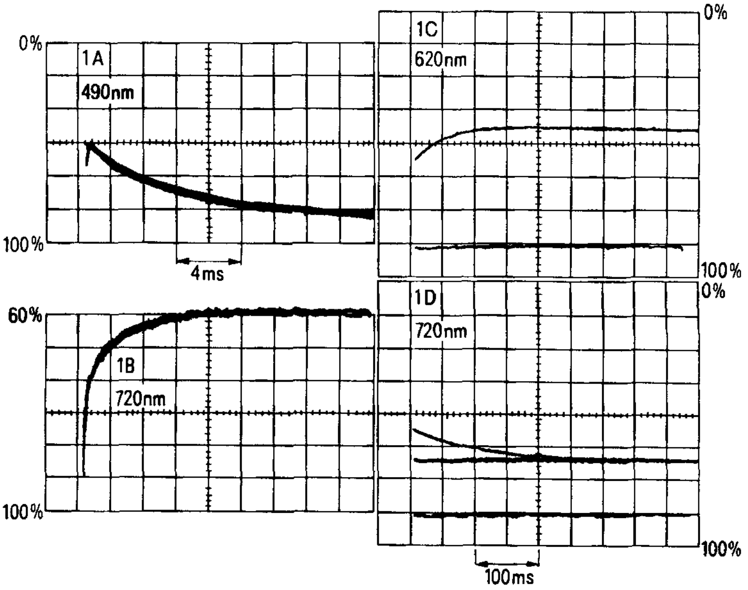

Fig. 1. *Original oscilloscope traces obtained with solutions of TMD in TA at −65°.* 1a and 1b: 1.8×10^{-5} M in 10 cm cells. Growing-in at 720 nm and decay at 490 nm. 1c and 1d: 10^{-4} M in 2 cm cells. Growing-in at 620 nm and decay at 720 nm. The relatively small changes are due to the spectral overlap of the D and B isomers, *cf.* [3].

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[1] We are indebted to Prof. *U. Wild* for putting his results at our disposal for comment before their publication, and agreeing to have his and our results to be published together.

fore deferred publication of our results until the experimental evidence for such an involvement became overwhelming, as detailed in our relevant papers [2] [3]. The present comments are intended to a) provide additional experimental evidence for the sequence of reactions A $\rightarrow$ $^3A^*$ $\rightarrow$ D $\rightarrow$ B for TMD in triacetin, unfortunately in direct contradiction to *Gschwind*'s and *Wild*'s results in the same system, and b) summarize the more indirect evidence in favour of the involvement of triplet $^3A^*$ in photocoloration.

a) *Direct experimental evidence.* Fig. 1 summarizes flash results obtained with a solution of TMD in triacetin at −56°. The flash consisted of two air-filled discharge tubes of 10 cm length each, operating in series, with a total electrical discharge energy of about 300 joules/flash. The growing-in of absorption at 720 nm, at the expense of the absorption at 490 nm, is clear, as is the subsequent decay at 720 nm, and the parallel increase at 620 nm. In view of previous spectral data this provides clear-cut evidence for the above reaction sequence. Similar results, but of course with different rates of change in absorption, were obtained at higher and lower temperatures, as summarized in Fig. 11 of our earlier paper [3]. These results differ markedly from those of *Gschwind* in Fig. 8 of the preceeding paper. In fact, the only similar feature is the decay rate of the absorption at 490 nm. The residual absorption at this wavelength is much higher in *Gschwind*'s experiments, and the behavior at 620 and 714 nm is radically different. (In the present context we shall confine ourselves to a comparison of 'conventional' flash results, in view of the low time resolution of the photographic method and other difficulties. The preceeding paper does not describe any experiments applying ***both*** methods to the TMD/TA system at ***the same*** temperature, and this makes it impossible for us to check the validity of the new

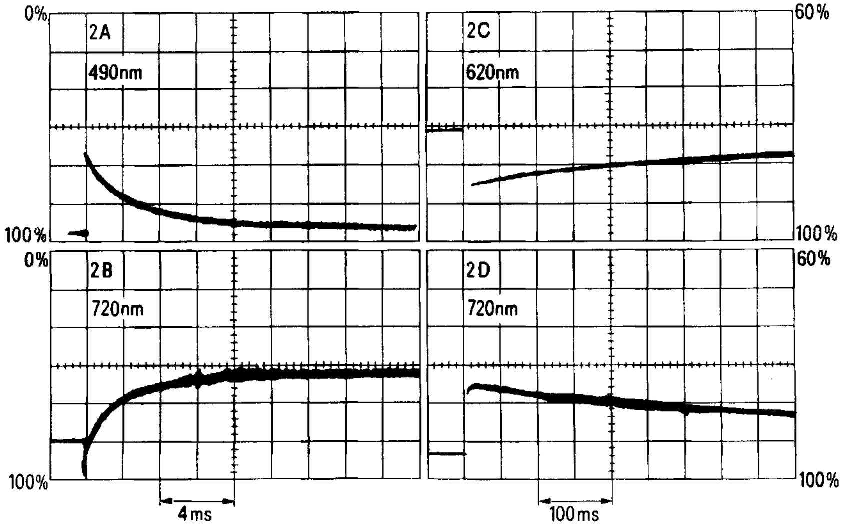

Fig. 2. *Original oscilloscope traces obtained with* 2×10^{-5} M *solutions of TMD in a 1:1 mixture of methylcyclohexane (MCH) and 2-methylpentane (2-MP), in a 10 cm cell.* (These are the experiments described in Fig. 10 of [3]. 1a and 1b: Decay at 490 nm and growing-in at 720 nm at −170°. 1c and 1d: Decay at 720 nm and growing-in at 620 nm, at −168°.

method.) We obtained similar results with a 2×10^{-5}M solution in 8 cm cells and in 1 cm cells, and with 2×10^{-5}M and 10^{-4}M solutions in 2 cm cells. The only major difference in *Gschwind*'s and our experimental conditions seems to be the very much higher intensity of the light flashes in *Gschwind*'s experiments (2000 joule), as evidenced also by the practically total absorption at 620 nm after the flash at –62° and at 488 nm at –68° (*Gschwind*'s Fig. 8 and 9). We wish to point out again that similar results were obtained by us with TMD solutions in the hydrocarbon mixture MCH/2-MP and also in methyltetrahydrofuran, at the appropriate temperatures. Representative results are shown in Fig. 2 and 3. It is worth emphasizing that the results in the latter two solvents are cleaner, because of the absence of isomer C (which absorbs at 490, 620, and 720 nm) and the less marked overlap of the adsorption spectra of ^{3}A* and isomers D and B. However, even the results in TA solvent leave no doubts about the validity of the concepts developed by us. The very considerable residual absorption at 490 nm in *Gschwind*'s results was explained as being due to the C isomer. If so, the absorption of C at the crucial wavelengths 490, 620, 720 nm may well overshadow that due to ^{3}A*, D and B.

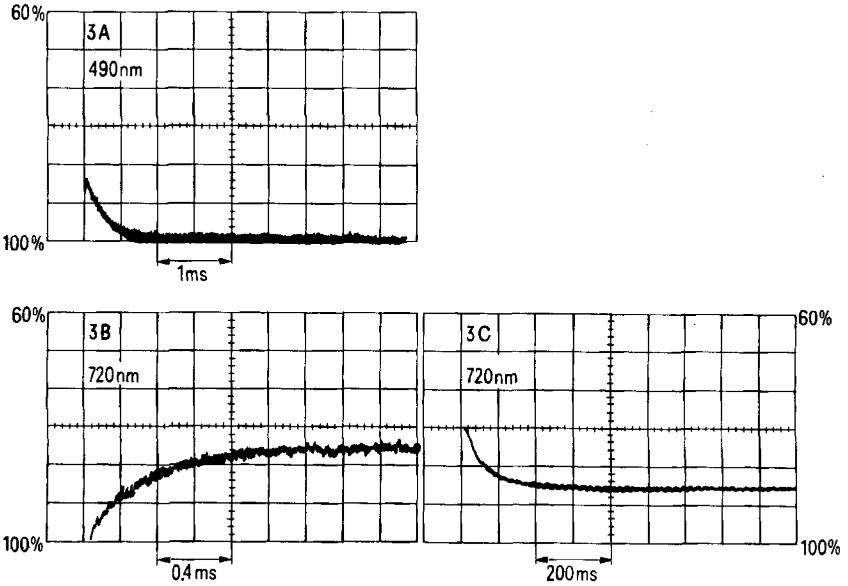

Fig. 3. *Original oscilloscope traces obtained with a 2×10^{-5}M solution of TMD in methyltetrahydrofuran (MTHF) in a 1 cm cell at –159°.* 3a and 3b: Decay at 490 nm and growing-in at 720 nm. 3c: Decay at 720 nm.

The low-temperature flash technique used was described before [3].

b) *Indirect evidence.* 1. The sequence: 'A $\xrightarrow{h\nu}$ ^{3}A* ⟶ colored form' was observed by us by means of flash experiments in dianthrone itself and all derivatives available to us, without exception. (The D isomer was observed both with static methods [4] and with flash methods [3], but only in TMD and two related derivatives. The lack of evidence for the existence of D in *Gschwind*'s experiments is surprising. Again only the very high light intensities of the flash might be blamed.) As with TMD, various solvents gave similar results at the appropriate temperatures.

2. Our recent results [5] with a pulsed nitrogen laser provide evidence for the growing-in of the absorption due to D or B, at a rate which, though enhanced by oxygen, is much slower than the singlet TMD decay rate observed in emission. It is difficult to reconcile these results with a singlet mechanism.

3. Recent sensitization experiments with biacetyl carried out by *Korenstein* in our laboratory showed that the formation of B can be sensitized even at low temperatures. No C is formed under these conditions, although *direct* photocoloration results in the almost exclusive formation of C. We conclude that this indicates the formation of C from singlet TMD. A similar pathway for the formation of B is therefore unlikely.

4. In the temperature range in which the quantum yield of photocoloration falls off sharply with the temperature [4], the rate of triplet decay (absorption at 490 nm in flash experiments) also declines sharply (Fig. 2 in [3]).

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109. Über Tris(siloxymethyl)-, Tris(silylmercaptomethyl)- und Tris(silylmethyl)amine

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(29. I. 73)

Summary. By the reaction of alkali salts of triorgano-silanols, -silanethiols and trimethylsilylmethanol as well as of triorganosilyllithium compounds with tris(chloromethyl)amine, silyl derivatives of tris(hydroxymethyl)-, tris(mercaptomethyl)- and tris(methyl)amine were prepared.

Silylderivate des nicht beständigen Tris(hydroxymethyl)amins und des Tris(mercaptomethyl)amins wurden bisher nicht beschrieben. Ebenso sind die vom Trimethylamin sich ableitenden Tris(silylmethyl)amine unbekannt. Durch die Umsetzung von

$$N(CH_2Cl)_3 + 3\ R_2R'Si{-}X{-}Me \longrightarrow N(CH_2{-}X{-}SiR_2R')_3 + 3\ MeCl \qquad (1)$$

	X	R	R'
1	O	CH_3	CH_3
2	O	C_6H_5	CH_3
3	S	C_6H_5	C_6H_5
4	OCH_2	CH_3	CH_3
5	CH_2	CH_3	CH_3