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PHOTOCHEMICAL *CIS*, *TRANS*-ISOMERIZATION IN THE 2,3-DIPHENYLPIPERAZINE SERIES

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Abstract - Irradiation of *cis* diphenyl substituted piperazines 2a, b (R = Me, H) in acetonitrile solution results in their conversion to *trans* compounds 1a, b (R = Me, H) while in the case of 2c (R = $CH_2\phi$) no isomerization is observed. On the other hand, none of the three *trans*-piperazines isomerizes under the same conditions. A general mechanism is proposed.

In the course of another study[1] the *trans* and *cis*-piperazines 1a-c and 2a-c were needed for the sake of comparison, and were synthesized according to methods reported in the litterature[2]. Mixtures of isomers were obtained in each case from which pure samples of *trans* and *cis* were separated. We were thus led to examine in some details the possibility of a photochemical isomerization of these compounds, such a type of *cis*, *trans*-interconversion appearing relatively rare for heterocyclic system[3,4,5]. We report here our results, the first ever published in this series.

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a R = Me ; b R = H ; c R = CH_2 Ph

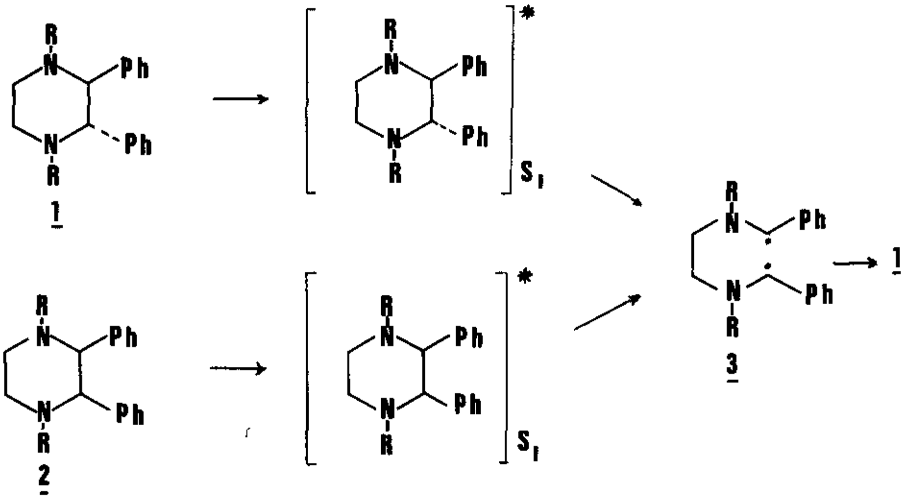
Results - All *trans* 1a-c and *cis* 2a-c piperazines were irradiated in acetonitrile degassed solutions (∿ 10^{-2} M) with a 100 watt medium pressure mercury lamp. *Cis* isomer 2a was also irradiated in degassed acetone as solvent.

Irradiation of trans 2,3-diphenylpiperazines 1 - None of the three *trans*-piperazines 1a-c isomerizes to *cis* compounds but rather decomposes smoothly after 4 hours of irradiation.

Irradiation of cis-2,3-diphenylpiperazines 2 - Complete isomerization of 2a (R = Me) to 1a is achieved within 5 hours. In acetonitrile solution, *cis*-piperylene a triplet quencher, fails to quench the photoisomerization at various concentrations (up to 0.3 M) and a *cis* $\rightleftarrows$ *trans* equilibrium in the diene is reached. When acetonitrile is changed by acetone as solvent, no trace of 1a is detected after the same irradiation time.

Piperazine 2b (R = H) isomerizes more slowly than 2a (R = Me). In acetonitrile solution, longer period of irradiation (∿ 10 hours) leads to the *trans* isomer (60 %) and to degradation products. Complete isomerization to the *trans* compound 1b is obtained starting from an enriched *trans* mixture (1b/2b = 3). N,N-dibenzyl-*cis*-piperazine 2c irradiated for 4 hours in acetonitrile solution decomposes smoothly and yields virtually no *trans* isomer.

Discussion - The sensitizing and quenching experiments performed with 2a indicate that the excited state responsible for the isomerization may be the singlet. The observed *cis*, *trans*-interconversion may be due in principle to C-N or C-C bond scission on excitation. This last process seems to be the most plausible in view of bond dissociation energy data for similar types of bonds ($\emptyset CH_2-CH_2\emptyset$ 45-48 Kcal/mole ; $\emptyset CH_2-NHCH_3$ 58 Kcal/mole)[4] and because it leads to a resonance stabilized biradical 3. Furthermore, homolytic cleavages of C-C bond have already been reported in the course of [2-2] paracyclophane irradiation[6], and photochemical isomerization of N-substituted 2,3-diphenylazyridines[3].



Trans 1a, b and *cis* 2a, b piperazines raising in their excited singlet state by absorption of light, give the same biradical 3 which recyclizes to the thermodynamically more stable *trans* isomer 1. Therefore only *cis*-piperazines 2a, b undergo photoisomerization.

The difference of reactivity observed with *cis*-piperazines (2a > 2b) and the inertness of 2c toward photoisomerization, show the influence of N-substitution as already reported in the case of diphenylaziridines[3]. The lack of isomerization of *cis* and *trans*-piperazines 1c, 2c, can be explained by the substantial change in the photochemical properties induced by the incorporation *of the second chromophore*[7]. *Whatever the* cis *or* trans *isomer is considered, the two phenyl rings* separated by four saturated bonds can adopt a sandwich configuration, in which the two chromophores parallel to each other at a distance $\simeq$ 3Å undergo maximum interaction. After irradiation, the excited molecule can deactivate radiatively or non-radiatively by intramolecular energy transfer.

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