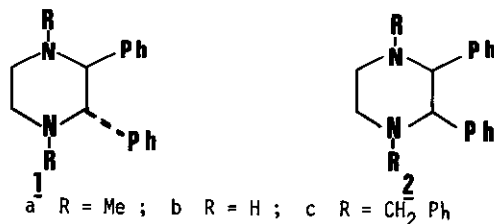


PHOTOCHEMICAL CIS, TRANS-ISOMERIZATION IN THE 2,3-DIPHENYLPYPERAZINE SERIESL. Benadjila-Iguertsira, J. Chastanet and G. Roussi<sup>2\*</sup>

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Abstract - Irradiation of cis diphenyl substituted piperazines 2a, b ( $R = \text{Me}$ ,  $\text{H}$ ) in acetonitrile solution results in their conversion to trans compounds 1a, b ( $R = \text{Me}$ ,  $\text{H}$ ) while in the case of 2c ( $R = \text{CH}_2\text{Ph}$ ) 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<sup>1</sup> 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 literature<sup>2</sup>. 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<sup>3,4,5</sup>. We report here our results, the first ever published in this series.



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

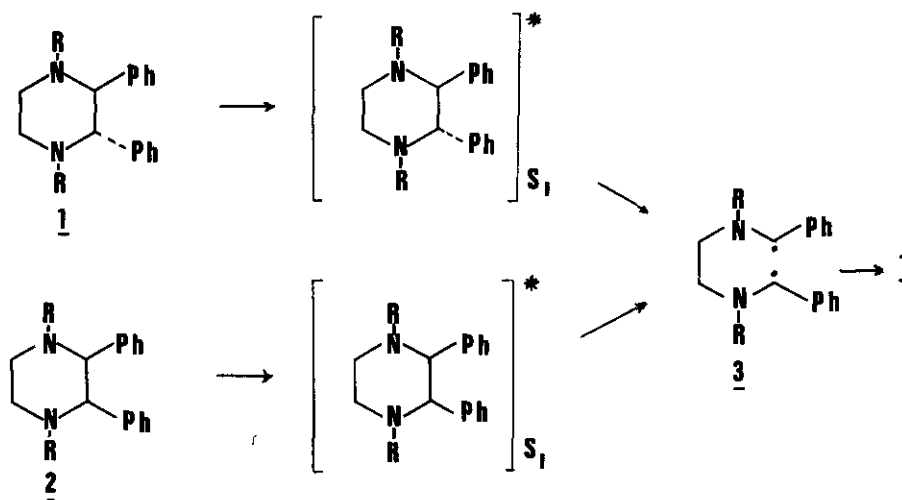
Irradiation of trans 2,3-diphenylpiperazines 1 - None of the three trans-piperazines 1a-c isomerizes to cis compounds but rather decomposes smoothly after 4 hours of irradiation.

Irradiation of cis-2,3-diphenylpiperazines 2 - Complete isomerization of 2a ( $R = \text{Me}$ ) 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  $\rightleftharpoons$  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 ( $\text{CH}_2\text{-CH}_2^\phi$  45-48 Kcal/mole ;  $\text{CH}_2\text{-NHCH}_3$  58 Kcal/mole)<sup>4</sup> 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<sup>6</sup>, and photochemical isomerization of N-substituted 2,3-diphenyl-aziridines<sup>3</sup>.



Trans 1a, b and cis 2a, b piperazines raising in their excited singlet state by absorption of light, give the same biradical 3 which recycles 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<sup>3</sup>. 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<sup>7</sup>. 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  $\sim 3\text{\AA}$  undergo maximum interaction. After irradiation, the excited molecule can deactivate radiatively or non-radiatively by intramolecular energy transfer.

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