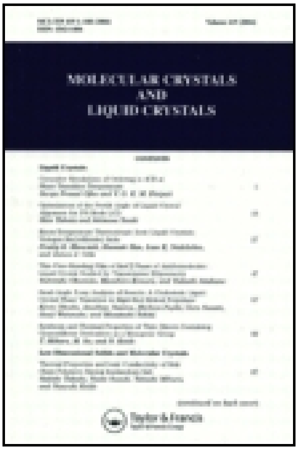

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On Photocolored Product Structure of Photochromic Azomethines in Solutions and Crystals

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ON PHOTOCOLORED PRODUCT STRUCTURE OF PHOTOCHROMIC AZOMETHINES IN SOLUTIONS AND CRYSTALS

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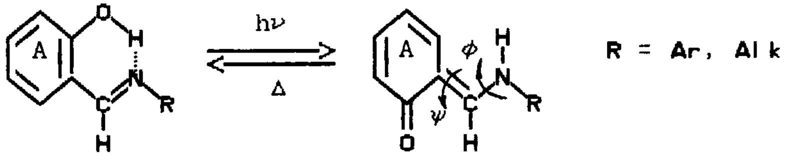
__Abstract__ Comparative data of the experimental and quantum-chemical investigations of the photochromic anils and model compounds lead to the conclusion about unusual "twisted" cis (with regard to C—N-bond) zwitterion N^+H-structure of photocolored form with nearly orthogonal Ar-C- and CH—NH$^+$-groups. This form is stabilized kinetically by the intermolecular interactions in the rigid media and crystals.

INTRODUCTION

From the most wide-spread point of view the photochromic properties of the molecules (I) are conditioned by the thermoreversible photoreaction (scheme 1) and colored photoproduct displaying the absorption bands with λ_{max}=480 and 540 nm has trans-keto-structure (II) with coplanar keto and CH—NH fragments ($\psi = \pi^{\circ}$, $\phi = 0^{\circ}$)[1,2].



(I) (II)

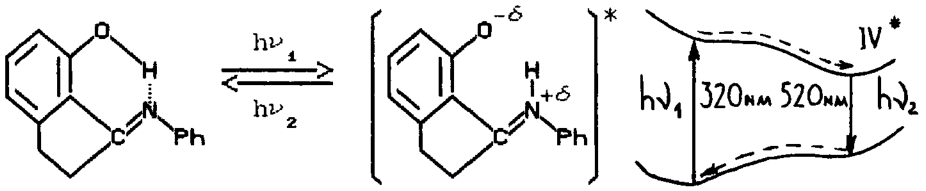
SCHEME 1

From our standpoint the conclusion about that photoproduct structure has not been grounded strictly and moreover it does not conform to some experimental results[3].

Therefore the experimental and quantum-chemical studies and literature data analysis are carried out to obtain a more grounded ideas about photocolored product structure.

RESULTS AND DISCUSSION

The activation energy of dark decoloration (30 Kj/mol)[4,5] is much lower than that of trans-cis isomerisation with respect to C=C -bond (160-170 Kj/mol)[4]. Therefore the suggestion about the trans-structure of photoproduct is doubtful. Meanwhile, model compound (III) where rotation around C—C -bond is impossible does not show any photochromic properties either in rigid matrices or in crytals notwithstanding the photochromically-favorable structure of last ones.



(III) (IV) (III)

SCHEME 2

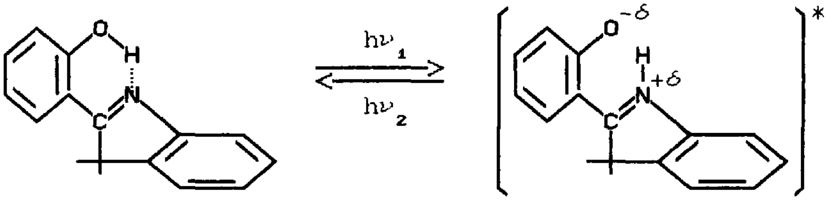
At the same time, compound (III), like non-photochromic anils[6], fluoresces with anomalous Stokes Shift (ASS) under above-mentioned conditions[3] due to adiabatic proton transfer (scheme 2). Hence, in molecule (I), the photocolored product formation is connected not only with excited-state intramolecular proton transfer (ESIPT) but with A-ring rotation around C—C-bond in competition with fluorescence.

On the other hand, CNDO/S calculations indicate that the longest wave-length transition in (II) accompanied by the charge transfer from A-ring onto C—N -group[3] in planar trans- and cis-structures ($\psi = \pi$ or 0) engenders absorption in the region no more than 440 nm and is shifted to the red up to λ=650 nm when ψ is changed from 0 to $\pi/2$.

This analysis presents strong evidence in favor of nearly orthogonal ($\psi=\pi/2$) structure of Ar-C-fragment in colored product which absorbs in the region of 480-540 nm.

Furthermore, according to CNDO/S computation, this structure has the large dipole moment of $\mu_{\pi/2}$=8D which leads to the "blue"-shift of short-lived band of colored form in liquid solutions with increasing polarity of solvents.

A key role in the colored structure formation is also played by the isomerisation with respect to C=N-bond. Really, in rigid structure (V) where such isomerisation is ruled out but the rotation around C—C-bond is still possible no stable structure is formed in rigid media and crystals but instead the ESIPT takes place resulting in very weak ASS-fluorescence.



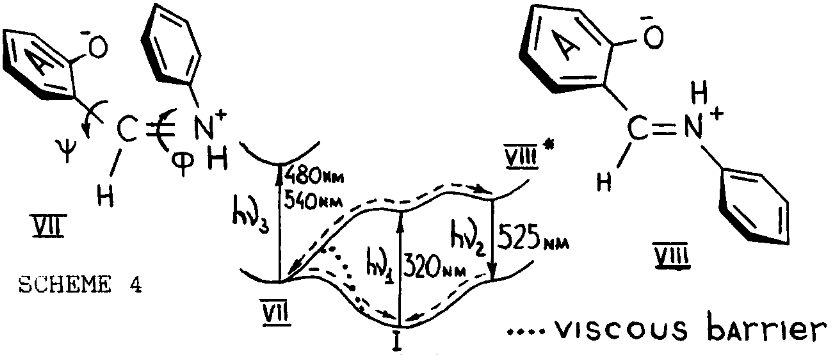
(V) (VI)

SCHEME 3

Absorption spectra of colored alkylimines (I)(R=Alk) provide a strong blue shift of the typical structured "photochromic" band when Alk is shortened from $(C_2H_5)_{11}CH_3$ (λ=480-540 nm) to CH_3 (λ=420-440 nm)^3, which may be due to acoplanar ($\psi=\pi/2$) structure stabilisation caused by sterical interaction of bulky Alk substituent with A-ring in NH-cis- ($\phi=\pi$) structure similar to (II). The position and shape of absorption bands of colored products of compound (I) whith R=$(C_2H_5)_{11}CH_3$ and R=Ar are practically the same which allows us to assume for them similar structures.

CONCLUSIONS

Obtained data suggest that colored forms of anils (I) have unusual twisted ($\psi=\pi/2$, $\phi=\pi$) NH-Zwitter-ion cis- (with respect to C—N-bond) structure resulting from the sterical interactions of N—R -group and Ar-C-ring (A) (VII).



SCHEME 4

Such structures are stabilized by intermolecular interactions in rigid matrices ("viscous" barrier)and crystals[1,9]. The diabatic formation of this weakly-fluorescent structure competes with adiabatic process of the fluorescent structure (VIII) formation (scheme 4).

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