

Photo and Thermal Isomerization of Azophenol and Bis-Azophenol Derivatives: Additional Evidences for a Concerted Inversion Mechanism

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Abstract

Photochemical and thermal isomerization behavior of 2,4-bis(*p*-tolylazo)phenol was studied and compared with its mono-azo analog.

Introduction

Azobenzenes are key components in several molecular photoswitches because of their efficient and reversible *E-Z* isomerization under appropriate light radiation, making this class of compounds an interesting prototype for molecular information, non-linear optics and controlled drug release systems. Among the azobenzene derivatives, hydroxyazobenzenes (azophenols) display particular and interesting properties such as red shifted π - π^* transitions, faster thermal isomerization rates, tautomerism, and intra or intermolecular hydrogen bonding.¹ In spite of the great interest generated by azophenols, there are no reported isomerization studies for bis-azophenols. In the present study has been investigated the isomerization behavior of the bis-azophenol 2,4b-TAP comparatively to an azophenol derivative (4'-TAP).

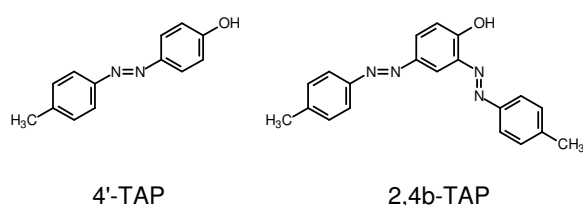


Figure 1 4-tolylazophenol (4'-TAP) and 2,4-bis(*p*-tolylazo)phenol (2,4b-TAP).

Results and Discussion

Benzene solutions of 4'-TAP and 2,4b-TAP were irradiated on the region of the π - π^* bands using a 370 nm LED until no changes in UV-Vis absorption were observed (photostationary state). The kinetic data along with the quantum yields are presented in Tab. 1.

The obtained photostationary states for the two azo dyes are significantly different: 80% conversion for 4'-TAP and 15% for 2,4b-TAP.

The “*mono*” azobenzene 4'-TAP behaves as a typical *p*-azophenol¹ in apolar solvents with detectable photoisomerization and thermal recovery

(minute range) using steady state techniques and rich ratios of *E* to *Z* in the photostationary state.

Table 1. Kinetic constants and quantum yields of isomerization of the azo dyes at 298K.

	$E \rightarrow Z$ k (s ⁻¹)	$Z \rightarrow E$ k (s ⁻¹)	$\Phi_{E \rightarrow Z}$
4'-TAP	1,8·10 ⁻²	2,6·10 ⁻³	0,41
2,4b-TAP	1,8·10 ⁻²	4,9·10 ⁻⁵	0,05

The obtained results for 2,4b-TAP can be rationalized taking in account a recently proposed isomerization mechanism for azobenzenes, the concerted inversion pathway (CIP)² and the properties of *ortho* and *para* azophenols¹. The main aspect of the CIP is that *both* phenyl rings simultaneously invert along the -N=N- bond in going from *trans* to *cis* form assuming a linear structure. Should be noted that in 2,4b-TAP both azo groups has a common phenyl ring (the *o/p* phenol ring). After excitation, the *o*-azophenol is rapidly converted thermally (ms range in apolar solvents) to the *E* form and due intramolecular hydrogen bonding blocks the inversion possibility of the common ring necessary for the isomerization of the *p*-azophenol moiety explaining the poor *E* to *Z* ratio and the low quantum yield. The unusual thermal recovery observed (hours range instead of min range) would be accounted for the absence of tautomeric structures for the *p*-azophenol moiety because the hydrogen of the hydroxyl group is strongly compromised with intramolecular hydrogen bond at the *o*-azophenol moiety.

Conclusions

The isomerization behaviour of 2,4b-TAP is mainly governed by the *o*-azophenol moiety and the results reinforce the recent proposed CIP for the isomerization of azobenzenes. Due to strong hydrogen bond at *o*-azophenol moiety the thermal recovery behavior of the *p*-azophenol is drastically changed resembling of that azobenzene.

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¹ García-Amorós, J.; Velasco, D. *Beilstein J. Org. Chem.* **2012**, *8*, 1003.

² Burdette, S.C.; et al. *J. Org. Chem.* **2010**, *75*, 4817.