# Photoinitiated azo-hydrazo tautomerizm of 1-*p*- toluenesulphonylazo-2,4,6,8-tetrakis (tert-butyl)phenoxazine

T. E. Ivakhnenko, N. I. Makarova, E. P. Ivakhnenko,
V. I. Minkin, and M. I. Knyazhansky

*Institute of Physical and Organic Chemistry of Rostov-on-Don State University Stachky av., 194/2, Rostov-on-Don, 344090, Russia*

ABSTRACT. A novel photochromic compound with NH−N intramolecular H-bond (1-*p*-toluenesulphonylazo-2,4,6,8-tetrakis(tert-butyl)phenoxazine) and the corresponding model structures (1-oxo-2,4,6,8-tetrakis(tert-butyl)phenoxazine, 2,4,5,7-tetrakis (tert-butyl )-1-( veratroylazo ) phenoxazine, 2,4,5,7-tetrakis ( tert-butyl )-N-acetyl-1-(*p*-toluenesulphonylazo)phenoxazine) have been synthesized and their spectral and photochemical properties are studied. The photochromic transformations observed are found to be conditioned by ESIPT (as a primary step) followed by E-Z isomerisation about N−N-bond.

## 1. INTRODUCTION

Various structurally nonrigid systems including intramolecular hydrogen bonds (IHB) OH · · · N, in which adiabatic Excited State Proton Transfer (ESIPT) is a first stage of the processes responsible for fluorescent [1] and (or) photochemical (including photochromic) [2] properties have been recently investigated in much detail [3–6]. On the other side, ESIPT in compounds with IHB NH−N is considerably less studied [7–9]. Although Anomalous Stocks Shift (ASS) fluorescence was supposed to be conditioned by ESIPT, investigation into possible stages of the processes related to adiabatic structural transformations and diabatic reactions leading to a metastable colored form (photochromizm) has not been carried out.

In this work, results of the investigation of photoinitiated processes including ESIPT in a structurally flexible molecular system containing IHB NH−N are presented. A series of novel compounds 1-*p*-toluenesulphonylazo-2,4,6,8-tetrakis(tert-butyl)phenoxazine (I) and 2,4,5,7-tetrakis(tert-butyl)-1-(veratroylazo)phenoxazine (III) and the model structures without IHB, 2,4,5,7-tetrakis(tert-butyl)-N-acetyl-1-(*p*-toluenesulphonylazo)phenoxazine (IV) and 1-oxo-2,4,6,8-tetrakis(tert-butyl)phenoxazine (II) [10] was synthesized and their spectral and photochemical properties are studied.

## 2. MATERIALS AND METHODS

Absorption spectra of the compounds were recorded with a spectrophotometer Specord M-40 (Germany) equipped with a high pressure mercury lamp DRSh-250 supplied with the changeable filters. The spectral investigations were carried out in a quartz Dewar vessel with 1 cm cell using liquid nitrogen. The polymeric films of the samples were prepared on the basis of the polymethylmetacrylate. IR-spectra were recorded with a spectrophotometer Specord-IR-71. $^1$H-NMR-spectra were recorded with a spectrometer Varian VXR-300.

Characterization of the initial compounds and the model structures has been performed by means of UV-, IR-Internal and $^1$H-NMR spectroscopy and by elemental analysis as well.

1-*p*-toluenesulphonylazo-2,4,6,8-tetrakis(tert-butyl) phenoxazine (I) was prepared by coupling 1.67 g (0.0046 mole) of 1H-1-1oxo-2,4,6,8-tetrakis(tert-butyl) phenoxazine (II) [10] solved in 25 ml toluene with 0.88 g (0.0046 mole) *p*-toluenesulphonylhydrazine. The mixture was heated until boiling (15–20 min) and the solvent was removed in vacuum. The product formed was washed out by cool hexane to clear off the unreacted phenoxazinone (II) and the unsolved precipitate was recrystallized from hexane. The yield of (I) was 0.69 g (26%). White crystal powder, m.p. 153–154 °C. I.R.(nujol), $\nu$: 3460, 1620 cm$^{-1}$. $^1$H NMR ($CDCL_3$), $\delta$, ppm: 1.20 (1H, s, t-Bu); 1.40 (1H, s, t-Bu); 1.80 (1H, s, t-Bu); 2.20 (1H, s, t-Bu); 2.30 (3H, s, $CH_3$); 6.92–7.10 (4H, m, aromat. protons); 7.19 (1H, s, phenoxaz.); 7.25 (1H, s, phenoxaz.); 7.50 (1H, s, phenoxaz.).

2,4,5,7-tertakis( tert-butyl )-1-( veratroylazo )phenoxazine (III) was prepared through reaction of solution of 4.21 g (0.01 mole) phenoxazinone (II) in 40 ml of absolute benzene with 1.92 g (0.01 mole) of 3,4-dimethoxybenzoic hydrazide added in small portions under stirring. The mixture was heated and boiled for 1 hour. Then the mixture was filtered and the solvent evaporated. The yield of (III) was 3.2 g (52%), m.p. 252 °C (from hexane). $^1$H NMR(toluene $D_8$), $\delta$, ppm: 1.54 (9H, s, t-Bu), 1.56 (9H, s, t-Bu), 1.58 (9H, s, t-Bu), 1.88 (9H, s, t-Bu), 2.10 (3H, s, $CH_3$), 2.15 (3H, s, $CH_3$), 6.85–7.42 (4H, m, Ph and 3H phenox.). I.R. (nujol), $\nu$: 3400 (NH), 1720 (C=O).

2,4,5,7-tetrakis ( tert-butyl ) -N - acetyl - 1- ( *p*-toluenesulphonylazo)phenoxazine (IV) was prepared by coupling the compound (III) in benzene solution with an equivalent quantity of acetic anhydride. The mixture was separated on a silica gel column. The yield of (IV)

was 35%. $^1$H NMR ($CDCl_3$), $\delta$, ppm: 1.18 (9H, s, t-Bu), 1.22 (9H, s, t-Bu), 1.26 (9H, s, t-Bu), 1.30 (9H, s, t-Bu), 2.3 (3H, s, $CH_3$), 2.5 (3H, s, $CH_3$), 6.62–7.31 (4H, m, Ph and 3H, phenox.). I.R.(nujol), $\nu$: 1750 (C=O).

## 3. RESULTS AND DISCUSSION

***Structure and absorption spectra of the initial product.***

The long wavelength absorption of 1-*p*-toluenesulphonylazo-2,4,6,8-tetrakis(tert-butyl)phenoxazine (I) has its maximum at 278–290 nm both in the polar (acetonitrile, ethanol) and in the nonpolar (toluene, hexane) solvents and in polymeric films as well. Figure 1: $\lambda_{max}$ = 278 nm, $\varepsilon$ = 7750 mole/l cm$^{-1}$ (hexane), $\lambda_{max}$ = 285 nm, $\varepsilon$ = 9515 mole/l cm$^{-1}$ (ethanol). From comparison of extinction and longwave absorption bands data for the compound (I) with those of various azobenzenes it follows that the spectral characteristics of the compound (I) are closer to *cis*-azobenzenes than to the planar *trans*-azobenzene ($\lambda_{max}$ = 320 nm, $\varepsilon$ = 20000 mole/l cm$^{-1}$ for *trans*-azobenzene, $\lambda_{max}$ = 281 nm, $\varepsilon$ = 5200 mole/l cm$^{-1}$ for *cis*-azobenzene). The vibralioual frequency 3460 cm$^{-1}$(hexane) in the IR-spectra of the compound (I) testifies to the existence of IHB (NH–N) between N-atoms of the phenoxazine fragment and the azo-group.

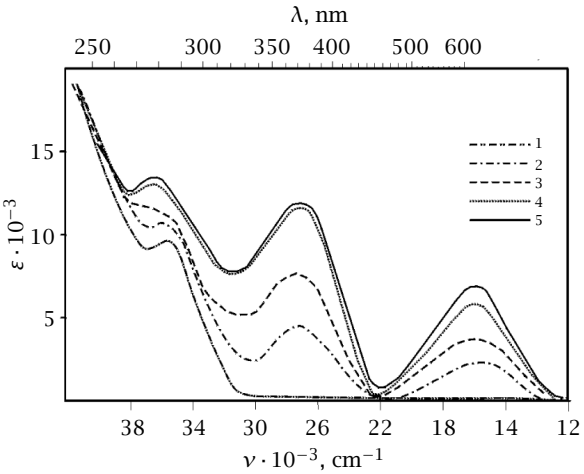



Figure 1. *Transformation of the absorption spectrum of the compound (I) under irradiation in ethanol,* T = 293 *K,* $\lambda_{exc}$ = 313 *nm. Curves 1,2,3,4 correspond to the time of irradiation-0,8,13,40 mins.5-the absorbtion spectrum of the phenoxazinone (II).*

Results of quantum chemical MNDO(MP3) calculations are in good agreement with the experimental data allowing interpretation of the longwave absorption band as the charge transfer band. The spectrum of (I) at solid glassy solution at 77 K is similar to that in solution at room temperature. See Figure 2.

The position and intensity of the longwave absorption maximum point to accoplanarization of the molecule (I) as compared with *trans*-azobenzene (see above) as the result of sterical interactions of azo-group

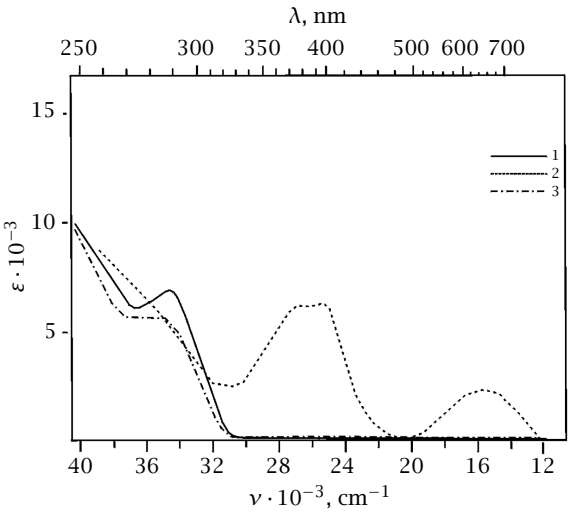


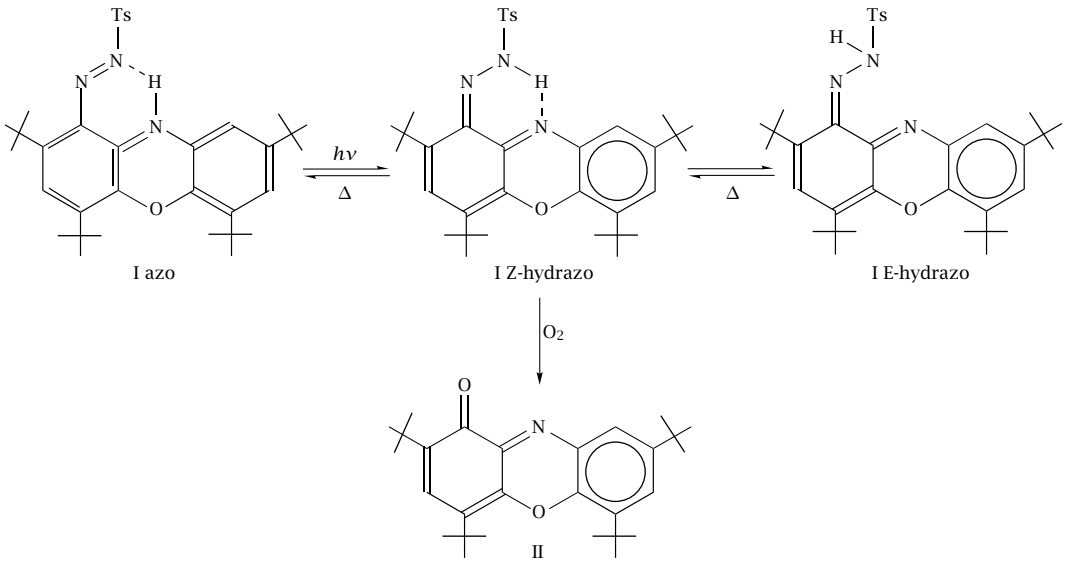

Figure 2. *Transformation of the absorption spectrum of the compound (I) in ethanol at 77 K. 1-before the irradiation, 2-after the irradiation (*T = 77 *K,* $\lambda_{exc}$ = 313 *nm,* $\tau_{exc}$ = 15 *min), 3-AFTER defreezing (*T = 293 *K).*

with a tert-butyl-group of the sterically crowded heterocycle. The sterical interactions lead to weakening IHB in the ground state of (I) as they disturb conjugation of the tozylazo-group with the phenoxazine fragment. These findings lead to a conclusion that sterically crowded hydrazone obtained by the interaction of 1-oxo-2,4,6,8-tetrakis(tert-butyl)phenoxazine with *p*-toluenesulphonylhydrazine exists in the azo-form, stabilized by IHB NH–N. Variations in temperature and solvent polarity do not shift tautomeric equilibrium to the hydrazonic form of the compound (I).

***About the photoreaction mechanism and photoproduct structure.***

UV-irradiation of the solutions or polymeric films of the 1-*p*-toluenesulphonylazo-2,4,6,8-tetrakis(tert-butyl) phenoxazine (I) with both filtered and nonfiltered light of the DRSh-250 lamp results in appearance of two intense absorption bands ($\lambda_{max}$ = 363, 617 nm in ethanol; $\lambda_{max}$ = 344, 571 nm in hexane; $\lambda_{max}$ = 361, 563 nm in polymeric films on the basis of polymethylmetacrylate). Visually, deep dark blue coloration of the solutions and the polymeric films is observed. In the case of short time irradiation (2–5 minutes) of the solutions of (I) the photocoloration is reversible. The UV-spectrum of the photocolored form of the compound (I) completely coincides with that of the model compound-phenoxazinone (II), which fact permits to suppose that prolonged UV-irradiation of the initial azo-compound (I) leads to its photodegradation giving rise to the phenoxazinone (II) (see Scheme 1).

UV-irradiation of the freezed glassy solutions (77 K) of (I) in polar (ethanol) and nonpolar (isopentane) solvents leads to deep photocoloration similar to that observed at room temperature. A difference is in the bathochromic shift of the photoproduct absorption bands observed at 77 K as compared with those at room temperature: $\lambda_{max}$ = 363, 617 nm in ethanol at room




Scheme 1

temperature, $\lambda_{max}$ = 380, 666 nm at 77 K and $\lambda_{max}$ = 344, 577 nm in isopentane at the room temperature, $\lambda_{max}$ = 380, 662 nm at 77 K. On warming up the photocolorated solutions they decolorize. The process of photocoloration with the next decoloration in the dark can be repeated many times without noticeable decomposition of the photochromic compound.

To clarify the mechanism of the process in the compound (I) model compounds were studied: 2,4,5,7-tetrakis(tert-butyl)-N-acetyl-1-(*p*-toluene-sulphonylazo) phenoxazine (IV) and 2,4,5,7-tetrakis- (tert-butyl)-1-(veratroylazo)phenoxazine (III). The compound (III) has an absorption band at $\lambda_{max}$ = 303 nm ($\varepsilon$ = 14000 mole/l cm$^{-1}$) with a shoulder at $\lambda_{max}$ = 322 nm ($\varepsilon$ = 9500 mole/l cm$^{-1}$) in ethanol. However, unlike the compound (I) irradiation of the compound (III) both at room temperature and at 77 K does not lead to photocoloration. The compound (III) shows no fluorescence in ethanol and isopentane solutions. Excitation at 77 K causes the ASS fluorescence at $\lambda_{max}$ = 480 nm, 500 nm, isopentane. At the same time no thermochromic conversion was observed in solutions of the compound (III). Therefore, there is no structures in the ground state responsible for ASS fluorescence. At the same time, the ASS fluorescence excitation coincides with the absorption spectrum of the azo-form of (III). Thus, the ASS fluorescence in the compound (III) is conditioned by the ESIPT, but not transformations in its ground state structure.

Neither photochromism nor fluorescence of 2,4,5,7-tetrakis(tert-butyl)-N-acetyl-1-(*p*-toluenesulphonylazo) phenoxazine (IV) were observed.

The above described findings lead to the conclusion about the mechanism of the photoinitiated processes in the studied compound (I) (Portrayed by Scheme 1). The ESIPT (from the nitrogen atom of phenoxazine heterocycle to the nitrogen atom of the azo-group) occurs under excitation of the initial azo-form of the compound (I) ($\lambda_{max}$ = 288 nm). The compound (I) rearranges to the dark blue colored hydrazonic-form ($\lambda_{max}$ = 360, 580 nm). Two absorption bands ($\lambda_{max}$ = 360, 580 nm) appearing after irradiation of solutions of compound (I) represent a superposition of the absorption bands of two isomers (E-Z) of the hydrazonic-form. Back thermal transformations are related to the reverse ground state proton transfer. Such the transfer is only possible in Z-isomer of the hydrazonic-form of the compound (I). Only Z-isomer of the hydrazonic-form of (I) is formed under UV-irradiation of (I) at 77 K (matrix) which fact is witnessed by full reversibility of the photoreaction.

## ACKNOWLEDGEMENTS

This work was supported by RFBR (Grants 96-15-97476, 98-03-33063, 99-03-32485)

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