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Photochemical Properties of 2,2′-Biquinoxalyl and Thieno[2,3—*b*:4,5—*b*′]biquinoxalyl

I. Baranowska

Department of Analytical and General Chemistry, Silesian Technical University,
PL-44-101 Gliwice, Poland

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2,2′-biquinoxalyl and thieno[2,3—*b*:4,5—*b*′]biquinoxalyl can be photoreduced in acidified alcoholic solutions and in aqueous solutions of acids. Quantum yields of the photochemical reaction have been determined. The fluorescence and phosphorescence spectra of these compounds have been recorded and the fluorescence quantum yields have been determined. A mechanism of the photoreduction has been proposed.

(Keywords: 2,2′-Biquinoxalyl; Fluorescence; Phosphorescence; Photoreduction; Thieno[2,3—b:4,5—b′]biquinoxalyl)

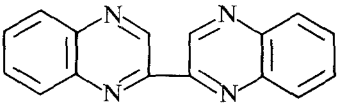
Photochemische Eigenschaften von 2,2′-Bichinoxalyl und Thieno[2,3—b:4,5—b′]bichinoxalyl

2,2′-Bichinoxalyl und Thieno[2,3—*b*:4,5—*b*′]bichinoxalyl unterliegen photochemischer Reaktion in angesäuerten Alkohollösungen und in wäßrigen Säurelösungen. Es wurde die photochemische Quantenausbeute bestimmt. Außerdem wurden die Fluoreszenz- und Phosphoreszenz-Spektren aufgezeichnet und die Fluoreszenz-Quantenausbeuten bestimmt. Zugleich wurde ein Mechanismus zur Photoreduktion vorgeschlagen.

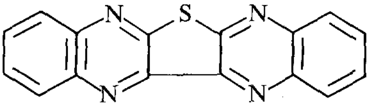
Introduction

The photochemical reactions of diazines have been widely studied for quinoxaline and pyrazine [1–4] and their photosubstitution, hydroxylation and isomerization have been described in details. In recent years there were a number of papers on the systems composed of two heterocyclic rings, especially 2,2′-bipyrazil and its derivatives [5, 6]. Ruthenium complexes, e.g., $\mathrm{Ru}(BPZ)_3^{2+}$, have been found to be new photocatalysts like the well-known complexes of ruthenium and bipyridyl. Photochemical reactions of 2,2′-biquinoxalyl and its derivative have not been reported yet.

In continuation of our studies on the properties of 2,2′-biquinoxalyl and thieno[2,3—*b*:4,5—*b′*]biquinoxalyl, in which we had found that these compounds were reduced electrochemically [7–10] and by tin(II) and titanium(III) [11–13] the present work deals with the behaviour of these compounds on irradiation with light of different wavelength. The reactions described in this paper were performed in alcoholic solutions acidified by mineral acids and in aqueous solutions of acids.



2,2′-Biquinoxalyl
(2,2′-*BQx*)



Thieno[2,3—*b*:4,5—*b′*]biquinoxalyl
(*TBQx*)

Experimental

An ultraviolet analytical lamp, EMITA VP-60 has been used to irradiate the solutions, and a high-pressure mercury lamp, HBO-200, equipped with a BC-7 filter and interference filters, $\lambda = 345$ nm and $\lambda = 365$ nm, has been used to determine quantum yields. The absorption spectra were recorded with a Unicam spectrophotometer, SP 1700, the fluorescence spectra and the phosphorescence spectra with a Jasny spectrofluorimeter [14]. 2,2′-biquinoxalyl and thieno[2,3—*b*:4,5—*b′*]biquinoxalyl were synthesized according to [15, 16], crystallized from dioxane and sublimed. Their purity was checked by thin-layer chromatography. Water was distilled four times over $KMnO_4$. Isopropanol was purified by shaking with active charcoal and by fractional distillation. CH_3COOH was distilled. CH_3OH (fluorescence grade, Merck), concentrated H_2SO_4, HCl, and $HClO_4$ (Merck) were used without further purification. All solvents were checked for fluorescence and absorption before use.

The photochemical reactions were performed in quartz or glass flasks or directly in spectrophotometric cells equipped with ground glass stoppers.

Before irradiation the solutions were purged for 15 minutes using argon to remove oxygen. The measurements were performed at ambient temperature. Only the phosphorescence spectra were performed in H_2SO_4 : *n*-propanol : ethanol (1 : 5 : 2) glass, at 77 K.

Results and Discussion

Photochemical Reactions of 2,2′-Biquinoxalyl and Thieno[2,3—b:4,5—b′]biquinoxalyl

The alcoholic solutions of 2,2′-biquinoxalyl and its thieno derivative acidified by hydrochloric acid become blue on irradiation. The compounds themselves do not absorb in the visible range and after the photochemical reaction the absorption maximum is at $\lambda = 680$ nm.

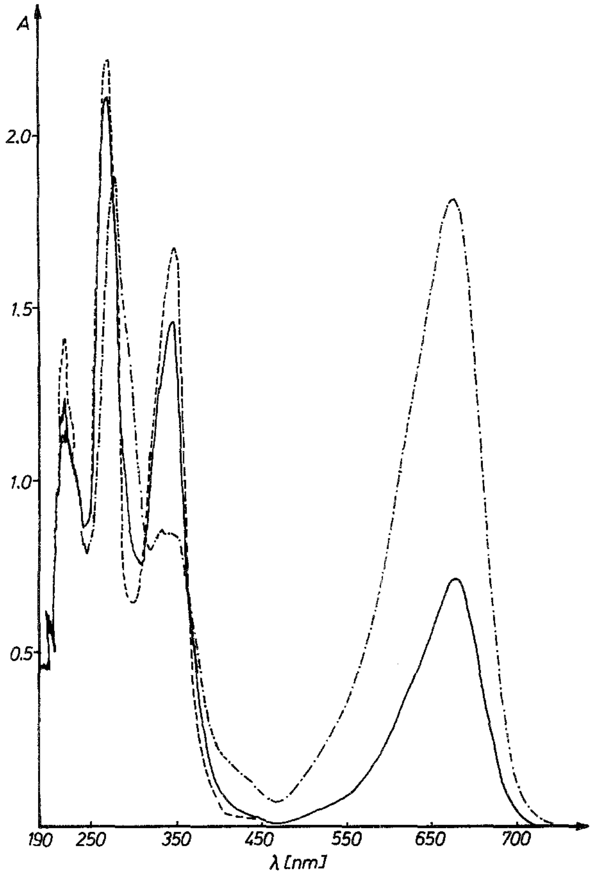


Fig. 1. Absorption spectra recorded in isopropanol acidified with hydrochloric acid. 2,2'-*BQx* ––––; product of photochemical reaction —·—·—; product of reaction, recorded during decolouration of the solution ———

Simultaneously with the occurrence of a maximum in the visible range, a decrease of absorbance in the range of 340 nm for 2,2'-biquinoxalyl and 360 nm for thieno[2,3—*b*: 4,5—*b*']biquinoxalyl (Figs. 1 and 2) has been observed. The blue colour of the solutions is stable in oxygen-free conditions, while in the presence of oxygen the solutions turn colourless again and the absorption spectrum becomes identical with that before irradiation. The irradiation and decolourization of the solutions can be repeated several times without observable changes in the absorption spectrum of the original compound. The photochemical reactions were investigated while irradiated with light of 345 nm, 365 nm, and the full

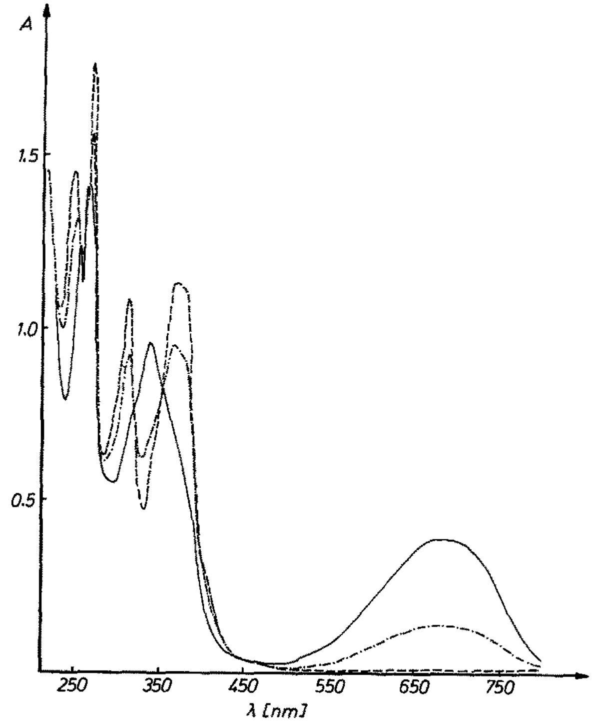


Fig. 2. Absorption spectra recorded in isopropanol acidified with hydrochloric acid. *TBQx* – – – – –; product of photochemical reaction ———; product of reaction, recorded during decolouration of the solution —·—·—

spectrum of the lamp. The reaction products were the same an all the alcoholic solution on the course of the reaction has been studied and the highest volume of the molar absorption coefficient 2,2'-*BQx*, $\varepsilon = 4.4 \cdot 10^4$ at $\lambda = 680$ nm and *TBQx*, $\varepsilon = 1.7 \cdot 10^4$ at 680 nm has been found for the concentration of 1 *M* HCl in 1 dm^3 of isopropanolic solution. The reaction is identical in a number of mineral acids (HCl, H_2SO_4, $HClO_4$, H_3PO_4) and in acetic acid. In concentrated acids the reaction is very slow or even does not take place at all, while dilution of the solution increases the rate of the reaction. Due to very low solubility of these compounds the concentration of 10^{-5} to 10^{-6} *M* can be obtained only in concentrated acid (above 4 *M*). In more diluted acids these compounds are insoluble. The maximum of absorption for the product of the photochemical reaction is the same in mineral acids and in acetic acid and it is equal to $\lambda = 680$ nm (Figs. 3 and 4).

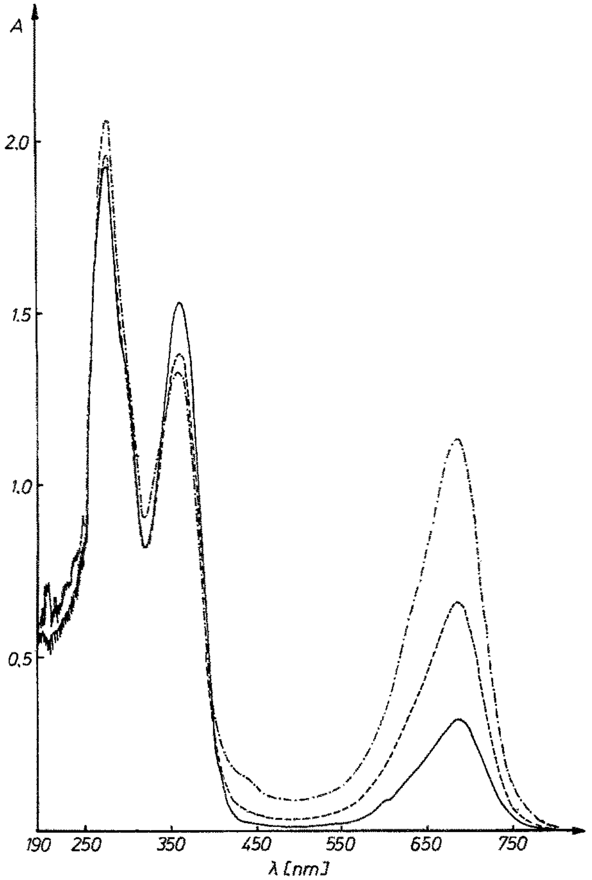


Fig. 3. Absorption spectra of N,N′-dihydrobiquinoxalyl in acetic acid. Product of photochemical reaction —·—·—; product of electrochemically reduction – – – – –; product of reduction by Sn(II) ———

Determination of the Reaction Quantum Yields

The quantum yield for the photochemical reaction of 2,2′-*BQx* and *TBQx* was determined in solution of isopropanol with an addition of HCl, for the concentration of 2,2′-*BQx* equal to $2.17 \cdot 10^{-5}$ *M* and that of *TBQx* to $1.94 \cdot 10^{-5}$ *M*. The measurements were performed on an optical bench and the solutions were irradiated in a spectrophotometric cell (1.0 cm thick). A mixtures of benzene solution of 0.1 *M* Q_2CO and of 0.1 *M* benzhydrol (1 : 1) has been used as actinometer.

The absorbance of the actinometer solution was measured at $\lambda = 345$ nm, for 2,2′-*BQx* at 345 nm, and for *TBQx* at 365 nm and 680 nm.

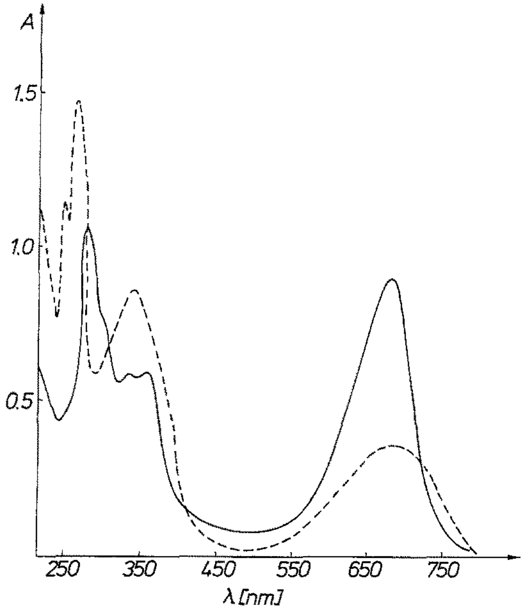


Fig. 4. Absorption spectra in perchloric acid. Product of photochemical reaction of 2,2′-*BQx* ———; product of photochemical reaction of *TBQx* — — — —

The quantum yield of the decay of the substrate and formation of the product was calculated from the following equation [17]:

$$\varnothing = \frac{\Delta c}{I_a} \tag{1}$$

$\varnothing$ is the quantum yield, Δc the difference of concentrations calculated from the $A_{\max}$ value, and I_a is the absorbed light.

$$I_a = I_0 \cdot t \frac{\Delta A}{\Delta A + \log \frac{1 - T_{(0)}}{1 - T_{(t)}}} \tag{2}$$

I_0 is the incidence light $\Delta A = A_{(0)} - A_{(t)}$, A_{345} is measured for *BQx*, A_{365} for *TBQx*, t is the time of irradiation, T the transmittance, I_0 is calculated for the actinometer according to [18].

$$I_0 = \frac{\Delta A_{345}}{\varepsilon \cdot l \cdot \varnothing \cdot t} \tag{3}$$

$\Delta A_{345} = A_{(0)} - A_{(t)}$; $\varepsilon_{345} = 130$; $l = 1.0$ cm, $\varnothing = 0.68$.

For the above conditions of the average values for the quantum yields are:

$I_0 = 3.05 \cdot 10^{-5}$ [Einstein $\mathrm{cm}^{-1}\,\mathrm{s}^{-1}$], $\varnothing_{2,2'\text{-}BQx} = 0.026$ and $\varnothing_{TBQx} = 0.023$.

The same magnitude of the quantum yield has been obtained for the reaction of substrate decay and product formation.

Fluorescence and Phosphorescence Spectra of 2,2′-BQx and TBQx and Quantum Yield of Fluorescence

The fluorescence spectra of 2,2′-*BQx* and *TBQx* were recorded in ethanolic solution at ambient temperature. A weak fluorescence observed was caused by a competition of photochemical reactions. Figures 5 and 6 show the fluorescence spectra of the above compounds—$\lambda_{\text{emission}} = 430\,\text{nm}$ for 2,2′-*BQx* and $\lambda_{\text{emission}} = 465\,\text{nm}$ for *TBQx*.

The fluorescence quantum yield ($\varnothing_f$) for 2,2′-*BQx* and *TBQx* has been determined. Quinine sulphate in 0.05 *M* sulphuric acid was used as a standard. The fluorescence spectra of the above solutions were recorded using an excitating light of 366 nm. The quantum yield of the standard was assumed to be 0.51 [19].

Applying the following expression:

$$\varnothing_f = \frac{I_f}{I_a} \tag{4}$$

and

$$\varnothing_f,\ \text{standard} = \frac{I_{f\,\text{standard}}}{I_{a\,\text{standard}}} \tag{5}$$

where $\varnothing_f$ is the quantum yield of fluorescence, I_f the intensity of fluorescence, and I_a the intensity of absorption, and applying the law of *Lambert-Beer*, $I_a = I_0\,(1 - 10^{-A})$, the following equation can be obtained for small absorbances:

$$\varnothing_f = \varnothing_{f\,\text{standard}} \cdot \frac{I_f}{I_{f\,\text{standard}}} \cdot \frac{A_{\text{standard}}}{A} \tag{6}$$

The fluorescence quantum yield determined for 2,2′-*BQx* is equal to $\varnothing_f = 0.006$, and for *TBQx* to $\varnothing_f = 0.008$.

The excited spectra of the compounds investigated have been also recorded and they were corrected with respect to rodamine B solution in ethylene glycol (Figs. 5, 6).

Phosphorescence spectra were records in glass (Fig. 7).

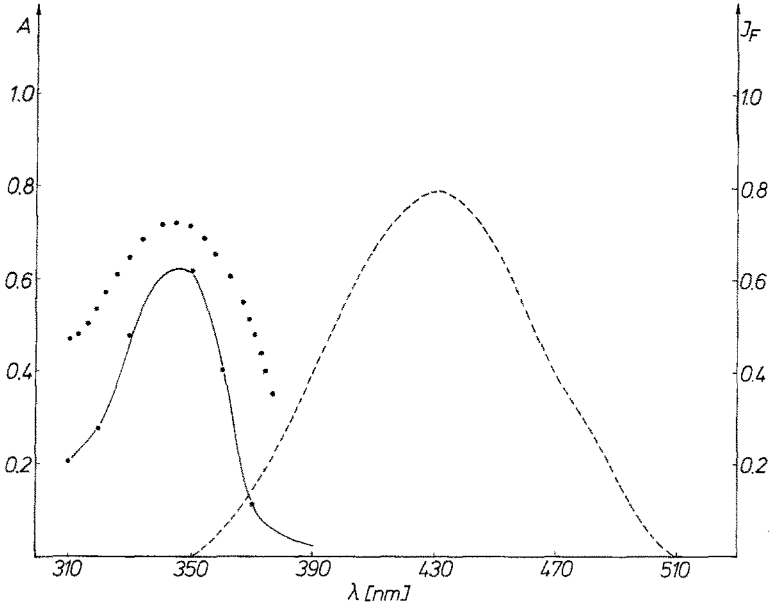


Fig. 5. Spectra of 2,2′-*BQx* in ethanol. ——— absorption; — — — — fluorescence, $\lambda_{exc} = 360$ nm; ····· fluorescence excitation, $\lambda_{obs} = 440$ nm

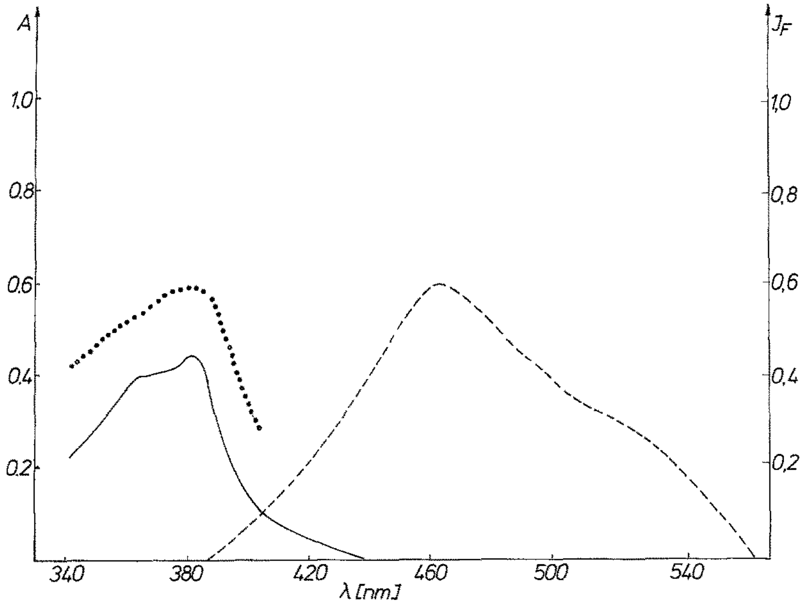


Fig. 6. Spectra of *TBQx* in ethanol. ——— absorption; — — — — fluorescence, $\lambda_{exc} = 380$ nm; ···· fluorescence excitation, $\lambda_{obs} = 470$ nm

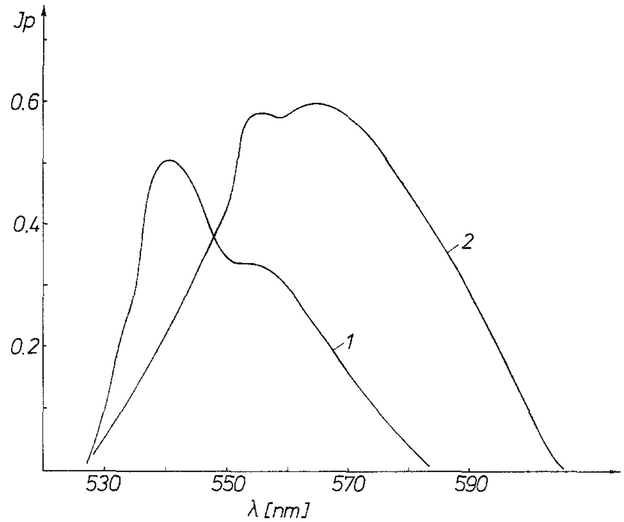


Fig. 7. Uncorrected phosphorescence spectra of 2,2'-*BQx* (*1*) and *TBQx* (*2*) in H_2SO_4 : *n*-propanol : ethanol (1 : 5 : 2) glass

Mechanism Proposed for the Photochemical Reaction of 2,2'-BQx and TBQx

The blue products of the photochemical reactions feature identical absorption spectra in the ultraviolet and the visible range as the products of reduction of 2,2'-*BQx* and *TBQx* using Sn(II) or Ti(III) and the products of electrochemical reductions. The products of the above reactions are also oxidized on air giving the original substrates. Therefore, the photochemical reactions investigated can be regarded as photoreduction processes. The products of photoreduction, reduction with strong reductors, and electrochemical reduction can be oxidized to original 2,2'-*BQx* and *TBQx* by such oxidizing ions as: Cr(VI), Sb(V), Au(III), Ru(IV).

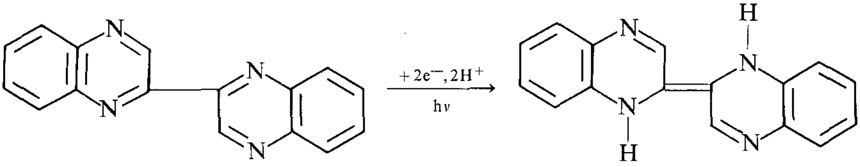
Moreover, it was found that the redox potential of 2,2'-*BQx* and its thieno derivative is the same for the products of electrode reduction and photochemical reaction. Therefore, a mechanism similar to that for the 2,2'-*BQx* reduction on a platinum electrode [7] can be proposed for the photoreduction of 2,2'-*BQx*:

It can be supposed that water is a donor of electrons in this reaction. In excited state the molecules of the above compounds are sufficiently strong oxidizers to remove the electrons from water molecules.

It was impossible to separate the products of the photochemical reactions because these substances were oxidized while removed from the solution and the original compounds were obtained again.

The mechanism proposed above will undergo further studies. Summing up, it can be stated that photochemical properties of the title compounds have been studied and unknown absorption spectra of the products of these reactions have been recorded, as well as their fluorescence and phosphorescence spectra.

The decolourating properties of the coloured reaction products can be utilized in chemical analysis to determine traces of oxidizing ions. Moreover, since the photochemical reactions of the compounds consisting of two heterocyclic rings are different than those for the monomer, i.e., quinoxaline, further investigations are required.



N,N-dihydrobiquinoxalyl

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