## Benzothiazole compounds XXXII. Photochemical isomerization of 3-substituted 2-styrylbenzothiazolium salts

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Photochemical *trans-cis* isomerization of 3-substituted 2-styrylbenzothiazolium salts has been studied. The composition of equilibrium mixture is dependent on the polarity of the solvent. Reverse thermal isomerization competes with the photochemical reaction. The structure of the cation affects the quantum yields only slightly.

Изучена фотохимическая *транс-цис* изомеризация солей 3-замещенного 2-стирилбензотиазолия. Состав равновесной смеси зависит от полярности растворителя. Обратная термическая изомеризация конкурирует с фотохимической реакцией. Структура катиона лишь в очень малой мере влияет на квантовый выход.

On the basis of the results obtained from the growth regulation tests of compounds of the general formula  $R_{het}$ —CH—CH—Ar, *Teitei* [1] had found that the biological activity of nonplanar *cis* isomers is markedly higher than the activity of the corresponding planar *trans* isomers. We wanted to verify this phenomenon with 3-substituted 2-styrylbenzothiazolium salts [2], by preparation of their *cis* isomers and testing these on the efficiency of growth of the root system of *Vicia sativa*.

The influence of the positive charge on the character of the ground and excited states had been studied on stilbazolium betaines [3-5], quaternary bipyridylethylene salts [6], and stilbazolium salts [7-10]. These investigations showed that the electron transfer from anion to cation competes with *cis-trans* photoisomerization. The extent to which these two processes compete depends not only on the solvent used but also on the electronic character of the substituents and the life-time of the corresponding excited state.

In the present investigation it was found that each of the absorption spectra of the *trans* isomers of 3-substituted 2-styrylbenzothiazolium salts exhibits relatively strong absorption band in the near UV region at  $\lambda_{max} = 380$  nm. The

## Table 1

UV spectral data of trans isomers and quantum yields (Q) of trans-cis photoisomerization of 3-substituted 2-styrylbenzothiazolium salts

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	R	<b>x</b> -	1		2		3		
Compound			$\frac{\lambda_{1, \max}}{nm}$	$\log \left( \varepsilon_{\rm l} / ({\rm m}^2  {\rm mol}^{-1}) \right)$	$\frac{\lambda_{2, \max}}{nm}$	$\log \left( \varepsilon_2 / (m^2 \operatorname{mol}^{-1}) \right)$	λ <sub>3, max</sub> nm	$\log \left( \varepsilon_3 / (m^2 \operatorname{mol}^{-1}) \right)$	Q
	CH <sub>3</sub>	I	367	3.48	372	3.28	372	3.61	0.43
II	CH <sub>2</sub> C=CH	Br	373	3.33	373	3.28	375	3.48	0.45
III	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	Br	377	3.29	378	3.31	378	3.55	0.48
IV	CH <sub>2</sub> COOCH <sub>3</sub>	Br	382	3.11	382	3.10	378	3.56	0.31
V	CH2COOC2H5	Br	378	3.30	378	3.27	378	3.57	0.39
VI	CH <sub>2</sub> COOCH=CH <sub>2</sub>	Br	378	3.34	378	3.32	380	3.45	0.39
VII	CH <sub>2</sub> COOC <sub>3</sub> H <sub>7</sub>	Br	382	3.33	382	3.30	378	3.52	0.33
VIII	CH2COOC3H2-i	Br	378	3.33	375	3.30	382	3.47	0.39
IX	CH <sub>2</sub> COOCH <sub>2</sub> CH=CH <sub>2</sub>	Br	378	3.32	378	3.30	378	3.46	0.41
X	CH <sub>2</sub> COOC <sub>7</sub> H <sub>15</sub>	Br	378	3.35	378	3.13	382	3.55	0.36
XI	CH2COOCH2C6H5	Br	382	3.28	382	3.26	375	3.36	0.35

1 — measured in H<sub>2</sub>O; 2, Q — measured in HBr ( $c = 0.2 \text{ mol dm}^{-3}$ ); 3 — measured in CH<sub>3</sub>CN.



position of this band is not very sensitive to the change of solvent, but its intensity grows with lowered polarity of the solvent (Table 1) or its solvation ability. This absorption band may be assigned to the singlet  $\pi \to \pi^*$  transition. This band also overlaps the electron transfer band, which can be observed in low polarity solvents as a shoulder at higher wavelengths, similar to pyridinium salts [9].

Absorption spectra of the *trans* isomer of 3-benzyl-2-styrylbenzothiazolium bromide (*III*) in aqueous solution before and after irradiation are shown in Fig. 1. Absorption maxima of the other compounds under observation are not significantly changed by a change of the substituent R.



Fig. 1. UV spectrum of 3-benzyl-2-styrylbenzothiazolium bromide (III).
1. Absorbance after thermal isomerization of equilibrium mixture 3; 2. absorbance of the *trans* isomer before

irradiation; 3. absorbance of equilibrium mixture of *cis* and *trans* isomers.

The absorption maxima of the photoproducts with lower values of the molar absorption coefficients than the *trans* isomers, are hypsochromically shifted with an isosbestic point at  $\lambda_{max} = 325$  nm. Equilibrium is attained after 10—30 min with an unchanged isosbestic point, which suggests that there are no side reactions competing with the photochemical isomerization of these salts.

The composition of equilibrium reaction mixture is strongly dependent on the polarity of the solvent or its solvation abilities. In the strongly polar solvent (distilled water acidified with HBr) conversion is about 70 %, in water 30 %, and in methanol approximately 15 %. In methanol, water, and some medium polarity solvents (chloroform, acetonitrile) we observed reversible thermal *cis-trans* isomerization. We assume, therefore, that the low *trans-cis* conversion in those solvents is due to the above-mentioned thermal reaction.

The half-life of this thermal *cis-trans* isomerization is approximately 10 min, which is comparable with the half-life of photochemical isomerization. A low ratio of *trans-cis* isomers may be a consequence of the relative reaction rates in either direction and is dependent on temperature. By increasing the temperature the rate of *cis-trans* isomerization grows, which ultimately leads to a lower *trans-cis* conversion. Differing rates of reverse thermal reaction (due to the polarity of the solvent) are probably caused by different degrees of dissociation of the salts in these solvents (Scheme 1).



Scheme 1

In strongly polar solvents the equilibrium, due to solvation, is shifted to the right and the salt exists mostly in a dissociated ionic form. In less polar solvents the salt is in the form of ion pairs and at concentrations lower than  $10^{-4}$  mol dm<sup>-3</sup> the equilibrium is shifted to the left. Interaction of the anion with the *trans* isomer of the cation is different from the interaction of the anion with the cis isomer of the cation. This difference is more pronounced in less polar solvents in which the salt exists in the form of ion pairs or associated ion pairs. The contribution of solvation energy in these solvents is not big enough to compensate for the energy changes which were caused by the change of interaction of the anion with the cation of the cis form. Therefore, the cis form of the cation possesses low stability and a low activation energy is enough to allow the reverse thermal reaction. In a strongly polar environment the ions are separated, their mutual interactions are minimal and the decrease of internal energy caused by solvation is such that at 25 °C there is no reverse reaction. For the reverse reaction the isosbestic point, which is identical with the point obtained from the photochemical isomerization, is retained strongly. When the thermal cis-trans isomerization equilibrium is achieved, the absorption is by approximately 20 % lower than the absorption of the starting compound at the time t = 0. This surprising discovery can be explained by the fact that the starting "trans" isomer is a mixture of trans and cis isomers (which however was not determined by IR or NMR spectroscopy) and several possible conformers.

The measured quantum yields (Q) of the photochemical *trans-cis* isomerization are almost independent of the substituent R (Table 1).

Due to the above problems, we were not able to isolate *cis* isomers of 3-substituted 2-styrylbenzothiazolium salts, and therefore it was impossible to determine their growth-regulation activity.

## Experimental

Methods for the preparation and identification of 3-substituted 2-styrylbenzothiazolium salts are given in the previous paper [2]. Quantum yields for the photochemical isomerization were measured using the apparatus described previously [11]. Solutions of salts ( $c = 10^{-4} \text{ mol dm}^{-3}$ ) in distilled water acidified by HBr ( $c = 2 \times 10^{-2} \text{ mol dm}^{-3}$ ) were irradiated with monochromatic light of wavelength 336 nm (isolated from polychromatic light of high-pressure mercury lamp HBO 50 with an interference filter). The decrease in the concentration of the *trans* isomer was monitored spectrophotometrically on a Perkin—Elmer 450 instrument.

Actinometric method (for determination of the hv amount) employed potassium ferrioxalate [12].

Quantum yields were calculated under conditions when the concentration of the *cis* isomer in the reaction mixture was close to zero. Reaction mixture was maintained at  $25 \,^{\circ}$ C.

## References

- 1. Teitei, T., Agr. Biol. Chem. 45, 1669 (1981).
- Chabreček, P., Sutoris, V., Foltínová, P., Sekerka, V., and Gáplovský, A., Chem. Papers 41, 655 (1987).
- 3. Ikada, N., Mataga, N., Steiner, U., and Abdel-Kader, M. H., Chem. Phys. Lett. 95, 66 (1983).
- 4. Steiner, U., Abdel-Kader, M. H., Fischer, P., and Kramer, H. E. A., J. Amer. Chem. Soc. 100, 3190 (1978).
- 5. Al-Hassan, K. A. and El-Bayoumi, M. A., Chem. Phys. Lett. 76, 121 (1980).
- 6. Gutierrez, A. R. and Whitten, A. R., J. Amer. Chem. Soc. 98, 6233 (1976).
- 7. Görner, H. and Schulte-Frohlinde, D., Chem. Phys. Lett. 101, 79 (1983).
- 8. Görner, H. and Schulte-Frohlinde, D., J. Phys. Chem. 89, 4105 (1985).
- 9. Güsten, H. and Schulte-Frohlinde, D., Tetrahedron Lett. 1970, 3567.
- 10. Briegleb, G., Jung, W., and Herre, W., Z. Phys. Chem. 38, 253 (1963).
- 11. Gáplovský, A., Donovalová, J., Toma, Š., and Hrnčiar, P., Chem. Listy 80, 989 (1986).
- 12. Hatchard, C. G. and Parker, C. A., Proc. Roy. Soc. (London) A253, 518 (1956).

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