

# STEREOSPECIFIC CROSS-[2+2]-PHOTOCYCLOADDITION OF COMPLEXES OF CROWN-CONTAINING AND AMMONIOALKYL DERIVATES OF STYRYL DYES



РОССИЙСКАЯ АКАДЕМИЯ НАУК  
ЦЕНТР ФОТОХИМИИ

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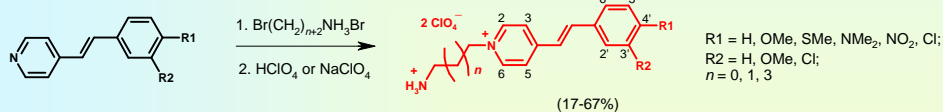


**INTRODUCTION:** Development of promising methods for self-assembly of organic molecules via various non-covalent interactions is the subject of numerous studies in the supramolecular chemistry. The self-assembly of photoactive compounds to supramolecular assemblies can considerably affect their photophysical and photochemical properties. Interaction of the photoactive sites located at short distances often gives rise to new useful properties of molecular assemblies not inherent in single molecules.

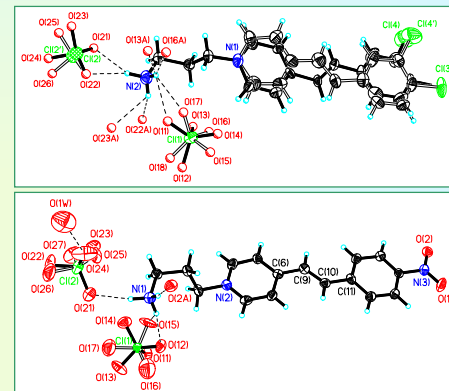
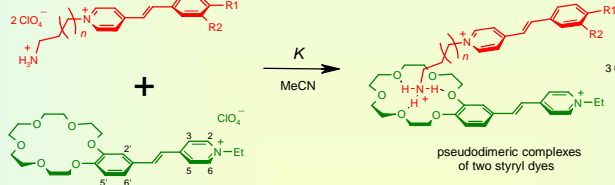
Benzo-18-crown-6 ether and its derivatives efficiently bind primary ammonium ions via hydrogen bonding. This feature underlies the supramolecular self-assembly of some

photoactive compounds in which the benzo-18-crown-6 ether moiety is a part of the conjugated system. The C=C double bond contained in the chromophores of 18-crown-6-substituted unsaturated compounds can be involved in photoinduced *E-Z* isomerization and [2 + 2] cycloaddition reactions. There are only few examples of using photoactive 18-crown-6-substituted unsaturated compounds in self-assembly involving the  $\text{RNH}_3^+$  ions. We suggested that two styryl dyes can be held together by interaction between the ammonioalkyl group and the crown ether moiety. Such pseudomeric complexes might be considered as promising objects for stereospecific cross-[2 + 2] photocycloaddition.

**1** A series of new 4-pyridine-derived styryl dyes containing an *N*-ammonioalkyl substituent was prepared by quaternization of respective neutral 4-styrylpyridines with  $\omega$ -bromoalkylamine hydrobromides and subsequent anion exchange for perchlorate:

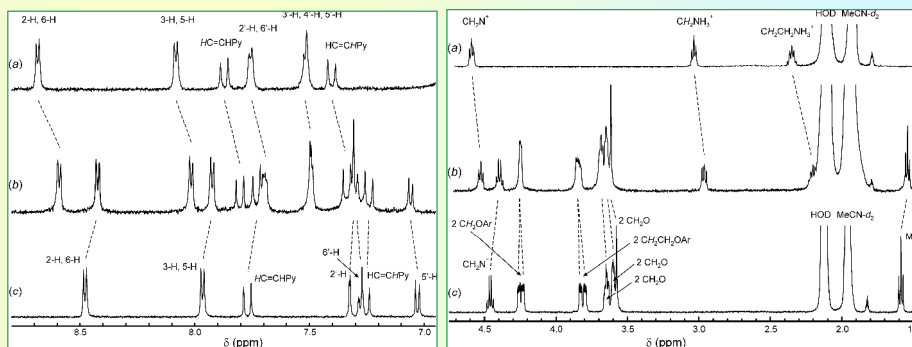


**2** We found that two different 4-pyridine-derived styryl dyes, one having an ammonioalkyl substituent and the other having a 18-crown-6 ether moiety, can be held together by interaction between the ammonioalkyl group and the crown ether moiety, thus forming a pseudomeric complex. Stacking interaction of the conjugated parts facilitates the complex formation.



X-ray structure determination of styryl dyes.

**3** The formation of pseudodimeric complexes is clearly seen from comparison of the <sup>1</sup>H NMR spectra of free components and equimolar mixtures. For example, in a solution in MeCN-*d*<sub>3</sub>, the signals of ethylene and most aromatic protons of mixed ammonioalkyl dye (R1 = R2 = H) and crown-containing dye are shifted upfield to  $\Delta\delta_{\text{H}} = -0.09$  ppm relative to free dyes. The signals for crown ether CH<sub>2</sub>O groups shift downfield by up to  $\Delta\delta_{\text{H}} = 0.07$  ppm upon mixing, which confirms hydrogen bonding of the ammonium group with the crown ether. Meanwhile, the signals of both *N*-substituents shift upfield on mixing by up to  $\Delta\delta_{\text{H}} = -0.15$  ppm. The observed upfield shift for mixed dyes can be attributed only to the preferred arrangement of the planar conjugated moieties of the dyes approximately one above the other in pseudodimeric complex and, hence, to substantial anisotropic effects in this complex. Thus, the complexes have "head-to-tail" arrangement of the chromophores.



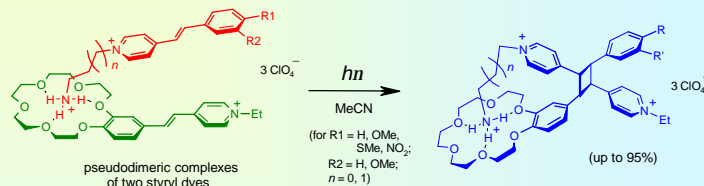
<sup>1</sup>H NMR spectra of ammonioalkyl styryl dye (R1 = R2 = H, C = 1.10<sup>-3</sup> M) (a), 18-crown-6-containing styryl dye (C = 1.10<sup>-3</sup> M) (c), and their 1:1 mixture (b) in MeCN-*d*<sub>3</sub>.

**4** Quantitative determination of the stability of complexes was performed by <sup>1</sup>H NMR titration in MeCN-*d*<sub>3</sub> and by spectrophotometric titration in MeCN (0.01 M Bu<sub>4</sub>NClO<sub>4</sub>).

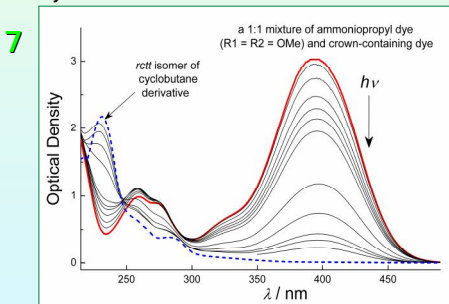
R1, R2, n	lg K	
	<sup>1</sup> H NMR titration	Spectrophotometric titration
MeO, MeO, 3	3.5	
MeO, MeO, 2	3.5	
Me <sub>2</sub> N, H, 3	3.4	3.89
Cl, Cl, 3	3.4	4.07
MeO, H, 3	3.3	4.10
MeS, H, 3	3.3	3.86
NO <sub>2</sub> , H, 3	3.3	
MeO, MeO, 5	3.3	
H, H, 3	3.1	3.99

**6** Visible light irradiation of solutions of free ammonioalkyl dyes in MeCN results in relatively fast decrease in long-wavelength absorption (LWA) intensity (down to 33–96% of the initial value), which is caused by *E-Z* isomerization of the dyes.

Visible light irradiation of solutions of equimolar mixtures of ammonioalkyl dyes with crown-containing dye results in a more pronounced decrease in the LWA intensity. The disappearance of absorption in the region of > 330 nm is caused by disruption of the conjugated system in the chromophores of both pseudodimer components as a result of cross-[2+2] photocycloaddition (PCA) to give asymmetrical 1,2,3,4-tetrasubstituted cyclobutanes.



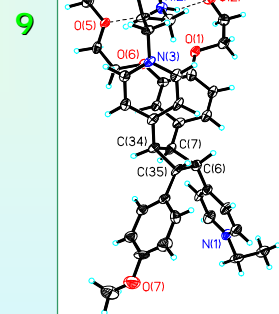
*rctt* isomers of cyclobutane derivative



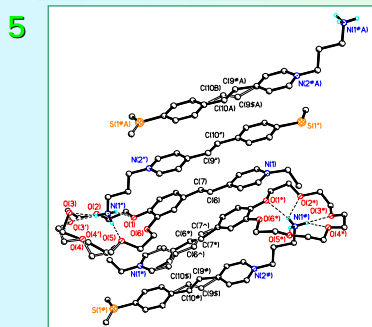
Photolysis of solution of an equimolar mixture of two dyes (MeCN, C = 5 × 10<sup>-4</sup> M, 0.1-cm quartz cell). The blue dash curve is the spectrum of corresponding cyclobutane (MeCN, C = 5 × 10<sup>-4</sup> M, 0.1-cm quartz cell).

**8** Quantum yield of cross-[2+2] photocycloaddition of pseudodimeric complexes in MeCN:

R1, R2, n	φ [2+2]-PCA
MeS, H, 3	0.016
MeO, H, 3	0.014
NO <sub>2</sub> , H, 3	0.014
H, H, 3	0.0052
Cl, Cl, 3	0.0018



X-ray structure determination of cyclobutane derivative.



X-ray structure determination of pseudodimeric complex.

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