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Stereo- and regioselective [2+2] photocycloaddition in a bis(styrylquinoline) dyad

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The dyad connecting two styrylquinoline chromophores by an *o*-xylylene bridge undergoes [2+2] photocycloaddition with quantitative formation of a single *rctt* cyclobutane derivative.

The [2+2] photocycloaddition (PCA) between two diarylethylenes leading to cyclobutanes attracts attention of investigators.[1–6] In contrast to other photochemical reactions of diarylethylenes such as photoisomerization (PI) and intramolecular photocyclization in dilute solutions ($< 10^{-5}$ M), the (intermolecular) PCA can take place only in (pre)organized supramolecular systems. Depending on the diarylethylene structure, pre-organization (or pre-orientation) can be achieved by coordination with metal or ammonium cations, as in the case of the crown containing styryl dyes,[1–4] or by means of cation-controlled π-stacking, as in the case of the protonated aza derivatives of stilbene.[5,6]

Pre-organization can also be achieved by covalent linking of two components.[7] In this case, the properties of supramolecular system should depend on the structure of a covalent bridge. For example, bichromophoric dyad with two styrylquinoline (SQ) fragments connected by a trimethylene bridge underwent only *E–Z* PI while no PCA was observed.[8] We supposed that connection of the SQ fragments by an *o*-xylylene bridge could promote photodimerization.

Here, we present a synthesis and some photochemical properties of a new dyad **1** with the SQ photochromic groups. Dyad **1** was synthesized in a moderate yield by alkylation of (*E*)-2-[2-(4-hydroxyphenyl)vinyl]quinoline with 1,2-bis(bromomethyl)benzene.† According to the values of the vicinal spin–spin coupling constants found for the olefinic protons ($^3J_{trans}$ 16.2 Hz), dyad **1** has (*E*,*E*)-configuration.

The absorption spectrum of the bichromophoric dyad (*E*,*E*)-**1** is double that of the model monochromophoric (*E*)-2-(4-methoxystyryl)quinoline (MeSQ), the long-wavelength absorption band (LWAB) has a maximum at 356 nm (in ethanol) and a molar absorption coefficient ε is 62 100 dm^3 mol^{-1} cm^{-1} (Figure 1, spectrum *1*).

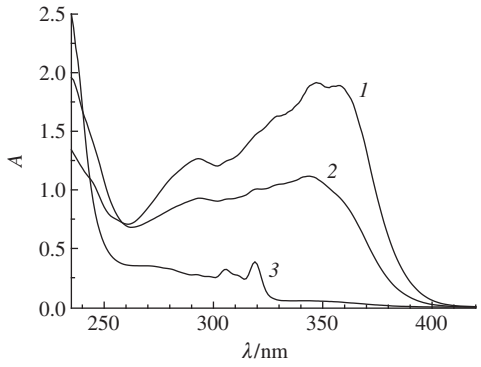
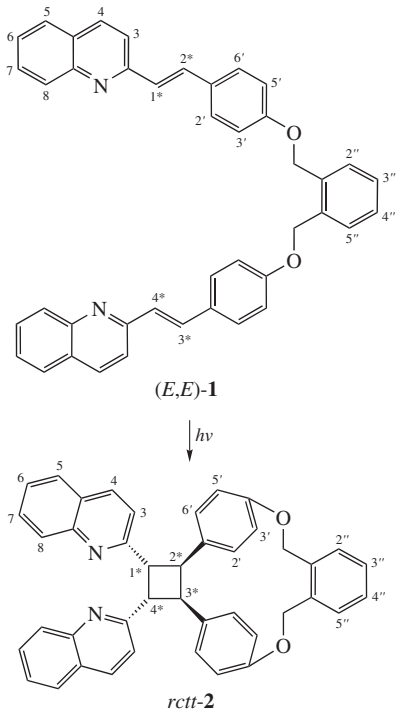


Figure 1 Spectral variations during irradiation of an air-saturated solution of (*E*,*E*)-**1** (2.9×10^{-5} mol dm^{-3}) in ethanol with light at 365 nm, intensity 5×10^{-9} Einstein cm^{-2} s^{-1}, irradiation time: (*1*) 0, (*2*) 30 s, (*3*) 5 h.

Irradiation of a solution of (*E*,*E*)-**1** with 365 nm light caused a fast reaction with spectral changes that corresponded to those observed under irradiation of the model MeSQ and thus were attributed to *E–Z* PI (Figure 1, spectrum *2*). PI, as a reversible reaction, should result in a photostationary state with definite ratio of *E* and *Z* isomers. However, spectrum *2* proved to belong not to a real but quasi-photostationary state; subsequent prolonged irradiation resulted in a gradual decrease and, finally, the absolute disappearance of the LWAB and appearance of a structured blue-shifted absorption band with maxima at 306 and 319 nm (spectrum *3*). These spectral changes had no analogy in the photochemistry of MeSQ. Comparison with the spectrum of quinaldine testified that spectrum *3* (Figure 1) was characteristic of the separate (without π-conjugation) quinoline rather than the styrylquinoline moieties. In the emission spectra we observed a blue-shift and decrease in luminescence intensity; these changes were also consistent with the appearance of the non-conjugated quinoline nucleus.

According to ESI mass spectrum, the reaction product had the same *m/z* value as the starting dyad **1** (597, MH$^+$). The IR spectrum had a broad intense peak at 1055 cm^{-1} in the range characteristic of ring deformations of substituted cyclobutanes.[10] Theoretically, PCA of dyad **1** can result in several possible cyclobutane regioisomers. However, analysis of the ^{1}H NMR spectrum, two-dimensional (2D) NOESY ^{1}H NMR (Figure S1) and ^{13}C NMR spectra of an evaporated reaction mixture showed that residue consisted of a single compound. The structure was assigned to *rctt*-**2**‡ (Scheme 1).

† *(*E,E*)-1,2-Bis{4-[2-(quinolin-2-yl)vinyl]phenoxymethyl}benzene* **1**. A mixture of (*E*)-2-[2-(4-hydroxyphenyl)vinyl]quinoline[9] (2 mmol) and K_2CO_3 (10 mmol) in 20 ml of 2-butanone was refluxed for 30 min. Then, 1,2-bis(bromomethyl)benzene (1 mmol) (Aldrich) was added and the mixture was refluxed for 5 h. After cooling, 20 ml of water was added followed by 50 ml of $CHCl_3$, and the organic layer was separated and dried with $MgSO_4$. The solvent was removed on a rotary evaporator. The residue was recrystallized first from ethanol, then from heptane to afford white crystals of product **1** (0.40 g, 67%), mp 133–134 °C (heptane). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 5.23 (s, 4H, CH_2), 6.99 [d, 4H, 2H(3′), 2H(5′), *J* 8.7 Hz], 7.26 [d, 2H, H(1*), H(2*), *J* 16.2 Hz], 7.39 [dd, 2H, H(2″), H(5″), *J* 3.4 Hz, *J* 5.6 Hz], 7.46 [ddd, 2H, H(6), *J* 1.0 Hz, *J* 6.8 Hz, *J* 7.9 Hz], 7.53 [dd, 2H, H(3″), H(4″), *J* 3.4 Hz, *J* 5.6 Hz], 7.55 [d, 4H, 2H(2′), 2H(6′), *J* 8.7 Hz], 7.59–7.64 [m, 4H, 2H(3), H(3*), H(4*)], 7.68 [ddd, 2H, H(7), *J* 1.5 Hz, *J* 7.0 Hz, *J* 8.4 Hz], 7.73 [d, 2H, H(5), *J* 8.0 Hz], 8.04 [dd, 4H, 2H(8), 2H(4), *J* 3.4 Hz, *J* 8.4 Hz]. IR (ν/cm^{-1}): 3041, 2979, 2884 (ν, CH_2), 1636 (ν, C=C), 967 (δ, –CH=CH). Found (%): C, 84.32; H, 5.22; N, 4.57. Calc. for $C_{42}H_{32}N_2O_2$ (%): C, 84.54; H, 5.41; N, 4.69.



Scheme 1

The ^{1}H NMR spectrum of the cyclobutane protons in *rctt*-**2** (Figure 2) is described by a symmetrical four-spin system of an AA′BB′ type with the typical 'roof effect' because of small relative chemical shifts between nuclei of A and B.[11] The following set

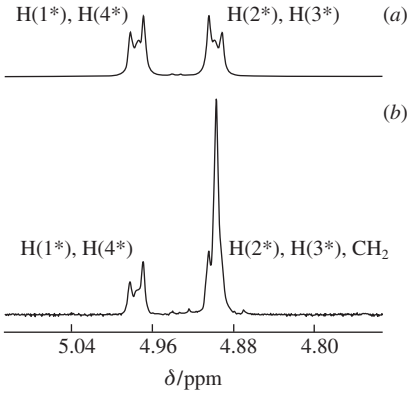


Figure 2 (*a*) Simulated AA′BB′ and (*b*) experimental ^{1}H NMR spectra in $CDCl_3$ of the cyclobutane protons of *rctt*-**2**.

‡ *3,4-Di(quinolin-2-yl)-10,19-dioxapentacyclo[16.2.2.2^{6,9}.0^{12,17}.0^{2,5}]-hexacosa-1(22),6,8,12,14,16,20,23,25-nonaene* **2**. A solution of compound (*E*,*E*)-**1** (2 mg, 3.4 μmol) in ethanol (50 ml, quartz flask) was irradiated for 22 h with a high-pressure Hg lamp (line 365 nm, intensity 5×10^{-9} Einstein cm^{-2} s^{-1}) and then evaporated *in vacuo*. According to ^{1}H NMR data, the residue consisted completely of photoadduct *rctt*-**2**. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.86–4.91 [m, 6H, 2CH$_2$, H(2*), H(3*), $J_{2*,3*}$ 8.5 Hz, $J_{1*,2*} = J_{3*,4*}$ = 6.4 Hz, $J_{1*,3*} = J_{2*,4*}$ = –0.4 Hz], 4.94–4.98 [m, 2H, H(1*), H(4*), $J_{1*,4*}$ 8.6 Hz, $J_{1*,2*} = J_{3*,4*}$ = 6.4 Hz, $J_{1*,3*} = J_{2*,4*}$ = = –0.4 Hz], 6.47 [dd, 2H, H(3′), *J* 2.5 Hz, *J* 8.3 Hz], 6.56 [dd, 2H, H(5′), *J* 2.5 Hz, *J* 8.4 Hz], 6.69 [dd, 2H, H(2′), *J* 2.3 Hz, *J* 8.3 Hz], 7.03 [dd, 2H, H(6′), *J* 2.3 Hz, *J* 8.4 Hz], 7.15 [d, 2H, H(3), *J* 8.5 Hz], 7.37 [ddd, 2H, H(6), *J* 0.9 Hz, *J* 6.9 Hz, *J* 8.0 Hz], 7.41 [dd, 2H, H(3″), H(4″), *J* 3.5 Hz, *J* 5.9 Hz], 7.55–7.61 [m, 4H, 2H(5), 2H(7)], 7.68 [d, 2H, H(8), *J* 8.7 Hz], 7.76 [dd, 2H, H(2″), H(5″), *J* 3.5 Hz, *J* 5.7 Hz], 7.97 [d, 2H, H(4), *J* 8.4 Hz]. ^{13}C NMR (CD_3CN, 126 MHz) δ: 47.0, 47.3, 72.2, 121.4, 121.6, 122.8, 126.5, 127.3, 128.0, 128.3, 128.4, 129.3, 129.9, 130.5, 132.1, 136.0, 136.7, 137.1, 148.2, 158.7, 162.1. IR (ν/cm^{-1}): 2922, 2854 (ν, CH$_2$), 1602, 1508, 1055 (C–C), 817, 753, 697.

of the spin–spin coupling constants fits best to the experimental spectrum: $^3J_{H(1*),H(4*)}$ 8.6 Hz, $^3J_{H(2*),H(3*)}$ 8.5 Hz, $^3J_{H(1*),H(2*)}$ = = $^3J_{H(3*),H(4*)}$ = 6.4 Hz, $^4J_{H(1*),H(3*)}$ = $^4J_{H(2*),H(4*)}$ = –0.4 Hz ($CDCl_3$). The approximate values of these constants were calculated first using formulas for the direct analysis of the AA′BB′-system[11] of the cyclobutane protons in the experimental ^{1}H NMR spectrum of *rctt*-**2**, and then were refined using the CALM iterative program.[2] Because of the spectral overlap for H(2*), H(3*) with CH$_2$-protons, only a part of AA′BB′-system in the range of 4.90–5.00 ppm was analyzed. The resulting set of vicinal constants agrees with the values obtained previously[1] for cyclobutane protons of crown-containing 1,2,3,4-tetrasubstituted cyclobutane with an arrangement of substituents similar to that in *rctt*-**2**.

Comparison of the ^{1}H NMR spectra of the starting dyad **1** and cyclobutane **2** (Figure 3) testifies that the linking of two SQ fragments in **2** results in distinctive shifts of the signals of three aromatic subsystems: quinoline nucleus, benzene rings of the styryl groups and benzene ring of the xylylene group. According to DFT calculations (B3LYP/6-31G*, the Gaussian 03 program package),[12] **2** has a cagelike cyclophane structure (Figure S2) where two benzene rings from the former styryl groups are located over and almost perpendicularly to the benzene ring of the xylylene group. This results in shielding and, respectively, upfield shifts of the H(2′)–H(6′) protons, especially for the H(2′) (–0.86 ppm) and H(3′) (–0.52 ppm) protons. On the contrary, the aromatic protons of the xylylene group [H(2″), H(5″)] are deshielded and undergo downfield shifts by 0.37 ppm. The H(3) and H(8) quinolinic protons are shielded by the neighboring quinoline nucleus (upfield shifts are –0.46 and –0.36 ppm, respectively).

Thus, linking of two SQ groups by an *o*-xylylene bridge in the dyad **1** promotes stereospecific PCA with formation of a single cyclobutane isomer. PCA occurs exclusively head-to-head between two E-SQ residues. Generally, PCA is reversible reaction. However, cyclobutane **2** has no absorption bands in the region $\lambda > 330$ nm, therefore, under irradiation with UV light at 365 nm, the PCA is irreversible and dyad **1** converts completely to the final product.

We can compare the pre-organizing action of different molecular bridges (or spacers) – trimethylene, *o*-, *m*- and *p*-xylylene – on the [2+2] photocycloaddition. The trimethylene bridge is the most flexible one and does not promote PCA. The bis-(styrylquinoline) dyad[8] with this bridge underwent only photoisomerization, as well as crown-containing bis(styrylbenzothiazole) dyad.[1] Nevertheless, the latter did form isomeric cyclobutanes upon irradiation of sandwich complexes with Ca^{2+} and Ba^{2+} cations (so called 'molecular pincers'). The photochemistry of

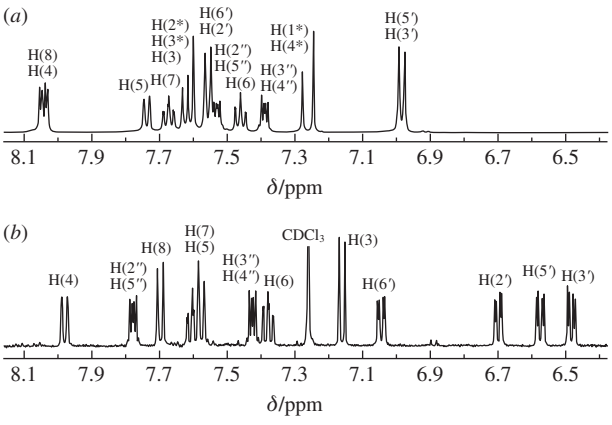


Figure 3 ^{1}H NMR spectra of (*a*) (*E*,*E*)-**1** and (*b*) *rctt*-**2** (aromatic region, $CDCl_3$, 23 °C).

the dyad with crown-containing styryl dyes connected by a *p*-xylylene bridge was limited to PI because intramolecular PCA was impossible for steric reasons, whereas the analogous dyad with a *m*-xylylene bridge underwent PI in free form but PCA in a pseudocyclic complex with the 1,3-diammoniumpropane dication.[2] Only in the dyad **1** with *o*-xylylene bridge PCA takes place without addition of special reagents that pulls together the two photoactive fragments forming a pseudocyclic structure.

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Online Supplementary Materials

Supplementary data associated with this article (the two-dimensional NOESY NMR spectrum of *rctt*-**2**, structure of *rctt*-**2** optimized at B3LYP/6-31G* level) can be found in the online version at doi:10.1016/j.mencom.2015.03.008.

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