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Regio- and stereoselective [2+2] photocycloaddition in Ba²⁺ templated supramolecular dimers of styryl-derivatized aza-heterocycles

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A B S T R A C T

The regio and stereoselective [2+2] photocycloaddition of 15 crown 5 containing styrylheterocycles resulting in formation of only one cyclobutane isomer out of eleven possible is described. It was shown that the cycloaddition takes place solely in the case of the supramolecular preorganization of the reactive molecules provided by both π π stacking interaction of the heterocyclic fragments and sandwich type coordination of the crown ether residues by the barium cation. The results point out the importance of the supramolecular approach for the synthesis of cyclobutane derivatives with desired structure and conformation.

1. Introduction

Organic compounds comprising a cyclobutane motif represent an important class of natural metabolites that have been found in various terrestrial and marine species [1,2]. The majority of naturally occurring cyclobutane derivatives demonstrates remarkable biological activity making them promising lead structures for the creation of novel anticancer, antibacterial and fungicidal drugs [2]. Besides that, cyclobutanes are important synthetic intermediates providing atom economic one step transitions from simple to complex structures that is especially important in the total synthesis of natural products and other intricate molecules [3].

High practical importance of cyclobutane derivatives stimulated the development of synthetic approaches to these compounds. The most commonly applied method of the cyclobutane scaffold construction is photochemical [2+2] cycloaddition of two ethylene double bonds that may occur in the inter or intramolecular way

[3c,4]. Nevertheless, a straightforward application of the photoinduced [2+2] cycloaddition in the synthesis of complex biologically related molecules is hindered in many cases by its low regio and stereoselectivity. To manage this problem, three main methodologies allowing performance of [2+2] cycloaddition reactions in a regio and stereoselective manner have been applied. The classic methodology is based on the attachment of appropriate substituents managing the preferred direction of the photochemical cycloaddition by steric and electronic effects [5]. In some cases, stereoselectivity of the photocycloaddition can be reached through chiral induction provided by introduction of chiral auxiliaries [5]. The second methodology relates to an emerging class of catalytic [2+2] cycloadditions that have been extensively developing within the last decade [6]. This group of reactions includes both photochemical and non photochemical transformations that are assisted by various catalysts, such as Lewis acids, amines or transition metal complexes, and lead to formation of enantiomerically enriched cyclobutanes. The third methodology is based on the supramolecular preorganization of substrate molecules that provides fixation of the reactive bonds in the desired mutual position prior to the cyclization process. In this field, several reports are devoted to the solid state template directed synthesis of cyclobutanes managed

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by confinement of the substrates in metal organic frameworks and hydrogen bond templates [7], zeolites [8], nanocages [9]. There are a few examples of the reversible single crystal to single crystal cyclobutane ring formation upon irradiation of stilbenoids in their crystal state [10]. In solution, supramolecular catalysis has been applied for complexes of macrocyclic hosts with photoactive guests that undergo stereospecific [2+2] photocycloaddition directly inside the host cavity [11]. Another type of supramolecular preorganization for [2+2] photocycloaddition was realized by self assembly of the substrates in solution assisted by the metal cation coordination, hydrogen bonding, π - π stacking interaction and partial covalent linking. The examples of the latter approach, however, are still rather rare [12–20].

Herein, we present simple yet efficient variation of the latter method resulting in the regio- and stereoselective light induced formation of cyclobutane derivatives in the series of crown containing styrylheterocycles **1a–4a** (Chart 1). The key process providing the closure of a cyclobutane ring is an intermolecular [2+2] photocycloaddition of the ethylene double bonds taking place upon irradiation of the supramolecular dimers of **1a–4a** (Chart 1). Noticeably, the photoreaction yields only one of eleven possible isomers of the cyclobutane product. Formation of the head to head dimeric complexes of **1a–4a** is driven by a delicate balance between the π - π stacking interaction of the heterocyclic fragments and the sandwich type coordination of Ba^{2+} cations by two 15 crown 5 ether residues. To estimate the role of the stacking interaction we varied the heterocyclic residue increasing the surface area from pyridine to phenanthroline. The effect of the sandwich type coordination with barium cations on the formation of dimers was studied by comparison with magnesium cations, whose size fits well to the 15 crown 5 ether cavity excluding the possibility of “sandwich” formation. Metal cation complexation, supramolecular dimerization and photocycloaddition reaction of compounds **1a–4a** were investigated by absorption spectroscopy, steady state and time resolved fluorescence spectroscopy as well as 1D and 2D NMR techniques.

2. Results and discussion

2.1. Steady state optical spectroscopy studies

Absorption spectra of styryl derivatives **1a–4a** exhibit intense long wavelength absorption bands at the spectral region of 300–400 nm (Fig. 1; Table 1; Figures S1–S7, ESI) that are associated with an intramolecular charge transfer from the electron rich

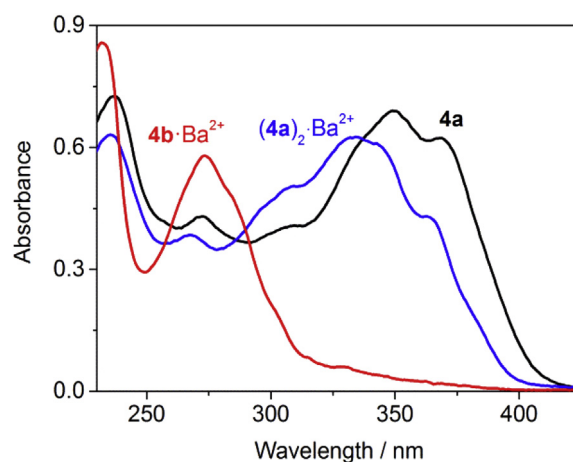


Fig. 1. Absorption spectra of **4a**, its sandwich complex $(4a)_2 \text{Ba}^{2+}$ and photocycloaddition product **4b** Ba^{2+} (c_{4a} 20 μM , λ 365 nm, irradiation time 30 min) in MeCN at 20 °C.

Table 1

Absorption maxima λ^{abs} , fluorescence lifetimes τ_{fl} and stability constants $\log K$ of **1a–4a** and their complexes with Mg^{2+} and Ba^{2+} in MeCN at 20 °C.

Compound	$\lambda^{\text{abs}}/\text{nm}$	$\tau_{\text{fl}}/\text{ps}$	$\log K$
1a	331	49	
1a · Mg^{2+}	317	17	5.98 \pm 0.01
$(1a)_2 \text{Ba}^{2+}$	319	24	10.62 \pm 0.04
2a	353	43, 100	
2a · Mg^{2+}	334	30, 150	5.89 \pm 0.07
$(2a)_2 \text{Ba}^{2+}$	341	20, 45, 1000	11.45 \pm 0.21
3a	358	345	
3a · Mg^{2+}	345	103, 500	5.56 \pm 0.06
$(3a)_2 \text{Ba}^{2+}$	342	170, 580, 2200	10.08 \pm 0.14
4a	348	160	
4a · Mg^{2+}	339	116, 580	5.06 \pm 0.04
$(4a)_2 \text{Ba}^{2+}$	332	220, 3600	11.75 \pm 0.02

crown residues to the electron poor heterocyclic fragments. The absorption maxima of compounds **1a–4a** shift to longer wavelength with increasing electron withdrawing effect of the heterocyclic part in the series **1a** < **4a** < **2a** < **3a**. Addition of $\text{Ba}(\text{ClO}_4)_2$ or $\text{Mg}(\text{ClO}_4)_2$ to the acetonitrile solutions of **1a–4a** results in the blue shift of the absorption bands due to binding of Ba^{2+} and Mg^{2+} cations by crown ether oxygen atoms involved in the chromophoric system of the ligands (Fig. 1; Table 1; Figs. S3–S7, ESI). In the case of

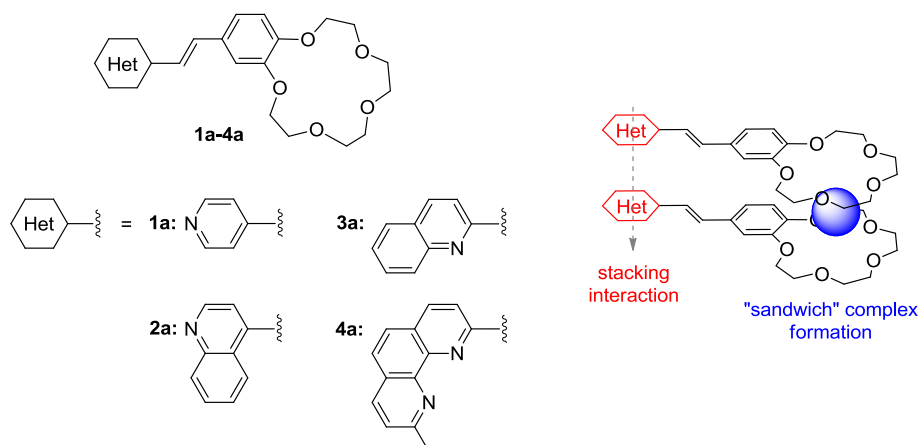


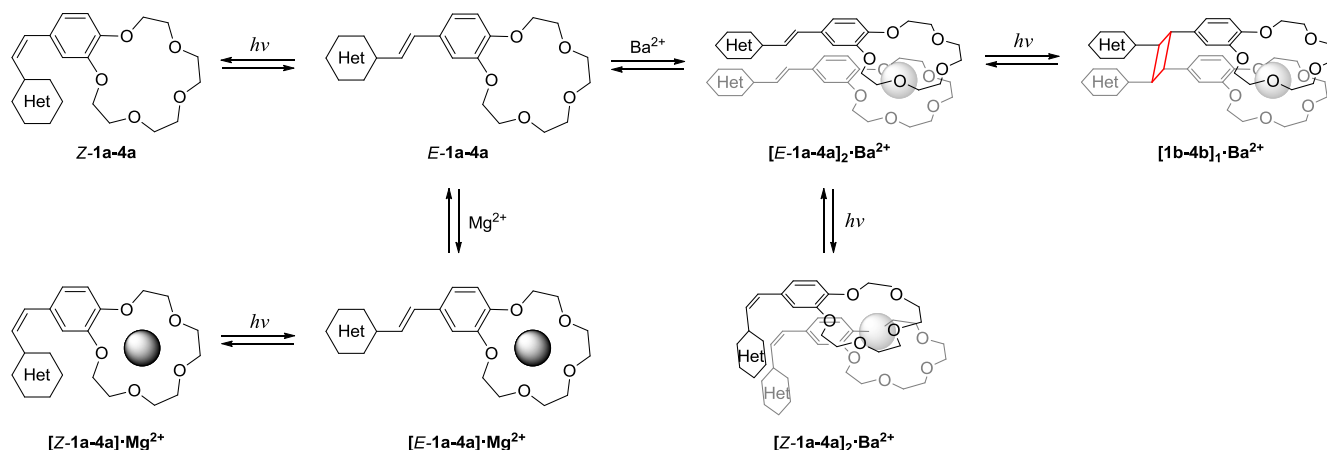
Chart 1. Chemical structures of **1a–4a** and schematic representation of their supramolecular dimerization in the presence of Ba^{2+} .

Mg²⁺, the inclusion complexes of 1:1 stoichiometry (metal/ligand) are formed due to the fine coincidence of the sizes of 15 crown 5 ether and magnesium cation [21,22]. At the same time, the cavity of 15 crown 5 ether is too small for binding of the barium cation.

Therefore, in the presence of Ba²⁺ formation of sandwich type complexes of 1:2 stoichiometry (metal/ligand) is expected (Chart 1) [21,22]. Spectrophotometric titrations of **1a–4a** with Ba(ClO₄)₂ and Mg(ClO₄)₂ in acetonitrile and following treatment of the obtained data confirmed the expected stoichiometries and allowed to determine stability constants of the complexes (Table 1).

Irradiation of the acetonitrile solutions of styryl derivatives **1a–4a** with filtered light (λ 365 nm) resulted in the decrease of the absorption intensities along with a slight blue shift of the absorption maxima that is indicative of the formation of the photo stationary mixtures of *E* and *Z* isomers of **1a–4a** (Scheme 1; Figs. S1 and S2, ESI) [23].

Photolysis of **1a–4a** under the same conditions in the presence of 0.5 eq. of Ba(ClO₄)₂ led to more pronounced and more complicated spectral changes. At first, a fast decrease of the absorption intensities of the long wavelength absorption bands and a slight blue shift of the absorption maxima were observed as in the case of *E/Z* photoisomerisation of styryl derivatives **1a–4a**. Prolonged irradiation of the barium complexes of **1a–4a** (λ 365 nm) caused the disappearance of the long wavelength absorption bands in the spectral region of 300–400 nm indicating destruction of the conjugated chromophoric system. At the same time, new significantly blue shifted bands appeared at 230–350 nm that is the characteristic absorption region of non conjugated aromatic and hetero aromatic fragments (Fig. 1; Figs. S5–S7, ESI). To explain this observation, we assumed that dimeric complexes L₂·Ba²⁺ undergo the [2+2] photocycloaddition reaction of the ethylene double bonds resulting in the formation of cyclobutane derivatives **1b–4b**, in which conjugation between aromatic rings is disrupted by the cyclobutane ring closure. (Scheme 1). Kinetic studies on the photochemical reactions of the complexes of **1a** and **3a** with Ba(ClO₄)₂ were carried out upon irradiation at 313 nm or 365 nm depending on the position of the absorption maxima of the corresponding species. Analysis of the kinetic data allowed us to determine the values of the quantum yields of the forward and reverse photoisomerisation and photocycloaddition reactions (Table 2). No cyclobutane species was detected in control experiments with Mg²⁺ cation that does not form dimeric complexes with **1a–4a**. Thus, irradiation (λ 365 nm) of the complexes L·Mg²⁺ just led to the decrease of the intensity of the long wavelength absorption bands with a small blue shift of the absorption maxima (Figs. S3–S4, ESI), as it was observed for free **1a–4a**.



Scheme 1. Photochemical transformations of styryl derivatives **1a–4a** and their complexes with Ba²⁺ and Mg²⁺.

Table 2

Quantum yields of the *E-Z*-photoisomerisation (φ_1), *Z-E*- photoisomerisation (φ_2), forward (φ_3) and reverse (φ_4) [2+2] photocycloaddition reactions of the supramolecular dimers L₂·Ba²⁺ at different irradiation wavelengths (λ).

Compound	λ , nm	φ_1	φ_2	φ_3	φ_4
(1a) ₂ ·Ba ²⁺	313	0.42	0.50	0.12	- ^a
(3a) ₂ ·Ba ²⁺	313	0.36	0.45	0.20	0.0044
(3a) ₂ ·Ba ²⁺	365	0.52	0.40	0.08	0.0014

^a Not determined due to low absorption of (**1b**)₂·Ba²⁺ at 313 nm.

Therefore, supramolecular preorganization of the ligands **1a–4a** in the Ba²⁺ templated supramolecular dimers is the key process managing the occurrence of [2+2] photocycloaddition.

2.2. NMR spectroscopy studies

Since binding of the barium cation to the crown ether residue has an intermediate rate in the NMR timescale, the addition of Ba(ClO₄)₂ to the solutions of styryl derivatives **1a–4a** in CD₃CN resulted in severe broadening of their ¹H NMR spectra at room temperature, owing to chemical exchange between various possible complexes. While at lower temperature (233 K) the intermolecular exchange is slow enough to allow observing the signals of complexes with different barium to ligand ratio (Fig. S15, ESI), the irradiation of these mixtures with 365 nm light produced heavily overlapped NMR spectra of the photocycloaddition and *E/Z* photoisomerisation products and their barium complexes. The spectra are dramatically simplified if a small amount of D₂O (15% v/v) is added to the sample and if the measurements are performed at room temperature, as the presence of water shifts the dynamic exchange processes to the high rate regime (Fig. 2).

In all cases, the main photochemical process was the formation of the only one cyclobutane derivative of **1b–4b**, as revealed by the presence of two doublets in a characteristic region of the cyclobutane ring protons (4.5–5.5 ppm), and the only side process was the *E/Z* isomerization of the initial compounds. Notably, irradiation (λ 365 nm) of compounds **1a–4a** in the absence of barium species resulted in the *E/Z* isomerization only, and no products of photocycloaddition were detected that is in agreement with the steady state optical spectroscopy data (*vide supra*).

The processes occurring upon addition of barium ions and following photoirradiation were analyzed by NMR in more details for 4 quinoline derivative **2a**. The addition of 0.5 eq. of Ba²⁺ to a solution of **2a** in CD₃CN caused two distinctive sets of signals to appear in the ¹H NMR spectrum (Fig. S15b, ESI); those are assigned to two isomers of sandwich (**2a**)₂·Ba²⁺ complexes with different

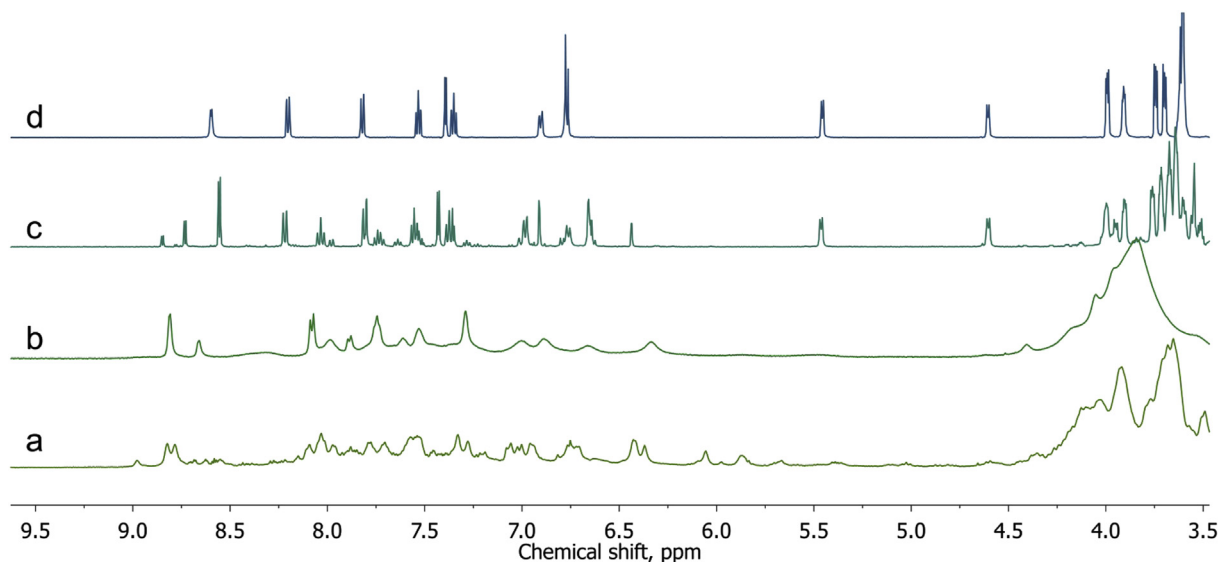


Fig. 2. ^1H NMR spectra in CD_3CN (600 MHz) of the mixture **2a** + 0.5 eq. Ba^{2+} irradiated for 2 h ($\lambda = 365$ nm) at 233 K (a), RT (b) and RT with addition of 100 μl D_2O (c) and the spectrum of the isolated cyclobutane product **2b** (d).

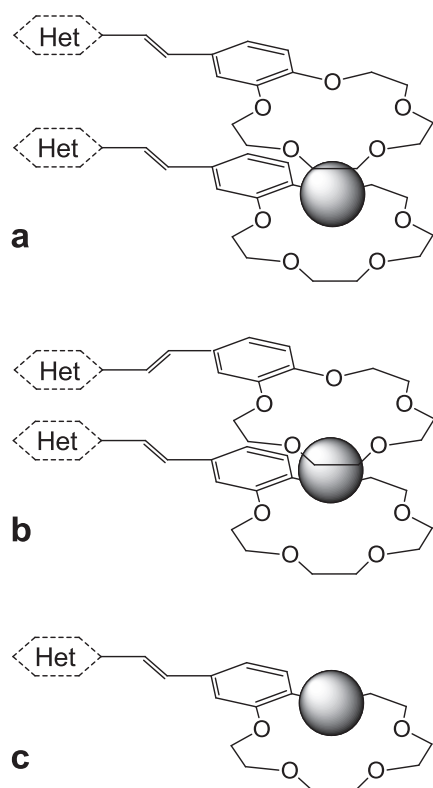


Fig. 3. Possible outcomes of Ba^{2+} complexation with styryl derivatives **1a–4a**.

orientations of the styryl fragments (Fig. 3a and b) [19]. In both cases, the downfield shift of the signals of the heterocyclic protons suggests the deshielding influence of a neighboring aromatic fragment of the second styrylheterocyclic fragment, which is possible only in a sandwich like coordination geometry. Further increase of the concentration of the metal ions results in a new set of signals (Fig. S15, ESI) assigned to a conventional 1:1 complex (Fig. 3c).

While the irradiation of different isomers of sandwich

complexes would result in different products of photo cycloaddition, in our experiments, only one cyclobutane isomer out of eleven possible [24] (Fig. 4) is formed. The presence of only two signals in the region of cyclobutane protons (4.5–5.5 ppm) limits the plausible structures to the symmetric ones, thus excluding isomers 2, 3, 8 and 9. Given the origin of the product, i. e. the geometry of the sandwich dimers, it leaves only four structures of the cyclobutane products with crown ether moieties located on the same side of the cyclobutane ring (compounds 1, 6, 7, 11 on Fig. 4).

Indeed, the formation of all other isomers is less probable, as the corresponding $\text{L}_2 \cdot \text{Ba}^{2+}$ sandwich complexes will not be stabilized by the $\pi \pi$ stacking of heteroaromatic fragments. The $\text{L}_2 \cdot \text{Ba}^{2+}$

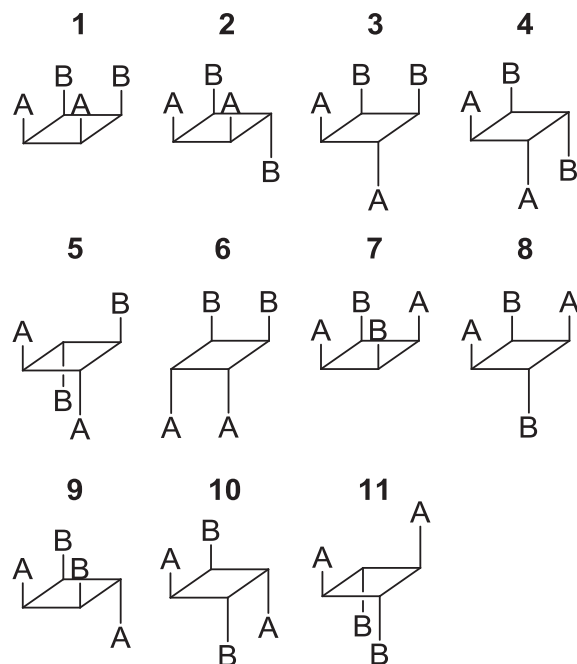


Fig. 4. Possible isomeric cyclobutane derivatives that can be formed from 1,2-disubstituted ethenes upon [2+2] cycloaddition.

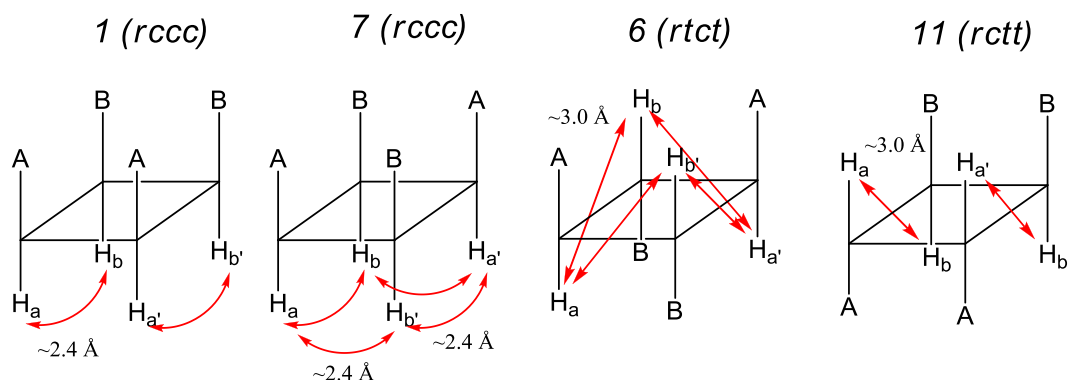


Fig. 5. Proton-proton through-space interactions in cyclobutane isomers. For clarity, the cyclobutane moiety is shown as a plane.

complexes shown on Fig. 3a and b would lead to cyclobutane derivatives **6** (*rctt*) and **11** (*rtct*), respectively, in the absence of *E Z* photoisomerisation, and to isomers **1** (*rccc*) and **7** (*rccc*), respectively, if *E Z* photoisomerisation would occur. The relative positions of the protons in the cyclobutane structure can be identified with the aid of the two dimensional NMR ROESY (Rotating frame nuclear Overhauser effect spectroscopy) pulse sequence, in which the intensity of cross peaks in 2D spectra depends on the distance between the corresponding nuclei [25]. Generally, *rccc* and *rtct* isomers would have stronger through space interactions between protons $H_{a,a'}$ and $H_{b,b'}$ than for *rctt* one (Fig. 5): in *rccc*, all protons H_a , $H_{a'}$, H_b , $H_{b'}$ are close to each other, as they are located on the same side of the cyclobutane ring, whereas in *rtct* isomer there are twice as many H_a H_b interactions as in *rctt* isomer. On a more quantitative level, the relative intensity of the ROE type cross peaks between different protons may be estimated from the ratio of distances between them; the pair of protons with a well determined internuclear distance may be used as a reference. [26] The approximate geometries of three possible isomers, as obtained by quantum chemical calculations using MM2 force field, were used to estimate expected $H_a(H_{a'}) - H_b(H_{b'})$ cross peak intensities relative to the cross peak of the neighboring aromatic protons H 5 and H 6 (~2.5 Å). The comparison with the experimental data (Table 3; Fig. S19, ESI) shows that the product **2b** is an *rctt* isomer (Fig. S20, ESI). Moreover, the value of the scalar coupling constant $^3J_{H_a-H_b}$ 6.6 Hz obtained from lineshape simulation of 1H NMR signals using DAISY module of Topspin 3 software (Fig. S21, ESI) is also indicative of a transoid geometry of H_a and H_b protons in **2b** [27].

2.3. Time resolved fluorescence spectroscopy studies

Time resolved fluorescence measurements showed the mono exponential fluorescence decay for free ligands **1a**, **3a**, **4a**, whereas for ligand **2a** two distinct fluorescence lifetimes were observed (Table 1). Most likely, the existence of two lifetimes for **2a** corresponds to the occurrence of two photoinduced processes in the excited state, namely, the equilibration of *syn* and *anti* populations (reflecting orientation of the 4 quinoline moiety with respect to the

double bond) and following *E Z* photoisomerisation [28]. Complexation of **1a–4a** with Mg^{2+} shortened the first fluorescence lifetime for all compounds and additionally led to the appearance of the second component for **3a** and **4a**. We assume that the second lifetime arises from the occasional formation of labile sandwich like structures of **2a–4a** complexes with Mg^{2+} due to the stacking interactions between the heterocyclic fragments and the exchange of magnesium cations between the two crown ether units [18]. Complexation of the ligands with Ba^{2+} resulted in the appearance of new very characteristic long living components in the timescale of 1000–3600 ps for compounds **2a–4a** that were assigned to the formation of the tight *syn* sandwich dimers with the Ba^{2+} cation (Table 1). Shorter lifetimes were associated with the relaxation of the monomeric and/or loose *syn* complexes as well as possible *anti* conformers of 4 quinoline derivative **2a**.

The value of the longest relaxation time of the excited state correlates with the bulkiness of the moving molecular fragments on the *E Z* isomerization pathway. In other words, formation of the sandwich complexes in the presence of Ba^{2+} cations hinders large amplitude rotations due to the tight stack arrangement of the molecules in the supramolecular dimers. This fact results in the increase of the excited state (fluorescence) lifetimes. Surprisingly, no long living component was detected for styrylpyridine derivative **1a** upon complexation with the barium cation. The most possible reason for this is quite weak $\pi-\pi$ stacking interaction between the small aromatic systems of the pyridine rings that does not allow a long living sandwich dimer of **1a** to be formed. On the other hand, irradiation of the complex $(\mathbf{1a})_2 \cdot Ba^{2+}$ still yields the single isomer of the cyclobutane species **1b** as it does in the cases of **2a–4a**. We assume, therefore, that the sandwich dimer of $(\mathbf{1a})_2 \cdot Ba^{2+}$ is formed, but it possesses high conformational lability that is reflected by the absence of the long living fluorescence lifetime. However, the lifetime of $(\mathbf{1a})_2 \cdot Ba^{2+}$ in the favorable conformation appears to be sufficient for the occurrence of the regio and stereoselective [2+2] photocycloaddition.

3. Conclusions

In summary, we have demonstrated that the regio and stereoselectivity of [2+2] photocycloaddition can be controlled in solution in an all supramolecular way by means of the appropriately balanced non covalent interactions. Thus, the [2+2] photocycloaddition of the crown derivatized styryl/heterocycles takes place only in their supramolecular dimeric complexes, in which a favorable arrangement of the reactive C=C double bonds is provided. The supramolecular dimerization is managed by $\pi-\pi$ stacking interaction of the heterocyclic fragments and sandwich type coordination of Ba^{2+} cations by two 15 crown 5 ether

Table 3
Experimental and theoretical ROE-cross-peak intensity for possible isomers of **2b**.

	ROE-cross-peak intensity
H-5 H-6 (reference)	1.00
1 (<i>rccc</i>)	1.65
7 (<i>rccc</i>)	3.30
6 (<i>rtct</i>)	0.67
11 (<i>rctt</i>)	0.33
Experimental value	0.33

residues. No [2+2] photocycloaddition occurs in the complexes of the ligands with Mg^{2+} due to the smaller size of the Mg^{2+} cation excluding the sandwich complex formation. Notably, for all studied compounds only one cyclobutane isomer out of eleven possible is formed. The obtained results represent a promising synthetic approach towards construction of the cyclobutane ring of the desired structure and conformation.

4. Experimental section

Crown derivatized styrylheterocycles **1a–4a** were synthesized according to published protocols [29,30]. 1H and ^{13}C NMR spectra were recorded from CD_3CN solutions using Bruker Avance 500 and Avance 600 spectrometers. The chemical shifts were referenced using the residual signals of the deuterated solvents. The temperature was calibrated using standard methanol sample. Samples in CD_3CN were irradiated in NMR tubes (5 mm) at 295 K in a home built apparatus that has been previously described [31]. The filtered emission spectrum of a 1000 W Xe–Hg high pressure short arc lamp (Oriol) (optical filter: L.O.T. Oriol 365FS10–50: $354 < \lambda < 378$ nm with λ_{max} 365 nm and T 25) was focused on the end of a silica light pipe (length 6 cm, diameter 8 mm), leading the light to the spinning sample tube, inserted into a quartz Dewar. After irradiation, the tube was transferred into the NMR spectrometer. To monitor the pathways of the photoreactions, the spectra were recorded at regular time intervals. The concentration of each photoproduct was obtained from the ratio of peak intensities.

Absorption spectra were recorded on a Varian Cary 100 double beam spectrophotometer. Preparation and handling of the solutions were carried out under red light. Photochemical reactions were carried out with a high pressure Hg vapor lamp (120 W) and an immersed Hg photoreactor (125 W). Kinetic studies on the phototransformations of the complexes were performed using a diode array fiber optic spectrometer AvaSpec 2048. Complex formation of **1a–4a** with $Mg(ClO_4)_2$ and $Ba(ClO_4)_2$ was studied by a spectrophotometric titration method in acetonitrile at 20 ± 1 °C; the stability constants of the complexes were determined from the photometric data using the SpecFit 32 program.

The fluorescence excitation light pulses for the time resolved measurements were obtained by frequency doubling and tripling of a Ti:sapphire femtosecond laser system (Femtopower Compact Pro) output. The depolarized excitation light was used to excite the samples. The highest pulse energies used to excite fluorescence did not exceed 100 nJ and the average power of excitation beam was 0.1 mW at a pulse repetition rate of 1 kHz focused into a spot with a diameter of 0.1 mm in the 10 mm long fused silica cell. The fluorescence emitted in the forward direction was collected by reflective optics and focused with a spherical mirror onto the input slit of a spectrograph (Chromex 250) coupled to a streak camera (Hamamatsu 5680) equipped with a fast single sweep unit M5676, temporal resolution 2 ps. The convolution of a rectangular streak camera slit in the sweep range of 250 ps with an electronic jitter of the streak camera trigger pulse provided a Gaussian (over 4 decades) temporal apparatus function with a FWHM of 20 ps (for more details see ESI).

Note

Authors declare no competing financial interests.

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