

Crown ether styryl dyes

25.* Application of molecular mechanics to the study of self-organization into dimeric complexes, regio-, and stereoselectivity of cation-dependent [2+2]-photocycloaddition in photochromic crown ethers

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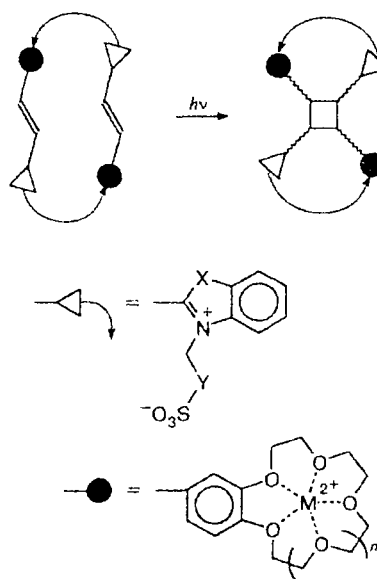
Regio- and stereoselectivity of [2+2]-photocycloaddition in complexes containing crown ether styryl dyes and alkaline-earth metal cations were studied using molecular mechanics. The main assumption is that the rate of the allowed concerted photocycloaddition correlates with the relative energies of the ground states of dimeric adducts, which are treated as pre-reaction complexes, and the resulting cyclobutanes. These energies are estimated by molecular mechanics within the MMX parameterization. The calculated characteristics of different dyes are studied as functions of the structure of the heterocyclic moiety, the structure and size of the N-substituent, the size of the crown ether cycle, and the nature of the metal cation. A comparison between the computational results and the experimental data showed that the observed quantum yield of the reaction is governed by the relative energies of the dimeric complexes and the resulting cyclobutanes as well as by the mutual arrangement of dye molecules in the dimeric complexes. Both factors are closely interrelated. The approach used in this work furnishes an explanation for the experimental data and provides a guideline for supramolecular control of regio- and stereochemistry of cation-dependent [2+2]-photocycloaddition.

Key words: crown ether styryl dyes; complexes with Ca^{2+} and Mg^{2+} , photocycloaddition; cyclobutane derivatives; molecular mechanics, MMX.

Crown ether styryl dyes (CSD) and their complexes with alkaline-earth metals were proposed as promising photoswitched molecular devices, because they can readily undergo *trans-cis*-photoisomerization when exposed to visible light, and the spectral and complexing properties of *cis*- and *trans*-isomers are substantially different.^{2,3} At the same time, it is shown that these compounds can enter into [2+2]-photocycloaddition (PCA) giving cyclobutanes in high quantum yield (Scheme 1).⁴ This reaction can also be of practical importance because it opens a way for obtaining a new class of complexones. Because of this, the possibility of predicting regio- and stereoselectivity of the cycloaddition is of substantial theoretical interest.

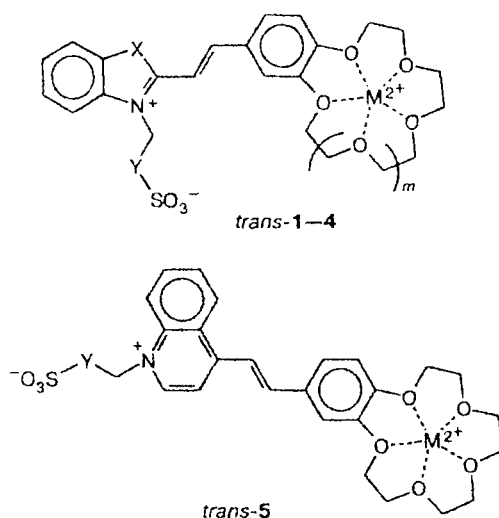
Our goal was to study the factors that govern regio- and stereoselectivity of PCA of CSD complexes 1–5 by molecular simulation. The molecules in the study are rather large; they contain about 70 atoms each. Therefore, only the simplest approaches like semiempirical

Scheme 1



* For Part 24, see Ref. 1.

quantum-chemical methods and methods of molecular mechanics can be applied to the molecules as large as this. Intermolecular interaction between initial monomers is the most important factor in [2+2]-photocycloaddition. As a rule, known semiempirical methods of quantum chemistry describe these interactions inadequately. We used molecular mechanics, because it was successfully applied earlier to the same or other crown ether styryl dyes (see ref.⁵). This method is commonly used in the study of supramolecular systems, molecular aggregation, conformational effects, structure of molecular crystals, etc. However, the possibility for using this method in the study of photochemical reactions needs special consideration.



X = S (1a-d, 3a,b, 4a,b), CH=CH (2a,b);
 Y = (CH₂)₂ (1a-5a), (CH₂)₃ (1b-5b), *o*-C₆H₄ (1c),
p-C₆H₄ (1d)
 M = Mg (1a-d, 2a,b, 5a,b), Ca (3a,b, 4a,b);
 m = 1 (1a-d, 2a,b, 3a,b, 5a,b), 2 (4a,b)

We assume that photochemical [2+2]-cycloaddition under consideration is concerted and *supra, supra*-facial. This mechanism is allowed according to the Woodward-Hoffmann rule. Therefore, we may suppose that its activation barrier is mainly governed by steric factors, i.e., how easily central double bonds in the initial dyes can be brought together for the reaction to occur. At the same time, the rearrangement of the electronic wavefunction due to the reaction does not cause the total energy to increase considerably and does not contribute to the formation of the barrier. This approach is usually applied to other barrier-free transitions, such as in the theory of electron transfer. Therefore, the reaction is sterically controlled and can be reliably studied by molecular mechanics.

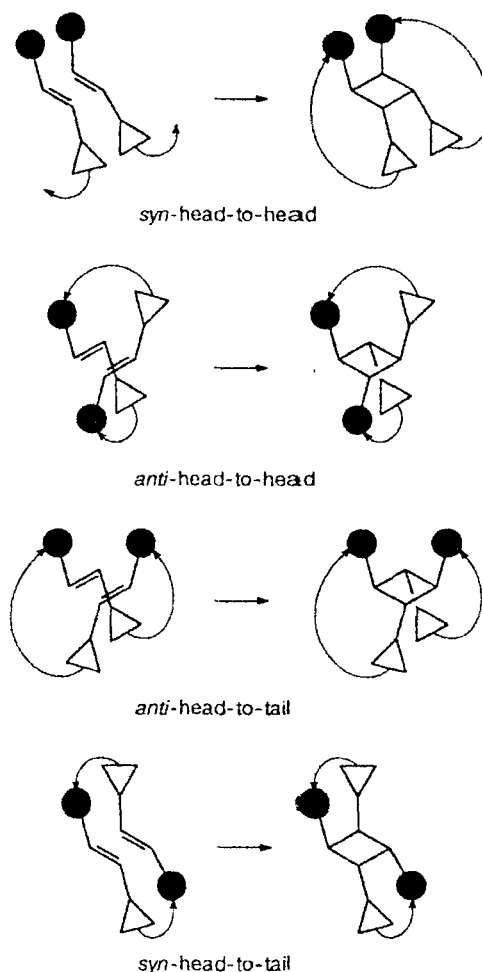
Molecular model. The dyes under consideration consist of an ethylene fragment (double C=C bond), a heterocyclic fragment with an N-substituent (spacer)

bearing a sulfo group, and a benzocrown ether fragment with an alkaline-earth metal cation in its cavity. In solution, the sulfo group of one dye molecule interacts with the metal cation in the crown ether cavity of the other molecule binding them into a supramolecular dimeric complex. The dye can be both in *cis*- and in *trans*-form.

One can easily see by exhaustive search that the reaction on Scheme 1 can give up to 11 cyclic isomers (Fig. 1). The reaction between *trans*-isomers gives four cyclobutanes (Fig. 1, a). The cycloaddition of *cis*-isomers to *trans*-isomers gives four cyclobutanes shown in Fig. 1, b. The three cyclobutanes shown in Fig. 1, c, are produced in the cycloaddition of *cis*-isomers. From here on, we consider only four isomers produced from the *trans*-form of the dye, because the latter is substantially more stable than the *cis*-form and dominates the reaction mixture.⁴

One can see four ways of cycloaddition of the *trans*-isomers (Scheme 2). In *syn*-head-to-head cycloaddi-

Scheme 2



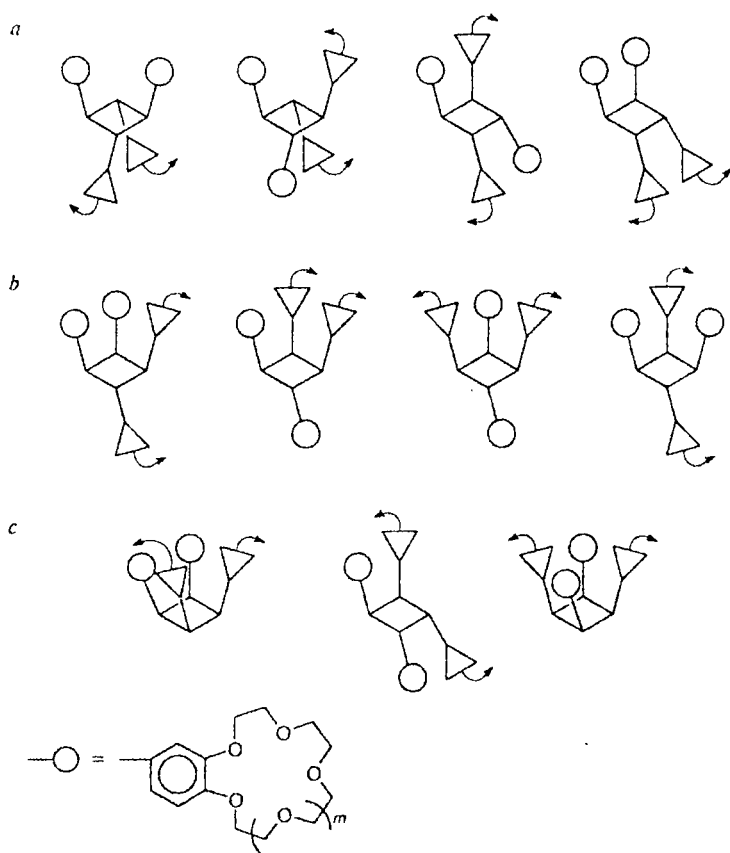


Fig. 1. Possible cyclobutanes produced by [2+2]-photocycloaddition of *cis*- and *trans*-forms of crown ether styryl dyes: photocycloaddition of *trans*-isomers (a); photocycloaddition of *trans*-isomer to *cis*-isomer (b); photocycloaddition of *cis*-isomers (c).

tion, the heterocyclic fragments of the two dye molecules are located at the neighboring carbon atoms on one side of the cyclobutane ring. In *anti*-head-to-head cycloaddition, the heterocyclic fragments are located at the neighboring carbon atoms at the opposite sides of the ring. In *anti*-head-to-tail cycloaddition, the heterocyclic fragments of the two dye molecules are located at the opposite carbon atoms on one side of the cyclobutane ring. In *syn*-head-to-tail cycloaddition, the heterocyclic fragments are located at the opposite carbon atoms at the opposite sides of the ring.

Concerted [2+2]-photocycloaddition of alkenes involves one of the reacting molecules in the lowest excited singlet state. In solution, the excited state easily relaxes due to the competitive processes of *trans*-*cis*-photoisomerization, fluorescence, etc.⁴ At the same time, the structure of the initial dyes does not favor photocycloaddition. In solution, the dye exists as a cation, which prevents its molecules from coming close together due to the Coulomb repulsion. The dye molecule is highly conjugated, which also hinders photocycloaddition. Therefore, bimolecular [2+2]-photocycloaddition is im-

possible, and the reacting molecules should be assembled into a supramolecular structure and arranged so that the reaction is possible. It is known⁴ that crown ether styryl dyes without the terminal sulfo group do not enter into photocycloaddition. Experiments^{4,13} show that in MeCN, two dye molecules and two metal cations give a supramolecular dimeric complex, which undergoes monomolecular [2+2]-photocycloaddition. Therefore, the mutual arrangement of the double bonds in the supramolecular dimer and the possibility of their coming close together for the reaction to begin govern to a large extent the possibility and efficiency of [2+2]-photocycloaddition.

We consider only intramolecular cycloaddition of dimeric complexes with two metal cations, because it is known from the experiments that such complexes dominate over a wide range of dye concentrations.¹² This is true for *anti*-head-to-head, *anti*-head-to-tail, and *syn*-head-to-tail dimeric complexes, but not for *syn*-head-to-head complex. In the latter case, Coulomb repulsion of metal cations in the crown-ether cavities prevents the molecules from coming close together. Hence, one can expect three different stereochemical ways for the photocycloaddition shown in Scheme 2: *anti*-head-to-head, *anti*-head-to-tail, and *syn*-head-to-tail.

We considered both the initial dimeric complexes and expected cyclobutane products. We assumed that the spatial structure of the dimeric complex should be close to the structure of the corresponding cyclobutane for the reaction to occur. Hence, we considered the energy differences between the cyclobutanes and corresponding dimeric complexes as a guideline in deciding whether this preliminary assembling is possible. Under these assumptions, comparing relative formation energies of cyclobutanes can assess the probability of the photocycloaddition occurring in the same dye by different regio- and stereochemical way. This can be done by molecular mechanics.

Method of calculation. Calculations were performed by the extended MMP2⁶ method implemented in MMX89⁷ and PCMODEL⁸ program packages. The MMX force field used within these programs is the standard MM2^{9,10} force field for the organic part of the molecule. Metal-crown ether-sulfo group interaction was simulated within the ionic (electrostatic) approximation,¹¹ when a point charge (here, +2) and an ionic radius characterize the cation. Complexing occurs through the interaction of the cation with the ligand lone pairs. Within this approximation, the Coulomb interaction of the point charges is explicitly described by the expression $U_{el} = f_{el} q_i q_j / (e R_{ij})$, where R_{ij} is the dis-

tance separating the charges, q_i and q_j are point charges, ϵ is the effective dielectric constant, and f_{el} is a unit conversion factor.

Preliminary calculations showed that, within MMX89 and PCMODEL, geometry optimization of the molecules in the study cannot be performed adequately with all hydrogen atoms and lone pairs taken into account, and the local energy minimum is not necessarily achieved. This is due to the complex character of the potential energy surface of such large molecules, which cannot be investigated by the methods developed for small molecules. Molecular dynamics and Monte Carlo techniques are more appropriate for these purposes.

However, MMX calculations are possible when all nonhydrogen atoms and four hydrogen atoms bonded to the double bonds in the initial dyes and to the cyclobutane rings in the products are taken into account. This reduces substantially the number of atoms to be treated and allows one to obtain unambiguous and reproducible results. In spite of some additional assumptions, this approach makes it possible to take into account the main factors that govern the stereochemistry of the reaction: the structure of the initial molecule, Coulomb interaction, and steric hindrances near the reaction center. This approach is used in this paper.

Because the local energy minimum is not necessarily achieved in the geometry optimization performed by MMX and PCMODEL, we repeated our calculations several times as recommended by the authors of the program.⁸ Each time, we started with the last obtained point until the difference between the last point and the next to the last point was less than 0.01 kcal. To obtain a global or a deep local minimum of energy, we used a randomization procedure implemented in MMX89 and PCMODEL. Each step of the procedure consists of multiple random movements of all or some of the atoms; next, the geometry is optimized.^{6,8} We generated about 1000 structures during the randomization. About 50 of them were stored with the energy less than 1.0 kcal·mol⁻¹ higher than the initial value. The best (lowest energy) structure was used for further energy minimization.

Results and Discussion

Calculation results were compared with the experimental data on quantum yields^{1,12–14} and the structures of related compounds from Cambridge Structural Database¹⁵. Calculated dye structures agree principally with X-ray data¹⁵.

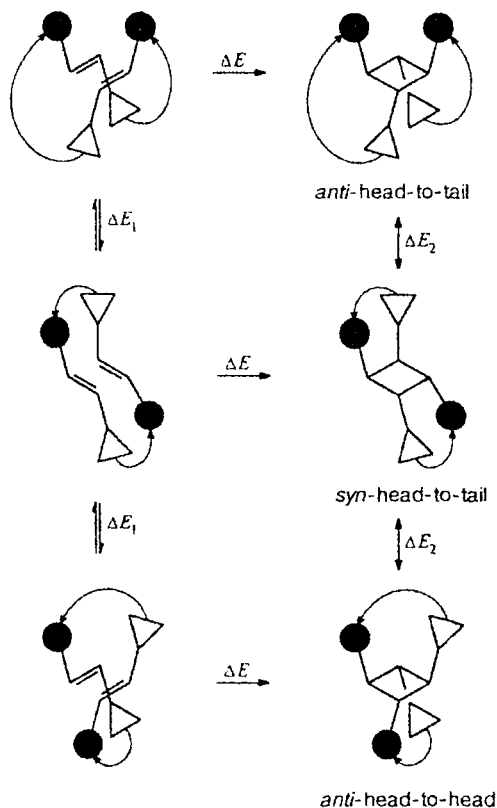
Our calculations showed that the photocycloaddition in the study is endothermic as expected. Hence, the assumption that the structure of its transition state is close to the structure of the corresponding cyclobutane is true. Therefore, the relative formation energies of the cyclobutane products rather than the energies of the initial dimeric complexes govern the quantum yield of the photocycloaddition.

Table 1. Calculated energy differences (ΔE_1) between the isomeric dimeric complexes and (ΔE_2) between the corresponding cyclobutanes according to Scheme 3

Dimeric complexes	ΔE_1	ΔE_2
	kcal · mol ⁻¹	
<i>anti</i> -head-to-tail— <i>syn</i> -head-to-tail		
(1a · Mg ²⁺) ₂	2.39	-4.92
(1b · Mg ²⁺) ₂	-1.19	-6.30
(1c · Mg ²⁺) ₂	3.27	-6.20
(1d · Mg ²⁺) ₂	-1.68	-11.23
(2a · Mg ²⁺) ₂	2.74	-7.19
(2b · Mg ²⁺) ₂	0.22	-9.31
(3a · Ca ²⁺) ₂	0.79	-7.22
(3b · Ca ²⁺) ₂	-1.65	-9.04
(4a · Ca ²⁺) ₂	-3.41	-7.18
(4b · Ca ²⁺) ₂	-3.00	-8.23
(5a · Mg ²⁺) ₂	0.58	8.30
(5b · Mg ²⁺) ₂	-0.83	3.99
<i>anti</i> -head-to-head— <i>syn</i> -head-to-tail		
(5a · Mg ²⁺) ₂	1.27	4.47
(5b · Mg ²⁺) ₂	0.18	4.97

For each studied dye, Table 1 gives the relative energies ΔE_1 for *anti*-head-to-head, *anti*-head-to-tail, and *syn*-head-to-tail isomeric dimers containing two metal cations (see Schemes 2 and 3). It also gives the

Scheme 3



relative energies ΔE_2 for corresponding cyclobutanes (see Scheme 3). The values of ΔE_1 show that the dimeric complexes of different stereochemistry have virtually the same (within 0.1–3.4 kcal·mol⁻¹) formation energies; that is, the relative formation energies of the dimeric complexes have little effect on the quantum yields of photocycloaddition. The small differences between the formation energies of the dimeric complexes point to the fact that both complexes exist in solution simultaneously. At the same time, ΔE_2 lies within 4–12 kcal·mol⁻¹. This points to the fact that one of the cyclobutanes substantially dominates, no less than 100 times, in the mixture at room temperature. This can be easily estimated by the formula $C_1/C_2 = \exp(\Delta E_2/RT)$, where C_1 and C_2 are cyclobutane concentrations. In this case, the stereoselectivity of the reaction can be judged from the values of ΔE_2 .

Table 2 gives the energies ΔE of the cyclobutanes relative to the dimeric complexes (they are arbitrarily called energies of photocycloaddition) and the quantum yields according to the papers^{1,12–14}. It also gives the calculated geometrical parameters of the dimeric complexes: the distance (r) and the dihedral angle (τ) between the double bonds (Fig. 2). Under the assumption that the structure of the transition state is close to the structure of the products, the value of ΔE should correlate with the quantum yield of the photocycloaddition.

We assumed that the parallel arrangement of the double bonds and the small distance between them favor photocycloaddition. However, in the case under study, the angle τ exhibited no correlation with the quantum yield. The distance r correlates with the quantum yield for different dyes. This means that the structure of the dye molecule in the general case determines the distance between double bonds in its dimeric complexes. The long distance prevents the dye molecules from being brought together, thus increasing ΔE . At the same time, the distance r exhibits no correlation with the energy of photocycloaddition ΔE for a given dye. Hence, r cannot be considered as an index of the stereoselectivity of photocycloaddition. This can be attributed to the fact that the calculated structures of the dimeric complexes are far from the transition state structure. Thus, the shortest distance between double bonds observed in the calculated structures was 6.4 Å, and the angle between them is rather large in most cases. Overlap of carbon π orbitals is virtually zero under these conditions, whereas it should be large enough to form a σ bond in the transition state.

We considered two types of crown ether styryl dyes: with the ethylene fragment in the *ortho*-position to the heterocycle nitrogen (benzothiazolium or 2-substituted quinolinium fragments) and with the ethylene fragment in the *para*-position to this nitrogen (4-substituted quinolinium fragment). For the former dyes, we studied the formation of *anti*-head-to-tail and *syn*-head-to-tail dimeric complexes. For the latter dyes, we studied the formation of *anti*-head-to-head, *anti*-head-to-tail, and

Table 2. Calculated energies of photocycloaddition ΔE for the dimeric complexes with two metal cations (Scheme 3), quantum yields Φ of the corresponding cyclobutanes according to papers^{1,12–14} and calculated geometrical parameters of the dimeric complexes^a

Dimeric complex	ΔE /kcal·mol ⁻¹	Φ	$r/\text{\AA}$	τ/deg
<i>anti</i> -head-to-tail				
(1a·Mg ²⁺) ₂	47.54	0.005	8.76	-43.3
(1b·Mg ²⁺) ₂	48.71	0.013	10.33	-11.2
(1c·Mg ²⁺) ₂	42.09	0.018	6.41	-28.0
(1d·Mg ²⁺) ₂	65.16	<i>b</i>	10.68	-32.6
(2a·Mg ²⁺) ₂	47.77	0.0007	7.34	-28.0
(2b·Mg ²⁺) ₂	47.63	<i>c</i>	8.37	-24.9
(3a·Ca ²⁺) ₂	43.91	0.001	8.26	-62.0
(3b·Ca ²⁺) ₂	44.74	0.01	8.45	-67.5
(4a·Ca ²⁺) ₂	47.50	0.0002	6.43	-54.3
(4b·Ca ²⁺) ₂	47.24	0.06	6.70	-52.2
(5a·Mg ²⁺) ₂	27.49	<i>b</i>	7.99	-79.9
(5b·Mg ²⁺) ₂	27.46	<i>b</i>	9.13	-80.0
<i>syn</i> -head-to-tail				
(1a·Mg ²⁺) ₂	54.85	<i>b</i>	8.40	-19.8
(1b·Mg ²⁺) ₂	53.82	<i>b</i>	9.59	-18.9
(1c·Mg ²⁺) ₂	51.56	<i>b</i>	7.65	-34.8
(1d·Mg ²⁺) ₂	74.71	<i>b</i>	11.29	-19.6
(2a·Mg ²⁺) ₂	57.70	<i>b</i>	8.42	-23.9
(2b·Mg ²⁺) ₂	57.16	<i>c</i>	8.80	-23.4
(3a·Ca ²⁺) ₂	51.92	<i>b</i>	7.90	-10.2
(3b·Ca ²⁺) ₂	52.13	<i>b</i>	8.73	-4.7
(4a·Ca ²⁺) ₂	51.31	0.0001	7.78	-10.3
(4b·Ca ²⁺) ₂	52.47	<i>b</i>	8.47	-11.8
(5a·Mg ²⁺) ₂	19.77	0.15	7.28	10.6
(5b·Mg ²⁺) ₂	22.64	<i>c</i>	9.03	8.0
<i>anti</i> -head-to-head				
(5a·Mg ²⁺) ₂	22.97	<i>b</i>	7.86	-72.2
(5b·Mg ²⁺) ₂	27.43	<i>b</i>	9.05	-63.7

^a The distance (r) and the dihedral angle (τ) between the double bonds are shown in Fig. 2.

^b Not obtained.

^c Data not available.

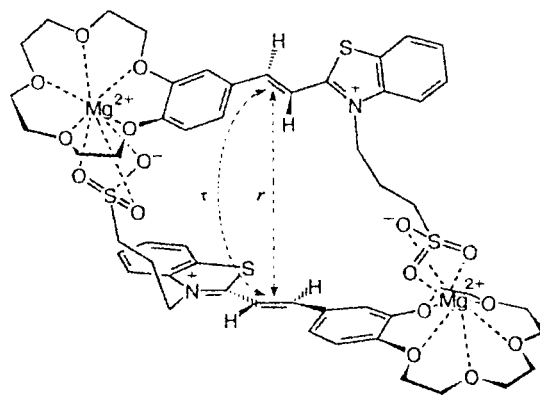


Fig. 2. Calculated structure of *anti*-head-to-tail dimer (1a·Mg²⁺)₂. One can see undistorted structure of the crown ether fragment. Arrows show the studied geometrical parameters: the distance (r) and the dihedral angle (τ) between the double bonds.

syn-head-to-tail dimeric complexes. 2-Substituted heterocyclic fragments favor *anti*-head-to-tail photocycloaddition, whereas 4-substituted ones favor *syn*-head-to-tail reaction. This is supported both by our calculations and by experiments.^{1,12–14} Additionally, 4-substituted heterocyclic fragments decrease the energy of photocycloaddition approximately twice as compared to dyes with 2-substituted heterocyclic fragments.

The energy of *syn*-head-to-tail photocycloaddition is the lowest for dye **5a** with a 4-substituted quinolinium fragment, and the double bonds in the corresponding dimeric complex are optimally arranged as compared to other structures in the study. This agrees with the fact that the highest quantum yield was observed in **5a**.¹³ Our calculations show that different dimeric complexes of this dye (as well as of its analog **5b**) differ in energy only slightly (0.1–2 kcal·mol⁻¹). Therefore, the three types of dimeric complexes can exist in solution simultaneously. However, even though the energies of photocycloaddition are rather low for all the dimeric complexes, only one cyclobutane, namely, *syn*-head-to-tail, is produced. This is possibly attributed to the almost parallel arrangement of the double bonds in the corresponding dimeric complex, which is observed neither in other dimeric complexes of **5** nor in other dyes (**1–4**).

Our calculations show that 2-substituted quinolinium fragment produces more steric hindrances near the reaction center than benzothiazolium fragment. This fact probably accounts for the lower quantum yield of photocycloaddition in **2a** (which contains 2-substituted quinolinium) as compared to its analog **1a** (which contains benzothiazolium fragment).^{12,13}

We considered spacers of different length and rigidity. Flexible polymethylene spacers (three and four methylene groups, dyes **1a–5a** and **1b–5b**, respectively) allow dye molecules in the complex to move and arrange their double bonds in the best way for photocycloaddition. At the same time, the rigid *o*-sulfo benzyl spacer (dye **1c**) holds the dye molecules at a relatively short distance, thus favoring photocycloaddition.¹ Conversely, the rigid *p*-sulfo benzyl spacer (dye **1d**) prevents the dye molecules in the complex from coming close together and holds the cation in the cyclobutane in a position that makes the stable conformation of the crown ether–cation complex impossible (Fig. 3). Thus, the structure of the crown ether fragment in the resulting cyclobutanes is distorted. This distortion is responsible for the highest calculated formation energy of cyclobutanes **1d** and for the fact that **1d** does not enter photocycloaddition in the experiment.¹

Benzo-15-crown-5-ether and benzo-18-crown-6-ether fragments differ in cavity size. Benzo-18-crown-6-ether does not give complexes with Mg²⁺, whereas benzo-15-crown-5-ether gives complexes with both Mg²⁺ and Ca²⁺. Benzo-15-crown-5-ether is rather rigid as

compared to benzo-18-crown-6-ether, and it is possible to find a global energy minimum for its complexes with Mg²⁺ or Ca²⁺, either free or incorporated into a dye. Benzo-18-crown-6-ether complexes have several different conformations with close energies (within 1 kcal·mol⁻¹), so that it is impossible to choose one of them as a global minimum.

There are some discrepancies in our calculations connected, possibly, with an inadequate treatment of electrostatic interactions of cations with crown ethers and sulfo group within MMX method. Thus, in experiment,¹⁴ the dimeric complex of **4b** dye with the sulfoethyl spacer gives the *anti*-head-to-tail cyclobutane with a rather high quantum yield, whereas its analog **4a** with the sulfopropyl spacer exhibits the lowest quantum yield among all studied dyes and gives both *anti*-head-to-tail and *syn*-head-to-tail cyclobutanes in the ratio 2 : 1. At the same time, our calculations give close energies of photocycloaddition and rather short distances between double bonds for both dyes (the same distances were observed in the *anti*-head-to-tail dimeric complex of **1c** dye, which exhibits relatively high quantum yield). These short distances result from the fact that the distance between the metal cation and crown ether plane in the complex of benzo-18-crown-6 with Ca²⁺ is shorter than that in the complexes involving benzo-15-crown-5. In spite of all this, quantum yields for the complexes of dyes with Ca²⁺ (**3a**, **3b**, **4a**, and **4b**) differ by 1–2 orders of magnitude in going from sulfopropyl to sulfoethyl spacers.¹⁴ The agreement between the size of the crown ether cavity and the length of the spacer may be important in this case. The elucidation of this problem needs special investigation. The electrostatic approximation implemented within MMX method possibly overestimates cation–sulfo group interaction and underestimates cation–crown ether interaction. This is supported by the overestimated distances between the metal cation and the oxygen of the crown ether and the underesti-

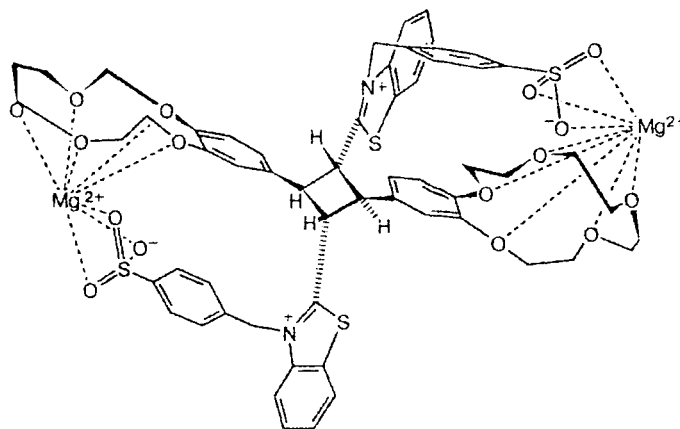


Fig. 3. Calculated structure of *anti*-head-to-tail cyclobutane formed by **1d**·Mg²⁺ dye. One can see distortion of the crown ether fragment through the interaction of the spacer with Mg²⁺ cation.

mated distances between the metal cation and the oxygen atoms of the sulfo group.

For each studied dye, the dimeric complexes have virtually the same global energy minima, which suggests that dimeric complexes of any possible structure can exist in solution (*anti*-head-to-tail, *syn*-head-to-tail, *etc.*). The quantum yields and stereochemistry of [2+2]-photocycloaddition seem to be governed mainly by the relative formation energies of cyclobutane products and, other conditions being equal, by mutual arrangement of the double bonds in the dimeric complexes.

The approach developed in this work makes it possible to interpret the experimental results and to predict regio- and stereoselectivity of cation-dependent [2+2]-photocycloaddition by molecular mechanics.

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