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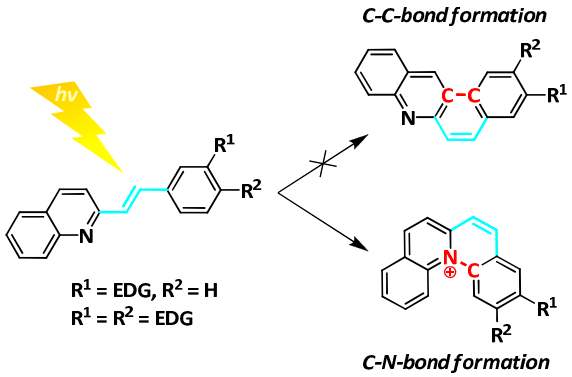
Abstract



Regiospecific C-N photocyclization of 2-styrylquinolines resulting in formation of potentially biologically active quino[1,2-*a*]quinolizinium derivatives was investigated. The presence of strong electron donating groups (EDG) in the phenyl ring reveals to be a crucial factor managing photocyclization effectiveness. Introduction of a crown ether moiety allows to change the photoreaction parameters by means of complexation with $Mg(ClO_4)_2$.

Introduction

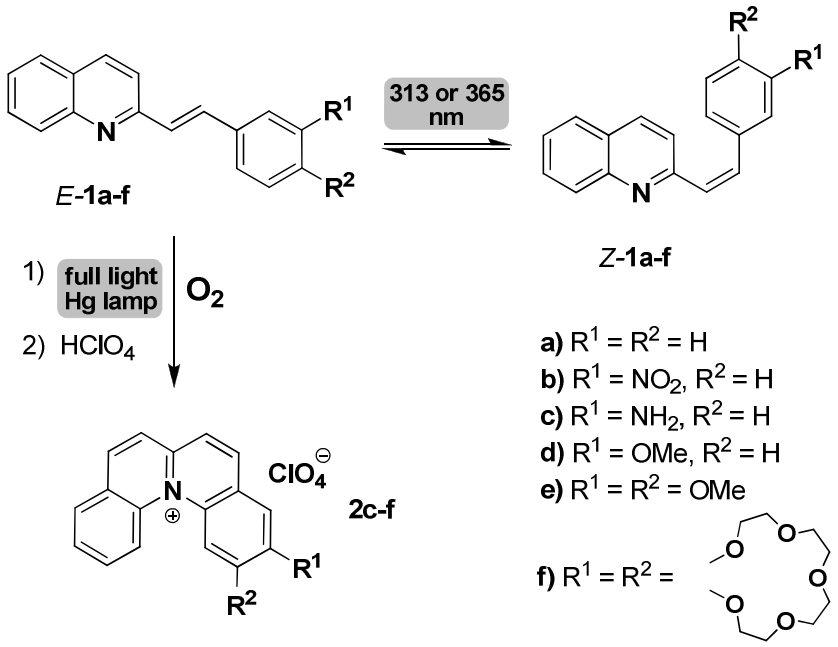
Biological activity of polycondensed heteroaromatic compounds recently has been the focus of considerable interest due to high potential in developing new anticancer, antibacterial and fungicidal drugs.[1] The main reason for the chemotherapeutic effect of the molecules possessing

extended heteroaromatic π-system is effective interaction with DNA,[2] which causes changes in the physiological functions of the nucleic acid and subsequently leads to the cell death. Significant difficulties of obtaining polycyclic aromatics by classical organic synthesis encouraged chemists to search for alternative approaches. One of the most powerful, however, not extensively studied methods is the photocyclization of stylbenes and their heterocyclic analogs.[3] The range of hetarylphenylethenes suitable for photochemical synthesis of biologically active heteroaromatic compounds is constantly expanding. Thus, photocyclization products of styryl-substituted benzimidazoles[4,5], benzopyrroles, naphthofurans, naphthothiophenes[6], phenanthridines[7] and imidazopyridines[8] demonstrated high potential as anticancer and fungicidal agents. Interestingly, that photocyclization of hetarylphenylethenes may lead to the formation of either neutral or charged products, which possess different biological activity. Particularly, fused heteroaromatics bearing a permanent positive charge are typical DNA-intercalators and therefore are of interest as potential DNA-targeting drugs.[2] From this point of view the investigation of phototransformation mechanism plays an important role in the development of practical applications of hetarylphenylethenes in biology and medicine.

Recently, we described novel oxidative photocyclization of indolinylphenylethenes and benzothiazolylphenylethenes leading to polycyclic heteroaromatic cations involving formation of a new C-N bond.[9,10] This photochemical transformation includes 6π-electron conrotatory electrocyclic ring closure followed by oxidation of an intermediary dihydroelectrocycle resulting in formation of fused products.[11,12,13] Moreover, we used the photocyclization reaction of 2-(3,4-dimethoxystyryl)benzothiazole for *in situ* generation of a DNA-binding photoproduct directly in the presence of the nucleic acid, thus realizing photocontrolled binding with DNA.[14] In this paper we extend our research to the phototransformations of 2-styrylquinolines **1a-f** containing various substituents in the phenyl ring (Scheme 1). Compound **1f** was additionally modified with 15-crown-5 ether residue providing the possibility to influence the photoreaction by complexation with Mg^{2+}

cation. Styrylquinolines **1a-f** was prepared by condensation of quinaldine with corresponding benzaldehyde derivatives in the presence of $KOBu^t$ in DMF according to published protocols.[15,16]

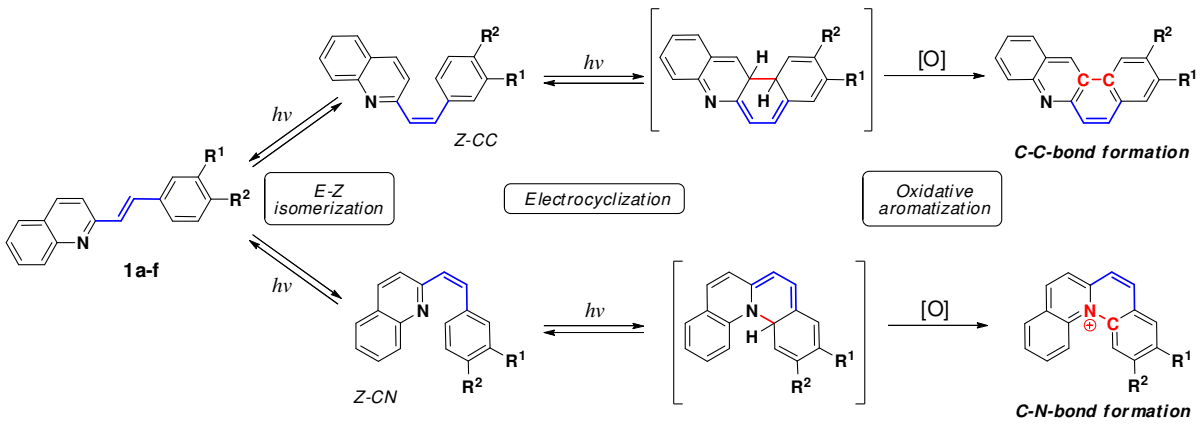
Scheme 1. Photochemical transformations of 2-styrylquinolines



Results and discussion

Theoretically, the photocyclization of 2-styrylquinolines **1a-f** may occur *via* C-C or/and C-N bond formation (Scheme 2). C-C photocyclization reveals to be the most common pathway for structurally related hetarylphenylethenes.[17] It should be noted, however, that products of C-C cyclization for 2-styrylquinolines were not reported up to now. At the same time 4-styrylquinoline derivatives undergo quite effective C-C photocyclization.[18] On the other hand, C-N photocyclization of 2-styrylazines was described by few authors earlier.[19] Nevertheless, in the cases reported so far all the studied compounds contained halogen in *ortho*-position of phenyl ring, thus resulting in the intramolecular nucleophilic substitution mechanism. In our study, we suppose the electrocyclic mechanism of the C-N bond formation that allows to avoid modification of the phenyl ring *ortho*-position without loss in C-N regiospecifity.

Scheme 2. Possible photocyclization pathways for 2 -styrylquinolines



To develop the possible phototransformation pathways of 2-styrylquinolines, first we examined the photoreaction of **1a-f** in acetonitrile upon irradiation with filtered light at 313 or 365 nm (Figure 1a, S1-6) in air saturated solutions. In these experiments photostationary equilibria of *E* and *Z* isomers were reached. Detailed characterization of the photolysis products was performed by NMR spectroscopy. Thus, comparison with the authentic spectra of *E*-**1a-f** showed that all obtained photostationary mixtures consisted of two species, namely, initial isomers *E*-**1a-f** and photoisomerization products *Z*-**1a-f** (Figure S7-12).

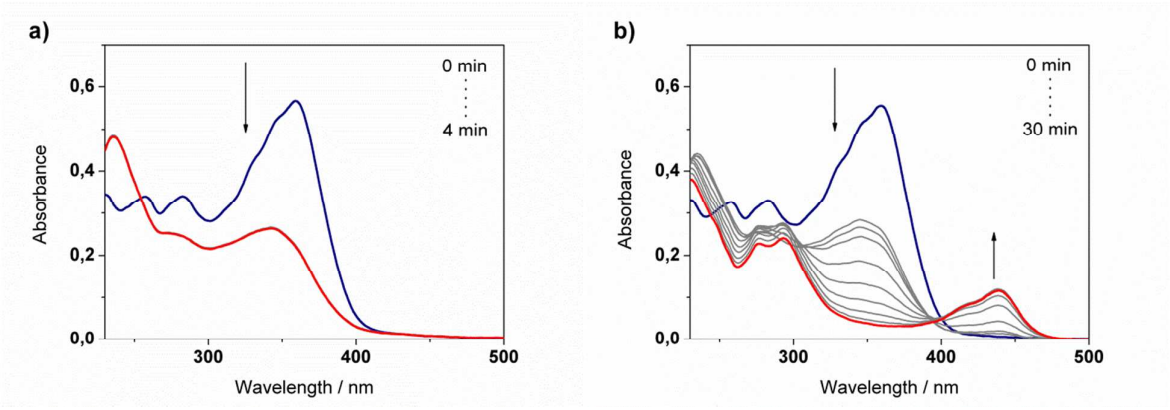


Figure 1. Spectral changes during the photolysis of the **1f** acetonitrile solution: (a) filtered light, λ = 365 nm; (b) full light; in both cases: $c = 2 \cdot 10^{-5}$ M, high pressure Hg lamp, 20 °C.

Irradiation of **1a-f** in the presence of air oxygen with unfiltered output of a high pressure Hg vapor lamp resulted in more complicated behavior. Under these conditions unsubstituted 2-styrylquinoline

1a and its nitro derivative **1b** underwent photodestruction of the molecular skeleton (Figure S1-2). At the same time, the photochemical transformation of amino-, methoxy- and crown-substituted styrylquinolines **1c-f** upon irradiation with full light showed sharp contrast with the previous experiments. In these cases the photoreaction resulted in the appearance of new absorption bands in the spectral region of 400-500 nm, which were assigned to heteroaromatic species **2c-f** (Figure 1b, S3-6, S13). The exclusive formation of C-N photocyclization products has been unambiguously proven by NMR data (Figure 2, S14-28). Moreover, no positional isomerism for the substituents was detected for **2c-f**. Heteroaromatic compounds **2d-f** were successfully isolated as perchlorate salts by recrystallization from MeOH with small addition of $HClO_4$ with moderate-to-good yields **2d**: 52%, **2e**: 70%, **2f**: 45%. Characterization of the amino derivative **2c** required purification by HPLC under special conditions (injection of $NaClO_4$ solution to elute the desired species) thus leading to a very reduced amount of the obtained product. However, according to the raw NMR data the yield of **2c** after ion-exchange to perchlorate was 80%.

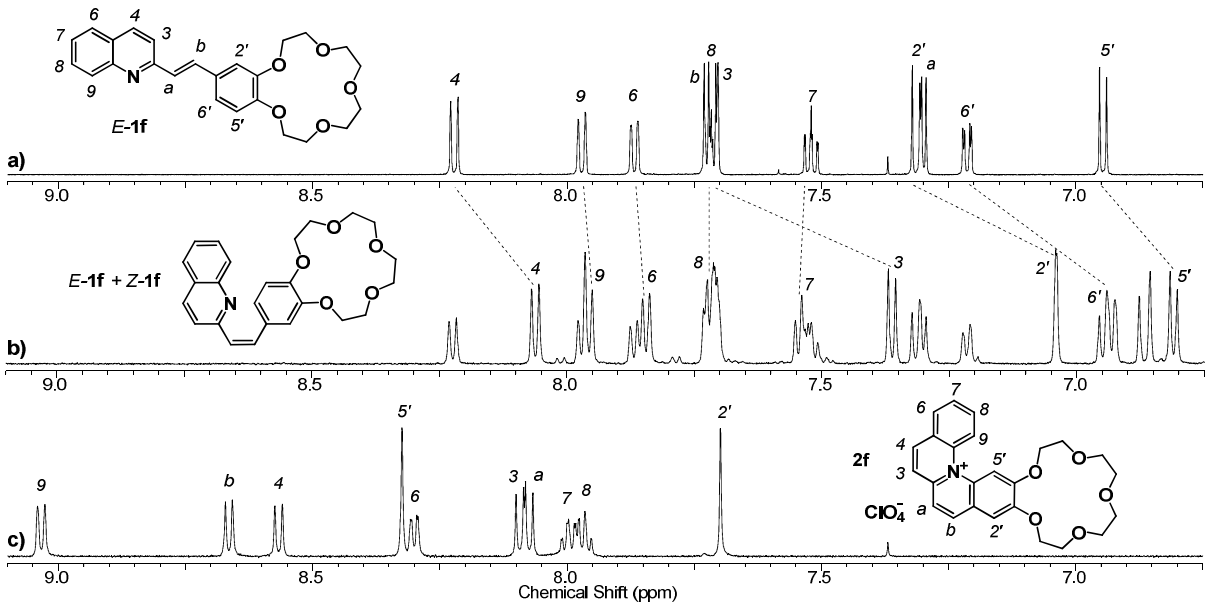


Figure 2. ^{1}H NMR spectra in CD_3CN: a) *E*-**1f**; b) photostationary mixture of *E*-**1f** and *Z*-**1f** obtained after irradiation of the *E*-**1f** solution with filtered light λ = 365 nm; c) isolated photocyclization product **2f**.

It is important to note that for the oxidative aromatization stage other mild oxidants may be applied such as iodine and Dess-Martin reagent. However, in these cases we run into significant difficulties during isolation of the photocyclization products due to the presence of hardly separable iodine-containing species. At the same time, irradiation of the initial styryl derivatives upon bubbling pure oxygen through the solution led to the complete photodegradation of organic molecules.

Our efforts to stop the reaction on the electrocyclization stage and isolate the intermediary non-charged dihydrocyclic derivatives were not successful. Thus, formation of the electrocyclization products was not detected upon irradiation of 2-styrylquinolines in the deaerated solutions under argon. Most likely, dihydrocyclic intermediates are highly unstable and rapidly rearrange back into initially formed *Z*-isomers of **1a-f** in the absence of oxidants (Scheme 2).

For a better understanding of the remarkable C-N regiospecifity of the studied reaction quantum chemical calculations were carried out. Thus, geometry optimization (PM6, MOPAC) of unsubstituted 2-styrylquinoline **1a** showed that the most stable conformation of the formed on the first step *Z*-isomer possesses non-planar structure with the phenyl ring located close to protons H-3 and H-4 of the quinoline moiety (*Z-CC*) (Figure 3, Scheme 2). Stability of this conformation is also supported by NMR data (Figure 2). Thus, upon *E-Z*-isomerization signals of protons H-3 and H-4 undergo significant upfield shift, while the positions of the rest quinoline proton signals remain almost unchanged. This pattern of the spectral changes discloses strong anisotropic effect provided by the phenyl ring, which, therefore, is located in the close proximity to the aforementioned quinoline protons in the most stable conformation of *Z*-isomer (*Z-CC*).

In terms of interatomic distances formation of a new C-C bond (3.3 Å) in *Z-CC* conformation is more favorable than formation of a C-N bond (4.0 Å). Therefore, formation of a C-N bond takes place from the other conformation of *Z*-isomer (*Z-CN*), where the distance between the reacting C and N atoms is short enough (3.3 Å) to ensure bond formation. Conformation *Z-CN* was found to be 6 kJ/mol less stable in comparison to conformation *Z-CC* (Figure 3). Nevertheless, calculated enthalpy of C-N cyclization product formation was found to be ~ 90 kJ/mol less than that of C-C

cyclization product, which completely matches with the experimental C-N regiospecifity of this reaction.

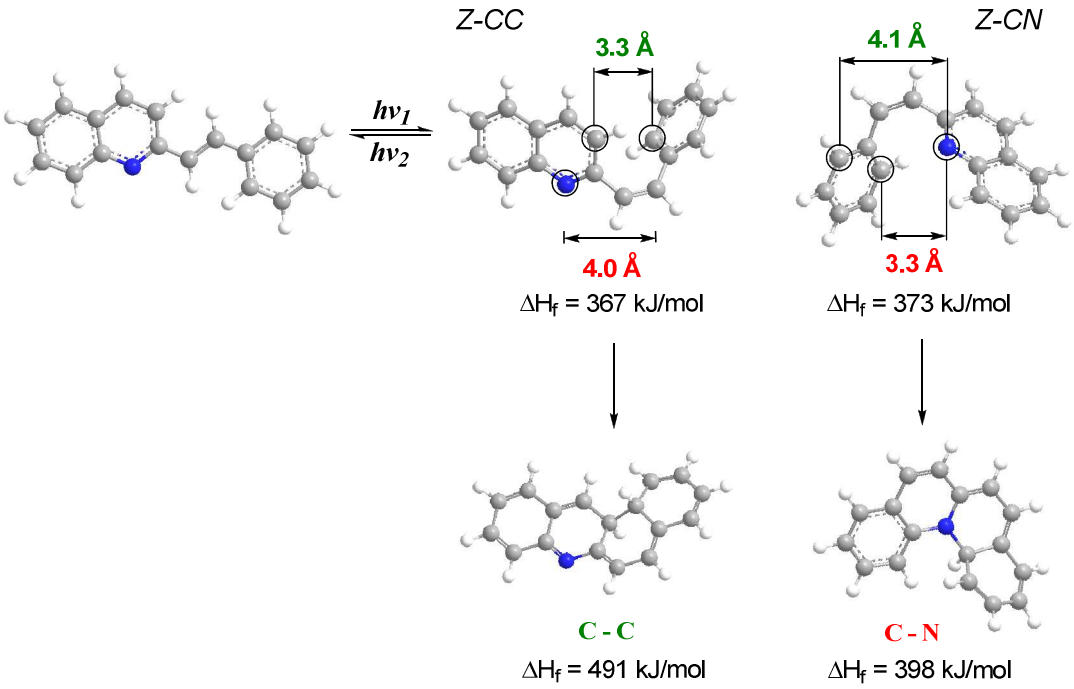


Figure 3. Optimized geometries (PM6, MOPAC) of unsubstituted 2-styrylquinoline *E*-**1a**, its *Z*-isomers and C-C/C-N electrocyclic intermediates including calculated enthalpy of formation.

The next point to be discussed is the influence of the substituents in the styryl moiety of **1a-f** on the occurrence of the cyclization. Apparently, effective photocyclization requires the presence of the electron donors in the phenyl ring, whereas electron withdrawing group (NO_2) does not favor the photocyclization. Additional evidence for the crucial role of donor substituents was provided in the experiments with crown-derived 2-styrylquinoline **1f**. Thus, complexation with Mg^{2+} cation reduces the donor strength of crown ether oxygen atoms, which leads to pronounced deceleration of the cyclization reaction in **1f**-Mg^{2+} complex in comparison with free **1f** (Figure 4).

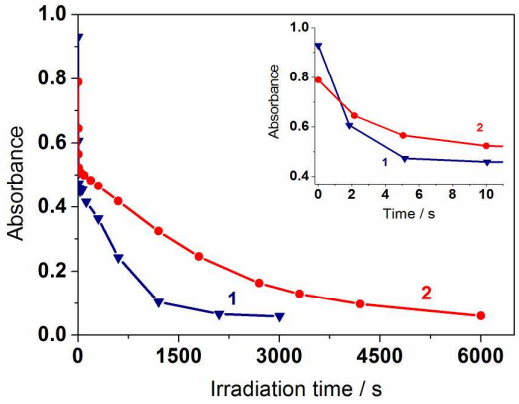


Figure 4. Dependence of the absorption of *E*-**1f** ($c_{\mathbf{1f}}$ = 0.03 mM) (at 358 nm) (*1*) and (*E*-**1f**)·Mg^{2+} ($c_{\mathbf{1f}}$ = 0.03 mM) (at 340 nm) (*2*) on the time of irradiation of the air-saturated solutions with a full light of a high pressure Hg lamp. Inset: development of the absorption changes during the first 10 seconds of irradiation.

These results can be reasonably interpreted if we consider the oxidative aromatization of the dihydrocyclic intermediate as a two-step process, where an electron transfer from the substrate to the oxidant precedes or follows the hydrogen abstraction. Thus, presence of the electron donating groups facilitates the electron transfer and, therefore, favors formation of the desired heteroaromatic cations **2c-f**. Indeed, the yield of the photoreaction increases with increasing donor strength of the substituents (*cf.* 52% for methoxy-derived compound **2d** *vs* 80% for amino-derived one **2c**). Introduction of the second donor group has the same effect of the yield increase for dimethoxy substituted product **2e** (70%) in comparison with monomethoxy substituted one **2d**. However, the yield of crown-containing product **2f** possessing similar substitution pattern as dimethoxy derivative **2e** was reduced (45%), most likely, due to lower photostability of the crown ether moiety. In the absence of donor substituents (**1a**) or in the presence of the acceptor (**1b**) the electron transfer is not effective enough overall resulting in predominant photodestruction rather than formation of the photocyclization products.

Conclusion

We have developed the regioselective C-N photocyclization of 2-styrylquinolines. It was found that irradiation of **1a-f** with filtered light (λ = 313, 365 nm) results only in *E–Z* isomerization whereas formation of polycyclic products **2c-f** requires irradiation with full light of Hg lamp, *i. e.* presence of the shorter wavelength UV light (λ < 300 nm) is essential for the occurrence of the cyclization. The photocyclization effectiveness is strongly dependent on the electronic factors of the substituents in the styryl moiety. Thus, the process is favored only in the presence of donor groups, whereas acceptor groups or the absence of any substituents do not support formation of the polycyclic products. Tuning of the donor strength allows to manipulate the photoreaction rate that was demonstrated by complexation of crown-modified styrylquinoline **1f** with Mg^{2+} cation. Overall, the studied phototransformation can be used as a very simple and effective approach towards synthesis of the potentially biologically active quino[1,2-*a*]quinolizinium derivatives.

Experimental section

All reagents and solvents were obtained from commercial sources and used as received. $Mg(ClO_4)_2$ for the complexation studies with crown-containing compounds was dried in vacuum at 230ºC. ^{1}H NMR spectra were recorded at 400 or 600 MHz, ^{13}C NMR spectra were recorded at 150 MHz at ambient temperature using 5 mm tubes. Chemical shifts were determined with accuracy of 0.01 ppm and 0.1 ppm for ^{1}H and ^{13}C spectra, respectively, and are given relative to the residual signal of the solvent that was used as internal reference. Spin–spin coupling constants were determined with accuracy of 0.1 Hz. Low-resolution electrospray ionization (ESI) mass spectra were detected in the mode of full mass scanning of positive ions on a tandem dynamic mass spectrometer equipped with a mass analyzer with an octapole ionic trap. High-resolution mass spectra were recorded on a time-of-flight instrument in a positive-ion mode using electrospray ionization method. Electronic absorption spectra were measured on a fiber-optic spectrometer connected to a computer at 20±1°C. 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).

Synthesis of the photocyclization products (2c-f)

The acetonitrile solutions (1 mM) of ***E*-1c-f** (50 mg; **1c**: 0.20 mmol, **1d**: 0.19 mmol, **1e**: 0.17 mmol, **1f**: 0.12 mmol) were irradiated with the immersed Hg photoreactor (125 W) under UV-Vis spectroscopy control. As soon as maximum conversion was reached the solvent was removed in vacuum, the residue was washed with hexane and recrystallized from MeOH with addition of $HClO_4$ to give the photocyclization products **2c-f** as perchlorate salts.

*3-aminoquinolino[1,2-a]quinolinium perchlorate (**2c**)*

Yield 80% (0.16 mmol), ^{1}H NMR (CD_3CN, 600 MHz) δ: 7.28 (splitted s, 1H, H-2', J = 2.7), 7.39 (dd, 1H, H-4', J = 9.6, 2.7), 7.92 (t, 1H, H-7, J = 6.9, 7.3), 7.97 (t, 1H, H-8, J = 6.9, 7.3), 8.01 (d, 1H, H-3, J = 8.7), 8.06 (d, 1H, H-a, J = 8.7), 8.26 (d, 1H, H-6, J = 8.2), 8.47 (d, 1H, H-4, J = 8.7), 8.56 (d, 1H, H-b, J = 8.7), 8.61 (d, 1H, H-5', J = 9.6), 8.83 (d, 1H, H-9, J = 8.2). ESI-MS **2c** in MeCN, *m/z*: calcd. 245.30; found 245.20 [**2c**]$^+$. HRMS *m/z* 245.1059 [**2c**]$^+$ (calcd. for $C_{17}H_{13}N_2$, 245.1073).

*3-methoxyquinolino[1,2-a]quinolinium perchlorate (**2d**)*

Yield 52% (0.10 mmol, 36 mg). ^{1}H NMR (CD_3CN, 600 MHz) δ: 4.07 (s, 3H, OCH_3), 7.64 (dd, 1H, H-4', J = 9.5, 2.9), 7.77 (splitted s, 1H, H-2', J = 2.9), 7.99-8.08 (m, 2H, H-7, H-8), 8.18 (d, 1H, H-a, J = 8.9), 8.20 (d, 1H, H-3, J = 8.6), 8.36 (d, 1H, H-6, J = 7.6), 8.71 (d, 1H, H-b, J = 8.9), 8.72 (d, 1H, H-4, J = 8.9), 8.85 (d, 1H, H-5', J = 9.5), 8.90 (d, 1H, H-9, J = 8.3). ^{13}C NMR (CD_3CN, 150 MHz) δ: 56.2, 108.6, 122.5, 123.2, 123.6, 123.7, 125.4, 125.5, 129.2, 129.5, 130.1, 131.3, 132.0, 132.8, 136.3, 139.3, 139.9, 160.1. Anal. calcd. for $C_{18}H_{14}ClNO_5$: C, 60.09; H, 3.92; N, 3.89; found: C, 60.12; H, 3.98; N, 3.95. ESI-MS **2d** in MeCN, *m/z*: calcd. 260.31; found 260.30 [**2d**]$^+$. HRMS *m/z* 260.1073 [**2d**]$^+$ (calcd. for $C_{18}H_{14}NO$, 260.1070).

*2,3-dimethoxyquinolino[1,2-a]quinolinium perchlorate (**2e**)*

Yield 70% (0.12 mmol, 47 mg). ^{1}H NMR (CD_3CN, 600 MHz) δ: 4.04 (s, 3H, OCH_3), 4.10 (s, 3H, OCH_3), 7.74 (s, 1H, H-2'), 7.95-8.03 (m, 2H, H-7, H-8), 8.07 (d, 1H, H-a, J = 5.7), 8.11 (d, 1H, H-3, J = 6.4), 8.31 (d, 1H, H-6, J = 8.3), 8.36 (s, 1H, H-5'), 8.58 (d, 1H, H-4, J = 8.9), 8.69 (d, 1H, H-b, J = 8.9), 9.03 (d, 1H, H-9, J = 8.3). ^{13}C NMR (CD_3CN, 150 MHz) δ: 57.5, 57.6, 105.7, 108.8, 122.1, 124.1, 124.3, 126.6, 130.0, 130.6, 131.0, 132.2, 134.7, 137.1, 138.6, 140.5, 145.3, 152.5, 155.3. Anal. calcd. for $C_{19}H_{16}ClNO_6$: C, 58.55; H, 4.14; N, 3.59; found: C 58.61; H, 4.11; N, 3.60. ESI-MS **2e** in MeCN, *m/z*: calcd. 290.34; found 290.20 [**2e**]$^+$. HRMS *m/z* 290.1175 [**2e**]$^+$ (calcd. for $C_{19}H_{16}NO_2$, 290.1176).

*11,12,14,15,17,18,20,21-octahydro[1,4,7,10,13]pentaoxacyclopentadecino[2,3-g]quino[1,2-a]quinolin-24-ium perchlorate (**2f**)*

Yield 45% (0.05 mmol, 28 mg), m.p. 224–226°C. ^{1}H NMR (CD_3CN, 600 MHz) δ: 3.64 (m, 4H, H-δ,δ'), 3.71 (m, 4H, H-γ,γ'), 3.89 (m, 2H, H-β), 3.92 (m, 2H, H-β'), 4.31 (m, 2H, H-α), 4.36 (m, 2H, H-α'), 7.70 (s, 1H, H-2'), 7.95-8.01 (m, 2H, H-7, H-8), 8.07 (d, 1H, H-a, J = 8.7), 8.09 (d, 1H, H-3, J = 9.2), 8.30 (d, 1H, H-6, J = 7.8), 8.32 (s, 1H, H-5'), 8.56 (d, 1H, H-4, J = 8.7), 8.66 (d, 1H, H-b, J = 8.7), 9.03 (d, 1H, H-9, J = 8.7). ^{13}C NMR (CD_3CN, 150 MHz) δ: 69.4, 69.5, 70.1, 70.5, 70.6, 71.8, 106.8, 110.1, 122.4, 124.4, 124.6, 126.8, 130.2, 130.9, 131.3, 132.6, 134.9, 137.4, 138.9, 140.8, 145.5, 152.0, 155.0. Anal. calcd. for $C_{25}H_{26}ClNO_9$: C, 57.75; H, 5.04; N, 2.69; found: C 57.81; H, 5.05; N, 2.74. ESI-MS **2f** in MeCN, *m/z*: calcd. 420.48; found 420.50 [**2f**]$^+$. HRMS *m/z* 420.1799 [**2f**]$^+$ (calcd. for $C_{25}H_{26}NO_5$, 420.1805).

Photochemical studies

The acetonitrile solutions of **1a-f** (*c* = 20 μM) were irradiated either with filtered light (λ = 313, 365 nm) or with full light of a high pressure mercury vapor lamp (120 W). Individual lines of the lamp emission spectrum (λ = 313, 365 nm) were isolated with the use of glass filters. All photoreactions were carried out in air-saturated solutions under stirring. The analysis of the reaction progress was performed by absorption spectroscopy.

Stability constant determination of the complex 1f·Mg^{2+}

Complex formation of **1f** with Mg^{2+} cation was studied by spectrophotometric titration in acetonitrile at 20 ± 1 °C. Upon addition of $Mg(ClO_4)_2$ the 1:1 (**1f**·Mg^{2+}) complex is formed due to the interaction of the magnesium cation with the crown-ether residue. The stability constant of the complex was determined using «SPECFIT/32» program. The stability constant value is log$K$ = 5.10 ± 0.02.

Associated content

Supporting Information

^{1}H and ^{13}C NMR spectra, HRMS data for all new compounds, optical spectroscopy and photochemical studies data, details of the computational methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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