

## Photoswitching of Redox Potentials and Spectroscopic Properties in the UV/vis Region

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The photoswitching of optical and electrochemical properties of di-donor, di-acceptor and donor-acceptor substituted photochromic tetrahydropyrene – [2,2]metacyclophanene and dihydropyrene – [2,2]metacyclophanediene systems has been studied theoretically. A switching of the half-wave oxidation and reduction potentials should be possible in the case of bis(pyridinium) and bis(hydroxyphenyl) substituted systems. Because of the relatively great perturbation of the planarity of the  $\pi$ -electron systems by large torsion of the substituents out of the  $\pi$ -electron structure of the photochromic system and the stair-like structure of the ring-opened isomer, relatively large excitation energies for CT transitions have been calculated with the AM1-CI procedure. The ring-closed structures should absorb in the visible spectral region, and the open-ring isomers should have a longest-wavelength absorption in the UV region.

*Key words:* Photoswitching, Redox Properties, Absorption spectra in UV/vis

### Introduction

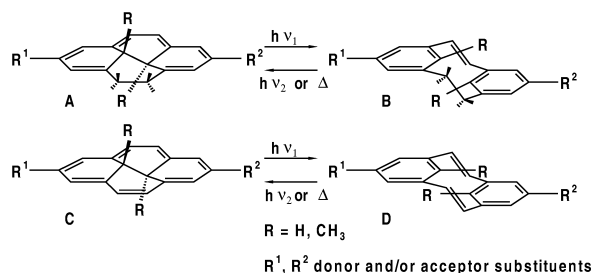
Photochromic diarylethenes, especially derivatives of dithienylethenes, have been used as photosensitive compounds for switching of different physical properties. These systems are potential candidates for active materials in photoswitching devices [1–3]. The reversible photochemically induced valence tautomerism was also realized with more rigid compounds, the 4,5,15,16-tetrahydropyrene-[2,2]metacyclophan-1-ene system [4], and the 15,16-dihydropyrene – [2,2]metacyclophanediene photochromic system [5–9] (see Scheme 1). The  $\pi$ -electron systems of the 4,5,15,16-tetrahydropyrene – [2,2]metacyclophan-1-ene photochromic system correspond to the  $\pi$ -systems of the 4a,4b-dihydrophenanthrene-*cis*-stilbene photochromic system. The [2,2]metacyclophan-1-enes contain rigidly constrained *cis*-stilbene moieties [4].

Contrary to most of diarylethenes, the ring-closed dihydropyrene isomer is the thermodynamically more stable photoisomer than the ring-opened isomer [6]. The ring closure of the [2,2]metacyclophanediene phototautomeric structure can be carried out either photochemically or in a thermal reaction.

Benzannulation [8] and acceptor substituents ( $R^1$ , see Scheme 1) and donor substituents ( $R^2$ , Scheme 1) in the *para*-like positions increase the reaction rate of both the thermal reaction and the photochemical reaction [6]. The photochemical ring-opening passes over an excited singlet state [6]. In the case of dithienylethenes with pyridinium cation substituents at both thiophene rings a very high cyclization quantum yield has been measured [10].

In a recent paper [11] we have investigated the photoswitching of dipole moment, absorption spectra, and the redox potentials of donor-acceptor substituted dihydropyrene-[2,2]metacyclophanediene photochromic systems with [2,2]metacyclophanediene betaine and merocyanine structure, respectively. The strong switching effect is due to the [2,2]metacyclophanediene fragment which acts as a  $\pi$ -electron conjugation barrier.

The aim of this paper is to investigate theoretically the possibility to switch photochemically the oxidation/reduction potentials and the absorption spectra in the UV and visible spectral region of di-substituted



Scheme 1.

tetrahydropyrene (**A**)–[2,2]metacyclophane (**B**), and dihydropyrene (**C**) – [2,2]metacyclophanediene (**D**) photochromic systems, respectively (Scheme 1).

### Objects of Investigations

The (model) compounds investigated in this paper are 2,7-disubstituted photochromic 4,5,15,16(dimethyl)-tetrahydropyrene  $\rightleftharpoons$  [2,2]metacyclophan-1-ene systems and (trans-15,16-dimethyl)dihydropyrene  $\rightleftharpoons$  [2,2]metacyclophanediene systems, respectively (Scheme 1). Different substituent patterns have been selected to switch the electrochemical and optical properties. In the first group of compounds (see Figs 1 and 2) the substituents R<sup>1</sup> and R<sup>2</sup> (Scheme 1) are both either electron donors or electron acceptors. In photochromic system **1(2)red(c)**–**1(2)red(o)** the substituents are phenolic groups which can be oxidized to quinonoid residues only in the closed-ring isomer (Fig. 1). In structures **3** and **4** the 1-pyridinium substituents are connected with the photochromic system, and in structures **5** and **6** the pyridinium groups are linked at the 4-positions to the photochromic system (Fig. 2). In the closed-ring isomers, **5(6)ox(c)**, the 4-pyridinium substituents could be reduced to dihydropyridine groups. In the reduced forms, **5(6)red**, the photochromic ring-opening reaction should be blocked up.

In (model) systems **7–14** the substituents R<sup>1</sup> and R<sup>2</sup> are of different type (Figs 3 and 4). Two types of conjugated  $\pi$ -electron systems can be considered. If the nitrogen atoms are separated by an even number of carbon atoms of the closed-ring isomer, then the conjugated  $\pi$ -electron system has an electron donor-acceptor substituted polyene-like structure (**7(c)**, **8(c)**, Fig. 3). When the N atoms are separated by an odd number of carbon atom (**9(c)** to **14(c)**, Fig. 4) then the conjugated  $\pi$ -electron system is a polymethine (asymmetrical cyanine) system.

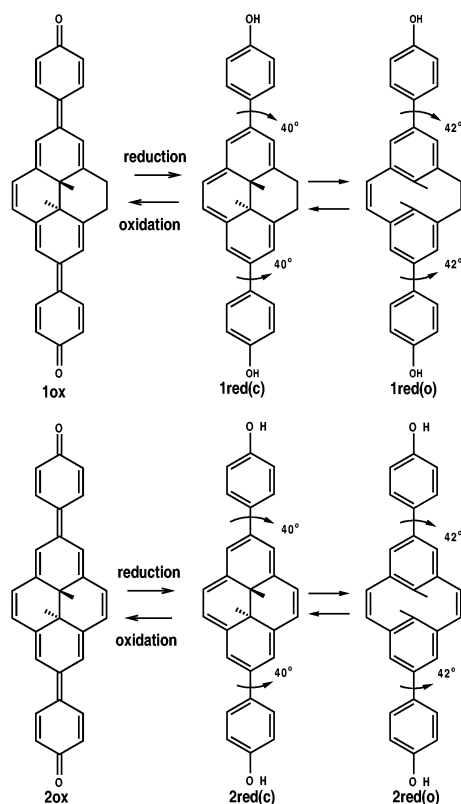


Fig. 1. Photochromic systems with phenolic – quinonoid redox pair substituents.

The photoswitching of optical and electrochemical properties of disubstituted 1,2-bis(thien-3'-yl)perfluoropentene photochromic systems with either both electron donor (acceptor) substituents or a donor and an acceptor substituent has been investigated experimentally by J.-M. Lehn *et al.* [12, 13] and by H. Port *et al.* [14]. F.D. Lewis *et al.* [15] have measured the change of the optical properties of push-pull substituted stilbene/4a,4b-dihydrophenanthrene photochromic systems.

### Methods of Investigations

Geometry optimization and calculation of the heats of formation (AM1) and total energies (*ab initio*) of the di-substituted valence tautomers **C** (closed-ring isomer) and **O** (open-ring isomer), Figures 1–4, have been performed with the semiempirical quantum-chemical AM1 method [16, 17] and with the *ab initio* method (basis set 6-31G\*) [17].  $S_0 \rightarrow S_n$  excitation energies and transition dipole moments are cal-

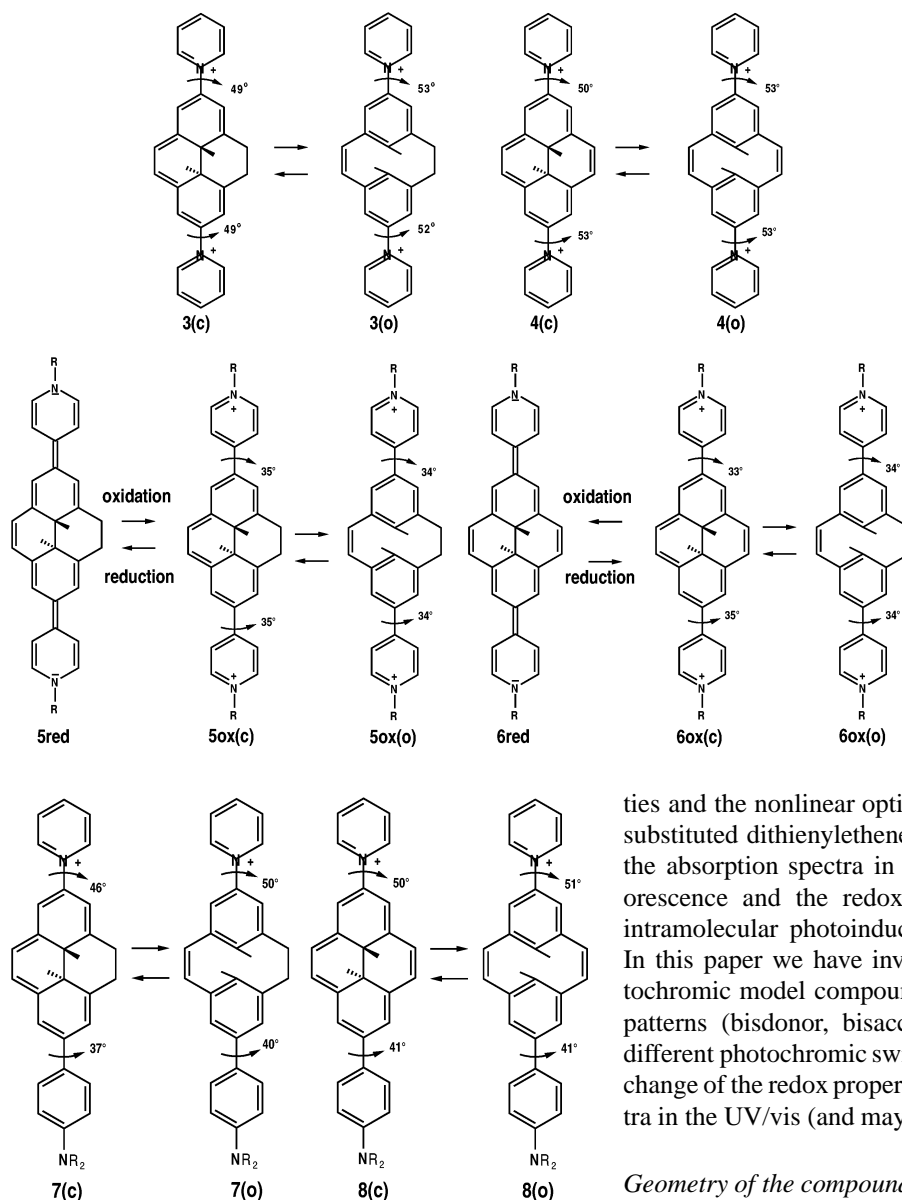


Fig. 3. Photochromic push – pull polyene systems.

culated within the singly-excited configuration interaction (SCI) approach for the AM1 Hamiltonian [18].

## Results and Discussion

Bisacceptor, bisdonor and donor-acceptor substituted dithienylethenes have been investigated as models of light-triggered molecular devices [12,13] to use the photochromic and electrochromic properties for switching the optical and electrochemical proper-

ties and the nonlinear optical activity. Donor-acceptor substituted dithienylethenes have been used to switch the absorption spectra in the UV/vis region, the fluorescence and the redox properties caused by the intramolecular photoinduced charge separation [14]. In this paper we have investigated theoretically photochromic model compounds with similar substituent patterns (bisdonor, bisacceptor, donor-acceptor) but different photochromic switching moieties to study the change of the redox properties and the absorption spectra in the UV/vis (and may be NIR) spectral region.

### Geometry of the compounds

While the conjugated  $\pi$ -electron system of the ring-closed photochromic tetrahydropyrene and dihydropyrene fragments are more or less planar, the ring-opened [2,2]metacyclophanene and [2,2]metacyclophanediene fragments have a stair-like structure. The donor and acceptor substituents are relatively strongly twisted at about  $30^\circ$  to  $50^\circ$  out of the  $\pi$ -electron system of the central photochromic part of the molecules. The dihedral angles of the AM1 optimized structures are given in Figs 1–4. Particularly large dihedral angles ( $\Theta > 50^\circ$ ) have been calculated for the 1-pyridinium

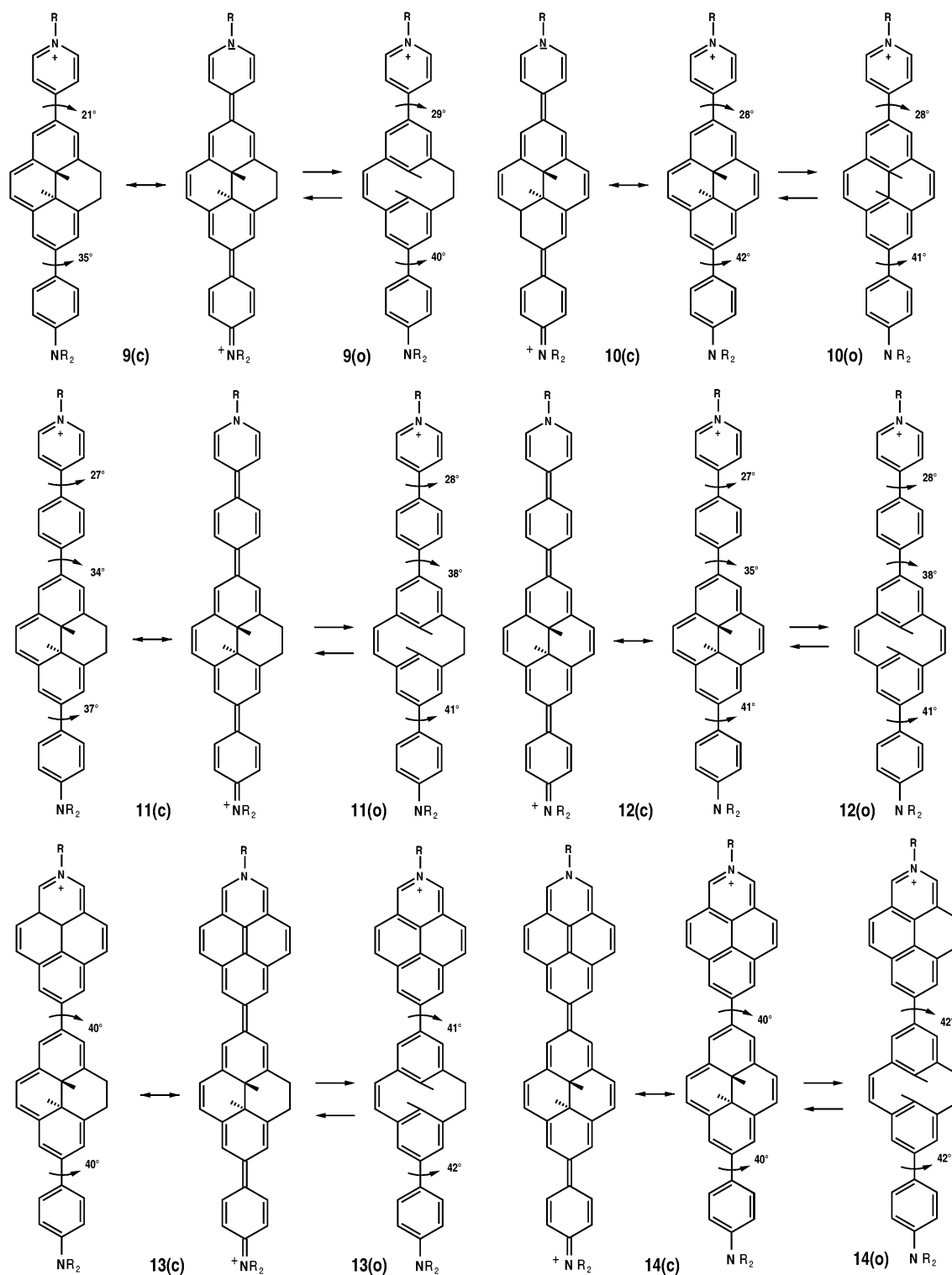


Fig. 4. Photochromic polymethine systems.

Table 1. Heats of formation,  $\Delta H^f$ , and energy difference between the isomers,  $\Delta\Delta H^f$ , (AM1, in kcal/mol) and total energies  $\Delta E$  (*ab initio*, 6-31G\*, in a. u.), and energy difference between the isomers  $\Delta\Delta E$  (*ab initio*, 6-31G\*, in kcal/mol) of geometry optimized structures of the photoisomers (see Figs 1–4).

Photoisomer	$\Delta H^f$	$\Delta\Delta H^f$	$\Delta E$	$\Delta\Delta E$
<b>1ox</b>	96.8		-1221.6102	
<b>1red(c)</b>	39.2		-1222.7954	
<b>1red(o)</b>	37.7	-1.45	-1222.8121	-10.48
<b>2ox</b>	122.0		-1220.4358	
<b>2red(c)</b>	62.8		-1221.6316	
<b>2red(o)</b>	70.9	2.11	-1221.6112	12.80
<b>3(c)</b>	500.8		-1105.7764	
<b>3(o)</b>	500.6	-0.24	-1105.7869	-6.59
<b>4(c)</b>	526.4		-1104.6056	
<b>4(o)</b>	534.5	8.07	-1104.5847	13.11
<b>5red</b>	155.3		-1106.1850	
<b>5ox(c)</b>	470.7		-1105.8037	
<b>5ox(o)</b>	469.6	-1.05	-1105.8131	-5.90
<b>6red</b>	179.5		-1105.0134	
<b>6ox(c)</b>	495.2		-1104.6327	
<b>6ox(o)</b>	503.3	8.05	-1104.6113	13.43
<b>7(c)</b>	290.9		-1144.4959	
<b>7(o)</b>	290.8	-0.15	-1144.5061	-6.40
<b>8(c)</b>	324.2		-1143.3280	
<b>8(o)</b>	324.2	10.32	-1143.3046	14.68
<b>9(c)</b>	277.8		-1144.5046	
<b>9(o)</b>	278.8	0.97	-1144.5145	6.21
<b>10(c)</b>	300.5		-1143.3427	
<b>10(o)</b>	312.1	11.58	-1143.3132	18.51
<b>11(c)</b>	306.1		-1374.0487	
<b>11(o)</b>	305.0	-1.11	-1374.0641	-9.66
<b>12(c)</b>	329.8		-1372.8842	
<b>12(o)</b>	338.3	8.45	-1372.8629	13.37
<b>13(c)</b>	323.7		-1525.5691	
<b>13(o)</b>	322.4	-1.32	-1525.5805	-7.15
<b>14(c)</b>	347.2		-1524.4010	
<b>14(o)</b>	355.7	8.50	-1524.3794	13.55

substituents in the para-like positions of the systems **3** and **4**. There is no significant difference in the dihedral angles of the ring-opened isomer and the corresponding ring-closed isomer. The significant deviations from planarity (relatively large dihedral angles, stair-like structure of the ring-opened structure) prevent an optimal delocalization of the conjugated  $\pi$ -electron system of the push-pull polyene structure and the polymethine structure, respectively. Therefore, in contrast with completely planar push-pull polyenes and polymethines, absorption in the NIR spectral region cannot be expected.

#### Energetic properties of the photoisomers

In Table 1 are summarized the heats of formation,  $\Delta H^f$ , and the total energies,  $\Delta E$ , of the optimized

Table 2. Energies of the highest occupied molecular orbital,  $\epsilon(\text{HOMO})$ , and the lowest unoccupied molecular orbital,  $\epsilon(\text{LUMO})$ , calculated with the AM1 and *ab initio* (6-31G\*) procedures, respectively. All values are in eV.

Photoisomer	AM1		<i>ab initio</i>	
	$\epsilon(\text{HOMO})$	$\epsilon(\text{LUMO})$	$\epsilon(\text{HOMO})$	$\epsilon(\text{LUMO})$
<b>1ox</b>	-8.43	-2.00	-7.55	0.32
<b>1red(c)</b>	-7.66	-0.94	-6.35	1.86
<b>1red(o)</b>	-8.32	-0.41	-7.29	2.57
<b>2ox</b>	-8.28	-2.24	-7.34	-0.10
<b>2red(c)</b>	-7.75	-1.00	-6.45	1.79
<b>2red(o)</b>	-8.31	-0.54	-7.27	2.25
<b>3(c)</b>	-13.37	-7.00	-12.42	-4.16
<b>3(o)</b>	-14.13	-6.86	-13.38	-3.95
<b>4(c)</b>	-13.53	-7.04	-12.63	-4.14
<b>4(o)</b>	-14.11	-6.87	-13.31	-3.95
<b>5red</b>	-6.63	-0.30	-5.38	2.67
<b>5ox(c)</b>	-12.65	-6.99	-11.74	-4.68
<b>5ox(o)</b>	-13.41	-6.88	-12.69	-4.29
<b>6red</b>	-6.46	-0.53	-5.10	2.31
<b>6ox(c)</b>	-12.80	-7.03	-11.92	-4.73
<b>6ox(o)</b>	-13.39	-6.89	-12.69	-4.34

structures of photoisomers calculated by the AM1 and *ab initio* method, respectively. From the energy differences between the photoisomers,  $\Delta\Delta H^f$  and  $\Delta\Delta E$ , it can be seen that in the case of the tetrahydropyrene  $\Leftrightarrow$  [2,2]metacyclophanene photochromic systems the ring-opened isomer is more stable than the ring-closed structure, while the ring-closed isomer of the dihydropyrene  $\Leftrightarrow$  [2,2]metacyclophanediene photoresponsive system is more stable than the ring-opened valence tautomer. The results obtained with the semiempirical all valence electron procedure AM1 are in good agreement with those calculated with the *ab initio* method.

#### Electrochemical properties

The energies of the highest occupied MOs ( $\epsilon(\text{HOMO})$ ) and the lowest unoccupied MOs ( $\epsilon(\text{LUMO})$ ) calculated with the semiempirical all valence electron method AM1 and with the *ab initio* method for the optimized structures of the photosensitive isomers **1–6** are collected in Table 2. In Fig. 5 are shown the energies of the frontier orbitals, HOMO and LUMO, to demonstrate the changes of these energies for the reduction process of the ring-closed photoisomers **1(2)ox** to **1(2)red(c)**, and for the oxidation of **5(6)red** to **5(6)ox(c)**, respectively. In the case of the quinonoid structures **1(2)ox** the ring-opening reaction is possible only when these structures are reduced to the phenolic structures **1(2)red(c)**. On the other hand, a direct photochemical or thermal ring-opening of the structures **5(6)red** is impossible, but after (may

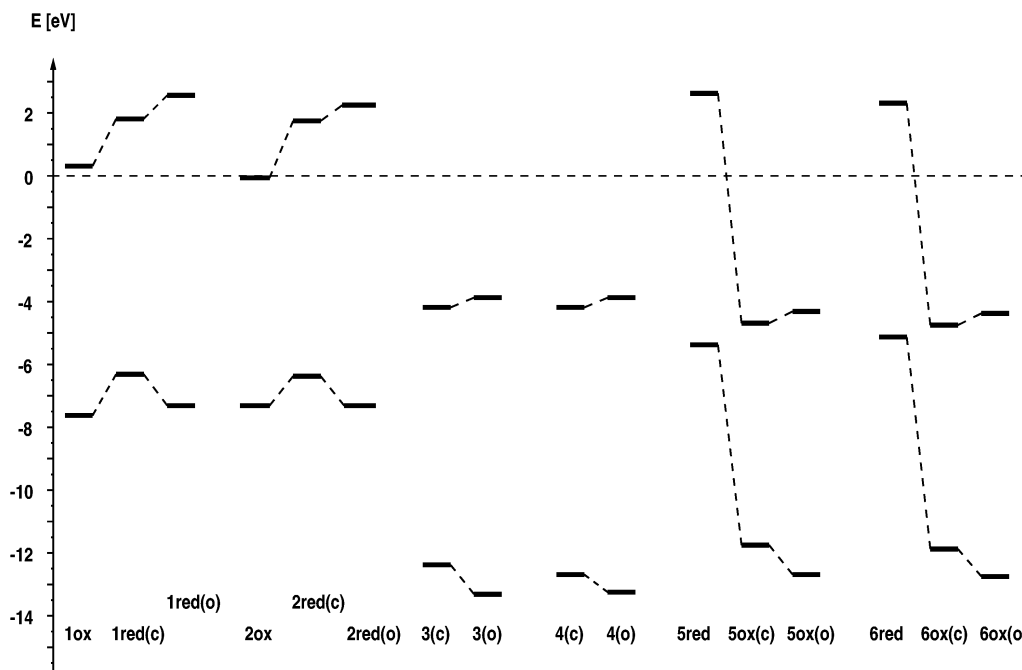


Fig. 5. Energies of the frontier orbitals,  $\epsilon(\text{HOMO})$  and  $\epsilon(\text{LUMO})$ , calculated by the *ab initio* method (6-31G\* basis set).

be two successive one-electron) oxidation steps to the viologen-like ring-closed forms **5(6)ox(c)** the ring-opening should be possible.

Especially the HOMO energies are changed at the photochromic reaction of systems **1** to **6**. Because of the lower lying HOMOs of the ring-opened forms the corresponding oxidation half-wave potential should be lower in value in comparison with those of the ring-closed forms. As can be seen from Fig. 5 the LUMO energies of the ring-closed and ring-opened photoisomers are of the same order of magnitude, and a switching of the reduction half-wave potentials should be less effective.

In the case of the ring-closed and ring-opened isomers of the photochromic systems **7–14** the energies of the frontier orbitals are comparable, and no switching of the redox properties should be effective.

#### Switching of the light absorption properties

In Tables 3–5 are summarized the absorption characteristics of the photochromic systems investigated in this paper. Generally, the closed-ring isomers should have a longest-wavelength absorption in the visible region, and the ring-opened isomers should have a longest-wavelength absorption in the UV spectral re-

gion. There are no significant differences in the excitation energies and the intensities of the tetrahydropyrene  $\rightleftharpoons$  [2,2]metacyclophanene and the dihydropyrene  $\rightleftharpoons$  [2,2]metacyclophanediene photoresponsive system, respectively.

In Table 3 are collected the data of the photochromic redox systems **1–6**. It is surprising that the quinonoid structures **1ox** and **2ox** have a relatively short-wavelength absorption at the short-wavelength visible region. The reduced phenolic closed-ring isomers should have an absorption in the visible region caused by a local excitation in the whole  $\pi$ -system, and the ring-opened isomers absorb in the UV region with low intensity caused also by a local electron excitation.

The ring-closed isomers as well as the ring-opened isomers of the bis(1-pyridinium)-substituted photochromic systems **3** and **4** are characterized by a longest-wavelength charge-transfer (CT) transition in the visible spectral region. The CT excitation energies of the ring-closed isomers of the oxidized forms of the 4-pyridinium disubstituted photochromic systems **5** and **6** are relatively small corresponding to an absorption in the visible region, while the ring-opened isomers absorb in the ultraviolet region.

Similar features of the CT excitation with relatively large excitation energies are characteristic for

Table 3. Vertical  $S_0 \rightarrow S_n$  transition energies  $\Delta E$  (in eV and nm), transition dipole moments,  $M$ , and oscillator strengths  $f$  for the substituted photochromic systems **1–6** in the ring-closed (**c**) and ring-opened (**o**) forms.

System		<b>c</b>			<b>o</b>		
		$\Delta E$ (eV)	$\Delta E$ (nm)	$M(f)^a$	$\Delta E$ (eV)	$\Delta E$ (nm)	$M(f)^a$
<b>1ox</b>	1	2.96	419	3.5 (3.15)	–	–	–
	2	3.62	343	0 (0)	–	–	–
<b>1red</b>	1	2.62	473	1.1 (0.28)	3.68	337	0.3 (0.03)
	2	3.81	325	0.4 (0.06)	3.69	336	0 (0)
<b>2ox</b>	1	2.87	432	3.8 (3.55)	–	–	–
	2	3.20	387	0 (0)	–	–	–
<b>2red</b>	1	2.44	509	0.5 (0.05)	3.51	353	0 (0)
	2	3.52	352	0.5 (0.08)	3.58	346	0.4 (0.05)
<b>3</b>	1	2.57	482	0.8 (0.14)	3.74	331	0.3 (0.03)
	2	3.84	323	1.1 (0.41)	3.75	331	0.2 (0.01)
<b>4</b>	1	2.44	508	0.3 (0.02)	3.55	349	0.0 (0)
	2	3.54	351	0.1 (0.00)	3.62	343	0.4 (0.05)
<b>5red</b>	1	2.89	430	3.2 (2.64)	–	–	–
	2	3.04	408	0.5 (0.08)	–	–	–
<b>5ox</b>	1	2.24	552	1.4 (0.40)	3.41	364	1.0 (0.33)
	2	3.09	402	0.8 (0.15)	3.51	354	0.3 (0.03)
<b>6red</b>	1	2.80	444	3.6 (3.14)	–	–	–
	2	2.99	414	0 (0.0)	–	–	–
<b>6ox</b>	1	2.24	555	1.2 (0.28)	3.32	373	0 (0.0)
	2	3.01	411	0.8 (0.17)	3.36	369	1.0 (0.32)

<sup>a</sup> The oscillator strength  $f$  has been calculated with the equation:  $f = 0.087516\Delta E(\text{eV})|M|^2$ .

Table 4. Vertical  $S_0 \rightarrow S_n$  transition energies,  $\Delta E$  (in eV and nm), transition dipole moments  $M$ , and oscillator strengths  $f$  for the substituted photochromic systems **7** and **8** in the ring-closed (**c**) and ring-open (**o**) forms.

System		<b>c</b>			<b>o</b>		
		$\Delta E$ (eV)	$\Delta E$ (nm)	$M(f)^a$	$\Delta E$ (eV)	$\Delta E$ (nm)	$M(f)^a$
<b>7</b>	1	2.23	556	1.1 (0.23)	3.50	354	0.3 (0.02)
	2	2.99	414	0.2 (0.01)	3.62	342	0.3 (0.04)
<b>8</b>	1	2.20	564	0.7 (0.09)	3.41	363	0.3 (0.04)
	2	3.02	411	0.5 (0.07)	3.45	360	0 (0.0)

<sup>a</sup> The oscillator strength  $f$  has been calculated with the equation:  $f = 0.087516\Delta E(\text{eV})|M|^2$ .

the donor–acceptor disubstituted photochromic systems which can be considered as push-pull polyenes **7** and **8** (see Table 4). The relatively great perturbation of the planarity of the  $\pi$ -electron system by large torsion angles of the donor and acceptor substituents and additionally by the stair-like structure of the ring-opened structure may be the reason for the relatively large excitation energies and the small intensities.

The spectral characteristics (Table 5), structural parameters, and electronic structure of the systems **9–**

Table 5. Vertical  $S_0 \rightarrow S_n$  transition energies  $\Delta E$  (in eV and nm), transition dipole moments  $M$ , and oscillator strengths  $f$  for the substituted photochromic systems **9–14** in the closed-ring (**c**) and open-ring (**o**) forms.

System		<b>c</b>			<b>o</b>		
		$\Delta E$ (eV)	$\Delta E$ (nm)	$M(f)^a$	$\Delta E$ (eV)	$\Delta E$ (nm)	$M(f)^a$
<b>9</b>	1	1.75	710	2.2 (0.72)	2.96	419	0.8 (0.18)
	2	3.05	407	0.9 (0.20)	3.23	384	0.3 (0.03)
<b>10</b>	1	1.89	656	0.4 (0.03)	2.94	421	1.0 (0.25)
	2	1.90	654	2.7 (1.20)	2.97	418	0.4 (0.05)
<b>11</b>	1	2.40	516	1.4 (0.43)	3.26	380	0.8 (0.20)
	2	2.88	431	0.1 (0.0)	3.37	368	0.2 (0.02)
<b>12</b>	1	2.40	516	1.1 (0.25)	3.24	382	0.8 (0.18)
	2	2.89	429	0.5 (0.06)	3.33	372	0.3 (0.04)
<b>13</b>	1	2.30	538	1.6 (0.52)	3.05	406	1.3 (0.44)
	2	2.82	439	0.5 (0.05)	3.25	381	0.9 (0.23)
<b>14</b>	1	2.30	540	1.4 (0.38)	3.10	400	0.8 (0.18)
	2	2.72	456	0.5 (0.05)	3.36	369	0.5 (0.08)

<sup>a</sup> The oscillator strength  $f$  has been calculated with the equation:  $f = 0.087516\Delta E(\text{eV})|M|^2$ .

**14** are not in agreement with a polymethine (cyanine) structure (maximum equilization of the bond lengths, charge alternation along the polymethine chain) [19] as it was described in Section 2. One reason may be also for these systems the relatively strong perturbation of the planarity of the  $\pi$ -electron system. Because of the relatively large twisting of the photochromic system from the substituents the local excitations (typically for a polymethine  $\pi$ -system) require relatively large energies, and therefore CT excitations are dominant. So, a switching of an absorption in the visible region to an absorption in the UV region should be realized.

## Conclusions

Based on quantum-chemical *ab initio* (basis set 6-31G\*), AM1 and AM1-CI calculations of the isomeric forms of 2,7-disubstituted photochromic tetrahydropyrene – [2,2]metacyclophanene and dihydropyrene – [2,2]metacyclophanediene systems the photoswitching of the following physical properties have been discussed:

(i) In the case of bis(4-hydroxyphenyl), bis(1-pyridinium) and bis(4-pyridinium) substituted photochromic systems, the switching of the oxidation and reduction half-wave potentials should be possible. The calculated HOMO and LUMO energies show that both the oxidation and the reduction should be more difficult for the ring-opened isomer in relation to the ring-closed form.

(ii) With all the systems investigated in this paper a photoswitching of the absorption spectra from a longest-wavelength absorption in the visible region of the ring-closed to a longest-wavelength band in the UV region of the ring-opened isomer should be possible.

(iii) The ring-opened photoisomer of the 2,7-disubstituted tetrahydropyrene - [2,2]metacyclophanene

photochromic systems is more stable than the ring-closed isomer, while the opposite is valid for the substituted dihydropyrene - [2,2]metacyclophanediene photochromic systems.

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