

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 π -electron systems by large torsion of the substituents out of the π -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

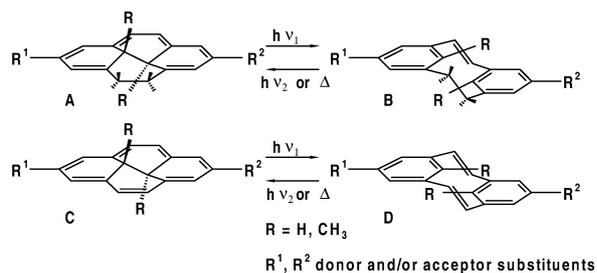
Photochromic diarylethenes, especially derivatives of dithienylethenes, have been used as photosensitive compounds for switching of different physical properties. These systems are potential candidates for active materials in photoswitching devices [1–3]. The reversible photochemically induced valence 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 π -electron systems of the 4,5,15,16-tetrahydropyrene – [2,2]metacyclophan-1-ene photochromic system correspond to the π -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 pho-

tochemically 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 π -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 R¹ and R² (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 R¹ and R² are of different type (Figs 3 and 4). Two types of conjugated π -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 π -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 π -electron system is a polymethine (asymmetrical cyanine) system.

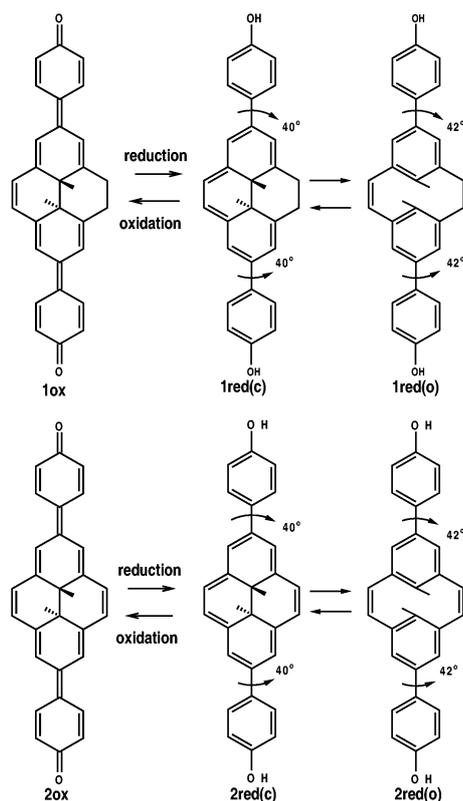


Fig. 1. Photochromic systems with phenolic – quinonoid redox pair substituents.

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-

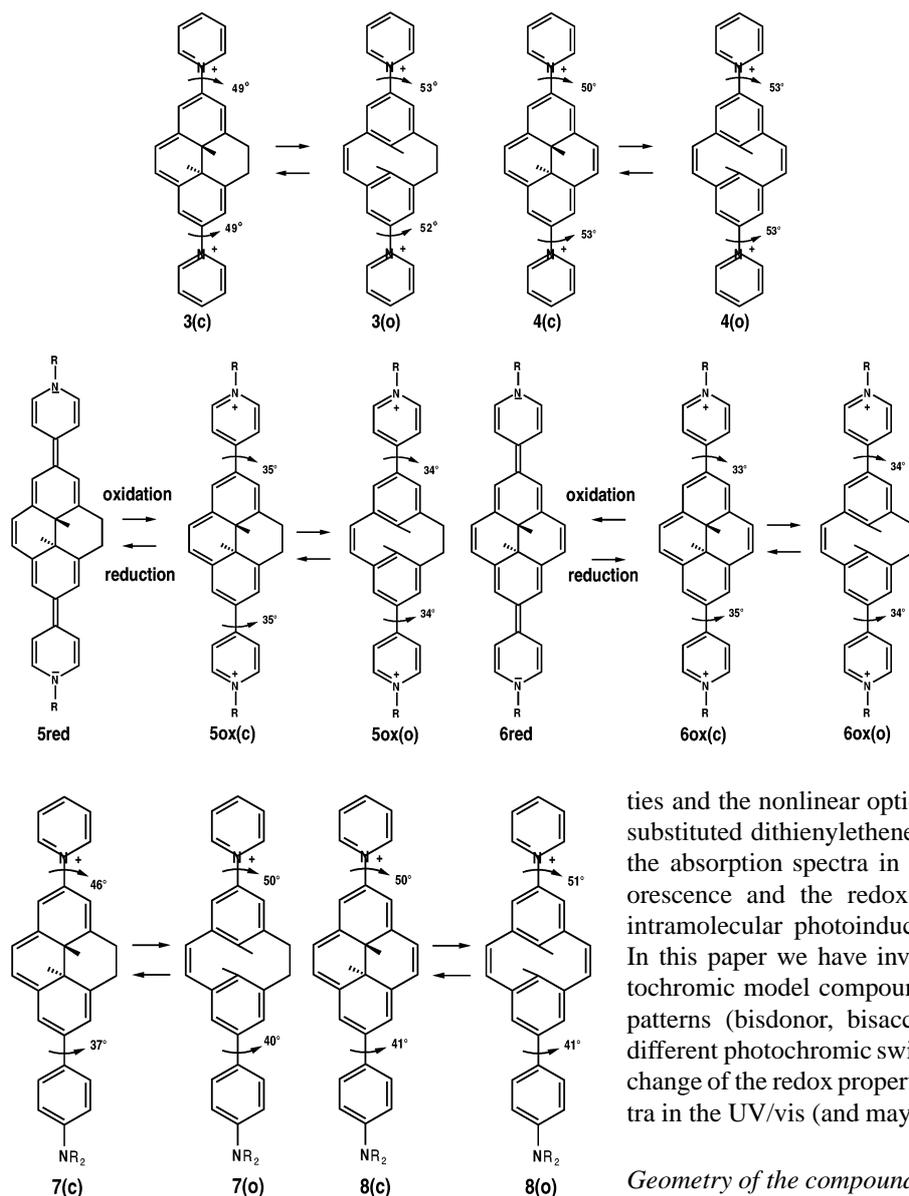


Fig. 3. Photochromic push – pull polyene systems.

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 π -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° to 50° out of the π -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

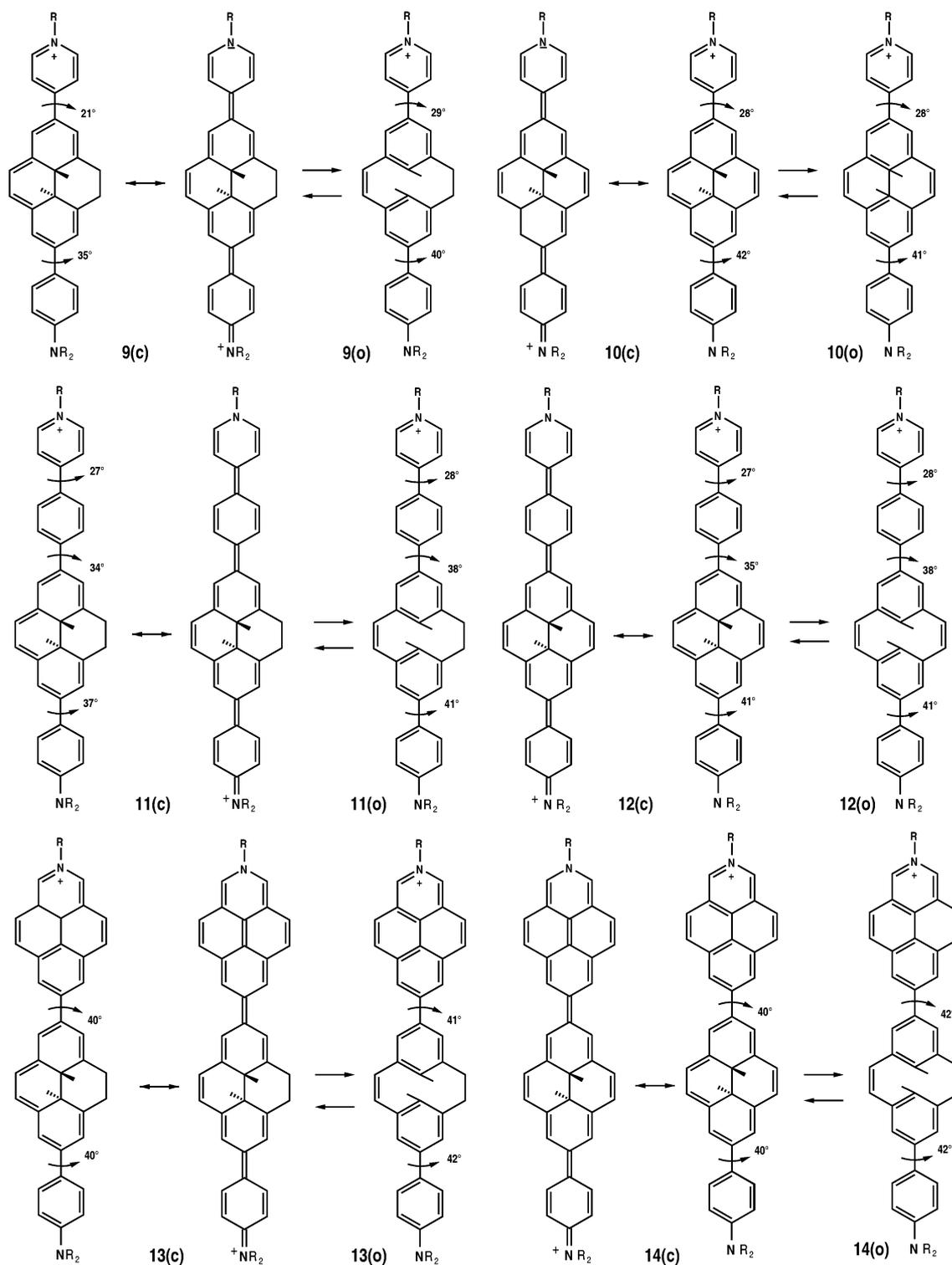


Fig. 4. Photochromic polymethine systems.

Table 1. Heats of formation, ΔH^f , and energy difference between the isomers, $\Delta\Delta H^f$, (AM1, in kcal/mol) and total energies ΔE (*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	ΔH^f	$\Delta\Delta H^f$	ΔE	$\Delta\Delta E$
1ox	96.8		-1221.6102	
1red(c)	39.2		-1222.7954	
1red(o)	37.7	-1.45	-1222.8121	-10.48
2ox	122.0		-1220.4358	
2red(c)	62.8		-1221.6316	
2red(o)	70.9	2.11	-1221.6112	12.80
3(c)	500.8		-1105.7764	
3(o)	500.6	-0.24	-1105.7869	-6.59
4(c)	526.4		-1104.6056	
4(o)	534.5	8.07	-1104.5847	13.11
5red	155.3		-1106.1850	
5ox(c)	470.7		-1105.8037	
5ox(o)	469.6	-1.05	-1105.8131	-5.90
6red	179.5		-1105.0134	
6ox(c)	495.2		-1104.6327	
6ox(o)	503.3	8.05	-1104.6113	13.43
7(c)	290.9		-1144.4959	
7(o)	290.8	-0.15	-1144.5061	-6.40
8(c)	324.2		-1143.3280	
8(o)	324.2	10.32	-1143.3046	14.68
9(c)	277.8		-1144.5046	
9(o)	278.8	0.97	-1144.5145	6.21
10(c)	300.5		-1143.3427	
10(o)	312.1	11.58	-1143.3132	18.51
11(c)	306.1		-1374.0487	
11(o)	305.0	-1.11	-1374.0641	-9.66
12(c)	329.8		-1372.8842	
12(o)	338.3	8.45	-1372.8629	13.37
13(c)	323.7		-1525.5691	
13(o)	322.4	-1.32	-1525.5805	-7.15
14(c)	347.2		-1524.4010	
14(o)	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 π -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, ΔH^f , and the total energies, ΔE , 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>	
	$\epsilon(\text{HOMO})$	$\epsilon(\text{LUMO})$	$\epsilon(\text{HOMO})$	$\epsilon(\text{LUMO})$
1ox	-8.43	-2.00	-7.55	0.32
1red(c)	-7.66	-0.94	-6.35	1.86
1red(o)	-8.32	-0.41	-7.29	2.57
2ox	-8.28	-2.24	-7.34	-0.10
2red(c)	-7.75	-1.00	-6.45	1.79
2red(o)	-8.31	-0.54	-7.27	2.25
3(c)	-13.37	-7.00	-12.42	-4.16
3(o)	-14.13	-6.86	-13.38	-3.95
4(c)	-13.53	-7.04	-12.63	-4.14
4(o)	-14.11	-6.87	-13.31	-3.95
5red	-6.63	-0.30	-5.38	2.67
5ox(c)	-12.65	-6.99	-11.74	-4.68
5ox(o)	-13.41	-6.88	-12.69	-4.29
6red	-6.46	-0.53	-5.10	2.31
6ox(c)	-12.80	-7.03	-11.92	-4.73
6ox(o)	-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

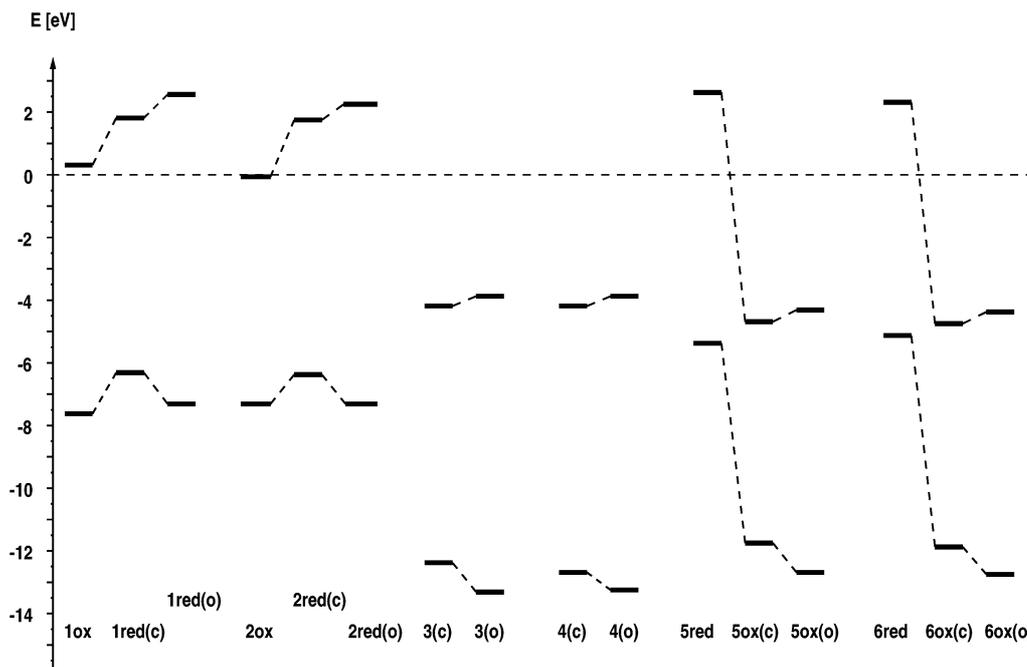


Fig. 5. Energies of the frontier orbitals, $\epsilon(\text{HOMO})$ and $\epsilon(\text{LUMO})$, calculated by the *ab initio* method (6-31G* basis set).

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 π -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 ΔE (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		c			o		
		ΔE (eV)	ΔE (nm)	$M(f)^a$	ΔE (eV)	ΔE (nm)	$M(f)^a$
1ox	1	2.96	419	3.5 (3.15)	–	–	–
	2	3.62	343	0 (0)	–	–	–
1red	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)
2ox	1	2.87	432	3.8 (3.55)	–	–	–
	2	3.20	387	0 (0)	–	–	–
2red	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)
3	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)
4	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)
5red	1	2.89	430	3.2 (2.64)	–	–	–
	2	3.04	408	0.5 (0.08)	–	–	–
5ox	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)
6red	1	2.80	444	3.6 (3.14)	–	–	–
	2	2.99	414	0 (0.0)	–	–	–
6ox	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)

^a 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, ΔE (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		c			o		
		ΔE (eV)	ΔE (nm)	$M(f)^a$	ΔE (eV)	ΔE (nm)	$M(f)^a$
7	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)
8	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)

^a 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 π -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 ΔE (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		c			o		
		ΔE (eV)	ΔE (nm)	$M(f)^a$	ΔE (eV)	ΔE (nm)	$M(f)^a$
9	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)
10	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)
11	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)
12	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)
13	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)
14	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)

^a 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 π -electron system. Because of the relatively large twisting of the photochromic system from the substituents the local excitations (typically for a polymethine π -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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