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Photoswitching of the magnetic properties of one-dimensional π-electron systems

III. Photochromic polymers with polymethine radicals in the elementary units

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Dedicated to Prof. Dr. Peter Welzel on the occasion of his 65th birthday.

Abstract

The switching of the magnetic properties of the photoisomeric structures of polymers with photochromic [2,2]-metacyclophanene, [2,2]-metacyclophanediene, 10-benzylidene-anthrone or 9-benzylidene-9,10-anthracene fragments and polymethine radical fragments of Wurster and Weitz type within the elementary units is investigated theoretically. The band theory is used to calculate the effective exchange interaction of the open-ring and closed-ring photoisomers, respectively. A real switching from a ferromagnetic to an anti-ferromagnetic state of the isomers has been found only for a few polymers, while in most cases an increase or decrease of the effective exchange integral at the photocyclization has been pointed out.

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Keywords: Photochromic polymers; Photoswitching; Magnetic properties; Polymethine radicals

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1. Introduction

Photochromic compounds—molecules, oligomers and polymers—are potential canditates for active materials in photoswitching devices [1–3]. Based on the reversible change in molecular and electronic structure of photoresponsive compounds upon irradiation with light, many physical properties can be switched [4]. Thus photocontrol of the magnetic properties of radical-substituted photochromic diarylethenes has been recently established ([5,6], and references given therein). In earlier papers [7,8] we have investigated theoretically the photoswitching of magnetic properties in model one-dimensional (1D) polymers containing di-(het)arylethenes and methylene groups ($–CH_2^\bullet$) as photoresponsive fragments and radical centers in the elementary units (EU), respectively. However, the photocyclizations of stilbenes (a), [2,2]-metacyclophanenes (b), and [2,2]-metacyclophanedienes (c), shown in Scheme 1 are even mode ubiquitous photochromic reactions.

The molecules above are viewed as bridging units, whose photoisomerization can modify or even reverse the effective spin-exchange coupling they provide to attached monoradicals, leading to cross-over from ferromagnetic to anti-ferromagnetic behavior (or vice versa).

The aim of the present work is to investigate theoretically that issue on the example of photochromic polymers containing stable polymethine radicals of Wurster and Weitz types in the EUs.

2. Photochromic polymers

The polymers addressed herein are assumed to be one-dimensional systems for which periodic boundary conditions are valid. The EU consists of a photochromic [2,2]-metacyclophanene (a), [2,2]-metacyclophanediene (b), 10-benzylidene-anthrone (c) or 9-benzylidene-9,10-dihydro-anthracene (d) fragments (Scheme 2), connected to

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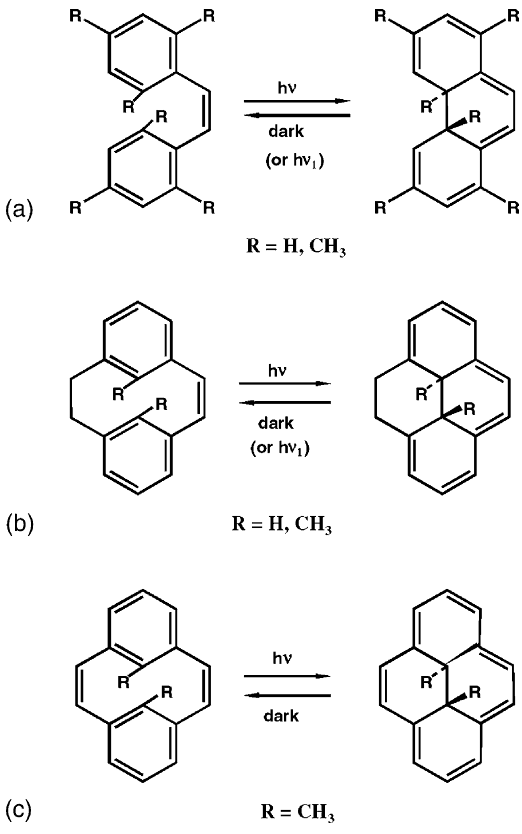
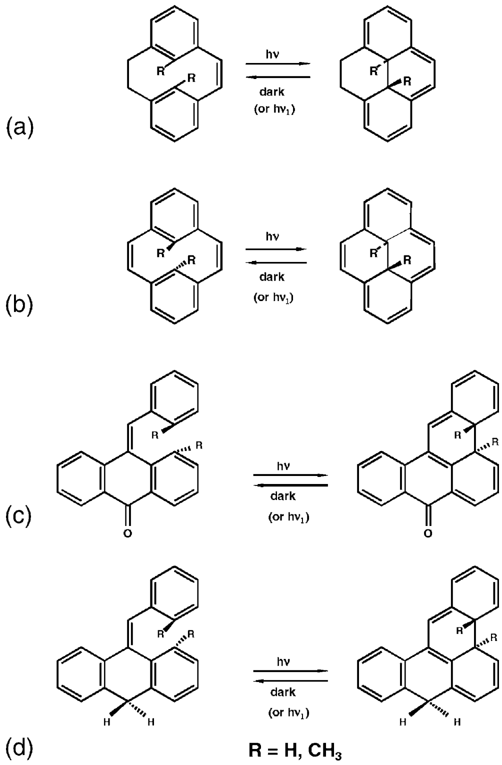
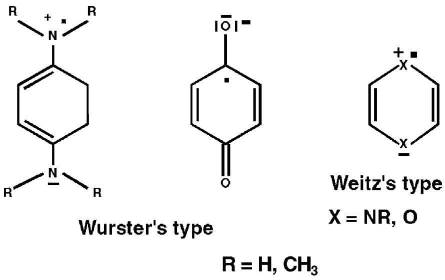


Scheme 1.



Scheme 2.



Scheme 3.

a polymethine radical of Wurster or Weitz type [9–12] (Scheme 3). The model polymers resulting from various combinations of radical units and photochromic exchange couplers are shown in Figs. 1–3.

There are several classes of high-spin systems [13], one of them are two classes of polaronic π-conjugated 1D polymers [13,14]. To the first class belong polymers in which a structural relaxation corresponding to a polaron delocalized in more EUs is not possible. This property is caused by the topology of the π-network and determines the good localization of the Wannier functions within the EUs and arising of a high-spin ground state with ferromagnetically (FM) coupled electrons within a narrow half-filled band (HFB). An example of this type is polymer **1a** given in Fig. 1. To the second class of polaronic systems belong polymers in which a structural relaxation corresponding to a polaron delocalized in more than one EU is possible, and the ground state is anti-ferromagnetic (e.g. polymer **1b** in Fig. 1).

3. Methods of investigation

3.1. Energy spectra of the polymers

The one-electron wavefunctions of a 1D system have the form of Bloch running waves:

$$|\boldsymbol{k}\rangle = N^{-1/2}\sum_{\mu}\sum_{r} C_r(\boldsymbol{k})\exp(-\mathrm{i}\boldsymbol{k}\mu)|r,\mu\rangle$$

with pseudomomentum $\boldsymbol{k} \in [-\pi, \pi]$. Here μ labels the EU, and $|r, \mu\rangle$ are the atomic orbitals within it. Band structure is obtained by means of the Hückel–Hubbard [15,16] version of the Bloch method, so that orbital energies $e(\boldsymbol{k})$ are eigenvalues of the energy matrix (for more details of the formalism see [17]):

$$\boldsymbol{E}(\boldsymbol{k}) = \boldsymbol{E} + \boldsymbol{V}\exp(\mathrm{i}\boldsymbol{k}) + \boldsymbol{V}^{+}\exp(-\mathrm{i}\boldsymbol{k}) \qquad (1)$$

In Eq. (1), $\boldsymbol{E}$ is the energy matrix of the EU, $\boldsymbol{V}$ the interaction matrix between neighboring EUs (μth and $(\mu+1)$th), and $\boldsymbol{V}^{+}$ the transposed matrix (the interaction matrix between the μth and $(\mu-1)$th EUs). The matrix elements of the matrices $\boldsymbol{V}$ and $\boldsymbol{V}^{+}$, respectively, are equal to the resonance integrals between connected π-centers of neighbouring EUs

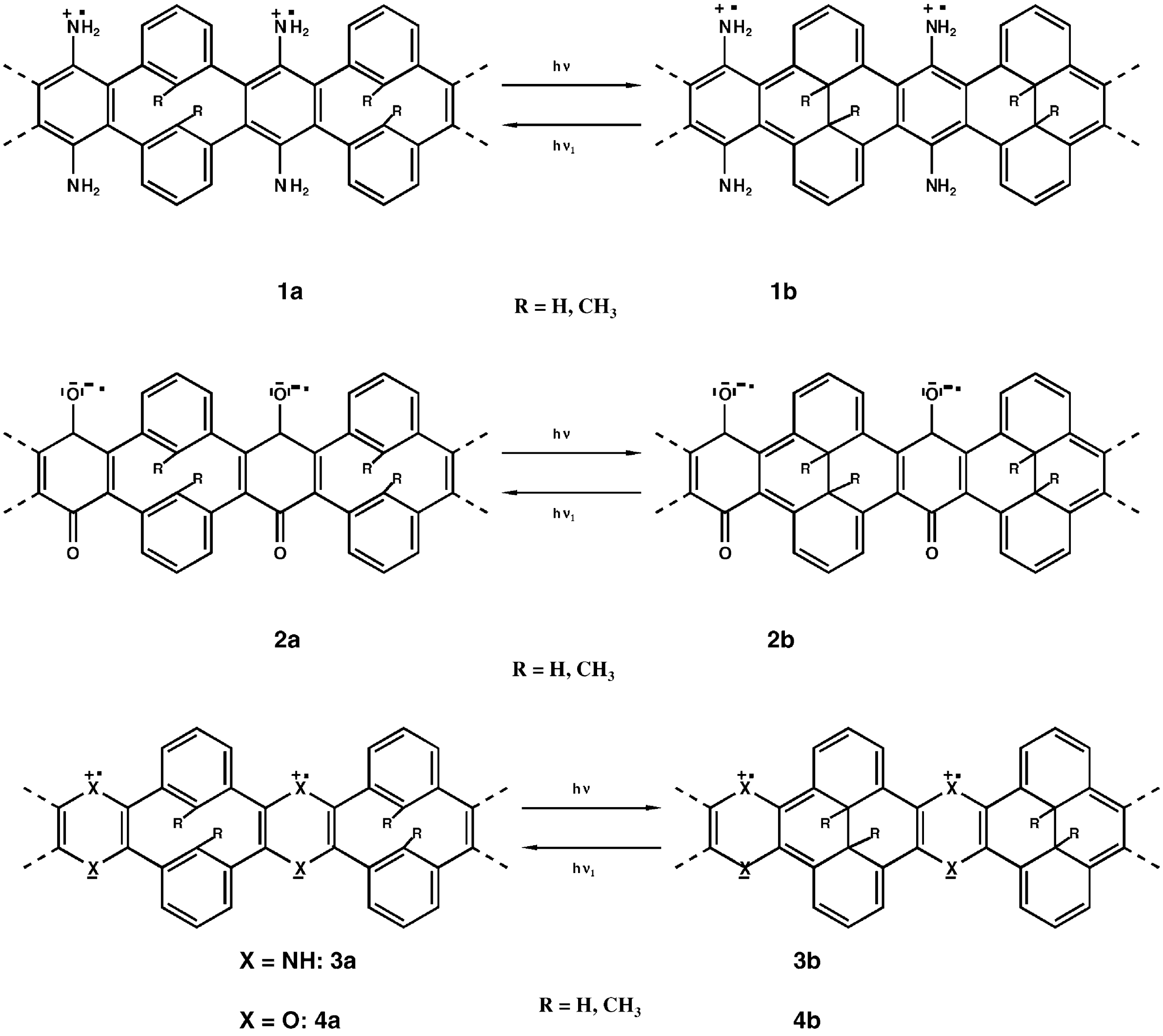


Fig. 1. Structures of polymers **1**–**4** with elementary units consisting of photochromic [2,2]-metacyclophanediene fragments annelated with polymethine radicals.

(μ and ($\mu+1$), and μ and ($\mu-1$), respectively, as it follows from the tight-binding approximation.

3.2. *Spin exchange interaction of the electrons in the half-filled band*

Based on Anderson's theory [18] it was shown [19,20] that the effective exchange integral, J_{eff}, between Wannier functions localized upon the νth and ρth EU in the Heisenberg-Dirac-Van Vleck Hamiltonian:

$$\boldsymbol{H} = -2\sum_{\nu\neq\rho} J_{\mathrm{eff}}(\nu,\rho)\boldsymbol{S}_\nu\boldsymbol{S}_\rho = -2\sum_{\nu\neq\rho} J_{\mathrm{eff}}(\tau)\boldsymbol{S}_\nu\boldsymbol{S}_\rho \tag{2}$$

can be expressed as a sum of three contributions (for the sake of simplicity the dimensionless distance parameter $\tau = |\nu-\rho|$ is omitted):

$$J_{\mathrm{eff}} = J + J_{\mathrm{kin}} + J_{\mathrm{ind}} \tag{3}$$

The terms in Eq. (3) have the following physical meaning: J is the Coulomb exchange integral between the localized Wannier states within the νth and ρth sites. The kinetic exchange parameter is:

$$J_{\mathrm{kin}} = -\frac{2t^2}{(U_0-U_1)} = -\frac{2t^2}{U} \tag{4}$$

where $U = U_0 - U_1$ is the renormalized Hubbard parameter [15], representing the anti-ferro-magnetic contribution to the spin exchange, t the transfer (hopping) parameter between adjacent Wannier functions: $t =< \mu|\boldsymbol{h}(1)|\mu+1 >$ ($\boldsymbol{h}$ is the one-electron periodic Hamiltonian). The exchange parameter (spin polarization exchange) J_{ind} expresses the indirect exchange ("superexchange") of the electrons in the HFB via delocalized π-electrons (along the polymer chain) in the filled energy bands (see [21,22]). The sign of J_{ind} is determined by the structure of the EU and by the interaction between the EUs. Depending on the exact balance of

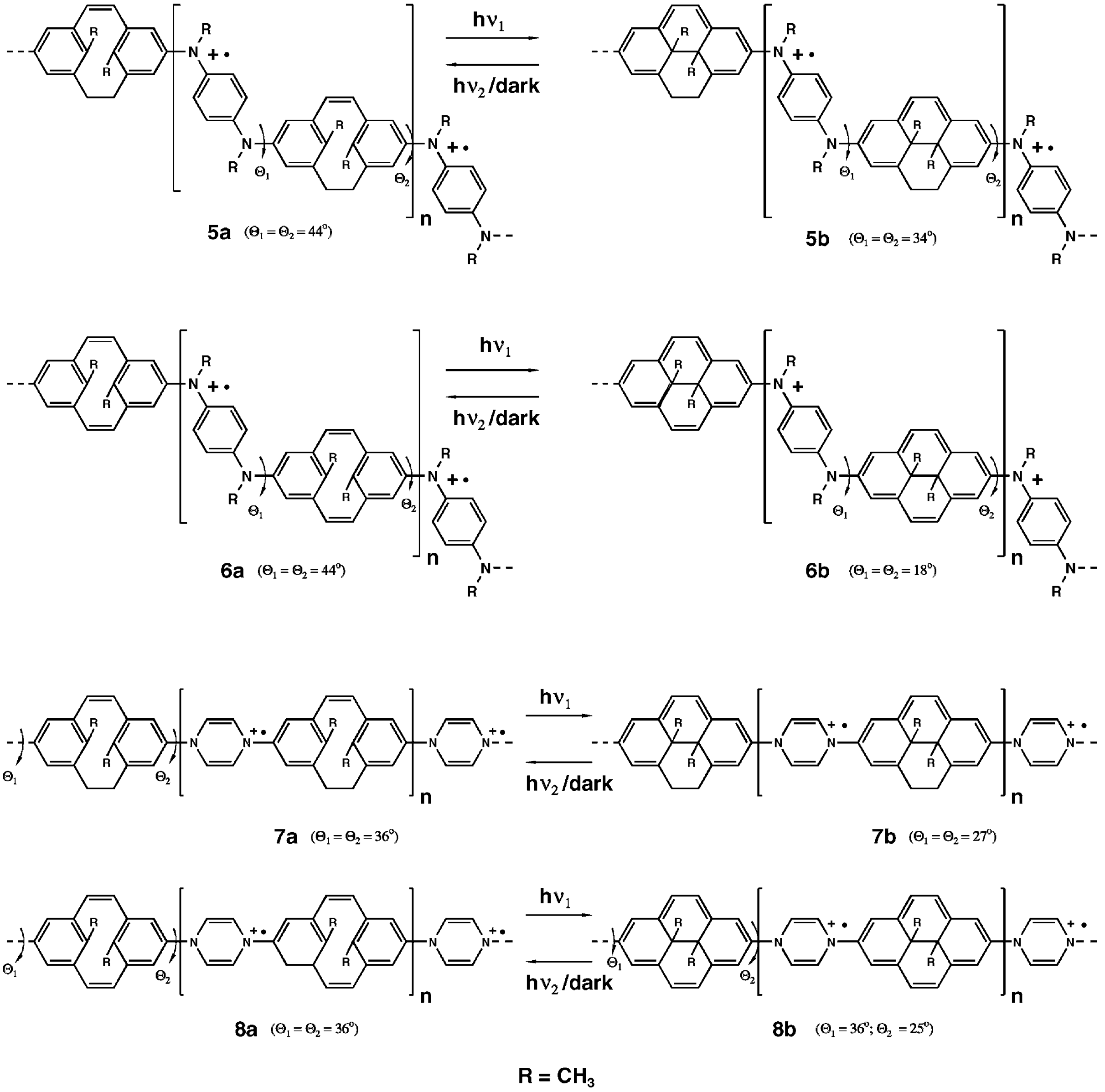


Fig. 2. Polymer structures (**5**–**8**) with [2,2]-metacyclophanene (**5** and **7**) and [2,2]-metacyclophanediene fragments (**6** and **8**), respectively, linked by a single bond with polymethine radicals of Wurster and Weitz type, respectively.

various contributions to J_{eff}, effective exchange can be ferromagnetic ($J_{\mathrm{eff}} > 0$) or anti-ferromagnetic ($J_{\mathrm{eff}} < 0$).

3.3. Parametrization and model geometry of the polymers

Band structure and Wannier functions were obtained for standard resonance integrals: $\beta_0(\mathrm{CC}, R_0 = 1.4\,\text{Å}) = -2.4\,\mathrm{eV}$ [23]; $\beta_0(\mathrm{CN}) = -2.3\,\mathrm{eV}$ [23]; $\beta_0(\mathrm{CO}) = -2.6\,\mathrm{eV}$ [23]. On-site Coulomb integrals for heteroatoms, α_X, were taken from [24]. Mulliken's relation [25] $\beta(R, \Theta) = \beta_0 S(R)/S(R_0)\cos\Theta$ was used to determine the dependence of the resonance integrals on the torsional angles Θ (the overlap integrals S have been calculated with the Slater orbital exponent $z_{\mathrm{C}} = 3.25$). Two-center Coulomb repulsion integrals $\gamma(R)$ were calculated with the Mataga–Nishimoto approximation [26],

$$\gamma_{\mu\nu} = \frac{e^2}{(a + R_{\mu\nu})} \tag{5}$$

with $a = 2e^2/(\gamma_{\mu\mu}+\gamma_{\nu\nu})$. The following standard values for one-center Coulomb integrals were used: $\gamma_{\mathrm{CC}} = 10.84\,\mathrm{eV}$ [27], $\gamma_{\mathrm{NN}} = 12.27\,\mathrm{eV}$ [28], $\gamma_{\mathrm{OO}} = 14.27\,\mathrm{eV}$ [29].

Equilibrium bond lengths $R_{\mu\nu}$ and dihedral angles Θ were obtained by means of all-valence electron AM1 method [30] (SPARTAN Program System, Version 3.0 [31]). Complete geometry optimization was performed for oligomers containing 3 repeat units (EUs).

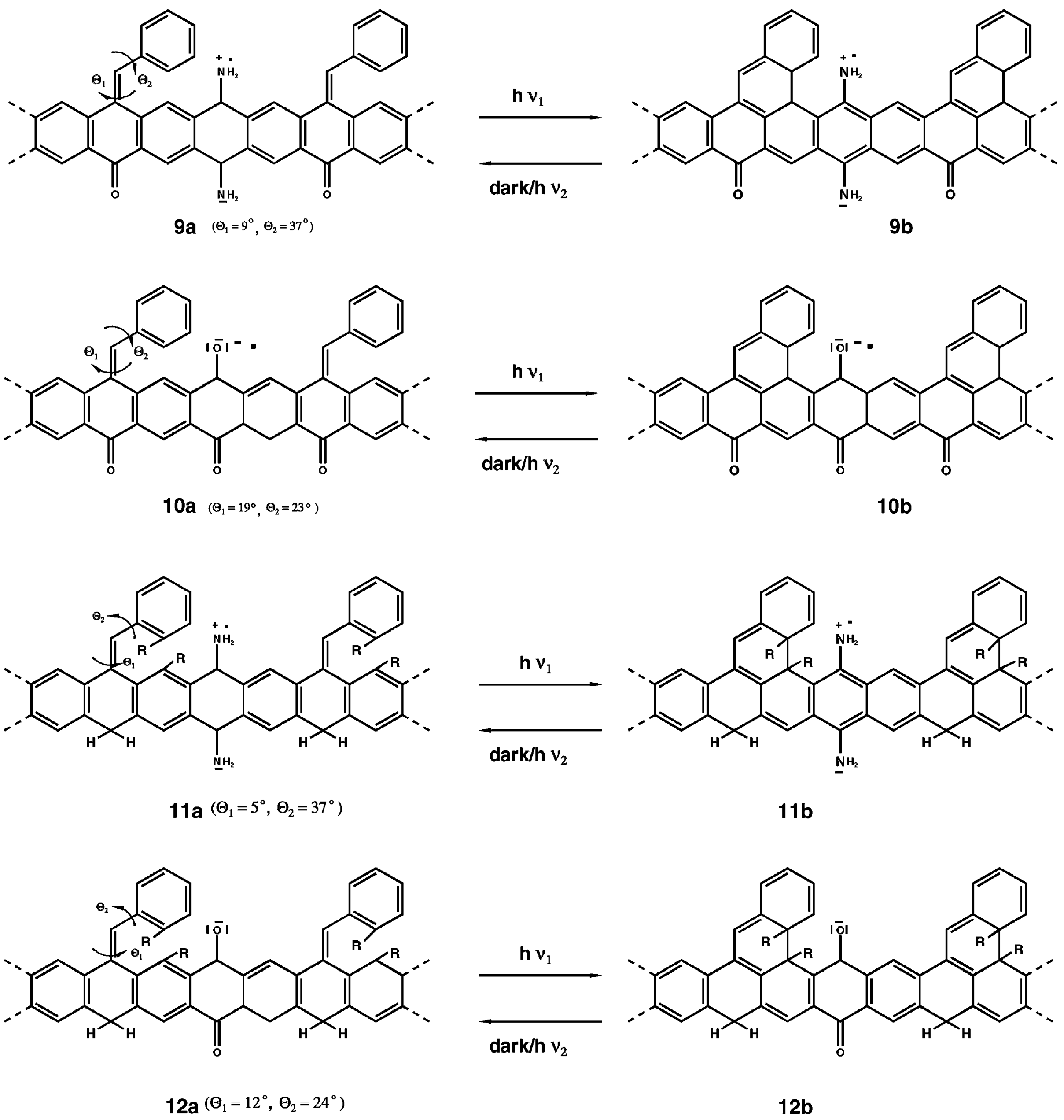


Fig. 3. Structures of polymers **9**–**12** with elementary units of photochromic 10-benzylidene-anthrone and 9-benzylidene-9,10-dihydroanthracene fragments, respectively, annelated with polymethine radicals of Wurster type.

4. Results and discussion

In all the Tables 1–3 are given the computed values of the energy gap (EG), ΔE, the width of the half-filled band $\Delta\varepsilon$, and the contributions to the effective exchange integral, J_{eff}. The values pertain the different model polymers as shown in Figs. 1–3.

In all cases the components of the effective exchange integral between the Wannier functions decrease rapidly with the distance parameter τ (see Eq. (2)). For this reason, the magnetic components in all Tables are given only for the value $\tau = 1$.

The energy spectra of the polymers, both in their open-ring and closed-ring forms, are characterized by a relatively wide EG, $\Delta E \sim 2\,\mathrm{eV}$. The width of the HFB, $\Delta\varepsilon$, mainly determines the character of the ground state and the spin exchange, respectively [18]. For polymers with ferromagnetic coupled electrons ($J_{\mathrm{eff}} > 0$) the width of the HFB has values $\Delta\varepsilon < 0.5\,\mathrm{eV}$ (see Tables 1–3). If the HFB width is larger than 0.5 eV, an anti-ferromagnetic or non-magnetic ground state is preferred. The larger HFB width for closed-ring photoisomers determines correspondingly larger anti-ferromagnetic contributions J_{kin} to the effective exchange J_{eff}.

Table 1
Calculated values of the energy gap, ΔE (in eV), the width of the half-filled band, $\Delta\varepsilon$ (in eV), and the contributions to the effective exchange integral, J_{eff}, (Coulomb J, kinetic J_{kin}, and indirect exchange integral J_{ind}, in meV) of polymers **1–4**

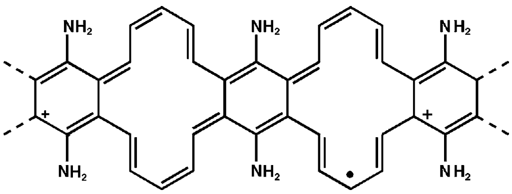
Polymer	ΔE	$\Delta\varepsilon$	J	J_{kin}	J_{ind}	J_{eff}
1a	2.32	0.11	15	−1	2	16
1b	1.44	1.10	92	−174	−34	−116
2a	2.33	0.12	19	−1	3	21
2b	1.43	1.15	96	−191	−36	−131
3a	2.37	0.04	195	0	10	205
3b	2.03	0.84	269	−258	2	13
4a	2.37	0.04	212	0	11	223
4b	2.07	0.83	290	−310	1	−19

Table 2
Calculated values of the energy gap, ΔE (in eV), the width of the HFB, $\Delta\varepsilon$ (in eV), and the contributions to the effective exchange integral, J_{eff}, (Coulomb J, kinetic J_{kin}, and indirect exchange integral J_{ind}, in meV) of polymers **5–8**

Polymer	ΔE	$\Delta\varepsilon$	J	J_{kin}	J_{ind}	J_{eff}
5a	2.41	0.01	3	0	0	3
5b	1.84	0.21	7	0	0	7
6a	2.14	0.01	13	0	0	13
6b	2.02	0.34	185	−1	6	190
7a	2.43	0.01	4	0	0	4
7b	1.75	0.49	9	−2	−2	5
8a	2.14	0.02	136	0	2	138
8b	1.97	0.55	263	−33	−9	221

Table 3
Calculated values of the energy gap, ΔE (in eV), the width of the HFB, $\Delta\varepsilon$ (in eV), and the contributions to the effective exchange integral, J_{eff}, (Coulomb J, kinetic J_{kin}, and indirect exchange integral J_{ind}, in meV) of polymers **9–12**

Polymer	ΔE	$\Delta\varepsilon$	J	J_{kin}	J_{ind}	J_{eff}
9a	2.04	0.10	213	−1	24	236
9b	1.64	0.58	80	−34	−17	29
10a	1.92	0.22	234	−4	28	258
10b	1.76	0.51	48	−21	−9	18
11a	2.44	0.16	166	−2	13	177
11b	1.86	0.60	69	−33	−14	22
12a	2.32	0.21	175	−3	15	187
12b	1.96	0.59	69	−30	−11	28



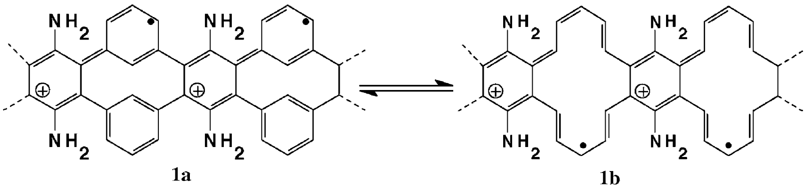
Scheme 5.

Scheme 6.

A real switching of the magnetic properties from a ferromagnetic state to an anti-ferromagnetic state upon radiation-induced ring closure is predicted for only a few polymer structures with [2,2]-metacyclophanediene fragments in the EU: polymers **1–4** (see Fig. 1 and Table 1). The ground state of **1a** is a ferromagnetic one, because the condition for a localization of a polaron in one EU is fullfilled, i.e. a structural relaxation corresponding to a polaron delocalized over more than one EU is not possible (see Scheme 4, here and below only one valence formula is given).

On the other hand, the ground state of **1b** is an anti-ferromagnetic one, because the condition for a localized polaron is not fulfilled. In this case, a structural relaxation corresponding to a polaron delocalized over more than one photochromic closed-ring fragments is possible as it is shown for a structure in Scheme 5.

In all the other cases effective exchange interaction changes with photoisomerization, but remains in the ferromagnetic range, e.g. polymers **6** and **8**. The ground state of the open-ring as well as the closed-ring form is ferromagnetic. In the case of the open-ring isomer **6a** the



Scheme 4.

ferromagnetic exchange interaction is weak ($J_{\mathrm{eff}} = 13\,\mathrm{meV}$) because a structural relaxation corresponding to a polaron delocalized over more than one EU is possible. In the photoisomeric closed-ring structur **6b** the polarons are strongly localized in each EU (Scheme 6), and therefore the ferromagnetic coupling is much more larger ($J_{\mathrm{eff}} = 190\,\mathrm{meV}$).

The switching of magnetic properties through photochromic [2,2]-metacyclophanediene couplers is most pronounced when the latter are annelated to polymethine radicals (see polymers **1**–**4**). In comparison, when photochromic and radical fragments are connected by a single bond (polymers **5**–**8**), exchange coupling is less affected by ring closure. No general trend in the nature and degree of change of magnetic properties for different types of polymethine radicals is observed. Generally, different photochromic fragments perform better or worse in combination with Wurster and Weitz type radicals, respectively.

5. Conclusions

Switching of magnetic properties by irradiation of the photochromic spin couplers has been predicted only for several selected polymers with polymethine radicals. For most of the structures addressed herein, ring closure is found merely to modify the strength of ferromagnetic exchange, without changing its sign. It has been shown that the switching from ferromagnetic to anti-ferromagnetic state is most likely for photochromic [2,2]-metacyclophanediene fragments, when annelated to the Wurster or Weitz type radical units.

No general trends concerning the relationship between polymer structure and efficiency in photoswitching of spin–spin interactions could be observed or deduced thus far.

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