

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

Part II.† Conjugated polymers with di-hetarylethene and benzylidene-anthrone fragments in the elementary units

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The change in the magnetic properties of the isomeric forms of photoresponsive model polymers with photochromic di-hetarylethene, 10-benzylidene-anthrone, and 9-benzylidene-9,10-dihydroanthracene fragments in the elementary units and substituted with radical centers is investigated theoretically. Based on the band theory, the effective exchange integral is calculated for the photoisomeric one-dimensional conjugated π -electron systems. In the case of the polymers with di-hetarylethene fragments, an increase or decrease in the antiferromagnetic exchange is connected with the photoisomerization. A photoswitching between non-magnetic and ferromagnetic intramolecular exchange interaction (or *vice versa*) of open-ring and closed-ring photoisomers should be possible with polymers containing photochromic 10-benzylidene-anthrone and 9-benzylidene-9,10-dihydroanthracene fragments.

1 Introduction

Many of the physical properties of photochromic molecules can be switched on irradiation. The most efficient photochromic systems for this are di-(het)arylethenes¹ which are converted to the closed-ring valence isomeric forms on irradiation with UV light. The closed-ring form returns to the open-ring di-arylethene in the dark or on irradiation with visible light if the reactive positions are substituted with methyl (alkyl) groups. The methyl (alkyl) groups prevent oxidation (elimination) but are not a precondition for the reverse reaction which yields the diarylethene. It has been shown^{2,3} that the photocyclization quantum yield of a photochromic polymer with di-thienylethene elementary units (EU) is much higher than that of the monomer. The polymeric closed-ring form is electrochemically dopable, in contrast to the open-ring isomer.

This principle of reversible photocyclization was realized experimentally to change the magnetic interaction. The intramolecular antiferromagnetic interaction between the nitronyl

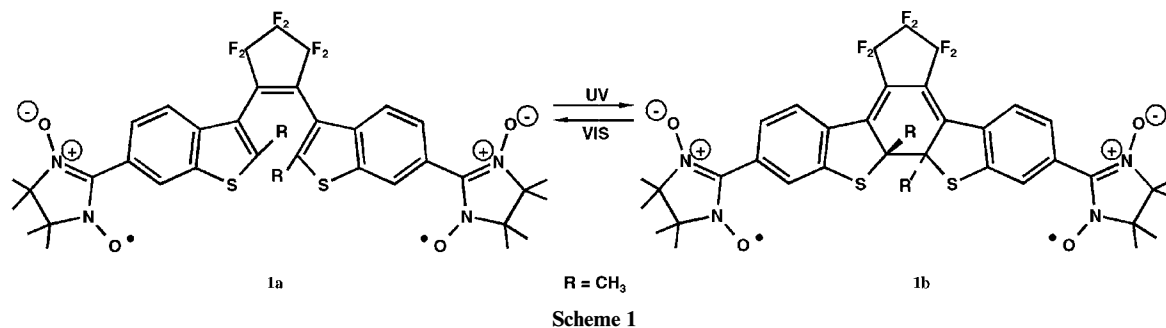
nitroxide radical centers of compound **1** is remarkably increased in the closed-ring isomer **1b** compared to the open-ring isomer **1a** (Scheme 1).^{4–6}

In an earlier paper⁷ we have investigated, based on the band theory, the change in the magnetic properties (effective exchange integral J_{eff}) of one-dimensional (1-D) homonuclear photoresponsive conjugated model polymers with photochromic stilbene-like elementary units substituted with radical centers. Two types of polymers have been characterized:

- (i) Polymers which show a real photoswitching from a ferromagnetic state ($J_{\text{eff}} > 0$) to a state without magnetic ordering ($J_{\text{eff}} = 0$) (or *vice versa*). This phenomenon is a topological effect.
- (ii) Polymers which show an increase or decrease in the (ferromagnetic) exchange interaction on irradiation.

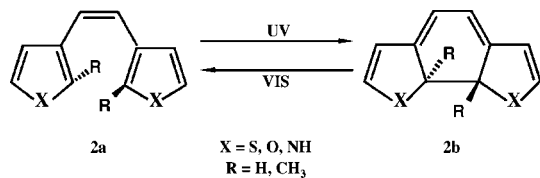
The realization of the photocyclization was estimated using reactivity indices in the excited state, calculated in the π -electron approximation,^{8,9} in comparison with corresponding limiting values.^{10,11}

There are many photochromic di-arylethenes which have been well investigated experimentally.¹² Besides the di-5-membered ring hetarylethenes **2a** (Scheme 2)^{13,14} the unsubstituted and substituted 10-benzylidene-anthrone **3a**¹⁵ are also photochemically converted to the closed-ring form **3b** (Scheme 3).

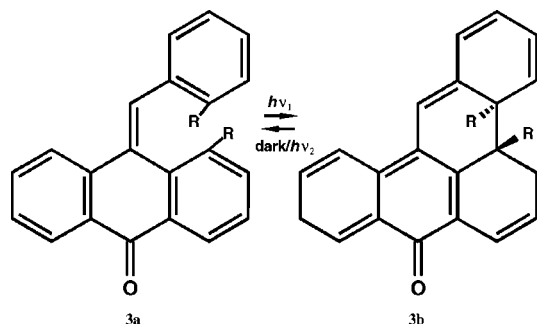


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Scheme 2



Scheme 3

The aim of this paper is to investigate the photoswitching of the intramolecular (ferro- or antiferro-) magnetic spin coupling¹⁶ of the open-ring and closed-ring isomers of 1-D photoresponsive conjugated polymers.

2 Model polymers investigated

We consider three classes of polymers, belonging to the photoresponsive conjugated ones with photochromic di-

hetarylethenes (4–7, see Fig. 1), 10-benzylidene-anthrone (8–10, see Fig. 2) and 9-benzylidene-9,10-dihydroanthracenes (12–16, Fig. 2) substituted with methylene groups as model radical centers in the EU. The effective exchange integral of the photoisomeric polymer structures with 10-benzylidene-anthrone fragments as EU (11a and 11b in Fig. 2) was also calculated.

3 Methods of investigation

3.1 Energy spectra of the polymers

If the molecular orbitals (MOs) of a 1-D system have the form of Bloch running waves

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

where $k \in [-\pi, \pi]$ is the wave vector, μ denotes the number of the EU, and $|r, \mu\rangle$ is the r th atomic orbital (AO) within the μ th EU, in the Hückel–Hubbard^{17–20} version of the Bloch method the MO energies $e(k)$ are eigenvalues of the energy matrix (for more details of the formalism see ref. 21):

$$E(k) = E + V \exp(ik + V^+ \exp(-ik) \quad (1)$$

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

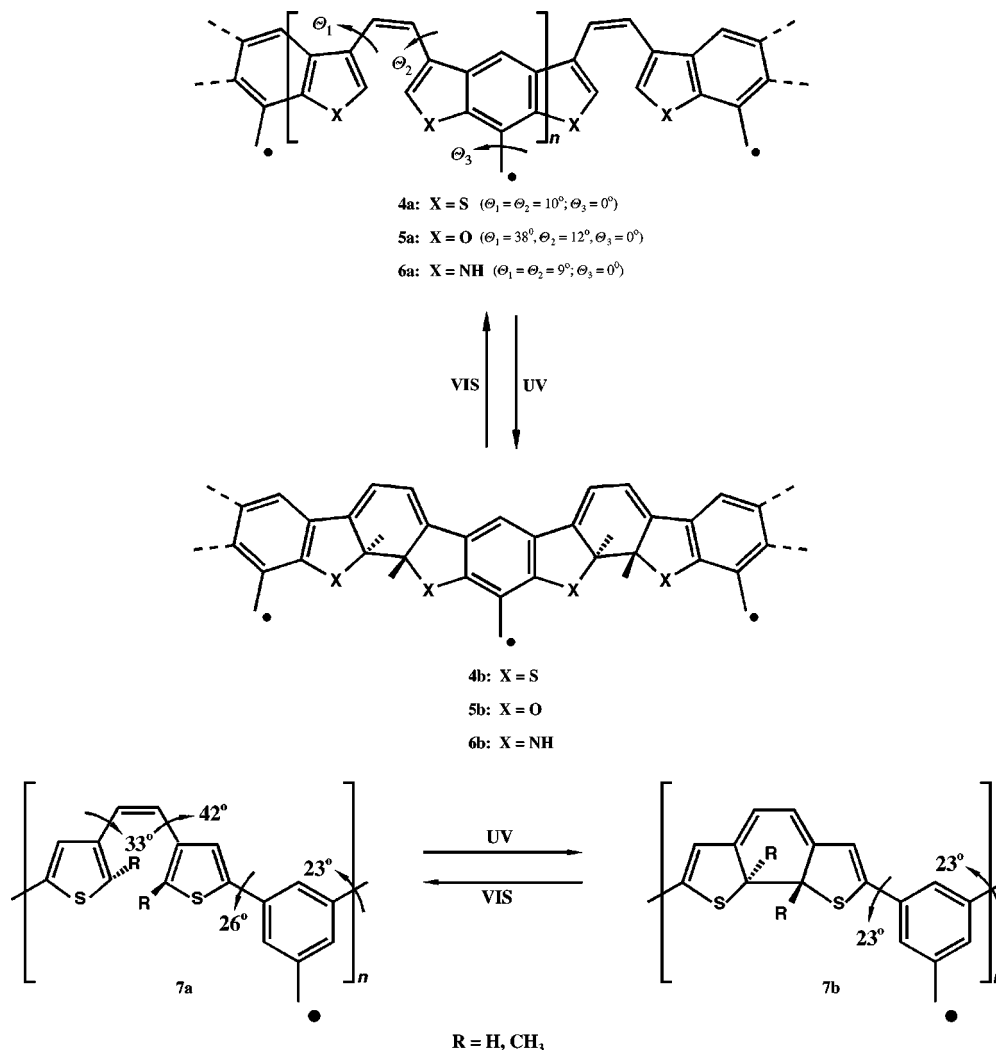


Fig. 1 Structures of polymers 4a–7a with photochromic di-hetarylethene fragments and the corresponding photoisomers 4b–7b.

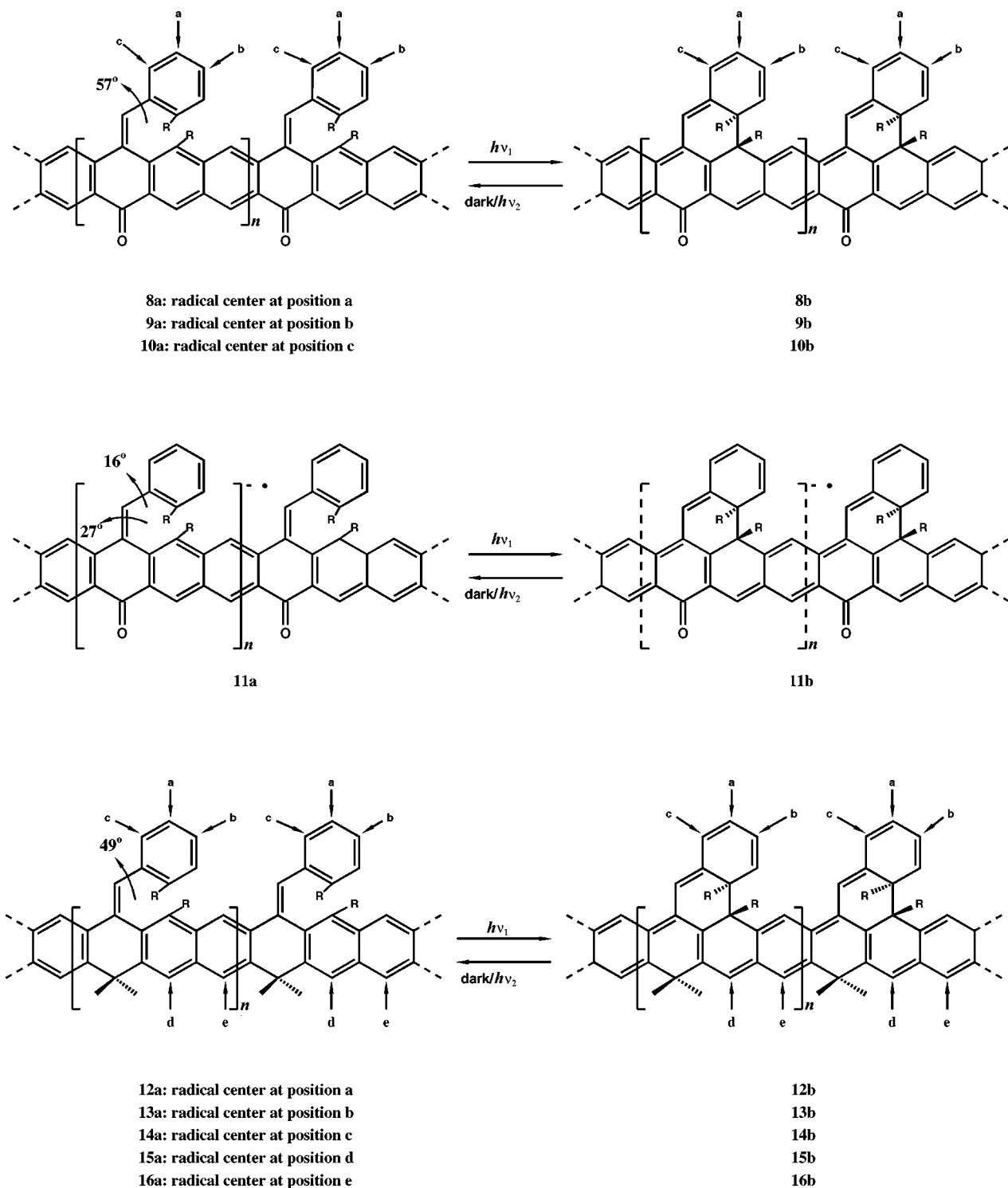


Fig. 2 Structures of polymers 8a–16a with photochromic 10-benzylidene-anthrone and 9-benzylidene-9,10-dihydroanthracene fragments and the corresponding photoisomers 8b–16b.

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

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

The method used for determination of the nature of the spin exchange interaction within the half-filled band (HFB) follows from Anderson's general theory of magnetism.²² It was shown^{23,24} that the effective exchange integral, J_{eff} , between Wannier functions localized upon the v th and ρ th EU in the

Heisenberg–Dirac–Van Vleck Hamiltonian:

$$H = -2 \sum_{v \neq \rho} J_{\text{eff}}(v, \rho) S_v S_\rho = -2 \sum_{v \neq \rho} J_{\text{eff}}(\tau) S_v S_r \quad (2)$$

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

$$J_{\text{eff}} = J + J_{\text{kin}} + J_{\text{ind}} \quad (3)$$

The terms in eqn. (3) have the following physical meaning: J is the Coulomb exchange integral between the localized Wannier states within the v th and ρ th sites. The kinetic

exchange parameter

$$J_{\text{kin}} = -2t^2/(U_0 - U_1) = -2t^2/U \quad (4)$$

represents the antiferromagnetic contribution to the spin exchange. t is the transfer (hopping) parameter between adjacent Wannier functions μ and $\mu + 1$, $t = \langle \mu | \hat{h}(1) | \mu + 1 \rangle$ (\hat{h} is the one-electron periodic Hamiltonian), and $U (= U_0 - U_1)$, U_0 and U_1 are the Coulomb repulsion integrals of two electrons residing in the same Wannier state and occupying adjacent Wannier states, respectively) is the renormalized Hubbard parameter.^{17–20} Details of the calculation of J_{kin} (eqn. (4)) are given in ref. 23 and 24.

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. This term can be calculated using a formalism described in ref. 25.

The sign of the effective exchange integral, J_{eff} , determines the character of the exchange interaction: $J_{\text{eff}} > 0 \Rightarrow$ ferromagnetic, and $J_{\text{eff}} < 0 \Rightarrow$ antiferromagnetic.

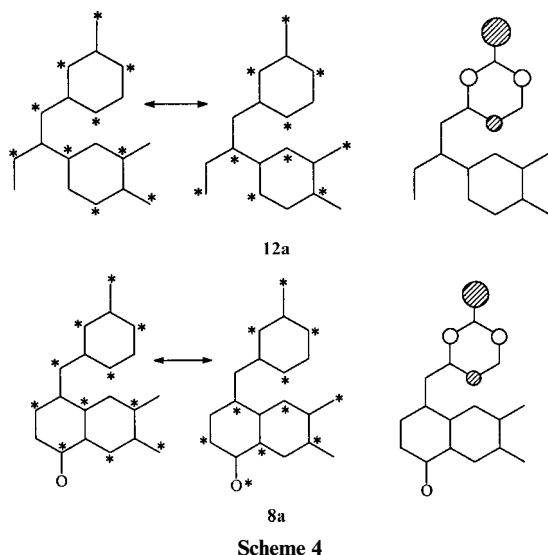
3.3 Topological effect of the exchange interaction²⁶

Based on the Coulson–Rushbrooke–Longuet–Higgins theorem (CRLH)^{27–32} and the extended CRLH theorem^{33,34} the number and the localization of non-bonding MOs (NBMO) within the energy spectra can be determined. As a result of the extended CRLH theorem^{33,34} the following corollary can be drawn: if the conjugated π -system has various maximal disjoint sets R_k , $k = 1, 2, \dots, p$, the NBMOs are composed only of the AOs of their intersection $R_1 \cap R_2 \cap \dots \cap R_p$. In the case of the EU of polymer **12a** and also polymer **8a** there are two maximal disjoint sets R_1 and R_2 (Scheme 4). It follows (from the corollary) that the NBMO coefficients are nonzero only for the π -sites in the benzyl fragment depicted in Scheme 4.

As a consequence the coefficients of the Wannier functions in the polymer chain are different from zero only for the π -sites in the benzyl fragment (they are identical with the AO coefficients of the benzyl radical). Thus, the π -conjugation among the elementary units is interrupted, and the exchange interaction vanishes. Only an indirect exchange among the benzyl fragments could be possible, but J_{ind} is practically zero because of the large distance between the radical centers (see Sections 4.2 and 4.3, and Tables 2 and 3).

3.4 Reactivity indices

The reactivity indices used to characterize the practicability of the photocyclization of di-arylethenes are defined as follows:^{7–9}



The free valence in the excited state of the position μ , F_{μ}^* , is defined analogously to the free valence in the ground state, F_{μ} :

$$F_{\mu}^* = \sqrt{3 - \sum_{\nu} p_{\mu\nu}^*} \quad (5)$$

where $p_{\mu\nu}^*$ is the bond order in the excited state. The sum of the free valences in the excited state at the photochemically reactive positions μ , $\sum F_{\mu}^*$, is formed with the F_{μ}^* -values at the positions μ of the ring closure.

The localization energy, $L_{\mu\nu}^*$, (in β units) is the difference of the total π -electron energies of the open-ring form in the excited state, M^* , and the closed-ring dihydro form in the ground state, $M_{\mu\nu}$:

$$L_{\mu\nu}^* = M^* - M_{\mu\nu} \quad (6)$$

The following limiting values of these reactivity indices for the realization of photocyclization of di-arylethenes have been formulated: photocyclization is possible if $\sum F_{\mu}^* \geq 1.0$ and $L_{\mu\nu}^* \leq 3.45 \beta^{10}$ (β is the energy unit in the HMO formalism), and $\sum F_{\mu}^* \geq 0.95$ and $L_{\mu\nu}^* \leq 3.54 \beta$.¹¹

3.5 Parametrization and geometry of the polymers

The terms in eqn. (1) were calculated using standard values of the resonance integral: $\beta_0(\text{CC}, R_0 = 1.4 \text{ \AA}) = -2.4 \text{ eV}$,³⁵ $\beta_0(\text{CN}) = -2.3 \text{ eV}$,³⁶ $\beta_0(\text{CO}) = -2.6 \text{ eV}$,³⁶ $\beta_0(\text{CS}) = -1.68 \text{ eV}$.³⁷ The parameters for the Coulomb integrals of the heteroatoms, α_X , were taken from ref. 38.

Mulliken's relation³⁹ $\beta(R, \Theta) = \beta_0 S(R)/S(R_0) \cos \Theta$ was used to determine the dependence of the resonance integrals on the torsional angles Θ (the overlap integrals S have been calculated with $Z_C = 3.25$ —the effective nuclear charge). The two-center Coulomb repulsion integrals $\gamma(R)$ were calculated with the Mataga–Nishimoto approximation,⁴⁰

$$\gamma_{\mu\nu} = e^2/(a + R_{\mu\nu}) \quad (7)$$

with $a = 2e^2/(\gamma_{\mu\mu} + \gamma_{\nu\nu})$. The following standard values of the one-center Coulomb integrals were used: $\gamma_{\text{CC}} = 10.84 \text{ eV}$,³⁵ $\gamma_{\text{NN}} = 12.27 \text{ eV}$,⁴¹ $\gamma_{\text{OO}} = 14.27 \text{ eV}$,⁴² $\gamma_{\text{SS}} = \gamma_{\text{CC}} = 10.84 \text{ eV}$.⁴³

The bond lengths $R_{\mu\nu}$ and the dihedral angles Θ were obtained by means of the all-valence electron quantum-chemical AM1 method⁴⁴ (SPARTAN Program System, Version 3.0⁴⁵). A complete geometry optimization was performed using a cluster with 3 repeating units.

4 Results and discussion

4.1 Polymers with di-hetarylethenes in the elementary unit

The calculated values of the energy gap (EG), ΔE , (in eV), the hopping parameter, t , (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 **4** to **7** shown in Fig. 1 are given in Table 1.

The energy spectra of the polymers, both the ring-open forms, and the photoisomeric ring-closed forms, are characterized by a more or less wide EG in the middle of which is situated a HFB. The EG of the ring-open forms, with the more aromatic character of the π -electron system, is larger than that of the ring-closed forms with the more polyenic π -electron system. The HFB consists of degenerate non-bonding MOs only in the case of polymers **7a** and **7b** in which the photochromic units are coupled through a *meta*-phenylene fragment. In all the other polymers the width of the HFB is larger for the ring-open isomeric forms than for the ring-closed photoisomers.

The character and magnitude of the intramolecular magnetic exchange interaction (J_{eff}) of the photoisomeric forms of the polymers depend on the type of the heteroatoms in the hetaryl residues, and also on the type of the connection of the

Table 1 Calculated values of the energy gap, ΔE (in eV), the hopping parameter, t (in eV) (see eqn. (4)), 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 **4** to **7** (see Fig. 1)

Polymer	ΔE	t	J	J_{kin}	J_{ind}	J_{eff}
4a ^a	2.12	0.015	0	0	0	~ 0
4b	1.61	~ 0	5	0	-10	-5
5a	2.51	0.161	32	-30	-28	-26
5b	1.54	0.001	1	0	-9	-8
6a	2.40	0.103	13	-9	-28	-24
6b	1.33	-0.002	3	0	-8	-5
7a ^a	2.29	0	0	0	0	0
7b	1.18	0	0	0	-5	-5

^a Non-magnetic spin coupling.

photochromic fragments. Generally, the intramolecular exchange interaction of the photoisomers is an antiferromagnetic one ($J_{\text{eff}} < 0$). While the antiferromagnetic interaction occurs at the photocyclization of polymer **4a** (non-magnetic) to **4b** ($X = S$), a decrease in the antiferromagnetic exchange interaction is observed at the photocyclization of polymers **5a** to **5b** and **6a** to **6b**, respectively.

Polymer **7a** is non-magnetic ($J_{\text{eff}} = 0$), and the photocyclization to the closed-ring isomer **7b** is accompanied by a switching on of an antiferromagnetic exchange interaction.

4.2 Polymers with 10-benzylidene-anthrone fragment in the elementary unit

In Table 2 are given the calculated values of the EG (ΔE , in eV), the hopping parameter, t (in eV), and the contributions to the effective exchange integral (J_{eff}) of polymers with a 10-benzylidene-anthrone fragment in the EU (**8–10**) shown in Fig. 2. The methylene group CH_2 as a model radical center in each EU is attached to various positions of the phenyl group of the benzylidene fragment (Fig. 2). In polymer **11** each EU is a radical anion fragment.

The energy spectra of the ring-open isomers are characterized by a larger EG than that of the ring-closed photoisomers. The HFB within the EG consists of degenerate or nearly degenerate (**9a**, **10a**) quantum states. Based on the calculated values of the effective exchange integral of the polymers a switching from a non-magnetic ring-open structure (**8a**, $J_{\text{eff}} = 0$) to a ring-closed photoisomer with intramolecular ferromagnetic exchange interaction (**8b**, $J_{\text{eff}} > 0$) and *vice versa* (**9a** and **10a** ($J_{\text{eff}} > 0$) \Rightarrow **9b** and **10b** ($J_{\text{eff}} = 0$)) should be realized on irradiation with light. The non-magnetic state of the photoisomers **8a**, **9b** and **10b** can be explained based on the extended CRLH theorem. The NBMOs in each EU are localized in benzyl fragments without a direct π -conjugation between the EUs. Therefore, only a negligible indirect exchange interaction ($J_{\text{ind}} \sim 0$) is acting (see also Section 3.3).

Table 2 Calculated values of the energy gap ΔE (in eV), the hopping parameter, t , (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 **8** to **11**

Polymer	ΔE	t	J	J_{kin}	J_{ind}	J_{eff}
8a ^a	1.85	0	0	0	0	0
8b	1.46	0	41	0	32	73
9a	2.00	-0.014	62	0	5	67
9b ^a	1.00	0	0	0	0	0
10a	1.97	-0.014	63	0	4	67
10b ^a	1.07	0	0	0	0	0
11a	1.52	-0.104	310	-47	24	287
11b	1.62	-0.134	63	-18	8	53

^a Non-magnetic spin coupling.

In the case of the poly(radical anion) polymer the ring-open isomer **11a** is characterized by a large value of the effective exchange integral which is strongly reduced on formation of the ring-closed photoisomer **11b** on irradiation.

4.3 Polymers with 9-benzylidene-9,10-dihydroanthracene fragment in the elementary unit

The calculated data characterizing the energy spectra (EG) and the magnetic exchange interaction of polymers **12–16** with a 9-benzylidene-9,10-dihydroanthracene fragment in the EU shown in Fig. 2 are collected in Table 3. The energy spectra of the polymers, both the ring-open forms and the photoisomeric forms, are characterized by a wide EG in the middle of which is situated a HFB of degenerate NBMOs. In all polymers of this type a change in the magnetic spin coupling at the photocyclization is observed, either from a non-magnetic state of the ring-open form ($J_{\text{eff}} = 0$: polymers **12a**, **15a**, **16a**) to the ring-closed photoisomer with intramolecular ferromagnetic exchange interaction ($J_{\text{eff}} > 0$: **12b**, **15b**, **16b**) or from the ring-open form with ferromagnetic exchange interaction ($J_{\text{eff}} > 0$: **13a**, **14a**) to the non-magnetic photoisomer ($J_{\text{eff}} = 0$: **13b**, **14b**). The only contributions to J_{eff} are the indirect exchange (J_{ind}) and the Coulomb (Hund) exchange (J) while the antiferromagnetic contribution (the kinetic exchange integral J_{kin}) is zero. This is a topological effect which is explained in more detail in Sections 3.3 and 4.2 as a consequence of the extended CRLH theorem.

4.4 Practicability of photocyclization

The reactivity indices for characterization of the practicability of the photocyclization—the sum of the free valence at the reactive positions in excited state ($\sum F_{\mu}^*$) and the localization energy in excited state ($L_{\mu, v}^*$)—of the model polymers **4a–8a** and **12a** are collected in Table 4. Only one polymer of the classes with photochromic 10-benzylidene-anthrone and 9-benzylidene-9,10-dihydroanthracene fragments (**8a** and **12a**), respectively, has been considered. The photocyclization should be possible with all the polymers because the calculated values

Table 3 Calculated values of the energy gap ΔE (in eV) and the contributions to the effective exchange integral J_{eff} (Coulomb J , and indirect exchange integral J_{ind} , in meV) of polymers **12** to **16**. The width of the HFB, $\Delta\epsilon$, the hopping parameter, t , and therefore the kinetic exchange integral, J_{kin} , are zero in each case (eqn. (4))

Polymer	ΔE	J	J_{ind}	J_{eff}	Polymer	ΔE	J	J_{ind}	J_{eff}
12a ^a	2.33	0	0	0	12b	1.73	36	30	66
13a	2.51	20	3	23	13b ^a	1.13	0	0	0
14a	2.46	21	3	24	14b ^a	1.20	0	0	0
15a ^a	2.62	0	0	0	15b	2.51	40	27	67
16a ^a	2.63	0	0	0	16b	1.52	171	60	231

^a Non-magnetic spin coupling.

Table 4 Calculated values of the sum of free valence indices in the excited state ($\sum F_{\mu}^*$) of the reactive positions for photocyclization and the localization energies in excited state ($L_{\mu, v}^*$, in β units) of diarylethene fragments within the EU of polymers **4a–8a**, **12a** (Fig. 1 and 2)

EU in polymer	$\sum F_{\mu}^*$	$L_{\mu, v}^*$
4a	1.12	3.19
5a	1.23	3.03
6a	1.09	3.42
7a	1.22	3.21
8a	1.02	3.59
12a	1.04	3.34

are outside the limiting values which determine the realization of the reaction. In the case of the polymers with photochromic di-hetarylethene fragments a tendency towards facility of photocyclization can be observed. However, the data should not be overestimated.

Conclusions

The change in the magnetic spin coupling upon reversible photocyclization of photoresponsive polymers with photochromic di-hetarylethene, 10-benzylidene-anthrone and 9-benzylidene-9,10-dihydroanthracene fragments in the elementary units (EU) and substituted with radical centers have been investigated based on the band theory. The following types of polymers can be characterized by the calculated values of the effective exchange integral, J_{eff} :

Polymers with the radical-substituted photochromic di-hetarylethene EUs show an increase or decrease in the intramolecular antiferromagnetic exchange interaction upon photocyclization.

Polymers with radical-substituted photochromic 10-benzylidene-anthrone and 9-benzylidene 9,10-dihydroanthracene EUs show a real photoswitching of their magnetic properties from a non-magnetic state to a ferromagnetic spin coupling ($J_{\text{eff}} > 0$) and *vice versa* upon photocyclization. The non-magnetic state ($J_{\text{eff}} = 0$) of a photoisomer is caused by a topological effect, and can be explained with the extended Coulson–Rushbrooke–Longuet–Higgins theorem. If this theorem is valid, then the Wannier function of the NBMO is localized in the benzyl fragment of the EU, the π -conjugation among the EUs is interrupted, and the (indirect) exchange interaction vanishes.

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