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Structure and Magnetic Interaction in Organic Radical Crystals. 6. Spin-Transfer Crystals: A Theoretical Study[†]

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The nature of the spin exchange interaction in half-filled bands of one-dimensional (1-D) stacks of mixed molecular radical crystals (MMRC) with the general formula $\cdots R^{\bullet} \cdots H \cdots R^{\bullet} \cdots H \cdots$ (R^{\bullet} is a π radical, and H is a diamagnetic polycyclic aromatic hydrocarbon (PAH)) has been investigated theoretically. The intermolecular interaction is accompanied by spin transfer from R^{\bullet} to H and determines the spin–spin interaction within the 1-D stacks of the MMRCs. The nature and the magnitude of the magnetic interaction in these structures are investigated using the band theory. At a given topology and geometry of the MMRC stacks the antiferromagnetic interaction in the parent molecular radical crystals $\cdots R^{\bullet} \cdots R^{\bullet} \cdots$ becomes ferromagnetic in the MMRCs and vice versa. It was found that the effective exchange integral J_{eff} of MMRCs, belonging to a given group with one and the same radical but different H, is proportional to the diamagnetic susceptibility $\chi(H)$. A new topological effect of the exchange interaction in MMRCs is formulated.

1. Introduction

In recent papers^{1,2} the band theory was applied to study the nature of the intermolecular spin exchange interaction in one-dimensional (1-D) mixed molecular radical crystals (MMRC) with a general structure



where R^{\bullet} is a homonuclear alternant π -radical and H is a diamagnetic alternant polycyclic aromatic hydrocarbon (PAH). The nature and the magnitude of the exchange interaction in MMRCs are significantly different when compared to those of the parent molecular radical crystals (MRC). At a given topology and geometry of the MMRC stacks, the antiferromagnetic interaction in the parent MRC changes to a ferromagnetic one in the MMRC and vice versa.

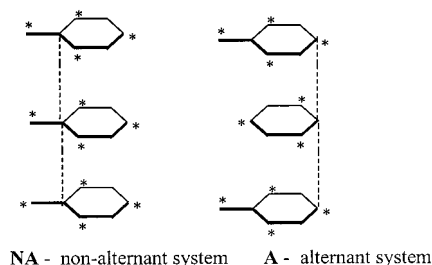
In general, our considerations follow from the fundamental theorem determining the structural principle of the homonuclear alternant π systems with degenerate MOs which is due to the Coulson, Rushbrooke, and Longuet-Higgins (CRLH theorem).^{3,4} A homonuclear alternant π system has

$$N = S^* - R^{\circ}$$

degenerate nonbonding MOs (NBMO) where S^* and R° are the number of the starred and unstarred π centers, respectively.

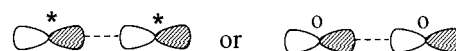
A model of a MMRC consisting of benzyl radical (R^{\bullet}) and benzene molecule (H) within the elementary unit (EU)

SCHEME 1

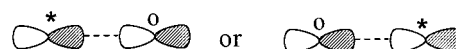


which demonstrates the mechanism and the nature of the magnetic interaction in MMRCs is illustrated schematically in Scheme 1.

In the case of the full face-to-face structure of the 1-D MRC stack, NA, the CRLH theorem does not apply since the system is nonalternant. The nearest π centers of the neighboring benzyl radicals are both starred or nonstarred, respectively:



The large width of the half-filled band (HFB), $\Delta\epsilon = 1.152$ eV, is the main reason for the negative value of the effective exchange integral, $J_{\text{eff}} = -47.0$ meV, and hence for the antiferromagnetic character of the spin exchange.¹ In the case of a face-to-face structure of the 1-D MMRC stacks, A, the elementary units and the stacks as a whole are alternant systems:



The CRLH theorem is valid for every EU comprising a benzyl radical and a benzene molecule, and $S^* - R^{\circ} = 1$; furthermore, the system has a HFB of degenerate NBMOs. The ferromagnetic

[†] Part 5 of this series is ref 2.

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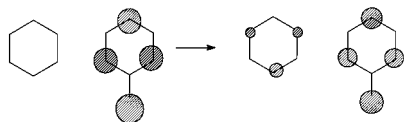
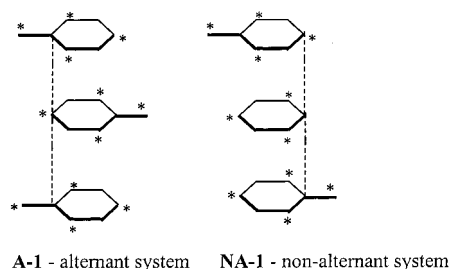
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TABLE 1: Calculated Values of J_{eff} (in meV) and P(H) Values (see eq 4) of MMRCs Al–Pc–Al and Bl–Pc–Bl (see Figure 2)^a

n	χ_M	χ_\perp	$J_{\text{eff}}(\text{Al–Pc–Al})$	$J_{\text{eff}}(\text{Bl–Pc–Bl})$	P(Al)	P(Bl)
0	55.6 (54.8)	91.6 (94.6)	33 (69)	9	0.028	0.012
1	92.2 (93.6)	163 (173.5)	64 (102)	15	0.026	0.015
2	130.3 (134.2)	238.3 (254.2)	106 (147)	20	0.034	0.017
3	168 (67)	312.6	148 (162)	52	0.046	0.019
4	205.4	386.9	192 (245)	37 ^b	0.058	0.021

^a Values for J_{eff} brackets correspond to the results from taking into account first and second neighboring π centers. The values of χ_M and χ_\perp (in $\text{cm}^3 \text{mol}^{-1} 10^{-6}$) of naphthalene ($n = 0$), anthracene ($n = 1$), tetracene ($n = 2$), and pentacene ($n = 3$) are taken from the paper of Akamatsu and Matsunaga.⁴⁴ In brackets are quoted the values of Weiss and Witte.⁴³ ^b It is not clear why this MMRC does not fit the linear relationship between J_{eff} and χ .

**Figure 1.** Spin density distribution in isolated (noninteracting) benzyl radical and benzene, and in the EU of the 1-D stacks.**SCHEME 2**

coupling of the electrons within the NBMO band is characterized by $J_{\text{eff}} = 9.0$ meV (see Table 1). The interaction between the benzyl radical Bl and the diamagnetic benzene molecule Bz in the stacks A is accompanied by spin transfer (ST) from Bl to Bz (see Figure 1). The intermolecular spin–spin interaction determines the ferromagnetic interaction of the electrons within the HFB of the 1-D stacks of MMRC. Qualitatively, this follows from the McConnell model Hamiltonian⁵

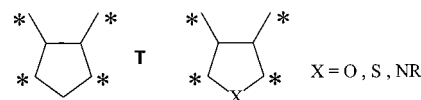
$$H = -S_R S_H \sum_{\langle k,l \rangle} J_{kl}^{\text{RH}} \rho_k^{\text{R}} \rho_l^{\text{H}}$$

where S_R and S_H are the spins on the subunits R and H, J_{kl}^{RH} is the exchange integral, and $\rho_k^{\text{R}}(\rho_l^{\text{H}})$ is the spin density at the $k(l)$ th π center of the subunit R(H).

The opposite case of MRC and MMRC with rotated face-to-face arrangement of the EUs is shown in Scheme 2. The electrons within the HFB of the stack of the 1-D crystals consisting of benzyl radicals, A-1, are ferromagnetically coupled, $J_{\text{eff}} = 24$ meV, but the electrons within the HFB of the stack of 1-D crystals consisting of benzyl radicals and benzene molecules, NA-1, are antiferromagnetically coupled, $J_{\text{eff}} = -1$ meV.

The CRLH theorem provides a sufficient but not necessary condition for the presence of NBMOs in π electron systems. The theorem has been generalized later on.^{6,7} Within the CRLH theorem one always considers two subsets of homonuclear nonbonded π centers: the subset of starred $\{S^*\}$ and the subset of unstarred $\{R^\circ\}$ ones. According to the generalized theorem,⁷ only one subset of nonbonded π centers is responsible for the appearance of NBMOs. A system with M π centers and a maximum set of $\{S^*\}$ homonuclear nonbonded π centers must have at least $N = 2S^* - M$ NBMOs. The NBMOs are present even if the π system is a nonalternant one and if the π centers belonging to the nonstarred subset $\{R^\circ\}$ are heteroatoms.

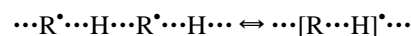
Representative examples are the nonalternant hydrocarbon T and the heteronuclear nonalternant systems:



$$N = 2 \times 4^* - 7 = 1 \text{ NBMO}$$

Such systems were investigated by Berson et al.^{8,9}

In previous work,¹ only MMRCs consisting of homonuclear alternant π radicals and PAHs have been studied. The model MMRCs are structures with 1:1 ratio between the R subunit and the PAH subunit within the EU. Now we extend the considerations to MMRCs with the following general structure

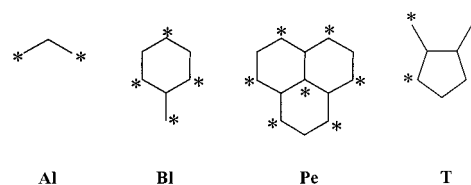


Here R^\bullet is a homonuclear or heteronuclear (polymethine) radical and H is a diamagnetic polycyclic molecule with a conjugated π system. As a further extension we included 1:2 MMRCs, i.e., MMRCs comprising R^\bullet and H in a ratio 1:2 within the EU.

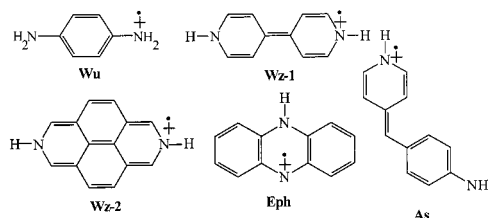
The diamagnetic susceptibility is the main magnetic feature of a diamagnetic molecule, in particular of a hydrocarbon. The purpose of the current investigation is to find a correlation between the values of the effective exchange integral J_{eff} (see eq 1) and the diamagnetic susceptibilities of the hydrocarbons H.

2. Objects of Investigations

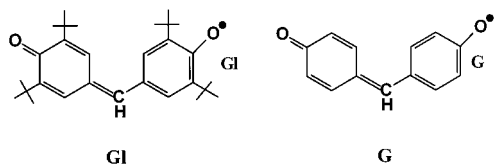
2.1. Radicals. We consider three homonuclear alternant π monoradicals R^\bullet , allyl (Al), benzyl (Bl), and perinaphthyl (Pe), and a nonalternant radical T:



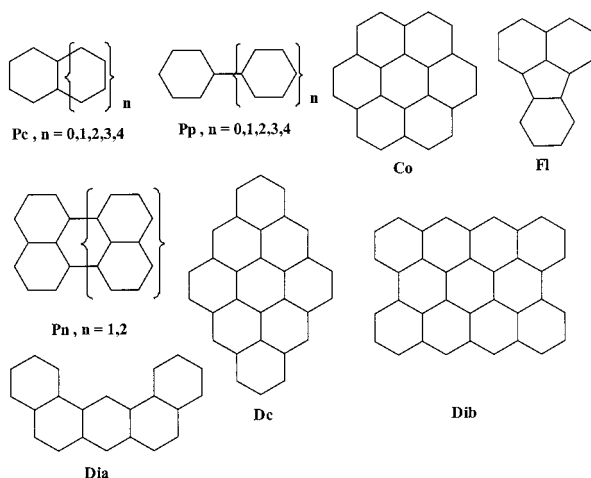
The following heteronuclear Weitz's (Wz) and Wurster's (Wu) type polymethine radicals^{10–13} are used as subunits of the EUs of the MMRCs:



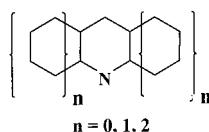
These polymethine monoradicals are stable open-shell systems and possess singly occupied MO (SOMO) within a large energy gap. The galvinoxyl radical GI (Coppinger's radical)¹⁴ also belongs to the group of the polymethine monoradicals; its magnetic properties were investigated experimentally and theoretically (see Section 4.3.). For this study the radical GI was simplified to G in which the *tert*-butyl residues are omitted to build up the MMRC stacks.



2.2. Diamagnetic Molecules as Subunits of the EUs of MMRCs. Different diamagnetic PAHs (H) have been used to separate the radicals R[•] in the 1-D stacks of MMRCs, viz., polyacenes (Pc), poly[perinaphthalene]s (Pn), poly[*para*-phenylene]s (Pp), coronene (Co), fluoranthene (Fl), 2,3,8,9-dibenz-coronene (Dc), 1,2,13,14-dibenzbisanthene (Dib), and 1,2,7,8-dibenzanthracene (Dia).



The following diamagnetic N analogues of the polyacenes have been also used:



2.3. 1-D Stacks of MMRCs. The MMRC stacks are considered to be 1-D systems complying with the Born-Karman cyclic conditions. The EUs of all 1-D MMRCs are built up of a radical R[•] and one or two diamagnetic subunits H, i.e., we consider 1:1 and 1:2 mixed crystals. The homo- and heteronuclear radicals and the diamagnetic molecules H are assumed to have ideal geometry with all bond lengths equal to $R_0 = 1.40 \text{ \AA}$ and regular hexagonal benzene rings. The numerical results, obtained with various values of the interplanar distance R between the radical and the hydrocarbon, $3.1 \text{ \AA} < R < 3.4 \text{ \AA}$, show that the character of the exchange interaction does not depend qualitatively on the value of R . Therefore, the calculations for all MMRCs are performed with an interplanar distance $R = 3.35 \text{ \AA}$ as in graphite¹⁵ (see also refs 1 and 16).

We consider two types of 1-D stacks of MMRCs: (i) *face-to-face* type. This model has a mirror plane perpendicular to the translation axis between the subunits, as in Figures 2, 3,

and 7–9. (ii) *slipped face-to-face* type with different slip angles α (see Figures 5 and 6).

3. Methods of Investigation

3.1. Spin Exchange of the Electrons within the HFB. Based on Anderson's theory,¹⁷ it has been shown^{18,19} that the effective exchange integral, J_{eff} in the Heisenberg Hamiltonian:

$$H = -2 \sum_{\nu, \rho} J_{\text{eff}}(\nu, \rho) S_{\nu} S_{\rho} = -2 \sum_{\nu, \rho} J_{\text{eff}}(\nu - \rho) S_{\nu} S_{\rho} = -2 \sum_{\nu, \rho} J_{\text{eff}}(\tau) S_{\nu} S_{\rho} \quad (1)$$

(ν and ρ denote EUs) can be expressed as a sum of three contributions (for the sake of simplicity the dimensionless distance parameter τ is omitted):

$$J_{\text{eff}} = J + J_{\text{kin}} + J_{\text{ind}} \quad (2)$$

where J is the Coulomb exchange integral between the Wannier states localized at the ν th and ρ th sites. J_{kin} is the kinetic exchange parameter

$$J_{\text{kin}} = -\frac{2t^2}{(U_0 - U_1)} = -\frac{2t^2}{U} \quad (3)$$

which represents the antiferromagnetic contribution to the spin exchange. 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. $U = U_0 - U_1$ is the renormalized Hubbard integral.²⁰ The transfer (hopping) parameter between adjacent Wannier functions is given by $t = \langle \mu | \mathbf{h}(1) | \mu + 1 \rangle$, where $\mathbf{h}(1)$ is the periodic one-electron Hamiltonian. The term J_{ind} in eq 2 expresses the indirect exchange caused by the spin polarization within the conjugated π electron system, the so-called "superexchange" via delocalized π electrons in the filled energy bands. This term can be calculated using a formalism described earlier.²¹ The sign of J_{ind} is determined by the structure of the EU and the interaction between the units.

3.2. Electron and Spin Densities. The interaction between the radical R[•] and the diamagnetic molecule (subunit) H is accompanied by spin transfer from R[•] to H. A quantitative measure of the spin transfer is the sum of all spin densities at the atoms of the subunit H:

$$P(H) = \sum_r \rho_r \quad (4)$$

By definition, the spin density at the r th atom is equal to

$$\rho_r = q_r^{\alpha} - q_r^{\beta}$$

where q_r^{σ} is the π electron density of the electrons with spin σ ($\sigma \in \alpha, \beta$). In the one-electron approximation, the charge densities in the doubly occupied bands are $q_r^{\alpha} = q_r^{\beta}$, and the expression for the spin densities transforms into

$$\rho_r = q_r = \sum_k |C_r(k)|^2 \xrightarrow{N \rightarrow \infty} 1/2\pi \int_{-\pi}^{\pi} |C_r(k)|^2 dk$$

where $C_r(k)$ are the coefficients of the Bloch function of the HFB

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

In accordance with the CRLH^{3,4} and the extended theorem,^{6,7} only the spin densities of the π centers belonging to the subset of starred centers $\{S^*\}$ are nonzero. π Centers belonging to the subset of the unstarred π centers $\{R^o\}$ have spin densities $\rho^o_r = 0$.

3.3. Parametrization. The calculations have been carried out using a standard set of parameters.^{1,16,19} The intermolecular resonance integrals between two $2p_z$ AOs have been calculated with Mulliken's formula,²² $\beta(R) = \beta_0 (S_{\sigma-\sigma}, S_{\pi-\pi})/S(R_0)$, taking into account the angular dependence of the overlap integrals S (calculated with $z_C = 3.25$). A standard value $\beta_0(R_0 = 1.40 \text{ \AA}) = -2.4 \text{ eV}$ has been used for the π type resonance integrals between the $2p_z$ AOs on adjacent carbon atoms. The two-center atomic Coulomb integrals γ_{pq} needed for the calculation of the various contributions to the effective spin exchange integral, J_{eff} , have been evaluated using the Mataga-Nishimoto potentials:²³

$$\gamma_{pq} = e^2/(a_{pq} + R_{pq}) \quad (5)$$

($a_{pq} = 2e^2/(\gamma_p + \gamma_q)$) with standard values of the one-center Coulomb integrals: $\gamma_C = 10.84 \text{ eV}$, $\gamma_N = 12.27 \text{ eV}$,²⁴ and $\gamma_O = 14.27 \text{ eV}$.²⁵

4. Results and Discussion

4.1. Homonuclear 1:1 MMRCs. The components of the effective exchange integral decrease rapidly with the distance parameter τ (see eq 1) in all cases. With $\tau > 1$, $J_{\text{eff}} \sim 0$. For this reason, the magnetic components in all tables are given only for the value $\tau = 1$. The results in the tables were obtained in the topological approximation, i.e., taking into account only the first-neighbor interaction between $2p\sigma$ – $2p\sigma$ AOs. Extending the interaction to second neighbors preserves the character of the exchange interaction. In Table 1 are the results for the MMRCs from of allyl radical and polyacenes displayed as examples.

The Coulomb exchange integrals between Wannier orbitals centered on units ν and ρ depend only on the index $\tau = |\nu - \rho|$ (see eq 1), $J_{\nu\rho} = J_{|\nu-\rho|} = J_\tau$, and decrease rapidly with its increment. At a distance r between two radicals (not separated by a diamagnetic molecule), $r > 6 \text{ \AA}$, the exchange integrals between neighboring Wannier orbitals are $J \sim 0$. However, in the MMRC the electrons (spins) are delocalized over the whole EU, and the coefficients of the Wannier orbitals within the EU are different from zero in the both subunits R and H. As a result, the value of the exchange integral between neighboring Wannier orbitals (ν and ρ)

$$J_{\nu\rho} = J_{|\nu-\rho|} = J_{\tau=1} = \int \int \nu^*(1)\rho^*(2)|1/r_{12}|\nu(2)\rho(1) d\nu_1 d\nu_2$$

may be, in the general case, different from zero. This means that the magnetic exchange interaction in the case of MMRCs results from the exchange between the spin density of the radical and the spin density $P(H)$ of the diamagnetic PAH. The diamagnetic subunit works such as a transmission. The magnetic exchange interaction in the case of MMRCs results from the exchange between the spin density of the radical and the spin density $P(H)$ of the diamagnetic PAH created by a spin-transfer from the radical to the PAH. The effective exchange integral J_{eff} and also the components J , J_{kin} , and J_{ind} have at a factor 10 smaller values in the case of MMRCs in comparison with those of the parent molecular radical crystals, e.g., NA-1 (Scheme 2): $J_{\text{eff}} = -1 \text{ meV}$, A-1 (Scheme 2): $J_{\text{eff}} = 24 \text{ meV}$. The values

TABLE 2: Calculated Values of J_{eff} (in meV) of MMRCs BI–Pp–BI (see Figure 3) and $P(H)$ Values (see eq 4)

n	χ_M	χ_\perp	$J_{\text{eff}} (\Theta=0^\circ)$	$J_{\text{eff}} (\Theta=30^\circ)$	$P(H)^a$
b	54.8	94.6	33		0.012
0	106	186	60	56	0.046
1	152	271	92	82	0.054
2	201	372	109	97	0.058
3	248 ^c		117	93	0.063

^a Calculated for $\Theta = 0^\circ$. ^b Benzene. ^c Calculated by means of the method of Hasato⁴⁵ and Pacault⁴⁶ (modified Pascal's empirical formula⁴⁷). The values of χ_M and χ_\perp (in $\text{cm}^3\text{mol}^{-1} \cdot 10^{-6}$) of poly[*para*-phenylene]s are taken from ref 43.

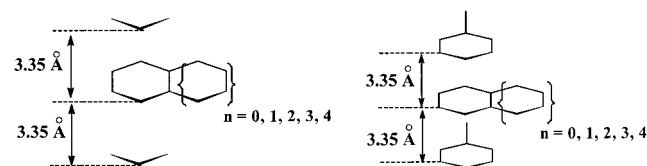


Figure 2. 1-D stacks consisting of polyacenes and allyl (Al) and benzyl (Bl) radicals, respectively.

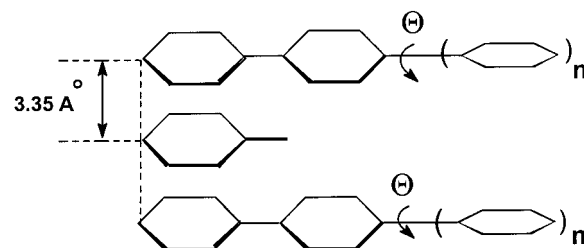
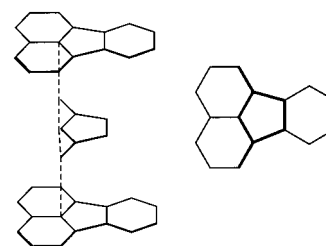


Figure 3. 1-D stacks consisting of poly[*para*-phenylene]s (Pp) and benzyl radical.

SCHEME 3



of J_{eff} , J , J_{kin} and J_{ind} are proportional to the spin-transfer efficiency expressed by $P(H)$ (see Tables 1, 2, 5, and 6).

The results for the face-to-face homonuclear MMRCs are contained in Tables 1 and 2. For those cases where the topology of the systems conforms to the stipulations of the CRLH theorem or its extension, the HFB consists of degenerate NBMOs. This HFB is situated within a large energy gap (see Figure 4) and results in zero values of the kinetic term, $J_{\text{kin}} = 0$, and positive values of the Coulomb (direct) exchange integral J . This is the main component of the effective exchange integral, J_{eff} . As a result, the magnetic interaction is ferromagnetic. The electrons within the HFB of the nonalternant MMRC, consisting of fluoranthene and the radical T shown in Scheme 3 are also ferromagnetically coupled with $J_{\text{eff}} = J + J_{\text{ind}} = 20 + 4 = 24 \text{ meV}$. The spin transfer from radical T to Fl is characterized by a value of $P(H) = 0.037$.

As can be seen from Tables 1 and 2 the effective exchange integral, J_{eff} , is proportional to the diamagnetic molsusceptibilities χ_M and the susceptibilities perpendicular to the molecular plane χ_\perp (both quantities $\times 10^6$ in $\text{cm}^3 \text{mol}^{-1}$). An exception (see Table 2) is the MMRC consisting of benzyl radical and pentacene. The MMRCs of allyl radical and polyacenes, and

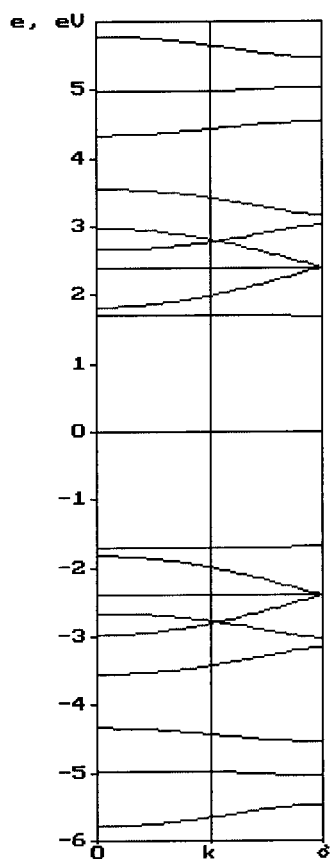


Figure 4. Energy dispersion of the bands (in π electron approximation) of an 1-D MMRC consisting of biphenyl and benzyl radical (see Figure 3, $n = 0$). The 7th and 13th bands are 2-fold degenerate.

TABLE 3: Calculated Values of J_{eff} (in meV) of MMRCs Pe–Pn–Pe and Bl–Pn–Bl (see Figure 5)

n	α [°]	$J_{\text{eff}}(\text{Pe–Pn–Pe})$	$J_{\text{eff}}(\text{Bl–Pn–Bl})$
1	0	114	42
1	57.9	28	~ 0
2	0	182	68
2	57.9	103	29
2	38.6	23	~ 0

benzyl radical and poly[*para*-phenylene]s exhibit a linear relationship between the values of J_{eff} and the susceptibilities χ_M and χ_L . A magnetic moment is induced in the diamagnetic molecule by the inhomogeneous magnetic field of the radical. The induced magnetic moment is proportional to the magnetic susceptibilities χ of the molecule. This phenomenon is analogous to the electrical moment induced in a molecule by an electric field. Therefore, it is expedient to search for a relationship between the effective exchange integral and χ . As can be seen from the data of Table 1, the dependence between the effective exchange integral and both the diamagnetic susceptibility and its normal component, χ_M and χ_L , is linear. This possibly results from the linear relationship between χ_M and χ_L .

For the MMRCs belonging to one and the same type, the effective exchange integral J_{eff} is proportional to the measure $P(H)$ of the spin transfer defined in eq 4,

$$J_{\text{eff}} \sim P(H)$$

and follows from the values in Tables 1 and 2.

In Table 3, the results of MMRCs with slipped face-to-face arrangement of poly[perinaphthalene]s (Pn, $n = 0, 1$) and perinaphthenyl and benzyl radicals, respectively, are collected

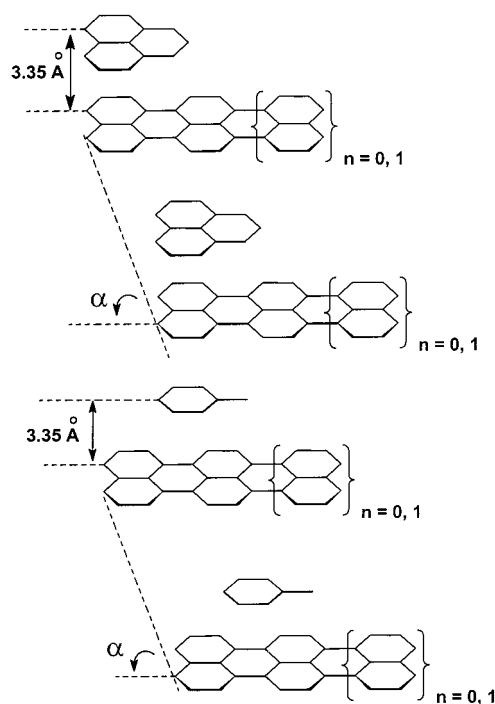


Figure 5. 1-D stacks consisting of poly[perinaphthalene]s and perinaphthenyl radical (Pe) and benzyl radical (Bl), respectively.

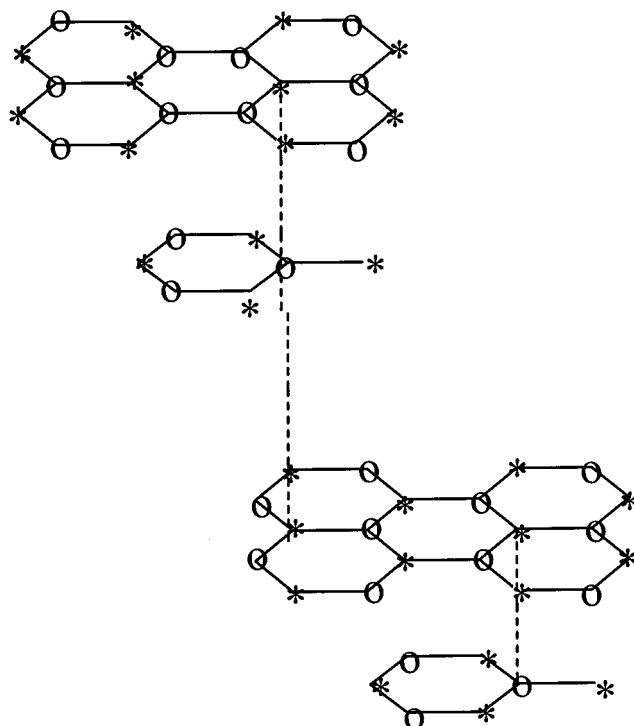


Figure 6. 1-D MMRC stacks, build up of benzyl radical and perylene (slip angle $\alpha = 57.9^\circ$, see also Figure 5). A doubling of the EUs arises and NBMOS are absent ($J_{\text{eff}} = 0$).

(see Figure 5). In stacks with *slipped face-to-face* structure a HFB with NBMOS does not necessary arise, depending on the arrangement and the topology of the EUs. For MMRCs consisting of benzyl radical and poly[perinaphthalene]s, the magnetic interaction vanishes, $J_{\text{eff}} = 0$, at slip angles $\alpha = 57.9^\circ$ and 38.6° (Figure 6). This causes a doubling of the EU and NBMOS are absent in these stacks.

The replacement of a PAH H by a heterocyclic one in an MMRC stack leads to a decrease of the effective exchange

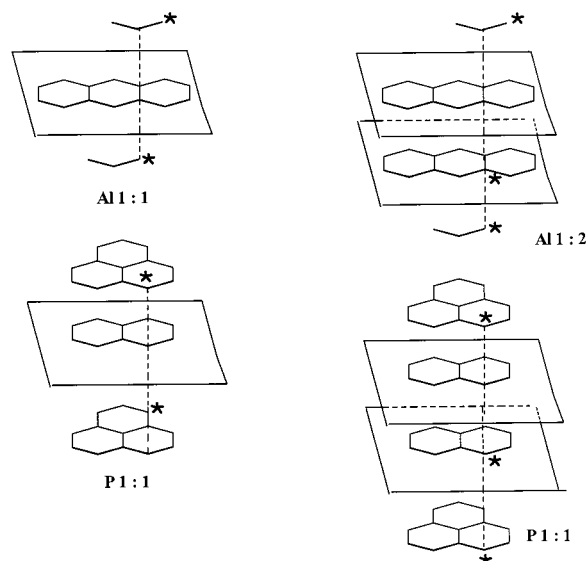


Figure 7. 1-D stacks of 1:1 and 1:2 MMRCs consisting of perinaphthyl radical (Pe) and naphthalene and allyl radical (Al) and anthracene.

TABLE 4: Calculated Values of J_{eff} (in meV) of the 1:1 and 1:2 MMRCs Shown in Figure 7

MMRC	J	J_{ind}	J_{eff}
Al1:1	62	5	67
Al1:2			<i>a</i>
P1:1	19	4	23
P1:2			<i>a</i>

^a Nonmagnetic state.

integral and the $P(H)$ value because of the smaller intermolecular resonance integrals and a smaller overlap between the subunits.

4.2. 1:1 and 1:2 MMRCs. Figure 7 displays stacks of 1:1 and 1:2 1-D mixed crystals with face-to-face arrangement. They are built up of allyl radical and anthracene and of perinaphthyl radical and naphthalene molecules, respectively. The interplanar distances between the radicals and the diamagnetic molecules and between the diamagnetic molecules are equal to $r = 3.35$ Å as in the 1:1 structures. In Table 4 are shown the calculated values of the effective exchange integral J_{eff} . The ground state of 1:2 MMRCs is a nonmagnetic. In the 1:2 stacks again a doubling of the EUs arises, similarly to some of the MMRCs with slipped face-to-face arrangement, and no NBMOs were found.

4.3. Heteronuclear MMRCs. **4.3.1. MMRC Stacks with Polymethine Type Radicals.** Different arrangements were found in the crystal structures of the polymethine radicals. In the crystalline state, some of the polymethine type radicals form radical pairs with paired spins ("pimerization";^{26–29} see also the paper of Gleiter et al.³⁰) or 1-D stacks with an antiferromagnetic ground state. In Wurster's blue salts (Wu), the radical cations in the stacks are shifted with respect to each other along the N–N axis.^{31–33} The structure and the magnetic properties of 1-D stacks of Wurster's radicals have been investigated theoretically in ref 34. The antiferromagnetic interaction between the radicals within the 1-D stacks is in qualitative agreement with the results for dimers, estimated experimentally by Yamaguchi et al.³⁵ The negative value of the effective exchange integral, $J_{\text{eff}} < 0$, is determined by the kinetic (antiferromagnetic) and indirect exchange interaction. On the other hand, in stacks of MMRCs consisting of Wurster's radicals and different PAHs (see Figure 8 and Table 5), the electrons within the HFB are ferromagnetically coupled.

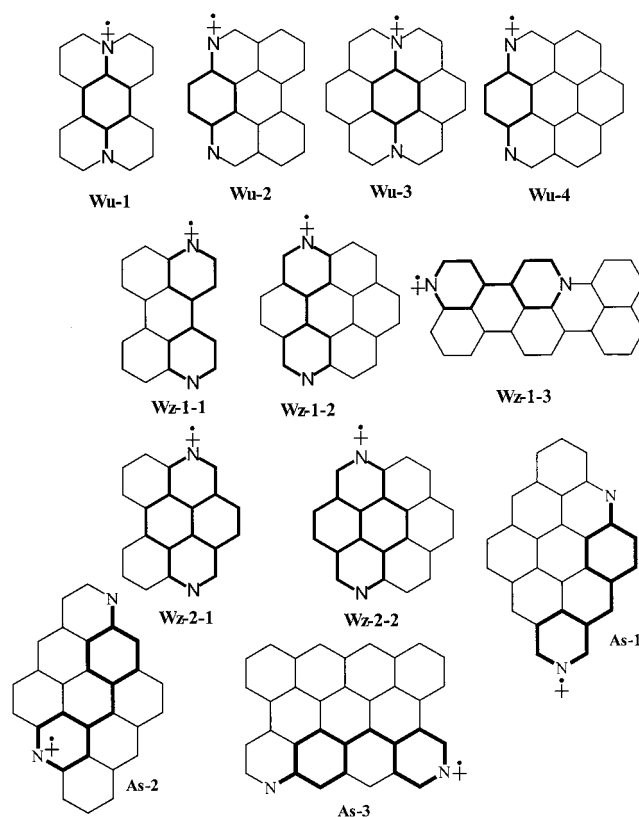
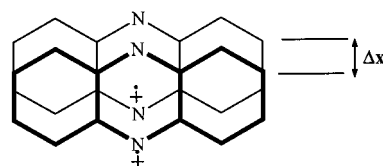


Figure 8. MMRCs, consisting of polymethine radicals and different polycyclic aromatic hydrocarbons. The distances between the subunits in the face-to-face stacks are 3.35 Å.

TABLE 5: Calculated Values of J_{eff} (in meV) of MMRCs Consisting of Weitz's (Wz) and Wurster's (Wu) Radicals (see Figure 8), $P(H)$ Values (eq 4), the Width of the HFB $\Delta\epsilon$ (in meV), and the Renormalized Hubbard Integral U (eq 3, in eV)

MMRC	J	J_{ind}	J_{kin}	J_{eff}	$P(H)$	$\Delta\epsilon$	U
Wu-1	32	1	0	33	0.014	49	3.035
Wu-2	142	8	−1	149	0.191	127	1.939
Wu-3	34	2	0	36	0.019	32	3.016
Wu-4	74	4	0	78	0.055	71	2.687
Wz-1-1	98	8	−3	103	0.324	233	1.100
Wz-1-2	145	9	−1	153	0.157	192	2.369
Wz-1-3	24	3	−1	26	0.100	111	1.222
Wz-2-1	34	4	0	38	0.028	75	1.602
Wz-2-2	193	18	22	189	0.312	392	0.806
As-1	99	45	0	144	0.208	90	1.625
As-2	63	9	0	72	0.082	62	1.185
As-3	87	12	0	99	0.098	73	1.533

SCHEME 4



The EU of the crystalline 10-Ethylphenacin-5(10H) (Eph, see Figure 9) consists of four independent radical pairs with close interplanar distances between 3.28 and 3.36 Å.³⁰ The ground state of the stacks is nonmagnetic. The magnetic interaction of the electrons within the HFB of 1-D MRC stacks consisting of Eph radicals has been calculated. The arrangement of the Eph radicals in the models shown in Scheme 4 corresponds to the radical pairs A and B within the EU of Eph crystals.³⁰

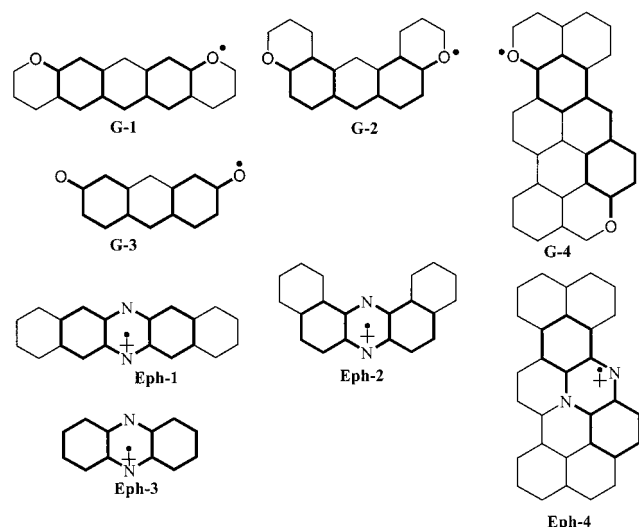


Figure 9. MMRCs consisting of galvinoxyl radical (G) and 10-Ethylphenacin-5(10H) (Eph), respectively, and different PAHs. The distances between the subunits in the *face-to-face* stacks are 3.35 Å.

TABLE 6: Calculated Values of J_{eff} (in meV) of MMRCs Consisting of Galvinoxyl Radical (G) and 10-Ethylphenacin-5(10H) Radical (Eph) and Various PAH (see Figure 9)

MMRC	J	J_{ind}	J_{kin}	J_{eff}	$P(\text{H})$	$\Delta\epsilon$	U
G-1	22	3	0	25	0.950	82	1.677
G-2	19	2	0	21	0.945	12	1.899
G-3	27	3	0	30	0.969	34	2.146
G-4	27	4	0	31	0.967	14	1.420
Eph-1	66	4	-2	68	0.119	191	2.050
Eph-2	34	2	-1	35	0.044	121	2.429
Eph-3	36	2	~0	38	0.063	165	2.341
Eph-4	30	3	0	33	0.039	25	2.465

The Eph radicals in 1-D stacks of MRCs are laterally shifted along the N–N axis. The character of the spin exchange is qualitatively independent of the Δx value. In all cases, the large value of the kinetic term, $J_{\text{kin}} = J_{\text{eff}} < 0$, determines the antiferromagnetic character of the spin coupling. For instance, at $\Delta x = 0$, corresponding to a full face-to-face arrangement $J_{\text{eff}} = J_{\text{kin}} = -68$ meV. As in the case of Wurster's radicals, in stacks of MMRCs comprising Eph radicals and different PAHs (see Figure 9 and Table 6), the electrons within the HFB are ferromagnetically coupled.

The stacks of MMRCs built up of Weitz's and Wurster's type polymethine radicals are nonalternant systems. Therefore, the width of the HFB, $\Delta\epsilon$, is different from zero; however, rather narrow: $\Delta\epsilon < 400$ meV (see Tables 5 and 6). This determines the ferromagnetic spin coupling between the electrons within the HFB, $J_{\text{eff}} > 0$, as can be seen from Tables 5 and 6.

This result is in qualitative agreement with that obtained from of Whangho's and Hubbard's conditions.

4.3.2. Whangho's and Hubbard's Conditions. Whangho³⁶ has derived a condition which allows to determine in a simple qualitative way the relative stability of the high-spin (magnetic) and the low-spin (nonmagnetic) states in the HFB, respectively:

$$\Delta\epsilon < (\pi/4)U \quad (6)$$

where $\Delta\epsilon$ is the width of the HFB and U is the renormalized Hubbard integral (see eq 3).

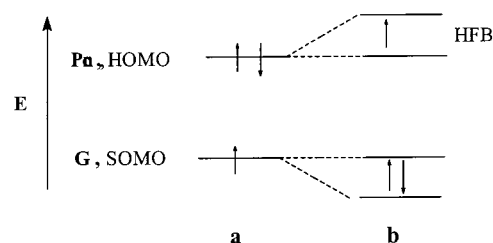


Figure 10. (a) Electron distribution in the frontier MOs for noninteracting subunits, galvinoxyl radical, G, and poly[perinaphthalene], Pn ($n = 2$) (see Figure 9). (b) Electron distribution in the frontier bands, arising by the interaction between the subunits within the stacks of MMRC, consisting of G and Pn ($n = 2$).

Equation 6 is similar to that derived by Hubbard²⁰ which takes the dynamics of the electrons in a narrow HFB into account:

$$\Delta\epsilon < (2/\sqrt{3})U \quad (7)$$

Table 5 contains the values of $\Delta\epsilon$ and the values of the renormalized Hubbard parameter U calculated for the MMRCs stacks with polymethine radicals investigated. A comparison of the values of $\Delta\epsilon$ and U reveals that all of the polymers have a high-spin magnetic ground state.

4.3.3. MMRC Stacks with Galvinoxyl Radicals. The magnetic properties of GI in solid state have been investigated experimentally and theoretically by Mukai et al.^{37,38} and by Awaga et al.^{39–41} In the high-temperature phase, which is stable above 85 K, the radical pairs in the 1-D stacks are ferromagnetically coupled with a value of the effective exchange integral $2J_{\text{eff}} = E_{\text{S}} - E_{\text{T}} = 1.5 \pm 0.7$ meV.^{37–39} A ferromagnetic interaction was also observed between the radical pairs in mixed crystals of GI and hydrogalvinoxyl.^{38–40} The crystal structure of GI below 85 K is unknown. An antiferromagnetic interaction between neighboring radicals was determined in this low-temperature phase.^{39,40} Models of 1-D MRCs of galvinoxyl radicals (G) were investigated theoretically in ref 42. It was shown that the character of the magnetic interaction depends essentially on the topology and geometry of the stacks. In the case of MMRCs considered in this study (see Figure 9) the electrons in the HFB are also ferromagnetically coupled (Table 6).

4.3.4. Spin Densities. In the case of the homonuclear alternant MMRCs there is some spin transfer (ST) within the EUs from the NBMO of the radical to the diamagnetic PAH, but the spin density is localized mainly in the radical. The value of $P(\text{H})$ is small: $P(\text{H}) < 0.1$ (see Tables 1 and 2). In the MMRCs consisting of heteronuclear ion radicals and PAHs, a ST also occurs from the radical to the PAH. However, if the HOMO energy of the PAH is higher than that of the SOMO energy of the radical

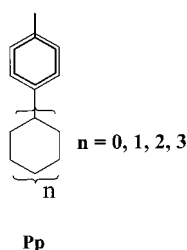
$$E(\text{HOMO, PAH}) > E(\text{SOMO, R})$$

then the spin density is localized in the PAH (see Figure 10). An example for such an interaction (see Figure 10) is the MMRC consisting of galvinoxyl radical (G) and poly[perinaphthalene] (G-4 in Figure 10): $E(\text{HOMO, Pn}) = -0.528$ eV $>$ $E(\text{SOMO, G}) = -1.776$ eV, and $P(\text{H}) = P(\text{Pc}) = 0.967$ (see Table 6).

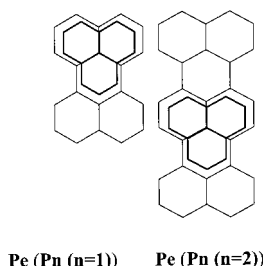
5. Topological Effect of the Exchange Interaction (TEEI) in MMRCs

The value of the effective exchange interaction (J_{eff}) in some MMRCs that consist of one and the same radical R^{\bullet} and different

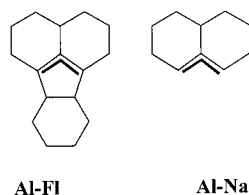
hydrocarbons H are identical. Typical examples are the MMRCs which are build up of benzyl (or allyl) radical and poly[*para*-phenylene]s (face-to-face type):



The magnetic susceptibilities χ_M of poly[*para*-phenylene]s vary from $54.8 \text{ cm}^3 \text{ mol}^{-1} \times 10^{-6}$ in H = benzene to $201.0 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ in H = quaterphenyl.⁴³ In all cases the exchange integral is identical, $J_{\text{eff}} = 9.0 \text{ meV}$. The magnetic susceptibility of perylene, Pe (Pn ($n = 1$)), is $\chi_M = 166.8 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$. The magnetic susceptibility of Pn ($n = 2$) calculated by means of the method of Pacault⁴⁶ is $\chi_M = 260.9 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$. However, in both cases the exchange integral is $J_{\text{eff}} = 114 \text{ meV}$.

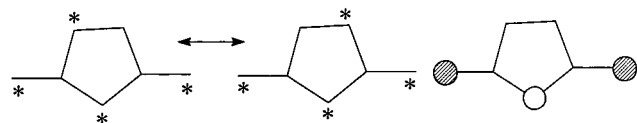


The magnetic susceptibilities of fluoranthrene, Fl, and naphthalene, Na, are significantly different. However, for the latter two molecules the exchange integral within the stacks Al-Fl and Al-Na, is $J_{\text{eff}} = 107 \text{ meV}$.



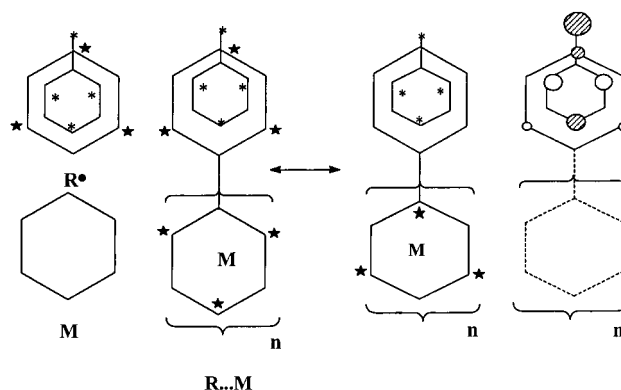
The physical nature of this effect is similar to that which appears in 1-D polymers with a continuous π -system of conjugation and indirect exchange interaction.⁴⁸ The special topological effect of the exchange interaction (TEEI) can be explained by means of the generalized CRLH theorem.^{6,7} Based on the extended CRLH theorem two corollaries follow.⁷

Corollary I: If the conjugated π -system has various maximum disjoint sets, R_k , $k = 1, 2, \dots, p$, then the NBMOs are composed only of the AOs of their intersection $R_1 \cap R_2 \cap \dots \cap R_p$. Corollary I yields the set of AOs from which the NBMOs are composed. In the case of the nonalternant hydrocarbon

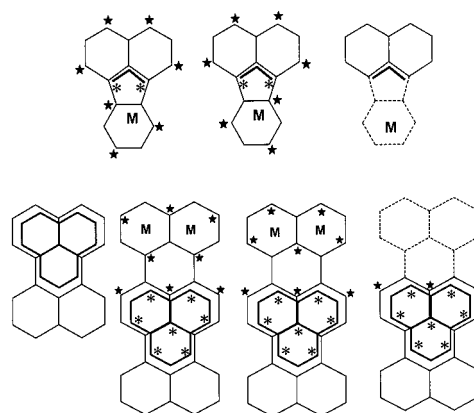


there are two different maximum disjoint sets of cardinality 4, and therefore the NBMO coefficients are nonzero for the π sites in the pentadienyl radical fragment.

SCHEME 5



SCHEME 6



Corollary II follows from corollary I and determines the structural principle of TEEI.

Corollary II: Let us consider a system consisting of a monoradical subunit R^\bullet for which the extended theorem is valid, linked with an even alternant closed-shell unit M:



If the π centers r of R^\bullet which are connected with the π centers of M belong to the set of the nonstarred ones $\{R^\circ\}$ (the MO coefficients are $C_r = 0$), then all the NBMO coefficients in the fragment M are zero, i.e., the NBMO coefficients are nonzero only for the starred π centers in R. A typical example is the EU of a MMRC which consists of benzyl radical and biphenyl shown in Scheme 5. The NBMO coefficients are zero for all π centers in the rings M which do not interact with the neighboring benzene rings and with neighboring EUs.

Scheme 6 shows that the conditions of Corollary II are valid for the MMRCs consisting of Al and Fl, and of Pe and Pn ($n = 1, 2$), respectively. The NBMO coefficients are zero for all π centers in the benzene rings M which do not interact with the neighboring benzene rings and with neighboring EUs.

The TEEI (Corollaries I and II) is valid only in topological approximation, which only takes into account the $2p\sigma-2p\sigma$ interaction between first neighbors. If one extends the interaction to the second (and third) neighbors, then no significant difference in the values of J_{eff} for the different systems occur.

6. Conclusions

As an essential result of this study it was possible to establish a relationship between the magnetic properties of mixed 1-D crystals, consisting of radicals and diamagnetic polycyclic aromatic hydrocarbons, and those of the parent 1-D crystals,

consisting only of radicals. The intermolecular interaction within the 1-D stacks of MMRCs is connected with a spin transfer from the radical to the diamagnetic molecule and determines the magnetic interaction within the half-filled band. In some cases, the antiferromagnetic interaction in the parent molecular radical crystals becomes ferromagnetic in MMRCs and vice versa.

The significantly higher values of the effective exchange integral, in some cases is $J_{\text{eff}} \sim 10^2$ meV, correspond to higher values of the critical temperature of the macroscopic system. Since MMRCs are 1-D systems, a magnetic ordering occurs only for $T_c = 0$ K.^{50,51} However, the real crystals of MMRCs, presumably synthesized, are 3-D systems. Even weak interaction between the separate 1-D stacks may cause the stabilization of the macroscopic spin configuration at $T_c > 0$ K.⁵² MMRCs are probably the only approach to the possibility of increasing the critical temperature of purely organic polymers (1-D stacks) with magnetic ordering.

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