

Nature of the Magnetic Interaction in Organic Radical Crystals. 3. Galvinoxyl Radicals in 1-D Crystals^{†,‡}

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Using the band theory, the nature of the spin exchange interaction between the unpaired electrons within the half-filled band of 1-D organic radical crystals, consisting of galvinoxyl radicals, is investigated theoretically. The various contributions to the Heisenberg effective exchange integral, J_{eff} , the direct, kinetic, and indirect spin exchange, are evaluated quantitatively for the experimentally determined crystal structure. To establish the dependence of J_{eff} on the crystal topology and geometry, the calculations are carried out for several artificial model 1-D crystals of the galvinoxyl radical and of the parent hydrocarbon radical. J_{eff} was also calculated for different interplanar distances of the stacking in the real crystal.

1. Introduction

The interest of the magnetic properties of low-dimensional pure organic systems, in particular of quasi one-dimensional (1-D) systems, is determined by the search of organic materials whose ground state is characterized by a magnetic ordering.¹

Theoretical investigations, so far, are directed mainly to 1-D extended π -systems: polymers with ferromagnetic coupling between the delocalized electrons in the half-filled band (HFB).^{2–4} For these systems, the correlation between the geometry, topology, and the type of the exchange interaction (ferro- or antiferromagnetic) is well established.^{2–4} From this point of view only a few studies have been done for molecular radical crystals⁵ (MRCs) in which the elementary units (EUs) are weakly interacting subsystems.

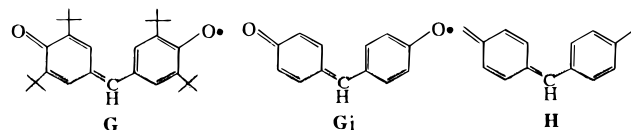
With the MO approach, the problem is considered in the papers of Yamaguchi and Fueno,⁶ Kollmar and Kahn,^{7–9} and Yoshizawa and Hoffmann¹⁰ (see also ref 11). However, in these papers the magnetic interaction was considered only for dimers and clusters, but not for infinite MRCs. The influence of the geometry on the nature of the magnetic interaction was studied experimentally for substituted verdazyl radicals by Wudl et al.¹²

The magnetic interaction of dimers of galvinoxyl radicals was investigated by Awaga^{13,14} by means of INDO open-shell calculations.

In the first communications of this series^{15,16} we have begun to study the correlation between the composition, topology, and geometry of MRCs and the nature of the exchange interaction using the band model. It was applied to 1-D crystals in which the EUs are radicals with delocalized π -electron systems.

One aim of this paper is to extend the study of the relation between the nature of the spin exchange interaction and the arrangement (topology and geometry) of galvinoxyl radicals (**G**) (Coppinger's radical¹⁷) in the MRC for which the crystal

structure and the magnetic properties are well investigated experimentally. Another aim is to compare the results of galvinoxyl with those of the parent hydrocarbon radical **H** in several models of MRCs. For the purpose of simplicity, the radical **Gi** (in which the *tert*-butyl residues are omitted in **G**) was used to build up all the stacks that were investigated:



2. Experimental Data of the Magnetic Properties of Galvinoxyl

The magnetic properties of **G** in the solid state were investigated by Mukai et al.^{18,19} and by Awaga et al.^{13,14,20} In the high-temperature phase (stable above 85 K), the radical pairs in the 1-D stacks are ferromagnetically coupled with an effective exchange integral $2J_{\text{eff}} = E_S - E_T = 1.5 \pm 0.7$ meV.^{13,14,20} A ferromagnetic interaction was also observed between the radical pairs in mixed crystals of **G** and hydrogalvinoxyl.^{13,14,20} The crystal structure of **G** below 85 K is unknown. In this low-temperature phase, an antiferromagnetic interaction was determined between neighboring radicals.^{14,20}

3. 1-D Models of the Radical Crystals

The molecular and crystal structure of galvinoxyl at room temperature has been determined by X-ray diffraction analysis.²¹ The EUs in the 1-D stacks consist of two galvinoxyl radicals. The radicals are rotated to each other at 180° in the radical pairs (screw axis 2₁). The distance between neighboring radicals R_0 (the shortest C...C distance is 3.71 Å)²¹ is relatively large in comparison with stacks of molecules or other radicals (e.g., $R_0 = 3.105$ Å in molecular crystals of Wurster's Red Bromide²²). The radicals are almost planar: the oxyphenyl residues are twisted relative to each other by about 12°.²¹ Therefore, in all our models we presume a planar structure. The bond lengths were optimized with the AM1 procedure of the SPARTAN 3.0 program package.²³

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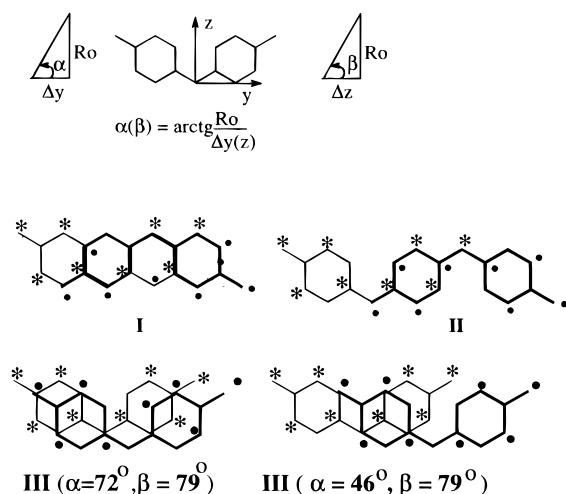


Figure 1. Arrangement of the radicals in the stack models which are alternant systems.

The galvinoxyl radical **G** can be considered as a perturbed hydrocarbon radical **H**. **H** is an odd-alternant π -system for which the Coulson–Rushbrooke–Longuet–Higgins (CRLH) theorem^{24,25} is valid. According to this theorem, an alternant hydrocarbon having S^* starred non-neighbored π -centers and R unstarred non-neighbored π -centers ($S^* > R$) possesses $S^* - R$ nonbonding MOs (NBMO). Hence, **H** has $8^* - 7 = 1$ NBMO.

To explain the dependence of the type of intermolecular spin exchange interaction on the topology of the radicals within the MRCs, we consider also stacks (corresponding to models **I–IV**, see below) that are build up from the homonuclear radical **H**. If a model 1-D stack of **H** has a topology (by taking into account the interaction only between the first neighboring π -centers) that corresponds to the CRLH theorem, the energy spectrum is characterized by a band of degenerate NBMOs within which the electrons are coupled ferromagnetically.^{15,26}

To be consistent with the above finding, we consider two classes of 1-D model stacks: (i) The first is stacks that are alternant systems (if they consist of the radical **H**). Then, they possess a HFB consisting of NBMOs. To this class belong the models **I**, **II**, and **III** shown in Figure 1. Besides the stack based on the experimental determined arrangement of **G** in the crystal (model **I**), the following model stacks were considered to investigate the dependence of the nature of the magnetic interaction on the topology and geometry of the radicals **Gi** in the crystal.

Model II: *rotated and slipped* (along the y axis) type with different slip angles α . The model **I** is a special case of this type with a slip angle $\alpha = 57^\circ$ (Figure 1).

Model III: *slipped face to face* along the short molecular axis (z) and along the long molecular axis (y) with different slip angles β and α .

(ii) The other class of 1-D model stacks is stacks for which the CRLH theorem is not valid. To this class belong the models **IV** shown in Figure 2.

Model IV: *slipped face-to-face* along the long molecular axis (y) with different slip angles α . In the case of face-to-face structures, the radicals are divided by a mirror plane of symmetry σ_h perpendicular to the translation axis. The *full face-to-face* arrangement of the radicals corresponds to the model **IV** with a slip angle $\alpha = 90^\circ$.

Here, we consider only those models in which the π -centers of neighboring radicals are situated one upon another ($R = R_0 = 3.71 \text{ \AA}$). If we take into account also the interaction between

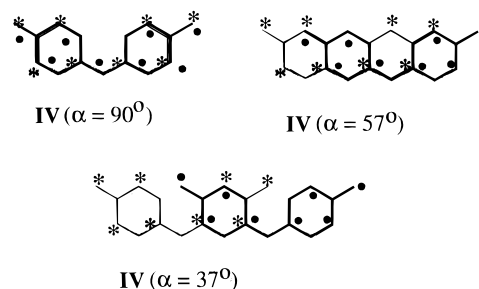


Figure 2. Radical pairs in 1-D stacks for which the conditions of the CRLH theorem for the existence of a HFB with degenerate NBMOs are not fulfilled.

the second neighboring π -centers, then the distances are larger than $R = 3.96 \text{ \AA}$, and the resonance integrals have very small values. To investigate the dependence of the absolute values of the effective exchange integral J_{eff} on the intermolecular distance R between the radicals, calculations were also done for $R = 3.0 \text{ \AA}$ and $R = 3.2 \text{ \AA}$.

4. Methods of Investigations

Energy Spectra. The radical crystals are considered as 1-D systems for which the Born–von Karman conditions are fulfilled. The band structure was calculated in the π -electron tight-binding approximation using a Hückel–Hubbard²⁷ version of the Bloch method. If for the 1-D system we adopt a Bloch form of the wave vector k ($k \in [-\pi, \pi]$):

$$|k\rangle = N^{-1/2} \sum_{\mu} \sum_p C_p(k) \exp(-ik\mu) |p, \mu\rangle \quad (1)$$

the MO energies $e(k)$ are obtained by numerical diagonalization of the matrix

$$\mathbf{E}(k) = \mathbf{E}_0 + \mathbf{V} \exp(ik) + \mathbf{V}^+ \exp(-ik) \quad (2)$$

where \mathbf{E}_0 is the energy matrix of the EU, \mathbf{V} is the interaction matrix between neighboring EUs (μ th and $(\mu+1)$ th), and \mathbf{V}^+ is the transposed matrix (for the detailed formalism, see refs 15, 26).

Spin Exchange of the Electrons within the Half-Filled Band. Let us denote by $J_{\text{eff}}(\nu, \rho)$ the effective exchange integral in the Heisenberg Hamiltonian:

$$\mathbf{H} = -2 \sum_{\nu \neq \rho} J_{\text{eff}}(\nu, \rho) S_\nu S_\rho = -2 \sum J_{\text{eff}}(\tau) S_\nu S_\rho \quad (3)$$

between the EUs ν and ρ upon which the Wannier functions are localized. Based on the results of Anderson,²⁸ it has been shown²⁹ that J_{eff} can be expressed as a sum of three contributions (in the following, the dimensionless distance parameter $\tau = |\nu - \rho|$ is omitted for simplicity):

$$J_{\text{eff}} = J - J_{\text{kin}} + J_{\text{ind}} \quad (4)$$

The terms in eq 4 have the following physical meaning. J is the Coulomb exchange integral between the localized Wannier states within the ν th and ρ th EUs. J_{kin} expresses the kinetic spin exchange representing the antiferromagnetic contribution to the spin exchange:

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

In eq 4a, t is the transfer (hopping) parameter between adjacent Wannier states, given by $t = \langle u|H|\mu + 1\rangle$, where H is the periodic one-electron Hamiltonian. U_0 and U_1 are the Coulomb

repulsion integral of two electrons, residing in the same Wannier state and occupying adjacent Wannier states, respectively. $U = U_0 - U_1$ is the renormalized Hubbard parameter.^{27,29} J_{ind} is the term of the indirect exchange of electrons (spin polarization exchange) via delocalized π -electrons in the filled energy bands. This term is calculated using a formalism described in ref 30. The sign of J_{ind} , plus or minus, is determined by the structure of the 1-D systems. The sign of the effective exchange integral J_{eff} determines the character of the ground state: a ferromagnetic (FM) high-spin state with $J_{\text{eff}} > 0$, or an antiferromagnetic (AFM) state with $J_{\text{eff}} < 0$.

Parametrization. A standard value $\beta_0 = -2.4$ eV^{15,16,26} has been used for the resonance integral between $2p\pi-2p\pi$ AOs of the carbon atoms at a distance $R_0 = 1.40$ Å. $\beta(\text{C-O}) = -2.4$ eV. The parameter used for the Coulomb integral of oxygen is $\alpha_O = \alpha_C - 1.5\beta_0$. The dependence of the resonance integrals between two $2p\pi$ atomic orbitals which belong to neighboring carbon π -centers in **Gi** (**H**) was calculated with Mulliken's relation³¹ $\beta(R) = \beta_0 S(R)/\beta(R_0)$. The resonance integrals between two π -centers belonging to neighboring radicals have been calculated also with Mulliken's relation³¹ taking into account the angular dependence of the overlap integrals. The overlap integrals (S) were calculated with the following standard values of the Slater orbital exponents: $z_C = 3.25$ and $z_O = 4.55$. The two-center atomic Coulomb integrals $\gamma_{\mu\nu}$ for the calculation of the various contributions to the effective spin exchange were evaluated using the Mataga-Nishimoto³² approximation according to eq 5:

$$\gamma_{\mu\nu} = e^2/(a + R) \quad (5)$$

with $a = 2e^2/(\gamma_{\mu\mu} + \gamma_{\nu\nu})$. The following standard values of the one-center Coulomb integrals were used: $\gamma_{\text{CC}} = 10.84$ eV³³ and $\gamma_{\text{OO}} = 14.27$ eV.³⁴

The resonance integrals between two nearest-neighboring $2p\sigma$ AOs at $R = R_0 = 3.71$ Å are $\beta_{\sigma\sigma}(\text{C-C}) = -0.145$ eV, $\beta_{\sigma\sigma}(\text{O-O}) = -0.0056$ eV, and $\beta_{\sigma\sigma}(\text{C-O}) = -0.038$ eV. At a distance $R = 3.20$ Å, the corresponding values are $\beta_{\sigma\sigma}(\text{C-C}) = -0.188$ eV and $\beta_{\sigma\sigma}(\text{C-O}) = -0.056$ eV; at $R = 3.00$ Å $\beta_{\sigma\sigma}(\text{C-C}) = -0.546$ eV and $\beta_{\sigma\sigma}(\text{C-O}) = -0.201$ eV.

5. Results and Discussion

Energy Spectra. The type and magnitude of the MO splitting resulting in energy bands depend on the topology and the geometry of the MRCs. In the case of 1-D stacks with the hydrocarbon monoradical **H** with a full face-to-face structure and if the radicals are divided by a mirror plane of symmetry σ_h perpendicular to the translation axis, an analytical expression can be derived for the MO energies. Each MO of the monoradical of energy e_p splits in the stacks into MOs of energies¹⁵

$$e_p(k) = e_p + 2\beta_{\sigma\sigma} \cos k \quad (6)$$

where $\beta_{\sigma\sigma}$ is the resonance integral between $2p\sigma-2p\sigma$ AOs. From the above equation, it follows that the bandwidth $\Delta\epsilon$ is equal to

$$\Delta\epsilon = 4|\beta_{\sigma\sigma}| = \Delta\epsilon_0 \quad (7)$$

From eq 7 also follows that the bandwidth $\Delta\epsilon$ depends only on the value of the resonance integral $\beta_{\sigma\sigma}$; that is, $\Delta\epsilon$ has the same value for two arbitrary homonuclear stacks with the same values of $\beta_{\sigma\sigma}$.

TABLE 1: Calculated Values (All Entries Are in meV) of the Width of the HFB $\Delta\epsilon$, the Transfer Parameter t , and the Components of the Effective Spin Exchange between the Unpaired Electrons in the HFB and J_{eff} for Models I, II, and III Consisting of Gi and H in 1-D Stacks and of Polymer P

model	$\Delta\epsilon$	$-t$	$-J_{\text{kin}}$	J	J_{ind}	J_{eff}
I(Gi)	194	35	1	5	2	6
II(Gi)	192	48	2	1	2	1
III(Gi-72°)	~0	~0	0	5	1	6
III(Gi-46°)	~0	~0	0	2	0.5	2.5
I(H)	0	0	0	15	11	26
II(H)	0	0	0	16	12	28
III(H-72°)	0	0	0	12	8	20
III(H-46°)	0	0	0	3	2	5
P	161	38	2	116	12	126

TABLE 2: Calculated Values (in meV) of the Width of the HFB $\Delta\epsilon$ and the Different Contributions to J_{eff} and J_{eff} for Different Distances of Neighboring Galvinoxyl Radicals in Model I(Gi)

R_0 (Å)	$\Delta\epsilon$	$-t$	$-J_{\text{kin}}$	J	J_{ind}	J_{eff}
3.71 ^a	137	35	1	5	2	6
3.20 ^a	494	121	21	33	10	22
3.20 ^b	546	120	25	70	13	58
3.00 ^a	615	157	45	82	23	60
3.00 ^b	793	126	33	119	18	104

^a Calculated with consideration of the interaction only between the first neighboring π -centers (of two radicals). ^b Calculated with consideration of the interaction between the first and the second neighboring π -centers (of two radicals).

TABLE 3: Calculated Values (in meV) of the Width of the HFB $\Delta\epsilon$ and the Contributions to J_{eff} and J_{eff} for Different Distances of Neighboring Radicals in Models II(Gi) and II(H)

model	R_0 (Å)	$\Delta\epsilon$	$-t$	$-J_{\text{kin}}$	J	J_{ind}	J_{eff}
II(Gi)	3.71	192	48	2	1	2	1
II(Gi)	3.20	495	125	17	6	10	-1
II(Gi)	3.00	691	175	36	10	19	-7
II(H)	3.71	0	0	0	16	12	28
II(H)	3.00	0	0	0	288	152	440

TABLE 4: Calculated Values (All Entries Are in meV) of the Width of the HFB $\Delta\epsilon$, the Transfer Parameter t , and the Components of the Effective Spin Exchange between the Unpaired Electrons in the HFB for Models IV of Gi and H Radicals in 1-D Stacks

model	$\Delta\epsilon$	$-t$	$-J_{\text{kin}}$	J	J_{ind}	J_{eff}
IV(Gi-90°)^a	468	117	17	0.3	-1	-17.7
IV(Gi-57°)	282	71	6	3	-0.4	-3.4
IV(Gi-37°)	126	32	1	1.5	-1.5	-1
IV(H-90°)^a	580 ^b	145 ^c	24	0	-6	-30
IV(H-57°)	324	81	7	0	-3	-10
IV(H-37°)	60	14	~0	~0	-1	-1

^a Full face-to-face arrangement. ^b $\Delta\epsilon = 4|t| = 4 \times 0.145 = 580$ meV (see eq 7). ^c $t = \beta_{\sigma\sigma}$ (see eq 8).

In the case of *slipped* or *rotated* and *slipped* types of stacks (consisting of homonuclear or heteronuclear radicals), the bandwidth $\Delta\epsilon < \Delta\epsilon_0$.

Spin Exchange of the Electrons in the Half-Filled Band. For all investigated 1-D models, the effective exchange integral J_{eff} and the corresponding components of J_{eff} decrease rapidly with increasing distances between the EUs (distance parameter τ in eq 3). At $\tau \geq 2$, $J_{\text{eff}} < 10^{-3}$ eV. Therefore, in Tables 1 and 4 are given only the values calculated with $\tau = 1$, i.e., values for neighboring radicals. This is also valid for models **I** and **II**, whose EU consists of two monoradicals.

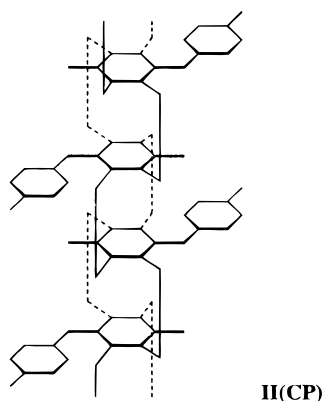
The intermolecular magnetic interaction is FM in nature in the case of the 1-D model **I (Gi)**, which corresponds to the

experimentally determined crystal structure of **G**, and for models **II(Gi)** and **III(Gi)**. In the case of the homonuclear alternant 1-D systems (stacks) **I(H)**, **II(H)**, and **III(H)**, whose topology corresponds to the CRLH theorem, the exchange interaction also has FM character; that is, if the hydrocarbon radical **H** built up the 1-D stacks in which the electrons are ferromagnetically coupled, then the unpaired electrons are also ferromagnetically coupled within the stacks consisting of the corresponding heteroanalogue galvinoxyl radicals (see Table 1).

The calculated value of $J_{\text{eff}}(\text{I(Gi)}) = 6 \text{ meV}$ is of the same order of magnitude as the experimental value of the galvinoxyl MRC, $2J_{\text{eff}} = 1.5 \pm 0.7 \text{ meV}$.^{13,14,20}

The relatively large intermolecular distance in the stacking models ($R_0 = 3.71 \text{ \AA}$) determines the small overlap between the interacting neighboring radicals. This indicates that the exchange interaction should be weak (Table 1). In contrast to galvinoxyl MRCs, the magnitude of the magnetic interaction (antiferromagnetic in nature) between neighboring Wurster's radicals in the 1-D stacks of Wurster's Red Bromide is large, $J_{\text{eff}} \sim 0.1 \text{ eV}$.¹⁶ This relative large absolute value of J_{eff} is caused by the short interplanar distance between the Wurster's radicals in the stacks ($R(\text{exp}) = 3.105 \text{ \AA}$).²²

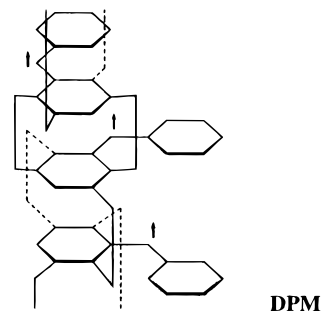
In Table 2 are given the calculated values of J_{eff} for different values of the distance between neighboring galvinoxyl radicals of model **I(Gi)**. The numerical results show clearly the dependence of the ferromagnetic exchange interaction on the intermolecular distance in the stacks. A short fixed interplanar distance ($\sim 3 \text{ \AA}$) may be achieved in a cyclophane-like linking of the radicals in a stack. Cyclophane diradicals with a short distance between the radicals were synthesized and characterized by Iwamura et al.^{35,36} and theoretically investigated by Yamaguchi et al.³⁷ and by Yoshizawa et al.³⁸ Unfortunately, a cyclophane-like connection of galvinoxyl radicals corresponding to model **I** is impossible. For model **II**, for which the CRLH theorem is fulfilled and the exchange interaction should be FM, such a cyclophane structure is shown in the scheme



In Table 3 are collected the calculated values of the width of the HFB $\Delta\epsilon$, the contributions to the effective exchange interaction, and J_{eff} for different interplanar distances of galvinoxyl radicals and the parent hydrocarbon radicals in models **II(Gi)** and **II(H)**, respectively. The width of the HFB increases dramatically on decreasing the interplanar distance from 3.71 to 3.0 \AA in the case of **II(Gi)**. The large splitting of the HFB is caused by the heteroatoms (O atoms). Through that, the kinetic term J_{kin} increases and the indirect exchange interaction (J_{ind}) changes sign from plus to minus. So, the character of the intermolecular exchange interaction becomes AFM at short interplanar distances. In the case of the parent hydrocarbon model **II(H)**, the HFB consists of degenerate

NBMOs and the FM exchange interaction increases by 1 order of magnitude on decreasing the interplanar distance from 3.7 to 3.0 \AA .

A similar problem with results comparable to our work was considered by Yoshizawa, Yamabe, and Hoffmann,³⁸ who have investigated the nature of the magnetic interaction (FM or AFM) in diphenylmethyl radical dimers in several stacking modes using the McConnell model. For all models investigated in ref 38, the results of the character of the spin exchange are in qualitative agreement with the results obtained with the band model. For instance, based on their *rotated face-to-face model* (see the scheme given below), we calculate $J_{\text{eff}} = 0.019 \text{ eV}$ ($J_{\text{kin}} = 0$; $J = 0.012 \text{ eV}$; $J_{\text{ind}} = 0.007 \text{ eV}$) for an infinite stack **DPM** in which the interplanar distance is 3.2 \AA .



If the topology of the MRC does not correspond to the conditions for the occurrence of a HFB with degenerate NBMOs, the ground state has antiferromagnetic character. The numerical results given in Table 4 illustrate these findings.

In the case of all the full face-to-face arrangements of homonuclear alternant hydrocarbon radicals in the 1-D stacks, the transfer parameter t is equal to

$$t = \langle \nu | H | \nu + 1 \rangle = \sum_s a_s^* \langle s^*, \nu | H | s^*, \nu + 1 \rangle = \beta_{\sigma\sigma} \quad (8)$$

Equation 8 is valid taking into account the interaction between not only the first but also the second neighboring AOs because the coefficients of the Wannier function are different from zero only for the starred disjoint set $\{s^*\}$. From eqs 7 and 8 one obtains

$$J_{\text{kin}} = -2t^2/U = -\Delta\epsilon_0^2/8U \quad (9)$$

The relatively large bandwidth, also for the full face-to-face stacking models of **H** and **Gi**, causes the large values of the term J_{kin} and the AFM character of the spin exchange, respectively (see Table 4). The Coulomb (J) and indirect (J_{ind}) contributions are equal to zero or have small values.

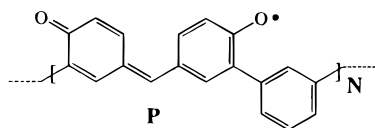
The negative sign of $J_{\text{eff}} \sim J_{\text{kin}}$ corresponding to an AFM exchange interaction between neighboring radicals in the case of an arbitrary full face-to-face stack can also be explained using the McConnell Hamiltonian:³⁹

$$\mathbf{H}^{\text{AB}} = -\mathbf{S}^{\text{A}}\mathbf{S}^{\text{B}} \sum_{\langle k,l \rangle} J_{kl}^{\text{AB}} \rho_k^{\text{A}} \rho_l^{\text{B}} = -\Omega \mathbf{S}^{\text{A}}\mathbf{S}^{\text{B}} \quad (10)$$

where \mathbf{S}^{A} and \mathbf{S}^{B} are the total spins of radical A and radical B, J_{kl}^{AB} is the exchange integral, and $\rho_{k(l)}^{\text{A(B)}}$ are the spin densities at the $k(l)$ th π -center of the radical A (B), respectively. The sum Ω in eq 10 is negative for all face-to-face stacks (all products $J_{kl}^{\text{AB}} \rho_k^{\text{A}} \rho_l^{\text{B}} < 0$), that is, the exchange interaction is AFM in nature.

For the slipped face-to-face stacking models (IV) with slip angles $\alpha < 90^\circ$, the magnetic interaction (of the electrons within the HFB) is also AFM in nature; however, the values of $|J_{\text{eff}}| \sim |J_{\text{kin}}|$ are significantly smaller (Table 4).

The magnitude of the *intermolecular* magnetic coupling within the MRCs is significantly smaller in comparison with those of the *intramolecular* exchange interaction within a 1-D polymer with a π -conjugated system. The calculated values of the magnetic characteristics of the polymer **P**,



collected in Table 1, show that the effective exchange integral of **P** is 1 order of magnitude larger than the corresponding value of the 1-D stack **I(Gi)**:

$$J_{\text{eff}}(\mathbf{P}) \sim 10^{-1} J_{\text{eff}}(\mathbf{I-Gi})$$

6. Conclusions

To understand the relation between the nature of the intermolecular magnetic interaction and the composition and arrangement (topology and geometry) of radicals in 1-D organic radical crystals, MRCs of galvinoxyl radicals were theoretically investigated using the band theory. This study is supposed to yield criteria for the arrangement of the radicals within the stacks to achieve the strongest intermolecular ferromagnetic interaction between neighboring radicals. From the numerical results obtained for several models of MRCs of galvinoxyl radicals and the parent hydrocarbon radicals with different topology and geometry, the following conclusions can be drawn.

The character of the intermolecular exchange interaction depends essentially on the topology and geometry of the stacks. If the topology of the stacks corresponds to the CRLH theorem, then the Coulomb exchange integral J determines the FM character. The arrangement of the galvinoxyl radicals in the molecular radical crystals (corresponding to model **I** in this paper) is obviously optimal for the FM character.

The AFM character of the magnetic interaction of stack models, whose topology does not correspond to the CRLH theorem, is determined mainly by the kinetic spin exchange J_{kin} , while J and J_{ind} are zero or have small values.

The kinetic term J_{kin} (which determines the AFM character of the magnetic interaction) is proportional to the resonance integral $\beta_{\sigma\sigma}$ between neighboring $2p\sigma$ – $2p\sigma$ AOs (eqs 7 and 9). In other words, J_{kin} is proportional to the bandwidth of the HFB $\Delta\epsilon$. The larger $\Delta\epsilon$, the weaker the intermolecular exchange interaction. $\Delta\epsilon$ depends on the topology and the geometry of the stacks: $\Delta\epsilon$ is zero (or has small values) in the case of models of class (i); $\Delta\epsilon$ has finite values which increase with increasing slip angle α . Quantitatively, the same conclusion was drawn from theoretical investigations of the nature of the magnetic interaction of Wurster's radicals in the solid state.¹⁶

The intermolecular magnetic coupling within the MRCs is 1 order of magnitude smaller in comparison with the intramo-

lecular magnetic coupling between galvinoxyl radicals connected by *meta*-phenylene units in an 1-D polymer.

The only way to achieve a strong intermolecular magnetic coupling in 1-D stacks is a fixed arrangement of radicals (or radical ions) with short intermolecular distances ($R \sim 3 \text{ \AA}$), e.g., by a cyclophane-like linking of the radicals.

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