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Structure and Properties of Non-Classical Polymers. XI. Heteroatomic Analogues of Poly(1,3-phenylenemethylene)'s [#]

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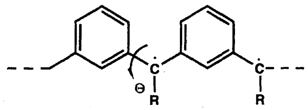
The magnetic properties of a new class of high-spin organic 1-D polymers were studied theoretically. The polymers have the same topology as poly(1,3-phenylenemethylene)s (PMP) and are derived from the latter by substitution of the exocyclic radical center $-\mathrm{C}^{\bullet}\mathrm{R}-$ by $-\mathrm{B}^{\bullet -}\mathrm{R}-$, $-\underline{\mathrm{N}}^{\bullet}-$, $-\mathrm{N}^{+\bullet}\mathrm{H}-$, $-\mathrm{O}^{+\bullet}-$ or $-\mathrm{S}^{+\bullet}-$. All of these polymers possess a narrow half-filled band (HFB) within the energy gap. The nature of spin-exchange interactions of π-electrons within the HFB has been investigated. The three components of the effective exchange integral, J_{eff}, in the Heisenberg Hamiltonian representing the potential (direct), kinetic and exchange (due to the spin polarization—indirect exchange) interaction of the π-electrons in the HFB were calculated. In all cases, the potential (Coulomb) exchange was the main contribution to the ferromagnetic ($J_{\mathrm{eff}} > 0$) exchange interaction.

Poly(1,3-phenylenemethylene)'s **1** are the simplest non-classical (non-Kekulé) alternant high-spin one-dimensional (1-D) systems with ferromagnetic coupled π-electrons in the half-filled band (HFB) (Chart 1). A theory of the energy spectrum and the magnetic properties of **1** has been proposed[1,2] (also see the paper of Yoshizawa and Hoffmann[3] and the references given therein). High-spin dendritic polyradicals having the same structural principle as **1** were synthesized by Rajca et al.[4]

The energy spectra and magnetic properties of **1** result from the topology of the π-electron network. The presence of a set of degenerate non-bonding MOs (NBMOs), a condition for the occurrence of a high-spin state (Hund's rule), is connected to the Coulson–Rushbrooke–Longuet-Higgins (CRLH) theorem.[5,6] This theorem defines the structural principle of Hückel π-systems with degenerate MOs. Systems arising by the substitution of the exocyclic $\mathrm{C}^{\bullet}\mathrm{R}$ group by a heteroatom (or ionic) $\mathrm{X}^{\bullet}$ or a heteroatomic group $\mathrm{X}^{\bullet}\mathrm{R}$ (which contributes one electron to the π-system) are iso-π-electronic with respect to the parent polymers **1**. For such heteronuclear systems the CRLH theorem is not valid. The NBMOs split in a HFB whose width depends on the nature of the substituent $\mathrm{X}^{\bullet}$ ($\mathrm{X}^{\bullet}\mathrm{R}$). Nevertheless, it has been shown[7,8] that poly(1,3-aniline) has a high-spin ground state in its dehydrogenated (**2**) and its cationic (**3**) forms (Chart 2).



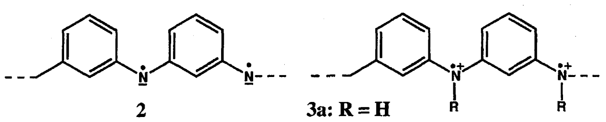
1a: R = H
1b: R = phenyl

Chart 1.

The spin exchange between the electrons within the HFB is of a ferromagnetic nature. This result explains the magnetic properties (high-spin states) of the poly(1,3-aniline) synthesized by Yoshizawa et al.[9]

Some results[7—9] raise the question whether iso-π-electronic high-spin polymers of **1**—**3** expressed by the general formula **4** exist (Chart 3), where X is a heteroatom (or heteroatomic group) donating one electron to the conjugated π-system. Theoretical predictions of the electronic properties of polymers in which X is boron-R (BR) **5**, sulfur (S) **6**, **7**, or oxygen (O) **8** (Chart 4) were made. This help to define this study and provide incentives in the search for purely organic materials with magnetic ordering. The results obtained below are compared with those for polymers **1**—**3**.[7,8]

The following experimental results motivated the authors in their investigations: i) Very recently, Rajca and coworkers[10] have published the synthesis of a stable triplet state molecule, the diradical dianion of a diborane, which is iso-π-electronic with Schlenk's hydrocarbon.[11] The cor-



2 **3a: R = H**
3b: R = phenyl

Chart 2.

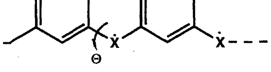


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Chart 3.

[#] Part X: *Mol. Eng.*, **4**, 353 (1995).

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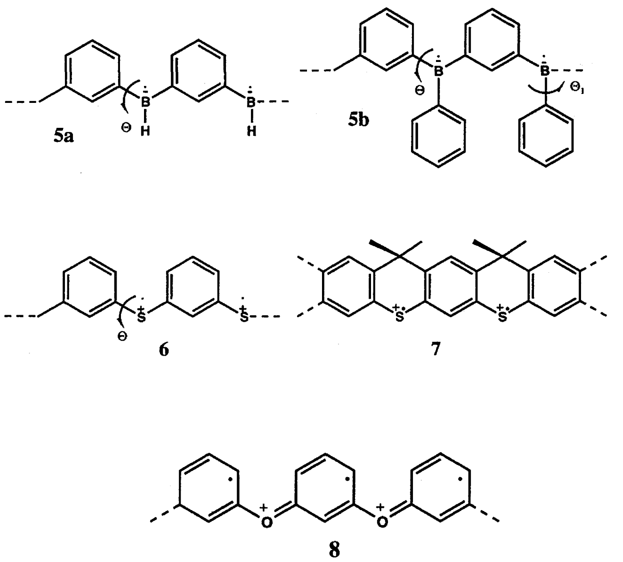

5a 5b 6 7 8

Chart 4.

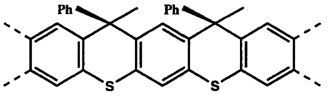


Chart 5.

responding polymers with $X=-B^{\bullet -}R-$ are iso-π-electronic with **1** and **3**. ii) The synthesis of a ladder type poly(thio-1,3-phenyle) (Chart 5):[12] which is a promising and existing candidate for polymer **7**.

The theoretical results in the papers of Yamaguchi et al.[13,14] have also motivated our investigations.

Method of Investigation

Energy Spectrum. The investigations were carried out in the π-electron tight-binding approximation using a Hückel–Hubbard version of the Bloch method.[15] The Bloch form of the wave vector k ($k \in [-\pi, \pi]$) was used,

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

where μ denotes the elementary unit (EU), and $|r,\mu\rangle$ the r-th AO (atomic orbital) within the μ-th EU, to calculate the MO energies, $E(K)$, by numerical diagonalization of the matrix[7,8]

$$E(k) = E_0 + V\exp(ik) + V^{+}\exp(-ik), \tag{2}$$

where E_0 is the energy matrix of EU in Eq. 2. V is the interaction matrix between neighbouring EUs (μ-th and ($\mu+1$)-th) and V^{+} is the transposed matrix.

The eigenvalues E(k) can also be represented by the roots of the characteristic polynomial (see Chapt. 3):

$$\det E(k) = P_n(y, \cos k) \tag{3}$$

with $y=[\alpha_C - E(k)]/\beta_0$ ($\beta_0 = \beta_{CC}$ is the standard resonance integral and α_C is the Coulomb integral of the C atom).

Spin Exchange of the Electrons within the Half-Filled Band. The transformation of the Bloch wave functions to Wannier states is more convenient for describing the spin correlation of the electrons within the HFB of an 1-D system if the Wannier states are well localized within the EU:

$$|\nu\rangle = N^{-1/2}\sum_{k}\exp(-ik\nu)\,|k\rangle = \sum_{\mu}\sum_{r} a_r(\mu-\nu)\,|\mu,r\rangle. \tag{4}$$

The coefficients a_r ($\mu-\nu$) of the Wannier functions (at the limit $N \rightarrow \infty$) are given by

$$a_r(\mu-\nu) = a_r(\tau) = N^{-1/2}\int_0^{2\pi}\exp[i(\mu-\nu)]C_r(k)\mathrm{d}k. \tag{5}$$

The norm of localization L is defined as

$$L = \sum_r |a_r(0)|^2. \tag{6}$$

Whangbo and Hubbard Conditions. The Whangbo condition (7)[16] is a qualitative expression used to determine the relative stability of the localized (high-spin) and the delocalized (low-spin) non-magnetic states in the HFB:

$$\Delta\epsilon < (\pi/4)U, \tag{7}$$

where $\Delta\epsilon$ is the width of the HFB and U is the renormalized Hubbard parameter (see Eq. 11). For a given polymer, this condition predicts a stabilization of the high-spin over the low-spin state if $\Delta\epsilon$ and U satisfy Eq. 7.

Equation 7 is similar to those derived by Hubbard[17] to consider the dynamics of the electrons in a narrow HFB:

$$\Delta\epsilon < (2/\sqrt{3})U. \tag{8}$$

Calculation of the Effective Exchange Integral between the Unpaired Electrons within the HFB. The effective exchange integral in the Heisenberg Hamiltonian is denoted by J_{eff} (ν,ρ),

$$H = \sum_{\nu \neq \rho} J_{\mathrm{eff}}(\nu-\rho)\boldsymbol{S}_{\nu}\boldsymbol{S}_{\rho} = J_{\mathrm{eff}}(\tau), \tag{9}$$

where $\boldsymbol{S}_{\nu}$ and $\boldsymbol{S}_{\rho}$ are the spin operators at the sites ν and ρ, respectively. The effective exchange integral, J_{eff}, depends on the relative distance, $\tau=\nu-\rho$, between the EUs ν and ρ where the Wannier functions are localized.

Based on the results of Anderson,[18] J_{eff} can be expressed as a sum of the following three contributions[19] (the dimensionless distance parameter τ is omitted for simplicity):

$$J_{\mathrm{eff}} = J - J_{\mathrm{kin}} + J_{\mathrm{ind}} = J - 2t^2/U + J_{\mathrm{ind}}. \tag{10}$$

Here, J is the Coulomb-exchange integral between the localized Wannier states within the ν-th and ρ-th EUs, and t is the transfer (hopping) parameter, calculated using the Wannier functions. $U = U_0 - U_1 - 2J$ is the renormalized Hubbard parameter,[17] where U_0 is the Coulomb-repulsion integral of two electrons residing in the same Wannier state. U_1 is the Coulomb-repulsion integral of two electrons occupying adjacent Wannier states. In the case of the renormalized Hubbard parameter,[17]

$$U = U_0 - U_1 >> J, \tag{11}$$

$$J_{\mathrm{kin}} = -2t^2/(U_0 - U_1). \tag{12}$$

J_{ind} expresses an indirect exchange of electrons (spin polarization exchange) via delocalized π-electrons in the filled energy bands. This term can be calculated using a formalism described elsewhere.[20] The sign of J_{ind} is determined by the structure of the EU and the interaction between the EUs.

The sign of the effective exchange integral, J_{eff}, determines the character of the ground state: a ferromagnetic high-spin state with $J_{\mathrm{eff}} > 0$ or an antiferromagnetic state with $J_{\mathrm{eff}} < 0$.

Parametrization. The MO energies, $E(k)$, were calculated using the following values of the resonance integrals: β_0 (CC, Θ=0)=β_0=−2.4 eV;[7,8] β_0 (BC, Θ=0)=−1.8 eV,[21] β_0 (CS, Θ=0)= −1.68 eV.[22] $\beta(\Theta)=\beta_0 \cos\Theta$ was used as the dependence of the resonance integrals on the torsion angles, Θ and Θ_1 (in structure **5b**).

The parameters used for the Coulomb integral were: $\alpha_B=\alpha_C-\beta_0(CC)$[23] and $\alpha_S=\alpha_C+\beta_0(CC)$,[22] where α_C represents the energy of an electron in the $2p_z$ atomic orbital of the carbon atom. It is a reference term of the Coulomb integral of heteroatoms.[23]

The hyperconjugation effect of the methylene group in polymer **7** was taken into account by the contribution $\delta\alpha$ to the Coulomb integrals of the π-centers connected to the $-CH_2-$ group: $\delta\alpha=-0.3\beta_0(CC)$ and $\delta\alpha=-0.5\beta_0(CC)$[24] (see Table 1). The two center Coulomb integrals ($\gamma_{\mu\nu}$) were calculated using the Mataga–Nishimoto approximation,[25]

$$\gamma_{\mu\nu} = e^2/(a+R_{\mu\nu}), \tag{13}$$

with $a=2e^2/(\gamma_{\mu\mu}+\gamma_{\nu\nu})$. The following standard values of the one-center Coulomb integrals were used: γ_{CC}=10.84 eV,[7,8] γ_{BB}=7.0 eV[21] and $\gamma_{SS}=\gamma_{CC}$.[26] The parameters used for carbon, boron, and sulfur were taken from papers in which the energy spectra of corresponding heteroatomic compounds were reproduced in good agreement with the experiment.

Geometry of the 1-D Polymers. The bond-length alternation and the dihedral angles, Θ and Θ_1, were obtained by means of the all-valence electron quantum-chemical AM1 method[27] (SPARTAN, Version 3.0, program[28]). A complete geometry optimization was performed using a cluster with 5 repeating units (3 repeating units in the case of **5b**.) The bond lengths and bond angles do not deviate significantly from those of the ideal geometry for the benzene rings (C–C bond lengths in the range between 1.39 and 1.41 Å). The C–B bond lengths are 1.51 Å (**5a**) and 1.55 Å (C(phenylene)–B) and 1.49 Å (C(phenyl)–B) in **5b**. The C–S bond lengths are 1.65 Å (**6**). The dihedral angles are:

Θ=23.9° for structure **5a**;
Θ=53°, Θ_1=2.7° for structure **5b**;
and Θ=24.3° for structure **6**.

Table 1. Calculated Values of the Width of the HFB $\Delta\epsilon$ (in eV), the Renormalized Hubbard Integral U (see Eq. 11) and the Various Contributions to the Effective Spin Exchange Interaction in the HFB of the Investigated Polymers

The results were obtained with the Mataga–Nishimoto approximation[25] for the two-center atomic Coulomb integrals (Eq. 13).

Polymer	$\Delta\epsilon$	$(\pi/4)U$	J	$-J_{kin}$	J_{ind}	J_{eff}	L
1a[a)]	0	1.911	0.199	0.000	0.070	0.269	0.751
1b	0	1.638	0.131	0.000	0.044	0.175	0.784
2[a)]	0.193	1.904	0.184	0.003	0.061	0.242	0.713
3a[a)]	0.431	1.237	0.196	0.014	0.026	0.208	0.617
3b[a)]	0.272	1.167	0.126	0.006	0.029	0.149	0.740
5a	0.332	1.257	0.171	0.008	0.018	0.181	0.710
5b	0.227	1.273	0.089	0.004	0.015	0.100	0.796
6	0.322	1.724	0.199	0.006	0.023	0.216	0.696
7[b)]	0.540	1.562	0.182	0.017	0.021	0.186	0.675
7[c)]	0.665	1.470	0.197	0.035	0.015	0.177	0.660

a) See Refs. 7 and 8. b) $\delta\alpha=-0.3\beta$. c) $\delta\alpha=-0.5\beta$.

Numerical Results and Discussion

Energy Spectrum. All polymers have a large energy gap (EG). A narrow HFB is situated within the EG (ΔE= $2\beta_0$). This can be seen from the characteristic polynomial of the polymers. In a topological approximation the polymers belong to the symmetry group $D_{(2n)d}$. It follows that the characteristic polynomial (see Eq. 3) has the form

$$P_n(y,\cos k) = (y^2-1)[yP_{n-3}(y,\cos k) + hQ(y,\cos k)] = 0. \tag{14}$$

For instance, the characteristic polynomial for polymers with 7 π-centers within the EU reads

$$\begin{aligned} P_7(y,\cos k) &= P_{7,M}(y,\cos k) + hQ_6(y) \\ &= (y^2-1)\{y[y^4-7y^2+10-2\cos k] + h(y^4-5y^2+4)\} \\ &\quad (k \in [-\pi,\ \pi]), \end{aligned} \tag{15}$$

where $P_{7,M}(y,\cos k)$ is the polynomial of the "parent" polymer **1a** and h is the parameter of the Coulomb integral, $\alpha_X= \alpha_C+h\beta_0(CC)$. If h=0, the roots y=0 correspond to a HFB with degenerate NBMOs. When $h\neq0$ the band width of the HFB, $\Delta\epsilon$, is non-zero and depends on the value of h. For $|h|<1.5$, $\Delta\epsilon\sim|h\beta_0(CC)|/6$ eV.

Whangbo's and Hubbard's Conditions. Table 1 contains the calculated values of $\Delta\epsilon$ and the values of the renormalized Hubbard parameter, $U=U_0-U_1$, for the investigated polymers. A comparison of the values for $\Delta\epsilon$ and U reveals that all of the polymers have a high-spin magnetic ground state, in accordance with Whangbo's (Eq. 7) and Hubbard's (Eq. 8) conditions. This result is in qualitative agreement with those obtained by means of calculating the effective exchange integral, J_{eff}, in the Heisenberg Hamiltonian.

Spin Correlation within the HFB. The calculated values of the various contributions to the effective spin-exchange interaction in the HFB of the investigated polymers are collected in Table 1. For all polymers the calculated effective exchange integrals are positive ($J_{eff}>0$). The predominant component to the ferromagnetic interaction is the direct (Hund) exchange, J.

The values for J_{eff} of the investigated heteronuclear polymers do not differ significantly from those of the homonuclear alternating PMPs. The dependence of J_{eff} on the parameter $h=(\alpha_X-\alpha_C)/\beta$ characterizing the Coulomb integral of the heteroatom X is given in Fig. 1, thus quantitatively illustrating the results. By comparing polymers **1a**-**1b**, **3a**-**3b**, and **5a**-**5b** it seems that an extension of the π-system by substituting the hydrogen atom with a phenyl group leads to diminishing values of J_{eff}.

Qualitatively, two structural factors determine the magnetic properties of the hetero-analogues of the PMP's: (i) the topological structure of the π-network and (ii) the values of h, i.e. the difference between the electronegativities χ of the heteroatom X and the carbon atom ($h[\beta]= \alpha_X-\alpha_C\sim(\chi_X-\chi_C)$).[29]

The dominant factor determining the magnetic properties of the heteroatomic PMPs (HPMP) is the topology of the polymers. The energy spectra and the magnetic properties of

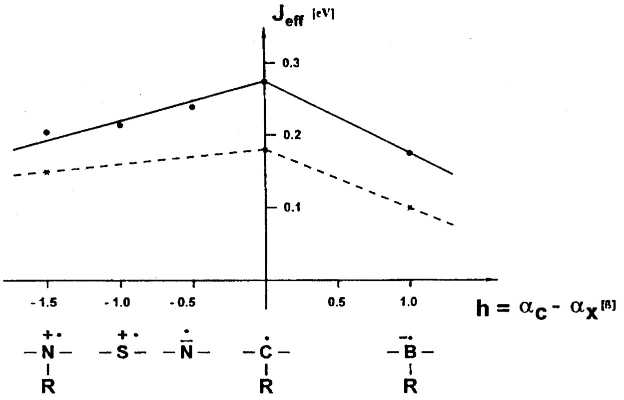


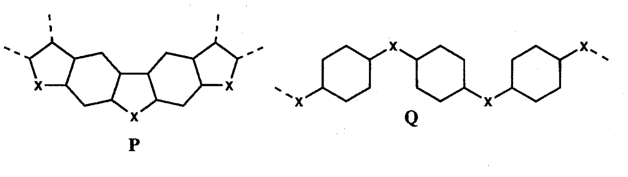
Fig. 1. Calculated values of $J_{\rm eff}$ for polymers **1a**, **2**, **3a**, **5a**, **6** (•) and **1b**, **3b**, **5b** (×) vs. the parameter $h=(\alpha_X-\alpha_C)/\beta$ of the heteroatom X. The numerical results of $J_{\rm eff}$ are taken from Table 1.

the alternant PMPs are determined solely by the topology,[1—3] which is identical to those of the investigated HPMPs **2**, **3**, **5**—**8**.

The change in topology of the PMPs is associated with a dramatic change in their band structure and magnetic properties.

The non-classical radicals C_6H_5-$X^\bullet$ can form either non-classical polymers **1**—**8** or iso-π-electronic polymers having different topologies. The structural graphs are shown below (Chart 6). The possibility for the existence of a high-spin state in the case of polymers *P* and *Q* follows from a theoretical artifact, that the high-spin structures **P-1** and **Q-1** can be formulated (Chart 7). The structures and properties of polymers **P** and **Q** are essentially different from those of the iso-π-electronic PMPs. The geometrical optimization of **P** and **Q** using a generalized[30] Su–Srieffer–Heeger method[32] led to a doubling of the elementary units with charcteristic para-quinonoide structural fragments.

The ground state of polymer structures **P-2** and **Q-2** is non-magnetic dielectrical (Chart 8). The width, $\Delta\epsilon$, of the highest (7-th) occupied band (HFB) of all polymer structures **P-2** and **Q-2** is large ($\Delta\epsilon>1.0$ eV). For instance, $\Delta\epsilon=1.108$ eV for X=–B⁻H–.



$(X = -\dot{C}H-, -\dot{N}^{+}H-, -\underline{\dot{N}}-, -\dot{B}^{-}H-, -\dot{S}^{+}-, -\dot{O}^{+}-)$.

Chart 6.

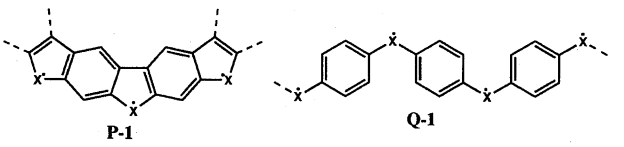


Chart 7.

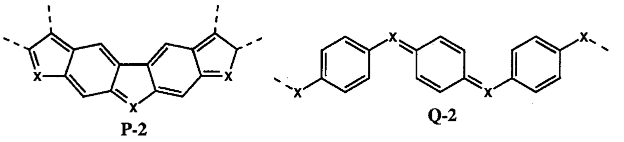


Chart 8.

In contrast to the polymers of the **P-2** or **Q-2** group, the width of the HFB of the polymers **1**—**3**, **5**, **6** is small. For $|h|<1.5$ $\Delta\epsilon<0.4$ eV, and almost satisfies $\Delta\epsilon<|h\beta|/6$ eV. The influence of the σ–π interaction of polymer **7** increases the width of the HFB to $\Delta\epsilon>0.54$ eV. The relatively small width of the HFB causes a favorable localization of the Wannier states and favors a ferromagnetic spin exchange.

If the value of $h<-1.5$, the norm of the localization of the Wannier states $L<0.5$. With such small values of L, the calculated values of $J_{\rm eff}$ are physically not relevant. Therefore, no reliable conclusions concerning the character of the ground state and the spin interaction can be drawn for the model polymer **8** with –$O^{\bullet+}$– radical centers.

Conclusions

The energy spectra and magnetic properties of new classes of polymers derived from the simplest homonuclear nonclassical high-spin 1-D π-systems with ferromagnetic exchange interaction between the electrons within the HFB (the PMPs) were studied. These polymers were designed by substituting the exocyclic radical π-center (–$C^\bullet$R–) in the PMP chain by a heteroatomic radical π-center $X^\bullet$. X is an atom (or an atomic group) of second-row elements of the periodic table: B, N, O or S (in an $(sp^2)^4$ p or $(sp^2)^3$ p^2 valence state). It has been shown that these polymers have qualitatively the same magnetic properties as the PMPs. The π-electrons in the HFB are coupled ferromagnetically. The ferromagnetic interaction results from the Coulomb (potential) interaction, which is the predominant contribution to the effective exchange integral, $J_{\rm eff}$, in the Heisenberg Hamiltonian.

It has been shown that the identical topology of the π-network of the PMPs and their heteroatomic analogues (connection of the radical π-centers through 1,3-phenylene groups) is the dominant factor determining the similar magnetic properties.

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References

1) N. Tyutyulkov, P. Schuster, and O. E. Polansky, *Theoret. Chim. Acta*, **59**, 123 (1983).

2) N. Tyutyulkov, O. E. Polansky, P. Schuster, S. Karabunarliev, and C. I. Ivanov, *Theoret. Chim. Acta*, **63**, 291 (1985).

3) K. Yoshizawa and R. Hoffmann, *Chem. Eur. J.*, **1**, 403 (1995).

4) A. Rajca, S. Utamapanya, and S. Tayumanavan, *J. Am.*

Chem. Soc., **114**, 884 (1992).

5) C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Phil. Soc.*, **36**, 139 (1940).

6) C. A. Coulson and H. C. Longuet-Higgins, *Proc. R. Soc. London, Sect. A*, **A191**, 9 (1947); **A192**, 16 (1947); **A193**, 447 (1947).

7) M. Baumgarten, K. Müllen, N. Tyutyulkov, and G. Madjarova, *Chem. Phys.*, **169**, 81 (1993).

8) G. Madjarova, M. Baumgarten, K. Müllen, and N. Tyutyulkov, *Makromol. Theory Simul.*, **3**, 803 (1994).

9) K. Yoshizawa, K. Tanaka, T. Yamabe, and J. Yamauchi, *J. Chem. Phys.*, **96**, 5516 (1992).

10) A. Rajca, S. Rajca, and S. R. Desai, *J. Chem. Soc., Chem. Commun.*, **1995**, 1957.

11) W. Schlenk and M. Brauns, *Chem. Ber.*, **48**, 661 (1915).

12) K. Müllen and Ch. Kübel, to be published.

13) K. Yamaguchi, M. Okumura, J. Maki, and T. Noro, *Chem. Phys. Lett.*, **207**, 9 (1993).

14) M. Okumura, K. Takada, J. Maki, T. Noro, W. Mori, and K. Yamaguchi, *Mol. Cryst. Liq. Cryst.*, **233**, 41 (1993).

15) O. E. Polansky and N. Tyutyulkov, *MATCH* (*Commun. Math. Chem.*), **3**, 149 (1977).

16) M. H. Whangbo, *Acc. Chem. Res.*, **16**, 95 (1983).

17) J. Hubbard, *Proc. R. Soc. London, Sect. A*, **A276**, 238 (1963); **A277**, 401 (1964).

18) P. W. Anderson, *Phys. Rev.*, **79**, 350 (1950); **115**, 2 (1959).

19) C. I. Ivanov, N. Tyutyulkov, and S. Karabunarliev, *J. Magnet. Magn. Materials*, **92**, 192 (1990).

20) N. Tyutyulkov and S. Karabunarliev, *Chem. Phys.*, **112**, 293 (1987).

21) J. Michl, J. Koutecky, R. S. Becker, and C. E. Earchart, Jr., *Theoret. Chim. Acta*, **19**, 92 (1970).

22) R. Mayer, H. Hartman, J. Fabian, and A. Mehlhorn, *Z. Chem.*, **7**, 209 (1967).

23) A. Streitwieser, "MO Theory," J. Wiley, New York (1965).

24) L. Pauling and G. W. Wheland, *J. Am. Chem. Soc.*, **57**, 2086 (1935); H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 283 (1950); M. H. Whangbo, R. Hoffmann, and R. B. Woodward, *Proc. R. Soc. London, Sect. A*, **A366**, 23 (1979).

25) N. Mataga and N. Nishimoto, *Z. Phys. Chem.*, **13**, 140 (1957).

26) J. Fabian, A. Mehlhorn, and R. Zahradnik, *J. Phys. Chem.*, **72**, 3975 (1968).

27) K. Ohno, *Theoret. Chim. Acta*, **2**, 219 (1964).

28) J. J. P. Stewart, MOPAC 6.00, QCPE, No 455.

29) "SPARTAN Program System, Version 3," Wavefunction Inc., Irvine, CA, USA.

30) C. A. Coulson, "Valence," University Press, London (1962), p. 242.

31) S. Karabunarliev, M. Baumgarten, K. Müllen, and N. Tyutyulkov, *Chem. Phys.*, **179**, 421 (1994).

32) W. P. Su, J. R. Schrieffer, and A. J. Heeger, *Phys. Rev. Lett.*, **42**, 1698 (1979); *Phys. Rev. B*, **B22**, 2099 (1980).