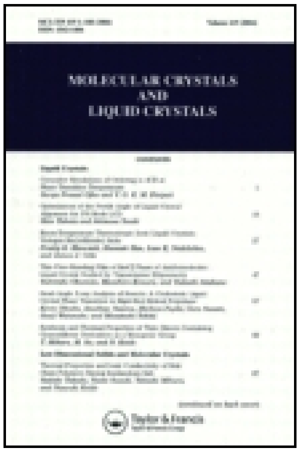

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Nature of The Magnetic Interaction in Organic Radical Crystals. I. Alternant Systems

Nikolai Tyutyulkov [a] , Galia Madjarova [a] & Fritz Dietz [b]

[a] University of Sofia, Faculty of Chemistry, BG-1126, Sofia, Bulgaria

[b] Universitüt Leipzig, Institut für Physikalische und Theoretische Chemie Talstraße 35, D-04103, Leipzig, Germany

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NATURE OF THE MAGNETIC INTERACTION IN ORGANIC RADICAL CRYSTALS. I. ALTERNANT SYSTEMS

NIKOLAI TYUTYULKOV; GALIA MADJAROVA
University of Sofia, Faculty of Chemistry, BG-1126-Sofia, Bulgaria
FRITZ DIETZ
Universität Leipzig, Institut für Physikalische und Theoretische Chemie
Talstraße 35, D-04103 Leipzig, Germany

Abstract A theoretical approach is applied for estimation of the nature (ferro- or antiferromagnetic) of the spin exchange interaction between the unpaired electrons within the half-filled band of 1-D organic radical crystals, consisting of weakly interacting alternant radicals. The various contributions to the Heisenberg effective exchange integral, J_{eff} – direct, kinetic, and indirect spin exchange – are evaluated quantitatively for several model crystals in order to establish the nature and magnitude of the exchange coupling between the unpaired spins. General rules are formulated showing the dependence of J_{eff} on the crystal topology and geometry.

INTRODUCTION

The magnetic properties of low-dimensional pure organic systems, in particular of quasi one-dimensional (1-D) systems have received much attention in the last decade. This interest is determined by the search for organic materials whose ground state is characterized by a magnetic ordering.[1-3] The investigations are focussed mainly on three classes of pure organic 1-D molecular systems with exchange coupled electrons in the half-filled band (HFB):

I) systems with intramolecular magnetic interaction - polymers with a continual π-system of conjugation (CP)[1,2];

II) molecular radical crystals (MRC) in which the elementary units (EU) are weakly interacting subsystems, namely radicals with delocalized π-electrons[3,4];

III) 1-D systems for which the magnetic ordering is caused by an intermolecular charge transfer (CT) mechanism.[5]

The theoretical investigations are directed mainly to 1-D high-spin CPs with ferromagnetic coupling between the delocalized electrons in the HFB.[1,2] The correlation between the geometry, topology and the type of exchange interaction is well established.[5-11] From this point of view little research of MRCs has been done. Usually, the magnetic coupling between the radicals is considered by means of the McConnell model Hamiltonian[5] (see for instance paper [12] and the references therein):

$$\mathbf{H} = -\mathbf{S}_A\mathbf{S}_B\sum_{(i,j)}\mathbf{J}_{ij}^{AB}\rho_i^A\rho_j^B = -\mathbf{S}_A\mathbf{S}_B\Omega \qquad (1)$$

where $\mathbf{S}_A$ and $\mathbf{S}_B$ are the spins on radicals A and B , J_{ij}^{AB} is the exchange integral and $\rho_{i(j)}^{A(B)}$ is the spin density on the i(j)-th π-center in the radical A(B). More correctly, with the MO approach, the problem was investigated in the work of Yamaguchi,[13] Kollmar and Kahn[14,15] and in a recent study by Yoshizawa and Hoffmann.[16] In these papers the magnetic interaction was considered only for dimers and clusters but not for infinite MRCs. The problem of the exchange interaction in infinite 1-D CT MRCs was studied in the papers of Soos[17] and McConnell et al.[18]

The aim of this paper is to study the relation between the nature of the spin exchange interaction and the arrangement – topology and geometry – of MRCs consisting of identical mono-radicals. The method used has been applied to examine the intramolecular spin exchange interaction in many high-spin CPs and various contributions to the Heisenberg effective exchange integral – direct, kinetic, and indirect – are evaluated quantiatively (see [19] and the references therein).

1-D MODELS OF THE RADICAL CRYSTALS

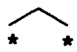
Mono-Radicals as Elementary Units

As elementary units of the MRCs we consider the following three types of mono-radicals which possess one nonbonding MO (NBMO) resulting from the molecular topology:

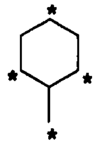
a) AS - Homonuclear alternant mono-radicals.

The fundamental idea determining the structural principle of the homonuclear alternant π-systems (AS) is connected with the theorem of Coulson-Rushbrooke-Longuet-Higgins (CRLH).[7] According to this theorem, an alternant hydrocarbon containing S^* non-neighboured π-centers and R^0 non-neighboured π-centers ($S^* > R^0$) possesses

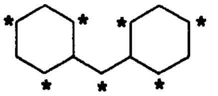
$S^* - R^0$ NBMOs. Typical examples are allyl (**Al**), benzyl (**Bl**), diphenyl-methyl (**Di**), and perinaphtenyl (**Pe**) radicals,



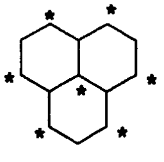
Al



Bl



Di



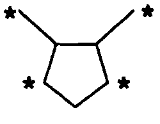
Pe

for which $S^* - R^0 = 1$, i.e. they have one singly occupied NBMO (SOMO).

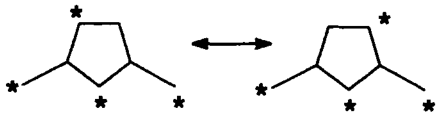
b) NA - Quasi-alternant homonuclear mono-radicals.

The CLRH theorem has been generalised[20,21] and it is the basis of a structural principle of a large class of π-systems denoted as *quasi-alternant* (NA). If, for a conjugated system with M π-centers and a maximum set of M* homonuclear disjoint π-centers, the condition 2M* > M is fulfilled, then the energy spectrum displays at least 2M* – M NBMOs. The NBMOs are present even if the π-centers not belonging to the disjoint subset are heteroatoms. The theorem is also valid for polymers, for which the condition 2M* > M holds not only for every elementary unit but also for the whole π-system.

Examples of homonuclear NA mono-radicals with one NBMO are the non-alternant systems **NA-1** and **NA-2**:

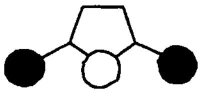


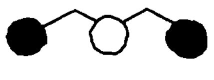
NA-1



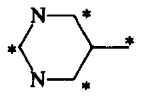
NA-2

As in the case of alternant radicals, the NBMOs contain only AOs of the disjoint set of starred π-centers. The NBMO of the monoradical **NA-2** is composed only of the AOs of the pentamethine radical because **NA-2** has two disjoint subsets of starred π-centers.[21]





c) HA - Heteratomic QA mono-radicals for which the extended CRLH theorem is also valid, for instance:



DA

The radicals are assumed to have ideal geometry – all bond lengths 1.40 Å, regular hexagons for the alternant system, and regular pentagon for **NA-1** and **NA-2.**

Models of 1-D Stacks

The radical crystals are considered as 1-D systems for which the Born-von-Karman conditions are fulfilled. The one-dimensional stacks of all the considered radicals are classified into the following 3 types:

i) *full face-to-face* type

In the case of the face-to-face structure the radicals are divided by a mirror plane of symmetry σ_h perpendicular to the translation axis (see Fig. 1, Tables 1, 2).

ii) *rotated face-to-face* type, characterised by a screw axis $\mathbf{n_m}$ (see Table 1).

iii) *slipped face-to-face* type with different slip angles α (see Table 2).

The intermolecular distance R_0 between the planes of two neighbouring monomers for different MRCs varies in the range between 3.1 and 3.7 Å.[12,22,23] The quantitative results obtained with various values of the intermolecular distance, 3.2 Å $\leq R_0 \leq$ 3.4 Å, show that, qualitatively, the nature of the exchange coupling between the unpaired spins does not depend on the value of R_0. Therefore, the numerical results for all models investigated in in this paper are given only for the interplanar distance R_0 = 3.35 Å.

METHODS OF INVESTIGATIONS

Energy Spectra

The investigations were carried out in the π-electron tight-binding approximation using a Hückel-Hubbard[24] version of the Bloch method. If, for the 1-D system, we adopt a Bloch form of the wave vector $\boldsymbol{k}$ ($\boldsymbol{k} \in [-\pi, \pi]$)

$$|k\rangle = N^{-1/2}\sum_{\mu}\exp(-ik\mu)\left[\sum_{s} C_s(k)\,|s^*,\mu\rangle + \sum_{r} C_r(k)\,|r,\mu\rangle\right] \qquad (2)$$

the MO energies $e(\boldsymbol{k})$ are obtained by numerical diagonalization of the matrix

$\mathbf{E}(\boldsymbol{k}) = \mathbf{E}_0 + \mathbf{V}\exp(i\boldsymbol{k}) + \mathbf{V} + \exp(-i\boldsymbol{k})$ where $\mathbf{E}_0$ is the energy matrix of the EU, $\mathbf{V}$ is the interaction matrix between neighbouring EUs (μ-th and μ+1-th). If the MRC is an AS or NA, the Bloch function of the HFB contains only AOs of the starred disjoint set$|s^*\rangle$.

Spin Exchange of the Electrons within the Half-Filled Band

Let us denote by J_{eff} (ν,ρ) the effective exchange integral in the Heisenberg Hamiltonian:

$$\mathbf{H} = \sum_{\nu \neq \rho} \mathbf{J}_{eff}(\nu - \rho)\mathbf{S}_{\nu}\mathbf{S}_{\rho} = \sum \mathbf{J}_{eff}(\tau)\mathbf{S}_{\nu}\mathbf{S}_{\rho} \qquad (3)$$

between the EUs ν and ρ upon which the Wannier functions

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

are localized. Based on the results of Anderson [25] it has been shown [26] that J_{eff} can be expressed as a sum of three contributions (in the following the dimensionless distance parameter τ is omitted for simplicity):

$$J_{eff} = J - J_{kin} + J_{ind} = J - 2t^2 / U + J_{ind} \qquad (5)$$

The terms in the sum (5) have the following physical meaning: J is the Coulomb exchange integral between the localized Wannier states within the ν-th and ρ-th EUs; t is the transfer parameter between adjacent Wannier states and $U = U_0 - U_1$ is the renormalized Hubbard parameter[24], where U_0 is the Coulomb repulsion integral of two electrons residing in the same Wannier state and U_1 is the Coulomb repulsion integral of two electrons occupying adjacent Wannier states, respectively. J_{ind} expresses the indirect exchange of electrons (spin polarization exchange) via delocalized π-electrons in the filled energy bands. This term was calculated using a formalism described in.[26] 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 high-spin state with $J_{eff} > 0$ or an antiferromagnetic state with $J_{eff} < 0$.

Parametrization

A standard value $\beta_0 = -2.4$ eV[11,190] has been used for the resonance integral between the $2p\pi$-$2p\pi$ AOs of the carbon atoms at a distance $R_0 = 1.40$ Å. The resonance integrals between two 2p orbitals which belong to neighbouring radicals (EUs) were calculated with Mulliken's formula.[27]

The two-center Coulomb integrals $\gamma_{\mu\nu}$ for the calculation of the various contributions to the effective spin exchange according to eq. (5) were evaluated using the Mataga-Nishimoto[28] approximation:

$$\gamma_{\mu\nu} = e^2 / (e^2 / \gamma_{\mu\mu} + DR) \qquad \text{with } \gamma_{\mu\mu} = \gamma_{CC} = 10.84 \text{ eV}. \tag{6}$$

RESULTS AND DISSCUSION

Energy Spectra

The type and magnitude of the MO splitting depends on the topology and the geometry of the MRCs. In the case of a face-to-face structure, an analytical expression can be derived for the MO energies. Each mono-radical MO of energy e_p splits into MOs of energies:

$$e_t(\boldsymbol{k}) = e_t + 2\beta_{\sigma\sigma} \cos \boldsymbol{k} \tag{7}$$

where $\beta_{\sigma\sigma}$ is the resonance integral between 2pσ-2pσ AOs. From the above equation it follows that the interaction between the monomers is nonbonding, i.e. the delocalization energy $\Delta\varepsilon$ is zero:

$$\Delta\varepsilon = 2\beta_{\sigma\sigma} \int_{-\pi}^{\pi} \cos \boldsymbol{k} \, d\boldsymbol{k} = 0 \tag{8}$$

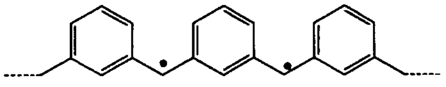
This is the reason why the MRCs tend[29] towards a configuration with a reduced symmetry by loss of the symmetry plane σ_h and lowering of the π-electron energy. In the real cases, the total energy balance of a MRC is not only determined by π–π interaction but also by interaction in which the σ-skeleton of the monomer takes part.[29] All these interactions are responsible for the geometry of MRCs. In the case of the full face-to-face structure the CRLH (or the extended CRLH) theorem is not valid, because in the stacks a doubling of the EU occurs, i.e. $S^* - R^0 = 0$ (see Fig. 1), and the width of the HFB $\Delta\varepsilon > 0$. It follows from eq. (8) that

$$\Delta\varepsilon = 4\beta_{\sigma\sigma} \tag{9}$$

If the conditions (topology) for the validity of the CRLH or extended CRLH theorem are fulfilled for a given MRC, the HFB is formed from degenerate NBMOs, e.g. for models **B** and **D** in Table 1.

Spin Exchange of the Electron in the Half-Filled Band

To compare the results of the exchange coupling (the magnitude of the exchange coupling) for both classes of 1-D systems (CP and MRC), the effective exchange integral for a typical representative of CPs, the poly(meta-phenylene-methylene) has been calculated:



$J_{eff} = J + J_{ind} = 0.252 + 0.075 = 0.327$ eV

The values of the components of the effective exchange integral have been calculated for all seven monoradicals (shown in Chapt. 2) and for the three types of 1-D stacks. Here, as a numerical illustration of the general qualitative conclusions only the results for **Al**-MRCs, **Bl**-MRCs and **NA-2**-MRCs are given.

Full Face-to-Face MRCs

For all full face-to-face MRCs the transfer parameter is equal to (see eqs.(4), (5)):

$$t = \langle \nu | \mathbf{H} | \nu + 1 \rangle = \sum_{s} a_s^{*2} \langle s^*, \nu | \mathbf{H} | s^*, \nu + 1 \rangle = \beta_{\sigma\sigma} \qquad (10)$$

Eq. (10) is valid by taking into account the interaction not only between the first but also the second neighboured AOs because the coefficients of the Wannier function are different from zero only for the starred disjoint set {*}. From eqs.(9) and (10) one obtains:

$$J_{eff} = -2t^2 / U = -\Delta\varepsilon^2 / 8U \qquad (11)$$

The relatively large band width causes the large values of the kinetic term J_{kin} and the anti-ferromagnetic character of the spin exchange, respectively (see Tables 1, 2). The Coulomb (J) and indirect (J_{ind}) contributions are equal to zero or have very small values. Hence,

$$J_{eff} \approx J_{kin} < 0. \qquad (12)$$

The antiferromagnetic interaction for all full face-to-face structures are in qualitative agreement with the results obtained in the papers.[13,15,17] The results also agree qualitatively with the results obtained by means of the McConnell model.

The sum Ω in eq. (1) is negative for all MRCs with a full face-to-face stacking. This proportionality is in disagreement with the physical meaning of eq. (11). The kinetic exchange is a spin polarization effect [27,28] and appears if, and only if, the electron correlation is taken into account.

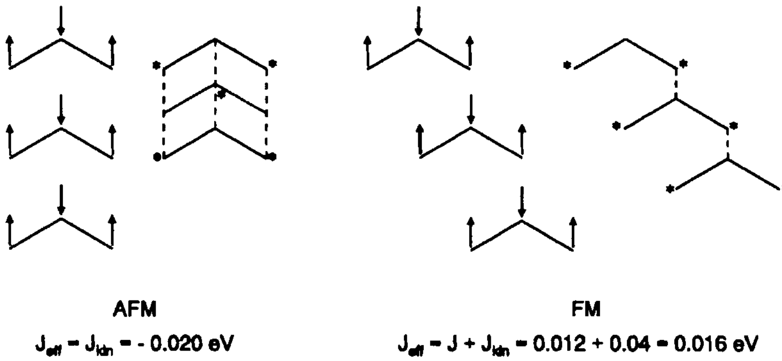


FIGURE 1 Ferromagnetic (FM) and antiferromagnetic (AFM) coupling between the electrons within the HFB of a MRC consisting of allyl radicals. AFM stack with full face-to-face configuration; FM stack with slipped face-to-face configuration.

Rotated and Slipped Face-to-Face MRCs

If the MRCs have a topology (by taking into account the interaction only between the (first) neighbouring AOs) which corresponds to the CRLH or extended CRLH theorem, the SOMOs build up a band of degenerate quantum states. In all these cases the effective spin exchange is ferromagnetic ($J_{eff} > 0$) with a predominant contribution from the Coulomb exchange J and, in part, from the indirect exchange. The kinetic term is zero (see Tables 1, 2). The consideration of the interaction between the first and second neighbours (see Table 2), i.e. by an increase of the overlap between the monomers, is connected with a small splitting of the degenerate HFB. However, the effective exchange integral remains positive, i.e. the interaction is ferromagnetic. The value of J_{eff} decreases because the kinetic term has a small, however negative, value. If the topology of a MRC does not correspond to the conditions for the occurance of a HFB with degenerate NBMOs, the ground state has antiferromagnetic character.

TABLE 1 Calculated values of the width of the HFB $\Delta\varepsilon$, the transfer parameter t, and the components of the effective spin exchange between the unpaired electrons in the HFB of the **BI**-MRCs (all values in eV).

Model (see below)	$\Delta\varepsilon$	t	J	$-J_{kin}$	J_{ind}	J_{eff}
A	1.148	−0.287	0.0	0.046	−0.001	−0.047
B	0.0	0.0	0.013	0.0	0.008	0.021
C	0.164	0.042	0.0	0.001	−0.010	−0.011
D	0.0	0.0	0.015	0.0	0.009	0.024

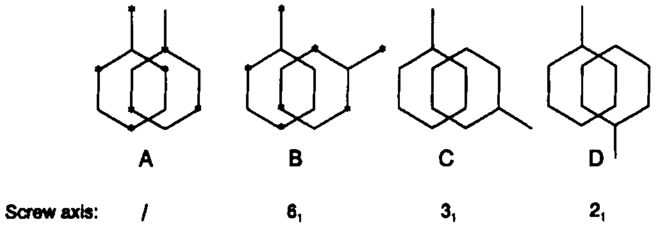
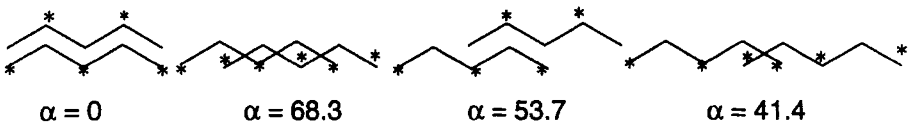


TABLE 2 Calculated values of $\Delta\varepsilon$ and the components (in eV) of J_{eff} for slipped face-to-face **NA-2** MRCs with various values of the slip angle α. The results were obtained by taking into account the interaction between the first and second neighbours.

α	$\Delta\varepsilon$	t	J	$-J_{kin}$	J_{ind}	J_{eff}
0.0	1.148	−0.287	0.0	0.052	−0.002	−0.054
68.3	0.231	−0.059	0.033	0.002	0.013	0.044
53.7	0.762	0.191	0.002	0.022	−0.007	−0.027
41.6	0.225	0.056	0.012	0.002	0.005	0.015



CONCLUSIONS

For the three types of MRCs, consisting of the three types of mono-radicals, (**AS**), (**NA**) and (**HA**), the main factor which determines the nature of the magnetic interaction is the topology. In all cases, the full face-to-face stacking determines the antiferromagnetic exchange interaction between the electrons within the HFB with the main contribution being the kinetic exchange. In the other two cases, rotated and slipped face-to-face stacking, the nature of the magnetic interaction is also determined by the topology. If the conditions (requirements) of the CRLH and the extended CRLH theorem are fulfilled (not only for the isolated mono-radicals but also for the stacks) the MRC exhibits a ferromagnetic alligment of the spins with a predominant contribution from the direct (Coulomb) and a partial contribution of the indirect exchange. The numerical results show that the effective exchange integral for ferro- or antiferromagnetic coupling is one order of magnitude smaller incomparison to the exchange coupling for CPs:

$$|J_{eff}(MRS)| \approx 10^{-1}|J_{eff}(CP)|.$$

ACKNOWLEDGMENT

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REFERENCES

1. H. Iwamura, in Adv. Phys. Org. Chem., 26, 179 (1990).
2. K. Yoshisawa and R.Hoffmann, Chem. Eur. J., 1, 403 (1995).
3. E. Dormann, Synth. Meth., 71, 1781 (1955).
4. M. Kinoshita, Jpn. J. Appl. Phys., 33, 5718 (1994).
5. H. M. McConnell, J. Chem. Phys., 39, 1910 (1963).
6. K. Itoh, Chem. Phys. Lett., 1, 235 (1967).
7. C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc., A193, 447(1947).
8. A. A. Ovchinnikov, Theoret. Chim. Acta, 47, 297 (1978).
9. D. J. Klein, C. J. Nelin, S. Alexander and F. A. Matsen, J. Chem. Phys., 77, 3101 (1982).
10. D. Maynau, M. Said and J. P. Malrieu, J.Am.Chem.Soc., 105, 5244 (1983).
11. N. Tyutyulkov,O. E. Polansky;P. Schuster, S. Karabunarliev and C. I. Ivanov, Theoret. Chim. Acta, 67, 211 (1985).
12. K. Takeda, H. Deguchi, T. Hoshiko, K. Konoshi, K. Takahashi and J. Yamaguchi, J. Phys. Soc. Jpn., 58, 3361 (1989).
13. K. Yamaguchi, and T. Fueno, Chem. Phys. Lett., 159, 465 (1989); K. Yamaguchi, Y. Toyoda and T. Fueno, Chem. Phys. Lett., 159, 459 (1989).
14. C. Kollmar and O. Kahn, Acc. Chem. Res., 26, 259 (1993).
15. C. Kollmar and O. Kahn, J. Chem. Phys., 96, 6026 (1993).
16. K. Yoshizawa and R. Hoffmann, J. Am. Chem. Soc.,117, 6921 (1995).
17. P. Strebel and Z. G. Soos, J. Chem. Phys., 53, 4077 (1970).
18. J. S. Krugler, C. G. Montgomery and H. M. McConnell, J. Chem. Phys., 41, 2421(1964).
19. N. Tyutyulkov, F. Dietz, K. Müllen, M. Baumgarten and S. Karabunarliev, Chem. Phys., 189, 83 (1994).
20. N. Tyutyulkov and O. E. Polansky, Chem. Phys. Lett., 139, 281 (1987).
21. S. Karabunarliev and N. Tyutyulkov, Theoret. Chim. Acta, 76, 65 (1989).
22. E. Dormann, H. Winter, W. Dyakonov, B. Gotschy, A. Lang, H. Naarmann and N. Walker, Ber. Bunsenges. Phys. Chem., 96, 922 (1992).
23. Y. Hosokoshi, M. Tamura, D. Shiomi, N. Iwasawa, K. Nosawa, M. Kinoshita, H. Aruga and T. Goto, Physica, B 201, 497 (1994).
24. J. Hubbard, Proc. Roy. Soc. London, A276, (1963); A277, 401 (1964).
25. P. W. Anderson, Phys. Rev. 79, 350 (1950); 115, 2 (1959).
26. C. I. Ivanov, N. Tyutyulkov and S. Karabunarliev, J. Magn. Magn. Materials, 92, 172 (1990).
27. R. Mulliken, J. Chem. Phys. 46, 497, 675 (1949).
28. N. Mataga and K. Nishimoto, Z.Phys.Chem., 13, 170 (1954).
29. C. A. Hunter and J. K. M. Sander, J. Am. Chem. Soc., 112, 5525 (1990).