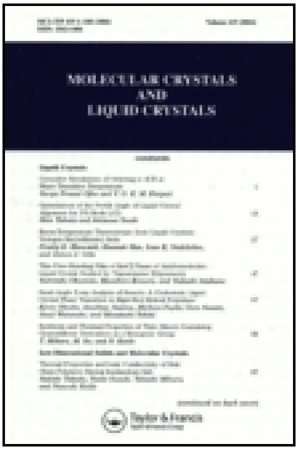


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Ab Initio Crystal Orbital Study of Ferromagnetic Interactions of Spins in Polymer Comprising Phenylenevinylene

Masaki Mitani [a], Yu Takano [a], Daisuke Yamaki [a], Yasunori Yoshioka [a] & Kizashi Yamaguchi [a]

[a] Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka, 560-0043, Japan

Version of record first published: 24 Sep 2006

To cite this article: Masaki Mitani, Yu Takano, Daisuke Yamaki, Yasunori Yoshioka & Kizashi Yamaguchi (1999): Ab Initio Crystal Orbital Study of Ferromagnetic Interactions of Spins in Polymer Comprising Phenylenevinylene, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 335:1, 613-622

To link to this article: http://dx.doi.org/10.1080/10587259908028902

Mol. Cryst. and Liq. Cryst., 1999, Vol. 335, pp. 613-622
Reprints available directly from the publisher
Photocopying permitted by license only

Ab Initio Crystal Orbital Study of Ferromagnetic Interactions of Spins in Polymer Comprising Phenylenevinylene

MASAKI MITANI, YU TAKANO, DAISUKE YAMAKI,
YASUNORI YOSHIOKA and KIZASHI YAMAGUCHI

*Department of Chemistry, Graduate School of Science, Osaka University,
Toyonaka, Osaka 560–0043, Japan*

Magnetic properties for models of poly(phenylenevinylene) having four types of chain structure with methylene radical were investigated by the *ab initio* crystal orbital approaches using UBLYP and UHF approximations. It was found that the stability of high-spin states increases from molecules to polymers which is caused by the ferromagnetic interactions between neighboring monomer units arising from the spin polarization through phenylenevinylene bridge.

Keywords: trans-stilbene bis(methylene radical); poly(phenylenevinylene); *ab initio* crystal orbital calculation; ferromagnetic interaction; spin density

INTRODUCTION

The design of polymers with high-spin ground state is important as an element in the organic ferromagnetic materials, because the magnetic exchange force is larger in a molecule than between molecules[1]. Thus, the experimental efforts to synthesize organic ferromagnetic polymers have been made in recent years[2-4]. On the other hand, we have performed theoretical investigations of the effective exchange integrals in molecular systems[5] and their size dependency in oligomer models comprising meta- and para-phenylene bis(methylene)[6] or trans-stilbene bis(nitroxide)[7] previously. But, it is difficult to extract the converged magnetic properties for chain length in an infinite polymer by applying the cluster models of dimer, trimer, and oligomers. This indicates that the crystal orbital approach should be employed to estimate the magnetic interaction in a periodic polymer. However, only Hückel[8-12], PPP[13,14], CNDO/2[15], and MINDO/3[16-19] studies have already been reported until now for one-dimensional magnetic polymers.

In this work, the *ab initio* crystal orbital investigations are performed for models of poly(phenylenevinylene) with methylene radical as a spin source. The purpose of our study is to clarify the change in magnetic properties from molecules to polymers. The electronic structure calculations at the spin-polarized density functional based on Becke exchange[20] with Lee-Yang-Parr correlation[21] terms (UBLYP) and unrestricted Hartree-Fock (UHF) levels using 4-31G basis set are carried out for methodological comparison. We consider four models of high-spin polymers which consist of trans-stilbene bis(methylene radical) units as monomers. Because the oligomers having poly(phenylenevinylene) skeletons with phenoxy or nitroxide radical groups were synthesized by Nishide et al.[22-24], the theoretical examination of magnetic properties in phenylenevinylene-bridged polymers is interesting as realistic model systems of pendant-type ferromagnetic polymer. We assumed geometrical parameters in planar molecules and polymers as C-C = 1.40Å, C-H = 1.08Å, C-C-C = C-C-H = 120.0°.

MAGNETIC PROPERTIES IN MOLECULES AND POLYMERS

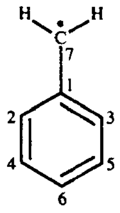
Spin Density in Benzyl Radical

First of all, the comparison among semi-empirical (INDO, PM3, and MNDO) and non-empirical (UHF, UBLYP, and UB3LYP) methods in the evaluation of spin densities in benzyl radical is given to show the reliability of approximation, since this fragment exists in phenylenevinylene systems with methylene radical. Table I lists the atomic spin densities on C atoms. UBLYP and UB3LYP give the comparable densities with the experiment while others (especially UHF) induce the large amplitude in density on benzene ring. Thus, it can be expected that these density functional methods are highly reliable rather than others.

TABLE I Atomic spin densities on C atoms in benzyl radical.

Atom	INDO	PM3	MNDO	UHF	UBLYP	UB3LYP	Exp.[a)]
C1	-0.270	-0.578	-0.614	-0.927	-0.165	-0.237	
C2,C3	0.312	0.635	0.678	0.934	0.220	0.268	0.190
C4,C5	-0.202	-0.552	-0.678	-0.874	-0.099	-0.155	0.065
C6	0.290	0.597	0.652	0.907	0.239	0.277	0.227
C7	0.881	1.066	0.995	1.153	0.781	0.843	

a) Absolute value of densities are shown.



Exchange Interaction in Isomers of Trans-Stilbene Bis(methylene radical)

Figure 1 shows the molecular structure of trans-stilbene bis(methylene radical) (**1**) examined here. As seen from Fig. 1, the molecule has isomers according to the different position of methylene radicals. Possible isomers are (3-2'), (3-3'), (3-4'), (3-5'), (4-2'), (4-3'), (4-4'), (5-2'), and (5-3') combinations of substitution at both benzene rings. Here, (a-b) indicates the position of radical groups in left (a) and right (b) rings, respectively, shown in Fig. 1 as numbered atoms.

In the construction of models for the polymer having high-spin character by connecting stilbene skeletons as monomers, we need to know that which isomers become more stable triplet than singlet. The spin configuration of ground state for these isomers can be easily predicted by the valence bond (VB) picture of spin polarization pattern alternating the sign of spins at each carbon atom. That is, four isomers with (3-2'), (3-4'), (4-3'), and (5-2') substitutions are expected to be triplet as illustrated in Figure 2 while others are singlet.

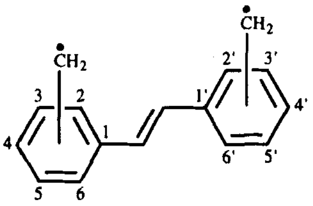


FIGURE 1 Molecular structure of trans-stilbene bis(methylene radical) (**1**).

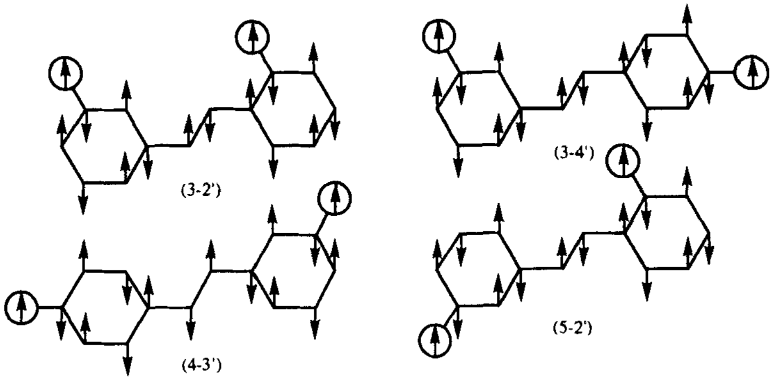


FIGURE 2 Spin polarization patterns in triplet isomers of **1** by VB picture.

UBLYP/4-31G energy calculations for both singlet and triplet states of all isomers of **1** were performed by Gaussian94 program[25] to confirm the ground spin state. We summarize the singlet-triplet energy gaps (ΔE) and the effective exchange integrals (J_{ab}) for nine possible isomers in Table II. It is found that the introduction of methylene radicals at (3-2'), (3-4'), (4-3'), and (5-2') positions lead to the positive ΔE, indicating that triplet state is more stable than singlet state. The obtained spin states of isomers for the ground state coincide with the predictions by spin polarization pattern. The J_{ab} seems to be sensitive to the radical placements. The isomers of **1** are classified by whether radical groups are at the ortho(o)- or meta(m)- or para(p)-positions. From such classification, we specify these isomers as (3-2') = (m-o'), (3-4') = (m-p'), (4-3') = (p-m'), and (5-2') = (m-o') for triplets and as (3-3') = (m-m'), (3-5') = (m-m'), (4-2') = (p-o'), (4-4') = (p-p'), and (5-3') = (m-m') for singlets. That is, the magnetic interactions are summarized as follows that the set of (m,o) and (m,p) indicates the high-spin character while the group of (m,m), (p,o), and (p,p) shows the low-spin nature.

TABLE II Energy gaps between singlet and triplet states (ΔE)[a)] and effective exchange integrals (J_{ab})[b)] for nine possible isomers of **1**.

Isomer	ΔE	J_{ab}	Isomer	ΔE	J_{ab}	Isomer	ΔE	J_{ab}
(3-2')	0.001294	277	(3-5')	-0.000357	-79	(4-4')	-0.015183	-1941
(3-3')	-0.000374	-83	(4-2')	-0.008991	-1356	(5-2')	0.001313	282
(3-4')	0.002018	432	(4-3')	0.002058	441	(5-3')	-0.000377	-84

a) ΔE is defined as $\Delta E = E(\text{singlet}) - E(\text{triplet})$ and ΔE is given in a.u.
b) J_{ab} is defined as $J_{ab} = \Delta E/({}^{triplet}\langle S^2\rangle - {}^{singlet}\langle S^2\rangle)$ and J_{ab} is given in cm^{-1}.

Models of High-Spin Phenylenevinylene Polymer

It is reasonable to construct the models for high-spin polymers including four isomers of **1** having the triplet ground states as monomer units. We can design four types of ploy(phenylenevinylene) structure with the different connectivity between stilbene skeletons. These model polymers (**2-5**) are given in Figure 3. The **2-5** polymers include four isomers of **1** as (3-2') in **2** and **3**, (4-3') and (5-2') in **4**, and (3-4') in **5**, respectively, according to the connective patterns described in Fig. 3. Since the monomers in these polymers are triplet units, the models of **2-5** have the high possibilities of ferromagnetic properties. It is noted that the chains **2** and **5** have the same skeletons as the synthesized oligomers have[22-24].

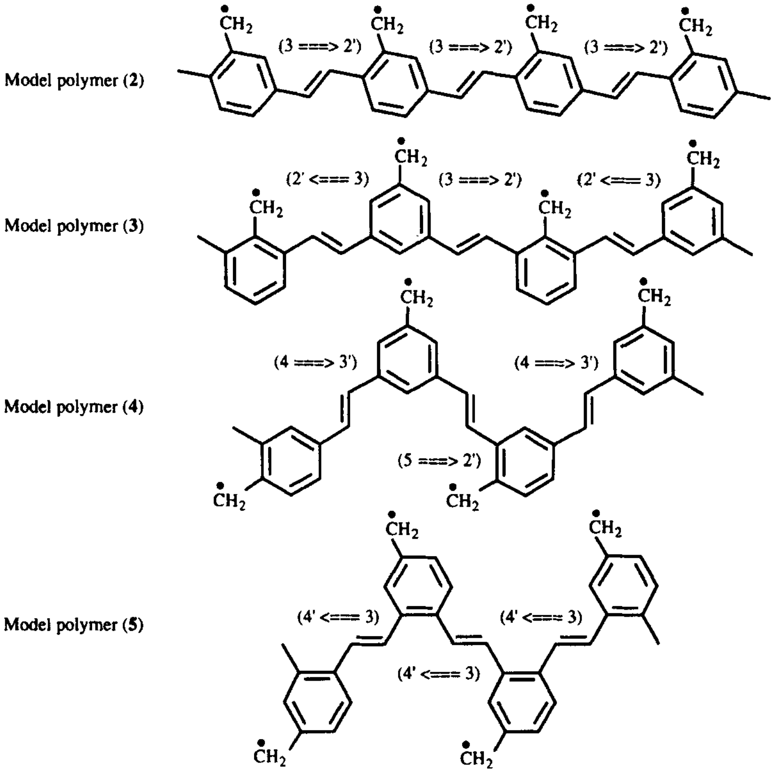


FIGURE 3 Models of high-spin poly(phenylenevinylene) (**2**-**5**).

Relative Stability for Low- and High-Spin States of Model Polymers

The energy differences between low- and high-spin states of **2**-**5** were estimated by UBLYP/4-31G and UHF/4-31G methods using CRYSTAL95 program[26] in order to compare the stability of ferromagnetic state between in molecules and in polymers. The obtained values of ΔE are presented in Tables III and IV for triplet monomers and model polymers, respectively.

UBLYP results in Table III indicate that the (3-4') and (4-3') isomers are more stable than the (3-2') and (5-2') isomers, and also, the formers have larger energy gaps than the latters. That is, E(m,p) < E(m,o) and ΔE(m,p) > ΔE(m,o). The similar tendency in stabilities among isomers appears in UHF energies but the difference in energy gaps is not detected and ΔE(UHF) >> ΔE(UBLYP). From Table IV, we observe that the stabilities of chain structure and of high-spin state in four polymers are ordered as follows that E(**4**) < E(**5**) < E(**2**) < E(**3**) and ΔE(**5**) > ΔE(**4**) > ΔE(**2**) > ΔE(**3**), respectively, by UBLYP computations. The conjugation between neighboring units induces the effective ferromagnetic interactions to increase the gap ΔE(polymer) > ΔE(molecule) by about twice.

The measured J_{ab} values for synthesized oligomers having 1,4-skeleton (**2**) and 1,2-skeleton (**5**) with phenoxy or nitroxide radicals are indeed ferromagnetic in the range of 20-40 cm^{-1} and J_{ab}(**5**) > J_{ab}(**2**) by the steric repulsion[22-24]. The UBLYP evaluation of ΔE(**5**) > ΔE(**2**) suggests that the ferromagnetic interactions between methylene radicals are stronger in the polymer chain of 1,2-structure than of 1,4-structure even if the molecular planarity is maintained. Judging from the experimental magnitude of J_{ab} results, UBLYP estimations seem to be more reliable than UHF calculations.

TABLE III Total energies for singlet and triplet states (E)$^{a)}$ and energy gaps between singlet and triplet states (ΔE)$^{b)}$ for triplet isomers of **1**.

	UBLYP/4-31G			UHF/4-31G		
Isomer	E(singlet)	E(triplet)	ΔE	E(singlet)	E(triplet)	ΔE
(3-2')	-616.929057	-616.930347	283	-613.106302	-613.136870	6709
(3-4')	-616.938129	-616.940154	444	-613.114773	-613.145297	6699
(4-3')	-616.938722	-616.940770	450	-613.115079	-613.145427	6661
(5-2')	-616.929743	-616.931037	284	-613.106622	-613.137011	6670

a) E(singlet) and E(triplet) are shown in a.u.
b) ΔE is defined as ΔE = E(singlet) - E(triplet) and ΔE is given in cm^{-1}.

TABLE IV Total energies for low- and high-spin states (E)$^{a)}$ and energy gaps between low- and high-spin states (ΔE)$^{b)}$ for polymers of **2**-**5**.

	UBLYP/4-31G			UHF/4-31G		
Model	E(low spin)	E(high spin)	ΔE	E(low spin)	E(high spin)	ΔE
2	-692.995556	-692.998136	566	-688.691854	-688.757985	14514
3	-692.990649	-692.993035	524	in calculation	-688.756069	-------
4	-692.999150	-693.002062	639	-688.700328	-688.763645	13896
5	-692.997153	-693.000934	830	-688.693434	-688.757480	14056

a) E(low spin) and E(high spin) per unit cell are shown in a.u.
b) ΔE is defined as ΔE = E(low spin) - E(high spin) and ΔE is given in cm^{-1}.

Spin Density in Triplet Molecule and High-Spin Polymer

Figure 4 depicts the spin population distributions by UBLYP/4-31G method in triplet isomers of **1** and high-spin polymers of **2-5**. Positive and negative spins appear alternatively to be consistent with the spin alignments from VB picture given in Fig. 2. Comparatively speaking, relatively large polarizations exist on the benzene ring with m-methylene radical than with o- or p-methylene radicals.

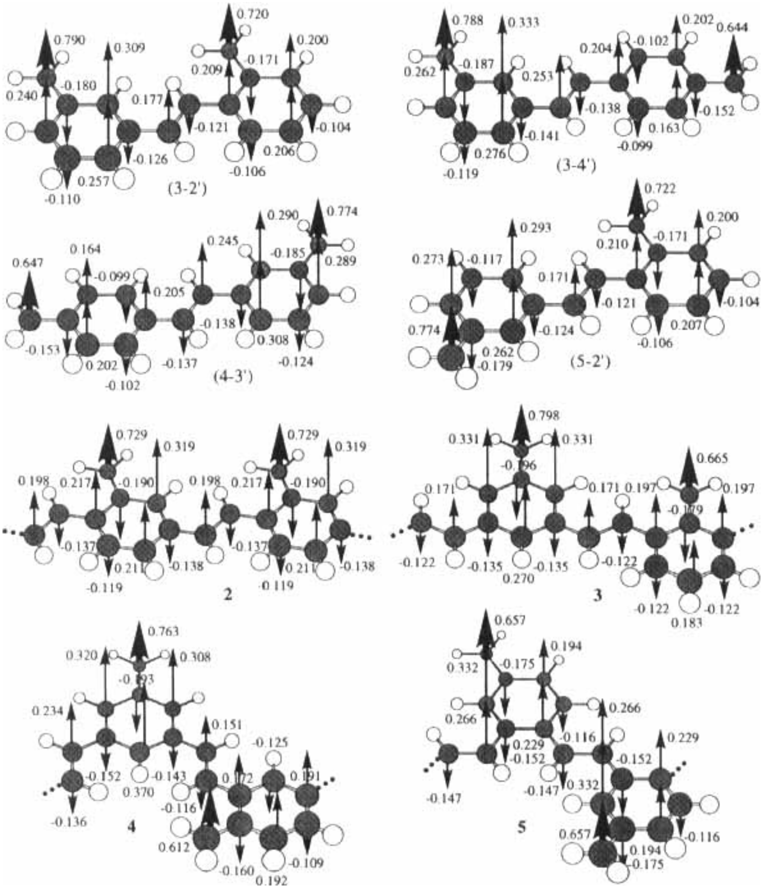


FIGURE 4 Atomic spin densities in triplet isomers of **1** and in polymers **2-5**.

On the other hand, although we did not show the numerical results in this figure, the values around ±1.0 were detected in UHF/4-31G densities at every sites on C atoms as similar as the densities in benzyl radical listed in Table I, which are too large for the experimental values.

In order to clarify the spin polarization induced by the π-conjugation within a chain structure, we plot the change in absolute value of spin density on each C atom included in stilbene unit from molecule to polymer in Figure 5.

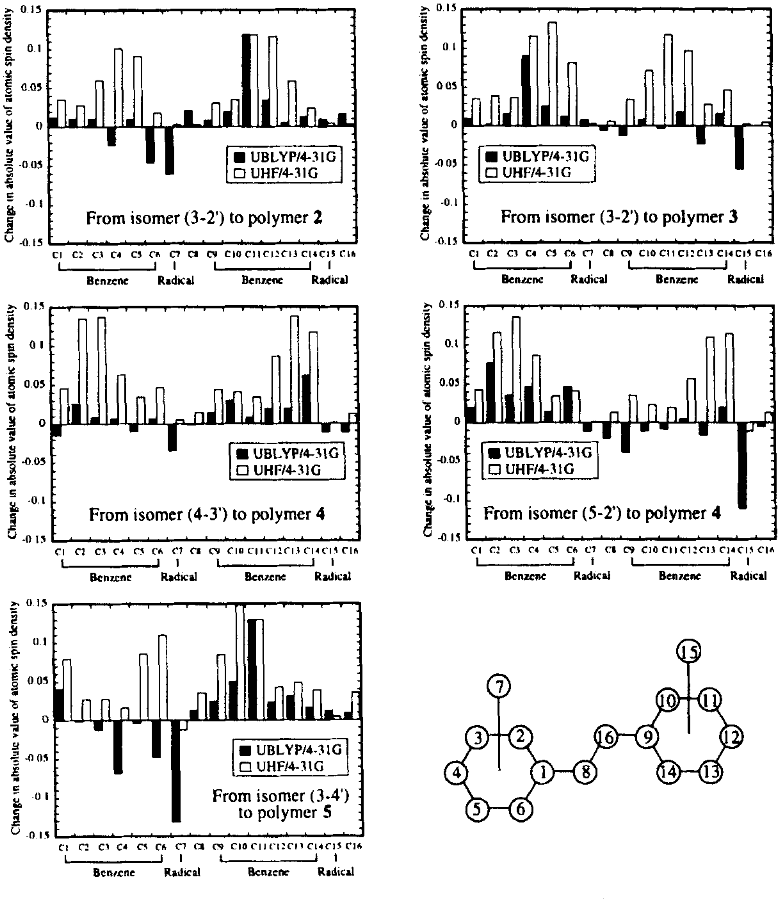


FIGURE 5 Change in spin density from triplet isomers of **1** to polymers **2**-**5**.

The effect of polymerization from monomer to polymer is clearly elucidated from this figure, that is, the polarization in spin density is enhanced in polymer than in molecule corresponding to the increment in ΔE given in Tables III and IV. UHF calculations show a large amount of the change in density in comparison with UBLYP calculations.

CONCLUDING REMARKS

The present *ab initio* calculations for magnetic molecules and polymers clearly indicate that the UBLYP/4-31G density functional approach is fairly applicable to the evaluation of the effective exchange interactions and the spin distributions in organic molecular systems, but UHF/4-31G is not. The four models examined as one-dimensional ferromagnetic polymers comprising phenylenevinylene with methylene radical have the high-spin ground states. The stability of high-spin configuration increases in polymer than in molecule by about twice which is caused by the conjugation between monomer units inducing the spin polarization through phenylenevinylene. Thus, it is concluded that phenylenevinylene bridge can effectively carry the ferromagnetic interactions between radical spins as one of the coupling units. This is consistent with the experimental observation by Nishide et al. that the oligomers having poly(phenylenevinylene) skeletons with phenoxy or nitroxide radical groups show the ferromagnetic character.[22-24]

The results in this study suggest that the *ab initio* periodic treatment based on the density functional formulation is useful to estimate the magnetic properties in an infinite periodic polymer. Therefore, further investigations by this approach will supply some guidelines to design and construct the organic ferromagnetic polymers. The computations for model polymers with nitroxide group are now in progress in our laboratory and we will report the results in the near future.

Acknowledgments

This work was supported by Grants-in-Aid for Scientific Research on Priority Areas (No. 283, "Innovative Synthetic Reactions") from Ministry of Education, Science, Sports and Culture of Japan. One of authors (M.M.) was also supported by Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists.

References

[1] K. Yamaguchi, Y. Toyoda, and T. Fueno, *Kagaku*, **41,** 585 (1986) (in Japanese); idem, *Synth. Met.*, **19,** 81 (1987).

[2] H. Iwamura, *Kikan Kagaku Sosetsu*, **35,** 57 (1998) (in Japanese).

[3] J. S. Miller and A. J. Epstein, *Angew. Chem. Int. Ed. Engl.*, **33,** 385 (1994).

[4] A. Rajca, *Chem. Rev.*, **94,**871 (1994).

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

[6] D. Yamaki, S. Yamada, G. Maruta, T. Kawakami, W. Mori, and K. Yamaguchi, *Mol. Cryst. Liq. Cryst.*, **279,** 9 (1996).

[7] G. Maruta, D. Yamaki, W. Mori, K. Yamaguchi, and H. Nishide, *Mol. Cryst. Liq. Cryst.*, **279,** 19 (1996).

[8] C. I. Ivanov, N. Tyutyulkov, and S. Karabunarliev, *J. Magn. Magn. Mater.*, **92,** 171 (1990).

[9] K. Müllen, M. Baumgarten, N. Tyutyulkov, and S. Karabunarliev, *Synth. Met.*, **40,** 127 (1991).

[10] N. Tyutyulkov, S. Karabunarliev, K. Müllen, and M. Baumgarten, *Synth. Met.*, **52,** 71 (1992).

[11] N. Tyutyulkov, F. Dietz, K. Müllen, M. Baumgarten, and S. Karabunarliev, *Theoret. Chim. Acta*, **86,** 353 (1993).

[12] N. Tyutyulkov, F. Dietz, K. Müllen, M. Baumgarten, and S. Karabunarliev, *Chem. Phys.*, **189,** 83 (1994).

[13] T. Hughbanks and M. Kertesz, *Mol. Cryst. Liq. Cryst.*, **176,** 115 (1989).

[14] T. Hughbanks and K. A.Yee, in *Magnetic Molecular Materials*, edited by D. Gatteschi et al. (Kluwer Academic Publishers, Dordrecht, 1991), p. 133.

[15] K. Yoshizawa, A. Takata, K. Tanaka, and T. Yamabe, *Polymer Journal*, **24,** 857 (1992).

[16] K. Tanaka, T. Shichiri, and T. Yamabe, *J. Mol. Struct. (THEOCHEM)*, **188,** 313 (1989).

[17] K. Yoshizawa, A. Chano, A. Ito, K. Tanaka, and T. Yamabe, *Synth. Met.*, **52,** 377 (1992).

[18] K. Yoshizawa, K. Tanaka, and T. Yamabe, *Synth. Met.*, **60,** 279 (1993).

[19] K. Yoshizawa, K. Tanaka, and T. Yamabe, *J. Phys. Chem.*, **98,** 1851 (1994).

[20] A. D. Becke, *Phys. Rev.*, **A38,** 3098 (1988).

[21] C. Lee, W. Yang, and R. G. Parr, *Phys. Rev.*, **B37,** 785 (1988).

[22] T. Kaneko, S. Toriu, Y. Kuzumaki, H. Nishide, and E. Tsuchida, *Chem. Lett.*, 2135 (1994).

[23] H. Nishide, T. Kaneko, T. Nii, K. Katoh, E. Tsuchida, and K. Yamaguchi, *J. Am. Chem. Soc.*, **117,** 548 (1995).

[24] H. Nishide, in *Bunnshi Jisei*, edited by K. Itoh (Gakkai Shuppann Center, Tokyo, 1996), p. 236 (in Japanese).

[25] Gaussian 94, M. J. Frisch et al., Gaussian, Inc., Pittsburgh PA, 1995.

[26] R. Dovesi, V. R. Saunders, C. Roetti, M. Causà, N. M. Harrison, R. Orlando, and E. Aprà, CRYSTAL95 User's Manual, University of Trino, Trino, 1996.