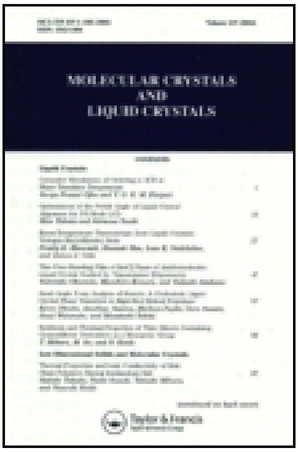


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Design of Donor Oligomers to Produce Parallel Spins Upon Charge Transfer

Hideo Mizouchi [a] , Atsushi Ikawa [a] & Hideo Fukutome [a]

[a] Department of Physics, Kyoto University, Kyoto, 606, Japan

To cite this article: Hideo Mizouchi , Atsushi Ikawa & Hideo Fukutome (1993): Design of Donor Oligomers to Produce Parallel Spins Upon Charge Transfer, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 233:1, 127-132

To link to this article: http://dx.doi.org/10.1080/10587259308054955

Mol. Cryst. Liq. Cryst. 1993, Vol. 233, pp. 127–132
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

DESIGN OF DONOR OLIGOMERS TO PRODUCE PARALLEL SPINS UPON CHARGE TRANSFER

HIDEO MIZOUCHI, ATSUSHI IKAWA AND HIDEO FUKUTOME
Department of Physics, Kyoto University, Kyoto 606, Japan

Abstract We design covalently bonded dimers of donor molecules to give parallel spin coupling owing to the dynamic spin polarization of linking bonds if the donors become cation radicals upon charge transfer. We show the triplet nature of the ground state of the dications of the dimers by UHF calculations in the PPP model.

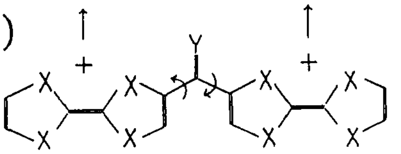
INTRODUCTION

One of the authors (H.F.) and collaborators designed polymers in which spins of polarons produced by doping couple parallely[1] (polaronic ferromagnets) owing to enhancing interference of the dynamic spin polarizations (DSP) produced by polarons. Such a polymer was synthesized[2]. At low dopings it gave in average five parallel polaronic spins but at high dopings it perhaps degraded to give only 1/2 spins. Hence it is necessary to avoid degradation at high dopings. It is also almost impossible to have crystals of such polymers.

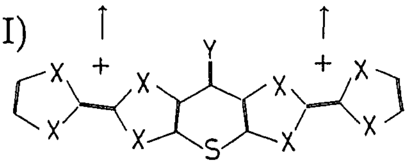
To overcome these difficulties we try to design oligomers of donors or acceptors to produce parallel spins upon doping, namely upon charge transfer (CT). An oligomer of donors or acceptors may make stable CT crystals even if all donor or acceptor moieties become ion radicals. If the ground state of the oligomer has a high spin upon CT, it may become a building block of new magnetic materials.

To demonstrate possibility of such oligomers, we consider here donor dimers of the following structures where $X = S, Se$ and $Y = C, O, S, C(CN)_2$. The donor monomer is tetrathiafuluvalene (TTF) for X=S and tetraselenafuluvalene (TSF) for X=Se. These dimers are designed so as to favor parallel spins in the dications owing to the DSP in the linking bonds with Y.

I)



II)



METHOD OF CALCULATIONS

The pi electronic structures of I and II are calculated in the UHF approximation of the PPP model[3]. We use the UHF program with direct optimization algorism that is capable to calculate instabilities and to get stable UHF wave functions[4]. The singlet (S) and triplet (T) UHF ground states are obtained. The S ground state may be a singlet diradical. As the electron-electron Coulomb interaction we examine the Mataga-Nishimoto (M-N) and Ohno potentials. They give qualitatively same but quantitatively much different results.

The molecules I have various conformers. We can not determine definitely which conformer is of the lowest energy. However, from comparisons of the pi energies and the extents of steric hindrance, we guess the conformer shown as I would be the most stable. Owing to the steric hindrance of hydrogen atoms, the connecting bonds in I are twisted by about $\theta = 27°$ if we put the H-H distance at the zero point of the Lennard-Jones potential. In the twisted bonds, the pi transfer is reduced by $\cos\theta$. The molecules II are considered to be plane. The geometries of TTF, TSF and connecting bonds are taken from[5].

RESULTS

Singlet-Triplet (S-T) Energy Separation

We show in TABLES I and II the energy separation $E_S - E_T$ (in meV) between the S and T ground states of the dications of I and II, respectively. They show that the pi electronic ground states in the dications of I and II are always triplet. We note that in all the other conformers of I also this is true. Both the M-N and Ohno potentials give the T ground state but the magnitudes of the S-T separation are very much different between them. The former give much larger S-T separations than the latter. The S-T separations in the plane dimers II are

		E_S - E_T (meV)	
X	Y	M - N	Ohno
S	C	14.41	0.54
	O	12.38	0.21
	S	17.53	0.80
	$C(CN)_2$	16.71	0.78
Se	C	11.17	0.19
	O	11.56	0.12
	S	15.84	0.38
	$C(CN)_2$	15.13	0.41

		E_S - E_T (meV)	
X	Y	M - N	Ohno
S	C	57.26	5.43
	O	24.75	1.89
	S	47.76	4.99
	$C(CN)_2$	52.93	5.80
Se	C	38.16	2.28
	O	15.29	1.57
	S	34.34	2.73
	$C(CN)_2$	22.31	1.19

larger than those in the twisted dimers I. The enhancements by planarity are more prominent in the Ohno potential than the M-N case. The S-T separations in I with the Ohno potential are in the order of about 0.5 meV. They are so small that inclusion of contributions of sigma electrons and correlations beyond the UHF might alter the order of the S and T states. We note also that Y=O, except for X=Se in I with the M-N potential and in II with the Ohno potential, gives the smallest S-T separations compared to the other cases.

We can estimate the exchange energies J between the spins of the cation radicals of donor moieties as the half of the S-T separation. They give ferromagnetic couplings of the spins in the orders of J=5.6 ∼ 8.8 meV (61.6° ∼ 96.8°K) for I with the M-N potential and 0.06 ∼ 0.4 meV (0.66° ∼ 4.4°K) for I with the Ohno potential and J=7.6 ∼ 28.6 meV (83.6° ∼ 314.6°K) for II with the M-N potential and 0.6 ∼ 2.9 meV (6.6° ∼ 31.9°K) for II with the Ohno potential. It is obvious that by making trimers, tetramers and so on in the similar manners to I and II we can get molecules with spins 3/2, 2 ⋯ upon CT. The M-N and Ohno potentials give so much different J's. We must determine experimentally which is the better description of the pi electronic systems. To get magnetic materials of this kind at high temperatures, it is desirable that the M-N potential would be the better approximation.

Electron and Spin Density Structures of the Singlet and Triplet States

We show in FIGURES 1 and 2 the pi electron densities (ED) and the spin densities (SD) in the S and T states of the dication of I for X=Y=S with the

M-N (FIGURE 1) and Ohno (FIGURE 2) potentials. The main differences in the pi electronic structures due to the difference of the M-N and Ohno potentials are as follows.

In TTF and TSF, S and Se atoms have two pi electrons. In their cation radicals, a hole produced in S or Se delocalizes over the whole donor. The extent of the hole delocalization is larger in the M-N potential than the Ohno case. The

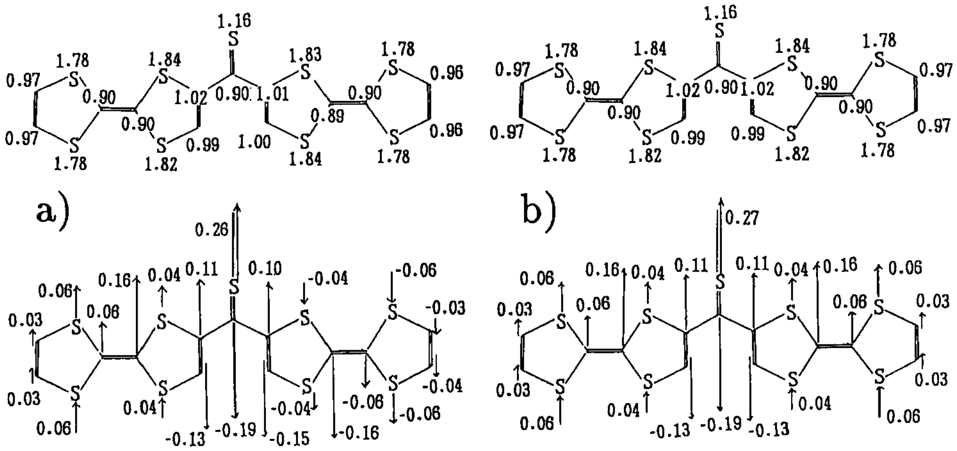


FIGURE 1 ED (upper) and SD (lower) structures in the S(a) and T(b) states of I with X=Y=S and the M-N potential

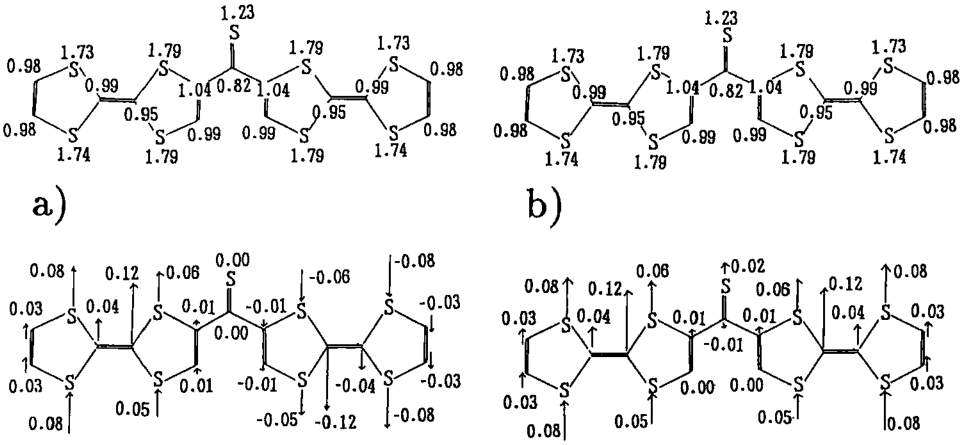


FIGURE 2 ED (upper) and SD (lower) structures in the S(a) and T(b) states of I with X=Y=S and the Ohno potential

electronic structures of the donors in a dimer are little different between the S and T states. The linking bonds with Y and the adjacent C=C bonds show DSP and charge polarization (CP). The DSP in the M-N potential is much larger than the Ohno case. In the M-N case, the DSP is very similar between the S and T states, but in the Ohno case no DSP is present in the S state and a small DSP occurs only in the T state. The DSP stabilizes the T state. On the contrary, the CP in the Ohno potential is larger than the M-N case.

The DSP for Y=O is the smallest. This is due to the fact that the O atom has much excess ED by 0.35 to 0.44 compared to the excess ED of the S atom in the linking bond by 0.16 to 0.30. This is why Y=O gives the smallest S-T separations. In the plane dimers II, the DSP decrease in the M-N case, though the S-T separations increase, but it increase in the Ohno case in accordance with the increase of the S-T separation. Thus the relation of the DSP to the stabilization of the T state is not so straightforward in the present systems.

These differences between the pi electronic structures in the M-N and Ohno potentials arise from the difference of their first neighbor values. Their on-site values V_0, for instance for carbon, are the common value 11.13 eV but their first neighbor values V_1 for the C-C bond linking the donors with the bond length 1.446 Å are 5.256 and 7.422 eV, respectively. The larger the difference $V_0 - V_1$, 5.855 eV for the M-N and 3.708 eV for the Ohno cases, the larger is the DSP, but the larger V_1, the larger is the CP.

DISCUSSION

If the donor dimers I and II are crystallized with suitable small acceptors, they will make CT crystals. The plane dimers II would be easier to make good crystals than the twisted dimers I. The separation between the HOMO and 2nd HOMO of the dimers are small, for instance in the range 0.2 to 0.03 eV for I with X=S depending on Y and the type of the potential. So, they will make overlapping bands in a crystal if it has stacking of donor moieties. Their bandwidths will be larger than the S-T separations given above. Because of this, all the dimers can not be in the T state even if the donor to acceptor ratio is one to one. Electrons will enter into the HOMO and 2nd HOMO bands making closed shells near their bottoms because the delocalization energy gain is larger than the S-T separation. However, in the energy range about the S-T separation near the Fermi level, two electrons will enter into the two bands with their spins parallel to gain the extra stabilization in the T state. All the electrons in this energy range of the two bands will have parallel spins to maximize the average number of the dimers in the T state. Therefore, itinerant ferromagnetism may be possible to occur in these systems. The strength of magnetization will be dependent on the bandwidths, band separation and S-T separation. The 3D interactions will also affect it. We note also that I and II may have varieties of 3D interactions and may provide organic superconductors of new kinds.

ACKNOWLEGDEMENTS

This work was supported in part by a Grant for International Joint Research Project from the NEDO, Japan and a Grant-in-Aid for Scientific Research on Priority Area (No. 228/04242101) from the Ministry of Education, Japan.

REFERENCES

1. H. Fukutome, A. Takahashi and M. Ozaki, Chem. Phys. Lett., 133, 34 (1987).
2. D.A. Dougherty and D.A. Kaisaki, Mol. Cryst. Liq. Cryst., 183, 71 (1990). D.A. Kaisaki, W. Chang and D.A. Dougherty, J. Am. Chem. Soc., 113, 2764 (1991).
3. J.N. Murrell and A.J. Harget, "Semi-empirical Self-consistent-field Molecular Orbital Theory of Molecules", (Wiley-Interscience, London, 1972).
4. A. Igawa and H. Fukutome, Prog. Theor. Phys., 54, 1266 (1975).
5. "Chemistry Handbook" 3rd edition, ed. Chemical Society of Japan, vol.II (Maruzen, Tokyo 1984).