Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 18 Oct 2010

To cite this article: Takeshi Taniguchi, Shuhei Nakano, Takashi Kawakami & Kizashi Yamaguchi (2003): Theoretical Studies with π-R• Cluster Models for Pure Organomagnetic Conductors, Molecular Crystals and Liquid Crystals, 379:1, 483-488

To link to this article: http://dx.doi.org/10.1080/713738659

Mol. Cryst. Liq. Cryst., Vol. 379, pp. 483-488

1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290090921

Theoretical Studies with π-R• Cluster Models for Pure Organomagnetic Conductors

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Model clusters $(NH_3)_4^{+2}$ and $(NH_3\text{-}H_2NO\bullet)_4^{+2}$ are introduced as simple models for a pure organic conductor. Then theoretical calculations of the total energies of ab initio solutions, in which the spin or charge density are arranged alternately, and intermolecular magnetic interactions are carried out by ab initio MO-DFT method. The result shows that these model clusters are efficient for ab initio investigation of the electronic properties of organomagnetic conductors.

Keywords ab initio MO calculation;pure organomagnetic conductors;effective exchange integrals;cluster model

INTRODUCTION

About ten years ago, our group proposed organic and organomagnetic conductors as possible analogs of copper oxides [1][2]. Nowadays, organic conductors with low dimensional electronic sheets have been focused, particularly, systems consisted of π-donor molecules coupled with localized spins have been intensely studied in the way of theoretical calculation or experimental measurement.

In this work, model clusters are introduced to calculate the electronic properties of organic conductors, being expanded to apply realization of pure organomagnetic conductors. Among the important properties, SDW- (spin density wave), CDW- (charge density wave) COS- (charge ordered

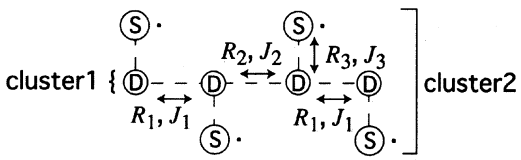
state) like solutions are evaluated in terms of their total energies calculated by ab initio MO method based on DFT (density functional theory). Moreover, magnetic interactions between the donor molecules and between the donors and the organic radicals (π-R• interaction) are evaluated employing effective exchange integrals in the Heisenberg model.

THEORETICAL BACKGROUNDS

1. Cluster models

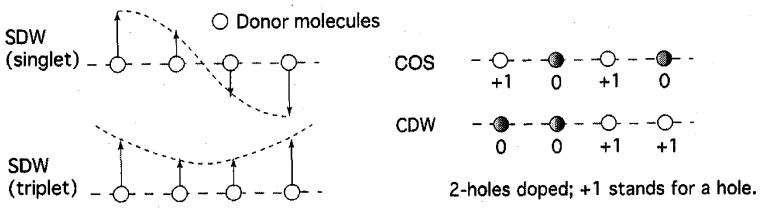
A model we introduce for organic conductor is generally represented as Figure 1, where donor molecules and spin sources (organic radicals) are as D and S in the illustration, respectively, and the donors are aligned in one-dimension. We can execute simple and useful ab initio MO calculations with these models in exchange for existing large systems. Interatomic distances defined as R_1 and R_2 are the parameters to express dimerization of two donors in the crystal[4]. Then SDW-, CDW- and COS-like solutions (Figure 2) have been evaluated for each of those distances.

Cluster 1 is designed as a simplified model for the donor planes of organic conductive salts, the D of which is an ammonium cation. The



Cluster 1; D = NH_3, **Cluster 2**; D = NH_3, S = H_2NO•

FIGURE 1 A schematic illustration of model clusters for organic conductors.



(a) (b)

FIGURE 2 Schematic illustrations for definition of (a) SDW-, (b) CDW- and COS-like solutions.

π-electrons on the ammonium cations is regarded as the conjugated π-electrons in typical organic conductors. This model has totally +2 electric charge [3], namely each ammonium cation is on charge of +1/2.

Cluster 2 is devised for a reduced model of pure organomagnetic conductors, the donor plane of which is placed between two organic radical layers. The D is also an ammoium caion and the S is a nitroxide radical that represents the radicals on the counter anion layer in organic conductors and are located on the same plane of the ammonium cation at a distance of R_3.

2. Computational details

First, the energy of each solutions were calculated by UB3LYP on several R_1 and R_2. Second, intermolecular magnetic intercations in Cluster 1 were estimated in terms of J, which is the effective exchange integral of the Heisenberg model and defined as;

$$\mathcal{H} = -\sum_{<i,j>} 2J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j \quad , \tag{1}$$

where $\mathbf{S}_i$ is a spin on the ith radical site and $<i, j>$ is the nearest pair of radical sites. Then the same investigations were performed on Cluster 2 and the stabilities of SDW-like solutions were evaluated also in terms of its energy by UB3LYP. Last, π-R• interactions between the donor cation radical and the organic radical were calculated as J-values.

The relative stabilities of SDW-, CDW- and COS-like solutions were estimated by DNO (density matrix-based natural orbital) -CASCI [6, 6] based on UB3LYP, while the dimerization effect and the J-values were examined by UB3LYP. The basis set 6-31+G* was employed for the molecules on both ends of the donor plane except for hydrogens atoms, in order to take account of crystallographic surroundings. The UDFT (spin-polarized DFT) method always brings us low spin states contaminated by spin states with higher spin-multiplicity. Hence approximated spin-projection (AP) has been applied to such a contaminated low spin state in our calculation;

$$E(\mathrm{AP}-\mathrm{X}) = {}^1E(\mathrm{X}) + f\left\{{}^1E(\mathrm{X}) - {}^3E(\mathrm{X})\right\}, \tag{2}$$

$$f = {}^1\langle \mathbf{S}^2 \rangle(\mathrm{X}) \Big/ \left\{ {}^3\langle \mathbf{S}^2 \rangle(\mathrm{X}) - {}^1\langle \mathbf{S}^2 \rangle(\mathrm{X}) \right\}. \tag{3}$$

where E(X) is an energy evaluated by method X such as UDFT, the superscripts are spin-multiplicity and the constant f is a contamination factor.

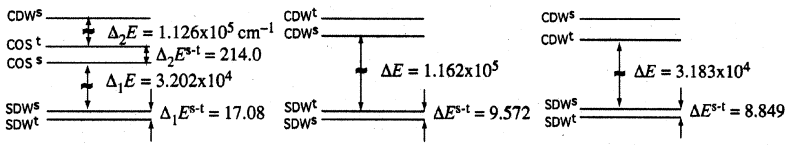
The J-values are also spin-projected, i.e., for two spin site,

$$J(\mathrm{AP}-\mathrm{X}) = \frac{{}^{1}E(\mathrm{X}) - {}^{3}E(\mathrm{X})}{{}^{3}\langle \mathbf{S}^2 \rangle(\mathrm{X}) - {}^{1}\langle \mathbf{S}^2 \rangle(\mathrm{X})} \ . \tag{4}$$

RESULTS AND DISCUSSION

Cluster1

The total energy of each solution is shown in Figure 3. The intermolecular distances are fixed as (R_1, R_2) = (3.0, 3.0) (a), (2.5, 3.5) (b) and (3.0, 4.0) (c) in Å unit in order to examine dimerization effects. Upon condition (a), the most stable state of these is triplet SDW-like solution (SDW^t), then next comes singlet SDW-like solution (SDW^s) and singlet COS-like solution (COS^s) is still more unstable than SDW^s, followed triplet COS-like solution (COS^t). The CDW-like solutions are the most unstable of these solutions. On the other hands, upon condition (b), the order of relative stability of these solutions is SDW^s, SDW^t, CDW^s (singlet CDW) and CDW^t (triplet CDW). The condition (c) have given the same rusult as (a) for SDW-like solutions, though the relative stability of CDW^s and CDW^t is reversed. The energy gaps between SDW- and CDW-like solutions are nearly 10,000 times as large as that between singlet and triplet of SDW ones throughout the three conditions. This means that we need further study, such as periodic boundary condition, to obtain more stable ab initio CDW- and COS-like solutions for this culster model. As shown on Table 1, comparison of each energy of the most stable solutions has shown us that (b) gives the lowest total energy among the three geometries, while (a) makes Cluster 1 most unstable, implying that these molecules tend to make pairs (i.e., dimerize) in the crystal. Besides, magnetic interactions



(a) (b) (c)

FIGURE 3 The relative energy levels of the SDW-, CDW- and COS-like solutions upon conditions (a) $R_1 = R_2 = 3.0$Å, (b) $R_1 = 2.5$Å, $R_2 = 3.5$Å and (c) $R_1 = 3.0$Å, $R_2 = 4.0$Å.

All the energies are calculated by DNO-CASCI [6, 6].

TABLE 1 Interdimeric effective exchange integrals; J_2 and relative energies of the lowest states, the ground state of which is the energy of SDW^s on (b).

case	(R_1, R_2) [Å]	$J_{2\,(AP)}$ [cm^{-1}]	relative energy [cm^{-1}]
(a)	(3.0, 3.0)	58.79	+7778.5 (triplet)
(b)	(2.5, 3.5)	–60.90	0 (singlet)
(c)	(3.0, 4.0)	1.975	+537.00 (triplet)

*All the values are evaluated by UB3LYP

between $(NH_3)_2^{\cdot+}$ dimres in Cluster 1 is weak antiferromagnetic on condition (b), which is an essential property for organic conductors observed such existing organics as BETS-TTF.

Cluster 2

Shown in Figure 4 is the comparison of relative energy levels of SDW-like solutions, keeping R_3 = 1.3Å, with their spin configurations. Intermolecular distances are the same values as Cluster 1, so that (a′), (b′) and (c′) correspond (a), (b) and (c), respectively. Through the three conditions SDW^t-1 solution is always below SDW^t-2, which shows that magnetic interactions among radicals on the counter anion layer are ferromagnetic and this solution is the ground state except for condition (a).

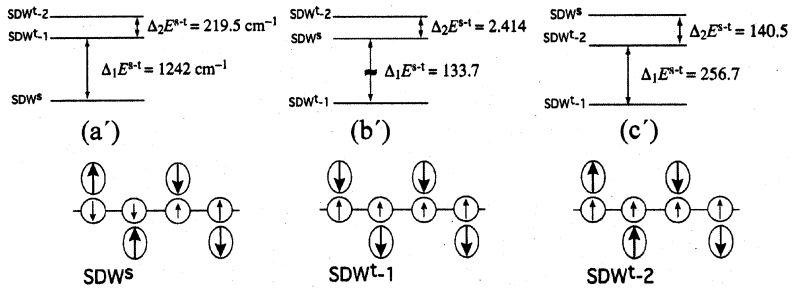


FIGURE 4 Diagrams of energy levels on the conditions (a′), (b′) and (c′), and the spin configuration in each state. All the energies are calculated by UB3LYP.

TABLE 2 Intermolecular effective exchange integrals, J_1, J_2 and J_3, and relative energies of the most stable state, the ground state of which is SDW^t-1 in (b). All energies are calculated by UB3LYP and the unit is cm^{-1}.

case	(R_1, R_2) [Å]	J_1	J_2	J_3	relative energy
(a)	(3.0, 3.0)	–1279	–1395	–109.7	+3631
(b)	(2.5, 3.5)	–1241	–2.404	–68.04	0
(c)	(3.0, 4.0)	~ –1280	143.4	–128.3	+2496

Table 2 summarizes intermolecular J-values calculated by the method in [5] and relative energies of the most stable solutions. The ferromagnetic ground state has appeared on condition (b) and (c), though J_2 on (b) are negative. This has suggested the interaction path R•-π-π-R• are dominant in this system, which is been examined in our further study. J_3 , meaning π-π interaction between D and S, affects the donor molecules to make SDW^t-1 stable on condition (b) and (c). The condition (b) may be regarded as a possible model for organomagnetic conductors since all J-values are negative and small. This impies that Cluster 2 with the periodic condition can procude an organic ferri/ferromagnetic conductor.

CONCLUSION

First, the SDW-like solutions are the ground level of each cluster model, although some of their spin configurations are different. Obtained CDW- and COS-like solutions are unstable because of trancation of the system, however the point is that this is the first work to evaluate such an ab initio solution on cluster models. Second, varing the intermolecular distances have shown the donor molecules of the clusters tend to dimerize, which has reproduced experimental results. Last, the SDW-like solution are still stable even under the magnetic perturbation of organic radical layer, only to change their spin-multiplicity. Considering above, the clusters introduced in this work are reliable and useful for theoretical studies on organomagnetic conductors. In addition, the compound synthesized by referring to these models and hole-doped with such devices as FET would turn into a pure organomagnetic metal.

Acknowledgements

This work has been supported by a Grant-in-aid for Scientific Research on Priority Areas (Nos. 10149105, 11224209 and 13740396) from Ministory of Education, Culture, Sports, Science and Technology, Japan.

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