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Theoretical Studies on Magnetic Properties of TCNQ Organic Crystals with Ab initio and DFT Methods

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The detailed theoretical studies for TCNQ/$TCNQ^{\bullet}$ salts, which possess ferromagnetic hysteresis at relative high temperature, were carried out. The calculations based on *ab initio* molecular orbital (MO) and density functional (DFT) theories were carried out to evaluate the intermolecular effective exchange integrals and transfer integrals. In addition, we employed the "hybrid DFT method" based on instability of chemical bonds and successfully studied their spin densities. From the results it was found the remarkable singlet dimer structure is dominant. In addition, quasi-one-dimensional structure was found because of nonzero charge transfer.

Keywords TCNQ; organic ferromagnetism; effective exchange integral; transfer integral; spin density; hybrid DFT method

INTRODUCTION

Organic ferromagnets and magnetic-metal crystals have been receiving continuous interest in recent years.[1] Many experimental and theoretical studies[2] have been carried out to elucidate the mechanism of the magnetic interaction and may reveal the new feature of organic crystals.

Recently, Sugimoto and his co-workers has reported ferromagnetic hysteresis at relative high temperature in the tetramethylammonium (NMe_4^+) and cesium (Cs^+) cations salts of tetracyanoquinodimethane

(TCNQ) and its radical anion ($TCNQ^{\bullet}$), where molecular ratio is equal to 1:2.[3,4] On the other hand, the salts in molecular ratio of 1:1 do not exhibit ferromagnetic behavior. It is interesting how these delocalized spin sources contribute to magnetic properties.

We here report the detailed theoretical studies on these salts. The calculations based on *ab initio* molecular orbital (MO) and density functional theories (DFT) were carried out to evaluate the intermolecular parameters in these crystals. In addition, we tried to introduce the "hybrid DFT method", which is the hybrid method between Hartree-Fock (HF) and DFT methods on the basis of instability of chemical bonds in open-shell systems.[5]

CRYSTAL STRUCTURES

The TCNQ/$TCNQ^{\bullet}$ mixed salts which consist of neutral molecules (TCNQ), its radical anion ($TCNQ^{\bullet}$) and counter ion, has been reported in detail by Sugimoto and co-worker.[3,4] They reported the salts of NMe_4^+ and Cs^+ in a molecular ratio of 1:2 in TCNQ/$TCNQ^{\bullet}$, i.e., (NMe_4^+•$TCNQ^{\bullet}$)•1/2TCNQ (**1**) and (Cs^+•$TCNQ^{\bullet}$)•1/2TCNQ (**2**), respectively.[4] Their papers propose that they exhibit peculiar magnetic behavior. On the other hand, (NMt_4^+•$TCNQ^{\bullet}$)•TCNQ (**3**) was also reported as 1:1 molecular ratio and no ferromagnetic hysteresis is found.[4]

Here, we employed the most accurate structural data for salt **1** mainly and Fig. 1A illustrated a unit cell of this crystal. The X-ray structural measurement shows accurate positions of carbon, nitrogen and oxygen atoms. We decided the positions of hydrogen atoms in TCNQ molecules by the semiempirical PM3 method because of lack of their detailed positions. The salt has the unit cells classified by a space group of P21/n and cell parameters are a = 7.808 Å, b = 9.692 Å, c = 27.417 Å, and β = 94.781 °. In Fig. 1B the more detailed molecular stacking was depicted. In this figure, molecules **A**, **B**, **C**, **D**, **E** and **F** are radical anions

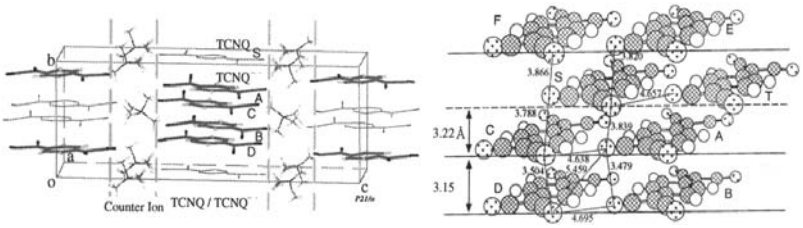


FIGURE 1 (A) Crystal structure of (NMe_4^+•$TCNQ^{-\bullet}$)•1/2TCNQ (**1**). (B) Stacking modes of radical anion and neutral molecules in TCNQ/$TCNQ^{-\bullet}$ sheet.

and molecules **S** and **T** are neutral molecules. The molecules **A** and **B** form a tight dimer with distance of 3.479 Å between nitrogen atoms along b axis. The TCNQ and $TCNQ^{-\bullet}$ networks with molecular closing face-to-face and side-by-side will compose two dimensional networks. In this studies we treated only the TCNQ/$TCNQ^{-\bullet}$ sheet and counter ions did not been taken into account.

MAGNETIC PARAMETERS BETWEEN EACH MOLECULE

First of all, we have to investigate effective exchange integrals (J_{ab}) between radical anions, i.e. **A**, **B**, **C** and **D** as shown in Fig. 1B. In addition to the magnetic interaction between radical anions, we also treated interaction between radical anions and neutral molecules when neutral molecules (**S** and **T**) turn to be anion with charge transfer (CT) mechanism. The evaluated J_{ab} values were summarized in Table 1. Here, INDO, *ab initio* UHF and DFT UB3LYP calculations were carried out and 4-31G basis sets were employed for our purposes. The pairs **AS** and **FS**, **CS** and **ES** give same values because of spatial symmetry of its crystal structure. From these result the evaluated J_{ab} values between radical anions are relatively small except for pair **AB**. It must emphasize that a singlet dimer is realized in pair **AB** and the energy gap between high and low spin states is larger than the energy splitting at root temperature as shown in Fig. 2A.

TABLE 1 Magnetic parameters evaluated by semiempirical, *ab initio* and DFT methods.

	J_{ab} /cm^{-1}			S_{ab}	h_{ab} /a.u.
Pair	INDO	UHF[a]	UB3LYP[a]	UHF[a]	
AB	-651.511	-286.710	-1542.202		
AC	0.135	-125.127	0.470		
AD	0.049	0.439	0.417		
BC	0.002	0.007	0.002		
AS (= FS)	-28.188	-62.909	-106.796	0.01104	0.33029
CS (= ES)	-1.034	25.248	-2.014	0.00236	0.06736

a) 4-31G bases set was employed.

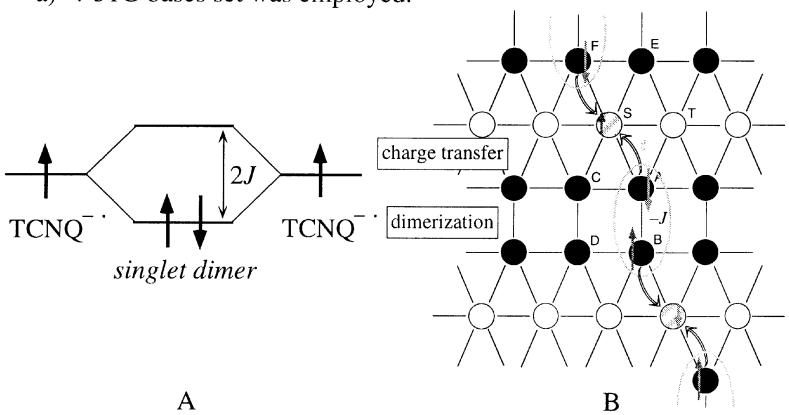
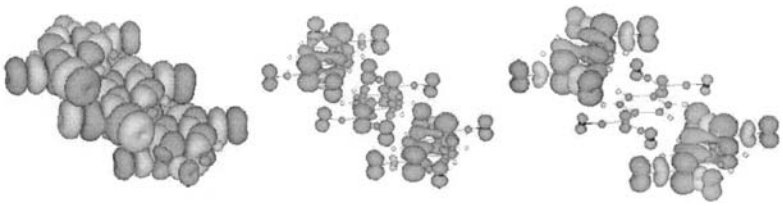


FIGURE 2 (A) Dimer structure between radical anions **A** and **B**. (B) Quasi-one-dimensional structure in TCNQ/TCNQ$^{-\bullet}$ sheet.

Next, let us analyze the overlap integrals (S_{ab}) and kinetic integrals (h_{ab}), which is related in transfer integrals (t_{ab}), for several pairs between radical anions and neural molecules. The CT from HOMO in a anion to LUMO in a neutral molecule may occurs. The formalism in order to evaluate S_{ab} and h_{ab} is described:

$$s^i_{ab} = \sum_{rs} c^{a*}_{ri} c^b_{si} \langle ra|sb\rangle, \quad h^i_{ab} = \sum_{rs} c^{a*}_{ri} c^b_{si} \langle ra|\frac{p^2}{2m}|sb\rangle \qquad (1)$$

and we had ensured its accuracy and effectivity for the case of simple H_2NO dimer models previously. The evaluated S_{ab} and h_{ab} values were



A B C

FIGURE 3 Spin densities calculated by UHF/4-31G (A), UBLYP (B) and hybrid-DFT (C) for trimer **ASF** (threshold 0.002).

summarized in Table 1. All the calculate values indicate existence of the CT mechanism. The values for path **AS** is larger than that for path **CS** and it is found the CT mechanism for direction **A**-**S**-**F** is dominant.

From these results, we can conclude that quasi-one-dimensional interaction chain (-**B**-**A**-**S**-**F**-) is dominant, though inter-chain interaction is not small. In Fig. 2B magnetic interaction was simply depicted. Here, black and white circles indicate radical anions and neutral molecules, respectively.

DETAILED STUDIES BY HYBRID-DFT METHOD

Here, let us examine the trimer pair **ASF** as anion-neutral-anion stacking, which is unit cell in one-dimensional model. It is suitable model in order to study the induced spin on center neutral molecule with the CT mechanism. Figures 3A and B depict the spin density populations by the UHF/4-31G and UBLYP methods, respectively. The densities by the UHF method are overestimated though those by the DFT method are very small.

Thus, we introduce the "hybrid DFT method", which is the hybrid method between HF and DFT methods.[5] The diradical character (y) for each orbital which indicates instability of chemical bonds with natural orbital analysis, was calculated. The diradical character (y_{sys}) for whole molecules was evaluated with summation of the y values and the mixing parameter was decided to be 0.363. Figure 3C illustrates the spin

densities with the hybrid-DFT method. The spin densities are induced even on the central molecule, though almost all spin densities locate in radical anions. In addition, we calculated J_{ab} values for trimer **ASF** with hybrid-DFT method and the obtained result is 10.481 cm^{-1}. It is found that indirect ferromagnetic coupling between anions **A** and **F** is expected.

CONCLUDING REMARK

Judging from the present calculations, singlet dimer structure between radical anion **A** and **B** is remarkable. Unfortunately, in this study we cannot decide what is responsible for peculiar magnetic behaviors in these crystals and the origin of ferromagnetic hysteresis is still open-question. More extended studies are now under progressing. It is expected that Investigation of this system is worth to study new magnetic-metal crystals. We have also successfully applied new "hybrid-DFT" method to this model. The hybrid-DFT approaches are expected to be employed for many computations of spin densities and J_{ab} values for many other organic radical crystals.

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