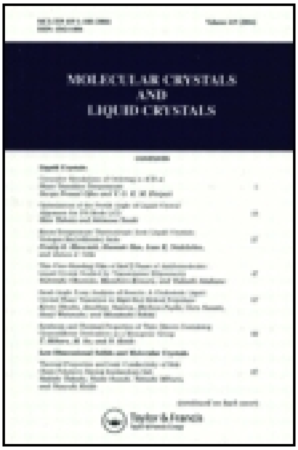

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: Shugo Suzuki, Shinichi Higai, Nobutada Nagai & Kenji Nakao (2000): The Electronic Structures of $(PH_4)_3C_{60}$ and $(ClO_4)_3C_{60}$, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 340:1, 587-592

To link to this article: http://dx.doi.org/10.1080/10587250008025530

Mol. Cryst. and Liq. Cryst., 2000, Vol. 340, pp. 587-592
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Printed in Malaysia

The Electronic Structures of $(PH_4)_3C_{60}$ and $(ClO_4)_3C_{60}$

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(Received May 30, 1999; In final form June 19, 1999)

We have studied theoretically the electronic structures of a hypothetical donor-type material, $(PH_4)_3C_{60}$, and a hypothetical acceptor-type material, $(ClO_4)_3C_{60}$ from first principles by using a full-potential linear-combination-of-atomic-orbitals method based on the density-functional theory within the local-density approximation. It is found that the charge transfer from the PH_4 molecules to the C_{60} molecules is perfect while the charge transfer from the ClO_4 molecules to the C_{60} molecules is not perfect. We compare the latter result with the electronic structures of two typical acceptor-type organic conductors, $(TMTSF)_2ClO_4$ and $(TMTSF)_2PF_6$, and discuss the differences.

Keywords: donor-type C_{60} compound; acceptor-type C_{60} compound; PH_4 molecule; ClO_4 molecule; electronic structure

INTRODUCTION

C_{60} compounds have been studied as a new class of molecular crystals[1]. In particular, the superconductivity found in a certain kind of C_{60} compound, e.g., alkali-metal-doped C_{60}[2–4], has become a strong driving force of the extensive studies in this field.

The superconductivity in alkali-metal-doped C_{60} shows a remarkable feature; the transition temperature increases with increasing the lattice constant. That is, there exits a scaling relation between the transition temperature and the lattice constant. This behaviour is understood as follows. Since the density of states at the Fermi level increases with increasing the lattice constant, the transition temperature also increases in accordance with the prediction of the BCS theory.

It is then natural to consider new materials with larger lattice constants because they can have higher transition temperatures than alkali-metal-doped C_{60}. A possible way is to use molecules as intercalates instead of atoms. This is analogous to the situation in the graphite intercalation compounds.

Recently, it has been proposed theoretically that NH_4 molecules can be used as donors[5]; a Born-Haber analysis predicts that the heat of formation of $(NH_4)_3C_{60}$ is -1.82 eV/mol and this material is stable with respect to the standard state reactants. The size of NH_4 molecules is however almost the same as the size of Rb atoms, so that $(NH_4)_3C_{60}$ is not expected to be a candidate for a new C_{60} superconductor with a higher transition temperature. Another possible candidate similar to this material but with larger molecular size is $(PH_4)_3C_{60}$. We study the electronic structure of this hypothetical material in the present work.

Furthermore, the use of molecules also opens a way to synthesize acceptor-type C_{60} compounds as in the graphite intercalation compounds although the synthesis of acceptor-type C_{60} compounds with good quality of samples has not been established yet. It is thus interesting to study the electronic structures of the candidates for this type of compound.

Several studies have been carried out to synthesize acceptor-type C_{60} compounds[6]. One of the compounds is $(AsF_6)_{0.38}C_{60}$. This material however shows semiconducting behaviour with the excitation energy of about 0.22 eV. The structure is body-centered tetragonal. This indicates that the face-centred cubic lattice of pure C_{60} is disturbed by the introduction of the intercalate molecules. Although the actual synthesis of samples with good quality has not been established yet, we also study the electronic structure of an ideal acceptor-type C_{60} compound, $(ClO_4)_3C_{60}$, in the present work as a starting point. Furthermore we compare the results on the electronic structure of this material with those of $(TMTSF)_2ClO_4$ and $(TMTSF)_2PF_6$ and discuss the differences.

RESULTS AND DISCUSSION

We have calculated the electronic structures of $(PH_4)_3C_{60}$ and $(ClO_4)_3C_{60}$ by using a full-potential linear-combination-of-atomic-orbitals method based on the density-functional theory within the local-density approximation[7].

The structures of $(PH_4)_3C_{60}$ and $(ClO_4)_3C_{60}$ are assumed as follows. We fixed the molecular structure of C_{60} throughout the calculations because the charge transfer causes no substantial changes in the molecular structure. On the other hand, we used optimized structures for PH_4^+ and ClO_4^- molecules; the optimized P-H and Cl-O distances are 1.42 and 1.46 Å respectively. For comparison, the optimized P-H and Cl-O distances in neutral PH_4 and ClO_4 molecules are 1.46 and 1.45 Å respectively. We then choose the lattice constants of the two compounds in such a way that the shortest distance between the C atoms and the H or O atoms is equal to the sum of the van der Waals radii of C atoms and H or O atoms; the estimated lattice constants for $(PH_4)_3C_{60}$ and $(ClO_4)_3C_{60}$ are 15.3 and 15.8 Å respectively.

The results of the calculations on the electronic structures of $(PH_4)_3C_{60}$ and $(ClO_4)_3C_{60}$ are shown in Figs.1(a) and (b), respectively. The zero of energy is the Fermi level in both figures.

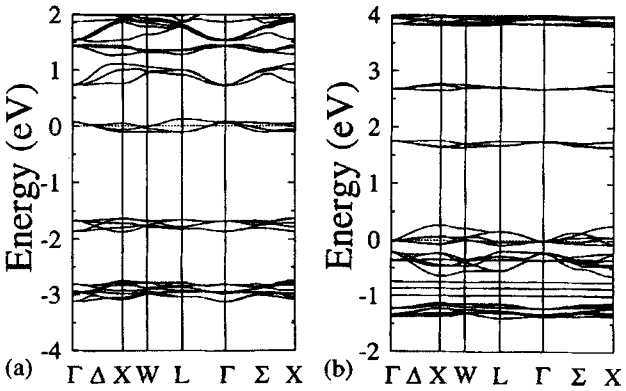

FIGURE 1 Electronic structures of (a) $(PH_4)_3C_{60}$ and (b) $(ClO_4)_3C_{60}$. The zero of energy is the Fermi level.

We first describe the characteristics of the electronic structure of $(PH_4)_3$-C_{60}. It is found that the charge transfer from the PH_4 molecules to the C_{60} molecules is perfect; the bands derived by the PH_4 molecules are located at about 1.5 eV and the conduction thus will primarily take place through the t_{1u} molecular orbitals of the C_{60} molecules. In this aspect, $(PH_4)_3C_{60}$ is similar to alkali-metal-doped C_{60}.

We also find that the width of the conduction bands in $(PH_4)_3C_{60}$ is about 0.2 eV. The width is extremely narrower than those in alkali-metal-doped C_{60}, about 0.4 eV. This is due to the large lattice constant, which corresponds to the superconducting transition temperature of about 70 K from the scaling relation between the transition temperature and the lattice constant, used for $(PH_4)_3C_{60}$ in the present study although this lattice constant is only a rough estimate and more precise determination is thus necessary in the future.

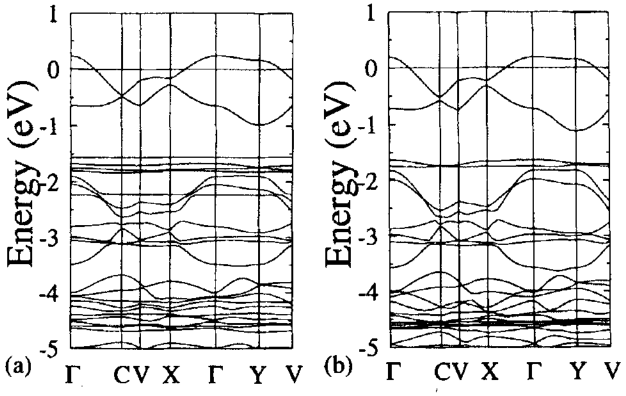

FIGURE 2 Electronic structures of (a) $(TMTSF)_2ClO_4$ and (b) $(TMTSF)_2PF_6$. The zero of energy is the Fermi level.

We next describe the characteristics of the electronic structure of $(ClO_4)_3C_{60}$. It is found that the charge transfer from the C_{60} molecules to the ClO_4 molecules in $(ClO_4)_3C_{60}$ is not perfect. That is, the bands derived from LUMO of the ClO_4 molecules are strongly hybridized with the bands derived from HOMO of the C_{60} molecules at −1 to 0 eV in Fig.1(b). This is in contrast with the situation in typical acceptor-type organic conductors. For example, we show the electronic structures of $(TMTSF)_2ClO_4$ and $(TMTSF)_2PF_6$ in Figs.2(a) and (b), respectively. The two bands near the Fermi level in each figure are derived from HOMO of the TMTSF molecules while the bands derived from LUMO of the ClO_4 molecules are located at about −1.6 eV in Fig.2(a) and the bands derived from LUMO of the PF_6 molecules are located at about −4.5 eV in Fig.2(b).

One reason for the imperfection of the charge transfer in $(ClO_4)_3C_{60}$ is that the HOMO level of C_{60} molecules, −6.9 eV, is relatively lower than those of other donor molecules. For example, the HOMO level of TMTSF molecules is −3.9 eV. At the same time the LUMO level of ClO_4 molecules, −9.1 eV, is relatively higher than other acceptor molecules. For example, the LUMO level of BF_4 molecules is −11.0 eV. As a result, the energy difference between HOMO and LUMO for $(ClO_4)_3C_{60}$ is 2.2 eV while that for $(TMTSF)_2ClO_4$ is 5.2 eV. The small energy difference between the HOMO and LUMO levels prevents the charge transfer in $(ClO_4)_3C_{60}$. We summarize the energies of the HOMO and LUMO levels of several donor and acceptor molecules in Table I. From Table I, possible candidates for acceptor-type C_{60} compounds to be synthesized are $(BF_4)_3C_{60}$ or $(AlF_4)_3C_{60}$.

Another possible reason for the above imperfection is that there are no positively charged portions in C_{60} molecules and thus the electrons on the ClO_4 molecules feel repulsive potential from the C_{60} molecules. This is in contrast with the situation in $(TMTSF)_2ClO_4$. Since TMTSF molecules have positively charged H atoms in methyl base at the ends of the molecule, the ClO_4 molecules are surrounded by these positively charged portions of the TMTSF molecules and thus the electrons on the ClO_4 molecules feel attractive potential from the H atoms in the TMTSF molecules.

TABLE I The energies in eV of the HOMO of C_{60} and TMTSF molecules and those of the LUMO of ClO_4, BF_4, and AlF_4 molecules.

Molecule	HOMO	LUMO
C_{60}	-6.9	
TMTSF	-3.9	
ClO_4		-9.1
BF_4		-11.0
AlF_4		-11.0

In the future studies, the following aspects are indispensable for carrying out further investigation. Firstly, it is necessary for calculating the heat of formation of a hypothetical C_{60} compound to optimize its geometrical structure because the heat of formation is very sensitive quantity to the geometrical structure although the electronic structure is not so sensitive. Secondly, new candidates for acceptor-type C_{60} compounds should be searched taking the two aspects mentioned above into consideration.

CONCLUSIONS

In the present work, we have investigated the electronic structures of two hypothetical compounds; one is a donor-type material, $(PH_4)_3C_{60}$, and the other is an acceptor-type material, $(ClO_4)_3C_{60}$. By calculating with a full-potential LCAO method based on the density-functional theory within the local-density approximation, we have found the following results. The charge transfer from the PH_4 molecules to the C_{60} molecules is perfect while the charge transfer from the C_{60} molecules to the ClO_4 molecules is not perfect. The latter imperfection can be understood by considering the energy difference between HOMO and LOMO and the structural characteristic of the C_{60} molecule that there are no positively charged atoms in this molecule in contrast with the H atoms in TMTSF molecules. It is thus necessary for the synthesis of acceptor-type C_{60} compounds to take the above aspects into consideration.

Acknowledgements
We would like to thank S. Miyamoto and T. Koike for helpful discussion.

References

[1] For example, see *Solid State Physics*, **48**, edited by H. Ehrenreich and F. Spaepen (Academic Press, New York, 1994).
[2] A. F. Hebard. M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, and A. R. Kortan, Nature, **350,** 600 (1991).
[3] M. J. Rosseinsky, A. P. Ramirez, S. H. Glarum, D. W. Murphy, R. C. Haddon, A F. Hebard, T. T. M. Palstra, A. R. Kortan, S. M. Zahurak, and A. V. Makhija. Phys. Rev. Lett., **66**, 2830 (1991).
[4] K. Tanigaki, T. W. Ebbesen, S. Saito, J. Mizuki, J. S. Tsai, Y. Kubo, and S. Kuroshima, Nature, **352**, 222 (1991).
[5] R. S. Ruoff, J. Phys. Chem., **100**, 8973 (1996).
[6] W. R. Datars, J. D. Palidwar, and P. K. Ummat, J. Phys. Chem. Solids, **57,** 977 (1996).
[7] S. Suzuki and K. Nakao, J. Phys. Soc. Jpn. **66,** 3881 (1997).