Crystalline and Electronic Structures of Molecular Solid C\textsubscript{50}Cl\textsubscript{10}: First-Principles Calculation

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A molecular solid C\textsubscript{50}Cl\textsubscript{10} with possible crystalline structures, including the hexagonal-close-packed (hcp) phase, the face-centered cubic (fcc) phase, and a hexagonal monolayer, is predicted in terms of first-principles calculation within the density functional theory. The stable structures are determined from the total-energy calculations, where the hcp phase is uncovered more stable than the fcc phase and the hexagonal monolayer in energy per molecule. The energy bands and density of states of states for hcp and fcc C\textsubscript{50}Cl\textsubscript{10} are presented. The results show that C\textsubscript{50}Cl\textsubscript{10} molecules can form either a hcp or fcc indirect-gap band insulator or an insulating hexagonal monolayer.

PACS numbers: 71.20.Tx, 31.70.Ks, 73.61.Wp

Fullerenes such as C\textsubscript{60}, C\textsubscript{70} and their larger homologs satisfy the so-called isolated pentagon rule (IPR)\textsuperscript{[1, 2]}. This rule states that the most stable fullerenes are those in which every pentagon is surrounded by five hexagons. For some time, people believe that the non-IPR fullerenes could be unstable due to their adjacent pentagons, and may be difficult to synthesize. In recent years, it has been uncovered, however, that the IPR can be violated by metallic endohedral or exohedral chemical deriving fullerenes\textsuperscript{[3, 4, 5, 7, 8]}.

On account of the adjacent pentagons and the high curvature of molecular surface, the non-IPR fullerenes might have unusual electronic, magnetic, and mechanical properties. Last year, Xie et al.\textsuperscript{[9]} had successfully synthesized a new exohedral chemical deriving non-IPR D\textsubscript{5h} fullerene\textsuperscript{[50]}, say, C\textsubscript{50}Cl\textsubscript{10}, with 10 chlorine atoms added to the pentagon-pentagon vertex fusions. The molecular structure of C\textsubscript{50}Cl\textsubscript{10} looks like a Saturn-shaped profile, as depicted in Fig. 1, which is compatible with the Euler theorem, ensuring that the fullerenes with fewer than sixty C atoms and comprised of only pentagons and hexagons do not satisfy the IPR. The existence of D\textsubscript{5h} C\textsubscript{50}Cl\textsubscript{10} is evidenced by mass spectrum, and \textsuperscript{13}C NMR spectra; and of particular interest is that C\textsubscript{50}Cl\textsubscript{10} could easily react with a variety of organic groups to form new compounds\textsuperscript{[2]}

Since its discovery, there have been several investigations\textsuperscript{[10, 11, 12, 13, 14, 15]} on the electronic and optical properties of C\textsubscript{50}Cl\textsubscript{10} clusters.

So far, none has discussed, however, the possibility if C\textsubscript{50}Cl\textsubscript{10} molecules can form a solid. As is well-known, C\textsubscript{60} clusters can condense to form a solid with either the face-centered-cubic (fcc) phase\textsuperscript{[16]} or the hexagonal-close-packed (hcp) phase\textsuperscript{[17]}. Although the molecular structure is different, there is no reason to believe that C\textsubscript{50}Cl\textsubscript{10} molecules cannot condense to form a solid. Therefore, it would be interesting to address this issue at least from a viewpoint of numerical simulations. In this paper, we report a first-principles study on the possible solid C\textsubscript{50}Cl\textsubscript{10} within the framework of density functional theory (DFT)\textsuperscript{[13]} with local density approximation (LDA)\textsuperscript{[14]}. From the total-energy calculations we have found that C\textsubscript{50}Cl\textsubscript{10} molecules could form a stable hcp or fcc crystal or a hexagonal monolayer, though the hcp phase is more stable than the fcc phase and the hexagonal monolayer in energy per molecule. The optimized lattice constants are $a_0 = 13.57 \text{ Å}$, $c_0 = 11.39 \text{ Å}$ for the hcp phase, $a_0 = 19.20 \text{ Å}$ for the fcc phase, and $a_0 = 13.52 \text{ Å}$ for the hexagonal monolayer. The energy bands and density of states (DOS) for three structures have been calculated. The results show that the solid C\textsubscript{50}Cl\textsubscript{10} is a band insulator with an indirect energy gap of 1.59 eV for the hcp phase or 1.79 eV for the fcc phase, and with a gap of 1.85 eV for the hexagonal monolayer, where the gap widths are comparable with those of C\textsubscript{60} solids\textsuperscript{[20, 21]}

The total energies, energy bands and DOS are calculated by means of the ABINIT package\textsuperscript{[22]}. This package is coded within the DFT framework based on pseudopotentials and plane waves, which relies on an efficient fast Fourier transform algorithm\textsuperscript{[23]} for the conversion of wave functions between real and reciprocal spaces, on the adaptation to a fixed potential of the band-by-band conjugate gradient method\textsuperscript{[24]}, and on a potential-based conjugate-gradient algorithm for the determination of the self-consistent potential\textsuperscript{[24, 25, 26]}. Troullier-Martins norm conserving pseudopotentials\textsuperscript{[27]} are applied to mimic the electron-ion interaction, and the Teter parametrization\textsuperscript{[28]} of the Ceperley-Alder exchange-correlation potential is used. The kinetic energy cutoff in the plane-wave basis is taken as 20 Hartree, and the tolerance for absolute differences of the total energy is set as $10^{-6}$ Hartree. The convergence of the total energy to the kinetic energy cutoff has been checked.

As shown in Fig. 1, the C\textsubscript{50}Cl\textsubscript{10} molecule has 4 unique...
types of carbon atoms (I to IV) within D$_{5h}$ symmetry, and ten Cl atoms are added to the most reactive C$_{IV}$ sites (i.e. to pentagon-pentagon vertex fusions). Such a structure obviously violates the IPR. The C-Cl bond length in C$_{50}$Cl$_{10}$ is 1.80 Å, which is comparable with that in CCl$_4$, 1.78 Å. We have calculated the valence-electron density of C$_{50}$Cl$_{10}$, and found that the high density of the C-Cl bond shows that the ten Cl atoms are indeed bonded with the C$_{50}$ cage, and a stable C$_{50}$Cl$_{10}$ molecule can be formed.

To seek for stable solid phases, by carefully analyzing the geometrical symmetry of C$_{50}$Cl$_{10}$ where it has the D$_{5h}$ symmetry in $xy$ plane with diameter (10.3 Å) almost twice larger than that along $z$ axis (5.4 Å), we find the crystal lattices such as tetragonal (tt), simple hexagonal (sh), fcc and hcp structures could be the most possible candidates. The former three are shown in Fig. 2, where the coordination systems of the lattices are coincident with those of the C$_{50}$Cl$_{10}$ molecule. Then, the total energy is calculated accordingly with respect to different lattice parameters for each presumed structure$^{[30]}$. The total energy is scanned in every 0.1 Å for lattice constants $a$ and $c$. Owing to the limits of the method and the capability of our computer system, a properly fixed orientation of C$_{50}$Cl$_{10}$ molecules, namely, the $xy$ plane of C$_{50}$Cl$_{10}$ molecule is arranged to be vertical to the $z$ axis in tt, sh, and hcp structures, and to be along the (111) plane in the fcc structure, is assumed in calculations, which makes the system bear a relatively high symmetry$^{[31]}$.

Table I gives the calculated minimal relative total energies per C$_{50}$Cl$_{10}$ molecule and the corresponding lattice constants for the presumed four solid structures, where the data with precision of 0.01 Å is obtained by a bicubic interpolation from the calculated data with precision of 0.1 Å. For both tt and sh structures, the total energy shows a series of minimums (labeled by A-F) with almost the same values, suggesting that these two structures are labile. For the hcp and fcc structures, only one minimal total energy is obtained, showing that the hcp and fcc C$_{50}$Cl$_{10}$ could be formed, though the hcp phase looks more stable than the fcc phase in energy per molecule, as the minimal energy of the hcp structure is about 0.6 eV per C$_{50}$Cl$_{10}$ molecule lower than those of tt, sh and fcc structures.

To show it clearly, the contour map of the total energy for the hcp C$_{50}$Cl$_{10}$ in the plane of lattice constants $a$ and $c$ is depicted in Fig. 3(a), where only one minimum of the total energy is observed at $a = a_0 = 13.57$ Å, and $c = c_0 = 11.39$ Å, as marked by the letter A. Figs. 3(b) and (c) present the total energy per C$_{50}$Cl$_{10}$ molecule of the hcp C$_{50}$Cl$_{10}$ crystal, which is measured from the total energy of isolated C$_{50}$Cl$_{10}$ clusters$^{[32]}$, as a function of lattice constants $a$ and $c$, respectively. The results reveal that the hcp structure is stable. Fig. 3(d) gives the total energy per C$_{50}$Cl$_{10}$ cluster in the fcc C$_{50}$Cl$_{10}$ crystal as a function of lattice constant $a$, where only one minimum of the total energy is seen at $a = a_0 = 19.20$ Å, indicating that the fcc C$_{50}$Cl$_{10}$ crystal could also be stable, though the minimal total energy of the fcc phase is larger than that of the hcp phase.

In order to confirm the relative stabilities of the obtained hcp and fcc lattices, we have optimized the atomic positions with fixed lattice parameters by 40 steps Broyden-Fletcher-Goldfarb-Shanno minimization. The results show that no notable atomic displacements are observed, and the total-energy changes are less than 0.0003% (0.04eV), indicating that the C$_{50}$Cl$_{10}$ molecules keep their shapes and sizes, and the lattice structures which we have obtained are stable.

The calculated cohesive energy per C$_{50}$Cl$_{10}$ molecule is 0.9 eV for the hcp solid, and 0.3 eV for the fcc solid, which is much smaller than the typical C-C bond energy (more than 3 eV). The cohesive energies of both solid phases are less than that of fcc C$_{60}$ solid (1.6 eV$^{[20]}$), implying that C$_{50}$Cl$_{10}$ solid is less stable than C$_{60}$ solid. The contour map of the valence-electron density for hcp C$_{50}$Cl$_{10}$ crystal is given in Fig. 4.

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Table I: The calculated minimal relative total energies per C$_{50}$Cl$_{10}$ molecule and the corresponding lattice constants for the presumed four solid structures.

| Minimums | Lattice constants (Å) | Energy (eV) |
|----------|----------------------|-------------|
| tt       |                       |             |
| A        | $a_0$ = 13.99        | 9.22        | 0.77        |
| B        | $a_0$ = 13.61        | 9.72        | 0.77        |
| C        | $a_0$ = 14.02        | 9.80        | 0.76        |
| D        | $a_0$ = 13.72        | 10.31       | 0.75        |
| E        | $a_0$ = 13.99        | 10.82       | 0.73        |
| F        | $a_0$ = 13.65        | 11.41       | 0.74        |
| sh       |                       |             |
| A        | $a_0$ = 13.37        | 9.75        | 0.55        |
| B        | $a_0$ = 13.38        | 10.42       | 0.58        |
| C        | $a_0$ = 13.33        | 10.79       | 0.57        |
| D        | $a_0$ = 13.39        | 11.36       | 0.54        |
| E        | $a_0$ = 13.38        | 12.37       | 0.54        |
| F        | $a_0$ = 13.38        | 12.99       | 0.55        |
| fcc      |                       |             |
| A        | $a_0$ = 13.57        | 11.39       | 0.00        |
| B        | $a_0$ = 19.20        | –           | 0.60        |
It is seen that the valence-electron density between $C_{50}Cl_{10}$ molecules is much lower than the density in a single $C_{50}Cl_{10}$ molecule. The similar situation occurs for the fcc phase of $C_{50}Cl_{10}$.

The energy bands, DOS $G(\varepsilon)$, as well as the integrated DOS $I(E) = \int_{-\infty}^{E} G(\varepsilon) d\varepsilon$ for solid $C_{50}Cl_{10}$ are calculated for the hcp and fcc phases with the optimized lattice constants $a_0$ and $c_0$. Fig. 5 presents the band structures of the hcp and fcc $C_{50}Cl_{10}$ crystals, respectively, where only several energy bands around the energy gap are shown. For the hcp crystal, the energy difference between the valence-band top (VBT) at the $\Gamma$ point and the conduction-band bottom (CBB) at the $K$ point is $1.59 \, eV$, and for the fcc crystal, the energy gap between the VBT at the $\Gamma$ point and the CBB at the $L$ point is about $1.79 \, eV$, showing that both hcp and fcc $C_{50}Cl_{10}$ solids may be indirect-gap band insulators. The present situation is in contrast to the fcc $C_{60}$ solid which is a direct-gap insulator with an energy gap of $1.5 \, eV$ [20]. We have also calculated the energy levels of $C_{50}Cl_{10}$ molecule, and found that the energy gap between the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) is around $1.9 \, eV$, which is in well agreement with a previous calculated result [11], and is comparable with that of $C_{60}$ cluster where the energy gap between the HOMO state, $h_s$, and the LUMO state, $t_{1u}$, is about $1.9 \, eV$ [20]. Obviously, the energy gap remains finite when the $C_{50}Cl_{10}$ molecules are condensed to form a solid. Like other typical molecular systems [12], the energy bands of these two $C_{50}Cl_{10}$ crystals become narrow, as they are formed through the overlap of $C_{50}Cl_{10}$ molecular energy levels.

Fig. 6 presents the DOS and the integrated DOS of the hcp $C_{50}Cl_{10}$ as an example, which are obtained by means of a smearing technique. An energy gap in the vicinity of the Fermi level is clearly seen. From the positions of peaks in the DOS around the energy gap, the information of the HOMO-derived and LUMO-derived bands as well as next
higher bands can be extracted. Evidently, the DOS of electrons at the LUMO-derived states appears to be smaller than that at the HOMO-derived states. With the increase of energy, the integrated DOS increases nonmonotonically below and above the energy gap, where the flat part in the vicinity of the Fermi level measures the width of the energy gap. The presented results in Fig. 6 are in agreement with the calculated electronic energy levels shown in Fig. 5. It should be remarked that the obtained DOS as a function of energy shows a very similar behavior for the hcp and fcc phases, though there are slightly quantitative changes. The reason is that owing to the quite weak interactions between C$_{50}$Cl$_{10}$ molecules, as manifested in Fig. 4, the DOS of electrons for solids would have profiles similar to that for clusters, yielding that the DOS is similar for both hcp and fcc C$_{50}$Cl$_{10}$.

Let us now address another interesting issue if C$_{50}$Cl$_{10}$ molecules can condense to form a monolayer structure. Recall that C$_{60}$ clusters can form a hexagonal monolayer structure, which has gained much attention recently[34]. From Table I, one may note that for the sh lattice, the minimal total energies have slight changes with the lattice constant $a$, but have remarkable changes with constant $c$. It hints that a stable layered structure with a single minimal total energy could probably be formed. To probe this possibility, we have taken the lattice constant $c$ of the sh supercell to 40 Å to decline the interactions between the C$_{50}$Cl$_{10}$ layers but keeping the molecular orientation the same as in the sh lattice. It turns out, after some efforts, that a single minimal total energy with the optimized lattice constant $a_0 = 13.52$ Å is indeed obtained. The cohesive energy per C$_{50}$Cl$_{10}$ molecule for this monolayer is found to be 0.3 eV. The energy bands and DOS show that the C$_{50}$Cl$_{10}$ hexagonal monolayer is a band insulator with an energy gap of 1.85 eV.

It would be emphasized that as manifested in Fig. 4, the molecule-molecule interactions in the solid C$_{50}$Cl$_{10}$ appear to be weak. Whether the interactions between C$_{50}$Cl$_{10}$ molecules in the solid phase are of the van der Waals force or not, is at present unclear within our calculations, because it is known that the LDA cannot correctly describe the van der Waals force as it assumes fundamentally that the electron density is flat like in metals (see, e.g. [35]). Nevertheless, our calculations indeed suggest that the molecular solid C$_{50}$Cl$_{10}$ with either the hcp, fcc or hexagonal monolayer phase can be somehow formed through weak interactions.

To summarize, in terms of first-principles calculation within the density functional theory, we have predicted a molecular solid C$_{50}$Cl$_{10}$ with either a hcp, fcc, or a hexagonal monolayer structure. These possibly stable structures are determined from the total-energy calculations, where the hcp phase is found more stable than the fcc phase and the hexagonal monolayer in energy per molecule. The energy bands and DOS for the hcp and fcc C$_{50}$Cl$_{10}$ as well as the hexagonal monolayer are discussed. Our results show that C$_{50}$Cl$_{10}$ solid can be a band insulator with an indirect energy gap of 1.59 eV for the hcp structure and 1.79 eV for the fcc structure, or with a gap of 1.85 eV for the hexagonal monolayer. Since the LDA calculation usually underestimates the energy gap[21, 36], our present simulations inevitably call for further theoretical studies [37] or experiments. We expect that the C$_{50}$Cl$_{10}$ solids can be successfully synthesized in near future.

The authors are grateful to B. Gu, H. F. Mu, X. B. Wang, and Z. C. Wang for helpful discussions. This work is supported in part by the National Science Foundation of China (Grant Nos. 90403036, 20490210), and by the MOST of China (Grant No. 2006CB601102).

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[28] For the tetragonal, simple hexagonal, and hcp structures, as we have two lattice constants \( a \) in \( xy \) plane and \( c \) along \( z \) axis, the total energy is a bivar function of \( a \) and \( c \). For the fcc structure, the total energy is a function of lattice constant \( a \).

[29] After we have determined the proper lattice structures and parameters, we calculated the change of the total energy by rotating \( C_{50}Cl_{10} \) molecules around \( z \) axis. It has been found that the change is no more than 0.0008% (0.09eV), suggesting that the effect of molecular rotations on the total energy could be ignored. As the \( C_{50}Cl_{10} \) diameter in \( xy \) plane is almost twice larger than that along \( z \) axis, being nearly the lattice parameter along \( z \) axis in the hcp structure, the rotation around \( x \) or \( y \) axis will break the lattice structure, and would not be possible. Similar situations occur for the other interested lattice structures.

[30] Note that the isolated \( C_{50}Cl_{10} \) molecule has been simulated, as usual, by a cubic supercell calculation with a lattice parameter 26 \( \text{Å} \).

[31] As the relative stability of different structures of molecular crystals would not be well determined by LDA, an independent confirmation by other methods for the structures predicted in the present paper is called on.