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Electronic properties of one-dimensional C₃₆ polymers

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Abstract

Electronic structures for several neutral and anionic one-dimensional (1D) C₃₆ polymers are investigated by using the *ab initio* self-consistent-field crystal orbital method based on the B3LYP (Becke–Lee–Yang–Parr) density functional theory. Calculations show that all the neutral polymers are semiconductors with energy gaps in the range from 0.55 to 2.04 eV. The possibilities of superconducting and Peierls phase transitions are also explored for these metallic anionic polymers at the same time. It is found that the intramolecular electron–phonon (e–p) coupling in metallic 1D C₃₆ polymers plays an important role in producing high superconducting transition temperatures (T_c). The estimated Peierls phase transition temperatures (T_p) are very small due to the very weak intermolecular e–p interactions.

1. Introduction

The recent discovery of a new solid, C₃₆ fullerene, has aroused great scientific interest. Because of the abutting pentagons, strong intermolecular bonds can be formed [1–4]. It has been pointed out that C₃₆ could be a uniquely suitable candidate for forming a covalent bond fullerene solid and a building block for oligomers, polymers and solids [5–9]. To achieve a better understanding of possible structures and properties of the compounds composed of C₃₆ cages, the investigation of low-dimensional C₃₆ polymers is necessary. In this work, the electronic structures of several 1D C₃₆ model polymers are calculated using a *ab initio* self-consistent-field crystal orbital (SCF-CO) method based on the Becke–Lee–Yang–Parr (B3LYP) [10, 11] density functional theory (DFT). Although we previously studied neutral 1D C₃₆ polymers using a semiempirical SCF-CO method at the CNDO/2 level [12], a comparison with higher-level calculations is useful. Since the band structures of neutral crystals are often used in discussing doped cases, it is necessary to investigate whether a change occurs in the bands of charged crystals. We pay special attention to whether rigid-band theory is valid or not for the anionic 1D C₃₆^{m-} ($m = 1-4$) polymers. The possibilities of superconductivity and metal–insulator phase transitions in metallic anionic polymers are discussed on the basis of the e–p coupling mechanism. Until now, no calculation for 1D C₃₆^{m-} crystals has been published.

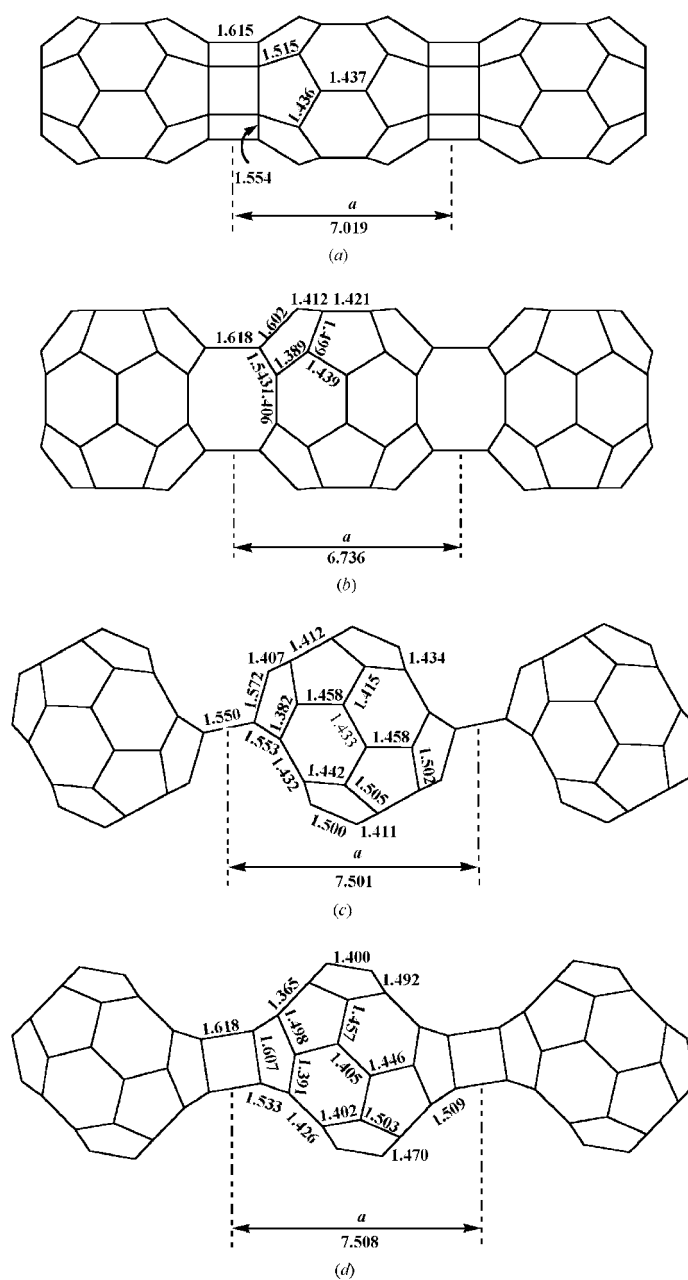


Figure 1. Models of 1D C_{36} polymers: (a) D_{6h} , (b) D_{2h} , (c) C_{2h-1} , (d) C_{2h-2} .

2. Models and methods

Four 1D C_{36} models are shown in figure 1, in which each unit cell contains a C_{36} cage. These 1D polymers have higher symmetries, D_{6h} , D_{2h} and C_{2h} . The geometrical parameters of C_{36} cages in the models are obtained from B3LYP-DFT optimization results for corresponding linear C_{36} trimers with the 3-21G basis set [13] and the Gaussian 94 program package [14].

Table 1. Electronic properties of neutral 1D C₃₆ models (in eV).

Polymer	ΔE	E_g	Top of HOB	Bottom of LUB	Width of HOB	Width of LUB
D _{6h}	0.52	0.55	-5.12	-4.57	0.123	0.177
D _{2h}	-3.11	2.04	-5.71	-3.67	0.463	0.993
C _{2h} -1	-2.60	1.85	-5.93	-4.09	0.006	0.169
C _{2h} -2	-1.58	0.91	-5.52	-4.65	0.014	0.067

The band structures of all neutral and anionic 1D C₃₆ polymers are calculated using *ab initio* B3LYP-DFT SCF-CO methods with the 3-21G basis set using the CRYSTAL 98 program [15]. Because the unit cell of a periodic system must be neutral [16], the charges are compensated by adding a uniform background charge density to neutralize the unit cell in the CRYSTAL 98 program for the calculations for charged systems. The translation length a for these 1D C₃₆ polymers is determined from the lowest-energy structures of 1D polymers through the pointwise optimization of SCF-CO calculations. When a is optimized, other geometrical parameters are kept unchanged. In the SCF-CO calculations, the shrinkage factors are all set to 20, and the default values of the convergence condition in the CRYSTAL 98 program are used.

3. Results and discussion

The intermolecular bond lengths (1.546–1.618 Å) marked in figure 1 are longer than those obtained by CNDO calculations and the bonds can be considered as C–C covalent bonds, not van der Waals interaction bonds. The shorter translation lengths for structures 1 and 2 manifest that face-to-face linking gives a tighter stack along the chain axis, though both structures have longer intermolecular bonds. Moreover, the translation length of the D_{2h} structure is close to 6.68 Å, suggested by electron diffraction patterns [2].

The calculated band structures are shown in figure 2. The energies per unit cell relative to that of the single C₃₆ molecule obtained with D_{6h} symmetry (ΔE) are 0.52, -3.11, -2.60 and -1.58 eV, as shown in table 1. Formation of the polymers decreases the energies of the complete systems except for the D_{6h} structure. The order of stability is thus D_{2h} > C_{2h}-1 > C_{2h}-2 > D_{6h}, which is in agreement with that for the optimized trimers. The structure with the highest symmetry, D_{6h}, has the narrowest energy gap and the highest energy.

From figure 2, the magnitudes of the energy gaps (E_g) between the highest occupied band (HOB) and the lowest unoccupied band (LUB) are in the range of 0.55–2.04 eV for these polymers. This result is different from the case for a proposed three-dimensional C₃₆ crystal, which is estimated to be metallic with partially filled conduction bands [4, 9]. Although SCF-CNDO-CO calculations also indicated that these polymers are semiconductors, the energy gaps are more than three times larger than those from B3LYP-DFT. It is well known that the HF SCF-CO method overestimates the value of E_g [17], usually giving values about 3–5 times that obtained experimentally. Therefore the smaller energy gaps given by the B3LYP-DFT method seem more reasonable for these model polymers, and can be attributed to the effect of the electronic correlation included in DFT calculations.

Now we discuss anionic polymers. The corresponding ΔE s are listed in table 2. It can be seen that the order of stability for 1D C₃₆^{m-} polymers is the same as that for the corresponding 1D neutral polymers for $m = 1$ and 2, but is changed for $m = 3$ and 4. Nevertheless, the most stable polymer is still the D_{2h} structure. We now focus on whether the rigid-band picture

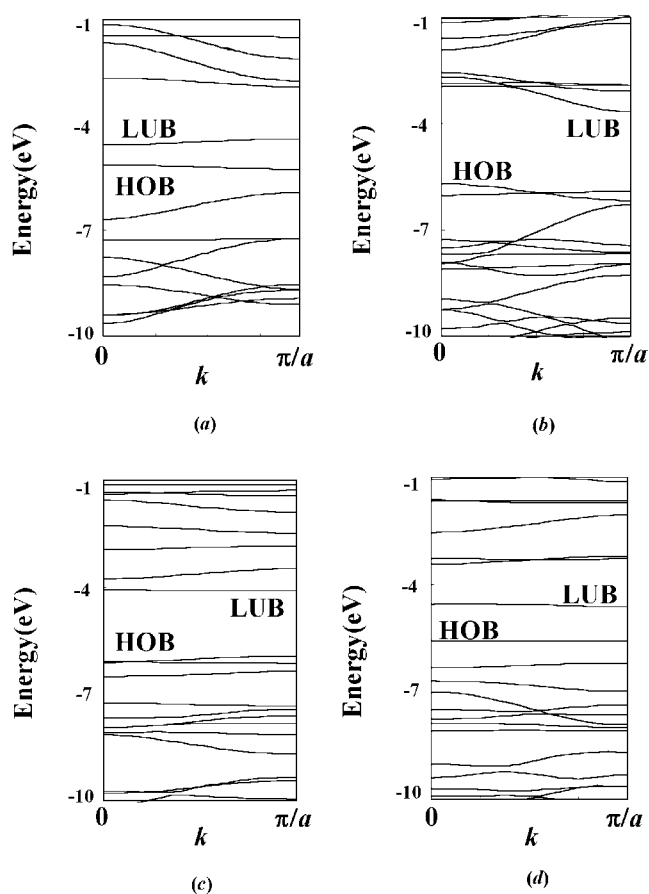


Figure 2. Band structures of the neutral 1D C_{36} polymers: (a) D_{6h} , (b) D_{2h} , (c) C_{2h-1} , (d) C_{2h-2} .

Table 2. Unit-cell energies of 1D C_{36}^{m-} polymers related to the neutral D_{6h} C_{36} molecule (in eV).

Polymer, m	D_{6h}	D_{2h}	C_{2h-1}	C_{2h-2}
1	-7.79	-10.58	-10.21	-9.71
2	-23.56	-25.42	-24.98	-24.83
3	-44.88	-48.31	-46.10	-41.16
4	-73.65	-79.01	-74.22	-73.10

can work for 1D C_{36}^{m-} polymers with increase of m . If 1D C_{36}^{m-} polymers follow rigid-band theory, we can easily deduce the electronic properties. For example, all anionic polymers ($m = 1-4$) for D_{2h} structure should be conductors, because of the crossing LU, LU + 1 and LU + 2 bands in the neutral condition. Our calculations confirm this expectation. The changes of band structures for all four structures are similar. Therefore, figure 3 gives the calculated band structures for the anionic D_{2h} structure only. The D_{2h} polymer is selected as an example because it is the most stable structure. From figure 3, it can be seen that the whole energy bands are lowered with increase of m . But compared to those in figure 2, the shapes of the energy bands are little different. Hence the extra electrons fill the unoccupied bands almost in a rigid-band manner, similarly to the case for Na-doped C_{36} crystal that relaxes slightly [9].

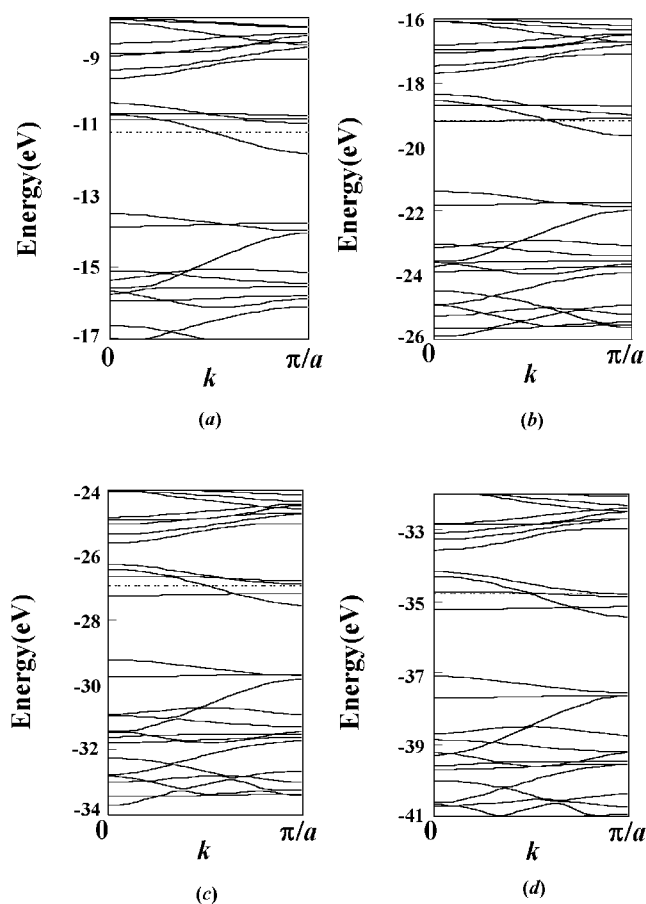


Figure 3. Band structures of 1D C_{36}^{m-} polymers for the D_{2h} structure: (a) $m = 1$, (b) $m = 2$, (c) $m = 3$, (d) $m = 4$.

The rigid-band theory can be used for the 1D C_{36} polymers if the change of the geometrical structures is not considered. It should be pointed out that the LUB + 1 is in contact with the LUB + 2 in the neutral C_{2h} -2 structure; it separates from the LUB + 2 when the LUB + 1 is filled with electrons and the polymer becomes a semiconductor for $m = 4$. Moreover, the D_{6h} tetra-anionic C_{36} polymer is a metal due to the doubly degenerate LU + 1 bands.

It is well known that the coupling of conducting electrons to the lattice vibration of the linear chain in a 1D conductor can result in a Peierls phase transition (metal–insulator phase transition). Hence, checking for the occurrence of the Peierls phase transition is important for the metallic 1D C_{36}^{m-} polymers. In a first study, we only consider longitudinal acoustic phonons. Under the mean-field approximation, the Peierls phase transition temperature (T_p) is given by [18]

$$T_p = 1.14E_F \exp\left(-\frac{1}{\lambda_p}\right). \quad (1)$$

E_F is the Fermi energy measured from the bottom of the partially filled bands. Using the results of applying deformation potential (DP) theory [19] to the 1D C_{36} polymers, and after [20], the

Table 3. The DOS at the Fermi level and e–p coupling constants for metallic 1D C_{36}^{m-} polymers.

	Polymer	$N(E_F)$	λ_{intra}	λ_{inter}	λ_{total}
$m = 1$	D _{6h}	3.5	0.46	0.001 4	0.46
	D _{2h}	0.66	0.089	0.000 031	0.089
	C _{2h} -1	9.5	1.28	0.003 6	1.28
	C _{2h} -2	5.5	0.74	0.002 2	0.74
$m = 2$	D _{2h}	6.5	0.88	0.023	0.90
$m = 3$	D _{6h}	5.7	0.77	0.019	0.79
	D _{2h}	3.3	0.45	0.000 74	0.45
	C _{2h} -1	1.9	0.26	0.002 9	0.26
	C _{2h} -2	3.0	0.41	0.008 7	0.42
$m = 4$	D _{6h}	5.6	0.77	0.034	0.80
	D _{2h}	9.7	1.31	0.25	1.56

intermolecular coupling constant $\lambda_{inter} = \lambda_p$ can be expressed as

$$\lambda_p = N(E_F) \frac{\varepsilon_1^2}{M_{C_{36}} v_F^2} \quad (2)$$

where $N(E_F)$ is the density of states (DOS) per electron volt per C_{36} per spin at the Fermi level, $v_F = (1/\hbar)(dE/dk)|_{k=k_F}$ is the Fermi velocity, ε_1 is the proportionality constant of the deformation potential, $M_{C_{36}}$ is the mass of a C_{36} cage. The variation of the energy at the Fermi level is linearly related to the small variation of a ; that is, $\delta\varepsilon = \varepsilon_1 \Delta$ and $\Delta = \delta a/a$. Here we choose 5–7 points near the intermolecular equilibrium distance in the range of $-0.02 \text{ \AA} \leq \delta a \leq 0.02 \text{ \AA}$ to calculate the band structures of these 1D polymers. The variations ($\delta\varepsilon$) of the Fermi energies with Δ form straight lines with the correction coefficient $r > 0.99$; the DP constants thus are obtained from the slopes of the straight lines. The calculated values of λ_p are listed in table 3 for the metallic 1D C_{36}^{m-} polymers.

From table 3, it can be seen that the intermolecular coupling constants are very small for all metallic 1D C_{36}^{m-} polymers except for the D_{2h} structure with $m = 4$. The very weak coupling leads to very small T_p ($< 6 \times 10^{-9}$ K). As to the tetra-anionic C_{36} polymer with D_{2h} structure, since $\lambda_p = 0.25$, a T_p of 21 K can be obtained from equation (1). However, the Peierls phase transition can break the translation symmetry in 1D conductors, which is concerned with the position of the Fermi wavevector (k_F) [21]. Because k_F for the polymer cannot be expressed as a simple fraction of π/a (meaning $k_F = l\pi/na$, where n and l are integers), the Peierls phase transition will possibly be suppressed somewhat. Hence the metallic 1D C_{36} polymers are predicted to remain metals down to very low temperature. In fact, the estimated T_p was also very small for other 1D fullerenes; e.g. $T_p < 1$ K for 1D C_{60}^- and carbon nanotubes [20, 22]. Possibly the weak intermolecular coupling plays little role in the phase transition in 1D fullerenes.

On the other hand, theoretical work had indicated that the rhombohedral C_{36} solid could have a high superconducting transition temperature (T_c) due to strong e–p coupling [4]. Thus we are also interested in whether the 1D C_{36} polymers are candidates for being 1D superconductors. Here, we make a roughly estimation of the possibility of superconductivity for the 1D C_{36} polymers.

Consider the metallic 1D C_{36} polymers. From the above discussion, the intermolecular coupling is very small, and hence cannot produce a high superconducting temperature in these 1D polymers. The intramolecular coupling should play an important role in the superconducting transition for these polymers. In fact, the partially filled bandwidths of

the D_{2h} structure are about 1 eV; those for other structures are even (much) smaller. Like the rhombohedral C₃₆ solid [4], therefore, 1D C₃₆^{m-} polymers are still mostly molecular-type crystals.

The intramolecular e–p coupling constant is expressed as $\lambda_{intra} = N(E_F)V_{ep}$, where V_{ep} is the intramolecular e–p interaction potential. The total coupling constant $\lambda_{total} = \lambda_{intra} + \lambda_{inter}$. According to the method for estimation of the e–p interaction in fullerenes given in [23], V_{ep} is about 135 ± 11 meV for the C₃₆ cage. This value of V_{ep} is close to that from the LDA calculation (136 meV) for the D_{6h} C₃₆ molecule due to the coupling of B_{2g} electrons with the A_{1g} phonon mode [4]. We set $V_{ep} = 135$ meV for all polymers studied here. The intramolecular and total e–p coupling constants obtained are also listed in table 3. Since $\lambda_{intra} \gg \lambda_{inter}$, the superconducting properties should be mainly determined by the intramolecular e–p coupling.

Because of using the same V_{ep} , higher $N(E_F)$ leads to larger e–p coupling constants. The largest λ_{intra} is 1.31 for the D_{2h}C₃₆⁴⁻ polymer, which is smaller than that for the rhombohedral C₃₆ solid [4]. But it is somewhat bigger than those for alkali-metal-doped C₆₀ crystals ($\lambda_{C_{60}} = 0.5$ – 1.0). If both intramolecular and intermolecular couplings are considered, the total coupling constant $\lambda_{total} = 1.56$. Therefore, the D_{2h}C₃₆⁴⁻ polymer may become a 1D superconductor with a T_c higher than those of the alkali-metal-doped C₆₀ crystals. In addition, the 1D C_{2h}-1 C₃₆⁻ polymer also gives $\lambda_{intra} > 1$. Perhaps low-dimensional superconductors with higher T_c can be produced among the 1D C₃₆ polymers.

4. Conclusions

To briefly summarize, band structures of several 1D C₃₆ polymers have been studied using the B3LYP SCF-CO method with the 3-21G basis set. It is found that all the polymers are usually semiconductors, which contrasts with the metallic property shown by the 3D crystal structure of the rhombohedral C₃₆ solid. The most stable polymer is the D_{2h} structure. The D_{6h} structure has the narrowest energy gap but is the most unstable among the 1D C₃₆ polymers studied here. Our calculations show that the extra electrons fill the unoccupied bands almost in a rigid-band manner for 1D C₃₆^{m-} polymers. The estimated Peierls phase transition temperature is very small due to very weak intermolecular e–p coupling; the metallic polymers can thus remain metals down to very low temperature. It is shown that the intramolecular coupling is much larger than the intermolecular coupling. The tetra-anionic D_{2h} polymer may be a good candidate for showing 1D superconductivity with a high superconducting transition temperature, because it gives an e–p coupling constant considerably bigger than those of alkali-metal-doped C₆₀ crystals.

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