## Polycubanes linked with C<sub>2</sub>, N<sub>2</sub>, NO, and NS: From insulating to metallic behavior

F. Valencia,<sup>1</sup> A. H. Romero,<sup>1</sup> M. Kiwi,<sup>2</sup> R. Ramírez,<sup>2</sup> and A. Toro-Labbe<sup>3</sup>

<sup>1</sup>Advanced Materials Department, IPICyT, Camino a la Presa San José, 2055 Col. Lomas 4ta. sección, San Luis Potosí (SLP), Mexico

<sup>2</sup>Facultad de Física, Pontificia Universidad Católica de Chile, Casilla 306, Santiago de Chile, Chile 6904411

<sup>3</sup>Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Santiago de Chile, Chile 6904411

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An interesting carbon structure is cubane ( $C_8H_8$ ). This molecule is a cube formed by carbons and  $sp^3$  bonds saturated with hydrogens. The fact that the bonding angle is 90°, rather than the ideal 109.5° value found in diamond, gives to this structure rather unusual properties. Here we report an electronic and structural characterization of polycubane chains linked with C<sub>2</sub>, N<sub>2</sub>, NO, and NS, and show that the electronic properties can be modified to obtain oligomeric chains with insulating, semiconducting and metallic behavior.

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Since 1985 research on a variety of carbon structures, which exhibit interesting molecular and electronic properties, has been the focus of intense attention. Carbon is an element that, depending on the molecular or crystal structure, can exhibit dramatically different electronic properties. Therefore, it is one of the most widely investigated systems in the quest to create new nanoelectronic devices. One of the most interesting realizations of a fascinating carbon structure is known as cubane (C<sub>8</sub>H<sub>8</sub>).<sup>1-4</sup> As the name suggests, this molecule is a cube formed by carbons and  $sp^3$  bonds saturated with hydrogens. The amazing property of this molecule is that although it shows  $sp^3$  hybridization it has a 90° C—C—C bond angle, quite different from the ideal  $109.5^{\circ}$ value found in diamond. Even though the molecule is under a large strain and has a very large heat of formation (+144 kcal/mol) it was successfully synthesized in 1964 by Eaton and Cole.<sup>1,3</sup> The same year it was x-ray characterized as a solid with a space group  $R\overline{3}$  by Fleischer *et al.*,<sup>2</sup> with carbon-carbon distances close to those of cyclobutane (1.548 Å). The molecule was found to be amazingly stable, the energy for thermal decomposition in the gas phase being almost 43 kcal/mol at 230-260 °C. Due to the large strain the chemistry and the physical properties are very different from those of normal hydrocarbons, which prompted scientists to suggest its use in the pharmaceutical, propellant, and explosive industries.

Most theoretical studies have dealt with solid cubane or the single molecule itself. The molecule has been characterized using different theoretical methods, yielding excellent agreement with experimental observations<sup>5–9</sup> on geometrical and electronic properties. The C—C distance is of the order of 1.57 Å, the C—H distance is of the order of 1.111 Å, and the C—C vibrational modes are of higher frequency than in any other hydrocarbon, mainly due to the molecule strain. The electronic gap is at least 4.5 eV,<sup>10</sup> which corresponds to a good insulator with strongly localized orbitals. The optical properties are determined by the electronic structure and thus the solid should be transparent. In its crystalline solid form cubane is a molecular organic solid, with weak interactions and properties dominated by its molecular counterpart, with very little dispersion.<sup>10–14</sup>

The stability of cubane geometries has been observed not only for carbon based structures, but also in systems like Fe—S (Ref. 15) and Cu—S clusters.<sup>16</sup> A molecular material with the cubane frame, but with the H atoms replaced by NO<sub>2</sub>, was recently reported for  $-NO_2$ ,<sup>17,18</sup> and  $-ONO_2$ .<sup>19</sup> These molecular species have attracted attention as potential explosives, mainly due to their large energy release and volume expansion. In fact, many of the properties of this type of molecule can be rationalized by using as framework the typical carbon cubane. The last few years have seen a renewed interest, generated by the development of a systematic experimental procedure by Eaton and co-workers, to create large molecular structures. For example, bicubylcubanes<sup>20</sup> are synthesized through nucleophilic additions on cubane (1,2-dehydrocubane) and 1,4-cubanediyl (1,2-dehydrocubane). Larger polycubane chains are obtained by using the same 1,4-cubanediyl as a precursor.<sup>21</sup> These are rigid rods, made up of cubanes, linked together at the 1 and 4 positions, and joined directly through cubanes or through other organic or inorganic molecules. A recent theoretical calculation<sup>22</sup> has found that a polymer formed by cubanes is a strong insulator, with an electronic band gap of about 4.5 eV, which corresponds to 83% of the 5.4 eV gap between the highest occupied and the lowest unoccupied molecular orbitals (HOMO-LUMO gap) of the cubane molecule. It was also shown that the electronic properties of finite oligomers approach the infinite chain behavior within reasonable oligomer sizes,<sup>22</sup> so that properties predicted for perfectly periodic systems can be obtained on the basis of moderately large finite systems.

Here we report an electronic and structural characterization of polycubane chains, with C, O, N, and S atoms intercalated as linkers between cubane molecules, thus combining different properties of these type of materials, which should open the possibility of manipulating their electronic properties by changing the linker atoms. We expect our results to motivate experimentalists to synthesize polycubanes with specific chemical and transport properties. In particular, we have considered nitrogen which could provide a way to further chemical functionalization. Also, nitrogen has a lone pair of electrons which are good donors, creating compounds with particularly useful chemical and electrical properties.



FIG. 1. Polycubanes linked with  $C_2$ ,  $N_2$ , NO, and NS. Distances are given in angstroms. The dark atoms on the corners of the cubic cages, as well as the linkers in the 1D  $C_2$  chain, correspond to carbon. The light gray atoms attached to the carbons are hydrogens. In the linkers of the 1D  $N_2$ , 1D NO, and 1D NS chains the dark atom depicts nitrogen and the gray ones the O and S, respectively.

Our calculations show how it is possible to change the transport properties, from insulator to metallic behavior, without losing the molecular cubane properties and the low electronic dispersion. We have obtained narrow bandwidths, for both the conduction and the valence electrons, which suggests the possibility of strong electron-lattice interaction and polaron formation. Consequently, coherent bandlike conduction is expected only for relatively low temperatures. The calculations reported here were performed within the density functional theory framework, using a plane wave basis set and a pseudopotential approach.<sup>23</sup> The pseudopotentials were of the ultrasoft Vanderbilt kind,<sup>24</sup> and the exchange correlation term was treated with the Perdew-Wang91 scheme.<sup>25</sup>

We have considered four different types of groups to link the cubanes: alkyl groups (C<sub>2</sub>), nitryl groups (N<sub>2</sub>), oxynitryl (NO), and sulfunitryl (NS). They are plausible species since a chemical path, able to create C<sub>2</sub> bridged polymers, is known<sup>4,26</sup> and nitryl enriched molecular cubane systems have been built. Thus, chemical reaction paths leading to nitryl bridged polymeric chains could be feasible. Total energies per atom were converged up to 0.01 eV, requiring kinetic energy cutoffs between 20 Ry for C<sub>2</sub> and 34 Ry for NS, and ten special *k* points in the one-dimensional (1D) Brillouin zone.

The geometries we considered are based on two premises: (i) that the properties of the system under consideration are dominated by those of the cubane molecule; and (ii) that Eaton's group's experimental results point out that the linker is positioned along the cubane molecule main diagonal,<sup>10-14</sup> as illustrated in Fig. 1. On this basis we assumed periodicity in the growth direction. The dimensions of the simulation box perpendicular to the growth axis are large enough to keep clear of interactions with the periodic images, just as in

TABLE I. Distances and energetics of the lowest polymer unit cells considered in this work.  $X^{(1)}$  denotes carbon in the first row and nitrogen in the second, third, and fourth.  $X^{(2)}$  denotes carbon, nitrogen, oxygen, and sulfur in the first, second, third, and fourth rows, respectively.  $W_b$  corresponds to the conduction bandwidth and *a* is the lattice parameter.  $K=d^2E/d\zeta^2$  is the elastic constant, where  $\zeta = a/a_0$  is the deformation along the chain axis.

Linker	C— <i>X</i> <sup>(1)</sup> (Å)	C— <i>X</i> <sup>(2)</sup> (Å)	$X^{(1)}-X^{(2)}$ (Å)	a (Å)	$W_b$ (eV)	K (eV)
C <sub>2</sub>	1.418	1.418	1.227	6.85	0.430	441
$N_2$	1.413	1.413	1.268	6.22	0.110	246
NO	1.372	1.404	1.416	6.12	0.055	180
NS	1.391	1.751	1.644	6.62	0.048	158

previous calculations.<sup>22</sup> Assuming this geometry we optimized the cubane-linker-cubane distances, as well as the positions of each atom in this configuration. The geometries and some electronic properties are reported in Table I. For the case of  $C_2$  the functionalizing groups tend to stay aligned with the cubyl diagonal, as shown in Fig. 1, and thus the resulting oligomer is a straight rod. The cubane geometry of the polymer is very close to the molecular one, since there is little deformation and the lattice parameter only reflects the linear addition of the extra groups. In the case of  $C_2$  the carbons in the alkyl group are *sp* hybridized and the bonding is very strong, as inferred from the elastic constant. In the  $N_2$ % bonded case, the elastic constant is a little bit smaller than in the alkyl case, but it still is very large.

It is also of interest to mention the reaction energy required to form the cubane chain from its basic constituents: the hydrogen saturated cubane molecule and the linkers. The reaction energy to form a complex of n-linked cubanes is given by

$$\Delta E = E_n(\text{chain}) + nE(\text{H}_2) - (n+1)E(\text{cubane}) - nE(\text{linker}),$$
(1)

and thus the energy per unit cell of an infinite (1D) linked polycubane is

$$\lim_{n \to \infty} \frac{1}{n} \Delta E = E(\text{chain}) + E(\text{H}_2) - E(\text{cubane}) - E(\text{linker}).$$
(2)

We have computed these reaction energies for the various linkers considered and they are 0.141, 1.322, -0.502, and 0.598 eV per unit cell, for C<sub>2</sub>, N<sub>2</sub>, NO, and NS, respectively. Thus, only the reaction leading to the NO linked chain is exothermic.

When linked by NO and NS the resulting polymers are gapless and have a very narrow conduction band. The presence of a nonsymmetric group contributes to the formation of a conjugated polymer with metallic properties. In fact, the synthesis of a NS chain was the first metallic polymer reported in the literature<sup>26,27</sup> with alternate bonding and different bond lengths. This feature is also present in the NS and NO linked polycubanes. The electronic density of states



FIG. 2. Electronic density of states of one-dimensional polycubane linked by  $C_2$ ,  $N_2$ , NO, and NS.

(EDOS) for all the systems we considered is illustrated in Fig. 2. The metallic character of NO and NS linked systems, where the conduction bands are half filled, is quite apparent. For  $N_2$  and  $C_2$  linkining a clearcut gap, of around 2 eV, is observed between the valence and conduction bands, which ranks them in the semiconductor category.

The electronic properties can be further characterized by looking at the highest occupied (HOMO) Kohn-Sham valence state, as shown in Fig. 3. It is observed that all these systems behave rather differently and we now point out the distinctions among them. For  $C_2$  linking  $\pi$  bonding is the dominating feature, and charge is shared between the alkyl and the  $\alpha$  positioned bonds, whereas N<sub>2</sub>, NO, and NS linked systems exhibit very localized orbitals centered on the included functional group, building up electronic density on the cubane bonding atoms. As represented in Fig. 4, excited electrons occupy the LUMO when linked by N2 and C2, or get promoted to the second conduction band when linked by NO and NS. In C<sub>2</sub> enriched cubanes we notice the charge on the  $\pi$  bond formed by the alkyl group, but there is also a significant charge accumulation at the cubane center, which constitutes a rather particular feature, not found in the other polycubanes. This behavior indicates a strongly delocalized state on the whole chain, and can be related to the EDOS



FIG. 3. (Color online) HOMO state densities of polycubanes with  $C_2$ ,  $N_2$ , NO, and NS as linkers. The atomic species illustrated here were identified in the caption of Fig. 1.



FIG. 4. (Color online) LUMO state densities of polycubanes with  $C_2$  and  $N_2$  linkers, and the first state of the second conduction band of NO and NS. The atomic species illustrated here were identified in the caption of Fig. 1.

depicted on Fig. 2: as a matter of fact  $C_2$  enriched cubanes exhibit a wide conduction band, consistent with stronger dispersion and with delocalized states. In the N<sub>2</sub> linked system the charge is again localized on the nitryl group, an indication of localization due to the N=N double bonding. In the NO and NS linked cases there are contributions due to the localization on the linker atoms and on the cubane, consistent with its metallic behavior. Charge delocalization in this second conduction band is clearly observed in NO enriched cubanes, while the first state in the second conduction band of NS enriched cubanes is still very localized, a feature that, of course, is also observable in the EDOS.

In order to specify the electronic charge distribution in the cubyl chains, and to characterize the bond character, we have calculated (by projecting the wave functions onto orthogonalized atomic wave functions<sup>23</sup>) the Löwdin charges reported in Table II. For the sake of comparison charges on the pure chain are also reported in the first row of the table. We have subtracted the nominal valence, so that the data in Table II must be understood as the electron fraction each atom gains or loses. According to the corresponding spilling parameters the Löwdin projections account for roughly the 99% of the total electronic charge. As expected, it is always the case that charge is transfered from the H atoms to the p-like states in their neighboring C atoms. The s-like to *p*-like charge ratios of the carbon atoms remain close to 1/3, indicating  $sp^3$  hybridization. The C—C, N—N, and N—O bonds in the linking groups are mainly covalent, with little charge being transferred from one atom to the next. However, for N—S bonding a significant amount of charge flows from the sulfur to the nitrogen atom. The  $C_{cage}$ — $C_{alkyl}$  bond exhibits a slight charge transfer from the cage to the alkyl group. This charge transfer between the cage atoms and the attached functional groups is noticeably more significant when nitrogen and oxygen are included, while sulfur only donates a slight amount of charge to the bonded C atom.

In summary, we have reported a set of theoretical calculations on polycubanes linked with four different com-

TABLE II. Electronic Löwdin charges for the atoms in the cubyl chain unit cell.  $X^{(1)}X^{(2)}$  denotes the linker. The first row corresponds to the pure chain.  $C^{(1)}$  and  $C^{(8)}$  are the cube diagonals in the growth direction, with  $C^{(1)}$  bonded to  $X^{(2)}$  and  $C^{(8)}$  to  $X^{(1)}$ . The subscripts *in* and *out* refer to the positions of the atoms in or out of the plane defined by the  $C - X^{(1)} - X^{(2)}$  bonds; if this plane is defined at all (N<sub>2</sub>, NO, and NS linking), the superscripts (1) and (2) signal whether those atoms are closer to  $X^{(1)}$  or to  $X^{(2)}$ .

$X^{(1)}X^{(2)}$	C <sup>(1)</sup>	C <sup>(8)</sup>	$C_{out}^{(1)}$	C <sup>(2)</sup> <sub>out</sub>	$\mathbf{C}_{in}^{(1)}$	$C_{in}^{(2)}$	$X^{(1)}$	$X^{(2)}$	$\mathbf{H}_{out}^{(1)}$	$\mathbf{H}_{out}^{(2)}$	$\mathbf{H}_{in}^{(1)}$	$\mathbf{H}_{in}^{(2)}$
	-0.059	-0.059	0.133	0.133	0.133	0.133			-0.182	-0.182	-0.182	-0.182
CC	-0.047	-0.047	0.112	0.112	0.112	0.112	0.024	0.024	-0.197	-0.197	-0.197	-0.197
NN	-0.176	-0.175	0.113	0.113	0.151	0.151	0.085	0.085	-0.198	-0.198	-0.203	-0.203
NO	-0.256	-0.176	0.127	0.139	0.109	0.129	0.141	0.139	-0.202	-0.205	-0.201	-0.200
NS	0.062	-0.169	0.142	0.119	0.117	0.118	0.449	-0.545	-0.198	-0.203	-0.200	-0.194

pounds, showing how the electronic properties can be modified so that oligomeric chains with insulating, semiconducting and metallic behavior could be achieved. Considering the recent advances in synthesis of oligomeric cubane enriched with alkyl and nitryl groups, this could prove useful in nanodevice technology. Potential applications in the polymer industry can be dominated by the very distinct properties of the cubane system and its large dissociation heat. Although it is probable that, due to the neutral properties of the cubane, different polymer chains interact through van der Waals forces we expect most of the electronic properties to be determined by the single, covalently bonded, chain behavior.

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