ELSEVIER

Journal of Molecular Structure: THEOCHEM 769 (2006) 183–187

THEO CHEM

www.elsevier.com/locate/theochem

# Cubane oligomers: A density functional theory study

Bárbara Herrera [a], Felipe Valencia [c], Aldo H. Romero [b,c], Miguel Kiwi [b],
Ricardo Ramírez [b], Alejandro Toro-Labbé [a,*]

[a] *QTC, Facultad de Química, Departamento de Química Física, Pontificia Universidad Católica de Chile, Casilla 306, Correo 22, Santiago 6094411, Chile*
[b] *Facultad de Física, Pontificia Universidad Católica de Chile, Casilla 306, Correo 22, Santiago 6094411, Chile*
[c] *Departamento de Materiales, CINVESTAV, Unidad Querétaro. Libramiento Norponiente #2000 Fraccionamiento Real de Juriquilla, Querétaro 76230, Mexico*

Received 7 November 2005; accepted 1 April 2006

**Abstract**

The cubane molecule, and a few representative oligomers built with cubane units, are examined in order to investigate the feasibility and likelihood of creating covalently bonded arrays with cubane units as building blocks. In this way, oligomers with a variety of structures were obtained, including rods and surface-like networks. B3LYP/6-311G** calculations indicate that, in the bulk limit, the cubane structures do not accept electrons. The electron transfer within the cubane network may occurs only through doping or substitution with donor/acceptor groups.
© 2006 Elsevier B.V. All rights reserved.

*Keywords:* Conceptual DFT; Hardness; Electron transfer

## 1. Introduction

The creation and investigation of new materials has received increasing attention in recent years, due to the growing demand for products with more adequate and/or different properties than already known materials. As a response to this challenge many new research areas have strongly developed. Among them nanotechnology has emerged as a science that investigates materials at the nanometric scale, which has led to many applications and exhibits a strong potential. These nanomaterials are often built up by small building blocks with special geometries and properties. When these blocks are assembled to create a nanostructure, they can give birth to a wide diversity of compounds, with many possible new architectures, interesting properties and a variety of potential applications.

Cubane, $C_8H_8$ (CB), illustrated in Fig. 1 is a perfect cubic and quite rigid structure, that has been studied extensively by different techniques, and has been found to be very stable [1–6]. A series of cubylcubane compounds can be obtained through nucleophilic additions on cubene (1,2-dehydrocubane) and 1,4-cubanediyl (1,4-dehydrocubane). X-ray structure analysis shows that the central cubylcubane bond is shorter than might be expected, since the exocyclic orbitals of cubane are s-rich and close to the nucleus. The intercage bond in cubylcubane (CCB), also illustrated in Fig. 1, is about as long as a bond between two $sp^2$ carbons, whereas the bond lengths and angles within the two cubyl cages are quite close to the values of cubane itself.

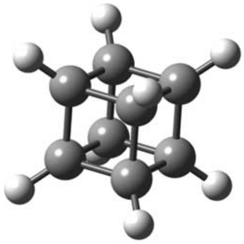
In this paper, we report DFT/B3LYP/6-311G** calculations of 1D and 2D polycubane networks. Energetic and electronic properties are calculated in order to characterize the patterns obeyed by several different properties, as the number of cubane units increases. Linear oligomers where built up using cubane (**1**) as the building block. This unit is added to the axial terminal carbons in CCB (**3** and **4** in Fig. 2(A)). Moreover, a series of structurally modified CCB's, as the structures **5** and **6** displayed in Fig. 2(B) were similarly obtained. This gave rise to a series of linear cubylcubane-like structures, (**3**,**4**) in Fig. 2(A), as well as another set of CCB's that was obtained by adding cubanes at one of the vertices of the cubane unit, thus yielding a series of structurally modified CCB's, as **5** and **6** illustrated in Fig. 2(B). Two-dimensional networks were built using CCB as the building unit, which leads to the structures **7**, **8** and **9** displayed in Fig. 3. Also displayed in Fig. 3 is a larger 2D cubane network, made up of nine cubane units, and labelled as structure **10**.

The energy and the electronic properties, which are related to the reactivity of these systems, were analyzed in detail. We have also investigated the behavior of these properties when

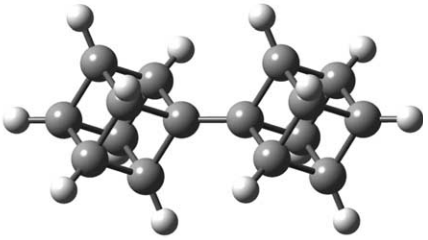
---

[*] Corresponding author. Tel.: +56 2 6864746; fax: +56 2 6864744.
*E-mail address:* atola@puc.cl (A. Toro-Labbé).

0166-1280/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.theochem.2006.04.053



**1**



**2**

Fig. 1. Structures of the cubane (**1**) and cubylcubane (**2**) systems.

these structures reach the so called surface bulk condition ($n \to \infty$, where $n$ is the number of cubane or cubylcubane units involved). The properties we report here are the ionization potentials (IP), electron affinities (EA) and the chemical potential ($\mu$). The latter is related to the electron transfer from sites of high to low $\mu$. We also studied the energy gap between HOMO and LUMO frontier orbitals ($\varepsilon$), which measures the escaping tendency of electrons, or the response to electromagnetic excitations. In addition to the above, an analysis of other properties derived from $\mu$ and the band gap is provided as well. This paper is organized as follows: Section 2 is devoted to the definition of the concepts used in the analysis of the various systems. Then, in Section 3, the computational details are presented. Section 4 is devoted to the discussion of the results and in Section 5 conclusions are drawn.

## 2. Theoretical background

Within the conceptual framework of DFT, the chemical potential of a system of $N$ particles, with total energy $E$ and subject to the external potential $v(\vec{r})$, is defined as [7]

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})} = -\chi. \tag{1}$$

In Eq. (1), $\chi$ is the electronegativity [8–13]. The use of the finite difference approximation and Koopmans's theorem [14] leads to the following working expressions for $\mu$

$$\mu \approx -\frac{1}{2}(\mathrm{IP} + \mathrm{EA}) = \frac{1}{2}(\varepsilon_\mathrm{L} + \varepsilon_\mathrm{H}), \tag{2}$$

where IP is the first ionization potential, EA is the electron affinity, $\varepsilon_\mathrm{L}$ and $\varepsilon_\mathrm{H}$ are the energies of the lowest unoccupied and the highest occupied molecular orbitals LUMO and HOMO, respectively.

On the other hand, the maximum electronic charge that the system can accept is $\Delta N_\mathrm{max} = -2\mu/\varepsilon$. Thus, $\Delta N_\mathrm{max}$ relates the electron transfer to the energy gap $\varepsilon = \varepsilon_\mathrm{L} - \varepsilon_\mathrm{H}$.

## 3. Computational details

All calculations were performed using the Gaussian 98/03 packages [15]. All the systems considered in this work, with the only exception of the cubane network (**10**), were fully relaxed at the B3LYP/6-311G** level [16,17]. Since, the geometrical parameters were quite constant along the series of linear and 2D structures, we used them to characterize the unrelaxed structure we labelled as **10**, on which we performed a single point calculation to obtain its properties of interest.

## 4. Results and discussion

### 4.1. Geometrical parameters

For the systems we studied it is possible to distinguish four different kinds of CC bonds: the intercage bond (CC1); the bonds located at the $\alpha$ position relative to one or two CC1 (CC2); the bonds located at the $\beta$ position relative to CC1 (CC3) and the bonds that are farthest from the intercage

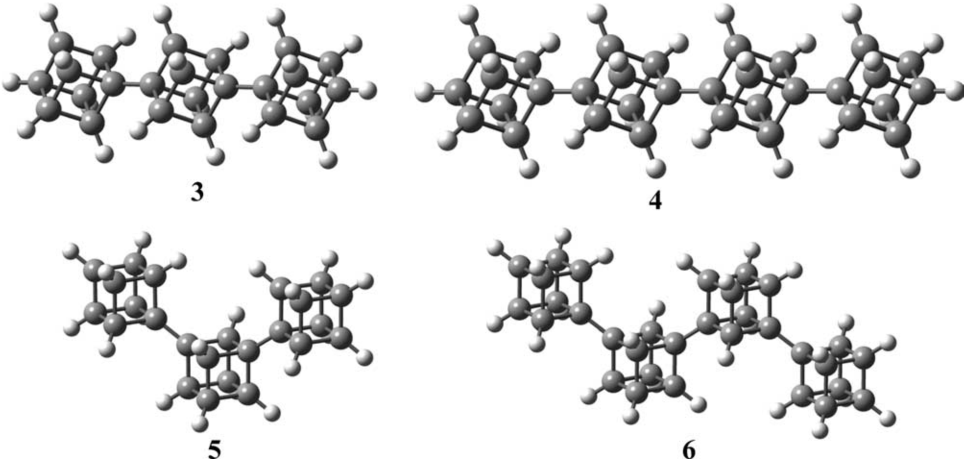


Fig. 2. Structures of the linear (**3, 4**) and zig-zag (**5, 6**) oligomers systems.

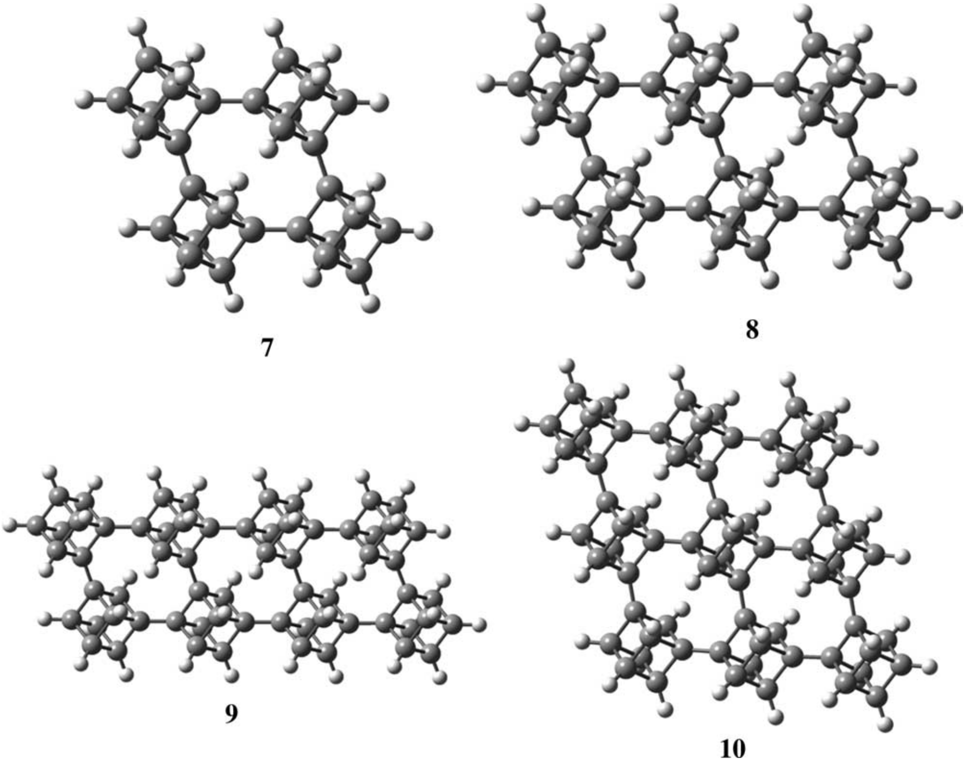


Fig. 3. Structures of the 2D oligomers **7**-**10**.

bond (CC4); their values are displayed in Table 1. It is interesting to notice that the optimized structures are in quite good agreement with X-ray data [18]. Besides, they change only slightly with the oligomer size (~0.01–0.02 Å). It is also interesting to point out that there are no marked structural distortions as the system grows in size, both for the chains and the 2D networks. Optimized bond distances indicate that the intercage bonds are significantly shorter than the other CC distances. Moreover, fluctuations of the coordinates and symmetry changes of the building blocks are also small, and amount to around ±0.005 Å. Experimental data on cubylcubane show a shortened intercage CC distance [19–21] that is in agreement with our results.

### 4.2. Size dependence of the ionization potentials (IP) and the electron affinities (EA)

Some properties of oligomeric systems are quite different from those of the monomer or the surface. In fact, the latter correspond to extremes cases that can be visualized as infinitely small and infinitely large polymers. This applies to the evolution of the ionization potentials (IP) and the electron affinities (EA) as a function of the size and the geometry of the oligomer. Both properties are expected to converge to a limit that we designate as the 'surface bulk limit'; it corresponds to the number of units, $n$, becoming very large $n \gg 1$. In this context, it has been shown that the evolution of a property $P$, such as IP and EA, as function of the number of building units of atomic or molecular aggregates, can be described by the following analytic form [22,23]

$$P(n) = P(\infty) + A_p n^{-1/3}, \tag{3}$$

where $P(\infty)$ corresponds to the property value in the surface bulk limit ($n \to \infty$) and $A_p$ is a fitting parameter. Fig. 4 displays the behavior of IP and EA for the 10 cubane oligomers we investigated. These values were obtained using Koopman's theorem, which indicates that IP and EA can be approximated by the energies of the frontier molecular orbitals: $\mathrm{IP} = -\varepsilon_{\mathrm{HOMO}}$ and $\mathrm{EA} = -\varepsilon_{\mathrm{LUMO}}$. Fig. 4 shows that the EA values increase slightly as they approach EA($\infty$), with rather small variations, indicating that these kind of structures are nearly saturated and thus unable to accept electrons. For the IP values the situation

Table 1
Bond lengths at B3LYP/6-311G** of the different systems studied here.

| System | CC1 | CC2 | CC3 | CC4 |
|---|---|---|---|---|
| **1** | – | – | – | 1.559 |
| **2** | 1.475 | 1.580 | 1.560 | 1.570 |
| **3** | 1.475 | 1.570 | 1.560 | 1.570 |
| **4** | 1.475 | 1.580 | 1.560 | 1.570 |
| **5** | 1.470 | 1.580 | 1.570 | 1.560 |
| **6** | 1.476 | 1.570 | 1.560 | 1.560 |
| **7** | 1.479 | 1.570 | 1.560 | 1.570 |
| **8** | 1.470 | 1.600 | 1.560 | 1.570 |
| **9** | 1.480 | 1.580 | 1.550 | 1.560 |
| **10** | 1.478 | 1.587 | 1.577 | 1.568 |

All distances are quoted in Å

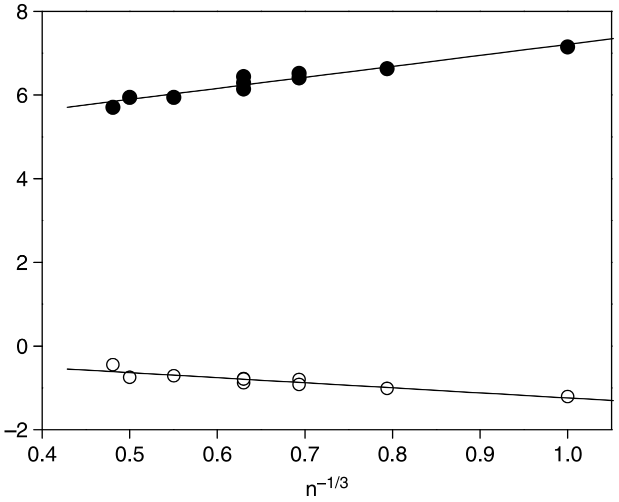


Fig. 4. EA (open circles) and IP (full circles), in eV units, versus $n^{-1/3}$ obtained at the B3LYP/6-311G** level. The straight lines are linear fits to the data. Notice that for $n=3$ (structures **3** and **5**), and $n=4$ (structures **4**, **6** and **7**) the corresponding EA and IP values are almost identical.

is different: the amount of energy needed to remove an electron becomes smaller as the number of units $n$ grows, reaching the surface bulk value IP($\infty$)=4.58 eV.

### 4.3. Size dependence of $\mu$ and $\varepsilon$

Fig. 5 displays the electronic chemical potential $\mu$ and the HOMO–LUMO energy gap, $\varepsilon$, of the cubane oligomers. Again $\mu$ and $\varepsilon$ depend linearly on $n^{-1/3}$. The corresponding analytic forms are

$$\mu(n) = 1.15 - 0.36n^{-1/3}, \tag{4}$$

$$\varepsilon(n) = 4.59 + 3.84n^{-1/3}, \tag{5}$$

and the values of $\mu(n)$ and $\varepsilon(n)$ are displayed in Fig. 5. Since, the chemical potential is a measure of the electron transfer between two systems that have different $\mu$ values, we observe in Fig. 5 that as the number of units increases from $n$ to $n+1$ the consequent charge transfer is very small. Moreover, as the number of units $n$ increases, $\mu$ becomes larger, reaching $\mu(\infty)=-2.27$ eV; the latter corresponds to one half of the work function of the bulk material. On the other hand, $\varepsilon$ decreases reaching $\varepsilon(\infty)=4.59$ eV, a value that is not small enough to allow electronic conductivity, which only occurs in materials with band gaps smaller [21,24] than 1–1.3 eV. In the surface bulk limit it is not possible to transport electrons, but doping or substituting with donor/acceptor atoms, or functional organic groups, may induce charge transfer.

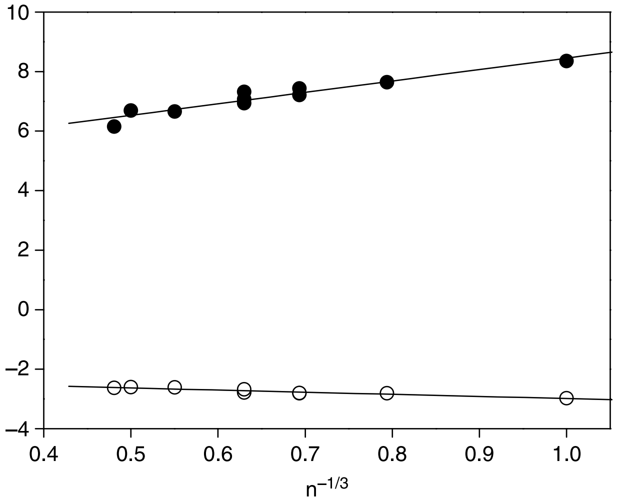


Fig. 5. $\varepsilon$ (full circles) and $\mu$ (open circles), in eV units, versus $n^{-1/3}$ obtained at the B3LYP/6-311G** level. The straight lines are least square fits to the data. Notice that for $n=3$ (structures **3** and **5**), and $n=4$ (structures **4**, **6** and **7**) the corresponding $\varepsilon$ and $\mu$ values are almost identical.

### 4.4. Charge transfer: $\Delta N_{max}$ and $\Delta N$

As defined above, the maximum electronic charge that the system can accept is $\Delta N_{\text{max}}=-2\mu/\varepsilon$. The way that $\Delta N_{\text{max}}$ varies as a function of $n^{-1/3}$, for the ten oligomers we examine in this paper, is given in Fig. 6. We observe that the number of electrons that saturate the molecular structure increases as a function of $n$, and that it also is strongly dependent on the structure of the oligomer. Relating this behavior to previous indices, we observe that both doping and substitution with donor/acceptor groups increases the likelihood of electron transfer in an extended 2D cubane network.

As a matter of fact, we have seen that the inclusion of electron enriched functional groups in cubane chains allows for states within the band gap, thus favoring electronic conduction and, in some cases, increasing the electronic density of states around the Fermi energy [25]. In this context, it is possible to estimate the quantity of electrons needed to make sure that the system becomes a conductor, through the reduction of the band gap to values that are typical of semiconductors. Following the equation $\Delta N_{\text{max}}=-2\mu/\varepsilon$, and having in mind that in

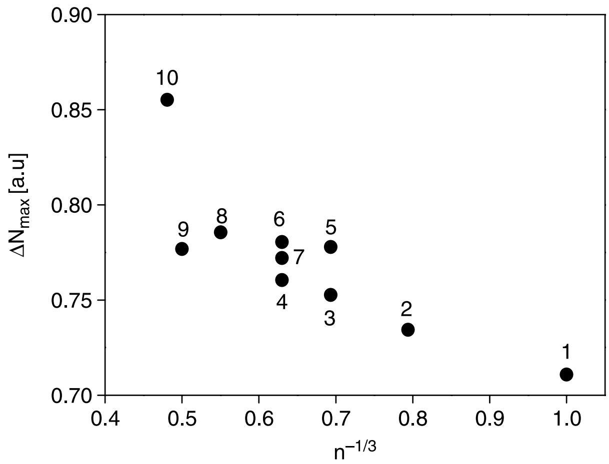


Fig. 6. $\Delta N_{\text{max}}$, in atomic units, at the B3LYP/6-311G** level for all the ten cubane oligomers displayed in Figs. 1–3 and denoted by the same labels. Notice that the values of $\Delta N_{\text{max}}$ for structures **1, 2, 3** and **4**, corresponding to $n=1$–4, respectively, lie on a straight line.

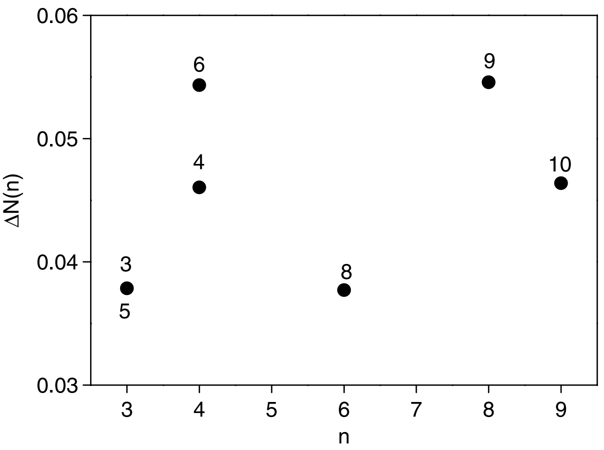


Fig. 7. Electron transfer $\Delta N(n)$, as given by Eq. (7), when a cubane unit is added to one of the cubane oligomers labelled and displayed in Figs. 1–3.

the infinite size limit $\mu$ is the half of the work function ($\mu = \Phi/2$) the last equation becomes $\Delta N_{\max} = \Phi/\varepsilon$. To allow conductivity to occur $\varepsilon$ must have values of 1–1.3 eV or smaller, and thus the necessary amount of charge that the system needs to incorporate through doping is given by values of $\Delta N_{\max}$ ranging from 3.5 to 4.5 electrons.

To discuss the charge transfer during the oligomer formation, it is convenient to use the following expression [7,10,23]:

$$\Delta N(n) = \frac{\mu_1 - \mu_n}{(\varepsilon_1 + \varepsilon_n)}. \tag{6}$$

Using Eq. (2), along with $\varepsilon = \varepsilon_L - \varepsilon_H$, $IP = -\varepsilon_{HOMO}$ and $EA = -\varepsilon_{LUMO}$, and knowing that $EA \to 0$ as $n \to \infty$, Eq. (6) becomes:

$$\Delta N(n) = \frac{IP_1 - IP_n}{IP_1 + IP_n} \quad n = 2,3\ldots 9. \tag{7}$$

In Fig. 7, we display the values of $\Delta N(n)$ for each one of the cubane oligomer formations, obtained using the above equation, when either one CB or one CCB unit is added to the original structure. The values of $\Delta N(n)$ turn out to be quite small, thus confirming a very slight electron transfer during the build up of these systems, which agrees with the experimental reports that cubane oligomers are built up from free radicals [26]. As expected Fig. 7 shows indicates that the electron transfer depends mainly on the number of units required to build the various oligomers.

## 5. Concluding remarks

We have studied different structures of cubane oligomers through the characterization of their energies, ionization potentials and electron affinities. It has been found that the IP's and EA's are only sightly dependent on the number of building blocks involved; the energy decreases with the number of cubane units no matter the type of structure considered.

From the values of IP and EA, we are able to predict that these structures, in the bulk limit, do not accept electrons, but that they might allow electron donation. The bulk bandgap ($\varepsilon$) also indicates that a surface made of cubanes is not capable of electron transfer to the conduction band, since it has almost four times the gap allowed for a molecule to be able to transfer electrons, opening the possibility of doping or substitution with donor/acceptor groups to make electron transfer feasible [25].

From $\Delta N_{\max}$, we found that to allow for conductivity to occur an amount close to four electrons is required to assure electron transfer, which can be achieved by doping or by the inclusion of electron enriched functional groups. On the basis of the $\Delta N$ values we found that weak delocalization and charge transfer are related to the formation of the intercage bond.

## Acknowledgements

Supported by FONDECYT under grants no. 1060590, 1030957, 1040356 and Proyecto Bicentenario en Ciencias y Tecnología (PBCT no. 8) de Inserción en la Academia. The authors also wish to thank MECESUP under projects PUC-0004 and Red Química UCH-0116, and by Fundación Andes A.H.R. is supported by project J-42647-F from CONACYT-Mexico.

## References

[1] P.E. Eaton, T.W.C. Jr, J. Am. Chem. Soc. 86 (1964) 962.
[2] P. Eaton, Angew. Chem. 31 (1992) 1421.
[3] W.W. Jr, J. Am. Chem. Soc. 75 (1953) 4224.
[4] E. Seidl, H.S. III, J. Am. Chem. Soc. 113 (1991) 1915.
[5] G.W. Griffin, A.P. Marchand, Chem. Rev. 89 (1989) 997.
[6] B. Herrera, A. Toro-Labbé, Chem. Phys. Lett. 344 (2001) 193.
[7] R.G. Parr, W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press, New York, USA, 1989.
[8] R.G. Pearson, Hard and Soft Acid and Bases, Dowden, Hutchinson and Ross, Stroudsberg, 1973.
[9] R.G. Pearson, Coord. Chem. Rev. 100 (1990) 403.
[10] R.G. Pearson, Chemical Hardness, Wiley–VCH, Oxford, 1997.
[11] P.W. Ayers, R. Parr, J. Am. Chem. Soc. 122 (2000) 2010.
[12] L. Pauling, The Nature of Chemical Bond, Cornell University Press, New York, 1960.
[13] K.D. Sen, C.K. Jorgensen, Electronegativity: Structure and Bonding, vol. 66, Springer, Berlin, Germany, 1987.
[14] A. Szabo, N.S. Ostlund, Modern Quantum Chemistry, first ed., Dover Publications, NY, 1989.
[15] J.M. Frisch, GAUSSIAN 98: Revision A.7, Gaussian, Inc, Pittsburgh, PA, 1998.
[16] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[17] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 5648.
[18] R. Gilardi, M. Maggini, P.E. Eaton, J. Am. Chem. Soc. 110 (1998) 7232.
[19] O. Ermer, J. Lex, Angew. Chem. 31 (1992) 5648.
[20] P. Jaque, A. Toro-Labbé, J. Phys. Chem. B. 108 (2004) 2568.
[21] H. Müller, H.G. Fritsche, L. Skala, Clusters of Atoms and Molecules I, Springer, Berlin, Ch. Analytic Cluster Models and Interpolation Formulae for Cluster Properties, p. (1995) 114.
[22] A.J. Heeger, J. Phys. Chem. B. 105 (2001) 8476.
[23] R.G. Parr, R.A. Donnelly, W.E. Palke, J. Chem. Phys. 68 (1978) 3801.
[24] A.J. Heeger, J. Phys. Chem. B. 105 (2001) 8476.
[25] F. Valencia, A.H. Romero, M. Kiwi, R. Ramirez, A. Toro-Labbe, Phys. Rev. B., 033410 (2005).
[26] P.E. Eaton, K. Pramod, T. Emrick, R. Gilardi, J. Am. Chem. Soc. 121 (1999) 4111.