Framework electron count and structural trends in Li_2X_2 rings

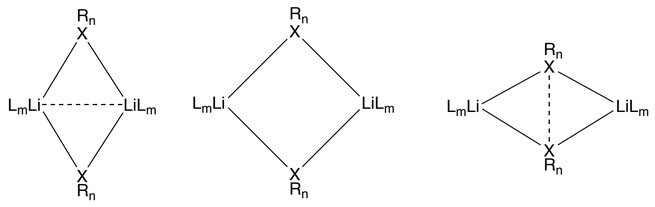
Juan Diego Velasquez, Jorge Echeverría and Santiago Alvarez

Departament de Química Inorgànica i Orgànica, and

Institut de Química Teòrica i Computacional, Universitat de Barcelona

Introduction

In spite of the highly ionic character of most lithium-element bonds, the bonding within the Li_2X_2 rings presents similarities with that found in similar transition metal systems, which obey simple framework electron counting rules (FEC) that allow us to predict whether they will form a regular ring or a squeezed one with short Li-Li or X-X distance (1a-c)[1-3]. The goal of this study is to disclose, through a combined structural and computational analysis, the orbital conditions that determine the framework electron counting rules. Therefore, we have studied the electronic structure of model compounds of the type $[L_mLi_2(\mu\text{-}XR_n)_2]$ by performing molecular orbital calculations of the Extended Hückel and DFT 3-21G type for m = 0-2 and n = 1-3.



1a 1b 1c

Methodology

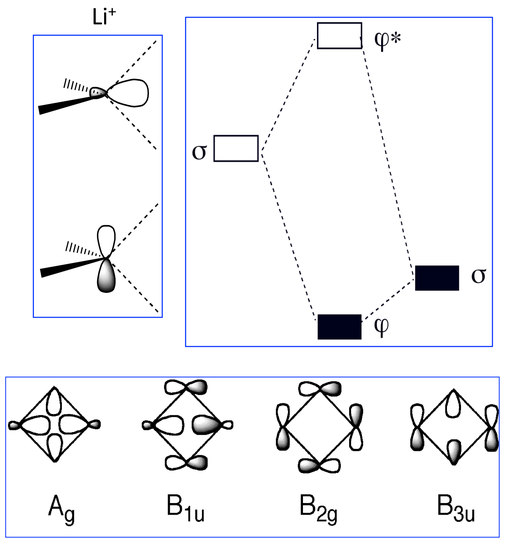
Molecular orbital calculations of the extended Hückel type[4] were carried out using the modified Wolfsberg-Helmholz formula[5] on the models compound with different net charges corresponding to FEC's of 8, 6 and 4. Standard atomic parameters[4,6] were used for the Extended Hückel calculations. The search for experimental structural data was carried out with the help of the Cambridge Structural Database.[7] Searches were performed for Li with XR_n bridges (n= 1-3), being X any group 14, 15 or 16 element. The terminal ligands were allowed to be any group linked to Li through a donor atom of groups 14-16.

Density functional calculations were carried out using the GAUSSIAN09 package. The hybrid (U)MO6-2X-DFT functional was applied with AUG-cc-pVTZ/TZVP basis set. The geometries were fully optimized using gradient techniques and were oriented preserving a C_{2h} symmetry for the $Li_2(\mu\text{-}XR_n)_2$ core. The "atoms in molecules" (AIM)[8] analysis of the electron density has been performed at the same level of the theory using the AIMAII program.[9]

Framework Electron Count Scheme

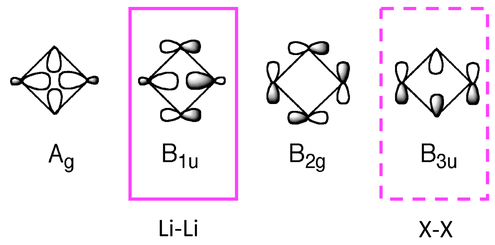
Two-lobes bridging donor atoms

- R_2P^-, R_2N^-, R_2S, RS^-, RO^-, RN^{2-}, Cl^-, I^-, S^{2-}, O^{2-}, $R_2C{=}C^{2-}$, $R_2C{=}N^-$, ...
- 2 Li^+: 2 empty orbitals
- $\mu\text{-}XR_2$ = 4 electrons donors
- 8 skeleton electrons = regular ring / **FEC = 8**

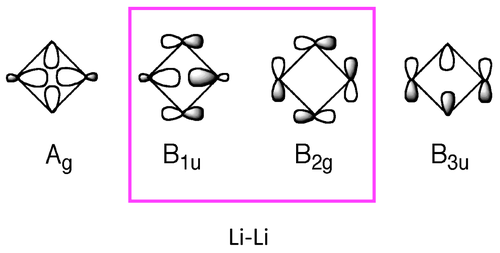


Emptying of φ orbitals

- **FEC=6**
  - ➢Li-Li o X-X

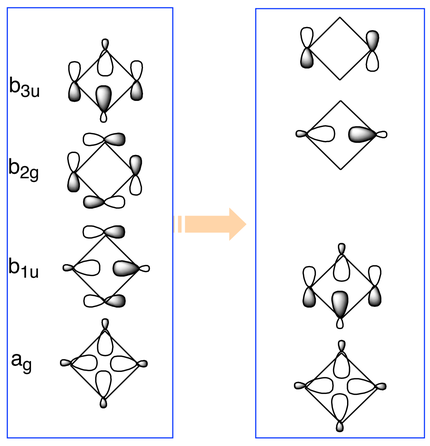


- **FEC=4**
  - ➢Li-Li



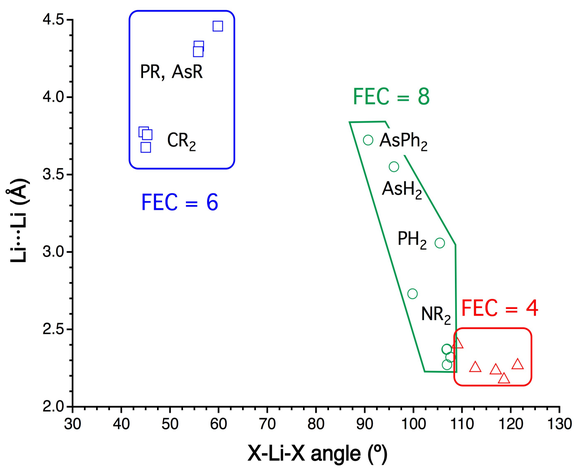
One-lobe bridging donor atoms

- $C^-_{(Ar)}$, py, H^-, R_3C^-, R_3P, CO, NO^+, ...
- Only 2 orbitals by skeleton
- $\mu\text{-}XR_3$ = 2 electrons donors
- 4 skeleton electrons= squeezed ring, short Li-Li/ **FEC=4**

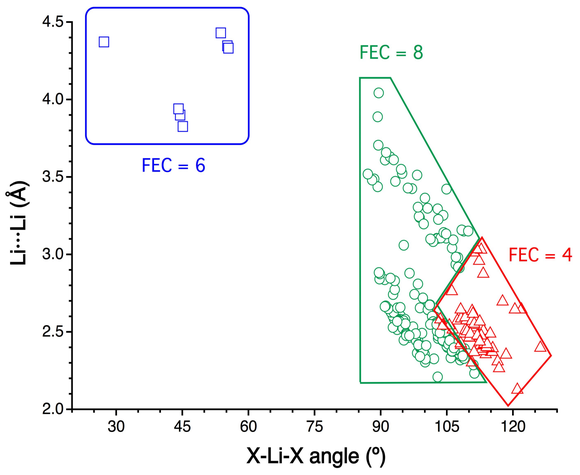


Li – Li interactions

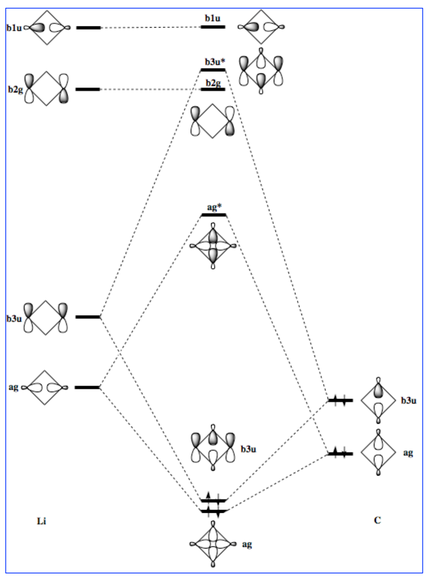
➢**Calculated data**

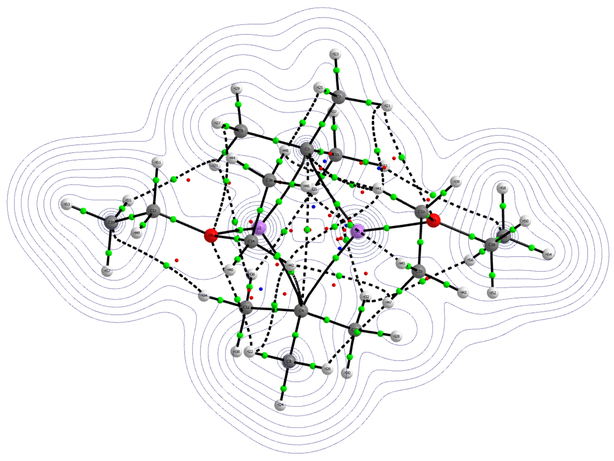


➢**Experimental data**

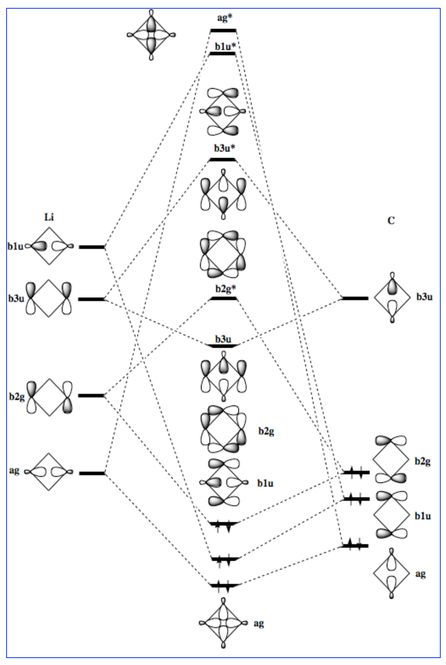


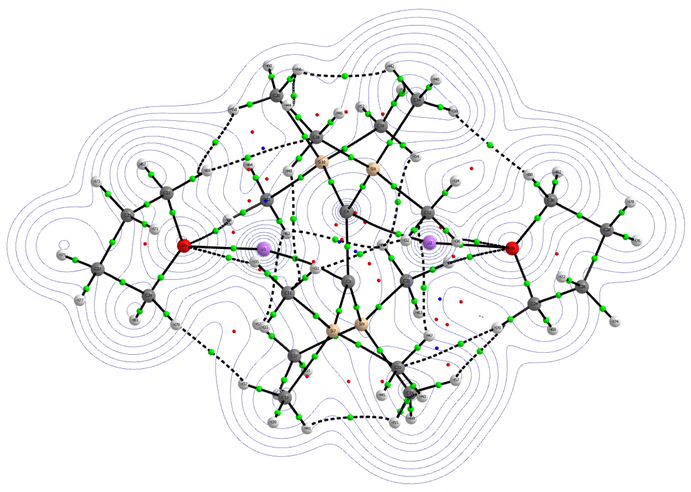
- **FEC=4**



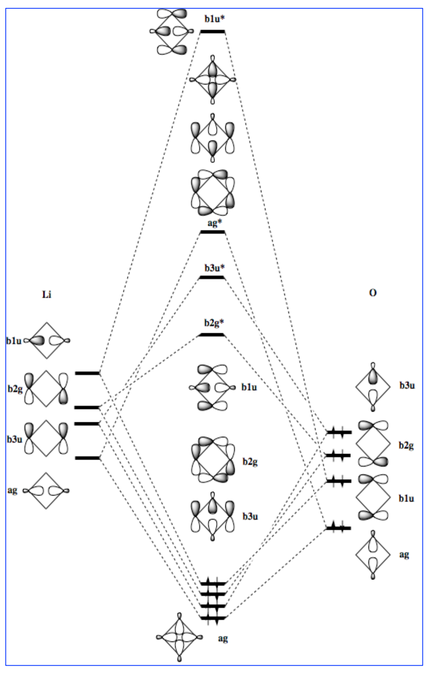


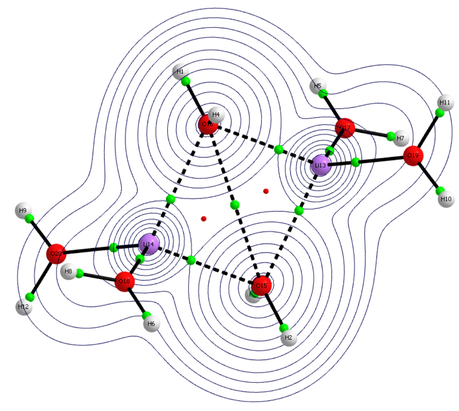
- **FEC=6**





- **FEC=8**





Summary

- FEC = 4 (One-lobe bridging donor orbital)
  d(Li-Li) < 3.0 Å; α(X-Li-X) > 110°
  Squeezed ring/ short Li-Li
- FEC = 6 (Two-lobes bridging donor orbital)
  d(Li-Li) > 3.8 Å; α(X-Li-X) < 60°
  Squeezed ring/ short X-X
- FEC = 8 (Two-lobes bridging donor orbital)
  d(Li-Li) = 2.2-3.8 Å; α(X-Li-X) = 90°-110°
  If X = atom of 2nd period, d(Li-Li) < 3.0 Å
  Regular ring

References

[1] Alvarez, S.; Alemany, P.; Aullón, G.; Palacios, A. A.; Novoa, J. J., Heterodox Bonding Effects Between Transition Metal Atoms. In *The Synergy Between Dynamics and Reactivity at Clusters and Surfaces*, Farrugia, L. J., Ed. Kluer Academic: Dordrecht, **1995**; pp 241-255.

[2] Alvarez, S.; Aullón, G., Ligand Orientation Effects on Metal-Metal Bonds. In *Metal Clusters in Chemistry*, Braunstein, P.; Oro, L. A.; Raithby, P., Eds. Wiley-VCH: New York, **1999**; Vol. 1, pp 308-322.

[3] Alvarez, S.; Palacios, A. A.; Aullón, G., Ligand Orientation Effects on Metal-Metal, Metal-Ligand and Ligand-Ligand Interactions. *Coord. Chem. Rev.*, **1999,** *185/186*, 431-450.

[4] Hoffmann, R., *J. Chem. Phys.*, **1963,** *39*, 1397.

[5] Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hofmann, R., *J. Am. Chem. Soc.*, **1978**, *100*, 3686.

[6] Summerville, R. H.; Hofmann, R., *J. Am. Chem. Soc.*, **1976**, *98*, 7240.

[7] Allen, F. H.; Kennard, O., *Chem. Des. Autom. News*, **1993**, *8*, 31.

[8] Bader, R. F. W., *Chem. Rev.*, **1991**, *91* , 893-928.

[9] Keith, T. A., *AIMAII (Version 13.05.06),* TK Gristmill Software, Overland Park KS, USA, 2013.

Funding

AGAUR (Generalitat de Catalunya), grant 2017 SGR 01289.

Spanish Structures of Excellence María de Maeztu program, grant MDM-2017–0767.

Ministerio de Ciencia, Investigación y Universidades, grant PGC2018-093863-B-C21 .