Aromaticity in Complex Consisting of Thiocarbons ($C_nS_n^{2-}$; $n = 3$ *e* 4)

Eder H. da Silva [1] (PG), Giovanni F. Caramori [2] (PQ), Renato L. T. Parreira [1] (PQ)

[1] *Núcleo de Pesquisa em Ciências Exatas e Tecnológicas, UNIFRAN - Franca - 14404-600, SP, Brazil*
[2] *Depto. de Química, UFSC, Campus Universitário Trindade, Florianópolis - 88040-900, SC, Brazil*
renato.parreira@unifran.edu.br / edersilva3@yahoo.com

Keywords: Aromaticity, Thiocarbons, Electronic effects, NICS.

INTRODUCTION

The thiocarbons ($C_nS_n^{2-}$), similarly to the oxocarbons ($C_nO_n^{2-}$), present important optical and photophysical properties.[1a] The continued interest in the family of thiocarbons is due, in part, to the aromaticity of this class of compounds, which exhibits electron delocalization stabilized by resonance.[1b] This work presents the study of the species $C_3S_3^{2-}$ (1) and $C_4S_4^{2-}$ (2), isolated and complexed with lithium (Li^+) and calcium (Ca^{2+}) ions, as models for the investigation of the structural and electronic characteristics of this class of compounds.

METHODS

Geometries were optimized at the B3LYP/6-311++G(3df,3pd) level of theory by using the Gaussian09 software. Methods based on magnetic (NICS) and structural (HOMA) parameters were used for the study of aromaticity.[2] The topological analysis of the electron density was performed with the use of the QTAIM theory.[4,5]

RESULTS AND DISCUSSION

The studied compounds are shown in Figure 1.

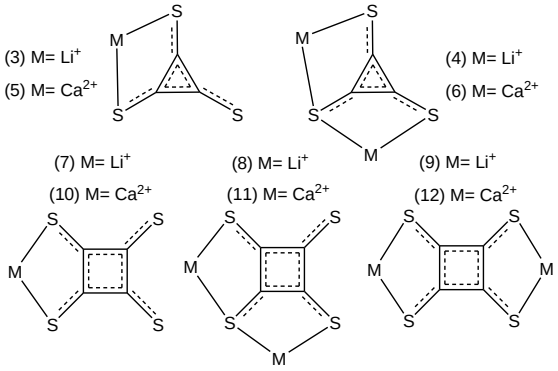

Figure 1. $C_3S_3^{2-}$ and $C_4S_4^{2-}$ complexes.

The NICS values (Table 1) indicate strong aromatic character to the complexes constituted by the $C_3S_3^{2-}$ ion. The increase in the ring size led to a reduction of aromaticity in complexes formed by $C_4S_4^{2-}$ion. It is observed that the symmetrical coordination with metal ions cause an increase in the aromaticity.

Table 1. NICS and HOMA values.

	NICS(1)	$NICS(1)_{zz}$	HOMA	EN	GEO
C_6H_6	-10,04	-29,84	0,998	0,002	0,000
1	-9,94	-13,96	0,974	0,026	0,000
3	-9,71	-13,96	0,952	0,037	0,010
4	-9,89	-14,82	0,963	0,028	0,010
5	$-7{,}52^{(in)}$ $-9{,}12^{(out)}$	$-10{,}51^{(in)}$ $-14{,}65^{(out)}$	0,871	0,107	0,023
6	-8,36	-12,98	0,956	0,044	0,001
2	-2,50	1,26	-0,568	1,568	0,000
7	-2,43	1,23	-0,568	1,440	0,128
8	-2,37	1,55	-0,590	1,317	0,272
9	-3,68	-0,44	-0,194	0,192	0,002
10	$-0{,}97^{(in)}$ $0{,}53^{(out)}$	$2{,}79^{(in)}$ $3{,}73^{(out)}$	-1,052	1,818	0,234
11	-1,37	2,35	-0,991	1,440	0,551
12	-3,09	1,37	-0,123	1,123	0,000

According to the HOMA index (Table1), only the complexes formed by the $C_3S_3^{2-}$ ion present aromatic character. The anti-aromatic character for $C_4S_4^{2-}$ compounds is related to the long lengths of the C-C bonds (EN term). The Laplacian of the electron density ($\nabla^2\rho_b$) indicates that metal-ligand bonds are classified as type "closed-shell".

CONCLUSIONS

The NICS index showed that the complexes formed by $C_3S_3^{2-}$ ion are aromatic. The complexation with symmetrical pattern promotes slight increase in the aromatic character to the complex formed by $C_4S_4^{2-}$ ions. The metal-ligand bonds were classified as "closed-shell".

ACKNOWLEDGMENTS

FAPESP (2011/07623-8 and 2012/22440-0) and CNPq (grant 470985/2011-9).

[1] (a) A. J. Fatiadi, J. Am. Chem. Soc. 100, 2586 (1978). (b) D. Quiñonero, C. Garau, A. Frontera, P. Ballester, A. Costa, PM Deya, Chem. Eur. J., 8, 433 (2012).
[2] D. Geuenich, K Hess, F. Köhler, R. Herges, Chem. Rev. 105, 3758 (2005).
[3] (a) R. F. W Bader, Atoms in Molecules. A Quantum Theory. Oxford University Press. Oxford, U. K., 1990. (b) R. F. W. Bader, Phys. Chem. A, 102, 7314 (1998).