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Article

Ab Initio, DFT and Semi-Empirical Studies on Interactions of Phosphoryl, Carbonyl, Imino and Thiocarbonyl Ligands with the Li^+ Cation: Affinity and Associated Parameters

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A afinidade do cátion Li^+ para uma série de ligantes fosforila, carbonila, imino e tiocarbonila substituídos na posição *para* de um anel aromático foi calculada com os métodos *ab initio* MP2/6-311+G(d,p), DFT B3LYP/6-311+G(d,p) e semi-empírico PM6. Cada série de ligante é constituída pelos seguintes grupos substituídos na posição *para*: NH_2, OCH_3, CH_3, H, Cl, CN and NO_2. A entalpia de interação foi calculada para quantificar a afinidade dos ligantes para o cátion Li^+. Parâmetros geométricos e eletrônicos foram correlacionados com a força da interação metal-ligante. A natureza eletrônica dos grupos substituintes é o principal parâmetro que modula a intensidade da ligação metal-ligante. Grupos doadores de elétrons tornam a entalpia de interação mais exotérmica, enquanto grupos aceptores de elétrons tornam a entalpia de interação menos exotérmica. Análise da decomposição da energia mostra que os grupos substituintes modulam a intensidade da componente eletrostática da interação sem afetar a componente covalente.

The affinity of the Li^+ cation for a set of *para*-substituted phosphoryl, carbonyl, imino and thiocarbonyl ligands was calculated with the *ab initio* MP2/6-311+G(d,p), DFT B3LYP/6-311+G(d,p) and semi-empirical PM6 methods. Each set of ligand is constituted by the following *para*-substituted groups: NH_2, OCH_3, CH_3, H, Cl, CN and NO_2. The interaction enthalpy was calculated to quantify the affinity of the ligands for the Li^+ cation. Geometric and electronic parameters were correlated with the strength of the metal-ligand interaction. The electronic nature of the *para*-substituted group is the main parameter that modulates the intensity of the metal-ligand binding energy. Electron donor groups make the interaction enthalpy more exothermic, whereas electron acceptor groups make the interaction enthalpy less exothermic. The energy decomposition analysis shows that the *para*-substituted groups modulate the intensity of the electrostatic component of the interaction without affecting the covalent component.

Keywords: lithium cation, substituent effect, interaction enthalpy, EDA, ligand interaction

Introduction

The interaction between metal cations and neutral bases is a subject of continuous interest in biochemistry, because of their relevant functions in many biological processes.[1,2] Alkaline metal cations are indispensable for the human body, playing an important role in DNA syntheses, hormonal regulation, muscle contraction and in the maintenance of blood pressure.[3,4] More specifically, the Li^+ cation can also inhibit multiple enzymes, such as cytochrome P_{450} and glutathione S-transferase, stabilize the structure of nucleotides, stimulate glycogen synthesis and interact with various types of neurotransmitters.[5] In all these processes the Li^+ cation interacts with a wide range of biological molecules with several different organic functional groups. The most common types of interactions are with oxygen atoms of alcohols,[6] ketones,[7] carboxylic acids[8,9] and phosphates,[10] nitrogen atoms of amines,[9,11] amides[12] and imides[13] and sulfur atoms of thiols.[14] In the biological media the Li^+ cation is surrounded by different

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types of atoms,[5] forming either electrostatic or polar interactions, due to its small size and high nuclear effective charge.[15]

The bond between the Li^+ cation and ligands can be described as an acid-base interaction. According to Pearson's acid base theory the Li^+ cation is classified as a hard acid and forms stable compounds when interacting with hard bases.[16] Interactions between the Li^+ cation and oxygen donor ligands (hard base) are stronger than those with ligands having nitrogen or sulfur atoms (less harder bases) due to its small van der Waals radius and strong polarization power. Nevertheless, the neighborhood of the atom interacting with the Li^+ cation is also important to define the strength of the interaction. Inductive and resonance effects of neighbor pendant groups can modulate the electron releasing or withdrawing ability of the ligand by rearranging the charges through the molecule.[17,18]

Computational studies have extensively contributed to the understanding of the strength of the interactions between the Li^+ cation and ligands by calculating the lithium cation affinity (LCA) and basicity (LCB). The LCA is defined as the negative of the enthalpy change (ΔH) of equation 1, whereas the LCB is the ΔG^{298} associated with the corresponding thermodynamic equilibrium.[19]

$$Li^+ + L \rightleftharpoons [Li\text{-}L]^+ \quad (1)$$

The widest LCA and LCB series were proposed by Burk *et al*.,[19] based on Taft's work,[20] and consist of an experimental and *ab initio* study of 205 neutral organic and inorganic ligands with a 29.6 kcal mol^{-1} LCB range. This scale has been widely used to convert relative basicities into absolute ones and to evaluate the strength of the binding energy between the Li^+ cation and ligands.[19] Monofunctional sulfuryl and phosphoryl ligands were evaluated by Buncel *et al.*[21] and Borrajo *et al.*[21] showing, as a general trend, that the Li^+ cation interaction is stronger with harder (Pearson) bases. A detailed DFT study of the influence of electron donor and electron acceptor groups in a set of *para*-substituted acetophenones on the lithium affinity was reported by Senapati *et al*.[22] It demonstrates that pendant aromatic groups can modulate the strength of the lithium interaction and that some specific electronics and geometrical parameters are strongly correlated to the affinity. Similar correlations were found by Palusiak[23] in *para*-substituted $Cr(CO)_5$–pyridine complexes, by Ma in silver complexes with carbonyl, nitrogenous, thio and aromatic ligands[24] and by Gal *et al.*[25] in lithium complexes with substituted phenyl rings. High level electronic structure calculations of lithium affinities show high degree of correlation between *ab initio* and DFT results.[19,24,26]

Continuing our previous investigations[27] about the effect of substituents on the interaction between oxo ligands and the alkaline earth cations, in the present work we quantify the intensity of the binding energy of several ligands, with different functional groups, to the Li^+ cation. As model ligands we studied some constitutive blocks of organic compounds, with C=O (carbonyl), C=N (imino), C=S (thiocarbonyl) and P=O (phosphoryl) groups, as shown in Figure 1. To mimic electronic effects of natural biomolecules we choose a set of simple and common substituents, having different properties for resonance and inductive effects.[28] The substituents H, Cl, OCH_3, CH_3, CN, NH_2 and NO_2 were selected. In previous works we showed that aromatic compounds substituted in the *para* position can modulate the strength of binding of phosphoryl and carbonyl ligands to the calcium and magnesium cations.[27] To rationalize the influence of the *para*-substituent on the strength of the metal-ligand interaction the energy decomposition analysis (EDA), as proposed by Ziegler and co-workers,[29] was employed.

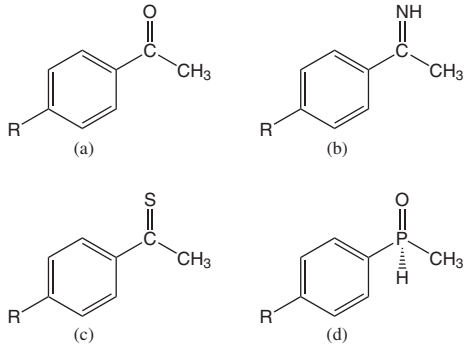

Figure 1. Structures of the adducts used for interaction with the Li^+ cation: carbonyl (a), imino (b), thiocarbonyl (c) and phosphoryl (d) ligands.

Computational Details

Geometry optimizations and energy calculations were carried out with the Gaussian 03W software,[30] using the B3LYP[31] functional and the MP2 frozen core[32] *ab initio* method with the 6-311+G(d,p)[33] basis set. After geometry optimization the second order force constant matrix was calculated to confirm the optimized geometry as a genuine minimum on the potential energy surface. It has been shown that these combinations of methods and basis set are able to yield structures in reasonable agreement with those obtained at higher level of theory.[34-37] To evaluate the ability of a less time consuming method to reproduce the lithium cation affinity, semi-empirical PM6[38] calculations were also carried out with the MOPAC 2009 package.[39] EDA calculations[29,40] were done using the B3LYP functional and the DZP basis set of the ADF software.[41]

Results and Discussion

Geometry optimization

The geometries of the 28 substituted lithium complexes were fully optimized with the MP2 frozen core, DFT and semi-empirical methods, without any restriction. In Figure 2 we show the optimized geometries for the carbonyl, imino, thiocarbonyl and phosphoryl complexes with the hydrogen atom in the *para* position. The optimized geometries of these complexes are similar, except for the point of interaction with the lithium cation. The optimized geometries for the several *para*-substituted derivatives are also similar, with the exception of the d_1 (bond length between the lithium cation and the O, N or S atom of the ligand) and d_2 (P=O, C=O, C=N or C=S double bond of the complex) distances.

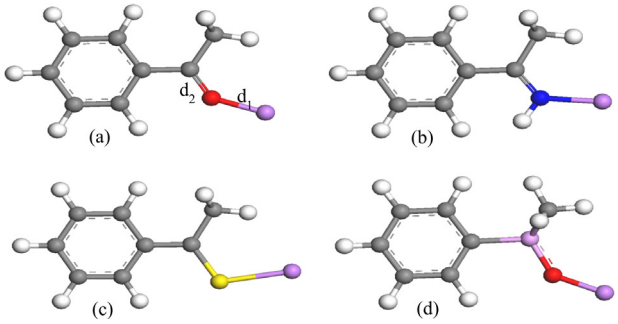

Figure 2. Optimized structures of the Li^+ complexes with the hydrogen atom as the *para*-substituted group. The d_1 (bond length between the lithium cation and the O, N or S atom) and d_2 (C=O, C=N, C=S and P=O double bond) distances for the (a) carbonyl, (b) imino, (c) thiocarbonyl, (d) phosphoryl compounds are shown. The lithium cation is shown in pink color. See online version for color visualization.

In Table 1 we list the MP2 and B3LYP d_1 and d_2 distances for each optimized structure. As the lithium-ligand interaction is predominantly electrostatic,[15] the distance between the cation and the ligand (d_1) must reflect the strength of that interaction. The smallest d_1 bond lengths are found in the phosphoryl complexes, followed by the carbonyl, imino and thiocarbonyl complexes, in agreement with other theoretical studies.[24,36,42] The d_1 bond lengths in the phosphoryl compounds are about 0.19 Å smaller than in the carbonyl, 0.21 Å smaller than in the imino and 0.57 Å smaller than in the thiocarbonyl compounds. Following this order we can predict that the phosphoryl ligands lead to the stronger interaction with the lithium cation, whereas the thiocarbonyl ligands lead to the weaker interaction. When seen within a given set of ligand, the d_1 distance shows a common trend, as previously reported.[27] The d_1 distance in complexes with electron donor groups in the *para*-position is smaller than in complexes with electron withdrawing groups. This behavior shows that the resonance effect inherent to the *para*-substituted group is also important to determine the d_1 distance. The resonance effect of electron donor groups increase the negative charge on the atom (O, N or S) that interacts with the lithium cation, making the d_1 distance smaller and the corresponding interaction stronger, whereas electron withdrawing substituents decreases the negative charge, weakening the interaction. The (MP2) difference in the d_1 distance between the amino (strongest resonance donor effect) and the nitro (strongest resonance acceptor effect) derivatives is 0.02 Å for phosphoryl, 0.05 Å for carbonyl, 0.03 Å for imino and 0.07 Å for thiocarbonyl compounds. The d_1 bond lengths are longer with MP2 than with B3LYP, in agreement with Petrie's work.[43] The d_2 bond lengths depend mainly on the atomic radii of the atoms that participate in the interaction and are not directly related to the strength of the interaction between the metal and the ligand. The carbonyl and imino d_2 bond lengths are essentially the same, circa 0.23Å and 0.39Å smaller than the d_2 distance in the phosphoryl and thiocarbonyl compounds, respectively. Analysis of the d_2 bond lengths in a given class of compound shows that the substituent has only marginal contribution to that distance, since they are almost constant in each set. In the complexation process the interaction between the Li^+ cation and the ligand is strengthened by electron delocalization from the double bond of the ligand to the cation. Part of the electron density of the double bond is dislocated to the O, N or S atom and increases its negative charge, making the metal-ligand interaction stronger and the d_2 distance longer. The double bond (P=O, C=O, C=N and C=S) lengths before complexation with the Li^+ cation are essentially constant for each set of ligands, being 1.30 Å for the carbonyl and imino, 1.50 Å for the phosphoryl and 1.64 Å for the tiocarbonyl ligands. After complexation they increase as a consequence of the electron delocalization. This effect is larger for the carbonyl (0.08Å), followed by the imino (0.05 Å), thiocarbonyl (0.05 Å) and phosphoryl (0.04 Å) derivatives. The MP2 and B3LYP d_2 bond lengths are essentially the same.

Interaction enthalpy

The affinity of each ligand for the metal cation was evaluated in terms of the interaction enthalpy, obtained as the heat of reaction of equation 1, corrected to 298K with the thermal contribution (using unscaled frequencies). The same approach has been used previously to determinate the interaction energy between metal cations and ligands.[6-9,11,22-27] In Table 1 we list the interaction enthalpies for the phosphoryl, carbonyl, imino and thiocarbonyl complexes using the *ab initio*, DFT and semi-empirical methods. As a typical ionic bond,[15] the strength of the Li^+-ligand

Table 1. Interatomic d_1 and d_2 distances (see Figure 2 for definition of the distances) in Å, MP2, B3LYP and PM6 interaction enthalpies (ΔH) in kcal mol^{-1} and Merz Kollman charges on the atom (O, N or S) that interacts with the Li^+ cation (q_X) in $|e^-|$ for the phosphoryl, carbonyl, imino and thiocarbonyl derivatives. B3LYP values are given in parenthesis

R group	d_1	d_2	ΔH	ΔH_{PM6}	q_X
			Phosphoryl ligands		
NH_2	1.71(1.69)	1.54(1.54)	−69.8(−66.6)	−55.2	−0.801
OCH_3	1.72(1.69)	1.54(1.54)	−67.5(−64.1)	−53.5	−0.796
CH_3	1.72(1.69)	1.54(1.54)	−66.6(−63.2)	−52.1	−0.789
H	1.72(1.70)	1.53(1.53)	−65.3(−62.2)	−51.8	−0.785
Cl	1.72(1.70)	1.53(1.53)	−63.1(−60.1)	−49.5	−0.782
CN	1.73(1.70)	1.53(1.53)	−59.3(−56.5)	−48.2	−0.780
NO_2	1.73(1.71)	1.53(1.53)	−58.1(−54.1)	−46.5	−0.775
			Carbonyl ligands		
NH_2	1.90(1.87)	1.31(1.31)	−59.9(−49.5)	−43.1	−0.682
OCH_3	1.91(1.88)	1.31(1.31)	−55.4(−47.5)	−40.3	−0.677
CH_3	1.92(1.89)	1.30(1.30)	−53.6(−45.8)	−38.9	−0.670
H	1.93(1.89)	1.30(1.30)	−51.5(−44.1)	−36.8	−0.668
Cl	1.93(1.89)	1.30(1.30)	−49.4(−42.5)	−34.5	−0.666
CN	1.95(1.90)	1.30(1.30)	−44.8(−38.0)	−32.3	−0.656
NO_2	1.95(1.91)	1.30(1.30)	−43.7(−37.4)	−29.3	−0.652
			Imino ligands		
NH_2	1.92(1.89)	1.31(1.31)	−55.9(−48.8)	−42.0	−0.670
OCH_3	1.93(1.90)	1.31(1.31)	−53.8(−48.1)	−39.5	−0.664
CH_3	1.94(1.91)	1.30(1.30)	−51.0(−44.9)	−37.2	−0.659
H	1.94(1.91)	1.30(1.30)	−49.7(−43.7)	−35.1	−0.655
Cl	1.94(1.91)	1.30(1.30)	−47.3(−41.3)	−32.9	−0.652
CN	1.95(1.92)	1.30(1.30)	−42.5(−37.8)	−31.3	−0.646
NO_2	1.95(1.92)	1.30(1.30)	−41.2(−37.0)	−27.1	−0.639
			Thiocarbonyl ligands		
NH_2	2.28(2.26)	1.70(1.70)	−47.6(−40.6)	−39.1	−0.328
OCH_3	2.30(2.28)	1.70(1.70)	−43.8(−37.7)	−38.0	−0.321
CH_3	2.32(2.29)	1.69(1.69)	−41.2(−36.0)	−35.5	−0.313
H	2.32(2.30)	1.69(1.69)	−38.8(−35.5)	−32.4	−0.309
Cl	2.32(2.30)	1.68(1.69)	−37.3(−32.9)	−30.5	−0.303
CN	2.34(2.31)	1.68(1.68)	−32.2(−28.2)	−26.5	−0.296
NO_2	2.35(2.31)	1.68(1.68)	−29.7(−24.6)	−23.0	−0.289

interaction is strictly correlated to the distance between the interacting atoms (d_1), where the smallest distances lead to the strongest interaction enthalpy. The phosphoryl compounds have the highest affinity for the Li^+ cation, with an (MP2) interaction enthalpy circa 12 kcal mol^{-1} more negative than for the carbonyl derivatives. The corresponding differences for the imino and thiocarbonyl compounds are 14 kcal mol^{-1} and 24 kcal mol^{-1}, respectively. This ligand affinity order was also found in previous studies with aminoacids[8-10] and other biological adducts.[6,7,24]

Analysis of the interaction enthalpy in each set of ligands shows an interesting trend related to the nature of the *para*-substituted group. Figure 3 shows the correlation between the interaction enthalpy and the values of the σ_p Hammet parameter of the substituents for the *para*-substituted derivative in each set of phosphoryl, carbonyl, imino and thiocarbonyl compounds. Ligands with electron releasing groups have more negative interaction enthalpies than the ones with electron withdrawing groups. This is due to the resonance structures inherent to each

group, which modulates the electronic charge on the atom that interacts with the metal cation. This behavior was previously seen for interactions of ligands with the lithium,[22] chromium[23] and calcium[27] cations. In each set of ligands the amino *para*-substituted group gives the most negative interaction enthalpy, whereas the nitro group gives the less exothermic enthalpy. The difference of interaction enthalpies for compounds containing the amino and the nitro *para*-substituted groups is above 10 kcal mol^{-1} in all the sets, showing that the resonance effect of the *para*-substituted group indeed determines the intensity of the interaction. Table 2 gives the linear fitting parameters for the data shown in Figure 3. They confirm the interaction enthalpy order given above and, additionally, indicate that the substituents have the strongest effect on the thiocarbonyl derivatives while the weakest effect is observed for the phosphoryl case. The effect of the substituents on the interaction enthalpy of carbonyl and imino derivatives is essentially the same.

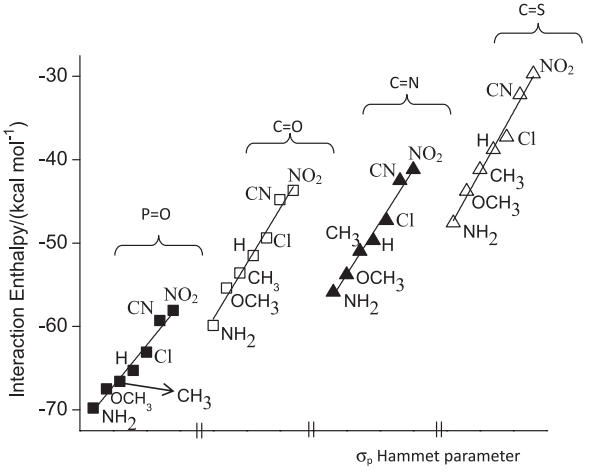

Figure 3. MP2(FC)/6-311+G(d,p) interaction enthalpy, calculated according to equation 1, for complexes of the Li$^+$ cation with the phosphoryl (■), carbonyl (□), imino (▲) and thyocarbonyl (△) ligands.

Table 2. Linear fitting analysis for the data shown in Figure 3

Complexes	Intercept	Slope	R-Square
Phosphoryl	−72.10	1.96	0.961
Carbonyl	−85.54	2.64	0.976
Imino	−104.09	2.51	0.975
Thiocarbonyl	−128.11	2.88	0.983

The qualitative effect of each *para*-substituted group is well reproduced by the semi-empirical and DFT methods employed, although a quantitative analysis show that the MP2 interaction enthalpies are more negative than those obtained with either the B3LYP or the PM6 methods, in accordance with our previous studies.[27] For the phosphoryl complexes the MP2 enthalpies are about 3 and 14 kcal mol^{-1} more negative than the B3LYP and PM6 values, respectively. For the carbonyl compounds this difference is in the order of 10 and 16 kcal mol^{-1}, respectively. For the imino derivatives the corresponding values are 6 and 13 kcal mol^{-1} and for the thiocarbonyl derivatives they are 5 and 7 kcal mol^{-1}, respectively.

The charge on the atom that interacts with the lithium cation is closely related to the strength of the interaction. Compounds with the most negative charge are also those that have the strongest interaction enthalpy. In Table 1 we list the MP2 Merz Kollman atomic charges on the atoms that interact with the Li$^+$ cation for all the sets of ligands (charges on the Li$^+$ cation are given in Table S1 of the Supplementary Information). The analysis of these charges shows that the charge on the oxygen atom of the phosphoryl compounds are about 0.120 e$^-$ more negative than those on the oxygen atom of the carbonyl derivatives, 0.132 e$^-$ more negative than those on the nitrogen atom of the imino derivatives and 0.479 e$^-$ more negative than those on the sulfur atom of the thiocarbonyl derivatives. This order was also found in previous studies.[6,7,22-24] The charge analysis in each set of ligands shows that the *para*-substituted group modulates the charges through its resonance effect. The difference between the charge of the amino and nitro *para*-substituted groups are 0.026e$^-$ for the phosphoryl, 0.030e$^-$ for the carbonyl, 0.031e$^-$ for the imino and 0.039e$^-$ for the thiocarbonyl derivatives. These results are in agreement with the interaction order found in this work.

Decomposition of the metal-ligand interaction

The nature of the interaction between the Li$^+$ cation and the ligands is predominantly electrostatic.[15] The main parameters that determine the strength of the interaction are the distance between the charged atoms and their charges, as shown before. However, some contribution of covalent interaction, due to charge polarization, may also add to the electrostatic component.[15] The covalent component is derived from the overlap of atomic orbitals and the electron exchange between the two partners of the interaction. The electrostatic component includes, mainly, ion-dipole and ion-induced dipole interactions. The energy decomposition analysis (EDA) method was employed to evaluate the changes in each component according to each ligand and in each set of ligand. In this method the molecule is divided into fragments and a linear combination of the fragment's orbitals is used to generate the molecular orbitals of the complex.[40] In the present study the fragments are the Li$^+$ cation and the ligand. The EDA approach divides the interaction between fragments

into three main terms: the Pauli repulsion, due to repulsion between electrons of the same spin; the orbital interaction, due to the overlap of the fragment's orbitals (covalent component) and the electrostatic interaction, due to the attraction of the charge distribution of each fragment (ionic component).[40] The calculated Pauli repulsion term is essentially constant and small for all compounds in the set and does not show significant variations for the different ligands. Figures 4 and 5 show the dependence of the covalent and electrostatic components of the metal-ligand interaction as a function of the class of ligand and the *para*-substituted group in each ligand (For the numerical values of each component see Tables S2-S5 in the Supplementary Information). The covalent component of the Li^+-ligand interaction is essentially constant for each set of ligand, with a variation of no more than 2.3 kcal mol^{-1} in each set. The effect of the *para*-substituted group on the covalent component is practically negligible in each set of ligand, showing that the substituent does not modify this component. In contrast, the ionic component undergoes significant decrease as the R group becomes stronger electron attractor. This behavior is in agreement with our previous calculations for the interaction of the Mg^{2+} cation with phosphoryl ligands.[27] The ionic component for the phosphoryl compounds are 12.1 kcal mol^{-1} more negative than for the carbonyl, 15.9 kcal mol^{-1} more negative than for the imino and 27.3 kcal mol^{-1} more negative than for the thiocarbonyl compounds. This difference was expected based on the d_1 distance and the charges on the interacting atom of the ligand (O, N, S) in the complex. The phosphoryl compounds have the smallest d_1 distance and the most negative charge on the atom interacting with the metal, followed by the analogous carbonyl, imino and thiocarbonyl complexes. The analysis of the electrostatic component in each set of ligand reinforces the modulation of the interaction by the *para*-substituted group. The differences in the ionic component between the compounds with the amino and nitro groups are −13.82 kcal mol^{-1} for the phosphoryl, −15.16 kcal mol^{-1} for the carbonyl, −16.48 kcal mol^{-1} for the imino and −21.79 kcal mol^{-1} for the thiocarbonyl derivatives. Therefore, there is a decrease in the contribution of the ionic component as we go through the sequence phosphoryl, carbonyl, imino and thiocarbonyl. For the thiocarbonyl complexes the ionic component becomes smaller than the covalent component for compounds with strong electron acceptor groups.

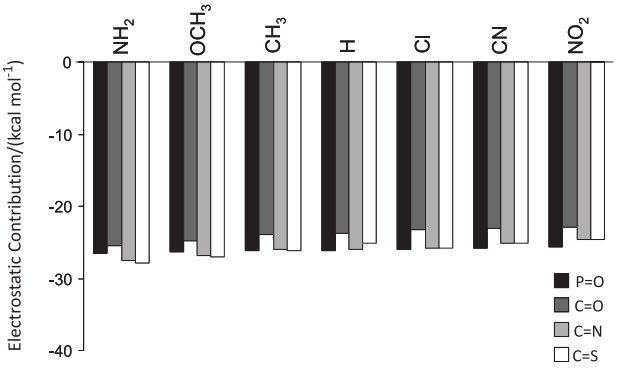

Figure 4. Covalent component of the metal-ligand interaction.

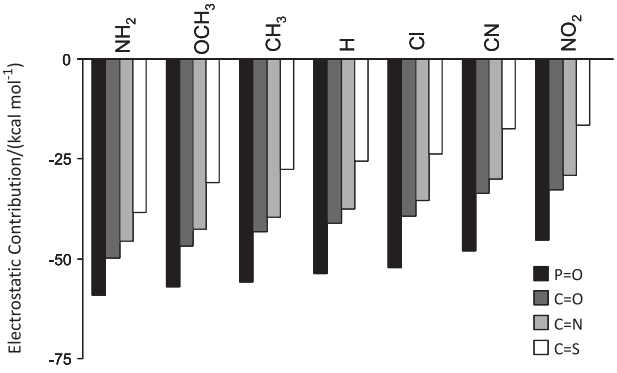

Figure 5. Electrostatic component of the metal-ligand interaction.

Conclusions

The ability of 28 phosphoryl, carbonyl, imino and thiocarbonyl ligands to complex the Li^+ cation was analyzed in terms of the distance between the cation and the ligand (d_1), charges on the O, N or S atom that interacts with the cation and the interaction enthalpy. Electron-donating substituents strength the ligand-cation interaction by shortening the d_1 distance, increasing the O, N or S atomic charges and increasing the negative value of the interaction enthalpy, while electron withdrawing substituents have the opposite effect. The Hammett σ_p parameter is strongly correlated with the interaction enthalpy, in agreement with the behavior cited above. Decomposition of the interaction energy showed that the differences in the ability of the ligands to complex the cation are mainly due to the *para*-substituted modulation of the electrostatic component of the interaction. Electron-donor substituents lead to higher charges on the interacting atom what results in stronger electrostatic interaction and, as a consequence, higher interaction enthalpy. The covalent component of the Li^+ cation-ligand interaction is almost constant for all ligands in the set. The Pauli repulsion component is also constant and small. The MP2, B3LYP and PM6 methods give qualitatively the same trends for the variation of the interaction enthalpy, according to the Hammett σ_p parameter. Quantitatively, the interaction enthalpies calculated with the MP2 method are more negative than those obtained with either the B3LYP or the PM6 methods.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

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