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Gas-phase lithium-cation basicities of some benzene derivatives An experimental and theoretical study

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This paper is dedicated to Dr. Yannik Hoppilliard on the occasion of her 60th birthday.

Abstract

The gas-phase lithium-cation basicities of a series of monosubstituted benzene derivatives, namely C_6H_5X (X = H, Me, $CH{=}CH_2$, OH, OMe, SH, Cl, Br) have been measured by means of Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. The structures of the corresponding complexes and their relative stabilities were investigated with B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) density functional theory calculations. In all cases, the π-complexes are favored with respect to those in which the metal monocation interacts with the substituent. These latter kind of complexes, which are entropically favored with respect to the π-complexes, are found to be chelated species, in which Li^+ bridges the heteroatom of the substituent and the *ipso* carbon atom. The Li^+ basicity of the benzene derivatives investigated reflects the electron-donor ability of the aromatic moiety as a function of the substituent. Consistently, there is a linear correlation between the Li^+ basicity and the frequency of the vertical displacement of Li^+ with respect to the aromatic ring. (Int J Mass Spectrom 219 (2002) 445–456) © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Li^+ basicities; Benzene derivatives; Density functional theory calculations; FT-ICR

1. Introduction

Along the last decades of the 20th century, a great deal of effort was devoted to building up a proton affinity scale which covers a very wide range of values from weak to very strong bases, usually called superbases [1]. The contribution to this goal of high-level ab initio calculations was of great relevance, and the actual scale was anchored in a combined experimental and theoretical work [2]. A similar large interest was concentrated on the study of reactions involving metal monocations instead of the proton [3]. However, and in spite of these efforts, the different metal cation basicity scales are much more limited than the proton affinity scale.

A large part of these studies was devoted to alkali-metal cations [4–19]. In their 1986 review on the thermochemistry of ion/molecule association and clustering, Keesee and Castleman included a number of data on the interaction between alkali-metal ions and neutral Lewis bases [6]. More recent reviews relevant to the determination of the interaction energy between alkali-metal cations and molecules have been published by Fujii [14] and Rodgers and Armentrout

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[17]. Among the metal cations, the lithium ion is one of the most studied. The early ion cyclotron resonance (ICR) Li^+ affinity measurements of Beauchamp and co-worker [4,5] were later extended in the Taft laboratory [7], using Fourier transform ICR (FT-ICR). A recent publication of an expanded scale of gas-phase lithium-cation basicities that included 205 different compounds [19] was the result of the joint efforts of Taft and co-workers, in particular the Estonian group of Koppel. The structural aspects of the Li^+/base interaction was studied in detail by our groups [8,20–30], from both the theoretical and the experimental points of view, showing for the first time, the crucial role played by chelated structures in order to explain the enhanced basicity of bidentate base [21–23].

A particular interesting subset is formed by aromatic compounds for which the interaction takes place preferentially with the π-system [31–33]. Such cation–π interactions are of particular relevance in biological systems and were reviewed by Ma and Dougherty [11].

In spite of the great interest on these kind of complexes, there are still some interesting open questions associated with their structural peculiarities, in particular when the aromatic system presents basic substituents susceptible of binding an alkali-metal cation. Hence, the aim of this paper was to investigate the possible competition between attachment to the substituent and attachment to the π-system. For this purpose, the gas-phase lithium-cation basicities (LCBs, also designated as $\Delta G(Li^+)$) of different benzene derivatives have been measured by Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry and compared with the values estimated by means of high-level density functional theory calculations.

2. Experimental

The method of determination of lithium-cation transfer equilibrium constants was similar to the one described by Burk et al. [19]. The main differences were the Li^+ source and the working temperature. The lithium cation was generated by laser ablation (pulsed nitrogen laser, 337 nm, 200 μJ per pulse) of a lithium benzoate target, in the form of a pellet obtained by compression of the salt [29]. A small amount of 2-chloropropane was added to the systems under scrutiny to generate the propene/Li^+ adduct, which in turn transfers Li^+ to ligands of larger LCB. Equilibrium constants were determined at about four different pressure ratios, the total pressure read on the ion gauge being in the 10^{-5} Pa range. Reaction times of about 10 s were used. As there was no heat source close to the ICR cell (except for the electromagnet poles at about 30 °C, which are external to the vacuum chamber), the experiments were conducted at a temperature close to 25 °C.

All the relative LCBs, except those concerning chloro- and bromobenzene, were simultaneously optimized by a multiple linear regression procedure, as used by Taft and co-workers [8] following the Free and Wilson treatment [34]. Each experiment (ΔLCB) is described by a series of presence (1), or absence (0) of LCB intervals, no constant term being included in the model. This treatment of 52 ΔLCBs, involving couples of reference/studied compounds, plus data on ethylbenzene, naphtalene, phenantrene, anthracene and azulene not reported here, led to a model explaining 99.1% of the variance in the experiments. These relative values were anchored to the extensive LCB scale recently reported [19], which was established at 373 K. Theoretical estimates of temperature effect on LCBs showed that the change in LCB, when going from 298 to 373 K, is almost constant, ranging from 5.5 to 6.7 kJ mol^{-1}. Therefore, the errors introduced by combining relative LCBs, determined at room temperature, with the 373 K scale, are expected to be less than 1.2 kJ mol^{-1} in general. We have referenced our relative values to this scale without temperature correction. The values thus obtained for substituted benzenes and auxiliary compounds used to link them are reported in Tables 1 and 2.

Uncertainties on absolute values are not well defined, because the scale is anchored to only a few data accurate to ±5–10 kJ mol^{-1}. The relative values are more accurate, with uncertainties of the order of 1 kJ mol^{-1} or better.

Table 1
Lithium-cation basicities (LCBs in kJ mol^{-1} at 373 K) for the benzene derivatives studied here

Compound (B)	Reference (Ref)	LCB (kJ mol^{-1})		
		Ref[a]	(B) Free–Wilson[b]	Deviation[c]
	CF_3CH_2OH	110.9		–
Ph-SH			112.1	
	CF_3COMe	113.0		0.0
Ph-H		112.5	114.6	+2.1
	MeOH	119.2 (114.6)		−4.2 (−0.4)
Ph-OH			117.6	
	$(n\text{-Pr})_2S$	120.9		−2.1
	Me_2O	123.4 (119.2)		−2.9 (+1.3)
$Ph\text{-}CH{=}CH_2$			122.6	
Ph-Me			124.3	
	1,4-Dioxane	126.8		−1.3
	CF_3CO_2Et	128.0		−1.3
Ph-OMe		126.4	127.2	+0.8
	MeCHO	133.1		−2.9
	EtCHO	137.2		−2.1
	n-PrCHO	139.3		−2.1
	Et_2O	139.3		−0.8
	HCO_2Et	141.8		−2.1
	MeCN	142.3 (141.0)		−1.7 (−0.4)
	$(n\text{-Pr})_2O$	145.6		+2.1
	Me_2CO	147.7		+1.3

Halogenated benzenes not included, see Table 2.

[a] At 373 K; G2 calculations in parenthesis for the same temperature [19].

[b] LCBs for the compounds of interest obtained by a Free–Wilson treatment, see text. All values are anchored to the experimental GB of CF_3CH_2OH, which is the less basic compound of the series.

[c] These deviations correspond to the difference between the result of the Free–Wilson optimization and the published experimental values [19]. In parenthesis: the difference between the result of the Free–Wilson optimization and LCBs calculated at the G2 level [19].

Table 2
Lithium-cation basicities (LCBs in kJ mol^{-1} at 373 K) for the two halogenated benzenes not included in the Free–Wilson treatment

Compound (B)	Reference (Ref)	LCB (Ref)[a]	ΔLCB[b]	LCB (B)[c]
Ph-Br	C_5F_5N	93.3	+8.41 ± 0.70	101.7
Ph-Cl	C_5F_5N	93.3	+5.86 ± 0.40	
	Ph-Br	101.7	−2.19 ± 0.29	99.3

[a] Literature lithium-cation basicities at 373 K [19].

[b] Relative lithium-cation basicities obtained using the equilibrium method at 298 K, see text; the indicated uncertainty correspond to the standard deviation.

[c] Absolute lithium-cation basicities. No temperature correction; see text.

3. Computational details

The geometries of the different bases included in this study and those of their complexes with Li^+ have been optimized at the B3LYP/6-31G(d) level of theory. The B3LYP method combines Becke's three-parameter non-local hybrid exchange potential [35,36] with the non-local correlation functional of Lee et al. [37]. In general, geometries obtained using the aforementioned DFT method are in fairly good agreement with experimental values [38–42]. The harmonic vibrational frequencies were evaluated at the same level of theory so we can assess that the different structures found are local minima of the potential energy surface.

Final energies were evaluated using a 6-311+G(3df,2p) basis set expansion, which has been found well suited to reproduce experimental metal cation binding energies.

In all relevant cases, we have considered the possibility of forming two different complexes, those in which Li^+ interacts directly with the π cloud, and therefore is located above the six-membered ring, and those in which Li^+ interacts with the substituent.

4. Results and discussion

The optimized geometries of the neutral bases and those of the stable Li^+-complexes are schematized in Fig. 1. The complete sets of optimized geometrical parameters are available from the authors upon request. The total energies, as well as the lithium-cation

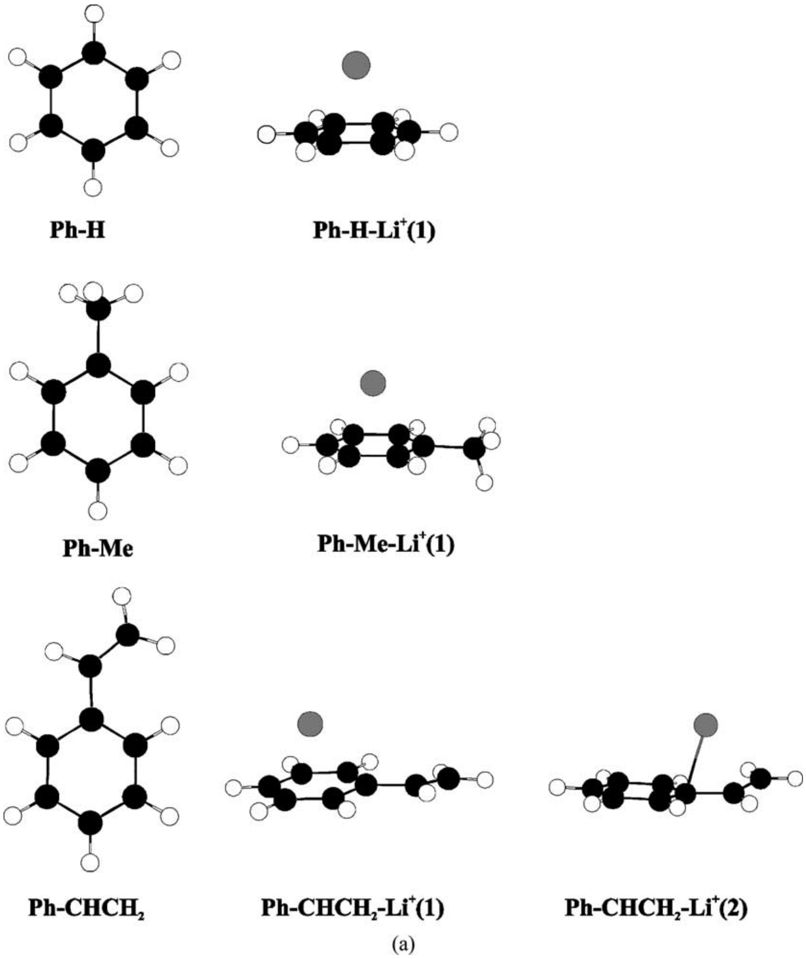

Fig. 1. Schematic representation of the B3LYP/6-31G(d) optimized geometries of the different Ph-X compounds included in this study and their Li^+ complexes.

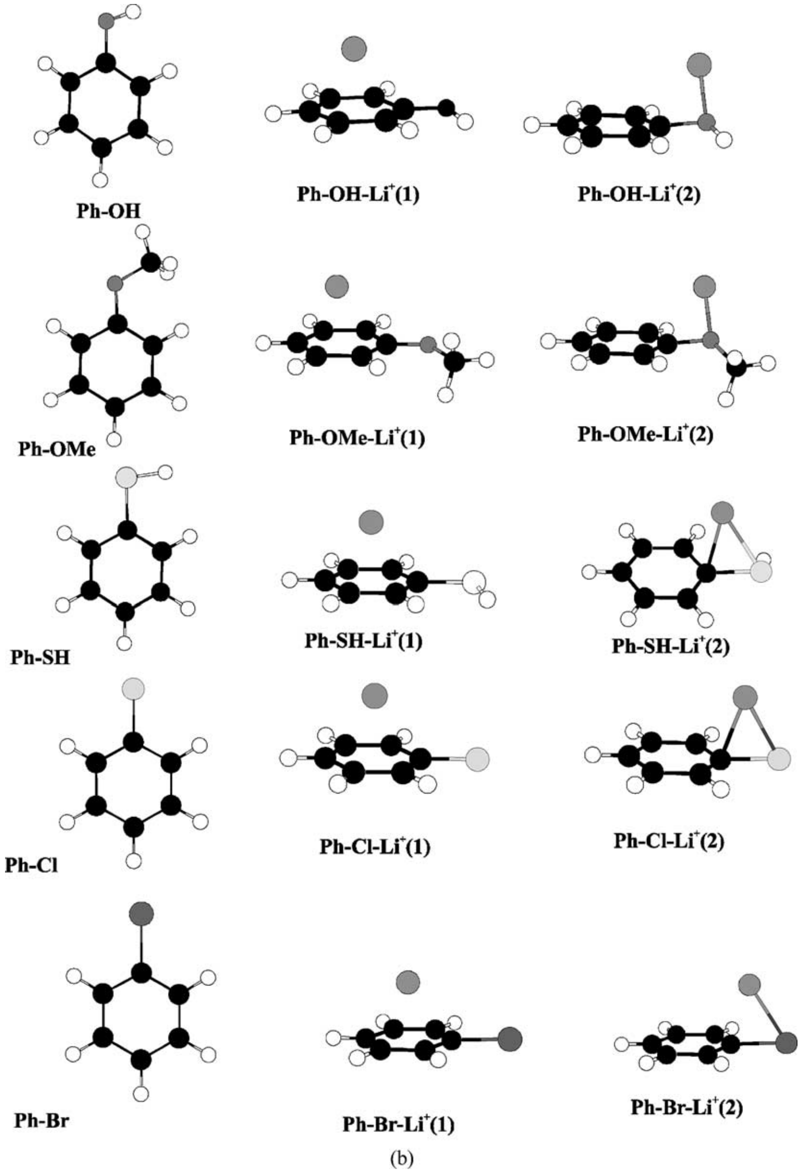

Fig. 1. (*Continued*).

binding enthalpies (BE(Li^+)) and lithium-cation basicities ($\Delta G(Li^+)$) are summarized in Table 3.

4.1. *Structures and vibrational frequencies*

Although a detailed analysis of the geometries of the complexes investigated was not the aim of this study, there are some structural features that deserve to be discussed in some detail. As it could be anticipated, with the only exception of toluene, and obviously benzene, two local minima are found for the different Ph-X-Li^+ complexes investigated. The first ones, designated hereafter as complex **1**, are those in which Li^+ locates above the benzene ring giving rise to

Table 3
Total energies[a] (E, hartrees), zero point energies[b] (ZPE, hartrees), entropy[b] (S, J K^{-1} mol^{-1}), Li$^+$ binding enthalpies[a] (BE(Li$^+$), kJ mol^{-1}), and Li$^+$ binding Gibbs free energies (ΔG(Li$^+$), kJ mol^{-1}) for different benzene substituted compounds[a]

System[c]	E	ZPE	S	BE(Li$^+$)[d]	ΔG(Li$^+$)[d]
Ph-H	−232.32747	0.10074	288.78		
Ph-H-Li$^+$ (1)	−239.67437	0.10352	307.78	161	118
Ph-Me	−271.65754	0.12832	333.38		
Ph-Me-Li$^+$ (1)	−279.00886	0.13119	345.09	172	127
Ph-CHCH$_2$	−309.75265	0.13373	345.23		
Ph-CHCH$_2$-Li$^+$ (1)	−317.10234	0.13642	364.35	167	125
Ph-CHCH$_2$-Li$^+$ (2)	−317.09332	0.13582	369.55	145	104
Ph-OH	−307.58060	0.10480	311.87		
Ph-OH-Li$^+$ (1)	−314.92873	0.10751	331.79	164	122
Ph-OH-Li$^+$ (2)	−314.92416	0.10641	346.15	154	117
Ph-Ome	−346.89301	0.13364	342.01		
Ph-OMe-Li$^+$ (1)	−354.24523	0.13625	362.70	175	133
Ph-OMe-Li$^+$ (2)	−354.24073	0.13534	378.68	162	128
Ph-SH	−630.54868	0.09960	333.64		
Ph-SH-Li$^+$ (1)	−637.89519	0.10236	349.12	160	116
Ph-SH-Li$^+$ (2)	−637.88787	0.10172	361.25	139	102
Ph-Cl	−691.95568	0.09122	318.95		
Ph-Cl-Li$^+$ (1)	−699.29477	0.09357	340.95	141	100
Ph-Cl-Li$^+$ (1)	−699.28704	0.09256	364.49	120	88
Ph-Br	−2805.87361	0.09083	330.28		
Ph-Br-Li$^+$ (1)	−2813.21307	0.09310	353.15	142	101
Ph-Br-Li$^+$ (2)	−2813.20628	0.09214	380.35	123	93
Li$^+$	−7.284918		133.04		

[a] Values obtained at the B3LYP/6-311+G(3df,2p) level.
[b] Values obtained at the B3LYP/6-31G* level.
[c] (1) stands for complexes where Li$^+$ lies above the aromatic ring; (2) stands for complexes where Li$^+$ interacts with the substituent.
[d] Values calculated at 373 K.

a π-complex. The second ones, designated as complex **2**, are those in which the cation interacts preferentially with the substituent. It is also worth noting that, even though in the latter complexes the starting point for our geometry optimizations corresponded to a complex in which the metal cation interacted with the heteroatom of the substituent, all of them collapsed to a "chelated" conformation in which the metal cation bridges between the heteroatom of the substituent and the *ipso* carbon atom. It is only in the case of toluene that all attempts to find a type **2** complex failed, and that only the π-complex **1** was obtained. It is also important to emphasize that for styrene there is no local minimum corresponding to the interaction of Li$^+$ with the C=C double bond of the substituent as it collapses also to a type **2** complex in which Li$^+$ bridges between the *ipso* carbon atom and the C$_\alpha$ carbon of the substituent. The formation of this kind of bridged structures is typical of those bidentate bases in which the two basic centers are neighbors. Actually, the formation of these "non-classical" bridged structures explained the enhanced basicity of some triazoles, tetrazoles [20] and diazines [22,23] and other polyfunctional compounds [19] with respect to alkali metals. In addition, the interactions of alkali-metal cations with disaccharides [43] and guanine [44] lead to the formation of chelated structures [43] in which the metal interacts with two or more basic centers of the neutral molecule.

For benzene, where only **1**-type complexes are possible, our optimized structure, in which Li$^+$ is found to be 1.876 Å above the center of the ring, is in good agreement with theoretical studies carried out at the MP2 ab initio level [32]. Also, our calculated BE (161 kJ mol^{-1} at 373 K; 159 kJ mol^{-1} at 298 K) is in fairly good agreement with the most accurate ab initio value reported in the literature (154 kJ mol^{-1} at

Table 4

C_{ipso}–X distances ($R_{C\text{–}X}$, Å), C–X stretching frequencies ($\nu_{C\text{–}X}$, cm^{-1}), ring-Li^{+} stretching frequency ($\nu_{\text{ring-Li}}$, cm^{-1}), C_{ipso}–Li^{+} stretching frequency ($\nu_{C_{ipso}\text{–Li}}$, cm^{-1}) and out-of-plane C–H bending frequencies ($\nu_{C\text{–}H}$, cm^{-1}) for Ph-X derivatives and their Li^{+} complexes

	$R_{C\text{–}X}$			$\nu_{C\text{–}X}$			$\nu_{\text{ring-Li}}$, complex **1**	$\nu_{C_{ipso}\text{–Li}}$, complex **2**	$\nu_{C\text{–}H}$		
	Neutral	Complex **1**	Complex **2**	Neutral	Complex **1**	Complex **2**			Neutral	Complex **1**	Complex **2**
H	1.087	1.086	–	3175	3213	–	388	–	864–969	1021–1042	–
Me	1.512	1.511	–	801	800	–	397	–	859–992	909–1027	–
$CHCH_2$	1.472	1.472	1.481	789	785	781	392	380	800–992	822–992	802–998
OH	1.369	1.343	1.414	833	839	809	394	563	823–980	879–1019	815–980
OMe	1.367	1.336	1.406	803	811	791	401	591	830–982	881–1014	829–982
SH	1.789	1.769	1.813	707	713	690	387	498	749–960	795–1009	762–995
Cl	1.761	1.733	1.790	710	722	702	373	497	756–994	803–1024	767–1032
Br	1.915	1.888	1.951	678	685	667	379	484	760–1002	803–1020	734–1000

298 K) [33] obtained using coupled cluster theory calculations, and with the experimental values of Woodin and Beauchamp (158.6 ± 8.4 kJ mol^{-1} at 298 K [5], corrected by Amicangelo and Armentrout, 155.2 ± 8.0 kJ mol^{-1} at 298 K [18]), and Amicangelo and Armentrout (164.4 ± 13.6 kJ mol^{-1} at 298 K [18]).

The formation of complexes **1** implies a sizable polarization of the aromatic π-electron density. As a consequence, there is a non-negligible charge transfer from the base toward the Li^+ cation, which in the complex has a net charge of +0.73e, in average. The withdrawing of charge from the π-cloud results in a slight weakening of all the C–C bonds of the benzene ring, which accordingly lengthen by 0.01 Å (1 Å = 0.1 nm), in average. These activation effects, although smaller, are also observed for complex **2**, where the metal cation bridges the *ipso* carbon and the heteroatom of the substituent.

However, the effects on the C–X bond for complexes **1** and **2** are opposite. The formation of complex **1** implies a reinforcement of the bond (see Table 4) whose stretching frequency is slightly blue-shifted. Conversely, in type **2** complexes, the C–X bond becomes longer, and its stretching frequency appears red-shifted (see Table 4). It is also worth noting that the former effect is very small for benzene, toluene and styrene. However, in the latter compound, the C=C stretching of the substituent appears red-shifted by 9 cm^{-1} in complex **1** and by 44 cm^{-1} in complex **2**, reflecting the polarization of this bond due to the presence of the metal cation. The interaction of Li^+ with the benzene moiety in type **1** complexes is also reflected in a systematic blue shifting of all the out-of-plane C–H bending modes (see Table 4). It is also worth noting that all the complexes investigated exhibit a vibration in the region 380–400 cm^{-1}, which corresponds to the vertical displacement of the metal cation with respect to the aromatic ring ($\nu_{\text{ring-Li}}$). In complexes of type **2**, one of the vibrational modes in the region between 380 and 590 cm^{-1} corresponds

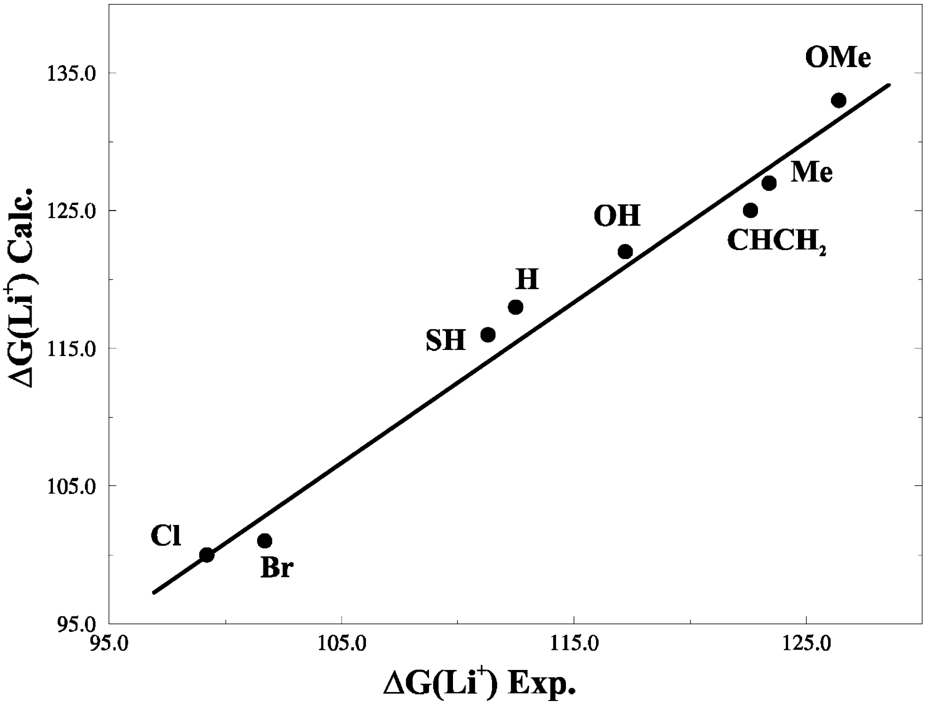

Fig. 2. Linear correlation between calculated and experimental lithium-cation basicities (LCB = $\Delta G(\text{Li}^+)$). All values in kJ mol^{-1}.

to the displacement of Li^+ with respect to the *ipso* carbon atom.

4.2. Lithium-cation basicities

The first conspicuous fact from Table 3 is that the π-complexes are systematically more stable than the complexes in which the metal monocation interacts with the substituent. For the particular case of anisole this finding is in agreement with previous ab initio studies [31] carried out at MP2/6-311+G* level, although our estimated binding energies are slightly higher than the ab initio ones. The gap between the Li^+ binding enthalpies for complexes **1** and **2** changes with the nature of the substituent, from about 10 kJ mol^{-1} for OH and OMe substituents to almost twice this value for substituents such as SH, Cl and Br. It is worth noting however, that the complexes in which Li^+ interacts with the substituent are entropically favored with respect to the π-complexes. As a consequence, the gaps between Li^+ cation basicities are smaller than for the corresponding enthalpies. Nevertheless, in terms of LCB = $\Delta G(Li^+)$ the π-complexes are still clearly favored.

There is a good agreement between the calculated LCB = $\Delta G(Li^+)$ values and the experimental ones (see Fig. 2). Actually, there is a good linear correlation ($r = 0.992$) between both sets of values with slope 1.169 and intercept −15.90, rather similar to that reported before in [19]. The fact that the slope of this correlation is close to unity can be taken as an indirect evidence that indeed the π-complexes are the ones experimentally formed in the gas phase.

It is well established that the gas-phase interactions between neutral molecules and alkali-metal cations are essentially electrostatic, also in complexes stabilized

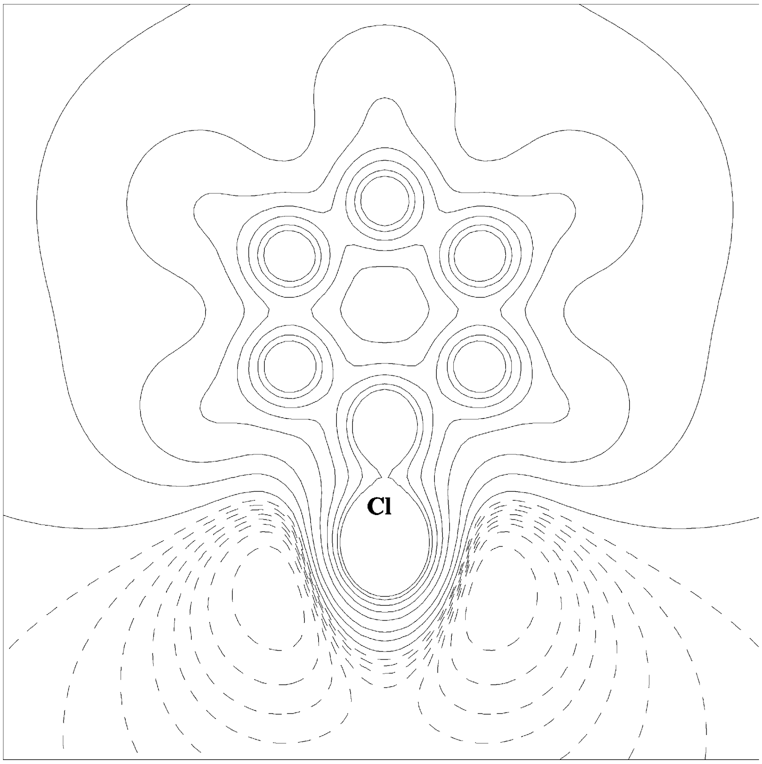

Fig. 3. Molecular electrostatic potential map of chlorobenzene evaluated in a plane parallel to the aromatic ring and 1.5 Å above it. Solid lines correspond to positive values of the potential and dashed lines to negative values.

by cation–π interactions [11]. However, polarization effects are crucial to understand the formation of the aforementioned chelated structures, when the base presents two neighbor basic centers. In these cases, the molecular electrostatic potential of the base presents typically two local minima associated with the lone pairs of both basic sites. However, as shown by Alcamí et al. [23], Li^+ is not trapped in any of these two local minima, as it would be the case for a proton, because of the presence of the $1s^2$ core of electrons, the metal cannot approach the base as much as a proton. The consequence is that Li^+ is normally located in a region where isopotential lines enclose the two local minima. Hence, in terms of purely electrostatic arguments, Li^+ would move freely from the vicinity of one minimum to the vicinity of the other. However, if polarization effects are taken into account, the most favored position corresponds to a point along the isopotential line and between both minima, in which Li^+ can polarize simultaneously both basic centers.

Let us take chlorobenzene as a suitable example. In Fig. 3, we show the molecular electrostatic potential map evaluated in a plane parallel to the aromatic ring and 1.5 Å above it. It can be seen that this map presents two regions in which the potential is attractive, one above the six-membered ring and another one above the lone pairs of the chlorine atom. This is consistent with the existence of two type of complexes. However, as illustrated in Fig. 4, where the molecular electrostatic potential map was evaluated in the plane which contains the chlorine atom and the *para* carbon atom and is perpendicular to the aromatic ring, the local minima associated with the chlorine lone pairs are deeper than that associated with the π-cloud. Then, in spite of this, the π-complex is more stable because when the Li^+ atom is located above the six-membered

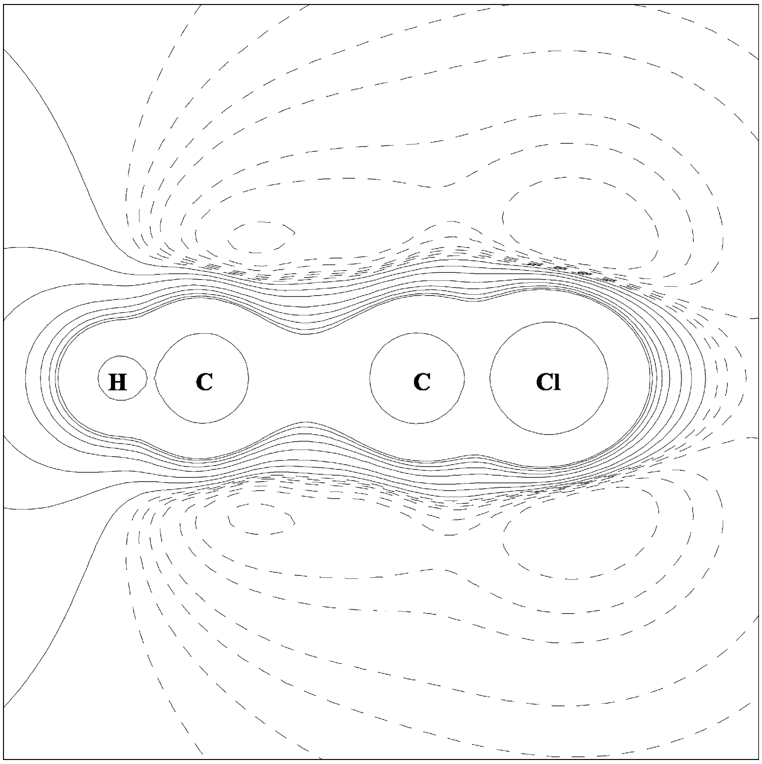

Fig. 4. Molecular electrostatic potential map of chlorobenzene evaluated in a plane perpendicular to the aromatic ring and which contains the chlorine and the *para* carbon atoms. Same conventions as in Fig. 3.

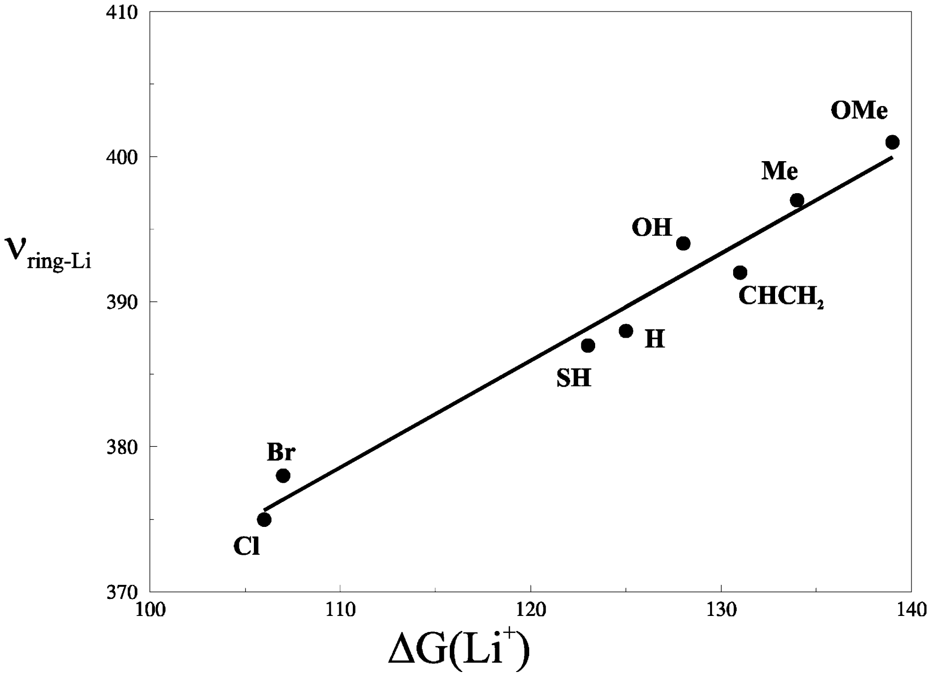

Fig. 5. Correlation between the frequency associated with the vertical displacement of Li^+ with respect to the aromatic ring (in cm^{-1}) and the calculated lithium-cation basicities (in $kJ\,mol^{-1}$).

ring it is able to polarize the whole π-system. For a similar reason, when the Li^+ interacts with the substituent it locates above the C–Cl bond, so that it polarizes simultaneously the chlorine lone-pairs and part of the π-system. A complete discussion of the role of "nonelectrostatic" interactions in complexes involving aromatics can be found in the review of Ma and Dougherty [11]. Also, in agreement with the conclusions presented in that review we have found, for the complexes under investigation, that the cation–π interaction cannot be explained in terms of ion–quadrupole interactions. Indeed, among all the neutrals considered, benzene is the one which exhibits the lowest quadrupole moment while it does not have the smallest binding energy.

It is also interesting to note that the intrinsic basicity of the aromatic π-system reflects the electron donor ability of the aromatic moiety as a function of the substituent. The derivatives with electron-withdrawing substituents are those which exhibit the lower LCBs. Consistently, there is also a good linear correlation between the frequency of the vertical displacement of the metal cation with respect to the aromatic ring, that we have called above $\nu_{\text{ring-Li}}$, and the calculated LCBs (see Fig. 5). Obviously, a similarly good correlation is found when using the experimental LCBs.

5. Conclusions

Our results show that for all the benzene derivatives investigated the π-complexes are favored with respect to those in which the metal monocation interacts with the substituent. These latter kind of complexes, which are entropically favored with respect to the π-complexes, are found to be chelated species, in which Li^+ bridges between the heteroatom of the substituent and the *ipso* carbon atom. The Li^+ basicity of the benzene derivatives investigated reflects the electron donor ability of the aromatic moiety as a function of the substituent. Consistently, there is a linear correlation between the LCB and the frequency of the vertical displacement of Li^+ with respect to the aromatic ring. There is also a very good linear correlation between LCBs calculated at the B3LYP/6-311+d(3df,2p) and the experimental ones. However, the slope of this correlation indicates that this method slightly overestimates the neutral–Li^+ interaction.

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