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Complexes between Lithium Cation and Diphenylalkanes in the Gas Phase: The Pincer Effect

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Abstract: The gas-phase lithium cation basicities (LCB values, Gibbs free energies of binding) of α,ω-diphenylalkanes Ph-$(CH_2)_n$-Ph ($n=2$, 3, or 7) and 1,1-diphenylethane Ph-CH(Me)-Ph were investigated by means of Fourier-transform ion cyclotron resonance (FTICR) mass spectrometry. Their structures, and those of the corresponding Li^+ complexes were optimized at the B3LYP/6-31G(d) level and their relative stabilities calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level. Whereas the most stable conformers of the free diphenylalkanes were found to adopt a completely stretched aliphatic chain connecting the two benzene rings, the most stable Li^+ complexes correspond to conformers in which the alkali metal cation interacts simultaneously with both benzene rings through the folding of the aliphatic chain ("pincer effect"). This chelation brings about a significant enhancement of the Li^+ binding enthalpies (LBE values), which were calculated to be approximately 75 kJ mol^{-1} higher than those evaluated for conventional (singly coordinated) π complexes in which the metal cation interacts with only one of the benzene rings. The increase of the corresponding lithium cation basicities, however, (Gibbs free energies of Li^+ binding, LCB values) was calculated to be smaller by approximately 15 kJ mol^{-1} as the pincer effect is entropically disfavored. The good agreement between the calculated LCB values, assuming a statistical distribution of the different conformers present in the gas phase, and the experimental LCB values measured by means of FTICR mass spectrometry are considered indirect evidence of the existence of the pincer effect.

Keywords: cation–pi interactions · density functional calculations · ion cyclotron resonance techniques · lithium · pincer effect

Introduction

In two series of articles, Allison and co-workers[1–5] and Schwarz and co-workers[6–10] showed that aliphatic chains might adopt a coiled conformation when interacting with a metal cation in the gas phase, due to an enhancement of polarization interactions. Significant coiling effects have also been described when different polyethers interact with alkali cations in the gas phase.[11] The important role of alkali metal cations in systems of biological significance is best understood when taking into account alkali cation–π interactions, as, for instance, in lariat ether receptors that exhibit enhanced interactions through the neutral arenes present in the system.[12] In the case of transition-metal ions, the coiling in such adducts is invoked as a driving force for a reaction remote from the initial binding center. This process was referred to as "remote functionalization".[8,9]

More recently, we have shown that binding in Li^+ and Cu^+ complexes of alkylbenzenes is enhanced by a similar effect that we called the "scorpion effect".[13,14] The interac-

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tion of alkylbenzenes with metal monocations in the gas phase triggers the coiling of the aliphatic chain in a manner that, besides the expected interaction between the metal and the aromatic π-electron system, enables an additional stabilizing interaction with a number of methylene groups of the aliphatic chain. In the present paper, we will show that an analogous folding and the simultaneous coordination of the two benzene rings of diphenylalkanes with the metal cation are responsible for an even larger basicity enhancement of these compounds when interacting with Li^+ in the gas phase.

Another interesting aspect of this study concerns our understanding of the cation–π interactions, among which the interactions with Li^+[15–23] and their role in molecular recognition phenomena[24] received a lot of attention. In particular, cation–π interactions are involved in protein side-chain orientation and protein folding, involving mechanisms similar to those described in this paper. Furthermore, [Li^+···diphenylalkane] adducts constitute a new category among conventional π complexes.

Finally, extended studies have shown that the reactivity of α,ω-diphenylalkanes with organic cations, such as *tert*-butyl and related cations, in the gas phase were found to be dominated by the solvation of the alkyl cation by both of the aromatic rings. Thus, the presence of the second ring was found to affect the competition between proton and hydride transfer within the [$tC_4H_9^+$···α,ω-diphenylalkanes] complexes[25–27] and the regiospecificity of the latter process,[26,28] in addition to the kinetics of gas-phase alkylation of α,ω-diphenylalkanes under radiolytic conditions ("spectator ring effect").[29,30] The simultaneous coordination of Fe^+ ions to the two aromatic rings of homologues α,ω-diphenylalkanes has also been invoked to explain the highly regioselective intramolecular dihydrogen abstraction,[31] and a similar coordination of Cr^+ ions to α,ω-diphenylalkanes has been deduced from the reactivity of the bare metal ions with these bidentate ligands.[32]

Results and Discussion

Experimental lithium cation basicities (LCB values): The experimental determination of the LCB values for Ph-CH(Me)-Ph and Ph-$(CH_2)_n$-Ph ($n=2, 3, 7$) was based on the nine reliable equilibrium measurements for which the resulting ΔLCB values and inferred LCB values are reported in Table 1. Absolute LCB values may be biased by the choice of the anchor point(s) of the scale, but the differences in LCB values between closely related compounds, within a short range of basicity, are likely to be much more reliable. These relative values (ΔLCB values) were anchored to the extensive absolute LCB scale recently reported,[18] which was established at 373 K. Theoretical estimates of temperature effects[19] 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 ΔLCB values determined at room temperature with the 373 K scale are expected to be less than 1.2 kJ mol^{-1} in general. Uncertainties on the ΔLCB values of the order of 1 to 4 kJ mol^{-1} can be evaluated by comparing the results obtained from the different references. Previous comparisons[19] of the values obtained for substituted benzenes with other published scales demonstrate that uncertainties in absolute LCB values are greater in general, in the ±5–15 kJ mol^{-1} range.

Table 1. Lithium cation basicities (LCB values in kJ mol^{-1} at 373 K) for diphenylalkanes.

Compound (B)	Reference (B_{Ref})	ΔLCB [kJ mol^{-1}][a]	LCB [kJ mol^{-1}]	
			B_{Ref}[b]	B[c]
Ph-CH(Me)-Ph	$(nPr)_2O$	+9.29 ± 1.71	145.6	
	$(iPr)_2O$	+10.92 ± 1.34	148.5	
	$(nBu)_2O$	−1.84 ± 0.75	152.7	155.2
Ph-$(CH_2)_2$-Ph	$HCONMe_2$	+2.72 ± 0.29	173.6	
	MeCONHMe	+2.43 ± 0.33	173.6	
	$MeCONMe_2$	−4.02 ± 2.97	179.1	175.7
Ph-$(CH_2)_3$-Ph	$MeCONMe_2$	+6.94 ± 0.46	179.1	
	$(MeOCH_2)_2$	−3.76 ± 0.50	187.9	184.9
Ph-$(CH_2)_7$-Ph	$MeCOCH_2COMe$	+3.76 ± 0.96	180.3	184.1

[a] Given uncertainties correspond to the standard deviation of several experiments carried out at different partial pressures of B_{Ref} and B. [b] LCB values for compounds used as references (B_{Ref}) see reference [18]. [c] The accuracy of these values is discussed in the Experimental Section.

Structures, relative stabilities, and bonding: In Figures 1 and 2, we have schematized the structures and the relative stabilities of the most stable conformers of Ph-CH(Me)-Ph and Ph-$(CH_2)_n$-Ph ($n=2, 3, 4, 7$) that we have named **A**, **B**, **C**, **D**, and **E**, respectively, followed by a number that, when needed, indicates their relative stability order. The most stable Li^+ complexes will also be named as **ALi**, **BLi**, etc. and, where necessary, will also be identified by a number that indicates their relative stability order. As a first member of the diphenylalkane series, we decided to study the complexation of Ph-CH(Me)-Ph, equivalent to Ph-CH_2-Ph in terms of aliphatic chain length, but more similar to Ph-$(CH_2)_2$-Ph in terms of the polarizability of the aliphatic chain. Their total energies, thermal enthalpy corrections, and entropies are provided in the Supporting Information.

The first conspicuous fact that can be deduced from Figures 1 and 2 is that for the neutral the global minimum corresponds systematically to the conformer in which the aliphatic chain connecting the two benzene rings is unfolded to its maximum extension. It is also worth noting that when the number of CH_2 groups is even ($n=2, 4$) the global minimum corresponds to the conformer in which the two benzene rings lie in parallel planes and perpendicular to the plane defined by the carbon skeleton of the aliphatic chain. Interestingly, a torsion angle of 90° for one of the benzene rings (Scheme 1) destabilizes the system by 10 kJ mol^{-1} or more in terms of Gibbs free energies, therefore these alternative conformers are not likely to be found in the gas phase at room temperature.

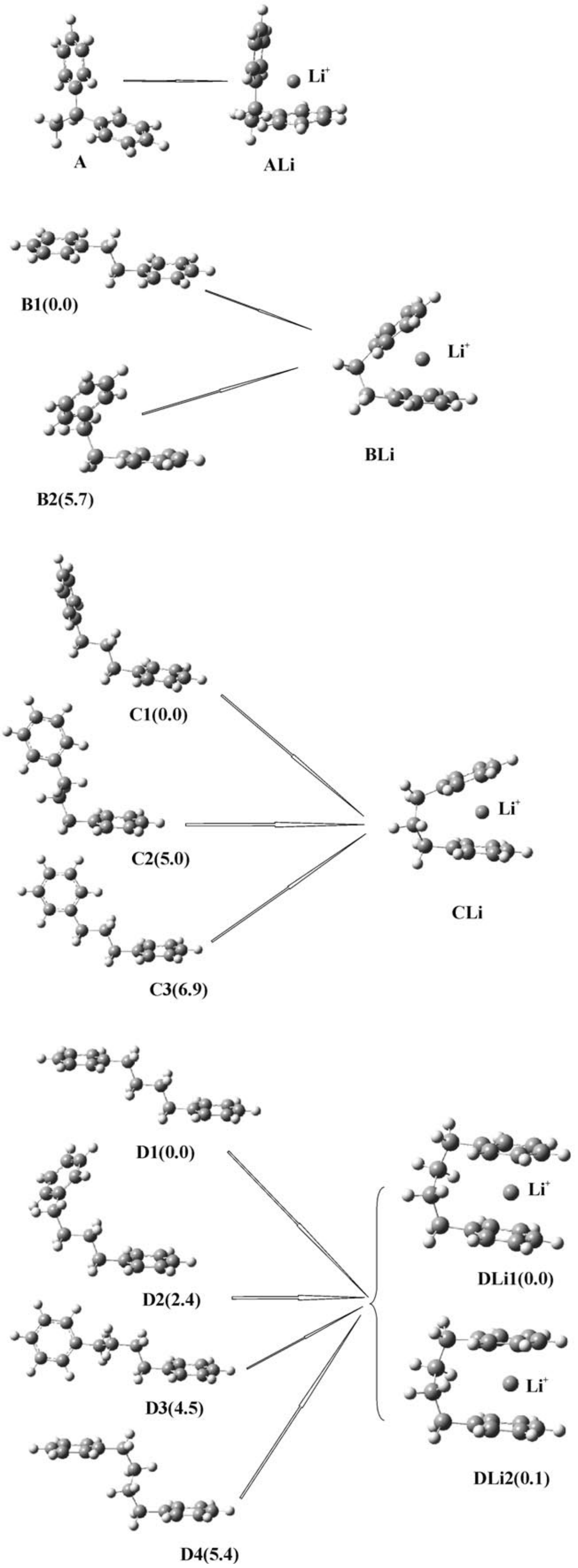


Figure 1. Structures of the most stable conformers of Ph-CH(Me)-Ph, Ph-$(CH_2)_n$-Ph ($n=2$, 3, 4), and their Li^+ complexes. Relative energies in $kJ\,mol^{-1}$.

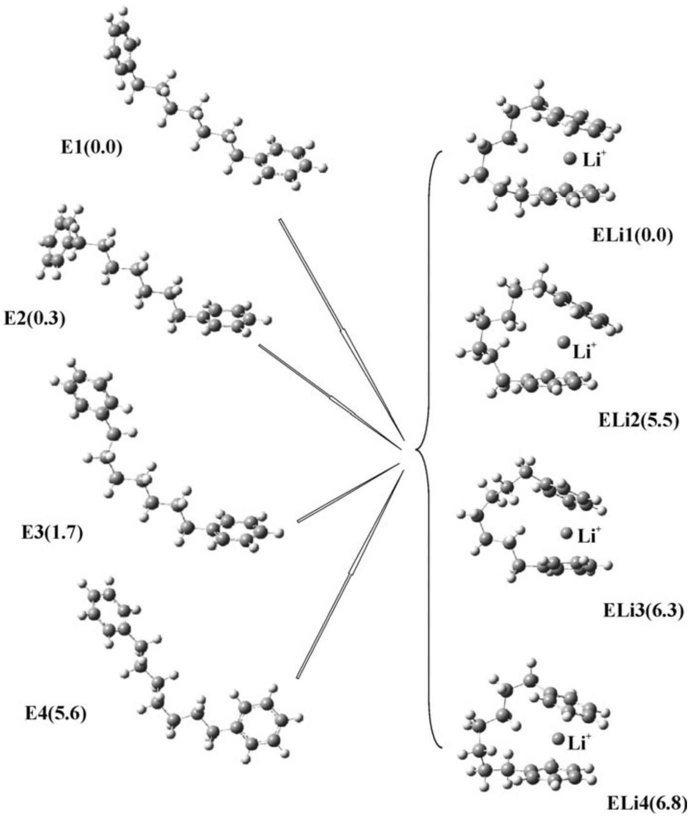
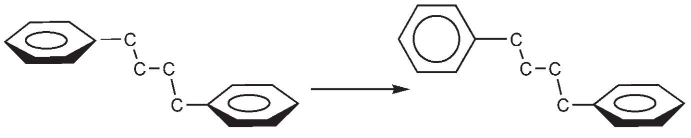


Figure 2. Structures of the most stable conformers of Ph-$(CH_2)_7$-Ph and its Li^+ complexes. Relative energies in $kJ\,mol^{-1}$.



Scheme 1.

The different Li^+ complexes can be classified into two subsets, those in which the metal cation interacts with only one of the benzene rings and those in which the aliphatic chain folds up to favor the interaction of the metal cation with both of the benzene rings. However, the most important finding is that the complexes of the first kind are much less stable than those of the second kind. For example, the complexes that can be formed by direct attachment of Li^+ to Ph-$(CH_2)_n$-Ph ($n=4$, 7) in their global minimum conformations, namely **DLi5** and **ELi5** (Figure 3), are 88 and 86 $kJ\,mol^{-1}$ less stable in terms of enthalpies than the coiled structures shown in Figures 1 and 2, respectively. When looking at the corresponding Gibbs free energies, this gap decreases to 75 and 74 $kJ\,mol^{-1}$, because the coiled structures are entropically less favored than the unfolded ones. We have named this binding enhancement the "pincer effect" as the two aromatic rings "grab" or "clutch" the metal cation similar to a crab pincer. It is worth noting that these coiled conformations are stable only when the metal

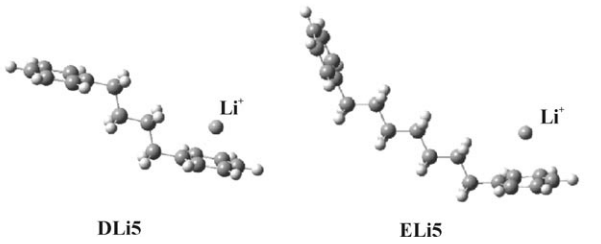


Figure 3. Structure of the complexes formed as Li^+ adducts to the most stable conformers of Ph-$(CH_2)_n$-Ph ($n=4$, 7)

cation is interacting with the two benzene rings. As a matter of fact, in the absence of this twofold interaction, for instance if the structure of the Ph-$(CH_2)_n$-Ph ($n=4$, 7) moiety in complexes **D1** and **E1** is reoptimized after eliminating the Li^+ ion, the initial structure evolves to a conformation in which the interaction between the two aromatic rings decreases, either by changing their relative orientations or by moving the rings apart from each other by partially defolding the aliphatic chain. In any case, the local minima found in this way are among the less stable of the potential energy surface (PES).

For neutral Ph-CH(Me)-Ph, only the conformer in which the planes containing both benzene rings form a dihedral angle of 51° was found to be a minimum of the PES. Obviously, in this case no coiling effect can be produced upon Li^+ association, but as clearly shown in Figure 1, the angle between both aromatic rings closes significantly (from 112.2 to 104.6°) upon association of the Li^+ ion and the hydrocarbon.

In the complexes that exhibit this pincer effect, the metal cation interacts with both aromatic rings, but this interaction is weaker than in complexes in which the metal attaches to only one benzene ring. This difference is reflected in the metal–ring distances and in the distortion of the rings. In the complexes in which the metal interacts only with one of the benzene rings, the distance between the metal cation and the plane of the ring (1.796–1.802 Å, 1 Å = 0.1 nm) is slightly shorter than that found, at the same level of accuracy,[19] for the benzene-Li^+ complex (1.876 Å), reflecting the electron-donating effect of the aliphatic chain and increasing consequently its intrinsic basicity. Conversely, in those complexes that exhibit a pincer effect, the distance between the metal cation and both benzene rings becomes longer (about 1.914 Å). This can be understood by taking into account the repulsive interaction between the two π systems. These findings are in line with the results reported by Amicangelo and Armentrout[33] on the binding of Li^+ to two benzene rings, which showed that the $(C_6H_6)Li^+{-}C_6H_6$ bond dissociation energy (BDE) is smaller than the $Li^+{-}C_6H_6$ BDE. In this respect, it is also worth noting that the stability enhancement of the complexes exhibiting the pincer effect is of the same order of magnitude (around 75 kJ mol^{-1}) as the $(C_6H_6)Li^+{-}C_6H_6$ BDE[33] (about 104 kJ mol^{-1}). The weaker interaction with the aromatic rings in complexes exhibiting the pincer effect is also mirrored in the electron density of the system. As illustrated in Figure 4, in these complexes a bond critical point (bcp) is located between the metal and each ring, but the electron density at these points is smaller than that associated with the bcp when the metal ion interacts with only one benzene ring. Accordingly, the polarization of the aromatic rings leads to an average lengthening of the C–C bonds of the ring of 0.01 Å in the complexes in which the metal cation interacts only with one aromatic ring and of only 0.008 Å in complexes in which the interaction involves the two benzene rings. Nevertheless, although the interaction with each of the aromatic rings in the complexes that exhibit a pincer effect is weaker than in the complexes for which Li^+ interacts only with one ring, the overall stabilization is larger. It is worth noting that in pincer-type complexes the Li^+ ion is located symmetrically at the same distance from both aromatic rings; accordingly, the charge densities at the corresponding bcps indicate that the strength of the interaction is the same with both rings.

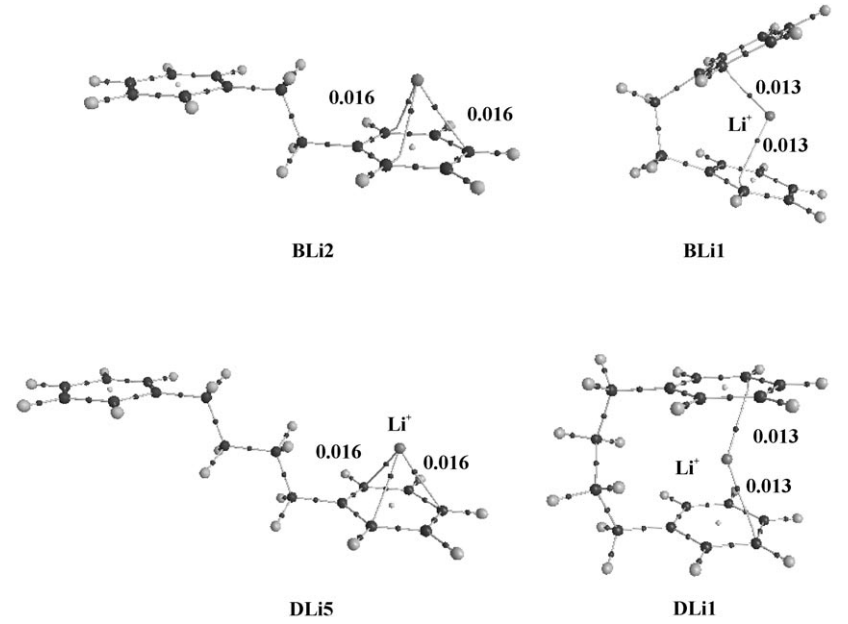


Figure 4. Molecular graph of complexes in which Li^+ interacts with only one benzene ring of Ph-$(CH_2)_n$-Ph ($n=2$, 4), and those which exhibit a pincer effect. The dots are bond and ring critical points. Electron density values are in a.u.

Calculated lithium cation basicities: The calculated LBE values and LCB values for the compounds under investigation are summarized in Table 2. Only for Ph-CH(Me)-Ph, in which only one conformer is found to be stable both for the neutral molecule and for the Li^+ complex, can a direct comparison be made between calculated and experimental values. As shown in Table 2, the agreement between the calculated and the experimental LCB values is very good. To evaluate the LCB values for the remaining systems under investigation, it is necessary to take into account the fact that both the neutral compounds and their Li^+ complexes are in fact a statistical mixture of the most stable conformers. Hence, based on the relative Gibbs free energies of the different conformers, evaluated at 298 K, the diphenylalkanes Ph-$(CH_2)_n$-Ph ($n=2$, 3) should be an equilibrium mixture of **B1** (86.3 %) and **B2** (13.7 %), and of **C1** (76.5 %), **C2** (15.3 %), and **C3** (8.3 %), respectively. In both cases, only one conformer, **BLi** and **CLi**, respectively, can be assumed to be the product of Li^+ association. Under this assumption the estimated LCB values are 175.3 and 186.7 kJ mol^{-1}, respectively, in fairly good agreement with the corresponding experimental values, and only for Ph-$(CH_2)_3$-Ph, the theoretical value overestimates the experimental one by 4 kJ mol^{-1}.

Table 2. Calculated[a] LBE and LCB values for diphenylalkanes.

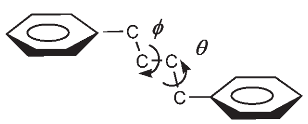
Compound	LBE	LCB
Ph-CH(Me)-Ph	198.6	153.8 (155.2)[b]
Ph-$(CH_2)_2$-Ph	228.7	175.3 (175.7)
Ph-$(CH_2)_3$-Ph	247.8	186.7 (184.9)
Ph-$(CH_2)_4$-Ph	245.8	186.4 –
Ph-$(CH_2)_7$-Ph	254.3	188.1 (184.1)

[a] Values in kJ mol^{-1} obtained at the B3LYP/6-311+G(3df,2p) level of theory. [b] Experimental values within parentheses.

Similarly, Ph-$(CH_2)_n$-Ph ($n=4$, 7) should be an equilibrium mixture of the structures shown in Figures 1 and 2 in the following proportions: $n=4$ (**D1** 53.4 %, **D2** 24.6 %, **D3** 12.5 %, **D4** 9.4 %) and $n=7$ (**E1** 37.7 %, **E2** 34.2 %, **E3** 21.8 %, **E4** 6.2 %). For $n=4$, the Li^+ complexes should also be a mixture of the **DLi1** (50.8 %) and **DLi2** (49.2 %), while for $n=7$, the mixture should include 70.8 % of **ELi1**, 12.0 % of **ELi2**, 9.3 % of **ELi3**, and 7.9 % of **ELi4**. As shown in Table 2, again the agreement between the calculated and the measured LCB values is very good, although for Ph-$(CH_2)_7$-Ph the calculated values are slightly too high.

Two points should be emphasized at this stage. Firstly, if the metal cation was attached to only one of the benzene rings, yielding structures, such as **DLi5** and **ELi5** (see Figure 3), the measured LBE and LCB values would be about 70 and 55 kJ mol^{-1} lower, respectively. In other words, the pincer effect is responsible for quite a significant enhancement in the basicity of diphenylalkanes with respect to Li^+. The enhancement is necessarily smaller in terms of LCB values, because the chelated structures associated with the pincer effect are entropically less favorable than those in which the metal cation interacts with only one of the benzene rings. Secondly, this enhancement is already observed for $n=2$ and does not change significantly with longer aliphatic chains between the aromatic rings. This is easily explained if one takes into account the fact that two methylene groups between the benzene rings are enough to allow them to reorient themselves to interact more efficiently with the metal cation (Figure 1). The existence of a significant pincer effect already in 1,2-diphenylethane, Ph-$(CH_2)_2$-Ph, is mirrored by its increased LBE and LCB (by more than 20 kJ mol^{-1}) with respect to the 1,1-isomer, Ph-CH(Me)-Ph, in which, as mentioned above, the interaction with the cation leads only to a decrease of the dihedral angle between the benzene rings.

Torsional barriers: As the most stable neutral conformation of diphenylalkanes corresponds to a completely unfolded arrangement of the aliphatic chain, the formation of the most stable Li^+ complexes requires that the system has enough internal energy for the aliphatic chain to coil up to favor the interaction of both benzene rings with the metal cation. This would be so if the exothermicity associated with the formation of the Li^+-complex is larger than the barriers involved in the corresponding torsions. To check if this is indeed the case we have used the Ph-$(CH_2)_4$-Ph homologue as a representative model system. The torsion barriers were estimated by increasing the value of φ and θ (defined in Scheme 2) in steps of 5°, starting from the completely stretched conformer **D1**.



Scheme 2.

The corresponding potential energy curves are plotted in Figure 5. Although, to the best of our knowledge these torsion barriers are not known experimentally, our calculated values, 12.6 and 12.0 kJ mol^{-1}, respectively, are in very good agreement with those reported previously for butylbenzene[13] and with the experimental rotational barrier for ethane (12.0 ± 0.04 kJ mol^{-1}).[34] We can safely assume that such barriers are easily overcome during the Li^+ cation exchange between $B_{ref}Li^+$ and the diphenylalkanes, as the interaction energy between the ion and the neutral molecule in the reaction intermediate is much higher. In fact, the conformational change in the diphenylalkanes arises in the presence of the electric field of the approaching ion. However, it has been shown for similar systems[13] that the value of the torsional barrier remains practically unchanged in the presence of the electric field. Hence, under normal experimental conditions, the system should have enough internal energy to coil the aliphatic chain to approach the two benzene rings to the metal cation, giving rise to what we have named the "pincer effect".

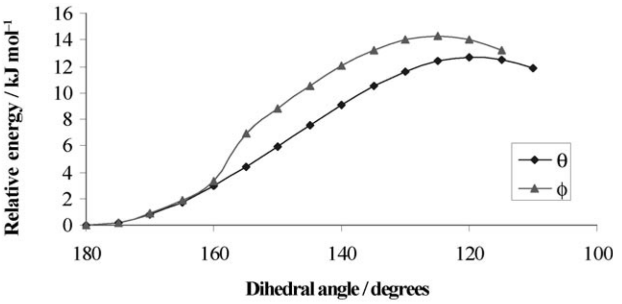


Figure 5. Potential energy curves corresponding to changes of the dihedral angles θ and φ defined in Scheme 2.

Conclusion

Our results show clearly that diphenylalkanes exert an enhanced basicity towards Li^+, and this enhancement has been named the "pincer effect". Upon Li^+ association in the gas phase, the aliphatic chain connecting the two benzene rings adopts a conformation favoring the interaction of both of the aromatic rings with the metal cation. The important finding is that those complexes in which the metal interacts with only one of the benzene rings are predicted to be about 75 kJ mol^{-1} higher in terms of enthalpies. The gap is about 15 kJ mol^{-1} smaller in terms of Gibbs free energies, because the pincer effect involves a decrease in the entropy of the system. Our study also shows that two methylene groups in the aliphatic chain are sufficient to fully observe this effect because the system has enough flexibility to bring both aromatic rings to interact with the metal cation. The main consequence of this is that the basicity enhancement by the pincer effect does not increase significantly further when the length of the chain is increased in the higher homologues of the α,ω-diphenylalkanes.

The importance of these findings is that these structural adjustments may also be possible in natural systems when they contain two or more aromatic subunits connected by flexible atomic chains, triggering their folding.

The good agreement between the calculated LCB values, assuming a statistical distribution of the different conformers present in the gas phase, and those measured by means of Fourier-transform ion cyclotron resonance (FTICR) mass spectrometry lend support to the existence of the pincer effect.

Experimental Section

Syntheses of the diphenylalkanes: The preparation of the hydrocarbons studied here and of various deuterium labeled analogues have been previously described.[35–39] 1,2-Diphenylethane is a crystalline solid of m.p. 52–53 °C,[35] which was recrystallized from ethanol prior to use.[36] By contrast, 1,3-diphenylpropane[37] and 1,7-diphenylheptane[38] are slightly oily liquids which were purified by microdistillation and later by kugelrohr distillation. The purities of the α,ω-diphenylalkanes were checked by ^{1}H NMR spectroscopy and EI mass spectrometry. The sample of 1,7-diphenylheptane used in this study was slightly contaminated by 1,4-diphenylbutane (approximately 3 %). 1,1-Diphenylethane was most conveniently synthesized by catalytic hydrogenolysis of commercially available 1,1-diphenylethanol (Aldrich): To a solution of this alcohol (1.0 g, 5.0 mmol) in ethanol (80 mL) was added palladium-on-charcoal (10 % Pd, Merck, 100 mg) and 2 drops of sulfuric acid (2 N). The mixture was shaken in a Parr apparatus under hydrogen (6.0 bar, 25 °C) for 20 h. TLC control revealed complete conversion of the starting material. The solution was filtered to remove the catalyst and then filtered through potassium carbonate to remove the traces of acid. Evaporation of the solvent under reduced pressure furnished a colorless liquid (750 mg, 82 %), which was virtually pure by ^{1}H NMR spectroscopy, but was subjected to Kugelrohr distillation (b.p. 155–158 °C, approximately 10 mbar). Final yield: 670 mg, 73 %; ^{1}H NMR (Bruker DRX 500, 500 MHz, $CDCl_3$): $\delta =$ 1.70 (d, $^3J=7.1$ Hz, 3 H), 4.21 (q, $^3J=7.2$ Hz, 1 H), 7.235 (t, $^3J=7.2$ Hz, 2 H^{para}), 7.282 (d, $^3J=7.1$ Hz, 4 H^{ortho}), 7.337 ppm (t, $^3J=7.3$ Hz, 4 H^{meta}).[39]

FTICR measurements. The gas-phase lithium cation basicity (LCB), defined as the Gibbs free energies of a base B for the process represented by Equation (1)

$$BLi^+ \rightarrow B + Li^+ \qquad (1)$$

has been determined by Fourier-transform ion cyclotron resonance (FTICR) mass spectrometry for the diphenylalkanes Ph-CH(Me)-Ph and Ph-$(CH_2)_n$-Ph ($n = 2, 3, 7$).

Lithium-cation-transfer equilibrium constants were determined by a method similar to that described by Burk et al.,[18] the lithium ion being exchanged between the phenylalkanes (B) and the reference compounds (B_{Ref}) [Eq. (2)].

$$B_{Ref} + BLi^+ \rightleftharpoons B_{Ref}Li^+ + B \qquad (2)$$

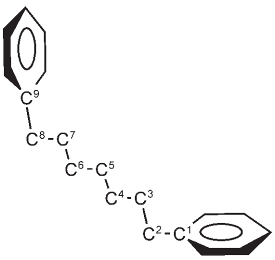
The FTICR mass spectrometer utilized was designed on the basis of an electromagnet (1.6 Tesla with a pole gap of 50 mm) and Bruker CMS 47 electronics. The cylindrical ICR cell has a diameter of 30 mm. The vacuum system (10^{-7} Pa range, obtained either with a turbopump or a diffusion pump) containing the cell is connected to a manifold equipped with four leak valves for the introduction of precise partial pressures of the compounds to be studied. This introduction system is evacuated by a diffusion pump. The pressure in the cell was monitored by a Bayard–Alpert ionization gauge, the readings of which were corrected by using calculated ionization cross sections.[18] The main differences with the method previously described[18] were the Li^+ source and the working temperature. In this work, the lithium cation was generated by laser ablation (pulsed nitrogen laser, 337 nm, 200 μJ per pulse) from a lithium benzoate target, as a pellet obtained by compression of the salt.[13] Direct adduct formation between Li^+ and B and B_{Ref} was observed, and addition of a promoter reactant, such as 2-chloropropane,[13] was not necessary. Equilibrium constants were determined at three or more different pressure ratios. The total pressure was in the 10^{-5} Pa range. Reaction times were about 10 s. As there was no heat source close to the ICR cell (except for the electromagnet poles at about 30 °C, which are outside the vacuum chamber), the experiments were conducted at a temperature close to 25 °C (298 K). The major difficulty encountered during the measurements was the formation of lithium-ion-bound dimers of reference compounds available in the range of basicity, mainly in the upper part. This was particularly the case for 1,7-diphenylheptane, for which equilibrium was achieved only with one reference compound.

Computational details: The geometries of the diphenylalkanes included in this study and their Li^+ complexes were optimized by use of standard B3LYP/6-31G(d) procedures. The same level of theory was used to calculate the harmonic vibrational frequencies, which allowed us to characterize the different stationary points as true local minima of the PES and to estimate the zero point energy (ZPE) corrections, as well as the different thermal corrections. Final energies were evaluated in single-point calculations carried out at the B3LYP/6-311+G(3df,2p) level. The B3LYP density functional theory method combines Becke's three-parameter nonlocal hybrid exchange potential[40] with the nonlocal correlation functional of Lee, Yang, and Parr[41] and it provides metal cation binding energies in fairly good agreement with the experimental values.[42,43] Although DFT methods do not properly describe dispersion interactions, these are a rather small component of LCB values and the good performance of these methods, as far as Li^+ complexes are concerned, has been assessed in several combined theoretical and experimental studies.[18–20,44]

Li^+ binding enthalpies, LBE values, were evaluated by subtracting the energy of the neutral ligand and that of Li^+ from the energy of the complex, after including the zero point energy (ZPE) corrections and the aforementioned thermal corrections at 373 K, which is the temperature of the reference scale used to anchor our data. The corresponding lithium cation basicities (LCB values, Gibbs free energy of binding) were obtained by using the entropy values evaluated at the B3LYP/6-31G(d) level. The use of a harmonic approximation induces errors in the low-frequency torsions of the systems under investigation, which are significantly anharmonic, and therefore in our estimates of the Gibbs free energies. Unfortunately, we have not found experimental information on the entropy for large saturated hydrocarbons, such as *n*-heptane, but this information is available for *n*-butane[45] and for tetramethylsilane,[46] which has four free-rotating methyl groups. Our calculated entropies at the B3LYP level differ from the experimental one by 7.5 and 7 $kJ\,mol^{-1}\,K^{-1}$, respectively, which implies an error in the Gibbs free energy at 373 K of 2.6–2.8 $kJ\,mol^{-1}$. Hence, we can estimate that our error of the Gibbs free energies for the compounds under investigation should not be larger than 4 $kJ\,mol^{-1}$. Given that, as discussed above, both neutral and cationized species are a mixture of several conformers in the gas phase, we have also included the corresponding entropy of mixing, evaluated as follows [Eq. (3)]:

$$\Delta S_{\mathrm{mix}} = -\sum \chi_i \ln \chi_i \qquad (3)$$

in which χ_i is the mole fraction of the i^{th} component within the mixture.



Scheme 3.

The different conformers of each neutral compound were generated in a systematic way by starting from the most stable conformer that corresponds to the one bearing a completely stretched aliphatic chain (Scheme 3).

The different conformers were generated by torsions around the C^n–C^{n+1} bonds ($n = 1$–9, numbering given in Scheme 1). Each of the conformers generated in this way can now be taken as a precursor of new conformers by successive C–C torsions. It is obvious that, in particular for $Ph(CH_2)_4Ph$, but mainly for $Ph(CH_2)_7Ph$, the number of conformers is so high that it would be an impossible task to calculate all of them. Nevertheless, from the exploration of the smaller compounds with two and three methylene groups in the aliphatic chain, it was possible to discard "a priori" many conformations that would lie very high in energy. Even though, more than one hundred structures were located. The calculations at the B3LYP/6-311+G(3df,2p) level were performed exclusively for conformers for which the energy differs from that of the global minimum by less than 7 $kJ\,mol^{-1}$, assuming that in terms of a Boltzmann distribution the population in the gas phase of the less-stable conformers would be negligibly small. To make our discussion more systematic, the different conformers were numbered following the stability order.

The situation is quite different for the $[Li^+\cdots Ph(CH_2)_nPh]$ complexes. Here again, the number of conformers is very high and increases dramatically as the number of carbon atoms in the aliphatic chain increases. However, as discussed above, all those complexes in which Li^+ interacts with only one of the benzene rings (which are the great majority of the local minima on the PES) are much less stable than those in which the metal interacts with both of the benzene rings. Hence, only the latter (which are very few) matter as far as the calculation of the Li^+ binding energies is concerned.

All calculations have been carried out by the Gaussian 03 series of programs.[47] The bonding characteristics of the complexes formed were analyzed by means of the atoms-in-molecules (AIM) theory.[48] For this purpose, the electron density was evaluated at the different bond critical points (bcps), and the corresponding molecular graph was obtained.

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