Aromaticity Analysis of Lithium Cation/π Complexes of Aromatic Systems

Mireia Güell,[a] Jordi Poater,[b] Josep M. Luis,[a] Otilia Mó,[c] Manuel Yáñez,[c] and Miquel Solà*[a]

The changes in the local aromaticity of aromatic rings on complexation with lithium cation are discussed for a series of polycyclic aromatic hydrocarbons by using, as probes of aromaticity, the para-delocalization index (PDI), the aromatic fluctuation index (FLU), the harmonic oscillator model of aromaticity index (HOMA), and the nucleus-independent chemical shift (NICS). In most cases, changes in the electronically based PDI and FLU indices are almost irrelevant. For this reason, the analysis is carried out mainly with the more sensitive HOMA and NICS descriptors. These indices indicate that changes in the local aromatic character of the different rings are small. In general, Li+ interacts more favorably with the ring having the largest π charge, but there is no correlation between these magnitudes. The ring directly interacting with the lithium cation suffers a slight but significant reduction of aromaticity, while the reduction of the local aromaticity of the adjacent rings is minor. For those rings located further away from the ring directly connected to Li+, we found generally a small increase in aromaticity. Although there is no clear correlation between aromaticity and Li+ binding enthalpies, there is a rough correlation between the latter and the change in the aromaticity of the ring directly interacting with the metal cation.

1. Introduction

In the last two decades, extensive experimental and theoretical investigations have been carried out for alkali metal cation/π complexes involving aromatic rings to investigate the participation of these complexes in important processes related to chemical and biological recognition.[1–20] With few exceptions,[4, 16] all of these works have concentrated mainly on gas-phase basicities of alkali metal cations. Only few of them[18, 19] have concisely analyzed the change in aromaticity of aromatic rings on complexation of alkali metal cations by using nucleus-independent chemical shifts (NICS)[21] as indicators of aromaticity. Garau et al.[18, 19] found that cation/π complexes have more positive NICS that indicate a reduction in aromaticity on complexation of the cation. The analysis of these authors was restricted to species derived from binding of alkali metal cations to monocyclic aromatic systems such as benzene, 1,3,5-trifluorobenzene, s-triazine, and 2,5-dichloropyrazine. Systems having more than one aromatic ring are particularly interesting because it is possible to discuss whether the strength of the binding to a given aromatic ring is related to its aromatic character or to the change in aromaticity on association with Li+. Thus, it seems pertinent to extend this analysis to fused aromatic species. Moreover, Garau et al.[18, 19] used only the NICS as a descriptor of aromaticity. However, as found by Katritzky, Krygowski et al. by means of principal component analyses[22–26] and also as pointed out by other authors,[27–29] aromaticity is a multidimensional property. This means that the different quantitative measures of aromaticity based on different physical phenomena (energetic, magnetic, geometric, or electron-delocalization properties) are not necessarily correlated. Indeed, some of these criteria are even considered to be orthogonal.[25] In addition, several studies have confirmed that different indices of aromaticity can afford divergent answers.[29–32] In this sense, it has been proposed that fully aromatic systems are those cyclic π compounds that fulfill most aromatic criteria. Those that fulfill only some should be considered only as partly aromatic.[26] As a consequence of this multidimensional character of aromaticity, aromatic compounds cannot be fully characterized by a unique index. Thus, to make reliable comparisons restricted to groups of relatively similar compounds it is usually recommended to employ a set of aromaticity descriptors.[26, 29–32] For this reason, it seems also convenient to analyze the changes in local aromaticity on complexation of alkali metal cations by using a series of indicators of aromaticity.

We have analyzed the changes in local aromaticity on Li+ association in a series of extended fused aromatic compounds. The aim is to discuss whether the strength of binding of the lithium cation to a given aromatic ring in a molecule is related

[a] M. Güell, Dr. J. M. Luis, Prof. Dr. M. Solà
Institut de Química Computacional and Departament de Química
Universitat de Girona, Campus de Montilivi
17071 Girona, Catalonia (Spain)
Fax: (+ 34) 972-418356
E-mail: miquel.sola@udg.es

[b] Dr. J. Poater
Afdeling Theoretische Chemie
Scheikundig Laboratorium der Vrije Universiteit
De Boelelaan 1083, NL-1081 HV Amsterdam (The Netherlands)

[c] Prof. Dr. O. Mó, Prof. Dr. M. Yáñez
Departamento de Química, C-9, Universidad Autónoma de Madrid
Cantoblanco, 28049-Madrid (Spain)

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to its aromatic character or to the change in aromaticity on complexation. To take into account the multidimensional character of aromaticity, local aromaticity changes are quantified by using several probes of local aromaticity based on structural, magnetic, and electron-delocalization properties. The series of polycyclic aromatic hydrocarbons (PAHs) is the same as that recently studied by some of us to analyze the effect of increasing the number of fused rings on gas-phase binding enthalpy and basicity of the lithium cation.[17] In addition, we have included in our study benzene as a reference system.

Computational Details

Molecular geometries of lithium cation/π complexes were taken from reference [17], in which geometries of all systems but circumcoronene complexes were fully optimized with the hybrid DFT B3LYP method[33–35] with the 6-31G(d) basis set[36–38] by means of the Gaussian 98 program suite.[39] For circumcoronene complexes, the optimization was carried out at the B3LYP/3-21G* level.

As a structure-based measure of aromaticity, we employed the harmonic oscillator model of aromaticity (HOMA) index, defined by Kruszewski and Krygowski as Equation (1):[40,41]

$$\text{HOMA} = 1 - \frac{\alpha}{n} \sum_{i=1}^{n} \left(R_{\text{opt}} - R_i \right)^2 \tag{1}$$

where n is the number of bonds considered, and α is an empirical constant fixed to give HOMA = 0 for a model nonaromatic system, and HOMA = 1 for a system with all bonds equal to an optimal R_{opt} value assumed to be achieved for fully aromatic systems. For C—C bonds $\alpha = 257.7$ and $R_{\text{opt}} = 1.388$ Å. R_i stands for a running bond length. This index has been found to be one of the most effective structural indicators of aromaticity.[23,42]

As a magnetic index of aromaticity, we used the NICS, proposed by Schleyer et al.[21] This is one of the most widely employed indicators of aromaticity. It is defined as the negative value of the absolute shielding computed at a ring center or at some other interesting point of the system. Rings with large negative NICS values are considered aromatic. The more negative the NICS value, the more aromatic the ring. The GIAO method[43] has been used to perform calculations of NICS at ring centers (NICS(0)) determined by the nonweighted mean of the heavy-atom coordinates. As shown by Lazzeretti and Aihara,[44–46] the NICS(0) values contain important spurious contributions from the in-plane tensor components that are not related to aromaticity. So, to complement the NICS analysis, we also calculated the NICS(1) values, that is, NICS measured 1 Å below the center of the ring, on the opposite face to the ion for species interacting with a lithium cation. NICS(1) is considered to better reflect aromaticity patterns, because at 1 Å the effects of the π-electron ring current are dominant and local σ-bonding contributions are diminished.[44,47,48] We also calculated the out-of-plane component of the NICS(1) value, NICS$_{zz}$(1), which is considered to better reflect the π-electron effects and therefore is probably an even better descriptor of aromaticity.[48]

Finally, as aromaticity criteria based on electron delocalization, we calculated the *para*-delocalization index (PDI)[49,50] and the aromatic fluctuation index (FLU).[51] The PDI is obtained by employing the delocalization index (DI)[52–54] as defined in the framework of the atoms in molecules (AIM) theory of Bader.[55–57] The PDI is an average of all DI of *para*-related carbon atoms in a given six-membered

ring (6-MR). Integrations of DIs were performed with the AIMPAC collection of programs.[58] Calculation of these DIs at the DFT level of theory cannot be performed exactly,[59] because the electron-pair density is not available at this level of theory. As an approximation, we used the Kohn–Sham orbitals obtained from DFT to calculate Hartree–Fock-like DIs [Eq. (2)].[59]

$$\delta(A,B) = 4 \sum_{i,j}^{N/2} S_{ij}(A) S_{ij}(B) \tag{2}$$

The summations in Equation (2) run over all the $N/2$ occupied molecular orbitals. $S_{ij}(A)$ is the overlap of the molecular orbitals i and j within the basin of atom A. The numerical accuracy of the AIM calculations has been assessed by using two criteria: 1) The integration of the Laplacian of the electron density $\bigtriangledown^2\rho(\mathbf{r})$ within an atomic basin must be close to zero; 2) The number of electrons in a molecule must be equal to the sum of all the electron populations of a molecule, and also equal to the sum of all the localization indices and half of the delocalization indices in the molecule.[53,54] For all atomic calculations, integrated absolute values of $\bigtriangledown^2\rho(\mathbf{r})$ were always less than 0.001 a.u. For all molecules, errors in the calculated number of electrons were always less than 0.01 a.u.

The FLU index[51] is based on the fact that aromaticity is related to the cyclic delocalized circulation of π electrons, and it is constructed not only by considering the amount of electron sharing between contiguous atoms, which should be substantial in aromatic molecules, but also by taking into account the similarity of electron sharing between adjacent atoms. It is defined as Equation (3):[51]

$$\text{FLU} = \frac{1}{n} \sum_{A-B}^{\text{RING}} \left[\left(\frac{\text{Flu}(A \rightarrow B)}{\text{Flu}(B \rightarrow A)} \right)^\delta \left(\frac{\delta(A,B) - \delta_{\text{ref}}(A,B)}{\delta_{\text{ref}}(A,B)} \right) \right]^2 \tag{3}$$

where the sum runs over all adjacent pairs of atoms around the ring, n is the number of members in the ring, $\delta_{\text{ref}}(C,C) = 1.4$ (the $\delta_{\text{ref}}(C,C)$ value in benzene at the HF/6-31G(d) level[51]), and the fluctuation from atom A to atom B reads as Equation (4):

$$\text{Flu}(A \rightarrow B) = \frac{\delta(A,B)}{\sum_{B \neq A} \delta(A,B)} = \frac{\delta(A,B)}{2(N(A) - \lambda(A))} \tag{4}$$

where $\delta(A,B)$ is the DI between basins of atoms A and B, $N(A)$ the population of basin A, and $\lambda(A)$ the number of electrons localized in basin A. δ in Equation (3) is a simple function to ensure that the enclosed term is always greater than or equal to 1, so it takes the values of Equation (5):

$$\delta = \begin{cases} 1 & \text{Flu}(A \rightarrow B) > \text{Flu}(B \rightarrow A) \\ -1 & \text{Flu}(A \rightarrow B) \leq \text{Flu}(B \rightarrow A) \end{cases} \tag{5}$$

FLU is close to 0 in aromatic species. The higher the FLU value, the less aromatic the ring.

The electronic (PDI and FLU), geometric (HOMA), and magnetic (NICS) aromaticity criteria were calculated at the B3LYP/6-31G* level of theory, with the exception of the HOMA indices of circumcoronene complexes, which were calculated for the B3LYP/3-21G* optimized geometries.

2. Results and Discussion

This section is organized as follows. First, we analyze the local aromaticity of the series of the free PAHs depicted in
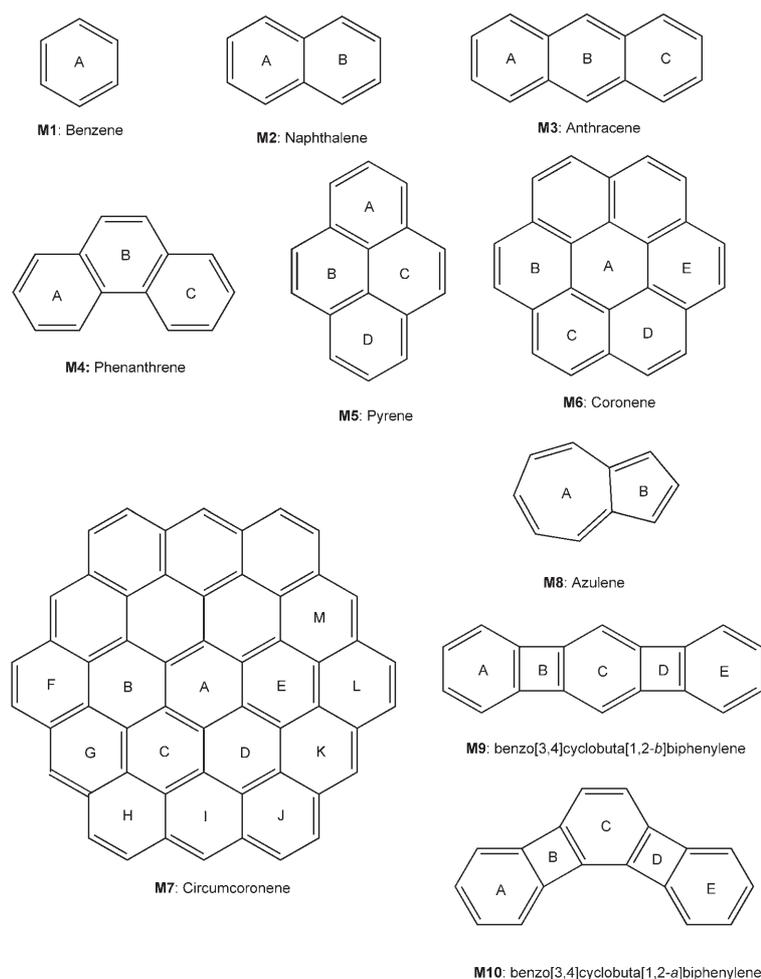
Scheme 1. Designation of the molecules studied (with labeling scheme of their rings).

Scheme 1. Second, we discuss the local aromaticity changes for this series of PAHs on complexation with a lithium cation. The local aromaticity of each PAH is evaluated by means of the electronic PDI and FLU, the geometric HOMA, and the magnetic NICS aromaticity descriptors applied to each nonequivalent ring of the molecules composing the series.

2.1. Local Aromaticity of the Free PAHs

Table 1 gathers the values of the NICS(0), NICS(1), $NICS_{zz}(1)$, HOMA, PDI, and FLU descriptors of aromaticity for the fully optimized free PAHs of Scheme 1, as well as the AIM π charge that can be assigned to each ring. In planar species, the AIM charge of the atomic basins can be split into σ and π components. The AIM π charge of each ring was calculated in two different ways. The first involved just adding the AIM π charges of all carbon atoms in the ring. Ring charges calculated this way do not sum the total number of π electrons. The second involved summing the AIM π charges of all carbon atoms in the ring, except for carbon atoms at a ring junction, for which the AIM π charge assigned to each ring is the total π charge of a given carbon atom divided by the number of rings sharing

it. The Mulliken counterparts of the AIM π ring charges calculated by adding the Mulliken populations of all np_z basis functions belonging to a given carbon atom in the ring can be found in the Supporting Information.

Benzene has higher PDI and lower FLU values (0.105 and 0.000 e) than naphthalene (0.076 and 0.019 e) and thus a greater local aromatic character. As already observed in previous works on PAHs,[49,51] the 6-MR in benzene has the highest PDI and the lowest FLU values, behaving as the most aromatic ring among the series in terms of these electron delocalization based descriptors. The HOMA values follow the same trend: 0.981 and 0.771 for the 6-MRs of benzene and naphthalene, respectively. The HOMA for benzene is not exactly 1.000, as we optimized this structure at the B3LYP/6-31G(d) level of theory, and the C–C distance obtained is slightly different than that taken as the reference in Equation (1). Finally, NICS values follow the opposite trend: 6-MRs in naphthalene (NICS(0) = −10.0 ppm) are slightly more aromatic than that of benzene (NICS(0) = −9.7 ppm). The larger NICS of naphthalene as compared to benzene is consistent with the ^{1}H NMR chemical shifts of these two species,[60] as well as with the ring currents calculated by Steiner et al.[60,61] The aromaticity difference between benzene and naphthalene 6-MRs yielded by NICS is small and it is quite dependent on the level of calculation. Indeed, this aromaticity order given by NICS is reversed at the HF/6-31G*//AM1 level.[50] Not only the electronic (PDI), geometric (HOMA), and in some cases the magnetic (NICS) descriptors of aromaticity find the aromatic character of the 6-MR of benzene to be greater than that of naphthalene, but also resonance energies (REs) point out to this conclusion.[62] To find indicators of aromaticity that afford different orderings for relatively similar 6-MRs is not completely unexpected[29] and it is considered a manifestation of the multidimensional character of aromaticity. In such a case, it is not possible to reach a definite conclusion on the relative local aromatic character of the compared 6-MRs,[29] although one may argue that there are more indicators pointing to the greater aromatic character of benzene than vice versa. So, in principle, the 6-MR of benzene should be considered more aromatic than that of naphthalene.

For anthracene, all probes of local aromaticity employed except the PDI indicate that outer 6-MRs are less aromatic than the inner one. The PDI values indicate that terminal 6-MRs have approximately the same aromaticity as the inner one. The greater aromatic character of the central 6-MR in anthracene was already observed by different authors[31,51,63,64] using aromatic stabilization energies (ASE), HOMA, NICS, and FLU indices. Going from benzene to anthracene, the aromaticity of the terminal ring decreases with the addition of rings for all indices, but for the inner ring, while FLU, PDI, and HOMA agree that its aromaticity decreases, the different NICS descriptors show exactly the opposite trend. This finding gives sup-

Table 1. B3LYP/6-31G* HOMA, NICS(0), NICS(1), NICS$_{zz}$(1), PDI, and FLU results and total π charge assigned to each ring for the fully optimized PAHs of Scheme 1.

Molecule	Ring	HOMA	NICS(0)[a]	NICS(1)[a]	NICS(1)$_{zz}$[a]	PDI[b]	FLU	Split ring π charge[b,c]	Total ring π charge[b,d]
benzene	M1-A	0.981	−9.7	−11.2	−29.0	0.105	0.000	5.873	5.873
naphthalene	M2-A	0.771	−10.0	−11.6	−29.0	0.076	0.019	4.914	5.899
anthracene	M3-A	0.618	−8.8	−10.7	−26.0	0.066	0.031	4.274	5.924
	M3-B	0.693	−12.6	−13.9	−34.7	0.066	0.020	3.618	5.933
phenanthrene	M4-A	0.853	−10.1	−11.7	−29.1	0.082	0.010	4.918	5.908
	M4-B	0.433	−6.8	−9.1	−20.4	0.047	0.040	3.950	5.930
pyrene	M5-A	0.834	−12.7	−14.0	−35.6	0.069	0.013	4.274	5.924
	M5-B	0.553	−5.1	−7.9	−16.5	0.044	0.039	3.618	5.933
coronene	M6-A	0.606	−1.3	−5.4	−7.7	0.032	0.035	1.994	5.891
	M6-B	0.716	−11.1	−12.9	−31.4	0.053	0.026	3.625	5.942
circumcoronene[e]	M7-A	0.739[f]	−13.8[g]	−16.1[g]	−39.0[g]				
	M7-B	0.635[f]	−4.9[g]	−8.7[g]	−17.3[g]				
	M7-F	0.446[f]	−6.3[g]	−9.0[g]	−19.1[g]				
	M7-G	0.698[f]	−16.3[g]	−17.5[g]	−43.9[g]				
azulene	M8-A	0.519	−6.8	−8.5	−21.2		0.021	5.784	6.774
	M8-B	0.290	−19.0	−19.1	−49.9		0.032	4.042	5.032
benzo[3,4]cyclobuta[1,2-*b*]biphenylene	M9-A	0.804	−3.7	−5.4	−10.5	0.088	0.007	4.944	5.930
	M9-B	−1.037	17.9	8.8	38.4		0.046	1.968	3.936
	M9-C	0.905	−0.5	−2.3	−0.8	0.081	0.003	3.963	5.928
benzo[3,4]cyclobuta[1,2-*a*]biphenylene	M10-A	0.862	−6.1	−7.5	−17.0	0.089	0.008	4.917	5.901
	M10-B	−0.967	13.6	4.7	25.6		0.098	1.982	3.964
	M10-C	0.363	0.9	−0.7	4.5	0.069	0.041	3.991	5.987

[a] Units are ppm. [b] Units are electrons. [c] Sum of the split AIM carbon atom charge populations in a given ring (see text for details). [d] Sum of the total AIM carbon atom charge populations in a given ring (see text for details). [e] Due to computational limitations, the AIM analysis was not carried out for this molecule. [f] B3LYP/3-21G* results. [g] B3LYP/6-31G*//B3LYP/3-21G* results.

port to the claimed overestimation by NICS of the local aromaticity of the central rings in polyacenes.[31,65,66]

An important change in local aromaticity trends occurs on going from anthracene to phenanthrene. Now the most aromatic rings are the terminal ones according to all indicators of aromaticity, and the values of the outer ring differ largely from those of the inner ring.[31,63] The different behavior between anthracene and phenanthrene agrees with previously reported current density maps that show an intense circulation mainly localized on the central hexagon of anthracene and on the external 6-MRs of phenanthrene.[67] The local aromaticity trends in phenanthrene are already anticipated by simple models such as the Clar's aromatic π sextets model.[68–70] Thus, phenanthrene has a single Clar structure in which the 6-MR A has an aromatic π sextet, which accordingly is predicted to be more aromatic than the B ring.

Pyrene, as compared to phenanthrene, has an additional ring of type B (inner 6-MR). Like in phenanthrene, the outer A rings (with three C—H bonds) are clearly more aromatic than the inner B rings (with two C—H bonds). This result is in agreement with Clar's model,[68,70,71] and also with previous NICS,[71–73] HOMA,[72] and ring critical point (RCP) calculations.[72] It is interesting to analyze the local aromaticity changes of outer (A) and inner (B) rings when going from phenanthrene to pyrene. All methods agree in finding similar local aromaticities for rings A and B of phenanthrene and pyrene. The various methods used differ, however, in the direction of the changes observed on going from phenanthrene to pyrene. Thus, all

NICS measures indicate an increase in the local aromaticity of ring A and a decrease in ring B in pyrene as compared to phenanthrene. The opposite trend is found according to HOMA and FLU indicators of aromaticity. Finally, the PDI results indicate that both rings suffer a reduction of local aromaticity in pyrene in comparison with phenanthrene.

Similar to what is found for phenanthrene and pyrene, all local aromaticity methods coincide in assigning a larger aromaticity to the outer B than to the inner A 6-MRs of D_{6h} coronene. This result is in line with previous NICS,[46,71,72,74,75] HOMA,[72] and RCP calculations,[72] as well as ring-current analysis.[61,76] All indicators of aromaticity in Table 1 indicate that ring B of coronene is more aromatic than the corresponding B rings of phenanthrene and pyrene.

Adding another layer of 6-MRs to coronene leads to circumcoronene, both with D_{6h} symmetry. Due to computational limitations, for this system only the NICS and HOMA values are reported. Somewhat unexpectedly from the previous results of this work and earlier studies,[50,77,78] both HOMA and NICS values indicate that inner ring A and outer ring G are more aromatic than inner ring B and outer ring F. Thus, according to the NICS indices, the order of aromaticity is G > A ≫ F > B, while the ordering A > G > B ≫ F is given by the HOMA indicator of aromaticity. Although, from the results for the previously analyzed systems, one might expect greater aromaticity for the outer ring F, the results obtained assigning a larger aromaticity to the 6-MRs A and G coincide with the predictions based on the Clar structure of circumcoronene depicted in Scheme 2
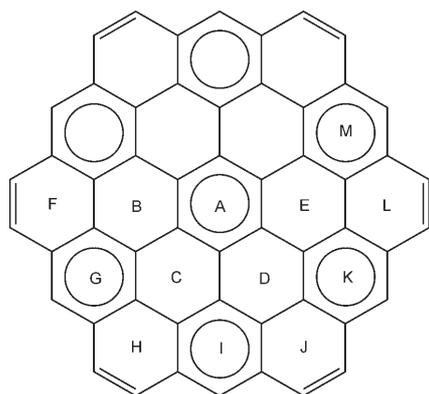
Scheme 2. The Clar structure of circumcoronene.

and with recent NICS calculations by Moran et al.[75] As shown recently, the predictions of local aromaticity based on Clar's model[68,69] for systems having a unique Clar structure, like circumcoronene, are totally in line with HOMA, NICS, and PDI results.[70] When coronene is surrounded by an additional layer of aromatic rings to yield circumcoronene all indices indicate a significant increase in the aromaticity of ring A and a concomitant decrease in the aromaticity of ring B. Similar findings in terms of NICS values have been reported before in the literature.[75] Finally, the NICS values for rings A and G as compared to those found for benzene seem to indicate that the aromaticity of these rings is overestimated by NICS. Several examples of NICS values that are seriously affected by ring currents in adjacent 5- or 6-MRs have been recently reported.[30,31]

The Mills–Nixon effect[79–83] is associated with distortions in aromatic rings fused to saturated or small strained rings. This effect reduces the aromaticity of the 6-MRs of annelated benzene derivatives such as benzo[3,4]cyclobuta[1,2-*b*]biphenylene or [3]phenylene (**M9**) and benzo[3,4]cyclobuta[1,2-*a*]biphenylene or angular [3]phenylene (**M10**), as compared to that of benzene, according to all indicators of aromaticity (see Table 1). Moreover, for **M10** all descriptors agree in a clearly larger aromaticity for outer ring A than for central ring C, with the same trend as for phenanthrene. The same result was obtained by Schulman et al.[84] using NICS(1) and proton chemical shifts calculated at the HF/3-21G//B3LYP/6-31G* level of theory. On the contrary, for **M9** the HOMA index yields ring C as the most aromatic ring, while PDI and FLU give an almost identical aromaticity for the two rings, and the magnetic-based index NICS affords ring A as most aromatic. This latter result was reported earlier by Schulman et al.[84] We have previously shown in pyracylene that paratropic currents in adjacent 5-MRs artificially reduce the NICS value of the 6-MRs.[30] It is likely that in **M9** also the paratropic ring currents of the antiaromatic 4-MRs produce the same effect on the NICS values of the adjacent 6-MRs, in particular that of ring C, which has two attached 4-MRs. In this sense, the local aromaticity of 6-MRs in **M9** and **M10** are probably underestimated by the NICS values, especially that of the central ring C. This could explain the greater local aromaticity of ring A as compared to C given by NICS in **M9**.

Azulene is a nonbenzenoid aromatic hydrocarbon with an electron-rich 5-MR, as indicated by its total π charge. This ring is found to be more aromatic according to the different NICS values, but not by the HOMA and FLU indices, which find the 7-MR to have a greater aromatic character than the 5-MR. The origin of this difference is unclear. No PDI values have been computed for azulene, since PDI can only be calculated for 6-MRs.

Finally, the ordering of the rings by local aromaticity given by NICS(0), NICS(1), and NICS$_{zz}$(1) is practically identical for the rings listed in Table 1. Thus, for this group of rings, the effect of spurious information in the NICS(0) values coming from the in-plane tensor components does not seriously affect the trends in local aromaticity.

2.2. Changes in Local Aromaticity Values after Complexation with the Lithium Cation

Tables 2 and 3 list the changes in NICS(0), NICS(1), NICS$_{zz}$(1), and HOMA descriptors of aromaticity on going from fully optimized free PAHs to fully optimized lithium cation/π complexes. These tables also give the lithium binding enthalpies and the relative energy of all possible lithium cation/π isomers extracted from reference [17]. The interaction of Li$^+$ occurs preferentially with the π electron richer 6-MRs, that is, those having the largest π charge calculated by uniformly distributing the total π charge for a given carbon atom at a ring junction between the different rings. However, there is no clear correlation between the two quantities, neither for the total ring π charges nor for the ring π charge obtained by dividing the π charge for the carbon atoms at the ring junctions. Apparently, the π charge that Li$^+$ feels when approaching the ring is the full π population of the carbon atoms belonging to this ring. Thus, LBEs should correlate better with the total than with the split ring π charges, but in both cases the correlation is rather poor. In fact, among the compounds investigated benzene has the largest split π charge but the smallest Li$^+$ binding enthalpy. Also in circumcoronene Li$^+$ interacts somewhat more favorably (by ca. 2 kcal mol^{-1}) with ring G than with ring F, despite the latter having a larger split π charge (see Table S1). For azulene, the interaction of the Li$^+$ occurs with the 5-MR, which also has less π charge than the 7-MR. However, in this case, π charges of the 5- and 7-MRs can not be compared because of the different ring size. Indeed, the 5-MR in azulene is considered to be electron-richer than the 7-MR.[17] It then seems clear that a model based only on the π charges cannot account for the trends in Li$^+$ basicity, because, among other things, the interaction energies have non-negligible polarization and dispersion components which cannot be accounted for by just looking at the π charges.[2] In many cases (but not always, as can be seen in Table 1 for anthracene and in Table S1 for circumcoronene) the rings having the largest split π charge coincide with the most aromatic rings. However, at least within the series of compounds under scrutiny, there is no correlation between Li$^+$ binding enthalpies and the aromaticity of the interacting ring, no matter which index is used to measure the latter (see Figure 1).

Table 2. B3LYP/6-31G* changes in HOMA, NICS(0), NICS(1), and NICS$_{zz}$(1) values for the different fully optimized lithium cation/π complexes considered. LBE is the Li$^+$ binding enthalpy and ΔE is the relative energy of a given lithium cation/π complex as compared to the most stable isomer (both from reference [17]).

Complex[a]	Ring[b]	LBE[c]	ΔE[c]	ΔHOMA	ΔNICS(0)[d]	ΔNICS(1)[d]	ΔNICS(1)$_{zz}$[d]
benzene–Li	M1-A (Li)	161		−0.064	1.6	1.4	0.5
naphthalene–Li	M2-A (Li)	169	0.0	−0.120	1.5	1.6	1.6
	M2-B			−0.076	1.4	0.8	−0.2
anthracene–Li(I)	M3-A		0.0	−0.079	1.4	0.9	−0.1
	M3-B (Li)			−0.164	1.6	2.0	3.5
anthracene–Li(O)	M3-A (Li)	179	−3.5	−0.126	1.7	1.9	2.3
	M3-B			−0.096	1.3	0.9	0.2
	M3-C			−0.025	−0.2	−0.7	−2.3
phenanthrene–Li(I)	M4-A		0.0	−0.064	1.5	1.1	0.3
	M4-B(Li)			−0.181	0.8	1.2	0.9
phenanthrene–Li(O)	M4-A (Li)	180	−6.8	−0.125	1.6	1.8	2.4
	M4-B			−0.051	1.2	0.9	0.3
	M4-C			0.005	−0.1	−0.5	−1.8
pyrene–Li(I)	M5-A		0.0	−0.056	1.2	0.9	0.1
	M5-B			−0.059	1.1	0.9	0.9
	M5-C(Li)			−0.166	1.4	1.6	2.1
pyrene–Li(O)	M5-A(Li)	184	−9.4	−0.152	2.3	2.4	4.3
	M5-B			−0.038	1.0	0.7	−0.1
	M5-D			0.014	0.0	−0.4	−1.4
coronene–Li(I)	M6-A (Li)		0.0	−0.213	1.9	1.9	4.3
	M6-B			−0.048	1.2	1.0	0.9
coronene–Li(O)	M6-A	186	−7.9	−0.046	0.9	0.8	0.8
	M6-B (Li)			−0.169	1.9	2.3	4.1
	M6-C			−0.067	1.7	1.3	1.6
	M6-D			0.014	−0.2	−0.4	−1.6
	M6-E			0.000	0.0	−0.3	−0.9
circumcoronene–Li(I1)	M7-A		0.0[f]	−0.066[e]	1.8[f]	−0.6[f]	3.1[f]
	M7-B (Li)			−0.277[e]	3.5[f]	−0.2[f]	9.6[f]
	M7-C			−0.038[e]	1.9[f]	−2.0[f]	4.1[f]
	M7-D			0.000[e]	−0.1[f]	−3.9[f]	−0.1[f]
	M7-E			0.010[e]	−0.4[f]	−4.1[f]	−0.6[f]
	M7-F			−0.038[e]	2.0[f]	−0.9[f]	3.5[f]
	M7-G			−0.038[e]	2.1[f]	0.8[f]	3.8[f]
	M7-H			0.000[e]	0.1[f]	−2.8[f]	−0.5[f]
	M7-I			0.028[e]	−0.1[f]	−1.4[f]	−0.6[f]
	M7-J			−0.038[e]	−0.3[f]	−3.2[f]	−1.2[f]
	M7-K			0.028[e]	−0.5[f]	−1.7[f]	−1.6[f]
	M7-L			0.000[e]	−0.4[f]	−3.3[f]	−1.5[f]
circumcoronene–Li(I2)	M7-A (Li)		0.0[f]	−0.208[e]	3.7[f]	1.8[f]	10.6[f]
	M7-B			−0.066[e]	2.3[f]	−1.7[f]	5.1[f]
	M7-F			0.000[e]	0.1[f]	−2.8[f]	−0.2[f]
	M7-G			0.000[e]	0.4[f]	−1.0[f]	0.4[f]

[a] (O) and (I) designate the outer and inner Li$^+$ complexes. [b] (Li) refers to the ring with the attached Li$^+$ cation. [c] Units are kJ mol^{-1}. The level of calculation is B3LYP/6-311 + G(3df,2p).[17] [d] Units are ppm. [e] B3LYP/3-21G* results. [f] B3LYP/6-31 + G**//B3LYP/3-21G* results.

or hexafluorobenzene leads to a gain in aromaticity of the ring measured by NICS.[18,19] The reduction of the aromaticity of benzene on complexation to Li$^+$ is also supported by the geometry-based HOMA index. Krygowski and Cyrański[23,63,85,86] showed that the HOMA value can be split into the energetic (EN) and geometric (GEO) contributions according to the relation HOMA = 1−EN−GEO. The GEO contribution measures the decrease/increase in bond length alternation, while the EN term takes into account the lengthening/shortening of the mean bond lengths of the ring. Withdrawal of charge from the π cloud results in a slight weakening of the C—C bonds of the aromatic ring, which accordingly lengthen by 0.01 Å. This geometry relaxation results in a reduction of the HOMA value of about six hundredths due totally to the EN term. Both the NICS and HOMA results point to a slight reduction of aromaticity on going from free benzene to the lithium cation/π complex of benzene. This small decrease in aromaticity is completely overlooked by the two indicators based on electron-delocalization effects employed here, PDI and FLU (see Table S2, Supporting Information). This result must be attributed to the small charge transfer from benzene to Li$^+$ (only 0.07 e for AIM charges). Apparently, the low charge transfer from benzene to Li$^+$ and the electronic polarization of the π cloud by Li$^+$ do not induce large changes in the electron density and higher order densities of the benzene fragment, which would remain almost unaltered. For this reason, these indices seem to be not especially well suited to discuss local aromaticity changes of aromatic rings on complexation of alkali metal cations, and we focus our discussion on the HOMA and NICS indices, which are more sensitive for this kind of systems. A table containing the changes in FLU and PDI on complexation of all PAHs studied except circumcoronene is given in the Supporting Information.

The HOMA and NICS values in Tables 2 and 3 also point to a clear reduction in local aromaticity for the 6-MR of naphthalene interacting with the Li$^+$ cation. These two indices show

Let us now discuss the results on our reference system, benzene. As found by Garau et al. using NICS(1) results,[19] there is a reduction of aromaticity on complexation of benzene with the lithium cation of about 1.5 ppm as indicated by NICS(0) and NICS(1) values and 0.5 ppm according to NICS$_{zz}$(1). Garau et al.[19] computed a ΔNICS(1) value of 0.2 ppm at the HF/6-31++G**//MP2/6-31++G** level of theory. Although qualitatively the trend is the same, these results seem to indicate that ΔNICS(1) values for these kind of systems are quite dependent on the level of calculation. Charge transfer from benzene to Li$^+$ reduces the number of π electrons available to generate the ring current, and this translates into a reduction of the absolute NICS value. Interestingly, complexation of anions to tri-

Table 3. B3LYP/6-31G* changes in HOMA, NICS(0), NICS(1), and NICS$_{zz}$(1) values for the different fully optimized lithium cation/π complexes considered. LBE is the Li$^+$ binding enthalpy and ΔE is the relative energy of a given lithium cation/π complex as compared to the most stable isomer (both from reference [17]).

Complex[a]	Ring[b]	LBE[c]	ΔE[c]	ΔHOMA	ΔNICS(0)[d]	ΔNICS(1)[d]	ΔNICS(1)$_{zz}$[d]
circumcoronene–Li(O1)	M7-A		−6.2[f]	0.000[e]	−0.2[f]	−2.5[f]	−0.7[f]
	M7-B			−0.028[e]	1.3[f]	−2.5[f]	2.5[f]
	M7-C			0.000[e]	−1.0[f]	−4.6[f]	−2.2[f]
	M7-D			−0.028[e]	−0.5[f]	−4.3[f]	−1.0[f]
	M7-E			0.000[e]	−1.1[f]	−4.7[f]	−2.3[f]
	M7-F (Li)			−0.229[e]	1.8[f]	−0.5[f]	3.9[f]
	M7-G			−0.049[e]	1.8[f]	0.5[f]	2.6[f]
	M7-H			0.000[e]	0.0[f]	−2.9[f]	−0.7[f]
	M7-I			0.000[e]	−0.5[f]	−1.8[f]	−1.7[f]
	M7-J			0.049[e]	−0.8[f]	−3.6[f]	−2.5[f]
	M7-K			0.028[e]	−0.7[f]	−1.9[f]	−2.0[f]
	M7-L			0.161[e]	−0.2[f]	−3.1[f]	−0.9[f]
circumcoronene–Li(O2)	M7-A	205[f]	−8.2[f]	−0.003[e]	0.1[f]	−2.2[f]	0.0[f]
	M7-C			−0.104[e]	1.4[f]	−2.4[f]	2.8[f]
	M7-D			0.000[e]	−0.4[f]	−4.2[f]	−0.7[f]
	M7-E			−0.028[e]	−0.6[f]	−4.4[f]	−1.1[f]
	M7-G (Li)			−0.160[e]	3.3[f]	2.6[f]	9.3[f]
	M7-H			−0.086[e]	1.5[f]	−1.4[f]	1.8[f]
	M7-I			0.000[e]	0.2[f]	−1.1[f]	−0.1[f]
	M7-J			0.000[e]	−0.4[f]	−3.3[f]	−1.5[f]
	M7-K			0.000[e]	−0.5[f]	−1.8[f]	−1.7[f]
	M7-L			0.000[e]	−0.4[f]	−3.3[f]	−1.6[f]
	M7-M			0.000[e]	−0.6[f]	−1.8[f]	−1.8[f]
azulene–Li(7)	M8-A (Li)		0.0	−0.257	2.0	2.1	3.5
	M8-B			−0.277	0.7	−0.4	−3.4
azulene–Li(5)	M8-A	189	−29.2	0.082	1.5	0.7	0.1
	M8-B (Li)			0.020	2.2	3.1	5.1
benzo[3,4]cyclobuta [1,2-*b*] biphenylene–Li(I)	M9-A			0.025	0.1	−0.2	−1.0
	M9-B		0.0	−0.093	0.2	0.8	−0.9
	M9-C (Li)			−0.120	1.9	1.8	2.9
benzo[3,4]cyclobuta [1,2-*b*]biphenylene–Li(O)	M9-A (Li)	192	−9.4	−0.180	4.1	3.5	7.3
	M9-B			0.110	1.4	1.5	2.0
	M9-C			−0.037	1.3	0.9	2.2
	M9-D			0.143	−0.8	−1.3	−3.9
	M9-E			0.051	−0.7	−0.8	−2.5
benzo[3,4]cyclobuta [1,2-*b*]biphenylene–Li(4)	M9-A		24.0	−0.060	2.7	2.2	2.8
	M9-B (Li)			−0.537	−0.6	1.4	0.7
	M9-C			−0.060	2.6	2.3	3.4
	M9-D			0.108	0.0	−0.5	−2.3
	M9-E			0.045	−0.3	−0.5	−1.3
benzo[3,4]cyclobuta [1,2-*a*]biphenylene–Li(I)	M10-A		0.0	0.028	0.0	−0.4	−1.6
	M10-B			−0.117	−1.0	−0.4	−3.7
	M10-C (Li)			−0.323	1.6	1.5	1.8
benzo[3,4]cyclobuta [1,2-*a*]biphenylene–Li(O)	M10-A (Li)	206	−7.5	−0.153	1.8	1.7	2.2
	M10-B			0.068	−0.5	0.1	−2.9
	M10-C			0.025	1.1	0.6	1.3
	M10-D			0.105	0.3	−0.3	−0.6
	M10-E			0.022	0.3	0.0	−0.1
benzo[3,4]cyclobuta [1,2-*a*]biphenylene–Li(4)	M10-A		18.7	0.028	1.1	0.9	−0.7
	M10-B (Li)			0.086	−2.8	−0.3	−4.7
	M10-C			−0.191	2.4	2.0	2.8
	M10-D			−0.470	−0.7	−1.1	−3.7
	M10-E			−0.015	0.1	−0.4	−1.3

[a] (O) and (I) designate the outer and inner Li$^+$ complexes, while (4), (5), an (7) denote four-, five- and seven-membered rings, respectively. [b] (Li) refers to the ring with the attached Li$^+$ cation. [c] Units are kJ mol^{-1}. The level of calculation is B3LYP/6-311+G(3df,2p).[17] [d] Units are ppm. [e] B3LYP/3-21G* results. [f] B3LYP/6-31+G**//B3LYP/3-21G* results.
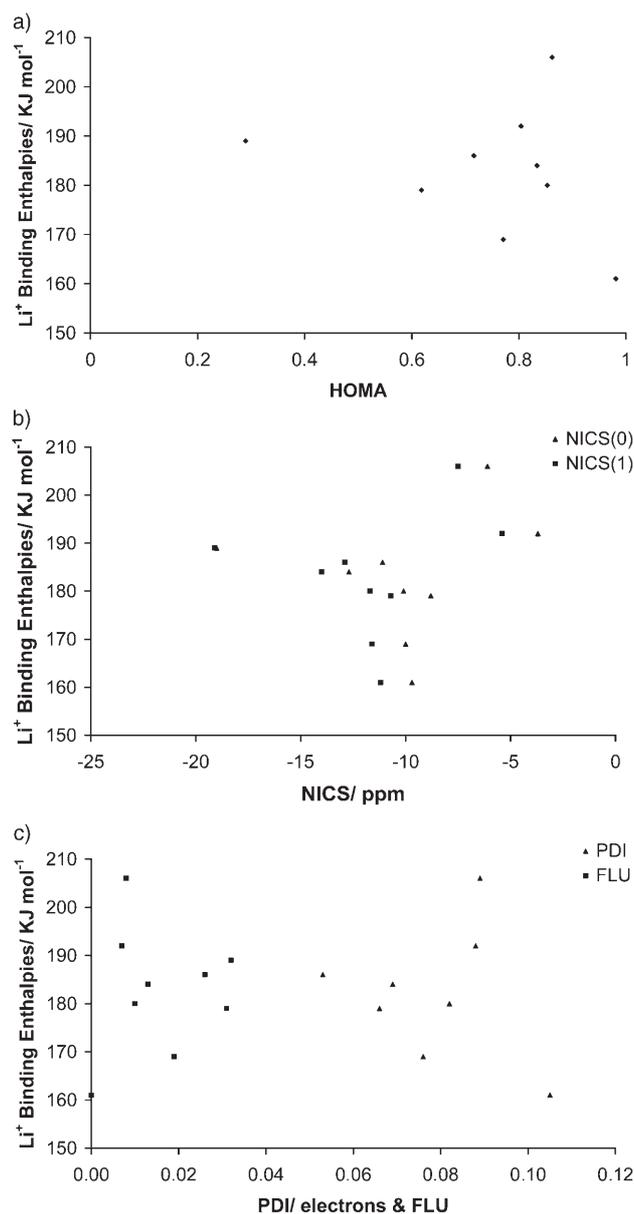
Anthracene and phenanthrene are the smallest PAHs considered to have two kinds of rings. For both systems, the interaction of Li$^+$ with the π electron richer (considering split ring π charges) outer 6-MRs is more stabilizing than the interaction with the inner 6-MR. The NICS results indicate that in the anthracene/Li(O) and phenanthrene/Li(O) complexes, the aromaticity of the 6-MR interacting with Li$^+$ is clearly reduced by about 2 ppm. There is also a reduction in the local aromaticity of the adjacent inner ring, albeit noticeably smaller. Finally, for the outer noninteracting ring, we found a slight increase in aromaticity. The HOMA trends are the same as those given by NICS, except for the noninteracting outer ring of the anthracene/Li(O) complex, which, according to HOMA, slightly reduces its local aromatic character on complexation.

For pyrene, the results are similar to those of phenanthrene, that is, the interaction of Li$^+$ is more favorable for the outer ring. This interaction leads to a small but clear reduction of the aromaticity in the ring directly attached to Li$^+$ and to a lesser extent in the adjacent inner rings, but to a small increase in the local aromatic character of the remaining outer ring.

Similarly, for coronene we have a larger stabilization when the lithium cation interacts with the outer and π electron richer 6-MR. Due to the interaction, the local aromaticity of the 6-MR B interacting with Li$^+$ is clearly reduced, as well as the aromaticity of the inner A and outer C rings fused to ring B, while those rings (D and E) not attached to ring B experience a minor increase in their aromatic character.

Complexation of circumcoronene with Li$^+$ also takes place preferentially with the outer F and G 6-MRs. Interaction with the G ring is more stabilizing than with the F ring by 2.0 kcal mol^{-1}, despite the F ring being π electron richer (see

that the reduction in aromaticity is smaller for the adjacent 6-MR. Indeed, the NICS$_{zz}$(1) descriptor, the preferred NICS indicator of aromaticity, points to a small increase in the local aromaticity of this noninteracting ring.

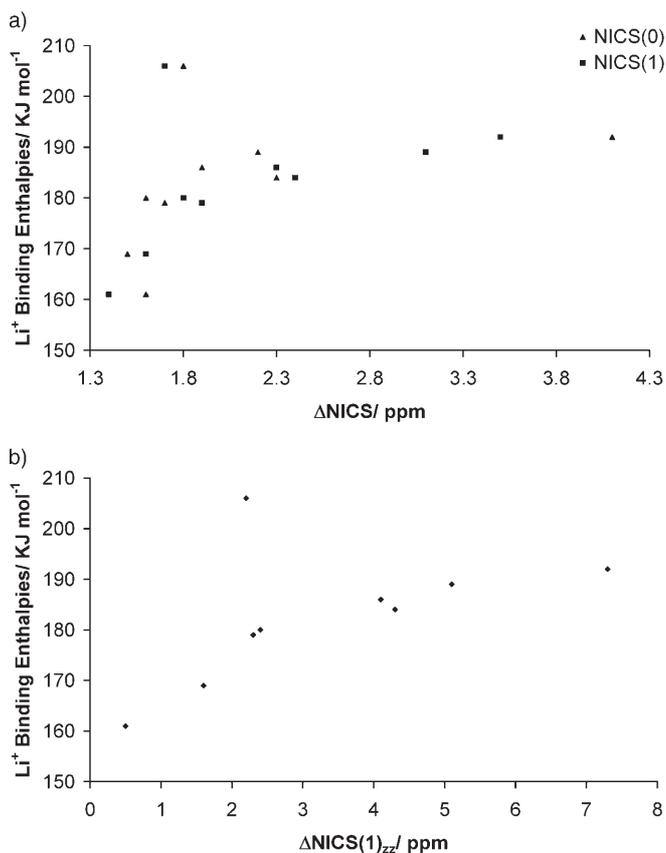**Figure 1.** Plots of calculated Li$^+$ binding enthalpies versus a) HOMA index, b) NICS, and c) PDI and FLU indices.

Compounds **M9** and **M10** interact with Li$^+$ also through the outer and electron richer 6-MR A. In the case of **M9**, formation of the lithium cation/π complex **M9-Li(O)** reduces the aromaticity of the 6-MRs A and C, and increases that of the other outer ring E and that of the 4-MR D. The behavior of the 4-MRs B is less clear. The HOMA yields an increase in the aromaticity of this 4-MR, while NICS indicates the opposite. For the **M10-Li(O)** complex, there is an apparent reduction of aromaticity for the 6-MR directly connected to Li$^+$. For the rest of the rings there is a minor intensification of the aromaticity according to the HOMA index that is also indicated by the NICS values for rings B and D, but not rings C and E. However, HOMA and NICS changes in rings other than the ring attached to Li$^+$ are in most cases very small and close to zero.

The NICS(0), NICS(1), and NICS$_{zz}$(1) results provide, with few exceptions, the same trends for the aromaticity changes experienced by the different rings on complexation.

In summary, Li$^+$ association implies a systematic decrease in the aromaticity of the ring with which the metal cation interacts. Furthermore, the change in aromaticity of the ring interacting with the metal cation qualitatively varies with the binding enthalpy. Indeed, a rough correlation exists between the calculated Li$^+$ binding enthalpies and the changes for both the NICS(0) and the NICS(1) indices (see Figure 2a). This correlation is even better when the NICS$_{zz}$(1) index is employed (see

Figure 2. Correlation between calculated Li$^+$ binding enthalpies and changes in aromaticity indices on Li$^+$ association for a) NICS(0) and NICS(1) values; b) NICS$_{zz}$(1) values.

Mulliken split ring π charges in Table S1, Supporting Information). After interaction the aromaticity in ring G decreases, and to a lesser extent in the rings directly attached to ring G (C and H). For the rest of the rings, the local aromaticity remains constant or undergoes a minor increase.

In azulene, the interaction is better with the 5-MR. On complexation both rings diminish their local aromaticity according to the NICS index. Unfortunately, the HOMA indicator of aromaticity yields the opposite result, so it is not possible to draw a definite conclusion on the aromaticity changes suffered by azulene when interacting with Li$^+$. The FLU changes (see Supporting Information) indicate an increase in the aromatic character of both rings on complexation, but they are very small and not fully conclusive either.

Figure 2b). In all cases, however, compound **M10** is a clear exception. In fact **M10** is predicted to be the most basic compound of the series, but the change in NICS values is similar to that of anthracene or phenanthrene, which are much less basic.

3. Conclusions

We have studied the changes in local aromaticity on complexation of lithium cation in a series of extended fused aromatic compounds. The main purpose was discussing whether the strength of binding of the lithium cation to a given aromatic ring in a molecule is related to its aromatic character or to the change in aromaticity on complexation. The analysis has been undertaken by means of NICS, HOMA, PDI, and FLU aromaticity criteria, in order to be consistent with the multidimensional character of aromaticity. However, we found that the PDI and FLU descriptors yield insignificant changes in the aromatic character of the rings on Li$^+$ association. For this reason, our discussion of aromaticity changes due to lithium cation binding was carried out mainly by using the HOMA and NICS criteria only.

On the whole, the interaction of Li$^+$ with fused PAHs occurs preferentially in the π electron richer rings, which in most cases are also the most aromatic. On complexation, there is a clear but small reduction of the aromaticity of the ring directly interacting with the lithium cation. The reduction of the local aromaticity of the adjacent rings is usually minor, and in some cases, HOMA and NICS indicators even point to a small increase in aromaticity, especially for those rings located further away from the ring directly attached to Li$^+$. Although there is no clear correlation between aromaticity and Li$^+$ binding enthalpies, there is a rough correlation between the latter and the change in the aromaticity of the ring directly interacting with the metal cation.

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