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Geometric Effects in Olefinic Cation−π Interactions with Alkali Metals: A Computational Study

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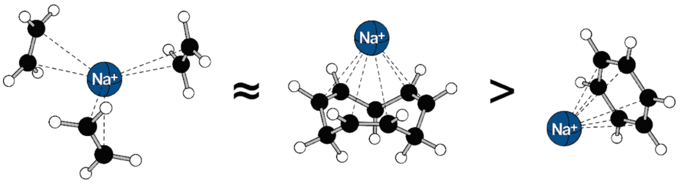

Although cation−π interactions commonly involve aromatic or heteroaromatic rings as the source of π-electrons, isolated and nonconjugated olefins are equally effective donors of π-electron density. Previous comparisons of these π-electron sources have indicated that the net energy of the binding interactions is not a simple additive function of the number of π-bonds involved. For instance, the enthalpy of binding ($\Delta H°$) of Li^+, Na^+, or K^+ cations to two ethylene molecules or to one benzene molecule is approximately the same, despite the 4:6 ratio of π-electrons involved. This present density functional theory study indicates that geometric factors can partially account for the proportionally greater interaction energies of olefins, but whether they are symmetrically placed around the cation or grouped on one hemisphere has little effect on the binding energy. Instead, flexible ligands that permit olefinic π-electrons to be oriented more favorably toward the metal than those in rigid aromatic rings can be correlated with greater bonding. For Li^+ complexes, this appears to be an appreciable factor, although it is less significant with Na^+ and K^+ complexes. For all three cations, stronger polarization interactions with olefins compared to arenes contribute to the strength of cation−π interactions involving olefinic π-bonds.

Introduction

Cation−π interactions involve the largely noncovalent attraction of a cation [commonly, but not necessarily, an alkali metal or NR_4^+ ion (R = H or alkyl)] with a ligand's π-electrons, which are often those of an arene or heteroarene.[1] Such interactions, which incorporate electrostatic, inductive, and charge transfer effects, and in some cases dispersion forces,[2] appear in numerous supramolecular and biological contexts, including cyclophanes,[3] calixarenes,[4,5] collarenes,[6] polyaromatics,[7,8] conjugated double bonds,[8] and amino acids such as tryptophan.[9] The interaction energies can be substantial: for example, those of K^+ with benzene and water in the gas phase are indistinguishable (∼17.7 ± 1.0 and ∼17.9 kcal/mol, respectively).[10,11] Even

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when weak, multiple cation−π(arene) interactions can critically influence ligand conformations and substrate binding.[12]

Although they have been less studied than those with arenes,[13−15] interactions of cations with olefinic π-bonds have revealed a distinctive feature of cation−π bonding, i.e., the nonadditivity of the energy contributions as a function of the number of π-bonds in a molecule. For example, the enthalpies of binding of Na^+ to ethylene and benzene have been determined to be -10.7 ± 1.0[16] and -23.2 ± 1.4[17] kcal/mol, respectively, which are not in the 1:3 ratio that would be estimated on the basis of the number of π-bonds. In another instance, the binding of 1,4-cyclohexadiene to Li^+, Na^+, and K^+ has been computationally modeled in the context of a study of [*n*]beltenes (cyclacenes),[14] and the enthalpy of binding of benzene to the same cations was found to be only 2−6% greater than that for binding to the cyclohexadiene, not the 50% increase that might be expected. These findings appear to be general; the binding of alkali metal cations to the double bonds in tris(allyl)zincates, $(M\{Zn[1,3\text{-}(SiMe_3)_2C_3H_3]_3\})$,[18] has been modeled with ethylenes as substitutes for the allyl bonds. Two ethylenes arranged in a staggered manner around Li^+, Na^+, and K^+ were found to be roughly equal in binding enthalpy to a benzene ring, and three ethylene units around the metal surpassed the arene binding enthalpy by ≥30%.

The reason that isolated or nonconjugated olefins should display binding to cations proportionally stronger than that of aromatic rings has been ascribed to general "geometrical considerations",[2,18] or more specifically in the case of 1,4-cyclohexadiene, to the flexibility in the -CH_2- linkages in the ring, which can deform to strengthen the cation−olefin interaction.[14] We were interested in examining this particular contributor to cation−π interactions in more detail, as it might be used as a guide to improving the binding properties of ionophores with judicious design of the π-system.[2,5,6,19] We report here the results of a density functional theory (DFT) study of geometric factors that could affect the strength of cation−π-olefin interactions.

Computational Methods

The computations were performed with the Amsterdam Density Functional (ADF2009) program package.[20] Many computational studies of cation−π interactions that include DFT results have used the hybrid B3LYP functional[21] either alone or in combination with other functionals or theoretical methods,[22] but given that there is no one "best" DFT method for studying cation−π interactions,[23] a preliminary screening of functionals was conducted with the $[K(C_6H_6)]^+$ cation, which has one of the better established energies of formation for a cation−π interaction (17.7 ± 1.0 kcal/mol).[10] The interaction enthalpy ($\Delta H°_{\text{int}}$) was calculated as the difference in the total enthalpy of the complex and sum of the enthalpies of the parent π-system and the metal under consideration (eq 1).

TABLE 1. Interaction Energies ($\Delta H°$, kilocalories per mole) for $[M(C_6H_6)]^+$ (C_{6v})

	Li^+	Na^+	K^+
P1	−41.3	−23.6	−16.0
P2	−36.1	−22.7	−17.9
experimental	-39.3 ± 3.3^{10}	-23.2 ± 1.4^{17}	-17.7 ± 1.0^{10}

$$\Delta H°_{\text{int}} = \Delta H°_{\text{complex}} - (\Delta H°_{\text{parent}} + \Delta H°_{M^+}) \qquad (1)$$

Even though hybrid functionals incur severe performance penalties when combined with the Slater-type orbitals used in the ADF program,[24] several examples (PBE0 and M06) were studied along with a range of nonhybrid functionals (BP86, BP86-D, BLYP, BLYP-D, PBE, mPBE, OPBE, M06L, and TPSS). In combination with basis sets of triple-ζ quality, those functionals that reproduced the experimental binding value of $[K(C_6H_6)]^+$ within ±3 kcal/mol (PBE0, M06, BP86-D, BLYP-D, PBE, mPBE, OPBE, and TPSS) were then examined with the $[Li(C_6H_6)]^+$ and $[Na(C_6H_6)]^+$ cations. The most consistent performance was found with the PBE functional[25] combined with the TZ2P basis with added diffuse functions (i.e., AUG TZ2P, taken from the ADF basis set library; the PBE/AUG TZ2P combination is denoted protocol 1, or P1) and the meta-GGA TPSS functional[26] combined with the even-tempered ET TZ1diff basis (which includes diffuse functions; the TPSS/ET TZ1diff combination is denoted protocol 2, or P2) (see Table 1). In some cases, P2 failed to give useful results, either because geometries failed to converge or frequency calculations did not reach completion; these cases are marked in the tables. Enthalpies were derived from the results of analytical frequency calculations; there were no imaginary frequencies for the optimized structures. Corrections for basis set superposition error (BSSE) were not applied; such errors are smaller with the Slater-type orbitals used in the ADF program than is the case with the more

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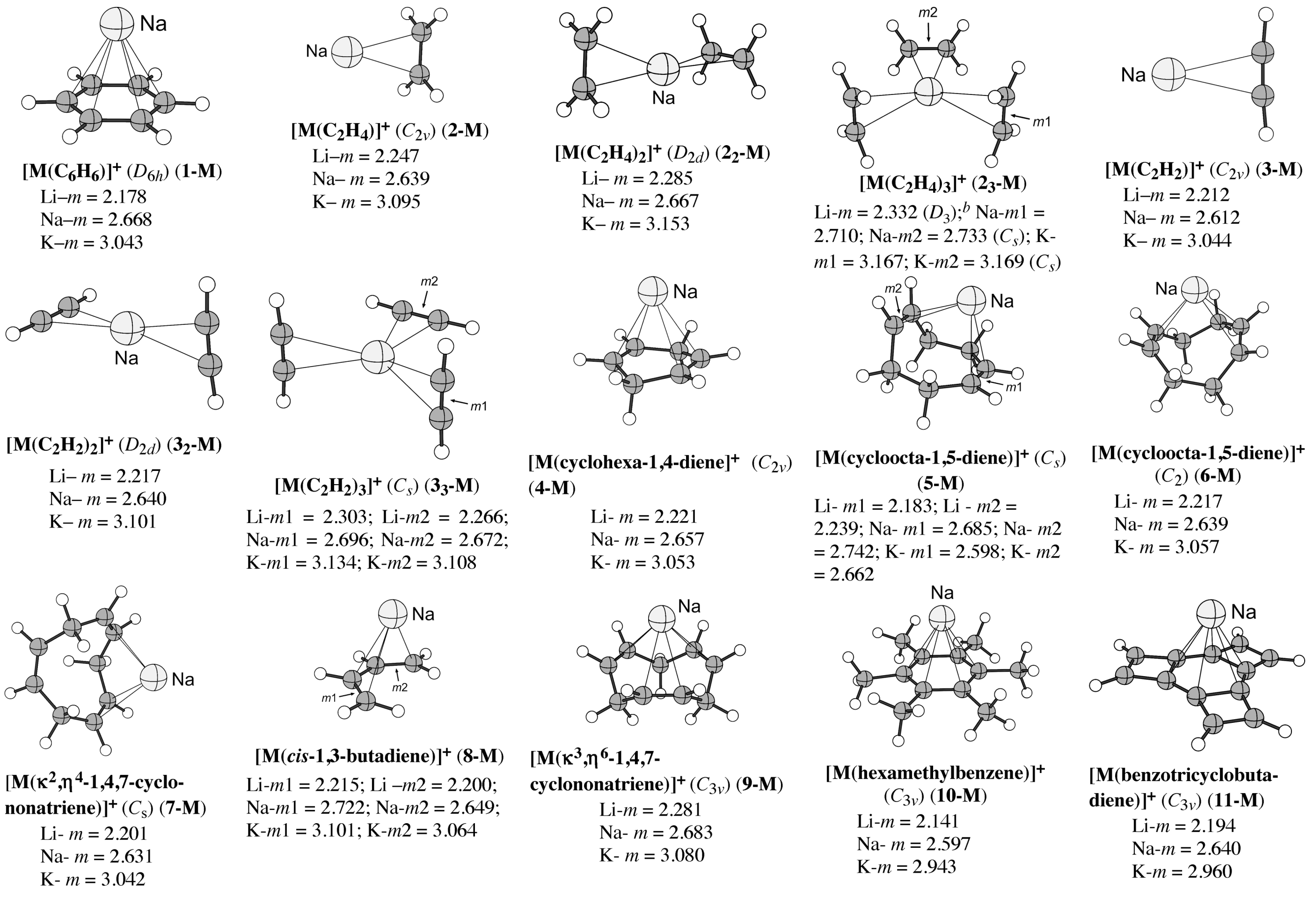

$[M(C_6H_6)]^+$ (D_{6h}) **(1-M)**
Li–m = 2.178
Na–m = 2.668
K–m = 3.043

$[M(C_2H_4)]^+$ (C_{2v}) **(2-M)**
Li–m = 2.247
Na– m = 2.639
K– m = 3.095

$[M(C_2H_4)_2]^+$ (D_{2d}) **(2_2-M)**
Li–m = 2.285
Na– m = 2.667
K– m = 3.153

$[M(C_2H_4)_3]^+$ (2_3-M)
Li-m = 2.332 (D_3);[b] Na-$m1$ = 2.710; Na-$m2$ = 2.733 (C_s); K-$m1$ = 3.167; K-$m2$ = 3.169 (C_s)

$[M(C_2H_2)]^+$ (C_{2v}) **(3-M)**
Li–m = 2.212
Na– m = 2.612
K– m = 3.044

$[M(C_2H_2)_2]^+$ (D_{2d}) **(3_2-M)**
Li– m = 2.217
Na– m = 2.640
K– m = 3.101

$[M(C_2H_2)_3]^+$ (C_s) **(3_3-M)**
Li-$m1$ = 2.303; Li-$m2$ = 2.266; Na-$m1$ = 2.696; Na-$m2$ = 2.672; K-$m1$ = 3.134; K-$m2$ = 3.108

$[M(cyclohexa-1,4-diene]^+$ (C_{2v}) **(4-M)**
Li- m = 2.221
Na- m = 2.657
K- m = 3.053

$[M(cycloocta-1,5-diene)]^+$ (C_s) **(5-M)**
Li- $m1$ = 2.183; Li - $m2$ = 2.239; Na- $m1$ = 2.685; Na- $m2$ = 2.742; K- $m1$ = 2.598; K- $m2$ = 2.662

$[M(cycloocta-1,5-diene)]^+$ (C_2) **(6-M)**
Li- m = 2.217
Na- m = 2.639
K- m = 3.057

$[M(\kappa^2,\eta^4-1,4,7-cyclononatriene)]^+$ (C_s) **(7-M)**
Li- m = 2.201
Na- m = 2.631
K- m = 3.042

$[M(cis-1,3-butadiene)]^+$ (8-M)
Li-$m1$ = 2.215; Li –$m2$ = 2.200; Na-$m1$ = 2.722; Na-$m2$ = 2.649; K-$m1$ = 3.101; K-$m2$ = 3.064

$[M(\kappa^3,\eta^6-1,4,7-cyclononatriene)]^+$ (C_{3v}) **(9-M)**
Li-m = 2.281
Na- m = 2.683
K- m = 3.080

$[M(hexamethylbenzene)]^+$ (C_{3v}) **(10-M)**
Li-m = 2.141
Na- m = 2.597
K-m = 2.943

$[M(benzotricyclobutadiene)]^+$ (C_{3v}) **(11-M)**
Li-m = 2.194
Na-m = 2.640
K-m = 2.960

FIGURE 1. Optimized geometries of the cation−π complexes. m is the midpoint of a π-bond. In the fourth strucure in the first row, the Li^+ complex optimized to a structure (not shown) with the ethylenes in a symmetrical, canted arrangement.

commonly used Gaussian-type orbitals, and in conjunction with basis sets of polarized triple-ζ quality or better (as used in this study), BSSE is typically on the order of ≤ 1 kcal/mol.[27]

The interaction energies (ΔE_{int}) of representative systems (the Li^+, Na^+, and K^+ cations with benzene, 1,3-ethylenes, 1,4-cyclohexadiene, and 1,4,7-cyclononatriene) were decomposed with a Morokuma-type scheme[28] into electrostatic interaction, exchange (or Pauli) repulsion, and (attractive) orbital interactions (eq 2).

$$\Delta E_{int} = \Delta V_{elstat} + \Delta E_{Pauli} + \Delta E_{oi} \tag{2}$$

The term ΔV_{elstat} represents the classical electrostatic interaction between the unperturbed charge distributions of the molecular fragments and is usually attractive. The Pauli repulsion (ΔE_{Pauli}) encompasses the destabilizing interactions between occupied orbitals of molecular fragments and is the source of steric repulsion. The orbital interaction (ΔE_{oi}) represents electron pair bonding, charge transfer, and polarization effects. It can be decomposed into kinetic, Coulombic, and exchange interaction terms; the sum of the kinetic and Coulombic terms expresses the polarization and charge transfer, which cannot be rigorously partitioned.[29] The electron density distribution was analyzed with the Voronoi deformation density (VDD) approach and the Hirshfeld method for computing atomic charges.[30]

In subsequent discussions, the cation−π species (Figure 1) will be numbered as L_n-M, where L refers to a specific hydrocarbon (benzene, ethylene, etc.; numbers given below), M is the metal involved (Li, Na, or K), and n is the number of hydrocarbons associated with the metal (1, 2, or 3; $n = 1$ is usually not explicitly shown, unless to prevent confusion). The following ligands were used: benzene (**1**), ethylene (**2**), acetylene (**3**), cyclohexa-1,4-diene (**4**), cycloocta-1,5-diene (C_s) (**5**), cycloocta-1,5-diene (C_2) (**6**), κ^2,η^4-cyclonona-1,4,7-triene (**7**), buta-1,3-diene (**8**), κ^3,η^6-cyclonona-1,4,7-triene (**9**), hexamethylbenzene (**10**), and benzotricyclobutadiene (**11**). Hence, for example, **2-Na** and **3_2-K** refer to $[Na(C_2H_4)]^+$ and $[K(C_2H_2)_2]^+$, respectively.

Results and Discussion

The discussion of cation−π bonding effects is divided into several parts, starting with isolated double and triple bonds, then double bonds constrained in a framework, followed by a brief examination of some substituent effects on bond strength, and finally a description of a geometric model of

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TABLE 2. Calculated Energies (kilocalories per mole) for 2_n-M

complex	energy	protocol	ref
2-Li	−18.99	MP2/6-31+G//MP2/6-31+G(d)	2
	−19.7	MP2(FULL)/6-311++G(d,p)//MP2(FULL)/6-31G(d)	8
	−22.3	PBE1PBE/aug-cc-pVTZ(C,H); cc-pCVTZ(Li)[a]	18
	−21.0	P1	this work
	−20.9	P2	
2_2-Li	−40.6	PBE1PBE/aug-cc-pVTZ(C,H); cc-pCVTZ(Li)[a]	18
	−39.0	P1	this work
	−38.6	P2	
2_3-Li	−51.8	PBE1PBE/aug-cc-pVTZ(C,H); cc-pCVTZ(Li)[a]	18
	−51.1	P1	this work
	−50.6	P2	
2-Na	−12.36	MP2/6-31+G//MP2/6-31+G(d)	2
	−12.7	MP2/6-311+G(2d,2p)//MP2/6-31G(d)	31
	−14.9	HF/6-31G(d)	32
	−14.6 ± 0.2	CCSD(T)/CBS(est.)//MP2(FC)/CBS	13
	−14.9	PBE1PBE/aug-cc-pVTZ(C,H); cc-pCVTZ(Na)[a]	18
	−13.9	P1	this work
	−13.5	P2	
	−10.7 ± 1.0	experimental (CID)	16
2_2-Na	−27.4	PBE1PBE/aug-cc-pVTZ(C,H); cc-pCVTZ(Na)[a]	18
	−26.4	P1	this work
	−26.8	P2	
2_3-Na	*b*	BP86/TZVPP	33
	−37.5	PBE1PBE/aug-cc-pVTZ(C,H); cc-pCVTZ(Na)[a]	18
	−36.4	P1[c]	this work
2-K	−7.05	MP2/6-31+G//MP2/6-31+G(d)	2
	−8.02	MP2/aug-cc-pVDZ//MP2/aug-cc-pVDZ	2
	−8.29	B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d)	34
	−8.9	PBE1PBE/aug-cc-pVTZ(C,H); cc-pCVTZ(K)[a]	18
	−8.0	P1	this work
	−6.8	P2	
2_2-K	−17.1	PBE1PBE/aug-cc-pVTZ(C,H); cc-pCVTZ(K)[a]	18
	−16.8	P1	this work
	−14.9	P2	
2_3-K	−23.8	PBE1PBE/aug-cc-pVTZ(C,H); cc-pCVTZ(K)[a]	18
	−23.4	P1[c]	this work

[a] The same functional/basis set combination was used for both geometry optimization and frequency calculation. [b] The binding energy was not reported; Na−C bond length of 2.852 Å. [c] The P2 job failed to complete.

cation−π interactions and an examination of their bonding energetics.

Isolated Double and Triple Bonds. The results of a series of calculations on **2_n-M** and **3_n-M** cations are provided in Tables 2 and 3 and Figure 1. These are closely equivalent to other calculations for alkali metal−ethylene−acetylene complexes in the literature, some of which are included for comparison. For the ethylene complexes, the results from P1 and P2 match each other for the Li^+ species and **2_1-Na** and **2_2-Na** within 0.5 kcal/mol; with **2_3-Na** and all the potassium ethylene complexes, the discrepancies are larger, up to 4.3 kcal/mol. Neither protocol consistently produces greater binding energy. For the acetylene complexes, the results from P1 and P2 are always within 1.5 kcal/mol of each other; neither consistently suggests a greater binding energy.

An examination of the trends in binding enthalpies for the ethylenes is instructive. As expected, the enthalpies decrease in the following order: $Li^+ > Na^+ > K^+$. If an average over both protocols is used, there is a roughly additive increase in the interaction energy with each additional ethylene molecule for Na^+ and K^+ of 12 and 9 kcal/mol, respectively. For Li^+, the second ethylene adds 18 kcal/mol to the binding energy, whereas the third adds only 12 kcal/mol. It is also clear that, as previously noted,[18] three ethylene molecules arranged around the metal center interact more strongly than does a single benzene molecule, and two ethylene molecules arranged on either side of the metal interact approximately as strongly as benzene does.

TABLE 3. Calculated Energies (kilocalories per mole) for 3_n-M

complex	energy	protocol	ref[a]
3-Li	−21.3	P1	
	−21.3	P2	
3_2-Li	−41.6	P1	
	−39.9	P2	
3_3-Li	−52.7	P1	
	−52.0	P2	
3-Na	−14.5	HF/6-31G(d)	32
	−14.3	B3LYP/cc-pVTZ(C,H); AVTZ(Na)[b]	35
	−13.9	P1	
	−13.6	P2	
3_2-Na	−26.2	P1	
	−27.1	P2	
3_3-Na	−35.8	P1	
	−37.1	P2	
3-K	−8.4	P1	
	−8.2	P2	
3_2-K	−17.0	P1[c]	
3_3-K	−24.3	P1	
	−23.5	P2	

[a] Reference is to this work, unless otherwise specified. [b] For geometry optimization, a truncated version of the AVTZ basis set was used. [c] The P2 job failed to complete.

The results for **3_2-M** complexes parallel those with ethylene (Figure 1 and Table 3). The binding enthalpies of the acetylenes tend to be slightly higher, but all are within 2 kcal/mol for comparable **3_n-M/2_n-M** systems.

Constrained Double Bonds. The results of a series of calculations on the **4-M**, **5-M**, **6-M**, **7-M**, and **8-M** cations are

TABLE 4. Calculated Energies (kilocalories per mole) for Complexes with Constrained Double Bonds

complex	energy	protocol	ref[a]
4-Li	−35.1	MP2/6-31+G(d)//MP2/6-31+G(d)	14
	−35.1	MP2/6-311++G(d,p)//MP2/6-311++G(d,p)	14
	−37.0	P1	
	−35.0	P2	
5-Li	−43.1	P1	
	−41.7	P2	
6-Li	−44.8	P1[b]	
7-Li	−40.9	P1	
	−41.3	P2	
8-Li	−26.6	MP2(FULL)/6-311++G(d,p)//MP2(FULL)/6-31G(d)	8
	−30.3	P1	
	−29.9	P2	
4-Na	−24.0	MP2/6-31+G(d)//MP2/6-31+G(d)	14
	−22.3	MP2/6-311++G(d,p)//MP2/6-311++G(d,p)	14
	−23.6	P1	
	−22.4	P2	
5-Na	−28.6	P1	
	−27.2	P2	
6-Na	−29.0	P1[b]	
7-Na	−26.1	P1	
	−25.2	P2	
8-Na	−18.4	P1	
	−17.9	P2	
4-K	−16.6	MP2/6-31+G(d)//MP2/6-31+G(d)	14
	−15.1	P1	
	−13.2	P2	
5-K	−18.1	P1	
	−16.0	P2	
6-K	−18.3	P1[b]	
7-K	−16.0	P1	
	−14.8	P2	
8-K	−11.9	P1	
	−10.5	P2	

[a] Reference is to this work, unless otherwise specified. [b] The P2 job failed to complete.

provided in Table 4 and Figure 1. Buta-1,3-diene (**8**) is a conjugated system. Its cation−π complexes have been studied previously in both cis and trans forms,[8] but the cis form was included here for comparison, as it allows the metal cation to interact with both double bonds. Two local minima were found for the complexes with cycloocta-1,5-diene and cyclonona-1,4,7-triene; for the latter, the conformation in which only two double bonds coordinate to the metal (**7-M**) is discussed in this section. In general, the results from the use of P1 and P2 are comparable, although the discrepancy in the binding energies is larger than in the case of the isolated double bonds and ranges up to 5 kcal/mol. For the sake of simplicity, only the results of the P1 calculations will be discussed in detail here.

TABLE 5. Calculated Energies (Δ*H*°, kilocalories per mole) for 9-M

protocol	**9-Li**	**9-Na**	**9-K**
P1	−49.9	−32.8	−20.9
P2	−46.3	−30.5	−16.0

Regardless of the metal, the bonding energy of **4-M** is only ca. 2−3 kcal/mol lower than that of **2_2-M** and, as previously noted, is similar to that of **1-M**.[14] This is true even though the π-electron density of cyclohexa-1,4-diene and benzene is confined to one hemisphere of the metal cation, rather than being distributed around the metal as with the ethylenes. The two local minima of the **5-M** and **6-M** complexes have very similar energies ($<$0.5 kcal/mol difference for the Na^+ and K^+ systems). Their bonding energy surpasses that for the **2_2-M** complexes (in the case of **6-K**, by only 1.5 kcal/mol, but for **6-Li**, by 6.2 kcal/mol). **7-M** displays bonding energies roughly comparable to those of the ethylenes (2.3 kcal/mol greater for **7-Li** and 0.8 kcal/mol less for **7-K**).

Noticeably different in this regard is the bonding energy of **8-M**, which ranges from 4.9 to 8.3 kcal/mol less than in the **2_2-M** complexes; in the case of **8-Na**, the 8 kcal/mol decrease represents a 30% drop in energy. Given the results with the ring systems described above, the discrepancy is probably not principally the result of the confinement of the π-electron density to one hemisphere of the metal; this is discussed in more detail below.

Constrained Bonds in the [M(κ^3,η^6-1,4,7-Cyclononatriene)]$^+$ Cations (9-M). The results of calculations on the **9-M** cations are provided in Table 5 and Figure 1. The P1 results indicate that the bonding to the cations is weaker than in the comparable **2_3-M** systems by an average of 2.4 kcal/mol, but this is still considerably stronger than in the benzene systems. As the π-bonds are concentrated on one face of the metal ion, these results corroborate the minimal importance of the uniform distribution of π-electron density around the metal center for optimal bonding. The results with P2 are less easily interpreted, as they indicate a progressive decrease in the binding energy from Li^+ to K^+ relative to the benzene

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TABLE 6. Calculated Energies ($\Delta H°$, kilocalories per mole) for Substituted Systems

M^+	complex	energy	protocol
Li	**10-Li**	−52.9	P1
		−51.8	P2
	11-Li	−42.7	P1
		−40.8	P2
Na	**10-Na**	−31.8	P1
		−32.1	P2
	11-Na	−30.1	P1
		−29.8	P2
K	**10-K**	−23.1	P1
		−22.1	P2
	11-K	−19.6	P1
		−17.9	P2

systems. The **9-Li** complex is 10.2 kcal/mol more stable than the **1-Li** cation (cf. the 8.6 kcal/mol difference with P1), but with P2, the **9-K** complex underbinds the comparable benzene system by 2 kcal/mol.

Substituted Arenes. Previous studies comparing the bonding of ethylene and 2,3-dimethylbut-2-ene (i.e., tetramethylethylene) have indicated that the enhanced electron density provided by the methyl groups increased the binding energies by 40−50% for the Li^+ complex and by ca. 30% for the Na^+ complex.[14] Enhancements of the binding energy are also observed on permethylation of the benzene ring (see Figure 1 and Table 6); with both P1 and P2, the increase in the **10-M** complexes is in the following order: $Li^+ > Na^+ > K^+$ (enhancement of 12−16 kcal/mol for **10-Li** and 4−7 kcal/mol for the **10-K** counterparts).

The molecule benzotricyclobutadiene (**11**) was examined as a planar analogue to benzene, but one in which the aromatic ring current has essentially disappeared.[36] Although current density maps indicate that the central π-system resembles that for three isolated double bonds, interaction between the π-bonds of the annelated rings and those of the central system generates new MOs that are spread over the entire system.[37] With P1, there is very little change in binding energy with **11-Li** compared to the complex with unsubstituted benzene (**1-Li**; 3% increase), although the sodium and potassium analogues display increases of 28 and 23%, respectively. As with **7-M** and **9-M**, the results from P2 differ somewhat from these: the **11-Li** complex shows greater enhancement compared to **1-Li** (13%), the increase in the level of binding of **11-Na** (31%) is roughly the same as with P1, but **11-K** and **1-K** are equal in energy.

Evaluation of the Angular Dependence on Binding. It is clear that on a per π-bond basis, olefinic bonds display greater interaction energy with alkali metal cations than benzene does.[14,18] What accounts for the difference? A topographical contribution to the interaction energy was evaluated first, given that "geometric considerations" have been previously suggested as the source of the enhanced binding of olefins.[2,18] A regularly spaced distribution of the electron density around the metal (as in the **2_2-M** and **2_3-M** systems) is not an adequate explanation for the difference, however, as the constrained olefinic systems (e.g., **4-M** and **9-M**) bind just as well to the cations, despite having their π-electron densities confined to a single hemisphere of the metal. A more likely source for the greater binding interaction is the greater ligand flexibility offered by olefins, which can optimize the orientation of the π-bonds toward the cations.[14] We tested a simple geometric model to examine this possibility in more detail.

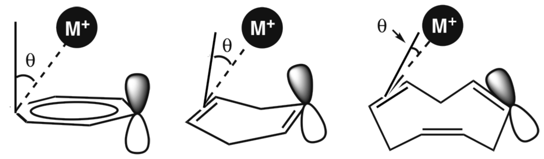

FIGURE 2. Definition of the angular displacement of the π-bonds toward the metal. The solid line is the normal to the π-bond, which is taken as being perpendicular to the ring plane in arenes (left) or assumed to lie above the plane defined by the two carbons generating the π-bond and the carbons bonded to them, as in **4-M** (middle) or **9-M** (right). For **2_n-M** (isolated olefins), the orientation angle equals 0°.

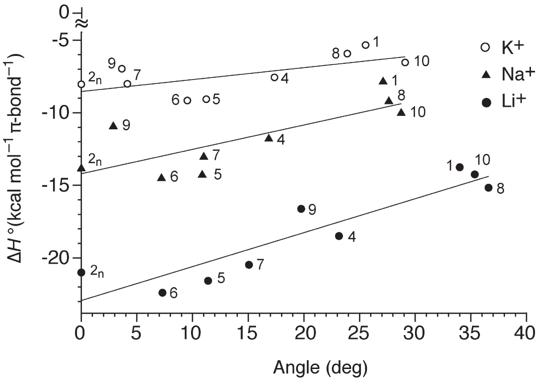

FIGURE 3. Plot depicting the decrease in the binding energy as a function of the displacement angle of the lone pairs. The best-fit lines for each metal center are also given. Numbers refer to the **X** in the **X-M** complexes of Table 1.

An angle θ can be defined by the normal to the π-bond and a line drawn from the midpoint of the π-bond to the cation; it serves as a measure of the orientation of the π-electron density (Figure 2). With this definition, the perpendicular orientation of ethylene toward a cation is set at $\theta = 0°$, and larger values of θ reflect increasingly greater rotation of the bonds. θ will also vary with the distance from the cation to the π-bond, becoming smaller with longer separations. In the case of benzene, for example, θ (using P1) varies from 34.0° in **1-Li** (Li−π-bond midpoint of 2.178 Å) to 25.5° in **1-K** (K−π-bond midpoint of 3.043 Å).

Plots of the P1 interaction energies versus orientation angle θ for the three different metals are given in Figure 3. The enthalpies were divided by the number of π-bonds in each system so that all the complexes could be considered in a single plot. The binding energies naturally group themselves into three areas, in the following order: $Li^+ > Na^+ > K^+$. For the lithium complexes, the relationship between θ and the binding energy proves to be quite strongly linear (slope = 0.23; $r^2 = 0.84$); there is a variation in energy of 8.6 kcal/mol over a $\Delta\theta$ range of 36.6°.[38] Besides **2-M** itself, the strongest interaction energies are found for **5-M** and **6-M**, i.e., in the large and flexible cycloocta-1,5-diene rings in which the

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[38] A somewhat more sophisticated model involving the cosine of the θ angle was also explored, but it did not provide appreciably better correlation with the binding energy.

TABLE 7. Cation Charges and Decomposition of Select Calculated Energies (kilocalories per mole)

compound	VDD charge	Hirshfeld charge	ΔV_{elstat}	ΔE_{Pauli}	ΔE_{oi} XC	ΔE_{oi} pol/CT	ΔE_{total}
2-Li	0.62	0.73	−13.95	8.00	−6.59	−10.29	−22.83
2_2-Li	0.29	0.49	−25.56	13.92	−12.62	−17.79	−42.06
2_3-Li	0.17	0.34	−37.93	20.21	−13.04	−24.16	−54.92
1-Li	0.44	0.52	−16.49	12.16	−22.54	−13.27	−40.14
4-Li	0.46	0.55	−20.64	13.48	−18.64	−13.35	−39.15
9-Li	0.32	0.42	−27.17	15.53	−22.11	−18.83	−52.57
2-Na	0.69	0.79	−11.41	5.76	−0.85	−9.23	−15.74
2_2-Na	0.42	0.61	−21.63	10.61	−3.18	−15.11	−29.31
2_3-Na	0.31	0.48	−28.46	13.06	−6.47	−17.70	−39.58
1-Na	0.62	0.68	−15.37	7.57	−13.85	−4.07	−25.71
4-Na	0.58	0.67	−18.15	9.27	−7.35	−10.50	−26.73
9-Na	0.47	0.58	−24.33	12.27	−9.09	−14.38	−35.55
2-K	0.70	0.85	−8.29	5.11	0.01	−6.43	−9.60
2_2-K	0.43	0.72	−15.00	8.36	−0.05	−11.39	−18.07
2_3-K	0.29	0.60	−21.55	12.07	0.67	−16.72	−25.53
1-K	0.61	0.74	−13.55	9.26	−7.16	−6.48	−17.93
4-K	0.57	0.75	−13.62	9.44	−4.77	−8.40	−17.36
9-K	0.47	0.67	−19.80	13.64	−4.28	−13.14	−23.58

double bonds are able to orient themselves more directly toward the cations than in the arenes. Noticeable here is the comparatively weak binding of **8-M**; the rigidity of its conjugated π-system places it in the same region of the plot as the arenes, with a less-than-optimal orientation of the π-bonds toward the cations.

The complexes with sodium display less angular dependence than do those of lithium; the slope of the line (0.17) has decreased, and the scatter is now greater ($r^2 = 0.60$). The potassium complexes continue the trend, with an even more nearly horizontal slope (0.08) and less correlation ($r^2 = 0.43$). The decrease in correlation with Na^+ and K^+ compared to Li^+ partially reflects the greater distance from the cations to the π-bonds with the former two, so that the exact positioning of the metals relative to the ligands is not as critical as for the smaller Li^+; the more limited range of θ values in potassium complexes compared to those for lithium ($\Delta\theta = 29.1°$ and $36.6°$, respectively) is an indication of this.

Charge Distribution Effects. Because the stronger binding of isolated and nonconjugated olefins relative to arenes is as evident in the Na^+ and K^+ complexes as with the Li^+ counterparts, other factors in addition to geometric orientations must be contributing to the relative strength of these cation−π interactions. Charge distribution effects were examined via calculation of Hirshfeld and Voronoi deformation density (VDD) charges for the systems involving benzene, ethylene (1−3), cyclohexadiene, and cyclononatriene and are listed in Table 7. Both charge schemes involve the partitioning of electron density distributions, rather than a population analysis of wave functions (as in Mulliken and NPA analysis). The VDD charges, in particular, are a measure of the amount of charge that moves out of or into the Voronoi cell of a given atom, i.e., the region of space that is closer to the nucleus of the atom than to any other nucleus.[30]

Several trends are evident in the VDD charges. One is that, as expected, their values decrease along the series **2-M**, **2_2-M**, and **2_3-M**, but also that the addition of the third ethylene makes a smaller change to the charge compared to the roughly comparable change made by the first two ethylenes. For example, the VDD charges for **2-Na**, **2_2-Na**, and **2_3-Na** are 0.69, 0.42, and 0.31, respectively, representing successive decreases from an initial +1 charge of 0.31e, 0.27e, and 0.11e, respectively. For the lithium complexes, the decreases are 0.38e, 0.33e, and 0.12e, respectively; for the potassium complexes, the decreases are 0.30e, 0.27e, and 0.14e, respectively. There may be a saturation effect functioning here. It should also be noted that the VDD charges for the benzene complexes (**1-M**) fall in every case between those of **2-M** and **2_2-M**; for the lithium and potassium species, the charge transfer from benzene is in fact close to the average of the **2-M** and **2_2-M** values.

The Hirshfeld charges are consistently somewhat larger than the VDD equivalent, and the values for the benzene complexes are closer to that of **2_2-M** than to that of **2-M**; in the case of potassium, the Hirshfeld charge on **1-K** is indistinguishable from that of **2_3-K** (0.61 and 0.60, respectively). Mirroring the trend in bonding energies, the Hirshfeld charges on the cations in the diethylene (**2_2-M**) and cyclohexadiene (**4-M**) systems are numerically close (0.49 and 0.52, 0.61 and 0.67, and 0.72 and 0.75 for Li^+, Na^+, and K^+, respectively) and underscore the relative unimportance of the location of the π-bonds around the metal cations. Finally, the generally increasing charge for the systems in the order Li < Na < K reflects the trend in the metal electronegativity.

Bond Energy Decomposition. The interaction energies (ΔE_{int}) of the **1-M**, **2_nM**, **4-M**, and **9-M** systems were decomposed as described in Computational Methods and are presented in Table 7. Of particular interest are the ethylene systems and their relationship to benzene. Focusing first on the electrostatic energy, we note that the successive addition of ethylenes around the metals has a similar effect on ΔV_{elstat}, regardless of the metal; the **2-M**:**2_2-M**:**2_3-M** energy ratio is 1.0:1.7:2.5 for Li, 1.0:1.8:2.3 for Na, and 1.0:1.6:2.4 for K. Given that the total binding enthalpies are similar for the benzene and diethylene systems, it is notable that the ΔV_{elstat} values for **1-M** are all midway between those of **2_1-M** and **2_2-M**. The larger **4-M** and **9-M** systems always display smaller ΔV_{elstat} values than their ethylene counterparts (**2_2-M** and **2_3-M**, respectively), but the ΔV_{elstat} values for **4-M** are consistently equal to or greater than those for **1-M**.

The ΔE_{Pauli} term, which stems from occupied orbital interactions and accounts for steric repulsion, is smaller for **1-Li** and **1-Na** than for **2_2-Li** and **2_2-Na** and smaller for **9-Li** and **9-Na** than for **2_3-Li** and **2_3-Na** but is approximately the same for **4-Li** and **4-Na** and **2_2-Li** and **2_2-Na**. The Pauli terms for the **1**, **4**, and **9** potassium systems are larger than for the corresponding ethylene systems **2_2-K**, **2_2-K**, and **2_3-K**, respectively.

The ΔE_{oi} term includes exchange interactions and polarization and charge transfer effects; although the exchange interactions can be separated out of the term, polarization and charge transfer, representing simultaneous intrafragment and interfragment interactions, respectively, cannot be rigorously partitioned. The latter two are consequently discussed together. The **2-M**:**2_2-M**:**2_3-M** polarization/charge transfer energy ratio is 1.0:1.7:2.3 for Li, 1.0:1.6:1.9 for Na, and 1.0:1.8:2.6 for K, i.e., roughly similar to the ratios observed for ΔV_{elstat}. The polarization/charge transfer energy for the **2_2-M** systems is consistently greater than for the benzene **2_2-M** counterparts, by ratios varying from 1.3 (Li) to 3.7 (Na). As a fraction of total energy, the contribution from the polarization/charge transfer term is always larger for two ethylenes than for benzene; the ratio increases from 0.42 for **2_2-Li** to 0.63 for **2_2-K**, and the corresponding ratio for **1-M** is 0.33 for Li, 0.36 for K, and, somewhat anomalously, 0.16 for Na. These values point to polarization/charge transfer effects as a key source of the bonding energies in the ethylene complexes, even more so than in the benzene systems.[39]

Such differences may be traceable in part to properties of the hydrocarbons themselves. For example, the magnitude of an induced dipole varies with the size of the dipole polarizability tensor along a line between the ion and the center of mass of the molecule.[40] The magnitudes of the dipole polarizability tensors for benzene and ethylene perpendicular to the molecular planes are 44.1 and 22.9 au, respectively,[41] i.e., in a 1.9:1 ratio. Polarization energy terms in molecules are not strictly additive,[42] but it appears that two ethylene molecules can be competitive with benzene in their contributions to the net binding energy.

Conclusions

The strength of cation−π interactions is a subject of considerable interest, particularly with regard to the way they might be strengthened with suitable modifications to the π-electron sources. In the course of this study, we have confirmed that the number of π-electrons in a ligand, per se, is not an adequate predictor of the strength of cation−π interactions to alkali metal cations. The equidistant distribution of electron density around a cation is not a critical element in the binding energy, either; e.g., three double bonds confined to one hemisphere of the metal are essentially as effective as three equally disposed π-bonds.

The orientation of the π-bonds toward the cation plays a role in the net cation−π interaction energy. The relative weakness of the cation−benzene interaction compared to the cation−ethylene interaction is partially a result of the aromatic ring's rigid structure, and the nonoptimal orientation of its π-electrons toward the metal center. This effect can account for a variation of up to almost 9 kcal/mol per π-bond in lithium systems; in complexes of sodium and potassium, with their longer metal−ligand distances, the variation is smaller. Polarization/charge transfer effects are an important component in cation−π binding in arenes, and they appear to play an even larger role in their olefin counterparts. Given that ligand substituents can enhance the polarizability of π-bonds,[43] their manipulation should provide a potentially fruitful avenue for improving cation−π binding in olefins.

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Supporting Information Available: Coordinates and absolute energies of the geometry-optimized structures and absolute energies of the molecules discussed here. This material is available free of charge via the Internet at http://pubs.acs.org.

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