Cation−π Interaction in Al(L)$^+$ Complexes (L = C_6H_6, C_5H_5N, C_5H_6, C_4H_4NH, C_4H_4O)

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The cation−π interactions between Al^+ and aromatic systems have been investigated by ab initio molecular orbital and density functional methods. The structures and bond dissociation energies (BDEs) of Al^+−L complexes (L = benzene, pyridine, cyclopentadiene, furan, pyrrole) have been calculated using Hartree−Fock (HF), Møller−Plesset perturbation, quadratic configuration interaction, pure density functional theory (DFT), and DFT/HF-hybrid methods. The following 0 K BDE data have been obtained: BDE(Al^+−benzene, C_{6v}) = 35.6 kcal/mol, BDE(Al^+−pyridine, C_{2v}) = 46.4 kcal/mol, BDE(Al^+−cyclopentadiene, C_s) = 33.9 kcal/mol, BDE(Al^+−furan, C_{2v}) = 22.2 kcal/mol, BDE(Al^+−furan, C_s) = 29.2 kcal/mol, and BDE(Al^+−pyrrole,C_s) = 41.6 kcal/mol. As a result from the molecular orbital analysis, the bonding mechanism of the Al^+−(π-L) complexes (π-L assigns the ligands L = C_6H_6, C_5H_6, C_4H_4O, interacting via their π-system with Al^+) is characterized by a π-type electron-donation HOMO(ligand) → LUMO(Al^+). Additionally, a deficiency of the widely applied Lee−Yang−Parr correlation functional is uncovered: As compared to the data obtained from ab initio correlation methods and the results from the Perdew−Wang correlation functional, the BDE(Al^+−(π-L)) are underestimated consistently by ca. 5−8 kcal/mol independent of the applied basis set and exchange functional.

Introduction

Noncovalent intermolecular forces play a major part in determining the structures and reactivity of organic,[1] organometallic,[2] and biological[3] molecules. An increasing interest concerning the description and prediction of cation−π interactions within aromatic systems[4−6] has emerged, because the attraction between cations and aromatic π-systems is found to be conceptually different compared to other noncovalent binding forces.[7] At least two extremes exist within the classification of cation−π interactions: (i) The bonding of transition metals with benzene[4c] as in $Cr(C_6H_6)_2$ or in the Ag(arene)$^+$ or Ag(olefin)$^+$ complexes,[8] which can be described by the Dewar−Chatt−Duncanson donor−acceptor model[9] and (ii) the interaction of Li^+ and other alkali-metal ions with arenes,[4d−h,7] being primarily electrostatic in nature.

Most of the bond-making and -breaking processes in homogeneous and heterogeneous catalysis occur at coordinatively unsaturated metal centers, e.g., electron-deficient aluminum complexes.[10] To develop catalysts for industrial applications, a more direct structure/reactivity information on "cation-like" catalytic centers is highly desirable.[11] For the characterization[12] of metal−ligand bonds, seemingly exotic techniques as matrix isolation,[13] gas−phase ion−molecule reactions[14] or molecular orbital (MO) theory[15−17] have been employed. It was recognized, that the coordination mode *n* in M(η^n-arene) complexes is of key importance in organometallic chemistry.[18] Interconversions of the form

$$M(\eta^6\text{-arene}) \rightleftharpoons M(\eta^4\text{-arene}) \rightleftharpoons M(\eta^2\text{-arene}) \qquad (1)$$

are expected to occur[18a,19] during (i) metal−arene bond formation or dissociation, (ii) hydrogenation of arenes, and (iii) inter- or intramolecular ("haptotropic shift")[20,21] exchange of arene ligands. With regard to the neutral $Al(C_6H_6)^\bullet$ complex, for example, three different minima structures have been proposed by McKee.[22]

The focus of the present theoretical investigation is set on the cationic singlet-state aluminum complexes[16,23] Al(L)$^+$ with L = benzene, pyridine, cyclopentadiene, furan, and pyrrole. Due to the polarizable $3s^2$ shell of Al^+ (^1S),[24] the Al(L)$^+$ complexes are expected to play an intermediate role considering the mostly electrostatic interaction of aromatics with singlet-state alkali ions and the more covalent character in benzene-multiplet transition-metal[25] ion complexes.[4c] The ligands L represent a selection of π- and σ-donor ligands and the mode of coordination is not always ad hoc predictable.[4g] The density functional formalism will be applied to answer the questions concerning (i) the origin and analysis of the attractive forces in the Al^+−L complexes, (ii) the determination of the bond dissociation energies (BDEs) of Al^+−L, (iii) the mode of the metal ion−ligand coordination (e.g., η^6 vs η^1 in Al^+−pyridine), and (iv) the structure of the ground-state Al(L)$^+$ complexes.

Computational Details

The quantum chemical calculations have been performed by using the GAUSSIAN 94 program package[26] on Digital DEC 3000/300 workstations and on a SGI Power Challenge R8000 with four processors. The density functional theory (DFT)[27,28] has been applied to the calculations because it was recognized as a promising alternative approach in the field of ab initio chemistry even in comparison with the electron-correlation formalisms. Bond dissociation energies, however, tend to be overestimated resulting from deficiencies in the treatment of exchange energies.[29] Recently, Becke proposed a hybrid of the exact Hartree−Fock (HF) theory and density functionals.[30] It was significantly more accurate compared to other density functionals with regard to the atomization energies and ionization potentials of 56 Gaussian 2 (G2)[31] molecules.[32]

In the present calculations, Slater's local (S)[26] and Becke's density gradient-corrected (B)[32g] exchange functionals combined with the correlation functionals reported by (i) Vosko, Wilk, and Nusair (VWN and VWN5),[32a] (ii) Lee, Yang, and Parr (LYP),[32e] (iii) Perdew (P86),[32c,d] and (iv) Perdew and Wang (PW91)[32h] have been employed. The abbreviations SVWN,

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TABLE 1: Bond Dissociation Energies (BDEs, in kcal/mol) Including the Zero-Point Vibrational Energies of the $Al^+-C_6H_6$ (C_{6v}, $^1A_1$) Complex As Obtained from Different Levels of Theory

	basis set						
method	3-21G	6-31G(d)	6-311+G(d)	6-311++G(3df,2p)	cc-pVDZ	cc-pVTZ	literature
HF	29.5	28.5	25.6	27.5	26.5	27.2[a]	
MP2(full)		40.1	36.5	39.1[b]	36.3	40.1[a]	39.0[c]
QCISD(T)		36.1[b]	33.3[b]		32.6[b]		
SVWN	51.9	49.9	44.9	46.1[d]	46.7	45.2[d]	
SVWN5	64.7	49.5	44.3	45.4[d]	46.2	45.1[a]	
SP86	63.5	61.5	56.8	58.4[d]	58.0	57.7[a]	
SPW91	62.9	61.2	56.8	58.6[d]	57.7	57.8[a]	
SLYP	57.3	55.0	48.9	50.0[d]	51.2	49.7[a]	
BP86	41.6	39.2	34.7	35.6[d]	36.3	35.5[a]	
BPW91	41.0	38.7	34.4	35.6[d]	35.9	35.4[a]	
B3PW91	40.1	38.3	34.5	36.0[d]	35.6	35.5[a]	
BLYP	36.5	34.1	28.3	28.9[d]	32.2	30.2[a]	
BHLYP	35.3	33.8	29.8	31.1[d]	31.3	30.8[a]	
B3LYP	36.5	34.5	29.6	30.4[d]	31.6	30.3[a]	
experiment							36(7)[e], 35(2)[f]

[a] ZPVE and geometry data taken from the corresponding method of calculation but with the cc-pVDZ basis set. [b] Single-point calculation on the MP2(full)/6-311+G(d) geometry. ZPVE-data from MP2(full)/6-311+G(d) calculations. [c] MP2(fc)/6-31G(d,p) calculation.[16d] [d] Single-point calculation employing the geometry and ZPVE data obtained from the corresponding method but with the 6-311+G(d) basis set. [e] Estimated from the linear fit of ligand−proton affinity vs ligand−aluminum affinity.[67] [f] Estimated from radiative association kinetics.[16f]

SVWN5, BLYP, BP86, and BPW91 indicate the pure DFT approaches. In addition, DFT/HF-hybride methods such as BHLYP,[30,33] B3LYP,[30] and B3PW91 have been applied.[34] In these cases a certain amount of Hartree−Fock exchange is added (50% in BHLYP, 20% in both, B3LYP and B3PW91). The numerical integration of the functionals was carried out with the standard "fine grid" procedure as implemented in GAUSSIAN 94.[26,35] According to previous suggestions,[23,36,37] basis set requirements are much less stringent for DFT than for post-HF methods. Therefore, Pople's split-valence basis sets (e.g.,"6-31G(d)") including polarization and diffuse functions[38] and the correlation-consistent basis sets "cc-pVDZ" and "cc-pVTZ" reported from the group of Dunning[39] have been used.[26,40] The ZPVE values obtained from the density functional treatment have been scaled uniformly by 0.98. The perturbational treatment second order (MP2)[41] or the quadratic configuration interaction including single, double, and estimated triple substitutions (QCISD(T))[42] have been applied for the reason of comparison. The MP2(full)/6-311+G(d) vibrational frequencies (scaled[43] by 0.94) and zero-point vibrational energies (ZPVE, scaled[43] by 0.96) have been combined with the QCISD(T) energies.

The B3LYP/6-311+G(d) and BPW91/6-311+G(d)-calculated geometries of the ligands L = benzene, pyridine, cyclopentadiene, furan, and pyrrole have been compared to experimental gas-phase data.[44] Concerning the bond lengths, a mean deviation of 0.005 Å and a maximum deviation of 0.011 Å has to be noted. The bond angles are reproduced with less than 1% error.[36b,45] The relative energies discussed in the text are given in kcal/mol and refer to the BPW91/6-311++G(3df,2p)//BPW91/6-311+G(d) total energies including the BPW91/6-311+G(d) calculated ZPVE contribution as described above. The bond lengths are given in angstroms and bond angles in degrees. The standard Mulliken MO population[46] and NPA charge analysis[47] were performed in all cases.

To estimate the charge-polarization (E_α),[12d] the charge-dipole (E_μ),[48,49] and the charge-quadrupole (E_Θ)[48,49] interactions within the Al^+-L complexes, the ligand's mean polarizabilities ($\alpha(L)$), the individual polarizability components (α_1, α_2, α_3), the dipole ($\mu(L)$), and molecular quadrupole ($\Theta(L)$, Θ_{aa}, Θ_{bb}, Θ_{cc}) moment data have been taken from the literature.[50] The charge on aluminum has been kept constant, $q_{Al} = 1\ e$. The amount of dispersion contribution (E_{disp}) has been calculated according to London.[51] In the case of **2** and **4a**, the Al^+-N and Al^+-O atom distances have been taken into account, since the HOMOs of the ligands pyridine and furan are dominantly located on N and O, respectively. The repulsive short-range interactions (E_{rep}) have been estimated following the treatment of Spackman.[52] By applying a simple addition scheme,[53] $E_\Sigma = E_\mu + E_\Theta + E_\alpha + E_{disp} + E_{rep}$ should provide an estimate of the total interaction energy between Al^+ (^1S) and L in the Al^+-L complexes.

Results and Discussion

In the beginning of this section, the results on the $Al(C_6H_6)^+$ complex as obtained with local and gradient-corrected density functionals are presented and compared. The accuracy of the present calculations has been estimated and a detailed analyses of the $Al^+-C_6H_6$ interaction will be provided. The $Al(L)^+$ complexes (L = benzene, pyridine, cyclopentadiene, furan, and pyrrole) will be characterized and the scheme of bonding will be reported. The section ends with a comparison of the present results and the literature-available data on the BDEs of metal cation−L complexes.

A. DFT Calculations on the BDE($Al^+-C_6H_6$). The BDE($Al^+-C_6H_6$) data as obtained at several levels of theory are summarized in Table 1. In comparison with the experimental data, i.e., BDE($Al^+-C_6H_6$) = 35 ± 2 kcal/mol,[16f,67a] (i) the HF method underestimates the BDE($Al^+-C_6H_6$) by roughly 10 kcal/mol, (ii) the MP2 calculations with the 6-31G(d), 6-311++G(3df,2p), and cc-pVTZ overestimate the BDE slightly, whereas for the MP2 level combined with the 6-311+G(d) and cc-pVDZ basis sets, the BDE is reproduced quite well, and (iii) the QCISD(T) predicted data are settled within the error bars of the experimental ones.

As expected,[29] the BDE($Al^+-C_6H_6$) data obtained from the SVWN, SVWN5, SLYP, SP86, and SPW91 approaches are overestimated. The BDE as predicted by the LSD approximations SVWN and SVWN5 are ca. 5−13 kcal/mol lower than those obtained with the local exchange and gradient-corrected correlation terms, i.e., SLYP, SP86, and SPW91. The three latter functionals yield an overestimation of the BDE by roughly 90%. Among them, it should be emphasized that the SLYP-calculated BDE data are lower by 5−8 kcal/mol as those from the SPW91 or SP86 methods for each of the given basis sets.

In line with the reports of other groups on gradient-corrected functionals,[32,36] the group of BP86, BPW91, and B3PW91 and the one of BLYP, B3LYP, and BHLYP perform similarly with regard to geometries and relative energies. Comparing the results on BDE($Al^+-C_6H_6$) from each group of functionals,

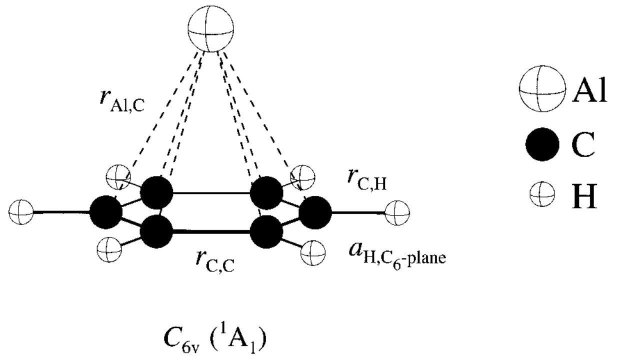

Figure 1. Definition of structural parameters in the C_{6v} symmetrical $Al(C_6H_6)^+$ ($^1A_1$) (**1**) complex. In Table 2 the respective data, $r_{Al,C}$, $r_{C,C}$, $r_{C,H}$, and $a_{H,C6\text{-plane}}$, are presented as obtained by different functionals.

however, the data from the LYP-containing functionals are consequently lower by ca. 5 kcal/mol.[54] These findings are independent from the applied exchange functional (Slater's local or Becke's gradient-corrected one, see above). Following the argumentation of Enzerhof et al.[55] and Barone et al.[36c] one reason for this distinct performance may be that the LYP correlation functional fails to reach the uniform electron gas limit. In contrast, the P86 and PW91 functionals respect the most important scaling and boundary conditions.[56] As it will be shown below, the underestimation of the BDE(Al^+-L) by applying the LYP correlation functional is not restricted to L $= C_6H_6$.

Considering different basis sets for a given density functional, the following trend is indicated. The BDE(Al^+-L) decreases approximately in the row 3-21G, 6-31G(d), cc-pVDZ, cc-pVTZ, 6-311++G(3df,2p), 6-311+G(d) for both the DFT and DFT/HF methods. The counterpoise correction[57] has been performed in order to estimate the amount of basis set superposition error (BSSE) in the Al^+-L complexes. The following BSSEs have been obtained employing the BPW91 density functional: 1−2 kcal/mol (6-31G(d)), 0.4−0.6 kcal/mol (6-311+G(d)), 0.2−0.5 kcal/mol (6-311++G(3df,2p)), ca. 1 kcal/mol (cc-pVDZ) and max 0.6 kcal/mol (cc-pVTZ).

The BPW91/6-311++G(3df,2p)//BPW91/6-311+G(d) calculated BDE (35.6 kcal/mol) fits perfectly with the latest experimental data[16f] of BDE($Al^+-C_6H_6$) = 35 ± 2 kcal/mol. Further, the respective BSSE is estimated comparatively low. Hence, the present calculations on the $Al(L)^+$ complexes have been performed employing this approach.[58] In addition, a comparison of the BPW91, B3LYP, and MP2 methods will be made, because they have been shown repeatedly to yield correct results on small molecular systems.[32,34,36,59]

B. Geometric Data of the $Al(C_6H_6)^+$ Complex. In Figure 1 the geometry of the $Al(C_6H_6)^+$ complex is displayed. Performing HF, MP2, and DFT frequency calculations, the C_{6v} symmetrical structure is proposed to be a local minimum in agreement with earlier results.[16d] The geometrical parameters (Table 2) have been obtained with the 6-31G(d), 6-311+G(d), and cc-pVDZ basis sets. The last two lines in Table 2 are statistical treatments over the given data indicating $r_{Al,C} = 2.72(9)$ Å, $r_{C,C} = 1.403(7)$ Å, $r_{C,H} = 1.093(10)$ Å, and $a_{H,C6\text{-plane}} = 0.2(4)°$, i.e., the hydrogens are bent away from the Al^+ center. If benzene is attached to Al^+ (^1S), an $r_{C,C}$ elongation does merely occur and the $r_{H,C}$ distance remains constant compared to the "free" benzene. The aluminum−C distance $r_{Al,C} = 2.72(9)$ Å, in $Al(C_6H_6)^+$ is slightly smaller as compared to the one in the Al(ethylene)$^+$ complex (2.856 Å) and similar to that in the Al(acetylene)$^+$ complex (2.748 Å).[16e] Employing different DFT and DFT/HF approaches, the predictions of the atom−atom distances are very similar contrary to the results on the BDE($Al^+-C_6H_6$) as discussed above.

TABLE 2: Comparison of the Calculated Geometrical Parameters of the $Al(C_6H_6)^+$ Complex As Defined in Figure 1

method	basis set	$r_{Al,C}$ (Å)	$r_{C,C}$ (Å)	$r_{C,H}$ (Å)	$a_{H,C6\text{-plane}}$ (deg)
HF	6-31G(d)	2.465	1.395	1.074	0.6
	6-311+G(d)	2.866	1.394	1.074	0.8
	cc-pVDZ	2.874	1.397	1.081	0.8
	cc-pVTZ	2.818	1.390	1.072	0.4
MP2(full)	6-31G(d)	2.687	1.404	1.087	0.4
	6-311+G(d)	2.756	1.406	1.087	0.6
	cc-pVDZ	2.765	1.413	1.094	0.5
SVWN	6-31G(d)	2.652	1.400	1.096	−0.2
	6-311+G(d)	2.675	1.395	1.095	0.0
	cc-pVDZ	2.685	1.401	1.102	0.0
SVWN5	6-31G(d)	2.660	1.402	1.098	−0.2
	6-311+G(d)	2.683	1.397	1.096	0.0
	cc-pVDZ	2.693	1.403	1.104	0.0
SP86	6-31G(d)	2.588	1.400	1.105	−0.4
	6-311+G(d)	2.605	1.395	1.104	−0.3
	cc-pVDZ	2.623	1.401	1.111	−0.2
SPW91	6-31G(d)	2.581	1.399	1.103	−0.4
	6-311+G(d)	2.597	1.394	1.102	−0.3
	cc-pVDZ	2.616	1.400	1.108	−0.2
SLYP	6-31G(d)	2.635	1.401	1.102	−0.3
	6-311+G(d)	2.659	1.396	1.101	−0.1
	cc-pVDZ	2.670	1.403	1.109	−0.1
BLYP	6-31G(d)	2.809	1.416	1.094	0.4
	6-311+G(d)	2.852	1.412	1.091	0.8
	cc-pVDZ	2.839	1.417	1.099	0.7
BHLYP	6-31G(d)	2.767	1.395	1.077	0.3
	6-311+G(d)	2.799	1.392	1.076	0.6
	cc-pVDZ	2.803	1.397	1.084	0.6
B3LYP	6-31G(d)	2.779	1.405	1.086	0.3
	6-311+G(d)	2.816	1.402	1.084	0.3
	cc-pVDZ	2.812	1.407	1.092	0.5
BP86	6-31G(d)	2.743	1.414	1.095	0.1
	6-311+G(d)	2.771	1.410	1.094	0.3
	cc-pVDZ	2.773	1.415	1.101	0.3
BPW91	6-31G(d)	2.733	1.413	1.093	0.0
	6-311+G(d)	2.760	1.409	1.092	0.3
	cc-pVDZ	2.763	1.414	1.099	0.3
B3PW91	6-31G(d)	2.723	1.404	1.086	0.0
	6-311+G(d)	2.746	1.400	1.085	0.3
	cc-pVDZ	2.755	1.405	1.092	0.4
averaged		2.72	1.403	1.093	0.2
standard deviation		0.09	0.007	0.010	0.4

C. MO Picture of the $Al^+-C_6H_6$ Interaction. To characterize the $Al^+-C_6H_6$ binding situation in a more detailed manner, a MO population analysis of the respective electronic wavefunction has been carried out. Similarly to the $Al^+-C_2H_4$ and the $Al^+-C_2H_2$ systems,[16b,16e] the traditional picture of Dewar, Chatt, and Duncanson[9] does not work for $Al^+-C_6H_6$ due to the lack of π-back donation from the metal to the ligand, because the electronic configuration of Al^+ (^1S) is [Ne] $3s^2$. Thus, compared to the free ligand, the C−C bond distances in $Al(C_6H_6)^+$ are not elongated remarkably, because benzene's antibonding orbitals are not occupied. Nevertheless, electron donation from the ligand to the cationic aluminum center occurs as illustrated by the results of the population analysis[46] and the charge distribution (NPA: $q_{Al} = 0.85\ e$).[47] According to Figure 2, the HOMO-2 and the HOMO-1 of $Al(C_6H_6)^+$ are identical in energy. They are characterized by a small π-type electron donation, $e_{1g}(C_6H_6) \rightarrow 3p_{x,y}(Al)$. The HOMO consists of more than 95 % of the Al's $3s^2$ orbital. The LUMO is 2-fold degenerated originating from the antibonding MO of the $e_{1g}(C_6H_6) \rightarrow 3p_{x,y}(Al)$ interaction, i.e., mostly from Al's unpopulated $3p_x$ and $3p_y$ orbitals parallel to the C_6 plane. The LUMO+2 and LUMO+3 originate solely from the antibonding e_{2u} orbitals of benzene.

D. Electrostatic Components of the $Al^+-C_6H_6$ Interaction. According to the primitive addition scheme of electrostatic and other interactions,[48,53,60] the overall attraction ($E_\Sigma = E_\mu +$

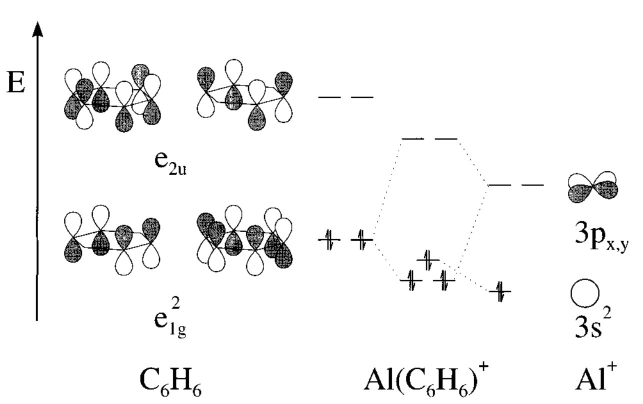

Figure 2. Schematic drawing of the interacting molecular orbitals in the $Al^+-C_6H_6$ complex as calculated from the HF, MP2, BPW91, and B3LYP methods. Note the increased energy of the HOMO in $Al(C_6H_6)^+$ relative to the $3s^2$ of the bare Al^+ (^1S).

$E_\Theta + E_\alpha + E_{disp} + E_{rep}$) between benzene and Al^+ (^1S) in the $Al^+-C_6H_6$ complex is composed as follows (Table 3): Ca. one-fourth results from the charge-induced polarization ($E_\alpha = 12.6$ kcal/mol) and three-fourths from the charge−quadrupole interactions ($E_\Theta = 41.3$ kcal/mol). The resulting $E_\Sigma = 36.0$ kcal/mol should not be taken as a quantitative measure since the amount of the short-range repulsive interaction, $E_{rep} = -20.7$ kcal/mol, has been estimated following the procedure of Spackman[52c] and the contribution of the dispersion energy ($E_{disp} = 2.8$ kcal/mol) has been calculated according to London.[51]

E. Al(L)$^+$ Complexes. To further analyze the interaction between Al^+ (^1S) and aromatic systems,[4g,61] the BDE(Al^+-L) data (Table 3) and the mode of the Al^+-L coordination (Figure 3) in $Al(C_5H_5N)^+$ (**2**, $^1A_1$), $Al(C_5H_6)^+$ (**3**, $^1A'$), $Al(C_4H_4O)^+$ (**4a**, $^1A_1$), $Al(C_4H_4O)^+$ (**4b**, $^1A'$), and $Al(C_4H_4NH)^+$ (**5**, $^1A'$) will be discussed in the following. The HF, MP2, and DFT frequency calculations indicate that Al^+ is η^1-coordinated to the heteroatom N in the electronic ground-state complex $Al(C_5H_5N)^+$ (**2**), resulting in the C_{2v} symmetrical complex. The potential energy surface (PES) is found to be very flat if Al^+ is positioned above the pyridine ring, but a corresponding minimum was not detected. In contrast, the ground-state complexes $Al(C_5H_6)^+$ (**3**) and $Al(C_4H_4NH)^+$ (**5**) posses C_s symmetrical structures and Al^+ is η^4-coordinated to the four unsaturated carbon atoms in **3** and **5**. Concerning the [Al^+,C_4H_4O] PES, two distinct isomers have been found. One consists of a C_{2v} geometrical symmetry structure (**4a**) and a $^1A_1$ electronic ground state, the other one belongs to the C_s symmetry point group (**4b**, $^1A'$). The reported structures[62] **1**−**5** are found to be the only minima of the respective ground-state [Al^+,L] PES. If the calculated geometrical parameters of the organic moiety in L and Al(L)$^+$ are compared, the complexation of the aluminum cation distorts the L's bond lengths and angles to less than 5%.

The effect of the applied basis sets on the BDE(Al^+-L) data shows qualitatively the same trend as in the case of the BDE($Al^+-C_6H_6$): The BDE(Al^+-L) decreases in the order 3-21G, 6-31G(d), 6-311++G(3df,2p), and 6-311+G(d) for both functionals, B3LYP and BPW91. Additionally, the applied correlation functional influences the BDE values. As mentioned above, the LYP and the PW91 correlation functionals perform distinctly. The former tends to underestimate the BDE of the $Al^+-C_6H_6$ complex by roughly 5 kcal/mol, whereas the latter seems to predict the BDEs more correctly. Similarly, concerning the BDE(Al^+-L) of **3**, **4b**, and **5** a difference in the BDE calculation of ca. 5 kcal/mol has been obtained *only for these π-bound complexes*, see below. The present calculations (BPW91/6-311++G(3df,2p)//BPW91/6-311+G(d), at 0 K) indicate that BDE($Al^+-C_5H_5N$) = 46.4 kcal/mol, BDE($Al^+-C_5H_6$) = 33.9 kcal/mol, BDE($Al^+-C_4H_4O$, $^1A_1$) = 22.9 kcal/mol, BDE($Al^+-C_4H_4O$, $^1A'$) = 29.2 kcal/mol, and BDE($Al^+-C_4H_4NH$) = 41.6 kcal/mol.

A comparison of the experimental[16f,67b] and calculated BDE data is possible only for the cases of **1**, **2**, and **4** (see above and Table 3). The accuracy of the BDE($Al^+-C_6H_6$) data have been discussed in section 3.A. Concerning **2** the ab initio calculated and experimental BDE(Al^+-L) data fit excellently. However, the DFT and MP2 calculations forecasts the BDE($Al^+-C_4H_4O$) too low by almost 15 kcal/mol. At the present time, we are not able to provide a satisfactory explanation for this discrepancy.

F. Analysis of the Al^+-L Interaction. According to the Mulliken MO population analysis,[46,47] the Al^+-L interaction is qualitatively very similar for the complexes **3**, **4b**, and **5**. The atomic charges on Al^+ as obtained from the NPA amount to $q_{Al}(\mathbf{3}) = 0.87\ e$, $q_{Al}(\mathbf{4b}) = 0.86\ e$, and $q_{Al}(\mathbf{5}) = 0.83\ e$.

In Figure 4, the cation−π interaction in the $Al(C_5H_6)^+$ complex is depicted schematically. It serves as a qualitative picture of the bonding mechanism in the Al(L)$^+$ complexes, **3**, **4b**, and **5**. The HOMO of these complexes consists dominantly of the $3s^2$-orbital of Al^+. The HOMO-1 and the HOMO-2 of the Al(L)$^+$ species result from the electron donation of the ligand's HOMO and HOMO-1 to the unpopulated 3p orbitals of aluminum. The low-lying unoccupied MOs of the complex are composed of the empty 3p(Al^+) and the ligand's LUMOs and LUMOs-1. It turns out from the present population analysis that the LYP correlation functional seems to underestimate the BDE(Al^+-L) in the cases of a π-type electron donation: HOMO(ligand) → LUMO(metal cation), as detected in the complexes **3**, **4b**, and **5**.

With regard to the Al^+-L binding analysis in the C_{2v} symmetrical complexes **2**,[46,47] we have found that the HOMO of **2** consists of a σ-type MO resulting from one sp^2-hybrid AO of the nitrogen atom and the Al's $3s^2$ and $3p_z$ orbitals. This HOMO is the only occupied MO with a significant interaction between the Al and C_5H_5N orbitals. The LUMO originates mainly from the Al's p-orbital perpendicular to the molecular plane. The NPA charge of aluminum has been calculated to be $q_{Al}(\mathbf{2}) = 0.92\ e$, indicating only a very small amount of electron transfer from the ligand.

For the isomer **4a**, the HOMO has been calculated to result from the diene system without any contributions from oxygen or aluminum. The HOMO-1 originates solely from furan's HOMO. The $3s^2$ orbital of aluminum and ca. 10% of the sp^2 orbital of O pointing to Al are dominating the HOMO-2. The LUMO consists mainly of the in-plane 3p(Al)-orbital perpendicular to the Al−O connection. The aluminum charge is $q_{Al}(\mathbf{4a}) = 0.96\ e$ according to the NPA. The PES in the region near to the C_{2v} symmetrical structure appears to be very flat: The barrier for the conversion **4a** → **4b** amounts to ca. 1 kcal/mol.

As indicated by the NPA calculated q_{Al} data given above, only a small charge-transfer component from the ligand L to the cationic aluminum center has been noticed for the complexes **1**−**5**. This is due to the huge difference between the IP data of the ligands L and the IP(Al^+)[50f] ranging from ΔIP = 15.06 eV for pyrrole up to 16.11 eV in the case of pyridine (Table 3). Considering the aluminum's NPA charges and the encountered problems concerning the BDE predictions applying either the LYP or the PW91 correlation functional, the following trend has been observed. In the π-bound Al complexes **1**, **3**, **4b**, and **5**, the NPA charges of Al^+ are slightly lower compared to those in the σ complexes **2** and **4a** (0.83−0.87 *e* vs 0.92−0.96 *e*). Apparently, further work is needed to analyze and eliminate the discrepancies connected with the LYP correlation functional.[63]

TABLE 3: BDE Values (kcal/mol) of the Singlet Complexes 1−5 Including ZPVE Corrections. The Estimated Charge-Induced Polarization (E_α in kcal/mol), Charge-Dipole (E_μ in kcal/mol), Charge−Quadrupole (E_Θ in kcal/mol), Dispersion (E_{disp} in kcal/mol), Repulsion (E_{rep} in kcal/mol) Interaction Energies and the Summed Energy (E_Σ) of the Complexes Al^+−L Are Given as Well as the Experimental Proton Affinities (PA in kcal/mol) and Ionization Potentials (IP in eV) of the Ligands L

method	$Al^+-C_6H_6$ (**1**) ($^1A_1$)	$Al^+-C_5H_5N$ (**2**) ($^1A_1$)	$Al^+-C_5H_6$ (**3**) ($^1A'$)	$Al^+-C_4H_4O$ (**4a**) ($^1A'$)	$Al^+-C_4H_4O$ (**4b**) ($^1A'$)	$Al^+-C_4N_4NH$ (**5**) ($^1A'$)
HF/6-31G(d)	28.5	42.8	23.6	20.6	21.2	34.5
HF/6-311+G(d)	25.6	40.5	21.1	18.5	18.6	31.0
B3LYP/3-21G	36.5	56.7	35.1	36.5	−	44.4
B3LYP/6-31G(d)	34.5	48.1	31.9	24.9	29.2	41.8
B3LYP/6-311+G(d)	29.6	44.4	27.2	21.9	24.1	36.1
B3LYP/6-311++(3df,2p)[a]	30.5	45.2	28.0	22.2	25.2	36.3
BPW91/3-21G	41.0	56.5	40.8	34.4	35.0	49.0
BPW91/6-31G(d)	38.7	49.0	37.0	24.7	33.2	46.3
BPW91/6-311+G(d)	34.4	45.7	32.7	21.9	28.5	41.2
BPW91/6-311++G(3df,2p)[b]	35.6	46.4	33.9	22.2	29.9	41.6
MP2(full)/6-31G(d)	40.1	50.3	35.9	25.8	32.9	47.4
MP2(full)/6-311+G(d)[c]	36.5	45.6	32.4	21.6	28.7	42.4
E_α[d]	12.6	18.2	13.0	13.2	12.4	13.1
E_μ	0.0	13.9	0.0	3.6	0.0	0.0
E_Θ[e]	34.4	8.3	17.3	−0.4	15.1	34.2
E_{disp}	2.8	24.3	2.7	17.0	2.9	2.7
E_{rep}	−14.8	−15.2	−14.8	−11.9	−13.2	−17.3
E_Σ	35.0	49.5	18.2	21.5	17.2	32.7
literature	36(7),[f] 35(2)[g]	44[h]		43[h]	43[h]	
PA[i]	181.3	220.8	199.6	192.2	192.2	207.6
IP[j]	9.246	9.25	8.56	8.883	8.883	8.208

[a] Single-point calculation, geometry, and ZPVE taken from the B3LYP/6-311+G(d) computation. [b] Single-point calculation, geometry, and ZPVE taken from the BPW91/6-311+G(d) computation. [c] ZPVE data taken from the MP2(full)/6-31G(d) computation. [d] The polarizability component parallel to the Al^+−L axis was taken. For more details, see text and ref 50. [e] The component of the quadrupole moment parallel to the Al^+−L axis was taken. For more details, see text and ref 50a−c. [f] Reference 67. [g] Reference 16f. [h] 298 K data from ligand−exchange equilibrium measurements,[67b] anchored on HF/6-31G(d) calculations.[17b] [i] PA data of the free ligands were taken from ref 68. [j] IP(Al) = 5.984 eV, IP(Al^+) = 18.823 eV, IP data taken from refs 50f and 68.

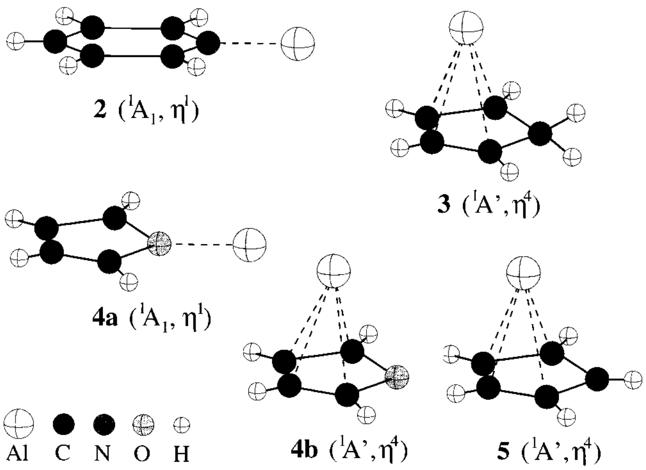

Figure 3. Modes of coordination (η^n, dashed line), and molecular symmetry of the ground-state minimum aluminum complexes $Al(C_5H_5N)^+$ (**2**), $Al(C_5H_6)^+$ (**3**), $Al(C_4H_4O)^+$ (**4a**), $Al(C_4H_4O)^+$ (**4b**), and $Al(C_4H_4NH)^+$ (**5**).[62]

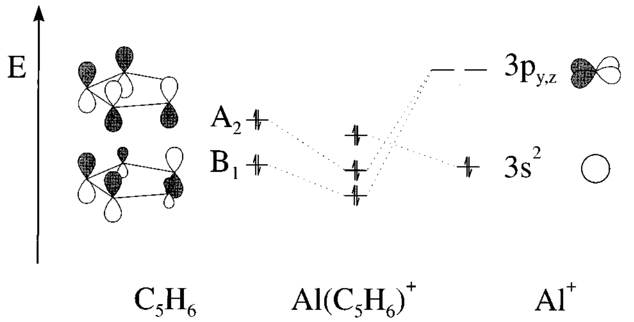

Figure 4. Schematic drawing of the interacting molecular orbitals in the $Al^+-C_5H_6$ complex as calculated from the HF, MP2, BPW91, and B3LYP methods. The π-type HOMO(ligand) → LUMO(Al^+) electron donation is found to be generally operative in the Al^+−(π-L) bonding mechanisms of the complexes **1**, **3**, and **4b**, and **5** (cf. Figure 2).

The application of the simple additive point-charge model results in quite a poor prediction of the Al^+−L bond dissociation energies: The amount of charge-induced polarization is similar for all aluminum complexes under investigation and varies from 12.4 kcal/mol (**4b**) to 18.2 kcal/mol (**2**).[64] E_μ adds to the attractive forces only in the case of **2** and **4a**. It vanishes in the complexes **1**, **3**, **4b**, and **5**, because (i) the molecular dipole moment of benzene is zero and (ii) Al^+ is oriented almost perpendicular relative to the molecular dipole moment of the ligands C_5H_6, C_4H_4O, and C_4H_4NH. With regard to the Al(L)$^+$ complexes except **4a**, the component of the L's molecular quadrupole moment[65] yields attractive interactions. Only in the cases of **1**, **2**, and **4a**, E_Σ predicts BDE values similar to the ab initio calculated ones. In comparison with the ab initio BDE, the classically estimated E_Σ for **3**, **4b**, and **5** appear too low (ca. 10−15 kcal/mol). The following explanations are reasonable: (i) The experimental data[66] of $\Theta_{cc}(C_4H_4NH)$ are connected with an error of ±20%. (ii) There may exist a significant octapole or higher-pole moment inducing additional contributions. (iii) The repulsive and dispersion forces have to be treated more accurately and/or (iv) the simple addition scheme of electrostatic forces does not work properly.[4i,53] (v) Further work is needed in order to elucidate the particular discrepancy concerning the experimental, the E_Σ and the ab initio data on the BDE($Al^+-C_4H_4O$).

G. Al^+ vs H^+ Affinities of L. In Figure 5 the BPW91/6-311++G(3df,2p)//BPW91/6-311+G(d) and B3LYP/6-311++G(3df,2p)//B3LYP/6-311+G(d) calculated BDE(Al^+−L) data are plotted vs the experimentally determined proton affinity (PA) of the ligands L.[67,68] This interpolation fits well for the BDE data of Al^+-H_2O,[16a] Al^+−HCN,[16c] and $Al^+-C_6H_6$.[16d] However, discrepancies have already been detected, in relation to the BDE values of the complexes $Al^+-C_2H_2$ and $Al^+-C_2H_4$.[16e] Similarly, in the present investigation the BDE(Al^+−L) vs. PA(L) prediction for **2**−**5** is 10−20 kcal/mol too low.[69] This failure may result from (i) different coordination modes comparing

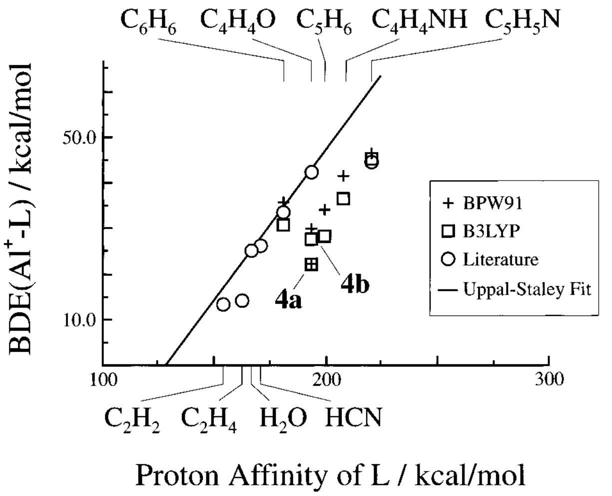

Figure 5. Plot of the BDE(Al$^+$−L) vs the proton affinities of the ligands L in kcal/mol. The literature-known experimental and theoretical data are compared with the present results obtained at the BPW91/6-311++G(3df,2p)//BPW91/6-311+G(d) and B3LYP/6-311++G(3df,-2p)//B3LYP/6-311+G(d) level of theory. Further, the Uppal−Staley fit from ref 67a has been included for reasons of comparison.

H$^+$−L and Al$^+$−L and in turn, the proposed model of a linear relationship between BDE(Al$^+$−L) and PA(L) does not necessarily apply (cf. the electrophilic attack of a proton toward an aromatic system leading to an intermediate σ-complex).[70] (ii) A stronger Pauli repulsion between the 3s^2 shell of Al$^+$ and the electrons of the ligands, in comparison to the proton−L case. (iii) The interaction of the ligand's MOs and the polarizable 3s^2 orbital of the aluminum cation, as being absent in the case of a proton.[17g,23,24] (iv) The amount of the covalent character[17g,24] comparing the interaction of a proton and Al$^+$ with L.

H. Comparison to M(L)$^+$ Complexes. The literature data of several M$^+$−L complexes (M$^+$ = metal ion) indicate that the BDE(M$^+$−L) values decrease as follows: transition metal ions > aluminum ≈ lithium > alkali ions. For example, BDE(Li$^+$−C$_6$H$_6$) = 38.3 kcal/mol (300 K),[4i,5f] BDE(Li$^+$−C$_5$H$_5$N) = 44 kcal/mol (300 K),[71a] BDE(Na$^+$−C$_6$H$_6$) = 28.0 kcal/mol (300 K),[5e] BDE(K$^+$−C$_6$H$_6$) = 19.2 kcal/mol (300 K),[5a] BDE(NH$_4$$^+$−C$_6H_6$) = 19.3 kcal/mol (300 K),[5b] BDE(Cu$^+$−C$_6$H$_6$) = 51.1 kcal/mol (0 K)[4c] and 50 ± 9 kcal/mol (300 K),[71c] BDE(Sc$^+$−C$_6$H$_6$) = 44.1 kcal/mol (0 K),[4c] and 49 ± 5 kcal/mol (300 K),[4c] BDE(Ti$^+$−C$_6$H$_6$) = 62.8 kcal/mol (0 K),[4c] and >49 kcal/mol (300 K),[71c] BDE(Co$^+$−C$_6$H$_6$) = 62.6 kcal/mol (0 K),[4c] and 68 ± 5 kcal/mol (300 K),[71b] BDE(Ag$^+$−C$_6$H$_6$) = 36.5 kcal/mol (0 K),[4c] and 30−37 kcal/mol (300 K),[4c] BDE(Pt$^+$−C$_6$H$_6$) = 82.2 kcal/mol (0 K),[71d] BDE(Au$^+$−C$_6$H$_6$) ≈ 70 kcal/mol (300 K),[71e] BDE(Fe$^+$−C$_6$H$_6$) = 48.6 ± 2.0 kcal/mol (473 K),[71f] 51.4 ± 2.0 kcal/mol,[71g] BDE(Fe$^+$−C$_5$H$_5$N) = 49 ± 3 kcal/mol (300 K).[61]

We consider two effects to be responsible for the differences of the absolute BDE data of the Al(π-L)$^+$ and M(π-L)$^+$ complexes (M = transition metal). From the population analysis by using the Mulliken scheme, the interacting orbitals appear to be *not* the same in these two systems. The π-MO back-bonding[9] from Al$^+$ to the unoccupied antibonding orbitals of the ligand L does not exist due to the unoccupied 3p$_{x,y,z}$ AO of the ground-state aluminum cation. Only a π-type electron donation from the ligand's HOMOs to the empty 3p(Al$^+$) orbitals can occur. The second distinction arises from the Pauli repulsion due to the 3s^2 orbital of Al$^+$, resulting in an increased Al$^+$−L distance and a less efficient overlap of bonding orbitals.

From the comparison of the Al$^+$−C$_6$H$_6$ and the alkali-metal ion−C$_6$H$_6$ interaction we conclude,[63] that the binding mechanism in Al$^+$−C$_6$H$_6$, i.e., $e_{1g}(C_6H_6) \rightarrow 3p_{x,y}(Al^+)$, also cannot occur in the alkaline cases, since the first vacant AO of the alkali-metal ions are the s orbitals and the $e_{1g}(C_6H_6) \rightarrow$ s-AO overlap is zero based on symmetry considerations. Therefore, Na$^+$ and K$^+$ are bonded less strongly to benzene than Al$^+$. In the case of Li$^+$ (1s^2), the Pauli repulsion is much smaller compared to Al$^+$ ([Ne]3s^2), leading to a smaller Li$^+$−C$_6$H$_6$ distance and a higher BDE value compared to Na$^+$ and K$^+$. In addition, we emphasize another difference between the M$^+$−C$_6$H$_6$ (M = Li, Na, K, Rb) and the Al$^+$−C$_6$H$_6$ interaction: As noted by Dougherty,[7] the dominant attractive force in the M$^+$−C$_6$H$_6$ complexes (M = Li, Na, K, Rb) originates from an electrostatic potential exhibiting a $1/r_{M-L}{}^n$ dependence with $n < 2$. In contrast, it is indicated by the present findings that the dominant part in the Al$^+$−(π-L) bond (L = benzene, cyclopentadiene, furan, and pyrrole) is due to ion-quadrupole and/or ion-induced polarization potentials, i.e., potentials exhibiting $1/r_{Al-L}{}^m$ dependence with $m \geq 3$. Nevertheless, due to the incorrect predictions by E_Σ in the cases of **3**, **4b**, and **5**, further studies are necessary in order to provide evidence for contributions by multipole terms or the actual existence of a new binding mechanism as postulated[7] by Dougherty.

Conclusions

The bond dissociation energies of the ground-state complexes Al(L)$^+$ (L = benzene, pyridine, cyclopentadiene, furan, pyrrole) have been determined applying HF, DFT, and DFT/HF hybrid methods. The obtained values[58] at 0 K are BDE(Al$^+$−benzene) ($^1A_1$) = 35.6 kcal/mol, BDE(Al$^+$−pyridine) ($^1A_1$) = 46.4 kcal/mol, BDE(Al$^+$−cyclopentadiene) ($^1A'$) = 33.9 kcal/mol, BDE(Al$^+$−furan) ($^1A_1$) = 22.2 kcal/mol, BDE(Al$^+$−furan) ($^1A'$) = 29.9 kcal/mol, and BDE(Al$^+$−pyrrole) ($^1A'$) = 41.6 kcal/mol. In the case of the Al(C$_4$H$_4$O)$^+$ complex, we were not able to reproduce the experimental BDE(Al$^+$−C$_4$H$_4$O) data.[67b]

The bonding mechanism in the Al$^+$−(π-L) complexes is characterized by (i) dominating attractive forces resulting from charge-induced polarization and charge−quadrupole interactions if classical electrostatic models are employed or (ii) a π-type HOMO(ligand) → LUMO(Al$^+$) electron donation according to the MO analysis. The BDE(Al$^+$−C$_6$H$_6$) value was found to be smaller as compared to the BDE(M$^+$−C$_6$H$_6$) (M = transition metal) and higher than the BDE of alkali-ion benzene complexes except for Li$^+$. In the Al(L)$^+$ systems under investigation, *minimum* structures corresponding to intermediates of an interconversion as depicted in eq 1 have not been detected.

In line with previous results on small aluminum complexes,[23] we suggest to use gradient-corrected functionals combined with basis sets of at least double-ζ quality, e.g., 6-311+G(d) or cc-pVDZ for the description of Al(L)$^+$ compounds (L = ligands with at least five second-row atoms, e.g., C, N, O). If larger basis sets are applied, e.g., 6-311++G(3df,2p) or cc-pVTZ, the differences with regard to relative energies compared to the results of calculations with double-ζ quality basis sets are within 1 kcal/mol.

Probably due to literature-known deficiencies,[36c,55,56] the LYP correlation functional does not perform satisfactory in the BDE calculation of the Al(π-L)$^+$ complexes **1**, **3**, **4b**, and **5**. Compared to results from the MP2, BP86, BPW91, or B3PW91 calculations, the BDE(Al$^+$−π-L) is predicted consistently too low by ca. 5 kcal/mol if the BLYP, BHLYP, or B3LYP functionals are used irrespective of the basis sets. The geometrical parameters, however, have been predicted consistently by the methods under investigation.

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Supporting Information Available: The molecular structures (*z* matrixes) of the complexes **1**−**5** (2 pages). Ordering information is given on any current masthead page.

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(63) Results from preliminary calculations on the experimentally and theoretically well-known BDE($Na^+-C_6H_6$) are as follows (given in kcal/mol at 0 K): 27.6 (B3LYP/6-31G(d)), 23.4 (B3LYP/6-311+G(d), 23.9 (B3LYP/6-311++G(3df,2p)//B3LYP/6-311+G(d)), 25.0 (BPW91/6-31G-(d)), 21.8 (BPW91/6-311+G(d)), and 22.3 (BPW91/6-311++G(3df,2p)//BPW91/6-311+G(d)). For the reason of comparison, the experimental data are listed in section 3.I. With regard to the $Al^+-C_6H_6$ complex, a different binding mechanisms is obviously operative in the $Na^+-C_6H_6$ case.

(64) The dipole polarizability components of L have been calculated according to Miller[50g] and are given pointing along the Al^+-L axis: $\alpha_\perp$-(C_6H_6) = 6.74 Å^3, $\alpha_{II}(C_5H_5N)$ = 10.84 Å^3, $\alpha_\perp(C_6H_6)$ = 6.20 Å^3, $\alpha_{II}(C_4H_4O)$ = 3.11 Å^3, $\alpha_\perp(C_4H_4O)$ = 2.91 Å^3, $\alpha_\perp(C_4H_4NH)$ = 5.79 Å^3.

(65) The molecular quadrupole moments of the ligands L pointing along the Al^+-L axis amount to $\Theta(C_6H_6) = -29.0 \times 10^{-40}$ Cm^2, $\Theta(C_5H_5N) = -11.7 \times 10^{-40}$ Cm^2, $\Theta(C_5H_6) = -17.0 \times 10^{-40}$ Cm^2, $\Theta(C_4H_4O) = +0.67 \times 10^{-40}$ Cm^2, $\Theta(C_4H_4O) = -20.3 \times 10^{-40}$ Cm^2, $\Theta(C_4H_4NH) = -41.4 \times 10^{-40}$ Cm^2. Data are taken from ref 50c.

(66) Sutter, D. H.; Flygare, W. H. *J. Am. Chem. Soc.* **1969**, *91*, 6895. Additionally, the authors compared the pyrrole data with those of the furan and thiophene and discussed some peculiarities.

(67) (a) The Uppal−Staley relationship was applied according to: Uppal, J. S.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 1235. For a further discussion, see refs 16c,d,e. (b) Gal, J.-F.; Taft, R. W.; McIver, Jr., R. T. *Spectrosc. Int. J.* **1984**, *3*, 96.

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(69) Predictions from the Uppal−Staley fit: $Al^+-C_6H_6$ (35.0 kcal/mol), $Al^+-C_5H_5N$ (62.6 kcal/mol), $Al^+-C_5H_6$ (47.8 kcal/mol), $Al^+-C_4H_4O$ (42.6 kcal/mol), $Al^+-C_4H_4NH$ (53.4 kcal/mol).[67a] Compared to the calculated values (Table 3) the *ordering* of these BDE data are predicted consistently with the present calculations except for benzene.

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