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DFT Study on the Reed Diethylaluminum Cation-like System: Structure and Bonding in $Et_2Al(CB_{11}H_6X_6)$ (X = Cl, Br)

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Electronic and molecular structure has been investigated in the diethylaluminum cation-like system $Et_2Al(CB_{11}H_6X_6)$ (**1**, X = Cl; **2**, X = Br) and neutral compounds AlX_3 (X = Cl, Br, Me, C_6H_5) with DFT B3LYP and BP86 levels of theory. The calculated geometries of $Et_2Al(CB_{11}H_6X_6)$ (**1**, X = Cl; **2**, X = Br) are in excellent agreement with those determined experimentally by X-ray crystallography. The Al–X bond distances 2.442, 2.445 Å in **1** and 2.579, 2.589 Å in **2** are longer than those expected for single bonds based on covalent radius predictions (Al–Cl = 2.15 Å and Al–Br = 2.32 Å) and those observed for bridged Al–X–Al bonds (2.21 Å in Al_2Cl_6, 2.33 Å in Al_2Br_6) and are close to sum of ionic radii of Al^{3+} and X^- (Al–Cl = 2.35 Å and Al–Br = 2.50 Å). The optimized geometries of the neutral compounds AlX_3 (X = Cl, Br, Me_3, C_6H_5) at BP86/TZ2P show Al–Cl = 2.088 Å in $AlCl_3$, Al–Br = 2.234 Å in $AlBr_3$, Al–C = 1.973 Å in $AlMe_3$, Al–C = 2.255 Å in $Al(C_6F_5)_3$. These bond distances are similar to those expected for single bonds based on covalent radius predictions. The calculated charge distribution indicates that the aluminum atom carries a significant positive charge while the ethyl and carborane groups are negatively charged. The Cl and Br atoms in compounds **1** and **2** are slightly positive while, in neutral compounds AlX_3 (X = Cl, Br, Me_3, C_6H_5), X is negatively charged. Energy decomposition analysis of $Et_2Al^{\delta+}(\text{carborane})^{\delta-}$ shows that the bonding between the fragments is more than half electrostatic. The ionic character of the Al···Cl bonds in compound **1** (59.8%) is greater than the Al···Br bonds in the compound **2** (57.9%). This quantifies and gives legitimacy to the designation of these types of compounds as “ion-like”. The Al–X bonding in AlX_3 is mainly covalent with percentage ionic character 28.2% in $AlCl_3$, 31.5% in $AlBr_3$, 25.6% in $AlMe_3$, 18.4% in $Al(C_6F_5)_3$.

Introduction

In recent times, the chemistry of reactive cations and catalysts has evolved from simplistic descriptions of “free” cations toward the concept of tight ion pairs or “ion-like” species. Even with the least coordinating counterions available to modern chemistry (e.g., carboranes,[1] fluorinated tetraphenylborates,[2] etc.),[3] coordinatively unsaturated cations such as trialkylsilylium ions (R_3Si^+) or group 4 alkyl metallocenes (Cp_2RM^+) have proved structurally elusive. Species such as R_3Si(carborane) and Cp_2RM(perfluoro-tetraphenylborate) show long bonds between the cationic moiety and the weakly coordinating anion indicative of considerable ionicity. They are not free ions but can behave like free ions. So, increasingly, they are referred to as “ion-like” and are written $R_3Si^{\delta+}(\text{carborane})^{\delta-}$ and $Cp_2RM^{\delta+}(\text{perfluoro-tetraphenylborate})^{\delta-}$ to reflect these realities.

A new class of compounds with apparently similar characteristics has recently been reported by Reed, Sen, and co-workers.[4] These are the products of pairing dialkylaluminium ions (R_2Al^+) with weakly coordinating carborane anions ($CB_{11}H_6X_6^-$ with X = Cl, Br). Diethylaluminum species of the type $Et_2Al(CB_{11}H_6X_6)$ (X = Cl, **1**; X = Br, **2**) were characterized by X-ray crystallography and shown to be active in cation-like catalysis.[4] The main goals of the present study are (i) to compare calculated and experimental structures and (ii) to analyze bonding interactions and ionicity in the Al···X bonds of “ion-like” compounds $Et_2Al(CB_{11}H_6X_6)$ and neutral compounds AlX_3 (X = Cl, Br, Me, C_6H_5).

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Methods

The calculations were performed at the nonlocal DFT level of theory using the exchange functional of Becke[5] and the correlation functional of Perdew[6] (BP86). Scalar relativistic effects have been considered using the ZORA formalism.[7] Uncontracted Slater-type orbitals (STOs) were used as basis functions for the SCF calculations.[8] Triple-ζ basis sets augmented by one set of polarization function have been used for all the elements. The $(1s)^2$ core electrons of the boron and carbon, $(1s2s2p)^{10}$ core electrons of aluminum and chlorine, and $(1s2s2p3s3p3d)^{28}$ core electrons of bromine were treated by the frozen-core approximation.[9] An auxiliary set of s, p, d, f and g STOs was used to fit the molecular densities and to present the coulomb and exchange potentials accurately in each SCF cycle.[10] The calculations were carried out using the program package ADF-2002.01.[11]

Calculations were also performed using the hybrid B3LYP density functional method, which uses Becke's 3-parameter nonlocal exchange functional[12] mixed with the exact (Hartree−Fock) exchange functional and Lee−Yang−Parr's nonlocal correlation functional.[13] The geometries of all complexes were optimized without any symmetry restrictions with standard 6-31G(d) basis sets[14] for all elements. Frequency calculations were performed to determine whether the optimized geometries were minima on the potential energy surface. The electronic structures of the complexes were examined by NBO analysis[15] using 6-311G(d) basis sets for all elements. These calculations were carried out with the Gaussian 98 program.[16]

The bonding interactions between the fragments $[Et_2Al]^+$ and $[CB_{11}H_6X_6]^-$ have been analyzed using the energy decomposition scheme of ADF which is based on the methods of Morokuma[17] and Ziegler and Rauk.[18] The bond dissociation energy ΔE between two fragments A and B is partitioned into several contributions that can be identified as physically meaningful entities. First, ΔE is separated into two major components ΔE_{prep} and ΔE_{int}:

$$\Delta E = \Delta E_{prep} + \Delta E_{int} \tag{1}$$

Here, ΔE_{prep} is the energy that is necessary to promote the fragments A and B from their equilibrium geometry and electronic ground state to the geometry and electronic state that they have in the compound AB. ΔE_{int} is the interaction energy between the two fragments in the molecule. The interaction energy, ΔE_{int}, can be divided into three main components:

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

ΔE_{elstat} gives the electrostatic interaction energy between the fragments that is calculated using the frozen electron density distribution of A and B in the geometry of the complex AB. The second term in eq 2, ΔE_{Pauli}, gives the repulsive interactions between the fragments that are due to the fact that two electrons with the same spin cannot occupy the same region in space. The term comprises the four-electron destabilizing interactions between occupied orbitals. ΔE_{Pauli} is calculated by enforcing the Kohn−Sham determinant of AB, which results from superimposing fragments A and B, to obey the Pauli principle through antisymmetrization and renormalization. The stabilizing orbital interaction term ΔE_{orb} is calculated in the final step of the energy analysis when the Kohn−Sham orbitals relax to their optimal form. The latter term can be further partitioned into contributions by the orbitals that belong to different irreducible representations of the point group of the system. The covalent and electrostatic character of the bond is given by the ratio $\Delta E_{elstat}/\Delta E_{orb}$.[19]

Geometries

Figure 1 shows the optimized geometries of the $Et_2Al(CB_{11}H_6X_6)$ (**1**, X = Cl; **2**, X = Br). The optimized bond lengths and angles at B3LYP and BP86 are presented in Table 1. The structures of the $Et_2Al(CB_{11}H_6Cl_6)$ and $Et_2Al(CB_{11}H_6Br_6)$ closely resemble those found by X-ray diffraction.[4] The B3LYP and BP86 values are very similar to each other. The Al−X bond distances 2.442, 2.445 Å in **1** and 2.579, 2.589 Å in **2** are longer than those expected for single bonds based on covalent radius predictions (Al−Cl = 2.15 Å and Al−Br = 2.32 Å)[20] and those observed for bridged Al−X−Al bonds (2.21 Å in Al_2Cl_6, 2.33 Å in Al_2Br_6) and

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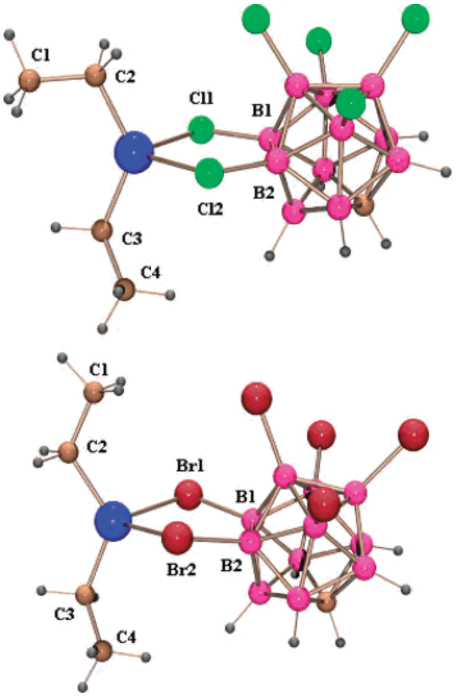

Figure 1. Optimized geometries of the $Et_2Al(CB_{11}H_6X_6)$ (**1**, X = Cl; **2**, X = Br). The most important bond lengths and angles are given in Table 1.

Table 1. Selected Optimized Geometrical Parameters for $Et_2Al(CB_{11}H_6X_6)$ (**1**, X = Cl; **2**, X = Br) and X-ray Data for **1** and **2**[a]

	1			**2**		
	B3LYP	BP86	X-ray	B3LYP	BP86	X-ray
Bond Distances						
Al−X1	2.438	2.442	2.4295(10)	2.580	2.579	2.5408(17)
Al−X2	2.441	2.445	2.4400(9)	2.591	2.589	2.5807(17)
B1−X1	1.866	1.865	1.831(2)	2.027	2.019	1.931(5)
B2−X2	1.866	1.864	1.828(2)	2.028	2.020	1.943(5)
Al−C1	1.961	1.964	1.921(5)	1.965	1.969	1.929(6)
Al−C3	1.967	1.970	1.934(2)	1.970	1.974	1.944(6)
C1−C2	1.541	1.540	1.460(7)	1.538	1.535	1.462(11)
C3−C4	1.543	1.542	1.502(3)	1.540	1.537	1.494(8)
Bond Angles						
X1−Al−X2	93.03	93.43	92.29(3)	93.71	94.03	93.36(5)
C1−Al−C3	130.41	129.92	133.8(4)	124.79	124.06	130.1(3)
C1−Al−X1	106.73	106.79	104.18(9)	107.86	108.05	106.71(19)
C3−Al−X2	106.91	106.96	105.0(3)	108.37	108.44	108.3(2)
Al−X1−B1	104.76	104.17	104.07(8)	101.88	101.17	101.99(16)
Al−X2−B2	104.83	104.23	104.27(8)	102.05	101.33	102.19(16)
Al−C1−C2	119.11	119.00	123.2(6)	121.58	121.24	122.3(6)
Al−C3−C4	114.46	114.66	118.7(5)	119.40	119.42	120.3(4)

[a] See Figure 1 for labeling of atoms. Distances are in angstroms and angles in degrees.

are close to the sums of ionic radii of Al^{3+} and X^- (Al−Cl = 2.35 Å and Al−Br = 2.50 Å). Using the relationship between covalent bond order and bond distance suggested by Pauling we find that the calculated Al−X distances correspond to a covalent bond order of 0.33 for Al−Cl bonds and 0.37 for Al−Br bonds.[21] These results reveal the ionic character of Al−X bonds in compounds **1** and **2**. The calculated C−Al−C bond angles are 129.92° and 124.06° at BP86 for compounds **1** and **2**. The NBO analysis of **2** shows $sp^{1.05}$ and $sp^{1.06}$ hybridization of Al along the Al−C bonds.

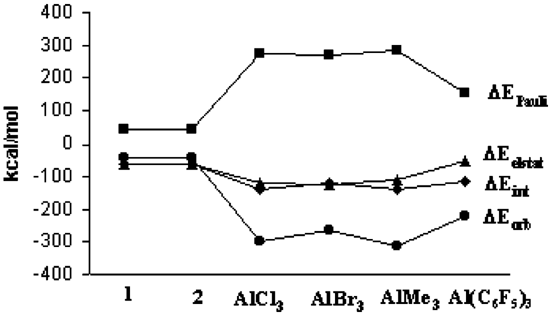

Figure 2. Trend of the energy contributions to the Al−X bonding interactions in $Et_2Al(CB_{11}H_6X_6)$ (**1**, X = Cl; **2**, X = Br), AlX_3 (X = Cl, Br, Me, C_6F_5).

The optimized geometries of the neutral compounds AlX_3 (X = Cl, Br, Me, C_6H_5) at BP86/TZ2P show Al−Cl = 2.088 Å in $AlCl_3$, Al−Br = 2.234 Å in $AlBr_3$, Al−C = 1.973 Å in $AlMe_3$, Al−C = 2.255 Å in $Al(C_6F_5)_3$. These bond distances are similar to those expected for single bonds based on covalent radius predictions. The Al−C bonds in $Al(C_6F_5)_3$ are relatively longer than the Al−C bond in $AlMe_3$.

Bonding Analysis of Al−Cl, Al−Br, and Al−C Bonds

We begin the analysis of the bonding with a discussion of the conventional indices, which are frequently used in order to characterize the bonding situation in molecules, i.e., bond orders and atomic charges. Table 2 gives the Wiberg bond indices (WBI)[22] and the natural bond orbital (NBO) charge distribution.

Table 2 shows that the WBI values of the Al−X bonds of the compounds **1** and **2** are significantly smaller (0.34 and 0.41 respectively) than the WBI values of the B−X bonds (0.93 and 0.96), Al−Cl (0.84) in $AlCl_3$, Al−Br (0.92) in $AlBr_3$, Al−C (0.63) in $AlMe_3$, Al−C (0.59) in $Al(C_6F_5)_3$. This is a first indication that the Al−X bonds in **1** and **2** have a substantial degree of ionic character. The ionic character of the Al−Cl bonds is greater than that of the Al−Br bonds. The bond indices of the Al−C bonds of the compounds **1** and **2** as well as of the $AlMe_3$ and $Al(C_6F_5)_3$ are not very different from each other.

The calculated charge distribution indicates that the aluminum atom carries a significant positive charge while the ethyl and carborane groups are negatively charged. The Cl and Br atoms in compounds **1** and **2** are slightly positive while, in neutral compounds AlX_3 (X = Cl, Br, Me, C_6H_5), X is negatively charged. The Et_2Al moiety in the compound **1** is more positively charged than in compound **2**. In order to quantify this information and to get a more detailed insight into the nature of the Al−X interactions we carried out an energy partitioning analysis. The results are given in Table 3. The trend of the different energy terms is shown in Figure 2.

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Figure 3. Plot of some relevant orbitals of $Et_2Al(CB_{11}H_6Cl_6)$ showing visualization of the Cl−Al−Cl and C−B−B−Cl bonding.

Table 2. Wiberg Bond Indices (WBI) and NBO Charges, *q*, in $Et_2Al(CB_{11}H_6X_6)$ (**1**, X = Cl; **2**, X = Br) and AlX_3 (X = Cl, Br, Me, C_6F_5)

	1	**2**	$AlCl_3$	$AlBr_3$	$AlMe_3$	$Al(C_6F_5)_3$
			WBI			
Al−X1/X2	0.34	0.41	0.84	0.92	0.63[a]	0.59[a]
B−X1/X2	0.93	0.96				
Al−C1	0.57	0.58				
Al−C3	0.58	0.59				
C1−C2	1.04	0.91				
C3−C4	1.04	0.91				
			NBO Charges			
q_{Al}	1.73	1.62	1.43	1.19	1.75	1.66
q_{Et}	−0.58	−0.58				
q_X	0.07	0.06	−0.48	−0.40	−0.58	−0.55
$q_{[Et_2Al]}$	0.57	0.47				
$q_{[CB_{11}H_6X_6]}$	−0.57	−0.47				

[a] W_{Al-C} values.

Table 3. Energy Decomposition Analysis of $Et_2Al(CB_{11}H_6X_6)$ (**1**, X = Cl; **2**, X = Br) at BP86/TZ2P[a]

	1[b]	**2**[b]	$AlCl_3$	$AlBr_3$	$AlMe_3$	$Al(C_6F_5)_3$
ΔE_{int}	−122.18	−123.21	−137.50	−118.80	−138.12	−114.71
$\Delta E_{Pauling}$	82.41	79.44	275.82	266.83	284.84	153.05
ΔE_{elstat}	−122.37	−117.33	−116.50	−121.47	−108.09	−49.14
ΔE_{orb}[c]	−82.22	−85.31	−296.83	−264.16	−314.87	−218.61
	(40.2%)	(42.1%)	(71.8%)	(68.5%)	(74.4%)	(81.6%)
ΔE_{prep}	10.66	13.62	0.75	1.57	11.37	27.69
$\Delta E(-D_e)$	−112.52	−109.59	−136.75	−117.57	−126.75	−87.02

[a] Energy contributions in kcal/mol. [b] Energy contributions for **two Al−X bonds**. [c] The values in parentheses are the percentage contribution to the total attractive interactions reflecting the covalent character of the bond.

The data in Table 3 show that the interaction energies of compound **1** (−61.09 kcal/mol per Al−Cl bond) and compound **2** (−61.60 kcal/mol per Al−Br bond) are nearly the same, but significantly smaller than the interaction energies of the Al−Cl bond (−137.80 kcal/mol) in $AlCl_3$, Al−Br bond (−118.80 kcal/mol) in $AlBr_3$, Al−CH_3 bond (−138.12 kcal/mol) in $AlMe_3$, and Al−C_6F_5 bond (−114.71 kcal/mol) in $Al(C_6F_5)_3$. We note that, for Al−Cl and Al−Br bonds in “ion-like” compounds **1** and **2**, the contribution of the electrostatic attractions ΔE_{elstat} is greater than the orbital interactions, while for neutral compounds AlX_3 (X = Cl, Br, Me, C_6H_5), the orbital interactions, ΔE_{orb} are significantly greater than the electrostatic interactions, ΔE_{elstat}. The contribution of the electrostatic attraction ΔE_{elstat} is greater for Al−Cl bonds in **1** than Al−Br bonds in **2**, and the covalent bonding ΔE_{orb} is smaller for Al−Cl bonds than Al−Br bonds. The $[Et_2Al]^+$−$[CB_{11}H_6X_6]^-$ bonding in **1** and **2** is more than half electrostatic. The Al−Cl bonds in **1** have a slightly lower degree of covalent bonding (40.2%) than the Al−Br bonds (42.1%) in **2**. The Al−X bonding in AlX_3 is mainly covalent with percentage ionic character 28.2% in $AlCl_3$, 31.5% in $AlBr_3$, 25.6% in $AlMe_3$, 18.4% in $Al(C_6F_5)_3$.

In order to visualize the X1−Al−X2 and X1−B1−B2−X2 bonding, envelope plots of some relevant orbitals of the **1** are shown in Figure 3. Figure 3a gives a pictorial description of the Cl−Al−Cl σ bonding orbital. Figure 3b and Figure 3c show mainly the Cl−B−B−Cl bonding and antibonding orbitals.

Summary and Conclusion

The first theoretical study has been presented where the bonding situations in diethylaluminum cation-like systems $Et_2Al(CB_{11}H_6X_6)$ (**1**, X = Cl; **2**, X = Br) are investigated at DFT B3LYP and BP86 levels. In order to compare the results between “ion-like” compounds **1** and **2** and related neutral compounds such as AlX_3 (X = Cl, Br, Me, C_6H_5), the calculations have been performed on AlX_3 compounds. The calculated geometries of $Et_2Al(CB_{11}H_6X_6)$ (**1**, X = Cl; **2**, X = Br) are in excellent agreement with experimental values. Energy decomposition analysis shows that bonding between the $[Et_2Al]^+$ moiety and the $CB_{11}H_6X_6^-$ anions is more than half electrostatic. The Al−Cl bonds in **1** have a slightly higher degree of ionic bonding (59.8%) than the Al−Br bonds (57.9%) in **2**. This provides support for designating their structures as “ion-like”. It should prove interesting to carry out comparable calculations with other chemically related alkyl cations. The Al−X bonding in AlX_3 is mainly covalent with percentage ionic character 28.2% in $AlCl_3$, 31.5% in $AlBr_3$, 25.6% in $AlMe_3$, 18.4% in $Al(C_6F_5)_3$.

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