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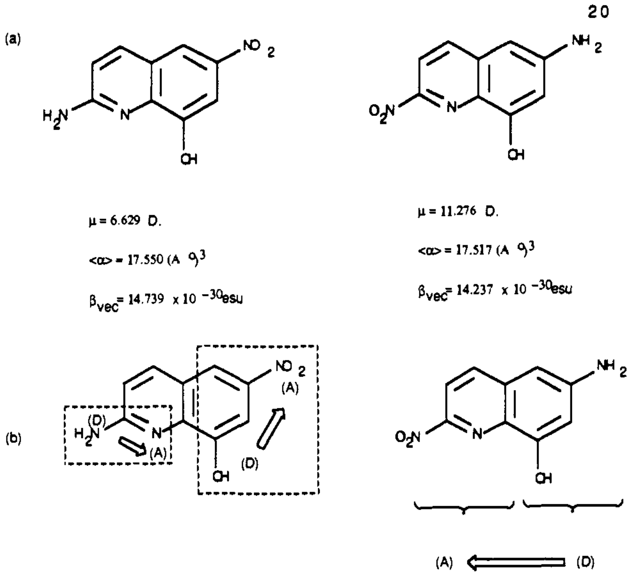

Figure 2. (a) Structures with μ, α, and β_{vec} values for the 2-amino-6-nitro-8-hydroxyquinoline and 2-nitro-6-amino-8-hydroxyquinoline molecules. (b) Sketch of the possible charge-transfer routes (denoted by the arrows) in the excited states of both molecules.

(inter-ring) conjugation path in this case. A comparison between these two molecules is shown in Figure 2.

On the basis of these findings we suggest that fused aromatic heterocyclic compounds may hold promise as potential candidates for future nonlinear optical applications. Not only could they have reasonably large molecular hyperpolarizabilities but they also meet the optical transparency criteria required for optimizing their optical nonlinearities. As for the molecular design of new nonlinear optical materials based on quinoline or similar heterocyclic compounds, the pyridine ring can be thought of as an acceptor group within the molecule while the benzene ring can be thought of as a donor. Therefore increasing the acceptor character of the pyridine ring and/or increasing the donor character of the benzene ring would substantially increase the optical nonlinearities of this class of compounds. We also would like to point out that the nitro/amino pair is not the best acceptor/donor pair, but it was chosen in this study for the sake of simplicity and comparison.

VI. Conclusion

The coupled perturbed Hartree–Fock ab initio extended basis set calculations have been successfully applied to the calculation of the geometric structures and static first-order and second-order polarizabilities of a series of 8-hydroxyquinoline molecules substituted by halogen, nitro, and amino groups. The effects of the nature and the position of the substituent on the geometry and the first-order and second-order polarizabilities are reported. 2-Amino-6-nitro-8-quinolinol is calculated to have a β_{vec} of 14.739 × 10^{-30} esu which is almost twice as large as that for *p*-nitroaniline. On the basis of these calculations, new trends for the molecular design of aromatic heterocyclic compounds for nonlinear optical applications are proposed.

Calculating the β values for the mixed ligand metal complexes, in addition to the synthesis of some of the newly identified ligands and their metal complexes, and determining their SHG activities is currently underway in our laboratory.

A Theoretical Investigation of the Aluminum–Benzene Complex

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Abstract: Five optimal structures for the aluminum–benzene complex have been determined theoretically: (1) Al centered (C_{6v}), (2) Al-centered boat (C_{2v}), (3) Al on-top (C_s), (4) Al σ-bridging (C_s), and (5) Al π-bridging (C_s). Structures 4 and 2 are most likely the forms of the complex observed in low-temperature electron spin resonance (ESR) experiments. Both structures involve a boat distortion of benzene and Al σ bonds with the benzene out-of-plane para C atoms. We find little evidence for a stable Al π complex. The high-temperature Al–benzene ESR spectra can be explained by the low distortion energy for the benzene boat. Structure 3 with Al bonding on top of a single C atom is also interesting since it may be prototypical for the chemisorption interaction of an Al atom on graphite. The optimized structures were obtained from Hartree–Fock calculations using a Dunning–Hay basis set.

Introduction

The interactions between an aluminum atom and various small organic molecules have recently attracted much theoretical[1-3] and experimental[4-10] interest. The organoaluminum σ bonds are typically strong, and their electronic structure can often be qualitatively understood by using Hartree–Fock (HF) calculations

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alone. The π-bonding complexes, such as AlC_2H_4 where the Al atom binds symmetrically above the C_2H_4 plane, have been more challenging to theory, requiring the inclusion of electron correlation effects before a sensible bond energy is attained.[3] Our own interest in organoaluminum compounds was stimulated by some scanning tunneling microscopy (STM) experiments which directly imaged single Al atoms adsorbed on the basal plane of graphite.[11] The STM image suggested that the Al atom was adsorbed either directly above a C atom at an on-top site or above a C–C bond at a bridging site. We attempted to use cluster calculations, a common technique for investigating chemisorption on surfaces,[12] to provide some theoretical interpretation of the STM images.[13] We simulated the graphite surface by using large polycyclic aromatic molecules. Unfortunately, the size of the aromatic molecules and computational limitations forced us to perform the calculations at a low level of sophistication, preventing us from making any definitive statement on the preferred adsorption site for Al on the graphite surface. Furthermore, our calculations raised the question as to whether the Al was strongly chemisorbed or only weakly physisorbed on the surface. However, recent experiments have shown that Al does form a molecular complex with benzene. It is this AlC_6H_6 complex which we theoretically examine in this paper.

Two matrix isolation experiments have reported electron spin resonance (ESR) spectra for AlC_6H_6 molecular complexes. In the first, Kasai and McLeod[7] observed a hyperfine interaction with only two of the six equivalent protons when the complex is stabilized in a neon matrix at 4 K. On the basis of these observations, Kasai and McLeod suggested that AlC_6H_6 forms a π complex similar to AlC_2H_4 in which the Al atom interacts with benzene through one C–C unit of the ring. They further envisaged the complex being formed by a dative interaction between the semifilled Al p_π orbital parallel to the C–C unit and the orbital given by the antibonding combination of p_π orbitals of the two C atoms. Kasai and McLeod also noted that there were smaller Al p-orbital spin densities in the benzene complex than in the ethylene complex. They estimated spin densities of 0.2 on Al and 0.4 on the neighboring C in AlC_6H_6 to be compared with 0.7 and 0.15, respectively, estimated earlier for the ethylene complex.[8] More recently, Howard et al. reinvestigated the ESR spectrum of the reaction product of an Al atom with benzene at 77 K in benzene and in inert hydrocarbon matrices.[8] At 4 K the ESR spectrum revealed resolvable hyperfine interactions with one Al atom and two equivalent protons similar to that found by Kasai and McLeod. The spectrum changed with an increase in temperature, and at 220 K it showed interaction with all six equivalent protons. On the basis of the observations, Howard et al. proposed a η^2 complex in which the Al lies along the C_{6v} axis and bridges two para C atoms with hyperfine interaction to the two para protons. This structure is quite similar to the 1,4 cheleotropic cyclization product of Al and buta-1,3-diene at 77 K in hydrocarbon matrices.[10] It is worth noting that theoretical calculations on AlC_4H_6 favored the formation of σ bonds over π bonds between the Al and the two terminal C atoms.[10] The temperature dependence of the proton couplings of AlC_6H_6 is consistent with a proposed 1,4 cheleotropic adduct at low temperatures, with the Al–C bonds moving from one para position to the other at a higher rate than the proton hyperfine frequency so as to simulate an η^6 complex. They estimated the barrier to C–Al–C para bond rotation to be 1–2 kcal/mol. Further, they argued migration of a bridging Al atom from one C–C unit of the benzene ring to the next, an alternative explanation for the equivalence of the six protons in the 1,2 π complex, to be less probable. However, Howard et al. were not able to produce definitive evidence in favor of a 1,4 cheleotropic product.

Mitchell et al. investigated Al atom association reactions with simple alkenes and arenes in the gas phase by time-resolved resonance fluorescence spectroscopy.[9] They found binding energies in the range 11–16 kcal/mol, indicating significant chemical interaction for these paramagnetic molecular complexes. From the equilibrium constant temperature variation in the range 283–333 K they determined the Al–benzene complex binding energy to be 10.5 ± 1 kcal/mol. Whey they estimated the complex binding energy using statistical mechanics, they obtained a value of 11.7 ± 1 kcal/mol. In making this estimate, they assumed AlC_6H_6 to have the π-complex structure, similar to that suggested by Kasai and McLeod, and low symmetry when computing the rotational partition function for the complex. Assuming AlC_6H_6 to have C_{6v} symmetry produces changes of ~1 kcal/mol and ~4 cal/(mol K) in the estimate of the complex binding energy and entropy, respectively.

Other metals are known to form complexes with benzene. Manceron and Andrews reported an infrared study of the interaction between a Li atom and benzene in solid argon.[14] Li atoms spontaneously formed mono- and diligand complexes (LiC_6H_6,$Li(C_6H_6)_2$) with benzene diluted in an inert argon medium. The Li isotopic shift for the Li–ring stretching mode indicates an axial position for the metal. Observation of a formerly E_{2g} ring stretching mode suggests that a small Jahn–Teller effect causes either a C_{3v} or C_{2v} symmetry reduction. The reaction of group 1B metal atoms (Cu, Ag, Au) with a range of arenes in inert hydrocarbon matrices at 77 K has been studied by Howard et al. using ESR spectroscopy.[15] In the case of benzene, the ESR spectra indicate formation of metal atom–monoligand complexes, MC_6H_6. They have predicted that the bonding in CuC_6H_6 may involve interaction between 3d and 4p orbitals of the correct symmetry with the upper $1e_{1g}$ benzene orbitals and leads to a singly occupied molecular orbital (SOMO) having metal 4p and 3d as well as 4s character, whereas in AgC_6H_6 and AuC_6H_6, bonding may involve interactions between the 4d and 5p or the 5d and 6p orbitals with the lower a_{2u} π benzene orbital resulting in an almost pure 5s or 6s SOMO. However, the mechanisms of formation and structures of most of these labile low-temperature complexes still remain obscure.

Recent ab initio quantum chemical studies of the chemical bond between transition metal atoms (Ni, Cu, Fe) and small organic molecules (C_2H_2, C_2H_4) have shown that strong coupling between different electronic states of the metal atom is an important factor in the bond formation.[16] It is therefore necessary, even for a qualitative understanding of the bonding, to go beyond the Hartree–Fock (HF) level. Below we present results of our theoretical determination for the geometry of the Al–benzene complex. The experimental work has suggested two likely structures: the Al π bridging a benzene C–C bond of Kasai and McLeod[7] and the Al bonding to two para benzene C atoms of Howard et al.[8] We have optimized the energy of a number of different AlC_6H_6 structures starting with different geometries and electronic states. The geometry optimizations were performed using HF calculations. All of the HF-optimized energies were higher than the total of the separate Al and C_6H_6 HF energies. Only after a CI calculation with a Davidson correction do some of the complexes become more stable than Al and C_6H_6. Full details of the method are given in the next section. Five optimal structures were obtained, including the two structures proposed experimentally, and these are described in Results and Discussion. Concluding remarks are given in the final section of the paper.

Method

Optimal energies of C_6H_6Al geometries constrained with either C_{6v}, C_{2v}, or C_s point group symmetries were found using restricted open shell Hartree–Fock (ROHF) calculations and analytical gradients.[17] All of

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Table I. Summary of Previous Theoretical Work on the $^2B_2$ State of C_2H_4Al

Geometry[a]

	method	C–C	C–H	C–Al
present basis	ROHF	1.407	1.079	2.267
DH + P[b]	ROHF	1.408	1.080	2.241
DH + P[b]	CISD	1.417	1.086	2.228
DH + P[c]	UHF	1.356	1.091	2.590
DH + P[c]	UMP2	1.416	1.076	2.245
TZ + P[c]	UMP2	1.407		2.256
6-31 + G(d)[d]	UHF	1.408		2.256
TZ + P[e]	ROHF	1.400	1.077	2.265
TZ + 2P[e]	ROHF	1.397	1.074	2.256

Al to C_2H_4 Binding Energy[f]

	HF	CISD	CISD + Davidson	UMP2	UMP4
present basis	–0.6	–9.3	–10.6		
DH + P[b]	–1.1	–10.1	–11.6		
TZ + P[c]					–12.2
6-31 + G(d)[d]	–0.1			–12.2	–11.2
TZ + P[e]	0.4	–9.3		–14.8	
TZ + 2P[e]	0.04	–10.2			

[a] In Å. [b] Reference 3a. [c] Reference 3b. [d] Reference 3c. [e] Reference 3d. [f] In kcal/mol. The experimental binding energy after a zero point energy correction is estimated to be >16 kcal/mol.[9]

the quantities reported in this paper have been computed using the Dunning–Hay split valence basis[18] for C [9s5p/3s2p], H [4s/2s], and Al [11s7p1d/6s4p1d] where the Al basis has been augmented with a d polarization function ($\zeta = 0.25$). The Dunning–Hay basis was chosen for computational convenience after making comparisons with several other calculations which utilized both larger and smaller basis sets. Some measure of the reliability of the Dunning–Hay basis is indicated by Table I where a summary of previous calculations on the C_2H_4Al π-complex $^2B_2$ state is presented. In addition we find a 1.974-Å Al–C distance in the optimized geometry of $Al(CH_3)_3$ which compares favorably with the 1.957-Å experimental distance.[19]

The HF Al–benzene complex binding energy is calculated by

$$BE = E_{HF}(AlC_6H_6) - E_{HF}(Al) - E_{HF}(C_6H_6) \qquad (1)$$

where $E_{HF}(X)$ is the total HF energy for species X. At the optimal SCF geometries single reference configuration interaction calculations were performed. The CI wavefunction included all single and double excitations (CISD) with respect to the ROHF wavefunction. The 11 core-like molecular orbitals (1s, 2s, 2p Al and 1s C) were constrained to be doubly occupied in all configurations; similarly the 11 highest virtual orbitals were also deleted from the CI procedure. In this way 219 545, 219 545, 438 539, 437 639, and 437 653 configurations were included in the CI calculations on structures 1–5, respectively, described in Results and Discussion. To include some of the size-extensive corrections, the CI Al–benzene binding energy was calculated by

$$BE = E_{CI}^{eq}(AlC_6H_6) - E_{CI}^{long}(Al \cdots C_6H_6) \qquad (2)$$

where $E_{CI}^{long}(Al \cdots C_6H_6)$ is the CI energy calculated with the Al atom 100 au above the center of the HF optimized benzene molecule. In both eqs 1 and 2 a positive BE indicates the complex to be unstable relative to the separate Al atom and benzene molecule. Negative BE values were only obtained after an estimate for quadruple excitations and size extensivity using the Davidson correction[20] was added to the CISD energy.

The ROHF geometry optimization calculations were performed on a Sun SPARCstation 1 using the American GAMESS program.[21] The CISD calculations were performed on a Cray Y/MP computer at the San Diego Supercomputer Center using the British GAMESS program.[22]

Table II. Mulliken Net Charges, Relative Hartree–Fock Energies (ΔE), and Bond Distances for Neutral and Anionic Benzene

	C_6H_6 optimized	C_6H_6 boat[a]	$C_6H_6^-$ benzene[b]	$C_6H_6^-$ optimized[c]	$C_6H_6^-$ boat
			Charges[d]		
C_1[e]	–0.192	–0.219	–0.280 (0.167)	–0.277 (0.167)	–0.340 (0.376)
C_2		–0.167			–0.221 (0.066)
H_1	0.192	0.167	0.113	0.110	0.064
H_2		0.193			0.108
			Relative Energies[f]		
ΔE	0	33.8	68.4	66.7	73.3
			Bond Distances[g]		
C–C	1.396		1.396	1.417	
C–H	1.071		1.071	1.079	

[a] Geometry same as C_6H_6 in the C_6H_6Al boat structure (2). [b] Calculation at optimized benzene geometry. [c] Calculation at optimized $C_6H_6^-$ geometry. [d] Spin densities are in parentheses. [e] C_1 and C_2 correspond to the out-of-plane and in-plane C atoms in the boat structure. [f] In kcal/mol. [g] In Å.

Table III. The Computed Restricted Open Shell Hartree–Fock and Configuratioin Interaction Al to Benzene Binding Energies[a]

	(1) centered	(2) boat	(3) on-top	(4) σ-bridge	(5) π-bridge
ROHF	35.5	22.6	19.7	21.8	17.4
CISD	16.7	3.1	5.1	2.0	0.7
CISD + Davidson correction	12.8	–1.4	1.4	–2.8	–3.5

[a] In kcal/mol. A negative binding energy occurs when the Al–benzene complex is more stable than the separated Al and benzene.

Results and Discussion

To serve as a reference point, in Table II we summarize the results of calculations on C_6H_6 using the Dunning–Hay basis. The optimized benzene C–C and C–H distances are in excellent agreement with the experimental values of 1.395 and 1.085 Å, respectively.[23] Theoretically treating the excited states of benzene is well-known to be a challenging task,[24] but largely for comparison with our AlC_6H_6 calculations we also include results from $C_6H_6^-$ in Table II. As expected, when an electron is added to the benzene $\pi^*(e_{2u})$ orbital the C–C bond is lengthened slightly. The spin populations show that the extra electron enters a SOMO which is delocalized only over the C atoms and not on the H atoms. However, the C atom charge only increases by ~0.09 e because some of the electrons in the previously occupied orbitals of benzene are now transferred to the H atoms.

By using different point group symmetries we were able to locate five stationary geometric structures for AlC_6H_6 where all the energy derivatives with respect to the nuclear coordinates are 0. This does not mean that all of the structures are true local minima with positive definite second derivative Hessian matrices. We used the symmetry constraints, in part to reduce the computer time requirements for the calculations, but largely to serve as a check on the possible isomer types for AlC_6H_6. Computing the Hessian matrix for the optimized AlC_6H_6 is also far too time consuming, and instead we have determined whether a structure is a saddle point by starting optimizations with the high-symmetry stationary AlC_6H_6 structures distorted into different lower point group symmetries. When the AlC_6H_6 returns to the original symmetry, the molecule must have a minimum energy with respect to that particular distortion direction; otherwise a new structure at lower energy will be obtained. The five stationary structures we have found are (1) Al-centered high symmetry (C_{6v}), (2) Al-centered boat (C_{2v}), (3) Al on-top (C_s), (4) Al σ-bridging (C_s), and (5) Al π-bridging (C_s). The high-symmetry isomer 1 resembles an η^6 complex, and this structure is found to be the most unstable

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Table IV. Mulliken Population Analysis of the HF Wavefunctions from the Five Optimized AlC_6H_6 Structures[a]

	AlC_2H_4	(1) centered	(2) boat	(3) on-top	(4) σ-bridge	(5) π-bridge
			Net Atomic Charges			
Al	0.294	0.442	0.422	0.416	0.341	0.298
C_1	−0.557	−0.290	−0.501	−0.580	−0.454	−0.118
C_2		−0.290	−0.168	−0.211	−0.169	−0.241
C_3		−0.290	−0.168	−0.169	−0.169	−0.241
C_4		−0.290	−0.501	−0.287	−0.454	−0.118
C_5		−0.290	−0.168	−0.169	−0.211	−0.415
C_6		−0.290	−0.168	−0.211	−0.211	−0.415
			Atomic Spin Densities			
Al	0.310	0.018	0.176	0.106	0.249	0.421
C_1	0.333	0.163	0.252	0.106	0.237	0.013
C_2		0.163	0.077	0.162	0.047	0.090
C_3		0.163	0.077	0.008	0.047	0.090
C_4		0.163	0.252	0.435	0.237	0.013
C_5		0.163	0.077	0.008	0.087	0.182
C_6		0.163	0.077	0.162	0.087	0.182

[a] The atom numbering is shown in Figure 1. Results from the HF geometry optimization of AlC_2H_4 are also included in the table.

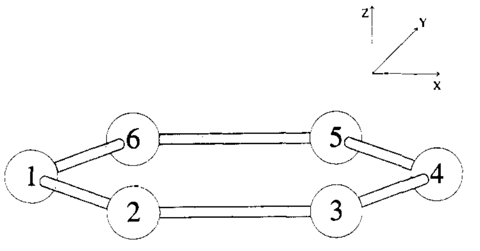

Figure 1. C atom labels and coordinate system used in the text.

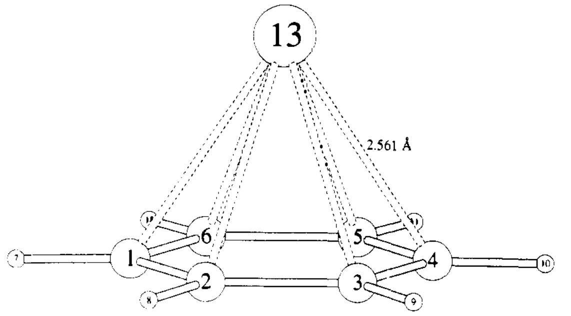

Figure 2. Structure 1, the Al-centered high-symmetry (C_{6v}) isomer.

of the optimal structures. However, in support of a 1,4 cheleotropic product proposed by Howard et al.,[8] we find structures 2 and 4 with the Al atom above the center of the carbon ring to be the most likely structures for the complex observed in the ESR experiments. Structure 5 resembles the π-like complex proposed by Kasai and McLeod,[7] but we find the computed spin densities of this structure not to be consistent with the experimental ESR data. In addition, we have found another AlC_6H_6 structure, 3, where the Al is on top of a single C atom. The HF and CI Al–benzene binding energies for the optimized structures are given in Table III. Table IV compares the Mulliken charges and spin densities, and Table V gives the Al–C and C–C distances for the different AlC_6H_6 isomers. Below we discuss each structure in turn using the atom labels and coordinate system shown in Figure 1.

(1) Al-centered high-symmetry C_{6v} structure. This isomer, shown in Figure 2, can be interpreted as a charge-transfer complex with the Al 3p electron being donated to the lowest empty π* molecular orbital of benzene. The Al binding energy and the relatively long 2.561-Å C–Al bond length indicate the complex to be not very stable. The benzene ligand resembles $C_6H_6^-$, by both having similar C–C distances and C atom spin and charge densities. The SOMOs for the high-symmetry AlC_6H_6 and $C_6H_6^-$ are essentially identical, only now in the Al complex some of the electrons in the occupied benzene orbitals are back transformed to Al instead of onto the H atoms. In AlC_6H_6 the H atom populations are close to the values computed for neutral benzene. As expected, an Al $3p_\pi$ population of 0.12 e develops via the Al interaction with the highest occupied π orbitals of benzene. However, there is little evidence for an Al–C_6H_6 π bond, and we note that instead the Al $3p_\sigma$ population is 0.26 e. The spin density on Al is derived from the d orbitals which have the same symmetry as the benzene π* orbitals. Finally, any likelihood of this structure being the isomer observed in the ESR experiments can be eliminated owing to the symmetry equivalence of the spin densities on each of the C atoms.

Table V. C–Al and C–C Bond Distances for the Five HF-Optimized AlC_6H_6 Structures[a]

	AlC_2H_4	(1) centered	(2) boat	(3) on-top	(4) σ-bridge	(5) π-bridge
Al–C_1	2.267	2.561	2.362	2.127	2.473	3.050
Al–C_2			2.693	2.679	3.000	3.528
Al–C_3			2.693	3.255	3.000	3.528
Al–C_4			2.362	3.255	2.473	3.050
Al–C_5			2.693	3.493	2.481	2.332
Al–C_6			2.693	2.679	2.481	2.332
C_1–C_2	1.407	1.422	1.458	1.479	1.452	1.370
C_2–C_3			1.369	1.373	1.364	1.444
C_3–C_4			1.458	1.428	1.452	1.370
C_4–C_5			1.458	1.428	1.441	1.436
C_5–C_6			1.369	1.373	1.385	1.450
C_6–C_1			1.458	1.479	1.441	1.436
C_1–C_4		2.843	2.715	2.876	2.734	2.817

[a] The atom numbering is shown in Figure 1. Bond distances in Å.

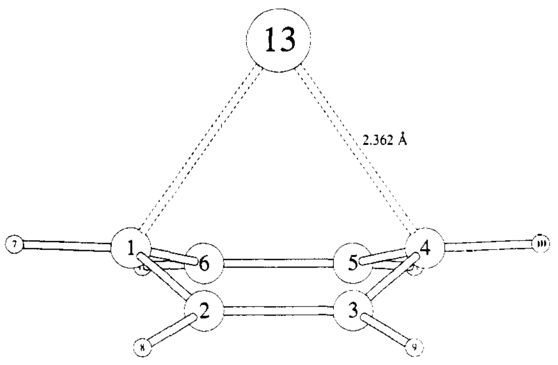

Figure 3. Structure 2, the Al-centered boat C_{2v} isomer.

(2) Al-centered boat C_{2v} structure. The degenerate $^2E_{2u}$ ground state for structure 1 should be expected to undergo a first-order Jahn–Teller distortion to lower symmetry. By reducing the symmetry of the complex to C_{2v} we do find an optimal structure at lower energy with Al above the center of the benzene ring. This Al-centered structure is illustrated in Figure 3. The C ring distorts, producing inequivalent C atoms which form a boat structure with stern and bow C atoms bent by 28° out of the benzene plane. The 2.362-Å Al–C distances with the out-of-plane C atoms is much shorter than that found in the C_{6v} structure, while the 2.693-Å Al–C distances with the in-plane C atoms have lengthened slightly. Some of the interaction energy needed to form structure 2 is shown in Table II, where we report the extra energy needed to distort benzene into a boat structure. At the HF level it requires 33.8 kcal/mol to distort the optimized planar benzene into the boat of structure 2 and 73.3 kcal/mol to arrive at the boat form of $C_6H_6^-$. If planar $C_6H_6^-$ is formed first, only 6.6 kcal/mol is needed to convert the ligand to the boat structure. The inequivalence of the C atoms is also evident in the calculated charge and spin densities. Only the two out-of-plane C atoms have large spin densities, in agreement with the low-temperature ESR spectra. The spin inequivalence of the C atoms is already present in the distorted $C_6H_6^-$ calculation. However, the out-of-plane C atom spin densities (0.376) in $C_6H_6^-$ are reduced in the complex because of Al 0.15 p_σ-orbital population in the SOMO. When benzene is distorted, one of the empty π* molecular orbitals has a symmetry which enables an interaction to

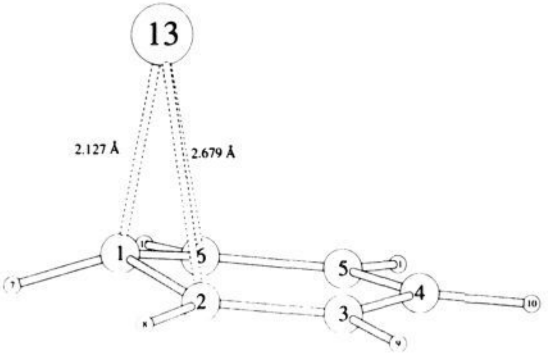

Figure 4. Structure 3, the Al on-top C_s isomer.

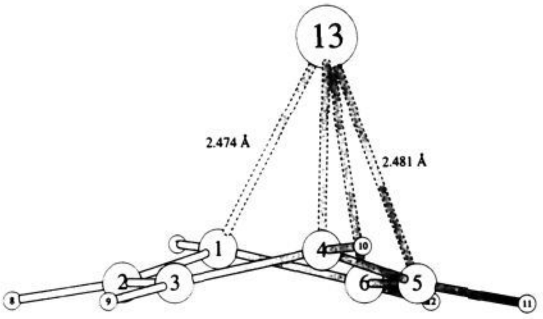

Figure 5. Structure 4, the Al σ-bridging C_s isomer.

take place with two of the C atoms and the Al p_σ orbital. We find C–Al bond orders, obtained from a Mulliken population analysis, of 0.316 with the out-of-plane and 0.044 with the in-plane C atoms, showing that the Al is mainly bonding with the out-of-plane C atoms. We find no evidence for the formation of a π complex; when we attempted to perform a geometry optimization with an Al p_π orbital populated in the SOMO, a much longer Al–C distance was obtained, and the optimized structure corresponded to a dissociated complex. The next two structures consider the effect of lowering the symmetry of the complex further.

(3) Al on-top C_s structure. This structure, shown in Figure 4, was optimized using C_s symmetry keeping the σ_{xz} mirror plane perpendicular to the y-axis. The optimization collapses back to structure 2 when the optimized structure 2 is distorted by moving the central Al atom by as much as ~0.3 Å along the x-direction. From this we conclude that structure 2 is a local minimum with respect to the x-coordinate of Al. However, when the Al displacements along the x-direction are large enough, we obtain structure 3, where the Al atom is essentially vertically above or on top of a benzene C atom. The ligand is again distorted, but forms a half-boat-like structure with only C_1 appreciably distorted out of plane. Among all of the five optimized structures, it is in this isomer we find the shortest Al–C distance of 2.127 Å and the largest Al–C bond order of 0.511 with the out-of-plane C atom. The SOMO again consists of contributions from the Al p_σ and the benzene π^* orbital, but the largest spin density is found on C_4, the atom furthest from Al. It is also interesting that this structure has the second-best Al binding energy at the HF level, but the Al CI binding energy is raised relative to the other isomers. An analysis of the natural orbital populations obtained in unrestricted HF (UHF) calculations suggests that a multiconfiguration SCF calculation might be required to more correctly describe the ground state for this Al on-top structure.[25] However, we do not expect this structure to correspond with the experimentally observed Al–benzene complex, since the computed spin densities suggest that an ESR spectra of this compound would have several inequivalent C atoms.

(4) Al σ-bridging C_s structure. This structure, shown in Figure 5, was obtained by starting the optimization from the Al-centered boat structure (2) but with the Al atom shifted slightly along the y-axis while preserving the σ_{yz} mirror plane. There is only a slight ~1-kcal/mol gain in energy, and the benzene boat is only slightly modified from structure 2. The energy to distort benzene into the boat is reduced by 9 kcal/mol, indicating that the Al–C interaction need not be as strong to form a stable complex. The Al atom moves substantially by 1 Å into a C–C bridging type structure resulting in the Al becoming equidistant from four C atoms. The C–Al equidistance is 2.48 Å, which is slightly less than the average of the 2.36-Å and 2.69-Å C–Al distances found in the centered structure 2. The large Al–C bond orders (0.276) with the out-of-plane C are slightly reduced from those in 2, but now the Al–C_5 and Al–C_6 bond orders (0.131) are more pronounced, resulting in an overall increase in the Al–C ring bond order. The spin densities of this bridging structure still resemble those of structure 2, and hence the ESR spectrum of this isomer should also match the one observed in the experiments. The Al spin density is enhanced relative to structure 2, and this is due to an increased Al s- and p_σ-orbital population in the SOMO. The Al–C bonding is σ-like, and we find no evidence for an Al π complex.

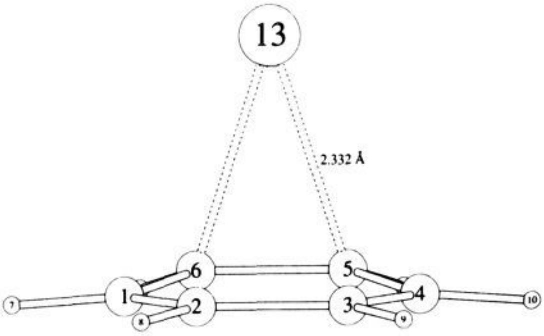

Figure 6. Structure 5, the Al π-bridging C_s isomer.

(5) Al π-bridging C_s structure. When a geometry optimization which maintains a σ_{yz} mirror plane is started with Al vertically above a benzene C–C bond and with the SOMO chosen to contain an Al p_π-orbital component perpendicular to the σ_{yz}, we finally obtain a π-complex structure like the one proposed by Kasai and McLeod. The π-complex structure is shown in Figure 6. The SOMO is still a benzene π^* orbital with two nodes, one along the y-axis and the other parallel to the x-axis intersecting bonds C_1–C_6 and C_4–C_5. At the optimal geometry the SOMO now has an Al p_π population of 0.30. When the Dunning–Hay basis was used, the structure proved difficult to optimize, a state crossing tended to occur once the energy gradients were below 0.002 au. The optimum structure of this lower energy state corresponds to the Al–benzene complex dissociating. However, when the optimization was performed using a 4-31G basis, a converged geometry for this π-bridging structure was relatively easy to find. The HF and CI Al binding energies suggest that the π complex is the most stable isomer. At the same time, the benzene ligand is only slightly distorted, having an energy 9 kcal/mol above that of the free molecule. This implies that the Al p_π-orbital interaction is not as strong as the p_σ-orbital interaction with benzene. In addition the spin density on the Al atom is significantly greater than that computed for AlC_2H_4, the reverse of what is found in the ESR experiments.

We feel after consideration of the Al–benzene computed spin densities and binding energies for the five optimal structures that the Al σ-bridging structure, 4, is the one most consistent with the complex observed experimentally. The ESR experiments estimate spin densities of 0.2 on the Al and 0.4 on the neighboring C atoms in AlC_6H_6, in fair agreement with the data given in Table IV. Our computed AlC_2H_4 spin density of 0.310 on Al is considerably less than the 0.7 estimated from ESR experiments, but it is still larger than the Al spin densities found in the AlC_6H_6 structures 2 and 4. In contrast, the π-bridging AlC_6H_6 structure, 5, has the highest Al spin density of all the compounds listed in Table IV. Thus we feel that the computed spin densities for structures 2 and

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4 are the ones most consistent with the ESR spectra recorded at low temperatures. Unfortunately, the binding energies indicate all of the possible isomer complexes to be unstable relative to the separated Al and benzene. Structures 2 and 4 both involve extensive distortion of the benzene ligand, and the complex binding energies are perhaps being underestimated because a much higher quality calculation is needed to compute the benzene distortion energy accurately. We have performed single point calculations on the isolated benzene ligands held at the different optimal complex geometries using larger basis sets which included polarization functions on the C and H but found little change in the benzene distortion energy. These large Al–benzene interactions, which must be taking place in order to cause the benzene to distort, suggest to us one further reason to favor structures 2 and 4 as being the most likely candidates for the complexes observed in the ESR experiments. The off-center isomer 4 would also have principal moments of inertia similar to those used by Mitchell et al. to estimate the Al–benzene complex binding energy.[9] In the ESR spectra at higher temperatures the Al starts to interact equivalently with all six C atoms. Our calculations provide two possible explanations. First, the planar $C_6H_6^-$ differs by $\sim$5 kcal/mol from the boat form of $C_6H_6^-$, allowing an easy interchange of the C atoms at the out-of-plane positions. Some support of this idea is given by previous work which shows $C_6H_6^-$ to undergo only a slight Jahn–Teller distortion giving rise to an ESR spectrum with six equivalent protons.[26] The alternative is that the Al on-top structure, 3, is a transition state interconnecting two Al σ-bridging structures with different out-of-plane C atoms. Structures 2, 3, and 4 have similar C–C bond length alternations, and for this reason we do not expect the on-top structure, 3, to serve as a transition state between different π-bridging structures 5.

The on-top structure, 3, is also interesting in its own right as it may be the prototypical structure formed when Al adsorbs on graphite. In our earlier Al on graphite cluster calculations we kept the positions of the C atoms rigidly fixed. The energetic demands for C honeycomb on the graphite surface to distort into a boat must be prohibitive. However, allowing a single C atom to move out of the surface plane is more reasonable. This is essentially what has happened in structure 3; the bond order between the out-of-plane C and Al suggests that a fairly strong Al–C bond is formed while the remaining benzene C atoms stay close to planar. Srivastava and Almlöf found a similar out-of-plane distortion when they performed calculations on the three-membered-ring compound $AlC_{13}H_9$.[27] In their optimum structure they found the central C to be 0.5 Å out-of-plane and the C–Al distance to be 2.1 Å, which is very similar to what we find for structure 3. A number of adsorbate-induced surface reconstructions have now been experimentally observed.[28] The Srivastava et al. calculations and our calculations demonstrate that substrate relaxation effects also need to be considered when using clusters to model adsorbate interactions on surfaces.

Conclusion

The Al–benzene complex is theoretically found to be a C–C bridging structure with the benzene ligand distorted into a boat shape. Close in energy is another structure with the Al centered above the benzene boat. In both complexes the Al interacts most strongly with the two out-of-plane para C atoms and the Al–C bonds are of σ type. These two structures are consistent with the low-temperature ESR spectra, which have a hyperfine interaction involving only two equivalent protons. The small barrier of interconversion between the two structures is the most likely explanation for the equivalence of the six protons in the higher temperature 220 K ESR spectrum. Our calculations do not provide support for an Al π-bridging complex being observed.

We have also found an on-top structure where the Al atoms bonds directly above a C atom. The on-top structure may be prototypical for Al chemisorbing on graphite and involve surface relaxation of the C substrate.

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Registry No. AlC_6H_6, 122358-77-4.

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Ab Initio/IGLO Study of Strained Bicyclic Olefins†

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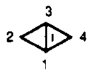
Abstract: The ^{13}C NMR chemical shifts of strained olefins **1**, **2**, **3**, and **6** were calculated using the ab initio/IGLO method(DZ/6-31G*). The calculated values resemble the experimental data closely but show a systematic drift with increased strain. The chemical shifts of the yet unknown olefins **1** and **2** were predicted to be extremely deshielded.

Introduction

Among olefins with colinear π orbital angle vectors[1b] the simplest and most strained symmetrical olefins are bicyclo[1.1.0]but-1,3-ene (**1**), bicyclo[2.1.0]pent-1(4)-ene (**2**), and bicyclo[2.2.0]hex-1(4)-ene (**3**). The former two olefins have been prepared only in the form of the substituted derivatives and characterized by trapping experiments.[2] Casanova and Rogers[3] and Wiberg et al.[3] prepared olefin **3** and studied its reactivity. Ca-



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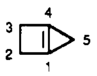

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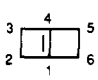

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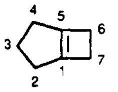

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† Dedicated to Professor George A. Olah on the occasion of his 65th birthday.

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