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Ab Initio studies of aryl σ- and π-complexes: neutral and charged electrophiles

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ABSTRACT: The *ab initio* MP2/6–311 ++ G** method was employed to examine the interaction of five electrophiles, Cl_2, Br_2 NO^+, SiH_3^+ and CH_3^+, with benzene. These groups exhibited a full range of complexation from true π-complexes to full σ-complexes (Wheland ions). The energy of complex formation increases in the order given above. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: electrophiles; aryl σ-complexes; aryl π-complexes; *ab initio* method

INTRODUCTION

The interactions of neutral and charged species with aryl π-systems have been recognized as important to various aspects of physical organic chemistry and to biochemistry. The study reported here deals with computations of the structures and energies of formation of a series of acceptor–donor complexes with benzene.

In 1949, Benesi and Hildebrand[1] examined the interaction of iodine with benzene and other solvents. They developed a procedure for determining concentrations for substances for which no molar absorptivity values were readily available. Their valuable research established the iodine–benzene complex to be formed in a 1:1 ratio. Keefer and Andrews[2] extended these studies to a variety of aryl complexes, and about this time the concept of electron donor–acceptor (EDA) complexes began to be seen in the literature. Mulliken provided a detailed quantum mechanical description of these complexes.[3] Based on valence bond theory, his work led to a more accurate description based on the concept of resonance between non-bonded components and those in which charge transfer (CT) from the electron donor to the acceptor had occurred. The existence of such CT complexes is now a matter of common knowledge.

Over the past decade, it has been established that mechanisms other than charge transfer may be operative between aryl π-systems and small molecules. Employing microwave spectroscopy, Blake and co-workers[4] demonstrated that water reacted with benzene to form what was described as a weak hydrogen bond calculated as 1.8 kcal mol^{-1} (1 kcal = 4.184 kJ). The approximate orientation of the water is indicated in Fig. 1(A). Gallivan and Dougherty[5] demonstrated that replacing the ring hydrogens with fluorine alters the orientation of the bound water to that depicted in Fig. 1(B). Owing to their symmetry, neither benzene nor perfluorobenzene possesses a permanent dipole moment. Both molecules, however, have appreciable quadrupole moments in the sense shown in the figure.[6] These reactions may be described then as dipole–quadrupole interactions. Similar considerations may be applied to the reported interactions of carbon monoxide and formaldehyde with benzene.[7]

It has been known since 1981 that in the vapor phase potassium ions bind more strongly to benzene than to water.[8] Based on STO-3G calculations, it was concluded that the most stable structure among the several considered poised the ion above the plane of the benzene on the sixfold axis. Extending this study, Caldwell and

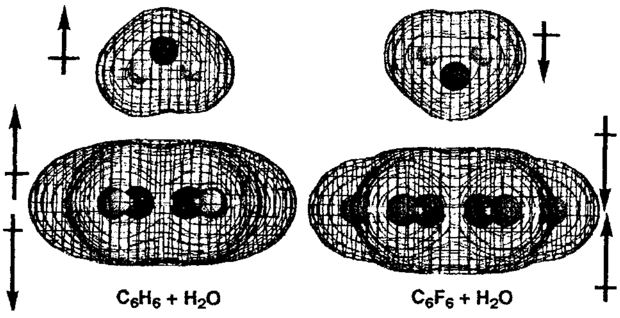

Figure 1. The interactions of water with (A) benzene and (B) perfluorobenzene. The grid displays the map of the electrostatic potential

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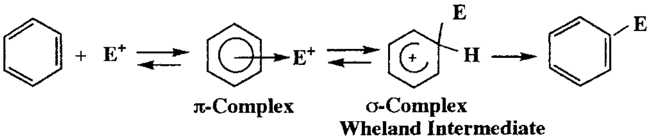
Kollman[9] employed a non-additive molecular mechanics approach that was parameterized for the quadrupole moment of benzene and incorporating electrostatic potential interactions. The binding energies for Li^+, Na^+, K^+ and NH_4^+ followed the experimentally observed values. Today these observations are categorized as cation–π interactions.

Dougherty and co-workers[10] published a review of cation–π interactions with particular reference to their biochemical implications. Among the subjects covered are (a) the interaction of acetylcholine with a synthetic receptor as a model for biological recognition,[10b] (b) potassium ion reactions with aryl-rich amino acid sequences which serve as potassium ion channels[10c] and (c) the reactions of alkali metal cations with benzene and several aryl-containing amino acids.[10d]

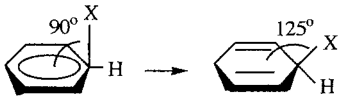
Dewar[11] appears to have been the first to propose that π-complex formation may precede the formation of the then established Wheland intermediate (σ-complexes) in electrophilic aromatic substitution reactions. The current mechanism is generally written as[12]



(1)

Based on detailed examinations of the benzylation of benzene–toluene mixtures, Olah *et al.*[13] proposed that the transition states for such reactions displayed characteristics varying from weak π-complexes to strong σ-complexes. Reed[14a] extended this thinking, describing true π-complexes with the acceptor poised above one of the ring carbons and bonded at an angle of 90° with reference to the plane of the ring; while true Wheland intermediate σ-complexes displayed acceptor angles near 125° in reference to the plane of the ring (Scheme 1). This postulation was based on the observation of the x-ray structure of the silver salt of $B_{11}CH_{12}^-$ which crystallized from benzene incorporating a benzene complexed in an η^1 fashion to the silver ion.[14b] Cowley and co-workers[15] extended this concept in their comparison of the complexation of aluminum alkyls and silylium ions with aromatic substrates.

Fukuzumi and Kochi[16] carried out detailed spectral examinations of a wide range of arene donor–acceptor complexes. They noted[16b] that for a series of arene halogenations and mecurations the spectral CT bands decreased in direct proportion to the rate of formation of the substituted products. More recently, Hubig and Kochi[17] carried out an experimental *tour de force* examining the complexes of hexamethylbenzene and related methylated arenes with seven electrophiles. Utilizing time-resolved UV–visible and NMR spectroscopic measurements and low-temperature accurate x-ray crystallography, they were able in several cases to determine very precise geometries. Low temperatures were required to insure adequate lifetimes, and it was necessary to include various counterions (i.e. $^-SbF_6$ or $^-BF_4$) chosen to enhance stability. The electrophiles employed were H^+, NO^+, NO_2^+, $^+CH_3$, $^+SiEt_3$, Cl^+ and Br^+. At this time, complexes of chlorine or bromine were not amenable to crystallization (see below). X-ray data on the $^+SiEt_3$ system were taken from the literature as the $^+SiMe_3$ derivative refused to form a proper crystal. NMR spectroscopy was found to be particularly useful in differentiating σ- and π-complex types. All of these complexes except one were of the σ-bonded type. The ^{13}C NMR spectra of the σ-complexes gave 1:2:2:1 intensity patterns. The exception was the complex formed by the nitrosonium ion, which formed an observable π-nitrosonium arene complex showing only one line in the ^{13}C NMR spectrum. Photochemical excitation was required to produce nitroso σ-complexes observable by UV spectroscopy.[18] Considerations of the C—X bond lengths plus the C—X bond angle made with the plane of the arene ring provided the best experimental evidence to date for the proposed continuum of σ–π-complexes.

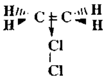


Scheme 1

It is pertinent here to mention the paper of Morokuma[19] addressing the general problem of molecular interactions utilizing *ab initio* methodology. Among the various causative effects listed were the attractive interactions comprising (a) electrostatic interactions such as ion–ion, ion–dipole, dipole–dipole, dipole–quadrupole, etc., (b) polarization effects due to the distortion of electron distributions as species approach each other and (c) charge transfer effects. Interactions brought about by dispersion were considered to be too small to require consideration in this study although the dispersion energy for the K^+–benzene interaction had been calculated to be ca -5 kcal mol^{-1}.[8]

The purpose of the computational study reported here was to examine the possibility of modeling these complexes in a meaningful fashion. Not only would such modeling offer savings in time and experimental difficulties, but one could also examine complexes derived from neutral species such as chlorine and bromine. It is known from earlier studies that these two elements and mercury(II) trifluoroacetate form stable CT complexes with substituted benzenes.[18] Computations employing benzene offer a chance to examine relatively weak electron donors. While it may well be that the ^{13}C NMR chemical shifts of the halogen CT complexes with benzene will never be accessible, the calculations of the expected chemical shifts are easily accomplished and offer a chance to compare characteristics of the benzene complexes with the observations of Hubig and Kochi.[17]

Table 1. Comparison of the charge transfer geometries for the chlorine–ethylene complex with the literature values[23]



Distance (Å)	Expt.	MP2[10a]	MP2/6–311 ++ G**[b]
d(C—C)	1.339[c]	1.341	1.342
d(Cl—Cl)	1.988[c]	2.044	2.039
d(Cl···plane)	3.128[c]	3.003	3.043

[a] A triple zeta plus polarization basis set was used.
[b] This study.
[c] Ref. 30.

Table 3. Ring bond lengths (Å) for the complexes in this study (MP2/6–311 ++ G**)[a]

	Bond		
Benzene complex	1–2	2–3	3–4
Benzene alone	1.400	1.400	1.400
Chlorine η^1	1.402	1.400	1.400
Bromine η^1	1.402	1.399	1.401
^+NO	1.417	1.392	1.412
$^+SiH_3$	1.428	1.395	1.411
$^+CH_3$	1.465	1.379	1.411
Benzene	1.401		

[a] The C—C bond lengths for the benzene rings in the chlorine and bromine η^2 complexes were all 1.401 ± 0.001 Å.

COMPUTATIONAL METHODOLOGY

All calculations were carried out at the MP2/6–311 ++ G** level with the Gaussian 98 program.[20] Results are given in Tables 1–3. NMR calculated chemical shifts were obtained by the GIAO method at the BPW91/6–311G** level (i.e. overall BPW91/6–311G**//MP2/6–311 ++ G**). All chemical shift data referenced to TMS are given in Table 4. Atomic charges were calculated from electrostatic potentials by the method of Kollman and co-workers.[21]

Since the processes under study involve the union of two entities into one, the problem of basis set superposition error (BSSE) may be introduced. To rule on this question the counterpoise method of Boys and Bernardi[22] was applied to the following pairs: chlorine with ethylene, benzene with bromine and benzene with the nitrosonium ion. The corrections amounted to 0.37, 0.27 and 0.59 kcal mol^{-1}, respectively. Since these errors are considerably less than those expected from single method energy optimizations (±2 kcal mol^{-1}), no further attention was given to this matter. It is mentioned parenthetically that density functional methods were found to be unsatisfactory for the purpose of finding the geometries of these complexes, presumably owing to their known lack of sensitivity to dispersion forces.[23,24]

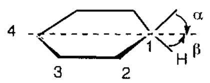
RESULTS AND DISCUSSION

To establish an accurate method and basis set for this study, a comparison was made with results on a known CT complex from the literature. Salahub and co-workers[23] explored in considerable detail the computational level required for an adequate geometry for the chlorine–ethylene CT complex. Since CT complexes will play a

Table 2. Total energies, energy of complexation, C–X (a), α and β[a]

Species	*E (hartrees)*	*ΔE (kcal/mol)*	*C—X* (Å)	α (°)	β (°)	Ring charge (e)[b]
C_6H_6	−231.584257				0.0	
Cl_2	−919.240978					
η^1 Complex	−1150.833270	−5.0	3.036	94.0	2.0	0.06
η^2 Complex	−1150.833377	−5.1	3.098,3.107	86.2, 84.7	2.1, 1.6	0.18
Br_2	−5144.972366					
η^1 Complex	−5376.565910	−5.8	3.118	86.9	1.8	0.10
η^2 Complex	−5376.565905	−5.8	3.144, 3.189	84.0, 85.8	1.8, 1.0	0.10
NO^+	−129.308567					
Complex	−360.947336	−34.2	2.410	103.2	0.4	0.48
SiH_3^+	−290.441923					
Complex	−522.113170	−54.6	2.096	96.9	15.5	0.56
CH_3^+	−39.356532					
Complex	−271.072769	−82.8	1.594	57.7	45.8	1.02

[a] Angles defined by



[b] Total charge remaining on the aryl ring in complex.

Table 4. Calculated carbon chemical shifts (ppm) referenced to TMS

CT	1	2	3	4	5	6	$\Delta\delta$ (ppm)[a]
η^1Cl_2	126.3	131.3	129.4	130.7	129.4	131.3	5.0
η^1Br_2	122.7	134.0	129.6	133.0	129.6	134.0	11.3
NO^+	154.1	140.3	142.4	157.5	142.4	140.3	17.2
Si^+H_3	82.9	160.2	138.2	152.6	138.2	160.2	77.3
C^+H_3	58.4	193.9	136.3	170.7	136.3	193.9	135.5
	56.7[b]	197.7[b]	139.2[b]	191.1[b]	139.2[b]	197.1[b]	

[a] The range of carbon chemical shifts in ppm for a given complex.

[b] See Ref.[16a]. These are the experimental chemical shifts for the hexamethylbenzene complexes. There is no immediate rationalization of the disparity in the calculated and experimental values for C4.

part in the following discussion, a brief examination of the chlorine–ethylene complex was carried out to verify the methodology to be employed. A summary of their pertinent values and the experimental parameters along with the results of the current calculations are given in Table 1, where it can be seen that the level chosen, MP2/6–311 ++ G**, is equivalent to their chosen best method. They point out that density functional methods, even the hybrid Becke3LYP method, did not give satisfactory results. This result was confirmed here for the bromine–benzene CT complex.

In 1999, two computational studies of the iodine–benzene CT complex were published.[25] The first of these[25a] employed several different computational methods including the MP2 method employed here. The authors concluded that an η^2 complex with the iodine at 3.333 Å from carbons 1 and 2 was the most stable form of the complex. It was also concluded that the potential energy surface for the complex was very flat. The second study also employed the MP2 method with the conclusion that the η^2 above-the-bond complex and the η^1 above-a-carbon complex were the two lowest energy forms very similar in energy and iodine–benzene separations.

During the course of the present investigation, Vasilyev *et al.*[26] published an x-ray study of bromine–benzene complex. Crystals were generated and measure-

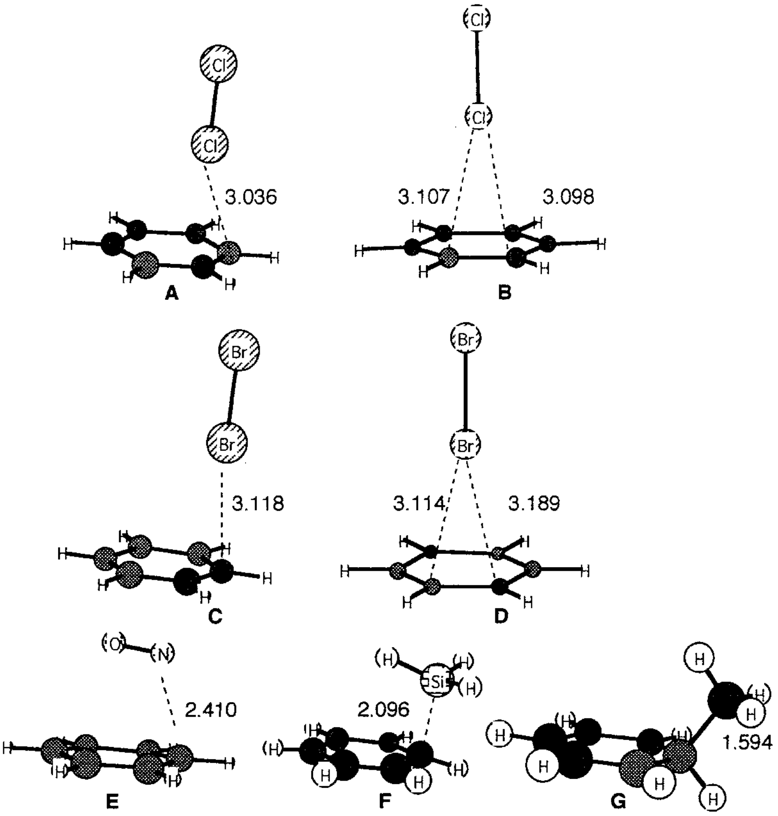


Figure 2. Ball and stick models for the benzene complexes with chlorine **A** and **B**, **C** and **D** bromine, nitrosonium ion **E**, silylium cation **F**, and **G** methyl carbocation

ments were taken at 123 K in a sealed capillary. No solvent was mentioned although many of their low-temperature studies employed methylene chloride.[17] Their x-ray results favored an unsymmetrical η^2 bromine complex above a C—C bond with bromine–carbon bond distances of 3.18 and 3.36 Å.

For the initial computations on the chlorine and bromine complexes with benzene, the halogens were poised parallel to the plane of the benzene ring centered about the sixfold axis and 4 Å above the ring. There was no contact of the van der Waals surfaces at these separations. Optimization (MP2/6–311 ++ G**) resulted in the η^1 complexes shown in Fig. 2(A) and (C). The formation energies are given in Table 2. Bond lengths for the benzene is various complexes are given in Table 3. Both complexes place the halogen directly above carbon 1 at angles close to the 90° predicted by Reed and co-workers[14] for π-complexes. The C—Cl and C—Br distances were both less than the corresponding sums for the van der Waals radii by 0.46 and 0.53 Å, respectively.

Subsequently, the x-ray structure for the bromine complex was used as a starting point for an optimization of the η^2 complex. The η^2 structure is shown as Fig. 2(D). The energy difference between the η^1 and η^2 structures is 3 cal only favoring the η^1 complex. This is not a computationally meaningful difference but may explain why only the η^1 complexes were formed in the initial calculation. Calculated at 0 K, the computed and experimental structures for the bromine complex are considered to be in satisfactory agreement. Furthermore, the perturbation of arene bond lengths is zero within computational accuracy (estimated as ±0.01–0.02 Å from known literature values). The energies of formation for both complexes fall within the range estimated for K^+–benzene dispersion interaction.[8] The amount of charge transferred to the halogens from the benzene rings is considerably less than that in the stronger complexes. It appears that both the dispersion interaction and charge transfer are taking place. Low barriers to structural variations in π-complexes are now well known and consistent with the above observations.[25,27]

While the structure of the η^2 complex of benzene with chlorine has not been reported, consistency required a similar computation of this complex. Shown in Fig. 2(B), the η^2 complex was also found not to be totally symmetric. The C—Cl bond distances were 3.098 and 3.107 Å, respectively. Within the error of the calculation, the two complexes had the same energy values.

The NMR ^{13}C chemical shifts (Table 4) were computed on the premise of static η^1 structures for both complexes. As will be noted in the table, carbons 2, 4 and 6 are deshielded with reference to carbons 3 and 5. This result corresponds to the expected charge effects based on the resonance structures that one can write for the cyclohexadienyl cation. The average calculated chemical shifts for the ring carbons of the chlorine and bromine complexes are 129.7 and 130.5 ppm, respectively, compared with 128.5 ppm for benzene. While appropriately downfield from benzene, these minor alterations in chemical shift confirm the weak interaction in these complexes. It would not be surprising if these two spectra were found to be single lines since rapid halogen exchange and/or fluxional rotations of the rings would lead to chemical shift averaging.

The x-ray crystal structure of the complex between benzene and the nitrosonium ion ($^+$NO) was determined by Brownstein *et al.*[28] in 1986. They produced the $^+$NO from a number of different sources, and there were some small structural changes and ^{13}C NMR chemical shift variations due to counterion effects. The N—O bond length in the hexamethylbenzene complex was reported as 1.128 Å, in excellent agreement with the value found here for the complex with benzene (1.120 Å). Kim and Kochi[18] reported an identical value. The calculated value for $^+$NO is 1.086 Å. In keeping with the results of the computation, they reported the nitrogen end of the ion to be closer to the ring plane than the oxygen. From considerations of the van der Waals radii both the nitrogen and the oxygen impinge on the benzene π-charge cloud.

Hubig and Kochi[17a] reported UV–visible observations of a transient π-complex that upon photoexcitation converted to a detectable σ-complex. For the mesitylene complex,[18] the x-ray data showed the $^+$NO to be obliquely oriented with reference to the aryl ring with the nitrogen 2.5 Å from the nearest carbon. The comparable value for the benzene–$^+$NO complex is 2.410 Å. Given the positive charge on the ion, the energy of formation for the benzene–$^+$NO complex is considerably more exothermic than for the halogen cases above. In keeping with the estimated charge transfer for a series of methylated benzenes,[18] charge transfer is considerably greater here than for the halogen complexes. The angle α is consistent with more σ-character as well. The C1—C2 bond length is closer to those characterizing σ-complexes as will be seen. Both the Brownstein group[28] and the report of Hubig and Kochi[17a] indicate the ^{13}C NMR spectrum for the complex to hexamethylbenzene to consist of a single line at ca 150–152 ppm.

The chemical shifts calculated here were based on the static structure and displayed a 1:2:2:1 pattern with the chemical shifts spread across the range 140–157 ppm. At least three possibilities exist for the observation of single aryl carbon resonance line. These may be listed as (1) the $^+$NO moiety is aligned on the sixfold axis of the arene ring; (2) a rapid exchange of bound and unbound $^+$NO exists in solution; and (3) the $^+$NO does a rapid transit from carbon to carbon around the ring. The latter is equivalent to a rapid fluxional motion of the ring with reference to the $^+$NO. Such motions are well documented for other aryl complexes.[29] Whatever the mechanism, by averaging the chemical shifts for the NO complex in Table 4 and correcting for the presence of the six methyl groups (3.8 ppm), the calculated result for the ^{13}C chemical shifts is 148.5 ppm, in very good agreement with the experimental values for the hexamethylbenzene–$^{+}$NO complex (150.8 ppm).

The complex between $(Et)_3Si^+$ and toluene has been the subject of a controversy which need not concern us here (see Ref. 15 for leading references to this subject). The $(Et)_3$ Si-toluene complex was reported to show a C4—Si bond length of 2.18 Å and an angle $\alpha = 76°$. When the H_3Si^+ cation was optimized from its starting position on the benzene sixfold axis, the structure shown in Fig. 2 was formed. The C1—Si bond length of 2.096 Å and angle $\alpha = 96.9°$ when coupled with the considerably greater formation energy ($-54.6\,\text{kcal mol}^{-1}$) suggests the structure to be a closer approach to a σ-complex than those discussed previously. For comparison, the C3—Si bond length in 3-silyl-1,4-pentadiene was calculated as 1.907 Å. The spread of ^{13}C chemical shifts is considerably larger (77.3 ppm) than others encountered to this point. Examination of the C1—C2 bond lengths for the five complexes (Table 3) shows a clear progression down the list. The H_3Si^+ cation forms a complex somewhat closer to a σ-complex, providing yet another point along the continuum path.

The σ-complex terminus is reached with the complex formed by the methyl carbocation with benzene. The C1—CH_3 bond length of 1.59 Å closely approximates that of an sp^3–sp^3 σ-bond. The C1—C2 bond length is within 0.03 Å of that reported for the heptmethylbenzenium ion.[17a] The ^{13}C chemical shifts follow closely those reported for the latter ion. The C4—C1—CH3 angle is 122.3°, and the energy of formation is the most exothermic of the cases considered.

CONCLUSIONS

The complexes of benzene with chlorine, bromine, nitrosonium, silylium and methyl cations when calculated at the MP2/6–311++G** level display the characteristics attributed to a continuum of complexes from pure π-complexes to true σ-complexes. Both η^1 and η^2 complexes were found for benzene with chlorine and with bromine. There is an increasing exothermicity of formation across the series. The C1—X bonds decrease in length from those of a loose complex to that of a typical σ-bonded complex. Progressing through the series the angle α approaches that expected of a tetrahedral C1. Accompanying this progression is an increasing transfer of electron density to the accept or partner.

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