# Haloalkane-Aromatic Complexes in the Ground and Excited States

## Molecular Orbital Calculation

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CNDO/2 calculations have been carried out on a series of haloalkane-aromatic 1 : 1 complexes in the ground and first excited singlet states and one 2 : 1 complex in the ground state. Calculated stabilities agree very well with reported experimental results for the ground state. Our calculations indicate that the substituent effect on complex stability in excited states will be the opposite of that found for the ground state.

## Introduction

The existence of complexes between haloalkanes and aromatic molecules has been known [1] for a long time. More recent experimental studies to determine the nature of these interactions have employed various experimental methods, such as ir [2], nmr [3], uv absorption spectroscopy [4], calorimetry [5], glc [6], and polarization measurements [7].

The general conclusions drawn have been that 1) a 1:1 complex is most probable, 2) that this complex is quite weak, 3) that completely halogenated haloalkanes form much weaker complexes than those with at least one hydrogen [8], and 4) that the haloalkane prefentially lies along the principal axis [9] of the aromatic ring.

There have been various calculations reported on similar systems, such as simple electrostatic model calculations [10] on dihalo-benzene complexes, an Extended Hückel treatment [11] of group IV chloride and bromide complexes with aromatics, and CNDO/2 calculations [12] on benzene-dihalogen and benzene carbon disulfide complexes. These studies were all limited to the ground state.

One apparent problem common to all of these studies is the neglect of dispersion forces in the formation of these weak complexes. Though dispersion forces are certainly essential to the stability of these complexes (and those treated in this paper), it has been pointed out [13] recently that the consideration of purely electrostatic interactions is sufficient for comparing relative stabilities of different orientations of a given complex, be it polar [14], or non-polar [15]. In addition, the CNDO/2 method has been shown to predict incorrect geometries in small dimers, such as $(HCN)_2$ [16], $(C_2H_4)_2$ [15] and $(H_2O)_2$ [17]. However, CNDO/2 apparently fares better in the treatment [12] of aromatic complexes.

We report CNDO/2 results of the complexes chloroform-benzene, carbon tetrachloride-benzene, chloroform-toluene, chloroform-p-xylene and 2:carbon tetrachloride-benzene as a function of the haloalkane-aromatic ring distance measured along the pseudo $C_6$ axis. Calculated stabilities are compared between these complexes in the ground ($S_0$) and first excited singlet ($S_1$) states.

## Calculations

All calculations were done on the Burroughs B6700 of the Núcleo de Computação Eletrônica – Universidade Federal do Rio de Janeiro. The Method was basically CNDO/2, modified for halogen atoms following the suggestions of Kollman, et al. [18]. The self-consistency criteria have been given [19] previously.

$S_1$ was calculated by a limited configuration interaction (CI) approximation in which only the 64 singly excited configurations corresponding to the excitations $N-7,\ldots,N\rightarrow N+1,\ldots,N+8$ ($N$ being the HOMO) were considered. The CI super matrix elements were constructed by use of the approximate equations.

$$(ij\,|\,\mathrm{A}\,|\,ij) = e_j - e_i - (ii\,|\,jj) + 2(ij\,|\,ij)\,, \qquad (1)$$

$$(ij\,|\,\mathrm{A}\,|\,kl) = -(ik\,|\,jl) + 2(ij\,|\,kl), \qquad (2)$$

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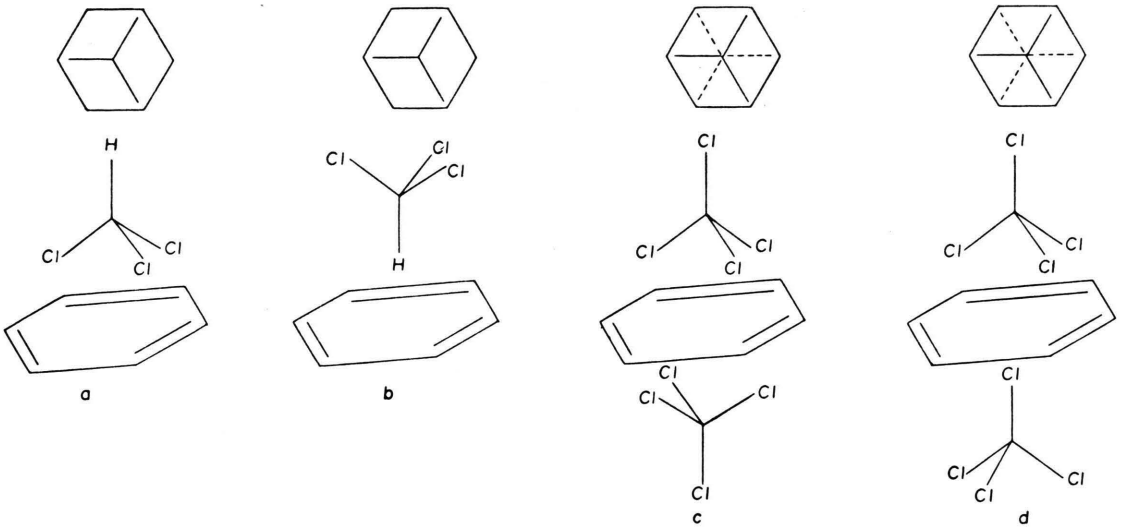


Fig. 1. Relative orientations of haloalkane-aromatic complexes considered. Chloroform-aromatic with a) the 3 chlorines toward the ring; and b) the 3 chlorines away from the ring, both $C_{3v}$. 2:carbon tetrachloride-benzene with c) the chlorines staggered and all six pointed toward the ring ($D_{3d}$), and d) the six chlorines staggered, with one molecule oriented towards the ring and the other away ($C_{3v}$).

where $e_i$ is the orbital energy of the $i^{\text{th}}$ molecular orbital,

$$(i\,j\,|\,k\,l) = \sum_{\mu}\sum_{\nu} c_{\mu i}\, c_{\mu j}\, c_{\nu k}\, c_{\nu l}\, \gamma_{\mu\nu},$$

where $\mu, \nu$ refer to atomic orbitals, $\gamma$ being a repulsion integral. The atomic coordinates used as input were obtained by applying Pulay's FORCE method [20] to $S_0$ each component molecule of the complex. These results were then used to fix all coordinates within each molecule, varying only the distance between molecules along the $C_6$ axis of benzene, by 0.1 Å in the region around the energy minimum, and up to 0.5 Å in regions of lesser interest. The relative orientations are shown in Fig. 1 a and b. In the 2:1 complex the only configurations tested were those in which the C-plane distance was equal for both $CCl_4$ molecules. These orientations are shown in Fig. 1 (c and d).

## Results

Figures 2 and 3 show the calculated energies as a function of intermolecular distance for the system chloroform-toluene and carbon tetrachloride-benzene, respectively. One notes in Fig. 2 that the $S_0$ complex shows a very shallow minimum (2.14 kcal/mole), however only when the hydrogen atom of the chloroform is oriented toward the toluene ring. The excited state has a reasonably deep energy trough, however the favored orientation in this state is the opposite of the ground state orientation. The energy vs distance curves of the chloroform-benzene and chloroform-p-xylene systems are not shown, being very similar to Fig. 2, the former having a shallower $S_0$ minimum and deeper excited state minima, and the latter having a slightly deeper minimum in

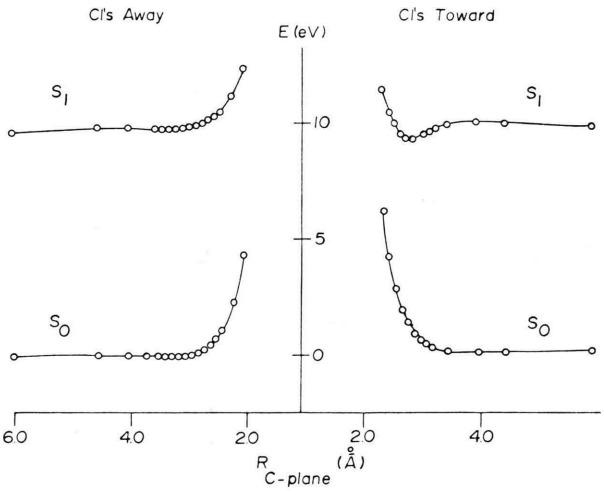


Fig. 2. CNDO/2 calculated energy as a function of donor-acceptor distance for the ground and first excited state of the chloroform-toluene complex.

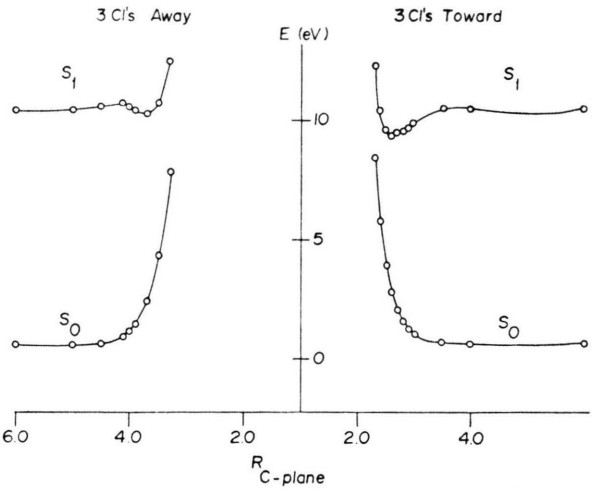


Fig. 3. CNDO/2 calculated energy as a function of donor-acceptor distance for the ground and first excited state of the carbon tetrachloride-benzene complex.

$S_0$, and shallower minima in the corresponding excited states (see Table 1). The carbon tetrachloride-benzene system is quite different, as shown in Figure 3. The $S_0$ complex shows no minimum. (We did calculate one intermolecular distance, 5.0 Å, to be more stable that infinite separation by a mere 0.14 Kcal/mole, however we attribute this to different rates of convergence to self-consistency rather than any real effect.) However this system is calculated to have the most stable excited state complexes. The 2:1 carbon tetrachloride-benzene complex was calculated to be unstable at any C-plane distance.

Table 1 shows the calculated depths of the energy wells, the distance (C-plane) at which each minimum occurs, and the calculated values of $(\partial\mu/\partial r)$ and $k$ (the force constants of the intermolecular vibration), evaluated at the calculated energy minimum by fitting the $\mu$ vs. $r$ and $E$ vs. $r$ curves to the parabolas $\mu = a + b(r - r_0) + c(r - r_0)^2$ and $E = 0.5\,k\,(r - r_0)^2$, using a least squares fit. Calculated charges on the haloalkane moiety at the energy minimum are also given.

## Discussion

In spite of the variations in calculated equilibrium constants, depending on the method of measurement, all studies on $S_0$ complexes agree that substitution of electron donating groups (such as methyl) increases the stability of the complex and that $CX_4$-aromatic complexes are much less stable that $CHX_3$-aromatic complexes. Our calculated results on the $S_0$ complexes clearly reflect these conclusions, and support the structure originally proposed [2, 8] for the chloroform-benzene system.

Even though the experimental energy of stabilization would not correspond to the depth of our calculated energy trough because of our neglect of dispersion force and solvation effects, these effects can be reduced by the comparison of the stabilities of two similar complexes. If we neglet entropy and PV terms we have $\Delta E = -RT \ln (K_1/K_2)$. We calculate the difference in trough depths between toluene-chloroform and benzene-chloroform complexes to be $E = 0.18$ kcal/mole. Based on nmr [3 a] and assuming no molar volume changes upon mixing, we calculate the equilibrium constants of the complexes to be $K$(benzene-chloroform) $= 0.032$ and $K$(toluene-chloroform) $= 0.060$ (Standard state: 1 M). These experimental $K$ values yield a value of $\Delta E =$ 0.38 kcal/mole, which we consider to be quite good agreement.

Table 1. Calculated properties of haloalkane-aromatic complexes at their energy minima ($E_{r_0}$).

| System | State | $r_0$ [Å] | $E_\infty - E_{r_0}$ [kcal/mole] | $\mu(D)$ | $\partial u/\partial r \cdot 10^{10}$ [esu] | $k$ [md/Å] | $^z$CYCl$_3$ [a] |
|---|---|---|---|---|---|---|---|
| $C_6H_6$—$CHCl_3$ | $S_0$ | 3.2 | 1.96 | 2.014 | − 0.268 | 0.162 | − 0.007 |
| | $S_1$ | 2.8 | 22.6 | 6.045 | − 1.52 | 1.91 | + 0.440 |
| $C_7H_8$—$CHCl_3$ | $S_0$ | 3.2 | 2.14 | 1.940 | − 0.243 | 0.165 | − 0.007 |
| | $S_1$ | 2.9 | 9.96 | 5.646 | − 1.75 | 1.34 | + 0.380 |
| $C_8H_{10}$—$CHCl_3$ | $S_0$ | 3.2 | 2.17 | 2.007 | − 0.241 | 0.162 | − 0.006 |
| | $S_1$ | 2.9 | 6.73 | 5.236 | − 2.94 | 1.81 | + 0.347 |
| $C_6H_6$—$CCl_4$ | $S_0$ | none | — | — | — | — | — |
| | $S_1$ | 2.6 | 26.1 | 5.526 | 9.36 | 1.51 | − 0.336 |

[a] Y = H or Cl.

We also calculate a much larger energy difference between the chloroform complexes of benzene and toluene than toluene and p-xylene, consistent with the experimental [3 a] value of $\Delta E = 0.15$ kcal/mole between the toluene-chloroform and mesitylene-chloroform complexes. The failure of our calculations to detect the ground state 2:1 carbon tetrachloride-benzene complex which has been reported [21] we attribute in part to the fact that our calculations do not consider d orbitals, consistent with the interpretation [11] that the stabiliies of $YX_4$-aromatic complexes can correlated with the electron affinities of the empty d orbitals of the appropriate halogen atoms. Bruns, et al. also found [12 a] that d orbitals needed to be included in the basis set in order to obtain an appreciable stabilization energy for the aromatic-dihalogen complexes. However, we recognize the possibility that the stability of the benzene-carbon tetrachloride complex may be due exclusively to dispersion forces, which are not considered in our treatment.

Other than stabilities, experimental data on these complexes are rare. However we could also point out from Table 1 that our calculated charges on the chloroform moiety in the various $S_0$ complexes are quite small, consistent with experimental ir results [2], and that our $S_0$ force constants are probably quite reasonable, comparing them to $k = 0.27$ md/Å obtained [21] from Raman spectra of the 2:1 carbon tetrachloride-benzene complex.

Possibly a more interesting aspect of our calculated results pertains to the complexes in their excited states. There are two striking failures with regard to our excited state energy curves. 1) The excitation energy is greatly exaggerated. This problem has been well known for the CNDO/2 method from its inception. Attempts [22] to rectify it suffer from the arbitrary distinction between the sigma and pi orbitals, which not only turns the method rotationally variant, but also becomes devoid of all significance in non-planar systems such as the complexes treated here. 2) The $S_1$ complexes have a shorter equilibrium C-plane distance than the $S_0$ complex. (The former also have greatly exaggerated transfers of charge.) This problem is undoubtedly due to overemphasis on delocalization stabilization, characteristic of all molecular orbital methods. However, in spite of these failures, we believe that reliable qualitative information can be abstracted from our calculated results.

Our calculations predict that electron donating substituents will destabilize the excited state complexes of chloroform. This substituent effect is reflected in both the calculated trough depths and the calculated charges on the chloroform moiety, being negative in the $S_0$ complex and positive in the excited state.

Simons and coworkers have reported [23] the fluorescence and phosphorescence spectra of the chloroform-benzene complex at 77 K. They have also investigated the effect of substituents on the benzene ring and the deuterium isotope effect on these emissions.

Their general conclusions on the excited state complexes can be summarized by 1) "the intermolecular interaction is weaker in the excited complex than in $S_0$" [23 c] and 2) there is a change in relative orientation between haloalkane and the aromatic ring which "cannot be ascribed simply to a change in the equilibrium internuclear molecular distance perpendicular to the ring" [23 c].

The first conclusion, based on the fact that both the absorption and fluorescence spectra of these complexes are blue shifted relative to the pure aromatic, is apparently in contradiction to our calculated curves, which predict a much more stable excited state complex. However we do predict blue shifted absorption spectra in the toluene ($1700\ cm^{-1}$ vs. $\sim 220\ cm^{-1}$ (exp.)) and p-xylene ($1550\ cm^{-1}$ vs. $\sim 370\ cm^{-1}$ (exp.)) complexes with chloroform. Our prediction of a red shifted fluorescence is strictly dependent on attaining the excited state equilibrium configuration during the lifetime of the appropriate state. However, Simons' [23 c] second conclusion and subsequent discussion is perfectly consistent with the chloroform moiety not attaining its equilibrium configuration, i.e., undergoing a rotation of 180°. If this is indeed the case, our suggestion that substitution on the aromatic ring by electron donors destabilizes excited states is apparently untestable for these complexes. However, the work of Martire and coworkers suggests [24] that fluoroform complexes might be more stable than the corresponding chloroform complexes, thus the complexes could be studied at a higher temperature. This would obviously favor the possibility of attaining equilibrium during the lifetime of the excited state. Another favorable factor to be expected in the use of fluoroform would be a decrease in the heavy atom effect, thus an expected increase in lifetimes.

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