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CNDO/2 Study of Benzene-Chlorine Complex

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We have carried out CNDO/2 calculations for the benzene-chlorine complex in a number of configurations. In order to obtain reasonable complexation energies, it was necessary to exclude chlorine 3*d*-orbitals from the basis set. When only *s*- and *p*-orbitals were included, we found maximum stability for the complex for an unsymmetrical geometry. The calculated complexation energy was -3.5 kcal/mole. Configuration-interaction calculations predicted a wavelength of about 270 nm for the charge-transfer band. Most, but not all, geometries were found to produce stable complexes.

Key word: Benzene-chlorine complex

The structure of the benzene-halogen charge transfer complexes in fluid phases is a question of long standing [1–3]. Although a variety of structures have been discussed, most investigators have favored the axial model which occurs in the solid state [4]. However, Fredin and Nelander have recently made infra-red absorption studies on several matrix-isolated complexes, and have concluded that, of all of the halogens, apparently only iodine forms an axial complex with benzene [5]. In recent years, several papers have been concerned with the study of these complexes by means of perturbation theory [6, 7]. The conclusions from these studies were: (a) At the equilibrium geometry it appears that most of the binding arises from the Coulombic and Polarization type interactions, with very little contribution from the charge-transfer resonance interaction; (b) for these weak complexes, it appears that a wide range of relative geometries probably lead to very similar binding energies (ca. 1 kcal/mole).

In this note, we wish to describe some results we have obtained for the Cl_2-benzene complex by application of the semi-empirical all-valence electron self-consistent-field (CNDO/2) theory developed by Pople and coworkers [8]. Several investigators have recently applied this theory to charge-transfer complexes, and obtained encouraging results [9–11].

The major problem encountered in the present calculations was that standard iteration procedures [12] failed to produce convergence when chlorine 3*d*-orbitals were included in the basis set. In most cases, convergence was achieved by the simple expedient of averaging the new calculated density matrix with the old one at each iteration. However, for several calculations at the shortest intermolecular separations considered, this procedure also failed. We therefore tried McWeeny's method [13] of directly determining the density matrix by minimizing the energy along the path of steepest descents, and found that it successfully produced convergence in every case. Calculations using McWeeny's procedure were always

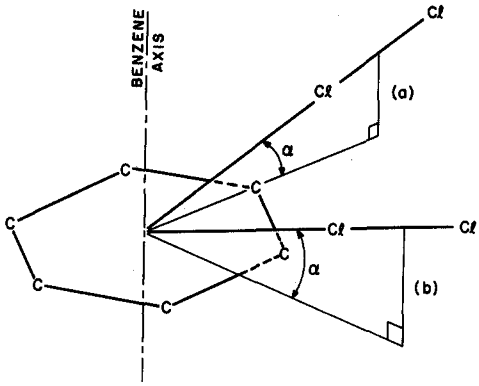

Fig. 1a and b. Illustration of two unsymmetrical geometries (a) and (b) investigated

followed by several iterations employing the standard Roothaan technique [12]. In all cases, calculations were continued until the energy converged to within 10^{-6} a.u. Except for the modifications necessitated by these additional methods for obtaining convergence, our computer program was essentially the one listed by Pople and Beveridge in their book [8].

The configurations which we investigated for the complex can be classified into two categories: (1) those in which the center of the Cl_2 molecule is situated on the six-fold axis of the benzene molecule; and (2) those in which the center of the Cl_2 molecule is not on benzene's six-fold axis. In the first category we treated: the axial model, with the Cl_2 molecule along the six-fold axis; the *resting* model, where Cl_2 is parallel to the benzene ring; and several oblique cases obtained by twisting Cl_2 to orientations intermediate between those of the axial and resting geometries. In the second category we have: a *planar* model, with the Cl–Cl bond along a C_2 axis of the benzene molecule; a *perpendicular* geometry, obtained from the former by twisting the Cl_2 molecule so it lies at right angles to the plane of the ring; and the two *unsymmetrical* configurations (a) and (b) illustrated in Fig. 1, for several values of the angles α.

The molecular geometries were assumed to be those of the isolated molecules ($R_{CC} = 1.397$ Å, $R_{CH} = 1.10$ Å, $R_{Cl-Cl} = 1.99$ Å). In general, the only geometric parameter that was varied was the distance between the molecular midpoints. However, where stable complexes were predicted, we also varied the internuclear distance in the chlorine molecule. This produced a slight increase in the calculated binding energy.

Just as Nelander reported for the ethylene-chlorine complex [10], we found that the inclusion of chlorine $3d$-orbitals always led to unsatisfactory results. The recommended $3d$-orbital exponent [8] is 0.94. When this value was used, the calculated intermolecular potentials continually decreased as the molecules were brought together; no minima were found even at separations as small as 2 Å. When the $3d$-orbitals were contracted by using exponents equal to those of the $3p$-orbitals, potential minima were found, but the potential well depths were always about two orders of magnitude too great (several hundred kcal/mole). Consequently, the only results that will be reported are those obtained by including only $3s$ and $3p$ orbitals on the chlorine atoms.

Table 1. Calculated results at potential minima–Category (1)

GEOMETRY		R_{min} (Å)(a)	INTERACTION ENERGY (kcal/mole)(b)	DIPOLE MOMENT (D)	CHARGE TRANSFER(c) (e)	POLARIZATION CHARGE(d) (e)	$\Delta k/k$(e) (%)
	Tilt From Axial Model						
AXIAL	0°	3.875	-0.41	0.095	+0.0026	0.0035	+2.3
OBLIQUE	22.5°	3.75	-0.60	0.14	+0.0042	0.0049	+1.8
	45°	3.75	-0.20	0.05	+0.0016	0.0014	-2.7
	67.5°	(Completely Repulsive)					
RESTING	90°	(Completely Repulsive)					

(a) Separation between molecular centers at potential minimum.

(b) $E(R_{min}) - E(\infty)$.

(c) Electrons transferred from benzene to chlorine.

(d) Polarization charge = $|q_{Cl_2} - q_{Cl_1}|/2$

(e) Calculated change in Cl-Cl stretching force constant, relative to isolated Cl_2 molecule.

Table 2. Results at potential minima–Category (2)*

GEOMETRY		R_{min}(Å)	INTERACTION ENERGY (kcal/mole)	DIPOLE MOMENT (D)	CHARGE TRANSFER (e)	POLARIZATION CHARGE (e)	$\Delta k/k$ (%)
PLANAR		5.495	- 0.25	0.05	+0.0007	0.0030	-2.4
PERPENDICULAR		(completely repulsive)					
	α						
UNSYMMETRICAL (a)	30°	5.17	-0.55	0.12	+0.0032	0.0053	+3.3
	45°	4.19	-2.90	0.56	+0.0161	0.0248	+2.7
	60°	3.75	-3.53	0.78	+0.0241	0.0332	+2.1
UNSYMMETRICAL (b)	30°	4.74	-0.51	0.21	+0.0051	0.0100	+3.4
	45°	4.19	-2.69	0.46	+0.0127	0.0221	+2.7
	60°	3.79	-3.23	0.63	+0.0186	0.0282	+2.7

* See Footnotes to Table I.

The important results obtained with this *sp* model at the minima found in the intermolecular potential are listed in Tables 1 and 2, for configurations of categories (1) and (2), respectively. For all of these calculations, the orbital exponents were those suggested by Pople and Beveridge [8] (1.2 for the H 1*s* orbital, 1.625 for C 2*s* and 2*p*, and 2.033 for Cl 3*s* and 3*p*). When potential minima were found upon varying the distance between molecular centers, we also optimized the Cl–Cl distance. The energies calculated as function of this distance were fit to a parabola for purposes of obtaining the optimum distance, the lowest energy, and the stretching force constant, *k*, for the Cl–Cl bond. The same calculation was also carried out for comparative purposes on an isolated Cl_2 molecule using the same parameters.

For all cases, the optimum Cl–Cl distance was found to be between 1.98 and 1.99 Å, showing no appreciable change as a result of complexation. Small changes were, however, found for the stretching force constant; the percent change from that in the isolated molecule is listed for each stable geometry in the last column of Tables 1 and 2. In all but one case, increases of the order of 2–3 % were found. Friedrich and Person have shown that on the basis of Mulliken's simple charge-transfer model, the change should be negative [14]. Experimentally, the Cl–Cl stretching frequency was reported to decrease by 2.8 % upon complexation [15], and this corresponds to a decrease of 5.6 % in the force constant.

The distances, $R_{\min}$, quoted in the tables are those between the centers of the two molecules. Interaction energy is defined as the energy of the complex at the potential minimum minus the energy of the two isolated molecules. The columns headed "Charge Transfer" indicate the total number of electrons transferred from benzene to chlorine. In all cases, the chlorine atom closer to the benzene ring had a net positive charge, while that farther away was negatively charged. The amount of internal charge reorganization in the chlorine molecule due to polarization was in most cases greater than the amount of charge transferred. This is shown as the "Polarization charge", which is defined as $|q(Cl_2)-q(Cl_1)|/2$, where the q's are the net charges of the chlorine atoms.

For those geometries that were treated by Schug and Dyson [7], the interaction energies obtained from the present MO calculations are generally in reasonable agreement with the earlier results based on perturbation theory [7]. The biggest difference occurred for the perpendicular model. The perturbation calculation [7] indicated this to be one of the most stable configurations, but the MO results predict that no stable complex is formed in this configuration.

However, the results of Table 2 indicate that the most stable complexes should correspond to the unsymmetrical configurations which are illustrated in Fig. 1, and which were not considered in the earlier work. This finding is in agreement with the conclusions of Fredin and Nelander [5]. Furthermore, the complexation energies determined for these structures, about -3 kcal/mole, compare favorably with the experimental value [6] of -1.1 kcal/mole. In addition, the intermolecular distances for these most stable configurations are close to the value of 4.24 Å measured in the solid complex [4].

In agreement with the earlier conclusions [7], we find that charge transfer is not very important. The greatest amount of charge transfer occurred, as expected, for the most stable complex, and amounted to about 0.02 e. The dipole moment of this complex has not been measured experimentally, but Hanna and coworkers [6] estimated that it should be about 1 D. The values calculated by us for the most stable configurations were very close to this. However, because all of these results were obtained with no *d*-orbitals in the basis set, the charge distributions should be viewed with some skepticism. Inclusion of *d*-orbitals invariably predicted considerably larger values for the amount of charge transfer and the dipole moment.

Since the most unique property of this type of electron donor-acceptor complex is the electronic spectrum, it is also of interest to note the predictions of this model concerning the charge-transfer absorption band. For this purpose, we used two methods: the virtual orbital approximation of Kroto and Santry [16]; and a direct configuration-interaction (CI) calculation employing about 30 of the lowest singly-excited configurations. The first excited state was predicted by the virtual orbital approximation to be about 0.25 a.u. above the ground state. This translates to a wavelength of about 182 nm, which is in poor agreement with the observed [17] wavelength of 278 nm. In contrast to Nelander's findings on the chlorine-ethylene complex [10], the lowest excited configuration does correspond to a charge-transfer state in the present case. The lowest virtual molecular orbital is highly localized on the chlorine molecule, and is essentially a σ-antibonding chlorine orbital; the highest orbital occupied in the ground state usually has about 30% chlorine character.

The CI calculations gave much better predictions of the charge-transfer band. The best value for the longest wavelength absorption band, 272 nm, was found for the axial configuration. This value shifted to 268 nm for the 22.5°-oblique model; for both unsymmetrical structures (a) and (b), the longest wavelength absorption was found to vary from 271 nm to about 263 nm as the angle, α, went from 30° to 60°. These were all clearly charge transfer transitions, but the calculated oscillator strengths were much too weak, being on the order of 10^{-5}. The agreement between the calculated and observed wavelengths is fortuitous, since the CNDO method with the original parametrization is known to give poor CI results [18].

Calculations of this type illustrate the inherent problems of the CNDO scheme in dealing with atoms beyond the first row of the periodic table [10, 19]. In the present case, we were fortunate to obtain complexation energies of the appropriate magnitude by eliminating the *d*-orbitals from the basis set. This is probably not entirely realistic. It would appear from our results that, if they are used, the 3*d*-orbitals should be very contracted, with orbital exponents larger than those of the 3*p*-orbitals. It should also be mentioned that the calculated results are quite sensitive to the *s*- and *p*-orbital exponents. We carried out a partial set of parallel calculations [20] employing the exponents suggested by Burns [21] for the chlorine 3*s* and 3*p*-orbitals, leaving all other parameters alone. These exponents are 2.183 for the 3*s* and 1.733 for the 3*p*-orbital, so the former is slightly contracted and the latter is expanded in comparison with the orbitals employed earlier. The results [20] parallelled those reported in Table 1, but stable complexes were predicted for all geometries considered and all complexation energies were larger. The calculated complexation energies were −12.5 kcal/mole for the axial and −17.6 kcal/mole for the oblique (22.5° off-axial) models.

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