Theoret. chim. Acta (Berl.) 25, 382—390 (1972)

A CNDO/2 Calculation on a Complex between Ethylene and Chlorine

BENGT NELANDER

Thermochemistry Laboratory, Chemical Center, University of Lund, S-220 07 Lund, Sweden

Received November 26, 1971

CNDO/2 calculations have been carried out for an ethylene chlorine complex, with the halogen orthogonal or parallel to the C–C bond. For comparison similar calculations were also carried out for ethylene and fluorine. The results are compared to estimates from experiments on related complexes and from Mulliken's resonance theory. It is concluded that the CNDO/2 calculations grossly overestimate the ethylene-chlorine interaction in particular if *d*-orbitals on chlorine are included in the AO-basis. The explanation for this may be the too high *d*-orbital exponent used here and the wrong asymptotic behaviour of the Slater orbitals.

Es werden CNDO/2-Rechnungen für zwei Konformationen eines Äthylen-Chlor-Komplexes und eines Fluor-Analogens berichtet und die Resultate mit der Resonanztheorie von Mulliken und mit experimentellen Daten verglichen. Es ergibt sich, daß bei CNDO/2-Rechnungen die Chlor-Äthylen-Wechselwirkung stark überschätzt wird, insbesondere, wenn *d*-Orbitale eingeschlossen werden. Letzteres könnte auch an einem großen Exponenten bei diesen Funktionen oder am falschen asymptotischen Verlauf von Slater-Funktionen liegen.

Calculs CNDO/2 pour un complexe ethylène-chlore avec l'halogène orthogonal ou parallèle à la liaison C—C. A titre de comparaison des calculs analogues ont été aussi effectués pour l'éthylène et le fluor. Les résultats sont comparés à des estimations expérimentales sur des complexes voisins et à des estimations provenant de la théorie de la résonance de Mulliken. La conclusion est que les calculs CNDO/2 surestiment beaucoup l'interaction éthylène-chlore, en particulier lorsque l'on inclut des orbitales *d* dans la base des orbitales atomiques. La raison peut s'en trouver dans les exposants trop élevés des orbitales *d* et dans le mauvais comportement asymptotique des orbitales de Slater.

Introduction

At present, experimental results on charge transfer complexes are in general interpreted using Mulliken's resonance theory [1]. While this theory has made it possible to systematize a large body of experimental results, it is quite often difficult to apply. It is for instance not easy to estimate the relative importance of pure electrostatic and charge transfer contributions to the energy of formation [2], or to find out the extent to which the complex forming molecules are deformed upon complex formation.

In recent years the CNDO approximation of Pople and coworkers [3] has been successfully applied to a large number of different problems. In view of these successful applications it seemed worth-while to calculate a number of properties of a simple charge transfer complex from the CNDO approximation in order to get an idea of the usefulness of such calculations. While this work was in progress a CNDO calculation on the benzene TCNE complex appeared

[4]. Its results, a too short equilibrium distance and a too large energy of formation are in general accord with the results of this paper.

Since there is available a large body of experimental results on halogen complexes, chlorine was chosen as electron acceptor as being the only complex forming halogen for which parameters are available. Ethylene was used as electron donor, since work is presently carried out in this laboratory on ethylene complexes [5].

Calculations

The calculations were carried out at the UNIVAC 1108 computer of the University of Lund computing centre. The CNDO/2 program used is based on QCPE 100, by Clarke and Ragle, supplied by the Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana. The program was rewritten to allow calculations with second row atoms, as described by Segal and Santry [6]. For these atoms calculations may be carried out both using basis sets with no *d*-orbitals and with *d*-orbitals (*sp*- and *spd*-approximations of Ref. [6]). The orbital exponent of the *d*-orbitals was the same as of the *s*- and *p*-orbitals on the same atom. Excitation energies were calculated in the virtual orbital approximation as described by Kroto and Santry [7]. Oscillator strengths were calculated using the formula of Giessner-Prettre and A. Pullman [8]. The parameters used were the original parameters of Pople and Segal [9] and Segal and Santry [6]. Vibration frequencies were obtained by fitting parabolas, or (in the case of ethylene-chlorine *sp*-approximation) a paraboloid to the energy values calculated within 0.02 (Cl–Cl-distance) or 0.03 Å from the equilibrium position. The use of Fues-potentialfunctions ($A + B/R + C/R^2$), which fit the calculated energies much further from the minimum than parabolas do, was found to have no effect on the calculated frequencies.

Results

Calculations were carried out for complexes between ethylene and fluorine or chlorine. In all calculations the experimental geometry of ethylene was used [10] and the fluorine internuclear distance was kept at the experimental value [11]. The chlorine internuclear distance was varied both for the most stable complex and for free chlorine. Two different relative orientations of the two interacting molecules were considered. In one series of calculations the halogen molecule was parallel to the C–C bond and the CCClCl plane was orthogonal to the ethylene plane (resting model). In the other series of calculations the halogen molecule was placed on the symmetry axis of ethylene, orthogonal to the ethylene plane (axial model). For each orientation the halogen ethylene distance was varied.

Ethylene-Fluorine

a) Axial Model. A minimum in the energy of 0.0584 a.u. (*ca.* 37 kcal/mole) below the energy of the free components was found for $R = 1.456$ Å (R, the distance between the nearest chlorine atom and the midpoint of the C–C bond). From the variation in the CNDO-charges, Q_A, ($Q_A = Z_A - \sum_{i \in A} P_{ii}$, where Z_A is the core charge of atom A and P_{ii} is the diagonal element of the CNDO density matrix for the i-th atomic orbital) with the fluorine ethylene distance, it was found that the charge transfered from ethylene to fluorine increases as the distance decreases, and that all charge transfered to the fluorine molecule becomes localised on the fluorine atom farthes away from the ethylene molecule. In fact the other fluorine atom even becomes positively charged. The charge transfered within the fluorine molecule is between one third and half of the charge transfered from ethylene to fluorine, depending on distance. The dipole moment rises rapidly with decreasing distance, reaching 3.58 D at the energy minimum.

b) Resting Model. As might be expected the energy rises rapidly when the fluorine ethylene distance is decreased. In fact, in this conformation the ethylene molecule acts as an electron acceptor, a rather unfavorable situation. Between 1.66 and 1.65 Å the calculated ground state changes abruptly from two interacting molecules to a highly deformed state of 1,2 difluoroethane. In the first excited state, where one electron is excited from the highest occupied to the lowest virtual orbital the energy changes smoothly from an excited state of the two interacting molecules to an excited state of difluoroethane. This kind of behavior was expected from considerations of orbital symmetry [12].

Ethylene-Chlorine

a) Axial Model, sp-Approximation. The energy decreases as the chlorine molecule is brought closer to the C–C bond (keeping the Cl_2 distance fixed) and reaches a minimum for $R = 2.259$ Å, the minimum energy is 0.00983 a.u. (*ca.* 6.2 kcal/mole) below the energy of the free components. When the chlorine internuclear distance was varied the energy minimum was found for $R = 2.242$ Å and $R_{ClCl} = 2.000$ Å (compared to 1.980 Å for free chlorine in the *sp*-approximation) and the energy was 0.00986 a.u. below the energy of the free components[1]. The axial energy minimum was found to be stable to small simultaneous variations of the parameters describing the relative orientations of the two interacting molecules. A number of properties calculated at equilibrium are given in Table 1a and 1b. As was found for the fluorine case, the only atom, which gains charge as the distance is decreased is the outer chlorine atom. In this case the charge transfer within the chlorine molecule is approximately equal to the ethylene chlorine charge transfer. Since the equilibrium distance obtained was much shorter than might be expected a number of properties were also calculated at a more reasonable distance, 3.25 Å, the results are given in Table 1.

The energy of the three lowest excited states of the complex, in the virtual orbital approximation, were also calculated as a function of distance. The two lowest states may be described as an excited chlorine molecule interacting with ethylene. Their energy curves are indistinguishable except at small distances. These states are repulsive. There is a very small dip in the energy at *ca.* 3 Å which

---

[1] The value in Table 1 has been corrected for the zero point vibration energy of the Cl_2 ... ethylene vibration, 237 cm^{-1}.

should not be taken seriously, since no variation of the chlorine distance was carried out. The vertical excitation energy is given in Table 1b for the *sp*-minimum. The third lowest excited state is obtained upon excitation of an electron from an orbital which is essentially a combination of the $2p\pi$ orbital of ethylene and the $3p\sigma$ orbital of chlorine to the $3p\sigma^*$ orbital of chlorine. It thus involves charge transfer from ethylene to chlorine and may therefore be identified with the charge transfer band of Mulliken's theory.

As expected the equilibrium distance of this excited state is somewhat shorter than for the ground state, 1.97 Å compared to 2.26 Å for the ground state. The

Table 1a. Calculated properties of the ethylene-chlorine complex

	$r_e(Cl_2)$ Å	$-\Delta E$ kcal/mole	Dipole moment D	$\nu(Cl_2)$ cm^{-1}	$(\nu_0-\nu)/\nu_0$	Dipole moment derivative D/Å(amu)$^{1/2}$
CNDO (*sp*-approx. equilibr.)	2.000	5.8	1.52	913	0.070	1.32
CNDO (*sp*-approx. 3.25 Å)	1.980	0.46	0.06	980	0.0005	0.031
CNDO (*spd*-approx. 3.25 Å)	—	2.74	0.15	—	—	—
CNDO (*spd*-approx. 3.25 Å Cl_2 distance relaxed)	1.752	2.6	0.13	1305	0.0021	0.013
CNDO Cl_2 (*sp* approx.)	1.980	—	—	981	—	—
CNDO Cl_2 (*spd* approx.)	1.751	—	—	1308	—	—
Estimates (see text)[a]	—	2.2[d]	0.4	—	0.011	0.16
Benzene-Cl_2 (experimental)	1.99[b]	1.1[e]	0.5 – 0.7[e]	526[f]	0.028	0.20[g]
Cl_2 (experimental)	1.988[c]	—	—	541[g]	—	—

[a] The energy of formation was estimated by adding the resonance and van der Waal's energies calculated above.

[b] Hassel, O., Strømme, Knut: Acta chem. scand. **13**, 1781 (1959).

[c] Herzberg, G.: Spectra of Diatomic Molecules, 2nd Ed. Princeton N.J.: Van Nostrand 1950.

[d] The resonance contribution was 1.4 kcal/mole.

[e] Estimated by Lippert, Joseph L., Hanna, Melvin W., Trotter, Philip J.: J. Amer. chem. Soc. **91**, 4035 (1969).

[f] Collin, J., D'Or, L.: J. chem. Physics **23**, 397 (1955).

[g] Friedrich, H. Bruce, Person, Willis B.: J. chem. Physics **44**, 2161 (1966).

Table 1b. Calculated excitation energies of the ethylene-chlorine complex

	ν "Cl_2" kK	Oscillator strength	CT-abs. kK	Oscillator strength
CNDO (*sp*-approx. equilibr.)	40.0	0.026	80.43	1.65
CNDO (*sp*-approx. 3.25 Å)	37.2	0.031	105.00	0.58
Cl_2, CNDO (*sp*-approx.)	36.8	0.030	—	—
Experimental	—	—	43.4[b]	0.19[c]
Experimental, Cl_2	30.5[a]	0.0017[a]	—	—

[a] Seery, D. J., Britton, D.: J. physic. Chemistry **68**, 2263 (1964).

[b] Dubois, J. E., Garnier, F.: Spectrochim. Acta **23 A**, 2279 (1967).

[c] Estimated, see text.

O–O excitation energy is 0.343 a.u.[2] (75.1 kK) compared to the vertical excitation energy of 0.366 a.u.

b) Resting Model, sp-Approximation. The potential curve obtained for this model has a very insignificant minimum around 3 Å, the energy is *ca.* 0.0007 a.u. (*ca.* 0.4 kcal/mole) below the energy of the free components. Inside this minimum the energy rises rapidly. As for the resting model of the fluorine complex, ethylene here acts as an electron acceptor.

c) Axial and Resting Models, spd-Approximation. For both models the calculated potential curves had very deep minima at very short equilibrium distances. For the axial model the energy is 0.23 a.u. (*ca.* 140 kcal/mole) below the energy of the free components at the equilibrium distance of *ca.* 1.7 Å. The energy minimum of the resting model is at *ca.* 1.9 Å and the stabilisation energy is *ca.* 0.14 a.u.

The inclusion of *d*-orbitals allows charge to be back donated from the outer to the inner chlorine atom, and thus the strong polarisation of the chlorine molecule in the *sp*-approximation is absent. The inclusion of *d*-orbitals also transforms the chlorine molecule into an electron acceptor in the resting conformation.

Because of the very poor results for stabilitsation energies and equilibrium distances, the *spd*-approximation was only used to calculate a few properties of the axial complex at 3.25 Å. The results are included in Table 1.

Estimates

At present, only the charge transfer band of ethylene chlorine complex has been observed experimentally [13]. It was therefore necessary to estimate other properties for comparison with the results of the CNDO calculation.

All estimates, except of the van der Waal's energy were made for an axial complex with $R = 3.5$ Å. The van der Waal's energy was calculated as a function of R as described by Eliel *et al.* [14]. A very flat minimum was found at $R = 3.3$ Å, where the interaction energy was -0.8 kcal/mole.

In order to estimate the resonance energy, the experimentally observed relation between ionisation potential and position of the charge transfer band was used as a startingpoint.

$$\begin{aligned} h\nu_{\mathrm{CT}} &= I - C_1 + C_2/(I - C_1) \\ C_2 &= \beta_0^2 + \beta_1^2 \,. \end{aligned} \tag{1}$$

(For detailed information on the physical interpretation of the parameters, and their values in different cases see Refs. [1] and [15].) The value of C_2 for the iodine complexes, given by Briegleb [15] was used directly, but the value of C_1 was changed to take into account the differences in electron affinity and in electrostatic interaction between the ethylene iodine and chlorine complexes. The change in vertical electron affinity was taken from Person [16]. The difference in electrostatic energy was calculated from a simple point charge model for the excited state of the complex, and the assumption that the ground states do not contribute.

---

[2] This is only a crude approximation to the true CNDO O–O excitation energy, since no variation in the internal structure of ethylene or chlorine was carried out.

The halogen ethylene distances were taken to be the sum of the van der Waal's radii [17] and the charges were divided even between the halogen atoms, and the two carbon atoms of ethylene. The resulting parameters were: $\beta_0 = -4.5$ kK, $\beta_1 = -8.8$ kK and $C_1 = 42$ kK. These parameters and formulas given in Ref. [1] were used to calculate the values given in Table 1. For the position of the charge transfer band, these parameters give 45.0 kK compared to the experimental value 43.4 kK.

Discussion

For ethylene and chlorine all calculations predict the existence of a stable complex with the chlorine molecule on the C_2 axis orthogonal to the ethylene plane. This structure is also expected from considerations of overlap between donor and acceptor orbitals. For the *sp*-approximation the equilibrium distance is 2.24 Å, which lies between the CCl single bond length 1.77 Å, and the sum of the van der Waal's radii, 3.5 Å [17]. However, since the ionisation potential of ethylene is higher than for benzene, the ethylene complex is expected to be weaker than the benzene-chlorine complex, and thus the equilibrium distance is expected to be longer than that of benzene chlorine complex, which is 3.28 Å in the crystal [18]. Considering the possibility that the benzene chlorine distance found by Hassel and Strømme may represent the average value of a long and a short distance [1] the ethylene-chlorine equilibrium distance may be shorter than 3.28 Å, but it seems very unlikely that it is shorter than 3.0 Å. The failure of the CNDO approximation to give reasonable equilibrium distances for complexes is in contrast to the reasonable bond distances which are obtained from such calculations.

It is very difficult to make any precise statements about the energy of formation of the ethylene-chlorine complex, in the gas phase. Olefin-iodine complexes have enthalpies of formation of about -1 to -2 kcal/mole at room temperature in solution [15]. Chlorine complexes are in general weaker and therefore should have more positive enthalpies of formation. Lippert *et al.* [2] estimate the energy of formation of the chlorine benzene complex to be -1.1 kcal/mole in solution, compared to -1.3 kcal/mole for the benzene-iodine complex. The energies of formation in the gas phase are expected to be more negative than in solution since van der Waal's interactions between the complex forming molecules are no longer compensated for by interactions with the solvent [1]. The van der Waal's energy of the ethylene complex was estimated above to be 0.8 kcal/mole. If this contribution is added to the experimental values for the olefine-iodine complexes and the change from iodine to chlorine is assumed to have no effect, the energy of formation of the ethylene chlorine complex is estimated to be -2 to -3 kcal/mole.

The resonance energy contribution to the energy of formation was estimated above to be *ca.* 1.4 kcal/mole, if the van der Waal's energy is added the energy of formation is estimated as *ca.* -2.2 kcal/mole. From these estimates it seems as if the calculated energy of formation -5.8 kcal/mole (*sp*-approximation) is at least too low by a factor two.

The interaction energy between axial chlorine calculated for 3.25 Å, -0.5 kcal/mole, seems too close to zero, while the interaction energies from the *spd*-approximation seem to be reasonable (-2.7 and -2.6 without and with relaxation of the Cl–Cl distance respectively).

As is seen from Table 1 the Cl–Cl stretching frequency decreases upon complex formation. A comparison with the frequency shift for the benzene-chlorine complex and with the estimated shift from the resonance theory makes it rather obvious that the shifts calculated at 3.25 Å are all too small, while the *sp*-approximation at equilibrium gives a much too large shift. It should be pointed out here that the calculations for the *sp*-minimum indicate a very strong coupling between the Cl_2–C_2H_4 vibration and the Cl–Cl vibration in the complex. If the Cl–Cl frequency shift is calculated from the corresponding force constant alone the relative change is only 0.040 compared to 0.070 when this coupling is included. The coupling although much exagerated by the CNDO calculation should be of importance also in real halogen complexes. A decrease in the halogen donor distance will increase the charge transfer to the halogen, and therefore weaken the halogen-halogen bond.

For the I_2 hexamethylenetetramine complex, Ichiba *et al.* [19] found that 0.37 electrons were transfered from the iodine closest to nitrogen to the outer iodine, while only 0.08 electrons were transfered from the donor to the iodine molecule. Of course the hexamethylenetetramine iodine complex is much stronger than the ethylene chlorine complex, which makes any extrapolations from the results of Ichiba *et al.* to this complex dangerous. It seems, however, that the *spd*-approximation grossly under estimates the importance of the halogen polarisation relative to that of the charge transfer.

When the overlap integrals were calculated between the free molecules and the axial complex at a distance close to the minimum (2.3 Å) in the *sp*-approximation, it was found that most orbitals of chlorine and ethylene are quite unaffected by complex formation. Two things should be noted, first the contribution of the $3p\sigma^x$-orbital of chlorine to the two highest occupied orbitals of a_1-symmetry of the complex. (Overlap integrals 0.145 and 0.069.) These contributions are responsible for the polarisation of the chlorine molecule, and also for the charge transfer. Second the strong mixing of the $2p\pi$-orbital of ethylene and the $3p\sigma$ orbital of chlorine. They contribute approximately equally to the two highest a_1 orbitals of the complex. This mixing leads to repulsion and therefore helps to precent the two molecules to get too close to each other.

Qualitatively, the calculated UV-spectra agree with experimental observations on halogen complexes. The chlorine absorption is shifted towards higher wavenumbers by *ca.* 3.4 kK. This shift may be compared to a shift of the visible iodine band of *ca.* 2.3 kK in the ethylene iodine complex at 20 K [5]. The shift of the chlorine band, although it seems a little too large, is thus of the expected magnitude. The calculated charge transfer excitation energy is much too high.

Conclusion

From the results of the calculations discussed above, it will seem as if the CNDO approximation gives a qualitatively correct picture of the structure of the complex, and of some of its properties, at least if *d*-orbitals are left out. The quantitative results are rather poor however. In view of the qualitative agreement it may be possible to obtain useful results from comparisons between calculations on closely related complexes. However, if the CNDO approximation is to be useful for more general investigations of molecular complexes, some changes in the method of calculation seem necessary. From the successful CNDO calculations on stable molecules it seems as if the approximations involved in the setting up of the F matrix balance each other at the relatively short distances between bonded atoms and next neighbour atoms. At the much longer distances involved in molecular complexes, the Slater orbitals used to calculate the overlap matrix go to zero much faster than Hartree Fock orbitals. This probably creates an unbalance in the approximations, since the exchange repulsion will be underestimated compared to nuclear repulsion and electron nuclear attraction, which may be the reason for the too short equilibrium distances etc. It might be of interest to calculate the overlap matrix using orbitals which approximate Hartree Fock orbitals more closely at large distances from the nucleus.

Another point which is of importance for chlorine complexes is the role of the *d*-orbitals. From an extrapolation of the trend in stabilisation energies of the fluorine and chlorine complexes in the *sp*-approximation it seems as if bromine and in particular iodine should be very weak acceptors compared to chlorine, while experimentally it is the other way around. This reverse of the trend may perhaps be due to the increasing importance of the *d*-orbitals when going from chlorine to bromine and iodine. The results of the calculations are very dependent on the *d*-orbital exponent, which makes the choice of the latter a very important problem. It may perhaps be as has been argued by Craig *et al.* [20] that the *d*-orbitals contract upon bond formation, which would make them sensitive to environment and make it more or less impossible to choose the correct orbital exponents in actual cases. Recently Keeton and Santry [21] stated from an investigation of the *d*-orbital exponents of phosphorus and sulfur, using minimal basis sets, that the *d*-orbital exponent is 0.9 of the 3*s* orbital exponent quite independently of the atoms surrounding the phosphorus or sulfur atom. There may thus be some hope that a "best" set of *d*-orbitals may be found.

References

1. Mulliken, R.S., Person, W.B.: Molecular complexes. New York: Wiley-Interscience 1969.
2. Lippert, J.L., Hanna, M.W., Trotter, Ph.J.: J. Amer. chem. Soc. **91**, 4035 (1969).
3. Pople, J.A., Beveridge, D.L.: Approximate molecular orbital theory. New York: McGraw-Hill 1970.
4. Chesnut, D.B., Wormer, P.E.S.: Theoret. chim. Acta (Berl.) **20**, 250 (1971).
5. Fredin, L.: Private communication.
6. Santry, D.P., Segal, G.A.: J. chem. Physics **47**, 158 (1967).
7. Kroto, H.W., Santry, D.P.: J. chem. Physics **47**, 792 (1967).
8. Giessner-Prettre, C., Pullman, A.: Theoret. chim. Acta (Berl.) **13**, 265 (1969).
9. Pople, J.A., Segal, G.A.: J. chem. Physics **44**, 3289 (1966).
10. Herzberg, G.: Electronic spectra of polyatomic molecules. Princeton, N.J.: Van Nostrand 1966.
11. — Spectra of diatomic molecules, 2nd Ed. Princeton, N.J.: Van Nostrand 1950.
12. Woodward, R.B., Hoffman, R.: The conservation of orbital symmetry. Weinheim/Bergstr.: Verlag Chemie, GmbH. 1970.
13. Dubois, J.E., Garnier, F.: Spectrochim. Acta **23A**, 2279 (1967).
14. Eliel, E.L., Allinger, N.L., Angyal, S.J., Morrison, G.A.: Conformational Analysis. New York: Wiley-Interscience 1965.

15. Briegleb, G.: Elektronen-Donator-Acceptor-Komplexe. Berlin: Springer-Verlag 1961.
16. Person, W. B.: J. chem. Physics **38**, 109 (1963).
17. Pauling, L.: Nature of the chemical bond. 3rd Ed. Ithaca, N.Y.: Cornell University Press 1960.
18. Hassel, O., Strømme, K.: Acta chem. scand. **13**, 1781 (1959).
19. Ichiba, S., Sakai, H., Negita, H., Maeda, Y.: J. chem. Physics **54**, 1627 (1971).
20. Craig, D. P., Maccoll, A., Nyholm, R. S., Orgel, L. E., Sutton, L. E.: J. chem. Soc. **332** (1954).
21. Keeton, M., Santry, D. P.: Chem. Physics Letters **7**, 105 (1970).

Dr. B. Nelander
Themochemistry Laboratory
Chemical Center
University of Lund
S-220 07 Lund
Sweden