tonation coordinates which include the O–H distance and the H–O–C angle are relatively constant, which suggests that the bond between the carbonyl oxygen and the proton may be classified as a polar covalent bond. Structural changes which occur upon protonation of the bases R_2CO are similar to the changes which occur upon protonation of the bases RCHO. From the computed results, a model for the protonation of carbonyl bases has been proposed.

References and Notes

(1) J. E. Del Bene, *J. Am. Chem. Soc.*, **100**, 1673 (1978).
(2) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).
(3) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
(4) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).
(5) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *Aust. J. Chem.*, **25**, 1601 (1972).
(6) J. E. Del Bene, G. T. Worth, F. T. Marchese, and M. E. Conrad, *Theor. Chim. Acta*, **36**, 195 (1975).
(7) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5417 (1977).
(8) J. E. Del Bene, *Chem. Phys. Lett.*, **55**, 235 (1978).
(9) J. E. Del Bene, *J. Am. Chem. Soc.*, **99**, 3617 (1977).
(10) H. Umeyama and K. Morokuma, *J. Am. Chem. Soc.*, **98**, 4400 (1976).
(11) J. E. Del Bene and A. Vaccaro, *J. Am. Chem. Soc.*, **98**, 7526 (1976).
(12) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).
(13) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Chapman and Hall, London, 1975; "Advances in Infrared Group Frequencies", Chapman and Hall, London, 1975.
(14) Implicit in this model is the assumption that the H–Y interaction is generally not a stabilizing one. This had been proposed by other investigators [A. C. Hopkinson and I. G. Csizmadia, *Can. J. Chem.*, **52**, 546 (1974)], who suggested that the H–F interaction in cis protonated $FCHOH^+$ is stabilizing due to the formation of an O–H · · · F hydrogen bond. Neither the small but negative H–F Mulliken overlap populations nor the changes in the cis O–C–F angles in $FCHOH^+$ and F_2COH^+ support this suggestion.

Theoretical Study of Some Ethylene–Halogen Molecule (Cl_2, Br_2, I_2) Complexes at Large and Intermediate Distances from ab Initio Calculations

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Abstract: Ab initio calculations have been carried out on several configurations of the $C_2H_4 \cdots Cl_2$ complex, adding the dispersion energy to the SCF supermolecule energy. It is found that the most stable configuration is the axial model. Similar calculations have been performed for the axial geometry of the $C_2H_4 \cdots Br_2$ and $C_2H_4 \cdots I_2$ complexes. The three axial complexes exhibit the same qualitative behavior for each intermolecular energy contribution: the charge transfer and induction energy are important but not able to give a really significant minimum depth; it is essential to take account of the dispersion energy, as in the case of van der Waals molecules. The depths of the minima and the corresponding intermolecular distances are evaluated. The nature of the binding is discussed.

I. Introduction

The special importance of ethylene–halogen molecules complexes is largely due to their possible role in the trans addition of halogen molecules to ethylene. It is most generally admitted that the first step of this reaction may begin by the formation of such complexes.[1–5]

The origin of the stability of these complexes is not clear and experimental data may support different interpretations.[6] Some authors[4] describe them as three-center covalently linked Dewar's π complexes.[7,8] This idea initiated the first theoretical work,[3] based on the use of an extended Hückel molecular orbital approach. Other authors[5] rather consider them as charge-transfer complexes, by analogy with the class of complexes described by Mulliken.[9] The difference between these two categories of complexes has been underlined by Banthorpe.[10] In particular, the possible role of van der Waals forces is discussed in the case of the second class of complexes.[9,10]

Clearly, theoretical information is necessary to understand the origin of the binding of these complexes since experimental data are not able to give a definitive answer. Unfortunately, difficulties are also encountered in theoretical treatments and we must be aware that artificial results are easily obtained. For instance, some approximations lead to a systematic overestimation of the binding energy with a too short intermolecular equilibrium distance. This happened with the two SCF calculations[11,12] based on the CNDO approximation which treated some geometrical configurations of the $C_2H_4 \cdots Cl_2$ or $C_2H_4 \cdots F_2$ systems. For the axial configuration of $C_2H_4 \cdots Cl_2$, both calculations give a very large SCF minimum depth (-6.2,[11] -2.38[12] kcal/mol) and a very short intermolecular distance (2.259,[11] 2.210 Å[12]) while our ab initio SCF calculations[13,14] give a stabilization energy of -0.64 kcal/mol and an intermolecular distance of 3.704 Å. In the latter paper,[14] we also showed that the dispersion energy contribution, not taken into account in a SCF treatment, is larger than the induction and charge transfer energy. Thus a correct minimum depth cannot be obtained from SCF calculations and it is absolutely necessary to take the dispersion energy contribution into account.

Experimental data[15] show that the ethylene chlorine complex has a C_{2v} symmetry. As discussed by Fredin and Nelander,[15] two models—the axial and the resting configurations—may be of particular interest. These two configurations are studied in the present work, along with an "X" configu-

ration deduced from the resting model by a 90° rotation of the Cl_2 molecular axis about the C_{2v} axis. For the sake of comparison with other systems, we also studied a dissymmetrical configuration which we call a "L" model. In this case, the Cl_2 molecular axis is perpendicular to the C_2H_4 plane, as in the axial model, but passes through a carbon atom.

The axial model, which is found to be the most stable configuration in $C_2H_4\cdots Cl_2$, is also studied for the $C_2H_4\cdots Br_2$ and $C_2H_4\cdots I_2$ systems.

II. Method

Using ab initio wave functions, the dispersion energy is obtained from the perturbation theory and computed according to the scheme described in a previous paper.[16] This contribution is added to the SCF supermolecule energy.[17] Such a procedure has been previously used[18] for other systems and takes advantage of the equivalence between the perturbation and the supermolecule treatment.[19] This is not a rigorous treatment. However, the main contributions to the intermolecular energy are taken into account and the general trends should be correctly described.

Two expressions of the dispersion energy have been proposed,[16] corresponding to two different partitions of the molecular Hamiltonians. Expressions 1 and 2 of ref 16 are denoted respectively by E'_{disp} and E_{disp} in the present paper. E'_{disp} is often used in the literature and the results obtained with this expression will be commented on here. However, when the perturbation series is limited to second order, it seems that the use of E_{disp} gives a better agreement with experiment.[16,18,20]

We denote by ΔE_{SCF} the difference between the SCF energy of the interacting system and the SCF energy of the isolated molecules. It may be convenient to start the SCF supermolecule calculation with Schmidt-orthogonalized SCF molecular vectors. It is commonly admitted that the difference, ΔE_1, between the energy of the first iteration performed with such vectors and the energy of the isolated molecules corresponds to the first-order electrostatic and repulsive energy of a perturbation treatment. We checked this equivalency[19] in the case of $(H_2)_2$ and $Li^+ + H_2$. The difference between ΔE_{SCF} and ΔE_1, or delocalization energy, would correspond to the second-order induction and charge transfer energy of the perturbation method. We denote this contribution by ΔE_{ind+CT} and have then $\Delta E_{SCF} = \Delta E_1 + \Delta E_{ind+CT}$.

Finally, we compute $E'_{tot} = E'_{disp} + \Delta E_{SCF}$ and $E_{tot} = E_{disp} + \Delta E_{SCF}$.

III. Detail of the Calculation

We described, in the Introduction, the geometric configurations studied in the present work. For the axial and the "L" models, the intermolecular distance d is the distance between the C_2H_4 plane and the nearer halogen atom. In the case of the resting and "X" configurations, d is the distance between the middle of the C–C bond and the middle of the halogen–halogen bond.

The C–H bond length (1.086 Å) and the HCH angle (117.3°) of C_2H_4 are taken from experiment.[21] The C–C, Cl–Cl, Br–Br, and I–I bond lengths are optimized in the isolated molecules for different basis sets. They are not varied in the intermolecular calculations and C_2H_4 is kept planar.

Basis Sets. Molecular orbitals are linear combinations of Gaussian functions. Since we have to work with truncated basis sets of Gaussian functions, the truncation must not strongly affect the description of the properties studied. The choice of an appropriate basis set is a delicate problem since the characteristics of a "good" basis set are not the same for the supermolecule treatment and for the description of the dispersion energy. A very large basis set would be able to correctly de-

scribe these two energy contributions but would be very time consuming. We have preferred to treat these two contributions separately, with an appropriate basis set for each of them.

(a) SCF Supermolecule Treatment. C_2H_4. Two basis sets are considered. In our first study of this system,[13] 9s and 5p uncontracted functions for C and 4s uncontracted functions for H, taken from ref 22, are contracted into a "double-ζ" basis set. This basis will be referred to as basis A in the present paper. With an optimized C–C bond length of 1.335 Å, the SCF energy of C_2H_4 is 78.0047 hartrees. The experimental bond length values[21] range from 1.332 to 1.339 Å.

In ref 14, the previous functions are not contracted and a polarization function, optimized to obtain the lowest SCF energy of C_2H_4, is added on each atom. This basis is referred to as basis A2, with exponents $\alpha_p(H) = 1.091\ 22$ and $\alpha_d(C) = 0.847\ 536$. The corresponding SCF energy is −78.054 992 hartrees with an optimized C=C bond length of 1.314 Å.

Cl_2. Three basis sets are considered. In ref 13, 11s and 7p functions[23] for each Cl atom are contracted into a "double-ζ" basis set. This basis is referred to as basis B. With an optimized Cl–Cl bond length of 2.190 Å, the SCF energy of Cl_2 is −918.8253 hartrees. The experimental bond length[21] is 1.988 Å.

The second basis set considered was also used in our first paper.[13] A d function on each atom, with exponent 0.518 142, is added to basis B. This basis is referred to as basis B_1. With an optimized Cl–Cl bond length of 2.029 Å, the SCF energy of Cl_2 is −918.8664 hartrees.

A third basis is referred to as basis B_2. In this case, the 11s and 7p functions are not contracted and a d function with exponent 0.532 392 is added on each atom. With an optimized Cl–Cl bond length of 2.011 Å, the SCF energy of Cl_2 is −918.9077 hartrees.

Br_2 and I_2. In these cases, we treat differently the functions describing the inner shells and those describing the two higher energy occupied shells (quantum number n and $n − 1$). The former group of functions is contracted into a "minimal" set, the latter into a "double-ζ" set.

For Br_2, the uncontracted functions (13s, 9p, and 5d) are taken from ref 24. The corresponding contracted basis is referred to as basis C. With an optimized Br–Br bond length of 2.443 Å, the SCF energy of Br_2 is −5136.7443 hartrees. The experimental bond length is[21] 2.284 Å. Our optimized bond length is 7% larger than the experimental one. This relative error is smaller than in the case of Cl_2.

A set of 15s, 11p, and 7d uncontracted functions has been optimized for the iodine atom, using the SCF atomic program described in ref 25. We obtain an SCF energy of −6917.6966 hartrees. The corresponding contracted basis set for I_2 is referred to as basis D. With an optimized I–I bond length of 2.826 Å, the SCF energy of I_2 is 13 804.3136 hartrees. The experimental bond length being[21] 2.666 Å, the relative error on the bond length is 6%.

(b) Dispersion Energy. The main characteristic of the bases used in this section is the need for diffuse polarization functions. Except for the H atoms, the unpolarized uncontracted functions are the same as in the previous section but the contraction may be different and will be described for each molecule. Generally, the contraction of the functions describing the valence shell is of the "double-ζ" type. However, because of size limitations in our system of programs, this was not possible in the case of I_2.

C_2H_4. For the H atoms, we used a basis set described in our previous studies on $(H_2)_2$[16] and CO + H_2.[26] It is a "double-ζ" set with a polarization function ($\alpha_p(H) = 0.2$). For the carbon atoms, a polarization function is added to the "double-ζ" set described in the previous section. The exponent of this function, $\alpha_d(C) = 0.17$, is taken from our work on CO + H_2.[26] This basis for C_2H_4 is referred to as basis A'. In all calculations, we used

Table I. C_2H_4 + Cl_2. First Iteration Intermolecular Energy (Electrostatic and Repulsive First-Order Energy) (kcal/mol), Basis (A_2 + B_2)

d,[a] Å	configurations			
	axial	"L"	resting	"X"
2.646	13.80 (13.70)[b]	12.83		
2.910	5.29 (5.40)	4.97		
3.175	1.74 (1.91)	1.69	5.75	5.04
3.440	0.34	0.38	2.65	2.38
3.704	-0.16 (-0.25)	-0.10	1.25	1.15
3.969	-0.30	-0.24		0.58
4.233		-0.25	0.34	
4.763				0.14

[a] See the definition of d in the text. [b] The values given in parentheses are obtained with basis (A + B).

Table II. C_2H_4 + Cl_2. Delocalization Energy (Induction and Charge Transfer Contribution) (kcal/mol), Basis (A_2 + B_2)

d, Å	configurations			
	axial	"L"	resting	"X"
2.646	-7.86 (-9.58)[a]	-6.35		
2.910	-3.58 (-4.55)	-2.95		
3.175	-1.72 (-2.16)	-1.45	-1.17	-0.72
3.440	-0.88	-0.76	-0.65	-0.45
3.704	-0.48 (-0.54)	-0.42	-0.43	-0.32
3.969	-0.28	-0.25		-0.25
4.233		-0.16	-0.26	
4.763				-0.10

[a] The values given in parentheses are obtained with basis (A + B).

the C–C bond length of 1.314 Å optimized with basis A_2. The SCF energy of C_2H_4 is then −78.020 233 hartrees.

The polarizability components have been computed[27] using basis A′. Comparison with the experimental values proposed by Landolt-Börnstein[28,29] or Buckingham et al.[30] shows that basis A′ is adequate to describe the polarizability. However, since there are no f functions in basis A′, the higher order terms of the multipole expansion may be not so well described, involving an error in the determination of the dispersion energy.

Cl_2. Two basis sets have been considered in this case. One of these bases has been described in another paper[31] and will be referred to as basis B′ in the present work. In this basis the contraction of the functions describing the valence shell is of the "double-ζ" type, that of the functions describing the inner shells of the "minimal" type. The exponent of the d polarization function has been optimized[31] to obtain the largest dispersion energy in $(Cl_2)_2$. With $\alpha_d(Cl) = 0.22$ and a Cl–Cl bond length of 2.029 Å (optimized with basis B_1), the SCF energy of Cl_2 is 918.780 66 hartrees. The determination of the polarizability components[27] confirms the adequacy of basis B′.

In order to estimate the reliability of the basis which will be used for I_2, an equivalent basis set has also been considered for Cl_2. It will be referred to as basis B'_1. In this case, the contraction of the functions is of the "minimal" type for any shell. The polarization function is the same as in basis B′. With a Cl–Cl bond length of 2.029 Å, the SCF energy of Cl_2 is 917.698 88 hartrees.

Br_2 and I_2. In both cases, the valence shells involve s and p atomic orbitals. Though there are d functions, they describe inner shells. Thus, in the calculation of the dispersion energy, we expect Br_2 and I_2 to have the same behavior as Cl_2. In particular, they should have the same need for diffuse d functions. The exponent of such diffuse d functions has been chosen to obtain the largest average molecular dipole polarizability.[27] There are no experimental data to check the adequacy of our basis sets.

In the case of Br_2, the contraction of the functions describing the valence shells is of the "double-ζ" type, that of the functions describing the inner shells of the "minimal" type. With $\alpha_d(Br) = 0.15$ and a Br–Br bond length of 2.443 Å (obtained with basis C), the SCF energy of Br_2 is −5135.4336 hartrees. The corresponding basis set is referred to as basis C′.

In the case of I_2, the contraction of the function is of the "minimal" type for any shell. With $\alpha_d(I) = 0.14$ and a I–I bond length of 2.826 Å (obtained with basis D) the SCF energy of I_2 is −13 800.5322 hartrees. The corresponding basis set is referred to as basis D'_1.

Let us underline that bases A′–D'_1 are adequate to describe the dispersion energy but would not be suitable for the supermolecule treatment: they are not "well-balanced" basis sets because of the use of one diffuse polarization function only.

Also we may notice that they give less good SCF molecular energies than equivalent bases with a larger polarization function exponent.

IV. Results

C_2H_4 + Cl_2. We shall comment on the different energy contributions separately.

(a) The Supermolecule Treatment: $\Delta E_{SCF} = \Delta E_1 + \Delta E_{ind+CT}$. Table I gives the intermolecular energies obtained at the first iteration of the calculation, starting from Schmidt-orthogonalized SCF molecular vectors. The results obtained with the large basis (A_2 + B_2) show that the resting and the "X" configurations are repulsive, while the axial and the "L" models are slightly attractive with a somewhat larger stabilization energy in the case of the axial geometry. In this last case, the results obtained with the "double-ζ" basis (A + B) are not very different of those given by the large basis (A_2 + B_2).

Table II gives the delocalization energy, mainly due to the induction and charge transfer contribution. Comparison of Tables I and II shows that the delocalization energy is very important for the axial and the "L" models, less essential for the resting and the "X" configurations. As expected, the smaller "double ζ" basis (A + B) overestimates this contribution: such bases generally give a nonnegligible superposition error. At $d = 2.910$ Å, the delocalization energy obtained with basis (A_2 + B_2) is about 79% of the value obtained with basis (A + B). We shall use this result in our discussion of bromine and iodine complexes.

It is very difficult to completely eliminate the superposition error and even to estimate it. The counterpoise method, where the dimer basis set is used instead of the monomer basis set to compute the SCF energy of the individual molecules, is probably the most known procedure proposed for such an estimate. The quantitative accuracy of this procedure is questionable for the following reason: in the dimer, the functions of the second molecule are mainly used to describe the second molecule and only partly able to improve the description of the first molecule while, in the counterpoise method, the functions of the second molecule, not required to describe this second molecule, are totally available to improve the description of the first molecule. This can lead to an overestimation of the superposition error. Recently,[31] we reported our estimate of the superposition error in the case of the $(Cl_2)_2$ dimer, using bases B and B_2 with the counterpoise method. In the region of the minimum, the error had been estimated for different geometrical configurations. The largest value was 0.34 kcal/mol, compared to the total energy of 1.68 kcal/mol. As explained above, this value of 0.34 kcal/mol is probably an upper limit and the exact value may be much smaller. Anyway, this value is not very large compared to the total energy and it is clear that when the stability of a system is largely due to the dispersion energy, as is the case in $(Cl_2)_2$ and in the present complexes, the superpo-

Table III. $C_2H_4 + Cl_2$. SCF Intermolecular Energy (kcal/mol), Basis $(A_2 + B_2)$

	configurations			
d, Å	axial	"L"	resting	"X"
2.646	5.94 (4.12)[a]	6.48		
2.910	1.71 (0.89)	2.01		
3.175	0.02 (−0.24)	0.24	4.58	4.32
3.440	−0.55	−0.38	1.99	1.92
3.704	−0.64 (−0.59)	−0.52	0.82	0.83
3.969	−0.58	−0.49		0.33
4.233		−0.41	0.08	
4.763				0.04

[a] The values given in parentheses are obtained with basis (A + B).

sition error is of relatively less importance than if the SCF intermolecular energy is predominant (this could not be true with smaller or unbalanced basis sets). Thus, in the present paper, our discussion of the superposition error is only qualitative and empirical, and we have not used the counterpoise method to estimate it.

Table III shows that, at the SCF level, the most stable configuration is the axial model, with a minimum depth of −0.64 kcal/mol at $d = 3.704$ Å. This value is nearly equal to that previously obtained[13] with basis (A + B_1). The "L" configuration is also attractive while the resting and the "X" models are repulsive. The induction and charge transfer contribution may increase the depth of the minimum when it exists, but does not modify the general behavior of the potential curves. The use of the "double-ζ" basis (A + B) gives an intermolecular SCF energy of −0.59 kcal/mol at $d = 3.704$ Å in the case of the axial model. The superposition error is not very important at this distance but becomes relatively larger in the repulsive part of the curve, when the first-order term and the delocalization energy are of opposite sign.

(b) Dispersion Energy. The SCF minimum depth, when it exists, is very small. To obtain the correct order of magnitude, it is essential to take account of the dispersion energy. Table IV gives the values of E_{disp} obtained with basis (A′ + B′). The axial and the "L" models have a similar behavior, the dispersion energies being slightly more attractive in the axial geometry; the resting and the "X" configurations are also close together. The values of E'_{disp} are not given here and may be easily deduced from those of E_{disp}, the ratio E_{disp}/E'_{disp} being about 1.35 for any intermolecular distance and any configuration.

In order to estimate the inaccuracy involved in the deter-

mination of the dispersion energies of $C_2H_4 + I_2$, basis (A′ + B_1′) has been used to compute the dispersion energy of $C_2H_4 + Cl_2$ in the axial configuration at $d = 2.910$ Å. The value of E_{disp} is then 5.32 kcal/mol. Basis (A′ + B_1′) gives about 99.3% of the value obtained with basis (A′ + B′). We may expect a similar result in the case of $C_2H_4 + I_2$. It is also interesting to note that, if d functions are absolutely necessary on C and Cl, the use of p functions on H is of much less importance: only 3% of the dispersion energy is lost when such p functions are suppressed in basis (A′ + B_1′). This result may be useful in the study of larger systems.

Special attention is paid to the possible approximation of the dispersion energy by semiempirical expressions. One of the most known among such expressions is probably the London formula,[29,32] $E = -3I_A I_B \alpha_A \alpha_B / 2(I_A + I_b) R^6$, which corresponds to the contribution of the leading term of the multipole expansion. I_A and I_B are the first ionization potentials of molecules A and B; α_A and α_B the mean polarizabilities. We give in Table IV the values obtained with this expression, using[28-30,33] $I(C_2H_4) = 10.5$ eV, $I(Cl_2) = 11.48$ eV, $\alpha(C_2H_4) = 4.26$ Å³, $\alpha(Cl_2) = 4.61$ Å³. Since the London formula is an average formula, the molecules being treated as spheres, the intermolecular distance R is the distance between the "center" of both molecules. Thus, referring to our definitions of d, we must choose $R = d$ for the resting and the "X" configurations, and $R = d + d(Cl-Cl)/2$ for the axial and the "L" model. Table IV gives two series of values, corresponding to these two definitions of R, for the same distance d. Our ab initio results must be compared to the first series of values in the case of the axial and the "L" models, and to the second series in that of the resting and the "X" configurations. The apparent agreement between the ab initio results for the axial model and the second series of values obtained with the London formula occurs by chance and has no significance. In fact, the London formula has been proposed for large intermolecular distances and is not justified when the intermolecular distances are hardly larger than the intramolecular bond lengths. This explains the large differences between the two series of values obtained with the London formula at intermediate intermolecular distances, while at $d = 42.334$ Å (80 bohrs) the values differ by only 13%. At this distance, ab initio calculations have also been performed in the case of the axial model. The ab initio result is larger than the London formula values by a factor of almost 2. Though some inaccuracies are involved in the ab initio calculations, we expect from our studies on other systems[16,18,20,26,31] and on static polarizabilities[27] that the error should not exceed 20-25%. Thus it appears that some care must be taken in the use of the London formula.

Table IV. $C_2H_4 + Cl_2$. Dispersion Energy (kcal/mol), Basis (A′ + B′)

	configurations				London
d, Å	axial	"L"	resting	"X"	formula[b]
2.646	−8.39	−7.81			−1.55; −10.86
	(−9.41)[a]	(−8.55)			
2.910	−5.36	−4.99			−1.02; −6.13
	(−5.52)	(−5.05)			
3.175	−3.43	−3.20	−5.44		−0.69; −3.64
	(−3.38)	(−3.12)	(−5.25)		
3.440	−2.21	−2.07	−3.50	−3.13	−0.48; −2.25
	(−2.15)	(−2.00)	(−3.37)	(−3.17)	
3.704	−1.44	−1.36	−2.27	−2.06	−0.34; −1.44
	(−1.42)	(−1.32)	(−2.23)	(−2.13)	
3.969				−1.38	−0.24; −0.95
				(−1.46)	
42.334	−1.06 × 10⁻⁶				−0.56 × 10⁻⁶; −0.64 × 10⁻⁶
	(−1.13 × 10⁻⁶)	(−1.13 × 10⁻⁶)	(−1.29 × 10⁻⁶)	(−1.29 × 10⁻⁶)	

[a] The values given in parentheses are obtained from the semiempirical determination described in the text. [b] Because of the different definitions of d according to the various configurations, the axial and the "L" model ab initio results must be compared to the first series of values ($R = d + d(Cl-Cl)/2$), the resting and the "X" configuration ones to the second series ($R = d$).

Table V. $C_2H_4 + Cl_2$. Total Intermolecular Energy (kcal/mol), $E_{tot} = \Delta E_{SCF} + E_{disp}$. Bases $(A_2 + B_2)$ and $(A' + B')$

	configurations			
d, Å	axial	"L"	resting	"X"
2.646	−2.46 (−4.27)^a	−1.33		
2.910	−3.65 (−4.47)	−2.98		
3.175	−3.40 (−3.67)	−2.96	−0.86	
3.440	−2.76	−2.45	−1.50	−1.21
3.704	−2.09 (−2.00)	−1.88	−1.45	−1.23
3.969				−1.04

^{a} For the values given in parentheses the SCF calculations have been performed using basis (A + B).

In our recent study of the $(Cl_2)_2$ system,[31] our ab initio calculations have been compared to the values obtained from a Lennard-Jones type atom–atom potential $(-\sum_{ij}A/R_{ij}{}^6$, i referring to the atoms of molecule 1, j to those of molecule 2). The agreement was quite acceptable and we have tried a similar approximation in the present work. Since the two polarizability components perpendicular to the C–C bond are nearly equal,[27-29] we have considered C_2H_4 as a linear diatomic molecule. The best agreement with our ab initio calculations is obtained when the bond length of this "diatomic" molecule is the C–C bond length and $A \simeq \frac{1}{4}(3I_AI_B\alpha_A\alpha_B/(I_A + I_B))$. It is easy to understand the origin of the factor $\frac{1}{4}$ in A since at large distances $1/R \simeq \frac{1}{4}(1/R_{13} + 1/R_{14} + 1/R_{23} + 1/R_{24})$, indices 1 and 2 referring to the first molecule, indices 3 and 4 to the second one. Comparing the term in parentheses with the London formula, we see that they differ by a factor of 2: we already commented on this in the previous section. The optimum bond length of the "diatomic" model molecule is not really surprising since we previously saw the relative unimportance of the polarization functions on H in the calculation of the dispersion energy, and we also noted the same phenomenon in our determination of the static polarizability.[27] The polarizability of the CH bonds is very probably due, in most part, to the carbon atom which is more polarizable than the hydrogen atom. Table IV gives the values obtained with this approximation (values in parentheses). Considering the simplicity of this approximation, the agreement with our ab initio results is quite satisfying for the four configurations.

(c) Total Intermolecular Energies. The total intermolecular energies are finally computed as the sum $E_{tot} = \Delta E_{SCF} + E_{disp}$. Table V gives the values obtained from Table III (basis $(A_2 + B_2)$) and Table IV (basis $(A' + B')$). The four configurations exhibit a minimum, the largest depth occurring in the axial model. This configuration was already favored at the first iteration of the SCF supermolecule calculation. As seen for other systems of nonpolar molecules,[18,31] the electrostatic energy, due to the quadrupolar moments of the molecules, is not able, or hardly able, to compensate the first-order repulsive energy but may determine the relative stabilities of the configurations. A parabolic interpolation of the values computed around the minima gives a minimum depth of −3.73, −3.18, −1.56, and −1.25 kcal/mol at $d = 3.00$, 3.04, 3.55, and 3.60 Å for the axial, "L", resting, and "X" models, respectively. No experimental data are available concerning the minimum well depths and the corresponding intermolecular distances. By analogy with some studies on the benzene–chlorine complex in solution, Nelander[11] estimates that the distance of $C_2H_4\cdots Cl_2$ should not be smaller than 3.0 Å and that the energy of formation should be about −2 to −3 kcal/mol. This last estimation is based on so many assumptions (estimation of the energy in solution, estimation of the van der Waals energy, assumption that in solution the van der Waals forces are compensated by the interaction with the solvent) that the value obtained must be considered only as an indication.

Tables I, II, and IV allow us to evaluate the relative importance of the different energy contributions. Considering the most stable configuration in the region of the minimum, for instance at $d = 2.910$ Å, we find respectively +5.29 kcal/mol for the first-order contribution, −3.58 kcal/mol for the induction and charge transfer component, and −5.36 kcal/mol for the dispersion energy. Clearly, though the induction and charge-transfer contribution is important, it is not able to compensate the repulsive first-order energy. The largest stabilization element is the dispersion energy, as in the case of van der Waals molecules. The role of the dispersion energy is the same at larger distances and is still more striking in the case of the resting and the "X" models which are strictly repulsive at the SCF level.

As mentioned above, the ratio E_{disp}/E'_{disp} is about 1.3. E'_{disp} being often considered, we have also used it instead of E_{disp}. It is easy to check that E'_{disp} is always larger than the charge transfer and induction contribution. Our previous conclusions are then also valid when E'_{disp} is used. The interpolated minimum depths are now −2.52, −2.14, −0.88, and −0.73 kcal/mol at $d = 3.15$, 3.22, 3.65, and 3.83 Å for the axial, "L", resting, and "X" models, respectively. Compared to the results obtained with the use of E_{disp}, the relative stabilities of the configurations are not changed but the minimum depths are now smaller for slightly larger intermolecular distances.

We already commented on the error involved in the SCF supermolecule treatment when the "double ζ" basis (A + B) is used. Table V gives the total energy results obtained with this basis in the case of the axial model. As expected from Tables II and III, the intermolecular energies are too attractive in the region of the minimum. The interpolated minimum depth is −4.51 kcal/mol at $d = 2.83$ Å. The use of the "double ζ" basis set overestimates the minimum depth by about 21% and decreases the intermolecular distance by 0.17 Å. We shall refer to this result to estimate the error involved in the calculations on $C_2H_4 + Br_2$ and $C_2H_4 + I_2$.

$C_2H_4 + Br_2$. The axial model of this complex has been studied, using bases (A + C) and (A' + C') in the SCF supermolecule treatment and in the determination of the dispersion energy, respectively. The results obtained are presented in Table VI.

Comparison with the values given in Table I for $C_2H_4 + Cl_2$ shows that the first iteration intermolecular energies (ΔE_1) are of the same nature for both complexes: they are only more repulsive with bromine than with chlorine at intermediate distances, the curve becoming attractive for a slightly larger intermolecular distance.

Comparison with Table II (basis (A + B)) shows that the induction and charge transfer contribution is larger with bromine than with chlorine by a factor of 1.4–1.6. The interpolated SCF minimum depth of $C_2H_4 + Br_2$ is −0.87 kcal/mol at $d = 3.57$ Å. It is larger than that of $C_2H_4 + Cl_2$ (Table III, basis (A + B)) by a factor of 1.47.

As with chlorine, the charge transfer and induction energy, though important, hardly compensates the repulsive energy, and we must add the dispersion energy to correctly describe the stability of the system. Comparison with Table IV shows that the ratio $E_{disp} (C_2H_4 + Br_2)/E_{disp} (C_2H_4 + Cl_2)$ is about 1.2–1.3. The interpolated minimum depth of $C_2H_4 + Br_2$, obtained from the values of E_{tot}, is −5.46 kcal/mol at $d = 2.95$ Å. This minimum depth is larger than that of $C_2H_4 + Cl_2$ by a factor of 1.2 (comparing to the equivalent basis (A + B) result) for a slightly larger intermolecular distance.

The ratio E_{disp}/E'_{disp} is about 1.35, as with chlorine. The interpolated minimum depth obtained when E'_{disp} is used instead of E_{disp} is −3.94 kcal/mol at $d = 3.03$ Å. The use of E'_{disp} instead of E_{disp} again gives a smaller minimum depth and a slightly larger intermolecular distance.

As discussed in the case of $C_2H_4 + Cl_2$, the use of the

Table VI. C_2H_4 + Br_2. Intermolecular Energy (kcal/mol) [a]

d, Å	ΔE_1	ΔE_{ind+CT}	ΔE_{SCF}	E_{disp}	E_{tot}
2.646	19.77	−13.75	6.03	−10.16	−4.14
2.910	8.03	−6.78	1.26	−6.69	−5.44
3.175	2.95	−3.26	−0.38	−4.40	−4.77
3.440	0.88	−1.69	−0.82		
3.704	0.06	−0.88	−0.82		
3.969	−0.19	−0.50	−0.69		
4.233	−0.25	−0.31	−0.56		

[a] Basis (A + C) is used in the SCF supermolecule treatment; basis (A' + C') is used to compute the dispersion energy.

Table VII. C_2H_4 + I_2. Intermolecular Energy (kcal/mol) [a]

d, Å	ΔE_1	ΔE_{ind+CT}	ΔE_{SCF}	E_{disp}	E_{tot}
2.646	34.59	−22.28	12.30		
2.910	15.13	−11.24	3.89	−8.19	−4.29
3.175	6.15	−5.90	0.25	−5.56	−5.31
3.440	2.20	−3.14	−0.94	−3.75	−4.70
3.704	0.50	−1.69	−1.19		
4.233	−0.19	−0.50	−0.69		

[a] Basis (A + D) is used is the SCF supermolecule treatment; basis (A' + D_1') is used to compute the dispersion energy.

"double ζ" basis (A + C) overestimates the delocalization energy, mainly due to the superposition error. Thus E_{tot} should be corrected. We saw, in the case of C_2H_4 + Cl_2, that the delocalization energy obtained with the large basis (A_2 + B_2) is, in the region of the minimum, about 79% of the value obtained with basis (A + B). If we arbitrarily correct the delocalization energy of C_2H_4 + Br_2 in a similar way at d = 2.646, 2.910, and 3.175 Å, the new values of E_{tot} become −1.25, −4.02, and −4.08 kcal/mol, leading to an interpolated minimum depth of −4.39 kcal/mol at d = 3.05 Å. This value of the energy is larger, by a factor of about 1.2, than the minimum depth of C_2H_4 + Cl_2 obtained with basis (A_2 + B_2). The intermolecular distance is slightly larger than the corresponding one in C_2H_4 + Cl_2. The same conclusions were previously obtained when we compared the uncorrected results given by the use of bases (A + C) and (A + B).

C_2H_4 + I_2. In this case, we used basis (A + D_1') in the supermolecule treatment and basis (A' + D_1') in the determination of the dispersion energy. The results obtained for the axial configuration are given in Table VII.

Tables I, VI, and VII show that ΔE_1 exhibits the same general behavior for all three complexes: the energy becomes slightly attractive at large intermolecular distances, owing to the electrostatic interaction between the quadrupoles of the molecules. At intermediate intermolecular distances, ΔE_1 becomes more and more repulsive when changing chlorine into bromine and bromine into iodine. Similarly, ΔE_{ind+CT} (Tables II, VI, and VII) becomes more and more attractive from chlorine to iodine, this trend being independent of any necessary correction of this term.

ΔE_{SCF} (Tables III, VI, and VII) exhibits the same general behavior for the three complexes, with a small SCF minimum. In the case of C_2H_4 + I_2, the interpolated SCF minimum depth is −1.21 kcal/mol at d = 3.76 Å. The minimum depth increases from chlorine to iodine and, at intermediate distances, the slope of the repulsive part of the curve becomes larger and larger.

As in the previous systems, the SCF minimum depth of C_2H_4 + I_2 is very small and we must take the dispersion energy into account to correctly describe the intermolecular interactions. Tables VI and VII show that the ratio E_{disp} (C_2H_4 + I_2)/E_{disp} (C_2H_4 + Br_2) is about 1.2–1.3. A similar ratio was previously obtained when we compared bromine and chlorine and we saw that the use of basis (A' + B_1') instead of basis (A' + B') involves only a very small change. The interpolated

minimum depth of C_2H_4 + I_2, obtained from the values of E_{tot} (Table VII), is −5.32 kcal/mol at d = 3.23 Å. The use of a basis of type (A' + D') instead of basis (A' + D_1') in the calculation of the dispersion energy would probably give about −5.40 kcal/mol. We may note that, while the intermolecular minimum distance increases from chlorine to iodine (and more from bromine to iodine than from chlorine to bromine), the minimum depth (obtained with equivalent bases) increases from chlorine to bromine but not from bromine to iodine.

The ratio E_{disp}/E'_{disp} is about 1.37, close to the value obtained with chlorine and bromine. The use of E'_{disp} instead of E_{disp} gives a smaller minimum depth (−3.99 kcal/mol) for a slightly larger intermolecular distance (3.28 Å). This trend was also observed with chlorine and bromine.

In the case of C_2H_4 + Br_2, we corrected the induction and charge transfer term by analogy with the change involved in the C_2H_4 + Cl_2 results when a larger basis set is used. In a similar way, we can correct the determination of ΔE_{ind+CT} given in Table VII, taking 79% of the value in the region of the minimum. The new values of E_{tot} become −1.93, −4.07, and −4.04 kcal/mol at d = 2.910, 3.175, and 3.440 Å, leading to an interpolated minimum depth of −4.33 kcal/mol at d = 3.30 Å. Comparing to the modified determinations obtained with bromine, both minimum depths are nearly equal, the intermolecular minimum distance being somewhat larger with iodine than with bromine. These two minimum depths are larger than the minimum depth of C_2H_4 + Cl_2 obtained with bases (A_2 + B_2) and (A' + B') and the intermolecular minimum distances vary as previously described with unmodified determinations. It then appears that the correction of ΔE_{ind+CT} modify the minimum depth but not the relative behavior of the three complexes.

V. The Nature of the Intermolecular Binding

We commented in the Introduction and in our previous studies[13,14] on the need for theoretical work in order to explain the origin of the stability of such complexes. In our early study[13] on C_2H_4 + Cl_2, we discussed the possibility of a three-center covalent bond and concluded to its inadequacy at the position of the SCF minimum: both chlorine atoms contribute only very little to the π ethylene bond and, from the sign of the coefficients, there is no possibility of binding between each carbon atom and the first chlorine atom. The situation is exactly the same with bromine and iodine: the contribution of both atoms to the π ethylene orbital is now larger

but with no possibility to form a three-center covalent bond. At the position of the total energy minimum, the π ethylene orbital is more perturbed by the presence of the halogen molecule but there is no qualitative change. Thus, we definitively exclude the possibility of a three-center covalent bond and we shall analyze the binding in terms of intermolecular interactions.

We saw, from Tables I, VI, and VII, that the first iteration intermolecular energy gives a very small minimum owing to the electrostatic interaction between the quadrupoles of the two molecules of the complex. Tables II, VI, and VII show the importance of the induction and charge transfer energy. However, this contribution, though not negligible, gives only a small part of the total minimum depth. This is compatible with experimental data which conclude the existence of a "charge transfer complex" [5,15] since we studied only the fundamental state while experimental work also considers the excited states of these complexes. Keeping in mind that the induction and charge transfer component is overestimated in Tables VI and VII, it is clear from Tables II, IV, VI, and VII that the dispersion energy is larger than the induction and charge transfer contribution in the region of the total energy minimum and becomes of the same order of magnitude in the repulsive part of the curve. Such an importance of the dispersion energy is also encountered in van der Waals complexes.

VI. Conclusions

We can summarize the main points discussed in this paper.

(1) Our calculations on the $C_2H_4\cdots Cl_2$ complex show that, among the different configurations studied, the most stable one is the axial geometry.

(2) In this axial configuration, the three complexes $C_2H_4\cdots Cl_2$, $C_2H_4\cdots Br_2$, and $C_2H_4\cdots I_2$ exhibit strictly the same general characteristics for each intermolecular energy component. The features are only more pronounced from Cl_2 to I_2.

(3) The nature of the binding must be described in terms of intermolecular interaction contributions and not as a three-center covalent bond. The charge transfer energy, though not negligible, is not able to ensure a really significant stabilization energy in the fundamental state. It is necessary to take account of the dispersion energy, as in van der Waals molecules.

(4) No experimental data are available concerning the minimum depths and the corresponding intermolecular distances of these complexes. From our calculations on the axial configuration, chlorine gives the smallest stabilization energy (-3.73 kcal/mol) and the smallest intermolecular distance

(3.00 Å); bromine and iodine give about the same stabilization energy (around -4.40 kcal/mol when $E_{\text{ind}+\text{CT}}$ is corrected) but for different intermolecular distances (3.05 and 3.30 Å, respectively).

References and Notes

(1) P. B. D. De la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems", Elsevier, Amsterdam, 1966, Chapters 6 and 7.
(2) R. C. Fahey, *Top. Stereochem.*, **3**, 237 (1968).
(3) R. D. Bach and H. F. Henneike, *J. Am. Chem. Soc.*, **92**, 5589 (1970).
(4) G. A. Olah, and T. R. Hockswender, Jr., *J. Am. Chem. Soc.*, **96**, 3574 (1974).
(5) J. E. Dubois and F. Garnier, *Tetrahedron Lett.*, 3961 (1965); 3047 (1966); *Spectrochim. Acta, Part A*, **23**, 2279 (1967); J. E. Dubois, "Reaction Transition States", 21st Meeting of Société Chimique de France 87, 1970.
(6) M. A. Wilson and P. D. Woodgate, *J. Chem. Soc., Perkin Trans. 2*, 141 (1976).
(7) M. J. S. Dewar, *Nature (London)*, **156**, 784 (1945).
(8) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C71 (1951).
(9) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).
(10) D. V. Banthorpe, *Chem. Rev.*, **70**, 295 (1970).
(11) B. Nelander, *Theor. Chim. Acta*, **25**, 382 (1972).
(12) A. Dargelos, D. Liotard, and M. Chaillet, *Tetrahedron*, **28**, 5595 (1972).
(13) M. Jaszunski and E. Kochanski, *J. Am. Chem. Soc.*, **99**, 4624 (1977).
(14) J. Prissette and E. Kochanski, *Nouveau J. Chim.*, **2**, 107 (1978).
(15) L. Fredin and B. Nelander, *J. Mol. Struct.*, **16**, 205 (1973).
(16) E. Kochanski, *J. Chem. Phys.*, **58**, 5823 (1973).
(17) The SCF calculations have been performed with "Asterix", a system of programs for the Univac 1110 developed in Strasbourg (M. Bénard, A. Dedieu, J. Demuynck, M.-M. Rohmer, A. Strich, and A. Veillard, unpublished work); M. Bénard, *J. Chim. Phys. Phys.-Chim. Biol.*, **73**, 413 (1976).
(18) E. Kochanski, *Theor. Chim. Acta*, **39**, 339 (1975); M. Jaszunski, E. Kochanski, and P. Siegbahn, *Mol. Phys.*, **33**, 139 (1977); J. Prissette and E. Kochanski, *Chem. Phys. Lett.*, **47**, 391 (1977).
(19) E. Kochanski and J. F. Gouyet, *Theor. Chim. Acta*, **39**, 329 (1975).
(20) E. Kochanski, *Chem. Phys. Lett.*, **25**, 381 (1974); **31**, 301 (1975).
(21) Interatomic Distances and Supplement, *Chem. Soc., Spec. Publ.* (1958, 1965).
(22) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965).
(23) S. Huzinaga, D. McWilliams, and B. Domsky, *J. Chem. Phys.*, **54**, 2283 (1971); S. Huzinaga, *Tech. Rep.*, **2** (1971).
(24) T. H. Dunning, Jr., *J. Chem. Phys.*, **66**, 1382 (1977), *Tech. Rep.* (1977).
(25) B. Roos, C. Salez, A. Veillard, and E. Clementi, IBM Report No. RJ 518 (1968).
(26) J. Prissette, E. Kochanski, and D. R. Flower, *Chem. Phys.*, **27**, 373 (1978).
(27) G. Seger and E. Kochanski, in preparation.
(28) Landolt-Börnstein, "Zahlenwerte und Funktionen", Vol. I, Part 3, Springer-Verlag, West Berlin, 1951, p 510 ff.
(29) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids", Wiley, New York, N.Y., 1967, p 950.
(30) N. J. Bridge and A. D. Buckingham, *Proc. R. Soc. London, Ser. A*, **295**, 334 (1966).
(31) J. Prissette and E. Kochanski, *J. Am. Chem. Soc.*, **100**, 6609 (1978).
(32) F. London, *Trans. Faraday Soc.*, **33**, 8 (1937); R. Eisenschitz and F. London, *Z. Phys.*, **60**, 491 (1930).
(33) "Handbook of Chemistry and Physics", 57th ed., CRC Press, Cleveland, Ohio, 1977.