Pergamon

Tetrahedron Vol. 50, No. 18, pp. 5387-5400, 1994

0040-4020/94 $6.00+0.00

0040-4020(94)E0216-G

ON THE NATURE OF THE ELECTRONIC INTERACTION BETWEEN CONJUGATED NUCLEOPHILES AND ELECTROPHILES

Alain SEVIN and Claude GIESSNER-PRETTRE

- Laboratoire de Chimie Organique Théorique, Université P. et M. Curie, Bât. F, 4 Place Jussieu, 75252 Paris Cedex 05 (France). (The laboratory is part of the URA N° 506 of the CNRS)

ABSTRACT

Morokuma's energy partition scheme has been used to calculate the electrostatic (ES), polarization (PL), exchange (EX), and charge transfer (CT) components of the total energy of interaction for various complexes between nucleophiles (vinylamines, vinylol) and electrophiles (BH_3, formaldehyde, Cl_2, methylchloride, CH_3^+ and NH_4^+). Simple geometry variations have been made in order to determine their influence on the studied complexes. When dealing with vinylamine, the role of nitrogen pyramidalization complexes has been studied. A particular emphasis has been given to the case of formaldehyde complexes for the study of nucleophilic additions to carbonyl compounds. The results showed that the classical HSAB concepts were generally not verified by our analysis. Neither the ES component which can be related to the charge contribution, nor the component CT which can be treated in terms of frontier MO interactions were sufficient to account for the actually calculated features. The strong geometry dependence of the component EX, whose value is related to the overlap of the occupied molecular orbitals of the two interacting species, was generally dominant when the studied complex did not carry any formal charge.

Introduction

Conjugated nucleophiles such as enamines or enolates and their derivatives react with a wide variety of electrophiles according to the general scheme of Figure 1.

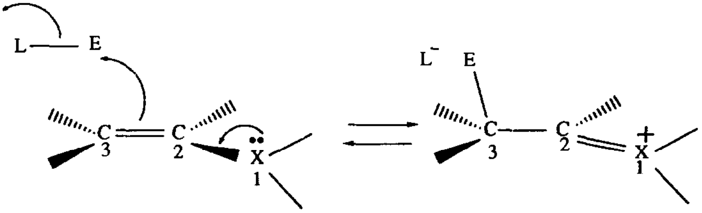
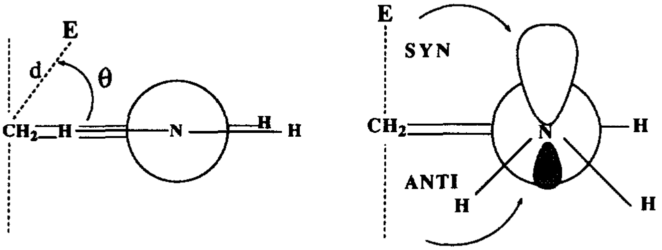


Figure 1. General reaction scheme. E stands for the electrophilic moiety of a molecule, e.g. C in CH_3Cl or in CH_2O, and L is either a leaving group (Cl^- in CH_3Cl) or a migrating double bond (C=O in CH_2O).

As the reaction proceeds, a bond is formed between carbon C_3 of the conjugated moiety and the electrophile, and the charge changes on X and L depend on the actual system under study. In order to account for the observed trends, various electronic models have been proposed on the basis of frontier MO analysis.[1] Most of them rely on the fact that the $X_1C_2C_3$ nucleophilic unit can be regarded as a distorted allylic anion, thus the shape of its HOMO, as well as that of the LUMO of the related electrophile are of crucial importance. In this perspective, HSAB theory [2] provides a simple ground for rationalizing most of the experimental observations, as long as only *regioselectivity* is concerned, *i.e.* attack of C_3 versus attack of X_1. This kind of approach relies more or less on commonly accepted assumptions that can be summarized as follows : i) prior to bond formation, the actual nature of the interaction between the nucleophile and the electrophile is supposed to result from a complex mixture composed of an electrostatic component (*charge control*) and of the best possible overlap between the frontier MOs of both partners (*orbital control*) ; usually, only the second factor can be qualitatively evaluated ; ii) in Figure 2(1a), one sees that the plane formed by NCC defines two that can be diastereotopic when suitable substituents are present on the system. But even when the substituents do not afford diastereotopic faces, two different half-spaces exist as long as the environment of N is not symmetrical with respect to the reference plane. This can be illustrated with vinylamine for which the pyramidalized structure such as that displayed in Figure 2(1b) opposes the planar structure represented in Figure 2(1a). In the latter case, we can define a *syn* and an *anti* half-space with respect to the N lone pair. This definition will be formulated later on in geometrical terms be seen (*vide infra*).



planar geometry 1a pyramidalized geometry 1b

Figure 2. Geometrical parameters and relative arrangements of the electrophilic moiety E used throughout the study. The syn and anti terms only stand in the case of pyramidalized vinylamine.

However, when looking at the available experimental[3] and theoretical data,[1] no clear-cut explanation of the observed facts arises, and in most cases, only *ad hoc* or *a posteriori* justification of the results is given. Thus, in a previous semi-empirical study on the Michael-type addition of chiral secondary amines to enones, we were able to relate the observed enantioselectivity to the energy of interaction between the two reactants.[1a] In addition, ab initio calculations carried out on the vinylamine-formaldehyde model complex showed that in all cases the syn complex was preferred. However, the wave functions of the different cases considered did not exhibit any notable difference. In order to get some insight into the nature of the electronic forces responsible for the variations of the energy of interaction, we undertook an exploratory study on two model conjugted nucleophiles, i.e. vinylamine **1** and vinyl alcohol **2**, that would afford complexes with, either neutral (BH_3 **3**, CH_2O **4**, Cl_2 **5**, CH_3Cl **7**) or charged (CH_3^+ **8**, NH_4^+ **9**) electrophiles as those defined in Figure 3.

Methodology

Ab initio calculations were achieved with the 6-31G** basis set[4] using the Monstergauss program,[5] which includes the energy partition scheme of Morokuma.[6] For each type of complex, the total energy of interaction, called TOT in Tables 1-3, appears as the classical sum of variouscontributions : electrostatic (ES), polarization (PL), exchange (EX), and charge transfer (CT) contributions. The formalism of this decomposition as well as the meaning of these various terms is well documented.[7] The values reported here are corrected from the basis set superposition error according to the computational procedure developped by Carri *et al.*[8] It is noteworthy that some qualitative link can be made with the aforementioned HSAB theory : following a crude and first approximation, we may say that the ES contribution amounts to the essential of the so-called "charge effect", while the CT contribution can be related to a summation over the perturbation terms arising from the frontier occupied MOs of each species and the empty MOs of the other one. Indeed, one must be aware of the fact that in our calculation, the four terms now deal with the complete set of electrons, and the total wavefunction of both partners as well as that of the complex[7], while in qualitative approaches, only a few terms are selected, and very often in an arbitrarily fashion. In Tables 1-3, the sum ES + PL + EX + CT,which is called Σ_{1-4} is generally very close to the total complexation energy which is the difference between the calculated energy of the complex and that of the isolated partners. When discrepancies are found between Σ_{1-4} and TOT, as in the case of Cl_2 complexes, it reveals that the energy partition does not take into account all the electronic factors. It is also clear that the lack of electron correlation inherent to our type of calculation leads us to only propose results that are only of semi-quantitative grade.

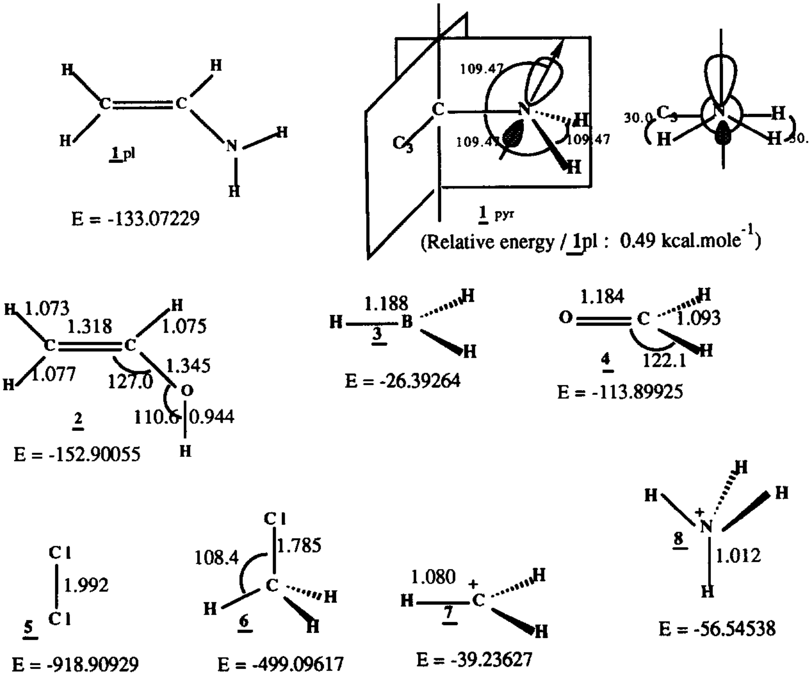


Figure 3. Geometries and energies of the species 1-8. All bondlengths are in Å. Unless noted, energies are in hartrees (1 hartree 627.50959 kcal.mole^{-1}).

The geometries of the various species considered in our study were optimized using the 631G** basis, and are reported in Figure 3. The structure of **1***pl* and its pyramidalization have been described in detail elsewhere.[1a] The geometrical parameters of **1***pyr* were set equal to those of optimal **1***pl*, except for the relative position of the N substituents for which tetrahedral valence angles were imposed (Figure 3, upper right). The CCNH dihedral angles were fixed in such a way that the fourth tetrahedral direction, arbitrarily assigned to the N lone pair direction of maximum electronic density, lies in a plane perpendicular to the CCN one, as displayed. The geometrical parameters and the calculated energies are reported. It is noteworthy that in the optimal structure of **2**, the O-H hydrogen lies in the plane of the heavy atoms and adopts the Z geometry with respect to the OCC linkage, in agreement with previous theoretical studies.[9]

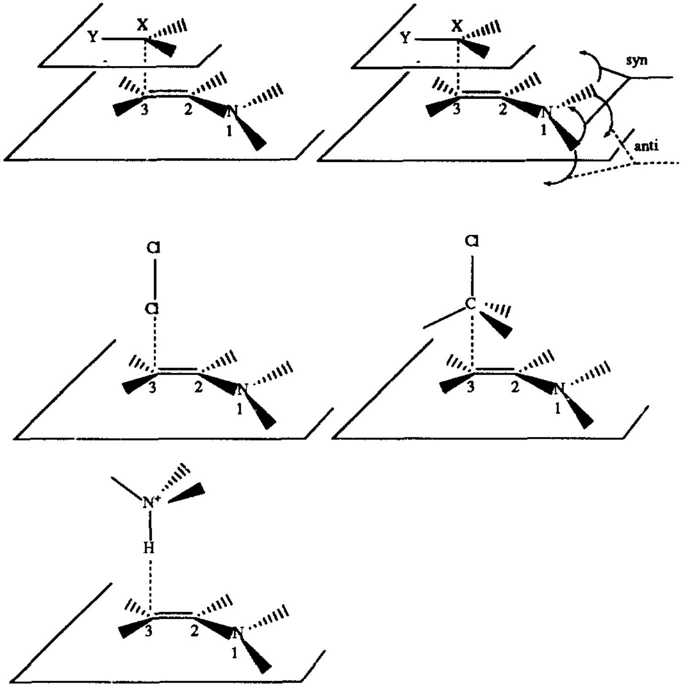


Figure 4. Relative arrangements in the various complexes. All distances between C_3 and the nearest electrophilic center have been set at 3 Å. X = $C(CH_2O, CH_3^+)$ or $B(BH_3)$; Y = $O(CH_2O)$ or $H(BH_3, CH_3^+)$.

In a second step, the complexes of vinylamine with compounds **3**-**8** were studied. Various geometries were explored : i) for structures **3**, **4**, **7**, the planar electrophile was fixed in a plane parallel to that of the CCN linkage (Figures 1 and 2), the electrophilic center (*i.e.* B or C) was set at the vertical of C_3, at a distance of 3 Å. Then, diehedral angles HBC_3C_2, OCC_3C_2 and HCC_3C_2 were fixed at 180°, respectively for **3**, **4**, and **7**, such as to afford a staggered arrangement of the substituents around the C_3-incipient bond. The calculation was then repeated keeping all geometrical parameters frozen, but upon pyramidalization of the N atom in a syn or anti fashion with respect to the electrophile. These requirements are schematically shown in Figure 4.). ii) When dealing with Cl_2 **5**, the Cl-Cl bond was aligned with C_3, such as the C_3-nearest Cl distance was of 3 Å, and then, N was pyramidalized to afford both syn and anti geometries. iii) The same procedure was repeated for complexes with **6** and **8**, and the C_3-C and C_3-H distances were set equal to 3 Å, with the geometries displayed such in Figure 4. The resulting calculated data are given in Table 1.

In a third step, the complexes formed by vinylamine and CH_2O were explored. This time, the complex were fixed in planar, syn or anti geometries, keeping all the preceding geometrical requirements, and the calculations were carried out for θ (C_2C_3C angle, Figure 2) values of 80° and 100°. The calculated energies of interaction are given in Table 2.

It is noteworthy that attempts to optimize the geometry of both partners at fixed d and θ do not yield significant energy changes, both in total and individual contributions. For example, with the data of table 2 (SYN, θ=90°), one gets : E(non relaxed) = -246.94087 au and : E(relaxed) = -246.94308 au, thus leading to an energy change of only 1.40 kcal.mole^{-1}, while in the meantime, the ES, PL, EX, and CT contributions remain practically unchanged within a margin of less than 1%. This shows that our choice of frozen geometries does not imply important restriction on the generality of the results.

Table 1. Complexes of vinylamine (**1**pl and **1**pyr) with compounds **3**, **5**-**8**, in planar, syn, and anti geometries. All geometries correspond to d=3Å, θ = 90°, as defined in Figure 2(1a).All values are in kcal/mole. The reported energy given in the last line (TOT) corresponds to the difference between the total energy of the complex and that of the isolated species. For the ES, PL, EX, and CT terms, a negative value has the usual meaning of a stabilizing (attractive) contribution.

	BH_3			Cl_2			CH_3Cl			CH_3^+			NH_4^+		
	plan.	syn	anti	plan.	syn	anti	plan.	syn	anti	plan	syn	anti	plan	syn	anti
ES	-3.2	-2.8	-3.2	-4.0	-3.6	-3.9	-3.3	-3.3	-2.5	-11.9	-13.1	-5.1	-6.7	-8.1	-1.6
PL	-0.3	-0.3	-0.3	-0.4	-0.4	-0.3	-0.3	-0.2	-0.2	-3.8	-3.8	-3.7	-1.4	-1.4	-1.3
EX	3.5	3.3	3.6	6.6	6.4	6.6	6.8	6.6	6.9	2.4	2.3	2.4	0.4	0.3	0.4
CT	-2.5	-2.2	-2.6	-3.3	-3.0	-3.3	-1.1	-0.9	-1.1	-14.5	-12.4	-14.2	-2.6	-2.3	-2.6
Σ1-4	-2.5	-2.0	-2.5	-1.1	-0.6	-0.9	2.1	2.2	3.1	-27.8	-27.0	-20.6	-10.3	-11.5	-5.1
TOT	-2.2	-1.6	-2.1	-0.3	0.3	0.1	2.8	2.6	3.8	-29.8	-28.2	-22.1	-9.9	-11.1	-4.8

Table 2. Complexes of vinylamine (**1**pl and **1**pyr) with CH_2O, at d = 3Å. All values are in kcal/mole. A negative value has the usual meaning of a stabilizing contribution

	PLANAR			SYN			ANTI		
θ	80°	90°	100°	80°	90°	100°	80°	90°	100°
ES	-2.6	-2.7	-2.8	-3.3	-3.1	-3.0	-1.6	-1.7	-1.9
PL	-0.4	-0.3	-0.2	-0.4	-0.3	-0.2	-0.4	-0.2	-0.2
EX	7.8	5.4	4.3	7.6	5.2	4.1	8.0	5.4	4.2
CT	-1.1	-1.2	-1.2	-1.1	-1.1	-1.0	-1.2	-1.3	-1.2
Σ 1-4	3.7	1.2	0.1	2.8	0.7	-0.1	4.8	2.2	1.1
TOT	4.4	1.8	0.7	3.4	1.2	0.3	5.5	2.8	1.6

At last, the calculations of the second step have been repeated replacing the vinylamine moiety by vinyl alcohol, and keeping all the remaining geometrical arrangements constant at θ = 90°. The corresponding data are given in Table 3.

Table 3. Complexes of vinylol **2** with compounds **3**-**8**, at d=3Å. For the definition of θ, see Figure 2(1a). All energy values are in kcal/mole. A negative value has the usual meaning of a stabilizing contribution.

	BH_3			CH_2O			Cl_2			CH_3Cl			CH_3^+			NH_4^+		
θ	80°	90°	100°	80°	90°	100°	80°	90°	100°	80°	90°	100°	80°	90°	100°	80°	90°	100°
ES	-3.1	-2.7	-2.1	-2.7	-2.5	-2.3	-4.2	-3.5	-2.8	-3.1	-2.4	-2.1	-6.9	-6.1	-5.1	-3.4	-3.0	-2.6
PL	-0.2	-0.2	-0.2	-0.3	-0.2	-0.2	-0.3	-0.3	-0.2	-0.2	-0.2	-0.2	-3.5	-3.4	-3.5	-1.3	-1.2	-1.3
EX	4.3	3.4	3.3	7.7	5.2	4.1	8.3	6.5	5.7	8.5	6.6	6.1	3.0	2.3	2.2	0.5	0.3	0.3
CT	-2.7	-2.2	-1.7	-1.1	-1.1	-1.0	-3.5	-2.8	-2.2	-1.3	-0.9	-0.7	-12.8	-11.6	-9.9	-2.4	-2.3	-1.9
Σ1-4	-1.7	-1.7	-0.7	3.6	1.4	0.6	0.3	-0.1	0.5	3.9	3.1	3.1	-20.2	-18.8	-16.3	-6.6	-6.2	-5.5
TOT	-1.2	-1.3	-0.4	4.2	2.0	1.1	1.3	0.8	1.2	4.6	3.8	3.7	-21.0	-19.4	-16.6	-6.3	-5.8	-5.2

For all types of complexes, we deliberately adopted the classical spatial arrangements that are generally assumed in qualitative discussion, without attempting further optimization. The "intermolecular distance" of 3 Å ensured us to have some results that would be quite meaningful in comparison with the previous ones.[1a-c] In fact, we were only able to tentatively rationalize the correlation that we had previously obtained between the energy of interaction and the enantioselectivity of the reaction studied. It must be clear that we do not pretend to analyze the actual electronic changes occuring during the *reaction paths*. In other words, we have restricted ourselves to answer the following questions : i) is the classical description of nucleophile and electrophile approach in terms of charge and frontier MOs legitimate? ii) Are the electronic trends simple enough so that one can propose models that would be of general and practical use ? The preceding points provide a guideline for the following discussion of the results.

Complexes of vinylamine with compounds 3-8

Planar structures (θ = 90°) Upon examination of Tables 1 and 2, several dominant features come to the fore. First of all, the complexes can be divided into three classes, depending on whether the complexation is exothermic (with BH_3, CH^{3+}, and NH_4^+), practically athermic (with Cl_2), or endothermic (with CH_2O and CH_3Cl). It is quite obvious that when dealing with charged electrophiles, an attractive complex is formed, but for **1**pl/**3**, only a weak electrostatic attraction is found, although **3** has a strong Lewis acid character. The weakly repulsive approach of **1**pl with CH_2O (**4**) has already been reported.[1c] For halogenated methyl derivatives, attractive complexes with the incoming charged nucleophile have been observed in the gas phase,[10] while a repulsive approach is observed in the present study. The case of Cl_2 might seem paradoxical in the sense that the electron rich extremity of this molecule is likely to interact in a repulsive fashion with a nucleophilic center, but it is less surprising when one recalls that Cl_2 yields complexes with alkenes (*vide infra*).[11] In fact, only little information can be extracted from these bulk thermodynamical data. They result from complex balances between terms of opposite signs as it will be shown below along with the detail of the calculated energy decomposition. The complexation with CH_2O, which has been the subject of many previous studies,[12] is noteworthy, and will be treated separately (*vide infra*).

Attractive complexes of ***1****pl with* ***3*** *,* ***7****,and* ***8***. As expected, the charged complexes **1**pl/**7** and **1**pl/**8** have large ES contributions, but the CT terms largely differ. The classical important two-electron term arising from the high-energy occupied π-MOs of **1**pl (two π MOs including the HOMO) and the low-energy empty π MO of the carbon of **7** has no equivalent when dealing with **8** for which no low-lying empty MO is available. A qualitative result thus emerges : the **1**pl/**8** complex is essentially of electrostatic nature, while the **1**pl/**7** complex is dominated by both electrostatic and charge-transfer interactions. The role of the CT term can be emphasized by the fact that in the **1**pl/**3** complex it drops to -2.5 kcal.mole^{-1}, in a similar way to the **1**pl/**8** complex. A qualitative argument can be advanced : the empty π MO of **3** lies at higher energy than that of CH_3^+, hence the 2-electron term perturbation arising from the π MOs of **1**pl, of the form $\delta E \approx S^2/\Delta E$, becomes weak due to a large denominator. A last remark must be made regarding the EX terms that vary according to the sequence

EX (**3**) ≈ EX (**7**) >> EX (**8**). The EX contribution is essentially caused by short-range repulsion due to the overlap of the electronic distribution of one molecule with that of its partner.[7a] The bonding frameworks of **3** and **7** are comparable in shape, but for **8**, the electronic distribution of the bonds is located much farther, hence yielding a much smaller overlap with **1**pl. It is noteworthy that the **1**pl/**7** complex is the one having the most important PL term. This strong polarization is caused by the close vicinity of the positively charged atoms of **7** and the very polarizable π system of **1**pl. The last feature is corroborated by the fact that in the **1**pl/**8** complex, this term decrease is mainly due to the fact that now only one partially charged atom (among five) interacts at short distance with **1**pl .

Complex formed between ***1****pl and* Cl_2 *(****5****)*. With the exception of the very weak PL term, the ES, EX, and CT terms are of comparable magnitude. The aforementioned repulsion between the electron lone pairs electrons of Cl_2 and those of **1**pl is important, as shown by the high value of EX (6.6 kcal.mole^{-1}), but this repulsion is practically cancelled by the sum ES + CT. The calculated SCF charges along the C_3.....Cl-Cl direction are : C_3 (-0.4151) Cl (+0.009) Cl (-0.054), indicating that some electrostatic interaction is present. The small excess of negative charge on the extreme Cl atom shows that some charge-transfer from the nucleophile takes place. However, it would be premature to draw a conclusion given our level of theory which does not include electron correlation.

Repulsive complex of ***1****pl with* ***6***. The dominant repulsive EX contribution of 6.8 kcal.mole^{-1} mainly arises from the three C-H bonds that are directed towards the nucleophilic moiety (see Figure 4). A comparison with the complexes derived from BH_3 and CH_3^+ for which the three C-H or B-H bonds of comparable length lie farther from the vinylamine plane is straightforward. The electrostatic term is important, while charge-transfer is weak, indicating that, at this distance, and without relaxation of the C-Cl bond, little electron transfer occurs through the 2-electron interactions arising from the occupied MOs of **1**pl and the empty MOs of **6** (little transfer is expected from **6** to **1**pl). This is in good agreement with the classical trends encountered in S_N2 reactions of halogenated methyl derivatives, where electron transfer from the nucleophile to the electrophile is rather progressive, and maximized in the transition state.

*Influence of N pyramidalization in complexes of **1pl** and **1pyr** with **3**, **5-8**.* First of all, it is worth emphasizing the fact that upon N-pyramidalization, rehybridization of N takes place. The pure N p orbital which was involved in conjugation with the C_2C_3 π bond acquires s character, thus yielding a directional hybrid pointing in the direction opposite to the half-space containing the NH bonds (see Figure 2). Namely, in what is a so-called syn geometry, the electrophile lies in the same half-space as that of the maximum extension of the electronic density of this hybrid, while it lies in the opposite half-space in the case of an anti geometry. For the rest of the discussion, it is practical to retain this classification of the complexes and accordingly, we will begin to treat the cases of BH_3, CH^{3+}, and NH_4^+. Moreover, as seen in Tables 1 and 2, the PL terms which remain practically constant upon N distorsion will not be taken into account.

Upon comparison of the complexes with CH_3^+ and NH_4^+, we see that the electrostatic terms ES vary significantly with N-pyramidalization, the best stabilization being found in syn complexes. This point clearly shows that the main electrostatic interaction comes from the positive atoms of the electrophile and the negative density which is concentrated around N. On the other hand, the positive hydrogens of both partners tend to avoid themselves. The case of BH_3 , for which the ES contribution of the anti geometry is greater than that of the syn geometry, is not paradoxical when one considers that the hydrogens bear some hydride character. The calculated SCF charges of BH_3 are +0.2314 on B and -0.0771 on the H atoms, while they are + 0.0782 on C and + 0.3072 on the H atoms of CH_3^+, that is to say the observed reverse trend. The repulsive EX terms do not exhibit important changes in the same conditions, nevertheless slightly more repulsion is found when the NH bonds point towards those of the electrophile, *i.e.* in the anti geometry. However, an interesting variation is found in the CT terms that are greater in the anti geometry than in the syn geometry, for all the entries of Tables 1 and 2. An explanation of this feature can be proposed by considering the HOMO/LUMO interactions as displayed in a very qualitative fashion in Figure 5. As schematically drawn, when the HOMO of vinylamine interacts with the LUMO of the electrophile symbolized by a p AO, a secondary negative overlap appears with the hybrid orbital centered on N.

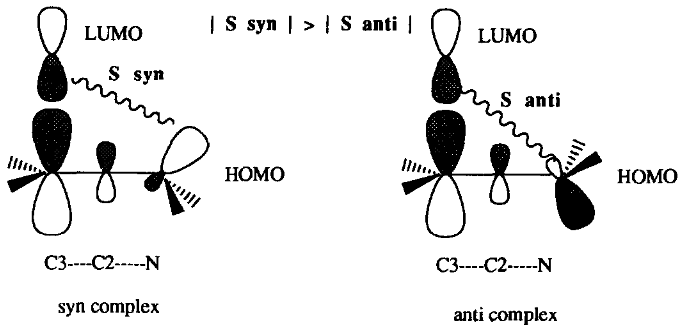


Figure 5. Schematic HOMO/LUMO interactions in the case of pyramidalized vinylamine. The p-type MO labelled LUMO symbolizes either an empty p MO (CH_3^+, BH_3) or the lowest antibonding MO of adequate symmetry for other compounds.

The latter is greater in the case of a syn geometry, thus favoring the anti geometry.[13]The last point is conflicting with the trends exhibited by the ES contributions since it goes the reverse way. This shows that an explanation which would only take into account the frontier orbitals analysis would lead to a wrong conclusion. *As an end result, the preference syn > planar >> anti observed for complexes with 7 and 8 mostly arises from electrostatic differential interactions and **not from** classical MO considerations.* The planar ≈ anti > syn preference for the complexes derived from 3 results from a complex balance between terms of comparable magnitude, but of opposite signs.

The complexes of Cl_2 have ES and CT contributions in favour of planar or anti geometries, while the EX contribution slightly favours the syn geometry. The differences are not significant, so that no clear-cut preference emerges. The case of CH_3Cl is less ambiguous : both ES and EX contributions are in favour of a syn complex. The latter EX contribution can be regarded as some kind of steric effect, as anticipated in the discussion of the planar complex. As previously shown, the CT term is slightly in favour of the anti complex, but once all of these terms are taken into account, the preferential sequence syn ≈ planar > anti is observed, though less pronounced than in the case of charged electrophiles. Here again, the bulk effect results from a balance where no leading term can be extracted.

In conclusion, we can put forward three kinds of arguments : i) the electrostatic interactions play a fundamental role and generally tend to place the so-called pyramidalized N lone pair close to the positive charges born by the electrophile (or far from the negative charges, as in the case of BH_3) ; ii) a weak but systematic and sizeable MO effect, that can be roughly described in terms of HOMO/LUMO interaction, is in favour of anti complexes ; iii) the repulsion arising from the electronic densities of both moieties is generally in favour of syn complexes, that is to say : "steric interactions" are minimal.

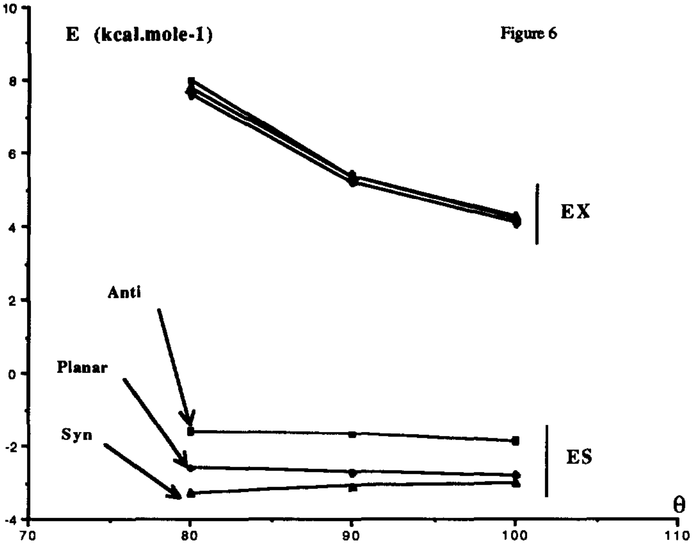
Complexes of vinylamine with CH_2O (4)

Nucleophilic attacks to carbonyl compounds is a key issue in chemistry, and has been the subject of numerous studies. Most of the classical models used to predict both reactivity and stereochemistry rely on the examination of complexes formed by the reactants. In this general perspective, we have tried to gain insights into the actual electronic nature of these complexes.

In their study of hydride addition to CH_2O, Bürgi and Dunitz have shown that the nucleophile approaches the carbonyl group with a θ angle greater than 90°, the latter angle varying as the reaction proceeds ; a simple MO explanation of this result has been proposed.[12a-c] On the other hand, a previous theoretical study of the reaction of CH_2O with vinylamine by one of us [1c] has shown that the complex leading to the product has a "compact geometry", different from those which have been studied in the present work. The latter point is not contradictory, since, as in the above discussion, our study is limited to the electronic aspects of complexation and does not presume of the reaction path leading to the products. In addition to the already discussed planar, syn, and anti geometries having θ fixed at 90°, the data of Table 2 include the values of 80° and 100° for this parameter, with the constraints fixed in the methodological part.

The data displayed in Table 2 exhibit simple important trends. First of all, the overall complexation energy is strikingly geometry dependent. N-pyramidalization leads to the following sequence for the relative complex stabilities : syn > planar > anti. The θ-dependence, in each of these geometries, yields the sequence :

$\theta = 100° > \theta = 90° > \theta = 80°$. It is worth attempting to solve both sequences in terms of the attractive and repulsive electronic contributions, as in the previous sections. A preliminary remark can be made : PL terms are generally small and almost constant , so that their role will not be treated. More surprisingly, the CT contributions are sizeable but remain practically constant when compared with the ES and EX contributions. *This indicates that at any rate, in our types of complexes, no clear-cut explanation based on frontier MOs can be proposed.* The latter point does not rule out the role of occupied-MO/empty-MO interactions, but shows that the cancellation of competing terms might occur, in such a way that no conclusion could be drawn on this ground. We are left with ES and EX terms exhibiting systematic trends that can be directly analyzed.



In Figure 6, the variations of ES and EX are displayed as a function of θ for the syn, planar, and anti geometries. Two main features are revealed : i) the splitting of the curves relative to the repulsive term EX (upper part) is very weak, thus indicating that syn, planar, and anti complexes behave similarly upon θ variation. The greatest repulsion is found in hindered geometries, *i.e* .when $\theta = 80°$; when θ increases, the repulsion sharply drops. The origin of this effect is clearly found in the short-range repulsion arising between the electronic density of CH_2O and the part of the electronic density of vinylamine which is involved. This short-range (compact) aspect is confirmed by the fact that it is practically not N-pyramidalization dependent, the geometry change occuring far away from the zone of maximum repulsion. ii) A reverse tendency is exhibited by the attractive ES terms (lower part), although the variation is less pronounced than when dealing with the EX term. Now, a weak θ-dependence is observed while a neat effect results from N-pyramidalization, and the stabilization decreases according to the sequence syn > planar > anti.

We thus see that two types of competing variations are found upon geometry changes : EX is strongly θ-dependent in favour of the $\theta = 100°$ geometry ; ES mostly varies with N-pyramidalization, but on a smaller range, in favour of the syn geometry. The algebraic sum of these two terms clearly shows that the syn complex having $\theta = 100°$ is preferred. However, it is noteworthy that this result does not arise from MO interactions (via the CT term), but from a complex balance between the electrostatic (ES) and repulsive (EX) terms, the latter ones being related to what is generally called "steric interactions".

Complexes of vinylol **2** with compounds (**3**, **5**-**8**)

The optimal geometry of **2** being planar, the only parameter that has been varied is θ with the same constraints similar to those of planar vinylamine. The calculated results are given in Table 3. At a first glance, the separation between attractive and repulsive complexes is roughly the same as in the complexes displayed in Table 1, with the exception of the **5**/**2** complex which is more repulsive than in the previous case. Indeed, **1**pl or **1**pyr and **2** are isoelectronic and therefore bear strong electronic analogy. However the electronic charge is more pronounced on the O atom in **2** : the SCF charge is -0.6302 by comparison to -0.3862 on N in **1**pl. Since the PL terms are either small or practically independent of θ, they will be omitted in the ensuing discussion that will follow the attractive/repulsive classification which is only of practical use.

Attractive complexes with **3**, **7** *and* **8**. The ES and CT terms undergo the same type of variation, that is to say a better stabilization according to the sequence : θ = 80° > θ = 90° > θ = 100°. For reasons similar to those encountered in the discussion of the **1**pl complexes, both ES and CT terms are very important for **7**, while they drop for **8** where they are of the same order of magnitude as for **3**. On the other hand, the EX contributions exhibit a reverse trend, being in favour of the θ = 100° geometry. Thus, we are left with competing interactions whose balance depends on the actual nature of the complex : for **7** and **8**, the ES and CT terms dominate over EX and act in favour of θ = 100°, while for **3** EX is large enough to overcome this trend, and then shift, to the preferred value of θ = 90°.

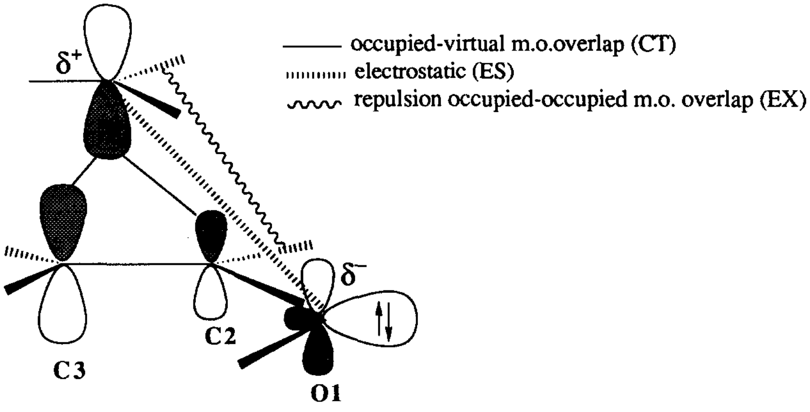


Figure 7. Schematic view of the various types of interactions existing between vinylol and an electrophile symbolized by an empty p-MO, with the same conventions as in Figure 5. The CT, ES, and EX contributions are displayed with different types of lines.

In Figure 7, the various parameters that are of concern for the ES, CT, and EX terms are schematically recalled. The electrostatic (ES, dashed line) leading term is self-evident. The EX term is only recalled in a symbolic fashion, and results from the repulsion between electronic distributions of both partners, and is therefore precisely defined with difficulty. The HOMO/LUMO interaction is more classical : the HOMO of **2** interacts with the empty pMO of **3** or **7** in order to optimize the overlap between these two orbitals : the primary overlap occurs with C_3, but a decrease of θ to 80° increases the positive overlap with C_2. The latter motion is nevertheless restricted by a negative overlap with O1 which increases when θ decreases.

Complexes with **5** *and* **6**. The complexation of **2** by Cl_2 (**5**) leads to a complex balance : here again, the ES and CT terms are in favour of a complex with θ = 80°, while the EX form is in favour of θ = 100° as ususal, and finally a compromise is found at θ = 90°. The case of CH_3Cl is not as complex : the geometry is ruled by the dominant amplitude of the EX term which tends to remove the steric constraint and leads to a preferential geometry with θ = 100°.

Complexes with CH_2O (**4**). As for vinylamine, a neat overall preference for θ = 100° is observed. As in most cases, the ES term is still in favour of θ = 80°, although the 80°-100° relative energy remains small (≈0.4kcal.mole^{-1}). The CT form is almost constant, as was observed for vinylamine, indicating again that the HOMO (**2**)/LUMO(**4**) interaction is not dominant and that cancelling effects arising from other types of MOs are to be taken into account. The most striking feature is found in the EX term which is very repulsive for θ = 80° and drops steeply upon θ increase. We thus reach the same conclusion than for vinylamine complexes : complexation by CH_2O is ruled by two competing terms, ES (attractive), which is slightly in favour of θ = 80°, and EX (repulsive), which strongly dominates and leads to a neat preference for θ = 100°. The essential of the analysis previously made for **1**pl and **1**pyr complexes remains valid and does not need to be repeated in the present case.

Conclusion

A complex balance between three kinds of terms that exhibit sizeable variation upon geometry change, namely ES, CT (both attractive in the present cases), and EX (repulsive) is observed. General trends can be emphasized : i) ES is always in favour of the geometry having the smallest distance between opposite dominant electrosatic charges, which is rather trivial ; ii) CT is of a more complex nature and can be explained in simple terms of HOMO (nucleophile) / LUMO (electrophile) interaction only when the electrophile bears a truly positive charge and has an empty p-type LUMO, *i.e* . for BH_3 (**3**) and CH_3^+(**7**).This simple kind of explanation fails for CH_2O where CT is practically independent of geometry changes, either via θ variation or N-pyramidalization, due to cancellation by competing effects. iii) The EX term is always the contribution to energy whose variation is the most geometry-dependent. In all cases, it is less repulsive in the geometry that avoids what is commonly called "steric hindrance". The magnitude of this term is determined by that of the overlap between the occupied orbitals of the two interacting entities. It is therefore very sensitive, not only to the intermolecular distance, but also to the relative orientations of the atomic orbitals at the "interaction site" and to the magnitude of their molecular orbital coefficient, and its variation is difficult to predict with precision.

Atlthough simple results are found, either as a function of θ or of N-pyramidalization, and in general agreement whith what is called "chemical intuition", this exploration of the various electronic contributions to energy which only deals with complexes and does not presume of the further reaction path, clearly shows that, they cannot in reality be explained by simple arguments, be they based on electrostatic forces and/or on MO considerations. Both indeed play a role, but it is not determinant in most cases. We thus reach the deceptive conclusion that the electronic aspects ruling the stereochemistry of these types of very commonly invoked complexes remain complex and subtle, and that no leading contribution appears evident.

Acknowledgements

We thank the CIRCE for giving us the opportunity to carry out this study during the test period of the AIX/370 system on the 3090/60. More especially, the assistance of J. D. Birman, F. Hamet, and Dr. M. Pelissier for the adaptation of the MONSTERGAUSS program to AIX/370 is gratefully acknowledged.

REFERENCES AND NOTES

1 - (a) A. Sevin ; D. Masure ; C. Giessner-Prettre ; M. Pfau ; *Helvetica Chimica Acta* **1990**, *73*, 552. (b) A. Sevin ; J. Tortajada ; M. Pfau ; *J. Org. Chem.* **1986**, *51*, 2671. (c) A. Sevin ; J. Maddaluno ; C. Agami ; *J. Org. Chem.* **1987**, *52*, 5611. (d) A.E. Dorigo ; K. Morokuma ; *J. Am. Chem. Soc.* **1989**, *111*, 6524. (e) Y. Li ; M.N. Paddon-Row ; K.N. Houk ; *J. Am. Chem. Soc.* **1988**, *110*, 3684. (f) P. Caramella ; N.G. Fondan ; M.N. Paddon-Row ; K.N. Houk ; *J. Am. Chem. Soc.* **1981**, *103*, 2438. (g) R.D. Bach ; G.J. Wolber ; *J. Am. Chem. Soc.* **1985**, *107*, 1352 and references cited therein.

2 - HSAB L. Pearson ; Hard and Soft Acid and Bases, Dowden, Hutchinson and Ross Inc., Strondsburg, Pa. USA ; 1973.

3 - (a) J. d'Angelo ; A. Guingant ; C. Riche ; A. Charioni ; *Tetrahedron Lett.* **1988**, *29*, 1989. (b) J.E. Bäckvall ; F. Rise ; *Tetrahedron Lett.* **1989**, *30*, 5347.

4 - W.J. Pietro ; M.M. Francl ; W.J. Hehre ; D.J. De Frees ; J.A. Pople ; J.S. Binkley ; *J. Am. Chem. Soc.* **1982**, *104*, 5039.

5 - M. Peterson, Department of Chemistry, University of Toronto (Canada); R. Poirier, Department of Chemistry, Memorial University of Newfoundland (Canada).

6 - K. Morokuma; *J. Chem. Phys.* **1971**, *55*, 1236.

7 - (a) K. Morokuma ; *Accounts Chem. Res.* **1977**, *10*, 294. (b) K. Kitaura ; K. Morokuma ; *Int. J. Quantum Chemistry* **1976**, *X*, 325.

8 - R. Carri ; R. Bonaccorsi ; J. Tomasi ; *Theoretica Chimica Acta* **1985**, *68*, 271.

9 - (a) B.J. Smith ; L. Radom ; *J. Am. Chem. Soc.* **1990**, *112*, 7525. (b) F.J. Lovas ; F.O. Clark ; E. Tiemann; *J. Chem. Phys.* **1975**, *62*, 1925. (c) K. Müller ; L. Brown ; *Helvetica Chimica Acta* **1978**, *61*, 1407.

10 - (a) T. Minato ; S. Yamabe ; *J. Am. Chem. Soc.* **1985**, *107*, 4621 and references cited therein. (b) S. Shi ; R.J. Boyd ; *J. Am. Chem. Soc.* **1989**, *111*, 1575. (c) M. J. Pellerite; J. I. Brauman; *J. Am. Chem. Soc.* **1983**, *105*, 2672.

11 -B. Toyonaga; M. R. Peterson; G. H. Schmid; I. G. Csizmadia; *J. of Molecular Structure-Theochem*, **1983**, *11*, 363.

12 - (a) H.B. Bürgi ; J.D. Dunitz ; E. Shefter ; *J. Am. Chem. Soc.* **1973**, *95*, 5065. (b) H.B. Bürgi ; J.M. Lehn ; G. Wipf ; *J. Am. Chem. Soc.* **1974**, *96*, 1956. (c) H.B. Bürgi ; J.D. Dunitz ; J.M. Lehn ; G. Wipf ; *Tetrahedron* **1974**, *30*, 1563. (d) H.B. Bürgi ; J.D. Dunitz ; *Acc. Chem. Res.* **1983**, *16*, 153. (e) N.T. Anh ; *Top. Curr. Chem.* **1980**, *88*, 145 for a review. (f) G.J. Mc Garvey ; J.M. Williams ; *J. Am. Chem. Soc.* **1985**, *107*, 1435. (g) E. Buncel ; S.S. Shaik ; I.H. Um ; S. Wolfe ; *J. Am. Chem. Soc.* **1988**, *110*, 1275. (h) R.R. Fraser ; M. Stanciulescu ; *J. Am. Chem. Soc.* **1987**, *109*, 1580. (i) E.P. Lodge ; C.H. Heathcock ; *J. Am. Chem. Soc.* **1987**, *109*, 2819.

13 - Another type of qualitative argument might be advocated, mostly based on experimental results : an antiperiplanar arrangement of the electronic densities is found in the anti geometry. This effect is likely to rely on dynamic aspects of reactivity, and therefore might not be taken into account in the present case where only static electronic effects are considered.

(*Received in Belgium* 22 *January* 1993; *accepted* 22 *February* 1994)