CROATICA CHEMICA ACTA CCACAA 57 (5) 911—925 (1984)

YU ISSN 0011-1643
CCA-1502 UDC 541
Original Scientific Paper

A Quantitative Analysis of the Role of Non-Bonded and Geminal Interactions in H_2N—X Molecules

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Received April 24, 1984

In this paper we describe the results obtained in a quantitative analysis of the role of the non-bonded and geminal interactions in the molecules H_2N—X with X = H, F, Cl, OH, SH. The analysis is performed in the framework of *ab initio* SCF—MO computations and the energy effects associated with the various types of orbital interactions are estimated using either a total energy approach or a quantitative PMO treatment. The energy effects of the non-bonded and geminal interactions are computed separately, using a suitable set of fragment orbitals. It is found that both types of interactions are important to determine the inversion barrier, with the geminal interactions playing the largest effect. It is also found that to rationalize the trend of the inversion barriers we have to include also the repulsive effects associated with the interactions of the singly occupied orbitals of the three ligands.

1. INTRODUCTION

Experimental and theoretical results[1] indicate that the geometry and the inversion barrier of NH_3 is significantly affected by the replacement of an hydrogen atom with an electronegative substituent. The preferred geometry of NH_3 seems to be adequately rationalized by simple MO theory[2-7]: the dominant factor has been suggested to be the geminal interaction between the original highest occupied MO (HOMO) and the original lowest unoccupied MO (LUMO), brought about by the pyramidalization. In the substituted molecules H_2N—X the situation is less clear. In fact, the replacement of an hydrogen atom with an electronegative substituent introduces significant changes in the magnitude of the HOMO-LUMO geminal interaction and introduces also large nonbonded interactions. Since both these effects can be large, it is very difficult to assess in terms of a qualitative analysis their relative importance.

In recent papers[8-10] we have described a procedure which provides estimates, in the framework of *ab initio* SCF-MO computation, of the energy effects associated with the various types of interactions occuring in a given molecule. This computational procedure is applied here for determining the relative magnitude of the energy effects associated with either the HOMO-LUMO geminal interaction or the non-bonded interactions in the H_2N—X molecules with X = F, Cl, OH, SH. For comparative purposes we have also determined the energy effect associated with the HOMO-LUMO interaction in NH_3. These energy effects are computed in terms of SCF-MO total energy values obtained in the absence of the interactions under examination (Total Energy approach) and also in terms of Perturbational MO expressions (PMO approach). We have already pointed out that the combined use of these two types of quantitative analysis provides a better understanding of the role played by the various factors which control a structural problem.

2. COMPUTATIONAL PROCEDURE

We describe first the procedures used here to compute the energy effects associated with the various types of orbital interactions occuring in NH_3, which are illustrated in Figure 1.

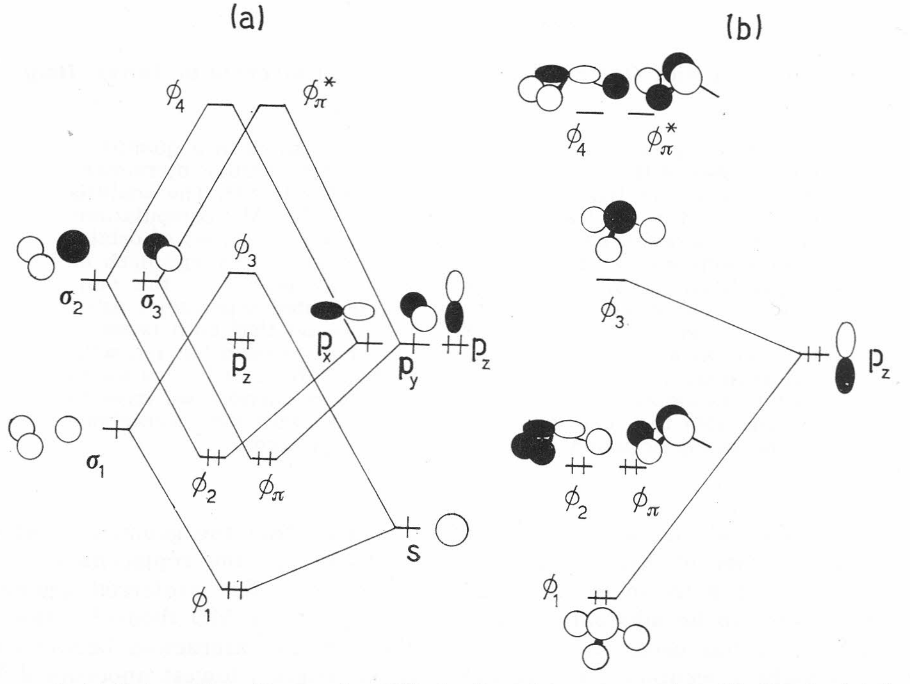

Figure 1. (a) Interaction digram for NH_3 in the planar geometry. (b) Geminal interactions occuring with pyramidalization.

We have first used a total energy approach[8,10] where we have carried out calculations of the total energy with (E_T) and without (E_T^0) the interactions involving the $2p_z$ orbital (*i. e.* $2p_z - \phi_1$ and $2p_z - \phi_3$). With these results we have constructed potential energy curves, with and without the energy effects associated with the geminal interactions involving the $2p_z$ orbital. From the comparative analysis of these curves it is possible to obtain information about the effect of these geminal interactions upon the geometry and the inversion barrier of NH_3. Furthermore the difference between the two curves at the same pyramidalization angle ($E_T - E_T^0$) provides an estimate of the energy effect associated with these geminal interactions.

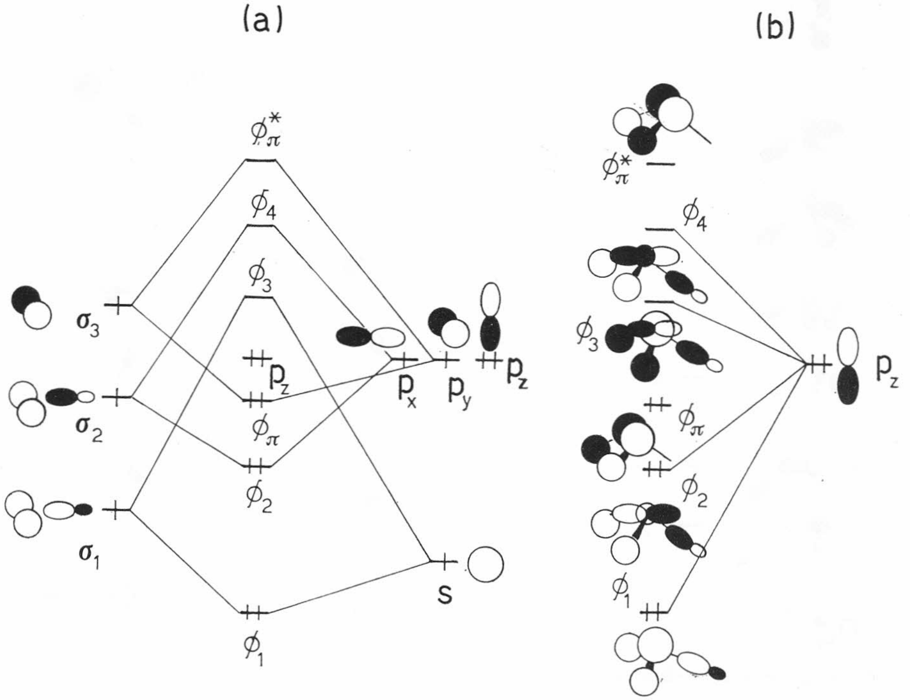

Figure 2. (a) Interaction diagram for H_2N—X in the planar geometry. (b) Geminal interactions occuring with pyramidalization.

We have also performed a quantitative PMO analysis[8-10] where the NH_3 molecule has been dissected according to the two interaction diagrams shown in Figure 1. Therefore this analysis provides information about the energy effects of all the interactions illustrated in Figure 1. However, since these interactions are large, a PMO treatment might not be able to provide reliable estimates of the related energy effects. For this reason we consider here as significant only the trend of these energy effects.

In H_2N—X type molecules the computation of the energy effects associated with the geminal interactions is complicated by the concomitant presence of non-bonded interactions. We have, therefore, defined a basis set of fragment orbitals which allows to compute separately the energy effects associated with these two types of orbital interactions. To this purpose we have dissected the molecule in the following fragments:

1. the $2p_z$ atomic orbital of the nitrogen atom;
2. the remaining orbitals of the H_2N — fragment;
3. the orbitals of the X substituent.

We have then computed the fragment localized MO's of X and we have allowed the σ_x singly occupied orbital to mix with the orbitals of fragment 2 The basis set obtained in such a way involves the following three sets of orbitals: the non-interacting $2p_z$ lone pair on nitrogen, the doubly occupied and

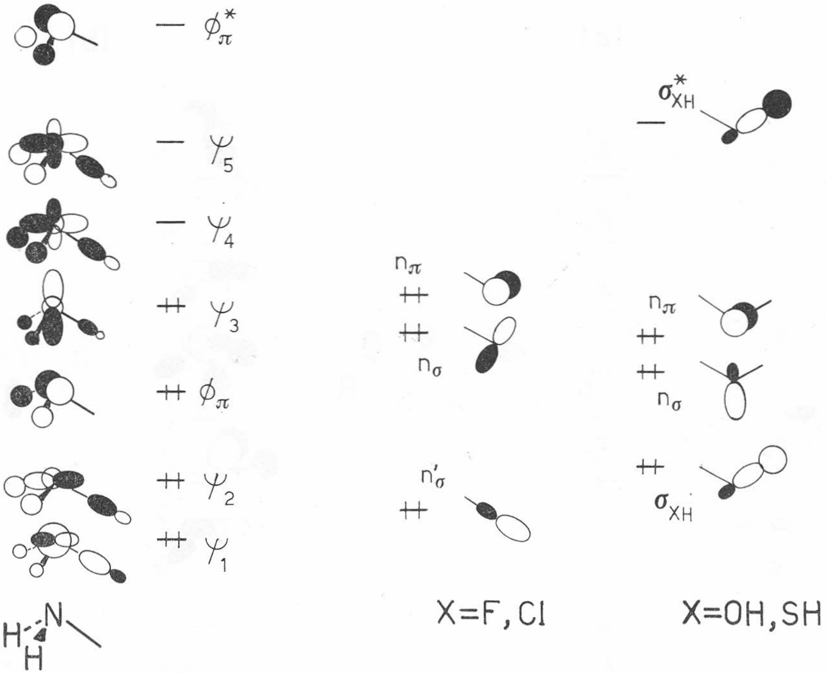

Figure 3. Non-bonded interactions occuring in the H_2N—X molecules.

vacant orbitals obtained by mixing σ_x with the remaining orbitals of the H_2N — fragment and the doubly occuiped and vacant orbitals of the *X* fragment. This basis set, which is illustrated in Figures 2b and 3 is particularly suitable to analyze separately the effects of the non-bonded and of the geminal interactions.

We have first computed the various energy effects with a total energy approach, where we have carried out the following total energy calculations:

i) calculations where all the interactions involving the orbitals of the X fragment have been decoupled. Therefore in this computation we have allowed the $2p_z$ orbital to mix with the orbitals of fragment 2: the resulting orbitals are illustrated in Figure 3 and correspond to the situation of a pseudo NH_3 molecule where a 1*s* hydrogen orbital has been replaced by the σ_X singly occupied orbital. This energy value is denoted with $E_T{}^0$ (1).

ii) calculations where, in addition to the non-bonded interactions described in i), also the geminal interaction involving the $2p_z$ orbital have been decoupled. This energy value is denoted with $E_T{}^0$ (2).

At both these computational levels we have computed potential energy curves with respect to the pyramidalization angle: therefore one curve is computed without the energy effects associated with the non-bonded interactions and the other curve is computed without the energy effects associated with either the non-bonded or the geminal interactions. The comparison between these two curves and the potential energy curve computed in terms of the total energy (E_T) provides information about the effect of the two types of interactions upon the geometry and the inversion barrier of the H_2N—X molecules under examination.

Furthermore the various energy differences provide estimates of the energy effects associated with these interactions. In particular $E_T - E_T^0\,(1)$ represents the energy effect associated with the non-bonded interactions and $E_T^0\,(1) - E_T^0\,(2)$ that associated with the geminal interactions involving the $2p_z$ orbital.

We have also performed the following two types of quantitative PMO analysis:

i) a quantitative PMO analysis of the non-bonded interactions where we have computed the energy effects between the two sets of orbitals described in Figure 3.

ii) a quantitative PMO analysis of the geminal interactions where we have computed the energy effects associated with the interactions between the $2p_z$ orbital and the doubly occupied and vacant orbitals of fragment 2, *i. e.* the interactions shown in Figure 2b.

These two types of analysis provide additional information on the factors determining the trends of the various types of energy effects.

3. RESULTS AND DISCUSSION

The computational results are summarized in the Tables I—IV and in the Figures 4—8. All the computations have been performed at the STO-3G level[11] and the SCF values have been computed with the GAUSSIAN 80 series of programs[12]. The potential energy curves for H_2N—OH and H_2N—SH have been computed for the trans conformers, which represent the most stable isomer at the STO-3G level.[13,14]

To facilitate the orbital decoupling in NH_3 we have used a reference system where the z axis coincides with the ternary symmetry axis and therefore with the direction of the non-interacting nitrogen lone pair. The situation is less clear in the H_2N—X molecules where there is not anymore a ternary axis. In such cases we have chosen a reference system where in the HOMO of the H_2N—X molecule computed in the absence of the non-bonded interactions (*i. e.* the ψ_3 orbital of Figure 3), the component of the $2p_x$ orbital is zero.

In the Tables I and II and in the Figures 4—9 the pyramidalization angle α is the complement to 180^0 of the angle between the C—X axis and the HNH plane, while the inversion barrier is the energy difference between the total energy values of the ground state and of the transition state to inversion.

Experimentally only the inversion barriers of NH_3[15] and H_2N—Cl[16] have been determined: the experimental values for NH_3 is 5.80 kcal/mol and that for H_2N—Cl a value in the range 10—11.4 kcal/mol. These values can be compared with those computed at the STO-3G level of 11.2 kcal/mol for NH_3 and 16.6 kcal/mol for H_2N—Cl. Therefore this computational level seems to overestimate the inversion barriers. However, since the trend of these values seems to be correct, this computational feature should not affect significantly the validity of the present study, which has the purpose of analyzing the nature and relative importance of the factors controlling the geometry and inversion barrier in H_2N—X type molecules.

TABLE I

Total Energy Values[a] *(a. u.) and Geometrical Parameters*[b] *Computed at the STO-3G Level for the Molecules* $H_2N—H$, $H_2N—F$, $H_2N—Cl$ *at various Values of the Pyramidalization Angle* α[c] *(degrees)*

α	0.00	20.00	35.00	50.00	MIN.[d]	80.00	95.00
$H_2N—H$							
r (N—H)	1.0054	1.0081	1.0135	1.0215	1.0325	1.0427	1.0567
< HNH	120.00	118.15	115.81	111.27	104.16	96.64	86.35
E_T	—55.437665	—55.440301	—55.445313	—55.451466	—55.455420	—55.450474	—55.426204
E_T^0	—55.437665	—55.438810	—55.440411	—55.440642	—55.434971	—55.419871	—55.379532
$H_2N—F$							
r (N—F)	1.3680	1.3684	1.3701	1.3751	1.3872	1.4053	1.4366
r (N—H)	1.0155	1.0191	1.0270	1.0378	1.0488	1.0544	1.0567
< HNH	124.26	121.02	115.16	108.62	103.24	101.12	101.56
< HNF	117.87	117.55	116.05	112.02	104.35	96.34	86.84
E_T	—152.843037	—152.847262	—152.855718	—152.866151	—152.872257	—152.866331	—152.843686
E_T^0 (1)	—152.697754	—152.700551	—152.706768	—152.715704	—152.722691	—152.719013	—152.698339
E_T^0 (2)	—152.697754	—152.698477	—152.699667	—152.700429	—152.697839	—152.688086	—152.663127
$H_2N—Cl$							
r (N—Cl)	1.7271	1.7303	1.7390	1.7552	1.7860	1.8101	1.8554
r (N—H)	1.0131	1.0163	1.0232	1.0329	1.0436	1.0473	1.0495
< HNH	124.88	121.88	116.38	110.00	103.96	102.30	102.10
< HNCl	117.56	117.16	115.58	111.64	102.67	96.26	86.86
E_T	—509.402518	—509.405998	—509.413087	—509.422277	—509.429033	—509.425998	—509.410406
E_T^0 (1)	—509.309489	—509.311661	—509.316730	—509.325318	—509.337753	—509.314520	—509.336617
E_T^0 (2)	—509.309755	—509.309989	—509.310216	—509.310231	—509.309209	—509.306872	—509.296146

[a] E_T is the Total Energy of the composite system, E_T^0 (1) is the Total Energy when the non-bonded Interactions are decoupled and E_T^0 (2) is the Total Energy when both the geminal interactions and the non-bonded Interactions are decoupled.

[b] Bond Lengths are in Å and angles in degrees.

[c] α is the complement to 180^0 of the angle between the bisector of the HNH angle and the N—X bond.

[d] This angle corresponds to the optimized pyramidalization angle and its value is 66.55^0, 66.48^0, 69.13^0, for $H_2N—H$, $H_2N—F$ and $H_2N—Cl$, respectively.

TABLE II

Total Energy Values[a] *(a. u.) and Geometrical Parameters*[b] *Computed at the STO-3G Level for the Molecules H_2N—OH, H_2N—SH at various Values of the Pyramidalization Angle* α[c] *(degrees)*

α	0.00	20.00	35.00	50.00	MIN.[d]	80.00	95.00
H_2N—OH							
r (N—O)	1.3933	1.3969	1.4025	1.4119	1.4270	1.4477	1.4804
r (N—H)	1.0153	1.0182	1.0250	1.0345	1.0438	1.0493	1.0512
r (O—H)	1.0012	0.9987	0.9968	0.9954	0.9950	0.9956	0.9968
$<$ HNH	121.78	119.20	114.18	108.30	103.36	101.08	101.20
$<$ HNO	119.11	118.39	116.43	112.11	104.55	96.34	86.83
$<$ HON	104.01	102.83	101.88	101.24	101.44	102.27	103.56
E_T	—129.235309	—129.239980	—129.248088	—129.257663	—129.263062	—129.257349	—129.235840
E_T^0 (1)	—129.248869	—129.254529	—129.261027	—129.266662	—129.265822	—129.252699	—129.221415
E_T^0 (2)	—129.247802	—129.248047	—129.246838	—129.242340	—129.230760	—129.210059	—129.172299
H_2N—SH							
r (N—S)	1.6861	1.6937	1.7076	1.7280	1.7431	1.7864	1.8293
r (N—H)	1.0123	1.0149	1.0207	1.0287	1.0336	1.0423	1.0451
r (S—H)	1.3415	1.3393	1.3370	1.3349	1.3339	1.3328	1.3330
$<$ HNH	116.33	114.64	111.14	106.86	104.42	100.86	100.82
$<$ HNS	121.81	120.49	117.59	112.52	108.40	96.35	86.82
$<$ HSN	97.88	96.76	95.87	95.14	95.07	96.19	97.72
E_T	—448.608451	—448.610836	—448.614992	—448.619234	—448.620237	—448.610998	—448.589599
E_T^0 (1)	—448.555725	—448.558822	—448.561728	—448.563846	—448.563089	—448.549396	—448.524102
E_T^0 (2)	—448.555703	—448.555031	—448.551821	—448.544704	—448.537170	—448.507657	—448.472716

[a] E_T is the Total Energy of the Composite system, E_T^0 (1) is the Total Energy when the non-bonded Interactions are decoupled and E_T^0 (2) is the Total Energy when both the geminal interactions and the non-bonded Interactions are decoupled.

[b] Bond Lengths are in Å and angles in degrees.

[c] α is the Complement to 180° of the angle between the bisector of the HNH angle and the N—X bond.

[d] This angle corresponds to the optimized pyramidalization angle and its value is 66.10°, 59.00° for H_2N—OH and H_2N—SH respectively.

3.1 *The Effect of the Geminal Interactions in NH_3*

The potential energy curves for NH_3, computed with respect to the pyramidalization angle, are shown in Figure 4. It can be seen that in the absence of the geminal interactions associated with the $2p_z$ orbital, the potential energy curve shows a very shallow minimum (~ 1 kcal/mol) at a pyramidalization angle of ~ 45^0. These results show very clearly that the geminal interactions $2p_z — \phi_1$, and $2p_z — \phi_3$ play a very important role in determining either the geometry or the inversion barrier of NH_3.

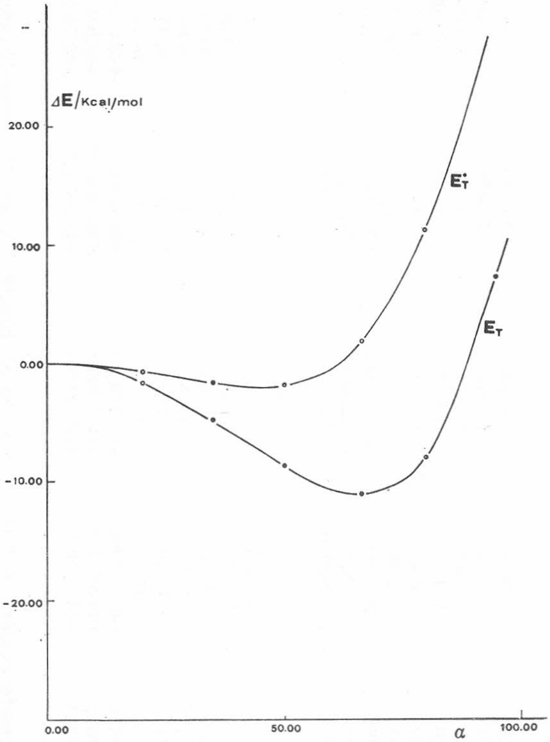

Figure 4. Potential energy curves for NH_3 computed with (E_T) and without (E_T^0) geminal interactions.

The difference between the two curves for a given pyramidalization angle (*i. e.* $E_T — E_T^0$) provides an estimate of the overall energy effect associated with the geminal interactions under examination. These values are listed in Table IV and it can be seen that at all points this energy effects is stabilizing and the stabilization increases with the increase of the pyramidalization angle.

The same result has also been obtained in terms of the quantitative PMO analysis, which shows that at all the pyramidalization angles the energy effect associated with the stabilizing two-electron interaction $2p_z — \phi_3$ dominates over that associated with the destabilizing four-electron interaction $2p_z — \phi_1$.

The quantitative PMO analysis provides also the following information:

(i) the energy effect associated with the interactions $2s — \sigma_1$, $2p_x — \sigma_2$ and $2p_y — \sigma_3$ tend to become less stabilizing with the increase of the pyramidalization angle.

(ii) the first order stabilization of the various MO's increases with the increase of the pyramidalization angle, as indicated by the trend of the various orbital energies.

(iii) the interaction of the three singly occupied 1*s* hydrogen orbitals becomes more destabilizing increasing the pyramidalization angle. This destabilizing effect should become dominant for large pyramidalization angles.

Therefore the behaviour of the potential energy curve in the absence of the geminal interactions suggest that the first order effect dominates for small values of the pyramidalization angle where the potential energy curve shows a slight decrease, while the other effects, and in particular that associated with the interaction of the three singly occupied 1*s* hydrogen orbitals, dominate at larger angle values where the potential energy curve rapidly increases. Therefore, the geometry and the inversion barrier of NH_3 seem to be mainly determined by the balance between the stabilizing energy effect associated with the geminal interactions involving the $2p_z$ lone pair and the repulsive effect associated mainly with the interaction of the three hydrogen orbitals.

3.2. *The Effect of the Non-Bonded Interactions in H_2N—X*

The potential energy curves computed in the absence of the energy effects associated with the non-bonded interactions show a shape similar to those computed in terms of the total energy values: in all cases, in fact, the molecules remain strongly pyramidal. The barrier, in the absence of these interactions, decreases in H_2N—OH (~ 5 kcal/mol), H_2N—SH (~ 2.5 kcal/mol) and H_2N—F (~ 2.5 kcal/mol) and increases in H_2N—Cl (~ 2 kcal/mol). These different effects are caused by the different behaviour of the energy effects associated with the non-bonded interactions with the pyramidalization. In all cases, in fact, this energy effect initially decreases with the increase of the pyramidalization angle (*i. e.* becomes more stabilizing or less destabilizing, see Table III) and then increases. However the extent of this decrease or the value of the pyramidalization angle at which the trend reverses vary in the various cases and cause different effects. In H_2N—OH, H_2N—SH and H_2N—F the energy effect decreases till large pyramidalization angles. The decrease is small in H_2N—F and H_2N—SH, so that the effect upon the barrier is also small, and larger in H_2N—OH, causing a larger effect on the barrier. In H_2N—Cl the energy effect initially decreases slightly and begins to increase earlier than in the other cases: as a consequence the pyramidalization angle and the barrier increase.

3.3. *The Effect of the Geminal Interactions in H_2N—X*

Information about the effect of the geminal interactions can be obtained from the comparison of the potential energy curve computed in terms of $E_T{}^0$ (1), the total energy in the absence of the non-bonded interactions, with that computed in terms of $E_T{}^0$ (2), the total energy in the absence of either the non-bonded or the geminal interactions. It can be seen from the Figures 5—9 that, when we remove also the geminal interactions, the potential energy curve shows a shallow minimum (for X = F and Cl) or becomes completely repulsive (for X = OH and SH). Therefore also in the H_2N—X molecules, these interactions are of critical importance for determining either the geometry or the inversion barrier.

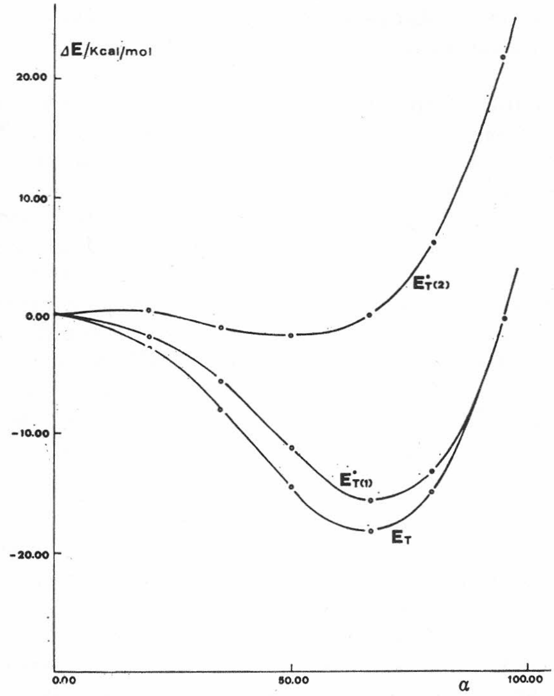

Figure 5. Potential energy curves for $H_2N—F$ computed with all types of interactions (E_T), without the non bonded interactions (E_T^0 (1)) and without either the non-bonded or the geminal interactions (E_T^0 (2)).

In all cases the energy effect associated with these interactions is stabilizing and becomes more stabilizing increasing the pyramidalization angle (see Table IV). Furthermore the energy effect associated with these interactions is significantly larger than the variation of the energy effect caused by the non-bonded interactions (see the IB values in Table III).

TABLE III

Energy Effects[a] (kcal/mol) Associated with the Non-Bonded Interactions Computed at various Values of the Pyramidalization Angle α (degrees)

α	F		Cl		OH		SH	
	IB	ΔIB	IB	ΔIB	IB	ΔIB	IB	ΔIB
0	—91.17	0.00	—58.38	0.00	8.51	0.00	—33.09	0.00
20	—92.06	—0.89	—59.20	— 0.82	9.13	— 0.62	—32.64	—0.55
35	—93.47	—2.30	—60.46	— 2.08	8.12	— 0.39	—32.42	—0.33
50	—94.41	—3.24	—60.84	— 2.46	5.65	— 2.86	—34.76	—1.67
Min.[b]	—93.85	—2.68	—57.28	— 1.10	1.73	— 6.78	—35.86	—2.77
80	—92.44	—1.27	—53.01	+ 5.37	—2.91	—11.42	—38.66	—5.57
95	—91.21	—0.04	—46.30	+12.08	—9.05	—17.56	—41.10	—8.01

[a] IB = $E_T — E_T^0$ (1); ΔIB = IB (α) — IB (o)

[b] See Tables I and II.

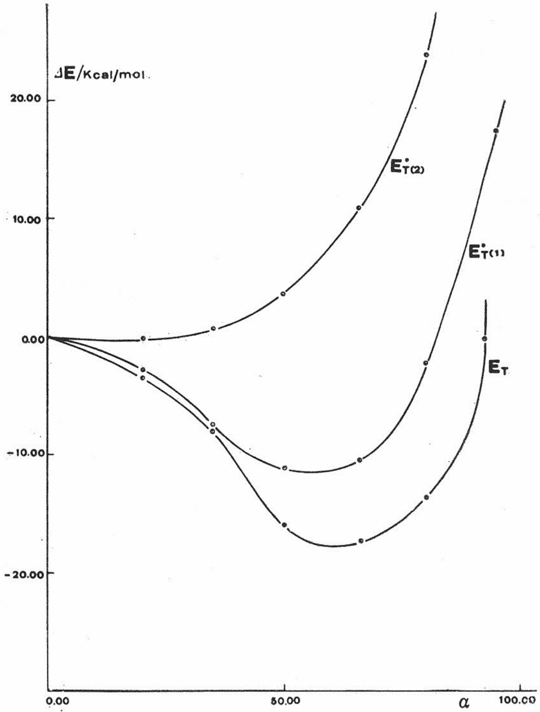

Figure 6. Potential energy curves for H_2N—OH computed with all types of interactions (E_T), without the non-bonded interactions (E_T^0 (1)) and without either the non-bonded or the geminal interactions (E_T^0 (2)).

This result indicates again the greater importance of the geminal over the non-bonded interactions for determining the inversion barrier and geometry of these molecules.

The analysis of the results obtained with the quantitative PMO analysis provides additional information about these interactions. In particular:

(i) the energy effects associated with the interactions $2p_z — \phi_1$ and $2p_z — \phi_3$ are significantly larger, in absolute magnitude, than those associated with the interactions $2p_z — \phi_2$ and $2p_z — \phi_4$, whose effect is small in all cases, except for $2p_z — \phi_4$ when X = Cl. The relevant geminal interactions, *i. e.* $2p_z — \phi_1$ and $2p_z — \phi_3$ are those which correspond more closely to the geminal interactions occurring in NH_3.

(ii) in all cases the dominant contribution is that associated with the two-electron stabilizing interaction $2p_z — \phi_3$ (the HOMO-LUMO) interaction. Both the absolute value of the matrix element and the energy gap associated with this interaction decrease when the substituent changes along a row or along a column of the periodic table. Along a column the two effects balance, so that the resulting effect is of similar order of magnitude for the pair of substituents OH, SH and F, Cl. On the other hand, along a row, the matrix element dominates and the effect for the pair OH, SH is more stabilizing than that for the pair F, Cl.

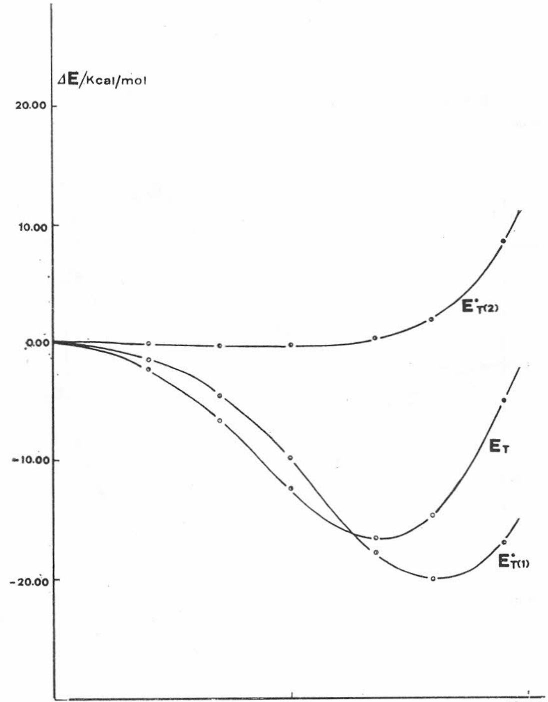

Figure 7. Potential energy curves for $H_2N—Cl$ computed with all types of interactions (E_T), without the non-bonded interactions (E_T^0 (1)) and without either the non-bonded or the geminal interactions (E_T^0 (2)).

The results of Table IV show that the overall energy effect associated with these interactions has a trend similar to that of the $2p_z — \phi_3$ energy effect, *i. e.* the overall energy effect has very similar magnitude for the pair OH, SH and for the pair F, Cl; furthermore the effect for the pair OH, SH is more stabilizing than that for the pair F, Cl.

TABLE IV

Energy Effects (E_T^0 (1) — E_T^0 (2), kcal/mol) Associated with the Geminal Interactions Involving the $2p_z$ Nitrogen Orbital (see Figures 1 and 2) Computed at various Values of the Pyramidalization Angle α (degrees)

α	H	F	Cl	OH	SH
0	0.00	0.00	0.00	0.00	0.00
20	— 0.94	— 1.30	— 1.05	— 4.07	— 2.38
35	— 3.08	— 4.46	— 4.09	— 8.90	— 6.22
50	— 6.79	— 9.59	— 9.47	—15.26	—12.01
Min.[a]	—12.83	—15.59	—17.91	—22.00	—16.26
80	—19.20	—19.41	—21.74	—26.76	—26.19
95	—29.29	—22.09	—25.40	—30.82	—32.24

[a] See Tables I and II.

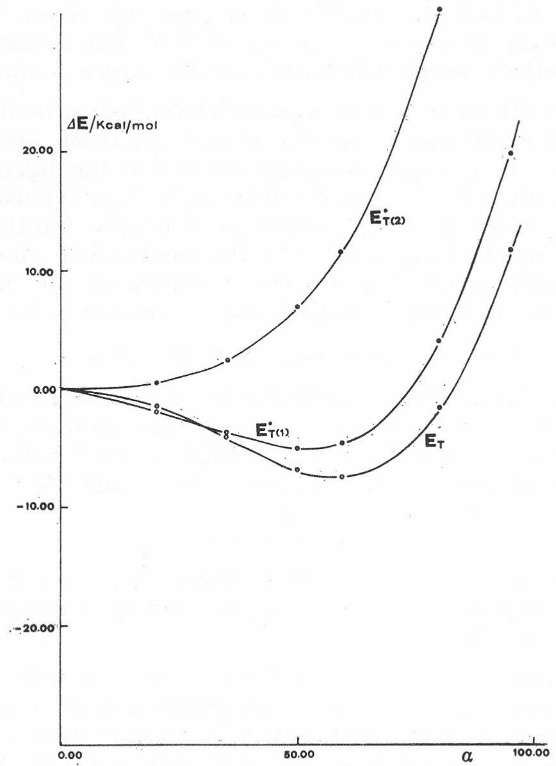

Figure 8. Potential energy curves for $H_2N—SH$ computed with all types of interactions (E_T), without the non-bonded interactions (E_T^0 (1)) and without either the non-bonded or the geminal interactions (E_T^0 (2)).

From the E_T^0 curve in Figure 4 and the E_T^0 (1) curves in Figures 5—8, it can be seen that the inversion barriers in the absence of the non-bonded interactions increase in the order:

$$H_2N—SH < H_2N—H < H_2N—OH < H_2N—F < H_2N—Cl$$

This trend can not be rationalized only in terms of the energy effects associated with geminal interactions. To obtain a better understanding we have to include into the analysis also the repulsive effects associated with the remaining interactions. Information about the relative magnitude of these effects can be obtained from a comparison of the E_T^0 (2) curves in the various $H_2N—X$ molecules (in the case of NH_3 we have to compare the E_T^0 curve). It can be seen that the repulsive effects increase in the order

$$H_2N—Cl < H_2N—F < H_2N—OH < NH_3 < H_2N—SH$$

The inversion barriers in the absence of the non bonded interactions arise from the combination of the geminal energy effects and of the repulsive effects: these two energy contributions have opposite signs and therefore largely cancel. Even if for determining the magnitude of the barriers both contributions are important, the trend of the barriers seems to be mainly controlled by the repulsive effects: in fact, the smaller is the repulsive effect, the larger is the barrier. In particular the smaller barrier in $H_2N—SH$ is associated with the larger repulsive effect, which dominates over the larger geminal energy effect.

The repulsive effects should be mainly determined, at least for large values of the pyramidalization angles, by the energy repulsion associated with the interaction of the three singly occupied orbitals of the ligands, *i. e.* the two 1*s* hydrogen orbitals and the hybrid orbital of X. This repulsive effect should critically depend on the geometry, and in particular on the HNH angle, whose value is, in turn, significantly affected by the non bonded interactions associated with the doubly occupied and vacant orbitals of the X substituent. In particular it can be seen that the HNH angle increases in the order

$$H_2N—SH < H_2N—OH < H_2N—F < H_2N—Cl$$

and the larger is this angle the smaller is the repulsive effect.

Therefore the non-bonded interactions operate upon the inversion barrier also indirectly through changes in the geometries, which affect the magnitude of the various contributions and therefore the magnitude of the inversion barrier.

4. CONCLUSIONS

In this paper we have analyzed the effect of the non-bonded and geminal interactions upon the geometry and inversion barrier of the molecules $H_2N—X$ with X = F, Cl, OH, SH.

It has been found that the non-bonded interactions affect in some extent the inversion barriers and only slightly the pyramidalization angles. The effect on the barrier varies with the molecule: in particular these interactions cause an increase of the barrier for $H_2N—OH$, $H_2N—SH$ and $H_2N—F$ and a decrease in $H_2N—Cl$. On the other hand the geminal interactions play a major role either for determining the geometry or the inversion barrier: in fact, in the absence of these interactions, the various molecules become planar or nearly so.

It has also been found that the trend of the inversion barriers can not be rationalized only in terms of the energy effects associated with the non-bonded and geminal interactions. To obtain a better understanding, we have to include also the repulsive effects which, at least for large values of the pyramidalization angles, should be mainly determined by the energy repulsion associated with the interaction of the three singly occupied orbitals of the ligands, *i. e.* the two 1*s* hydrogen orbitals and the hybrid orbital of X.

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SAŽETAK

Kvantitativna analiza uloge neveznih i geminalnih interakcija kod $H_2N—X$ molekula

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Opisani su rezultati kvantitativne analize uloge neveznih i geminalnih interakcija kod $H_2N—X$ ($X = H$, F, Cl, OH, SH) molekula. Analiza je provedena u okviru *ab-initio* SCF—MO-scheme, a energijski efekti orbitalnih interakcija procijenjeni su s pomoću kriterija ukupne energije i/ili kvantitativnog PMO-postupka. Efekti neveznih i geminalnih interakcija izračunani su odvojeno, uporabom pogodnih skupova orbitala molekularnih fragmenata. Proizlazi da su obje vrste interakcija važne za računanje barijera inverzije proučavanih molekula, pri čemu je utjecaj geminalnih interakcija veći. Ustanovljeno je također da se trend promjena inverzijskih barijera može racionalizirati samo ako se uzmu u obzir i efekti odbijanja povezani s interakcijama jednostruko zaposjednutih orbitala liganada.