CHAPTER TWO

"RESULTS AND DISCUSSIONS"

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PART ONE : EFFECT OF SUBSTITUENTS ON THE STABILITY AND GEOMETRY OF METHYL AND SILYL RADICALS.

PART TWO : CONFORMATIONAL ANALYSIS FOR SILICON AND CARBON CENTERED RADICALS .

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PART ONE

(A) EFFECT OF SUBSTITUENTS ON THE STABILITY OF METHYL AND SILYL RADICALS.

(B) EFFECT OF SUBSTITUENTS ON THE GEOMETRY OF METHYL AND SILYL RADICALS.

(A) EFFECT OF SUBSTITUENTS ON THE STABILITY OF METHYL AND SILYL RADICALS

The structure of methyl radical has been studied extensively by experimental[1-8] and theoretical techniques. On the other hand, the structure of silicon radicals was determined mainly by experimental studies but few theoretical treatments are reported[44-49]. In this section the geometry and energetic properties of both methyl and silyl radicals are theoretically investigated.

To start with, a full geometry optimization was carried out using MNDO procedure at the UHF (unrestricted Hartree-Fock) level. The analysis of the electronic spectrum as well as the electron spin resonance (ESR) spectrum[5-8], in addition to a theoretical[25-30] treatment have shown that methyl radical is planar or nearly so. This is consistent with the results of this work since the bond angles in the methyl radical were found to be 119.999° and 120.005°. The heat of formation equals 25.79 kcal/mole and the total energy is -169.29 ev. On the other hand silyl radical has been found to aquire tetrahedral structure consistent with previous experimental results[46-50]. The bond angles were found to be 109.96° and 110.04°. The heat of formation is 38.22 kcal/mole and the total energy is -136.07 ev.

The pronounced difference in geometry on changing the

central atom from carbon to silicon was explained by Pauling[40] in terms of a simple quantum mechanical argument involving the electronegativity differences between the central atom and the substituent atom (hydrogen atom in both cases of methyl and silyl radicals). In case of methyl radical hydrogen is less electronegative than carbon and so the C-H bond orbitals will contain more s-character and the orbital occupied by the unpaired electron is of less s-character than in case of a tetrahedral bond orbitals which possess approximately 25% s-character.

The more s-character in the C-H bond leads to increased planarity of the radical. In other words one can say that the more s-character in the hybrid orbital the more it is expanded in space. As a result the bond pair-bond pair repulsion is large and this requires the maximum space separation between them which is attained by aquiring a bond angle of 120°. This rationalization explains the planarity of methyl radical and the use of almost a pure p-orbital for the odd electron. Conversely, in the case of silyl radical, hydrogen is more electronegative than silicon. This leads to an electron withdrawal of the bond pair towards the hydrogen atom. This in turn leads to a less s-character in the bond pair. Experimental as well as theoretical investigations have shown an sp^3 hyperdization on the silicon atom in silyl radical. The less s-character and the more p.character in an sp^3 hybrid orbital (compared to the high s-character and

less p-character in an sp^2 hybrid one) led to a more localized (less expanded) orbitals. Thus, the bond pair-bond pair repulsion is not as large as in the case of the sp^2 hybrid on the methyl radical. This explains the tetrahedral geometry of silyl radical and the planar geometry of methyl one (Fig. 1). Begum et al[132] have used similar arguments in studying other species of the type AlR_3^-, SiR_3, and PR_3^+.

The difference in electronegativity between the central atoms [carbon = 2.5 , silicon = 1.8] was also reflected on the electron density on the central atom. In methyl and silyl radicals it has been found that the charge density on carbon atom in the methyl radical equal -0.09 and that on silicon atom in the silyl radical equal +0.686.

Radical Stabilization Energy (RSE).

The effect of a substituent X on the stabilization or destabilization of methyl and silyl radicals is of considerable importance. Recently, many researches were devoted to study the effect of substituents on a radical stability and, to understand the nature of interactions between the orbitals of the substituents and the singly occupied molecular orbital SOMO of the radical center. The vast majority of these researches have involved kinetic studies[41-46]. However, Since the kinetic data provide

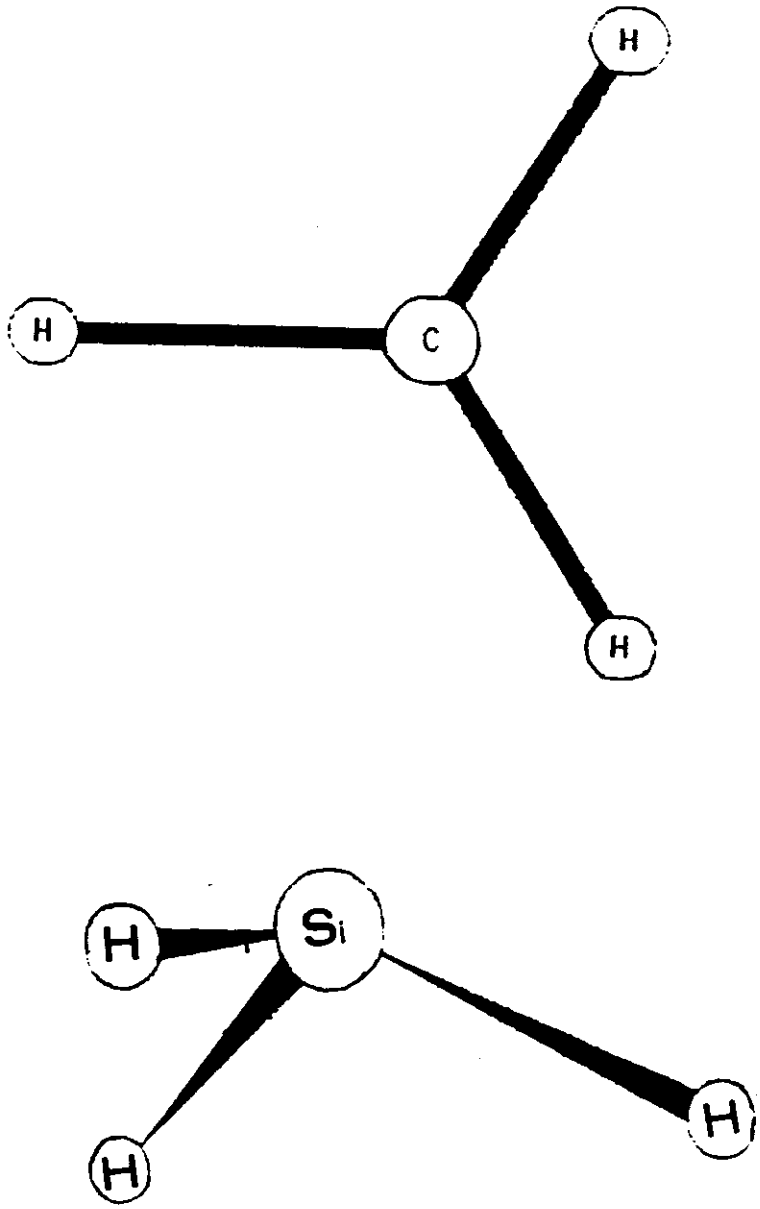


Fig (1) : Geometry of Methyl and Silyl Radicals.

informations only on the extent of interactions in the transition state, all the kinetic procedures were found to suffer from their inability to provide a quantitative determination of the completely formed free radical, and on the thermodynamic stabilizing effect of the substituents. To understand this effect in a very good way, one requires data derived on the completely formed free radicals that can be directly related to the radical stabilization energy (RSE) of the substituents. Dust and Arnold[84,85], had used the electron spin resonance methoed in studying the effect of substituents on benzyl radicals. They measured the ESR hyperfine coupling constants in substituted benzyl radicals and related them to the relative extents of spin delocalization, and this in turn is related to the stabilization exerted by the substituents on the benzyl radical. However,the main disadvantage of this method is that it is limited to the experimentally known compounds.

The thermodynamical stabilization energy of a chemical species was defined by Sana[61] and Leory on the basis that, the heat of atomization ΔH_a° of compound under consideration may be written as a sum of standard bond energy terms, that is determined from heats of atomization of reference compounds.

$$\Delta H_a^\circ = \sum N_{AB} E_{AB}^\circ \qquad [1]$$

They then considered that any compound having ΔH_a° which does

not obey equation [1] as stabilized or destabilized. Hence, they define the thermodynamical stabilization energy (SE°) by the relation :

$$SE^\circ = \Delta H^\circ_a - \sum N_{AB} \; E^\circ_{AB} \qquad [2]$$

SE° could aquire positive or negative values depending on whether the corresponding species is stabilized or destabilized. To calculate (SE°) of a radical using equation [2], one needs to know its heat of atomization and therefore its heat of formation. However, free radicals are experimentally not determined.

Recently a semiemperical procedure for determining radical stabilization energy RSE was developed. In this procedure the RSE is considered as the differences between the abilities of the attached groups to stabilize or destabilize a center relative to hydrogen atom as a substituent. It can be calculated by the isodesmic reaction

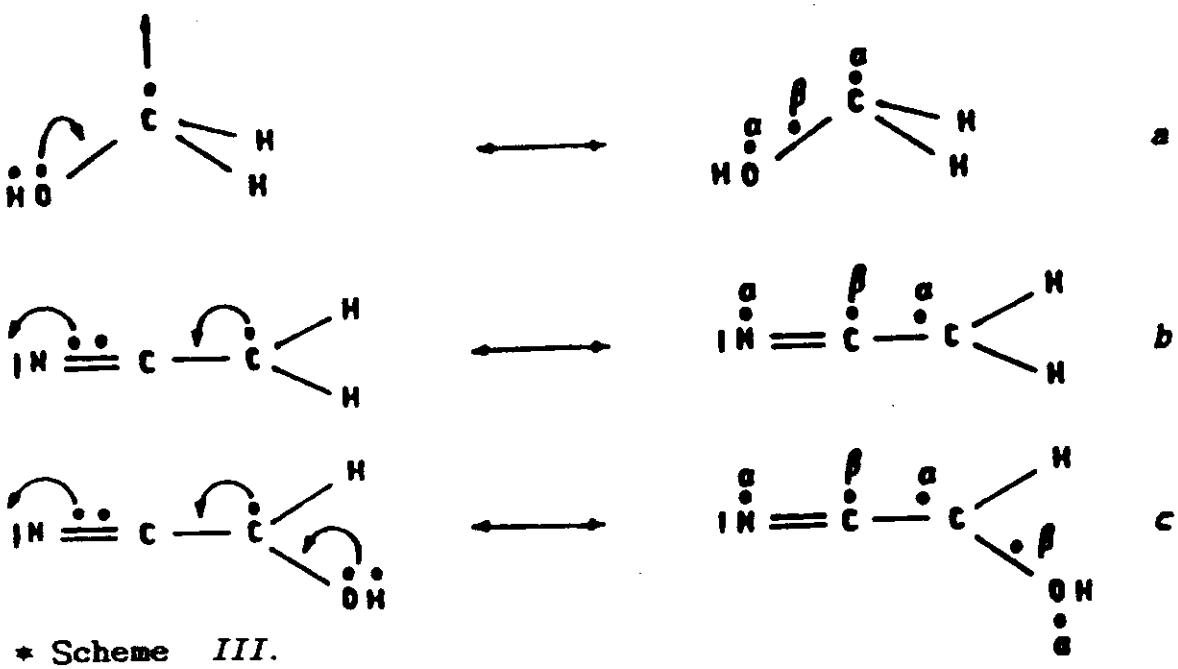
$$X_n\dot{A}H_{3-n} + AH_4 \longrightarrow X_nAH_{4-n} + \dot{A}H_3$$

$$RSE=\left[E_{tot}(X_n\dot{A}H_{4-n})+E_{tot}(\dot{A}H_3)\right]-\left[E_{tot}(X_n\dot{A}H_{3-n})+E_{tot}(AH_4)\right] \qquad [3]$$

This method was used by Daniel J.Pasto.[75]

The ability of a certain substituent on stabilizing or destabilizing a radical center is determined by the electronic nature of the substituent, the induced bond pair-

bond pair repulsion and the size of both the central atom and the substituent. It was found that stabilization or destabilization of a substituted radical can be correlated to the ability of that substituent on delocalizing or localizing the odd electron on the central atom. For example π-donor substituents such as hydroxy group remove the unpaired electron from α-carbon atom and the C_α-substituent bond has a three-electron bond character (Scheme *III-a*). On the other hand, π-acceptor substituents such as cyanide withdraw the unpaired electron towards the C_α-substituent bond which also has a three-electron bond character (Scheme *III-b*). Finally, a pair of substituents of opposite polarity (one is electron donor and the other is electron acceptor) delocalizes the unpaired electron, and the bonds between C_α (C-carrying the unpaired electron) and the substituents will both have a three electron bond character (Scheme *III-c*).



* Scheme *III*.

- Table (1). Spin densities of some carbon centered radicals

R·	$\rho_{\pi}^{a}(C_{\alpha})$
·CH_3	0.229
·CH_2 CH_3	0.249
·$CH(CH_3)_2$	0.262
·CH_2OH	0.283
·$CH(OH)_2$	0.366
·CHF_2	0.435
·CF_3	0.619

- Table (2). Theoretical and empirical values of some spin densities

R·	$\rho_{\pi}^{C_{\alpha}}$ emp	$\rho_{\pi}^{C_{\alpha}}$ theo
·CH_3	1.000	1.000
·CH_2 CN	0.906	0.855
·$CH(CN)_2$	0.832	0.769
·CH(CN)(OH)	0.786	0.757

The unpaired electron of π-carbon radicals is generally delocalized, this effect is important in captodative species, but in σ-carbon radicals it is more centered on the C_α atom. (Table 1) shows that $\rho_s(C_\alpha)$ increases upon substituting the hydrogen atom by an electron- donating group. It also indicats that as the number of electron donating group increases, $\rho_s(C_\alpha)$ increases. However, the effect of σ-donor groups such as CH_3 is small as compared to that of π-donor groups for example OCH_3, OH, F. If one considers the localization of the unpaired electron on the C_α- is maximum in $\cdot CH_3$, then delocalization increases by the substitution of an electron donor group for Hydrogen atom (Table 2) gives the values of π-spin densities of the α-carbon atom. The values of $\rho_s^\pi(C_\alpha)$ reflect that the unpaired electron in the hydroxycyano methyl radical has a maximum delocalization. This captodative effect - due to the presence of two groups with opposite polarity - is expected to be particularly important in the aminocyano- and amino ethyl radicals.

In this work, equation [3] was used to calculate the RSE for some carbon centered and silicon centered free radicals. The results are listed in (Table 3) for substituted methyl radicals and (Table 4) for substituted silyl radicals. A positive sign in these tables indicates stabilization of the radical. The results obtained are rationalized in the following manner.

Table (3). Radical stabilization energy for some carbon centered radicals.

Molecule	Total Energy EV	Radical	Total Energy EV	RSE EV
CH_4	- 185.1	CH_3	- 169.3	0.0
CH_3NH_2	- 406.5	CH_2NH_2	- 391.2	0.5
$CH_2(NH_2)_2$	- 627.9	$CH(NH_2)_2$	- 613.0	0.9
CH_3OH	- 507.5	CH_2OH	- 492.2	0.5
$CH_2(OH)_2$	- 830.1	$CH(OH)_2$	- 815.0	0.7
$CH(OH)_3$	-1152.8	$C(OH)_3$	-1137.8	0.8
CH_3F	- 647.7	CH_2F	- 635.2	3.3
CH_2F_2	-1116.1	CHF_2	-1100.9	0.6
CHF_3	-1581.7	CF_3	-1566.4	0.5
CH_3CN	- 505.0	CH_2CN	- 489.3	0.1
CH_2FNH_2	- 872.0	$CHFNH_2$	- 857.0	0.8

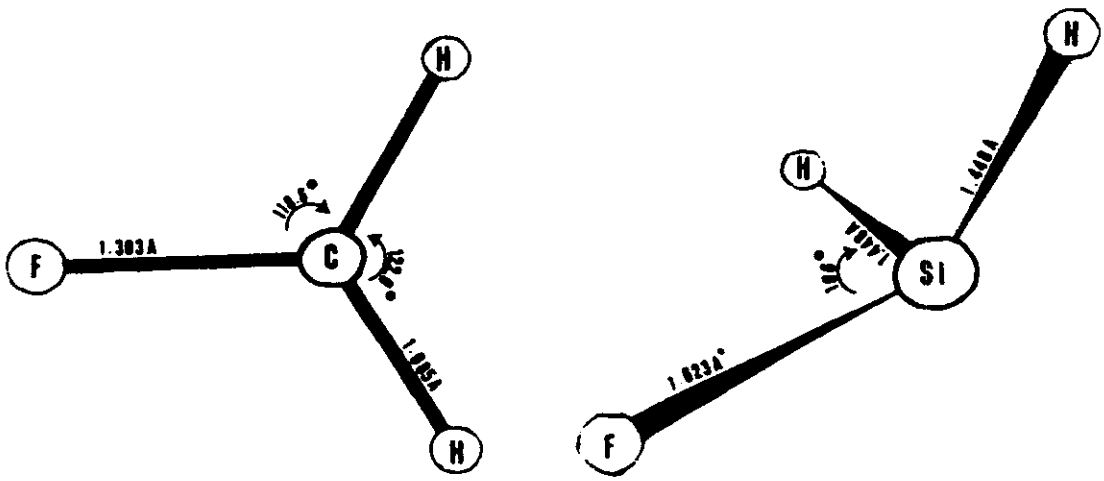
- Table (4). Radical stabilization energy for some silicon centered radicals.

Molecule	Total Energy EV	Radical	Total Energy EV	RSE EV
SiH_4	- 151.4	SiH_3	- 136.1	0.0
SiH_3NH_2	- 373.9	SiH_2NH_2	- 359.2	0.6
$SiH_2(NH_2)_2$	- 596.5	$SiH(NH_2)_2$	- 582.2	1.0
SiH_3OH	- 475.2	SiH_2OH	- 460.4	0.5
$SiH_2(OH)_2$	- 799.1	$SiH(OH)_2$	- 784.6	0.8
$SiH(OH)_3$	-1123.0	$Si(OH)_3$	-1108.7	1.0
SiH_3F	- 619.0	SiH_2F	- 604.1	0.4
SiH_2F_2	-1086.6	$SiHF_2$	-1072.1	0.7
$SiHF_3$	-1554.1	SiF_3	-1539.4	0.6
SiH_3CN	- 472.6	SiH_2CN	- 457.4	0.1
SiH_2FNH_2	- 841.6	$SiHFNH_2$	- 827.2	0.9

(I) Fluoro - Substituted Radicals.

In case of fluoro-substituted methyl radical it was noted that a single fluorine atom stabilizes the radical relative to a hydrogen atom. This is attributed to the delocalization of the odd electron on the radical center into the C-F bond. This delocalization will decrease the electron density on carbon atom and leads to stabilization. Such delocalization is promoted by the electron withdrawal properties of the electronegative fluorine atom. However, further fluorine substitution results in a decrease in the stabilization of the radical center. This is clear from the radical stabilization energy since it dropped from 3.3 ev in the case of fluoromethyl radical to a value of 0.6 ev in the case of di-fluoromethyl radical. This can be explained on the basis of lone pair-lone pair repulsion between the three lone pair of electrons on one fluorine atom and those on the other fluorine atom. The small size of both carbon and fluorine atoms (C-F bond length = 1.304 A°) makes this repulsion more significant in cases of di- and tri- fluoro-methyl radical. Hence, as the number of fluorine atom in the radical increases the repulsion increases and so the stabilization energy decreases (radical stabilization energy for $\cdot CHF_2$ equals 0.6 ev and that for $\cdot CF_3$ equals 0.5 ev). These results are consistent with previous calculations at the *ab initio* level[75,76].

It is interesting to compare the RSE as well as the geometry of $^{\cdot}CH_2F$ and $^{\cdot}SiH_2F$ radicals. To start with one has to remember that methyl radical is almost exactly planar whereas silyl radical is almost exactly tetrahedral. Substitution by a fluorine atom did not change the geometry of any of the two radicals significantly.



This is expected on the basis of the similarity in size of both hydrogen and fluorine atoms. The greater electronegativity of fluorine as compered to hydrogen did not affect the geometry, though it did affect the RSE. The RSE of $^{\cdot}CH_2F$, (3.3 ev) is much higher than that for $^{\cdot}SiH_2F$ (0.4 ev). Substitution by fluorine in methyl radical to give $^{\cdot}CH_2F$ has lowered significantly the charge density on carbon atom from - 0.09 in the case of $^{\cdot}CH_3$ to +0.007 in case of $^{\cdot}CH_2F$ and led to that stabilization. On the other hand substitution of F in silyl radical to give $^{\cdot}SiH_2F$ did not lower the charge density on silicon atom significantly. The charge density on silicon atom in silyl radical is not very high due to the large size of silicon atom, and the long

silicon- hydrogen bond. Concerning the case of difluorosilyl radical, it is more stabilized than the mono-substituted derivative [RSE for $\cdot SiH_2F$ = 0.4 ev for $SiHF_2$ = 0.7 ev]. This indicates that the electron withdrawing property of F-atom is thedominant factor in radical stabilization as it leads to a decreased charge density on the central atom. The big size of silicon atom (Si-F bond length is 1.63 A°) tenders the space separation between the F-atoms (in $\cdot SiHF_2$) to be large and thus decreases the repulsion between the lone pair of electrons on them. Meanwhile the second fluorine atom with its high electronegative character induces further delocalization of free electron on the central atom. Hence, the stabilization of the radical increases. In case of tri-fluorosilyl radical electron de-localization will definitly be greater than in the difluoro derivative, but the lone pair-lone pair repulsion between the lone electrons on the fluorine atoms becomes apparent. Hence, it has been found that $\cdot SiF_3$ is still more stabilized than $\cdot SiH_3$ but less stabilized than $\cdot SiHF_2$.

A comparison of RSE between $\cdot CHF_2$ and $\cdot SiHF_2$, $\cdot CF_3$ and $\cdot SiF_3$ is important. In both cases the RSE is larger for the silicon radicals than it is for carbon-centered radicals. In these cases, the charge density on the central atom is smaller in case of silicon radicals than it is in the case of carbon centered radicals. In addition the large size of silicon atom and consequently, the longer Si-F bond than the

C-F bond lowers the lone pair-lone pair electron repulsions on the different fluorine atom.

(II) Hydroxy Substituted Radicals.

Substitution by a hydroxy group in methyl radical leads to a relative stability of 0.5 ev. This indicates that hydroxymethyl radicals are more stabilized than methyl radicals. However, the stabilization energy is not directly proportional to the number of hydroxy groups substituted in the methyl radical. A mono- hydroxymethyl radical has a stabilization energy of 0.5 ev whereas a dihydroxymethyl radical has a stabilization energy of 0.7 ev and the trihydroxymethyl radical has a stabilization energy of 0.8 ev. In the case of the dihydroxy methyl radical two of the C-O bonds will have three-electron bond character, whereas in the trihydroxymethyl radicals the three C-O bonds have three electron bond character. As a result in the cases of both di- and tri- hydroxyradicals bond pair- bond pair repulsion is getting larger and larger and this lowers the stabilization expected to be proportional to the number of hydroxy substituents in the radical.

A similar behaviour is expected to be found in amino-substituted methyl radicals. Table (3) shows that this is the case. Radical stabilization energy is the same for $\cdot CH_2NH_2$ and $\cdot CH_2OH$ radicals although it is slightly higher

(0.9 ev) for $\cdot CH(NH_2)_2$ radical than for $\cdot CH(OH)_2$ radical (0.7 ev). The higher electronegativity of the oxygen atom over that of nitrogen atom is the reason for that behaviour.

An important result is the behaviour of hydroxy substituted silyl radicals. They behave almost exactly as the corresponding carbon-centered radicals. The RSE is the same for $\cdot CH_2OH$ and $\cdot SiH_2OH$, slightly higher for $\cdot SiH(OH)_2$ than for $\cdot CH(OH)_2$ and for $\cdot Si(OH)_3$ than for $\cdot C(OH)_3$. The larger size of silicon atom as well as its lower electronegativity (than that of carbon atom) leads to a less steric interaction between the hydroxy groups and also less lone pair-lone pair repulsion. This in turn leads to a slightly higher stability for di- and tri- hydroxy silyl radicals. A similar behaviour is found in the case of amino-substituted silyl radicals. Thus, RSE increases on increasing the amino substitution and it is higher than that incountered with methyl amino substituted radicals.

It is interesting to find that the RSE for $\cdot CHF(NH_2)$, 0.8 ev, larger than that for $\cdot CH_2(NH_2)$. The captodative effect is pronounced in the former radical than in the later one. The high electronegativity of fluorine atom will facilitate the donating properties of the amino group and lead to a lower charge density on the C_α atom.

It is found that the cyanomethyl and cyanosilyl

radicals have the lowest RSE compared to other substituted radicals. The difference in electronegativity between carbon atom and nitrogen atom is not so pronounced (2.5 and 3.0) and hence the electron withdrawing property of the cyano group is not significant. The captodative effect is weak and the $\rho_s^{\pi}(C_\alpha)$ is relatively large, 0.906, (Table 2) compared with 1.0 for methyl radical. This explains the small RSE for cyano methyl radical which is nicely reflected in its relatively large positive heat of formation (52.87 kcal/mol).

B: EFFECT OF SUBSTITUENTS ON THE GEOMETRY OF METHYL AND SILYL RADICALS.

The shape of radicals of the type AX_3 is determined by the nature of substituents as well as by the nature of the central atom A. Concerning the methyl and silyl radicals where both share the same substituents (X=H), the former was found to be planar (equilateral-triangular following the D_{3h} symmetry point group) consistence with theoretical and experimental results. While the latter was found to be pyramidal following the C_{3v} symmetry point group. Also for the same central atom while methyl radical is planar, tri-fluoromethyl radical is pyramidal. As a matter of fact the methyl radical is the only member among the studied series which is known to be completely planar. In most cases upon replacing any of the hydrogen atoms by another atom or group (X) the geometry of the radical deviates from planarity. The degree of deviation from planarity *i.e.* the degree of pyramidalisation depends mainly on the number of the valence electrons and on the electronegativity difference between the central atom (carbon or silicon in our case) and the substituents.

In this section the planar/pyramidal shapes of the studied radicals and the effect that substituents and the central atom induce in favour of one shape are rationalized quantitatively on the basis of the simple MO model

formulated by Mulliken[133] and Walsh[134], known as "Walsh diagrams". This MO model is based on Walsh's rule of maximization of overlap between atomic orbitals forming the occupied molecular orbitals. This implies that, changes in the molecular shape which increase the in-phase overlap between two atomic orbitals in the same molecular orbital will lower the energy of that molecular orbital, and changes in shape which increase out-of-phase atomic orbital's overlap will raise the energy of the molecular orbital. Since the total energy of the radical is the sum of the energies of the individual valence electrons, therefore, the radical shape of minimum total energy is that which allows for maximum in-phase overlaps between the atomic orbitals in the occupied molecular orbitals.

It should be noted that the MO model can only predict and explain the prefered shape for the radical. However, the magnitude of the induced degree of pyramidalization can be measured in various ways. One method is by consideringthe out of plane angle[135] (called α or θ), which is the angle between a plane defined by the radical center with two attached atoms and the third bond to the radical center. Another method is to measure $\hat{h}$, which is the perpendicular distance between the radical center and the plane defined by three points 1.0 A° away from the radical center along the bonds of the attached atoms[135,136]. The planar-pyramidal energy barrier, known as the inversion barrier is another

good and adequate way of expressing the pyramidalization. This energy barrier correlateswith the degree of pyramidalization measured in terms of $\hat{h}$. This conclusion was proved by Cartledge[136] in his study on tri-methyl and trifluorosilyl radicals. The inversion barrier is calculated from the difference in total energy between the radical in its optimized form and in the planar position. Before going through the results, it would be advantageous to present in some details the approach that had been followed, in this work, as applied to the methyl and silyl radicals.

(I) Unsubstituted Methyl and silyl radicals.

Although both radicals belong to the same isoelectronic series AH_3 with seven valence electrons, yet the methyl radical is planar and silyl radical is pyramidal. The Walsh correlation diagram for the planar and pyramidal forms of a typical AH_3 species is shown in (Fig. 2). This diagram shows that upon bending, the 1s-1s in-phase overlaps increase and this lowers the energy of the related molecular orbital $2A_1$ relative to the planar $2A_1'$. But this energy change is relatively small and can not control the shape of the radical. However, the shape is determined by the three molecular orbitals obtained from the in-phase overlap between the three degenerate p-atomic orbitals and the three 1s-hydrogen orbitals. The change from planar to pyramidal form raises the energy of the degenerate $1E'$ orbitals of D_{3h}

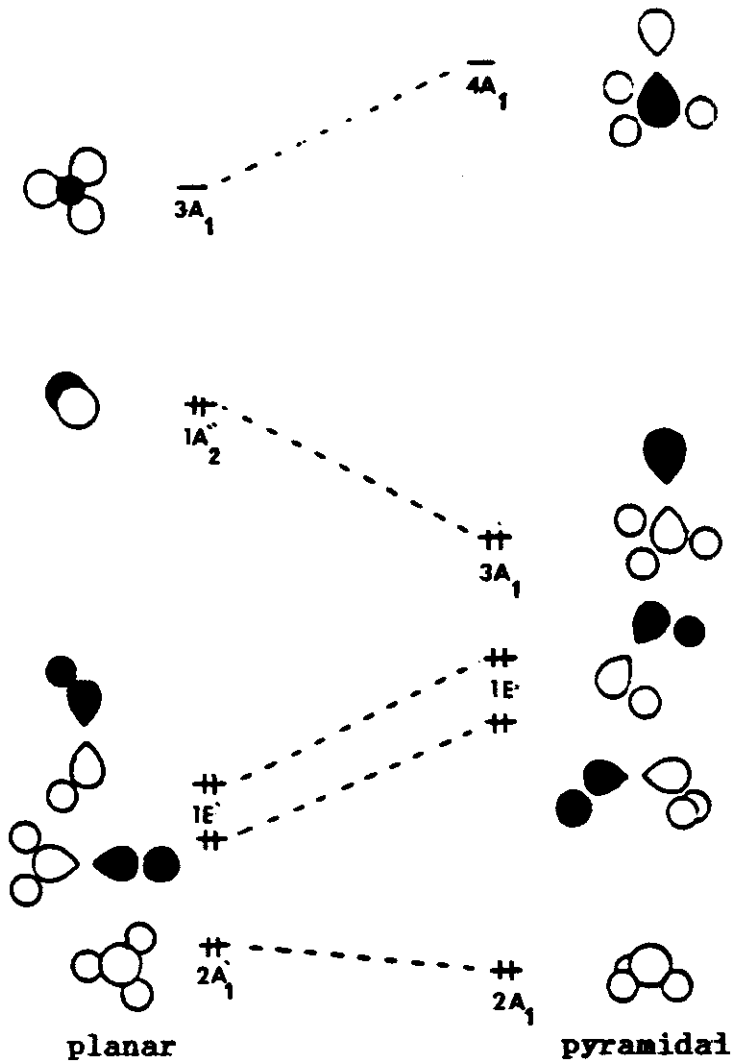


Fig (2) : The correlation diagram for an AH_3 molecule in the planar and pyramidal geometries.

due to the decrease of the in-phase overlap between the 1s orbitals and the p.orbitals. This is accompanied by a decrease in the energy of the singly occupied molecular orbital $1A_2''$ due to its mixing with the lowest unoccupied molecular orbital, and also due to the now possible overlap between 1s orbitals and the lower lobe of the p orbital to form the $3A_1$ molecular orbital (C_{3v}). Since methyl radical contains seven valence electrons with one electron occuping the $3A_1$ molecular orbital Walsh predicted a non-planar geometry for the methyl radical[134]. However, on the basis of experimental and SCF-MO results[38,119],Gimarc concluded that the seven-electron methyl radical is planar because a single electron in $3A_1-1A_2''$ cannot override the planar preference of four electrons in $1E-1E'$. In other wards one can say that the total energy for the pyramidal form is more than the total energy for the planar one.

From the foregoing argument it is clear that, the shape of the seven electron radical cannot be determined by a single factor namely, the balance between the decrease in the $1A_2''$ (SOMO) energy and the increase in the $1E'$ energy induced by pyramidalisation , or else one would expect all seven-electron radicals to have the same shape. This of course is not the case.

An important factor which determines not only the shape but also, the degree of pyramidalisation and consequently

the inversion barrier, is the extent of interaction between the singly occupied molecular orbital and the lowest unoccupied molecular orbital[137]. It was found that as the energy difference between the SOMO and the LUMO orbitals decreases, the extent of the interaction between them increases. This factor was first postulated by Cherry and Epiotis[137] for AH_3 molecules (A = N and P), and is considered to be the most rational explanation that can account for the larger barrier in case of third-row elements (e.g Si and P) as compared to the corresponding second-row elements (C and N). It also accounts for the effect of substituent's electronegativity on the inversion barrier (vide supra). Cartledge[136] had used this assumption to compare the shape of trimethyl silyl and trifluoro silyl radicals with their carbon counterparts.

In their theory, Cherry and Epiotis established that, in the planar form the SOMO-LUMO interaction is nil since they are mutually orthogonal. However, upon pyramidalization they tend to interact. According to the perturbation theory, the degree of their interaction is inversely proportional to the SOMO-LUMO energy difference and directly proportional to the square of their overlap. As have already been mentioned this interaction will lower the energy of the SOMO and raises the energy of $1E'$ and LUMO orbitals. Hence, if lowering in energy is more than the concomitant rise in the $1E'$ energies, the pyramidal shape will be favoured and vise

verse. Consequently, when the radical changes from the planar form to the pyramidal form, the extent of the SOMO-LUMO overlap will increase. This in turn increases the inversion barrier and $\hat{h}$ of the radical. This can be simply achieved by increasing the electronegativity of the substituents, or by altering the central atom from a second-row element to a third-row one. Electronegative substituents affect the electronic nature of the radical by lowering the LUMO energy, thus, decreasing the SOMO-LUMO energy gap and increasing their interaction. On the other hand, electropositive substituents are expected to increase the ΔE_{S-L}, and to decrease the interaction, accordingly, decrease $\hat{h}$ and the inversion barrier.

The above analysis was applied to the radicals studied in this work. The MNDO calculations were performed on the planar shape of methyl and silyl radicals. It indicated a large SOMO-LUMO energy gap for the methyl radical as compared with silyl radicals (Tables 5,6). The obtained eigenvalues for the two radicals are represented in (Fig 3). The large ΔE_{S-L} of the methyl radical revealed the difficulty of SOMO-LUMO mixing and accounts for the preferred planar shape of the methyl radical. On the other hand, the small ΔE_{S-L} for the silyl radical allows and even favours this mixing. The drop in ΔE_{S-L} on going from carbon to silicon is attributed to the change in electronegativity (H=2.2, C=2.5, Si=1.8). Although hydrogen is electropositive with respect

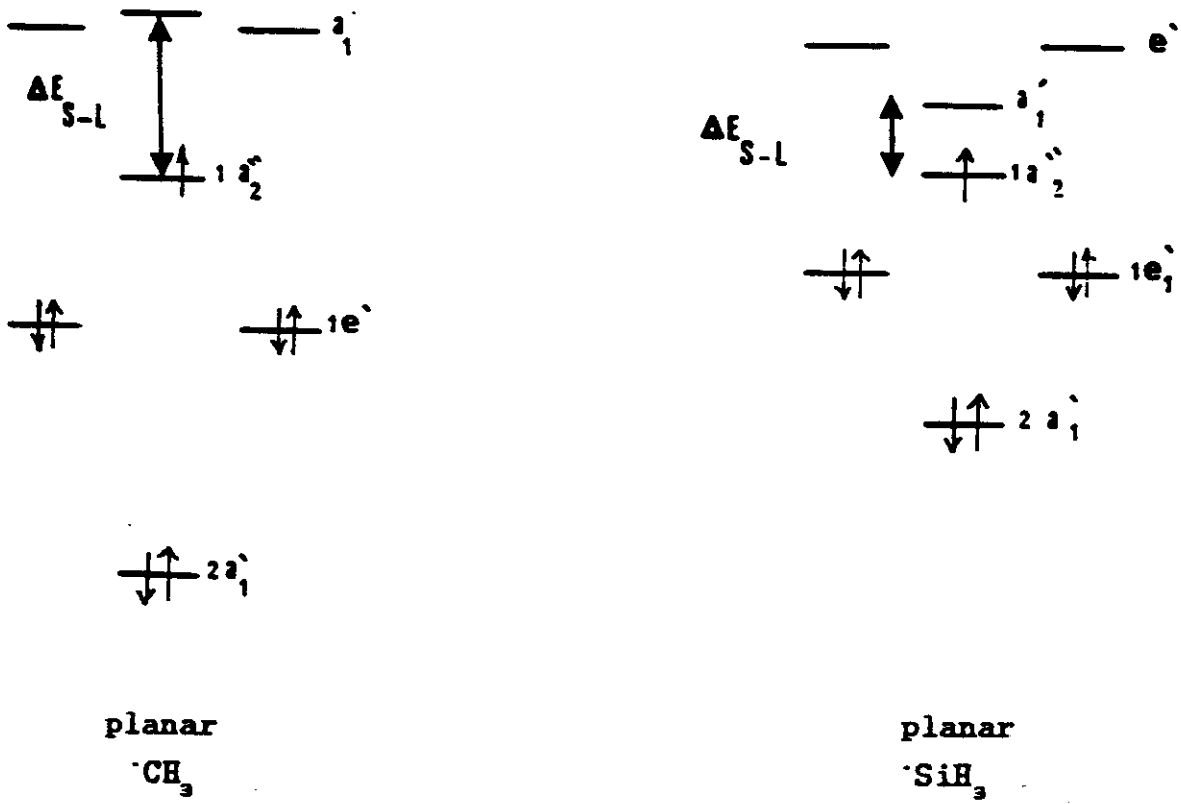


Fig (3) : The relative energies of the valence MO's for planar $\cdot CH_3$ and $\cdot SiH_3$ as calculated by MNDO method.

to carbon, it is an electronegative substituent with respect to silicon. Consequently, it decreases the energy of LUMO and increases the SOMO-LUMO interaction for silicon radical. This is the main reason for pyramidal shape of the silyl radical ($\hat{h}$ =0.327 A°) and the planar shape ($\hat{h}$ =0.0 A°) of the methyl radical. At this point, it should be noted that substituted methyl radicals show lower ΔE_{S-L} which allows for some pyramidalization, the degree of which depends on the substituents. This rationalization is in consistence with Pauling's analysis[40] based on the electronegativity difference between the substituents and the central atom.

(II) Substituted Methyl Radicals.

As have been mentioned above, substituting one hydrogen atom or more with another substituent will alter the inversion barrier. The effect exerted by different substituents on ΔE_{S-L}, the calculated $\hat{h}$ and the height of the inversion barrier are shown in (Table 5). Introduction of a cyano group, though electron withdrawing, expected to induce pyramidalization was found not to affect the shape of the radical. So, both the monocyano- and dicyanomethyl radicals are nearly planar with a very small inversion barrier (0.0 and 0.08 kcal/mol respectively). The calculated $\hat{h}$ for both radicals is zero. These results are in consistence with previous calculations[75] at the *ab initio* 4-31 G level which predicted planar geometry for cyanomethyl

radical. Nevertheless, as expected the cyano groups do lower the LUMO energy and decrease the ΔE_{S-L} (Table 5) The reason that the radicals did not deviate from planarity is attributed to the π. electron accepting nature of the cyano-group. This means that, it is capable of stabilizing the planar radical by delocalizing the odd electron on the carbon atom in its π- system.

This delocalization forces the radical to attain its planar shape, in which the p.orbital occupied by the odd electron and the p-orbitals of the π-system are parallel and can overlap. This stabilizing effect, however, dose not exist in the pyramidal form, since any deviation from planarity will break down the π.overlap. Thus in the cyano substituted radical. The π-overlap effect overcome the electronegativity effect.

As expected from an electronegative substituent which is not a π-electron acceptor, replacing the methyl hydrogen by an amino group reduces ΔE_{S-L} and induces pyramidalization. This is reflected on the values of both $\hat{h}$ and ΔE. Further substitution of hydrogen atom by a second amino group was found to induce further pyramidalization.

- Table (5). Effect of substituents on the value of pyramidalization parameters of carbon centered radicals CXYZ.

X , Y , Z	$\hat{h}_{A^\bullet}$	ΔE_{S-L} EV	ΔE kcal/mol
H , H , H	0.0	9.04	0.00
H , H , CN	0.0	6.86	0.01
H , CN , CN	0.0	7.01	0.08
H , H , OH	0.001	7.51	0.28
H , OH , OH	0.104	6.83	0.94
OH , OH , OH	0.212	6.27	5.32
H , H , NH_2	0.043	7.09	0.22
H , NH_2 , NH_2	0.109	6.59	1.25
H , H , F	0.00	8.34	0.11
H , F , F	0.054	7.45	1.61
F , F , F	0.221	7.02	6.90
H , F , NH_2	0.090	6.83	0.57
H , H , SiH_2	0.001	4.82	0.41

Since the hydroxy group (oxygen atom) is more electronegative than the amino group (nitrogen atom), it reduces ΔE_{s-L}, and increases the inversion barrier (from 0.0 to 0.28 kcal/mol) slightly more than the amino group does (from 0.0 to 0.22 kcal/mol). Introducing a second and a third hydroxy group increases the pyramidalization even more and shows a pronounced effect on both $\hat{h}$ and ΔE. Experimental results supporting the effect of hydroxy group on the inversion barrier was reported for amines. Thus, the determined inversion barrier (ΔE) for dibenzyl methyl amine is 6.5 kcal/mol[138], while the reported value for dibenzyl hydroxyl amine is 12.8 kcal/mol[139].

Substituting the methyl hydrogen by the most electronegative atom fluorine, affected the shape only slightly. The calculated inversion barrier is very small (0.11 kcal/mol), and $\hat{h}$ is nearly zero. Although the electronegativity of fluorine is more than that of oxygen and nitrogen, but its effect on the planarity is smaller than them. This is because of the absence of the steric hinderence effect which exist in the case of hydroxy group or amino group substitution. Upon introducing a second fluorine atom the inversion barrier (ΔE) and $\hat{h}$ were found to increase to 1.61 kcal/mol and 0.054A° respectively. They reached their maximum values ΔE = 6.9 kcal/mol and $\hat{h}$ = 0.221A° in the studied series, when a third fluorine atom was introduced to the radical. It should be noted that ΔE_{s-L}

decreases in the order as the inversion barrier and $\hat{h}$ increases, *i.e.* the SOMO-LUMO interaction increases in the order $^{\cdot}CH_2F$ < $^{\cdot}CHF_2$ < $^{\cdot}CF_3$.

Although monofluoro-substituent was predicted to have little effect on pyramidalization, its combination with an amino group explored their effect. Thus, fluoroamino methyl radical has an inversion barrier equals 0.57 kcal/mol, and $\hat{h}$ = 0.09 A°, which are higher than the values calculated for monofluoro- or amino methyl radicals (0.11 and 0.22 kcal/mol respectively). It is interesting to refer to the combined effect of fluorine atom and amino group on ΔE_{S-L}. Although ΔE_{S-L} decreased considerably with respect to methyl radical, and to a value which is even smaller than that calculated to the most pyramidal radical CF_3, yet ΔE and $\hat{h}$ are small in comparison. This can be rationalized on the basis of the captodative nature of both substituent. Both fluorine atom and amino group are individually electron withdrawing groups, thus they will lower the LUMO energy, and this in turn will decrease ΔE_{S-L}. However, in this system the fluorine atom acts as an electron acceptor while the amino group acts as an electron donor. The outcome of this electronic redistribution is an increased mixing between the molecular orbitals which is responsible for the marked decrease in ΔE_{S-L}.

Finally in order to cover all types of substituents, an

example of electropositive substituent is considered. The chosen example is silyl methyl radical. One would expect the introduction of the silyl group to increase the LUMO energy in the planar form, increase the value of ΔE_{S-L} and as a consequent decrease the SOMO-LUMO interaction. All these factors are in favour of a planar shape. However, although silyl methyl radical was predicted to be planar on the bases of a neglectable $\hat{h}$ value (0.001 A°), the SOMO-LUMO interaction seems to be very high on the basis of a small ΔE_{S-L} value (4.82 ev). This is attributed to the stabilization of the odd electron via hyperconjugation with the silyl group in the planar form. Therefore, the planar form is predicted in this case due to the electropositive effect of the silyl group and more importantly due to the possible hyperconjugation between the orbitals. This σ hyperconjugation stabilizes the planar form relative to the pyramidal one.

(III) Substituted Silyl Radicals.

The effect of substituents on the shape of silyl radicals was expressed in terms of the degree of pyramidalization as reflected by the value of $\hat{h}$. The value of the inversion barrier ΔE, were inconsistent due to the exclusion of the 3d-orbitals in the MNDO-SCF procedure. This conclusion was previously reached by Santry[140] from CNDO calculations and Hillier[53] from *ab initio* SCF molecular orbital calculations at different levels in studying the

- Table (6). Effect of substituents on the value of pyramidalization parameters of silicon centered radicals SiXYZ.

X , Y , Z	$\hat{h}_{A^\circ}$	ΔE_{S-L} EV	ΔE kcal/mol
H , H , H	0.327	3.72	19.35
H , H , CN	0.323	3.52	19.58
H , CN , CN	0.317	3.45	19.14
H , H , OH	0.324	4.54	12.58
H , OH , OH	0.332	5.29	10.81
OH , OH , OH	0.357	8.74	0.00
H , H , NH_2	0.335	4.55	11.49
H , NH_2 , NH_2	0.325	7.17	0.00
H , H , F	0.324	4.34	15.31
H , F , F	0.341	4.97	15.99
F , F , F	0.375	5.90	19.16
H , F , NH_2	0.346	5.17	11.79
H , H , SiH_2	0.265	4.15	6.96

structure of some triagonal radicals. They concluded that the exclusion of 3d orbitals does not affect the molecular shape, however, their inclusion is important for determining the inversion barrier. The calculated values of $\hat{h}$, ΔE_{S-L} and ΔE for substituted silyl radicals are listed in (Table 6). Silyl radical itself is pyramidal with a value of $\hat{h}$ equals 0.327 A°. The value of the inversion barrier calculated by *ab initio* method ranged between 3.0 to 5.77 kcal/mol, depending on the basis set used in the calculation. Replacement of hydrogen atoms by cyano group did not increase the degree of pyramidalization. As a matter of fact it slightly reduces $\hat{h}$ due to the possible interaction between the odd electron and the π-system of the cyano group. This effect, combined with steric repulsion between the cyano groups will reduce the pyramidalization of the dicyanosilyl radical ($\hat{h}$ = 0.317 A°) relative to the silyl radical.

As in the case of aminomethyl radical, the introduction of the electronegative amino group in silyl radical increasesthe pyramidalization of the radical due to the induced lowering in the LUMO energy. Thus $\hat{h}$ increased to 0.335 A°. However, introduction of a second amino group decreases $\hat{h}$ due to steric effect.

Mono hydroxy group has a minor decreasing effect on the pyramidalization of the silyl radical. However, replacement

of two hydrogen atoms by two hydroxy groups induced more pyramidalization on the shape of silyl radical. It worth mentioning that the effect induced by the two hydroxyl groups is slightly less than that induced by one amino group. This is a consequent result of the steric repulsion between the two hydroxy groups. Introduction of a third hydroxy group increases $\hat{h}$ even more.

Likewise, introduction of one fluorine atom - although very electronegative - has a slight reductive effect on the pyramidalization, but the introduction of a second and a third fluorine atoms increased it considerably, $\hat{h}$ equals 0.341 and 0.375 A° respectively. This effect is similar to that observed in the methyl radical in that trifluorosilyl radical is the most pyramidal radical in the present series. This is because it has the most electronegative substituents, which are of small size, Thus the radical does not suffer from steric effects as in the case of di- and trihydroxysilyl radical. An evidence for this conclusion is the effect of combination of amino and fluoro groups on the value of $\hat{h}$ which becomes 0.346 A°, compared to the effect of combination of two amino and fluoro groups, which gave rise to an $\hat{h}$ equal 0.325 A° and 0.341 A° respectively. Thus, although an amino group increases the pyramidalization a second group decreases it due to steric effects. The two fluorine atoms increased $\hat{h}$ but to a lesser extent than did a fluorine atom and an amino group together. However, the

introduction of a third group whatever it will be, is expected to induce steric hinderence on the radical. Consequently, the combination of three fluorine atoms is the only possible way to maximize the SOMO-LUMO interaction and in the same time offer the lowest possible steric effect.

As expected the introduction of silyl group on the silyl radical reduces the degree of pyramidalization $\hat{h}$ to 0.265 A°. this is because there is no difference in electronegativity of the substituent and the central atom. On the other hand, there is a stabilizing effect which results from the hyperconjugation of the odd electron and the silyl group which prefers the planar shape. Hence, the radical tends to escape from the pyramidal form as much as it can, and the equilibrium shape of the radical is less pyramidal than the silyl radical. A second silyl radical will certainly reduces the pyramidalization even more due to the steric effect between the two silyl groups.

In the above analysis, the effect of variety of substituents on the shape of the radical was explained. The examples were chosen to cover a large number of different types of substituents. A few conclusive aspects can be stated. Electronegative substituents such as amino group increases the SOMO-LUMO interaction and induces the pyramidalization on the methyl radical and increases it for silyl radical. However, the introduction of a second group

decreases $\hat{h}$ in case of silyl radical due to steric interaction.

On the other hand, introduction of one hydroxy group did not affect the shape of either radicals, and pyramidalization was only induced upon the introduction of the second hydroxyl group.

The successive replacement of hydrogen atoms by fluorine atoms increased the pyramidalization of the methyl and silyl radicals and in the same trend. In each case AF_3 was found to be the most pyramidal radical. This is attributed to the high electronegativity of the fluorine atom and due to the absence of the steric factor. Combination of two electronegative groups e.g fluorine atom and amino group also increased the pyramidalization.

As an example of electronegative substituent having a π-electron acceptor character, the cyano group was selected. In case of methyl radical, the group was found to decrease ΔE_{S-L} but did not affect the inversion barrier nor $\hat{h}$. A result which is expected from π-electron acceptor groups which favour the planar shape of the radical to allow for the delocalization of the odd electron in the π-system. As for the silyl radical, these groups were predicted to decrease the pyramidalization as a result of its electronic and steric effects. Similar effect was encountered by the

introduction of an electropositive substituent such as the silyl group. Thus, for methyl radical this group favoured planar shape to allow for hyperconjugation. For silyl radical $\hat{h}$ decreased considerably upon the introduction of the silyl group.

Finally, it is quite important to point out that the different substituents follow the same trend in the carbon and the silicon series. However, the effect of the substituent which induces pyramidalization is more pronounced on silicon centered radical (a third-row element) than on carbon centered radicals (second-row element). This is reflected on the high $\hat{h}$ values for silicon radicals as compared with their values for carbon centered radicals.

PART TWO

CONFORMATIONAL ANALYSIS FOR SOME SILICON CENTERED AND CARBON CENTERED RADICALS.

A : CONFORMATIONAL ANALYSIS FOR SOME SILICON CENTERED RADICALS.

(i) Hydroxy Silyl Radical.

(ii) Dihydroxy Silyl Radical.

(iii) Tri hydroxy Silyl Radical.

(iv) Amino Silyl Radical.

(v) Fluoro-amino Silyl Radical.

B : CONFORMATIONAL ANALYSIS FOR SOME CARBON CENTERED RADICALS.

(i) Hydroxy Methyl Radical.

(ii) Dihydroxy Methyl Radical.

(iii) Tri hydroxy Methyl Radical.

(iv) Amino Methyl Radical.

(v) Fluoro-amino Methyl Radical.

CONFORMATIONAL ANALYSIS

The conformational analysis for the selected radicals was studied by constructing a potential energy surface (PES). The construction of the (PES) is of considerable importance as it shows the way in which the energy of a molecule - a radical in this study - changes as a result of rotation about a single bond. Consequently it helps in locating the potential minima, in identifying the geometry of the stable rotational isomers (rotomer) at these minima, and in calculating the height of the rotational barrier, that is the energy required for the interconversion between the different isomers. The potential energy surface also helps in knowing if any of the different conformers are metastable; *i.e.*thermodynamically stable. The most important outcome of the potential energy surface calculation is the ability to predict the species (conformer) that are accessible experimentally[141].

A potential energy surface is constructed by calculating the molecular geometry as a function of the full set of the geometrical parameters (bond lengths, bond angles and dihedral angles).[125]

The potential function $V(\phi)$ which describes the internal rotation about a single bond, may be readily generated theoretically by carrying out calculations for an appropriate number of rotational angles ϕ. However, it is

more difficult to generate full potential functions from experimental data since only conformations in the vicinity of the potential minima are appreciably populated. The full rotational function $V(\phi)$ is a complicated function and, in order to facilitate its interpretation, it is desirable to break it down into simpler components. A method that has been successfully used to this end is to expand the potential function $V(\phi)$ as a Fourier series[93]:

$$V(\phi)= 1/2\sum_{n} V_n(1-\cos n\ \phi) + 1/2\sum_{n} V_n \sin n\ \phi \qquad [1]$$

Frequently the potential is symmetric about $\phi=0$ so that the sine terms disappear. In addition, the series is generally truncated after three terms. The most commonly used form of the expansion is then:

$$V(\phi)=1/2\ V_1(1-\cos\ \phi)+1/2V_2(1-\cos\ 2\phi)+1/2V_3(1-\cos 3\phi) \qquad [2]$$

which is generally written as :

$$V(\phi)= V_1(\phi) + V_2(\phi) + V_3(\phi) \qquad [3]$$

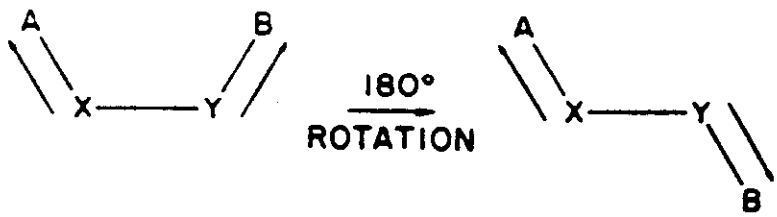
In some simple symmetrical molecules such as ethane, methylamine and methanol, the internal rotation is adequately described by a simple threefold potential function :

$$V(\phi)= 1/2\ V_3\ (1-\cos\ 3\phi) \qquad [4]$$

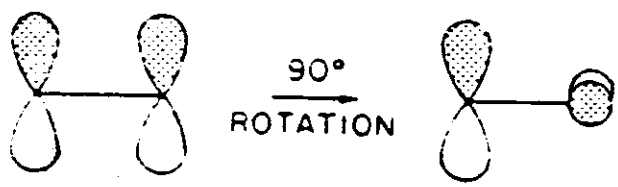
Where V_3 is the threefold barrier and ϕ is a dihedral angle defining the molecular conformation.

The individual components $V_1(\phi)$, $V_2(\phi)$ and $V_3(\phi)$ of the

total potential function $V(\phi)$ can be identified with specific physical effects because of their periodic properties. For example, the one fold term $V_1(\phi) = 1/2\ V_1(1-\cos\phi)$ moves from a maximum value to a minimum one as ϕ changes by 180°. Consequently, the value of V_1 is interrelated to the dipolar or steric interactions



The twofold term, $V_2(\phi) = 1/2\ V_2(1-\cos 2\phi)$ moves from a maximum value to a minimum value as ϕ changes by 90°. Thus its value frequently corresponds to the conjugative or hyperconjugative interaction.



Finally, the three fold term $V_3 = 1/2\ V_3(1-\cos 3\phi)$, moves from a maximum value to a minimum value as ϕ changes by 60°. The value of V_3 is generally correlated with the repulsion between electrons of bond pairs[94].

As the substituent rotates around a bond, each of the three components V_1, V_2 and V_3 would favour one of the conformers over the others, depending on the substituents around the single bond and the specific physical properties of each of them (e.g size, electronegativity, ...).

The outcome of the competing effect of these components determines the shape of the rotational potential curve with its maxima and minima. On the other hand, the resultant potential function is more difficult to analyse than the components because it includes other contributions from several reinforcing or competing effects. Consequently, the energy barrier between any two conformers could be analysed in terms of V_1, V_2 and V_3.

A : CONFORMATIONAL ANALYSIS FOR SILICON CENTERED RADICALS.

Although the structure of the silicon centered radicals was extensively and throughly studied both experimentally and theoretically at different basis set levels, to the best of our knowledge none of these studies included detailed conformational analysis for these radicals. One of the aims of this project was to carry out a fairly detailed conformation analysis for some silicon centered radicals. The examples studied were selected to include the most important bonds around which intramolecular rotation can occur, such as Si-Si, Si-O and Si-N bonds. The effect of captor, donor and captodative substituents on the height of the rotational barrier was investigated through using substituents as fluorine atom, amino and hydroxy groups. The potential curves were constructed by carrying out MNDO molecular orbital calculations at different rotational angles in the range from 0° to 360°. For each molecular conformation the

geometry was fully optimized for all bond lengths and bond angles except the dihedral angle of rotation ϕ which was fixed each time at the desired examined angle. The potential energy function describing the internal rotation in the studied radical was constructed by plotting the relative energy (the difference in total energy between the most stable conformer and any other conformer at angle ϕ) versus the dihedral angle of rotation ϕ. The height of the energy barrier, that is the energy required to convert the stable conformer to the less stable form was then calculated (results are given in Table 7). The complete results of potential energy analysis are represented graphically in (Figs. 4a - 8a).

The separation of $V(\phi)$ into components was obtained by utilizing the Fourier expansion. An examination of the potential energy curves (Figs. 4a - 8a) indicated the asymmetrical nature of the potential function about $\phi = 180^{\circ}$, consequently it was necessary to use form [1] of Fourier expansion - including the sine terms - in calculating the detailed potential energy curves. The theoretical values for the potential V_i and V_i for all radicals under investigation are listed in (Table 8). As an aid in understanding the decomposition of the potential function, the components $V_1(\phi)$, $V_2(\phi)$ and $V_3(\phi)$ are plotted along with the overall potential function $V(\phi)$ (Figs. 4b-8b). It should be noted that the overall potential function represents not only the

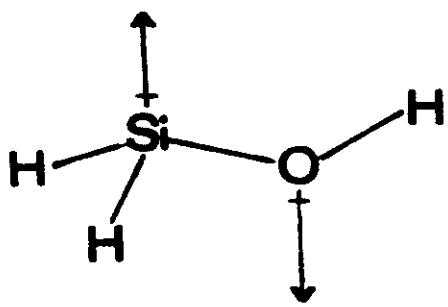
- Table (7). Calculated Energy Barriers For The Studied Silicon-centered Radicals.

Radical	Rotation axis	Dihedral angle ϕ	Energy Barrier kcal/mol
SiH_2OH	H_2Si— OH	HSiOH = 0°	1.33
		= 37°	0.0
		= 120°	2.67
		= 195°	0.02
		= 300°	4.89
$SiH(OH)_2$	(HO)HSi— OH	HSiOH = 0°	0.61
		= 27°	0.00
		= 127°	3.32
		= 187°	2.50
		= 275°	5.14
$Si(OH)_3$	$(HO)_2Si$— OH	OSiOH = 0°	1.37
		= 45°	0.00
		= 286°	4.73
SiH_2NH_2	H_2Si— NH	HSiNH = 0°	1.89
		= 37°	0.00
		= 120°	7.90
		= 201°	0.00
		= 300°	0.08

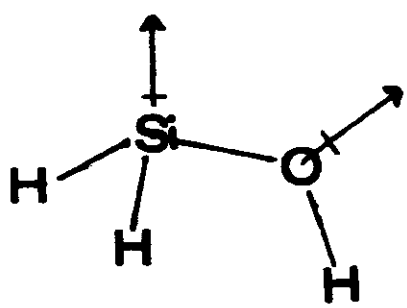
sum of $V_n(\phi)$ but it also includes the sum of $V_n'(\phi)$. In the following section an attempt is made to relate these constants to the physical effects contributing to the resultant potential functions.

(i) Hydroxy Silyl Radical $\dot{S}iH_2OH$

The potential energy surface of hydroxysilyl radical shows two nearly equivalent minima at ϕ=37° and 195° (Fig. 4a). The Fourier decomposition of the potential function is dominated by a positive V_2 term (Table 8) which reflects a preference for a cis conformer (ϕ=0°) and a trans conformer (ϕ=180°).



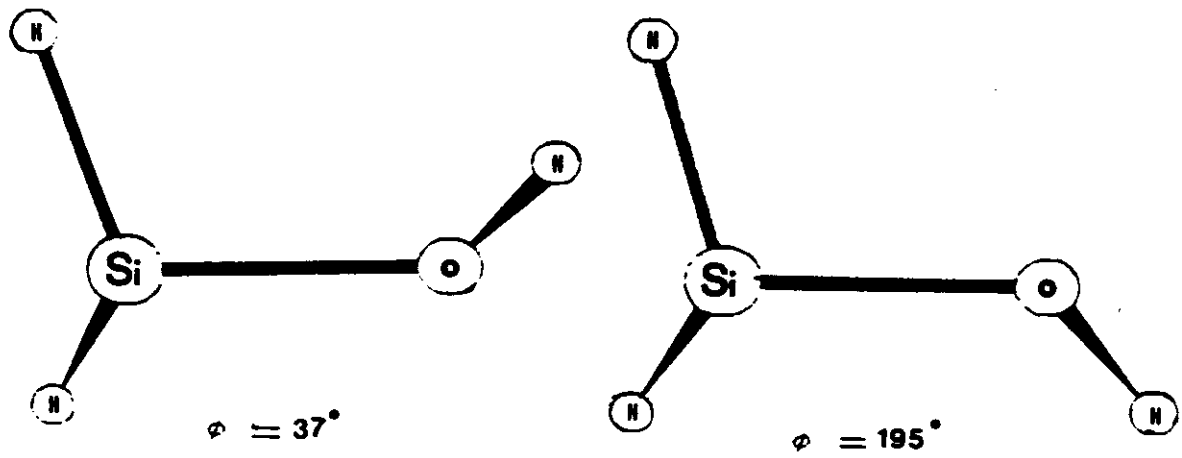
trans. form



Cis form

These conformations support both the hyperconjugation (*i.e.* the overlap between the oxygen lone pair orbital with the orbital of the odd electron) and the formation of a stable three electron bond. The V_1 term is negative indicating a preference for the trans form over the cis conformation. The trans conformer leads to a weak dipolar interaction since the direction of the two electric dipoles (O-H) and of the

free electron on silicon atom will be opposed. The steric interaction will also be at a minimum in the trans form. The value of V_1 is negative suggesting a preference for the staggered (ϕ=180°) and gauche (ϕ=60°) conformations over the eclipsed (ϕ=0°) conformation. This result is based on minimizing the repulsion between bond pairs of electrons, (electrons forming the Si-O bond and those forming the O-H bond), which favours staggering of bonds. However, this repulsion is very small due to the long Si-O bond length (1.68 Å) which minimizes the repulsion between bond electrons The influence of V_3 on the overall outcome of the potential function is insignificant. The negative values of V_1' and V_2' show that conformations with ϕ between 0° and 180° are preferred to the corresponding conformations at dihedral angles (360-ϕ).



From the foregoing analysis, one expects two minima at ϕ = 180°, which is favoured as indicated by the values of V_1, V_2 and V_3, and at ϕ = 0°, but the relatively large negative V_1' value displaces these minima from their values

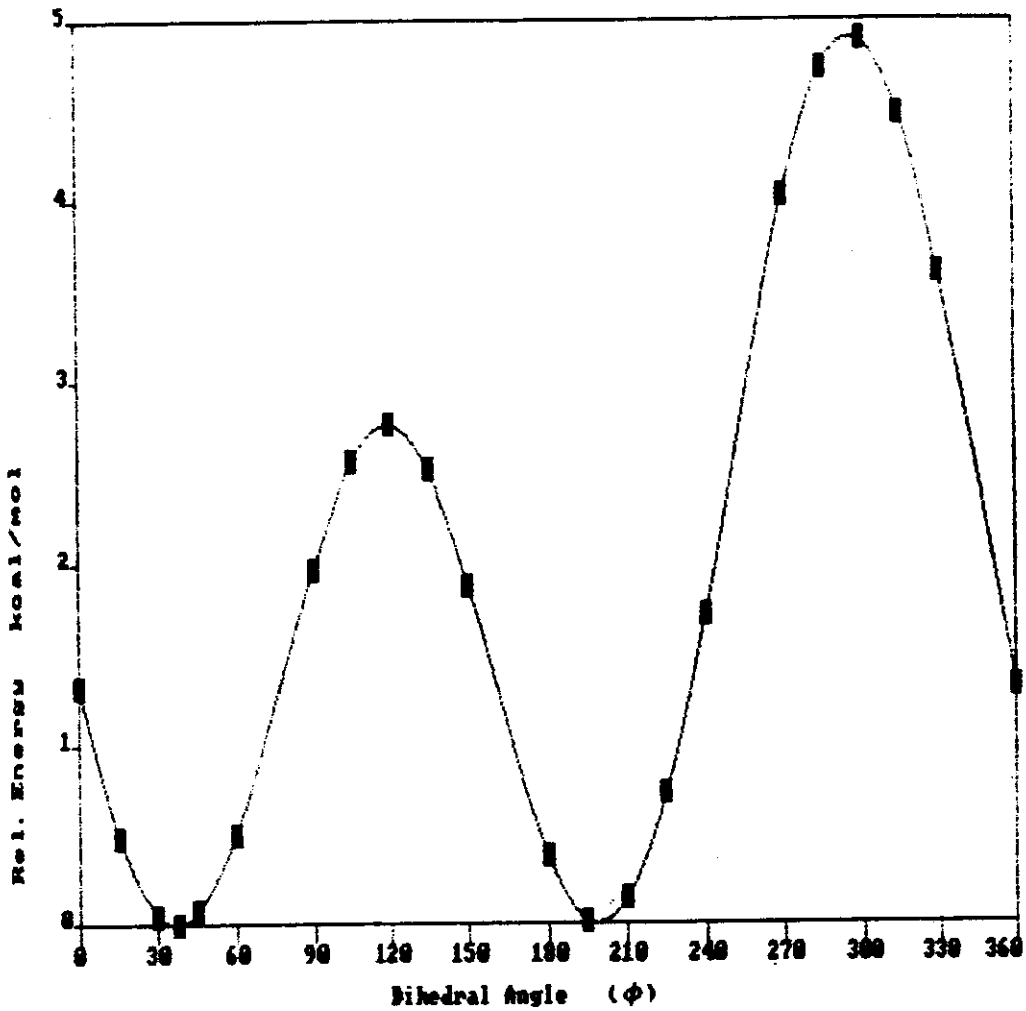


Fig (4a): Potential Energy Surface (PES) describing internal rotation in $^{\cdot}SiH_2OH$.

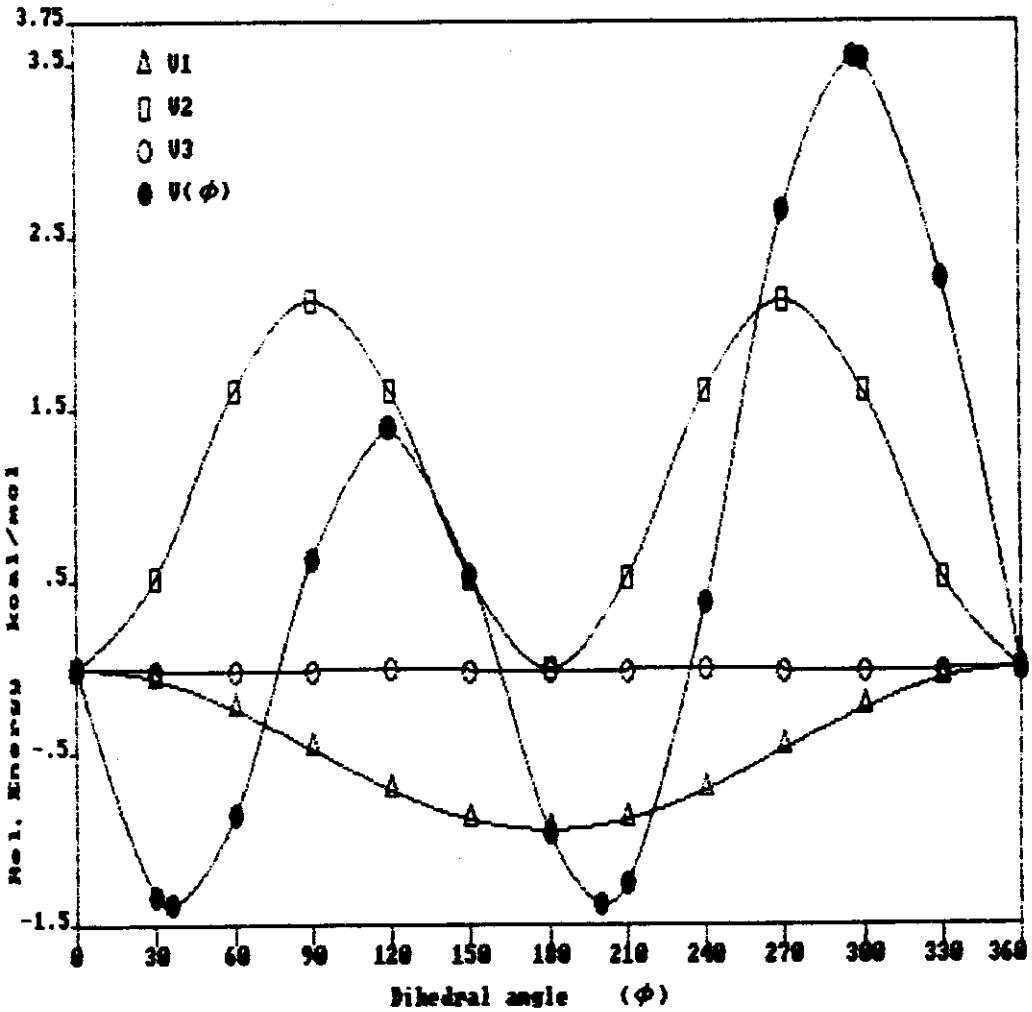
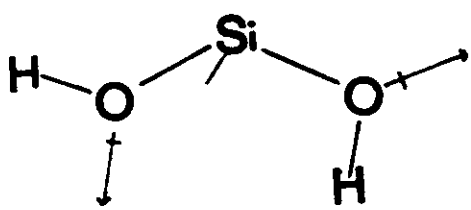


Fig (4b): Fourier components, $V_n(\phi)$ and potential energy function, $V(\phi)$ describing internal rotation in $^{\cdot}SiH_2OH$.

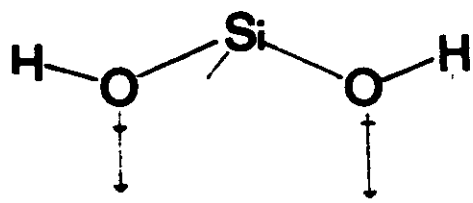
at the cis and trans forms. They occur at ϕ = 37° and 195° with only 0.01 kcal/mol energy difference. Barriers at the cis (ϕ=0°) and the gauche (ϕ=120°) conformers are 1.33 and 2.76 kcal/mol respectively (Table 7).

(ii) Dihydroxy Silyl Radical

The calculated potential energy function V(ϕ), describing the internal rotation of the above radical - rotation of one of the hydroxy groups around the Si-O bond - is displayed in (Fig. 5a) and the contributions of $V_i(\phi)$ to V(ϕ) are shown in (Fig. 5b). The potential function is dominated by the large values of V_1 and V_2 (Table 8). Thus V_1 is large and positive indicating a preference for the cis form over the trans conformer. This is because of the minimized opposing dipole-dipole interaction in the cis form where μ_{calcd}= 1.54 while μ_{calcd} in the trans form where μ_{calcd} = 2.24D.



Cis form



trans. form

The large positive value of V_2 (Table 8) indicates the preference for the configuration in which the Si-O bond (where oxygen is more electronegative than silicon) is

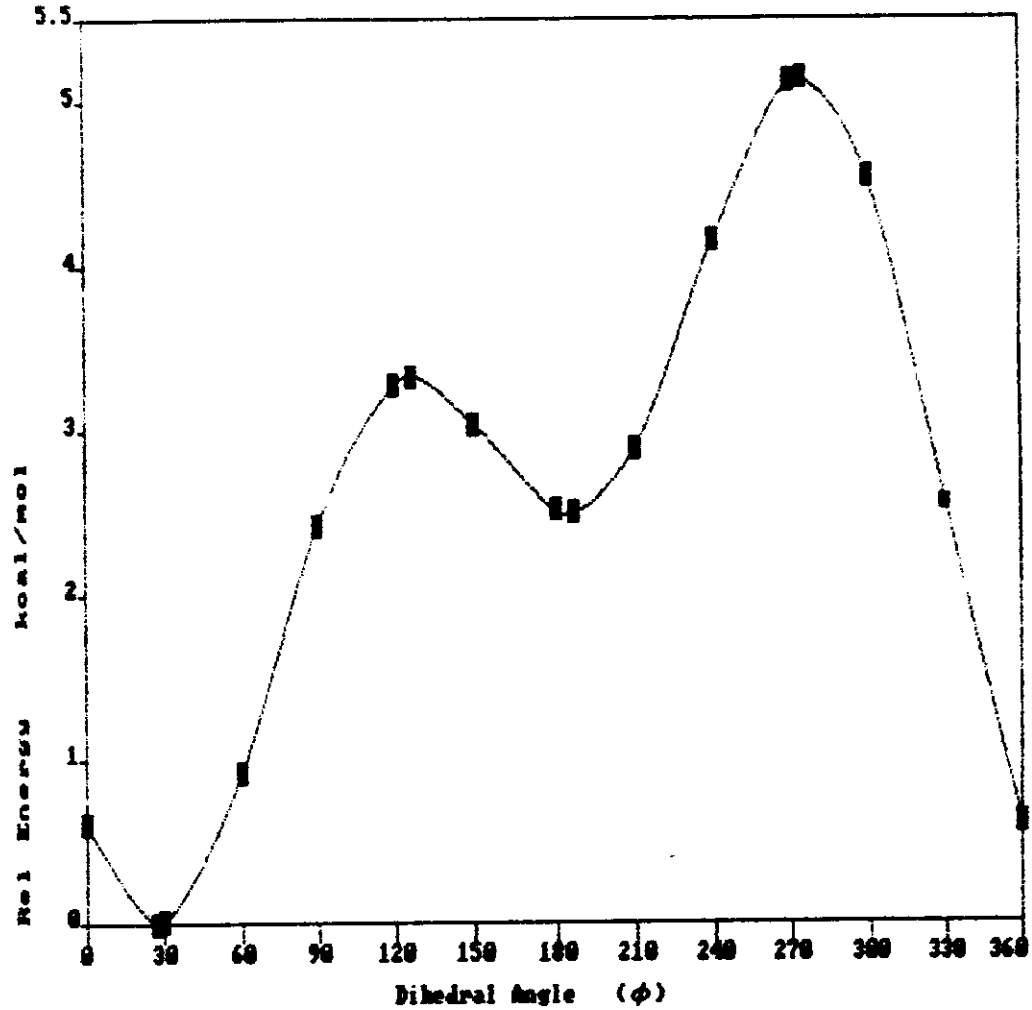


Fig (5a): Potential Energy Surface (PES) describing internal rotation in $^{\bullet}SiHCOHD_2$.

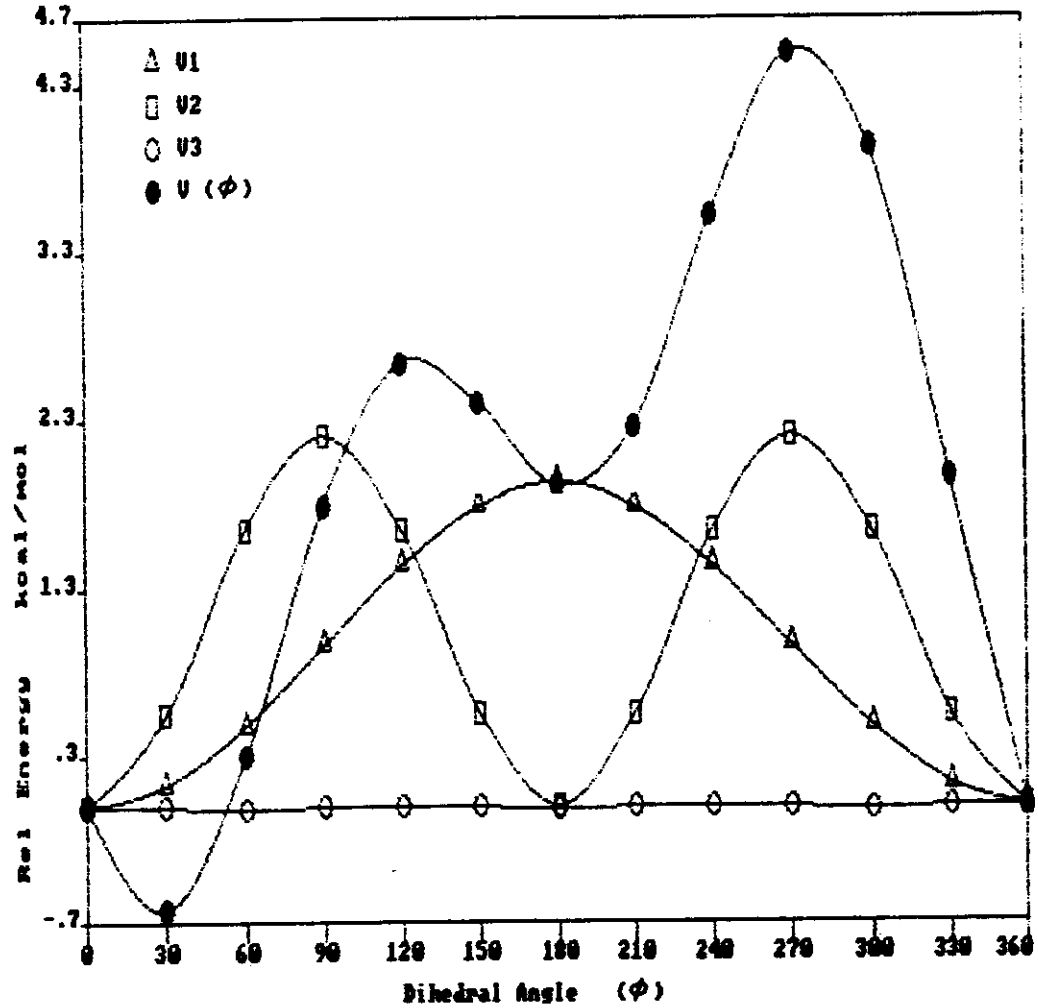
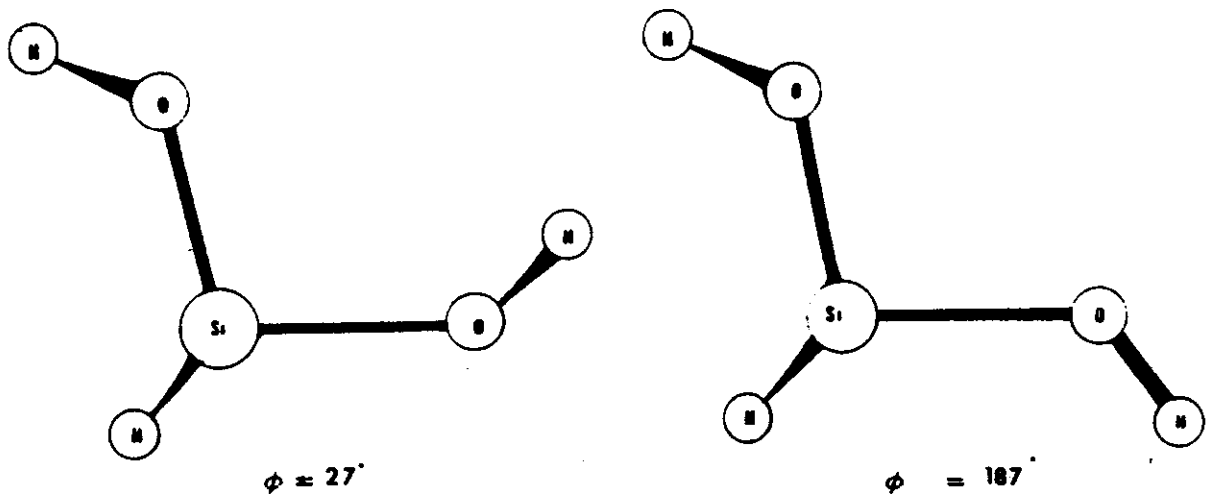


Fig (5b): Fourier components, $V_n(\phi)$ and potential energy function, $V(\phi)$ describing internal rotation in $^{\cdot}SiHCOHD_2$.

coplanar with the axis of the lone pair orbital (ϕ=0,180°) than to be orthogonal with it (ϕ=90°). This configuration facilitates the formation of a three-electron bond and also encourage the overlap between the orbitals (vide supra). As in the case of the hydroxy radical V_3 is very small and negative indicating a slight preference for the staggered conformation (ϕ=60,180°) over the eclipsed conformation (ϕ=0,120°). Eclipsed conformer suffers from a weak steric interaction. However, due to the long Si-O bond, the influence of V_3 on the overall potential curve is negligable. The overall result of rotation is a potential function $V(\phi)$ with minima at dihedral angles ϕ=27°,187° with the former being favoured by 2.5 kcal/mol.

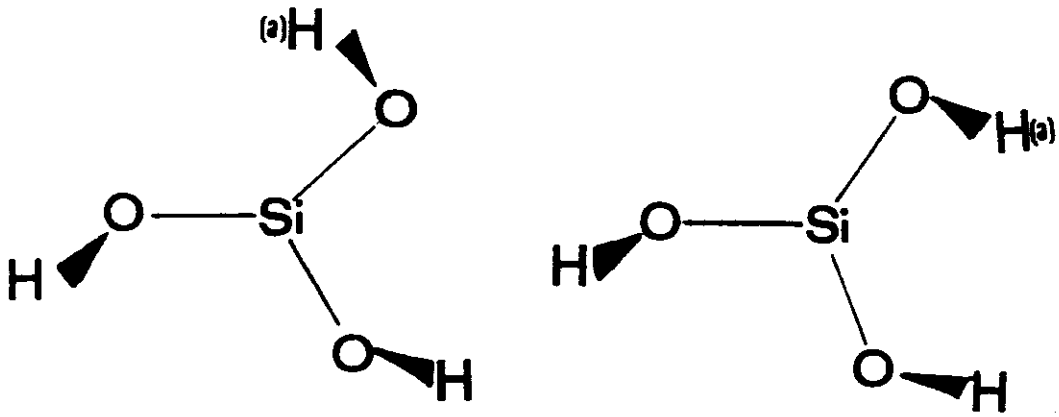


ϕ = 27° ϕ = 187°

The minima were displaced from the expected cis and trans positions (ϕ=0,180°) due to the contribution of the negative V_1'. There is a large barrier equals 5.14 kcal/mol. at ϕ=275° and a smaller barrier 3.32 kcal/mol at ϕ=127° (Table 7).

(iii) Trihydroxy Silyl Radical

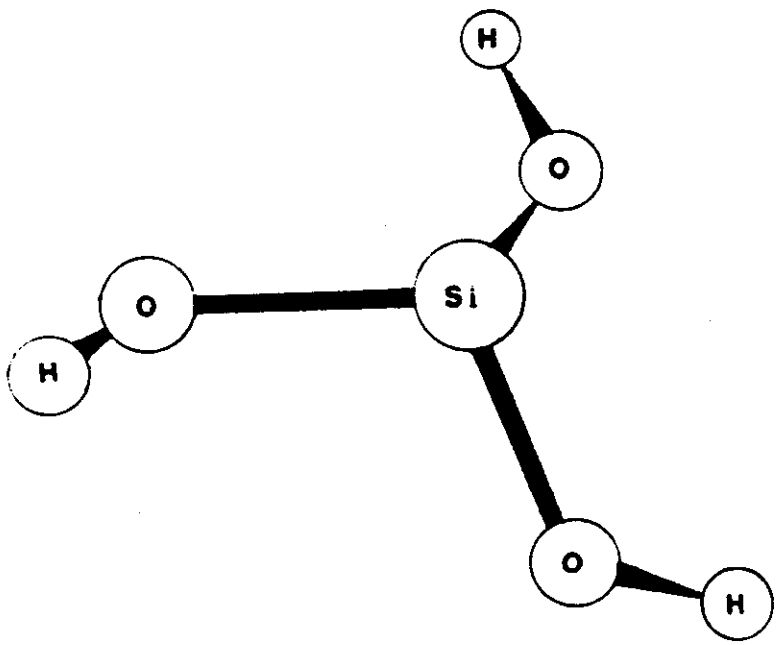
The potential energy curve for the internal rotation $V(\phi)$ of the hydrogen atom a around the Si-O axis is given in (Fig. 6a). The way in which $V_1(\phi)$, $V_2(\phi)$ and $V_3(\phi)$ components contribute to the overall $V(\phi)$ function is represented in (Fig. 6b). As in the previous cases the potential function is dominated by V_1, V_2 and V_1 terms (Table 8). The positive V_1 reflects a preference for cis over trans structures whereby the dipole interactions is at its minimum values.



Cis form trans. form

The V_2 term is positive and of the same magnitude as V_1. Its positive value (not favoured conformer) indicates that the orbitals of the lone pair of electrons on oxygen and that of the odd electron on the silicon atom prefer to be coplanar i.e. ($\phi = 0^\circ$ or 180°) rather than orthogonal and this is expected since this orientation will increase the overlap between the orbital which increases the stabilization of the radical. This coplanar conformation also facilitates the formation of more than one three-electron

bonds and hence the radical will also be in a more stable orientation. The non-bonded oxygen interactions (hydrogen bonding) are favoured in the eclipsed form leading to a positive values for the three fold term. In other wards, the eclipsed form is prefered over the staggered structures. However, because of the long si-O bond length, the magnitude of V_3 is relatively small and its contribution to $V(\phi)$ is minimal. The net result is a potential function with a single minimum at 45° and the potential curve is fairly flat in the region ϕ = 150°-180° due to the opposing effects of V_1 and V_2 terms. There is a maximum at 285° with an energy barrier equal 4.73 kcal/mol.



It is interesting to note that all the hydroxy silyl radicals discussed above have some common features. First, both V_1 and V_2 terms are negative showing a preference for conformations with ϕ<180° over those with ϕ>180°. Consequently all minima were located in the region between (0°-180°).

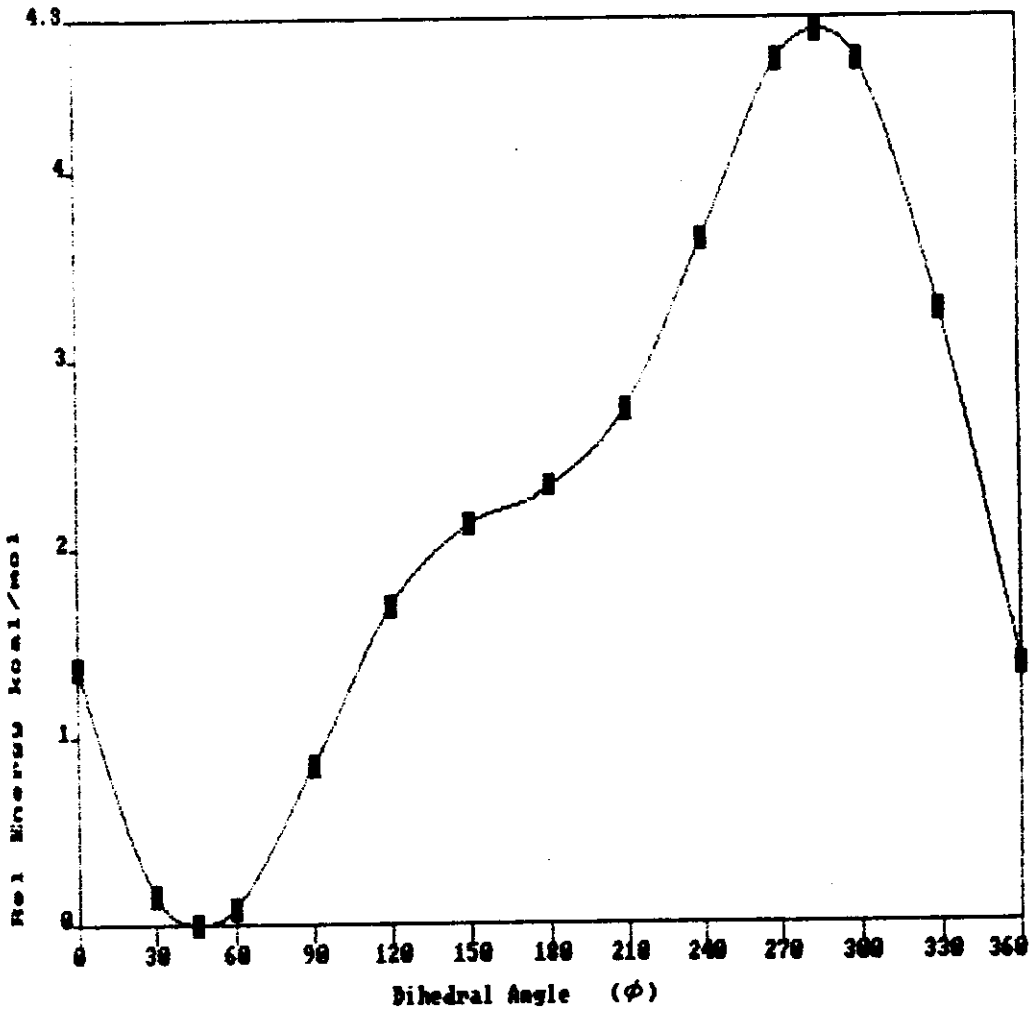


Fig (6a): Potential Energy Surface (PES) describing internal rotation in $^{\bullet}Si(OH)_3$.

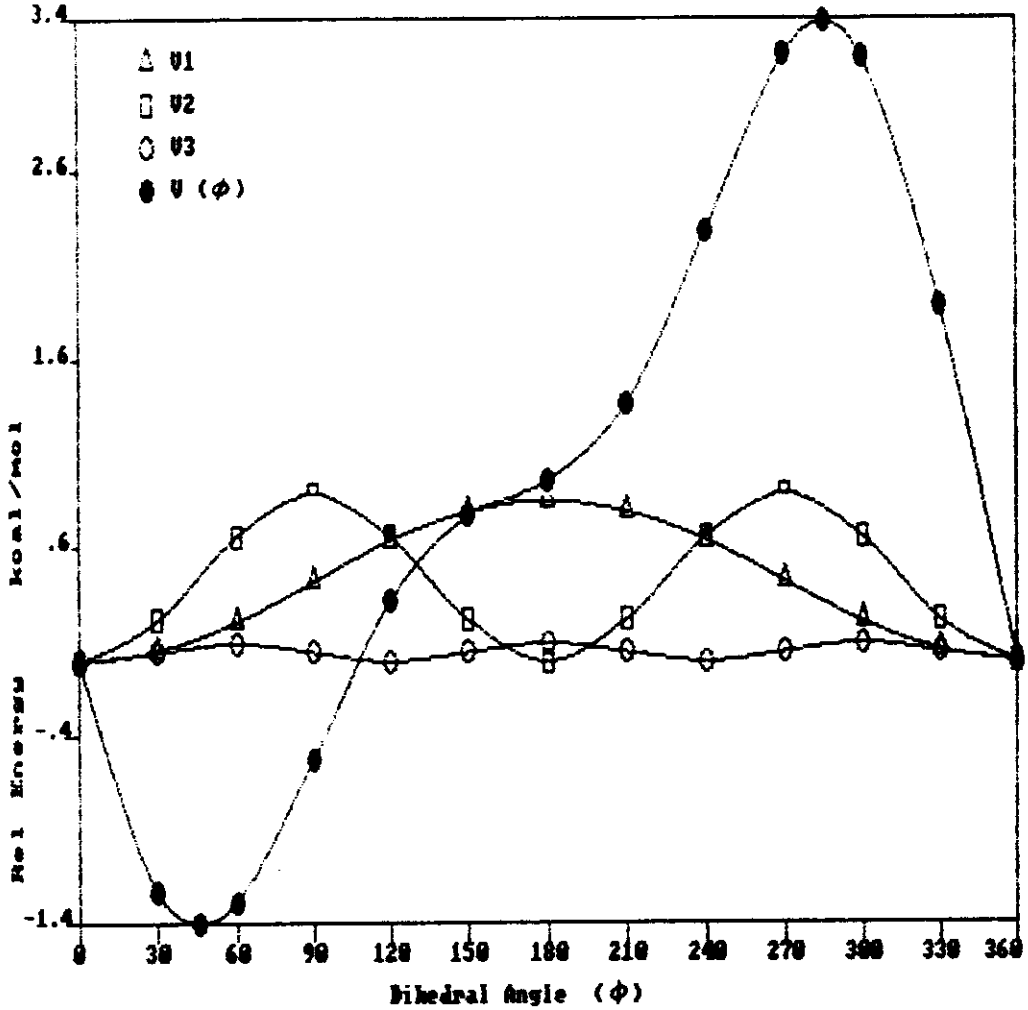


Fig (6b): Fourier components, $V_n(\phi)$ and potential energy function, $V(\phi)$ describing internal rotation in $^{\cdot}Si(OHD)_3$.

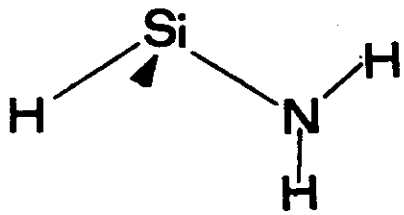
However, due to the large negative value of V_1' the minima were displaced from the expected positions. Second, the long length between the silicon and oxygen atoms decreased the interaction (bond pair-bond pair repulsion) between bond electrons relatively, the dipole-dipole interaction between the oxygen lone pair of electrons and the contribution of the V_3 component to the total potential function describing the internal rotation about the Si-O bond.

(IV) Aminosilyl Radicals

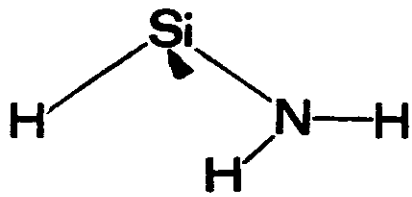
The rotational barrier about Si-N bond in aminosilyl radical (Fig. 7a) shows a great resemblence to that about Si-O bond in hydroxysilyl radical (Fig. 4a). In both cases the potential curve has two equivalent minima at ϕ = 37° and $\phi \approx 195\text{-}201°$, and both curves are dominated by the positive V_2 term.

The amino group can be considered as a strong electron-donor, even more donor than the hydroxy group. This permits an easier formation of a stable three electron bond. This will only be feasible at ϕ = 0 and ϕ = 180°. The difference in electronegativity between the nitrogen atom and the oxygen atom is reflected on the delocalization of the lone pair of electrons and hence on the magnitude of V_2 (Table 8) Therefore, the value of V_2 of aminosilyl radical (4.31) is larger than that of hydroxy silyl (2.13).

The V_1 term is negative indicating a preference for the trans form over the cis conformer. This conformation minimizes the dipole-dipole interaction between the lone pair of electrons on the nitrogen atom and the odd electron on the silicon atom.



trans. form



Cis form

Finally the values of V_3 are negative, and this result indicates the preference of the staggered conformer over the eclipsed one. The net result of all these contributing factors is a curve with two equivalent minima at (-2.7 kcal/mole) deviated from the expected position at $\phi = 0^\circ$ and 180° due to the negative value of V_1'. There are two energy maxima at $\phi = 120^\circ$ and 300° having energy barriers equal 7.9 and 10.08 kcal/mol respectively (Table 7). At these values of ϕ ,the delocalization of the odd electron and the formation of the three electron bond is at a minimum.

(V) Fluoroamino Silyl Radical

Fluorine atom has two important features, the first one is its small size and the second is its highest electro-negativity. Consequently, fluoro compounds are expected to have characteristic electronic features. The potential

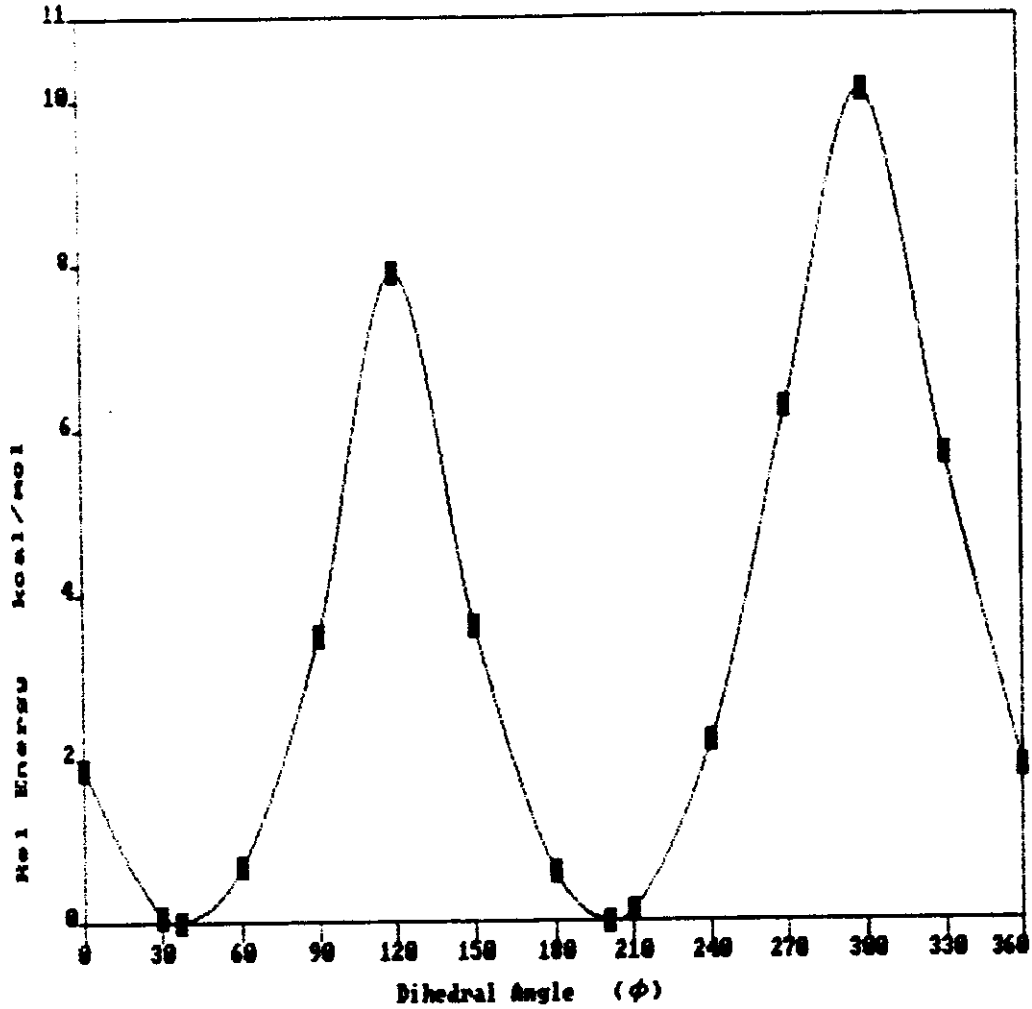


Fig (7a): Potential Energy Surface (PES) describing internal rotation in $^{\cdot}SiH_2NH_2$.

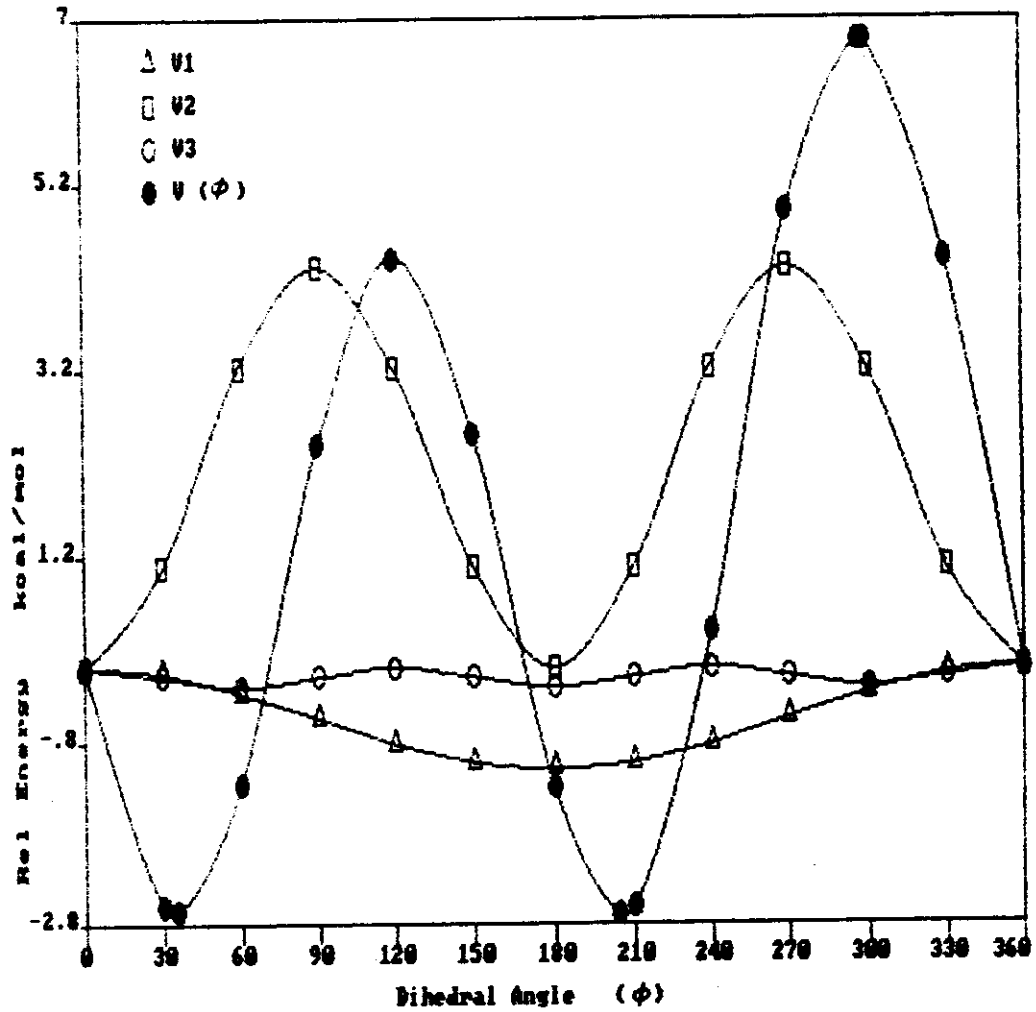


Fig (7b): Fourier components, $V_n(\phi)$ and potential energy function, $V(\phi)$ describing internal rotation in $^{\cdot}SiH_2NH_2$.

energy curve in case of fluroaminosilyl radical is dominated by the large V_2 term (Table 8). The large positive value of V_2 reflects a preference for the coplanar conformations (ϕ=0°,180°) where V_2 has minimum values over the orthogonal conformation (ϕ=90°). A sigma electron withdrawal (from the silicon- fluorine bond) and an "n" electron donation from the lone pair of electrons on the fluorine atom is involved and favoured in these positions (ϕ=0°,180°). The very strong electronegative fluorine atom withdraws the electrons of the Si-F bond, consequently shifts the odd electron towards the bond and thus facilitates donation from the nitrogen lone pair in that direction. It should be noted that, the electron withdrawing substituent, fluorine, enhanced the electron donation of the donor, amino, as compared with that in amino silyl radical. This is known as the captodative effect of the substituent and is reflected in the large positive magnitude of V_2.

The V_1 term is small and negative showing a slight preference for the trans form over the cis form, but this does not affect the overall potential energy curve. Finally, the negative value of V_3 indicate a preference for staggering of bonds to minimize the repulsion between bond pairs of electrons. The net result is a potential energy curve with two nearly equivalent minima at 29° and 189° with energy difference between the minima of 0.2 kcal/mol.

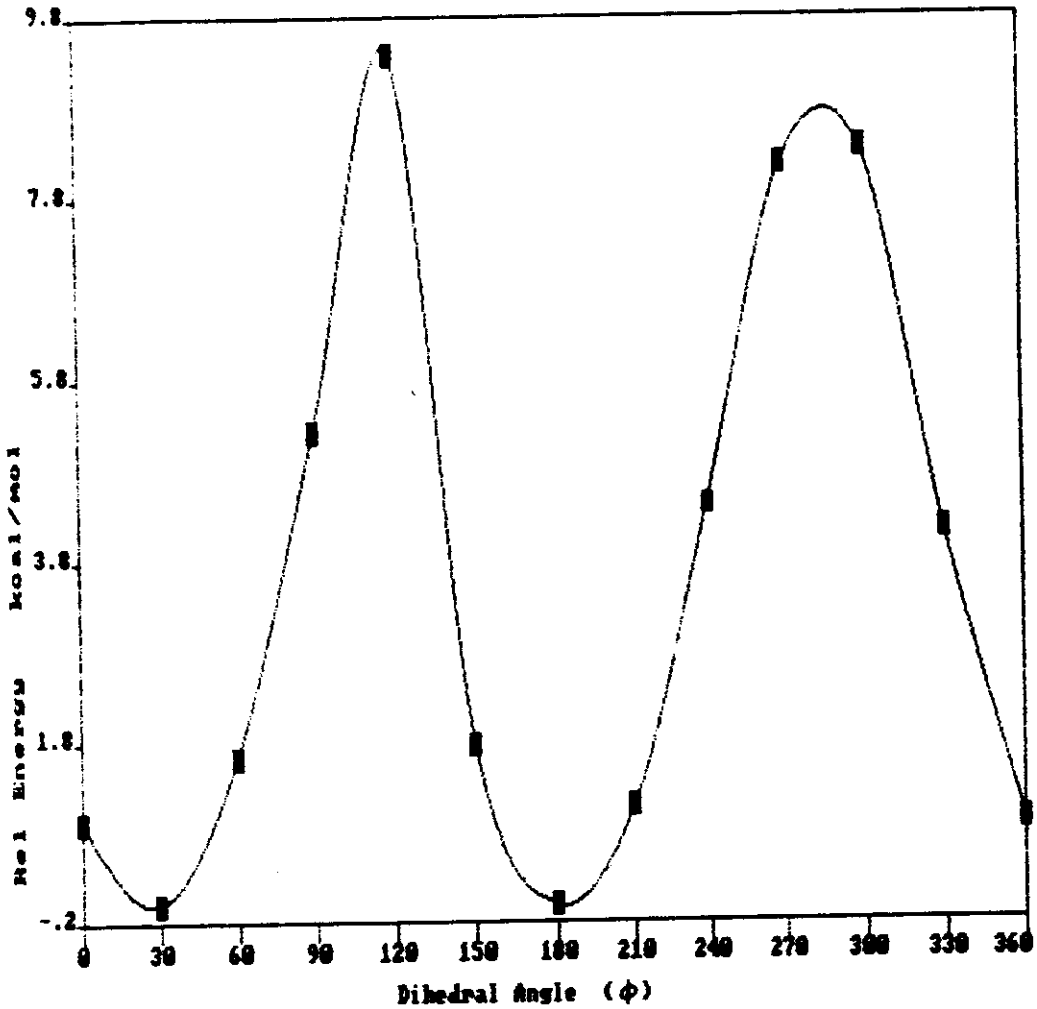


Fig (8a): Potential Energy Surface (PES) describing internal rotation in $^{\bullet}SiHFNH_2$.

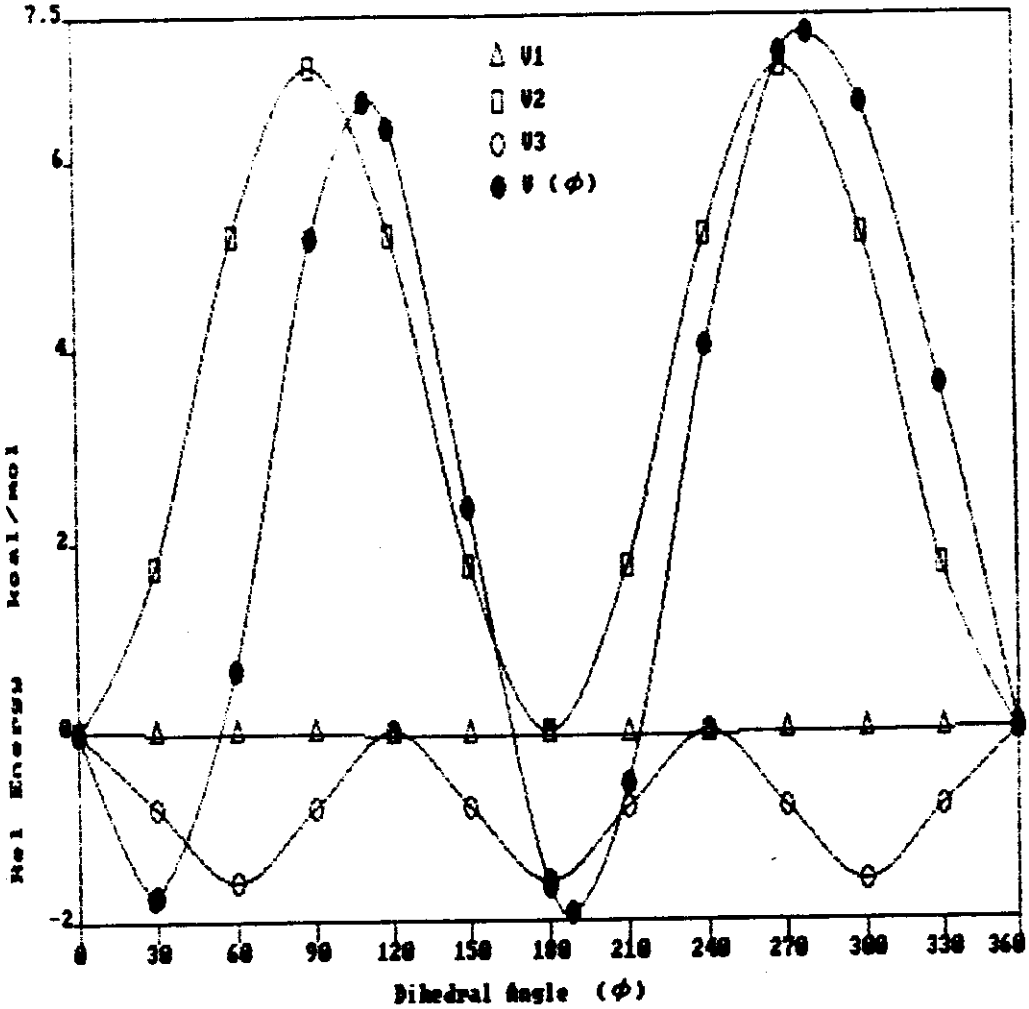


Fig (8b): Fourier components, $V_n(\phi)$ and potential energy function, $V(\phi)$ describing internal rotation in $^{\cdot}SiHFNH_2$.

Computation results have shown that in all the studied cases the height of the energy barrier between any two conformers is less than 10 kcal/mol. This means that there is free rotation around all the silicon-substituent bonds. Consequently, the substituted silyl radicals can adopt many interconvertable conformation in the space. But there is always a one most stable conformer. The geometry of this conformer is governed by the sum of the polar and steric factors exerted by the substituent attached to the silicon atom. As polarity is concerned, since in all the studied examples, the substituent has one or more lone pair of electrons on the atom α - to the silicon atom, and this lone pair is capable of overlapping with the odd electron on the silicon atom as well as forming three electron bond. Hence, one expects that these substituents will exert relatively the same stabilizing or destabilizing effect on the opposed configuration and as a result the studied radicals will have a common stable conformer. However, small deviation from this configuration is expected. This is attributed to the difference in electronegativity of the substituents as well as to the steric factors. This steric factor was most pronounced in the di- and tri- hydroxysilyl radicals.

B : CONFORMATIONAL ANALYSIS OF CARBON CENTERED RADICALS.

The primary concern of this work is to compare the behaviour, properties and energetics of silyl centered

- Table (8).

Potential constants for different substituted silyl radical

Radical	V_1	V_2	V_3	V_1'	V_2'
SiH_2OH	-0.94	2.13	-0.02	-0.98	-1.55
$SiH(OH)_2$	1.92	2.20	-0.013	-1.30	-0.79
$Si(OH)_3$	0.35	0.88	0.10	-1.86	-0.73
SiH_2NH_2	-1.10	4.31	-0.21	-1.16	-3.49
$SiHFNH_2$	-0.05	6.96	1.59	1.05	-2.38

- Table (9).

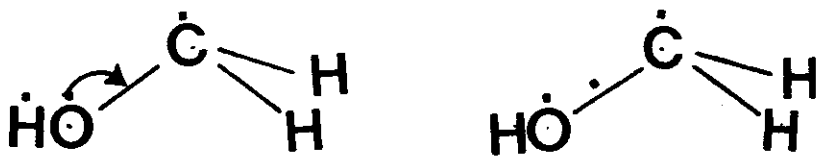
Potential constants for different substituted methyl radicals

Radical	V_1	V_2	V_3	V_1'	V_2'
CH_2OH	0.36	4.27	-0.41	---	---
$CH(OH)_2$	3.20	0.63	0.41	---	---
$C(OH)_3$	-4.35	0.90	0.47	-0.34	0.003
CH_2NH_2	-1.23	3.07	1.37	2.40	0.97
$CHFNH_2$	-0.14	1.18	-0.07	0.76	-0.74

radicals with those of carbon centered ones. It seemed imparative to perform the conformational analysis for carbon centered radicals. To allow for a fair comparison, exactly the same substituents were selected and the rotational barrier was studied around the same bonds (C-O and C-N) as was the case in the silicon centered radicals.

(I) Hydroxy Methyl Radical.

The potential energy surface of hydroxymethyl radical showed a symmetric behaviour about ϕ=180° (Fig. 9a), so that the sine terms should disappear. Consequently, Equation [2] of the Fourier expansion was applied. The (PES) (Fig. 9a) shows one minimum at 180° and the Fourier decomposition of the potential function is displayed in (Fig. 9b). As in the case of hydroxy silyl radical the potential function is dominated by a positive V_2 term (Table 9) which reflects a preference for cis (ϕ=0°) and trans (ϕ=180°) conformations due to the hyperconjugation interaction which facilitates the overlap between the orbital of the odd electron and the lone pair electron orbital.



These conformations also encourage the delocalization of the lone pair of electrons on the oxygen atom which results in the formation of a stabilized three electron bond.

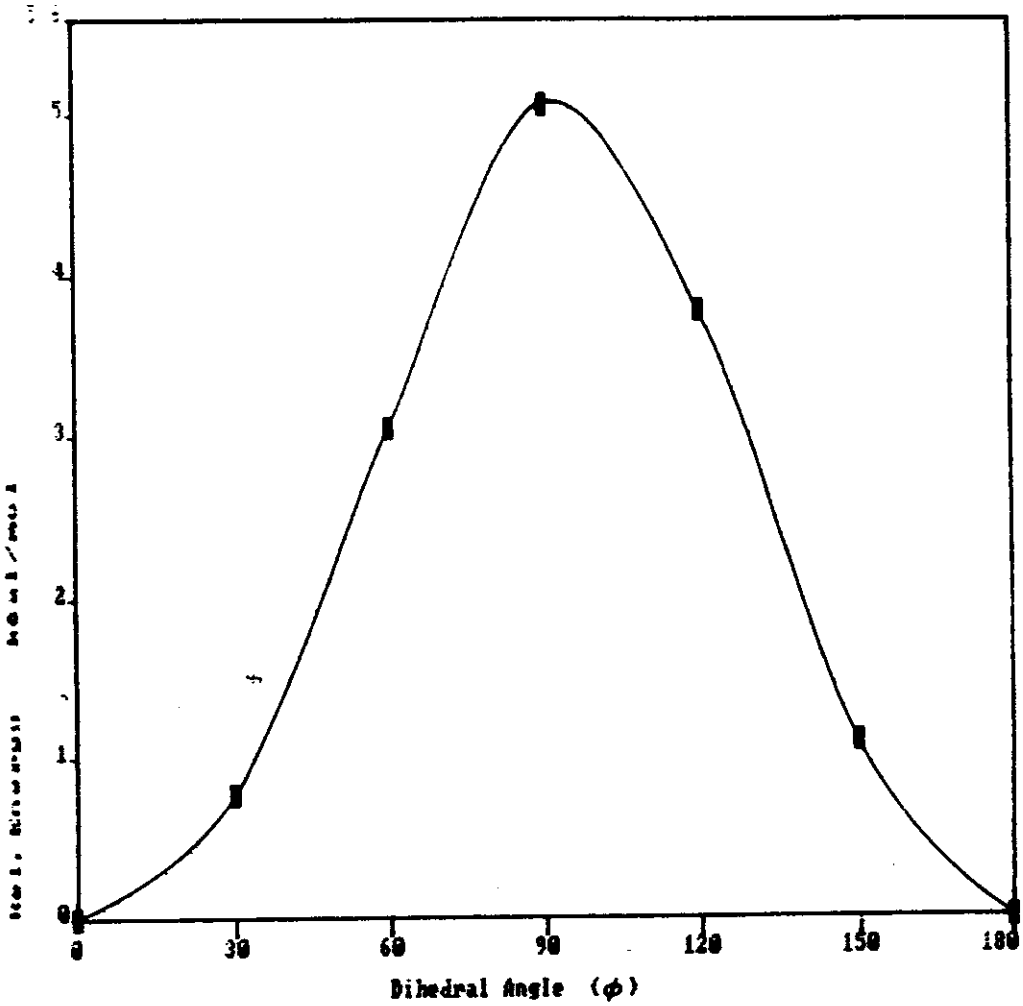


Fig.(9a): Potential Energy Surface (PES) describing internal rotation in $^{\cdot}CH_2OH$

The value of V_2 in the case of hydroxymethyl (4.27) is greater than that of hydroxsilyl radical (2.13). This result is attributed to the difference in the bond lengths of C-O (1.337 A°) and that of Si-O (1.68 A°). The shorter C-O bond allows for a better overlap between the interacting orbitals (the orbital of the lone pair electron on the oxygen atom and the odd electron orbital). The values of V_1 term is positive indicating a preference for the cis form over the trans form. It should be noted that this is not the case in hydroxysilyl radical where the trans form is favoured over the cis form. hydroxymethyl radical resembles the hydroxy silyl one in having negative V_3 term suggesting a preference for the staggered conformer (ϕ=180°) and gauche (ϕ=60°) one over the eclipsed conformation. These conformers minimize the repulsion between the bond pair-bonpair electrons. However, the value of V_3 in case of hydroxymethyl (-0.414) is relatively greater than that of hydroxysilyl radical (-0.02) due to the shorter C-O bond. This in turn results in a greater repulsion between bond pairs of electrons in the hydroxymethyl radical.

(II) Dihydroxy Methyl Radical.

The calculated potential energy function describing the internal rotation is displayed in (Fig. 10a). It shows a symmetric behaviour around the (ϕ=180°) and so equation [2] of Fourier expansion should be applied. The contributions of

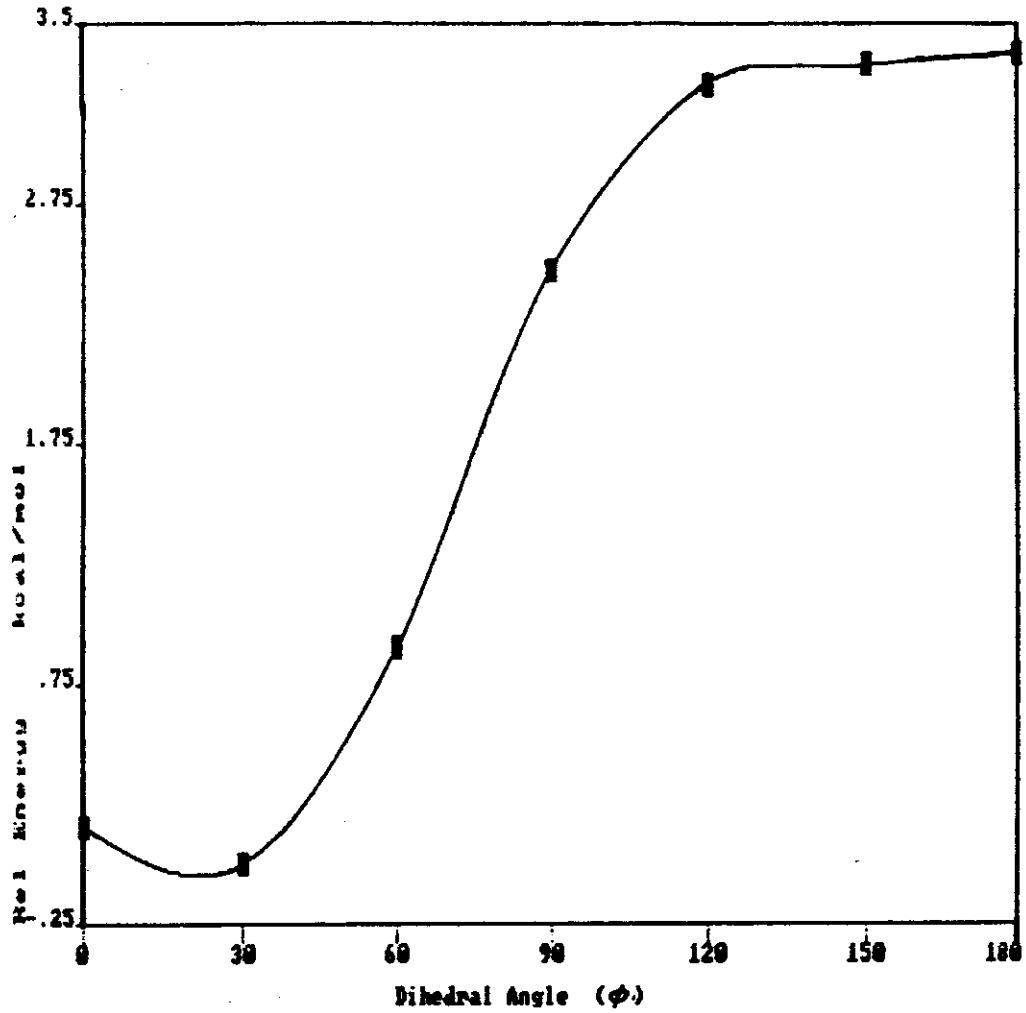


Fig (10a): Potential Energy Surface (PES) describing internal rotation in $^{\bullet}CHCOHD_2$.

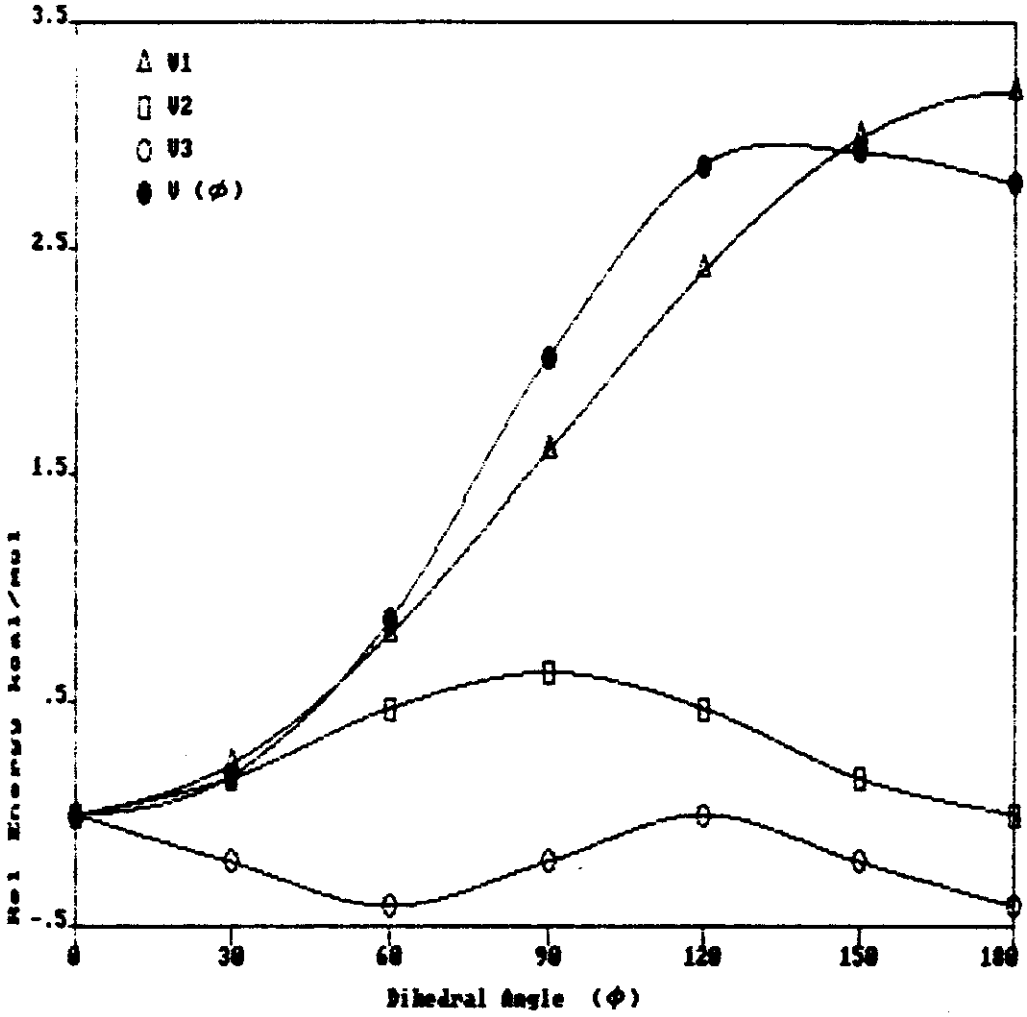


Fig (10b): Fourier components, $V_n(\phi)$ and potential energy function, $V(\phi)$ describing internal rotation in $^{\bullet}CHCOHD_2$.

$V_1(\phi)$ to $V(\phi)$ are shown in (Fig. 10b). From (Table 9) it is obvious that the potential function is dominated by the large value of V_1. The term V_1 is large and positive indicating a preference for the cis form over the trans one.This is consistent with the dipole-dipole interaction which favours the cis form having opposite dipoles (μ_{calcd}= 1.30D) over the trans form with reinforced dipoles (μ_{calcd}= 2.82D).

The positive value of V_2 indicates the preference for the configuration in which the C-O bond is coplanar with the axis of the lone pair orbital (ϕ=180°) than to be orthogonal to it *i.e.*(ϕ=90°). As in the case of dihydroxy silyl radical the term V_3 is small (compared with $V_1$and V_2) and negative indicating a preference for the staggered conformation (ϕ=60°,180°) over the eclipsed conformation (ϕ=0°,120°) since the latter suffers from a weak (but rather greater than that of hydroxysilyl radical) steric interaction. By compairing the mono- and di- hydroxy radical, it is found that V_1 for the di-substituted radical is greater than that of the mono-substituted one, while V_2 for the mono substituted radical is greater than that of the disubstituted one. This is also the case in the substituted silyl radicals.

(III) Trihydroxy Methyl Radical.

The potential energy curve of internal rotation is given

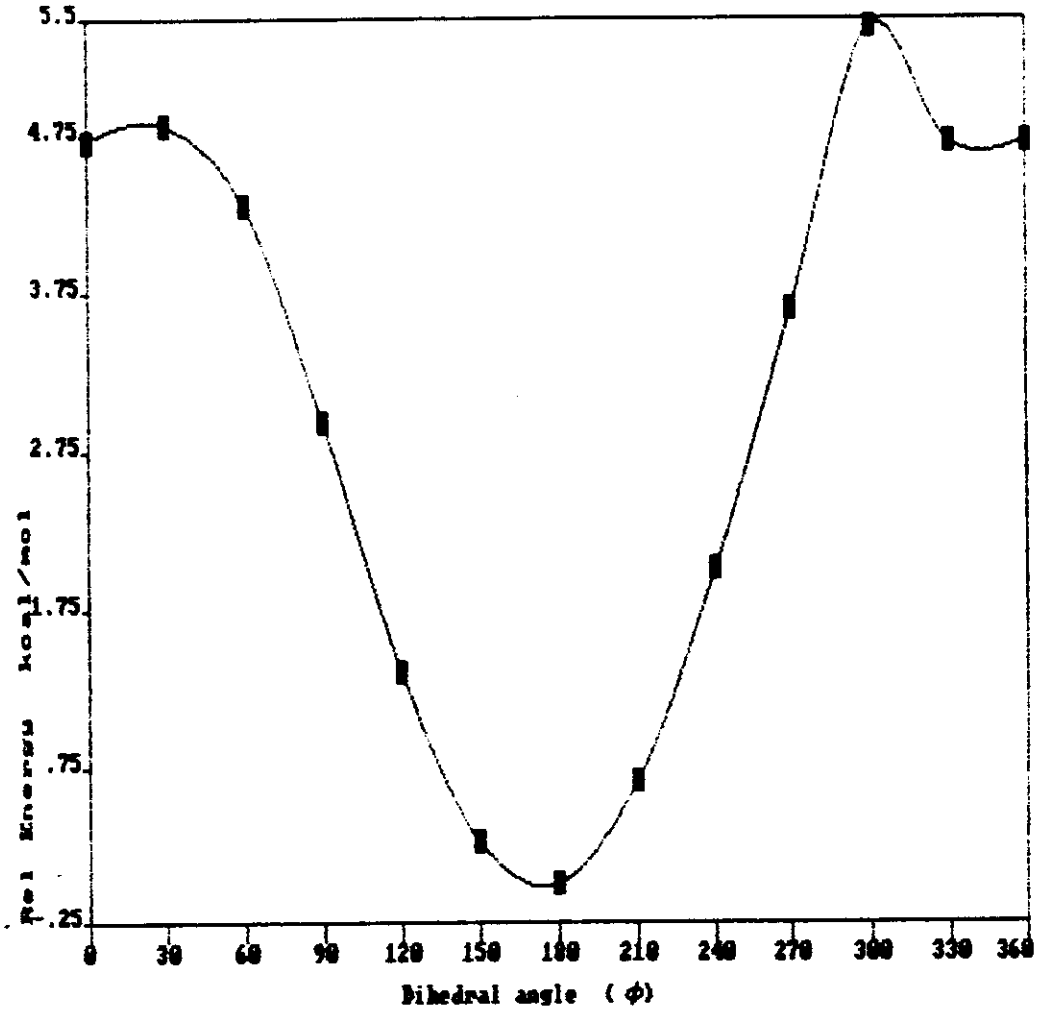


Fig (11a): Potential Energy Surface (PES) describing internal rotation in $^{\bullet}C(OH)_3$.

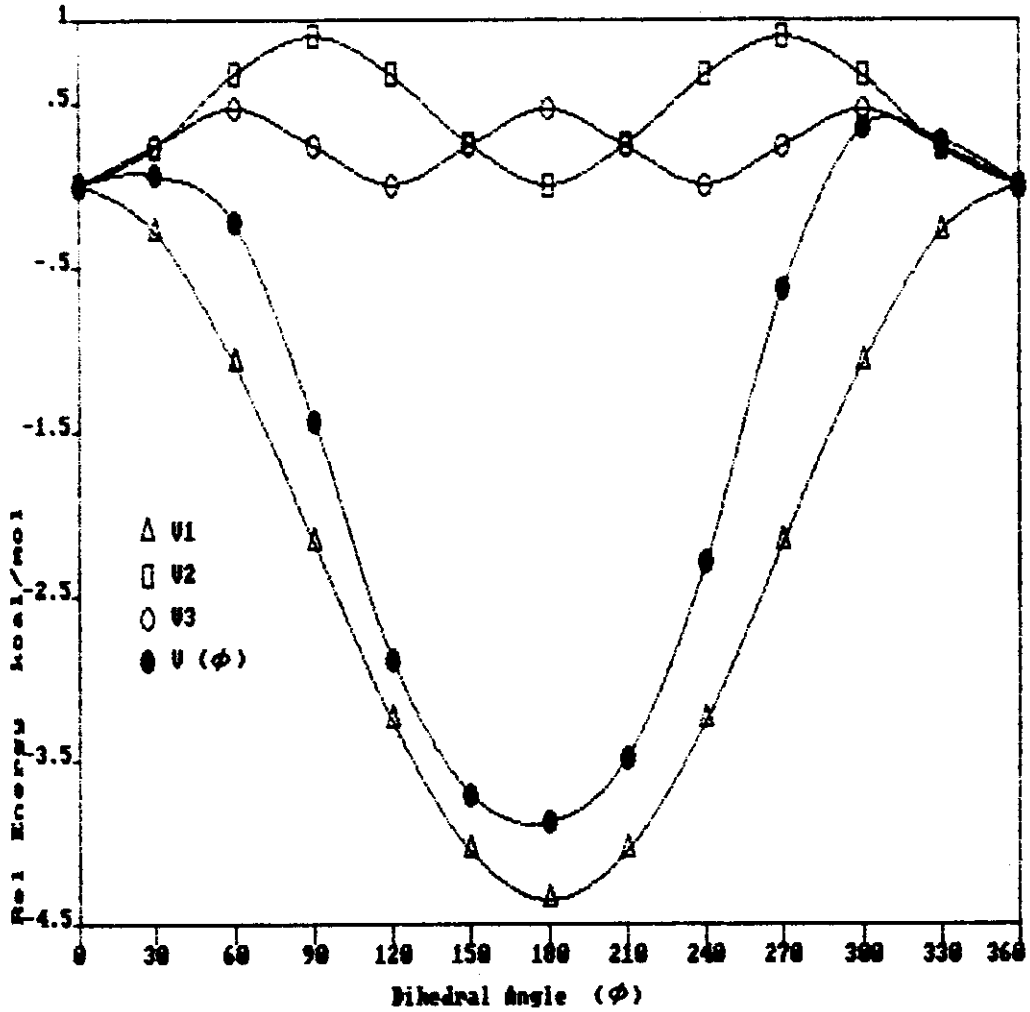


Fig (11b): Fourier components, $V_n(\phi)$ and potential energy function, $V(\phi)$ describing internal rotation in $^{\cdot}CC(O)HD_2$.

in (Fig. 11a) and the way in which the $V_1(\phi)$, $V_2(\phi)$ and $V_3(\phi)$ components contribute to the overall $V(\phi)$ function is represented in (Fig. 11b). The (PES) (Fig. 11a) indicates an asymmetrical behaviour of the potential function about $\phi=180^\circ$, so equation [1] of Fourier expansion of the potential energy equation should be applied in calculating the detailed potential energy curve. As in the case of dihydroxy methyl radical the potential function is dominated by V_1 term. The negative value of V_1 indicates preference for the trans ($\phi=180^\circ$) conformer over the cis ($\phi=0^\circ$) one.

The positive value of V_2 indicates preference for the coplanarity of the orbitals of the lone pair of the oxygen atom (around which the rotation occurs) and the odd electron orbital on the carbon center over the orthogonal conformers. This behaviour enhances the configurations with $\phi=0^\circ$ and $\phi=180^\circ$. The positive value of V_3 shows preference for the eclipsed configuration where ($\phi=0^\circ, 120^\circ$) over the staggered configuration ($\phi=60^\circ, 180^\circ$). But because it is small compared with V_1 and V_2 so it still does not have a significant effect. It should be noted that the value of V_3 in the case of trihydroxy radical is more than its value in the case of both mono- and di- hydroxymethyl radicals. This is because of the repulsion between bond pair electrons. It has been found that the value of V_3 in case of trihydroxymethyl radical is greater than that of trihydroxysilyl radical. This indicates that the repulsion in the first case is

greater than in the second. This is logically expected due to the difference in bond lengths between C-O and Si-O bonds. The negative value of V_1' shows a preference for conformations with $\phi < 180^\circ$ over those with $\phi > 180^\circ$, while V_2' has a very small positive value which can be neglected.

(IV) Amino-methyl Radical.

The (PES) of aminomethyl radical shows two minima (Fig. 12a) one at 210° and the other at 330°. As in the case of aminosilyl radical the potential function is dominated by the value of V_2. The large positive value of V_2 at $\phi=90^\circ$, 270° where the overlap between the orbital of the odd electron atom and the orbitals of the nitrogen lone pair of electrons is at a minimum. This indicates a preference for configuration with $\phi=0^\circ, 180^\circ$ where such overlap is not a maximum. The value of V_2 in case of aminomethyl radical is smaller than that in case of hydroxymethyl radical and this arises from the difference in size and electronegativity between the nitrogen and the oxygen atom. The term V_1 is negative indicating a preference for the trans form where ($\phi=180^\circ$) over the cis conformer. This is expected so long as this conformation minimize the dipole-dipole interaction as well as steric effects.

The term V_3 is positive indicating a preference for the eclipsed configuration ($\phi=0^\circ, 120^\circ$) over the staggered

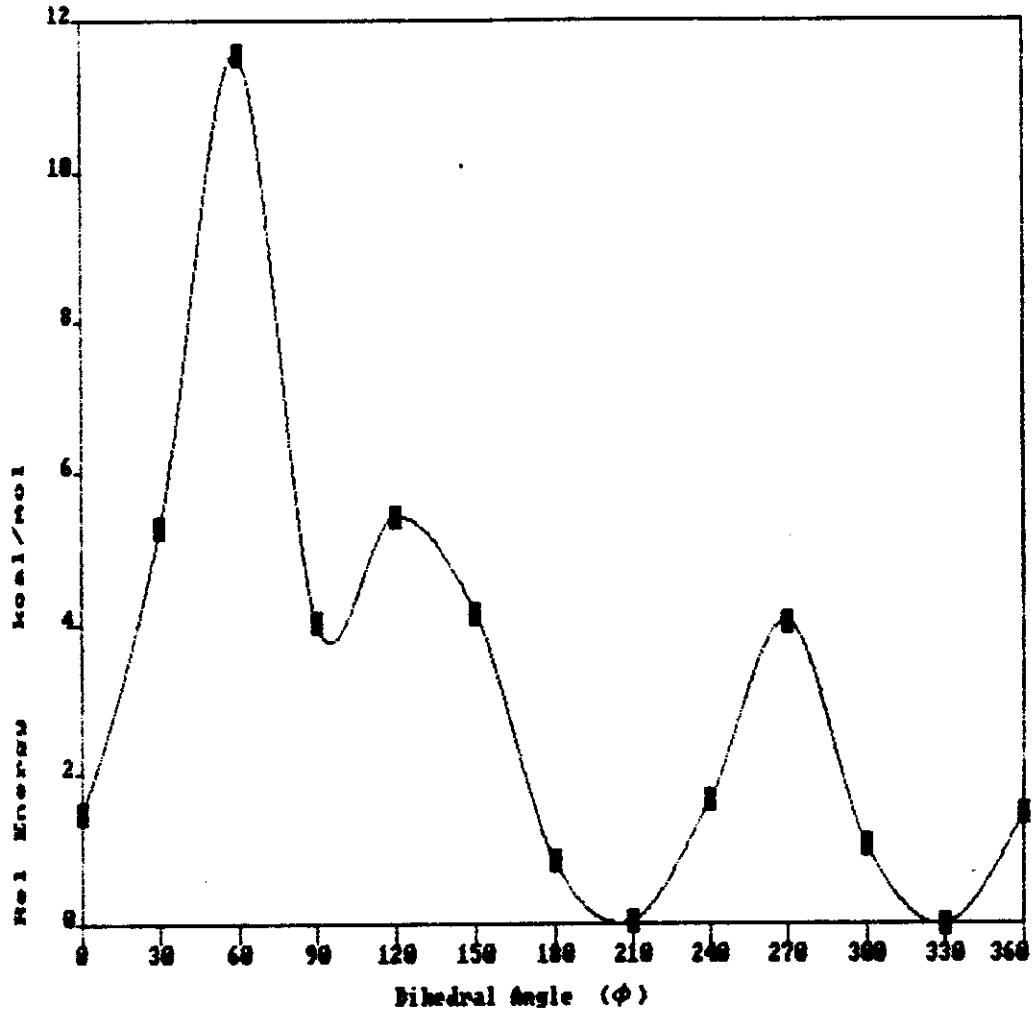


Fig (12a): Potential Energy Surface (PES) describing internal rotation in $^{\bullet}CH_2NH_2$.

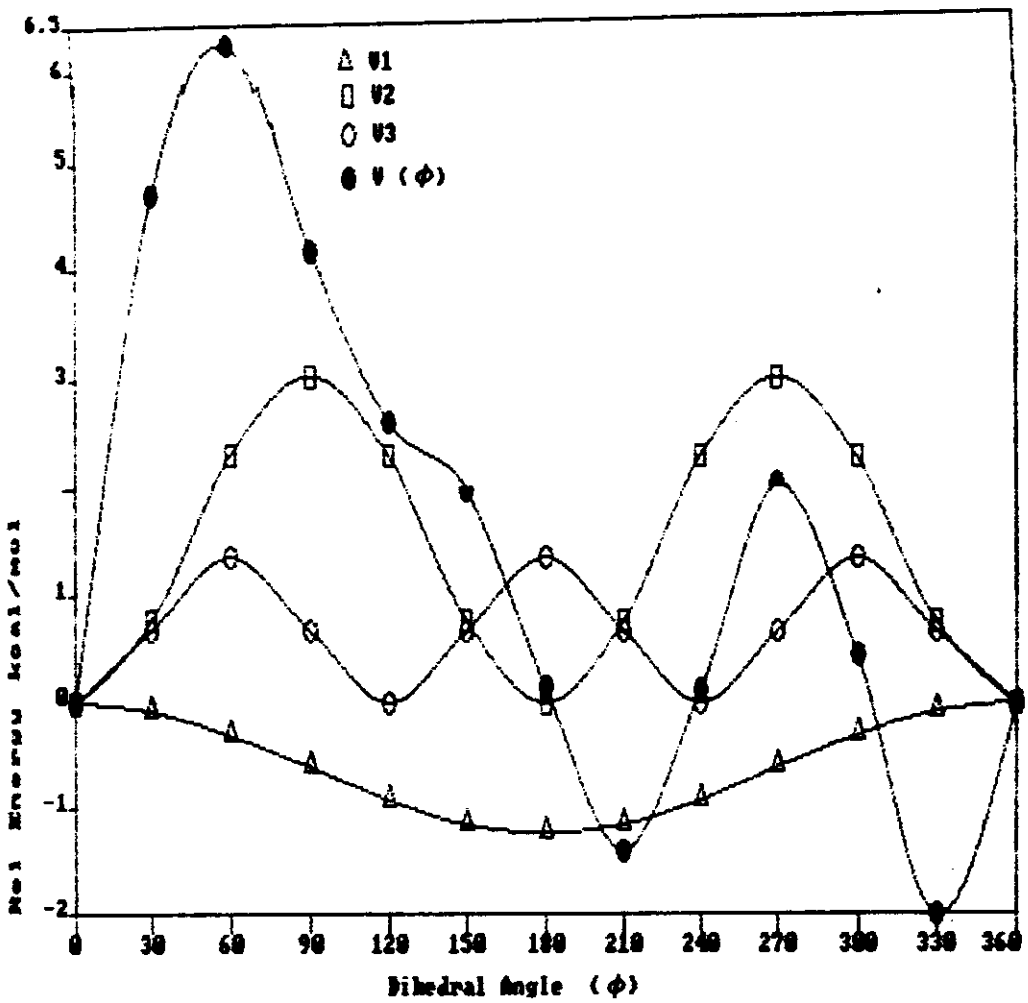


Fig (12b): Fourier components, $V_n(\phi)$ and potential energy function, $V(\phi)$ describing internal rotation in $^{\bullet}CH_2NH_2$.

configuration (ϕ=60°,180°). It is noted that the value of V_3 in case of aminomethyl radical is more than its value in the aminosilyl one. This is because the C-N bond is shorter than the Si-N and this allows a stronger repulsion between the bond pair- bond pair electrons. Both terms V_1' and V_2' have positive values which is responsible for the appearance of the two minima at angles more than 180°.

(V) Fluoro - amino Methyl Radical.

The potential energy of the fluoroamino methyl radical shows one sharp minimum at 240°. There are three maxima at 70°,150° and 330°. From studying the components of the potential energy it is obvious that V_2 and V_1' are the predominant factors. The value of V_2 is positive which is the case when the substituents possess one or more lone pair of electron. Positive values of V_2 show a preference for a configuration with rotational angles equal to ϕ=0°,180°. The value of V_1 though is small and negative value yet it supports to some extent the trans conformer where ϕ=180° over the cis conformer. V_3 has a negative value indicating a preference for staggered configurations (ϕ=60°,180°) over eclipsed form (ϕ=0°,120°). The combination of these three factors prefer the conformer with ϕ=180°. However the minimum at (PES) is shifted from position at 180° to 240°(Fig. 13a). This is a result of the large positive magnitude of V_1' which favours position with ϕ>180°.

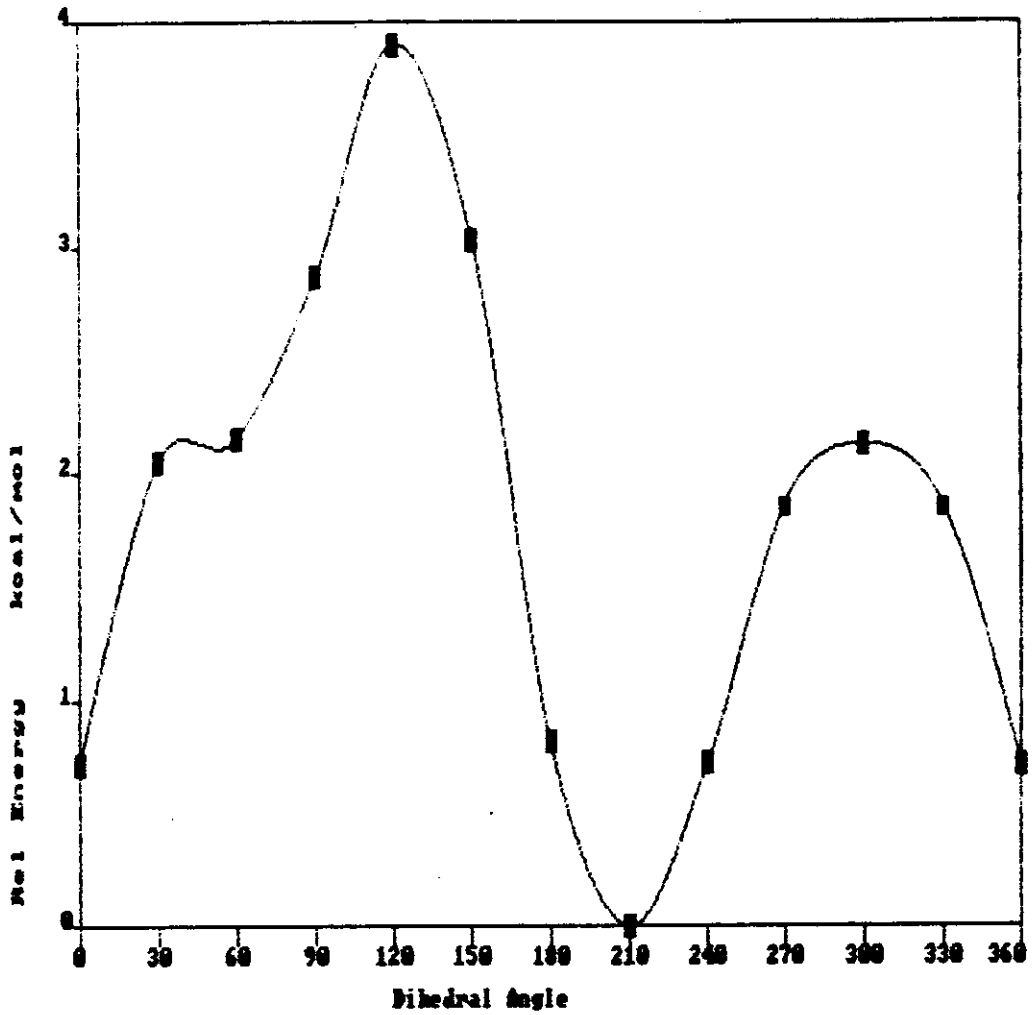


Fig (13a): Potential Energy Surface (PES) describing internal rotation in $^{\bullet}CHFNH_2$.

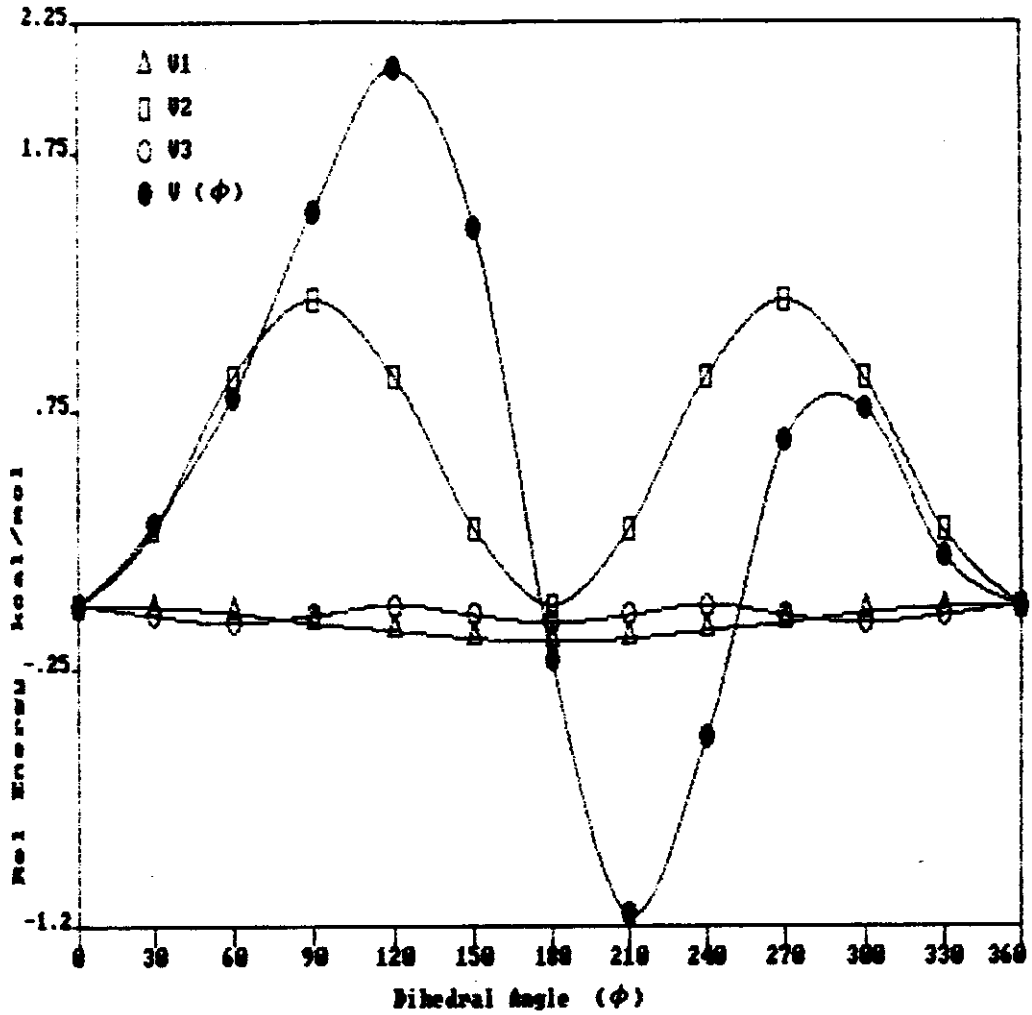


Fig (13b): Fourier components, $V_n(\phi)$ and potential energy function, $V(\phi)$ describing internal rotation in $^{\cdot}CHFNH_2$.