Journal of Organometallic Chemistry, 434 (1992) 19–33
Elsevier Sequoia S.A., Lausanne
JOM 22543

Ab initio study of the molecule $C_6H_5SiH_3$ and the molecular anion $C_6H_5SiH_2^-$: geometries and rotational barriers

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(Received October 10, 1991)

Abstract

This work reports the results of *ab initio* calculations at the split-valence basis set level for the species $C_6H_5SiH_3$ and $C_6H_5SiH_2^-$. The geometries and rotational barriers of the silicon compounds are compared with those of the carbon analogues $C_6H_5CH_3$ and $C_6H_5CH_2^-$ calculated at uniform levels of theory. Minimal π-conjugation is predicted for $C_6H_5SiH_2^-$, with the negative charge primarily localized on the silicon atom. π-Polarizations of the benzene ring are significant for $C_6H_5SiH_2^-$ and lead to charge-induced, conformationally dependent interactions. The π-electron-accepting properties of the phenyl group influence the value of the inversion barrier at silicon without changing appreciably the $CSiH_2$ geometry.

Introduction

Organosilicon chemistry is an especially fruitful area for investigation by gas-phase ion chemistry and ionic organosilanes are a subject of current interest [1]. However, experimental structural studies of charged organosilicon compounds and, in particular, of silyl anions are quite difficult and therefore are still limited. Structural information concerning silyl anions has been obtained only for SiH_3^- [2] which is the simplest molecular anion containing a silicon atom. Thus *ab initio* molecular orbital calculations assume a particularly important role in the investigation and in the prediction of structures and geometries of organosilicon compounds [3]. A variety of silyl anions has been studied by means of *ab initio* calculations [4–10] and their geometries have been determined at various levels of theory. With exception of the planar $BH_2SiH_2^-$ [5,6], all the structures deduced by theoretical investigation are pyramidal at silicon [4–10] with Si–substituent bond distances significantly longer than in the neutral precursors. For example, the potentially conjugated silacyclopentadienyl anion is found to be pyramidal at

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silicon and has an appreciable barrier to inversion [9,10]. In contrast to silyl anions, the molecular properties of the analogous carbanions are more affected by the electronic properties of the substituent. Indeed, the carbon lone-pair readily conjugates with π-electron-accepting substituents, and the corresponding carbanions are found in nearly all cases to be planar or almost planar at carbon [11].

The weak π-conjugation in silyl anions was inferred from electronic spectra [12] and NMR studies [13]. The wavelength of the UV absorption of phenylsilyllithium compounds is lower than that of phenylmethyllithium systems by about 150 nm and independent of the number of phenyl rings in the series $PhMe_2SiLi$, $Ph_2MeSiLi$ and Ph_3SiLi suggesting that negative charge delocalization from the substituent onto the phenyl ring is lower in silyl anions than in the analogous carbanions. NMR studies [13] provide direct information on negative charge delocalization on the benzene ring in phenylmethyl and phenylsilyl anions. Comparisons between ^{13}C chemical shifts of Ph_3CLi and Ph_3CCl indicate that phenylmethyl carbanions show remarkable localization of negative charge on the *ortho* and *para* carbon atoms of the benzene ring, in agreement with the usual predictions of resonance delocalization. On the other hand, the ^{13}C chemical shifts of Ph_3SiLi and Ph_3SiCl suggest a smaller charge on the phenyl ring in the silyl anion than in the carbanion. In addition, the charge distribution on the benzene ring of the silyl anions is mainly controlled by π-polarization [14] induced by the negative charge on the silicon atom.

The purpose of the present work is to study the molecular structure of $C_6H_5SiH_3$ and $C_6H_5SiH_2^-$, by *ab initio* calculations, and to discuss the nature of the interactions between silicon and benzene ring in both the organosilicon compounds by considering geometry and rotational and inversion barriers. A self-consistent-field (SCF) molecular orbital study of the $C_6H_5SiH_3$ and $C_6H_5SiH_2^-$ system is reported, and the results for these species are compared with the carbon analogues $C_6H_5CH_3$ [15,16] and $C_6H_5CH_2^-$ employing uniform levels of theory. Previous studies concluded that *d*-functions are essential for describing correctly the geometry of double-bonded silicon molecules [17,18]. On the other hand, it is well known that the inclusion of diffuse atomic orbitals is desirable for obtaining reliable molecular properties of silicon [4] and carbon [11] anions. Therefore, the optimized geometries reported in this study were obtained using split-valence basis sets including polarization and/or diffuse functions.

The extent of negative charge delocalization on the phenyl ring of $C_6H_5SiH_2^-$ can be inferred on geometrical grounds. Charge sharing between the substituent and the ring is likely to cause substantial alternations in the CC bond distances of the benzene ring, as previously shown for $C_6H_5CH_2^-$ in a 3-21G study [19]. The geometrical changes occurring upon rotation of the substituent about the CSi and CC exocyclic bonds, as well as the rotational barrier heights, are expected to reflect the strength of π-conjugation between substituent and phenyl group. Orthogonal orientations of CH_2 and PH_2 with respect to the benzene ring were purposely considered and the relative stabilities of the conformations were evaluated within the second-order perturbation level of the Møller–Plesset theory [20].

Alternatively, the extent of π-interaction between silicon and phenyl group in $C_6H_5SiH_2^-$ can be inferred from the values of the inversion barrier at silicon. Different orientations of the SiH_2 group with respect to the benzene ring are likely to influence the energy barrier to the planar configuration indicating the existence of conformationally dependent interactions between the substituent and the ring. In this context, it is also useful to compare the rotation and inversion barriers of $C_6H_5SiH_2^-$ with the values calculated for the isoelectronic phenylphosphine, $C_6H_5PH_2$.

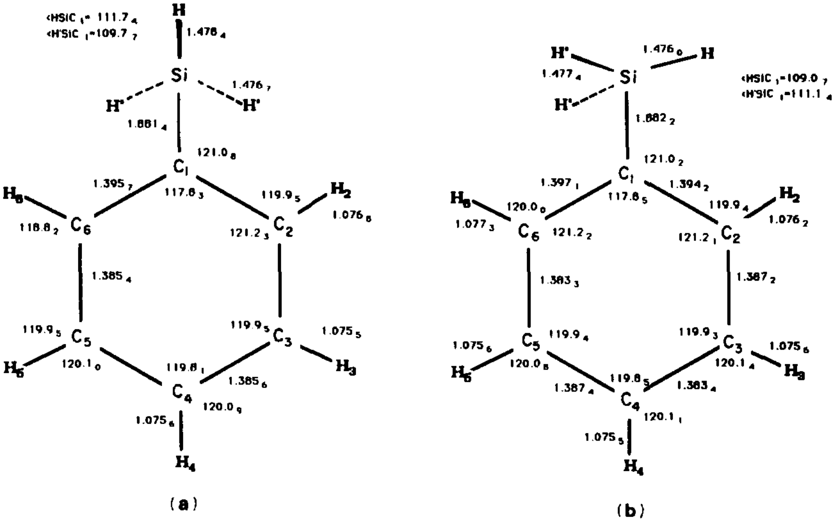
Lastly, an estimate of the stability of $C_6H_5SiH_2^-$ relative to different silyl anions is obtained from the energy changes for a series of isodesmic reactions [21].

Method

Computations were carried out with the IBM-VM/CMS version of the program GAUSSIAN 88 [22] running on an IBM 3090-600J computer. Geometry optimizations were carried out at the Hartree-Fock(HF)-SCF level by an analytical gradient-based technique [23] with the 6-31G* (6D) and 6-31 + G* (6D) basis sets [24]. The geometries calculated at the SCF 6-31G* level are reproduced in Figs. 1–5, and the HF/6-31 + G* geometries of the most stable conformers of $C_6H_5SiH_2^-$ and $C_6H_5CH_2^-$ are reported in square brackets (Figs. 2a and 3a). Electron correlation in the frozen core approximation, by the second order of the Møller–Plesset perturbation theory (MP2), was included at the HF/6-31G* geometries. The designation of these calculations is MP2(fc)/6-31G*//HF/6-31G* and MP2(fc)/6-31 + G*//HF/6-31G* where // means "at the geometry of" and in the remainder of the paper (fc) will be omitted. Total energies and rotational barriers about the CSi and CC bonds are reported in Table 1 and the results of additional computations are available upon request.

Results and discussion

The SCF/6-31G* geometry of $C_6H_5SiH_3$ is shown in Fig. 1. There are two distinct preferred orientations of the SiH_3 group with respect to the phenyl ring. The conformation where a hydrogen atom of SiH_3 is oriented perpendicularly to the ring plane and the two remaining hydrogen atoms are located on the opposite side of the benzene plane is described as the orthogonal conformer (Fig. 1a); the other rotamer (Fig. 1b), designated as eclipsed, has an SiH bond lying in the plane of the phenyl ring. Geometry optimizations within the C_s symmetry constraint were carried out for the eclipsed conformer assuming that the ring and the silicon atom are coplanar, while relaxation of the planarity constraint was introduced for the orthogonal structure. Nonplanar benzene ring structures were actually predicted for a wide number of derivatives where the substituent group is oriented unsymmetrically with respect to the benzene ring, but the predicted deviations from planarity were extremely small [25]. The ring of the orthogonal structure of $C_6H_5SiH_3$ adopts a very shallow inverted boat-type conformation, similar to that found for the orthogonal conformer of $C_6H_5CH_3$ [25], with the displacement of the silicon atom with respect to the C(1) ··· C(4) reference axis in the opposite direction to that of the ring carbon atoms. The energy difference between the two rotamers of $C_6H_5SiH_3$ is only 0.1 kJ/mol (HF/6-31G*) and 0.2 kJ/mol (MP2/6-31G*//HF/6-31G*), in favour of the orthogonal conformer. The low rotational barrier of the SiH_3 group compares with freely rotating property (0.03 kJ/mol) of the CH_3 group of $C_6H_5CH_3$ predicted at the HF/6-31G* level [15,16]. Preference for the orthogonal structure of $C_6H_5CH_3$ (0.2 kJ/mol) is also calculated at the MP2/6-31G*//HF/6-31G* level (Table 1).



(a)

(b)

Fig. 1. Geometries of the orthogonal (a) and eclipsed (b) conformers of $C_6H_5SiH_3$ (bond lengths in Å and bond angles in °).

Previous results on $C_6H_5CH_3$ [15,16] indicate that the geometry of the benzene ring is sligthly affected by the orientation of the substituent. Similarly, the variations of the CC and CSi bond distances of $C_6H_5SiH_3$ with the SiH_3 rotation are only a few thousands of an Ångström and the internal ring angles are nearly unchanged. The rotation of the substituent cause only small changes in the geometry of the SiH_3 group. Figure 1 shows that the length of the SiH bond depends on the value of the dihedral angle (ϕ) between the ring plane and the SiH bond. As for the methyl group of $C_6H_5CH_3$ [15], the largest SiH bond distance (1.478_4 Å) is found when the bond is perpendicular to the phenyl ring ($\phi = 90°$), while the SiH bond length progressively decreases from 1.447_4 to 1.476_7 and to 1.476_0 Å, at dihedral angle values equal to 60, 30 and 0°, respectively.

In addition, the HSiC(1) bond angle shows an appreciable dependence on the orientation of the SiH bond, decreasing progressively from 111.7_4°($\phi = 90°$) to 109.0_7°($\phi = 0°$). Such SiH_3 geometric changes suggest the tendency of the sub-

Table 1

Total energies (a.u.) for stable conformations of $C_6H_5CH_3$, $C_6H_5SiH_3$, $C_6H_5CH_2^-$, $C_6H_5SiH_2^-$, $C_6H_5PH_2$ and rotational barriers ΔE [a] (kJ/mol)

	$C_6H_5CH_3$	$C_6H_5SiH_3$	$C_6H_5CH_2^-$	$C_6H_5SiH_2^-$	$C_6H_5PH_2$
HF/6-31G*	−269.74016 [b]	−521.78034	−269.07853	−520.16382	−571.99486
ΔE HF/6-31G*	0.03 [b]	0.07	102.1	3.4	4.6
MP2/6-31G* [c]	−270.62710	−521.61425	−269.97492	−521.00721	−572.85245
ΔE MP2/6-31G* [c]	0.20	0.20	113.1	6.9	1.7
MP2/6-31+G* [d]			−270.01601	−521.03576	
ΔE MP2/6-31+G* [d]			92.5	4.9	

[a] Hartree = 2625.5 kJ/mol. [b] Ref. 15. [c] Short for MP2/6-31G*//HF/6-31G*. [d] Short for MP2/6-31+G*//HF/6-31G*.

stituent to tilt away from the π-system of the benzene ring. These structural features are not found in $C_6H_5CH_3$ for which the asymmetry of the methyl group concerns primarily the CH bond lengths. A reliable estimate of the deformation of the benzene ring geometry caused by the SiH_3 substituent can be obtained by comparing the theoretical values of the ring bond lengths and ring bond angles of $C_6H_5SiH_3$ with those of the unsubstituted C_6H_6 (HF/6-31G*: CC 1.386_3 Å) [26]. The largest deviations from the geometry of C_6H_6 concern the C(1)C(2) bond length and the C(6)C(1)C(2) bond angle. The C(1)C(2) bond distance of $C_6H_5SiH_3$ is about 0.01 Å longer than that of C_6H_6, with smaller variations for the other CC bond distances; the C(6)C(1)C(2) bond angle, the *ipso* angle, is 2.2 less than 120° and this value reasonably agrees with the result of an electron diffraction study on $C_6H_5SiH_3$ [27].

In order to test the influence of the basis set on the molecular geometry, optimization of both the rotamers of $C_6H_5SiH_3$ was performed by employing a slightly more extended basis set (DZP) [24]. At this level, the CC bond distances are systematically longer by 0.003 Å (*ortho* bonds) and by 0.005 Å (*meta* and *para* bonds) with respect to the 6-31G* basis set determination; likewise, the DZP lengths of the CSi and SiH bonds are longer by 0.005 Å. Except for these changes, both basis sets describe the geometrical distortions of the benzene ring of $C_6H_5SiH_3$ consistently; in fact, the values of the internal ring angles and of the difference between the ring CC bond distances are almost unaffected by the choice of basis set.

Taking into account these results and those of previous theoretical [15,16], and experimental studies on $C_6H_5CH_3$ [28] and on $C_6H_5SiH_3$ [27], it emerges that the structural differences between the silyl and methyl compounds are not very large. On the contrary, the $C_6H_5SiH_2^-$ and $C_6H_5CH_2^-$ anions have noticeably different structures. Geometry optimizations were carried out on $C_6H_5CH_2^-$ assuming a perpendicular orientation of the carbon lone-pair with respect to the ring plane.

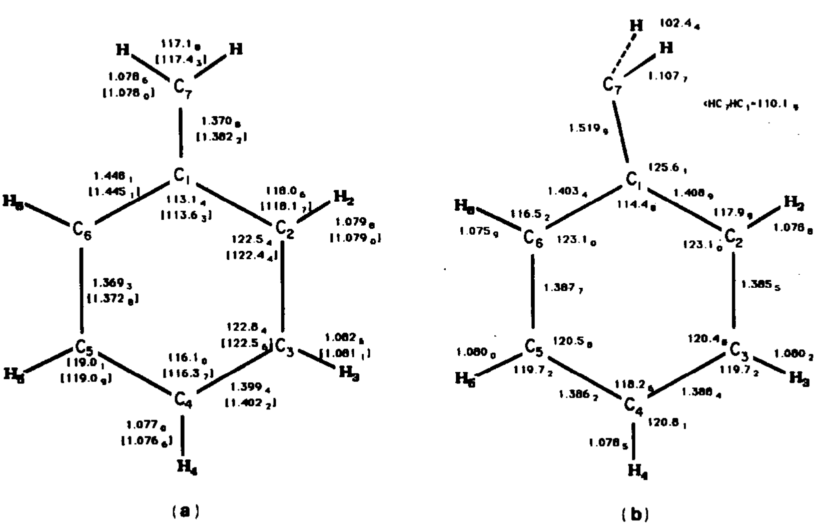


Fig. 2. HF/6-31G* geometries of (a) the planar and (b) orthogonal structures of $C_6H_5CH_2^-$. The HF/6-31+G* parameters are in square brackets (bond lengths in Å and bond angles in °).

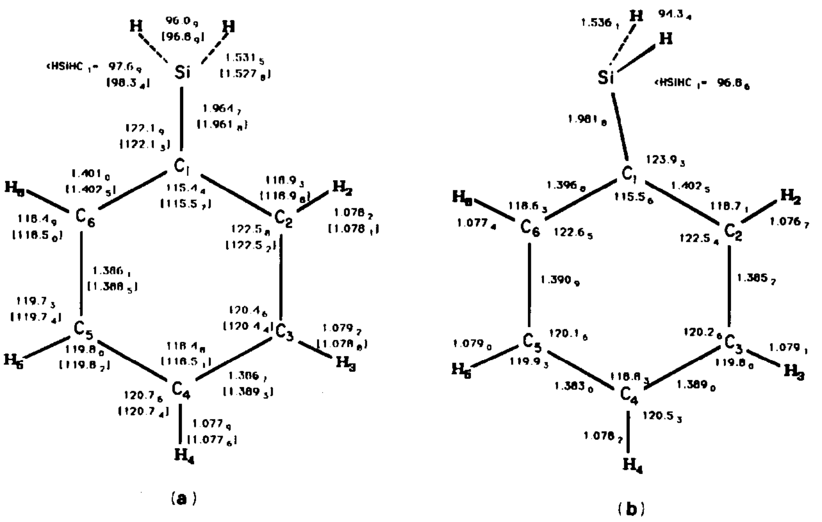


Fig. 3. HF/6-31G* geometries of the two rotamers of $C_6H_5SiH_2^-$. The HF/6-31+G* parameters are in square brackets (bond lengths in Å and bond angles in °).

HF/6-31G* calculations indicate that the benzyl anion has a planar structure (Fig. 2a); attempts to allow the CH_2 group to converge to a nonplanar configuration were made, but preference for the planar arrangement was confirmed. A pyramidal configuration at silicon (Fig. 3a) was found to correspond to a stationary point for $C_6H_5SiH_2^-$; this structure was obtained by imposing a perpendicular orientation of the silicon lone-pair with respect to the ring plane. As already described for the orthogonal rotamer of $C_6H_5SiH_3$, relaxation of the ring planarity constraint was taken into account during the optimizations and a boat-type deformation of the ring was obtained. Although nonplanarity of the ring is similar in $C_6H_5SiH_3$ and in $C_6H_5SiH_2^-$, the displacements of silicon with respect of the C(1) $\cdots$ C(4) reference axis, are different. In $C_6H_5SiH_2^-$ the silicon atom lies on the same side of the carbon atoms, while in the neutral precursor it is found on the opposite side. The dihedral angle between the SiH_2 plane and the CSi bond, henceforth indicated as the pyramidal angle, is 97.7°. In addition, as will be discussed below, HF/6-31G* geometry optimizations on $C_6H_5SiH_2^-$ constrained to be planar at silicon destabilize the system by 137.4 kJ/mol. The value of the pyramidal angle, as well as the high barrier to planarity at silicon, suggest strong configurational stability of the $CSiH_2$ moiety.

For both the stable conformations of $C_6H_5CH_2^-$ and $C_6H_5SiH_2^-$, geometries were optimized employing the 6-31 + G* basis set and these are reproduced in Figs. 2a and 3a, respectively. The largest changes in the molecular geometry passing from the 6-31G* to the 6-31 + G* basis set are calculated for $C_6H_5CH_2^-$ and, in particular, for the C(1)C(7) bond length and for the C(6)C(1)C(2) bond angle which increase by 0.011 Å and 0.5°, respectively.

Geometrical distortions of the benzene ring are predicted for both the molecular anions but the effects for $C_6H_5SiH_2^-$ are less pronounced than for $C_6H_5CH_2^-$. The benzyl anion shows a noticeable alternation in the CC bond distances. The C(1)C(7) and C(2)C(3) bond lengths are the shortest whereas the C(1)C(2) bond length is the longest one. This is consistent with the predictions of resonance theory for systems with significant π-interactions between the substituent and the ring [19]. Comparison of $C_6H_5CH_3$ [15] with the deprotonated species reveals an increase of the π-contribution in the exocyclic bond upon deprotonation, indicated by the shortening of the C(7)C(1) bond distance (0.02 Å) and by the decrease of the *ipso* angle by *ca.* 5°. On the ground of these results, considerable π-delocalization of negative charge from C(7) atom onto the ring is expected for the $C_6H_5CH_2^-$ anion.

Deprotonation of SiH_3 of $C_6H_5SiH_3$ results in a smaller structural reorganization as compared to $C_6H_5CH_3$. HF/6-31G* calculations indicate that $C_6H_5SiH_2^-$ has a ring geometry similar to that of $C_6H_5SiH_3$, with a small increase of the C(1)C(2) and C(1)C(6) bond distances by *ca.* 0.005 Å and a decrease of the *ipso* angle by *ca.* 2°. The differences among the CC bond lengths of the ring are less marked than those predicted for $C_6H_5CH_2^-$. On the ground of the 6-31 + G* geometry, the longest CC bond distance is C(1)C(2) (1.403 Å) whereas both the C(2)C(3) and C(3)C(4) bond lengths are shorter by *ca.* 0.014 Å. A minor alternation of the ring CC bond distances is therefore calculated for $C_6H_5SiH_2^-$. The most noticeable change occurring upon deprotonation of SiH_3 concerns the CSi bond distance, which increases from 1.881 to 1.962 Å. This is opposite to the carbon system, where deprotonation of CH_3 results in the shortening of the exocyclic bond distance. A similar elongation of the Si-substituent bond is also observed upon SiH_3 deprotonation of CH_3SiH_3, NH_2SiH_3, $OHSiH_3$ and $FSiH_3$ [5] and indicates a substantial decrease in the π-conjugation between silicon and the substituent moving from the neutral precursors to silyl anions.

Information about the variations of the benzene ring electron distribution following the deprotonation of the substituent bonded to the phenyl group is provided by the change of the atomic charges and, in particular of the π-charges. Table 3 summarizes the variations in the HF/6-31 + G*//HF/6-31G* π-gross orbital populations of the ring carbon atoms occurring upon deprotonation of the CH_3 and SiH_3 groups. As far as the carbon system is concerned, a large amount of negative π-charge (0.51 e.s.u.) is passed to the phenyl ring; the largest π-charge changes are calculated for the *ortho* and *para* carbon atoms, which gain 0.17 e.s.u., C(2) and C(6), and 0.31 e.s.u., C(4), whereas the *ipso* and *meta* carbon atoms lose π-charge 0.13 e.s.u., C(1), and 0.03 e.s.u., C(3) and C(5). These changes are consistent with the extensive π-charge delocalization from the substituent onto the *ortho* and *para* carbon atoms predicted by the usual resonance structures of the planar isomer. The analogous population data of the silicon compounds (see Table 3) show that the phenyl ring gains a negligible amount of negative π-charge (0.04 e.s.u.) upon deprotonation of SiH_3 and that the small π-charge changes occurring on each carbon atom have a pattern different from that expected if conjugative effects were important. In fact, the largest variations occur at the *ipso* and *para* carbon atoms, whereas the *ortho* carbon atoms gain a small amount of negative charge. On the ground of these population data, mesomeric effects seem to be negligible for $C_6H_5SiH_2^-$ and this result parallels previous conclusions based on ^{13}C NMR chemical shifts [13]. The charge pattern predicted for $C_6H_5SiH_2^-$ can be interpreted as the result of the polarization of the π-electrons of the benzene ring due to the negative charge localized on the silicon atom.

Alternatively, the degree of π-conjugation between the substituent and the ring in the molecular anions can be evaluated by rotating the CH_2 and SiH_2 groups

Table 2

Inversion barriers [a] (kJ/mol) at silicon for SiH_3^-, $CH_3SiH_2^-$, $C_2H_3SiH_2^-$ and $C_6H_5SiH_2^-$ and at phosphorus for $C_6H_5PH_2$

Theoretical method	SiH_3^-	$CH_3SiH_2^-$	$C_2H_3SiH_2^-$		$C_6H_5SiH_2^-$		$C_6H_5PH_2$	
			$\Theta^b = 90$	$\Theta^b = 0$	$\Theta^c = 90$	$\Theta^c = 0$	$\Theta^d = 90$	$\Theta^d = 0$
HF/6-41G*	145.2	167.9	133.8	173.2	137.4	171.9	157.7	156.1
MP2/6-31G*//HF/6-31G*	134.4	151.7	109.8	152.6	111.2	150.1	142.2	142.1
MP2/6-31+G*//HF/6-31G*	109.9	126.7	91.3	127.4	97.7	127.5		
MP2/6-31+G*	110.0							
MP2/6-31+G**	109.7							
MP4/6-31+G**//MP2/6-31+G**	110.1							
CCSD/TZ2P+diff(Si) [e]	106.3							
Exp [f]	108 ± 24							

[a] Inversion barriers calculated as difference between the energies of the pyramidal and planar structures where SiH_2 and PH_2 maintain the same orientation with respect to the vinyl and phenyl groups. [b] Dihedral angle (°) between the vinyl plane and the Si lone-pair. [c] Dihedral angle (°) between the phenyl plane and the Si lone-pair. [d] Dihedral angle (°) between the phenyl plane and the P lone-pair. [e] Ref. 4. Short for coupled cluster with single and double excitations method with triple-zeta plus polarization and diffuse functions on Si. [f] Ref. 2.

and by optimizing the corresponding geometries. Forcing the substituent to take orthogonal conformation orients the silicon and carbon lone-pairs of $C_6H_5SiH_2^-$ and $C_6H_5CH_2^-$ in the plane of the phenyl ring and prevents π-interactions. The geometries of the rotated conformations are reproduced in Figs. 2b and 3b and the energy variations with rotation of the substituents are reported in Table 1. Preference for pyramidal CH_2 and SiH_2 groups are found for both the rotated molecular anions; the pyramidal angle at silicon is 96.9° and the corresponding value at carbon is 110.2°. A high rotational barrier about the C(1)C(7) bond (113.1 kJ/mol) is calculated at the MP2/6-31G*//HF/6-31G* level for $C_6H_5CH_2^-$ and a lower value (92.5 kJ/mol) is obtained at the MP2/6-31 + G*//HF/6-31G* level, and these values indicate considerable π-conjugation for the planar structure of $C_6H_5CH_2^-$. On the other hand, free rotation of the SiH_2 group is predicted at

Table 3

Gross π-atomic population changes [a] of carbon-ring atoms: upon deprotonation of CH_3 (**A**) and SiH_3 (**B**); upon rotation of CH_2 (**A′**) and SiH_2 (**B′**)

Atom [b]	(**A**) $C_6H_5CH_3/C_6H_5CH_2^-$	(**A′**) $C_6H_5CH_2^-$	(**B**) $C_6H_5SiH_3/C_6H_5SiH_2^-$	(**B′**) $C_6H_5SiH_2^-$
C(1)	−0.131	−0.010	−0.230	0.090
C(2)	0.165	−0.144	0.045	−0.041
C(3)	−0.030	0.075	0.033	0.008
C(4)	0.314	−0.230	0.112	−0.030
C(5)	−0.030	0.075	0.033	0.003
C(6)	0.165	−0.179	0.045	−0.033

[a] HF/6-31+G*//HF/6-31G* level; positive value indicates a negative charge gain. [b] See Figs. 1, 2 and 3.

the MP2/6-31G*//HF/6-31G* level for $C_6H_5SiH_2^-$, with a small preference (6.9 kJ/mol) for the C_s conformer (Fig. 3a); this structure is also preferred upon addition of diffuse functions (MP2/6-31 + G*//HF/6-31G*) by 4.9 kJ/mol.

The geometric changes due to the torsion of the substituent strictly parallel the barrier heights. The largest change of the bond lengths in going from the planar to the orthogonal structure of $C_6H_5CH_2^-$ is predicted to occur for the C(1)C(7) bond distance, which increases by 0.149 Å. The large alternation in the C(1)C(2), C(2)C(3), and C(3)C(4) bond lengths for the planar structure becomes less marked in the orthogonal isomer, where the C(1)C(2) and C(1)C(6) bond distances are the longest ones and the remaining CC ring bonds show unchanged lengths within a few thousands of an Ångström. With regard to the bond angles of the ring, the torsion of the substituent is associated with an increase of the C(6)C(1)C(2) (1.4°) and C(3)C(4)C(5) (2.2°) angles. Such a structural change is a consequence of the shortening of the bonds subtending these bond angles. In addition, the orthogonal structure of $C_6H_5CH_2^-$ shows a tilt angle of the CH_2 group with respect to the C(1) ··· C(4) axis of 5.7°. The asymmetry of the substituent in orthogonal orientation is reflected also in the values of the C(2)H(2) and C(6)H(6) bond lengths and of the H(2)C(2)C(1) and H(6)C(6)C(1) angles. The C(6)H(6) bond distance is about 0.003 Å shorter than the C(2)H(2) and the H(6)C(6)C(1) angle is 1.5° smaller than H(2)C(2)C(1); probably such asymmetry of the benzene ring can be justified by an interaction between the H(6) atom and the C(7) lone-pair which lies in the ring plane and is located on the same side of the C(6)H(6) bond. Evidence of this fact is the charge on the H(6) atom, which is less than that on the H(2) atom by 0.03 e.s.u. Similar geometric features were found for C_6H_5OH [29] and for C_6H_5CHO [30], and are indicative of an attractive interaction between the oxygen lone-pair and the nearest hydrogen atom of the CH bond.

Minor changes are calculated to occur upon rotation of SiH_2. The ring geometry remains substantially unchanged with variations of the CC bond distances less than 0.005 Å and of bond angles less than 0.2°. The most appreciable changes are predicted for the CSi bond length (0.017 Å) and for the HSiH angle (1.8°). The tilt angle at Si with respect to the C(1) ··· C(4) axis is 3.4°, but the differences between the C(6)H(6) and C(2)H(2) bond lengths (0.0007 Å) and between the H(6)C(6)C(1) and H(2)C(2)C(1) (0.08°) bond angles are negligible.

The slight geometric changes associated with the SiH_2 torsion reflect small variations of the gross π-orbital population of the carbon atoms (see Table 3). The rotation of SiH_2, as well as the deprotonation of SiH_3, affect the π-electron distribution on each carbon atom of the benzene ring without altering the total π-charge. With exception of the *ipso* carbon atom of $C_6H_5SiH_2^-$, which gains π-charge 0.09 e.s.u. in going from the most stable isomer to the rotated conformation, the remaining carbon atoms are relatively unaffected. In contrast, the orientation of CH_2 in $C_6H_5CH_2^-$ influences more effectively the gross π-orbital population (Table 3). A net loss of negative π-charge (0.41 e.s.u.) on the whole benzene ring is observed on moving from the planar to the C_s orthogonal $C_6H_5CH_2^-$, with changes at the C(2), C(4) and C(6) atoms occurring in line with the prediction of the resonance theory. Moreover, the π-charge on C(1) atom does not depend on the orientation of CH_2. From the π-charge change patterns collected in Table 3, it is clear that the mesomeric effects are very slight for $C_6H_5SiH_2^-$; deprotonation or rotation of the SiH_2 group can only redistribute the

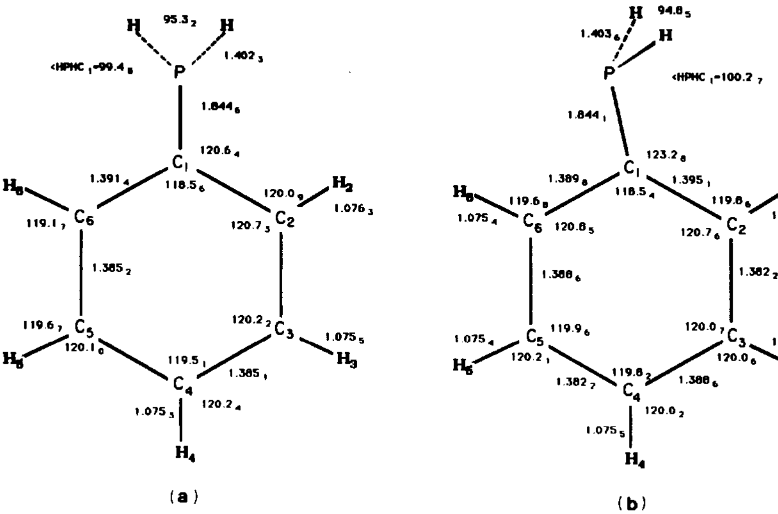


Fig. 4. Geometries of the two rotamers of $C_6H_5PH_2$ (bond lengths in Å and bond angles in °).

π-charge of the benzene ring without net gain or loss from the silicon atom to the phenyl group.

The extent of π-conjugation between silicon and aromatic ring in $C_6H_5SiH_2^-$ is suggested by the values of the inversion barrier at silicon. HF/6-31G* geometry optimizations were carried out by imposing the planarity constraint on $C_6H_5SiH_2^-$ within C_{2v} symmetry. In this structure, favourable alignment of the silicon lone-pair allows the maximum overlap with the C(1) *p*-orbital and a consequent appreciable charge delocalization on the phenyl ring. As evidence of this, the geometry of the planar $C_6H_5SiH_2^-$ (Fig. 5a) differs significantly from that predicted for a pyramidal conformation of the $CSiH_2$ moiety. The salient structural features are that the

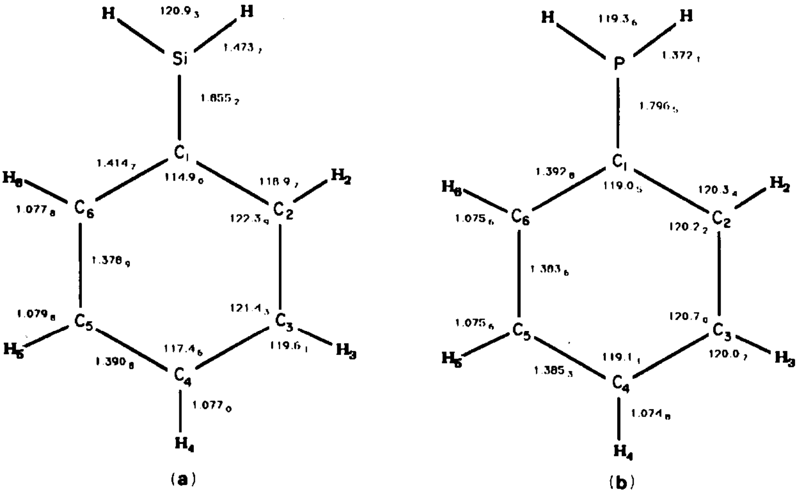


Fig. 5. HF/6-31G* geometries of the planar structures of (a) $C_6H_5SiH_2^-$ and (b) $C_6H_5PH_2$ (bond lengths in Å and bond angles in °).

CSi bond is *ca.* 0.110 Å shorter than the value in the pyramidal $C_6H_5SiH_2^-$, and that the C(1)C(2), C(2)C(3) and C(3)C(4) bond distances show a significant long/short/long type alternation. However, this structure is no less than 137.4 kJ/mol above the most stable C_s isomer. Although the addition of diffuse functions and the inclusion of electron correlation at the MP2/6-31 + G*//HF/6-31G* level lowers the inversion barrier to 97.7 kJ/mol, the high energetic requirement to planarization at silicon indicates that the extent of π-conjugation in the ground state of $C_6H_5SiH_2^-$ is very small.

The size of to the parent anion SiH_3^- allows the application of more sophisticated levels of theory. Geometry optimizations were performed considering the C_{3v} pyramidal structure and the D_{3h} planar isomer. Calculations of the relative stabilities of the two structures are reported in Table 2 and indicate that the inversion barrier converges in the electron correlation treatment to about 110 kJ/mol, employing the 6-31 + G* and the 6-31 + G** [24] basis sets. This value is not significantly different from that obtained at higher levels of theory (106.3 kJ/mol) [4] and agrees with the experimental value 108 ± 24 kJ/mol [2]. Moreover, calculations at the MP4/6-31 + G**//MP2/6-31 + G** level lead to a barrier to planarity very close to the result obtained at lower levels of electron correlation treatments, suggesting that the MP2/6-31 + G*//HF/6-31G* energy difference between the planar and nonplanar structure of $C_6H_5SiH_2^-$ is a reliable estimate of the inversion barrier at silicon.

Notwithstanding the high inversion barrier of $C_6H_5SiH_2^-$, a significant stabilization is present in the planar structure. In fact, MP2/6-31 + G*//HF/6-31G* calculations indicate that the inversion barrier of $C_6H_5SiH_2^-$ is lower than that of SiH_3^-. Table 2 reports the values of the barrier to planarity at silicon calculated for a perpendicular orientation of SiH_2 with respect to the benzene ring. HF/6-31G* geometry optimizations were carried out for the C_{2v} orthogonal structure with a planar $CSiH_2$ moiety and were compared with the results obtained for the C_s structure with the same orientation of the SiH_2 group. At the MP2/6-31 + G*//HF/6-31G* level the C_{2v} structure is destabilized by 127.5 kJ/mol with respect to the C_s orthogonal isomer whereas the C_{2v} planar structure is 97.5 kJ/mol above the most stable isomer. Therefore the barrier to planarization at silicon depends on the orientation of the SiH_2 group and this is a consequence of the fact that, as previously pointed out, the C_{2v} planar structure can be stabilized by electron delocalization from silicon to the benzene ring and, on the contrary, such an additional stabilization is not present in the C_{2v} orthogonal structure.

In order to investigate how the π-electron properties of the groups bonded to the silicon atom influence the inversion barrier of the $CSiH_2$ group, calculations at uniform levels of theory were carried out on the parent methylsilyl anion, $CH_3SiH_2^-$. The C_s-staggered ethane-type conformation and the transition state with $CSiH_2$ planar moiety were optimized at the HF/6-31G* level. The π-electron-donating properties of the methyl group are reflected in a higher inversion barrier at silicon. In fact, the MP2/6-31 + G*//HF/6-31G* value (126.7 kJ/mol) compares with that calculated for $C_6H_5SiH_2^-$ in the perpendicular orientation, indicating that the electronic properties of the group bonded to silicon significantly affect the energetic requirements for planarization at silicon [6]. On the other hand, the geometry of the $CSiH_2$ moiety is only slightly influenced by the electron properties of the substituent. The pyramidal angle at silicon in $C_6H_5SiH_2^-$ does not depend on the orientation of SiH_2 and its value is very close to that calculated for $CH_3SiH_2^-$ (97.0°). Thus, different substituents can lower the inversion barrier at silicon without altering the pyramidal geometry.

An interesting comparison may be made between $C_6H_5SiH_2^-$ and the isoelectronic molecule phenylphosphine, $C_6H_5PH_2$. HF/6-31G* geometries of two different orientations of the PH_2 group are reproduced in Fig. 4. As previously described, relaxation of the ring planarity constraint was allowed for the structure of Fig. 4a which prefers a nonplanar arrangement similar to that predicted for $C_6H_5SiH_2^-$. Slight geometric changes of the ring and of the CPH_2 moiety are associated with rotation about the CP bond. In particular, the exocyclic bond distance CP is unaffected by the orientation of PH_2 while, as described above, this parameter significantly changes upon rotation of SiH_2 in $C_6H_5SiH_2^-$. A very low torsional barrier (1.7 kJ/mol) is calculated at the MP2/6-31G*//HF/6-31G* level with preference for the C_s symmetry structure with the PH_2 group perpendicular to the ring (Fig. 4b). The inversion barrier at phosphorus was calculated by HF/6-31G* geometry optimizations of $C_6H_5PH_2$ assuming the CPH_2 group to be planar (see Fig. 5b). MP2/6-31G*//HF/6-31G* calculations predict high barriers to planarity at phosphorus both when PH_2 is forced to lie in the benzene plane (142.2 kJ/mol) and when PH_2 is perpendicular to it (142.1 kJ/mol). The free rotation of PH_2 and SiH_2, the remarkable configurational stability of phosphorus and silicon suggested by the high inversion barriers, as well as the poor phosphorus–carbon and silicon–carbon *p–p* overlap coupled with the marked pyramidalization of the CPH_2 and $CSiH_2$ moieties, indicate greatly reduced conjugation for the silicon and phosphorus systems compared to the analogous carbon and nitrogen [31] compounds. Notwithstanding the strict structural analogies, the negative charge retained on the silicon atom of $C_6H_5SiH_2^-$ gives rise to π-polarization on the benzene ring leading to charge-induced stabilization, which does not occur in $C_6H_5PH_2$. As previously described, the π-interactions slightly stabilize the structure with the silicon lone-pair perpendicular to the benzene ring and influence more effectively the barrier to planarization at silicon.

An alternative estimate of the strength of π-interaction between phenyl group and silicon atom in $C_6H_5SiH_2^-$ can be derived from the isodesmic reaction 1.

$$C_6H_5SiH_2^- + CH_3SiH_3 \rightarrow C_6H_5SiH_3 + CH_3SiH_2^- \tag{1}$$

This provides a measure of the stabilization of phenylsilyl anions relative to the methyl substituted parent compounds. The energy change for reaction 1 was estimated (see Table 4) from the total energies reported in Table 1 and from the total energies of $CH_3SiH_2^-$ and CH_3SiH_3 determined by calculations on the HF/6-31G* optimized staggered conformers. At all the levels of theory employed, a high stabilization energy is predicted for $C_6H_5SiH_2^-$ relative to $CH_3SiH_2^-$. In addition, the rotational barrier about the SiC bond of $C_6H_5SiH_2^-$ is smaller than the energy change in reaction 1 by 46.9 kJ/mol (MP2/6-31 + G*//HF/6-31G*). The extra stabilization of the orthogonal $C_6H_5SiH_2^-$ is rationalized by the fact that the σ-inductive withdrawing effects of electronegative sp^2 carbon atoms stabilize the negative charge on the adjacent silicon atom better than does the sp^3 carbon atom of the methyl group. Thus these calculations suggest that π- as well as σ-interactions cooperate to stabilize $C_6H_5SiH_2^-$ with respect to $CH_3SiH_2^-$, although the σ-electron contribution is clearly the dominant factor. In order to

Table 4

Energy changes [a] (kJ/mol) for the isodesmic reactions

$C_6H_5SiH_2^- + CH_3SiH_3 \rightarrow C_6H_5SiH_3 + CH_3SiH_2^-$ (1)

$C_6H_5SiH_2^- + C_2H_3SiH_3 \rightarrow C_6H_5SiH_3 + C_2H_3SiH_2^-$ (2)

$RSiH_2^- + RCH_3 \rightarrow RCH_2^- + RSiH_3$ (3)

Theoretical model	1	2		3 ($R = CH_3$)	3 ($R = C_6H_5$)	
		$\theta^b = 90$	$\theta^b = 0$		$\theta^c = 90$	$\theta^c = 0$
HF/6-31G*	38.2	16.1	13.4	249.1	118.5	217.1
MP2/6-31G*//HF/6-31G*	49.9	21.9	18.6	257.7	118.5	224.7
MP2/6-31+G*//HF/6-31G*	51.8	21.6	19.4	188.9	83.5	171.1

[a] Calculated as difference between the total energies of the products and those of the reagents. [b] Dihedral angle (°) between the vinyl plane and the SiH_2 bisector for $C_2H_3SiH_2^-$ and between the phenyl plane and the SiH_2 bisector for $C_6H_5SiH_2^-$. [c] Dihedral angle (°) between the phenyl plane and the SiH_2 bisector for $C_6H_5SiH_2^-$ and between the phenyl plane and the C lone-pair direction for $C_6H_5CH_2^-$.

$$C_6H_5SiH_2^- + C_2H_3SiH_3 \rightarrow C_6H_5SiH_3 + C_2H_3SiH_2^- \qquad (2)$$

assess the role of the σ-inductive interactions in the stability of silyl anions, it is useful to consider reaction 2 in which the C atom of CH_3 in reaction 1 is replaced by a more electronegative atom, the carbon atom of the vinyl group (C_2H_3). The energy change of the corresponding isodesmic reaction was estimated from the total energies of $C_2H_3SiH_2^-$ and those of $C_2H_3SiH_3$ obtained from HF/6-31G* geometry optimizations. As far as the $C_2H_3SiH_2^-$ anion is concerned, two different orientations of the pyramidal $CSiH_2$ moiety relative to the vinyl group were identified as stationary points on the potential energy surface. The most stable rotamer (Fig. 6a) corresponds to a structure where the silicon lone-pair is oriented towards the π-system of the vinyl group and the isomer where the SiH_2 bisector is lying on the vinyl plane (Fig. 6b) is destabilized by only 2.7 kJ/mol (MP2/6-31 + G*//HF/6-31G*). As expected from previous considerations, the HF and MP2 results of Table 4 indicate that the energy change of reaction 2 is smaller than that calculated for the reaction 1. However, both the stable and rotated conformers of $C_6H_5SiH_2^-$ are thermodynamically favoured relative to those of $C_2H_3SiH_2^-$. With these results, it appears that the extent of π-interaction between silicon and substituent is comparable in the phenyl and vinyl anions, and this strictly parallels the inversion barrier heights at silicon, which are calculated to be very similar for $C_6H_5SiH_2^-$ and $C_2H_3SiH_2^-$ (see Table 2). Thus,

Fig. 6. Lower energy structure (a) and rotated isomer (b) of $C_2H_3SiH_2^-$.

the stabilization of $C_6H_5SiH_2^-$ seems to be due mainly to the fact that C_6H_5 has a slightly larger σ-withdrawing effect than C_2H_3.

Finally, the relative stabilities of the carbon and silicon anions were evaluated by means of the isodesmic reaction 3 where $R = C_6H_5$.

$$RSiH_2^- + RCH_3 \rightarrow RCH_2^- + RSiH_3 \tag{3}$$

The calculation indicates that $C_6H_5SiH_2^-$ is more stable than $C_6H_5CH_2^-$ by 83.5 kJ/mol (MP2/6-31 + G*//HF/6-31G*) and this suggests that silicon accomodates a negative charge much more effectively than carbon. Indeed, the proton affinity for SiH_3 has been calculated to be lower than for CH_3^- [5]. However, the extensive delocalization of negative charge from carbon to the benzene ring occurring in $C_6H_5CH_2^-$ lowers the difference in stability between $C_6H_5CH_2^-$ and $C_6H_5SiH_2^-$ as compared to unconjugated systems. In fact, a greater difference in the abilities of silicon and carbon to accommodate negative charge is calculated when the *p*-orbitals are not involved in π-interactions. The energy change for reaction 3 calculated from the total energies of rotated $C_6H_5SiH_2^-$ and $C_6H_5CH_2^-$ is higher than the value predicted from the total energies of the most stable isomers and comparable to the value calculated for a system ($R = CH_3$) where π-bonding is eliminated.

Conclusions

The geometries and the rotational barriers of $C_6H_5SiH_3$ and $C_6H_5SiH_2^-$ were determined by *ab initio* molecular orbital calculations. Structural properties of the silicon compounds were compared with those determined for the carbon analogues $C_6H_5CH_3$ and $C_6H_5CH_2^-$ at uniform level of theory. The reluctance of silicon to form double bonds is responsible for several of the large structural differences between $C_6H_5CH_2^-$ and $C_6H_5SiH_2^-$. HF/6-31 + G* calculations indicate that $C_6H_5CH_2^-$ has C_{2v} planar structure whereas $C_6H_5SiH_2^-$ shows a pyramidal configuration at silicon. The strength of π-conjugation between the substituent and the benzene ring is estimated by calculating the barriers to rotation about the CC and CSi exocyclic bonds. MP2/6-31 + G*//HF/6-31G* calculations predict a high torsional barrier for $C_6H_5CH_2^-$ and free rotation for the SiH_2 group of $C_6H_5SiH_2^-$. The geometric changes and the π-charge variation patterns associated with the torsion of the substituent are reported for both the anions. An extensive π-delocalization from carbon onto the benzene ring is predicted for $C_6H_5CH_2^-$. In contrast, a large amount of negative charge is retained on the silicon of $C_6H_5SiH_2^-$, suggesting that mesomeric effects are negligible for the silicon-containing anion. The marked pyramidalization of the $CSiH_2$ moiety which decreases the efficiency of silicon–carbon *p–p* overlap and the ability of silicon to accommodate a negative charge much more effectively than carbon, is consistent with the minor importance of mesomeric effects for $C_6H_5SiH_2^-$. However, the population data of $C_6H_5SiH_2^-$ suggest that the silicon lone-pair perpendicular to the phenyl group induces a significant and stabilizing π-polarization in the benzene ring. In addition, the π-electron-accepting properties of the phenyl group can influence the barrier to planarization at silicon but do not affect the geometry of the $CSiH_2$ moiety. Thus the $C_6H_5SiH_2^-$ anion is an example where π-interactions can lower the inversion barrier without changing the pyramidal conformation at silicon.

Acknowledgements

Dr. L. Bencivenni is acknowledged for interest in this work. The author acknowledges the MURST for financial support and the "Progetto NIC-Italia" for a generous grant of computer time.

References

1 H. Schwarz, in S. Patai and Z. Rappoport (Eds.), Positive and negative ion chemistry of silicon-containing molecules in the gas phase, The Chemistry of Organic Silicon Compounds, Wiley, New York, 1989, p. 445; J.B. Lambert and W.J. Schulz, Jr., Trivalent silyl ions, p. 1007.
2 M.R. Nimlos and G.B. Ellison, J. Am. Chem. Soc., 108 (1986) 6522.
3 Y. Apeloig, in S. Patai and Z. Rappoport (Eds.), Theoretical aspects of organosilicon compounds, The Chemistry of Organic Silicon Compounds, Wiley, New York, 1989, p. 57.
4 M. Shen, Y. Xie and H.F. Schaefer III, J. Chem. Phys., 93 (1990) 8098.
5 A.C. Hopkinson and M.H. Lien, Tetrahedron, 37 (1981) 1105.
6 E. Magnusson, Tetrahedron, 41 (1985) 2945.
7 A.C. Hopkinson and M.H. Lien, J. Organomet. Chem., 206 (1981) 287.
8 A.C. Hopkinson and M.H. Lien, J. Mol. Struct., 104 (1983) 303.
9 M.S. Gordon, P. Boudjouk and F. Anwari, J. Am. Chem. Soc., 105 (1983) 4972.
10 J.R. Damewood, Jr., J. Org. Chem., 51 (1986) 5028.
11 R.H. Nobes, D. Poppinger, W.K. Li and L. Radom, in E. Buncel and T. Durst (Eds.), Molecular Orbital Theory of Carbanions, Comprehensive carbanion chemistry, Part C: Ground and excited state reactivity, Elsevier, Amsterdam, 1987.
12 A.G. Evans, M.A. Hamid and N.H. Rees, J. Chem. Soc. B, (1971) 1110.
13 E. Buncel, T.K. Venkatachalam, B. Eliasson and U. Edlund, J. Am. Chem. Soc., 107 (1985) 303.
14 W.F. Reynolds, Prog. Phys. Org. Chem., 14 (1983) 165.
15 P. George, C.W. Bock, J.J. Stezowski, T. Hildenbrand and J.P. Glusker, J. Phys. Chem., 92 (1988) 5656.
16 H. Berko, G.J. Mains, P. Maker and H. Niki, J. Photochem. Photobiol. A: Chem., 40 (1987) 219.
17 B.T. Luke, J.A. Pople, M.-B. Krogh-Jespersen, Y. Apeloig, M. Karni, J. Chandrasekhar and P. v. R. Schleyer, J. Am. Chem. Soc., 108 (1986) 270.
18 M.W. Schmidt, P.N. Truong and M.S. Gordon, J. Am. Chem. Soc., 109 (1987) 5217.
19 A.E. Dorigo, Y. Li and K.N. Houk, J. Am. Chem. Soc., 111 (1989) 6942.
20 C. Møller and M.S. Plesset, Phys. Rev., 46 (1934) 618.
21 W.J. Hehre, L. Radom, P. v. R. Schleyer and J.A. Pople, Ab initio Molecular Orbital Theory, Wiley, New York, 1986.
22 M.J. Frisch, M. Head-Gordon, H.B. Schlegel, K. Raghavachari, J.S. Binkley, C. Gonzalez, D.J. De Frees, D.J. Fox, R.A. Whiteside, R. Seeger, C.F. Melius, J. Baker, R. Martin, L.R. Kahn, J.J.P. Stewart, E.M. Fluder, S. Topiol and J.A. Pople, GAUSSIAN 88, Gaussian Inc., Pittsburgh, PA, USA, 1988.
23 H.B. Schlegel, J. Comput. Chem., 3 (1982) 214.
24 R. Poirer, R. Kari and I.G. Csizmadia, Handbook of Gaussian Basis Sets, Elsevier, Amsterdam, 1985.
25 P. George, C.W. Bock, M. Trachtman and G.H. Penner, J. Mol. Struct. (Theochem.), 180 (1988) 37.
26 C.W. Bock, M. Trachtman and P. George, J. Comput. Chem., 6 (1985) 592.
27 F.A. Keidel and S.H. Bauer, J. Chem. Phys., 25 (1956) 1218.
28 A. Domenicano, G. Schultz, M. Kolonits and I. Hargittai, J. Mol. Struct., 53 (1979) 197.
29 C.W. Bock, M. Trachtman and P. George, J. Mol. Struct. (Theochem.), 139 (1986) 63.
30 G.H. Penner, P. George and C.W. Bock, J. Mol. Struct. (Theochem.), 152 (1987) 201.
31 C.W. Bock, P. George and M. Trachtman, Theor. Chim. Acta, 69 (1986) 235.