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Ab initio study of α- and β-silyl substituent effects on vinyl radicals

S LALITHA and JAYARAMAN CHANDRASEKHAR*
Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India

Abstract. The geometries of α- and β-silyl substituted vinyl radicals and of α, β-disilylvinyl radical have been optimised with the STO-3G and the STO-3G* basis sets. The relative stabilities of various conformers have been determined at the UMP2/6-31G* level. The stabilisation of vinyl radicals through α-silyl substitution is larger than that due to corresponding alkyl groups. The presence of an α-silyl group also leads to a tendency towards linearisation of the vinyl radical centre and a corresponding reduction in the inversion barrier. In marked contrast, the β-silyl effect is negligible. The geometric, conformational and energetic consequences are insignificant. Overall, the silyl substituent effect at vinyl radicals is very different from that computed earlier for the vinyl cations, but qualitatively similar to that found in carbanions.

Keywords. *Ab initio*; MO calculations; silyl substituent effect; vinyl radical.

1. Introduction

Some of the most rewarding applications of *ab initio* MO theory have been in characterising the structures and energetics of reactive intermediates and in quantifying substituent effects (Hehre *et al* 1986). Such studies are of fundamental interest from the bonding point of view as they lead to valuable insights concerning electronic interactions operating in reactive chemical species. The results are also of direct significance for experimentalists since reactivity patterns can be readily discerned from the computed energetics. In this paper, we report one such application of *ab initio* MO theory by determining the structural and energetic consequences of silyl substitution at different positions of the vinyl radical.

The silyl substituent effects at carbocations and carbanions have been thoroughly characterised experimentally and theoretically. The stabilising effect of an α-silyl group in alkyl and vinyl carbocations is found to be less effective than that due to an alkyl group (Apeloig and Stanger 1985; Wierschke *et al* 1985; Lambert 1990). However, β-silyl substitution leads to exceptional stabilisation as a result of hyperconjugation by the C–Si bond (Wierschke *et al* 1985; Lambert *et al* 1987; Hajdasz and Squires 1988; Li and Stone 1989; Lambert 1990; Wang *et al* 1990). The α- and β-substituent effects are quite different in carbanions. While alkyl groups generally destabilise carbanions (Schleyer *et al* 1986), the silylmethyl anion is calculated to be significantly stabilised (Schleyer *et al* 1984). Experimental studies support these conclusions (Peterson 1972; Eaborn *et al* 1975; Seyferth and Mammarella 1978). The stabilisation of carbanions by a directly connected silyl group has been attributed to negative

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*For correspondence

hyperconjugative interactions between the carbanion lone pair and Si–H σ^* orbitals, rather than to *d* orbital participation (Schleyer *et al* 1984). The energetic effect of electropositive groups at the β-position of a carbanion has been shown to be destabilising on the basis of early *ab initio* calculations (Hoffmann *et al* 1972).

The silyl effect in radicals has also evoked interest. The unusual modes of cyclisation in sila-radicals have been rationalised (Wilt 1985; Wilt *et al* 1988) on the basis of conformational control effected by silyl units (Krusic and Kochi 1971; Chen and Kochi 1974). The silyl substituent effects have been quantified in a few alkyl radicals. For example, bond energy data have been interpreted in terms of negligible α-substituent effect but a β-stabilisation of about 3 kcal/mol (Auner *et al* 1986). *Ab initio* calculations have also been reported on the magnitude of the α-silyl effect (Coolidge and Borden 1988) as well as on conformations and energies of β-silyl alkyl radicals (Bernardi *et al* 1986; Bernardi and Fossey 1988; Guerra 1988; Ibrahim and Jorgensen 1989).

We have now carried out *ab initio* calculations on α- and β-silyl substituted vinyl radicals. The magnitudes of substituent interactions in alkyl and vinyl derivatives are generally different. For example, the α-silyl effect is more dominant in the vinyl cation as compared to the methyl cation (Wierschke *et al* 1985). The present study extends our understanding of the substituent effect to a wider range of reactive intermediates. The results are also of interest in the context of the reported ESR study on the structures and spin densities of the α-silylvinyl radical and the α,β-disilylvinyl radical (Rhodes and Symons 1988). The spectral parameters suggested an important linearisation effect at the radical centre due to α-silyl substitution. This structural feature is specifically examined through geometry optimisations.

2. Computational details

Ab initio calculations were carried out on the unsubstituted vinyl radical, $CH_2{=}CH^{\cdot}$, with a bent and linear radical centre (1 and 2, respectively) and on different conformers of α-silylvinyl (bent: 3, linear: 4), β-silylvinyl (*trans*: 5, *cis*: 6, linear: 7), and α,β-disilylvinyl (*trans*: 8, *cis*: 9, linear: 10) radicals. The structures and energies of the various silyl substituted vinyl radicals were examined at a uniform theoretical level (Hehre *et al* 1986). Full geometry optimisations were carried out with a minimal basis set (STO-3G) as well as a basis augmented with *d* orbitals on silicon (STO-3G*). In the latter basis, six cartesian *d* functions, instead of the 5 spherical harmonics components, were used. The basis set thus differs from the standard STO-3G* basis in this respect. For the linear forms of β-silylvinyl (7) and α,β-disilylvinyl (10) radicals, no minimum energy structure could be obtained on geometry optimisation. In order to obtain approximate estimates of the inversion barrier in these systems, single point calculations were carried out assuming the geometries of 5 and 8, respectively, with linearity enforced at the radical centre. Further, additional single point calculations were carried out at the MP2 level with the 6-31G* basis set (split-valance basis with *d* type polarisation functions on all non-hydrogen atoms) using STO-3G* geometries for all the radicals. The corresponding results represent the most reliable estimates of the current study. The restricted open-shell Hartree–Fock procedure was used for the STO-3G and STO-3G* calculations, whereas the UHF method was employed for the 6-31G* calculations (Hehre *et al* 1986).

The choice of the methodolygy needs some comments. Geometry optimisations have been carried out with rather small basis sets. The STO-3G* basis is especially unbalanced. However, early calculations (Collins *et al* 1976) have suggested that it represents a significant improvement over a minimal basis set wherever hypervalency is involved. To allow for potential negative hyperconjugative interactions involving the silyl group, which has been proposed to be an alternative description of hypervalency (Reed and Schleyer 1990), calculations with the augmented basis set have been carried out. The most reliable energy estimates in the present study, of course, correspond to UMP2/6-31G* values, in which the effect of polarisation functions as well as corrections due to electron correlation are included.

3. Results and discussions

The total energies of the various α and β silyl substituted vinyl radicals computed using the STO-3G, STO-3G* and 6-31G* basis sets are given in table 1. The relative energies of the various conformers with respect to the most stable form are also indicated in the table. Results for the parent vinyl radical are provided for comparison. The optimised values of key structural parameters are indicated in figure 1.

The unsubstituted vinyl radical prefers a bent radical centre (1), with a C=C–H

Table 1. *Ab initio* total energies (hartrees) of 1–10 and relative energies (kcal/mol).

Radical	ROHF/STO-3G //STO-3G	ROHF/STO-3G*[a] //STO-3G*	UHF/6-31G* //STO-3G*	UMP2/ 6-31G*
CH$_2$CH$^{\cdot}$, 1 (bent)	−76·41678 (0·0)	—	−77·39029 (0·0)	−77·61279 (0·0)
CH$_2$CH$^{\cdot}$, 2 (linear)	−76·39879 (11·3)	—	−77·37773 (7·9)	−77·60346 (5·9)
CH$_2$CSiH$_3^{\cdot}$, 3 (bent)	−363·21573 (0·0)	−363·28797 (0·0)	−367·47846 (0·0)	−367·78934 (0·0)
CH$_2$CSiH$_3^{\cdot}$, 4 (linear)	−363·20865 (4·4)	−363·28481 (2·0)	−367·47628 (1·4)	−367·78813 (0·8)
SiH$_3$CHCH$^{\cdot}$, 5 (trans)	−363·20933 (4·0)	−363·27890 (5·7)	−367·46918 (5·8)	−367·78164 (4·8)
SiH$_3$CHCH$^{\cdot}$, 6 (cis)	−363·20839 (4·6)	−363·27790 (6·3)	−367·46827 (6·4)	−367·78008 (5·8)
SiH$_3$CHCH$^{\cdot}$, 7[b] (linear)	−363·18925 (16·6)	−363·25866 (18·4)	−367·45551 (14·4)	−367·76970 (12·3)
SiH$_3$CHCSiH$_3^{\cdot}$, 8 (trans)	−650·00678 (0·0)	−650·14634 (1·5)	−657·55624 (0·6)	−657·95732 (0·2)
SiH$_3$CHCSiH$_3^{\cdot}$, 9 (cis)	−650·00563 (0·7)	−650·14867 (0·0)	−657·55715 (0·0)	−657·95769 (0·0)
SiH$_3$CHCSiH$_3^{\cdot}$, 10[b] (linear)	−649·99797 (5·5)	−650·14541 (2·0)	−657·55515 (1·3)	−657·95645 (0·8)

[a] Using a set of 6 cartesian *d* functions on silicon

[b] Fixed point calculations using the *trans* geometry but keeping the radical centre linear

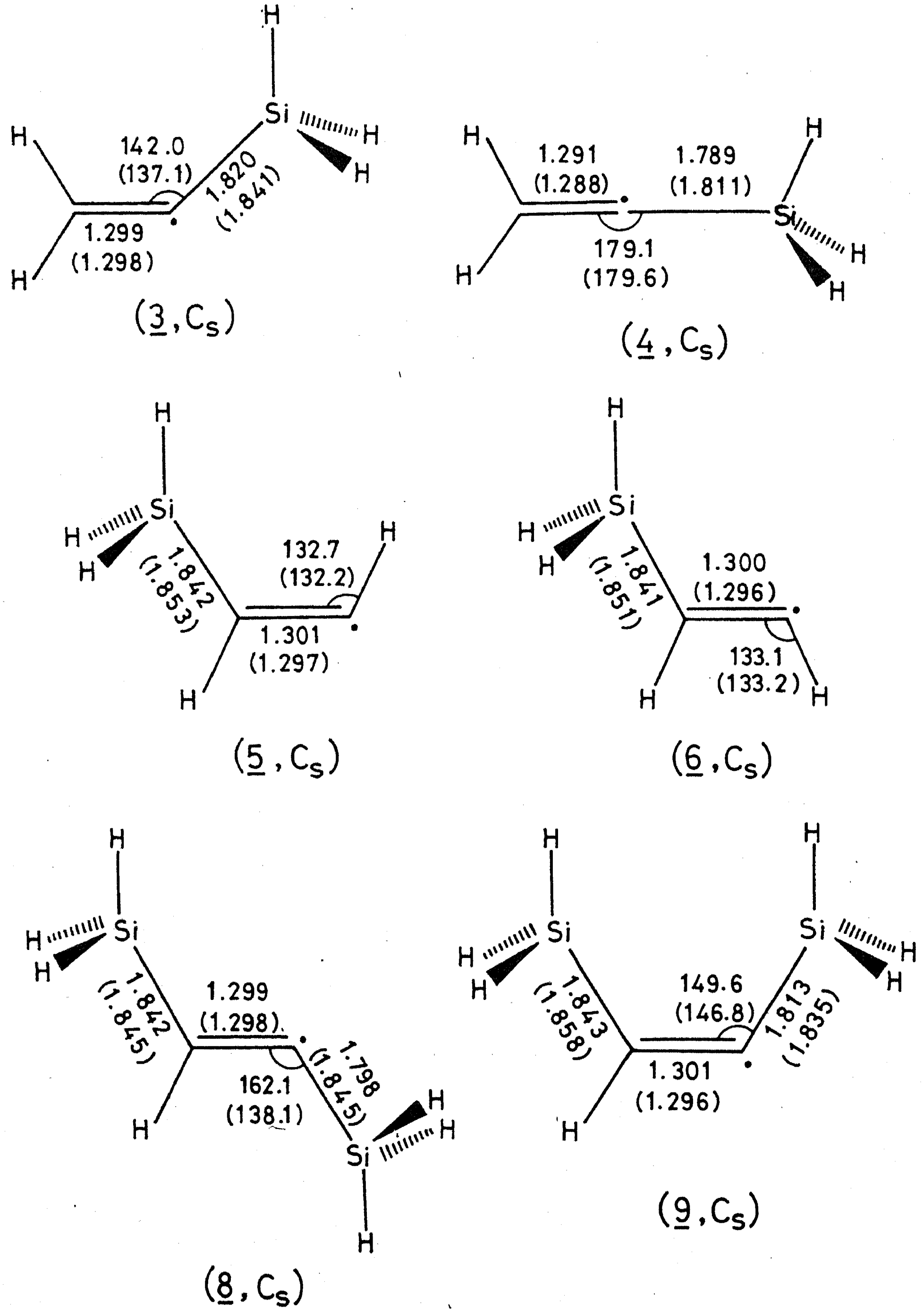

Figure 1. Optimised values of key geometric parameters (bond lengths in Å, angles in degrees) obtained using the STO-3G* basis set for the silyl substituted vinyl radicals 3–6, 8 and 9. The corresponding STO-3G values are shown in parentheses.

angle of 133° (STO-3G). This is in accord with experimental results (Fessenden 1967) and qualitative expectations, since the bent geometry allows for increased 's' character in the SOMO leading to stabilisation. Linearisation of the C=C–H unit requires around 11 kcal/mol with the minimal basis set (table 1). At the UHF/6-31G* level, the inversion barrier is 7·9 kcal/mol, which reduces further to 5·9 kcal/mol on inclusion of electron correlation with the MP2 procedure.

The optimised geometry of the α-silylvinyl radical also corresponds to a bent form (3). However, the C=C–Si angle is wider, 137° at the STO-3G level and 142° with the more reliable STO-3G* basis set. Interestingly, a near-linear structure (4) is also obtained on geometry optimisation. The corresponding energy yields an estimate of the inversion barrier of just 4·4 kcal/mol (STO-3G) for the α-silylvinyl radical. With the STO-3G* basis, the barrier is still smaller, 2·0 kcal/mol. At the highest level employed (UMP2/6-31G*), the inversion barrier via the linear α-silylvinyl radical, 4, is only 0·8 kcal/mol. Thus, α-silyl substitution reduces the inversion barrier in vinyl radical by ≈ 5–7 kcal/mol at all theoretical levels.

The ESR spectrum of the α-trimethylsilylvinyl radical (Rhodes and Symons 1988) indicates a linear structure on the basis of the equivalence of the two β-proton hyperfine coupling. The result can also be reconciled with two bent structures undergoing rapid interconversion. The computed small inversion barrier of 0·8 kcal/mol in the related α-silylvinyl radical is consistent with the latter interpretation.

In contrast to the above results, β-silicon substitution has virtually no effect on the geometries and inversion barrier (table 1). The preferred geometry of the β-silylvinyl radical is similar to that of the unsubstituted radical (figure 1). Of the two possible bent forms, the conformer with the two hydrogen atoms *trans* (5) is slightly more stable than the alternative *cis* isomer (6). The radical site is bent, with C=C–H bond angles similar to that in 1. No minimum corresponding to the linear form (7) could be obtained. On the basis of the energy of an assumed linear structure, the inversion barrier for the β-silylvinyl radical is estimated to be large – around 12·6 kcal/mol from the *trans* form, 5, and 12·0 kcal/mol from the *cis* structure, 6 – at the STO-3G level. These barriers are reduced to 7·5 and 6·5 kcal/mol for 5 and 6, respectively, at the MP2/6-31G* level. These values are quite similar to those computed for the vinyl radical at the same levels of theory.

Comparison of the energies of the α- and β-substituted vinyl radicals clearly shows that at all theoretical levels considered the former is more stable (table 1). The energy difference between the most stable forms of the α- and the β-substituted vinyl radicals (3 and 5) ranges from 4 to 5·8 kcal/mol depending on the theoretical level employed. This result is consistent with the fact that geometric and conformational effects of the silyl group are noted only for the α-substituted form 3. The interactions are obviously stabilising in nature. The computed energy difference provides a measure of the α stabilising interaction of the silyl group at a vinyl radical centre.

A more direct measure of the stabilisation energies of the silyl group can be obtained by means of suitable isodesmic equations (table 2),

$$\mathrm{H_2C{=}C{-}SiH_3^{\cdot} + H_2C{=}CH_2 \rightarrow H_2C{=}CHSiH_3 + H_2C{=}CH^{\cdot}}. \qquad (1)$$

The computed energy of reaction (1) reveals an α-stabilising effect of 4·6 to 6·0 kcal/mol, depending on the theoretical level. These values span the estimates made above based on computed relative energies. If the linearised forms are used as reference, the α-silyl effect is quite substantial. The interaction is greater than 11 kcal/mol. The corresponding stabilisation energy obtained for the methyl group is much smaller. At the STO-3G level, the value is 3·4 kcal/mol for the bent methylvinyl radical.

The modest α-silyl effect can be attributed to a combination of inductive, polarisation, and hyperconjugative interactions. The one-electron stabilising interaction between the radical SOMO and the SiH_3 σ^* orbitals is operative,

Table 2. Computed energies of isodesmic reactions (kcal/mol).

Reaction	Geometry of vinyl radicals	STO-3G	6-31G*
(1)	Bent	6·0	4·6
(1)	Linear	12·9	11·2
(2)	Bent, trans	2·0	−1·2
(2)	Bent, cis	1·4	−1·8
(2)	Linear	0·7	−1·9
(3)	Bent, trans	0·5	—
(3)	Bent, cis	0·8	—
(4)	Bent, trans	7·9	(9·2)[a]
(4)	Bent, cis	10·3	(13·0)[a]

[a]STO-3G* values

particularly in the linearised form. In this geometry, the SOMO is a pure '*p*' type orbital which is relatively high in energy. Interaction with the adjacent empty orbital is correspondingly enhanced. The *sp*-hybridisation at the radical centre would also enhance its sensitivity to induction, as noted in the silyl effect on vinyl cations (Lambert 1990).

The energetics of the reaction corresponding to the β-silyl effect are nearly thermoneutral ((2), table 2). Even using the most stable conformers, a mild destabilisation is computed at the 6-31G* level. When alternative bent or linear conformers are considered, the destabilisation increases to nearly 1·9 kcal/mol. The interaction energies are predicted to be weakly attractive at the STO-3G level. The values are quite similar to those obtained for the β-methyl effect at vinyl radicals, (3),

$$SiH_3CH{=}CH^{\cdot} + CH_2{=}CH_2 \rightarrow SiH_3CH{=}CH_2 + CH_2{=}CH^{\cdot}, \tag{2}$$

$$CH_3CH{=}CH^{\cdot} + CH_2{=}CH_2 \rightarrow CH_3CH{=}CH_2 + CH_2{=}CH^{\cdot}. \tag{3}$$

In principle, a number of interactions are possible between the β-sily group and the vinyl radical centre (Bernardi *et al* 1986). While the inductive and polarisation effects may be diluted at the β-position, hyperconjugative as well as negative hyperconjugative interactions are possible. The 3-electron interaction between the C–Si σ bond and the radical SOMO as well as the 1-electron interaction between the C–Si σ^* orbital and the SOMO are potentially stabilising. However, the computed energetics clearly indicate that these orbital interactions are not more effective than those involving C–H σ and σ^* orbitals and hence do not amount to significant stabilisation.

Experimentally, the β-silylvinyl radical has not been spectrally characterised. However, a disubstituted vinyl radical has been examined (Rhodes and Symons 1988). We have theorefore examined the corresponding α,β-disilylvinyl radical.

The most stable conformers, 8 and 9, of the disilylvinyl radical have a bent radical centre. The C=C–Si bond angle at the radical carbon is quite large in both forms, especially when silicon *d* orbitals are included. While the *trans* isomer, 8, is more stable than the alternative *cis* form, 9, at the STO-3G level, addition of *d* orbitals reverses the preference. The variation is probably due to the significant differences in the computed geometries (figure 1), especially for the *trans* isomers. However, the energy difference between the *cis* and the *trans* conformers is quite small, certainly beyond the limits of accuracy of the theoretical levels employed.

The computed inversion barrier, assuming that the structure with the C=C–Si angle fixed at 180° (10) represents the true transition state for the inversion process, is similar to that obtained for the α-silylvinyl radical. At the STO-3G level, the value is 5·5 (4·8) kcal/mol for 8 (9). However, at the MP2/6-31G* level the barrier reduces to 0·6 (0·8) kcal/mol.

Experimentally, the *trans* structure related to 8 has been assigned to the α,β-$(SiMe_3)_2$-substituted vinyl radical based on its ESR spectrum (Rhodes and Symons 1988). The proton coupling was found to be much greater than in the α-trimethylsilylvinyl radical as well as in the vinyl radical. This was suggested to be due to the greater hyperconjugation possible between the C–H bond and the radical SOMO when the two are antiperiplanar, as in 8. The fluxional character indicated by the computed results for 8–10 is probably offset by strong steric interactions in the trimethylsilyl derivatives.

The isodesmic reaction (4) can be used to derive the energetic magnitude of substitution in the α,β-disubstituted silylvinyl radical (table 2),

$$SiH_3CH{=}CSiH_3^{\cdot} + CH_2{=}CH_2 \rightarrow SiH_3CH{=}CHSiH_3 + CH_2 = CH^{\cdot}. \qquad (4)$$

Since α-silyl substitution is stabilising and the β-silyl substitution is thermoneutral, the combined effect is also overall stabilising. The magnitude varies from 8 to 13 kcal/mol, depending on the conformation and the theoretical level used.

4. Conclusions

Vinyl radicals are calculated to be stabilised by α-silyl substitution. The stabilisation is larger than that due to corresponding alkyl groups. The presence of an α-silyl group also leads to a tendency towards linearisation of the vinyl radical centre and a corresponding reduction in the inversion barrier.

In contrast, the β-silyl effect is negligible. The geometric, conformational and energetic consequences are meagre. The results are comparable to those obtained for the unsubstituted vinyl radical.

Overall, the silyl substituent effect at vinyl radicals is very different from that computed earlier for the corresponding vinyl cations. The behaviour is qualitatively similar to that found in carbanions, although the magnitude of interactions is much less in the radicals. The α-silyl effect has considerable potential for synthetic applications, e.g., in directing the course of radical cyclisation reactions.

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