

The Effect of Substituents on the First Transition in the Visible Spectra of Silanediyls (Silylenes)

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Ab initio calculations show that the first transition in the visible spectra of silanediyls (silylenes), RSiR' , is due to an $n(\text{Si}) \rightarrow 3p(\text{Si})$ excitation and that this absorption is shifted to shorter wavelengths by π -donors and to longer wavelengths by bulky substituents; the calculations for Me_2Si are more consistent with a λ_{max} of 450 nm than with 350 nm.

There has been a recent surge of interest in the chemistry of silanediyls (silylenes);¹ a major development has been the ability to isolate these species and measure their spectra.^{2–4} However, knowledge on the effect of substituents on the electronic spectra of silanediyls is so limited that in many cases it is difficult to decide if the observed spectra are indeed of the desired compound.³ This point is emphasized in a recent paper⁴ that challenges the previous assignment of the u.v.–visible spectrum of Me_2Si .² In this communication we use *ab initio* calculations to provide a reliable guide for predicting the spectral shifts which are caused by various substituents.

The parent silanediyl, H_2Si , is a ground-state singlet⁵ with a bent geometry ($\angle\text{H-Si-H}$ 93.2° at 6-31G*, *expt.*² 92.1°). In the 1A_1 state two electrons occupy an orbital of σ -symmetry [$n(\text{Si})$] while the 3p orbital on silicon of π -symmetry is vacant [see structure (1)]. The lowest electronic transition in H_2Si involves the promotion of one of the $n(\text{Si})$ electrons to the empty 3p(Si) orbital [*i.e.* (1) \rightarrow (2)].⁶

What is the effect of substituents on the $n(\text{Si}) \rightarrow 3p(\text{Si})$ transition? To answer this question we have performed⁷ *ab initio* unrestricted Hartree–Fock (U.H.F.)^{8a} calculations for a series of monosubstituted silanediyls RSiH , where R is varied along a representative series of substituents, *i.e.*: R = Me, $\text{HC}=\text{CH}_2$, $\text{C}\equiv\text{CH}$, CN, NH_2 , OH, F, SiH_3 , SH, and Cl. The geometries of the ground-state singlets were fully optimized with the 3-21G basis set,^{8b} and the energies of both the ground states ($^1A'$, 1A_1 in H_2Si) and the first excited singlet ($^1A''$, 1B_1 in H_2Si) and triplet ($^3A''$, 3B_1 in H_2Si) states were calculated at these geometries using the polarized 6-31G* basis set.^{8c} We assume that the $^1A' \rightarrow ^1A''$ energy differences (ΔE) correspond to 'vertical' electronic transitions. This simple theoretical model is not expected to duplicate the absolute excitation energies but experience suggests that substituent effects and trends in spectral shifts can be reproduced even with this simple theory.^{9†} Furthermore, the limited number of previous related calculations are in good agreement with the available spectra of H_2Si , FHSi , and F_2Si .¹⁰ The use of U.H.F. theory^{8a} raises a special problem. The excited singlets which are calculated at U.H.F. (more appropriately described as mixed states with $m_s = 0$) are nearly 1 : 1 mixtures of the wavefunctions of the 'pure' excited singlets and of the corresponding 'pure' triplets (*i.e.*, the $^1A''$ and $^3A''$ states respectively).^{11‡} The energy of the 'pure' excited singlets can be derived from equation (1) where E is the total energy, S and T denote the singlet and the triplet states respectively, and $\langle S^2 \rangle$ are the calculated expectation values of S^2 for the 'mixed states'. The ΔE values which are calculated using these energies (Table 1)

Table 1. Calculated energy differences (ΔE) between the $^1A'$ and the $^1A''$ states of RSiH and the calculated substituent shifts ($\Delta\Delta E$).^a

R	ΔE^b	$\Delta\Delta E^{b,c}$	R	ΔE^b	$\Delta\Delta E^{b,c}$
H ^d	53.6	0.0(0)	NH_2	87.8	34.2(208)
Me	56.1	2.5(24)	OH	74.9	21.3(152)
(Me) ₂ ^e	57.9	4.3(40)	F	72.6	19.0(140)
$\text{CH}=\text{CH}_2$	60.7	7.1(62)	H_3Si	36.6	-17.0(-248)
$\text{C}\equiv\text{CH}$	61.8	8.2(71)	HS	70.4	16.8(127)
CN	62.4	8.8(75)	Cl	66.5	12.9(104)

^a At 6-31G*. ^b In kcal mol⁻¹. Using the $E(S)$ values calculated by equation (1), see text. ^c $\Delta\Delta E$ kcal mol⁻¹ = $\Delta E(\text{HSiR}) - \Delta E(\text{H}_2\text{Si})$. Positive and negative values indicate 'blue' and 'red' shifts respectively. Values in parentheses are the calculated shifts ($\Delta\lambda$, in nm) calculated using the relationship: $\Delta\lambda(\text{nm}) = \Delta\Delta E(\text{kcal mol}^{-1}) \lambda(\text{H}_2\text{Si}) \cdot \lambda(\text{HSiR}) \cdot 3.494 \times 10^{-5}$. Note that calibration of the calculated $\lambda(\text{H}_2\text{Si})$ according to the experimental value may change slightly the $\Delta\lambda$ values. ^d For the 1A_1 and 1B_1 states. ^e For Me_2Si .

are as expected too small§ but yet in reasonable agreement with experiment. *E.g.* for H_2Si T_0 for the $^1A' \rightarrow ^1B_1$ state (*i.e.* for the 000–000 transition) is 44.4 kcal mol⁻¹,⁶ compared to the calculated values of 42.1 (6-31G*) and 50 kcal mol⁻¹ with the inclusion of correlation energy (1 cal = 4.184 J).¹⁰

$$E(\text{'mixed state'}) = [\langle S^2 \rangle \cdot E(T) + (2 - \langle S^2 \rangle) \cdot E(S)]/2 \quad (1)$$

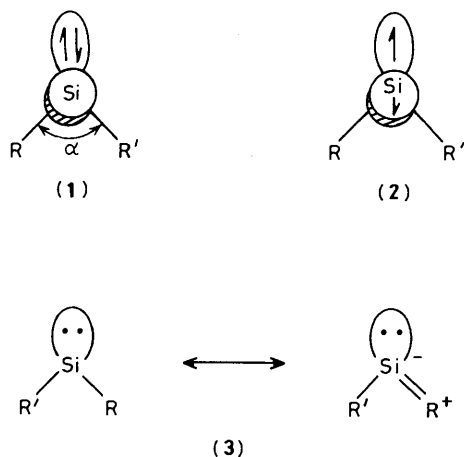
The calculated vertical transitions (Table 1)¶ are consistent with expectations based on resonance and perturbation molecular orbital (P.M.O.) arguments. π -Donors such as NH_2 , OH, SH, Cl, *etc.* stabilize substantially the ground state, by electron donation to the empty 3p(Si) orbital [see structure (3)]. The corresponding stabilization of the excited singlet is much smaller, because in (2) the 3p(Si) orbital is singly occupied and the π -interaction involves 3 electrons. Consequently, the $^1A' \rightarrow ^1A''$ splitting (ΔE) increases as R becomes a better π -donor; *i.e.* $\Delta E = 87.8, 74.9$, and 56.1 kcal mol⁻¹ for R = NH_2 , OH, and Me respectively (Table 1). Inductive effects are also important; electronegative substituents increase ΔE (compare R = F and Cl) while σ -donors decrease the $^1A' \rightarrow ^1A''$ gap (*e.g.*, SiH_3). We note that substitution changes the HOMO–LUMO energy differences (in the ground states of RSiH) and ΔE in the same direction. For example, fluorine, a π -donor σ -acceptor substituent, shifts the

† The calculations apply strictly only to the gas-phase. Solvent or matrix effects⁴ have to be evaluated separately.

‡ For most silylenes $\langle S^2 \rangle$ is indeed close to 1 and equation (1) reduces to $E(\text{'mixed state'}) = [E(S) + E(T)]/2$.

§ The $^1A'$ state is stabilized by correlation energy more than the excited $^1A''$ states.

¶ We use throughout the U.H.F./6-31G* values although we note that the $\Delta E(\text{U.H.F./MP3/6-31G*})$ values are very similar.



$n(\text{Si})$ orbital inductively to a lower energy and the empty $3p(\text{Si})$ orbital (due to π -conjugation) to a higher energy; consequently, both the HOMO–LUMO gap and ΔE increase.

The ‘blue shifts’ (*i.e.*, higher ΔE) which are predicted theoretically for π -donors are indeed observed experimentally. One example is the 40 nm ‘blue shift’ in $\text{MeSiC}_6\text{H}_4\text{-OMe-}p$ compared with MeSiPh . Similarly, MesSiNMe_2 ($\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$) absorbs at λ_{max} 404 nm compared with 497 nm in MesSiH or MesSiMe .³ Note that the calculated shift for $\text{R} = \text{NH}_2$ is much larger (208 nm). This discrepancy may result at least partially from steric interactions between the bulky mesityl groups and the NMe_2 group. These interactions impose rotation of the nitrogen lone-pair out of maximum conjugation with the empty $3p(\text{Si})$ orbital and also cause a widening of the bond angle around silicon. Ethynyl and vinyl substituents which can π -conjugate with the empty $3p(\text{Si})$ orbital are also calculated to induce a ‘blue shift’, but 3–4 times smaller than that for $\text{R} = \text{NH}_2$, OH , SH , *etc.* For σ -donors, *e.g.*, $\text{R} = \text{SiMe}_3$ we predict a significant ‘red shift.’ Experimental data for $\text{R} = \text{ethynyl}$, vinyl , and SiMe_3 are not yet available.

The angle around the divalent silicon atom [α , structure (1)] affects strongly the first electronic transition. Calculations for H_2Si show that the equilibrium value of α is much larger in the excited ${}^1\text{B}_1$ state than in the ${}^1\text{A}_1$ state (120.0 and 93.2° respectively, 6-31G*). (Similar results were obtained for Me_2Si .) As α increases beyond 93.2 (up to *ca.* 140°, where the 6-31G* potential curves of the ${}^1\text{A}_1$ and the ${}^1\text{B}_1$ states intersect) the energy of the ${}^1\text{A}_1$ state rises and that of the excited ${}^1\text{B}_1$ state drops. Thus, as α increases ΔE decreases and a ‘red shift’ is expected. ‘Red shifts’ are indeed observed for bulky substituents that increase the steric congestion around the silicon enforcing α to widen. The following three series demonstrate this point: Bu^tSiMe (470 nm) > EtSiMe (459 nm) > Me_2Si (453 nm); Bu^tSiMes (505 nm) > $\text{Bu}^t\text{CH}_2\text{SiMes}$ (500 nm) > MeSiMes (496 nm); Mes_2Si (577 nm) || > PhSiMes (530 nm) > Ph_2Si (495 nm).³

Finally we comment on the discrepancy between the two reported λ_{max} values for Me_2Si : 450 nm according to West *et al.*^{2a–c,3} and 350 nm according to Griller *et al.*⁴ Unfortunately at the present level of theory the calculated absolute excitation energies are not sufficiently reliable for deciding decisively between these values. However, the calculated ΔE values and the general good agreement between our calculations and

West’s spectroscopic data for a significant number of substituted silanediyls, are more consistent with λ_{max} of 450 nm. Furthermore, West finds a modest ‘blue shift’ of 30 nm on going from HSiMe (480 nm) to Me_2Si (450 nm),^{2a,3} in agreement with the calculated shift of 16 nm. The 30 nm shift reflects a balance between an hyperconjugative (π -donation) ‘blue shift,’ and a ‘red shift’ which results from the increase in α upon successive methyl substitution [$\alpha = 93.2$, 95.5 (6-31G*), and 98.2° (3-21G) in H_2Si , HSiMe , and Me_2Si respectively]. We point out that it may be possible to resolve the discrepancy by measuring λ_{max} for the well characterized H_2Si .⁶ Using the calculated 40 nm shift for a *gem*-dimethyl substitution one expects to find for H_2Si a λ_{max} value of *ca.* 490 or of *ca.* 390 nm depending on whether the correct λ_{max} for Me_2Si is 450^{2a–c} or 350 nm.⁴ Note that Dubois reports an absorption band at 485 nm which may correspond to λ_{max} (intensities are unfortunately not reported), but there is no report of an absorption band around 400 nm.^{6b} This also appears to support West’s assignment of λ_{max} 450 nm for Me_2Si .^{2a–c} We hope that this paper will prompt the measurement of λ_{max} for H_2Si as well as other experiments and theoretical studies of silanediyls.

We are grateful to Professor Robert West for allowing us to quote his spectroscopic data prior to publication and we thank him and Professors John Pople, E. R. Davidson, and P. Certain for numerous valuable discussions. This research was supported by the United States – Israel Binational Science Foundation (B.S.F.), Jerusalem, Israel, and by the Fund for the Promotion of Research at the Technion.

Received, 9th January 1985; Com. 047

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|| Calculations show that at $\alpha > 125^\circ$ H_2Si is a ground state triplet. The isoelectronic Mes_2C has a nearly linear geometry around the carbenic carbon; see: A. S. Nazran and D. Griller, *J. Am. Chem. Soc.*, 1984, **106**, 543. Thus, Mes_2Si may have a triplet ground state.