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AIM and ELF Electronic Structure/G2 and G3 π-Bond Energy Relationship for Doubly Bonded Silicon Species, $H_2Si{=}X$ ($X = E^{14}H_2, E^{15}H, E^{16}$)[1]

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π-Bond energies in doubly bonded silicon species, $H_2Si{=}X$ ($X = E^{14}H_2, E^{15}H, E^{16}$), were determined using G2 and G3 procedures. In addition, the distribution of electron density in the internuclear area between silicon and the element in $H_2Si{=}X$ and $H_3Si{-}XH$ was estimated using quantum-topological approaches AIM (MP2/6-311++G(2d,p)) and ELF (HF/6-311++G(2d,p)). Both parameters, an increase of electron density at the critical point of the silicon−element bond and π-bond energy, appeared to correlate linearly, increasing on going from group 14 to group 16 elements. The contribution of the ion-component to the Si=E π-bond energy increases as the negative inductive effect of the element grows, attaining the maximum for silanone.

Introduction

The chemistry of hetero-π-systems of silicon originates in works[2] in which the first transient silene, $Me_2Si{=}CH_2$, was cleanly generated in the gas phase by 1,1-dimethyl-1-silacyclobutane 2+2 thermocycloreversion.[3] Nonhindered compounds of doubly bonded silicon such as silenes, silanimines, silanones, disilenes, silaphosphenes, and silanthiones are the intermediates in many high-temperature processes taking place in the gas phase.[3,4] The most important energetic feature of the doubly bonded silicon species is the value of the π-bond energy, $D_\pi(Si{=}E)$. There are a few theoretical approaches to estimate the $D_\pi(Si{=}E)$. Two of them consist in evaluation of its contribution to the enthalpies of dehydrogenation (reaction i)[5] and isodesmic reaction ii.[6−9]

$$H_3Si{-}XH \rightarrow H_2Si{=}X + H_2 \qquad \text{(i)}$$

$$H_2Si{=}X + SiH_4 + XH_2 \rightarrow 2H_3Si{-}XH \qquad \text{(ii)}$$

Obviously, the accuracy of $D_\pi(Si{=}E)$ values obtained mainly depends on the reliability of Si−H and E−H bond dissociation energies, BDEs. In particular, the disadvantage of $D_\pi(Si{=}E)$ calculations via enthalpy of reaction ii was that the authors[6] assumed Si−H and E−H BDEs to be constant in SiH_4, XH_2, and $H_3Si{-}XH$.[10] It seems that the use of reaction i is preferable because only two BDE values, Si−H and E−H in $H_3Si{-}XH$, are required. However, the availability of reliable BDEs still remains the main problem. Therefore, instead of E−H BDEs in H_3SiXH, the somehow corrected E−H bond dissociation energies in H_3CXH or XH_2 were used.[5] To our knowledge, the most appropriate Si−H and E−H BDEs obtained from G2 calculations are now available only for H_3SiCH_3[10] and H_3SiOH.[11]

Another method of calculation of $D_\pi(Si{=}E)$ involving the estimation of the covalent and ionic structure contributions (resonance mixture) in terms of the valence bond (VB) theory was recently extended.[12] However, the data appeared to be rather overestimated. For instance, $D_\pi(Si{=}O)$ was 29 kcal/mol higher than the value resulting from ab initio calculation.[5] Since the G2 formalism is known to be remarkably able to reproduce experimental data, we used it as well as G3 in this work to obtain the more reliable new set of $D_\pi(Si{=}E)$ data.

Schleyer and Kost[6] discovered a distinct trend of $D_\pi(Si{=}E)$ to grow as electronegativity of the element E increases, which was confirmed indirectly by others.[5,12] Since electronegativity

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(7) In the third approach π-bond energy is taken as a barrier of hindered rotation about the double bond in $H_2Si{=}X$, ref 5. Noteworthy, the latter method is not universal, because it cannot be applied to the molecules with Si=O or Si=S bonds.

(8) The values of $D_\pi(Si{=}C)$ in $R_2Si{=}CH_2$ (R = H, CH_3, SiH_3, CH_3O, NH_2, Cl, F) were also calculated through the enthalpy of cycloreversion of silacyclobutanes, ref 9.

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Table 1. G2 and G3 Total Energies of Silanes, Related Radicals, and Derived Silenes, in Hartrees

molecule	G2/G3 energy (0 K)	radical	G2/G3 energy (0 K)
SiH_3CH_3	−330.65783/−330.99520	${}^{\bullet}SiH_2CH_3$	−330.01063/−330.34873
$H_2Si{=}CH_2$	−329.41260/−329.74890	$SiH_3C^{\bullet}H_2$	−329.99662/−330.33534
SiH_3NH_2	−346.72454/−347.06388	${}^{\bullet}SiH_2NH_2$	−346.08038/−346.42065
$H_2Si{=}NH$	−345.48220/−345.81975	$SiH_3N^{\bullet}H$	−346.04891/−346.38893
SiH_3OH	−366.61171/−366.95303	${}^{\bullet}SiH_2OH$	−365.96416/−366.30625
$H_2Si{=}O$	−365.37968/−365.71952	$SiH_3O^{\bullet}$	−365.91718/−366.26402
SiH_3SiH_3	−581.66809/−582.24977	$SiH_3Si^{\bullet}H_2$	−581.02700/−581.60936
$H_2Si{=}SiH_2$	−580.42938/−581.00976		
SiH_3PH_2	−632.93409/−633.52443	${}^{\bullet}SiH_2PH_2$	
$H_2Si{=}PH$	−631.71922/−632.30807	$SiH_3P^{\bullet}H$	−632.30524/−632.89619
SiH_3SH	−689.19839/−689.79669	${}^{\bullet}SiH_2SH$	−688.55546/−689.15461
$H_2Si{=}S$	−687.99256/−688.58928	$SiH_3S^{\bullet}$	−688.55709/−689.15592
H_2	−1.16635/−1.167388	$H^{\bullet}$	−0.50000/−0.50100

is an integral characteristic of the electronic properties of the element,[13] we aimed to disclose how an increase of π-bond energy is related to the changes in electronic structure of $H_2Si{=}X$.[14] Evidently, the variety of $D_\pi(Si{=}E)$ should be related to the peculiarities of the electronic structure of the doubly bonded silicon species. To study the allocation of electron density, we used quantum topological methods AIM[15] and ELF.[16] Earlier the ELF method was used to study the allocation of electron density in the Si=Si area of $H_2Si{=}SiH_2$[17] and the Si=P bond in $H_2Si{=}PH$.[18] In addition, a series of silenes, $R_2Si{=}CH_2$ (R = H, CH_3, SiH_3, CH_3O, NH_2, Cl, F),[19,20] 1,1-bis[*N*-(dimethylamino)acetamidato]silene,[21] $(HO)_2Si{=}O$, and $(HS)_2Si{=}S$[22] were studied by the AIM method.

Herein, we aimed at (i) using G2 and G3 levels of theory to obtain the more reliable set of $D_\pi(Si{=}E)$ values, (ii) searching the relationship between the electron structures and π-bond energies of the doubly bonded silicon species, and (iii) uncovering the subtle peculiarities of electron density allocation in the silicon−element internuclear area of $H_2Si{=}X$ (X = $E^{14}H_2$, $E^{15}H$, E^{16}).

Computational Methods

Full geometry optimization of the series of molecules $H_2Si{=}X$, $H_3Si{-}XH$, and related radicals was performed by an ab initio method at the MP2 level of theory with 6-311++G(2d,p) basis sets in term of G2 and G3 procedures using GAUSSIAN 03 packages.[23] G2 and G3 (0 K) energies of the species are given in Table 1. The correspondence of optimized structures to the local minima on the potential energy surface was proved by positive eigenvalues of the related Hessians. In Table 2 geometrical parameters of doubly bonded silicon species are listed. $D_\pi(Si{=}E)$ were calculated at the G2 and G3 levels of theory in terms of a thermochemical approach for dehydrogenation reaction i using eq 1, like it was done previously for carbon analogues.[10]

$$D_\pi(Si{=}E) = D(Si{-}H) + D(E{-}H) - D(H{-}H) - \Delta H^0(0\ K) \tag{1}$$

The bond dissociation energies $D(Si{-}H)$, $D(E{-}H)$, and $D(H{-}H)$ were calculated as the enthalpies of reactions iii−v.

$$H_3Si{-}XH \rightarrow {}^{\bullet}SiH_2{-}XH + H^{\bullet} \tag{iii}$$

$$^{\bullet}SiH_2{-}XH \rightarrow H_2Si{=}X + H^{\bullet} \tag{iv}$$

$$H^{\bullet} + H^{\bullet} \rightarrow H_2 \tag{v}$$

Analysis of the electron density in terms of the atoms in molecules (AIM) theory[15] was performed using the MORPHY 1.0[24] program at the MP2(Full)//MP2(FC)/6-311++G(2d,p) level of theory.[25] The electron localization functions of Bekke and Edgecombe[16] (ELF) were calculated with the TopMod[26] program package at the HF/6-311++G(2d,p)//MP2/6-311++G(2d,p) level of theory and visualized using the GopenMol[27] package of programs. Overviews of AIM and ELF theories as applied to organosilicon compounds were given in a previous paper.[28]

Results and Discussion

Geometries. Geometrical parameters of the doubly bonded silicon species, $H_2Si{=}X$, optimized at various ab initio levels of theory are listed in Table 2.

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Table 2. Geometric Parameters of $H_2Si{=}X$ Optimized at the MP2/6-311++G(2d,p) Level of Theory, Bond Lengths (Å) and Bond Angles (deg) (experimental data are given in parentheses)

molecule	rSi═E	rSi−H	rE−H	∠HSiH	∠HSiE	∠HEH	∠HESi
$H_2Si{=}CH_2$	1.708 (1.7039)[a]	1.467 (1.4671)[a]	1.084	115.0	122.5	116.0	122.0
$H_2Si{=}NH$	1.609	1.464[b] 1.477[c]	1.017	112.4	117.0[b] 130.6[c]		120.7
$H_2Si{=}O$	1.534 (1.515)[d]	1.471 (1.472)[d]		111.6 (112.0)[d]	124.2 (124.0)[d]		
$H_2Si{=}SiH_2$[e]	2.165	1.469	1.469	112.9	118.9	112.9	33.8[f]
$H_2Si{=}PH$	2.083	1.471[g] 1.469[h]	1.416	112.5	120.9[b] 126.6[c]		
$H_2Si{=}S$	1.936/1.956	1.469/1.471		109.9	125.0		91.4

[a] Ref 29. [b] *Trans*-position to NH bond. [c] *Cis*-position to NH bond. [d] Ref 30. [e] *Trans*-bent geometry. [f] HSiH out-of-plane angle. [g] *Trans*-position to PH bond. [h] *Cis*-position to PH bond.

Table 3. Si−H and E−H Bond Dissociation Energies in H_3SiXH, in kcal/mol

	BDE			
bond cleaved in H_3SiXH	this work G2/G3	other G2	BAC/MP4(SDTQ)/6-31**	other data
$CH_3SiH_2{-}H$	92.4/91.3	92.3[c]	92.4[b]	89.6[a], 92.7 ± 1.2[j]
$SiH_3CH_2{-}H$	101.2/99.7	101.1[c]	100.9[b]	99.2[a]
$NH_2SiH_2{-}H$	90.5/89.2		91.5[d]	90[a]
$SiH_3NH{-}H$	110.2/109.1		114.8[d]	98[a]
$HOSiH_2{-}H$	92.6/91.5	94[e]	93.7[f]	90[a]
$SiH_3O{-}H$	122.1/118.0	120.6[e]	122.7[f]	104[a]
$SiH_3SiH_2{-}H$	88.5/87.5			86.3[a], 89.1 ± 2[j]
$PH_2SiH_2{-}H$	−[g]		90.6[h]	86[a]
$SiH_3PH{-}H$	80.8/79.8		83.7[h]	80[a]
$HSSiH_2$-H	89.7/88.5			88[a]
$SiH_3S{-}H$	88.7/87.7			89[a]
H−H	104.4/103.8			104.2[i]

[a] Ref 10. [b] Ref 31. [c] Data cited in ref 5. [d] Ref 32. [e] Ref 33. [f] Ref 11. [g] Refs 34, 35. [h] We failed to optimize $^{\bullet}SiH_2PH_2$ because starting the optimization procedure from the different geometries resulted in the structure of $SiH_3P^{\bullet}H$. Therefore, the value of 90.6 kcal/mol for the $PH_2SiH_2{-}H$ bond energy was taken from ref 36. [i] Ref 36. [j] Ref 37.

Table 4. G2 and G3 Dehydrogenation Enthalpies of Silanes, in kcal/mol

	$\Delta H_{\mathrm{dehydr}}$			
molecule	this work (G2/G3)	MP4/6-311G(d,p)+ ZPE(3-21G), ref 5	BAC/MP4(SDTQ)/ 6-31**	CI(S+D+QC)/ 6-31G**/6-31G*
H_3SiCH_3	49.5/49.5	49	49.4[a]	
H_3SiNH_2	47.7/48.2	49	52.4[b]	
H_3SiOH	41.2/41.5	41	42.3[c]	51.6[d]
H_3SiSiH_3	45.4/45.6	46	43.8[e]	
H_3SiPH_2	30.4/30.7	32	31.9[f]	
H_3SiSH	24.8/25.1	26		31.4[d]

[a] Ref 31. [b] Ref 33. [c] Ref 34. [d] Ref 39a. [e] Calculated via ΔH_f taken from ref 40. [f] Ref 36.

Excluding disilene, all the molecules are planar. In every period the Si═E bond length, r(Si═E), decreases on going from group 14 to group 16 elements (Table 2), i.e., as the atom E electronegativity, χ, grows.[6] Shortening of r(Si═E) is accompanied by the diminishment of the ∠HSiH valence angle. Si═C and Si═O bond lengths in silene and silanone are somewhat overestimated, when compared to those obtained by the rotation spectroscopy.[29,30]

Si═E π-bond energies were calculated via eq 1. The accuracy of the D_π(Si═E) calculation is affected by the reliability of the Si−H and E−H bond dissociation energies (BDEs) and the enthalpies of reaction i. Both our and literature data on Si−H and E−H BDEs are provided in Table 3.

It is seen that our G2 and G3 values for the BDE Si−H in H_3SiCH_3 and H_3SiSiH_3 are in good agreement with experimental reference data.[32] Also G2 and G3 BDEs fit data obtained at the BAC/MP4(SDTQ)/6-31** level of theory that has been proven reliable in calculating the thermochemical properties of radicals and closed-shell species.[38]

In Table 4 the enthalpies of dehydrogenation reaction i, $\Delta H_{\mathrm{dehydr}}$, obtained by us at the G2 and G3 levels of theory, are listed.

As is seen from Table 4, in total our data fit literature values. Obviously $\Delta H_{\mathrm{dehydr}}$ of silanol and silylsulfide obtained by Kudo and Nagase[39a] are substantially overestimated, which might be due to the insufficiency of the level of theory used. Also

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Table 5. Si═E *π*-Bond Energies, in kcal/mol

	D_π(Si═E)				
molecule	G2/G3 data this work	MP4/6-311G(d,p)+ ZPE(3-21G), ref 5	MP4(SDTQ)/6-31*// 6-31*+ZPE, ref 6	VB, ref 12a	other data
$H_2Si{=}CH_2$	39.6/37.7	37	36.1	47.1	39.3[a], 40.3[b], 41.1[c], 34.9 ± 1[d]
$H_2Si{=}NH$	48.6/46.5	36	37.0	58.4	
$H_2Si{=}O$	69.1/64.2	50	55.8	79.0	70.0[e], 33[f], 61.2 ± 6[d], 58.5[g]
$H_2Si{=}SiH_2$	27.3/25.6	23	24.2	35.1	28.7[h], 27.0 ± 2[d]
$H_2Si{=}PH$	36.6/35.9	35	29.7	41.9	
$H_2Si{=}S$	49.2/47.3	50	43.6	57.7	42[f], 47.0[g]

[a] Rotational barrier, ref 25. [b] Calculated via 2+2 cycloreversion enthalpy, MP4/6-311G*//MP2/6-31G*, ref 9. [c] BAC/MP4(SDTQ)/6-31**, ref 31. [d] Ref 32. [e] BAC/MP4(SDTQ)/6-31**, ref 34. [f] CI(S+D+QC)/6-31G**/6-31G*, ref 39a. [g] B3LYP/TZ(d,p), ref 39b. [h] BAC/MP4(SDTQ)/6-31**, ref 40.

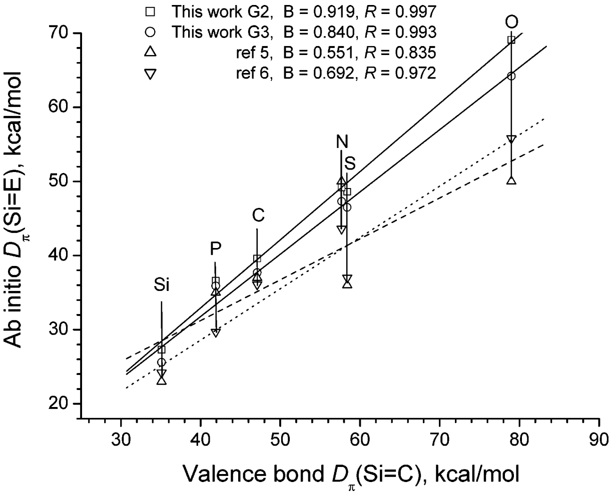

Figure 1. Relationships between D_π(Si═E) calculated by ab initio and valence bond[12a] methods.

dehydrogenation enthalpy of silylamine calculated at the BAC/MP4 level of theory seems to be incorrect especially because all the other BAC/MP4 data are in reasonable agreement with G2 and G3 data.

The Si═E *π*-bond energies obtained using G2 and G3 data on BDE and ΔH_{dehydr} are given in Table 5.

It is seen that all the D_π(Si═E) values vary substantially. Noteworthy, our G2 D_π(Si═E) values are in a good agreement but somewhat lower than those calculated at the BAC/MP4-(SDTQ)/6-31** level of theory combined with empirical bond additivity corrections: cf., D_π(Si═C) 39.6 and 41.1 kcal/mol,[31] D_π(Si═O) 69.1 and 70.0 kcal/mol,[34] D_π(Si═Si) 27.3 and 28.7 kcal/mol.[40] G3 D_π(Si═E) values are 0.7 to 2.1 kcal/mol lower than those calculated by the G2 method. An exception is D_π-(Si═O), for which the decrease reaches 4.9 kcal/mol. The worst values of D_π(Si═O) (33 kcal/mol) and D_π(Si═S) (42 kcal/mol) were from calculations at the CI(S+D+QC)/6-31G**/6-31G* level of theory.[39a] The VB data evidently exceed all the ab intio values. Since both approaches are based on different principles, it seemed of interest to estimate the relationships between ab intio and VB Si═E *π*-bond energies (Figure 1).

It is seen that the best correlation coefficient (0.997) and slope being fairly close to unit are achieved for our G2 D_π(Si═E). In the case of G3 calculations these parameters are also reasonably good. Since G2 and G3 and VB approaches result in mutually consistent data, in further discussions of ab initio thermochemical data we will use more reliable G2 and G3 data. Last, Figure 1 indirectly confirms a distinct tendency of D_π(Si═E) to increase as the electronegativity of atom E increases.[6]

Table 6. Properties of Bond Critical Points of $H_3Si{-}XH$ and $H_2Si{=}X$, at the MP2(Full)/6-311++G(2d,p) Level of Theory

	ρ [a]			$\nabla^2\rho$ [c]		−*E* [d]	
X	Si−	Si═	$\Delta\rho_\pi$ [b]	Si−	Si═	Si−	Si═
CH_2	0.810	1.003	0.193	−0.859	10.2	0.102	0.691
NH	0.886	1.117	0.232	−1.607	20.8	0.100	0.672
O	0.910	1.232	0.322	−1.421	32.4	0.095	0.639
SiH_2	0.590	0.681	0.090	2.075	−3.64	0.055	0.374
PH	0.628	0.772	0.144	0.353	−1.86	0.088	0.592
S	0.638	0.858	0.220	−0.733	3.809	0.094	0.637

[a] ρ, e/Å^3. [b] $\Delta\rho_\pi = \rho(Si{=}X) - \rho(Si{-}X)$, the difference between electron density at the critical point of $H_3Si{-}XH$ and $H_2Si{=}X$, e/Å^3. [c] $\nabla^2\rho$, e/Å^5. [d] E_c, hartree/Å.^{3}

AIM Analysis. There is a bond critical point (BCP) of rank (3, −1) in the internuclear area between atoms of silicon and element of the all compounds studied.[41] In Table 6 electron density (ED) values, ρ, in BCP of $H_3Si{-}XH$ and $H_2Si{=}X$, the ρ increment due to the double from single bond formation, $\Delta\rho_\pi$, Laplacian, $\nabla^2\rho$, ellipticity, ϵ, and local energy density, −*E*, calculated by AIM are listed.

As it is seen, ρ grows on going from single to double bonds and on changing E from group 14 to group 16 elements. This growth of ED could be rationalized by the shortening of the SiE bond due to the decrease in covalent radius and shrinking of E, because of nucleus charge accumulation. The increment of electron density, $\Delta\rho$, determined via eq 2 as a difference between ρ in BCP of the $H_2Si{=}XH$ molecules and their precursors, i.e., silanes $H_3Si{-}XH$, grew similarly.

$$\Delta\rho_\pi = \rho(\text{BCP}_{H_2Si=X}) - \rho(\text{BCP}_{H_3Si-XH}) \qquad (2)$$

The increment of the electron density at the BCP in the internuclear silicon−element area, raising as the increase of the negative inductive effect of the E atom, correlated with the *π*-bond energy of the double Si═E bond (Figure 2), being described by eqs 3 and 4.

$$\text{G2 } D_\pi(\text{Si=E}) = 9.6 + 177.1\Delta\rho_\pi \qquad (3)$$

$$\text{G3 } D_\pi(\text{Si=E}) = 10.3 + 162.5\Delta\rho_\pi \qquad (4)$$

In terms of AIM the negative value of the Laplacian unambiguously points to the covalent nature of the chemical bond.[15] This condition is held true for Si═Si and Si═P bonds

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(39) (a) Kudo, T.; Nagase, S. *Organometallics* **1986**, *5*, 1207. (b) Suzuki, H.; Tokitoh, N.; Okazaki, R.; Nagase, S.; Goto, M. *J. Am. Chem. Soc.* **1998**, *120*, 11096.

(40) Ho, P.; Melius, C. F. *J. Phys. Chem.* **1990**, *94*, 5120.

(41) The BCP of the rank (3, −3) indicated that the doubtful non-nuclear attractor was found in disilene, in the center of the Si═Si bond when calculating at the MP2/6-31G(d,p) level of theory. However, the attractor disappears when using the HF/6-311++G(2d,p) basis set. Therefore, the latter was used in further AIM calculations.

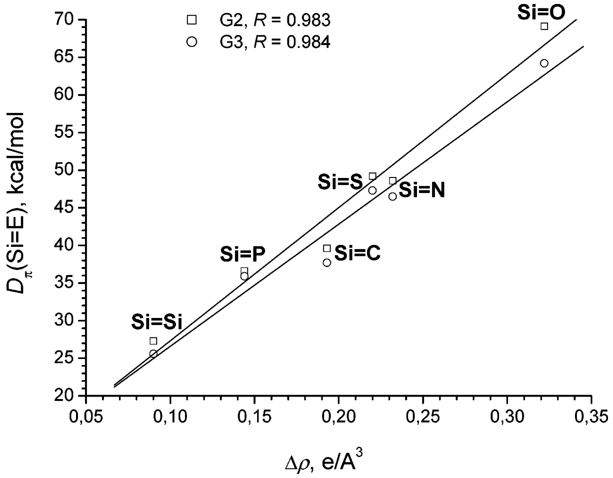
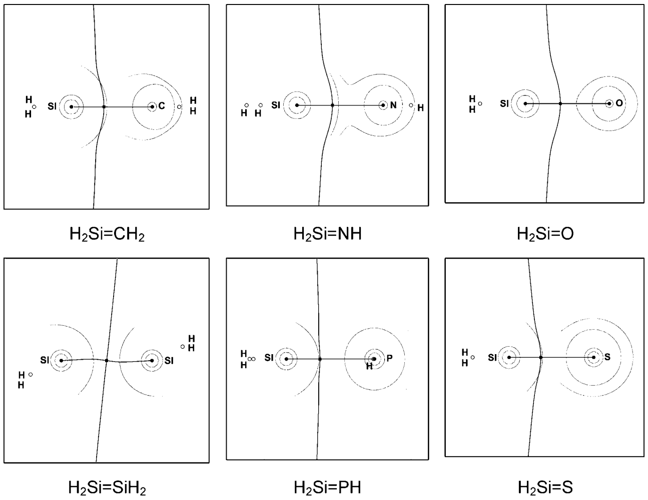


Figure 2. Plot of Si=E π-bond energy, D_{π}(Si=E), versus an increase of electron density at the silicon−element bond critical point upon dehydrogenation of H_2SiXH, $\Delta\rho_{\pi}$.



$H_2Si{=}CH_2$ $H_2Si{=}NH$ $H_2Si{=}O$

$H_2Si{=}SiH_2$ $H_2Si{=}PH$ $H_2Si{=}S$

Figure 3. Laplacian maps for $H_2Si{=}X$ species (plane of π-bond). The diagrams are superimposed with the selected bond paths. Critical points (3, −1) are denoted by solid squares. Dashed lines correspond to $\nabla^2\rho(\mathbf{r}) > 0$ (regions of charge depletion) and solid lines to $\nabla^2\rho(\mathbf{r}) < 0$ (regions of charge concentration). The contour values in e/a_0^5 are ±0.002, ±0.004, and ±0.008.

in disilene and silaphospene (Table 6), respectively. The other Si=E bonds (E = C, N, S, O) are covalent and polar, because at the positive Laplacian $\nabla^2\rho$ the following condition is met: the negative sign of the local electron energy, E, and $|E| > 0.4$ hartree/Å^3 (Cremer and Kraka criterion).[42] The Laplacian growth indicated a more polar Si=E bond, cf. $\nabla^2\rho$ is equal to −3.64 for the homonuclear Si=Si bond and 32.4 for the most polar heteronuclear Si=O bond (Table 6).

The disposition of BCP(Si=C) and BCP(Si=S) close to the border of the area of charge concentration also pointed to a covalent interaction in the Si=C and Si=S bonds (see Figure 3).

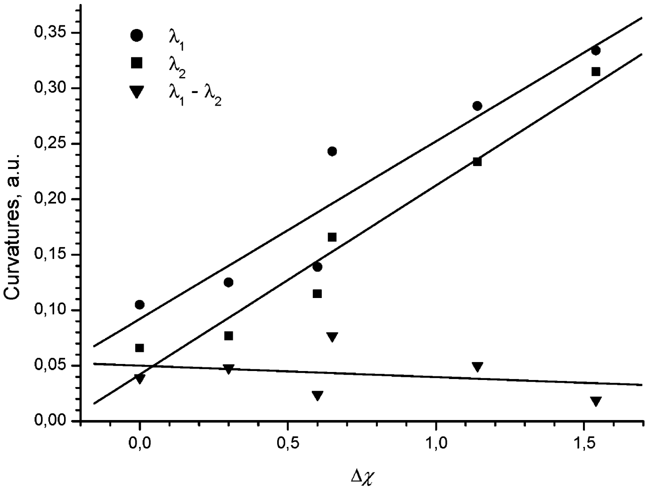


Figure 4. Plot of curvatures, λ_1 and λ_2, of the Laplacian of electron density at the Si=E bond critical point, $\nabla^2\rho(\mathbf{r})$, versus differences of electronegativities, $\Delta\chi = \chi_E - \chi_{Si}$.

Table 7. Values of Curvature, λ_1, λ_2, and λ_3, of the Laplacian Hessian of Electron Density (au) and Ellipticity at the BCP of Silicon−Element in $H_2Si{=}X$

molecule	ϵ	λ_1	λ_2	λ_3
$H_2Si{=}CH_2$	0.467	−0.243	−0.166	0.832
$H_2Si{=}NH$	0.211	−0.284	−0.234	1.383
$H_2Si{=}O$	0.061	−0.334	−0.315	1.994
$H_2Si{=}SiH_2$	0.595	−0.105	−0.066	0.019
$H_2Si{=}PH$	0.614	−0.125	−0.077	0.125
$H_2Si{=}S$	0.213	−0.139	−0.115	0.412

The Laplacian maps showed that for all compounds (except silanone) the area of negative charge, originating from the accumulation of electron density on the π-plane of Si=E, also involved the atomic basin of silicon (see Figure 3). The measure of the predominating charge concentration on this plane, pointing to the π-character of the Si=E bond, is the ellipticity, ϵ (Table 7).

A comparatively great value of ϵ indicates a pronounced "π-character" of Si=P, Si=Si, and Si=C bonds. It is significantly smaller for Si=S and Si=N bonds. The smallest ϵ indicating almost cylindrical symmetry is inherent to the Si=O bond in silanone.

Within the AIM theory the ellipticity is attributed to the relation of curvatures of the Laplacian, λ_1 and λ_2, which characterizes the charge concentration at the BCP in the directions orthogonal to the Si=E bond vector. It is described as follows:

$$\epsilon = \lambda_1/\lambda_2 - 1 \tag{5}$$

We plotted curvatures and their difference versus the difference in electronegativity of the element and silicon of the Si=E double bond, $\Delta\chi$ ($\Delta\chi_E = \chi_E - \chi_{Si}$) (Figure 4).

It is seen that curvatures λ_1 and λ_2 increase and get closer to each other as $\Delta\chi$ grows. At that ρ contraction toward transverse directions to the Si=E bond line results in shifting the electron density into the atomic basin of element E; that is, longitudinal curvature λ_3 increases. In other words, as the Si=E bond becomes more polar, the charge that is concentrated at the BCP becomes greater and the shape of the charge distribution tends to the cylindrical symmetry. Indeed, in silanone, the compound with the most polar bond, the curvatures become almost equal. Therefore, the ellipticity and thus "π-character" of the Si=E bond decrease in the order

$$\mathrm{Si{=}Si} \approx \mathrm{Si{=}P} > \mathrm{Si{=}C} > \mathrm{Si{=}S} \approx \mathrm{Si{=}N} \gg \mathrm{Si{=}O}$$

ELF Analysis. The aim of the ELF approach is to partition the space occupied by a molecule into the definite adjacent regions that are called "basins". In particular, they correspond

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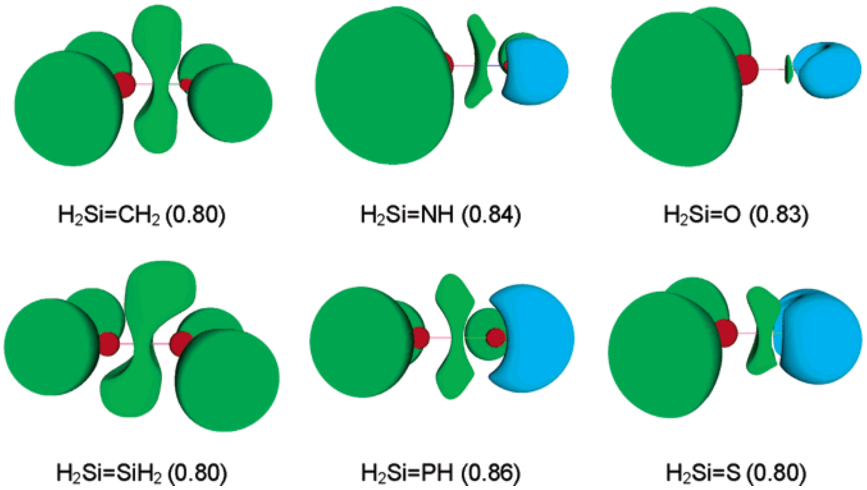
[42] (a) Cremer, D.; Kraka, E. *Croat. Chem. Acta* **1984**, *57*, 1259. (b) Cremer, D.; Kraka, E. *Angew. Chem.* **1984**, *96*, 612; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 627. (c) Ritchie, J. P.; Bachrach, S. M. *J. Am. Chem. Soc.* **1987**, *109*, 5909.


$H_2Si{=}CH_2$ (0.80) $H_2Si{=}NH$ (0.84) $H_2Si{=}O$ (0.83)

$H_2Si{=}SiH_2$ (0.80) $H_2Si{=}PH$ (0.86) $H_2Si{=}S$ (0.80)

Figure 5. Localization domains of the species $H_2Si{=}X$ as shown by ELF (isosurfaces are given in parentheses). Green demonstrates the disynaptic binding basins, red shows the spanning basins of silicon and E atoms, and light green is the disynaptic basins, surrounding hydrogen atoms. Monosynaptic basins of lone pairs are denoted by cyan.

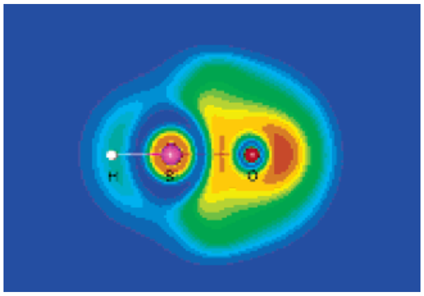


Figure 6. Two-dimentional cross-section of $H_2Si{=}O$ in the plane of the π-bond. Blue to red colors correspond to ELF change from 0 to 1.

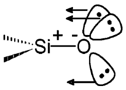


Figure 7. Model of bonding in the $H_2Si{=}O$ species.

Table 8. Volume, *V*, Mean Population, *N*, and Dispersion, σ^2, for the Valence Mono- and Disynaptic Basins of $H_2Si{=}X$

molecule	basin	*V*	*N*	σ^2
$H_2Si{=}CH_2$	V1(Si,C)	111.9	1.84	0.96
	V2(Si,C)	111.9	1.84	0.95
$H_2Si{=}NH$	V1(Si,N)	66.6	1.61	0.94
	V2(Si,N)	66.7	1.61	0.95
	V(N)	108.8	2.67	1.16
$H_2Si{=}O$	V1(Si,O)	44.4	1.33	0.96
	V2(Si,O)	10.2	0.8	0.64
	V(O)	169.8	5.67	1.42
$H_2Si{=}SiH_2$	V1(Si_1,Si_2)	169.9	1.91	0.93
	V2(Si_1,Si_2)	170.0	1.92	0.93
$H_2Si{=}PH$	V1(Si,P)	95.2	1.56	0.90
	V2(Si,P)	95.9	1.61	0.92
	V(P)	228.2	2.68	1.11
$H_2Si{=}S$	V1(Si,S)	58.1	1.28	0.84
	V2(Si,S)	58.3	1.31	0.85
	V1(S)	156.8	2.63	1.23

to bonds, lone pairs, and single-electron domains, which are characterized by volume, population, and dispersion. Disynaptic basins characterized a two-center covalent bond V(Si,E), while a lone pair V(E) is monosynaptic. In ELF topology[16] multiple bonds manifest as two clearly distinct disynaptic basins[17,43] with two weakly separated maxima above and below the Si−E axis and a local minimum on the Si−E vector (Figure 5).

Disynaptic basins between silicon and element cores shown in Figure 5 attest that Si=Si, Si=C, Si=N, Si=P, and Si=S bonds possess pronounced "π-character". Unlike other planar species, the bent shape of a disynaptic basin of the Si=Si bond is due to the *trans*-bent structure of disilene.[17] In accordance with numerical data (Table 8) the disynaptic basins look most extensive for Si=Si and Si=C bonds. These are somewhat less extensive for Si=P, Si=N, and Si=S bonds and being dramatically negligible for the Si=O bond in silanone. Presumably, the distinct "π-character" of most Si=E bonds is due to the rather small change of the electronegativity of element E, which does not exceed 0.65. On the other hand, the minor "π-character" of the Si=O bond seems to rather result from a huge difference in electronegativity of the silicon and oxygen atoms (1.54). Therefore, according to AIM and ELF studies the Si=O bond holds a special position in the series of doubly bonded silicon compounds due to its pronounced zwitterionic rather than π-character structure.[44]

Volumes and populations of the valence mono- and disynaptic basins of ELF are listed in Table 8. It may be seen that populations of disynaptic basins of Si=Si and Si=C double bonds exceed those of other Si=E bonds. Indeed, sums of populations, $2N$[V(Si,Si)] and $2N$[V(Si,C)] are 3.83 and 3.68, respectively. These are close to 4.0, the value expected for two binding electron pairs, and substantially transcend 2, the lowest value of $2N$[V(Si,E)], indicating the multiple bond in the ELF approach.[12b] In fact, all the other Si=E bonds satisfy the later criterion, cf. $2N$[V(Si,E)] 3.22, 3.17, 2.59, and 2.13, for Si=N, Si=P, Si=S, and Si=O double bonds, respectively. Noteworthy, basin population fluctuations of Si=E bonds expressed in terms of σ^2 satisfy the ELF condition[12b] $\sigma < N$[V(Si,E)] typical for two-center bonds. The volumes and populations of disynaptic basins of every double bond are equal and decrease in the order Si=Si > Si=C > Si=P ≈ Si=N > Si=S. The exception is the Si=O bond, which is characteristic of nonequivalent volumes and populations of disynaptic basins. Noteworthy, the population of a monosynaptic basin of oxygen is as high as 5.67, whereas

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(43) ELF localization domains of disilene are similar to those calculated using teh Stuttgart quasirelativistic pseudopotential, ref 17.

(44) The VB calculations of Shaik, Hiberty, et al. (ref 12a) suggested all the Si=E bonds to be neither covalent nor ionic but charge-shift bonds.

the population of other monosynaptic basins varies within 2.63−2.68. Unexpectedly the small disynaptic volume of the V2(Si,O) basin and the high population of the monosynaptic basin, V(O), suggest that the electron pair responsible for Si═O π-bond formation is "sucked" into the valence shell of oxygen, indicating a weak π-character of the Si−O bond, which is fairly clearly demonstrated by a 2D image of ELF (Figure 6).

Therefore, the most realistic model of describing silanone is a zwitterionic structure (Figure 7). The increase in the volume of the electron cloud around the oxygen atom promotes its polarization in the direction of the arrows in Figure 7.

Conclusion

Si═E π-bond energies in doubly bonded silicon species $H_2Si{=}X$ (X = $E^{14}H_2$, $E^{15}H$, E^{16}) were calculated using G2 and G3 formalisms for the thermochemical cycle involving the H_3SiXH dehydrogenation reaction. It was found that D_π(Si═E) increases on going from group 14 to group 16 elements: 39.6/37.7, 48.6/46.5, and 69.1/64.2 kcal/mol in the first period and 27.3/25.6, 36.6/35.9, and 49.2/47.3 kcal/mol in the second period. Using quantum-topological approaches AIM (MP2/6-311++G(2d,p)) and ELF (HF/6-311++G(2d,p)) the distribution of electron density in the internuclear area between silicon and the element in $H_2Si{=}X$ and $H_3Si{-}XH$ was studied. It was shown that the loss of two hydrogen atoms by H_3SiXH and the formation of $H_2Si{=}X$ results in an increase of electron density at critical point of the silicon−element bond, $\Delta\rho_\pi = \rho(\mathrm{Si{=}E}) - \rho(\mathrm{Si{-}E})$. D_π(Si═E) appeared to correlate linearly with $\Delta\rho_\pi$. The nature of Si═E bonds in $H_2Si{=}X$ has been found to be covalent and polar. The exception is the nonpolar double bond in disilene. The π-electron pair participates in a covalent bonding of the silicon atom to all the elements, except oxygen. In silanone the electron cloud of the highly polar covalent Si═O bond does not seize the silicon atom and has atypical to π-bond cylindrical symmetry. ELF calculations showed that π-electrons take part in π-bond formation in all $H_2Si{=}X$ molecules, except silanone. The most realistic is the zwitterion structure of the latter: σ-bond $Si^+{-}O^-$ with three lone pairs in the valence shell of oxygen. Therefore, as the negative inductive effect of element E increases, the contribution of the ion-component to D_π(Si═E) increases, attaining the maximum for silanone.

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Supporting Information Available: Tables of coordinates for $H_2Si{=}X$ species used in calculations of G2 and G3 energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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