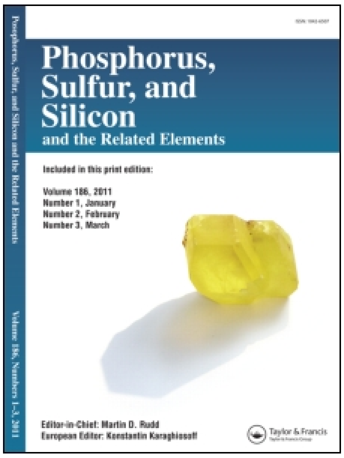

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Carbo-siloles, Part 1: A Theoretical Study

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To cite this Article Lepetit, Christine and Chauvin, Remi(2009) '*Carbo*-siloles, Part 1: A Theoretical Study', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 6, 1561 — 1572

To link to this Article: DOI: 10.1080/10426500902947906

URL: http://dx.doi.org/10.1080/10426500902947906

Phosphorus, Sulfur, and Silicon, 184:1561–1572, 2009

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500902947906

Carbo-siloles, Part 1: A Theoretical Study

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The ring carbo-*mer of silole, termed as* carbo-*silole, was investigated at the DFT level of theory (B3PW91/6-31G**) and compared to its* carbo-*cyclopentadiene and carbo-cyclopentadienone analogues. The electronic delocalization of these species and their parent molecules is analyzed indirectly from their optimized geometry, and directly from their canonical and NBO molecular orbitals by comparison of the HOMO-LUMO gaps. All criteria indicate that the π electron systems of* carbo-*silole and* carbo-*cyclopentadiene are delocalized to a similar extent, in particular through a $\pi - \sigma^*_{AH2}$ conjugation (A = C, Si). The cyclic component of the delocalization, i.e., aromaticity, has been more directly appraised by calculation of NICS values at the center of the rings: the latter definitely confirm that in contrast to* carbo-*cyclopentadienone (NICS = −8.1 ppm), both* carbo-*silole (NICS = −1.1 ppm) and* carbo-*cyclopentadiene (NICS = +2.4 ppm) are non-aromatic. The electron affinity is significantly increased by* carbo-*merization of silole (from 0.25 to 1.95 eV), suggesting that the* carbo-*silole ring might be a relevant unit for the design of functional materials. Studies of the* carbo-*silolylium cation show that its aromaticity is comparable to that of the long studied* carbo-*cyclopentadienyl analogue.*

Keywords Aromaticity; *carbo*-mers; cyclopentadiene; electron affinity; silole

INTRODUCTION

The relevance of ring *carbo*-merization of aromatic annulenes proved to be quite general.[1] Beyond *carbo*-benzene, for which several substituted representatives are known experimentally,[1,2] *carbo*-[N]annulenic ions

Received 18 January 2008; accepted 12 February 2008.

Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

The authors would like to thank CALMIP (Calcul intensif en Midi-Pyrénées, Toulouse, France), IDRIS (Institut du Développement et des Ressources en Informatique Scientifique, Orsay, France), and CINES (Centre Informatique de l'Enseignement Supérieur, Montpellier, France) for computing facilities and the Ministère de l'Education Nationale de la Recherche et de la Technologie for ACI financial support.

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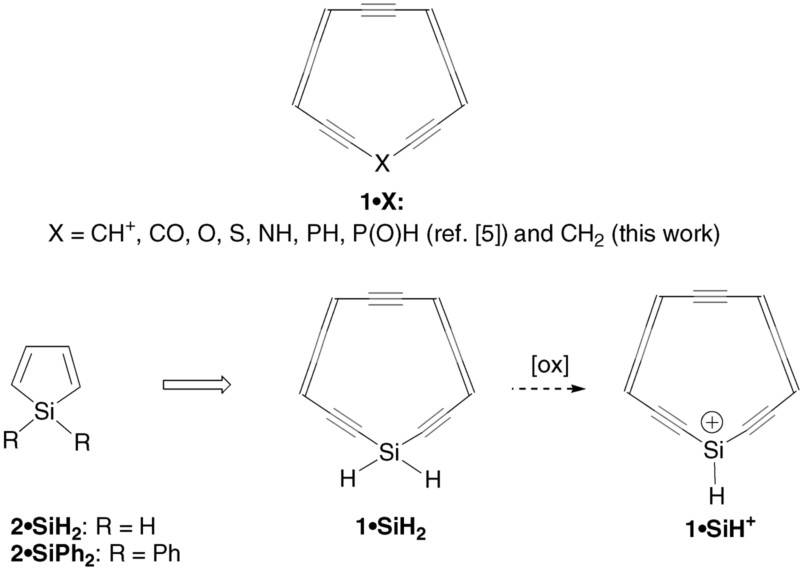
(N = 3, 5, 7) were submitted to various theoretical treatments, showing that they preserve the qualitative aromatic character of their parent counterions.[3] Similar *carbo*-meric comparisons also applied to less aromatic parent unsaturated carbocycles, such as radialenes[4] and related oxo-derivatives (cyclopentadienone,[5] [N]oxocarbones[6]). Carrying on the generalization, *carbo*-merization of heterocycles was considered.[5] In the six-membered series, *carbo*-pyridine and *carbo*-phosphinine were shown to exhibit the strong aromatic character of their parent molecules. In the less aromatic five-membered series, *carbo*-X-oles $C_{14}H_4X$ (**1•X**, Scheme 1) have also been investigated for X = CH^+ , O, S, NH, PH, P(O)H.[5] The missing links X = CH_2 (*carbo*-cyclopentadiene), X = SiH_2 ("*carbo*-silole"), and X = SiH^+ ("*carbo*-silolylium") are hereafter addressed.



SCHEME 1 Ring *carbo*-mers of five-membered "aromatic" carbocycles and heterocycles.

Siloles **2• SiR$_2$** possess high electron acceptability (their mono- and dianions exhibit aromatic properties) and fast electron mobility.[7] They are therefore candidates for building chromophores with bulk nonlinear optical properties, electron transporting materials,[8] or organic electroluminescent devices.[9] Their ring *carbo*-merization is therefore not only natural to complete the **1•X** series, but also a priori attractive in terms of possible applications.

RESULTS

Carbo-silole 1•SiH_2

Electron delocalization and the cyclic component thereof, namely aromaticity in the strict sense, are appraised on the basis of the three classical criteria: structural, energetic, and magnetic.

Structural Criterion

The selected level of calculation, B3PW91/6-31G**, is validated by confrontations of optimized geometries with available X-ray diffraction data for diphenylsilole **2•$SiPh_2$** (Table I, entry 1) and related benzene ring *carbo*-mers.[2a] At this level, both silole **2•SiH_2** and *carbo*-silole **1•SiH_2** are C_{2v} symmetric (Figure 1). As it is intrinsically deducible from the introduction of —C≡C— and =C=C= bonds, *carbo*-merization results in a decrease of the overall cyclic delocalization: this is measured by the root mean square deviation from the average C—C bond lengths (rms) over the rings of **2•SiH_2** (0.06317 Å) and **1•SiH_2** (0.07083 Å). The C—Si bonds are much shorter in **1•SiH_2** (1.823 Å) than in the parent **2•SiH_2** (1.873 Å): This shortening reflects an increase of the orbital overlap driven by the difference in hybridization state (and thus in electronegativity) of the sp^2- and sp—C atoms bonded to the Si atom.[10]

By contrast, the Si—H bond length is little affected upon *carbo*-merization. The *carbo*-silole ring involves 14π electrons stemming from the parallel non-hydridized p_z OAs of the 14 carbon atoms of the ring. Although conjugative transmission through the silicon vertex remains questionable, the 4n+2 electron count (for n = 3) fits with the Hückel rule for aromaticity. The planarity of the ring might thus a priori be dictated by the driving force of aromaticity (or equivalently, results in the development of aromatic characters). For comparative purposes, both the *carbo*-cyclopentadiene analogue **1•CH_2** and the *carbo*-cyclopentadienone **1•CO** have been considered (Scheme 1). The latter is selected as a carbon "isostructural" reference for **1•SiH_2**: the role of the carbon p_z OA of the partially polarized C^+—O^- bond of **1•CO** can be indeed regarded as a possible equivalent of the σ^* Si—H orbitals of **1•SiH_2**.

1•CH_2, **1•SiH_2**, and **1•CO** are all planar and C_{2v} symmetric (Table I), and their structural cyclic delocalization increases in the given order: This is measured by the rms over all the C—C bonds, which decreases from 0.07424 (**1•CH_2**) to 0.06923 (**1•CO**). It is noteworthy, however, that **1•CO** and **1•SiH_2** exhibit very similar rms values, showing that the Si atom allows for a π -conjugation at the same extent as a C^+—O^- vertex does. The average C—C bond length has also been calculated:

TABLE I Selected Structural Data in the Silole Series 2• Si and in the *Carbo*-silole and Pericyclynic Series 1• X (B3PW91/6-31G Level of Calculation)**

	X–C	XC≡C	$C_{sp}\overset{..}{=}C_{sp}$	$C_{sp2}\overset{.}{-}C_{sp2}$	$C_{sp}\overset{..}{-}C_{sp2}$	Si–H, Si–Ph C–H, or C=O	C–X–C	average C-Cbond length[c]	Rms[c]
2• Si	1.874	—	—	1.357	—	1.874	93.2	1.405	0.06788
Ph$_2^a$	1.862			1.501		1.864			
2• SiPh$_2$	1.882	—	—	1.348 1.485	—	1.884	91.8	1.394	0.06458
2• SiH$_2^b$ C_{2v}	1.877	—	—	1.349 1.487	—	1.489	n/a	1.395	0.06505
2• SiH$_2$ C_{2v}	1.873	—	—	1.349 1.483	—	1.491	92.7	1.394	0.06317
2• SiH$^+$	1.823	—	—	1.350 1.520	—	1.476	99.3	1.407	0.08014
1• CH$_2$ C_{2v}	1.466	1.215	1.257 1.224	—	1.413 1.338 1.343 1.402	—	109.7	1.320	0.07424
1• SiH$_2$ C_{2v}	1.823	1.225	1.255 1.225	—	1.408 1.341 1.344 1.398	1.487	106.4	1.321	0.07083

1• CO	1.441	1.223	1.251	—	1.398	1.226	110.5	1.319	0.06923
C_{2v}			1.228		1.347				
					1.350				
					1.391				
1• CH$^+$	1.369	1.238	1.238	—	1.369	—	118.5	1.325	0.06175
D_{5h}			1.238						
1• SiH$^+$	1.743	1.238	1.245	—	1.382	1.466	115.9	1.319	0.06382
C_{2v}			1.232		1.357				
					1.358				
					1.380				

Distances are in Å, and angles in degrees. Bond length are listed in consecutive order from the vertex X.

[a] X-ray crystal structure from reference [7].

[b] B3LYP/6-31G** level of calculation from reference [19].

[c] calculated over the carbon chain only.

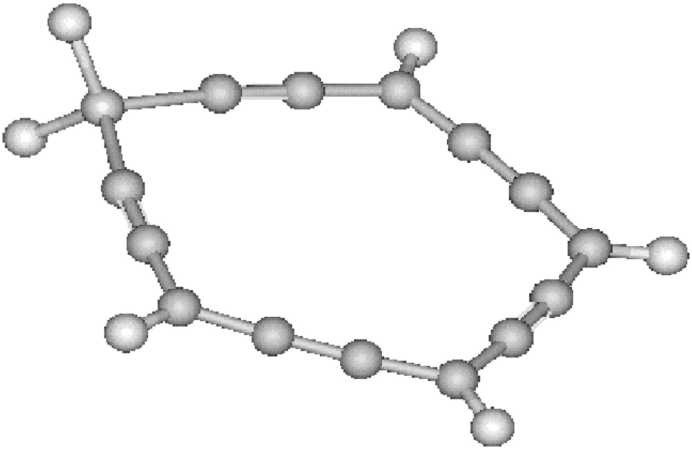


FIGURE 1 Calculated structure of *carbo*-silole **1•SiH$_2$** (B3PW91/6-31G**).

Its constancy over the series (1.320 ± 0.001 Å) indicates that the structural delocalization has no energetic effect on the "compactness" of the rings (the average bond length is indeed proportional to Krygowski EN parameter).[11]

The similar electron delocalization occuring in **1•SiH$_2$** and **1•CO** is thus directly supported by the similarity of their geometries. The main geometrical difference is indeed locally limited to the endocyclic bond angle at the SiH$_2$ vertex (106.4 degrees) which is smaller than the corresponding "carbon" angles occuring in **1•CH$_2$** (109.7 degrees) and **1•CO** (110.5 degrees). The same trend is observed in the parent series **2•SiH$_2$** (92.7 degrees), **2•CH$_2$** (102.8 degrees),[12] and **2•CO** (105.8 degrees to 106.2 degrees),[13] and is thus attributable to the elemental nature (Si or C) of the vertex atom.

Electronic-Energetic Criterion

Despite "accessible" σ^* Si–H orbitals, the silole ring is known to be essentially non-aromatic: The π-electron delocalization through the butadiene part of the ring is interrupted by the sp^3 silicon vertex (or even "reversed" by anti-aromaticity). Although peripheral conjugation to phenyl subtituents at the Si atom[9] [or to a η^4-coordinated Fe(CO)$_3$ fragment[8b]] should a priori result in a decrease of the HOMO-LUMO gap, this was not confirmed by our calculations on **2•SiPh$_2$**. Nevertheless, as compared to **1•SiH$_2$**, internal conjugation by *carbo*-merization induces a decrease of the HOMO-LUMO gap of **2•SiH$_2$** by a factor of two (Table II).

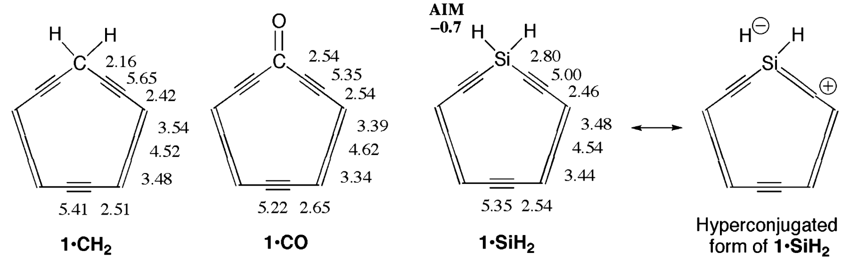
TABLE II Selected Structural, Energetic, and Magnetic Criteria of Aromaticity or Electronic Delocalization in the Silole Series 2• Si and in the *Carbo*-silole and Pericyclynic Series 1• X (B3PW91/6-31G Level of Calculation)**

	Average C–C bond length (Å)	rms[b] (Å)	NICS (ppm)	HOMO-LUMO GAP (eV)	$\sigma_X \rightarrow \pi_z^*$ ($\sigma_X \rightarrow \pi_{xy}^*$) interaction (kcal/mol)	$\pi_z \rightarrow \sigma_X^*$ ($\pi_{xy} \rightarrow \sigma_X^*$) interaction (kcal/mol)	EA[e] (eV)
2• $SiPh_2$[f] (XRD)	1.405	0.06788	—	—	—	—	—
2• $SiPh_2$ (calcd)	1.394	0.06458	+2.9	4.74	0.59 0.81	3.49 3.35	+0.139
2• SiH_2 C_{2v}	1.395	0.06317	+0.1	4.92	1.08	3.01	–0.254
2• SiH_2[a] C_{2v}	1.395	0.06505	+0.3[c]	n/a	—	—	–0.06
2• SiH^+	1.407	0.08014	+16.5 +12.8[g]	3.05	0.63	27.87	—
1• CH_2 C_{2v}	1.320	0.07424	+2.4	2.47	4.27 (0.78)	2.21 (0.75)	—
1• SiH_2 C_{2v}	1.321	0.07083	−1.1	2.51	1.92 (—)	2.21 (0.62)	+1.946
1• CO C_{2v}	1.319	0.06923	–8.1[d]	2.66	7.11	19.05	+2.140
1• CH^+ D_{5h}	1.325	0.06175	−16.9[d]	3.37	—		—
1• SiH^+ C_{2v}	1.319	0.06382	—13.7	2.83	—		—

[a] B3LYP/6-31G** level of calculation from reference [19]; [b] Calculated for the carbon chain only; [c] By the GIAO-HF/6-311G* method, from reference [15]; [d] From reference [5]; [e] Includes zero-point energy corrections; [f] X-ray crystal structure from reference [7]; and [g] From reference [21].

The electronic features of *carbo*-silole are more finely appraised below by analysis of the electron density or by analysis of the contribution of fragment orbitals.

The electron localization function (ELF) analysis of **1•SiH$_2$** and **1 •CH$_2$** has been performed. The scaled populations are listed in Scheme 2 and compared to those of **1•CO**.[5] The populations of the butatriene and butyne C_4 edges are similar (especially for X = CH_2 and SiH_2), but the populations of the X–C and XC≡C bonds strongly depend on X. The depleted populations of the C≡C basins (lower than 6) could be described by oscillating zwitterionic resonance forms also accounting for the concomitant overpopulated adjacent basins (larger than 2).[3d] However, the large population of the Si–C bonds suggests that the hyperconjugated Lewis form of Scheme 2 also possesses a substantial weight. The latter may be related to the π–$\sigma^*_{\mathrm{Si-H}}$ conjugation revealed by the canonical out-of-plane LUMO+1 of **1•SiH$_2$** (Figure 2). The stabilization energy of the $\pi_z \rightarrow \sigma^*_{\mathrm{Si-H}}$ interaction has been analyzed in terms of localized orbitals constructed within the NBO method (Table II).[14] The $\pi_z \rightarrow \sigma^*_{\mathrm{Si-H}}$ stabilization in **1•SiH$_2$** (2.21 kcal/mol) has the same order of magnitude as in the parent silole **2•SiH$_2$** (3.01 kcal/mol), and is identical to the $\pi_z \rightarrow \sigma^*_{\mathrm{C-H}}$ stabilization in the carbon analogue **1•CH$_2$**. As expected, it is also much lower than the $\pi \rightarrow \pi^*_{\mathrm{C-O}}$ conjugation energy occuring in *carbo*-cyclopentadienone **1•CO** (19.05 kcal/mol). In both **1•CH$_2$** and **1•SiH$_2$**, a secondary in-plane $\pi_{xy} \rightarrow \sigma^*_{\mathrm{X}}$ stabilization of *ca* 0.7 kcal/mol is also present (Table II). Criteria based on either orbital (NBO) or density (ELF) analyses thus indicate a contribution of zwitterionic $^+$ C=C=[X]$^-$ resonance forms for all the molecules. These criteria are not expected to be simply correlated, but comparison of the ELF basin populations gives a crude picture of the mesomeric electron shifts in the order: **1•SiH$_2$** > **1•CO** > **1•CH$_2$** (Scheme 2).



SCHEME 2 Comparison of scaled ELF populations of **1•CH$_2$, 1•CO** and **1•SiH$_2$** (*left*), and secondary Lewis form accounting for the $\pi_z \rightarrow \sigma^*_{\mathrm{Si-}H}$ hyperconjugation in **1•SiH$_2$** (*right*). Level of calculation: B3PW91/6-31G**.

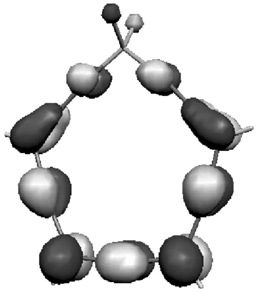


FIGURE 2 Canonical LUMO+1 featuring the out-of-plane π–σ $^*_{\text{Si–H}}$ conjugation in *carbo*-silole **1• SiH$_2$**.

The electron affinity of silole **2• SiH$_2$** increases upon *carbo*-merization and becomes positive. This variation is parallel to that of the $\sigma_{\text{Si}-H} \rightarrow \pi^*$ interaction, which is twice more stabilizing in **1• SiH$_2$** than in the parent silole (Table II). These trends suggest that *carbo*-siloles may be even better candidates than siloles for building electroluminescent devices.

Magnetic Criterion

According to the NICS measure of the magnetic criterion of aromaticity (Table II), the parent siloles **2** are not aromatic (NICS[**2• SiH$_2$**] = +0.3 ppm).[15] The magnetic aromatic character increases slightly upon ring *carbo*-merization (NICS[**1• SiH$_2$**] = –1.1 ppm), but remains much weaker than in the reference *carbo*-cylopentadienone (NICS[**1• CO**] = –8.1 ppm).

Carbo-silolylium 1• SiH$^+$

While siloles and cyclopentadienes are essentially non-aromatic,[15] the cyclopentadienyl and silolyl anions are aromatic,[16] while their corresponding cations are antiaromatic. In agreement with the predictions of the Hückel rules, these aromatic/anti-aromatic characters have been independently demonstrated on the basis of structural, energetic, and magnetic criteria. After having theoretically shown that the *carbo*-cyclopentadienyl cation **1 • CH$^+$** is definitely aromatic,[3] *carbo*-merization of the silolyl cation is here considered as a natural perspective.

Carbo-silolylium **1• SiH$^+$** exhibits strong analogies with **1• CH$^+$** (Table II): Both the cations are definitely aromatic in the structural and magnetic sense. The static and dynamic electron delocalizability is just slightly lower in **1 • SiH**$^+$ than in **1• CH**$^+$: This is indicated by the rms value of their C—C bond lengths (0.06175 Å for **1• CH**$^+$, 0.06382 Å for **1 • SiH**$^+$) and by their NICS values (–16.9 ppm for **1• CH**$^+$, −13.7 ppm for **1• SiH**$^+$), respectively.

CONCLUSION

Beyond their specific academic and aesthetical interest in *carbo*-mer chemistry, the theoretical results show that the delocalized-but-non-aromatic electronic structure of *carbo*-silole is a priori attractive for a future design of functional materials. Examples of *carbo*-silole rings thus deserve to be considered as valuable synthetic targets. The first results in this direction will be disclosed: They consist in the synthesis and characterization of an isohypsic equivalent of a substituted *carbo*-silole ring, namely a tetraoxy-*carbo*-silolane.[17]

COMPUTATIONAL DETAILS

Geometries were fully optimized (under symmetry constraint when possible) at the B3PW91/6-31G** level in the singlet spin state, using Gaussian98.[18] Vibrational analysis was performed at the same level in order to check that a minimum was obtained on the potential energy surface. This level of calculation was shown to be suitable for describing both the parent siloles[19] and previously studied ring *carbo*-mers.[20]

Adiabatic electron affinities (EA) were calculated as the total energy difference of the relaxed neutral and reduced species. Total energies were corrected from the zero-point energy. NICS (nucleus independent chemical shifts) were computed at the B3LYP/6-31+G** level according to the procedure described by Schleyer et al.[21] The magnetic shielding tensor was calculated for a ghost atom located at the geometric center of the ring using the gauge-independent atomic orbital (GIAO) method implemented in Gaussian98.[18]

NBO analysis[14] was performed using NBO3.1 implemented in Gaussian98.[18] In NBO analysis, deviations from idealized Lewis structures due to conjugation are interpreted in terms of orbital interactions between anti-bonds and localized bonds or lone-pairs. The energetic contributions from these interactions may be quantified with the help of the second-order perturbation theory: $E^{(2)} = n<F_{ij}>^2/\varepsilon_{ij}$, where F_{ij} is the Fock matrix element between occupied orbital i and unoccupied orbital j and can be taken as proportional to the overlap between those orbitals, ε_{ij} is the energy difference between orbital i and orbital j, and n is the occupancy of orbital i. Since perturbation theory is valid for small perturbations only, absolute stabilizations become less reliable as their value increase. General trends are therefore more meaningful than the absolute values of the energetic contributions.

ELF topological analysis was carried out with TopMoD.[22] Atomic charges were derived from atoms-in-molecules (AIM) analysis[23] using TopMoD.[22]

Visualization of molecular orbitals were done with the Molekel freeware.[24]

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