Intrinsic Bond Strengths of Multiple C–C, Si–Si, and C–Si Bonds**

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Like other chemical concepts, for example aromaticity[1] or hybridization,[2] the idea of bond orders recently led to a heated discussion in the literature.[3–5] Though those concepts often lack a solid physical ground, without a classification of different bonding situations as single or multiple bonds, there would be no systematic representation of the boundless diversity of possible chemical structures. Nevertheless, though modern quantum chemistry is able to predict a variety of observable quantities, it is by no means trivial to decide whether there *is* a bond between two specific atoms at all.[6] This dilemma led to a number of methods, which analyze the complexity of the wavefunction, with the aim to obtain information about local data.[7, 8] Unfortunately, there are many ways to localize the unique set of canonical molecular orbitals,[8, 9] which most of the electronic structure calculations are based on. Furthermore, any partition scheme of the basis functions or electrons between atomic centers is, strictly speaking, arbitrary. Given this, it is then not surprising that different methods of population analysis or charge-density analysis give different results when studying specific bond strengths or partial charges.[10] For example, the computed bond orders of a multiple Ga–Ga bond in a recently synthesized organogallium compound, range between less than two[5] and higher than three.[4]

Therefore, it might be useful to consider the quantum-chemical calculation of the inverted matrices of all energy second derivatives (compliance force constants).[3h] These calculations offer a complete, different, and simple way to compute directly intrinsic bond strengths, without using sophisticated analysis methods. A quantum-chemical calculation of the complete set of force constants overturns the classical way of evaluating a small number of force constants from experimental frequencies of vibrations by using a constrained force field.[11a] Such selected force constants (or better potential constants) are of limited use as a description for intrinsic bond strength[11b] since their transferability and hence their comparison is difficult. Furthermore, even if the complete matrix of force constants is available—which is now computational feasible for medium-sized systems by using correlated wave functions—their numerical value strongly depends on the internal coordinate system.[12] However, real-space theoretical force constants are frequently used in chemical literature.[13] Only after inversion of the complete set of theoretical force constants, is their numerical stability guarantied. Doing so, a higher compliance force constant is connected unambiguously and directly with a higher intrinsic bond strength.[14]

Herein the method of compliance force constants is used to study the strength of a triple bond between carbon and silicon atoms by comparing the bond strengths of different single and multiple C–C, Si–Si, and C–Si bonds. Theoretical studies on the C–Si triple bond date back to the 1970s and 1980s,[15] while experimental hints first appeared in 1994.[16] Only recently was the first experimental evidence of a C–Si triple bond published.[17] Earlier, in 1997, Apeloig and Karni used high-level quantum-mechanics calculations followed by population analysis to predict a bond order of three for a C–Si bond in a *trans*-bent RCSiR arrangement.[18] Interestingly, this study found no strengthening of the C–Si bond going from a *trans*-bent arrangement to linear acetylene-like RCSiR geometry.

In the present study, the compliance matrix method was used to learn more about the C–Si triple bond. All the quantum-chemical calculations used are based on hybrid density functionals, B3LYP.[19] Geometry optimizations and calculations of Cartesian force constants were performed with the Gaussian 98 program.[20] The setup of non-redundant internal coordinates and the transformation of the Cartesian force constants were carried out with Fogarasi's and Pulay's INTC/FCTINT set of algorithms.[21] The inversion of the internal Hessian matrix was accomplished by standard methods.[22]

The results are compiled in Table 1 and Figure 1. The well-known special position of C–C bonds is evident. There is more than a doubling of the intrinsic bond strength going from typical C–C (4.035 aJ Å^{-2}) to a C=C bond (9.551 aJ Å^{-2}) and it nearly doubles in going from a C=C to a C≡C (17.301 aJ Å^{-2}) bond (Figure 1). In the case of Si–Si single (1.617 aJ Å^{-2}), double (2.127 aJ Å^{-2}), and triple (2.654 aJ Å^{-2}) bonds, we again see a linear trend, though the slope is not as steep (Figure 1, solid line with squares). Both, the double and the triple bond strengths are diminished relatively to their planar or linear arrangement, which are not minima on the energy surface (dotted line, squares in Figure 1). It is noteworthy, that these findings are in contrast to a study by West et al., which concludes that "deformations have only a small influence on the electronic characteristics of the Si=Si bond".[23] Now we turn to C–Si bonds. Only, if a linear HCSiH geometry (second order saddle point) is assumed, is this near linear relationship also present for C–Si single (2.744 aJ Å^{-2}), double (5.402 aJ Å^{-2}), and triple (8.818 aJ Å^{-2}) bonds (dotted line with triangles in Figure 1). However, when the C–Si bond strength of the *trans*-bent minimum geometry (5.464 aJ Å^{-2}) is compared with the strength of a C=Si bond (5.402 aJ Å^{-2}) there is hardly a difference (solid line, triangles in Figure 1). The bending of the H-Si-C angle in the *trans*-bent HSiCH minimum geometry leads to a pronounced weakening (~40%) of the C–Si bond in comparison with a linear HSi≡CH arrangement (second order saddle point). Because the C=Si bond (in contrast to the Si=Si bond) does not suffer from any pyramidalization, there is no significant strengthening of the C–Si bond going from $H_2C{=}SiH_2$ to *trans*-bent HSi≡CH.

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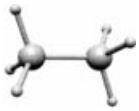
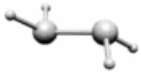
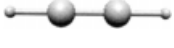
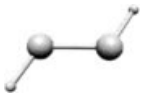
[**] Thanks are given to Prof. Y. Apeloig and Dr. M. Karni for the discussions. I would also like to thank Prof. H. Hopf and Prof. R. Herges for providing me with computing time.

  1433-7851/01/4021-4027 $ 17.50+.50/0

Table 1. Total energy (E_{tot}), bonding distance (r(X–X)), and reciprocal compliance force constants (F(X–X); relaxed force constants) of several systems containing single and multiple C–C, C–Si, and Si–Si bonds by using the B3LYP/6-311++G(d,p) method.

X–X						
C–C	E_{tot}[a]	–79.85657	–78.61553	nsp[i]	–77.35662	nsp
	r(X–X)[b]	1.531	1.329	nsp	1.199	nsp
	F(X–X)[c]	4.035	9.551	nsp	17.301	nsp
Si–Si	E_{tot}[a]	–582.63864	–581.37580[d]	–581.37706	–580.08511[f]	–580.11845
	r(X–X)[b]	2.354	2.139	2.173[e]	1.967	2.106[g]
	F(X–X)[c]	1.617	3.030	2.127	5.039	2.654
C–Si	E_{tot}[a]	–331.25362	–329.98423	nsp	–328.67656[f]	–328.68670
	r(X–X)[b]	1.884	1.708	nsp	1.588	1.649[h]
	F(X–X)[c]	2.744	5.402	nsp	8.818	5.464

[a] Total energies in Hartree. [b] Å. [c] aJ Å^{-2}. The actual unit of a compliance stretching force constants is Å^{2}aJ^{-1}. Nevertheless, the values are given as reciprocal values (relaxed force constants) for comparability reasons. [d] nimag (number of imaginary frequencies) = 1. [e] Out-of-plane angle: 30.81°. [f] nimag (number of imaginary frequencies) = 2. [g] H-Si-Si angle: 124.82°. [h] H-Si-C angle: 120.42°; H-C-Si angle: 154.11°. [i] nsp = no stationary point.

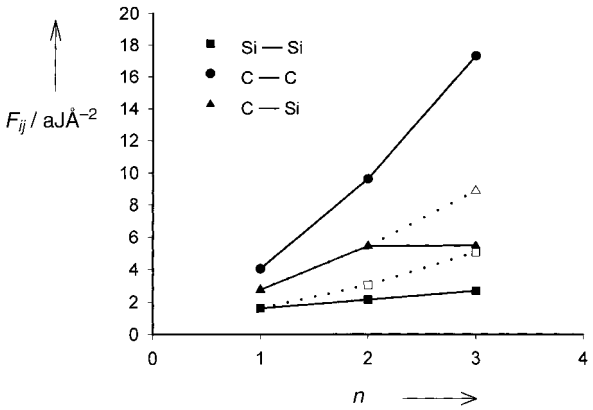


Figure 1. Reciprocal compliance force constants (relaxed force constants) of the five systems (see Table 1) containing single and multiple C–C, C–Si, and Si–Si bonds at the B3LYP/6-311++G(d,p) level of theory as a function of the formal bond order (n). The dotted lines correspond to theoretical ethylene- or acetylene-like geometries for the C–Si and Si–Si series (see text).

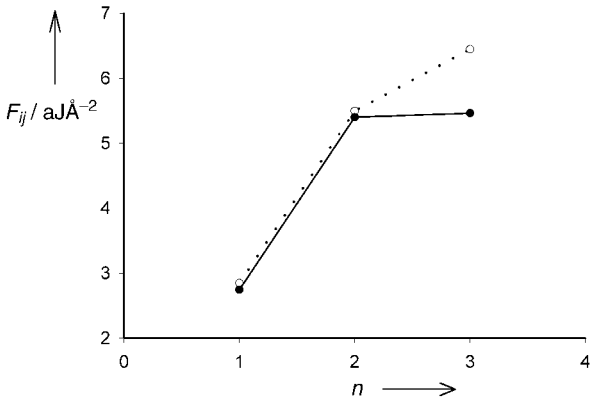
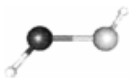


Figure 2. Comparing reciprocal compliance force constants (relaxed force constants) and real space force constants of the C–Si bond in H_3C–SiH_3, H_2C–SiH_2, and HC–SiH at the B3LYP/6-311++G(d,p) level of theory. ○ = real-space force constants, ● = compliance force constants.

Figure 2 compares real-space and compliance force constants. According to real-space force constants, which are used exclusively in the literature, the C–Si bond strength in the *trans*-bent HCSiH minimum geometry reaches 6.447 aJ Å^{-2}. This seems to be in line with an interpretation as a triple bond (C=Si double bond: 5.495 aJ Å^{-2}; real space coordinates). The reason for the discrepancy between real-space force constants and reciprocal compliance force constants is to be found in Table 2. The strong coupling between the C–Si stretching and the H-Si-C angle bending (0.431 aJ Å^{-1} rad^{-1}) excessively raises the numerical values of the diagonal elements (C–Si bonds). Since compliance matrices do not depend on the definition of the coordinate system and there is no such strong coupling in the force fields of H_3C–SiH_3 and H_2C=SiH_2, the difference between real-space force constants and reciprocal compliance force constants is most pronounced in *trans*-bent HCSiH.

To summarize, the major results of this study are as follows: 1) In contrast to real-space force constants, compliance force constants provide a unique description of bond strengths. 2) Pyramidalization (Si–Si)or *trans*-bent distortion (C–Si) of the atoms involved in (Si–Si or C–Si) multiple bonds has a

Table 2. B3LYP/6-311++G(d,p) matrix of force constants of the *trans*-bent HCSiH minimum geometry expressed in internal, real space coordinates.

	Si–H stretch [aJ Å^{-2}]	C–H stretch [aJ Å^{-2}]	C–Si stretch [aJ Å^{-2}]	C-Si-H bend [aJ rad^{-2}]	Si-C-H bend [aJ rad^{-2}]	H-Si-C-H torsion [aJ Å^{-1} rad^{-1}]
Si–H stretch	**2.829**	–0.006	–0.088	0.102	0.034	0.000
C–H stretch	–0.006	**5.861**	–0.131	0.043	0.073	0.000
C–Si stretch	–0.088	–0.131	**6.447**	0.431	0.218	0.000
C-Si-H bend	0.102	0.043	0.431	**0.197**	0.095	0.000
Si-C-H bend	0.034	0.073	0.218	0.095	**0.330**	0.000
H-Si-C-H torsion	0.000	0.000	0.000	0.000	0.000	**0.035**

  1433-7851/01/4021-4028 $ 17.50+.50/0 *Angew. Chem. Int. Ed.* **2001**, *40*, No. 21

strong influence on the bond strength. 3) There is no strengthening of the formal C–Si triple bond in a *trans*-bent HCSiH arrangement relative to a linear C=Si arrangement. Similar to the Ga–Ga multiple bonds, the notion "triple bond" is at least misleading.

Received: May 18, 2001 [Z17136]

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