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[17] Crystal data for **4b**: single crystals were obtained by recrystallization from diethyl ether. The substance ($C_{45}H_{40}NO_7P$ $M_r = 737.75$) crystallized in the monoclinic space group $P2_1$, $a = 15.052(2)$, $b = 10.1503(14)$, $c = 27.203(4)$ Å, $\beta = 95.738°$, $V = 4135.2(10)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.185\ \mathrm{g\,cm^{-3}}$, $F(000) = 1552$, $T = 147(2)$ K. Data collection: Siemens-Smart diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Crystal dimensions: $0.03 \times 0.08 \times 1.55$ mm $3.0° \leq 2\theta \leq 54.4°$; 41782 measured reflections, of which 16113 were independent and were used for the structure refinement of 994 parameters. Empirical absorption correction (SADABS). The structure was solved by direct methods (SHELXS), the hydrogen atoms were placed at idealized positions and refined according to the riding model. Disordered solvent was described with five isotropic C and O atoms. The structure was refined according to the full-matrix least-squares method on F^2 (SHELX-96). At convergence $R1 = 0.0618$ ($I > 2\sigma(I)$) and $wR2 = 0.1036$; min./max. residual electron density: $-0.26/+0.41$ e Å^2., Flack parameter 0.07(9). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147316. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Breakdown of Bond Length-Bond Strength Correlation: A Case Study[**]

Martin Kaupp,* Bernhard Metz, and Hermann Stoll

"Shorter bonds are stronger bonds". This is still the tenet of essentially all interpretations of molecular structure, for example in the analysis of crystallographic data,[1] formalized by a plethora of empirical bond length–bond strength correlations.[2] However, the number of cases where shorter bonds have been found to exhibit smaller bond energies or force constants has increased slowly but steadily during the past decade. Most examples (see, however, refs. [3, 4]) pertain to the effects of substitution by very electronegative groups, such as fluorine. Thus, for example, increased fluorine substitution in the $NH_{3-n}F_n$ and $OH_{2-n}F_n$ series shortens the N–F or O–F bonds but apparently reduces the force constants and dissociation energies.[5] Fluorine substitution in lead(IV) compounds $PbR_{4-n}F_n$ ($R = H, CH_3$) was shown computationally to contract bonds but to facilitate reductive elimination.[6] Similarly, in a number of titanium–phosphane complexes $[Ti(2,4\text{-}C_7H_{11})_2PX_3]$, Ti–P bond lengths *and* dissociation energies were found experimentally to decrease along the series $X = CH_3, OC_2H_5, F$.[7] In contrast, in some polyfluorinated hydrocarbons, C–C bond lengths *and* dissociation energies apparently *increase* with increasing fluorine substitution.[8]

There is clearly a need for systematic studies aimed at elucidating under which circumstances and in which direction deviations from the usual correlations may be expected. Here we report a high-level ab initio case study on the Sn–Sn bond lengths, homolytical dissociation energies, and force constants in distannane, Sn_2H_6, and several of its fluorine-substituted derivatives. This particular choice of model systems has several advantages: 1) a homonuclear bond is studied, and thus polar bonding contributions may be minimized or, for symmetrical substitution, eliminated; 2) in contrast to first-row compounds,[8] complicating effects of negative hyperconjugation are expected to be minor for the properties discussed; 3) the systems are still sufficiently small to obtain definite results from highly accurate coupled-cluster calculations with extended basis sets.[9]

Table 1 provides computed Sn–Sn bond lengths, dissociation energies, and force constants.[9] We will concentrate on the CCSD data, as the available computational resources did not allow CCSD(T) calculations at this basis-set level for all systems (the available data indicate that contributions from triple excitations will not alter the conclusions). Figure 1 shows clearly that bond lengths and dissociation energies do

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Table 1. Sn–Sn bond lengths d, homolytic dissociation energies D_e, and force constants k of $Sn_2H_{6-n}F_n$.[a]

Compound	d [Å]		D_e [kJ mol^{-1}][b]		k [10^{-2} au][c]	
	CCSD	CCSD(T)	CCSD	CCSD(T)	CCSD	CCSD(T)
$H_3Sn{-}SnH_3$	2.759	2.758	248.7 (250.9)	256.4 (258.5)	8.26–8.28	8.13–8.15
$H_2FSn{-}SnFH_2$	2.765	2.767	242.5 (245.4)	249.1 (251.9)	8.34–8.35	8.13–8.14
$HF_2Sn{-}SnF_2H$	2.764	2.767	226.0 (230.0)	231.5 (236.3)	8.47–8.49	8.17–8.18
$F_3Sn{-}SnF_3$	2.758	–	206.8 (208.6)	–	8.59–8.61	–
$F_3Sn{-}SnH_3$	2.767	–	230.1 (235.1)	–	7.91–7.93	–
$H_3Sn{-}SnFH_2$	2.761	2.761	246.9 (249.1)	253.9 (256.0)	8.23–8.24	8.08–8.09

[a] Bond angles, Sn–H, and Sn–F distances, as well as monomer structures, optimized at the MP2 level. [b] Values in parentheses were computed with monomers frozen at the optimized dimer structural parameters. [c] A range of values is given, due to the inherent uncertainties of the fitting procedure.

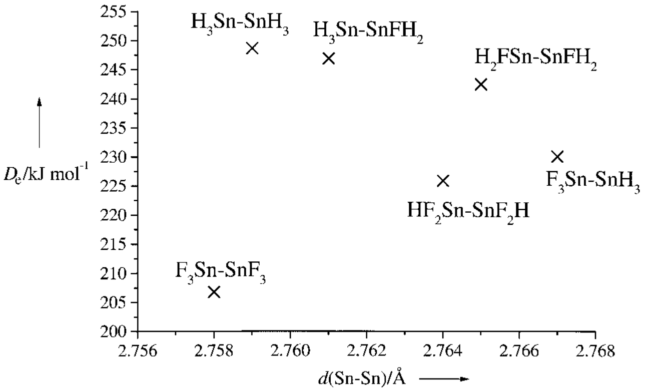

Figure 1. Plot of CCSD dissociation energy D_e versus CCSD bond length d.

not correlate. While the dissociation energies decrease significantly with increasing fluorine substitution, the bond lengths change very little, in a nonmonotonous fashion. Nuclear reorganization energies of the fragments amount to only a few kJ mol^{-1} (cf. Table 1). Electronic reorganization of the monomers is of course substantial. However, it appears that the breakdown of bond length–bond strength correlation in this series of systems is related predominantly to intrinsic properties of the Sn–Sn bond in the dimers (see below).

The range of force constants is significantly smaller (ca. 8%) than that of the dissociation energies (ca. 20%) and becomes even more attenuated at the CCSD(T) level. Figure 2 indicates that, for the symmetrical systems, larger dissociation energies are accompanied by *smaller* force constants. Interestingly, the unsymmetrically substituted $F_3Sn{-}SnH_3$ has by far the lowest force constant, in spite of exhibiting an intermediate dissociation energy. As a consequence of this nonintuitive behavior, no correlation between force constants and bond lengths may be discerned either (Table 1).

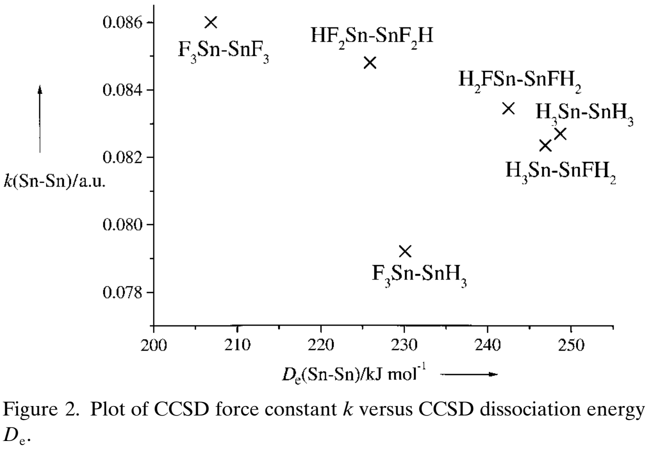

Figure 2. Plot of CCSD force constant k versus CCSD dissociation energy D_e.

What is the reason for the weaker but partly even shorter bonds in the fluorine-substituted species? It has already been shown that fluorine substitution removes electronic charge from the central atom (in this case Sn) and thereby reduces its effective size. At the same time, the relative size of the valence s and p orbitals on Sn is rendered even more disparate than before.[6] As a consequence, "hybridization defects"[10] become more dramatic: the p orbitals are too large to effectively hybridize with the compact s orbitals. Thus, they cannot contribute efficiently to covalent bonding. This weakens the Sn–Sn bonds, but also the Sn–H and Sn–F bonds.[6] Figure 3 shows that, indeed, the relative p character of the Sn hybrids used for the homonuclear bond (and also for the other bonds to Sn; cf. Figure 4) decreases dramatically with increasing charge. "Hybridization-deficient" bonds are weaker, and thus the dissociation energies decrease (Figure 3). However, the weaker bonds do not become longer, as the effect is compensated (or partly even overcompensated) by the reduced size, and the related larger net s character, of the Sn atom. Weakening of the bonds would also be expected to reduce the force constants. However, the reduced atom size may again contribute in the opposite direction.

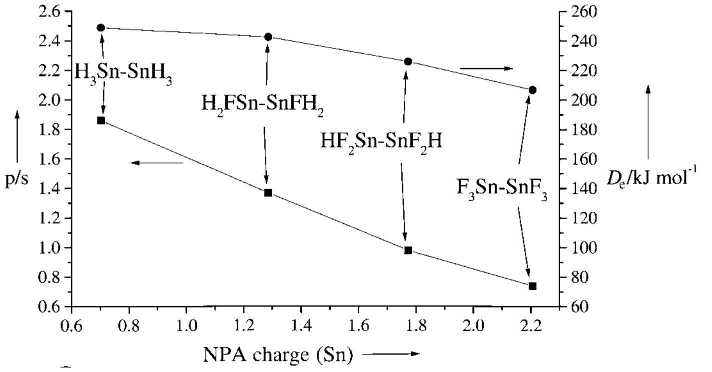

Figure 3. Dependence of p/s hybridization ratios (■) of the Sn–Sn bonding natural localized molecular orbitals (NLMO), and of the dissociation energies (●) on the natural population analysis (NPA) charges for the symmetrically substituted distannanes. Bonding analyses for HF wavefunctions at the MP2-optimized structures; CCSD dissociation energies taken from Table 1.

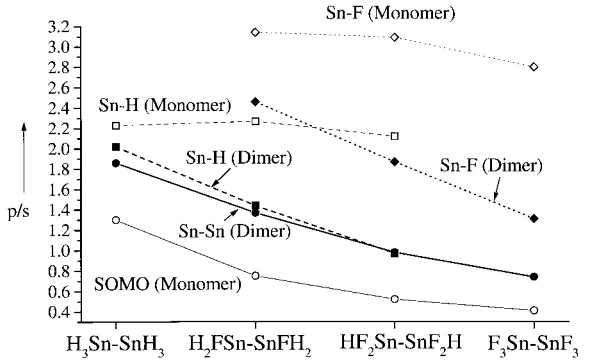

Figure 4. Changes in p/s hybridization ratios of various NLMO upon Sn–Sn bond dissociation. Bonding analyses for HF wavefunctions at the MP2-optimized structures. Average of α and β NLMO hybridization for the monomers.

Figure 4 shows the p/s hybridization ratio of the relevant localized MOs. In the dimers, hybridization defects increase dramatically with increasing fluorine substitution, not only for the Sn–Sn bonds (cf. also Figure 3), but also for the Sn–H and Sn–F bonds. In the monomers, the s character may concentrate more in the singly occupied molecular orbital (SOMO). The effect of fluorine substitution on Sn–H and Sn–F bonding (cf. corresponding NLMO hybridization) is therefore much less pronounced than in the dimers. As the hybridization defects are directly related to the bond strength, it is clear that changes in the bonding of the dimers are largely responsible for the observed trend in the dissociation energies. Our bonding analyses confirm furthermore, that delocalization effects are of only minor importance. The distannane series provides thus a particularly clearcut case in which hybridization defects are directly responsible for the observed lack of correlation between bond lengths, force constants, and dissociation energies.

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[1] The assumed correlation with bond strength is one of the primary reasons for measuring accurate interatomic distances. The implicit assumption of bond length–bond strength correlation may be found in essentially any chemistry textbook and in an uncountable number of scientific works.

[2] Two examples: M. L. Huggins, *J. Am. Chem. Soc.* **1953**, *75*, 4126; P. Politzer, S. Ranganathan, *Chem. Phys. Lett.* **1986**, *124*, 527, and references therein. Similarly, bond lengths are frequently correlated with force constants. See, for example: R. M. Badger, *J. Chem. Phys.* **1934**, *2*, 710; W. Gordy, *J. Chem. Phys.* **1946**, *14*, 305.

[3] It has long been known that monoionization of the alkali-dimers increases the bond lengths *and* binding energies; see, for example: W. Müller, W. Meyer, *J. Chem. Phys.* **1984**, *80*, 3311, and references therein.

[4] The (formal) double bonds in disilenes are shorter but weaker than the single bonds in the corresponding disilanes. The same holds for the heavier homologues of silicon; see, for example: H. Jacobsen, T. Ziegler, *J. Am. Chem. Soc.* **1994**, *116*, 3667, and references therein.

[5] See, for example: D. Christen, O. D. Gupta, J. Kadel, R. L. Kirchmeier, H. G. Mack, H. Oberhammer, J. M. Shreeve, *J. Am. Chem. Soc.* **1991**, *113*, 9131; P. Politzer, D. Habibollahzadeh, *J. Chem. Phys.* **1993**, *98*, 7659.

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[8] See, for example: J. M. Martell, R. J. Boyd, Z. Shi, *J. Phys. Chem.* **1993**, *97*, 7208; B. E. Smart in *Molecular Structures and Energetics, Vol. 3* (Eds.: J. F. Liebmann, A. Greenberg), Verlag Chemie, Weinheim, **1986**, pp. 141–189, and references therein.

[9] a) We used a modern quasirelativistic small-core (22-valence-electron) pseudopotential and extended (12s12p9d3f)/[6s6p4d3f] valence basis for Sn[9b] together with extended (11s6p2d)/[5s4p2d] and (6s3p1d)/[4s3p1d] all-electron basis sets for F and H, respectively.[9c] The structures of monomers and dimers were first fully optimized at the MP2 level of theory with the Gaussian98 program.[9d] Subsequently, the Sn–Sn distances were optimized numerically at the coupled-cluster singles–doubles (CCSD) and partly at the CCSD(T) levels (i.e. with a perturbational treatment of triple excitations), keeping the other degrees of freedom (and the monomer structures) at their MP2 values (five equidistant points in intervals of ca. 0.02–0.04 Å around the minimum distance were fitted to a polynomial, to determine the minimum and the force constant). The MOLPRO program[9e] was employed. Open-shell fragments were calculated at RCCSD, RCCSD(T), and UMP2 levels. Natural population and hybridization analyses (A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899) used the MP2-optimized structures, the Hartree–Fock (HF) densities, and the built-in subroutines of the Gaussian98 program. We have restricted our study to ethane-like staggered structures. A detailed exploration of the potential energy surface in these systems is beyond the scope of the present work. b) B. Metz, H. Stoll, M. Dolg, *J. Chem. Phys.* **2000**, *113*, 2563; c) These basis sets were derived from the aug-cc-pVTZ basis (T. H. Dunning, Jr., *J. Chem. Phys.* **1989**, *90*, 1007; R. A. Kendall, T. H. Dunning, Jr., R. J. Harrison, *J. Chem. Phys.* **1992**, *96*, 6796), but truncated in the polarization space. d) Gaussian98, Revision A.7, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Lui, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**; e) MOLPRO is a package of ab initio programs written by H.-J. Werner and P. J. Knowles, with contributions from R. D. Amos, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, T. Leininger, R. Lindh, A. W. Lloyd, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, K. Peterson, R. Pitzer, P. Pulay, G. Rauhut, M. Schuetz, H. Stoll, A. J. Stone, and T. Thorsteinsson.

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