Bond Moments, Molecular Moments, Electronegativity, and the Dipole Moment of Methylsilane

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Abstract: Contrary to statements in the literature, the dipole moment of methylsilane is not expected to coincide with the bond moment, Si–C+→. Various methods of estimating the total molecular moment predict the direction to be CH_3SiH_3+→ in agreement with experiment. One method accurately reproduces (0.7 D) the experimental value (0.73 D). The importance of the large Si–H+→ moment is shown by all methods. Further, the lower the assumed electronegativity of silicon, the greater is the CH_3SiH_3+→ moment in contrast to a naive prediction based only on the Si–C+→ bond moment. Finally, methylsilane provides another example of difficulties in assigning meaningful atomic charges from populational analysis.

Although the absolute value of the electric dipole moment of methylsilane has long been known accurately (0.73 D),[2–4] the direction of the moment has only recently been determined, first by measurement of the molecular Zeeman effect[5] and confirmed by a complete *ab initio* calculation.[6] Both of the latter studies indicate that the direction of the dipole is CH_3SiH_3 +→. Contrary to statements in the literature,[6] this result is not in contradiction to expectations based upon electronegativity considerations. It is the purpose of this paper to illustrate some misconceptions with regard to electronegativity theory and to illustrate that simple methods allow accurate predictions of the magnitude and direction of molecular dipole moments. A further, unexpected result of the present work is that the molecular moment of a molecule such as methylsilane varies with the assumed electronegativity of silicon in a way which is exactly opposite to what one might have assumed from a naive model.

I. The Relation of the C–Si Bond Moment to the Total Molecular Moment. It is obvious that any reasonable assignment of electronegativity values to carbon and silicon will result in a Si–C+→ bond moment. To assume that the molecular moment will be in the same direction is to ignore completely the three H–C+→ bond moments and the three Si–H+→ bond moments, all of which oppose the moment of the central bond. Further, a corollary of the electroneutrality principle[7] suggests that the charge separation in the C–H and Si–H bonds will be greater than that based on electronegativities alone: *Molecules are stabilized if charges are delocalized to peripheral atoms.* Perhaps a more explicit statement of the general principle would be that adjacent similar charges destabilize a molecule but adjacent (or alternating) opposite charges stabilize molecules through their contribution to the Madelung ("electrostatic") energy. To the extent that such accentuations of alternating charge do not lessen the overlap ("covalent") energy, they will be favored[8] and the charges, $H^{\delta+}C^{\delta-}$-$Si^{\delta+}H^{\delta-}$, enhanced. Thus we may expect the hydrogen atoms attached to carbon to be more positive than otherwise and the hydrogen atoms attached to silicon to be more negative. Thus the bond moments involving hydrogen which oppose the central bond moment will be especially large, and qualitatively we may expect them to be the dominant dipoles.[5] We discuss the bond moments quantitatively in part II. We might attempt a calculation involving the ionic character relationship of Pauling[9] or Hannay and Smyth,[10] but improved methods of estimating charge distribution have been developed and will be discussed in part III. *The essential point is that predicting a molecular moment on the basis of a single bond moment to the complete neglect of six others is not valid.*

II. The Use of Empirical Bond Moments. It has long been established that the dipole moment of polyatomic molecules (μ) can be considered as the resultant of the vectorial combination of the moments belonging to the individual bonds, or $\mu = \Sigma_{i=1}{}^{n}\mu_i$. Thus, if the geometry of the molecule is known, calculation of the dipole moment is carried out by vectorial combination of the bond moments.[11]

The above equation may be used not only to calculate the dipole moment of a molecule from the moments of the individual bonds but also to solve the inverse problem, *i.e.*, to resolve the total moment into its components. If only one bond is considered at a time, the number of terms in the equation is limited to two and the case is simplified to the combination of two vectors directed relatively to one another at an angle ϕ.

$$\mu = (\mu_1{}^2 + \mu_2{}^2 + 2\mu_1\mu_2 \cos \phi)^{1/2}$$

Therefore, upon knowing the geometry and two of the three moments, it is easy to calculate the third moment. In a species such as CH_3SiH_3, in which the bonding is

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[3] R. W. Kilb and L. Pierce, *J. Chem. Phys.*, 27, 108 (1957).

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[5] R. L. Shoemaker and W. H. Flygare, *J. Amer. Chem. Soc.*, **94**, 684 (1972).

[6] D. H. Liskow and H. F. Schaefer III, *ibid.*, **94**, 6641 (1972).

[7] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 172–173.

[8] (a) R. S. Evans and J. E. Huheey, *J. Inorg. Nucl. Chem.*, **32**, 777 (1970); (b) R. S. Evans, M.S. Thesis, University of Maryland, College Park, Maryland, 1971; (c) R. S. Evans and J. E. Huheey, submitted for publication.

[9] Reference 7, p 98.

[10] N. B. Hannay and C. P. Smyth, *J. Amer. Chem. Soc.*, **68**, 171 (1946).

[11] V. I. Minkin, O. A. Osipov, and Yu. A. Zhdanov, "Dipole Moments in Organic Chemistry," Plenum Press, New York, N. Y., 1970, pp 79ff.

essentially tetrahedral,[3] each M–H bond has a component $\mu_{M-H} \cos (180 - 109.5°) = \mu_{M-H}/3$ directed along the C–Si axis. Consequently, the total moment contributed by the three M–H bonds acting as a group is μ_{M-H}, which is directed along the C–Si axis. Therefore, the entire CH_3SiH_3 molecule can be represented as the vector sum of three bond dipoles which are linearly arranged, *i.e.*, H → C ← Si → H.

The Altshuler and Rosenbloom[12] Si–H+→ (1.0 D), Si–C+→ (0.6 D), and Si–alkyl+→ (0.2 D) bond moments, which Eaborn[13] assigns for organosilicon compounds, have been successfully used to calculate the molecular moments of a number of organosilicon species.[14] The magnitude and orientation of the C–H bond dipole have been the subject of some discussion,[15,16] though we know of no one who has seriously suggested that carbon is less electronegative than hydrogen. The moment has recently been calculated by Rothenberg[17] to be H–C+→ = 0.3 D. Therefore, the calculated molecular moment for CH_3SiH_3 would be +0.3 D (H–C+→) − 0.6 D (C–Si←+) + 1.0 D (Si–H+→) = 0.7 D, a value which agrees well with the experimental value of 0.73 D,[2-4] and which indicates that the negative end of the *molecular* dipole is oriented in the opposite direction from the C–Si *bond* dipole. The orientation of the molecular dipole, therefore, is actually determined by the not at all insignificant M–H bond moments and in particular by the magnitude and orientation of the Si–H bond moment.

Although estimates of the electronegativity of silicon have ranged from 1.90 to 2.30 (see section III), the Si–H bond moment is certainly (a) substantially larger than expected from the electronegativity difference between the atoms and (b) oriented with the silicon being the positive end of the dipole. The rather large moment can be rationalized on various grounds such as the electroneutrality principle (section I) or hyperconjugative structures ($H^+CH_2{=}Si^-H_3$), and it should be noted that even larger Si–H bond moments have been previously suggested.[18]

The question of the electronegativity of silicon in a hyperconjugative structure is similar to the question of the electronegativity of silicon when d orbital mixing is included in the valence state (section III). In the hyperconjugative structure the electronic environment about the silicon is augmented; thus, when in such a structure, the silicon would experience a decrease in its "effective electronegativity" exhibited toward other species. Alternatively, one could regard this structure as representing d orbital mixing and consequent lowering of the electronegativity of the silicon (section III). In either case, the Si–H+→ bond dipole would be larger than might otherwise be expected.

The assignment of the orientation of the Si–H bond moment is consistent with direct chemical evidence. The direction of addition of Si–H compounds to olefinic double bonds, the fact that on hydrolysis of Si–H containing compounds the hydrogen leaves the silicon as a hydride anion, the reaction of triorgano-substituted silanes with alkyl lithium compounds, the failure of experiments aimed at effecting the interchange of silane hydrogen for deuterium in EtOD, D_2O, and Et_2ND, and the success in effecting isotope interchange between deuteriosilane and lithium aluminum hydride have all been interpreted[19] as evidence for Si–H+→ polarization of the bond, and similar chemical evidence supports the orientation of the other bond.

Table I. Calculated Atomic Charges

Atom	χ_{Si} 1.90	χ_{Si} 2.25
H_C	+0.05	+0.15
C	−0.19	−0.37
Si	+0.02	+0.18
H_{Si}	+0.01	−0.09

Thus, it is readily apparent from an examination of the constituent bond moments that prediction of the orientation of the molecular moment of CH_3SiH_3 on the basis of the relative electronegativities of carbon and silicon gives an incomplete and erroneous picture. M–H bond moments must also be considered.

III. The Use of Mulliken–Jaffé Electronegativities. Mulliken–Jaffé electronegativities[20] have shown two advantages over other systems: (1) specificity with respect to orbital hybridization; (2) ability to adjust for partial charges on the atoms. A method has been proposed[8] for the calculation of total bond energies as sums of: (1) electronegativity energy; (2) Madelung ("ionic") energy; (3) covalent bond energy.[21] Although the method was developed for estimation of bond energies, partial charges on the constituent atoms are estimated as intermediate results of the calculation. These charges have been shown[22] to correlate well with those obtained from more rigorous quantum mechanical calculations.[23]

We have used this method to calculate atomic point charges for methylsilane. The results are listed in Table I. The only difficulty presented by the present calculation is the appropriate choice of electronegativity value for silicon, those of the other atoms in the molecule being well defined. The uncertainty in silicon arises from consideration of the amount of d orbital mixing in the valence state. This is in many ways comparable to the inclusion, or not, of d orbital wave functions in the basis set of an *ab initio* calculation.[6,24] Estimates of the electronegativity of silicon range from

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(12) A. P. Altshuler and L. Rosenbloom, *J. Amer. Chem. Soc.*, 77, 272 (1955).

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(14) J. M. Bellama and A. G. MacDiarmid, *J. Organometal. Chem.*, 24, 91 (1970); J. M. Bellama, submitted for publication.

(15) C. A. Coulson, "Valence," Oxford University Press, London, 1952, p 208.

(16) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill, New York, N. Y., 1955, pp 239–245.

(17) S. Rothenberg, *J. Amer. Chem. Soc.*, **93**, 68 (1971).

(18) H. O. Spauschus, A. P. Mills, J. M. Scott, and C. A. MacKenzie, *ibid.*, 72, 1377 (1950).

(19) Reference 13, Chapter 3; V. Bažant, V. Chvalovský, and J. Rathouský, "Organosilicon Compounds," Academic Press, New York, N. Y., 1965, Chapter 7.

(20) R. S. Mulliken, *J. Chem. Phys.*, 2, 782 (1934); 3, 573 (1935); J. Hinze and H. H. Jaffé, *J. Amer. Chem. Soc.*, 84, 540 (1962); J. Hinze, M. A. Whitehead, and H. H. Jaffé, *ibid.*, **85**, 148 (1963); J. Hinze and H. H. Jaffé, *J. Phys. Chem.*, 67, 1501 (1963). For an extensive list of Mulliken–Jaffé values, see J. E. Huheey, "Inorganic Chemistry: Principles of Structure and Reactivity," Harper and Row, New York, N. Y., 1972, pp 160–161.

(21) See ref 8a and 8b for the details of the calculation.

(22) R. S. Evans and J. E. Huheey, *Chem. Phys. Lett.*, 19, 114 (1973).

(23) P. Politzer and R. R. Harris, *J. Amer. Chem. Soc.*, 92, 6411 (1970); P. Politzer and R. S. Mulliken, *J. Chem. Phys.*, **55**, 5135 (1971); P. Politzer, *Theor. Chim. Acta*, **23**, 203 (1971); P. Politzer and P. H. Reggio, *J. Amer. Chem. Soc.*, **94**, 8308 (1972).

(24) See K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969), and references therein.

about 1.90[25] to about 2.30.[26] The former value has been determined from thermochemical data by the method of Pauling[27] and has been shown[26] to be artificially low if silicon forms p → d π bonds with oxygen, fluorine, etc., as is almost certain. The upper limit comes from Mulliken–Jaffé values for the sp^3 (te) valence state. Since d orbitals lie at higher energies than s and p orbitals, their inclusion in the hybridization will result in lower electronegativity values.[28] The only direct evidence for a silicon electronegativity higher than that of hydrogen is the work of Quane[26] based on a Pauling-type calculation from bond energies of silanes in which π bonding is impossible. Unfortunately, uncertainties in bond energies and the limited number of compounds available place rather wide error limits on his estimates.

We have performed calculations[29] using electronegativity values of both 1.90 Pauling (= 6.26 V, Mulliken) and 2.25 Pauling (= 7.30 V, Mulliken). Our results range from 0.2, Si–C+→ (χ = 2.25), to 2.2 D, C–Si+→ (χ = 1.90). The interesting result of the calculations is to indicate that *the lower the electronegativity of silicon the greater is the total* CH_3SiH_3 *moment*, in complete contradiction to the prediction based on the Si–C+→ moment alone, but in agreement with the empirical bond moment work which gives the Si–H+→ moment the dominant effect in the total molecular moment. The empirically determined bond moments have "built-in" accommodations for the greater polarizability of silicon, the longer Si–H bond length, the electroneutrality principle, and similar factors treated implicitly by the Mulliken–Jaffé electronegativity treatment.

Finally, we would call attention to the statement of Liskow and Schaefer[6] that although the expectation value of the dipole moment operator clearly indicates the molecular moment is in the direction CH_3SiH_3+→, point charges obtained from their Mulliken populational analysis yield a moment SiH_3CH_3+→. This is yet another example indicating that populational analysis fails to yield values corresponding to the chemist's concept of partial charge and should either be used cautiously or replaced by alternate methods.[22,23]

(25) A. L. Allred, *J. Inorg. Nucl. Chem.*, 17, 215 (1961).

(26) D. Quane, *ibid.*, **33**, 2722 (1971).

(27) Reference 7, Chapter 3.

(28) For example, see J. E. Huheey and J. C. Watts, *Inorg. Chem.*, 10, 1553 (1971).

(29) We calculated the molecular moment using a point-charge approximation. We should like to thank a referee for reminding us to note that this approximation is valid only, as is the case with CH_3-SiH_3, where lone pair moments can be ignored.[30]

(30) See F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Wiley, New York, N. Y., 1972, pp 120–122; J. E. Huheey, "Inorganic Chemistry: Principles of Structure and Reactivity," Harper and Row, New York, N. Y., 1972, pp 168–170.

Ab Initio Self-Consistent Field and Configuration Interaction Study of Beryllium Borohydride

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Abstract: Optimized geometries and relative energies are reported for many possible structures of beryllium borohydride. These calculations are at the *ab initio* minimum basis set self-consistent field level of approximation, with near optimum exponents. Configuration interaction calculations on the bound conformers with all valence shell single and double excitations included suggest that two or three conformers may coexist in the gas phase. This result is also based on the available experimental evidence. The previous experimental work on the gas phase is discussed in view of the above possibility.

The structure of gas-phase beryllium borohydride is currently one of the most interesting and frustrating problems in structural inorganic chemistry. To date at least six unique structures have been proposed, all of which have had some kind of experimental "verification." Although beryllium borohydride has been the subject of a few theoretical studies,[1,2] no extensive geometry optimizations using accurate molecular orbital techniques have yet been reported. In this paper we present a series of *ab initio* self-consistent field (SCF) and configuration interaction (CI) calculations on many possible conformers of this molecule and we report relative energies and optimized geometries for these conformers. By comparing our theoretical results with the available experimental data, we arrive at some tentative conclusions concerning the structure of this molecule in the gas phase.

Beryllium borohydride was first synthesized[3] by Burg and Schlesinger *via* the reactions

$$Be(CH_3)_2 \xrightarrow{B_2H_6} CH_3BeBH_4 \xrightarrow{B_2H_6} Be(BH_4)_2$$

They reported a vapor pressure of about 6 mm at room temperature and vapor density measurements which suggested that the gas phase is monomeric. Later, the monomeric nature of the gas phase was confirmed.[4] Remarkably, they also suggested that the crystalline phase might be polymeric. Our single-crystal X-ray

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(4) J. W. Nibler, *ibid.*, 94, 3349 (1972).