Calculation of NMR Chemical Shifts — The Third Dimension of Quantum Chemistry

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Dedicated to Professor John A. Pople in recognition of his many excellent contributions to Quantum Chemistry. Both as a teacher and a scientific leader, he has strongly influenced our work over the years.

Abstract. NMR chemical shift calculations provide the basis for an intensive collaboration between quantum chemists and experimentalists. Calculated shift data can be used to describe the magnetic properties of a molecule, to identify unknown compounds by comparison of experimental and theoretical shift values, to determine equilibrium geometries, to investigate conformational changes, to elucidate the mechanism of molecular rearrangements, to determine solvent effects on NMR data, to identify complexation or coordination of soluted molecules by solvent molecules, to detect electronic structure changes caused by the medium, and to describe chemical bonding. This is demonstrated by three examples, namely the determination of the equilibrium structure of the homotropylium cation, the description of BH_3NH_3 in solution or condensed phases, and the investigation of stannyl cation complexes in solution. IGLO calculations of ^{13}C, ^{11}B, ^{15}N, and ^{119}Sn chemical shifts with DZ+P or TZ+P basis sets lead to the following results: (1) The homotropylium cation possesses an equilibrium 1,7 distance of 2 Å that is indicative of strong through-space interactions and, as a consequence, homoaromatic character. (2) In solution, the charge transfer from NH_3 to BH_3 is increased, which leads to a decrease of the BN bond length, an increase of the dipole moment, and a shielding of both the B and the N nucleus. The experimental $\delta(^{11}B)$ and $\delta(^{15}N)$ values can be reproduced when the geometry effect and the direct solvent effect are included in the shift calculations. (3) Stannyl cations form strongly-bounded coordination complexes with solvent molecules (binding energy: ≥ 50 kcal/mol) that make the cation properties, in particular $\delta(^{119}Sn)$ values, similar to those of covalently-bounded stannyl compounds. An experimental detection of stannyl cations in solution by NMR spectroscopy should only be possible by extensive solvent variations.

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INTRODUCTION

Quantum chemistry has always been judged on the basis of what solutions it can offer to the problems of general chemistry. Therefore, it is not astonishing that the work of the pioneers in quantum chemistry between 1925 and 1950, although well-appreciated among the experts, had little or no impact on general chemistry. The beginning of

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modern quantum chemistry is generally dated from the early fifties for three reasons: First, Boys introduced gaussian-type functions for electronic structure calculations in 1950.[1] Second, in 1951 Roothaan and Hall independently published their classic papers on the LCAO-SCF approach.[2] And finally, one realized in these years, probably for the first time, the importance of electronic computers as valuable tools in quantum chemistry, which was emphasized at the first American conference on theoretical chemistry at Shelter Island.[3]

One can look upon the past four decades of modern quantum chemistry in several ways; for example, on the basis of how its tools were developed or on the basis of the impact quantum chemistry had on general chemistry. In the first two decades quantum chemists essentially learned how to use computers and how to set up programs that could carry out Hartree–Fock (HF) and some simple correlation-corrected calculations. Programs such as POLYATOM,[4] IBMOL,[5] MOLE,[6] and ALCHEMY,[7] characterized a development that culminated in the publication of general purpose ab initio programs for nonspecialists. The best known among the latter is John Pople's GAUSSIAN program package[8] that was started in the late sixties and still continues with new updates and program improvements. In the last two decades ab initio programs such as MOLECULE/MOLCAS,[9] HONDO,[10] GAMESS,[11] and CADPAC,[12] emerged. These, together with the GAUSSIAN package, tremendously pushed forward the use of quantum chemical methods in chemistry.

It is fair to say that only after 1970 did quantum chemistry have a steadily increasing impact on chemistry. Three factors influenced this development: (a) a rapid development of new methods, algorithms, and techniques for electronic structure calculations; (b) the development of sophisticated ab initio programs that can be used for routine as well as expert calculations of many molecular properties; and (c) the availability of modern supercomputers with steadily increasing computing power.

Although any classification is certainly very subjective, two major phases in the development of ab initio methods should be stressed here. The seventies were the decade of correlation-corrected methods that made it possible to accurately calculate energy differences such as reaction energies, activation energies, and ionization potentials. Many of the method developments of the seventies were already started in the sixties or even in the fifties. For example, the Møller–Plesset (MP) perturbation methods of Pople and coworkers[13] were based on developments in many-body perturbation theory that had already taken place in theoretical physics in the fifties and were introduced into quantum chemistry by Kelly in 1963.[14]

Method development in the seventies focused on how to get better energies, while in the eighties the emphasis was more on how to calculate molecular properties via analytical energy derivatives. Starting in the late seventies analytical energy gradients for the calculation of molecular geometries became available for most ab initio methods.[15] This development was already initiated in the late sixties when Pulay[16] and Gerratt and Mills[17] published their landmark papers on analytical gradient methods and the coupled-perturbed HF approach.

Certainly, the calculation of molecular geometries was the second most important contribution quantum chemistry has given to chemistry. For small and medium-sized molecules, the ab inito calculation of geometry and conformation is a reliable and economic alternative to X-ray, electron diffraction, microwave, or other structure determinations. In the last decade, more structural data have been determined by ab initio calculations than have been measured experimentally. The calculation of accurate geometries and energies, in particular, for short-lived reaction intermediates, compounds not synthesized, or transition states of reactions, had a large impact on general chemistry. This continues and is obvious from almost any issue of a chemical journal.

Where analytical energy derivative methods were implemented into general purpose ab initio programs, the calculation of molecular properties for both HF and correlation-corrected methods became routine. Although the computation of electrical moments, vibrational frequencies, infrared intensities, zero-point energies, entropies, etc. clearly enhanced the importance of quantum chemistry, none of these possibilities turned out to be as important for general chemistry as the calculation of molecular energies and geometries. Actually, the next big step forward in this regard was only reached when methods for the routine calculation of NMR parameters became available.

CALCULATION OF NMR CHEMICAL SHIFTS

If a chemist synthesizes a new compound, one of the first investigations to be carried out will be the measurement of the NMR spectrum. NMR spectral data provide in a relatively easy way useful information on the identity and structure of the new compound. There exist in most cases sufficient reference data that provide the basis for a qualitative structure determination or verification. Only after these first NMR investigations have been done is it normally decided whether a direct structure determination with other methods such as X-ray, electron diffraction, or microwave spectroscopy should be performed or whether other investigations for a spectroscopic, thermochemical, etc. characterization are desirable. However, all these

additional investigations require in most cases much more time and effort than the NMR measurements and, therefore, they are only done for interesting compounds. This is why for many compounds there is just an NMR spectrum available, which does not provide all the information and insights an experimentalist wants to have on a new compound.

Therefore, an experimentalist expects additional information from quantum chemical calculations that use the existing NMR data in some way. This is best done if for some appropriate trial structure NMR chemical shifts are calculated and compared with the existing NMR data. If the two sets of NMR data agree, the compound in question must possess the molecular structure used in the calculation and, therefore, is clearly identified. All the molecular properties that come out of the calculation can be assigned to the new compound and, accordingly, the experimentalist gets a detailed description of this compound. If the quantum chemical description of the molecule can be obtained in a faster and more economical way than additional experimental investigations, an ideal basis for the collaboration between experimentalists and quantum chemists will exist.

For a long time, this information could not be provided by quantum chemists since routine calculations of NMR parameters with sufficient accuracy were not possible. There were several approaches to calculating NMR chemical shift data, of which the best known is probably the method based on *gauge independent atomic orbitals* (GIAOs),[18] originally suggested by London.[19] GIAOs were used at the semiempirical level by Pople[20] and later at the ab initio level by Ditchfield[21] and other authors.[22] However, the computer-time-consuming integral evaluation over GIAOs prevented applications to larger molecules. Computer timings only improved when Pulay and coworkers[23] improved the GIAO method by implementing modern techniques for integral and integral-derivative evaluation. However, this development took place years after the routine calculation of NMR chemical shifts at the ab initio level had been mastered by Kutzelnigg and Schindler.[24] These authors solved the gauge problem inherent in all calculations of magnetic properties with the help of localized MOs rather than GIAOs. Accordingly, they coined their method *individual gauge for localized orbitals* (IGLO).[24,25]

The work by Kutzelnigg and Schindler triggered further developments in the field of NMR chemical shift calculations. Beside the IGLO program, several other computer programs are presently available for routine calculations of magnetic properties of molecules: (1) The LORG (localized orbital/local origin) method by Hansen and Bouman;[26] (2) GIAO-HF in the version of Pulay and coworkers;[23] (3) GIAO-MBPT2 by Gauss to calculate

correlation-corrected NMR chemical shifts with second-order many-body perturbation theory;[27] (4) MC-IGLO by Kutzelnigg et al. for problems that require an MCSCF wave function.[28] In addition, other methods to obtain correlation-corrected NMR chemical shift values have been described in the literature.[29]

The use of ab initio methods for the calculation of NMR chemical shifts was pushed forward by Schleyer and his coworkers who, either in collaboration with the Kutzelnigg group or other groups, published more than 40 papers in the last five years on the investigation of NMR chemical shifts. The success of this research tremendously increased the acceptance of ab initio results in general, and ab initio NMR results in particular, among experimental chemists.

Calculations with IGLO, LORG, or GIAO have led to a wealth of NMR chemical shift data and to a new dimension in the cooperation between quantum chemists and experimentalists, as is amply documented in the literature.[25-30] Besides energies and geometries, quantum chemists can nowadays offer experimentalists detailed NMR chemical shift data which provide a direct link between theory and experiment so that calculated energies and geometries become more meaningful for the experimentalist. NMR chemical shift calculations have been used not only to describe the magnetic properties of molecules, but also to identify unknown compounds by comparison of experimental and theoretical shift values, to determine equilibrium geometries, to investigate conformational changes, to elucidate the mechanism of molecular rearrangements, to determine solvent effects on NMR data, to identify complexation or coordination of soluted molecules by solvent molecules, to detect electronic structure changes caused by the medium, and to describe chemical bonding — to mention just some of the many possibilities that have opened to quantum chemists.[25-32.]

In the following, three examples will be discussed that demonstrate the usefulness and applicability of NMR chemical shift calculations. These examples deal with (a) the determination of the equilibrium structure of the homotropylium cation, (b) the description of BH_3NH_3 in solution, and (c) the identification and investigation of organotin cations in solution.

THE USE OF NMR CHEMICAL SHIFTS FOR STRUCTURE DETERMINATION — THE HOMOTROPYLIUM CATION

The determination of NMR chemical shifts either by IGLO, LORG, or GIAO turns out to be very sensitive with regard to the geometry used.[30-34] Experimental geometries are not that useful in this connection since

very often they are not accurate enough, represent different geometries (r_z, r_s, r_o, r_a, r_g, r_v, etc.), or suffer from intermolecular interactions in condensed phases. Ab initio geometries provide a consistent description of molecules that does not suffer from the ambiguities of experimental geometries. Many calculations have shown that reasonable NMR chemical shifts are obtained if the geometry of the molecule in question has been optimized at a correlation-corrected level of theory such as second-order MP (MP2) using DZ, DZ+P, or better basis sets. Since the calculated NMR chemical shifts clearly depend on the geometry, an agreement between experimental and theoretical shifts not only provides a clear identification, but also a geometry determination of the molecule in question. On the other hand, if theoretical and experimental shifts differ considerably, other possible geometries or structures have to be tested.

Schleyer was the first who fully realized the sensitivity of calculated NMR chemical shifts with regard to molecular geometry, and he used this for ab initio/IGLO/NMR-based structural determinations in many cases including carbocations, boron, and organolithium compounds.[30,31] A recent assessment of this approach suggests that "structural assignments based on the ab initio/IGLO/NMR method are quickly approaching a confidence level that rivals modern-day X-ray diffraction determinations of molecular structures."[32] To illustrate this method we describe in the following our investigation of the equilibrium structure of the homotropylium cation (I).

HF/STO-3G, as well as semiempirical calculations, predict for I the bicyclic structure Ia while HF/6-31G* calculations suggest the open structure Ic.[33,34] Experimental NMR chemical shift data, on the other hand, are in line with a nonclassical (homoaromatic) structure Ib with a delocalized 6π system.[35] X-ray structure determination of substituted homotropylium cations makes the situation even more confusing.[36,37] For example, 2-hydroxy-I was found to possess a relatively short 1,7 distance, in line with the bicyclic structure Ia,[36] while 1-ethoxy-I has a 1,7 distance of 2.4 Å, in line with the open structure Ic.[37]

Ia   Ib   Ic
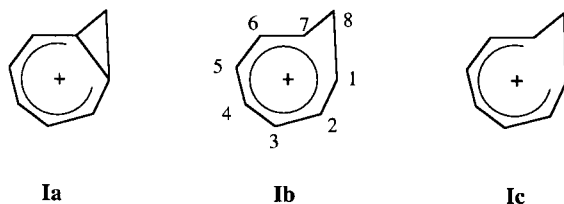
The normal way of solving such a problem is to apply correlation-corrected methods for an accurate geometry determination. For example, MP2,[13] which covers important pair correlation effects, can give a better account of critical geometry parameters than HF or semiempirical
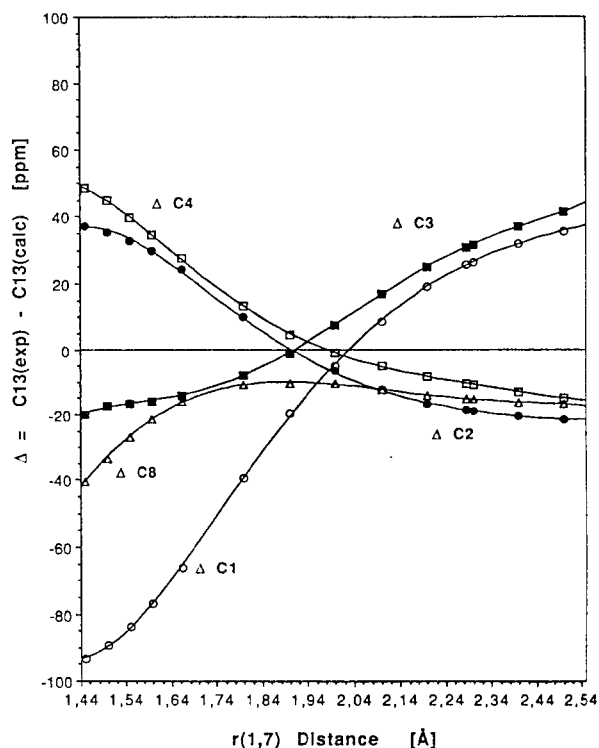

Fig. 1. Difference (Δ) between experimental and IGLO/6-31G(d)//HF/6-31G(d) ^{13}C NMR chemical shifts of the homotropylium cation as a function of the 1,7 distance. The zero line ($\Delta = 0$) indicates that theoretical and experimental shift values are identical.

methods. However, MP2 is known to overestimate the importance of biradical states and structures with elongated bond lengths.[38,39] Because of this, the MP2 geometry of a molecule with nonclassical structure should be better confirmed at higher levels of theory. Third-order MP (MP3)[13] is not sufficient in this regard since it only partially corrects the exaggeration of pair correlation effects without introducing new correlation corrections and, therefore, leads to results that are normally shifted in the direction of the corresponding HF data. Both MP2 and MP3 results have to be tested by fourth-order MP (MP4) calculations,[13] which introduce correlation effects resulting from single (S), triple (T), and quadruple (Q) excitations. But with MP4, there is the danger that, for example, T effects are overestimated since TT coupling as well as ST, DT, and QT couplings do not come in before fifth-order MP (MP5).[13,40] MPn geometries oscillate very often between MP1 (= HF) and MP2 values, and in critical cases it is difficult to predict at what level oscillations are dampened out.[39,40]

Of course, one can avoid problems with MPn geometries by using coupled-cluster (CC) methods.[41] They include infinite-order effects and, therefore, results
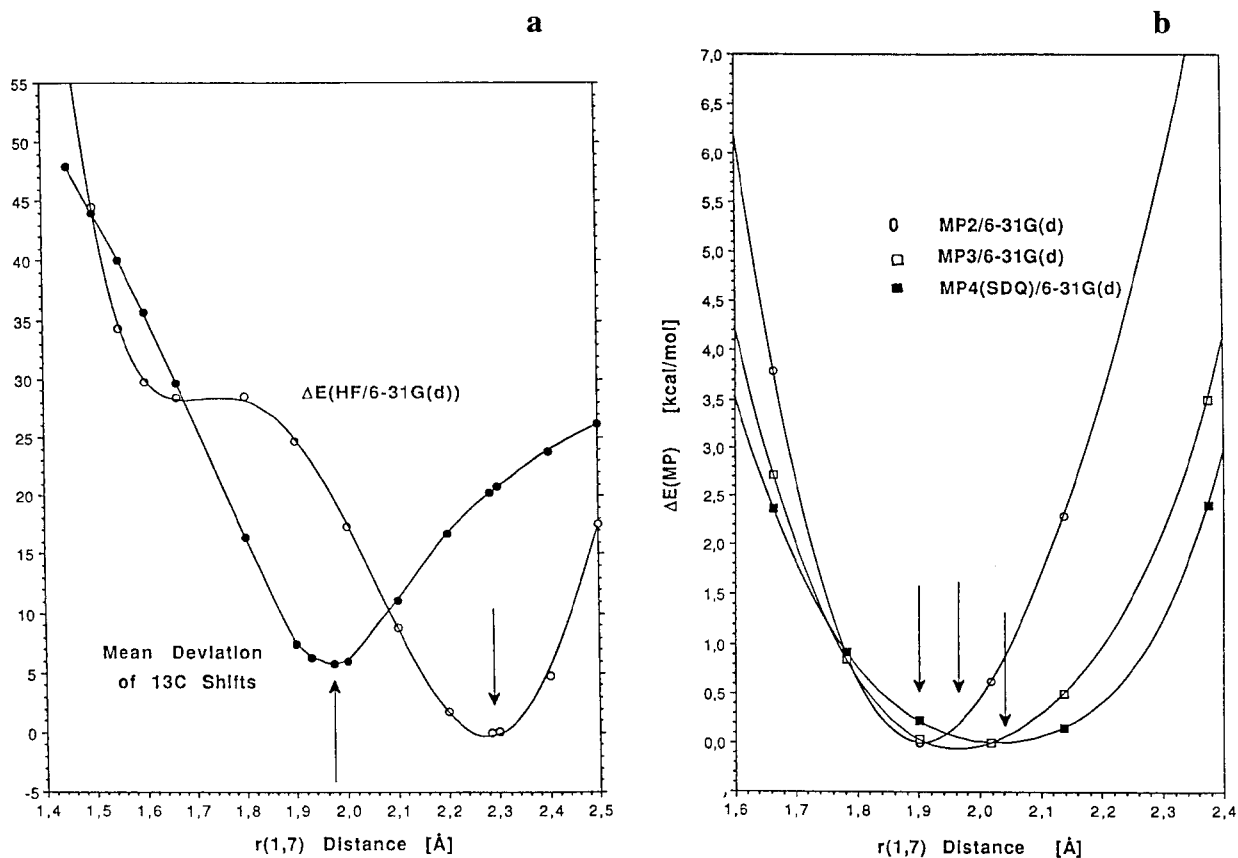
Fig. 2. **a**. Determination of the equilibrium value of the 1,7 distance of the homotropylium cation by α) HF/6-31G(d) calculations (o points) and β) IGLO/6-31G(d) ^{13}C chemical shift calculations. In the latter case, the mean deviation of calculated and experimental ^{13}C chemical shifts is plotted (• points). Minimum values of r(1,7) are α) 2.28 Å (downward-directed arrow) and β) 1.98 Å (upward-directed arrow). **b**. MP2, MP3, and MP4(SDQ) potential energy surface of the homotropylium cation in the direction of the 1,7 distance. The position of the minimum is indicated in each case by an arrow.

do not oscillate. But the price one has to pay is to move from a one-step (MPn) to an iterative method that is needed to calculate CC amplitudes. In the case of the homotropylium cation, CC calculations would imply a large amount of computer time that is not available under normal circumstances.

An alternative, less costly way of determining the correct structure of **I** is provided by NMR chemical shift calculations for **Ia, Ib**, and **Ic**. Since two of these structures are just transient points on the HF potential energy surface (PES), a prerequisite for structure determination by NMR chemical shift calculations is that the PES is systematically explored in the direction that connects possible structures. In the case of **I** the three structural alternatives **Ia, Ib**, and **Ic** correspond to three different ranges of the 1,7 distance: **Ia** implies a relatively short distance (r(1,7) < 1.7 Å), **Ic** a relatively long distance (r(1,7) > 2.3 Å), and **Ib** corresponds to intermediate values (2 Å ± 0.2 Å). By fixing r(1,7) to a number of

discrete values ranging from 1.6 Å to 2.4 Å and by optimizing the remaining geometrical parameters of **I**, the PES in the 1,7-direction is explored. Even though HF is not sufficient to give the correct value of the equilibrium 1,7 distance, one can expect that HF describes the changes of the other geometrical parameters of **I** in dependence on r(1,7) in a consistent way.

If for each of the optimized HF geometries, IGLO ^{13}C NMR chemical shifts are calculated, the dependence of the δ(^{13}C) shifts of **I** on the 1,7 distance is obtained and can also be investigated. One gets for all C atoms δ(^{13}C) as a function of r(1,7), which for some 1,7 distance becomes identical with the corresponding experimental value. In Fig. 1, deviations from experimental ^{13}C chemical shifts rather than calculated ^{13}C shifts themselves are plotted against r(1,7). The five curves cross or approach the zero line between 1.9 and 2 Å, which means that the best agreement with the experimental ^{13}C NMR chemical shifts is achieved in this region. The minimum of the

mean deviation between calculated and theoretical ^{13}C chemical shifts for **I** is calculated for $r(1,7) = 1.98$ Å (see Fig. 2) which suggests that the equilibrium structure of **I** corresponds to **Ib** rather than **Ia** or **Ic**.[42] Cation **I** neither possesses a bicyclic structure with a long 1,7-bond nor an eight-membered ring with weak 1,7 through-space interactions. At $r(1,7) = 2$ Å, the through-space interactions are sufficiently strong to influence π-delocalization in the conjugated system: Bond equalization and uniform charge distribution result, thus giving **I** the typical character of a homoaromatic compound.[33,34]

Clearly, the determination of the equilibrium geometry of a compound such as **I** by IGLO//HF NMR chemical shift calculations cannot lead to high accuracy since there are several approximations involved. But such a procedure is sufficiently accurate to characterize basic structural features. In addition, it can be improved by going to IGLO//MP2, IGLO//MP4, or GIAO-MP2//MP4.[33,43] This is reflected by comparing the IGLO/6-31G(d)//HF/6-31G(d) value of $r(1,7) = 1.98$ Å with the corresponding MP2/6-31G(d), MP3/6-31G(d)//MP2/6-31G(d), and MP4(SDQ)/6-31G(d)//MP2/6-31G(d) values: 1.901, 1.985, 2.031 Å (compare with Fig. 2b). The agreement with the IGLO result is satisfactory in view of the approximations involved. MP4(SDQ) leads to the most reliable geometry of **I**, which again can be checked with the calculated ^{13}C NMR chemical shift parameters. While the smallest mean deviation between theoretical and experimental ^{13}C shifts at the HF level is 6 ppm, it is reduced to 4.9 ppm using the optimized MP4(SDQ)/6-31G(d) geometry.[33] Hence, MP4(SDQ)/6-31G(d) provides a reasonably accurate prediction of the equilibrium geometry of **I**.

The procedure described above for the homotropylium cation is particularly useful if the molecule in question depends on just one or two critical geometry parameters that can only be determined by expensive correlation-corrected ab initio calculations. Variation of these parameters at the HF level in connection with NMR shift calculations helps to determine their equilibrium value. We have applied this approach in a number of cases, in particular to compute interaction distances of potentially homoaromatic compounds.[43]

CALCULATION OF NMR CHEMICAL SHIFTS IN SOLUTION — BORANE MONOAMMONIATE

Borane monoammoniate, BH_3NH_3, has been investigated as a prototype of Lewis acid–base complexes.[44,45] An r_s geometry of the molecule has been reported by Thorne et al.,[46] which is largely reproduced by the MP2/6-31G(d,p) equilibrium geometry of BH_3NH_3 (Table 1). The HF/6-31G(d,p) geometry gives a BN bond length that is 0.3 Å

too large, which shows that electron correlation corrections are important to correctly describe the charge transfer from N to B and by this also the BN bond length.

In Table 1, IGLO/[5s4p1d/3s1p]//HF/6-31G(d,p), IGLO/[5s4p1d/3s1p]//MP2/6-31G(d,p) ^{11}B, and ^{15}N NMR chemical shifts[47] are compared with experimental values measured in an aqueous solution of BH_3NH_3.[48] Theoretical shifts differ as much as 10 and 20 ppm, respectively, from experimental shifts. This is surprising in view of the fact that ^{11}B IGLO chemical shifts are normally correct within 5 ppm, provided the equilibrium geometry of the boron compound is accurately reproduced by theory and used in $\delta(^{11}B)$ calculations.[25h,30b] Since the latter is true for the MP2 geometry, something other than calculational deficiencies must be responsible for the discrepancy between theoretical and experimental shift values.[45]

A clue is given by the large dipole moment of 5.22 debyes for BH_3NH_3,[46] which suggests that the molecule will be strongly solvated in polar solvents because of dipole–dipole interactions. Therefore, one can expect strong solvent shifts for $\delta(^{11}B)$ and $\delta(^{15}N)$. To test this hypothesis, we have simulated the influence of the medium by the PISA solvent model[49] where the wave function of the solute is recalculated in a solvent cage under the influence of a polarizable continuum that is characterized by the dielectric constant of the solvent. IGLO NMR chemical shifts are then obtained for a solvent-dependent SCF wave function. Such an approach may be denoted as PISA-IGLO.[34]

PISA-IGLO/[5s4p1d/3s1p] shifts change by 2 and 5 ppm to higher field when the dielectric constant of water ($\varepsilon = 80$) is used. Changes in the shift values are accompanied by an increased charge transfer from NH_3 to BH_3 and an enlargement of the dipole moment. Obviously, the B and the N nuclei are more shielded, thus leading to chemical shift values closer to the experimental δ-values than the gas-phase δ-values. However, the differences between theoretical and experimental shifts are still too large to be acceptable.

In a second step, we have reoptimized the equilibrium geometry of BH_3NH_3 under the influence of the solvent. A similar investigation has been carried out by Schleyer and coworkers,[45] but since this investigation differs from ours in several ways, we find it desirable to present also the results of our PISA geometry optimizations. The PISA/6-31G(d,p) geometry shown in Table 1 reveals a significant decrease in the BN bond length (1.610 Å) of as much as 0.05 Å, which, according to the calculated charge distribution, is the result of an increase in charge transfer from N to B. The calculated PISA geometry gains credibility by the fact that X-ray structural analysis of crystalline BH_3NH_3[50] and various crown ether complexes of BH_3NH_3[51] have led to BN bond lengths between 1.564

Table 1. Geometry, dipole moment, and NMR chemical shifts of BH3NH3[a]

Parameter	HF	MP2	PISA	MW [b]	X-ray [c]
r(BN)	1.687	1.657	1.610	1.658	1.564 – 1.605
r(BH)	1.209	1.202	1.213	1.216	
r(NH)	1.003	1.014	1.005	1.014	
<HBN	104.4	104.5	106.8	104.7	
<HNB	110.7	111.1	111.6	110.3	
μ	5.54	5.60	6.61	5.22	

	IGLO //HF	IGLO //MP2	IGLO //PISA	PISA-IGLO //MP2	PISA-IGLO //PISA	exp. [d]
$\delta(^{11}B)$	−13.2	−15.0	−17.8	−16.8	−19.5	−23.8
$\delta(^{15}N)$	2.7	8.0	4.9	3.0	−0.8	−13.0

[a] bond lengths in Å, angles in deg, dipole moment μ in debyes, $\delta(^{11}B)$ in ppm relative to $BF_3 \cdot OEt_2$, $\delta(^{15}N)$ in ppm relative to NH_3. IGLO $\delta(^{11}B)$ values have first been calibrated with regard to B_2H_6 and, then, adjusted with the experimental value of B_2H_6 (16.6 ppm) to the $BF_3 \cdot OEt_2$ scale. Geometry otimizations have been carried out with the 6-31G(d,p) basis, IGLO calculations with a [5s4p1d/3s1p] basis set denoted by Kutzelnigg and Schindler as basis II in their IGLO calculations.[25h] The notation *method 1// method 2* indicates that method 1 calculations have been carried out at method 2 geometries.

[b] r_s-geometry from ref 46.

[c] X-ray geometries from refs 50 and 51.

[d] NMR chemical shifts measured in water, ref 48.

Dipole moment μ
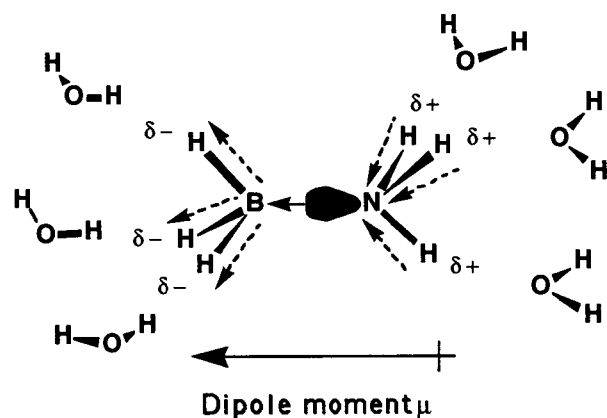
and 1.604 Å. According to these investigations, BH_3NH_3 is embedded in the crown ether and interacts with it by H bonds in a similar way as it does in water solution.

When recalculating chemical shifts with either the PISA/6-31G(d,p) or the X-ray geometry,[50] both $\delta(^{11}B)$ and $\delta(^{15}N)$ are shifted upfield by about 3 ppm. Adding the geometry effect (3 ppm) and the direct solvent effect on the shift calculation (2 ppm), a $\delta(^{11}B)$ value is obtained (−19.6 ppm, Table 1) that is within 5 ppm of the experimental $\delta(^{11}B)$ value obtained in an aqueous solution.[48] For ^{15}N, geometry and direct solvent effect also improve the IGLO $\delta(^{15}N)$ value considerably, but the difference to the experimental $\delta(^{15}N)$ value is 13 ppm, still large. This, however, simply reflects the fact that larger basis sets are needed to reach the same accuracy for $\delta(^{15}N)$ as that obtained for IGLO ^{11}B NMR chemical shifts.[30b]

Schleyer and coworkers, in their study on BH_3NH_3 and related borane adducts, obtained an even larger reduction of the BN bond length when using the PISA method with different physical constants for the solvent.[45] As a consequence, these authors calculated an upfield shift of 5 ppm for $\delta(^{11}B)$, thus leading to −20.5 ppm at IGLO/DZ/ /PISA/6-31G(d), in reasonable agreement with experiment. They concluded that "medium effects on NMR chemical shifts may be indirect," caused by a solvent-dependent change in molecular geometry rather than by a direct influence of the solvent on NMR chemical shifts.[45]

Our calculated $\delta(^{11}B)$ data seem to confirm this conclusion (2.8 ppm geometry effect, 1.8 ppm direct solvent effect), but the computed $\delta(^{15}N)$ values, which were not reported by Schleyer and coworkers, suggest a larger direct influence of the solvent on the chemical shift (3.1 ppm geometry effect, 5 ppm direct solvent effect, Table 1). We conclude that neither of the two effects can be neglected, and taken together they lead to a good description of the total solvation effect (4.5 ppm for $\delta(^{11}B)$ and 8.8 for $\delta(^{15}N)$, Table 1). PISA-IGLO//PISA calculations can provide a reasonable approximation of NMR chemical shifts of solvated molecules, while the combination of IGLO//MP2, IGLO//PISA, and PISA-IGLO//MP2 calculations leads to the determination of geometry and direct solvent effect. Accordingly, IGLO chemical shift and PISA solvent calculations provide a basis for the analysis of solvent–solute interactions and help us to understand electronic structure changes under the impact of the surrounding medium.[34]

INVESTIGATION OF SOLUTE–SOLVENT COMPLEXES BY NMR CHEMICAL SHIFTS — ORGANOTIN IONS IN SOLUTION

In recent years, there has been much dispute on the question whether triorganosilyl cations can be generated in solution and whether some of the carbocation chemistry can also be found for silicon.[52] Since this question has not been clearly answered so far because of experimental difficulties, it is interesting to extend the question to tin and ask whether triorganostannyl cations in solution show some similarities to carbocations. Indeed, evidence for the formation of organotin cations was reported as early as 1923[53] and the detection of SnH_3^+ in aqueous fluorosulfonic acid by ^{119}Sn NMR spectroscopy was published in 1971.[54] Nevertheless, little is known about the electronic structure of tin cations in solution and it remains to be proven whether they are comparable to carbocations.

Again, NMR spectroscopy in combination with ab initio calculations seems to be an appealing method for describing the electronic structure of organotin compounds in solution. Some NMR investigations have focused on the detection of stannyl cations[54–56] while relatively little has been done on the ab initio calculation of tin compounds.[57] Most of the theoretical work has been performed with pseudopotential methods that do not provide a good starting point for NMR chemical shift calculations.[58] There are no ab initio investigations on tin compounds that include the calculation of both energy, geometry, and NMR chemical shift parameters. Therefore, we have taken up the problem of calculating [119]Sn chemical shifts for organotin compounds pursuing two objectives; first, to learn more about the electronic nature of stannyl cations in solution and, second, to test the potential of NMR chemical shift calculations for heavy elements.

As a suitable basis set, we have taken for Sn the (15s11p6d) basis of Stromberg et al.[59] that is between DZ and TZ quality and have combined it with various Dunning TZ and DZ basis sets for first- and second-row elements.[60] Since our IGLO program does not contain f-functions we had to perform shift calculations without polarization functions at Sn. Nevertheless, we have also tested the effect of p-type and d-type polarization functions added to the Dunning basis set. A reasonable compromise between accuracy and costs was already obtained with a mixed basis set of close to TZ quality for Sn and DZ+P quality for all other elements, which we will denote as DZ+(P) in the following, where the parentheses indicate that f-type polarization functions for Sn are missing.[61]

In Figs. 3, 4, and 5, calculated geometries of compounds **1–12** are shown. There are some microwave and electron diffraction investigations on methylstannanes that can be used for comparison.[62] They reveal that both the SnH and

the SnC bonds calculated at the HF/DZ level are 0.01–0.02 Å and at the MP2/DZ level 0.02–0.03 Å longer than experimental values. Including polarization functions at all atoms but the Sn atom leads to a significant decrease of SnH and SnC bond lengths so that HF/DZ+(P) geometries show good agreement with experimental values. Inclusion of f-type polarization functions at the Sn atom leads to another small reduction of SnX (X = H, C, O, Cl, etc.) bond lengths but leaves other geometrical parameters unchanged. For example, the SnH bond is decreased to 1.707 Å at the HF/DZ+P level and to 1.689 Å at the MP2/DZ+P level. Hence, MP2/DZ+P calculations provide the best agreement with experimental geometries.[61] But since f-functions could not be used in the NMR shift calculations, we used the DZ and the DZ+(P) basis sets for the geometry calculations.

When replacing the H atoms of **1** consecutively by methyl groups, both the SnH and the SnC bond lengths increase steadily from 1.709 to 1.722 Å and from 2.153 to 2.167 Å (HF/DZ+(P)). At the same time the positive charge at the Sn atom becomes larger (Table 2) because of electron withdrawal by the methyl groups. Obviously, the SnC and SnH bond lengths increase with increasing bond polarity. The experimental bond lengths do not show any clear trends (Fig. 3). In view of the difficulties and approximations involved in the experimental measurements,[62] the calculated geometries probably provide a more accurate description of general trends than the few experimental data available.

Alkyl groups lead to some destabilization of stannanes. From isodesmic reactions

$$(CH_3)_n SnH_{4-n} + (n-1) SnH_4 \rightarrow n\, CH_3 SnH_3$$
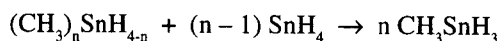
SnC bond, bond interaction energies of –1.1 (n = 2), –2.8 (n = 3), and –4.8 kcal/mol (n = 4) are calculated with the energies listed in Table 2. This is different from CC bond, bond interaction energies which are stabilizing, as can be seen when replacing H atoms in CH_4 by methyl groups. Since the methyl group functions in $CH_3 SnH_3$ as a σ-acceptor, a second methyl group could lead to stabilization provided it acts as a π-donor, thus giving the SnC bond some double bond character. However, $2p\pi(C)$-$5p\pi(Sn)$ overlap is rather poor and, therefore, the π-donor ability of CH_3 is strongly reduced. As a consequence, both methyl groups become negatively charged (see Table 2 and Fig. 6), thus repelling each other. The more methyl groups are attached to Sn, the larger the electrostatic repulsion between them and the greater the stannane molecule destabilization.

In Table 3, calculated ^{119}Sn NMR chemical shifts are shown. When comparing calculated [119]Sn chemical shifts with experimental ones,[63–65] one has to keep in mind that the latter can change very much in dependence on the
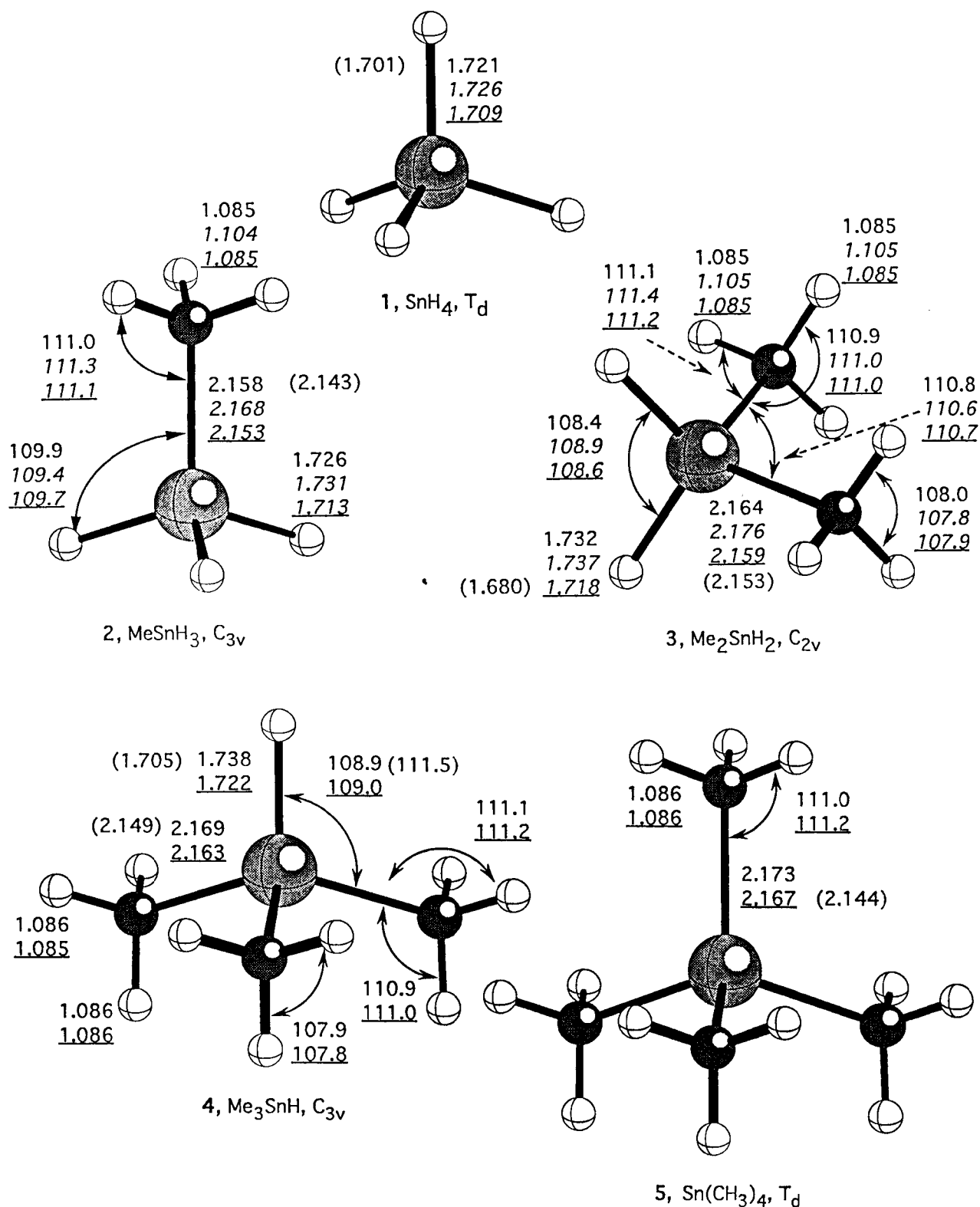
Fig. 3. Calculated geometries of methylstannanes $(CH_3)_n SnH_{4-n}$ **1–5**. Numbers in normal print: HF/DZ values; in italics: MP2/DZ values; in underlined italics: HF/DZ+(P) values; in parentheses: experimental values.
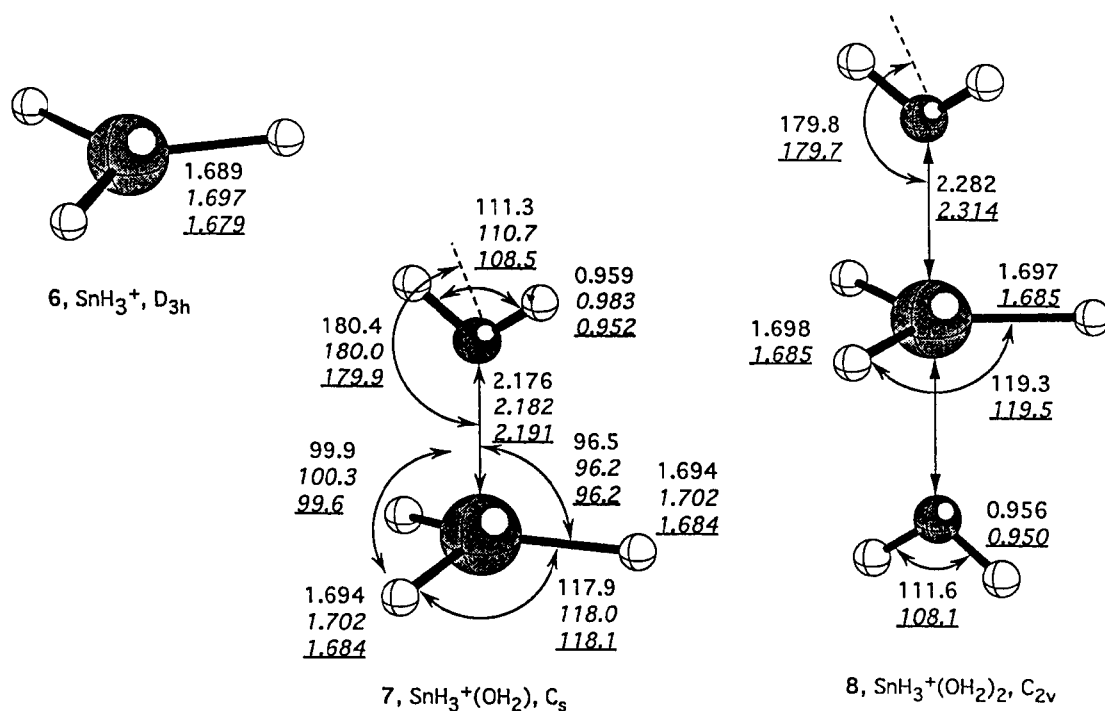
Fig. 4. Calculated geometries of stannyl cations $SnH_3^+(H_2O)_n$ **6–8**. Numbers in normal print: HF/DZ values; in italics: MP2/DZ values; in underlined italics: HF/DZ+(P) values.
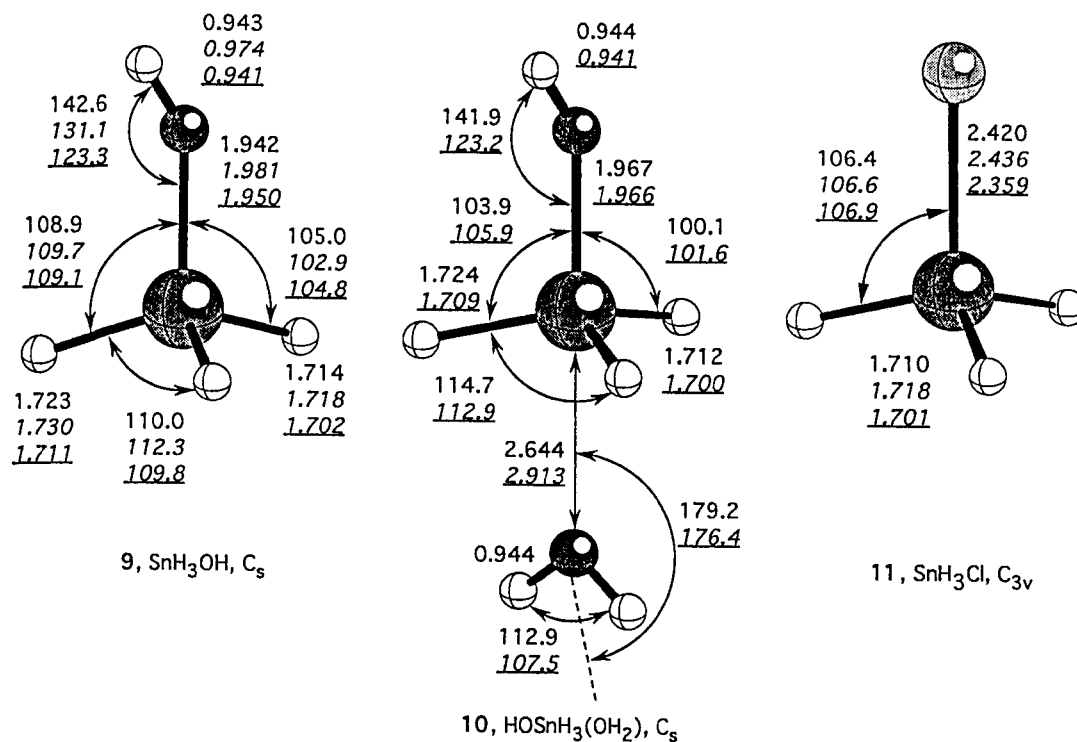

Fig. 5. Calculated geometries of stannyl compounds SnH_3X **9–11**. Numbers in normal print: HF/DZ values; in italics: MP2/DZ values; in underlined italics: HF/DZ+(P) values.
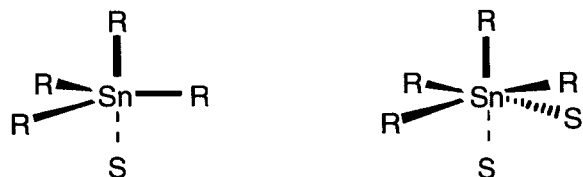
Table 2. Calculated energies and Sn charges q [a]

Molecule	Sym	Energy		q(Sn)	q(SnH$_n$)	q(Sn)	q(SnH$_n$)
		HF/DZ	HF/DZ+(P)	HF/DZ		HF/DZ+(P)	
1. SnH$_4$	T$_d$	−6024.51685	−6024.53845	0.926	0.000	1.018	0.000
2. CH$_3$SnH$_3$	C$_{3v}$	−6063.55801	−6063.59331	1.139	0.430	1.209	0.433
3. (CH$_3$)$_2$SnH$_2$	C$_{2v}$	−6102.59735	−6102.64636	1.356	0.877	1.403	0.880
4. (CH$_3$)$_3$SnH	C$_{3v}$	−6141.63583	−6141.69863	1.585	1.344	1.607	1.344
5. (CH$_3$)$_4$Sn	T$_d$	−6180.67384	−6180.67384	1.825	1.825	1.823	1.823
6. SnH$_3$$^+$	D$_{3h}$	−6023.66346	−6023.68194	1.330	1.000	1.409	1.000
7. SnH$_3$$^+$ H$_2$0	C$_s$	−6099.75755	−6099.79827	1.362	0.899	1.438	0.904
8. SnH$_3$$^+$ 2 H$_2$0	C$_{2v}$	−6175.82247	−6175.88849	1.417	0.843	1.487	0.855
9. HOSnH$_3$	C$_s$	−6099.41327	−6099.45191	1.417	0.676	1.463	0.657
10. HOSnH$_3$ H$_2$0	C$_s$	−6175.43729	−6175.50605	1.466	0.663	1.501	0.651
11. ClSnH$_3$	C$_{3v}$	−6483.46006	−6483.49166	1.199	0.552	1.317	0.575

[a]Energies in hartrees, Mulliken charges q in electron. q(Sn) is the charge at the Sn atom, q(SnH$_n$) is the charge of the SnH$_n$ group. The H$_2$O reference energies are: −76.01100 (HF/DZ), −76.06163 (HF/DZ+P).

medium. Polar coordinating solvents can produce shift changes of 200 ppm and more if five-coordinated or six-coordinated adducts with trigonal bipyramidal or octahedral configuration are formed between the Sn compound and the solvent molecule (S):[63,64]

Also, dimerization of Sn compounds in solution is possible.[63] Therefore, comparison of calculated and experimental [119]Sn chemical shifts requires a careful consideration of environmental and structural effects.

The IGLO [119]Sn chemical shifts show a clear dependence on the partial charge at Sn, as is shown in Fig. 6. Since the electronegativity of a C atom is larger than that of a H atom, the positive charge at the Sn atom increases with increasing methyl substitution (see Table 2). Accordingly, the Sn nucleus becomes more and more deshielded and δ([119]Sn) is shifted downfield, which is in line with experimental shift values (Table 3). However,

the latter are between 120 and 30 ppm more negative than the IGLO shift values. Media effects can be partially responsible for these differences, but since experimental measurements have been carried out in weakly or noncoordinating solvents, solvent corrections should be smaller than 10 ppm. On the other hand, inspection of the calculated charge distributions in dependence on basis set and correlation corrections reveals that the major part of the differences between theoretical and experimental ^{119}Sn NMR shifts results from calculational deficiencies:
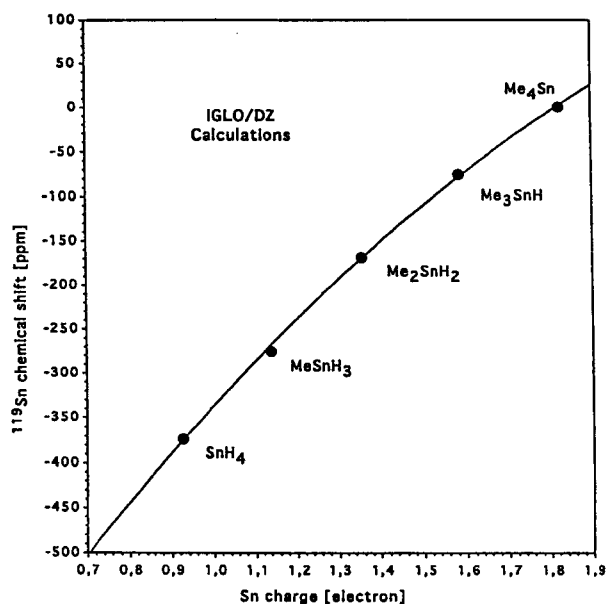1. The use of f-type polarization functions at Sn leads to

Fig. 6. Dependence of IGLO δ([119]Sn) values on the charge at the Sn atom (Mulliken values calculated with the DZ basis).

a redistribution of 0.1 electron from the H atoms to the Sn atom in 1, thus shielding the Sn nucleus. Utilizing the linear relationship between [119]Sn chemical shifts and the charge at the Sn atom (Fig. 6), a δ-value of −440 ppm is calculated for 1.
2. Response density calculations at the MP2/DZ+P level of theory lead to further screening of the Sn nucleus (q(Sn) = 0.790 e). This is because MP2 emphasizes biradical states and, therefore, decreases the polarity of SnH and SnC bonds. We expect that correlation-corrected NMR chemical shift calculations lead to a

Table 3. Calculated ^{119}Sn NMR chemical shifts[a]

Molecule	Sym	DZ	DZ+(P)	exp. value
1. SnH_4	T_d	−374	−380	−493 [b]
2. CH_3SnH_3	C_{3v}	−275	−273	−346 [b]
3. $(CH_3)_2SnH_2$	C_{2v}	−169	−162	−225 [b]
4. $(CH_3)_3SnH$	C_{3v}	−76		−104 [b]
5. $(CH_3)_4Sn$	T_d	0	0	0 [a]
6. SnH_3^+	D_{3h}	777	774	
7. $SnH_3^+ H_2O$	C_s	54	84	
8. $SnH_3^+ 2 H_2O$	C_{2v}	−238	−181	−186 [c]
9. $HOSnH_3$	C_s	−215	−181	
10. $HOSnH_3 H_2O$	C_s	−310	−221	
11. $ClSnH_3$	C_{3v}	−138	−179	
12. $Sn(CH_3)_3^+$		(1075)		
13. $Sn(CH_3)_3^+ H_2O$		(352)		
14. $Sn(CH_3)_3^+ 2 H_2O$		(60)		54 [d]
15. $HOSn(CH_3)_3$		(83)		77 [b]
16. $HOSn(CH_3)_3 H_2O$		(−12)		−47 [e]
17. $ClSn(CH_3)_3$		(160)		153 [b]

[a]Shifts relative to that of **5**. Numbers in parentheses are estimated from methyl group increments.
See text.
[b]From refs 63 and 64.
[c]SnH_3^+/FSO3H, ref 54.
[d]$SnBu_3^+$/2 CH_3CN, ref 56.
[e]Ref 65.

δ([119]Sn) value close to −450 ppm in the case of SnH_4.
3. For δ([119]Sn) also relativistic corrections have to be considered. Judging from NMR shift calculations of other heavy elements, these can be very large.[66] However, there are no data for δ([119]Sn) available that suggest a reasonable correction.
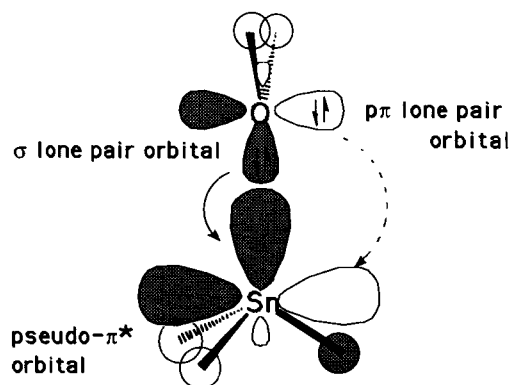
To get better δ([119]Sn) values, calculations have to be performed with a correlation-corrected method and basis sets including f-type polarization functions.[61] In this paper, however, we are more interested in trends than in accurate values and the former are satisfactorily reproduced at the IGLO/DZ and IGLO/DZ+(P) levels of theory.

In Fig. 4, three different SnH_3^+ cations **6**, **7**, and **8** are shown. The naked cation **6** is planar and has a SnH bond length that is clearly shorter (1.679 Å) than that of **1** (1.709 Å). Because of the deshielding of the Sn nucleus (q(Sn) = 1.33 e, Table 2), δ([119]Sn) is shifted to 774 ppm (Table 3), which is ca. 960 ppm lowfield from the experimental value of −186 ppm measured in FSO_3H acid.[54] Clearly, **6** does not exist in solution, but forms donor–acceptor complexes with solvent molecules. Depending on the donor strength of the solvent, the negative charge is transferred to cation **6**, thus leading to shielding of the Sn nucleus. To model this process we have calculated the mono- and di-water complex of SnH_3^+, **7**, and **8** (Fig. 4).

Complex **7** is characterized by a rather short Sn,O

distance of 2.19 Å and a significant pyramidalization of the SnH_3 group (<OSnH = 96.2 and 99.6°, Fig. 4). The OH bonds arrange in a staggered conformation with regard to the SnH bonds, but move from a bent position (start of the geometry optimization: flipping angle SnO(HH) < 180°) into a linear arrangement with SnO(HH) close to 180°. In this way, 2-electron stabilization interactions between the σ(O) lone pair orbital and the empty pπ(Sn) orbital become possible while interactions between the pπ(O) lone pair orbital and the pseudo-π*(SnH_3) orbital are probably negligible because of insufficient 2pπ–5pπ overlap.

This is confirmed by a complexation energy of 54 kcal/mol (HF/DZ+(P); 52 kcal/mol, HF/DZ), a charge transfer of 0.10 electrons from water to SnH_3^+, a

σ lone pair orbital

pπ lone pair orbital

pseudo-π* orbital

lengthening of the SnH bonds by 0.005 Å to 1.684 Å, and a widening of the HOH angle to 108.5° (HF/DZ+(P)). The value of $\delta(^{119}Sn)$ is strongly shifted upfield from 774 ppm to 84 ppm (IGLO/DZ+(P); 54 ppm, IGLO/DZ, Table 3).

Complexation by another water molecule leads to a trigonal bipyramidal geometry with a planar SnH$_3^+$ cation in the center. The SnO interaction distance is significantly increased from 2.19 (7) to 2.31 Å (8), indicating that the two water molecules hinder each other in their interactions with the cation. This is in line with the calculated charge transfer of just 0.079 e from each water molecule, leading to a reduction of the positive charge from +1 (6) and +0.899 (7) to +0.843 e (8). As a consequence, the Sn nucleus is more shielded and $\delta(^{119}Sn)$ becomes −181 ppm (IGLO/DZ+(P); −238 ppm, IGLO/DZ, Table 3) for 8. This value comes close to the −186 ppm measured in aqueous fluorosulfonic acid[49] and suggests that in this medium a similar SnH$_3^+$ complex exists.

Clearly, electronic structure, geometry, NMR shift values, and other properties of SnH$_3^+$ in solution will depend on the donor capacity of the solvent molecule and, therefore, it may be erroneous to speak in this case of stannyl cations. For example, some of the properties of complexes 7 and 8 are very close to those of a covalently-bonded SnH$_3$OH (9) molecule (Fig. 5, Tables 2 and 3). The SnO bond length of 9 (1.950 Å) is just 0.241 and 0.364 Å shorter than the SnO distances calculated for the two water complexes. More important, the Sn atom carries a positive charge that is comparable to that of the water complex 8 (Table 2). These similarities between 7, 8, and 9 become understandable if one no longer considers 7 and 8 as SiH$_3^+$–water complexes but as protonated SnH$_3$OH (7), or protonated SnH$_3$OH–water complex (8) with covalent SnO bonds. Protonation will lead to SnO bond lengthening and to charge redistributions as found for 7 and 8. On the other hand, it is still true that for both 7 and 8 the positive charge is predominantly located at the Sn atom (see Table 2) and, therefore, one can consider 7 and 8 as coordination complexes of SiH$_3^+$. In any case, relationship between 7, 8, and 9 *will make it difficult to distinguish covalently bonded SnR$_3$X compounds and coordination complexes of stannyl cations*. For example, 9 has a similar $\delta(^{119}Sn)$ value (−181 and −215 ppm) to that of 8 (−238 and −181 ppm) (Table 3).

Of course, $\delta(^{119}Sn)$ of coordination complexes of tin cations with solvent molecules should show a strong dependence on the donicity of the solvent. For example, NMR measurements of Bu$_3$SnCl, Bu$_3$SnClO$_4$, and Bu$_3$SnBF$_4$ in different solvents ranging from CH$_2$Cl$_2$ to hexamethylphosphoramide have found upfield shifts of $\delta(^{119}Sn)$ by 200 to 260 ppm, with the less ionized starting compound having the more positive and, hence, more

deshielded Sn nucleus.[56] This is in line with our calculations that suggest a relatively high positive charge at Sn in the covalently-bonded compounds SnH$_3$X, with X being an electronegative group or atom such as OH (9) or Cl (11) (See Table 3). Hence, the detection of the cation requires a series of NMR measurements for a variety of solvents with increasing donicity.

There is, however, some ambiguity with this procedure for detecting stannyl cations. Because of the relatively high positive charge at Sn in a covalently-bonded tin compound, the latter can coordinate at least one solvent molecule without dissociating into cation and anion. In Tables 2 and 3 and in Fig. 5, calculated energies, Sn charges, and geometry parameters of the mono-water complex of 9, 10, are shown. The properties of 10 are much more sensitive to changes in the basis set than has been found for the other tin compounds listed in Table 2. The charge transfer from water to Sn (0.036 (HF/DZ) and 0.024 e (HF/DZ+(P)) is one-third smaller if calculated with the larger basis set, but in any case it is much smaller than that found for complexes 7 and 8. This is due to the fact that the σ lone pair orbital of H$_2$O interacts in 10 with the energetically higher-lying σ*(SnO) orbital and, therefore, interactions are weaker than in the case of a stannyl cation.

As a consequence, complex 10 has a binding energy of just 8.2 (HF/DZ) and 4.7 kcal/mol (HF/DZ+(P)), respectively, much smaller than that of 7 or 8. Experimental complexation enthalpies measured by Torocheshnikov et al. for Me$_3$SnCl and Et$_3$SnCl in acetone, acetonitrile, and dioxane range from 2.8 to 4.2 kcal/mol.[67] Accordingly, HF/DZ+(P) seems to give a better description of complex 10 than HF/DZ, which is in line with the discussion above. The relative weakness of the interactions between water and 9 is also reflected by the calculated Sn,O interaction distance that with 2.644 (HF/DZ) and 2.913 Å (HF/DZ+(P)), respectively, is much larger than Sn,O distances obtained for cations 7 and 8 (Fig. 4). Nevertheless, complexation of 9 changes the electronic structure of the SnH$_3$ group in the direction of that of a SnH$_3^+$ cation. This can be seen from the beginning planarization of the SnH$_3$ group (reduction of the OSnH angles) and the increase in the SnO bond length (0.015 Å, Fig. 5) as a consequence of the population of the σ*(SnO) orbital.

The $\delta(^{119}Sn)$ value of 10 is shifted to highfield because of charge transfer from water to Sn and stronger shielding of the Sn nucleus. However, for the DZ+(P) basis this shift is moderate ($\delta(^{119}Sn) = -221$ ppm), while it is much larger for the DZ basis ($\delta(^{119}Sn) = -310$ ppm, Table 3). On the basis of these results we cannot exclude that H$_3$SnX compounds such as 9 and 11 show a relatively strong dependence on the coordinating capacity of the solvent. Definitely, careful NMR investigations and a broad

variation of the solvent are required to distinguish R_3Sn^+ cations from R_3SnX compounds in solution. This is illustrated by some examples from the literature.

For $HOSn(CH_3)_3$, **15**, and $ClSn(CH_3)_3$,**17**, $\delta(^{119}Sn)$ values of 77 and 153 ppm have been measured.[63,64] Utilizing the shift values obtained for compounds **1–5**, we can predict IGLO/DZ values of 83 (**15**) and 160 ppm (**17**), in good agreement with experiment. These ^{119}Sn chemical shifts have to be compared with an estimated $\delta(^{119}Sn)$ value of 60 ppm for $Sn(CH_3)_3^+ \cdot 2\,H_2O$, (**14**). In a careful NMR investigation of Bu_3Sn^+ ions using CH_2Cl_2, acetonitrile, pyridine, N,N-dimethylpropylenurea, dimethylsulphoxide, and hexamethylphosphoramide as solvents, $\delta(^{119}Sn)$ values between 130 and –47 ppm resulted when starting from Bu_3SnCl, between 220 and –43 ppm for Bu_3SnClO_4 and between 160 and –44 ppm for Bu_3SnBF_4.[56] When comparing our model solvent, water, with these solvents, we predict that with regard to its electron-donating capacity H_2O should be located somewhere between sulfolan ($\delta(^{119}Sn)$ = 139 ppm for Bu_3SnClO_4) and acetonitrile ($\delta(^{119}Sn)$ = 54 ppm for Bu_3SnClO_4). Hence, an estimated $\delta(^{119}Sn)$ value of 60 ppm for **14** is in line with experimental results.

In view of the results obtained here the following conclusions can be drawn.

a. R_3SnX compounds with an appropriate leaving group such as Cl, OH, etc. have $\delta(^{119}Sn)$ values at lower field than R_3Sn^+ cations in solution. Although one would expect the cation to have a much more deshielded nucleus, this is not the case since only strongly-coordianted Sn cations exist in solution.

b. Increasing the donicity of the solvent leads to trigonal bipyramidal $R_3SnX\cdot S$ (S = solvence) complexes. The $\delta(^{119}Sn)$ value appears at higher field because of charge transfer from S to Sn and resultant higher shielding of the Sn nucleus.

c. Formation of the cation probably involves another S molecule and the reaction steps (1) and (2) or (1) and (3).

d. For an electronegative X, $R_3Sn\,(S)_2^+$ cations should posses $\delta(^{119}Sn)$ values at higher field than either R_3SnX or $R_3SnX\cdot S$. However, for any R-X-S combination this has to be tested.

In view of the high binding energies between R_3Sn^+ and solvent molecules (in the case of H_2O more than 50 kcal/mol) it is certainly not justified to speak of stannyl cations in solution. In reality, there exist different pentacoordinated $R_3Sn\,(S)_2^+$ cations with strong Sn,S interactions that lead to properties that differ considerably from those of a

$$(1)$$

$$(2)$$

$$(3)$$
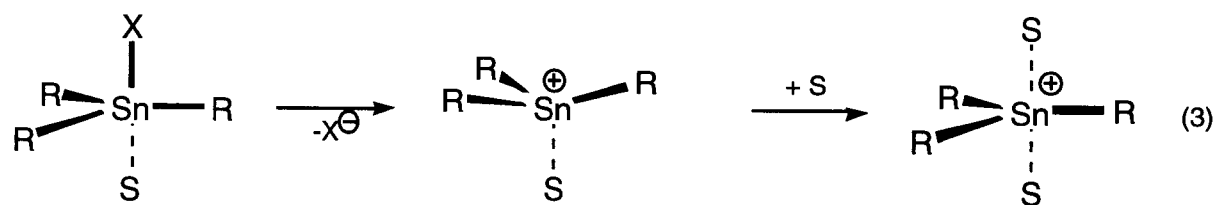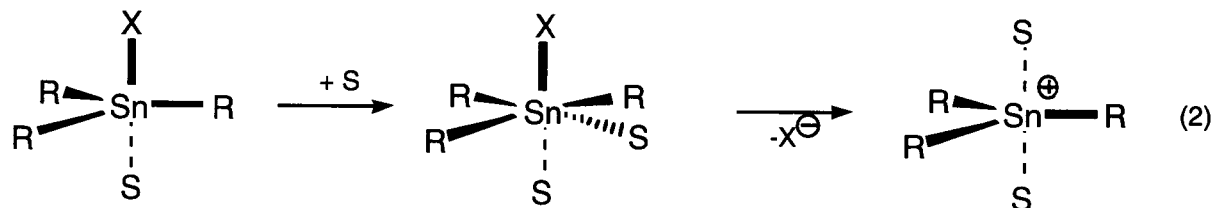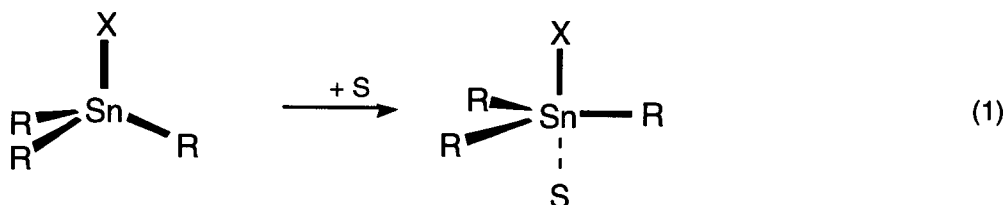
naked stannyl cation. This is best reflected by a $\delta(^{119}Sn)$ value that, according to our calculations, appears ca. 1000 ppm at higher field than that of an isolated cation in the gas phase.

CONCLUSIONS

The calculation of NMR chemical shifts by ab initio methods means an important addition to the repertoire of quantum chemistry. It has started the third phase of collaboration between experimentalists and quantum chemists, since theoretical NMR chemical shifts can be useful to solve a variety of chemical problems. This has been demonstrated in the present paper for three examples, namely, the structure determination of the homotropylium cation, the description of BH_3NH_3 in solution, and the investigation of organostannyl cation–sovent complexes.

REFERENCES AND NOTES

(1) Boys, S.F. *Proc. R. Soc. London* 1950, **A200**: 542.

(2) Roothaan, C.C.J. *Rev. Mod. Phys.* 1951, **23**: 69. Hall, G.G. *Proc. R. Soc. London* 1951, **A205**: 541.

(3) Light, J.C. *J. Phys. Chem.* 1982, **86**: 2111.

(4) Barnett, M.P. *Rev. Mod. Phys.* 1963, **35**: 571. POLYATOM, Version 2. Neumann, D.B.; Basch, H.; Kornegay, R.L.; Snyder, L.C.; Moskowitz, J.W.; Hornback, C.; Liebmann, S.P. *Program 199, QCPE*, Indiana Univ., Bloomington, Indiana.

(5) Clementi, E.; Davis, D.R. *J. Comput. Phys.* 1966, **1**: 223.

(6) Rothenberg, S.; Kollman, P.; Schwartz, M.E.; Hayes, E.F.; Allen, L.C. *Int. J. Chem., Symp.,* 1970, **3**: 715.

(7) Bagus, P.S.; Liu, B.; McLean, A.D.; Yoshimine, M. In *Wave Mechanics: The First Fifty Years*; Price, W.C.; Chissick, S.S.; Ravensdale, T., Eds.; Butterworth: London, 1973. McLean, A.D.; Yoshimine, M.; Lengsfield, B.H.; Bagus, P.S., Liu, B. In *MOTECC, Modern Techniques in Computational Chemistry;* Clementi, E., Ed.; ESCOM Science Publishers: Leiden, 1990, p. 593.

(8) GAUSSIAN 70. Hehre, W.J.; Lathan, W.A.; Ditchfield, R.; Newton, M.D.; Pople, J.A. *Program 236, QCPE*, Indiana Univ., Bloomington, Indiana. See also, GAUSSIAN 90. Frisch, M.J.; Head-Gordon, M.; Trucks, G.W.; Foresman, J.B.; Schlegel, H.B.; Raghavachari, K.; Robb, M.A.; Binkley, J.S.; Gonzalez, C.; DeFrees, D.J.; Fox, D.J.; Whiteside, R.A.; Seeger, R.; Melius, C.F.; Baker, J.; Martin, R.L.; Kahn, L.R.; Stewart, J.J.P.; Topiol, S.; Pople, J.A., Gaussian Inc., Pittsburgh, PA., 1990.

(9) Almlöf, J. *USIP Rep. 72–09*, Univ. Stockholm, 1972. Almlöf, J. *USIP Rep. 74–29*, Univ. Stockholm, 1974. Roos, B.O.; Karlström, G.; Malmqvist, P.Å.; Sadlej, A.J.; Widmark, P.O. In *MOTECC, Modern Techniques in Computational Chemistry*; Clementi, E., Ed.; ESCOM Science Publishers: Leiden, 1990, p. 533.

(10) Dupuis, M.; Rys, J.; King, H.F. *J. Chem. Phys.* 1976, **65**: 111. Dupuis, M.; Farazdel, A.; Karna, S.P.; Maluendes, S.A. In *MOTECC, Modern Techniques in Computational Chemistry*, Clementi, E., Ed.; ESCOM Science Publishers: Leiden, 1990, p. 277.

(11) GAMESS. Guest, M.F.; Kendrick, J.; Pope, S.A. SERC Daresbury Laboratory, England, 1983. Dupuis, M.; Spangler, D.; Wendolowski, J.J. *NRCC Software Catalog*, Vol. 1, Program QG01, 1980.

(12) CADPAC: The Cambridge Analytic Derivative Package, 4.0 ed. Amos, R.D.; Rice, J.E., Cambridge, 1987.

(13) Møller, C.; Plesset, M.S. *Phys. Rev.* 1934, **46**: 618. Pople, J.A.; Binkley, J.S.; Seeger, R. *Int. J. Quantum Chem., Symp.* 1976, **10**: 1. Krishnan, R.; Pople, J.A. *Int. J. Quantum Chem.* 1978, **14**: 91. Krishnan, R.; Frisch, M.J.; Pople, J.A. *J. Chem. Phys.* 1980, **72**: 4244. Raghavachari, K.; Pople, J.A.; Replogle, E.S.; Head-Gordon, M. *J. Phys. Chem.* 1990, **94**: 5579.

(14) Kelly, H.P. *Phys. Rev.* 1963, **131**: 684.

(15) For reviews on analytical derivative methods, see Jørgensen, P.; Simons, J., Eds.; *Geometrical Derivatives of Energy Surfaces and Molecular Properties*; Reidel: Dordrecht, 1986. Pulay, P. *Adv. Chem. Phys.* 1987, **67**: 241. Schlegel, H.B. *Adv. Chem. Phys.* 1987, **67**: 249. Amos, R.D. *Adv. Chem. Phys.* 1987, **67**: 99. Gauss, J.; Cremer, D. *Adv. Quantum Chem.* 1990, **27**: 101.

(16) Pulay, P. *Mol. Phys.* 1969, **17**: 197.

(17) Gerratt, J.; Mills, I.M. *J. Chem. Phys.* 1968, **49**: 1719.

(18) Hameka, H. *Mol. Phys.* 1958, **1**: 203. Hameka, H. *Rev. Mod. Phys.* 1962, **34**: 87. Zeroka, D.; Hameka, H.F. *J. Chem. Phys.* 1966, **45**: 300.

(19) London, F. *Naturwissenschaften* 1937, **15**: 187. London, F. *J. Phys. Rad.* 1937, **8**: 397.

(20) Pople, J.A. *J. Chem. Phys.* 1962, **37**: 53. Pople, J.A. *J. Chem. Phys.* 1962, **37**: 60.

(21) Ditchfield, R. *J. Chem. Phys.* 1972, **56**: 5688. Ditchfield, R. *J. Chem. Phys.* 1976, **65**: 3123. Ditchfield, R. *Mol. Phys.* 1974, **27**: 789. Ditchfield, R. In *Topics in Carbon-13 NMR Spectroscopy;* Wiley: New York, 1974; Vol 1.

(22) Galasso, V. *Theor. Chim. Acta* 1983, **63**: 35. Jaszunski, M.; Adamowicz, L. *Chem. Phys. Lett.* 1981, **79**: 133. Lazzeretti, P.; Zanasi, R. *J. Chem. Phys.* 1983, **105**: 12.

(23) Wolinski, K.; Hinton, J.F.; Pulay, P. *J. Am. Chem. Soc.* 1990, **122**: 8251.

(24) Kutzelnigg, W. *Isr. J. Chem.* 1980, **19**: 193. Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* 1982, **76**: 1919.

(25) (a) Schindler, M.; Kutzelnigg, W. *J. Am. Chem. Soc.* 1983, **105**: 1360. (b) Schindler, M.; Kutzelnigg, W. *Mol. Phys.* 1983, **48**: 781. (c) Schindler, M.; Kutzelnigg, W. *J.*

Am. Chem. Soc. 1987, **109**: 1021. (d) Schindler, M. *J. Am. Chem. Soc.* 1987, **109**: 5950. (e) Schindler, M. *Magn. Reson. Chem.* 1988, **26**: 394. (f) Schindler, M. *J. Am. Chem. Soc.* 1988, **110**: 6623. (g) Schindler, M. *J. Chem. Phys.* 1988, **88**: 7638. (h) Kutzelnigg, W.; Schindler, M.; Fleischer, U. *NMR, Basic Principles and Progress*; Springer: Berlin, 1989; Vol. 23.

(26) Hansen, Aa.E.; Bouman, T.D. *J. Chem. Phys.* 1985, **82**: 5035.

(27) Gauss, J. *Chem. Phys. Lett.* 1992, **191**: 614. Gauss, J. *J. Chem. Phys.* 1993, **99**: 3629.

(28) Kutzelnigg, W.; van Wüllen, Ch.; Fleischer, U.; Franke, R. *Proceedings of the NATO Advanced Workshop on The Calculation of NMR Shielding Constants and their Use in the Determination of the Geometric and Electronic Structures of Molecules and Solids*, 1992.

(29) Bouman, T.D.; Hansen, Aa.E. *Chem. Phys. Lett.* 1990, **175**: 292. Geertsen, J.; Oddershedde, J. *J. Chem. Phys.* 1984, **90**: 301. Geertsen, J.; Jørgensen, P.; Yaeger, D.L. *Comput. Phys. Rep.* 1984, **2**: 33. Darborn, G.T.; Handy, N.C. *Mol. Phys.* 1983, **49**: 1277. Jaszunski, M.; Sadlej, A. *Theoret. Chim. Acta* 1975, **40**: 157.

(30) Summaries of the work on carbocations, boron, and organolithium compounds can be found in (a) Buzek, P.; Schleyer, P.v.R.; Sieber, S. *Chem. Unserer Zeit* 1992, **26**: 116. (b) Bühl, M.; Schleyer, P.v.R. In *Electron Deficient Boron and Carbon Clusters*; Olah, G.A.; Wade, K.; Williams, R.E., Eds.; Wiley: New York, 1991. (c) Bühl, M.; Hommes, N.J.R. v.E.; Schleyer, P.v.R.; Fleischer, U.; Kutzelnigg, W. *J. Am. Chem. Soc.* 1991, **113**: 2459.

(31) See, e.g., Hnyk, D.; Vajda, E.; Buehl, M.; Schleyer, P.v.R. *Inorg. Chem.* 1992, **31**: 2464. Buehl, M.; Schleyer, P.v.R. *J. Am. Chem. Soc.* 1992, **114**: 477. Buehl, M.; Schleyer, P.v.R.; McKee, M.L. *Heteroat. Chem.* 1991, **2**: 499. Buehl, M.; Schleyer, P.v.R. *Angew. Chem.* 1990, **102**: 962. Schleyer, P.v.R.; Buehl, M.; Fleischer, U.; Koch, W. *Inorg. Chem.* 1990, **29**: 153. Schleyer, P.v.R.; Koch, W.; Liu, B.; Fleischer, U. *J. Chem. Soc., Chem. Commun.* 1989: 1098. Bremer, M.; Schoetz, K.; Schleyer, P.v.R.; Fleischer, U.; Schindler, M.; Kutzelnigg, W.; Koch, W.; Pulay, P. *Angew. Chem.* 1989, **101**: 1063.

(32) Onak, T.; Tseng, J.; Diaz, M.; Tran, D.; Arias, J.; Herrera, S.; Brown, D. *Inorg. Chem.* 1993, **32**: 487.

(33) Cremer, D.; Reichel, F.; Kraka, E. *J. Am. Chem. Soc.* 1991, **113**: 9459, and references therein.

(34) Reichel, F. Ph.D. Dissertation, Univ. of Köln, 1991.

(35) Paquette, L.A.; Broadhurst, M.J.; Warner, P.; Olah, G.A.; Liang, G. *J. Am. Chem. Soc.* 1973, **105**: 3386.

(36) Childs, R.F.; Varadarajan, A.; Lock, C.J.L.; R. Faggiani, R.; Fyfe, C.A.; Wasylishen, R.E. *J. Am. Chem. Soc.* 1982, **104**: 2452.

(37) Childs, R.F.; Faggiani, R.; Lock, C.J.L.; Mahendran, M. *J. Am. Chem. Soc.* 1986, **108**: 3613.

(38) Kraka, E.; Gauss, J.; Cremer, D. *J. Mol. Struct. (Theochem)* 1991, **234**: 95.

(39) Gauss, J.; Cremer, D. *Adv. Quantum Chem.* 1990, **27**: 101.

(40) Zhi He; Cremer, D. *Int. J. Quantum Chem., Symp.* 1991, **25**: 43. Zhi He; Cremer, D. *Theor. Chim. Acta* 1993, **85**: 305.

(41) See, e.g., Bartlett, R.J. *J. Phys. Chem.* 1989, **93**: 1697.

(42) Schleyer and coworkers have carried out an IGLO/DZ/ /MP2/6-31G(d) investigation of **Ib**, which led to similar results.[30a] However, the agreement between experimental and IGLO ^{13}C chemical shifts obtained in this work is lower because of the deficiencies of the MP2 method to describe nonclassical carbocations such as **Ib**.

(43) (a) Cremer, D.; Svensson, P.; Kraka, E.; Ahlberg, P. *J. Am. Chem. Soc.* 1993, **115**: 7445. (b) Cremer, D.; Svensson, P.; Kraka, E.; Konkoli, Z.; Ahlberg, P. *J. Am. Chem. Soc.* 1993, **115**: 7457. (c) Svensson, P.; Reichel, F.; Ahlberg, P.; Cremer, D. *J. Chem. Soc., Perkin Trans.* 1991, **2**: 1463. (d) Sieber, S.; Schleyer, P.v.R.; Otto, A.H.; Gauss, J.; Reichel, F.; Cremer, D. *J. Phys. Org. Chem.* 1993, **6**: 445.

(44) See, e.g., Redmon, L.T.; Purvis, G.D.; Bartlett, R.L. *J. Am. Chem. Soc.* 1974, **101**: 2856. Zirz, C.; Ahlrichs, R. *J. Chem. Phys.* 1981, **75**: 4980. Binkley, J.S.; Thorne, L.R. *J. Chem. Phys.* 1983, **79**: 2932. Brint, P.; Sangchakr, B.; Fowler, P.W. *J. Chem. Soc., Faraday Trans.* 2, 1989, **85**: 29, and references therein.

(45) Bühl, M.; Steinke, T.; Schleyer, P.v.R.; Boese, R. *Angew. Chem., Int. Ed. Engl.* 1991, **30**: 1160.

(46) Thorne, L.R.; Suenram, R.D.; Lovas, F.J. *J. Chem. Phys.* 1983, **78**: 167.

(47) The [5s4p1d/3s1p] basis is called basis II in ref 25.

(48) Nöth, H.; Wrackmeyer, B. *Chem. Ber.* 1974, **107**: 3070.

(49) Miertus, S.; Scrocco, E.; Tomasi, J. *J. Chem. Phys.* 1981, **55**: 117. Bonaccorsi, R.; Cimiraglia, R.; Tomasi, J. *J. Comput. Chem.* 1983, **4**: 567. Bonaccorsi, R .; Pala, P.; Tomasi, J. *J. Am. Chem. Soc.* 1984, **106**: 1945. Pascual-Ahuir, J.L.; Silla, E.; Tomasi, J.; Bonaccorsi, R. *J. Comput. Chem.* 1987, **8**: 778.

(50) Shore, S.G.; Parry, R.W. *J. Am. Chem. Soc.* 1955, **77**: 6084. Hughes, E.W. *J. Am. Chem. Soc.* 1956, **78**: 502. Lippert, E.L.; Lipscomb, W.N. *J. Am. Chem. Soc.* 1958, **80**: 503. Schleyer and coworkers, who have redetermined the X-ray structure of BH_3NH_3, give for the B–N bond length 1.564(6) Å.[45]

(51) See, e.g., Colquhoun, H.M.; Jones, G.; Maud, J.M.; Stoddart, J.F.; Williams, D.J. *J. Chem. Soc., Dalton Trans.* 1984, 63. Alston, D.R.; Stoddart, J.F.; Wolstenholme, J.B.; Allwood, B.L.; Williams, D.J. *Tetrahedron* 1985, **41**: 2923. Pears, D.A.; Shahriari-Zavareh, H.; Stoddart, J.F.; Crosby, J.; Allwood, B.L.; William, D.J. *Acta Crystallogr.* 1988, **C44**: 1101, 1106, 1112, 1118.

(52) See, e.g., Olah, G.A.; Rasul, G.; Heiliger, L.; Bausch, J.; Prakash, G.K.S. *J. Am. Chem. Soc.* 1992, **114**: 7737, and references therein.

(53) Kraus, C.A.; Callis, C.C. *J. Am. Chem. Soc.* 1923, **45**: 2624.

(54) Webster, J.R.; Jolly, W.L. *Inorg. Chem.* 1971, **10**: 877.

(55) Tobias, R.S. *Organomet. Chem. Rev.* 1966, **1**: 93.

(56) Edlund, U.; Arshadi, M.; Johnels, D. *J. Organomet.*

Chem. 1993, **456**: 57.

(57) See, e.g., Marquez, A.; Sanz, J.F. *J. Am. Chem. Soc.* 1992, **114**: 10019. Schleyer, P.v.R.; Kaupp, M.; Hampel, F.; Bremer, M.; Mislow, K. *J. Am. Chem. Soc.* 1992, **114**: 6791. Nguyen, K.A.; Gordon, M.S.; Wang, G.; Lambert, J.B. *Organometallics* 1991, **10**: 2798. Kudo, T.; Nagase, S. *J. Phys. Chem.* 1992, **96**: 9189. Nagase, S. *Angew. Chem.* 1989, **101**: 340.

(58) In principle, NMR chemical shift calculations should be possible with pseudopotential methods. However, with the existing ab initio programs for chemical shift calculations pseudopotentials cannot be used.

(59) Stromberg, A.; Gropen, O.; Wahlgren, U. *J. Comput. Chem.* 1983, **4**: 181.

(60) Dunning, T.H.; Hay, P.J. In *Methods in Electronic Structure Theory, Modern Theoretical Chemistry*; Schaefer, H.F., Ed.; Plenum: New York, 1977; Vol. 3, p. 1.

(61) For the corresponding TZ+P data, see Olsson, L.; Cremer, D. *Inorg. Chem.*, in press.

(62) Vilkov, L.V.; Mastryukov, V.S.; Sadova, N.I. *Determination of the Geometrical Structure of Free Molecules*; Mir Publishers: Moscow, 1983, and references therein. Wilkinson, G.R.; Wilson, M.K. *J. Chem. Phys.* 1956, **25**: 784. Beagley, B.; McAloon, K.; Freeman, J.M. *Acta Crystallogr.* 1974, **B30**: 444. Clark, H.C.; Furnival, S.G.; Kwon, J.T. *Can. J. Chem.* 1963, **41**: 2889. Fujii, H.; Kimura, M. *Bull. Chem. Soc. Jpn.* 1970, **44**: 2643.

(63) Smith, P.J. *Annu. Rep. NMR Spectrosc.* 1978, **8**: 291.

(64) Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* 1985, **16**: 73.

(65) Holecek, J.; Nadvornik, M.; Handlir, K.; Lycka, A. *J. Organomet. Chem.* 1983, **24**: 177. Nadvornik, M.; Holecek, J.; Handlir, K.; Lycka, A. *J. Organomet. Chem.* 1984, **275**: 43. Al-Allaf, T.A.K. *J. Organomet. Chem.* 1986, **337**: 177. Holecek, J.; Handlir, K.; Cerny, V.; Nadvornik, M.; Lycka, A. *Polyhedron* 1987, **6**: 1037.

(66) See, e.g., Tossell, J.A.; Lazzeretti, P. *J. Magn. Reson.* 1988, **80**: 39.

(67) Torocheshnikov, V.N.; Tupciauskas, A.P.; Sergeyev, N.M.; Ustynyuk, Y.A. *J. Organomet. Chem.* 1972, **35**: C25.