

Final Report

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MARIE CURIE ACTIONS

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“Nitroso Compounds”



One aim of the project was the synthesis and characterization of nitroso tetrel compounds, in particular nitroso silanes (R_3SiNO). These nitroso silanes possess an NO functionality which is directly bound to the silicon atom and which is responsible for the predicted low singlet-triplet energy gap ΔE_{S-T} . In the first phase of the project, comprehensive quantum chemical calculations (DFT, HF, B3LYP each at different levels of theory) on several model compounds R_3SiNO have been performed ($R=H, CH_3, NH_2, OH, F, Cl$) to guide the experimental work. Besides information on the geometry around the silicon atom ($dSi-N, dNO, wSiNO$) also information on spectroscopic properties was derived in dependence of the substituent. In addition, reaction enthalpies of the reaction between the NO radical and different silyl radicals $R_3Si\cdot$ have been calculated. The main findings can be summarized as follows:

The silicon-nitrogen bond lengths in all calculated nitroso silanes are much longer (1.807-1.919 Å depending on substituent, method and basis set) than in silylamines with average Si-N bond lengths of 1.70-1.75 Å. This is an indication that the Si-N bonds in nitroso silanes are much weaker than in silylamines. The NO bond lengths vary only slightly for different substituents within a basis set and method. A comparison of $dSi-N, dNO,$ and $wSiNO$ at the 6-311++g* level of theory is depicted in Fig. 1-3. For the determination of ΔE_{S-T} the lowest lying triplet states have been calculated. The geometries of these triplet states exhibit two surprising features. The Si-N bond lengths are significantly shorter (1.712-1.805 Å), and the SiNO angles are much wider (130.6-134.8°) than for the singlet species (114.0-116.9°). A comparison is depicted in 4 and 5. The ΔE_{S-T} was calculated 6.2 to 10.3 kcal/mol at the B3LYP 6-311++g* level of theory. Finally, reaction energies of NO with $R_3Si\cdot$ have been calculated. The results indicated an instantaneous formation of the nitrososilanes with ΔH_f ranging from -28 to -35 kcal/mol (B3LYP/6-311++g*). A reaction barrier cannot be found due to the radical nature of these reactions. These results made us very optimistic for the synthesis of these compounds in the laboratory, however, although several different synthetic routes have been followed (Fig. 6 and 7), nitroso silanes, germanes and stannanes could not be detected by any analytical method. It seems that these compounds are highly unstable and decompose or rearrange immediately after they have been formed.

The second goal of the project deals with structure determination by means of gas electron diffraction (GED). Originally, it was intended to characterize the nitroso compounds by this method. However, the inaccessibility of these substances forced us to turn our attention to other molecules with unusual bonding situations. The first molecule which was investigated in the course of this project was *tert*-butylsilanetriol, which bears three OH groups at the silicon center. This compound shows strong intermolecular interactions in the solid as well as in the liquid phase with other silanetriol molecules. Therefore, we became interested whether such interactions do also exist in the gas phase. Quantum chemical calculations predicted such interactions (acc. to Fig. 8) in the gas phase at 0 K. Nevertheless, the determination of the molecular structure in the gas phase unambiguously revealed the presence of free, isolated silanetriol molecules. The three Si-O bond lengths (1.640(1) Å, r_{hl} distance type) dominate the final radial distribution curve (Fig. 9). Such strongly polarized bonds are often described inadequately by quantum chemical calculations; therefore experiments such as gas electron diffraction can help to validate quantum chemical methods. Calculations yield quite different results for these Si-O bond lengths and depend on basis set and method (1.645 to 1.670 Å). Of the method/basis set combinations tested here, HF/6-31G* yields the closest agreement with the experimental value of this parameter (1.645 Å); the worst fit is predicted by MP2/6-31G*. This observation has also been reported in several other studies and originates from error cancellation for HF/6-31G* and insufficiencies of the double-zeta basis sets in connection with MP2. In contrast, for other bond lengths experimental (Si-C 1.879(3), C-C 1.540(2) Å) and computed values are in the same range (Table 1). The geometry around the silicon atom can be considered as approximately tetrahedral with

O-Si-O and C-Si-O angles of $107.7(3)^\circ$ and $111.2(2)^\circ$, which is in good agreement with computed values.

Another molecule of interest is BiPh₃ which may be used as starting material for the preparation of main group metal based OLEDs. However, for the fabrication of microelectronics and related high tech materials very often vapor deposition techniques are applied. It is obvious that for the final properties of the films (thickness, roughness, wettability, purity, homogeneity), the knowledge of the gas phase related processes is a substantial issue. For these processes, in turn, the knowledge of the molecular structure in the gas phase is of particular importance. As depicted in Fig. 10, the final radial distribution curve of BiPh₃ obtained by GED is dominated mainly by contributions of atomic distances involving bismuth which can be attributed to the large cross-scattering section of the bismuth atom. There is an interesting feature of this radial distribution curve at ca. 2.2 Å. A shoulder appears although there are no atomic distances present in this region. This behavior is an illustrative example of phase relativistic effects which occur when a heavy element such as bismuth is bonded to a lighter element such as carbon. The use of complex scattering factors nowadays employed in nearly every refinement procedure in GED consider these effects concomitant with an adjustment of the theoretical model to yield a double rather than a single peak. The interesting geometric parameters in BiPh₃ include $d_{\text{Bi-C}}$, $w_{\text{C-Bi-C}}$, and τ (torsion angle between least-square planes of the phenyl rings). When comparing the geometries of BiPh₃ obtained by RI-DFT and RI-MP2 with those obtained experimentally by GED, it can be concluded that RI-DFT performs better than RI-MP2 for this molecule at the employed level of theory. The Bi-C bond lengths of 2.278 Å (RI-DFT) are much closer to the experimental values (2.263(3) Å) than RI-MP2 (2.227 Å). A similar observation is made for the C-Bi-C angle where the experimentally derived parameter $94.7(9)^\circ$ matches better the RI-DFT (95.4°) rather than the RI-MP2 (92.0°) method. The torsion angles between the planes of the phenyl rings have been determined to $94(2)^\circ$. Also this torsion is better described by the RI-DFT (94.1°) method which is closer to the experimental values than RI-MP2 (92.7°).

The third topic which was investigated by means of GED deals with metallophilic interactions. Metallophilic interactions have been found in the solid state for several copper, silver and gold containing organometallic compounds. The reason for these interactions is not fully understood and it is still under debate whether packing effects in the solid state may be responsible for this phenomenon. In such cases, GED is able to exclude at least packing effects in such metallophilic interactions. For this purpose, we investigated a phosphorylide, $[(\text{CH}_3)_2\text{P}(\text{CH}_2)_2\text{Cu}]_2$, which exhibits metallophilic interactions between the copper atoms in the solid state and determined its molecular structure in the gas phase by GED. As depicted in Fig. 11, it can be clearly seen, that the radial distribution curve shows a Cu-Cu distance of 2.922(5) Å which is only slightly longer than the distance obtained in the solid state structure (2.849(1) Å). The copper atoms seem to exhibit an attractive interaction and the C-Cu-C angle is slightly bent showing a value of $177.1(3)^\circ$ which is a proof that packing effects cannot be made responsible for metallophilic interactions of $[(\text{CH}_3)_2\text{P}(\text{CH}_2)_2\text{Cu}]_2$.

In the end of the project Cl₃CSCN was investigated by GED. This compound is interesting due to its bonding situation at the thiocyanate moiety. The sulfur atom exhibits two different bond lengths to the neighboring carbon atoms (S-C1: 1.831(10) Å, S-C2: 1.713(10) Å). While S-C1 is probably longer due to negative hyperconjugation of $n \rightarrow \pi^*$ type caused by the equatorial chlorine atoms (C1-Cl4: 1.767(10) Å), S-C2 exhibits an additional shortening due to a delocalization of the π -electrons of the C-N triple bond. As a consequence, the C-N triple bond is lengthened (1.170(10) Å). In Fig. 12 the radial distribution curve is depicted which shows good agreement between the employed model and the experimental data.

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