The ^{13}C Chemical Shift of the *ipso* Carbon Atom in Phenyllithium

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Phenyllithium was labeled with ^6Li and ^{13}C at the *ipso* carbon atom, and the tetramer was measured by solid-state NMR. The chemical shift tensor data were obtained by a moment analysis of the spinning side bands and were compared with the results obtained by calculations with the IGLO method. Although no splitting by dipolar spin coupling to ^6Li was found the very good agreement between IGLO predictions and experimental results allowed alignment of the tensor axis to the molecular frame and interpretation of the data. The large deshielding of the isotropic chemical shift is mainly due to a decrease of the ΔE term in σ^p.

Phenyllithium plays a role in organometallic chemistry, both as an important reagent for preparative chemistry[1] and as a model compound for quantum mechanical calculations[2]. Numerous papers were published on its preparation[3], reaction[4], and structure[5]. UV spectra were reported[6], ebullioscopic measurements have been performed[7], and several crystal structures of complexes with different ligands forming tetramers, dimers, and monomers are known[8–10]. Similarly, many NMR studies were reported both in the liquid[11–21] and the solid state[22–24]. Astonishingly, however, is the lack of understanding of the ^{13}C-chemical shift data with respect of the *ipso* carbon atom and the C–Li bond. Normally, if in an aliphatic compound H is replaced by Li, the corresponding carbon signal is shifted to lower frequencies. This is usually interpreted in terms of the higher electron density at the anionic carbon atom. On replacement of one hydrogen atom by lithium in benzene, however, in phenyllithium the signal of *ipso* carbon atom is shifted to higher frequencies ($\Delta\delta \approx 58$ ppm). Several interpretations have been forwarded for this effect. Grant and Fraenkel[21] were the first to argue that a lower averaged excitation energy would be responsible for a larger σ^p term and therefore yielding the high frequency shift. Seebach and coworkers[19] distinguished on a qualitative basis between a σ and a π electron density at the metalated carbon atom and proposed enhanced σ density vs lowered π density. Similar arguments were put forward by Schleyer and coworkers[17].

Understanding ^{13}C-chemical shift data on a molecular level is only possible, when the chemical shift tensor and its alignment with respect to the molecular frame are known. This approach has been amply forwarded by the research group of Grant, who succeeded in measuring the chemical shift tensors of many basic molecules, such as acetylene, benzene, ethylene, and others[25–27]. We have therefore set up a project to measure the chemical shift tensor of the *ipso* carbon in phenyllithium in order to see whether a congruence with the theoretical predictions by the IGLO method can be obtained. This should lead to a more profound interpretation of the chemical shift in solution. Initially it was hoped that alignment of the principal axis of the chemical shift tensor with respect to the molecular frame would be achievable by an observation of the dipolar ^6Li,^{13}C spin coupling.

Results and Discussion

The measurement of the ^{13}C-chemical shift tensor still requires labeled compounds in most cases. We therefore developed a short and efficient synthesis of [1-^{13}C]bromobenzene which furnished this compound in seven steps and 6% overall yield starting from $Ba^{13}CO_3$[28]. From the labeled bromobenzene phenyllithium was prepared under argon by halogen-metal exchange with [^6Li]-*n*-butyllithium in benzene. The pyrophoric material was transferred to a 7-mm rotor for solid-state NMR which was tightly closed and kept under argon. The phenyllithium prepared by this procedure is known to be mainly the tetrameric material, from which a crystal structure exists[10]. However, the compound can loose ether to form a polymer, the solid state NMR spectrum of which is not different[22,23]. It is therefore assumed that if parts of polymeric material are present, these may have a similar relevant structure. The solid-state NMR spectra were recorded with a 400-MHz spectrometer both as static spectra and at various spinning speeds between 500 and 4000 Hz. In additional experiments the sample was measured with spinning, however using the TOSS sequence[29] to suppress the spinning side bands. A typical spectrum with the side band pattern is shown in Figure 1, in which also some unavoidable impurities due to the preparation and transfer to the solid-state rotor can be seen.

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These impurities, however, could all be identified by a comparison with the corresponding TOSS spectra and the high-resolution spectra in solution.

Figure 1. CPMAS spectra of [^{6}Li, 1-^{13}C]phenyllithium with a spinning speed of 1500 Hz. The isotropic chemical shift at $\delta = 186$ is marked with an asterisk, sharp signals stemming from benzene and butylbenzene are indicated, an impurity with broad signals between $\delta = 250$ and 70, probably stemming from phenolate is indicated by a dotted line

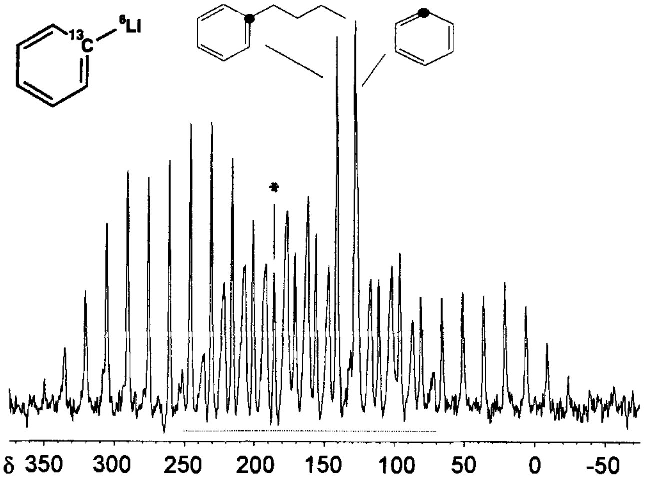


Figure 1 immediately reveals that the chemical shift tensor reaches from about 330 to −20 ppm. Unfortunately, none of our spectra revealed a pattern stemming from dipolar coupling between ^{6}Li and ^{13}C which would have allowed an alignment of the tensor axis to the molecular frame based on experimental data. The line width of the static spectrum apparently was too large to allow an expected splitting of about 360 Hz as calculated from the known C−Li distance in the tetramer. The line width in our static spectra is probably also due to the tetrameric structure where the carbon atoms of different phenyllithium moieties are dipolarly coupled to each other.

The moment analysis of our CPMAS spectra[30] is based on four spectra with spinning speeds of 1500, 3000, 3500, and 4000 Hz. Up to 12 side bands for each spectrum were evaluated, and the overall agreement between the different spectra used was good. The linewidth of the individual side bands was in the order of 120 Hz, which again rendered a resolution of the dipolar coupling unlikely. From these calculations the experimental results in Table 1 (first row) are compiled.

In the other rows of Table 1 the theoretical values as obtained from IGLO calculations are given not only for the tetramer but also for the monomer and dimer with and without complexation with water molecules. For all calculations we used structures optimized at the Hartree Fock level with a 3-21G basis set; the structures were constrained to D_{2d}, C_{2v}, and D_{2h} symmetry, respectively. For the tetramer the crystal structure of the tetrameric phenyllithium served as template for our geometry optimization. We used four water molecules to model the diethyl ether solvation present in the crystal structure. Two different basis sets were used for the IGLO calculations. Monomer and dimer were calculated with a larger one, II′, consisting of a TZP quality basis set on carbon and lithium and a DZ basis set on hydrogen[30−32]. The smaller one used for the tetramer is a DZ basis set, augmented with diffuse functions on the *ipso* carbon. The calculated shieldings σ were transformed into TMS-based chemical shifts δ using the IGLO shielding and the known gas-phase chemical shift of methane ($\delta = -2.3$). Earlier calculations were performed for monomeric phenyllithium and other organolithium compounds[33].

Table 1. Comparison of theoretical and experimental data of [^{6}Li, 1-^{13}C]Phenyllithium, obtained by different methods

Method	δ_{11}	δ_{22}	δ_{33}	δ_{iso}
solid-state NMR	327.1 ± 10	248.2 ± 10	−18.4 ± 10	185.6
IGLO: monomer	312	250	-24	179
IGLO: monomer complexed with one H_2O	330	252	-25	186
IGLO: dimer	308	240	-29	173
IGLO: dimer, complexed with 2 H_2O	333	248	-32	183
IGLO tetramer, complexed with 4 H_2O	334	254	−30	186
solution NMR[17]				
monomer				196.7
dimer				188.5
tetramer				176.2

As seen from Table 1, there is a very good agreement between the tensor components obtained by experiment and by theoretical calculation, also the isotropic values are well matched. This leads to the conclusion that also the alignment of the tensor axes, which can be taken from the IGLO calculation but not from our experiment due to the lack of an observable dipolar splitting, should be of high confidence. Otherwise, the agreement between the three components should not be as perfect. As can be seen from Table 1 there is some influence of the degree of oligomerization and solvation on the calculated data, but this influence is not very large, which is in line with results found for other organolithium compounds[31]. Therefore, one might attempt an interpretation of the experimental data using the calculated orientation of the tensor axes. Additionally, the calculated MO contributions to the tensor components can be used as a helpful tool for the qualitative interpretation of the trends observed.

We discuss our data in comparison with the orientation of the chemical shift tensor in benzene[26], which is shown in Figure 2. Here the most shielded direction (corresponding to δ_{33}) is perpendicular to the aromatic ring. A magnetic field along this direction cannot induce any interactions with the π^* orbitals; thus, the shielding (of 9 ppm) is comparable to an aliphatic system. The other components are distinctly deshielded, since a magnetic field in the plane of the aromatic ring induces deshielding interactions with the π^* orbitals. The deshielding contribution of the CH bond is large for a magnetic field perpendicular and zero for a field parallel to it. Nevertheless, the mostly deshielded direction (corresponding to δ_{11}) is the one parallel to the CH bond, since the contributions of the CC σ bonds overcompensate the effect of the CH contribution.

Figure 2. Orientation and values of the chemical shift tensor in benzene

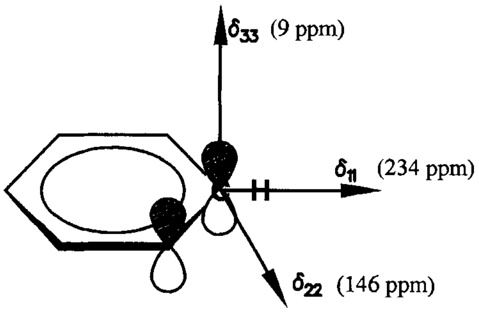
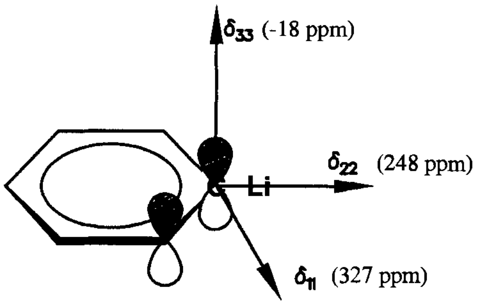


Figure 3. Orientation and values of the chemical shift tensor of the *ipso* carbon atom in phenyllithium



Very interesting are the changes induced by the lithium atom in phenyllithium as seen from Figure 3. δ_{33} still corresponds to the direction perpendicular to the aromatic plane, however shielded by about 40 ppm. This reflects the electron density for the σ electrons at the anionic carbon atom as known for aliphatic lithium compounds and as proposed by Seebach for phenyllithium[19]. The directions corresponding to δ_{11} and δ_{22} have interchanged, with the mostly deshielded direction now being perpendicular to the CLi bond direction. The shielding along this axis is about 180 ppm smaller than the corresponding value in benzene. For the direction nearly parallel to the CLi bond the deshielding as compared to benzene is only about 20 ppm. That the largest changes occur for the direction perpendicular to the CLi bond can be understood quite easily. Within an unsaturated (or aromatic) system like the one discussed here, it is a magnetic field in the molecular plane perpendicular to a given bond which induces the largest deshielding contributions for this bond. Although, of course, the electronic structure of the whole system changes on going from benzene to phenyllithium, the most important change is the formal exchange of a CH and a CLi bond. This might be considered as an oversimplification, however this crude model can be justified since the calculated data for the monomeric and tetrameric material do not differ principally[34]. It is thus the contributions of these different bonds which differ mostly, and hence it is the direction perpendicular to these bonds (in the molecular plane) which show the largest differences of the shielding. The contribution of a CLi is more deshielding than that of a CH bond, since ΔE which occurs as $1/\Delta E$ in the expression of σ^P is smaller. Additionally, the $1/r^3$ value is most probably larger for a CLi bond than for a CH bond. Both effects result in a larger σ^P and thus in a larger deshielding. A situation comparable to the one described above is expected for the "free" anion. Similar orientations of the chemical shift tensors were recently found for azines[35,36], phospholid anions[37], and carbenes[38] which bear also free electron pairs at the corresponding atom.

Conclusion

We have shown in this work that the chemical shift tensor of the *ipso* atom in phenyllithium as calculated by the IGLO method is in very good agreement with experimentally determined values. Compared with benzene an interchange of the indices of the tensor components takes place. The increased shielding occurring for the out-of-plane direction is overcompensated by a large deshielding in plane perpendicular to the CLi bond mainly due to the decrease of ΔE yielding a larger contribution to σ^P. The overall deshielding of the isotropic value by 54 ppm in phenyllithium is thus explained.

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Experimental

[^{6}Li,1-^{13}C]Phenyllithium: In a 10-ml nitrogen flask with septum 1.0 g (6.33 mmol) of [1-^{13}C]bromobenzene was dissolved in 3 ml of dry benzene. Under argon 4.3 ml of a 1.47-mol [^{6}Li]-*n*BuLi solution (*n*-hexane) was slowly added. After stirring overnight the white residue was filtered off using a frit, washed twice with pentane, and dried in high vacuum. This material was placed in a 7-mm solid-state NMR rotor by using a glove box under argon.

^{13}C-NMR solid-state measurements were performed with a Bruker wide bore AM-400 spectrometer at the University Gießen using a 7-mm ^{1}H,^{13}C dual MAS probe head. Prior to the measurement the magic angle was adjusted by means of glycine. CP/MAS spectra were typically recorded by using a relaxation delay of 10 s, a ^{1}H 90° pulse width of 7 μs and a contact time of 5 ms. The fids were recorded on 8 k data points for 128 scans and processed with an exponential window by employing a line broadening of 50–100 Hz.

Ab initio calculations were performed on a Silicon Graphics workstation (Personal Iris) using the TURBOMOLE[39] and DIGLO[40] programs.

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