Solid-State ^{13}C-NMR Spectroscopy, 3[◇]

Solid-State ^{13}C-NMR-Spectroscopic Investigations of α-(Dimethylamino)benzyllithium Complexes

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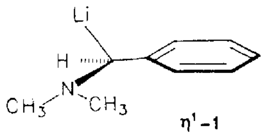
α-(Dimethylamino)benzyllithium (**1a**) and its complexes, **1b**–**f**, have been characterized by their solid-state ^{13}C-NMR spectra. The spectra are comparable to those recorded in solution and can be used to reveal the structures of the different solvates of the title compound.

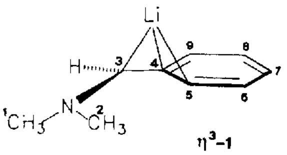
The stereoselective reactions of organolithium compounds can only be understood if their detailed structure is known. Unfortunately, the constitutional elucidation of metallated reagents is difficult to achieve. NMR-studies in *solution* are complicated by the fact that fast dynamic equilibria can exist between several species varying in their aggregation, coordination, solvation, complex formation etc., and only averaged spectra can be obtained. *Solid-state* structures can be determined by X-ray investigations only if crystalline material is available. It is, however, very often impossible to isolate lithiated molecules in crystalline form; in addition, the isolated compounds may differ from those in solution. In an attempt to fill this gap and obtain the information needed, we measured the solid state ^{13}C-NMR spectra of the powders which precipitate during metallation or which remain after evaporation of the solvent.

We selected α-(dimethylamino)benzyllithium (**1a**) as a test molecule. This compound has already been studied intensively[1–3]. MNDO calculations predict that **1a** should possess a trihapto structure, η^3-**1**, even if complexation with a unidentate or bidentate ligand is present. The coordination of the Li atom should occur, not only with the benzylic C atom, but also with the *ipso*- and one of the *ortho*-C atoms of the phenyl ring[1]. A monohapto structure, η^1-**1**, with a single contact of the Li atom to the benzylic C atom should be favored only in the case of tridentate ligands. These predictions were confirmed by ^{1}H-, ^{13}C-NMR and ^{1}H-, ^{6}Li-HOESY spectra of α-(dimethylamino)benzyllithium in the presence of different complex-forming donor molecules. In addition, a fast temperature-dependent equilibrium of the η^1 and η^3 structure in THF, **1c**, has been observed for the first time. The thermodynamic and kinetic data for this equilibration were evaluated from variations of the chemical shifts and line widths of the averaged signals in the ^{1}H- and ^{13}C-NMR spectra. At room temperature, η^3 coordination dominates[1]. The level of aggregation of **1a** and its derivatives, **1b**–**f**, also depends on the conditions. Dissolved **1c** (THF, 165 K) is monomeric[1,2], whilst the crystalline ether adduct, **1b**, is dimeric[3]. From the structure of **1b**, determined by Boche[3], it is also concluded, that in the dimer of **1b**, no contact with the *ipso*- or *ortho*-C atoms, or at least, only a very weak one, exists (no η^3 coordination).

In a continuation of our studies on the application of solid-state ^{13}C-NMR spectroscopy we used this method to reveal the structure of α-(dimethylamino)benzyllithium (**1a**) and its complexes containing various ligands, namely diethyl ether (Et$_2$O; **1b**), tetrahydrofuran (THF; **1c**), dimethoxyethane (DME; **1d**), pentamethyldiethylenetriamine (PMDTA; **1e**), and tetramethylenediamine (TMEDA; **1f**). In addition, we investigated the possibility of "freezing out" the fast equilibrium by the isolation of one or both isomers in the solid state. The parent compound, **1a**, was prepared by the "stannane route"[1]. The solvents, which functioned as ligands, were either already present during the transmetallation (**1d**, **e**), or were added after the isolation of **1a** (or **1c**). This procedure did not work with **1b** and **1e**. In these cases Boche's variant[3] was applied.



η^1-**1**



η^3-**1**

The observed ^{13}C chemical shifts of **1a**–**f** are summarized in Table 1 and Figure 1. The assignments of the signals are mainly based on experiences with the solid-state ^{13}C-NMR spectrum of benzyllithium itself[4], and the solution spectra of **1** under different conditions. In addition, the two signals for the non-identical *ortho*-C atoms and the single signal for the *para*-C atom were identified by the solid-state NMR pulse sequence, NQS[5]. The α-(dimethylamino)-

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[◇] Part 2: G. Maier, H.-O. Kalinowski, C. Weber, M. Henrich, *Magn. Reson. Chem.* **1995**, *33*, 290–296.

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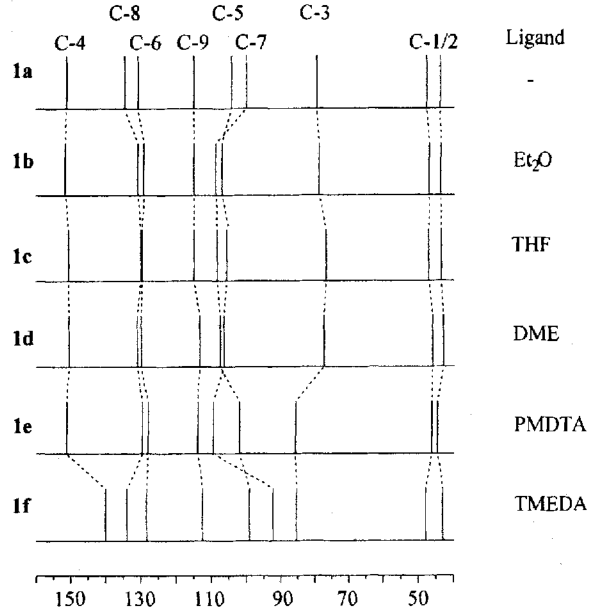
benzyllithium compounds were therefore deuterated in one *ortho* position of the phenyl ring. This was achieved by lithiation of benzyldimethylamine, deprotonation with *n*-butyllithium to give 2-lithiobenzyldimethylamine[6] and quenching with D_2O, followed by the routine treatment of the 2-deuteriobenzyldimethylamine ("stannane route"). By comparison of the NQS spectrum of **[2-D$_1$]1a** (deuteration in C-5/9 position in formula **1**), which shows only C atoms not bearing an H atom, with the spectrum of non-deuterated **1a**, the signals of the *ortho*- and *para*-C atoms could be assigned unambiguously (Figure 2). The fact that the signals of the dimethylamino group can be seen in the NQS spectrum is probably due to the rapid rotation of the methyl groups.

Table 1. ^{13}C chemical shifts (δ values relative to TMS) of the α-(dimethylamino)benzyllithium species **1a–f**; solution NMR data in parentheses

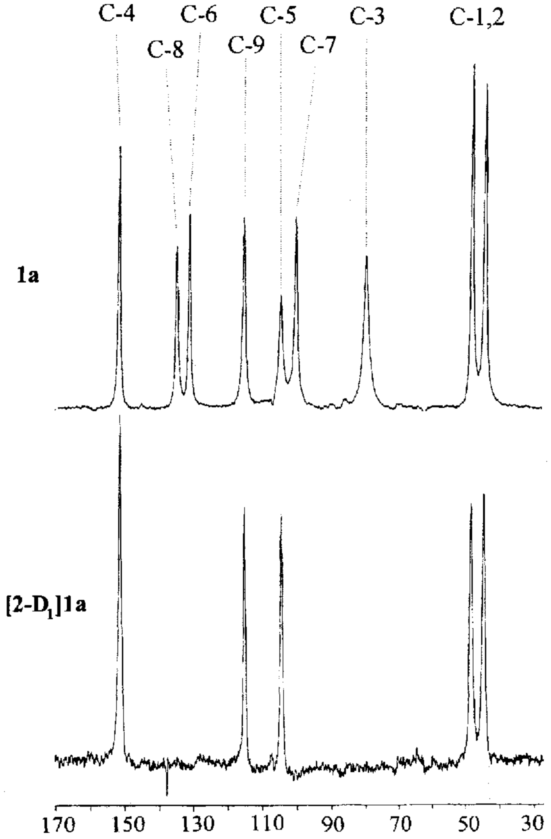
	Ligand	C-1/C-2	C-3	C-4	C-5/C-9	C-6/C-8	C-7	Others
1a	—	43.8/47.6	79.5	151.2	104.2/114.9	130.7/134.5	99.9	—
1b	Et_2O	43.7/47.0	78.8	151.6	107.0/114.9	129.1/130.8	108.7	14.5/65.9
1c	THF	43.5/47.0	76.7	150.7	105.6/114.9	129.6/130.0	108.3	25.6/68.7
		(47.3	84.3	149.8	105.4/114.2	128.7/130.6	103.4)	
1d	DME	42.9/45.9	77.3	150.5	106.4/113.3	129.9/131.0	107.5	58.9/68.6
1e	PMDTA	44.5/46.1	85.7	151.2	109.4/113.8	128.0/129.5	101.9	44.5/46.1/ca. 58
		(48.4	85.3	152.2	110.2/114,3	128.8/130.0	104.7)	
1f	TMEDA	43.1/48.0	85.4	140.1	92.4/112.6	128.4/133.9	99.1	ca. 44/ca. 56/ca. 58
		(46.2	85.1	142.0	93.9/113.9	129.5/132.7	100.8)	

Figure 1. Comparison of the ^{13}C chemical shifts (δ values relative to TMS) of the α-(dimethylamino)benzyllithium species **1a–f**



As shown in Figure 1, the ^{13}C chemical shifts of the THF complex, **1c**, are very similar to those of the η^3-**1a** species obtained in THF solution (presence of η^3-**1c**) at room temperature. This is especially true of the *ipso*-, *ortho*- and *meta*-C atoms and indicates that the same η^3 coordination also exists in the solid state. This is in accordance with the observation that at room temperature, at which the solid was prepared, the η^3 structure is also preferred in solution.

Figure 2. Comparison of the ^{13}C-NMR spectrum of undeuterated α-(dimethylamino)benzyllithium **1a** (top) with the NQS spectrum of *ortho*-monodeuterated **[2-D$_1$]1a** (bottom)



All attempts to isolate the second η^1 isomer by preparation of the solid at lower temperatures, at which it predominates in solution, failed. In all cases a solid spectroscopically identical to η^3-**1a** was obtained. Obviously the η^3 species has a lower solubility and always precipitates first during the evaporation of the solvent.

In all spectra of the solids, two signals for the methyl groups were obtained. The rotation of the dimethylamino group, which is fast in solution on the NMR time-scale, is frozen out in the solid state. Remarkably, for unknown reasons[*] the signals for the methyl groups in the solid state are shifted to higher field compared to the averaged signals in solution.

A strange temperature-dependent phenomenon could be observed in the case of the diethyl ether adduct, **1b**. In an attempt to prepare **1b**, α-(dimethylamino)benzyltri-*n*-butylstannane was treated with *n*-butyllithium in hexane. Subsequent addition of diethyl ether resulted in an orange solution, from which no crystals separated. Upon evaporation of the solvent at room temperature, a yellow powder was obtained. This compound did not show the signals for the

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[*] One referee raised the question whether the dimethylamino group is eventually located above the aromatic ring. In the monomeric compound this is impossible because of steric reasons. But interestingly enough, the inspection of the dimeric **1b** solid-state structure reveals that one monomeric unit places an *N*-methyl group above the aromatic ring of the second monomer subunit, and vice versa. This arrangement could, at least partially, explain the observed high-field shift.

ether adduct, **1b**. Instead, the spectrum was practically identical with that of uncomplexed **1a**. Surprisingly, three additional absorptions at δ = 101.8, 133.4 and 150.9 (signals for C-7, C-6,8 and C-4) could be measured. When the ether was evaporated at −30°C, these three additional peaks were even more intense. If the other peaks of the new ether-free compound overlap with those of pure **1a**, then it is possible that as a result of this process, a second solvent-free α-(dimethylamino)benzyllithium compound, **1a'**, may be isolated. It may be assumed that in an ether solution an equilibrium exists between **1a** and **1b**. At room temperature the evaporation of the solvent yields, preferentially, **1a**; if the same is done at −30°C then the yield of the species, **1a'**, which has a different aggregation or a crystal modification relative to **1a**, is enriched.

The comparison of the ^{13}C chemical shifts of solid-state **1a**−**f** with the spectra recorded in solution reveals some interesting features of the structures of these compounds. In particular, the chemical shifts of the benzylic and *para*-C atoms allow conclusions to be drawn about the ionic character of **1a**−**f**. If the C−Li bond becomes more ionic, then the signal for the *para*-C atom is shifted to higher field by a resonance effect; in contrast, the signal for the benzylic C atom is shifted to lower field as a result of hybridization. This change in bonding occurs in the transition from the solid state of the ether complexes to the THF solution [e.g. **1c**: C-7: δ = 108.3 (solid), 103.4 (solution); C-3: δ = 76.7 (solid), 84.3 (solution)]. In the solid state the lithium contact to C-3 seems to be tighter, i.e. a less ionic bond. This effect is less pronounced within the nitrogen complexes, where the match between the solution and solid-state spectra is nearly perfect.

All of the species, **1a**−**f**, must, however, in principle be regarded as η^3 species, independent of these details. In particular, this can be deduced from the field shifts of the *ortho*-C atoms. In all of the compounds studied, the signals for the two *ortho*-C atoms are separated. The signal of one *ortho*-C atoms has practically the same position throughout the whole series whilst that of the other *ortho*-C atom, with the lower δ value (high-field shift), covers a relatively large range. This latter *ortho*-C atom is coordinated with the Li atom and the contact causes a high-field shift, which is observed[1]. An additional proof of this assignment is the observation that this high-field signal is always broadened, due to coupling with the nearly quadrupolar ^{7}Li atom. Similarly, the signal of the benzylic C is also broadened.

Inspection of Table 2 shows that the ^{13}C chemical-shift differences between the two signals for the *ortho*-C atoms in **1a**−**f** are quite different. This may well reflect the varying extent of the contact between the Li and one of the *ortho*-C atoms, much better than the values obtained in solution, since no $\eta^1 \rightleftharpoons \eta^3$ equilibrium is expected in the solid state. It can be assumed that the strength of the η^3 coordination parallels the observed "limiting" $\Delta\delta$ values if the shift difference ($\Delta\delta$ = 4.4 ppm) of the PMTDTA complex, **1e**, is taken as a reference. As mentioned previously, the form of this adduct has been calculated and proved to adopt preferentially, in solution, an η^1 structure[1]. The observed non-equivalence of the two *ortho*-C atoms in **1e** originates mainly from the partial double-bond character of the bond between the *ipso*- and the benzylic C atom (the barrier of rotation for **1c** is 15.2 kcal/mol[1]). Since none of the signals for the *ortho*-C atoms in the solid-state spectrum of **1e** is broadened, it is further shown that there is no Li coordination to one of the *ortho* positions as a consequence of complexation to the tridentate ligand. In all the other complexes, with stronger contacts to the Li ion, the shift differences must therefore be larger; this is, indeed, observed to be the case.

Table 2. ^{13}C chemical shift differences ($\Delta\delta$) of the two signals for the *ortho*-C atoms in **1a**−**f**

	Ligand	$\Delta\delta$(*ortho*-C)
1f	TMEDA	20.3
1a	—	10.7
1c	THF	9.3
1b	Et_2O	7.9
1d	DME	6.7
1e	PMDTA	4.4

Very interesting are the values of the ether adduct **1b** which was obtained by exactly the same procedure as the dimer used for the X-ray structure determination[3]. Although in this solid-state structure no strong contact between the lithium and the aromatic carbon atoms could be detected [shortest distances between the lithium and the *ipso*- (C-4) and *ortho*-C atom (C-5) = 270−285 pm, i.e. definitely larger than the widely accepted border value of 250 pm], a remarkable shift difference of 8 ppm and a clear broadening of the high-field *ortho* signal for C-5 in **1b** was observed. The Li−C distance in π-complexed lithium compounds is thus possibly larger than the border value mentioned above for a normal C−Li contact.

The largest $\Delta\delta$ value, the most remarkable high-field shift for the *ipso*-C atom and the best agreement between the solid-state and solution spectra are found for the TMEDA complex, **1f**, which seems to be the most likely compound to have an η^3 structure. The strong interaction between the Li atom and the ligands obviously makes this structure rather inflexible. The solution and solid-state structures are therefore very similar.

The total effect observed in the experimental data is the sum of several factors, e.g. field, inductive, resonance, hybridization and packing effects, which cannot be distinguished easily. In particular, the solid-state spectra cannot be used to differentiate between η^3 coordination in a monomer or a dimer. If the powders of **1a**−**d** were dimers (as shown by X-ray structure determination for at least **1b**[3]), the lithium contact responsible for the observed ^{13}C chemical shifts would possibly be caused not only by coordination within one of the two components of the dimer, but by intermolecular contacts between the Li ion of one unit and the carbon atoms of the other.

Conclusion

Solid-state ^{13}C-NMR spectra may be helpful in obtaining information about the structure of organolithium compounds, especially in those cases where crystalline samples cannot be prepared. Although rapid equilibria exist in solution, only the least soluble species may be obtained by evaporation of the solvent. The investigations carried out with the lithiated *N*,*N*-dimethylbenzylamine **1a–f**, complexed with various ethers or amines, therefore demonstrate that the structural information which can be drawn from solution and solid-state ^{13}C-NMR spectra complement each other well.

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Experimental Section

NMR Spectra: The solid-state ^{13}C-NMR spectra were run on a Bruker AM 400 WB spectrometer with a double-bearing probehead at 100.6 MHz under MAS/CP conditions with the pulse sequence TOSS[7] at a rotation rate of 4.500 Hz with ^{1}H decoupling. For each spectrum about 2000 free-induction decays were taken with 8 K data points. The contact time for cross-polarization was 50 ms. For the NQS spectra a 50 µs dephasing delay was used. The spectra was referred to tetrakis(trimethylsilyl)silane ($\delta = 2.7$)[8].

Preparation of α-(Dimethylamino)benzyllithium (**1a**) *and Its Complexes* **1b–f**: All manipulations were carried out in preheated glassware under inert gas. All reagents and solvents were distilled before use. The lithium salts were either precipitated during transmetallation or were isolated after evaporation of the solvent. All compounds were very sensitive to air and moisture. **1a**: ref.[1], yellow powder; **1b**: ref.[3], orange crystals; **1c**: ref.[1], yellow powder; **1d**: according to ref.[1], yellow powder; **1e**: ref.[1], orange powder; **1f**: ref.[3], red crystals.

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