[α-(Dimethylamino)benzyllithium–Diethyl Ether]$_2$, (*S*)-α-(Methylpivaloylamino)benzyllithium – (–)-Sparteine, and [3-Iodo-2-lithio-1-methylindole – 2 Tetrahydrofuran]$_2$: Crystal Structure Investigations of α-Lithiated Amines

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Received March 3, 1993

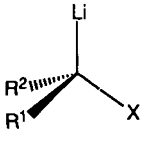
Key Words: α-Lithiated amines / Carbenoids

In order to determine whether α-metalated (lithiated) amines are carbenoids, as are α-lithiated halides and ethers, we have determined the crystal structures of the title compounds. In [α-(dimethylamino)benzyllithium–diethyl ether]$_2$ ([**9** · OEt$_2$]$_2$) lithium bridges the anionic carbon and the nitrogen atom which corresponds to the most stable calculated model structure of LiCH$_2$NH$_2$. The C–N bond is only slightly (≈ 3 pm) elongated (compared to the neutral species). If one of the *N*-methyl groups in [**9** · OEt$_2$]$_2$ is replaced by a pivaloyl group as in (*S*)-α-(methylpivaloylamino)benzyllithium – (–)-sparteine (**10** · sparteine), a five-membered ring chelate is formed with Li being bound to the benzylic carbon atom and the oxygen atom of the pivaloyl group. In agreement with model calculations avoidance of the bridged structure as in [**9** · OEt$_2$]$_2$ is compensated energetically by the chelate. Again a very small C–N bond elongation (≈ 3 pm) is observed. In [3-iodo-2-lithio-1-methylindole – 2 THF]$_2$ ([**12** · 2 THF]$_2$) lithium again does not bridge to the indole nitrogen atom because it is a weak donor. The C–N bond length to the anionic C atom is slightly longer (2 – 3 pm) than in the non-lithiated compound. Other α-lithiated amines, which have been published, although not analyzed so far under this particular aspect, show also a marginal C–N bond lengthening. However, since α-lithiated amines – in contrast to α-lithiated halides and ethers – until now have not been reported in the literature to react with nucleophiles RLi, there is no need to include them into the group of the above mentioned carbenoids – at least not to date.

I. Introduction

The knowledge of structures and reactivities (selectivities) of organolithium compounds has increased strongly within the last decade. This is especially the case with acceptor-substituted organolithium compounds bearing typical acceptor substituents (see Scheme 1).

Scheme 1. Acceptor-substituted organolithium compounds; X = acceptor substituent



- Typical acceptor substituents:

  X = C(O)R, SO$_2$R, S(O)(NR)R, S(O)R, SR, SiR$_3$, CN, NO$_2$, C(N-NR)R, NC, P(O)(OR)$_2$, etc.

- Carbenoids

  X = F, Cl, Br, I, OR

Seebach[1] and Williard[2] have summarized the results on enolates. A review of lithium sulfones, sulfoximides, sulfoxides, thioethers, dithianes, nitriles, nitro compounds, and hydrazones has been published by us[3]. Undoubtedly, all of the compounds contain acceptor substituents which are known to stabilize effectively a negative charge[4]. One common structural feature of these "carbanions" is the *shortened* C–X bond in the lithiated compound. An example is given in Scheme 2: sulfones **1** have a C–S bond length of 180.6 pm (mean value) while it is 164.1 pm in the lithiated benzyl phenyl sulfone **2**.

A completely different situation arises in the case of *carbenoids* as we have shown recently[5–7]. Thus, the crystal structure determination of the first "classical" carbenoid **4** · 2 THF · TMEDA discloses a length of the C–Cl bond of 185.5 pm which is ca. 12 pm *longer* than the mean value in vinyl chlorides **3** (172.9 pm)[5]. Furthermore, X-ray diffraction studies of four α-lithiated ethers[6], their reactions with nucleophiles RLi, the downfield chemical shifts of the signals of the carbenoid ^{13}C carbon atoms, and IGLO calculations which confirm these downfield shifts[7] demonstrate quite clearly that α-lithiated ethers are carbenoids, too. The C–O bond length in the carbenoid [**6** · O*i*Pr$_2$]$_2$ (147.0 pm) and the bond lengths in non-lithiated benzofurans **5** (mean value 138.5 pm) illustrate the bond *lengthening*.

How is the situation with X = NR$_2$, that is in the case of α-lithiated amines? In the following we report on the X-ray structures of the title compounds and compare them with the carbenoid structures of α-lithiated ethers and the α-lithiated halide **4** · 2 THF · TMEDA. The importance of α-lithiated amines in synthesis, especially in stereoselective reactions, requires a brief literature review first[8]. α-Lithiated amines are intimately related to what has originally been called "dipole-stabilized" carbanions[9,10]. Other publications deal with amine-substituted allyl-[11] and benzyllithium species[12], lithium compounds with an amino and other acceptor

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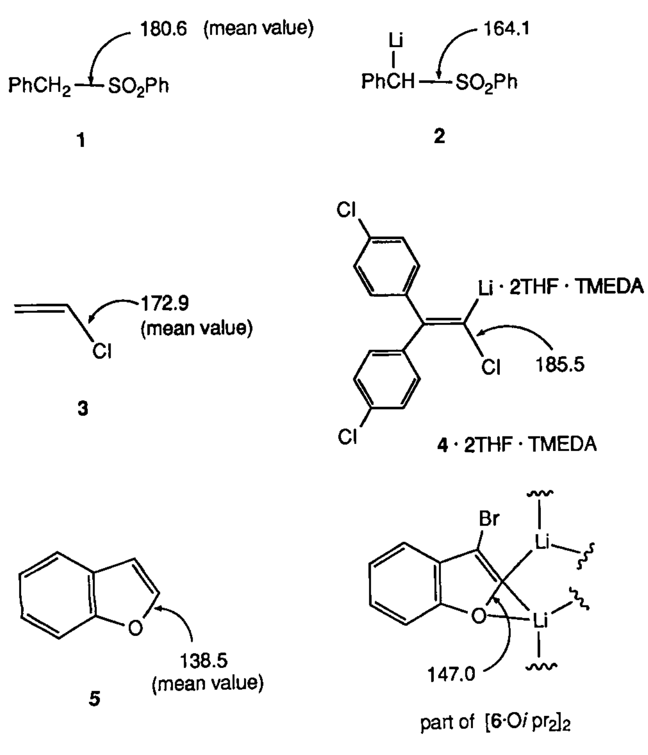
Scheme 2. Bond lengths [pm] in "carbanions" and carbenoids



substituents at the same carbon atom[13], BF_3-complexed amine-substituted organolithium reagents[14], amine-substituted alkyllithium compounds[15], α-lithiated pyrroles, and indoles[16].

II. Solid-State Structures of α-Lithiated Amines

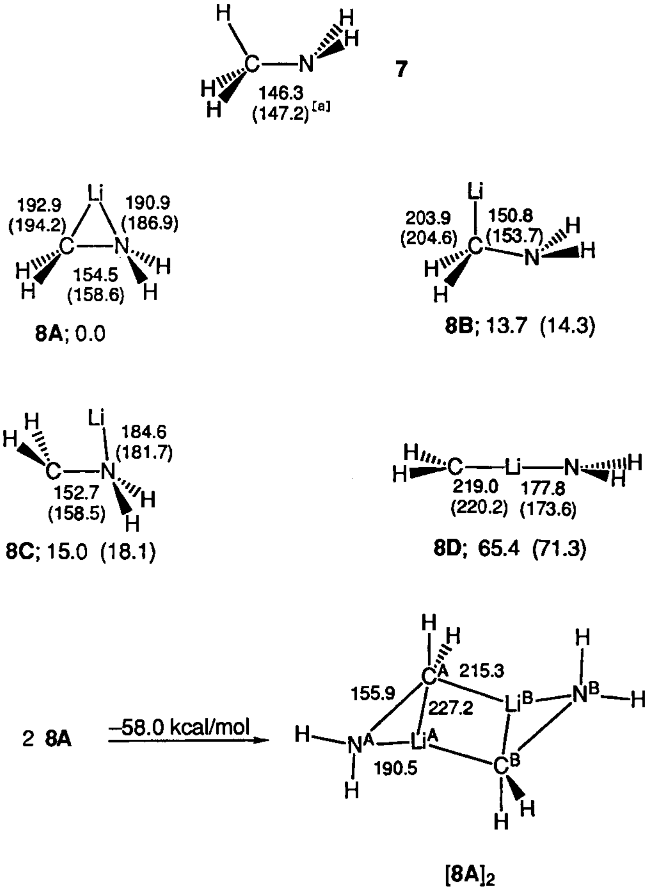
1. Model Calculations

Structural investigations of amine-substituted organo*lithium* compounds especially under the aspect as outlined in the introduction are not available yet. What structural type does one expect? The first model calculations have been performed by Clark, Schleyer, Houk, and Rondan[17]. In Scheme 3 we summarize our MP2/6-311++G(d,p)//MP2/6-311++G(d,p)+ZPE calculations together with the earlier results (in parentheses) which have been performed on a smaller basis [MP2/6-31G(d)//3-21G].

The most stable calculated isomer of $LiCH_2NH_2$ is **8A** with the lithium atom bridging the anionic carbon atom and nitrogen. The C–N bond is elongated to 154.5 pm – the calculated value for $H_3C{-}NH_2$ (**7**) is 146.3 pm (experimentally: 146.5 pm[18]). In the next stable isomer **8B** the Li–N bond is broken which raises the energy by 13.7 kcal/mol. If lithium is only attached to nitrogen (**8C**) the energy is slightly higher than that of **8B** (15.0 kcal/mol). In **8B** as well as in **8C** the C–N bonds are also longer (150.8 and 152.7 pm, respectively) than in $H_3C{-}NH_2$ (**7**). Isomer **8D**, a carbene–$LiNH_2$ complex, is much more unfavorable (65.4 kcal/mol) than **8A**. A calculation [MP2/6-31G(d)//3-21G] of the energy of dimerization of the most stable isomer **8A** to give [**8A**]$_2$ reveals a favorable reaction (–58 kcal/mol). Dimerization occurs along the C–Li bond of **8A**. In [**8A**]$_2$ the C–N bonds are also elongated (155.9 pm). The C–Li bonds of the bridging Li atoms are longer (CA–LiA 227.2 pm) than those of the non-bridging Li atoms (CA–LiB 215.3 pm). Qualitatively, and not unexpectedly, this situation corresponds to that of the calculated $LiCH_2OH$ isomers[6,7,17].

The structure of a "normal" α-lithiated amine (as of a "normal" α-lithiated ether[6,7]) thus should correspond to the theoretical model **8A** or its dimer [**8A**]$_2$. If the more unfavorable situations as in **8B** or **8C** are surmounted by other effects it is expected to detect structures of these model types. This indeed is the case.

Scheme 3. MP2/6-311++G(d,p)//MP2/6-311++G(d,p) + ZPE calculations of CH_3NH_2 (**7**) and $LiCH_2NH_2$ isomers **8A**–**8D**; earlier[17a] MP2/6-31G(d)//3-21G values in parentheses



[a] See ref.[17b]; the dimerization of **8A** was calculated on the MP2/6-31G(d)//3-21G level; relative energies in kcal/mol; bond lengths in pm.

2. Crystal Structure of [α-(Dimethylamino)benzyllithium–Diethyl Ether]$_2$ [**9** · OEt_2]$_2$

The crystal structure of [**9** · OEt_2]$_2$ is shown in Figure 1. The anionic carbon C1 and N1 are bridged by Li1, and a dimer is formed along the C–Li bonds. A diethyl ether molecule occupies the fourth coordination site at lithium. The distance of C1 to the bridging Li1 [247.5(6) pm] is longer than C1–Li1A [223.0(7) pm]. The structure of [**9** · OEt_2]$_2$ therefore corresponds exactly to the calculated

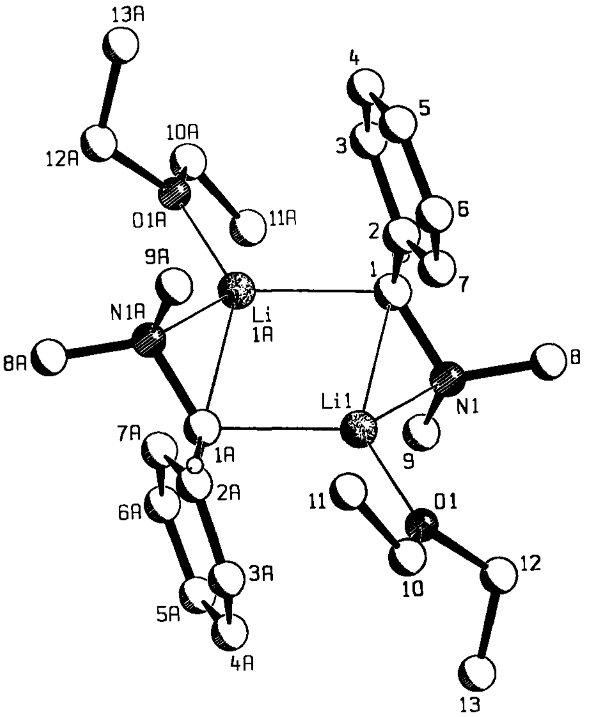


Figure 1. Crystal structure of [α-(dimethylamino)benzyllithium – diethyl ether]$_2$ [**9** · OEt$_2$]$_2$

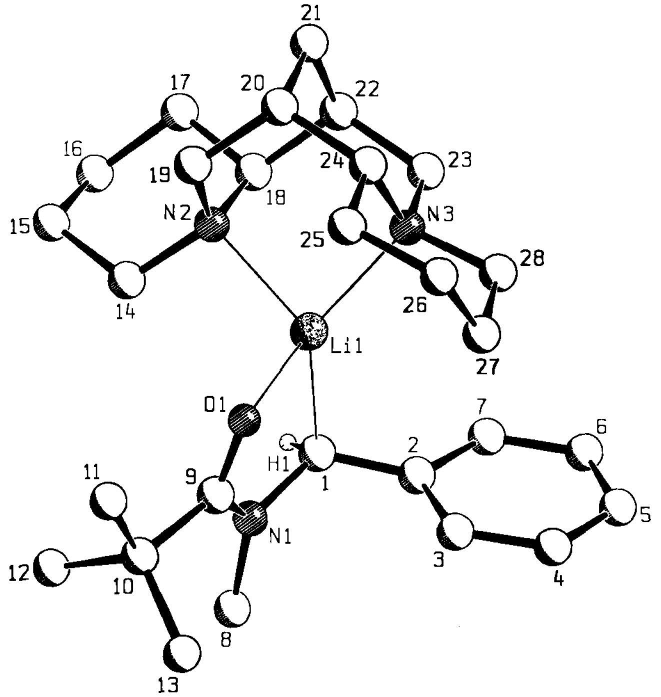


Figure 2. Crystal structure of (*S*)-α-(methylpivaloylamino)benzyllithium – (–)-sparteine [**10** · sparteine]

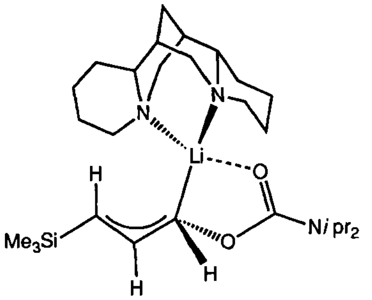
model [**8A**]$_2$. A carbon–lithium "bond" to one of the phenyl carbon atoms is not observed in this solid-state structure [Li1–C2A, e.g., amounts to 272.1(7) pm], at least not a strong one. Apparently, the lithium ion prefers in the solid state bonding with the anionic carbon atom and the adjacent nitrogen atom to η^2 or η^3 coordination with the *ipso* and *ortho* carbon atoms of the phenyl ring as often observed in benzyllithium compounds[19]. NMR investigations in THF solution, on the other hand, show a temperature-dependent behavior with η^1 coordination at low temperature and η^3 coordination at higher temperatures[12c]. ^{1}H-, ^{13}C-, ^{6}Li-NMR, and ^{6}Li,^{1}H HOESY experiments, however, do not allow us to detect specifically whether there is a Li–N contact or not.

The benzylic carbon is strongly pyramidalized: the sum of the bond angles at C1 amounts to 341° (sp^3: 328.5°; sp^2: 360°). The C1–N1 bond [146.9(4) pm] corresponds exactly to the mean value of C–N bonds in C_{sp^3}-hybridized Ph-CH(R)–NMe$_2$ compounds (146.8 pm)[20]. The mean value for C_{sp^2}–NMe$_2$ bonds as in enamines is shorter (140.0 pm)[21]. An estimation of the C–N bond length in a neutral compound with carbon having the same hybridization as in [**9** · OEt$_2$]$_2$ by means of the C–N bond lengths mentioned above leads to the conclusion that C1–N1 in the α-lithiated [**9** · OEt$_2$]$_2$ should be *slightly elongated* ($\approx$3 pm). This result is in agreement with the calculations although the experimentally determined bond elongation is remarkably smaller than the calculated ones (see Scheme 3).

3. Crystal Structure of (*S*)-α-(Methylpivaloylamino)-benzyllithium – (–)-Sparteine [10 · Sparteine]

In the structure of **10** · sparteine in which the lithiated amine **10** differs from the lithiated amine **9** by the replacement of an *N*-methyl group (**9**) by an *N*-pivaloyl group (**10**) one observes characteristic structural changes (see Figure 2).

As in the structure of [**9** · OEt$_2$]$_2$ Li1 is attached to the benzylic carbon atom C1. Li1 does not bridge C1 and N1, however. This is due to two reasons: 1. The donor qualities of the amide nitrogen N1 in **10** · sparteine are less pronounced than those of the amine nitrogen N1 in [**9** · OEt$_2$]$_2$. 2. The alternative Li1–O1 bond in **10** · sparteine resembles closely the situation in the structure of the related η^1-(1*S*,2*E*)-1-(diisopropylcarbamoyloxy)-3-(trimethylsilyl)allyllithium – (–)-sparteine [**11** · sparteine][22,6].



11 · sparteine[22]

The crystal structure of **10** · sparteine is the first example of a chelate-dipole-stabilized *lithiated* amine. Is there any "dipole stabilization", that is, a shortening of the N1–C9 and a lengthening of the C9–O1 bond in the lithiated species? Indeed, both structural changes are observed: The mean value of C–N bonds in structurally related non-lithiated amides is 135.3 pm[20] – N1–C9 in **10** · sparteine is shortened to 133.7(4) pm; the mean value of C=O bonds in the neutral species is 123.4 pm[20] – C9–O1 is lengthened to 125.0(4) pm. Both bond alterations, however, are very small which agrees with the observations made in the case of **11** · sparteine[22,6]. Once more, therefore, the major part for this favorable arrangement results from the chelation effect as indicated by model calculations[23]. It is also of interest that the calculated energies gained by chelation (ester: –13.2 kcal/mol[23]; amide: –28.2 kcal/mol[10b]) are in the range of or surmount the energy difference between the most stable bridged structure **8A** and **8B** (+13.7 kcal/mol) (see Scheme 3), in which Li is only attached to carbon – the model for the crystalline **10** · sparteine.

The sum of the bond angles at C1 in **10** · sparteine adds up to 341°, a value also found in [**9** · OEt$_2$]$_2$. Again C1 is strongly pyramidalized. In comparison with neutral species with the same hybridization at C1, the C1–N1 bond [146.2(4) pm] in **10** · sparteine should thus be somewhat longer, as also observed in the case of [**9** · OEt$_2$]$_2$.

4. Crystal Structure of [3-Iodo-2-lithio-1-methylindole – 2 Tetrahydrofuran]$_2$ ([**12** · 2 THF]$_2$)

Figure 3 shows the crystal structure of [**12** · 2 THF]$_2$.

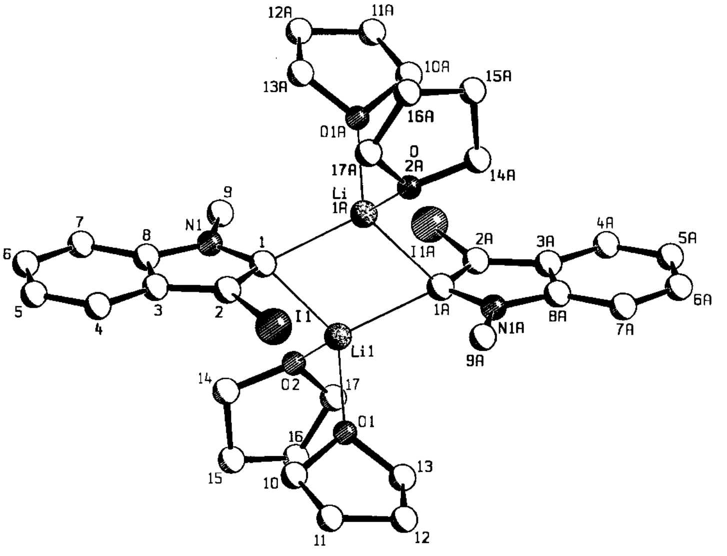
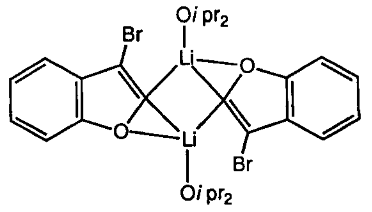
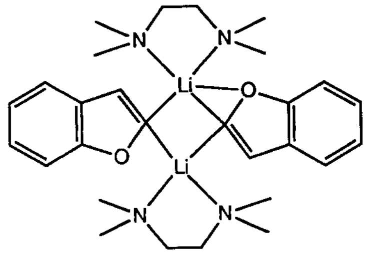


Figure 3. Crystal structure of [3-iodo-2-lithio-1-methylindole – 2 tetrahydrofuran]$_2$ ([**12** · 2 THF]$_2$)

Since [**12** · 2 THF]$_2$ has no chelating group like **10** · sparteine (Figure 2) one might have expected a structure similar to that of [**9** · OEt$_2$]$_2$ (Figure 1) with lithium bridging the anionic carbon atom C1 and the adjacent nitrogen N1. This, however, is not the case (see Figure 3): The lithium atoms Li1 and Li1A are only bound to the anionic carbon atoms C1 and C1A, respectively. A coordination to N1 and/or N1A is not observed [e.g. Li1–N1 310.5(7) pm]. Two further coordination sites at each Li atom are occupied by two THF molecules. The reason for the non-bridging situation in [**12** · 2 THF]$_2$ and the bridging in [**9** · OEt$_2$]$_2$ is evident: N1 in [**9** · OEt$_2$]$_2$ has much more pronounced donor qualitites than N1 (N1A) in [**12** · 2 THF]$_2$, the electron pair of which is involved in the formation of a five-membered aromatic ring system. This situation is strikingly different from that in the comparable lithiated benzofurans [**6** · O*i*pr$_2$]$_2$[6,24] and [**13** · TMEDA]$_2$[25].



[**6** · O*i*pr$_2$]$_2$[6,24]



[**13** ·TMEDA]$_2$[25]

In [**6** · O*i*Pr$_2$]$_2$ each lithium atom bridges the bond between the anionic carbon and the oxygen atoms; in [**13** · TMEDA]$_2$ this is at least so with one Li atom (although it is thus pentacoordinated). The difference between the situations in the lithiated indole [**12** · 2 THF]$_2$ and the lithiated benzofurans [**6** · O*i*pr$_2$]$_2$ and [**13** · TMEDA]$_2$ results from the extra electron pair at oxygen in the latter ones.

The C1–N1 bond length in [**12** · 2 THF]$_2$ is in agreement with what has been observed for the C1–N1 bond lengths in the crystal structures of the α-lithiated compounds [**9** · OEt$_2$]$_2$ and **10** · sparteine: The value 141.4(5) pm indicates a small elongation if compared to the mean value for the same C–N bond in indoles (139.0 pm[20]). The other C–N bond in [**12** · 2 THF]$_2$, namely C8–N1, is also slightly shorter [137.9(5) pm].

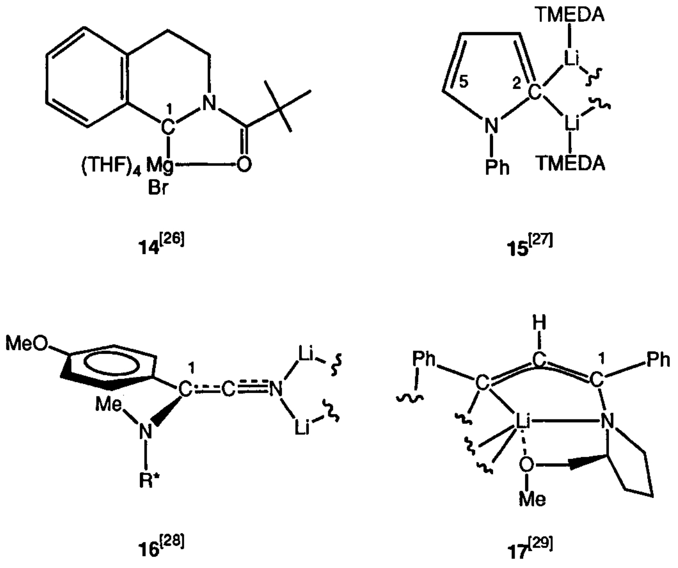
A comparison with the lithiated benzofurans [**6** · O*i*pr$_2$]$_2$[6,24] and [**13** · TMEDA]$_2$[25] shows a much more pronounced elongation of the C1–O1 bonds in these oxygen analogs of [**12** · 2 THF]$_2$. The bond lengths amount to 147.0 and 145.3 pm, respectively, while the mean value of the corresponding bond in neutral benzofurans amounts to 138.5 pm[6,24,25].

The structure of [**12** · 2 THF]$_2$ is also of interest because of the iodine atoms I1 and I1A attached to C2 and C2A, respectively, that is in β-position to the corresponding Li atoms. This leads normally to facile β-elimination of LiI. In the case of five-membered ring heterocycles like [**12** · 2 THF]$_2$ (as well as [**6** · O*i*pr$_2$]$_2$ with a bromine atom located next to lithium[6,24]), however, the elimination does not occur because of the strain which would be induced by the triple bond to be formed[24,16b]. This stability towards elimination is corroborated by the bond length C2–I1 [209.4(4) pm] which corresponds almost exactly to the mean value of C_{sp^2}–I bonds (209.5 pm[20]). A similar situation holds for the C–Br bond length in [**6** · O*i*pr$_2$]$_2$[6,24]. These observations are in remarked contrast to what was mentioned in the introduction for the Li/Cl carbenoid **4** which eliminates LiCl already at low temperatures (–60°C): correspondingly, the C–Cl bond is strongly elongated (ca. 12 pm)[5].

5. Structures of Other α-Metalated Amines

The small elongation of the C–N bonds between the anionic carbon and the nitrogen atoms in the solid-state structures of [**9** · OEt$_2$]$_2$, **10** · sparteine, and [**12** · 2 THF]$_2$ as outlined above raises the question about the generality of this phenomenon. For this purpose, we examine four other α-metalated amines (**14**–**17**), the crystal structures of which have been determined (Scheme 4).

Scheme 4. α-Metalated amines **14**–**17** with known crystal structures



14[26]

15[27]

16[28]

17[29]

The first crystal structure of an α-metalated amine has been reported by Seebach et al., namely that of **14**[26]. The bond of interest, C1–N, is 148.2(13) pm long. In a nonmetalated compound with an *sp*^{3}-hybridized carbon atom used for comparison, "C1–N" amounts to 147.2(4) pm. The almost negligible elongation of C1–N in **14**, however, needs to be related to the hybridization of C1 in **14** which is unknown because the position of the hydrogen atom at C1 has not been determined. Any hybridization of C1 in **14** with an s character higher than sp^3, however, is equal to a more pronounced lengthening of the C1–N bond in **14** as indicated by the bond lengths given above. The five-membered ring chelation as observed in **14** agrees well with the observations made in the cases of **10** · sparteine and **11** · sparteine[22].

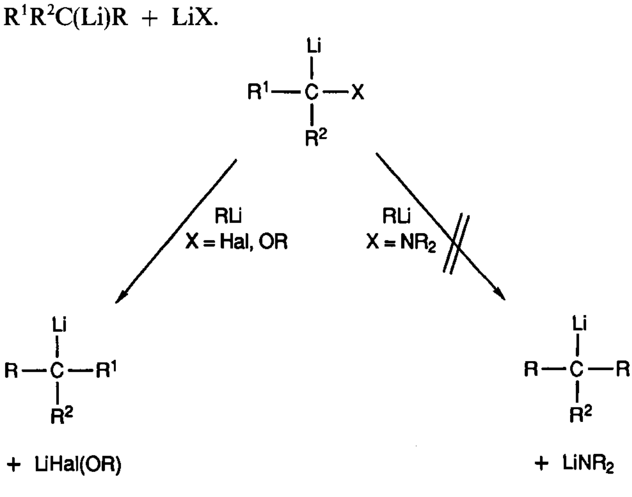
The crystal structure of the dimeric [2-lithio-1-phenylpyrrole–TMEDA]$_2$ (**15**)[27] offers the advantage of an intramolecular comparison of C–N bond lengths. C2–N (141.2 pm) is slightly longer than C5–N (139.5 pm) which confirms nicely the results of the structures of [**9** · OEt$_2$]$_2$, **10** · sparteine, and [**12** · 2 THF]$_2$. Furthermore, a coordination of lithium to the N atoms of pyrrole is also not observed as in the case of the lithiated indole [**12** · 2 THF]$_2$.

Lengthened C1–N bonds are also found in **16** [145.2(5) pm][28] and **17** [146(1) pm][29]. Because of the planarity of the corresponding anionic carbon atoms one has to compare these C–N bond lengths with the earlier mentioned C–N bond lengths in enamines (mean value 140.0 pm)[21].

6. Conclusions

The bond lengths between the anionic carbon atoms and the nitrogen atoms C1–N in the α-metalated amines known to date [**9** · OEt$_2$]$_2$, **10** · sparteine, [**12** · 2 THF]$_2$, **14**, **15**, **16**, and **17** are slightly elongated (2–5 pm) if compared to appropriate nonlithiated reference substances. A (somewhat more pronounced) elongation of the C–N bond on α-lithiation has been predicted in model calculations (see Scheme 3). Furthermore, the calculated model structures of Li-CH$_2$NH$_2$, especially of **8A** and **8B**, agree nicely with the essential structural features of [**9** · OEt$_2$]$_2$, **10** · sparteine, [**12** · 2 THF]$_2$, **14**, and **15**. In the lithiated amino nitrile **16** the nitrile functionality determines the position of the metal, while in the amine-substituted allyllithium species **17** lithium bridges rather four atoms than two, a structural feature which is also observed in **10** · sparteine, **11** · sparteine, and **14**.

The (slight) elongation of the C1–N bonds in the α-metalated amines described and discussed in this work is one of the criteria for a possible carbenoid nature of an organometallic compound as outlined in the introduction. Another one is the reaction of species of the type R^{1}R^{2}C(Li)X with nucleophiles RLi to give the substitution products R^{1}R^{2}C(Li)R + LiX.



Since this reaction is well-known in the Li/Hal carbenoid series[30] and is also observed in the case of Li/oxygen carbenoids[7], however is so far *unknown* in the literature of α-lithiated amines (LiNR$_2$ is a very weak leaving group), there is no reason to include *α-lithiated amines* into the above mentioned class of *carbenoids* – at least not to date. The bond elongations as observed on lithiation agree with this characterization: they are much stronger in the cases of Li/Hal and Li/oxygen carbenoids (see Scheme 2). α-Lithiated amines thus behave like "normal carbanions".

We are very grateful to the *Deutsche Forschungsgemeinschaft, Sonderforschungsbereich 260*, and to the *Fonds der Chemischen Industrie* for supporting this work.

Experimental

The preparations of the single crystals were carried out in oven-dried glassware under dry argon. – Solvents: THF and ether were freshly distilled from potassium and sodium, respectively. – Yields refer to analytically pure samples. – ^{1}H and ^{13}C NMR: Bruker AC 300, AM 400. – MS: Varian MAT 771. – Elemental analyses: Fachbereich Chemie der Universität Marburg.

Tributyl[α-(dimethylamino)benzyl]stannane was prepared according to Ahlbrecht et al.[12c] On the basis of IR and NMR spectroscopic data it corresponded in all respects to the substance described in ref.[12c]

N-Benzyl-N-methylpivalamide: To a solution of 10.0 g (82.5 mmol) of benzylmethylamine in 200 ml of pyridine 10.3 g (85.4 mmol) of pivaloyl chloride was added. The mixture was stirred at room temp. for 1 h. After removal of the solvent the residue was extracted with ether. The crude product was recrystallized from petroleum ether (60/95), yield 16.8 g (99%), m.p. 49°C. – ^{1}H NMR (CDCl$_3$): δ = 7.29–7.11 (m, 5H, Ph), 4.57 (s, 2H, NC*H*$_2$Ph), 2.91 (s, 3H, NCH$_3$), 1.26 (s, 9H, *t*Bu). – ^{13}C NMR (CDCl$_3$): δ = 177.7 (C=O), 137.5 (aromat. C), 128.5, 127.2, 127.0 (5 × aromat. CH), 53.1 (PhCH$_2$N), 38.8 (NCH$_3$), 36.0 [*C*(CH$_3$)$_3$], 28.3 [C(*C*H$_3$)$_3$]. – FD-MS, *m/z* (%): 205.0 (22.4) [M$^+$]. – $C_{13}H_{19}NO$ (205.1): calcd. C 74.11, H 9.84, N 6.82; found C 74.17, H 9.47, N 6.73.

3-Iodo-1-methylindole: According to a modified method of Bocchi and Palla[31] a solution of 5.00 g (38.1 mmol) of *N*-methylindole in 100 ml of DMF was treated with stirring with 19.4 g (76.2 mmol) of solid iodine. After 5 min 8.55 g (150.0 mmol) of potassium hydroxide pellets was added. After stirring overnight at 20°C the reaction medium was poured into 1.5 l of ice/water containing 40 ml of conc. ammonia and 2 g of sodium disulfite. The yellow precipitate was filtered off, washed with cold water, and dried in vacuo (9.40 g, 96%). The product was light-sensitive and thermally unstable. At 20°C it decomposed within a few hours. It had to be kept at –28°C in the dark. – ^{1}H NMR (CDCl$_3$)[31]: δ = 7.47 (d, *J* = 7.7 Hz, 1H, aryl-H), 7.31–7.20 (m, 3H, 3 × aryl-H), 7.06 (s, 1H, CH$_3$NC*H*), 3.83 (s, 3H, NCH$_3$). – ^{13}C NMR (CDCl$_3$): δ = 136.8 (aromat. C), 132.6 (CH$_3$NCH), 130.5 (aromat. C), 122.7, 121.3, 120.3, 109.3 (4 × aromat. CH), 55.0 (CI), 33.0 (NCH$_3$).

Preparation of Single Crystals of [PhCH(NMe$_2$)Li · OEt$_2$]$_2$ ([**9** · OEt$_2$]$_2$): A solution of 100 mg (0.24 mmol) of tributyl[α-(dimethylamino)benzyl]stannane in 0.5 ml of *n*-hexane was treated with 0.17 ml (0.28 mmol) of a 1.6 M solution of *n*-butyllithium in *n*-hexane at 0°C. After 1 h a yellow precipitate had formed. The *n*-hexane was removed at 10^{-3} Torr/20°C and the residue suspended in 1.5 ml of diethyl ether. TMEDA was added dropwise until the residue had dissolved (about 0.06 ml of TMEDA). The deep red solution was kept for 2 h at –26°C and then for 12 h at –5°C, after which time crystals suitable for structural analysis had formed (26.0 mg, 50%).

Crystal Structure Investigation of [**9** · OEt$_2$]$_2$: $C_{13}H_{22}LiNO$ (215.3). A colorless crystal with the dimensions 0.3 × 0.3 × 0.35 mm was used for the data collection with an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Cu-K_α radiation. Monoclinic space group $P2_1/n$, lattice constants: $a = 932.0(1)$, $b = 1283.2(1)$, $c = 1184.2(1)$ pm; $\beta = 106.47(1)°$, $V = 1358.1(2) \cdot 10^6$ pm^3; derived by centering of 25 reflections with $\Theta > 35°$; $Z = 4$, $D_{\text{calcd.}} = 1.053$ g cm^{-3}; $\mu = 0.491$ mm^{-1}; $F(000) = 472$. 1902 measured reflections; $T = 193 \pm 5$ K, $3.5° \leqslant \Theta \leqslant 55°$, *h* (0/9), *k* (0/13), *l* (–12/12); ω scans; scan width $(0.9 + 0.14\ \text{tg}\Theta)°$ ±25% for the background scans; 2 intensity control reflections every hour. After the Lp correction and merging of equivalent reflections there were 1672 unique reflections ($R_{\text{int}} = 0.118$) and 1206 observed with $F_o \geqslant 4\sigma(F_o)$. – All non-hydrogen atoms were refined anisotropically, ether hydrogen atoms "riding", the other refined with common isotropic temperature factors for different groups; extinction parameter $\chi = 0.0061(11)$ {expression used: $F^* = F \cdot [1 + 0.002 \cdot \chi \cdot F^2/\sin(2\Theta)]^{-0.25}$}; $R = 0.0586$; $wR = 0.0526$; 185 parameters; quantum minimized: $\Sigma w(\| F_o | - | F_c \|)^2$; weighting scheme: $w = 1/\sigma^2(F_o)$. Mean "shift/error" 0.000 in the last refinement cycle; largest difference peak 0.21 e/Å^3. – Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-320424, the names of the authors, and the journal citation.

Preparation of Single Crystals of [tBu(CO)NMeCHPhLi–(–)-Sparteine] (**10** · Sparteine): 100 mg (0.49 mmol) of *N*-benzyl-*N*-methylpivalamide, dissolved in 5 ml of diethyl ether in the presence of 15.0 mg (0.63 mmol) of (–)-sparteine, was deprotonated with 0.34 ml (0.54 mmol) of a 1.6 M solution of *tert*-butyllithium in *n*-pentane at –78°C. The yellow precipitate dissolved at room temp. Overnight yellow crystals were obtained (137 mg, 63%).

Crystal Structure Investigation of **10** · Sparteine: $C_{28}H_{44}LiN_3O$ (445.6). A yellow crystal with the dimensions 0.3 × 0.3 × 0.5 mm was used for the data collection with an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Cu-K_α radiation. Orthorhombic space group $P2_12_12_1$, lattice constants: $a = 946.6(3)$, $b = 1290.7(3)$, $c = 2126.8(3)$ pm; $V = 2598.5(11) \cdot 10^6$ pm^3; derived by centering of 25 reflections with $\Theta > 30°$; $Z = 4$, $D_{\text{calcd.}} = 1.139$ g cm^{-3}; $\mu = 0.520$ mm^{-1}; $F(000) = 976$. 3683 measured reflections; $T = 193 \pm 5$ K, $2.0° \leqslant \Theta \leqslant 55°$, *h* (0/10), *k* (0/13), *l* (–22/22); ω scans; scan width $(0.8 + 0.14\ \text{tg}\Theta)°$ ± 25% for the background scans; 3 intensity control reflections every hour. After the Lp correction and merging of equivalent reflections there were 3248 unique reflections ($R_{\text{int}} = 0.0318$) and 2781 observed with $F_o \geqslant 4\sigma(F_o)$. – All non-hydrogen atoms were refined anisotropically, hydrogen atoms "riding" with common isotropic temperature factors for different groups; extinction parameter $\chi = 0.0032(3)$ {expression used: $F^* = F \cdot [1 + 0.002 \cdot \chi \cdot F^2/\sin(2\Theta)]^{-0.25}$}; $R = 0.0410$; $wR = 0.0357$; 306 parameters; quantum minimized: $\Sigma w(\| F_o | - | F_c \|)^2$; weighting scheme: $w = 1/\sigma^2(F_o)$. Mean "shift/error" 0.000 in the last refinement cycle; largest difference peak 0.22 e/Å^3. – Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-400061, the names of the authors, and the journal citation.

Preparation of Single Crystals of [(C$_9$H$_7$IN)Li · 2 THF]$_2$ [**12** · 2 THF]$_2$: A solution of 46.1 mg (0.43 mmol) of LDA in 1 ml of THF, prepared by deprotonation of 48.0 mg (0.47 mmol) of diisopropylamine with 0.27 ml (0.43 mmol) of a 1.6 M solution of *n*-butyllithium in *n*-hexane at 0°C, was treated with a solution of 100 mg (0.39 mmol) of 3-iodo-1-methylindole in 0.5 ml of THF. After

15 min at 0°C 3.4 ml of *n*-hexane was added. Crystals suitable for X-ray structural analysis had formed after 24 h at −28°C (89 mg, 56%). − ^{1}H NMR ([D$_8$]THF, 293 K): δ = 7.40 (d, *J* = 7.6 Hz, 1H, aryl-H), 6.95 (d, *J* = 7.3 Hz, 1H, aryl-H), 6.8−6.7 (m, 2H, 2 aryl-H), 3.84 (s, 3H, NCH$_3$). − ^{13}C NMR ([D$_8$]THF, 163 K): δ = 200.5 [q, *J*(^{13}C,^{7}Li) = 39.0 Hz, CH$_3$NCLi], 140.6, 134.0 (2 aromat. C), 116.9, 116.7, 116.3, 107.2 (4 aromat. CH), 71.3 (CI), 36.7 (NCH$_3$). The quartet of the ^{13}C-^{7}Li coupling showed that only one lithium is bound to the anionic C atom when [**12** · 2 THF]$_2$ was dissolved in [D$_8$]THF and measured at 163 K.

Crystal Structure Investigation of [**12** · 2 THF]$_2$: $C_{34}H_{46}I_2Li_2N_2O_2$ (814.4). A colorless crystal with the dimensions 0.3 × 0.3 × 0.4 mm was used for the data collection with a Siemens P4 diffractometer with graphite-monochromated Mo-K_α radiation. Triclinic space group $P\bar{1}$, lattice constants: $a = 947.8(8)$, $b = 1091(6)$, $c = 2026.8(16)$ pm; $\alpha = 81.44(6)$, $\beta = 76.61(6)$, $\gamma = 69.23(5)°$, $V = 1758(2) \cdot 10^6$ pm^3; derived by centering of 25 reflections with $\Theta > 10°$; $Z = 2$, $D_{\text{calcd}} = 1.538$ g cm^{-3}; $\mu = 1.826$ mm^{-1}; $F(000) = 816$. 6594 measured reflections; $T = 193 \pm 5$ K, $1.5° \leqslant \Theta \leqslant 25°$, *h* (0/11), *k* (−11/12), *l* (−23/24); ω scans; scan width 1.20°, stationary background measuring; 3 intensity control reflections every 150 reflections. After the Lp correction and merging of equivalent reflections there were 6181 unique reflections ($R_{\text{int}} = 0.0127$) and 5418 observed with $F_o \geqslant 4\sigma(F_o)$; semi-empirical absorption correction (minimal and maximal transmission: 0.6322, 0.9566). − All non-hydrogen atoms were refined anisotropically, hydrogen atoms "riding" with fixed isotropic temperature factors; $R = 0.0287$; $wR = 0.0290$; 403 parameters; quantum minimized: $\Sigma w(\| F_o | - | F_c \|)^2$; weighting scheme: $w = 1/\sigma^2(F_o)$. Mean "shift/error" 0.000 in the last refinement cycle; largest difference peak 0.22 e/Å^3. − Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-320425, the names of the authors, and the journal citation.

All three structures were solved with direct methods and refined according to the full-matrix least-squares procedure with the Siemens SHELXTL PLUS (VMS) program system[32]. The calculations were performed with a Micro-Vax II and a VAX 6000−420[33,34].

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