

N-Aryl Anions: Half Way between Amides and Carbanions

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

A ‘carbanion’ can coordinate to a metal like an ‘amide’ if there is a nitrogen atom present to withdraw electron density from the formally negatively charged carbon center. On the other hand, shifting the negative charge from the amido nitrogen atom to the carbon substituent should convert an ‘amidic’ into a ‘carbanionic’ coordination behavior. This seems feasible with various substituents at the aromatic ring in a primary amide. This paper is concerned with the influence of aromatic substitution, as well as with the nature of the metal ion on the coordination mode of an amide ligand. Discussed are the parent lithium anilide [(thf)₂LiNH(C₆H₅)]₂ (**1**), the pentafluorinated lithium anilide [(thf)₂LiNH(C₆F₅)]₂ (**2**) and the lithium amino benzonitrile [(thf)₂LiNH(C₆H₄^{*p*}CN)]₂ (**3**). All amide ligands coordinate the lithium cation exclusively with their amido nitrogen atom. In the dimeric structure of **1** the atom can be regarded to be sp²-hybridized. Fluorine substitution of the ring results in a slightly more pronounced coupling of the negative charge to the aromatic ring. A *para*-nitrile group further enhances quinoidal perturbation of the C₆-perimeter from six-fold symmetry. Consequently, the *ipso*- and *ortho*-carbon atoms of the ring are partially negative charged. Those carbon atoms are only attractive for the soft rubidium cation in an *aza* allylic coordination in [(thf)₂RbNH(C₆H₄^{*p*}CN)]_n (**4**) but not to the hard lithium cation.

Key words: Alkali Metals, Amides, Ligand Effects, Lithium, Rubidium

Introduction

The directing influence of the metal cation in polar metal organic compounds concerning the structural assembly, reactivity and energy is a recent focus of research, both in organic and organometallic chemistry [1]. In addition, alkali metal amides are important starting materials in a vast number of synthetic routes to new target compounds [2]. Their aggregation and reactivity is mainly determined by the three parameters: sort of the alkali *metal*, donor *solvent* and type of the *substituent* at the central nitrogen atom [3]. For instance in the alkali metal triphenyl methyl system [MCPh₃]_n (M=Li, Na, K, Rb, Cs) the metal shifts from the central carbon atom to the center of a single phenyl ring as the ordering number increases [4]. Substitution of a single phenyl ring

by a 2-pyridyl ring (Py) interlocks the metals at almost the same position close to the nitrogen atom [5]. Hence, ‘carbanions’ can coordinate as ‘amides’ if there is a nitrogen atom able to withdraw electron density from the formal negative carbon center. In the dipyridyl methyl contact ion pairs MCHPy₂ (M = Li, Na) no metal-carbon contact is observed, not even to the hard lithium cation. Metal coordination is exclusively maintained by the ring nitrogen atoms without significant negative charge being accumulated at the central deprotonated carbon atom [6]. Obviously, there is a considerable intersection of the fuzzy classes ‘carbanions’ and ‘amides’. The same holds for ‘carbanions’ and ‘phosphides’ [7]. The three parameters *metal*, *solvent* and *substituent* also predominantly determine the aggregation in metal amides. For lithium amides their impact is well elaborated and lead to the

ring-stacking-and-laddering principle [8]. Examples are the structures of lithium/sodium *t*-butyl amides. Whereas $[\text{LiNH}^t\text{Bu}]_8$ [9] crystallizes as a cyclic eight-rung ladder ('double crown'), $[\text{NaNH}^t\text{Bu}\cdot\text{NH}_2^t\text{Bu}]_\infty$ forms infinite wavelike ladders [10]. This paper is concerned with the influence of the metal ion on the coordination mode of an amide ligand. To tie down the effect, first we kept the lithium metal and varied the amides from $\text{HN}(\text{C}_6\text{H}_5)^-$ *via* $\text{HN}(\text{C}_6\text{F}_5)^-$ to $\text{HN}(\text{C}_6\text{H}_4^p\text{CN})^-$ and then kept the parameters *solvent* and *substituent* constant and varied the metal from lithium to rubidium. We favored the deprotonated 4-aminobenzonitrile $\text{H}_2\text{N}(\text{C}_6\text{H}_4^p\text{CN})$ in this metal variation for two reasons: firstly the negative charge at the deprotonated nitrogen atom will couple into the aromatic ring because of the electron withdrawing CN-group in the *para*-position [11] and secondly the nitrile nitrogen atom might be an attractive donor, at least to the rubidium cation. It was anticipated that the soft rubidium would shift from the coordination site of the lithium, close to the N(H)-function of the amide, towards the C_6 perimeter, as this gets electronically more attractive at the expense of the amide center. In the following, we present the alkali metal amidobenzonitriles $[(\text{thf})_2\text{LiNH}(\text{C}_6\text{H}_4^p\text{CN})]_2$ (**3**) and $[(\text{thf})_2\text{RbNH}(\text{C}_6\text{H}_4^p\text{CN})]_n$ (**4**) in comparison to the parent lithium anilide $[(\text{thf})_2\text{LiNH}(\text{C}_6\text{H}_5)]_2$ (**1**) [11] and the lithium pentafluoro anilide $[(\text{thf})_2\text{LiNH}(\text{C}_6\text{F}_5)]_2$ (**2**) [12].

Results and Discussion

Lithium anilide and lithium pentafluoroanilide

Both, the lithium anilide $[(\text{thf})_2\text{LiNH}(\text{C}_6\text{H}_5)]_2$ (**1**) and the lithium pentafluoro anilide $[(\text{thf})_2\text{LiNH}(\text{C}_6\text{F}_5)]_2$ (**2**), feature a planar Li_2N_2 four membered ring [12]. In addition to the anilido ligands, two thf molecules complete the coordination sphere of each lithium atom inhibiting further association of lithium anilide moieties (Fig. 1, top). These dimers can be regarded as the final fragmentation products in the stepwise disassembling processes of unsolvated laterally connected lithium anilides to tetrasolvated dimeric lithium anilides [13]. The asymmetric bridging of lithium by the anilido nitrogen centers ($\text{N1} - \text{Li1} = 198.9(3)$, $\text{N1} - \text{Li1A} = 208.7(3)$ pm in (**1**); $\text{N1} - \text{Li1} = 200.6(7)$, $\text{N1} - \text{Li1A} = 206.7(7)$ pm in **2**) as well as the sum of the bond angles at nitrogen, disregarding the longer N–Li bond, (358° in **1** and 348° in **2**) deserves particular attention (Fig. 1, center): the

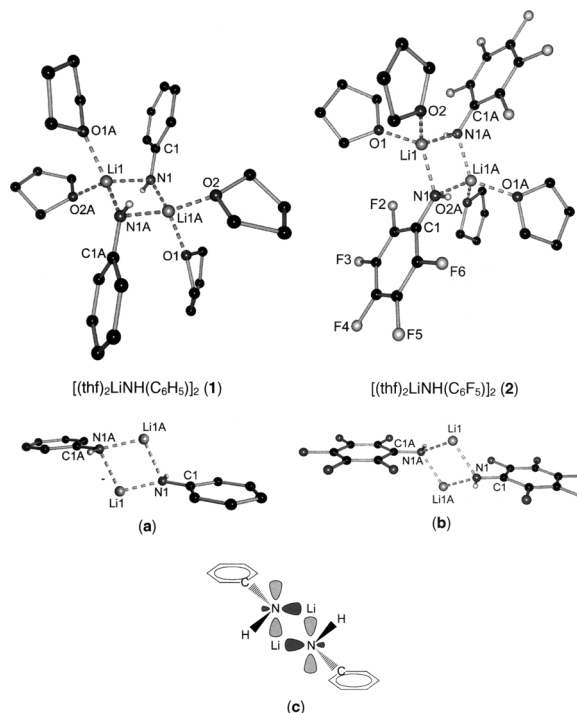


Fig. 1. Solid-state structures of $[(\text{thf})_2\text{LiNH}(\text{C}_6\text{H}_5)]_2$ (**1**) and $[(\text{thf})_2\text{LiNH}(\text{C}_6\text{F}_5)]_2$ (**2**), depicting the deviation of the C_6 perimeter from the NLi_2 bisecting of the central N_2Li_2 four membered ring (**a**, **b**) and indicating smaller sp^2 -character of the nitrogen atom in the lithium pentafluoro anilide than in the parent anilide (**c**).

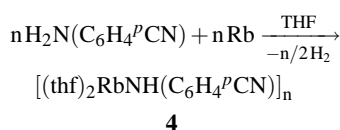
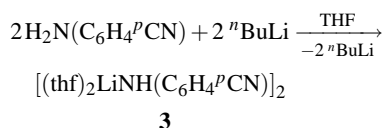
position of the lithium atom almost within the plane of the anilide ligand indicates sp^2 -hybridization of the nitrogen atom (Fig. 1, bottom) especially for **1**. Two sp^2 -orbitals are involved in σ -bonding of the hydrogen and the *ipso*-carbon atom, while the lone pairs occupy the remaining hybrid orbital and the non-hybridized *p*-orbital which is oriented orthogonal to the anilide plane. The short $\text{N1} - \text{Li1}$ distance is due to the interaction of lithium with the sp^2 -lone pair, the weak interaction with the nitrogen *p*-orbital is reflected by the longer $\text{N1} - \text{Li1A}$ distance. The approximate coplanarity of the C_6 perimeter with the plane defined by Li1 , N1 , and H1 can be rationalized in terms of a π -interaction of the aromatic system with the nitrogen *p*-orbital. However, the geometrical parameters in **2**, compared to **1**, clearly indicate that the preference for an sp^2 -hybridization of the nitrogen atom appears less pronounced in **2** (*vide infra*).

In **2** there is no Li–F contact to the ortho-fluorine atom at the aromatic ring like observed in $[(\text{thf})_2\text{LiN}(\text{Si}^t\text{Bu}_2\text{F})(\text{C}_6\text{F}_5)]$ [14].

Lithium and rubidium amidobenzonitriles

Preparation of $[(\text{thf})_2\text{LiNH}(\text{C}_6\text{H}_4^p\text{CN})]_2$ (**3**) and $[(\text{thf})_2\text{RbNH}(\text{C}_6\text{H}_4^p\text{CN})]_n$ (**4**)

3 was synthesized by adding *n*-butyllithium to a solution of 4-aminobenzonitrile in THF solution (eq. (1)). For the preparation of **4** elemental rubidium was reacted with 4-aminobenzonitrile in THF solution (eq. (2)).

Crystal structure of $[(\text{thf})_2\text{LiNH}(\text{C}_6\text{H}_4^p\text{CN})]_2$ (**3**)

Like in the structures of $[(\text{thf})_2\text{LiNH}(\text{C}_6\text{H}_5)]_2$ (**1**) and $[(\text{thf})_2\text{LiNH}(\text{C}_6\text{F}_5)]_2$ (**2**) [12], **3** adopts a dimeric structure in solid state (Fig. 2).

Like in most lithium amides the central structural feature is a Li_2N_2 four membered ring. Different to the solid-state structures of **1** and **2**, there is no center of inversion present in that ring. In addition to the amide nitrogen atoms, two thf molecules complete the coordination sphere of each lithium atom. The endocyclic ring angles at nitrogen ($75.2(5)^\circ$ and $76.3(5)^\circ$) and lithium ($101.0(6)^\circ$ and $101.5(6)^\circ$) are well within the range of corresponding values in related dimers [7b, c]. In **3** however, the four membered Li_2N_2 -ring adopts a butterfly conformation (Fig. 3). The deviation from planarity corresponds to a bending along the $\text{Li1}\cdots\text{Li11}$ vector by 156.5° (Fig. 3b and c). The four symmetrically independent Li–N distances (av.

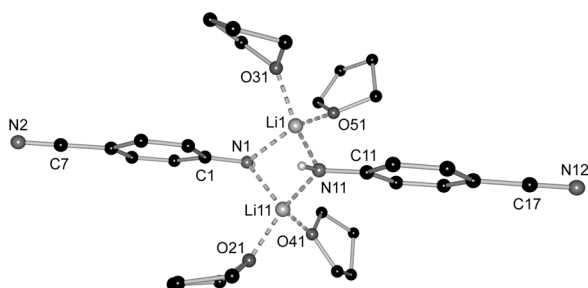


Fig. 2. Solid-state structure of $[(\text{thf})_2\text{LiNH}(\text{C}_6\text{H}_4^p\text{CN})]_2$ (**3**).

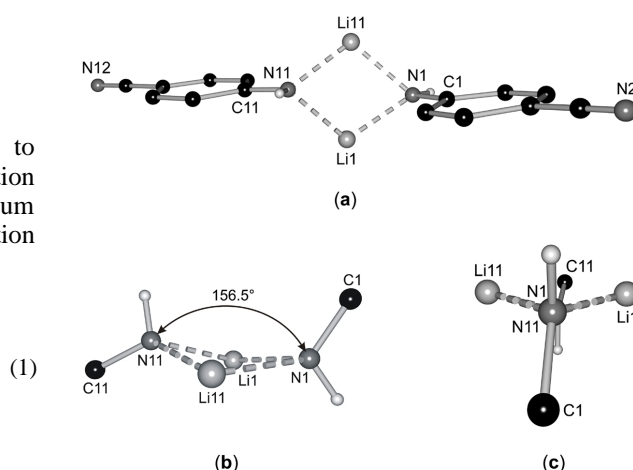
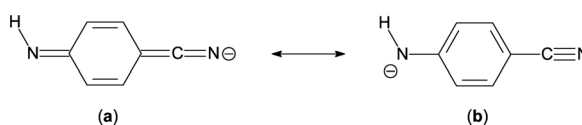


Fig. 3. Views of the Li_2N_2 four membered ring in $[(\text{thf})_2\text{LiNH}(\text{C}_6\text{H}_4^p\text{CN})]_2$ (**3**); with the Li_2N_2 ring in the plane of the paper (a) and $\text{N}\cdots\text{N}$ (c) orthogonal to the plane of the paper.

208 pm; range from 205(1) to 209(1) pm) correspond to the long distances in **1** and **2** (Table 1). The planes of the phenyl rings are arranged almost perfectly orthogonal to the $\text{Li1}\cdots\text{Li11}$ vector (av. of the best planes: 80.5° , Fig. 3a).

It seems worthy to note that the $\text{N}-\text{C}_{\text{ipso}}$ bond lengths in **3** are remarkably short (134.8(8) and 134.2(8) pm; Table 1). Standard N–C bond lengths vary from 147 (N(sp^3)–C(sp^3)) via 143 (N(sp^3)–C(sp^2)) and 140 (N(sp^2)–C(sp^2)) to 129 pm for an N=C double bond [15]. Hence the distances in **3** are more than 5 pm shorter than any N–C single bond. Methylation even shortens the N–C bond compared to the parent 4-aminobenzonitrile of 137.0(3) pm [11]. The partial double bond character is emphasized and the resonance form a in Scheme 1 contributes most to the description of the bonding situation. As a consequence, the phenyl ring systems show a considerable quinoidal perturbation (see structural comparison).



Scheme 1. Resonance forms of the 4-amidobenzonitrile anion.

Crystal structure of $[(\text{thf})_2\text{RbNH}(\text{C}_6\text{H}_4^p\text{CN})]_n$ (**4**)

To study the coordination behavior of the 4-amidobenzonitrile anion to bigger and softer alkali metal

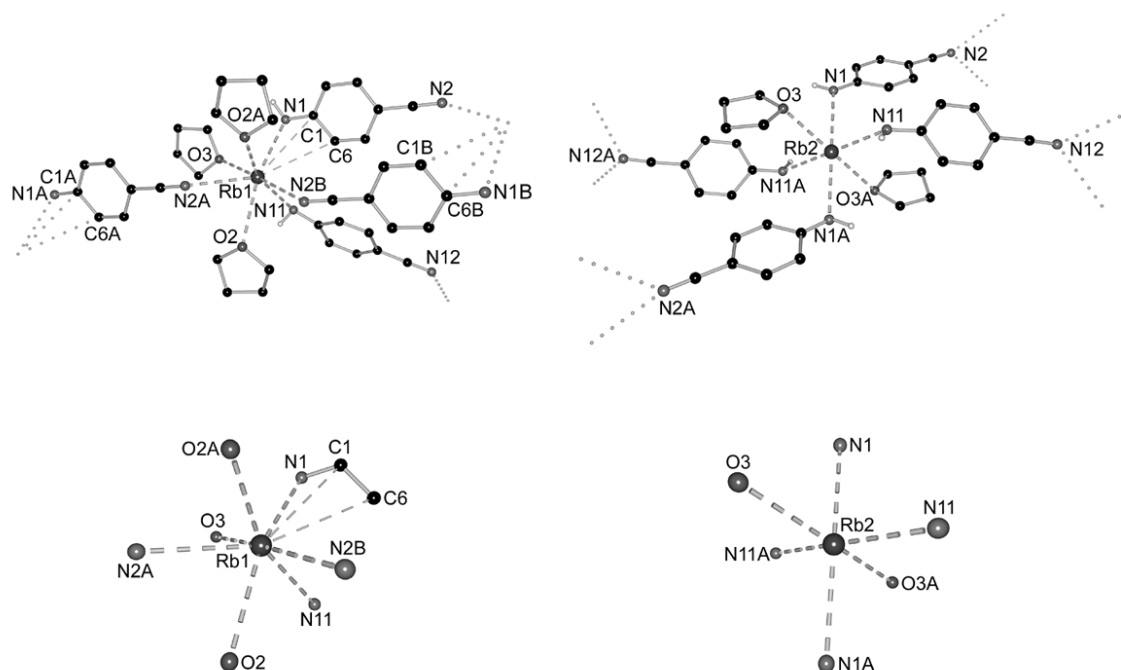


Fig. 4. Coordination spheres of both symmetry independent rubidium cations Rb1 and Rb2 in the polymeric solid-state structure of $[(\text{thf})_2\text{RbNH}(\text{C}_6\text{H}_4^p\text{CN})]_n$ (**4**).

cations, the 4-aminobenzonitrile was reacted with rubidium metal. Fig. 4 displays the coordination spheres of both symmetry independent rubidium cations in the polymeric solid-state structure.

The coordination sphere of Rb1 is made up of four anionic ligands and three coordinated thf molecules (Fig. 4, left). Three of the amide ligands are crystallographically equivalent (center of inversion). They are coordinated to cations in an aza allylic way (Rb1–N1 299.8(6), Rb1–C1 359.1(6), Rb1–C6 367.9(6) pm) and represent the bridging groups between the rubidium chains employing both nitrogen atoms (Rb1–N2: 303.5(6) and 310.5(6) pm). The aza allylic coordination mode has also been reported by Mulvey *et al.* for $[(\text{pmdeta})\text{K}\{\text{PhC}(\text{H})\text{–N–C}(\text{H})\text{Ph}\}]_\infty$ [16].

Obviously, the amide nitrogen atom in the deprotonated 4-aminobenzonitrile ligand is as attractive for the coordination to rubidium as the nitrile nitrogen. Therefore, the ligand is disordered about the crystallographic center of inversion, which is positioned half way between the two nitrogen atoms.

The fourth anionic ligand is only connected by the amide nitrogen atom (Rb1–N11: 314(2) pm) and not by the carbon atoms. The Rb–C distances in **4** are

located at the long end of the observed range for related distances. However, they fit the values observed for Rb– $\eta^6\text{C}$ -distances (η^6 in $[(\text{pmdeta})\text{RbCPh}_3]_\infty$ [4]: 335.1(4)–364.3(3) (pmdeta = $\text{MeN}(\text{CH}_2\text{CH}_2\text{NMe}_2)_2$), η^6 in $[(\text{pmdeta})\text{RbCH}_2\text{Ph}]_\infty$ [17] 314(2)–357(2), η^6 in $[(\text{pmdeta})\text{RbNC}_{12}\text{H}_8]$: [18] 342–368 pm). Both the Rb–(amido)N and Rb–(nitrile)N distances are within the wide range covered by rubidium amides (294.6(6) and 314.1(6) in $[(\text{dioxane})_{1.5}\text{RbN}(\text{SiMe}_2)]_\infty$ [19], 291.7(4) and 298.9(2) pm in $[(\text{thf})\text{Rb}\{\text{N}(\text{SiMe}_2)_2\text{PPh}_2\}_2]$ [20]) and rubidium donor base complexes (296.4(7)–317.3(9) in $[(\text{pmdeta})\text{RbCPh}_3]_\infty$, [4] 298(1)–307(1) pm in $[(\text{pmdeta})\text{RbCH}_2\text{Ph}]_\infty$ [17]). Hence the initial expectations could be verified: the exclusive Li–N coordination in **3** is converted into a Rb– $\eta^3(\text{NC}_2)$ coordination in **4** and the nitrile nitrogen atom proves to be an attractive donor. The coordination sphere of the second symmetry independent rubidium atom Rb2 (located on a center of inversion) is not so crowded. Different to Rb1, Rb2 is only six fold coordinated (Fig. 4, right). The coordination polyhedron can be described as a distorted octahedron formed of three different types of ligands: Two anionic ligands bonded

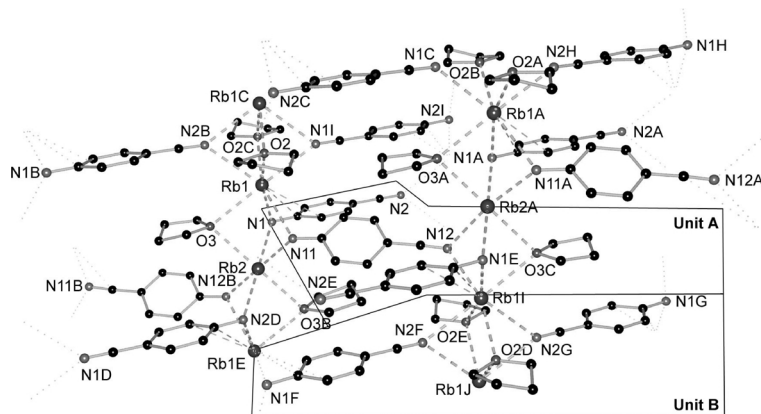


Fig. 5. Polymeric network arrangement of $[(\text{thf})_2\text{RbNH}(\text{C}_6\text{H}_4^p\text{CN})]_n$ (**4**).

exclusively *via* the amide nitrogen atoms and two disordered ligands coordinating Rb2 by the amide, as well as the nitrile nitrogen atoms, 50% each. Two coordinating thf molecules complete the coordination sphere. The 4-amidobenzonitrile ligands in **4** display an even shorter N–C distance than the analogous distances in **1**, **2**, and **3** (av. 132(8) pm, Table 1). This is one of the shortest $\text{N}(\text{sp}^2)\text{--C}(\text{sp}^2)$ -distances ever observed. It is very close to a $\text{N}=\text{C}$ double bond, explaining aza allylic coordination to the rubidium. As a consequence, the quinoidal character of the system is even more pronounced (see structural comparison). Although very rarely observed in solid state [21], the lithium aza allylic coordination has recently been calculated [22] to be very important in the mechanism of the anionic two-step [3+2] cycloaddition [23,24] and asymmetric induction [25]. This coordination mode is obviously favored when heavier alkali metals are employed. Due to the big radius of the metal and to the two coordination sites of the 4-amidobenzonitrile ligand, **4** forms a polymeric network structure in solid state (Fig. 5).

In unit A two rubidium atoms are μ_2 -bridged by two amide nitrogen atoms and a single thf molecule, which is a relatively rare coordination mode for thf [26]. The metal $\text{Rb}_2\text{N}_2\text{O}$ polyhedron can be described as a trigonal bipyramid. In unit B the two rubidium atoms are μ_2 -bridged by two nitrile nitrogen atoms of the anionic ligands and two thf molecules. The resulting polyhedron is a distorted octahedron.

The single polymeric chain results from an apical connection of the octahedron and the trigonal bipyramid *via* a common rubidium atom. Because one of the rubidium atoms is located on a center of inversion, the

sequence is not an A, B, A, ...-arrangement of 1:1 ratio, but a 1:2 structural motif. Every bipyramid is connected to one octahedron and one bipyramid each (A, A, B, A, A, ...). Another center of inversion is located in the center of every octahedron. The metals along the chains in **4** ($\text{Rb1}\cdots\text{Rb1A}$ across the octahedron: 368.6 and $\text{Rb1}\cdots\text{Rb2}$ across the trigonal bipyramid: 380.5 pm) are in remarkably close contact. The single chains within the polymer are not isolated, but interconnected by the amidobenzonitrile ligands, because the amide as well as the nitrile nitrogen atoms are involved in the metal coordination but to metals of different chains.

Structural comparison

The differently substituted lithium anilide derivatives **1–3** establish a structural trend which admits to draw conclusions according the electron density distribution in the amido ligand. In the dimeric structure of the parent lithium anilide $[(\text{thf})_2\text{LiNH}(\text{C}_6\text{H}_5)]_2$ (**1**) one lithium cation is located in the plane of the ligand and forms a close contact to the amido nitrogen atom. The second interacts with the non-hybridized *p*-orbital of the sp^2 nitrogen, resulting in an about 10 pm longer Li–N distance (Table 1). These distances elongate and equilibrate proceeding from $[(\text{thf})_2\text{LiNH}(\text{C}_6\text{F}_5)]_2$ (**2**) to $[(\text{thf})_2\text{LiNH}(\text{C}_6\text{H}_4^p\text{CN})]_2$ (**3**). In the last two dimeric structures none of the lithium atoms is located in the plane of the anion (Fig. 1 and 3). This feature is more pronounced in **3** ($60.6(2)^\circ$ between the phenyl/CNH-plane and the closest Li–N vector *vs.* $40.2(3)^\circ$ in **2**). Apparently, the amido nitrogen atom gets less attractive for the cations. The impact of a single *para*-nitrile group is bigger than that of five fluorine

Table 1. Li–N and Li–O bond distances [pm] in the lithium derivatives **1**–**3**.

Compound	1	2	3
Li–N	198.9(3) 208.7(3)	200.6(7) 206.7(7)	205(1) 208(1) 208(1) 209(1)
Li–O	196.6(3) 200.1(3)	198.2(9) 198.2(8)	190(1) 191(2) 191(2) 195(1)

atoms. Different to the first, fluorine has got a considerable π -donating effect. The nitrile group, however, is π - and σ -accepting. The more loosely bonding to the anion in **3** is compensated by closer bonding to the donating thf molecules.

1 belongs to a group of compounds in which one of the lithium atoms of the N_2Li_2 -ring is almost in plane with the phenyl/CNH-plane and the Li–N distances differ noticeably [27]. As explained earlier this hints to a sp^2 -hybridization of the nitrogen. **3** in contrast features quite similar Li–N distances and its $Li1 \cdots Li1A$ vector is oriented orthogonal to the phenyl/CNH-plane, *i.e.* the lithium atoms are remarkably dislocated from the planes. This is well known from literature [27a, 28]. **2** resides half-way between these two extremes. Although Li1 is not in the plane of the phenyl ring, there is still a distinct difference between the Li–N distances.

The increasing coupling of the negative charge at the amido nitrogen atom into the aromatic ring causes an increasing localization of double bonds and quinoidal character in **3** and **4** (Table 2). The N– C_{ipso} bond length decreases continually from 139.2(6) in aniline [29] to 131.7(8) pm in $[(thf)_2RbNH(C_6H_4^pCN)]_n$ (**4**). The deviation from sixfold symmetry of the C_6 -perimeter, already detected in the solid-state structure of aniline [29], is enhanced in the anilide anions of **1** and **2**. The short $N_{amide}-C_{ipso}$ bonds, in tune with the long $C_{ipso}-C_{ortho}$ -bonds, indicate coupling of the negative charge into the aromatic ring and accumulation at the *ortho*-carbon atom. Perfluorination of the ring results in further shortening of the $N_{amide}-C_{ipso}$ and $C_{meta}-C_{para}$ bonds in **2**, compared to **1**. The quinoidal perturbation of the aromatic ring, like in parent 4-aminobenzonitrile [11], is emphasized in the corresponding anions of **3** and **4**. The long $C_{ipso}-C_{ortho}$ and $C_{meta}-C_{para}$ -bonds as well as the short $C_{ortho}-C_{meta}$ -bonds indicate major contribution from resonance form a in Scheme 1. Different to the hard lithium cation, only the soft and easy to polarize rubidium cation main-

Table 2. Bond lengths [pm] in the anions of **1**–**4** in comparison to aniline and 4-aminobenzonitrile (ABN).

	Bond 1 ($N_{amide}-C_{ipso}$) ^a	Bond 2 ($C_{ipso}-C_{ortho}$) ^a	Bond 3 ($C_{ortho}-C_{meta}$) ^a	Bond 4 ($C_{meta}-C_{para}$) ^a
Aniline [25]	139.2(6)	139.6(6)	137.9(7)	138.1(7)
ABN [10]	137.0(3)	140.5(3)	136.9(3)	139.8(3)
1	136.6(2)	141.7(2)	138.4(2)	138.7(3)
2	135.1(9)	139.8(7)	137.6(6)	135.7(6)
3	134.5(8)	140.8(8)	135.3(9)	138.9(9)
4 ^b	131.7(8)	142.7(8)	136.0(8)	141.4(8)

^a Average of chemically equivalent bonds, esds represent extremes;

^b average of non-disordered ligands.

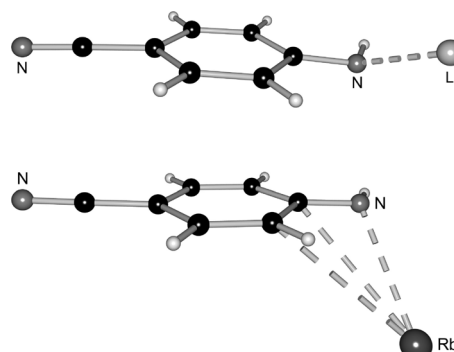


Fig. 6. Different coordination of the 4-amidobenzonitrile anion to the lithium and rubidium cation.

tains coordination to the partially negatively charged *ipso*- and *ortho*-carbon atom in an aza allylic fashion (Fig. 6).

These structural findings are further substantiated by NMR-spectroscopic investigations in solution. The most striking feature in the 1H NMR-spectra are the shifts of the amide protons in the presented metalated compounds. In comparison to aniline, **1** and **2** show strong up field shifts for the N(H)-groups which indicate higher electron density at the amido nitrogen atom. Compared to the neutral 4-aminobenzonitrile, only **3** shows an upfield shift for N(H), whereas in **4** it is strongly deshielded. Because of the electron withdrawing effect of the *para*-nitrile group, the amide lone pair couples into the ring system and the charge is accumulated at the nitrile nitrogen atom. However, the N(H)-protons of the two 4-amido-benzonitrile ligands

Table 3. ^1H -NMR-spectroscopic shifts δ of the anions in **1**–**4**^a.

	Aniline	2	1	ABN	3	4
N(H)	3.57	2.83	2.54	4.31	4.07	5.00
2	6.62	–	6.23	7.38	6.82	6.83
3	7.12	–	6.63	6.64	6.07	6.05

^a In $[\text{D}_8]\text{THF}$ at room temperature, TMS ext.

in **3** and **4** both are much more deshielded than in the two anilide ligands of **1** and **2**. Due to the quinoidal perturbation the protons in positions 2 and 3 in **3** and **4** are shifted upfield, indicating higher electron density in these positions than in the starting material.

Conclusion

Like in all contact ion pairs, the molecular organization in solid state heavily depends on the nature of the metal and the electron distribution in the anion. The nitrogen atom in the dimeric structure of lithiated aniline $[(\text{thf})_2\text{LiNH}(\text{C}_6\text{H}_5)]_2$ (**1**) can be regarded as sp^2 -hybridized with a short in-plane Li–N σ -contact (presumably to the in-plane lone pair) and a longer additional Li–N π -coordination (probably to the non-hybridized p -orbital). Fluorine substitution, as in $[(\text{thf})_2\text{LiNH}(\text{C}_6\text{F}_5)]_2$ (**2**), results in slightly more pronounced coupling of the negative charge into the aromatic ring. The anion also moves slightly towards the NLi_2 -bisection. Substitution of a nitrile group in the *para*-position of the ring further decreases the electron density at the amido nitrogen atom and the anion is positioned at the NLi_2 -bisection. Due to the partial negative charge at the nitrile nitrogen atom is less attractive to lithium coordination. However, it is only the big and soft rubidium cation that takes advantage from this density shift. In addition to the amido nitrogen atom the nitrile nitrogen, as well as the *ipso*- and *ortho*-carbon atoms are involved in metal coordination in the polymeric structure of $[(\text{thf})_2\text{RbNH}(\text{C}_6\text{H}_4\text{CN})]_n$ (**4**) in an aza allylic way. Nevertheless, there is no complete shift to a carbanionic behavior of the ligand. This coordination mode is a blend of the two extremes amide and carbanion.

Experimental Section

All manipulations were performed under an inert atmosphere of dry nitrogen gas with Schlenk techniques or in

Table 4. Crystal data of **3** and **4** at 153(2) K.

	3	4
Formula	$\text{C}_{30}\text{H}_{42}\text{Li}_2\text{N}_4\text{O}_4$	$\text{C}_{37}\text{H}_{47}\text{N}_6\text{O}_4\text{Rb}_3$
CCDC-no.	111502	111503
Mass	536.56	896.22
Cryst. size [mm]	$0.2 \times 0.2 \times 0.1$	$0.5 \times 0.3 \times 0.1$
Space group	$P\bar{1}$	$P\bar{1}$
a [pm]	873.5(9)	1074.2(2)
b [pm]	932.4(6)	1080.9(2)
c [pm]	2014.6(6)	1126.5(2)
α [°]	99.69(6)	116.09(3)
β [°]	92.16(12)	104.26(3)
γ [°]	108.09(4)	106.14(3)
V [nm ³]	1.530(2)	1.0202(3)
Z	2	1
ρ_c [g/cm ³]	1.164	1.459
μ [mm ^{−1}]	0.076	3.627
$F(000)$	576	454
2θ Range [°]	6–40	8–45
No. of refls measd	2928	3194
No. of unique refls	2843	2645
No. of restraints	693	315
Refined params	419	297
$R1^a$ [$I > 2\sigma(I)$]	0.0927	0.0539
$wR2^b$ (all data)	0.2479	0.1129
$g1, g2^c$	0.0986, 2.5301	0.0317, 2.476
Highest diff peak [10 ^{−6} e pm ^{−3}]	0.27	0.39
Absorption correction	–	semi-empirical
Max/min transmission.	0.98/0.73	0.98/0.64

^a $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; ^b $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; ^c $w = 1/[\sigma^2(F_o^2) + (g1P)^2 + g2P]$; $P = (F_o^2 + 2F_c^2)/3$.

an argon drybox. Solvents were dried over Na/K alloy and distilled prior to use. NMR spectra were obtained with a Bruker MSL 400 or AM 250 instrument. All NMR spectra were recorded in $[\text{D}_8]\text{THF}$ with SiMe_4 (^1H , ^{13}C) and LiCl (^7Li) as external standards. EI mass spectra were measured on Finnigan MAT 8230 or Varian MAT CH 5 instruments. Due to the low melting points and the high sensitivity of the reported compounds, no C, H, N analysis could be obtained.

1 and **2** were prepared as described previously in ref. [6].

3: Dried 4-aminobenzonitrile (1.18 g, 10.0 mmol) was solved in THF (30 ml). An equimolar amount of $n\text{BuLi}$ (11.9 ml of a 1.68 molar solution in hexane, 10.0 mmol) was added dropwise to the solution at 0 °C. Stirring for 24 h at room temperature gave a dark green solution with a little bit of a white precipitate. After filtration, toluene (10 ml) was added. Crystallization from this solution at room temperature yielded crystals suitable for an X-ray diffraction experiment after 10 days. Yield: 1.30 g; 48.5%. M.p: 43 °C. – ^1H NMR ($[\text{D}_8]\text{THF}$, room temperature): δ = 4.07 (s, NH), 6.07 (d, $^3J_{3,2}$ 8.5 Hz, H3), 6.82 (d, $^3J_{2,3}$ 8.5 Hz, H2). – ^{13}C NMR ($[\text{D}_8]\text{THF}$, room temperature): δ = 86.2 (s, C4), 116.4 (s, C2), 124.0 (s, C5), 133.3 (s, C3), 167.6 (s, C1). – ^7Li NMR

([D₈]THF, room temperature): $\delta = 0.50$. – MS (70 eV): m/z (%) = 118 (100) NC(C₆H₄)NH₂, 91 (15) C₆H₅N.

4: Elemental rubidium (1.00 g, 11.7 mmol) under THF (20 ml) was reacted with 4-aminobenzonitrile (1.38 g, 11.7 mmol) solved in THF (20 ml) at 0 °C. Stirring for 24 h at 0 °C gave a dark red solution. Crystallization from this solution at 3 °C for 2 d yielded red crystals suitable for X-ray diffraction. Yield: 2.22 g; 54.7%. M.p: 28 °C. – ¹H NMR ([D₈]THF, room temperature): $\delta = 5.00$ (s, NH), 6.05 (d, ³J_{3,2} 5.0 Hz, H3), 6.83 (d, ³J_{2,3} 5.0 Hz, H2). – ¹³C NMR ([D₈]THF, room temperature): $\delta = 87.2$ (s, C4), 115.4 (s, C2), 123.6 (s, C5), 133.5 (s, C3), 164.0 (s, C1). – MS (70 eV): m/z (%) = 118 (100) NC(C₆H₄)NH₂.

X-ray measurements of 3 and 4: Crystal data for the two structures are presented in Table 1. All data were collected at low temperatures using an oil-coated shock-cooled crystal [30] on a STOE-Siemens AED with Mo-K α ($\lambda = 71.073$ pm) radiation. A semi-empirical absorption correction was employed for structure **4** [31]. The structures were solved by direct methods using SHELXS-90 [32] and refined with all data on F^2 with a weighting scheme of $\omega^{-1} = \sigma^2(F_o^2) + (g_1 \cdot P)^2 + (g_2 \cdot P)$ with $P = (F_o^2 + 2F_c^2)/3$ using SHELXL-93 [33]. All non-hydrogen atoms were refined

anisotropically. The hydrogen atoms of the molecules were geometrically idealized and refined using a riding model. In **3** three of the four thf groups are disordered. In **4** the thf group bonded to Rb1 and one amide ligand is disordered. All disordered groups were refined with distance restraints and restraints for the anisotropic displacement parameters. Selected bond lengths and angles of **1–4** can be found in Table 1 and 3, relevant crystallographic data for **3** and **4** are presented in Table 4. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication (numbers see Table 4). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, GB-Cambridge CB2 1EZ (UK), [Fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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- [1] For review see: C. Lambert, P. v. R. Schleyer, *Angew. Chem.* **106**, 1187 (1994); *Angew. Chem. Int. Ed. Engl.* **33**, 1129 (1994).
- [2] a) M. F. Lappert, P. P. Power, A. R. Sanger, R. C. Srivastava, *Metal and Metalloid Amides*, Wiley, New York (1980); b) L. Brandsma, H. D. Verkruijsse, *Preparative Polar Organometallic Chemistry*, Vol. 1, Springer, Berlin (1987); c) B. J. Wakefield, *Organolithium Methods*, Academic Press, London (1987); d) M. Schlosser, *Organometallics in Synthesis*, Wiley, New York (2001).
- [3] T. Stey, D. Stalke, Lead structures in lithium organic chemistry, in Z. Rappoport, I. Marek (eds): *The Chemistry of Organolithium Compounds*, p. 47, John Wiley & Sons, New York (2004).
- [4] D. Hoffmann, W. Bauer, P. v. R. Schleyer, U. Pieper, D. Stalke, *Organometallics* **12**, 1193 (1993).
- [5] U. Pieper, D. Stalke, *Organometallics* **12**, 1201 (1993).
- [6] a) H. Gornitzka, D. Stalke, *Angew. Chem.* **106**, 695 (1994); *Angew. Chem., Int. Ed. Engl.* **33**, 693 (1994); b) H. Gornitzka, D. Stalke, *Organometallics* **13**, 4398 (1994).
- [7] For review: T. Kottke, D. Stalke, *Chem. Ber./Rec.* **130**, 1365 (1997).
- [8] a) D. R. Armstrong, D. Barr, W. Clegg, R. E. Mulvey, D. Reed, R. Snaith, K. Wade, *J. Chem. Soc., Chem. Commun.* 869 (1986); reviews; b) K. Gregory, P. v. R. Schleyer, R. Snaith, *Adv. Inorg. Chem.* **37**, 47 (1991); c) R. E. Mulvey, *Chem. Soc. Rev.* **20**, 167 (1991); d) R. E. Mulvey, *Chem. Soc. Rev.* **27**, 339 (1998); e) A. Downard, T. Chivers, *Eur. J. Inorg. Chem.* 2193 (2001).
- [9] N. D. R. Barnett, W. Clegg, L. Horsburgh, D. M. Lindsay, Q.-Y. Liu, F. M. Mackenzie, R. E. Mulvey, P. G. Willard, *J. Chem. Soc. Chem. Commun.* 2321 (1996).
- [10] W. Clegg, K. W. Henderson, L. Horsburgh, F. M. Mackenzie, R. E. Mulvey, *Chem. Eur. J.* **4**, 53 (1998).
- [11] A. Heine, R. Herbst-Irmer, D. Stalke, W. Kühnle, K. A. Zachariasse, *Acta Crystallogr. Sect. B* **50**, 363 (1994).
- [12] R. v. Bülow, H. Gornitzka, T. Kottke, D. Stalke, *J. Chem. Soc. Chem. Commun.* 1639 (1996).
- [13] W. Clegg, L. Horsburgh, F. M. Mackenzie, R. E. Mulvey, *J. Chem. Soc. Chem. Commun.* 2011 (1995).
- [14] D. Stalke, U. Klingebiel, G. M. Sheldrick, *Chem. Ber.* **121**, 1457 (1988).
- [15] P. Rademacher, *Strukturen organischer Moleküle*, VCH, Weinheim, New York (1987).
- [16] P. C. Andrews, D. R. Armstrong, W. Clegg, F. J. Craig, L. Dunbar, R. E. Mulvey, *Chem. Commun.* 319 (1997).
- [17] D. Hoffmann, W. Bauer, F. Hampel, N. J. R. van Eikema Hommes, P. v. R. Schleyer, P. Otto, U. Pieper, D. Stalke, D. S. Wright, R. Snaith, *J. Am. Chem. Soc.* **116**, 528 (1994).
- [18] K. Gregory, Ph. D. thesis, Universität Erlangen-Nürnberg (1991).

- [19] F. T. Edelmann, F. Pauer, M. Wedler, D. Stalke, *Inorg. Chem.* **31**, 4143 (1992).
- [20] A. Steiner, D. Stalke, *Inorg. Chem.* **32**, 1977 (1993).
- [21] D. Colgan, R. I. Papasergio, C. L. Raston, A. H. White, *J. Chem. Soc. Chem. Commun.* 1708 (1984).
- [22] F. Neumann, C. Lambert, P. v. R. Schleyer, *J. Am. Chem. Soc.* **120**, 3357 (1998).
- [23] For reviews see: a) T. Kaufmann, *Top. Curr. Chem.* **92**, 109 (1980); b) T. Kaufmann, *Angew. Chem.* **86**, 715 (1974); *Angew. Chem. Int. Ed. Engl.* **13**, 627 (1974).
- [24] For examples see: a) T. Kaufmann, H. Berg, E. Köppelmann, *Angew. Chem.* **82**, 396 (1970); *Angew. Chem. Int. Ed. Engl.* **9**, 380 (1970); b) G. Boche, D. Martens, *Angew. Chem.* **84**, 768 (1972); *Angew. Chem. Int. Ed. Engl.* **11**, 724 (1972); c) T. Kaufmann, R. Eidenschink, *Chem. Ber.* **110**, 651 (1977).
- [25] R. I. Papasergio, B. W. Skelton, P. Twiss, A. H. White, C. L. Raston, *J. Chem. Soc. Dalton Trans.* 1161 (1990).
- [26] a) T. Kottke, D. Stalke, *Organometallics* **21**, 4552 (1996); b) S. A. Brooker, F. T. Edelmann, T. Kottke, H. W. Roesky, G. M. Sheldrick, D. Stalke, K. H. Whitmire, *J. Chem. Soc. Chem. Commun.* 144 (1991).
- [27] a) W. Clegg, L. Horsburgh, S. T. Liddle, F. M. Mackenzie, R. E. Mulvey, A. Robertson, *J. Chem. Soc., Dalton Trans.* 1225 (2000); b) R. E. Allan, M. A. Beswick, N. Feeder, M. Kranz, M. E. G. Mosquera, P. R. Raithby, A. E. H. Wheatley, D. S. Wright, *Inorg. Chem.* **37**, 2602 (1998); c) R. E. Allan, M. A. Beswick, M. K. Davies, P. R. Raithby, A. Steiner, D. S. Wright, *J. Organomet. Chem.* **550**, 71 (1998); d) W. Clegg, L. Horsburgh, F. M. Mackenzie, R. E. Mulvey, *Chem. Commun.* 2011 (1995).
- [28] a) S. S. Al-Juaid, C. Eaborn, I. B. Gorrell, S. A. Hawkes, P. B. Hitchcock, J. D. Smith, *J. Chem. Soc., Dalton Trans.* 2411 (1998); b) D. Barr, W. Clegg, L. Cowton, L. Horsburgh, F. M. Mackenzie, R. E. Mulvey *Chem. Commun.* 891 (1995).
- [29] M. Fukuyo, K. Hirotsu, T. Higuchi, *Acta Crystallogr. Sect. B* **38**, 640 (1982).
- [30] a) D. Stalke, *Chem. Soc. Rev.* **27**, 171 (1998); b) T. Kottke, R. J. Lagow, D. Stalke, *J. Appl. Crystallogr.* **29**, 465 (1996); c) T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **26**, 615 (1993).
- [31] A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr. Sect. A* **24**, 351 (1968).
- [32] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **46**, 467 (1990).
- [33] G. M. Sheldrick, *Program for Crystal Structure Refinement*, Universität Göttingen (1996).