Picolyllithium

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Carbanion or Amide? First Charge Density Study of Parent 2-Picolyllithium**

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Dedicated to Professor Helmut Werner on the occasion of his 75th birthday

Organolithium compounds have gained in importance ever since their discovery by Schlenk and Holtz in 1917.[1] Today, they are well-established reagents in organic and inorganic synthesis and are readily applied to suit various preparative protocols.[2] These range from deprotonation of weakly acidic reagents to bond formation (transfer of organic groups) and anionic polymerization reactions.

The introduction of coordinating pyridyl side chains (i.e. methylpyridyl) in ligands is one example of a C−C bond formation reaction conducted using organolithium compounds. The design of pyridyl-substituted ligands[3] usually starts with the deprotonation of 2-picoline (2-methylpyridine) with commercially available *n*-butyllithium.[4]

The reactivity determines the yields and is mainly based on the basicity, steric demand, and the Pearson hardness of the nucleophile. Moreover, the aggregation state of the lithium compound in solution, which can be deduced from single crystal structure determination, influences the behavior of the nucleophile.[5] More detailed information on the reactivity of the molecule is available from diffraction experiments.[6] High-resolution X-ray diffraction experiments enable the accurate determination of the molecular electron density distribution in the crystal. The experimental results can be compared to densities derived from gas-phase calculations under the provisions of Bader's quantum theory of atoms in molecules (QTAIM).[7]

Thus we synthesized and grew single crystals of two unsubstituted 2-picolyllithium compounds differing only in the donor bases. This approach eliminates effects on the anion that derive from additional side-arm groups. The structural analyses should provide undisguised insight into the electron distribution in the aromatic heterocyclic carbanion as a whole,[8] which has been a matter of discussion ever since the first crystal structural analysis of a substituted picolyllithium compound.[9] In particular, the controversially discussed properties of Li−X (X = C, N, O) bonds should be elucidated.[10] Scherer et al. even chose a derivative of 2-picolyllithium in their pioneering experimental charge density study on Li···H agostic interactions.[11]

2-Picolyllithium (PicLi) was prepared by slowly adding *n*-butyllithium to an equimolar amount (to give **1**) or a 2.5-fold excess (to give **2**) of 2-picoline in diethyl ether at −20 °C. Storage in the refrigerator yielded single crystals suitable for crystal structure analysis. The crystals consisted of the dimers $[2\text{-PicLi}\cdot\text{OEt}_2]_2$ (**1**) and $[2\text{-PicLi}\cdot\text{PicH}]_2$ (**2**). The compounds crystallize in centrosymmetric space groups (**1**: $P\bar{1}$; **2**: $C2/c$) with half of each dimer in the asymmetric unit. Since **1** and **2** show similar structural features, a joint discussion of the PicLi motif will be presented (Figure 1).[12]

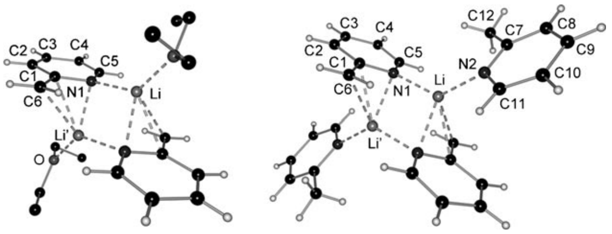

Figure 1. Molecular structures of $[2\text{-PicLi}\cdot\text{OEt}_2]_2$ (**1**, left) and $[2\text{-PicLi}\cdot\text{PicH}]_2$ (**2**, right).

The PicLi dimer is linked by two different lithium–anion interactions: a Li−N bond with the lithium atom located almost ideally in the pyridyl ring plane (deviation: 0.26 Å; angle between Li−N and the plane: 8°) and a η^3-aza-allylic contact in which the lithium cation is coordinated by the π system of the methylene group (C6), the *ipso*-carbon atom (C1), and the ring nitrogen atom (N1). The coordination sphere of the lithium cation is completed with one donor molecule per metal atom (**1**: Et_2O; **2**: 2-picoline). The in-plane Li−N bonds (2.031(2) (**1**), 2.021(1) Å (**2**)) are about 0.1 Å shorter than the contacts to the respective aza-allyl nitrogen atoms (2.133(2) (**1**), 2.136(1) Å (**2**)). The lithium–carbon distances are 2.29 Å to the *ipso*-carbon atom (2.297(2) (**1**), 2.284(1) Å (**2**)) and slightly longer to the methylene carbon atom (2.321(3) (**1**), 2.328(1) Å (**2**)).

Similar bonding situations are reported in the 2-(tri methylsilylmethyl)pyridyllithium-diethyl ether adduct[13] (**3**) and the 2-(bis(trimethylsilyl)methyl)pyridine adduct[14] (**4**). There, the aza-allyl nitrogen–lithium bonds (2.19(1) (**3**),

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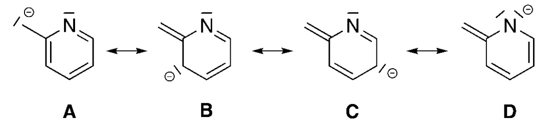
2.14(1) Å (**4**)) are also longer than the in-plane lone-pair-mediated ones (2.04(1) (**3**), 2.06(1) Å (**4**)). The Li–C separations are in the same range (2.34–2.39 Å) as in PicLi. The lithium–donor bonds in PicLi are 1.908(9) Å (O) and 2.018(1) Å (N) and are comparable in length to those known from the literature (Li–O e.g., 1.91(1) Å;[13] Li–N e.g., 2.01(1),[13] 2.05(1) Å[14]).[15]



Scheme 1. Resonance formulas of the anion in PicLi.

The diversity of feasible electronic situations in the picolyl anion is reflected by the variety of different resonance formulas in Scheme 1. In light of the solid-state structures, **A** and **D** appear to contribute most to the appropriate description of bonding. **A** emphasizes the carbanionic form, while **D** interprets the anion as an enamide. The natural bond order (NBO) analysis of the energy-minimized structure of PicLi in the gas phase with subsequent frequency calculation at the B3LYP/6-311+G(d) level of theory for the confirmation of the stationarity results in the natural Lewis structure **D** of Scheme 1.[16] In addition to the obtained structure, the NBO charges were also determined. The most distinct charges are found for N1 (−0.78 e) and C6 (−0.69 e), followed by well-separated less distinct values. This result renders resonance structure **D** to be the most dominant, followed by structure **A**. Others play only a minor role, if any. The sum of NBO charges over the anion yields in total −0.88 e, whereas the sum over the 2-picoline donor base yields a charge of +0.04 e.

The two main coordination modes (**A** and **D**) to the cation influence the electronic and structural features in the picolyl moieties of **1** and **2**. Pure crystalline 2-picoline (**5**)[17] can serve as an external reference for the deprotonation effects. The N–C bonds are of the same length (1.343 Å), and the C–C bonds in the pyridine ring vary only from 1.375 to 1.394 Å (mean value 1.383 Å). The H_3C–C bond is significantly longer (1.502(3) Å) and is almost as long as a standard C_{sp^3}–C_{sp^2} bond (1.510 Å).[18]

When the picoline molecule acts as a donor, similar bond lengths are adopted. The N–C bond lengths are 1.345 Å, and the H_3C–C bond is 1.498(1) Å. The aromatic C–C bonds are almost identical (mean value 1.392(3) Å, Figure 2). Thus, the donation to the metal atom increases the bond lengths only slightly but does not affect the π system, which is consistent with the donor concept.

In contrast, the deprotonation in **1** and **2** leads to a tremendous change in the bonding situation of the aromatic rings. The N–C bonds differ considerably (N–C1 1.394(1) and N–C5 1.358(1) Å.). The first is close to a standard N_{sp^2}–C_{sp^2} single bond (1.40 Å),[18] while the second is slightly elongated compared to the corresponding bond in the donor molecule. Moreover, there is a strong tendency toward localization of the double bonds. The bond to the methylene group is shortened by at least 0.12 Å (0.23 Å in **1**) compared to 2-picoline (**5**) and therefore is much closer to a standard double bond (C_{sp^2}=C_{sp^2}: 1.335 Å) than to a corresponding single bond (C_{sp^2}–C_{sp^2}: 1.466 Å).[18] This shortening is also observed for the C2–C3 and C4–C5 bonds. By contrast, C1–C2 and C3–C4 are closer to values for a single bond (1.453(2) and 1.417(2) Å). Therefore, from bond-length considerations of the anion, the enamide resonance formula (Scheme 1 **D**) seems most suitable to describe the electronic situation in PicLi.

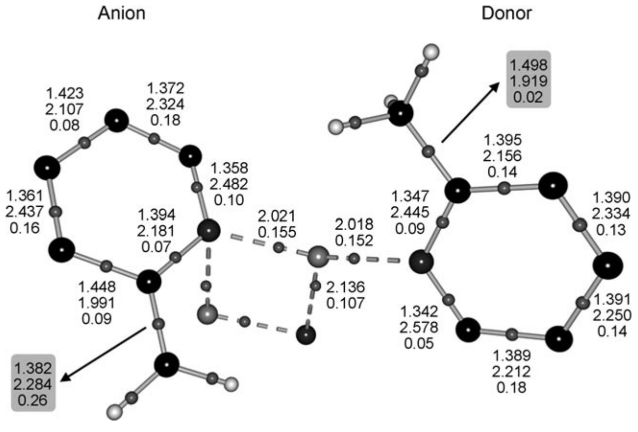


Figure 2. Representative fragment of [2-PicLi·PicH]$_2$ (**2**) showing BCPs (small spheres) with corresponding bond lengths [Å] (top), $\rho(\mathbf{r}_{BCP})$ values [e Å^{-3}] (middle), and $\varepsilon(\mathbf{r}_{BCP})$ values (bottom).

Even though the bond lengths can give a first hint as to the electronic properties of a given molecule, the method of choice is the direct investigation of the electron density distribution. Therefore, we carried out a multipole refinement[19] on a low-temperature high-resolution diffraction data set of [2-PicLi·PicH]$_2$ (**2**), measured on a Bruker TXS Mo rotating anode equipped with Helios mirror optics.[20] We analyzed the topology of the derived charge density distribution $\rho(\mathbf{r})$ within the framework of QTAIM[7] to gain more specific information on the bond characteristics.

A bond-path analysis[21] revealed the anticipated bond (BCPs) and ring critical points (RCPs) as well as the bond paths between all nonmetal atoms in **2**.[22] Furthermore, bond paths between the lithium and nitrogen atoms could be quantified, but those to the aza-allylic carbon atoms could not be. This result supports the idea of dominant Li–N bonds in the dimer and an auxiliary interaction with the formal anionic carbon atom C6. These experimental findings were substantiated by an AIM analysis of the energy-minimized structure. All determined bond paths in the experiment were matched by theory, but in addition, a BCP between Li′ and C6 was established, which might be caused by geometrical changes during the optimization.[23,24]

The electron-density values at the bond critical points of the donor molecule can serve as a reference for the bond order (Figure 2).[25] The carbon–carbon bonds within the donor pyridyl ring exhibit $\rho(\mathbf{r}_{BCP})$ values from 2.16 to 2.33 e Å^{-3}, in the range of the values in phenyl systems (2.11–2.26 e Å^{-3}).[26] The N–C bonds show elevated electron density values (2.45 and 2.58 e Å^{-3}), mainly owing to the shift of the BCP towards the more electronegative nitrogen atom.

Nevertheless, $\rho(\mathbf{r}_{BCP})$ is substantially higher than the average 1.85 e Å^{-3} for previously investigated N–C single bonds.[26] Consistently, we find distinct $\varepsilon(\mathbf{r}_{BCP})$ values in the C–C bonds (0.13–0.18), which are typical for aromatic systems. The H_3C–C bond, by contrast, reveals a reduced density ($\rho(\mathbf{r}_{BCP}) = 1.92$ e Å^{-3}) and a negligible ellipticity $\varepsilon(\mathbf{r}_{BCP})$ of 0.02; these values are close to those expected for a single bond.

The deprotonation at the methyl group changes the electronic situation in the whole ring drastically. The C–C bonds are no longer of equal length. As the bond-length alteration already indicates, the charge density distribution supports the hypothesis that the double bonds are localized at the expense of the aromatic system. Consistent with the enamide resonance formula, the highest $\rho(\mathbf{r}_{BCP})$ values are found between C2–C3 and C4–C5 (2.44 and 2.32 e Å^{-3}), accompanied by distinct $\varepsilon(\mathbf{r}_{BCP})$ values (0.16 and 0.18). Consequently, the electron density and the ellipticity between C1–C2 and C3–C4 are lower than in the donor molecule (1.99, 2.11 e Å^{-3}, and 0.09, 0.08 respectively). The N–C bonds are also influenced. The perturbation of aromaticity results in reduced $\rho(\mathbf{r}_{BCP})$ values of 2.18 and 2.48 e Å^{-3} in the nitrogen–carbon bonds. The C1–C6 bond is most affected by the deprotonation (Figure 3). Values typical for a bond order close to two (ethene as a prototype[27]) are found in **2** ($\rho(\mathbf{r}_{BCP}) = 2.28$ e Å^{-3}; $\varepsilon(\mathbf{r}_{BCP}) = 0.26$).

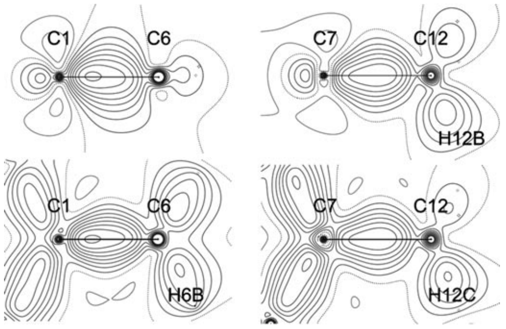


Figure 3. Deformation density map of the C1–C6 (anion, left) and C7–C12 (donor, right) bonds orthogonal to (top) and in the ring planes (bottom, step size between contours: 0.1 e Å^{-3}).

An appropriate tool to distinguish a single bond from a double bond is the inspection of the ellipticities along the whole bond paths rather than only the $\varepsilon(\mathbf{r}_{BCP})$ values (Figure 4).[11] The perturbation of the aromatic π system in the anion and the different bonding types between the *ipso*-carbon atoms and C6 or C12 are evident. While all C–C ring bonds in the donor show moderately elevated ellipticity values (mesomeric π contribution) along the bond paths with gradual asymmetry relative to the BCP, the ellipticity of the exocyclic C7–C12 bond is close to zero, as expected for a single bond. In comparison, the C1–C6 bond in the anion reveals the highest $\varepsilon(\mathbf{r})$ value among all C–C bonds under investigation. Therefore, we can include the methylene carbon bond in the series of localized formal double bonds in the conjugated π system of the picolyl anion. The closer to C6 $\varepsilon(\mathbf{r})$ is calculated, the more pronounced this feature gets, probably owing to charge accumulation at the methylene carbon atom and deformation caused by an interaction with Li′. The ellipticities along the carbon–carbon bonds in the anionic ring support the interpretation of C2–C3 and C4–C5 as having appreciable double bond character, while C1–C2 and C3–C4 show values that are about half as large; these bonds thus display less π character. From these $\varepsilon(\mathbf{r})$ distributions, we postulate the enamide form to be appropriate in describing the bonding properties in the anion.

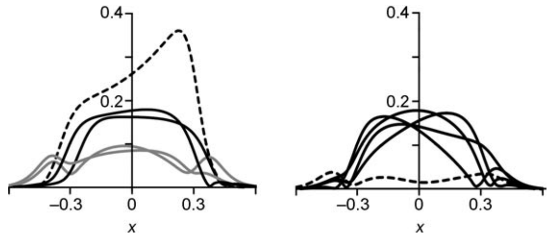


Figure 4. Ellipticities of the C–C bonds along the bond paths in the anion (left; ——: C2–C3/C4–C5, ——: C1–C2/C3–C4, -----: C1–C6) and the donor (right; ——: ring C–C bonds, -----: C7–C12) of [2-PicLi·PicH]$_2$ (**2**, x axis [Å] relative to the BCP).

Keeping the resonance formulas of Scheme 1 in mind, an inspection of the atomic charges[28] should consolidate these interpretations. The lithium cation exhibits a charge of +0.93 e, which is counterbalanced by the anion (sum of atomic contributions: −0.80 e) and the donor molecule (−0.13 e group charge). Thus, the main portion of the negative charge is located on the anion. Within the donor base, negative charge is exclusively concentrated at the ring nitrogen atom (−0.94 e). This situation results in a polarization of the neighboring carbon atoms (C7: +0.37, C11: +0.12 e) so that the negative charge is relativized.

Interestingly, despite the deprotonation, the negative charges at N1 (−1.04 e) and the methylene group (−0.19 e) show just a marginal increase compared to the donor (N2: −0.94 e; methyl group: +0.02 e). Thus, the negative charge is distributed over the whole ring system with the largest increase at the methylene group (Δ = −0.21 e). Hence, we suggest from the investigation of the group charges that the carbanionic resonance form **A** in Scheme 1 is suitable, even though the absolute values of the negative charges are relatively low. It is noteworthy that we find an atomic charge of about −1 e at N1 of the anion, but also at N2 of the donor. Therefore, the nitrogen charge originates mainly from polarization of neighboring atoms instead of deprotonation. On the other hand, the bonding properties derived from $\rho(\mathbf{r}_{BCP})$ and the ellipticities at the BCPs and along the bond paths support the interpretation of PicLi as an enamide (**D** in Scheme 1).

The question remains as to why the coordination of the lithium atom is accomplished first and foremost by the nitrogen atom, even though the charge at N1 (in the anion) is only slightly higher than that at N2 (in the donor). The charge accumulation in the lone-pair region seems to be the driving force in the arrangement of the four-membered $[LiN]_2$ ring. A search of extrema in the Laplacian field $\nabla^2\rho(\mathbf{r})$ around both nitrogen atoms gives three valence shell charge concentrations (VSCCs)[29] in the ring planes, thus indicating sp^2 hybridization. An isosurface representation of $\nabla^2\rho(\mathbf{r})$ around N1 reveals the expected VSCC (maximum value $-69.1\,e\,\text{Å}^{-5}$) of a Li-directed in-plane lone pair, which is deformed towards Li′ (Figure 5).[30] Differently, the donor nitrogen atom N2 exhibits a more symmetrical distribution of $\nabla^2\rho(\mathbf{r})$ on the same isosurface level and an even more pronounced maximum ($-73.5\,e\,\text{Å}^{-5}$). No such accumulation was found around C6. Three VSCCs towards the bonding partners could be quantified, but no explicit concentration facing the aza-allyl coordinated lithium atom was found. Only polarization towards the cation on a lower level is visible in the isosurface representation, but no well-defined VSCC can be detected (Figure 5). Obviously, the Lewis basicity of C6 cannot compete with the lone pair at N1. Nevertheless, the polarization around C6 towards Li′ suggests at least co-coordination of the aza-allyl system.

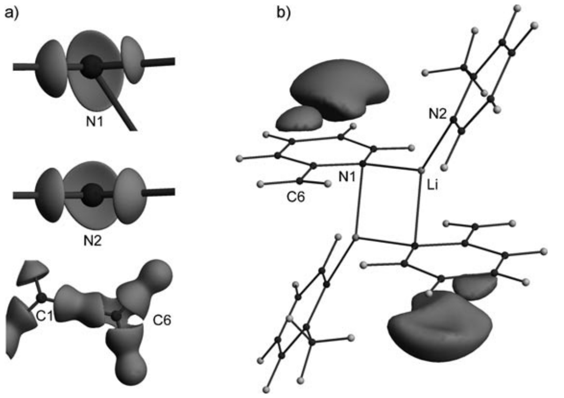


Figure 5. Isosurface representation of a) $\nabla^2\rho(\mathbf{r})$ around N1, N2 ($-45\,e\,\text{Å}^{-5}$), and C6 with the backside facing Li′ ($-8.5\,e\,\text{Å}^{-5}$) and b) of the ESP ($-0.1\,e\,\text{Å}^{-1}$).

The astonishing similarities of the nitrogen atoms in the donor and the anion are also mirrored in the topological properties of the σ-donor Li–N bonds. For both we find low electron density values at the BCPs (N1: $0.16\,e\,\text{Å}^{-3}$; N2: $0.15\,e\,\text{Å}^{-3}$) and slightly positive $\nabla^2\rho(\mathbf{r}_{\mathrm{BCP}})$ values ($4.5\,e\,\text{Å}^{-5}$). These values are in the expected range of dative bonds.[10c,26,31] Even less density is accumulated in the Li′–N1 bond ($\rho(\mathbf{r}_{\mathrm{BCP}}) = 0.11\,e\,\text{Å}^{-3}$ and $\nabla^2\rho(\mathbf{r}_{\mathrm{BCP}}) = 3.1\,e\,\text{Å}^{-5}$), which indicates the lone-pair–lithium σ bond to be dominant.

Remarkably, an electrophilic attack on 2-picolyllithium generally occurs at the methylene group. Is this in accordance with the electron density distribution? The three-dimensional distribution of the electrostatic potential (ESP) displayed in Figure 5 provides an answer. Opposite to the Li′–N bond, we find a vast region of negative ESP above the picolyl anion plane. We found a comparable distribution in a benzyllithium derivative.[26] The spatial distribution suggests that potential electrophiles are guided by the negative potential towards the nucleophilic C6 atom. Most probably, it is the π system of the anion as a whole that leads to the observed ESP, not a local charge concentration at the formal carbanion. We thus conclude that deprotonation in the benzylic position leads to similar density features in the ESP and the Laplacian distribution.

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[25] The value of $\rho(\mathbf{r}_{\mathrm{BCP}})$ is a measure for the strength of the bond. $\nabla^2\rho(\mathbf{r}_{\mathrm{BCP}})$ indicates charge concentrations (negative values) or charge depletions (positive values), and $\varepsilon(\mathbf{r}_{\mathrm{BCP}})$ gives the deviation from cylindrical symmetry of $\rho(\mathbf{r})$ at the BCP ($\varepsilon = \lambda_2/\lambda_1 - 1$, where λ_1 and λ_2 are the two eigenvalues of the Hessian perpendicular to the bond).

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[29] Valence shell charge concentrations are $(3,+3)$ critical points (minima) in $\nabla^2\rho(\mathbf{r})$.

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