



Crystal structure and Hirshfeld surface analysis of 2-picollythium·3thf

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In the title compound, (2-methylidene-1,2-dihydropyridinium- κN)tris(tetrahydrofuran- κO)lithium, $[\text{Li}(\text{C}_6\text{H}_6\text{N})(\text{C}_4\text{H}_8\text{O})_3]$, the lithium ion adopts a distorted LiNO_3 tetrahedral coordination geometry and the 2-picollyl anion adopts its enamido form with the lithium ion lying close to the plane of the pyridine ring. A methylene group of one of the thf ligands is disordered over two orientations. In the crystal, a weak $\text{C}-\text{H}\cdots\text{O}$ interaction generates inversion dimers. A Hirshfeld surface analysis shows that $\text{H}\cdots\text{H}$ contacts dominate the packing (86%) followed by $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$ and $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$ contacts, which contribute 3% and 10.4%, respectively.

1. Chemical context

Among the various synthetic approaches for the introduction of 2-picoline ($\text{C}_6\text{H}_7\text{N}$) into a wide range of chemical products, the route *via* a metallated intermediate (*i.e.*, the 2-picollyl anion, $\text{C}_6\text{H}_6\text{N}^-$) followed by trapping with an electrophile has proven to be particularly attractive due to the large number of possible electrophilic compounds. The formation of these metal-containing intermediates usually takes place by reaction with organometallic bases such as lithium organyles (Gessner *et al.*, 2009), resulting in deprotonation of the picoline and consequent anion formation (Beumel Jr *et al.*, 1974). Due to resonance-stabilizing effects, there are different possibilities to stabilize the negative charge formed at the 2-picoline moiety. In addition to the delocalization of charge across the aromatic ring, further anionic motifs in the sense of a carbanion, an aza-allyl anion, or an enamide anion are possible: see Fig. 1.

Charge-density studies by Ott *et al.* (2009) confirmed the existence of the aza-allyl carbanionic 2-picollyl motif by solid-state analysis of two dimeric 2-picollylithium structures ($(2\text{-PicLi}\cdot\text{OEt}_2)_2$ (**2**) and $(2\text{-PicLi}\cdot\text{PicH})_2$ (**3**)). Both structures are defined by two different lithium–anion interactions within one complex (Fig. 2). On the one hand there is an $\text{Li}-\text{N}$ bond such that the metal ion lies almost coplanar to the aromatic pyridyl ring and on the other hand an η^3 -aza-allylic contact can be identified. While NBO analysis determined partial negative charges at the nitrogen atom ($-0.78 e$) and formed carbanion

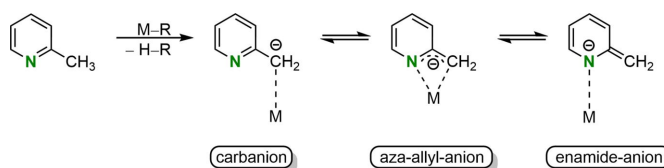
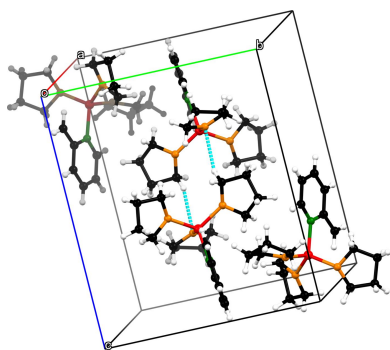
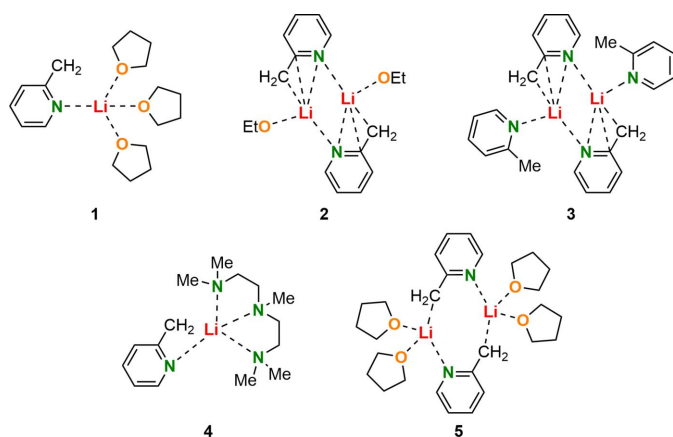


Figure 1
Transformation of 2-picoline into its carbanion, aza-allyl anion and enamide anion forms.

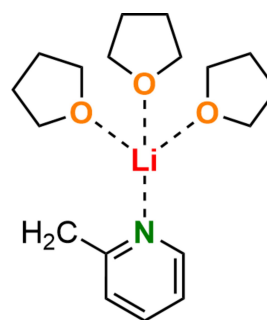
**Figure 2**

Structures of the title compound (2-PicLi·3thf) (**1**), (2-PicLi·OEt₂)₂ (**2**), (2-PicLi·PicH)₂ (**3**), enamido (2-PicLi·pmdta) (**4**) and dimeric carbanionic [2-PicLi·(thf)₂]₂ (**5**).

(−0.69 e), which indicates aza-allylic character, bond-path analysis could only identify a bond path between the lithium and nitrogen atoms. In conclusion, the Li–N interaction was described as more dominant and the Li–carbanion contact as an auxiliary interaction (Ott *et al.*, 2009).

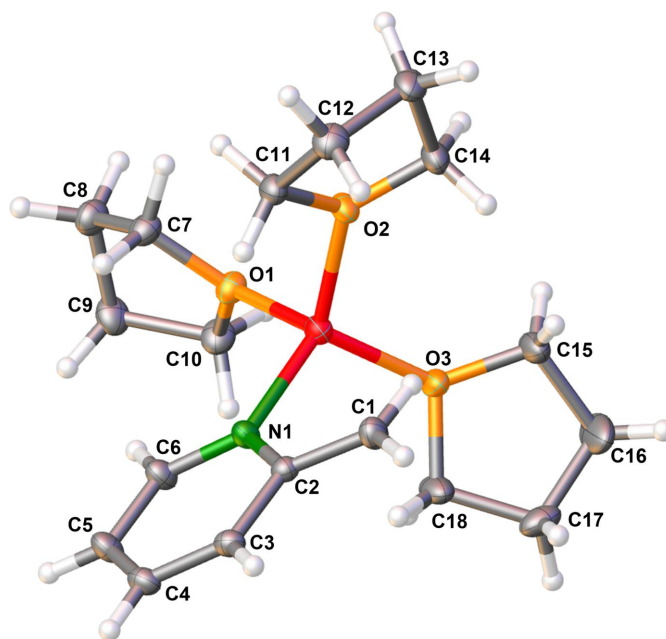
The group of Mulvey (Kennedy *et al.*, 2014) followed up on these studies and reported the monomeric solid-state structure (2-PicLi·pmdta) (**4**) (pmdta = *N,N,N',N'',N'''*-pentamethyl-diethylenetriamine, C₉H₂₃N₃). In contrast to the dimeric aza-allyl motif **2** of Stalke *et al.*, Mulvey and co-workers identified the monomeric structure **4** as an enamido motif due to the sole Li–N interaction (Fig. 1). Saturation of the lithium coordination sphere is accomplished by the chelating pmdta ligand. To characterize the described solid-state structures, the location of the lithium cations relative to the aromatic pyridyl ring serves as an important tool. Therefore aza-allylic structures like **2** or **3** were defined by *sp*²-hybridized nitrogen atoms and *C*_{para}–N–Li bond angles of about 180°, representing an almost planar arrangement. The enamido motif shows a divergent *C*_{para}–N–Li angle of about 146° indicating *sp*³-hybridization of the nitrogen center (Kennedy *et al.*, 2014). Due to the usage of different solvents, a follow-up dimeric structure [2-PicLi·(thf)₂]₂ (**5**) could be obtained by Brouillet *et al.* (2020) (Fig. 2). Unlike the previous dimeric structure **2** of Stalke *et al.*, NBO calculations determined negative charges at N (−0.68 e), O (−0.65 e) and C2 (−0.80 e) suggesting a carbanionic structural motif. Thus, all three possible structural motifs have been detected and characterized in the solid state (Brouillet *et al.*, 2020).

In this work, using an excess amount of the tetrahydrofuran (thf) ligand, a related structure to [2-PicLi·(thf)₂]₂ (**5**) by Mulvey *et al.* was obtained in the form of the title lithiated monomeric 2-picoline saturated by three thf molecules [2-PicLi·(thf)₃] (**1**) (Fig. 1). Interestingly, this monomeric structure shows an inconsistent *C*_{para}···N–Li angle of 179.9° regarding to former enamido motifs, indicating an *sp*²-hybridized nitrogen in contrast to usual *sp*³-hybridization.



2. Structural commentary

Fig. 3 shows the molecular structure of **1** and selected bond lengths and angles are given in Table 1. The solid-state structure consists of a lithiated 2-picoline unit forming an enamido motif. The lithium cation is coordinated by the N atom of 2-picoline as well as by three thf molecules. The O–Li1–N1 angles of 106.33 (7), 115.29 (7) and 111.51 (7)° indicate a slightly distorted tetrahedral coordination, probably due to packing effects (see *Supramolecular features*). Lithiation led to deprotonation of the methyl substituent resulting in *sp*²-hybridization of the C1-carbon atom, which is recognizable due to shortening of the C1–C2 bond and the changing sum of bond angles to 360° at the carbanionic center, compared to the solid-state structure of 2-picoline (Bond & Davies, 2001). With a length of 1.3804 (10) Å, the C1–C2 bond is significant shorter than typical *Csp*²–*Csp*² single bonds (1.466 Å) but too long for *Csp*²–*Csp*² double bonds (1.335 Å; Rademacher, 1987). This is caused by stabilization of the negative charge by the aromatic ring. Due to the shortened

**Figure 3**

The molecular structure of compound **1** with displacement ellipsoids drawn at the 50% probability level. Only the major disorder component is shown.

Table 1

Selected geometric parameters (Å, °).

Li1—O1	1.9493 (16)	N1—C6	1.3479 (10)
Li1—O2	1.9698 (15)	C2—C3	1.4548 (10)
Li1—O3	1.9576 (15)	C3—C4	1.3664 (11)
Li1—N1	2.0131 (16)	C4—C5	1.4196 (12)
N1—C2	1.4017 (10)	C5—C6	1.3855 (11)
O1—Li1—O2	103.75 (7)	O2—Li1—N1	115.29 (7)
O1—Li1—O3	105.69 (7)	O3—Li1—O2	113.22 (7)
O1—Li1—N1	106.33 (7)	O3—Li1—N1	111.51 (7)

C1—C2 bond, the overall bonding situation in the aromatic ring is changed as well, displayed by extended C2—C3 [1.4548 (19) Å], C4—C5 [1.4196 (12) Å] bonds and shortened C3—C4 [1.3664 (11) Å] and C5—C6 [1.3855 (11) Å] bonds. While the N1—C2 bond length increased by about 0.06 Å, the N1—C6 bond length is comparable to the equivalent bond in the educt structure (Bond & Davies, 2001).

The coordination distance Li1—N1 is only slightly longer than in the related monomeric structure of lithiated 2-picoline with pmdta, **4**. However, this can be explained by stronger coordinating thf ligands characterized by shorter Li—O distances [1.9493 (16) to 1.9698 (15) Å] compared to the nitrogen coordination distance of pmdta [2.138 (7) to 2.147 (7) Å]. One thf ligand of **1** shows disorder of one of its methylene groups over two adjacent positions in a 0.717 (5):0.283 (5) ratio.

Another striking feature of the monomer **1** is the planar arrangement of the lithium cation relative to the aromatic ring. As indicated by the angle Li1—N1⋯C4 of 179.9°, the cation hardly deviates from the ring plane. Together with the angular sum of 360° around N1, an sp^2 -hybridized nitrogen atom can be assumed. According to this, the lithium cation should be coordinated by a dative bond based on the free

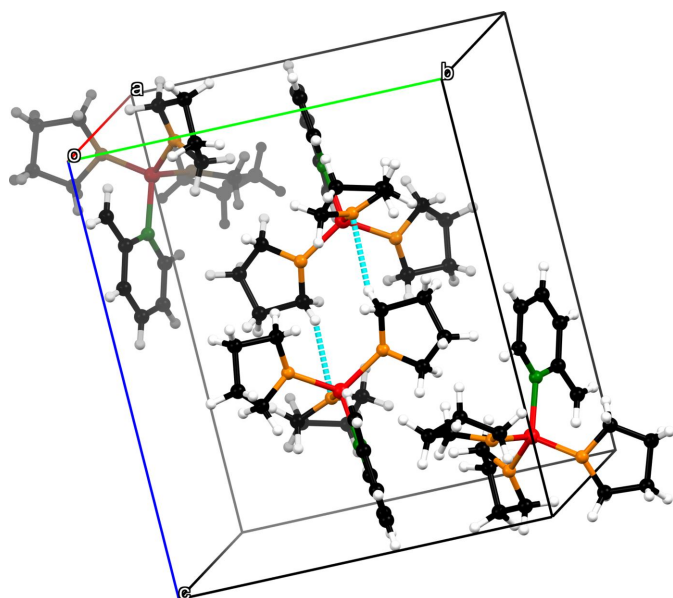
electron pair of the nitrogen. This is in strong contrast to the monomeric compound **4** observed by Mulvey *et al.* in which an Li1—N1—C4 angle of 145.9 (2)° was observed, which suggests sp^3 -hybridization of the nitrogen center and coordination of the lithium cation *via* a localized negative charge.

A greater similarity with **1** is shown by the dimeric carbanionic structure of lithiated 2-picoline with thf, **5**. The dimer consists of a non-planar eight-membered (NCCLi)₂ ring in the solid state. A planar arrangement of the lithium cation with the aromatic ring was observed and the authors describe a dative coordination of the cation *via* an sp^2 -hybridized nitrogen atom. However, the Li1—N1 coordination in **5** is described as a weaker interaction, as in the case of the sp^3 -hybridized nitrogen atom in structure **4**. Therefore, the carbanionic CH₂ substituent of **5** induces a stronger coordination to the lithium cation. In **1**, less carbanionic character of the CH₂ substituent is detectable, due to delocalization of the charge to the aromatic ring. The significantly shortened C1—C2 bond and the angular sum at the C1 atom of 360° indicate sp^2 hybridization. This would be more comparable to the monomeric structure of Mulvey *et al.*

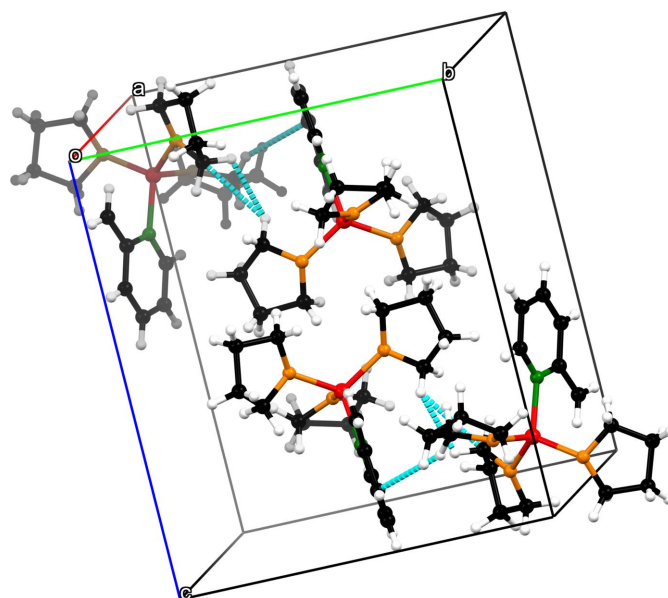
In summary, the here-presented structure **1** shows features of both structures **4** and **5**. While the sp^2 hybridization of the CH₂ substituent is more similar to the monomeric structure **4**, the linear arrangement of Li1—N1⋯C4 and the resulting presumed sp^2 hybridization of the nitrogen atom is more comparable to the dimeric structure **5**.

3. Supramolecular features

An important supramolecular structural element of compound **1** is the two close contacts between O1 and H15B across the inversion center (Fig. 4). With a coordination distance of O1ⁱ⋯C15 = 3.3695 (14) Å [symmetry code: (i)


Figure 4

The crystal packing of compound **1**. C—H⋯O hydrogen bonds are shown as dashed blue lines.


Figure 5

The crystal packing of compound **1**. C11ⁱ/H11Bⁱ⋯H19B and H7Aⁱ⋯C3 van der Waals interactions are shown as dashed blue lines.

Table 2
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C15-H15B\cdots O1^i$	0.99	2.63	3.3695 (14)	131

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

$1 - x, 1 - y, 1 - z$], fairly long-range interactions are represented. Due to two intermolecular C–H interactions (Table 2) between $C11^i/H11B^i$ and $H19B$ as well as $H7A^i$ and $C3$, further coordination points are given in the solid state (Fig. 5).

Fig. 6 shows the van der Waals interactions in the form of a Hirshfeld surface analysis mapped over d_{norm} in the range -0.02 to 1.61 a.u. (Spackman & Jayatilaka, 2009) generated by *CrystalExplorer21* (Spackman *et al.*, 2021) using red dots to represent close contacts. To visualize the percentages of the respective interactions, two-dimensional fingerprint plots (McKinnon *et al.*, 2007) were generated and are illustrated in Fig. 7. They show that interactions between $H\cdots H$ have the greatest influence (86%) to the packing of molecules in the solid state. Interactions between $O\cdots H$ and $C\cdots H$, as well as reciprocal contacts, contribute less to the crystal packing and can only be seen as spikes in the fingerprint plots with 3% and 10.4% contributions, respectively.

Due to its deprotonation, a partial negative charge at the CH_2 substituent would be expected, but no distinct coordination points could be observed. The closest contact is $C1\cdots H13B$ at 2.97 \AA but no specific intermolecular interactions can be observed.

4. Database survey

A search of the Cambridge Crystallographic Database (WebCSD, November 2023; Groom *et al.*, 2016) for lithiated

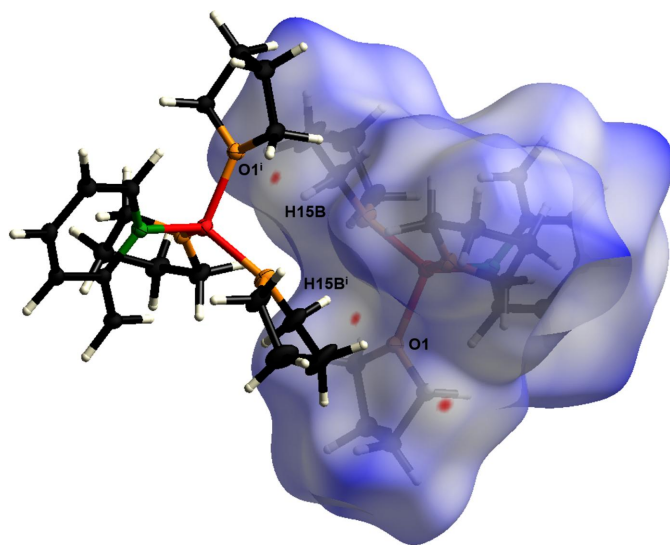


Figure 6
Hirshfeld surface analysis of **1** showing close contacts in the crystal. The weak hydrogen bond between $O1^i$ and $H15B$ is labeled. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$].

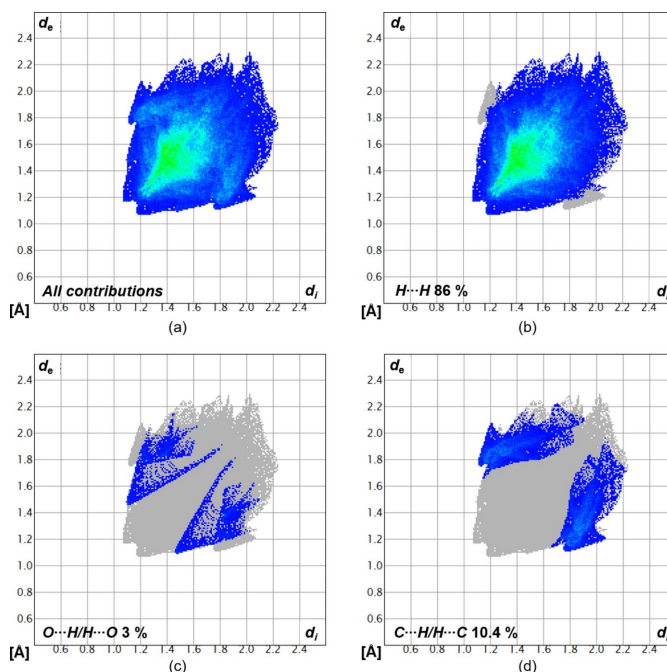


Figure 7

Two-dimensional fingerprint plots for compound **1**, showing (a) all contributions and (b)–(d) contributions between specific interacting atom pairs (blue areas).

2-picoline or lithiated 2-methylpyridine leads to the previously discussed structures **2** (Ott *et al.*, 2009), **2** and **5** (Kennedy *et al.*, 2014; Brouillet *et al.*, 2020). A few other lithiated solid state structures of 2-picoline were published, for example bis(μ_2 -dimesitylborinato)bis(2-methylpyridine)dilithium (ROLRIU; Saravana *et al.* (2009). However, it should be mentioned that the above structure and many other lithium 2-picoline complexes do not include the deprotonation of the methyl substituent and thus differ from the solid-state structures, accordingly this research. For example, bis(μ_2 -tetrahydroborato)tetrakis(2-methylpyridine)dilithium (HIWYOC; Gálvez Ruiz *et al.*, 2008). Compared to the few lithiated structures of 2-picoline, there are many other coordination complexes with neutral 2-picoline. For example, between 2-picoline and transition metals, such as *trans*-diiodobis(2-picoline)platinum(II) (KARVEE; Tessier & Rochon, 1999) or between 2-picoyl cations and different anions, for example bis(2-methylpyridinium)tetrabromocopper(II) (BACHOD; Luque *et al.*, 2001).

5. Synthesis and crystallization

On account of the air-sensitive nature of organolithium compounds, it was crucial to work with Schlenk techniques under an argon atmosphere. Pre-dried and distilled tetrahydrofuran (1.00 ml) was added to an evacuated 25 ml Schlenk flask and 2-picoline (0.09 g, 1.00 mmol, 1.00 eq.) was added. After cooling down the reaction mixture to 193 K, *n*-butyllithium (2.5 M in hexane, 0.44 ml, 1.10 mmol, 1.10 eq.) was added. The resulting orange-colored suspension was heated up to 233 K over the period of 1 h. Afterwards the

mixture was layered over by *n*-pentane (2.00 ml) and stored at 193 K. After 24 h, orange block-shaped crystals of the title compound were obtained.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Hydrogen atoms except for H1A and H1B were positioned geometrically ($C-H = 0.95-1.00 \text{ \AA}$) and were refined using a riding model, with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$ for CH_2 and CH hydrogen atoms and $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(C)$ for CH_3 hydrogen atoms. The hydrogen atoms H1A and H1B were refined freely.

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Table 3
Experimental details.

Crystal data	
Chemical formula	[Li(C ₆ H ₆ N)(C ₄ H ₈ O) ₃]
M_r	315.37
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	9.267 (3), 13.178 (4), 15.053 (5)
β (°)	94.437 (6)
V (Å ³)	1832.7 (10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.08
Crystal size (mm)	0.39 × 0.29 × 0.21
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
$T_{\text{min}}, T_{\text{max}}$	0.493, 0.570
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	58129, 10326, 7724
R_{int}	0.048
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.909
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.052, 0.159, 1.04
No. of reflections	10326
No. of parameters	226
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.68, -0.39

Computer programs: *APEX2* and *SAINT* V8.40B (Bruker, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL2014/7* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

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supporting information

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Crystal structure and Hirshfeld surface analysis of 2-picolyllithium·3thf

Tristan Mairath, Annika Schmidt and Carsten Strohmann

Computing details

(2-Methylidene-1,2-dihydropyridinium- κ N)tris(tetrahydrofuran- κ O)lithium

Crystal data

[Li(C₆H₆N)(C₄H₈O)₃]

$M_r = 315.37$

Monoclinic, $P2_1/n$

$a = 9.267$ (3) Å

$b = 13.178$ (4) Å

$c = 15.053$ (5) Å

$\beta = 94.437$ (6)°

$V = 1832.7$ (10) Å³

$Z = 4$

$F(000) = 688$

$D_x = 1.143$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 812 reflections

$\theta = 2.7$ – 17.2 °

$\mu = 0.08$ mm⁻¹

$T = 100$ K

Block, orange

$0.39 \times 0.29 \times 0.21$ mm

Data collection

Bruker APEXII CCD
diffractometer

φ and ω scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.493$, $T_{\max} = 0.570$

58129 measured reflections

10326 independent reflections

7724 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.048$

$\theta_{\max} = 40.2$ °, $\theta_{\min} = 2.1$ °

$h = -15 \rightarrow 14$

$k = -23 \rightarrow 20$

$l = -27 \rightarrow 23$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.052$

$wR(F^2) = 0.159$

$S = 1.04$

10326 reflections

226 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0816P)^2 + 0.2483P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.68$ e Å⁻³

$\Delta\rho_{\min} = -0.39$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	0.54688 (6)	0.40545 (4)	0.69990 (4)	0.02005 (10)	
O2	0.25473 (6)	0.37020 (4)	0.59195 (3)	0.01990 (10)	
O3	0.40664 (7)	0.59499 (4)	0.60466 (4)	0.02251 (11)	
N1	0.27503 (7)	0.50208 (5)	0.78389 (4)	0.01709 (10)	
C1	0.05286 (9)	0.55119 (6)	0.70141 (5)	0.02052 (13)	
H1A	0.0958 (14)	0.5399 (11)	0.6444 (9)	0.031 (3)*	
H1B	-0.0492 (14)	0.5759 (10)	0.6979 (8)	0.026 (3)*	
C2	0.13184 (8)	0.53679 (5)	0.78198 (4)	0.01576 (11)	
C3	0.07194 (8)	0.55663 (5)	0.86681 (5)	0.01810 (12)	
H3	-0.0262	0.5774	0.8673	0.022*	
C4	0.15372 (9)	0.54601 (6)	0.94577 (5)	0.02027 (13)	
H4	0.1128	0.5601	1.0004	0.024*	
C5	0.29996 (9)	0.51389 (6)	0.94596 (5)	0.02199 (14)	
H5	0.3600	0.5070	0.9997	0.026*	
C6	0.35063 (8)	0.49311 (6)	0.86368 (5)	0.01989 (13)	
H6	0.4479	0.4704	0.8635	0.024*	
C7	0.55077 (9)	0.30305 (6)	0.73460 (5)	0.02141 (13)	
H7A	0.5091	0.2547	0.6892	0.026*	
H7B	0.4956	0.2983	0.7882	0.026*	
C8	0.70987 (9)	0.28060 (6)	0.75781 (6)	0.02488 (15)	
H8A	0.7577	0.2567	0.7051	0.030*	
H8B	0.7231	0.2292	0.8057	0.030*	
C9	0.76766 (10)	0.38425 (7)	0.78926 (6)	0.02664 (16)	
H9A	0.7487	0.3970	0.8521	0.032*	
H9B	0.8729	0.3902	0.7828	0.032*	
C10	0.68127 (9)	0.45639 (6)	0.72633 (6)	0.02482 (15)	
H10A	0.6625	0.5210	0.7570	0.030*	
H10B	0.7351	0.4714	0.6736	0.030*	
C11	0.17241 (9)	0.29871 (6)	0.64195 (5)	0.02126 (13)	
H11A	0.1476	0.3291	0.6990	0.026*	
H11B	0.2288	0.2359	0.6549	0.026*	
C12	0.03647 (10)	0.27587 (7)	0.58261 (6)	0.02632 (16)	
H12A	-0.0410	0.3257	0.5917	0.032*	
H12B	0.0002	0.2066	0.5933	0.032*	
C13	0.09069 (11)	0.28551 (6)	0.48928 (6)	0.02723 (16)	
H13A	0.1429	0.2237	0.4726	0.033*	
H13B	0.0101	0.2991	0.4438	0.033*	
C14	0.19207 (10)	0.37589 (6)	0.50112 (5)	0.02495 (15)	
H14A	0.2684	0.3722	0.4587	0.030*	
H14B	0.1380	0.4402	0.4910	0.030*	
C15	0.37218 (13)	0.62291 (7)	0.51309 (5)	0.0318 (2)	
H15A	0.2719	0.6025	0.4934	0.038*	
H15B	0.4393	0.5896	0.4741	0.038*	
C16	0.3882 (2)	0.73688 (8)	0.50938 (7)	0.0516 (4)	
H16A	0.4885	0.7565	0.4988	0.062*	0.717 (5)

H16B	0.3209	0.7666	0.4621	0.062*	0.717 (5)
H16C	0.4604	0.7554	0.4670	0.062*	0.283 (5)
H16D	0.2945	0.7684	0.4889	0.062*	0.283 (5)
C17	0.3499 (2)	0.76969 (9)	0.60076 (10)	0.0299 (4)	0.717 (5)
H17A	0.3994	0.8339	0.6188	0.036*	0.717 (5)
H17B	0.2441	0.7792	0.6021	0.036*	0.717 (5)
C17A	0.4337 (5)	0.7718 (2)	0.59564 (19)	0.0232 (9)	0.283 (5)
H17C	0.3801	0.8339	0.6100	0.028*	0.283 (5)
H17D	0.5385	0.7874	0.6000	0.028*	0.283 (5)
C18	0.40128 (13)	0.68536 (6)	0.65944 (6)	0.0325 (2)	
H18A	0.4987	0.7009	0.6879	0.039*	0.717 (5)
H18B	0.3344	0.6749	0.7068	0.039*	0.717 (5)
H18C	0.4750	0.6825	0.7106	0.039*	0.283 (5)
H18D	0.3045	0.6938	0.6821	0.039*	0.283 (5)
Li1	0.36132 (16)	0.47086 (10)	0.66828 (9)	0.0189 (2)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0182 (2)	0.0180 (2)	0.0236 (2)	-0.00114 (17)	-0.00041 (18)	0.00186 (17)
O2	0.0242 (3)	0.0201 (2)	0.01507 (19)	-0.00422 (18)	-0.00091 (17)	-0.00015 (16)
O3	0.0354 (3)	0.0150 (2)	0.0172 (2)	-0.00083 (19)	0.0025 (2)	0.00046 (16)
N1	0.0175 (3)	0.0193 (2)	0.0143 (2)	0.00114 (19)	0.00059 (18)	-0.00134 (17)
C1	0.0204 (3)	0.0227 (3)	0.0180 (3)	0.0024 (2)	-0.0009 (2)	0.0007 (2)
C2	0.0176 (3)	0.0134 (2)	0.0163 (2)	-0.00083 (19)	0.0013 (2)	-0.00071 (18)
C3	0.0199 (3)	0.0164 (2)	0.0184 (3)	-0.0007 (2)	0.0041 (2)	-0.0020 (2)
C4	0.0243 (3)	0.0205 (3)	0.0164 (3)	-0.0030 (2)	0.0042 (2)	-0.0035 (2)
C5	0.0241 (3)	0.0269 (3)	0.0146 (2)	-0.0008 (3)	-0.0007 (2)	-0.0039 (2)
C6	0.0189 (3)	0.0244 (3)	0.0161 (3)	0.0010 (2)	-0.0005 (2)	-0.0029 (2)
C7	0.0211 (3)	0.0172 (3)	0.0257 (3)	-0.0014 (2)	-0.0002 (2)	0.0007 (2)
C8	0.0222 (3)	0.0237 (3)	0.0281 (4)	0.0028 (3)	-0.0017 (3)	0.0016 (3)
C9	0.0239 (4)	0.0303 (4)	0.0247 (3)	-0.0053 (3)	-0.0056 (3)	0.0020 (3)
C10	0.0244 (4)	0.0222 (3)	0.0271 (3)	-0.0064 (3)	-0.0027 (3)	0.0016 (3)
C11	0.0278 (4)	0.0185 (3)	0.0173 (3)	-0.0030 (2)	0.0007 (2)	0.0015 (2)
C12	0.0244 (4)	0.0244 (3)	0.0298 (4)	-0.0050 (3)	-0.0006 (3)	0.0003 (3)
C13	0.0362 (4)	0.0227 (3)	0.0213 (3)	-0.0047 (3)	-0.0076 (3)	-0.0016 (2)
C14	0.0351 (4)	0.0234 (3)	0.0156 (3)	-0.0047 (3)	-0.0025 (3)	0.0016 (2)
C15	0.0580 (6)	0.0211 (3)	0.0163 (3)	-0.0044 (3)	0.0028 (3)	0.0001 (2)
C16	0.1042 (11)	0.0230 (4)	0.0273 (4)	-0.0134 (5)	0.0030 (6)	0.0074 (3)
C17	0.0322 (10)	0.0159 (4)	0.0408 (7)	0.0010 (4)	-0.0016 (5)	-0.0044 (4)
C17A	0.028 (2)	0.0150 (9)	0.0251 (12)	-0.0041 (9)	-0.0038 (10)	0.0015 (8)
C18	0.0597 (6)	0.0175 (3)	0.0201 (3)	-0.0080 (3)	0.0022 (3)	-0.0030 (2)
Li1	0.0223 (6)	0.0184 (5)	0.0159 (5)	-0.0007 (5)	0.0011 (4)	-0.0001 (4)

Geometric parameters (Å, °)

Li1—O1	1.9493 (16)	C10—H10A	0.9900
Li1—O2	1.9698 (15)	C10—H10B	0.9900

Li1—O3	1.9576 (15)	C11—H11A	0.9900
Li1—N1	2.0131 (16)	C11—H11B	0.9900
O1—C7	1.4465 (10)	C11—C12	1.5170 (12)
O1—C10	1.4433 (10)	C12—H12A	0.9900
O2—C11	1.4577 (10)	C12—H12B	0.9900
O2—C14	1.4454 (10)	C12—C13	1.5335 (14)
O3—C15	1.4384 (11)	C13—H13A	0.9900
O3—C18	1.4515 (10)	C13—H13B	0.9900
N1—C2	1.4017 (10)	C13—C14	1.5189 (12)
N1—C6	1.3479 (10)	C14—H14A	0.9900
C1—H1A	0.985 (14)	C14—H14B	0.9900
C1—H1B	0.998 (13)	C15—H15A	0.9900
C1—C2	1.3804 (10)	C15—H15B	0.9900
C2—C3	1.4548 (10)	C15—C16	1.5107 (14)
C3—H3	0.9500	C16—H16A	0.9900
C3—C4	1.3664 (11)	C16—H16B	0.9900
C4—H4	0.9500	C16—H16C	0.9900
C4—C5	1.4196 (12)	C16—H16D	0.9900
C5—H5	0.9500	C16—C17	1.510 (2)
C5—C6	1.3855 (11)	C16—C17A	1.411 (3)
C6—H6	0.9500	C17—H17A	0.9900
C7—H7A	0.9900	C17—H17B	0.9900
C7—H7B	0.9900	C17—C18	1.4755 (16)
C7—C8	1.5177 (12)	C17A—H17C	0.9900
C8—H8A	0.9900	C17A—H17D	0.9900
C8—H8B	0.9900	C17A—C18	1.535 (3)
C8—C9	1.5288 (13)	C18—H18A	0.9900
C9—H9A	0.9900	C18—H18B	0.9900
C9—H9B	0.9900	C18—H18C	0.9900
C9—C10	1.5248 (12)	C18—H18D	0.9900
C7—O1—Li1	119.84 (6)	H12A—C12—H12B	109.2
C10—O1—C7	109.73 (6)	C13—C12—H12A	111.4
C10—O1—Li1	125.99 (7)	C13—C12—H12B	111.4
C11—O2—Li1	113.13 (6)	C12—C13—H13A	111.5
C14—O2—C11	109.51 (6)	C12—C13—H13B	111.5
C14—O2—Li1	131.57 (6)	H13A—C13—H13B	109.3
C15—O3—C18	108.65 (6)	C14—C13—C12	101.59 (6)
C15—O3—Li1	129.97 (7)	C14—C13—H13A	111.5
C18—O3—Li1	112.93 (7)	C14—C13—H13B	111.5
C2—N1—Li1	119.19 (6)	O2—C14—C13	105.66 (6)
C6—N1—C2	118.22 (6)	O2—C14—H14A	110.6
C6—N1—Li1	122.58 (7)	O2—C14—H14B	110.6
H1A—C1—H1B	116.7 (11)	C13—C14—H14A	110.6
C2—C1—H1A	121.5 (8)	C13—C14—H14B	110.6
C2—C1—H1B	121.8 (7)	H14A—C14—H14B	108.7
N1—C2—C3	117.74 (6)	O3—C15—H15A	110.5
C1—C2—N1	119.98 (6)	O3—C15—H15B	110.5

C1—C2—C3	122.28 (7)	O3—C15—C16	105.94 (7)
C2—C3—H3	119.3	H15A—C15—H15B	108.7
C4—C3—C2	121.43 (7)	C16—C15—H15A	110.5
C4—C3—H3	119.3	C16—C15—H15B	110.5
C3—C4—H4	120.1	C15—C16—H16A	111.2
C3—C4—C5	119.83 (7)	C15—C16—H16B	111.2
C5—C4—H4	120.1	C15—C16—H16C	110.0
C4—C5—H5	121.7	C15—C16—H16D	110.0
C6—C5—C4	116.52 (7)	H16A—C16—H16B	109.1
C6—C5—H5	121.7	H16C—C16—H16D	108.4
N1—C6—C5	126.19 (7)	C17—C16—C15	102.72 (9)
N1—C6—H6	116.9	C17—C16—H16A	111.2
C5—C6—H6	116.9	C17—C16—H16B	111.2
O1—C7—H7A	110.7	C17A—C16—C15	108.27 (13)
O1—C7—H7B	110.7	C17A—C16—H16C	110.0
O1—C7—C8	105.16 (6)	C17A—C16—H16D	110.0
H7A—C7—H7B	108.8	C16—C17—H17A	111.0
C8—C7—H7A	110.7	C16—C17—H17B	111.0
C8—C7—H7B	110.7	H17A—C17—H17B	109.0
C7—C8—H8A	111.4	C18—C17—C16	104.00 (10)
C7—C8—H8B	111.4	C18—C17—H17A	111.0
C7—C8—C9	102.00 (7)	C18—C17—H17B	111.0
H8A—C8—H8B	109.2	C16—C17A—H17C	110.5
C9—C8—H8A	111.4	C16—C17A—H17D	110.5
C9—C8—H8B	111.4	C16—C17A—C18	105.94 (18)
C8—C9—H9A	111.3	H17C—C17A—H17D	108.7
C8—C9—H9B	111.3	C18—C17A—H17C	110.5
H9A—C9—H9B	109.2	C18—C17A—H17D	110.5
C10—C9—C8	102.13 (7)	O3—C18—C17	107.55 (8)
C10—C9—H9A	111.3	O3—C18—C17A	103.68 (13)
C10—C9—H9B	111.3	O3—C18—H18A	110.2
O1—C10—C9	106.36 (7)	O3—C18—H18B	110.2
O1—C10—H10A	110.5	O3—C18—H18C	111.0
O1—C10—H10B	110.5	O3—C18—H18D	111.0
C9—C10—H10A	110.5	C17—C18—H18A	110.2
C9—C10—H10B	110.5	C17—C18—H18B	110.2
H10A—C10—H10B	108.6	C17A—C18—H18C	111.0
O2—C11—H11A	110.6	C17A—C18—H18D	111.0
O2—C11—H11B	110.6	H18A—C18—H18B	108.5
O2—C11—C12	105.55 (6)	H18C—C18—H18D	109.0
H11A—C11—H11B	108.8	O1—Li1—O2	103.75 (7)
C12—C11—H11A	110.6	O1—Li1—O3	105.69 (7)
C12—C11—H11B	110.6	O1—Li1—N1	106.33 (7)
C11—C12—H12A	111.4	O2—Li1—N1	115.29 (7)
C11—C12—H12B	111.4	O3—Li1—O2	113.22 (7)
C11—C12—C13	101.94 (7)	O3—Li1—N1	111.51 (7)
O1—C7—C8—C9	34.54 (8)	C14—O2—C11—C12	-11.21 (8)

O2—C11—C12—C13	31.49 (8)	C15—O3—C18—C17	4.90 (13)
O3—C15—C16—C17	-30.31 (15)	C15—O3—C18—C17A	-26.28 (19)
O3—C15—C16—C17A	1.4 (2)	C15—C16—C17—C18	32.73 (16)
N1—C2—C3—C4	2.67 (10)	C15—C16—C17A—C18	-17.3 (3)
C1—C2—C3—C4	-177.20 (7)	C16—C17—C18—O3	-23.87 (15)
C2—N1—C6—C5	0.86 (12)	C16—C17A—C18—O3	26.7 (3)
C2—C3—C4—C5	-0.71 (11)	C18—O3—C15—C16	16.25 (13)
C3—C4—C5—C6	-1.14 (11)	Li1—O1—C7—C8	-175.91 (7)
C4—C5—C6—N1	1.12 (13)	Li1—O1—C10—C9	150.06 (8)
C6—N1—C2—C1	177.20 (7)	Li1—O2—C11—C12	145.25 (7)
C6—N1—C2—C3	-2.67 (9)	Li1—O2—C14—C13	-164.78 (8)
C7—O1—C10—C9	-5.96 (9)	Li1—O3—C15—C16	161.28 (10)
C7—C8—C9—C10	-37.15 (9)	Li1—O3—C18—C17	-146.62 (11)
C8—C9—C10—O1	27.22 (9)	Li1—O3—C18—C17A	-177.80 (17)
C10—O1—C7—C8	-18.19 (8)	Li1—N1—C2—C1	-1.37 (10)
C11—O2—C14—C13	-14.18 (9)	Li1—N1—C2—C3	178.76 (6)
C11—C12—C13—C14	-39.06 (8)	Li1—N1—C6—C5	179.37 (8)
C12—C13—C14—O2	33.23 (9)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C15—H15B...O1 ⁱ	0.99	2.63	3.3695 (14)	131

Symmetry code: (i) $-x+1, -y+1, -z+1$.