Electronic Supplementary Information (ESI) For

The Annular Tautomerism of Lithium 1,2,3-Triazolate

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X-ray Diffraction Data

Table S1 Assignment of selected Bragg reflections of lithium 1,2,3-triazolate.

2θ (°)	I_{rel} (%)	d (Å)	d^{-2} (Å^{-2})	*Index* h	k	l	d_{cal} (Å)	d_{cal}^{-2} (Å^{-2})	d-d_{cal} (Å)	d^{-2} - d_{cal}^{-2} (Å^{-2})
11.35	42.3	7.794	0.016	1	1	0	7.835	0.016	– 0.040	0.000
16.04	1.0	5.526	0.033	2	0	0	5.540	0.033	– 0.014	0.000
17.60	5.0	5.039	0.039	1	0	1	5.068	0.039	– 0.029	0.000
19.37	7.8	4.582	0.048	1	1	1	4.609	0.047	– 0.027	0.001
22.50	10.6	3.952	0.064	2	0	1	3.972	0.063	– 0.021	0.001
22.74	35.2	3.910	0.065	2	2	0	3.917	0.065	– 0.007	0.000
23.91	12.1	3.721	0.072	2	1	1	3.739	0.072	– 0.018	0.001
25.47	100.0	3.497	0.082	3	1	0	3.504	0.081	– 0.007	0.000
30.07	5.1	2.972	0.113	3	1	1	2.985	0.112	– 0.013	0.001
32.41	5.0	2.762	0.131	4	0	0	2.770	0.130	– 0.008	0.001
33.27	2.0	2.693	0.138	3	2	1	2.705	0.137	– 0.012	0.001
34.38	26.5	2.609	0.147	3	3	0	2.612	0.147	– 0.003	0.000
36.25	3.1	2.478	0.163	4	2	0	2.478	0.163	0.000	0.000
36.47	10.7	2.463	0.165	2	1	2	3.739	0.072	– 0.007	0.001
37.12	3.0	2.422	0.170	4	1	1	2.431	0.169	– 0.009	0.001
38.00	0.7	2.368	0.178	3	3	1	2.374	0.177	– 0.006	0.001
39.85	2.4	2.262	0.195	4	2	1	2.272	0.194	– 0.010	0.002
41.64	7.2	2.169	0.213	5	1	0	2.173	0.212	– 0.004	0.001
46.58	3.9	1.950	0.263	4	1	2	1.955	0.262	– 0.005	0.001
50.87	2.4	1.795	0.310	5	3	1	1.803	0.308	– 0.008	0.003
52.30	12.0	1.749	0.327	4	3	2	1.749	0.327	0.000	0.000
55.31	4.8	1.661	0.362	3	1	3	1.670	0.359	– 0.009	0.004

Table S2 Refined atom positions and bond lengths of lithium 1,2,3-triazolate (see Figure S1 (b) for assignment).

Atom	*Position*		
	x	*y*	*z*
N1	0.6950	1.0563	0.2963
N2	0.7281	1.1090	0.0969
N3	0.6899	1.0385	– 0.0761
C4	0.6327	0.9418	0.0120
C5	0.6361	0.9532	0.2509
H4	0.5989	0.8751	– 0.0869
H5	0.6053	0.8972	0.3757
Li	0.7342	1.1244	0.6158

Bond	*Length* (Å)
N1 - N2	1.32
N2 - N3	1.32
N3 - C4	1.34
C4 - C5	1.36
C5 - N1	1.34
C4 - H4	1.00
C5 - H5	1.00
Li - N1	2.00
Li - N2	2.14
Li - N3	2.05

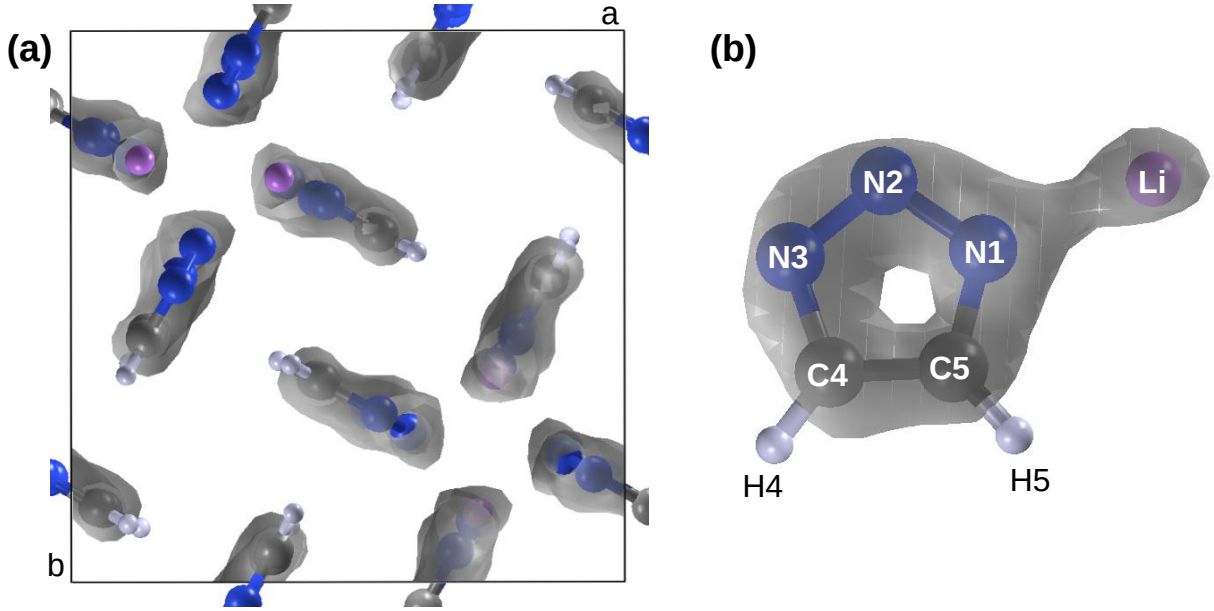

Fig. S1 Refined Fourier map of the electron density of lithium 1,2,3-triazolate (a) in the tetragonal unit cell and (b) of the asymmetric unit. The atoms are labeled for the assignment of the positions and bond lengths in Table S2.

Thermal Properties

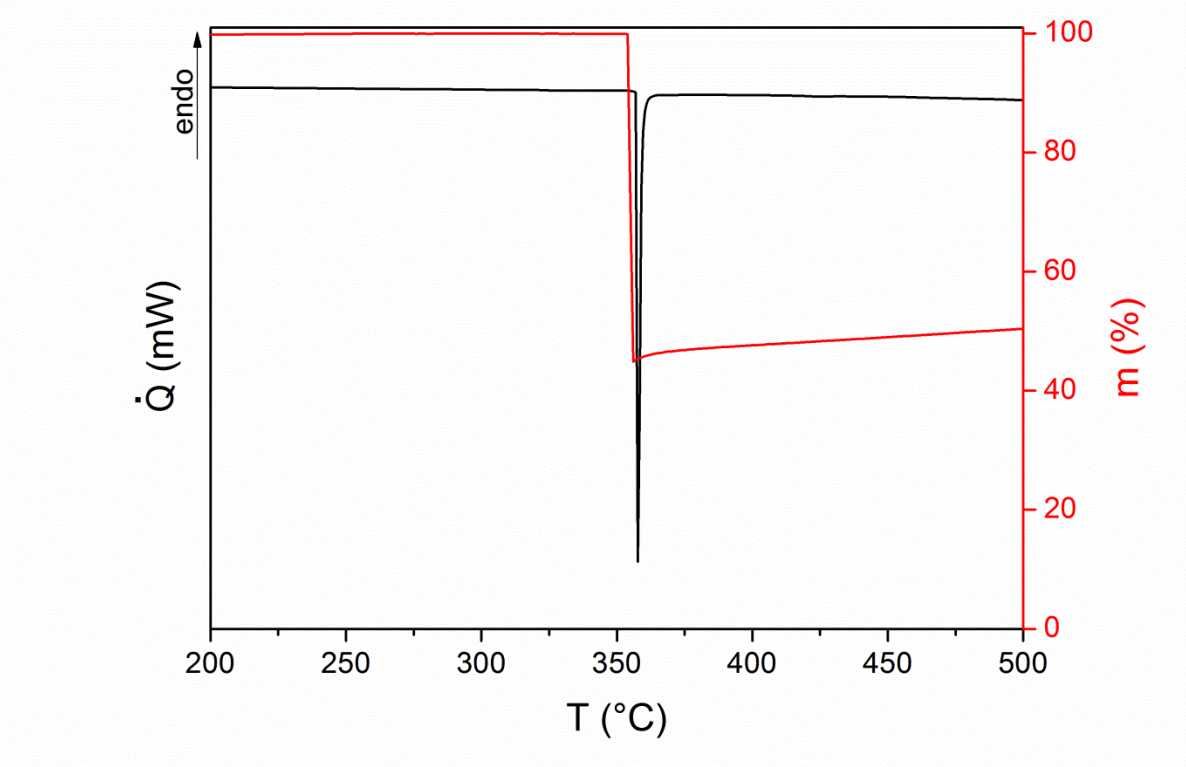

Fig. S2 Combined DSC and TGA plot of lithium 1,2,3-triazolate. The heat flow is plotted in black color and the red curve belongs to the mass.

NMR Spectroscopy Data

Table S3 NMR characterization data of 1,2,3-triazole and lithium 1,2,3-triazolate obtained from the NMR spectra measured in CD_3OD at room temperature, confirming the successful conversion.

Sample	^{1}H NMR[a]		^{7}Li NMR[b]
	δ (ppm)	$^1J_{C\text{-}H}$ (Hz)	δ (ppm)
1,2,3-Triazole	7.82	194.2	---
Lithium 1,2,3-triazolate	7.51	184.3	– 0.34

[a] NMR spectra recorded at 500 MHz and [b] at 194 MHz.

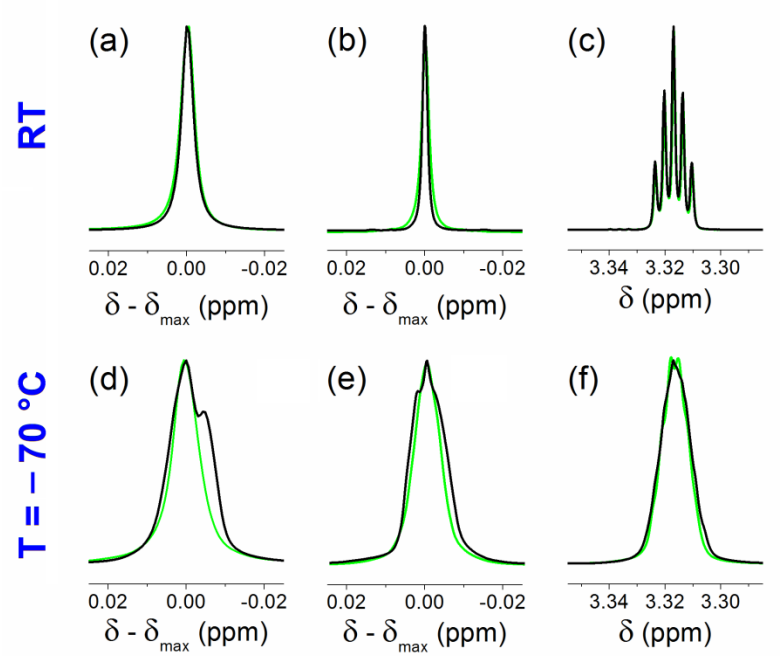

Fig. S3 NMR spectra of lithium 1,2,3-triazolate (black) and lithium 1,2,4-triazolate (green) in CD_3OD at RT (a)-(c) and at T = – 70 °C (d)-(f). The ^{7}Li NMR spectra are shown in (a) and (d) and the others are ^{1}H NMR spectra of the triazoles ((b) and (e)) and the methanol signal ((c) and (f)). All signals are normalized to their intensities and the chemical shift of their maximum intensity ($\delta - \delta_{max}$). The resonances of the NMR spectra of Li-TR and its isomer have the same line shape at RT but after cooling to T = – 70 °C, the NMR signals of the two isomers significantly differ. This is not an artefact caused by an inhomogeneous magnetic field since the resonances of the methyl group of the solvent do not show this difference, i.e. the splitting of the signals of Li-TR can be explained exclusively by the presence of the two lithiotropic tautomers.

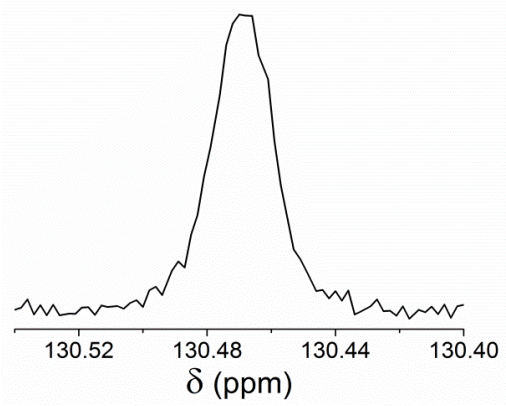

Fig. S4 ^{13}C NMR spectrum of lithium 1,2,3-triazolate at T = – 70 °C in CD_3OD recorded with a frequency of 125 MHz.