Electronic supplementary information (ESI) for

Completing a family: $LiCN_3H_4$, the lightest alkali metal guanidinate

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Table S1. Optimized hydrogen atom positions in the $LiCN_3H_4$ structure, obtained from plane-wave DFT computations with all other structural parameters fixed to the experimental values; see discussion in the Article. All atoms on Wyckoff site 4*e*. It is evident that the hydrogen atoms' *positions alone* do not depend much on whether the "D2" dispersion correction is switched on or off, as noted in our previous study (ref 28 in the Article): for positioning the H atoms alone, the covalent N–H bond plays the key role. *(Supplement to Table 2 in the Article.)*

	PBE, no dispersion correction			"PBE+D2" dispersion correction		
atom	*x*	*y*	*z*	*x*	*y*	*z*
H1	0.686	0.369	0.508	0.687	0.370	0.509
H2	0.563	0.625	0.384	0.564	0.627	0.384
H3	0.580	0.607	0.150	0.580	0.608	0.149
H4	0.910	0.065	0.251	0.912	0.065	0.252

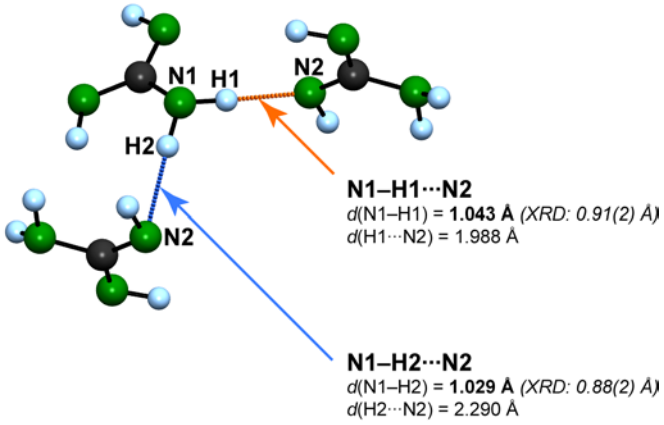

Figure S1. Fragment from the $LiCN_3H_4$ crystal structure with computationally optimized H positions, outlining two types of putative $^{(amino)}$N–H···$^{(imino)}$N hydrogen bonds. Optimized distances are given at the PBE+D2 level; XRD results are given in italics for comparison. The visible elongation of *one* of the covalent $^{(amino)}$N–H bond compared to the other is indicative of hydrogen-bonding interaction. Note that the shortest H···$^{(imino)}$N contacts are formed with N2 as acceptor, in both cases.

Table S2. Energetic data at the CCSD(T)/aug-cc-pVTZ level for the MP2-relaxed PES scan of the $LiCN_3H_4$ gas-phase entity. *(Supplement to Figure 3b in the Article.)*

Δd(Li···C) (Å)		E (CCSD(T), absolute)	ΔE (rel. to Li^+ and $CN_3H_4^-$)[a]
relative	absolute	(Hartree)	(kJ/mol)
-0.8	1.41328	-211.86962785	-439.7643715083
-0.7	1.51328	-211.90830729	-541.3179985702
-0.5	1.71328	-211.95818398	-672.2702247489
-0.4	1.81328	-211.97235100	-709.4660131486
-0.3	1.91328	-211.98192169	-734.5940471373
-0.2	2.01328	-211.98813806	-750.9152482886
-0.1	2.11328	-211.99174482	-760.3848672888
0	2.21328	-211.99288991	-763.3913235046
0.1	2.31328	-211.99168919	-760.2388096345
0.2	2.41328	-211.98848261	-751.8198710599
0.4	2.61328	-211.97752752	-723.0570677646
0.6	2.81328	-211.96287589	-684.5889263213
0.8	3.01328	-211.94677707	-642.321159197
1	3.21328	-211.93067794	-600.0525781617
1.2	3.41328	-211.91536567	-559.849913463
1.4	3.61328	-211.90120133	-522.6611614558
1.6	3.81328	-211.88828898	-488.7595337075
1.8	4.01328	-211.87661373	-458.1059362315
2	4.21328	-211.86609507	-430.4889884466
2.4	4.61328	-211.84810097	-383.2451265728
2.8	5.01328	-211.83345495	-344.7917142943

[a]Relative to: $E(Li^+, HF)$ = -7.236380389 Ha; no post-HF correction is applied since the Li 1s orbital was kept frozen in all computations. $E(CN_3H_4^-, CCSD(T))$ = -204.46575133 Ha (C_s symmetry), with the isolated guanidinate anion in the same conformation as in the $LiCN_3H_4$ monomer.

Table S3. Same as Table S2, but using plane-wave based density-functional theory at the PBE+D2 level and $(25\ \text{Å})^3$ supercells (as supplement to Figure 3b in the Article).

d(Li···C) (Å)	E (PW-DFT, PBE+D2, absolute) (eV)	ΔE (rel. to Li^+ and $CN_3H_4^-$)[a] (kJ/mol)
1.34481	-47.334942	-377.8919412635
1.56894	-49.660545	-602.2784606786
1.79308	-50.779853	-710.2752366862
2.01721	-51.26142	-756.7393765223
2.24135	-51.414376	-771.4973831398
2.46548	-51.271237	-757.6865727811
2.68962	-50.913894	-723.2082237218
2.91375	-50.421317	-675.6817806557
3.13789	-49.887983	-624.2228859321
3.36202	-49.385248	-575.7163451175
3.58616	-48.934203	-532.1971298217
3.81029	-48.583022	-498.3133232241
4.03443	-48.31896	-472.8352200871
4.25856	-48.114058	-453.0651877121
4.48270	-47.954157	-437.6370906375
4.70683	-47.828768	-425.5388944781
4.93097	-47.729738	-415.9839545259
5.15510	-47.650906	-408.3778248045
5.37924	-47.587755	-402.2846811821

[a]Relative to: $E(Li^+$, PW-DFT) = 5.294293 eV; $E(CN_3H_4^-$, PW-DFT) = -48.71266 eV. The latter values have been obtained by switching on image charge corrections in VASP (IDIPOL = 4) with both the molecule and the dipole (DIPOL tag) centered at (0.5, 0.5, 0.5). Note that for the computation of sublimation energies (Table 4 in the Article), a different, more stable anion structure was used (namely, that conformation found in the RbCN3H4 structure): for the latter, E = -48.994646 eV at the same level. For an energetic ranking and discussion of different guanidinate anion monomers, see ref 4 in the Article.

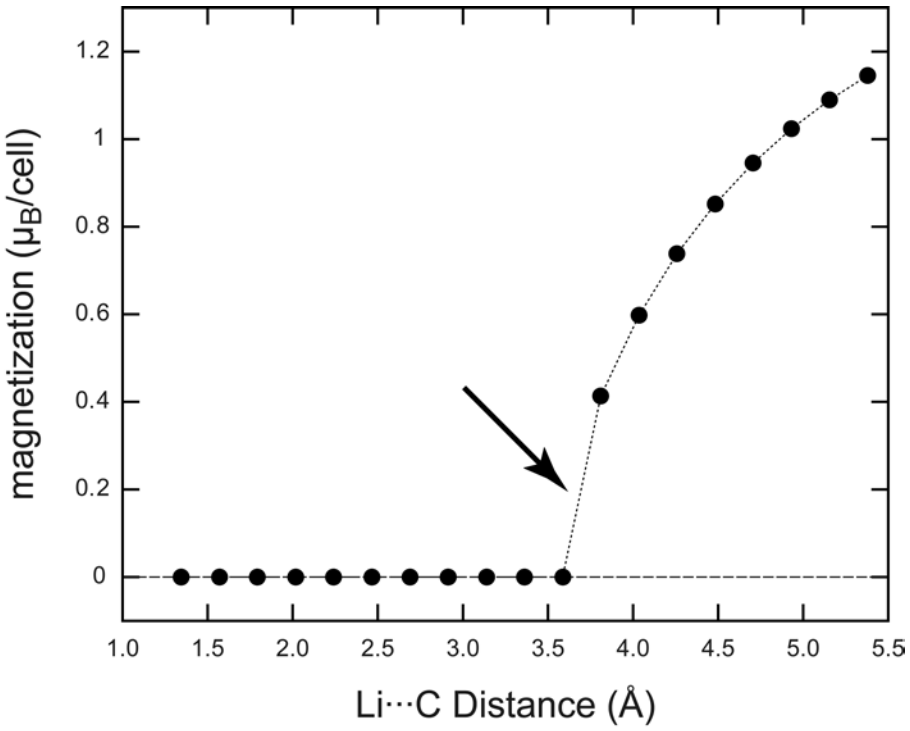

Figure S2. Course of magnetization in the simulation box (difference between "up" and "down" spin populations) during the PES scan of the $LiCH_3H_4$ monomer. For small Li···C distances, the magnetization is zero indicating an "Li^+" ion. Between a distance of 3.5 and 4.0 Å, the magnetization increases abruptly. This is exactly the Li···C separation at which the DFT and CCSD(T) results begin to differ significantly (see Figure 3b in the Article). In turn, we conjecture that the DFT description is suitable for the near-equilibrium region (d < 3.5 Å).

Listing S1. Output of a frequency computation for the $LiCN_3H_4$ monomer in conformation as shown in Figure 3a in the Article, in Gaussian 09 archival format. The username has been replaced by "USERNAME" and relevant parts have been highlighted in boldface.

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Listing S2. Computed structure of the $LiCN_3H_4$ gas-phase monomer (VASP output format; at the PBE+D2 level).

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