Protonation sequence of linear aliphatic polyamines from intramolecular atomic energy and charge distributions

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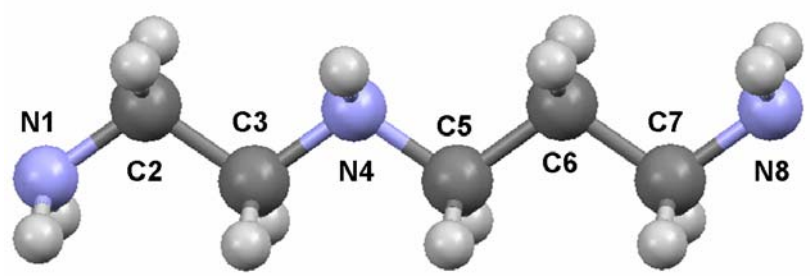
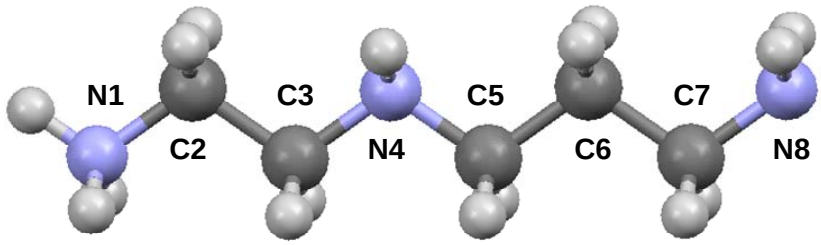
SUPPLEMENTARY INFORMATION

(L)



$(HL^{+})_{N1}$



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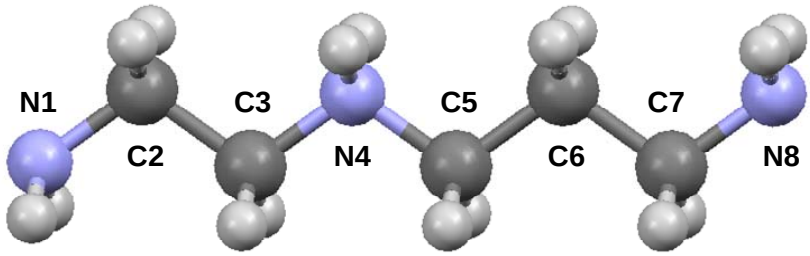

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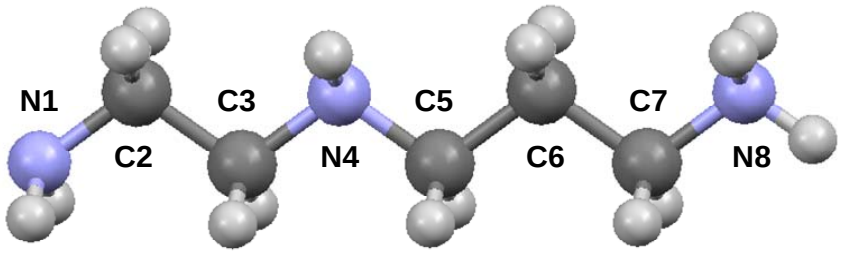
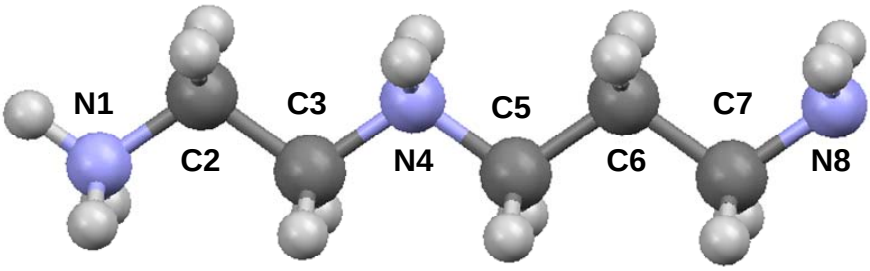


$(H_2L^{2+})_{N1,N4}$



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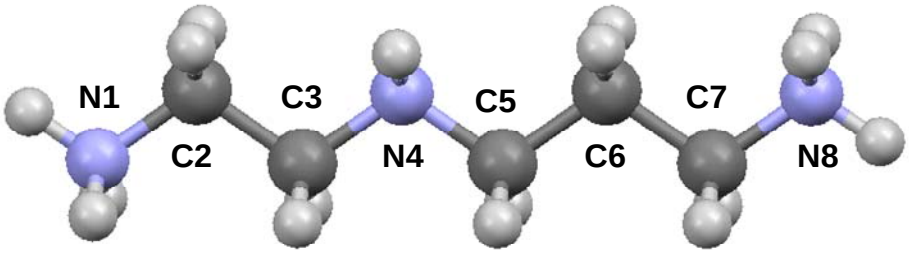

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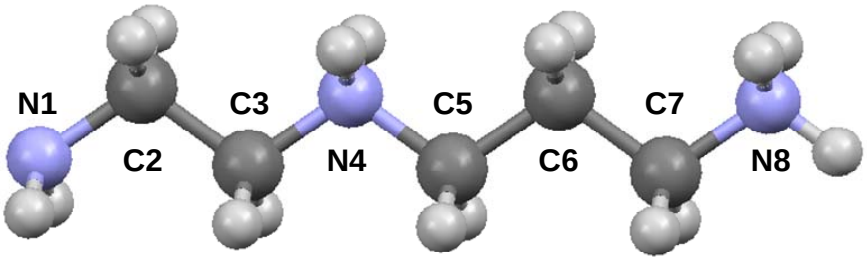

H_3L^{3+}

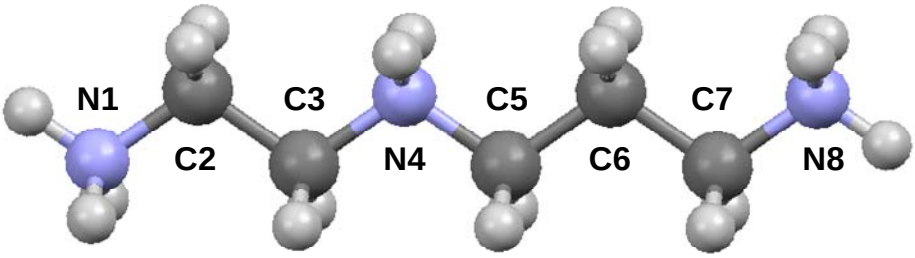

Fig. S1 All possible protonated forms of the linear aliphatic triamine 2,3-tri discussed in this work

Table S1 Net charges and atomic energies in a gas phase (RB3LYP/6-31+G(d,p)) of N-atoms in all H_nL^{n+} forms of 2,3-tri. Lowest energies of N-atoms of each H_nL^{n+} form are shown in bold

H_nL^{n+}	Atom	q(N) / e	E(N) / au	$\Delta E(N)_1$ [a]	$\Delta E(N)_2$ [b]	$\delta E(N)$ [c]	$\delta q(N)$ [d]
	N1	–1.052	–55.16972	36.8	158.1		
L	N4	–1.026	**–55.22840**	0.0	121.3	–1.2	–0.005
	N8	–1.047	–55.16776	38.1	159.4		
	N1	–1.124	**–55.42171**	0.0	0.0		
$(HL^+)_{N1}$	N4	–0.999	–55.12731	184.7	184.7	–197.8	–0.078
	N8	–1.046	–55.10656	197.8	197.8		
	N1	–1.074	–55.20261	80.5	137.5		
$(HL^+)_{N4}$	N4	–1.019	**–55.33096**	0.0	57.0	–3.5	–0.007
	N8	–1.067	–55.19696	84.1	141.0		
	N1	–1.059	–55.18170	95.9	150.6		
$(HL^+)_{N8}$	N4	–1.023	–55.22797	66.8	121.6	95.9	0.003
	N8	–1.063	**–55.33449**	0.0	54.7		
	N1	–1.075	**–55.32140**	0.0	62.9		
$(H_2L^{2+})_{N1,N4}$	N4	–1.004	–55.29725	15.2	78.1	–64.0	0.015
	N8	–1.090	–55.21943	64.0	126.9		
	N1	–1.072	–55.33161	0.4	56.5		
$(H_2L^{2+})_{N1,N8}$	N4	–1.011	–55.21390	74.3	130.4	0.4	–0.004
	N8	–1.068	**–55.33228**	0.0	56.1		
	N1	–1.103	–55.22411	65.6	124.0		
$(H_2L^{2+})_{N4,N8}$	N4	–1.013	–55.30751	13.3	71.7	65.6	–0.031
	N8	–1.072	**–55.32870**	0.0	58.4		
	N1	–1.077	–55.31396	4.9	67.6		
H_3L^{3+}	N4	–1.010	–55.27443	29.7	92.4	4.9	–0.002
	N8	-1.075	**–55.32182**	0.0	62.7		

[a]) relative energy, in kcal mol^{-1}, calculated versus lowest energy N-atom within a molecule

[b]) relative energy, in kcal mol^{-1}, calculated versus lowest energy N-atom, N1 in $(HL^+)_{N1}$, among all protonated forms of 2,3-tri

[c]) $\delta E(N) = E(N1) - E(N8)$ in kcal mol^{-1}

[d]) $\delta q(N) = q(N1) - q(N8)$

Table S2. Net charges and atomic energies in a gas phase (RB3LYP/6-31+G(d,p)) of C-atoms in all H_nL^{n+} forms of 2,3-tri

H_nL^{n+}	Atom	q(C) / e	E(C) / au	$\Delta E(C)_1$[a]	$\Delta E(C)_2$[b]	δE(C)[c]	δq(C)[d]
	C2	0.421	–37.82921	136.5	138.5		
	C3	0.391	–37.86214	115.8	117.8		
L	C5	0.400	–37.84007	129.7	131.7	–5.3	0.006
	C6	0.071	–38.04671	0.0	2.0		
	C7	0.414	–37.82071	141.8	143.8		
	C2	0.348	–37.85907	94.5	119.7		
	C3	0.418	–37.82364	116.7	142.0		
$(HL^+)_{N1}$	C5	0.408	–37.81757	120.5	145.8	–45.9	–0.089
	C6	0.102	–38.00965	0.0	25.2		
	C7	0.437	–37.78597	140.4	165.6		
	C2	0.459	–37.79855	157.7	157.7		
	C3	0.275	–37.93623	71.3	71.3		
$(HL^+)_{N4}$	C5	0.290	–37.90978	87.9	87.9	–4.5	0.004
	C6	0.056	–38.04987	0.0	0.0		
	C7	0.455	–37.79131	162.2	162.2		
	C2	0.438	–37.81779	139.7	145.6		
	C3	0.375	–37.86862	107.8	113.7		
$(HL^+)_{N8}$	C5	0.424	–37.82580	134.7	140.6	56.5	0.163
	C6	0.075	–38.04049	0.0	5.9		
	C7	0.274	–37.90782	83.2	89.1		
	C2	0.299	–37.88302	104.6	104.7		
	C3	0.320	–37.88362	104.2	104.3		
$(H_2L^{2+})_{N1,N4}$	C5	0.237	–37.93449	72.3	72.4	–70.9	–0.179
	C6	0.050	–38.04970	0.0	0.1		
	C7	0.478	–37.76998	175.5	175.6		
	C2	0.290	–37.90823	75.5	88.9		
	C3	0.413	–37.83549	121.1	134.5		
$(H_2L^{2+})_{N1,N8}$	C5	0.406	–37.82676	126.6	140.0	–8.5	0.003
	C6	0.078	–38.02852	0.0	13.4		
	C7	0.286	–37.89475	83.9	97.3		
	C2	0.482	–37.77959	150.0	169.6		
	C3	0.238	–37.95534	39.8	59.3		
$(H_2L^{2+})_{N4,N8}$	C5	0.320	–37.87897	87.7	107.2	63.0	0.183
	C6	0.071	–38.01869	0.0	19.6		
	C7	0.299	–37.87992	87.1	106.6		
	C2	0.306	–37.87094	85.5	112.3		
	C3	0.296	–37.88531	76.5	103.3		
H_3L^{3+}	C5	0.275	–37.89184	72.4	99.2	–2.8	–0.001
	C6	0.071	–38.00722	0.0	26.8		
	C7	0.307	–37.86645	88.3	115.1		

[a]) relative energy, in kcal mol^{-1}, calculated versus lowest energy C-atom within a molecule

[b]) relative energy, in kcal mol^{-1}, calculated versus lowest energy C-atom, C6 in $(HL^+)_{N4}$, among all protonated forms of 2,3-tri

[c]) δE(C)= E(C2) – E(C7) in kcal mol^{-1}

[d]) δq(C) = q(C2) – q(C7) in e.