Isomers of *cyclo*-Heptasulfur and their Coordination to Li⁺
– an ab initio MO Study

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Table S1. Absolute energies E_0 (hartree) of nine isomeric structures of S₇ and of the transition state (**1c**) for the pseudorotation of **1a**, calculated by the G3X(MP2) method.

species	E_0 (B3LYP)	E_0 [G3X(MP2)]
chair 1a	−2787.40892	−2784.35789
boat 1b	−2787.40173	−2784.35328
transition state 1c	−2787.40664	−2784.35577
branched ring 1d	−2787.37830	−2784.33581
branched ring 1e	−2787.37701	−2784.33070
branched ring 1f	−2787.36752	−2784.32152
singlet chain 1g	−2787.35190	−2784.31529
singlet chain 1h	−2787.35643	−2784.31155
triplet chain 1i	−2787.36853	−2784.30635
triplet chain 1j	−2787.36764	−2784.30078

Table S2. Absolute energies E_o (hartree) of 13 isomers of composition $[\text{LiS}_7]^+$, calculated by the G3X(MP2) method.

species	E_o (B3LYP)	E_o [G3X(MP2)]
$[\text{LiS}_7]^+ \mathbf{2a}$	−2794.75432	−2791.65127
$[\text{LiS}_7]^+ \mathbf{2b}$	−2794.74833	−2791.64342
$[\text{LiS}_7]^+ \mathbf{2c}$	−2794.74513	−2791.64236
$[\text{LiS}_7]^+ \mathbf{2d}$	−2794.74328	−2791.64060
$[\text{LiS}_7]^+ \mathbf{2e}$	−2794.74193	−2791.63796
$[\text{LiS}_6=\text{S}]^+ \mathbf{2f}$	−2794.72801	−2791.63476
$[\text{S}_6-\text{SLi}]^+ \mathbf{2g}$	−2794.72947	−2791.63002
$[\text{LiS}_7]^+ \mathbf{2h}$	−2794.73342	−2791.62946
$[\text{S}_6-\text{SLi}]^+ \mathbf{2i}$	−2794.72379	−2791.62410
$[\text{LiS}_6=\text{S}]^+ \mathbf{2j}$	−2794.72104	−2791.61980
$[\text{S}_6-\text{SLi}]^+ \mathbf{2k}$	−2794.71291	−2791.61240
$[\text{LiS}_6=\text{S}]^+ \mathbf{2l}$	−2794.70983	−2791.60977
$[\text{S}_6-\text{SLi}]^+ \mathbf{2m}$	−2794.70846	−2791.60815

Table S3. Calculated [B3LYP/6-31G(2df,p)] vibrational spectra of selected S₇ isomers and of [S₇Li]⁺ (**2a**); frequencies (ν) in cm⁻¹, infrared intensities (first number in parentheses) in km mol⁻¹ and Raman intensities (second number in parentheses) in A⁴ amu⁻¹.

1b	559 (11.5, 3.8), 552 (12.6, 8.3), 490 (0.4, 10.2), 446 (13.2, 6.6), 372 (0.8, 0.0), 353 (9.2, 41.9), 314 (0.6, 6.1), 291 (0.1, 5.2), 284 (4.1, 26.7), 221 (0.7, 7.4), 203 (0.0, 3.4), 155 (0.0, 14.1), 152 (0.2, 10.0), 135 (0.1, 6.6), 11 (0.0, 0.6)
1d	658 (85.1, 8.2), 513 (3.4, 19.8), 508 (8.9, 0.7), 440 (3.1, 11.1), 409 (8.5, 7.3), 340 (1.2, 3.1), 267 (4.6, 15.0), 256 (2.9, 4.7), 241 (9.0, 51.7), 217 (2.6, 16.9), 217 (0.1, 6.8), 173 (0.0, 17.7), 148 (0.1, 7.1), 133 (0.0, 4.3), 60 (1.7, 6.4)
1e	639 (100.9, 13.1), 494 (1.6, 21.5), 481 (8.7, 0.2), 449 (0.1, 6.6), 418 (5.3, 7.9), 360 (18.5, 14.3), 342 (4.8, 3.6), 289 (1.7, 0.9), 234 (6.5, 32.0), 187 (1.0, 21.3), 180 (0.0, 16.4), 164 (0.8, 18.9), 135 (1.9, 9.9), 111 (0.2, 1.3), 71 (0.5, 0.9)
1g	632 (25.6, 31.0), 622 (161.9, 3.5), 468 (1.9, 7.5), 440 (3.2, 4.3), 395 (12.1, 22.3), 379 (11.2, 11.3), 324 (0.4, 8.5), 283 (1.4, 8.5), 224 (0.3, 11.6), 167 (2.8, 6.7), 155 (0.5, 11.1), 113 (0.1, 49.7), 101 (5.1, 3.0), 70 (0.1, 5.7), 38 (1.9, 0.8)
1h	647 (0.2, 35.3), 646 (62.1, 5.8), 505 (0.1, 20.0), 463 (11.7, 3.0), 329 (0.0, 65.8), 314 (33.7, 7.9), 288 (2.3, 1.3), 279 (0.0, 18.7), 185 (0.4, 13.0), 162 (0.4, 0.6), 84 (0.0, 13.8), 62 (0.1, 0.2), 49 (0.0, 3.3), 25 (0.2, 3.5), 24 (0.5, 1.1)
2a	527 (3.8, 3.2), 520 (4.0, 8.2), 478 (1.1, 15.1), 446 (0.2, 0.9), 386 (2.6, 11.3), 375 (0.4, 1.2), 318 (10.8, 34.2), 282 (0.1, 4.3), 279 (28.4, 1.7), 257 (37.1, 5.8), 242 (15.3, 14.0), 222 (11.8, 1.2), 205 (28.3, 8.2), 174 (1.9, 4.9), 167 (11.6, 1.0), 155 (0.9, 11.5), 119 (0.1, 3.4), 81 (0.1, 0.5)

Table S4. NBO atomic charges of the various isomers of S₇, calculated at the B3LYP/6-31G(2df,p) level.

atom ^a	1	2	3	4	5	6	7
chair 1a	0.01	−0.02	0.03	−0.02	−0.02	0.03	−0.02
boat 1b	0.03	−0.03	0.03	−0.02	−0.02	0.03	−0.03
transition state 1c	−0.01	−0.01	0.01	0.01	0.00	0.01	−0.01
branched ring 1d	0.28	−0.07	0.05	−0.01	0.05	−0.07	−0.23
branched ring 1e	0.34	−0.04	0.01	0.01	0.01	−0.04	−0.29
branched ring 1f	0.30	−0.07	0.06	−0.04	0.01	−0.00	−0.26
singlet chain 1g	−0.23	0.16	0.04	0.05	0.03	0.17	−0.23
singlet chain 1h	−0.23	0.20	−0.03	0.03	0.02	0.21	−0.20
triplet chain 1i	−0.13	0.13	−0.04	0.07	−0.04	0.13	−0.13
triplet chain 1j	−0.10	0.12	−0.04	0.03	−0.04	0.12	−0.10

^a See Figures 1 and 2 for atom labeling.

Table S5. NBO atomic charges of the various isomers of $[\text{LiS}_7]^+$, calculated at the B3LYP/6-31G(2df,p) level.

atom ^a	Li	1	2	3	4	5	6	7
$[\text{LiS}_7]^+$ 2a	0.86	0.11	−0.05	0.12	−0.05	−0.05	0.12	−0.05
$[\text{LiS}_7]^+$ 2b	0.88	−0.05	0.07	−0.07	0.08	0.08	−0.07	0.07
$[\text{LiS}_7]^+$ 2c	0.90	−0.09	0.07	0.14	−0.11	−0.11	0.14	0.07
$[\text{LiS}_7]^+$ 2d	0.88	0.12	−0.08	−0.03	0.11	0.11	−0.03	−0.08
$[\text{LiS}_7]^+$ 2e	0.95	−0.13	0.06	0.06	0.07	0.06	0.06	−0.13
$[\text{LiS}_6=\text{S}]^+$ 2f	0.88	0.28	−0.20	0.15	−0.20	−0.05	−0.20	0.15
$[\text{S}_6-\text{SLi}]^+$ 2g	0.88	0.39	0.09	−0.01	0.07	−0.01	0.09	−0.49
$[\text{LiS}_7]^+$ 2h	0.96	0.04	−0.27	0.04	0.07	0.05	0.07	0.05
$[\text{S}_6-\text{SLi}]^+$ 2i	0.88	0.40	−0.09	0.11	0.05	0.11	−0.09	−0.35
$[\text{LiS}_6=\text{S}]^+$ 2j	0.87	0.36	−0.15	0.11	−0.04	0.11	−0.15	−0.11
$[\text{S}_6-\text{SLi}]^+$ 2k	0.91	0.34	0.08	0.08	0.05	0.10	−0.14	−0.42
$[\text{LiS}_6=\text{S}]^+$ 2l	0.89	0.42	0.09	−0.03	−0.06	0.11	−0.25	−0.17
$[\text{S}_6-\text{SLi}]^+$ 2m	0.95	0.26	0.03	0.06	0.04	0.12	0.03	−0.48

^a See Figures 3 and 4 for atom labeling.

Table S6. Cartesian coordinates of optimized [B3LYP/6-31G(2df,p)] geometries of S₇ (**1**) and S₇Li⁺ (**2**) isomeric structures.

1a				1b			
S	2.222681	0.258725	-0.565405	S	1.696510	0.447952	0.931969
S	-0.460570	-1.879098	-0.300038	S	-0.039786	-1.523379	-1.101060
S	-2.072842	0.883902	0.455365	S	-1.670814	0.535897	0.931969
S	0.668300	1.289849	-1.312563	S	1.193990	1.758447	-0.460335
S	-0.398247	2.097614	0.344065	S	-1.100573	1.818375	-0.460335
S	1.508963	-1.744814	0.074756	S	1.640253	-1.562520	0.078896
S	-1.468284	-0.906178	1.303821	S	-1.719578	-1.474771	0.078896
1c				1d			
S	0.000000	0.000000	2.377090	S	2.151513	0.245565	-1.019562
S	-1.913469	-0.706301	-0.372130	S	-0.639102	-1.753716	-0.792385
S	0.999276	-0.276599	-1.980448	S	-0.909896	-0.148152	2.069065
S	1.582749	-0.644843	1.164033	S	-0.981808	1.629800	-0.700958
S	1.913469	0.706301	-0.372130	S	-0.171611	1.597488	1.152180
S	-1.582749	0.644843	1.164033	S	0.392535	0.087806	-1.772384
S	-0.999276	0.276599	-1.980448	S	0.158369	-1.658792	1.064044
1e				1f			
S	-0.075666	0.000000	-3.216332	S	-0.430323	-0.306746	1.780034
S	-0.405618	-1.695654	-0.393313	S	0.286340	1.494177	1.191324
S	-0.550699	0.000000	2.417673	S	-1.148029	2.347719	-0.048431
S	-0.405618	1.695654	-0.393313	S	0.513375	-0.127226	-1.530856
S	0.404973	1.618388	1.498693	S	-1.230677	0.866535	-1.654643
S	0.627654	0.000000	-1.412102	S	0.142335	-1.723996	0.000742
S	0.404973	-1.618388	1.498693	S	1.866979	-2.550463	0.261830
1g				1i			
S	0.008149	0.033763	1.915268	S	-0.863895	0.000000	-0.610540
S	0.886902	2.474220	-0.586607	S	-0.852024	0.000391	1.428545
S	0.632674	-1.369722	-1.034895	S	1.062194	-0.000391	-1.280011
S	-1.566108	0.512230	0.665317	S	-0.731605	2.151682	2.000478
S	-0.889502	-2.485607	-0.576889	S	1.641519	-2.151682	-1.357414
S	-0.647609	1.377367	-1.038334	S	-0.500584	3.264720	0.436532
S	1.575494	-0.542252	0.656140	S	0.244395	-3.264720	-0.617589
1j				1h			
S	0.296564	0.391095	3.898878	S	-0.695160	0.866934	1.012387
S	1.638556	0.410374	2.483290	S	-1.586058	0.142452	-2.963745
S	1.102348	-0.948934	0.890973	S	0.335937	0.102482	-3.149919
S	-0.782366	-0.390376	0.261568	S	-0.248380	-1.024816	-0.062774

S	-0.615666	1.191644	-1.053616
S	-1.489930	-0.986306	-3.499971
S	-0.149505	0.332503	-2.981122
2a			
S	2.213974	0.307071	-0.542254
S	-0.441029	-1.926036	-0.304834
S	-2.149495	0.865588	0.334836
S	0.659234	1.239058	-1.423799
S	-0.460149	2.070856	0.204218
S	1.506126	-1.729149	0.177640
S	-1.486271	-0.880935	1.247754
Li	0.840580	0.285583	1.634346
2c			
S	-1.664835	-1.088850	-0.191343
S	-1.718715	0.238098	1.486996
S	-0.037062	1.419772	1.290021
S	-1.186164	-0.103423	-1.851728
S	1.721641	0.325251	1.472709
S	1.210906	-0.108717	-1.848794
S	1.670277	-1.049131	-0.148863
Li	0.021082	1.957337	-1.114657
2e			
S	-1.787528	0.672901	0.411899
S	-1.661210	-0.370635	-1.409437
S	-0.000225	0.492404	-2.300664
S	-1.138761	-0.637950	1.834454
S	1.661548	-0.369113	-1.409437
S	1.139345	-0.636907	1.834454
S	1.786911	0.674537	0.411899
Li	-0.000427	0.932075	3.343112
2g			
S	-1.653160	1.257732	1.487169
S	-0.283503	0.488464	-1.916073
S	-1.240050	-0.631380	1.118107
S	1.748447	0.047780	-1.575135
S	0.913978	-1.034897	1.455941
S	1.875375	0.492371	0.480463
S	-1.351248	-1.038997	-1.058652
Li	-0.052472	2.234282	0.043625

S	1.228776	-0.719007	-1.359778
S	0.584582	1.030156	2.603078
S	0.380302	-0.398201	3.920751
2b			
S	0.293424	-1.722352	1.554260
S	1.185301	-0.412238	-1.530898
S	-0.802483	2.032502	-0.593080
S	0.341432	0.264982	1.931770
S	-1.450545	1.163270	1.187709
S	0.802262	-2.130703	-0.533666
S	-0.665141	0.532970	-2.035058
Li	1.577332	1.448366	0.101136
2d			
S	1.773217	0.513298	0.869375
S	-0.039932	-1.509460	-1.177870
S	-1.743024	0.604073	0.872205
S	1.170809	1.808906	-0.485571
S	-1.076752	1.866801	-0.483866
S	1.626420	-1.582644	0.026743
S	-1.705761	-1.496720	0.029590
Li	-0.026544	-1.089358	1.863433
2f			
S	-1.382890	1.742397	-0.175133
S	0.653389	0.023084	-1.859035
S	-1.900534	-0.004976	0.307289
S	2.126069	-0.066261	-0.327585
S	-0.144256	-0.636337	1.992028
S	1.176357	0.763544	1.384717
S	-0.688820	-1.408869	-1.390756
Li	0.856988	-2.200434	0.365201
2i			
S	-0.197875	0.005010	-3.083919
S	-0.146079	-1.690536	-0.398418
S	-0.749210	0.001034	2.336041
S	-0.127892	1.693022	-0.394073
S	0.355898	1.612850	1.613555
S	0.885296	-0.002946	-1.436481
S	0.338547	-1.620678	1.609405
Li	-1.912984	0.011970	-1.312586

2j				2k			
S	-0.141245	-0.000344	-3.252363	S	-1.766341	0.148520	-0.328830
S	-0.334201	-1.715688	-0.370053	S	0.200224	0.752879	-1.429128
S	-0.481753	0.001970	2.415688	S	-1.084398	-1.138363	1.132466
S	-0.324165	1.717441	-0.370852	S	1.639280	-0.193056	-0.043063
S	0.479893	1.648280	1.530916	S	-0.352935	0.065085	2.612275
S	0.709138	-0.002433	-1.546990	S	1.421064	0.923766	1.605945
S	0.470250	-1.650345	1.531684	S	0.264633	-0.304972	-3.104159
Li	-2.015554	0.005969	0.330510	Li	-1.714804	-1.353917	-2.376027
2l				2m			
S	-0.694449	0.310449	-1.704102	S	1.472431	-0.930707	-0.525788
S	-0.638289	1.616771	0.436691	S	-0.608277	-0.614199	-1.309623
S	0.908022	-0.951356	-1.488143	S	1.715103	0.620124	0.761338
S	0.681770	0.164629	1.507413	S	-1.408016	0.716918	0.267917
S	0.178920	-2.562113	-0.392839	S	0.883951	0.004662	2.563251
S	-0.411568	-1.531809	1.498227	S	-1.186646	-0.337829	1.952973
S	0.349400	3.229294	0.269781	S	-0.549796	0.648814	-2.874081
Li	-1.993632	-1.471281	-0.677487	Li	-1.700001	-0.574845	-4.458596