Electronic supplementary information (ESI)

Thermodynamic aspect of sulfur, polysulfide anion and lithium polysulfide: Plausible reaction path during discharge of lithium-sulfur battery

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Heats of redox reactions in solid phase, Number of initial geometries used for geometry optimizations of S_n, $S_n^{\cdot -}$, S_n^{2-} and Li_2S_n, Energies of S_n, $S_n^{\cdot -}$ and S_n^{2-} relative to S_8 per one sulfur atom, Heats of reduction and oxidation reactions of S_8 and Li_2S_n, Optimized geometries of S_n, $S_n^{\cdot -}$, S_n^{2-}, $[LiS_n]^-$ and Li_2S_n, Basis set and electron correlation effects on relative energies of S_8 isomers, Molecular orbitals of S_4, $S_4^{\cdot -}$ and S_4^{2-}.

Heats of redox reactions in solid phase

Heats of redox reactions in solid phase (ΔE_{solid}) were calculated from those in the gas phase (ΔE_{gas}) and heats of sublimation of reactants and products ($\Delta E_{sub(reactant)}$ and $\Delta E_{sub(product)}$) according to the equation,

$$\Delta E_{solid} = \Delta E_{gas} + (\Delta E_{sub(product)} - \Delta E_{sub(reactant)}).$$

The heats of sublimation (ΔE_{sub}) of S_8, Li and Li_2S_n summarized in Table 2 were used for the calculations. The ΔE_{sub} of Li_2S_n (n = 2-8) were assumed to be identical to the ΔE_{sub} of Li_2S, since we were unable to calculate the ΔE_{sub} of other Li_2S_n (n = 2-8) owing to the lack of crystal structures.

In this study, quantum espresso code was employed to calculate the solid phase of Li, Li_2S, and S_8 within B86R exchange functional with the nonlocal correlation functional of vdW-DF2 and ultra-soft pseudo-potentials [1,2]. We assumed that Li, Li_2S, and S_8 were bcc, anti-fluorite, and α-S phase. The structure α-S belongs to a space group *Fddd* (No. 70) [3].

For the total energy calculations, the cutoff energies of plane wave basis set and charge density were 30 Ry and 270 Ry, respectively. The cell parameters of α-S were optimized by stress tensor with the cutoff energies of plane wave basis set and charge density of 50 Ry and 450 Ry, respectively. The k-samplings of 12x12x12, 12x12x12, and 2x2x1 were adopted for bcc-Li, Li_2S, and α-S, respectively. Only the Γ-point is sampled for molecules. The optimized lattice constants of bcc-Li, and Li_2S, were 3.435, and 5.967 Angstrom, respectively. Obtained lattice constants of α-S were a=10.363 A, b=12.741 A, c=24.496 A. These lattice parameters are close to the corresponding experimental values. The molecules were isolated in the unit cell with volume of 15x15x15 A^3.

References

[1] D. Vanderbilt, Phys. Rev. B 41, 7892 (1990).

[2] K. F. Garrity, J. W. Bennett, K. M. Rabe, and D. Vanderbilt, Computational Materials Science 81, 446 (2014).

[3] S. J. Rettig, and J. Trotter, Acta Cryst. C**43**, 2260-2262 (1987).

TABLE 1S. Number of initial geometries used for geometry optimizations of S_n, $S_n^{\cdot -}$, S_n^{2-} $[LiS_n]^-$ and Li_2S_n

n	S_n	$S_n^{\cdot -}$	S_n^{2-}	$[LiS_n]^-$	Li_2S_n
1	–	–	–	1	1
2	1	1	1	3	5
3	2	2	2	7	4
4	8	8	8	12	21
5	7	6	5	12	21
6	16	15	15	47	30
7	42	42	42	15	30
8	122	122	122	49	48

TABLE 2S. Energies of S_n, $S_n^{\cdot -}$ and S_n^{2-} relative to S_8 per one sulfur atom[a]

n		S_n		$S_n^{\cdot -}$		S_n^{2-}
1	**1**	88.1 (3.82)	**9**	22.5 (0.98)	**17**	166.5 (7.22)
2	**2**	19.3 (0.84)	**10**	−4.3 (−0.19)	**18**	51.4 (2.23)
3	**3a**	8.5 (0.37)	**11a**	−7.8 (−0.34)	**19a**	20.9 (0.91)
4	**4a**	6.3 (0.27)	**12a**	−5.6 (−0.24)	**20a**	9.1 (0.39)
5	**5a**	3.2 (0.14)	**13a**	−4.0 (−0.17)	**21a**	3.4 (0.15)
6	**6a**	1.0 (0.04)	**14a**	−3.4 (−0.15)	**22a**	0.4 (0.02)
7	**7a**	0.8 (0.04)	**15a**	−3.8 (−0.16)	**23a**	−1.3 (−0.06)
8	**8a**	0.0 (0.0)	**16a**	−3.7 (−0.16)	**24a**	−2.2 (−0.10)

[a] Relative energies for the most stable isomers calculated at the CCSD(T)/cc-pVTZ//MP3/cc-pVDZ level. Energies are in kcal/mol. Energies in eV are shown in parentheses.

TABLE 3S. Heats of reduction reactions of S_8

	ΔE_{gas}		ΔE_{solid}	
	kcal/mol	eV	kcal/mol	eV
Li + 1/2 S_8 -> 1/2 Li_2S_8	−74.54	−3.23	−75.59	−3.28
Li + 1/4 S_8 -> 1/4 Li_2S + 1/4 Li_2S_7	−58.03	−2.52	−64.97	−2.82
Li + 1/4 S_8 -> 1/4 Li_2S_2 + 1/4 Li_2S_6	−64.62	−2.80	−71.56	−3.10
Li + 1/4 S_8 -> 1/4 Li_2S_3 + 1/4 Li_2S_5	−67.80	−2.94	−74.74	−3.24
Li + 1/4 S_8 -> 1/2 Li_2S_4	−69.74	−3.02	−76.67	−3.33
Li + 1/6 S_8 -> 1/3 Li_2S + 1/6 Li_2S_6	−52.75	−2.29	−61.66	−2.67
Li + 1/6 S_8 -> 1/6 Li_2S + 1/6 Li_2S_2 + 1/6 Li_2S_5	−56.59	−2.45	−65.49	−2.84
Li + 1/6 S_8 -> 1/6 Li_2S + 1/6 Li_2S_3 + 1/6 Li_2S_4	−58.66	−2.54	−67.57	−2.93
Li + 1/6 S_8 -> 1/3 Li_2S_2 + 1/6 Li_2S_4	−60.38	−2.62	−69.28	−3.00
Li + 1/6 S_8 -> 1/6 Li_2S_2 + 1/3 Li_2S_3	−61.16	−2.65	−70.06	−3.04
Li + 1/8 S_8 -> 3/8 Li_2S + 1/8 Li_2S_5	−49.70	−2.16	−59.59	−2.58
Li + 1/8 S_8 -> 1/4 Li_2S + 1/8 Li_2S_2 + 1/8 Li_2S_4	−52.54	−2.28	−62.43	−2.71
Li + 1/8 S_8 -> 1/4 Li_2S + 1/4 Li_2S_3	−53.13	−2.30	−63.01	−2.73
Li + 1/8 S_8 -> 1/8 Li_2S + 1/4 Li_2S_2 + 1/8 Li_2S_3	−54.41	−2.36	−64.30	−2.79
Li + 1/8 S_8 -> 1/2 Li_2S_2	−55.70	−2.42	−65.58	−2.84
Li + 1/10 S_8 -> 2/5 Li_2S + 1/10 Li_2S_4	−47.84	−2.07	−58.31	−2.53
Li + 1/10 S_8 -> 3/10 Li_2S + 1/10 Li_2S_2 + 1/10 Li_2S_3	−49.33	−2.14	−59.81	−2.59
Li + 1/10 S_8 -> 1/5Li_2S + 3/10 Li_2S_2	−50.36	−2.18	−60.84	−2.64
Li + 1/12 S_8 -> 5/12 Li_2S + 1/12 Li_2S_3	−45.95	−1.99	−56.82	−2.46
Li + 1/12 S_8 -> 1/3 Li_2S + 1/6 Li_2S_2	−46.81	−2.03	−57.68	−2.50
Li + 1/14 S_8 -> 3/7 Li_2S + 1/14 Li_2S_2	−44.27	−1.92	−55.42	−2.40
Li + 1/16 S_8 -> 1/2 Li_2S	−42.36	−1.84	−53.72	−2.33

−1.8 <
−1.8 ～ −2.0
−2.0 ～ −2.2
−2.2 ～ −2.4
−2.4 ～ −2.6
−2.6 ～ −2.8
−2.8 ～ −3.0
−3.0 ～ −3.2
< −3.2

22 reactions

TABLE 4S. Heats of reduction reactions of Li_2S_8

	ΔE_{gas}		ΔE_{solid}	
	kcal/mol	eV	kcal/mol	eV
Li +1/2 Li_2S_8 -> 1/2 Li_2S + 1/2 Li_2S_7	−41.51	−1.80	−54.34	−2.36
Li +1/2 Li_2S_8 -> 1/2 Li_2S_2 + 1/2 Li_2S_6	−54.69	−2.37	−67.53	−2.93
Li +1/2 Li_2S_8 -> 1/2 Li_2S_3 + 1/2 Li_2S_5	−61.06	−2.65	−73.90	−3.20
Li +1/2 Li_2S_8 -> Li_2S_4	−64.93	−2.82	−77.76	−3.37
Li + 1/4 Li_2S_8 -> 1/2 Li_2S + 1/4 Li_2S_6	−41.86	−1.82	−54.69	−2.37
Li + 1/4 Li_2S_8 -> 1/4 Li_2S + 1/4 Li_2S_2 + 1/4 Li_2S_5	−47.61	−2.06	−60.45	−2.62
Li + 1/4 Li_2S_8 -> 1/4 Li_2S + 1/4 Li_2S_3 + 1/4 Li_2S_4	−50.72	−2.20	−63.56	−2.76
Li + 1/4 Li_2S_8 -> 1/2 Li_2S_2 + 1/4 Li_2S_4	−53.29	−2.31	−66.13	−2.87
Li + 1/4 Li_2S_8 -> 1/4 Li_2S_2 + 1/2 Li_2S_3	−54.47	−2.36	−67.30	−2.92
Li + 1/6 Li_2S_8 -> 1/2 Li_2S + 1/6 Li_2S_5	−41.42	−1.80	−54.25	−2.35
Li + 1/6 Li_2S_8 -> 1/3 Li_2S + 1/6 Li_2S_2 + 1/6 Li_2S_4	−45.20	−1.96	−58.04	−2.52
Li + 1/6 Li_2S_8 -> 1/3 Li_2S + 1/3 Li_2S_3	−45.99	−1.99	−58.82	−2.55
Li + 1/6 Li_2S_8 -> 1/6 Li_2S +1/3 Li_2S_2 + 1/6 Li_2S_3	−47.70	−2.07	−60.53	−2.63
Li + 1/6 Li_2S_8 -> 2/3 Li_2S_2	−49.41	−2.14	−62.25	−2.70
Li + 1/8 Li_2S_8 -> 1/2 Li_2S + 1/8 Li_2S_4	−41.16	−1.78	−53.99	−2.34
Li + 1/8 Li_2S_8 -> 3/8 Li_2S + 1/8 Li_2S_2 + 1/8 Li_2S_3	−43.03	−1.87	−55.87	−2.42
Li + 1/8 Li_2S_8 -> 1/4 Li_2S + 3/8 Li_2S_2	−44.32	−1.92	−57.15	−2.48
Li + 1/10 Li_2S_8 -> 1/2 Li_2S + 1/10 Li_2S_3	−40.23	−1.74	−53.06	−2.30
Li + 1/10 Li_2S_8 -> 2/5 Li_2S + 1/5 Li_2S_2	−41.26	−1.79	−54.09	−2.35
Li + 1/12 Li_2S_8 -> 1/2 Li_2S + 1/12 Li_2S_2	−39.22	−1.70	−52.05	−2.26
Li + 1/14 Li_2S_8 -> 4/7 Li_2S	−37.76	−1.64	−50.60	−2.19

21 reactions

TABLE 5S. Heats of reduction reactions of Li_2S_7

	ΔE_{gas}		ΔE_{solid}	
	kcal/mol	eV	kcal/mol	eV
Li + 1/2 Li_2S_7 -> 1/2 Li_2S + 1/2 Li_2S_6	−42.21	−1.83	−55.04	−2.39
Li + 1/2 Li_2S_7 -> 1/2 Li_2S_2 + 1/2 Li_2S_5	−53.72	−2.33	−66.55	−2.89
Li + 1/2 Li_2S_7 -> 1/2 Li_2S_3 + 1/2 Li_2S_4	−59.94	−2.60	−72.77	−3.16
Li + 1/4 Li_2S_7 -> 1/2 Li_2S + 1/4 Li_2S_5	−41.37	−1.79	−54.21	−2.35
Li + 1/4 Li_2S_7 -> 1/4 Li_2S + 1/4 Li_2S_{2b}+ 1/4 Li_2S_4	−47.05	−2.04	−59.88	−2.60
Li + 1/4 Li_2S_7 -> 1/4 Li_2S + 1/2 Li_2S_3	−48.23	−2.09	−61.06	−2.65
Li + 1/4 Li_2S_7 -> 1/2 Li_2S_2 + 1/4 Li_2S_3	−50.80	−2.20	−63.63	−2.76
Li + 1/6 Li_2S_7 -> 1/2 Li_2S + 1/6 Li_2S_4	−41.04	−1.78	−53.88	−2.34
Li + 1/6 Li_2S_7 -> 1/3 Li_2S + 1/6 Li_2S_2 + 1/6 Li_2S_3	−43.54	−1.89	−56.37	−2.44
Li + 1/6 Li_2S_7 -> 1/6 Li_2S + 1/2 Li_2S_2	−45.25	−1.96	−58.09	−2.52
Li + 1/8 Li_2S_7 -> 1/2 Li_2S + 1/8 Li_2S_3	−39.91	−1.73	−52.75	−2.29
Li + 1/8 Li_2S_7 -> 3/8 Li_2S + 1/4 Li_2S_2	−41.20	−1.79	−54.03	−2.34
Li + 1/10 Li_2S_7 -> 1/2 Li_2S + 1/10 Li_2S_2	−38.76	−1.68	−51.60	−2.24
Li + 1/12 Li_2S_7 -> 7/12 Li_2S	−37.14	−1.61	−49.97	−2.17

14 reactions

TABLE 6S. Heats of reduction reactions of Li_2S_6

	ΔE_{gas}		ΔE_{solid}	
	kcal/mol	eV	kcal/mol	eV
Li + 1/2 Li_2S_6 -> 1/2 Li_2S + 1/2 Li_2S_5	−40.54	−1.76	−53.37	−2.31
Li + 1/2 Li_2S_6 -> 1/2 Li_2S_2 + 1/2 Li_2S_4	−51.89	−2.25	−64.73	−2.81
Li + 1/2 Li_2S_6 -> Li_2S_3	−54.25	−2.35	−67.08	−2.91
Li + 1/4 Li_2S_6 -> 1/2 Li_2S + 1/4 Li_2S_4	−40.46	−1.75	−53.29	−2.31
Li + 1/4 Li_2S_6 -> 1/4 Li_2S + 1/4 Li_2S_2 + 1/4 Li_2S_3	−44.21	−1.92	−57.04	−2.47
Li + 1/4 Li_2S_6 -> 3/4 Li_2S_2	−46.77	−2.03	−59.61	−2.58
Li + 1/6 Li_2S_6 -> 1/2 Li_2S + 1/6 Li_2S_3	−39.15	−1.70	−51.98	−2.25
Li + 1/6 Li_2S_6 -> 1/3 Li_2S + 1/3 Li_2S_2	−40.86	−1.77	−53.69	−2.33
Li + 1/8 Li_2S_6 -> 1/2 Li_2S + 1/8 Li_2S_2	−37.90	−1.64	−50.73	−2.20
Li + 1/10 Li_2S_6 -> 3/5 Li_2S	−36.13	−1.57	−48.96	−2.12

10 reactions

TABLE 7S. Heats of reduction reactions of Li_2S_5

	ΔE_{gas}		ΔE_{solid}	
	kcal/mol	eV	kcal/mol	eV
Li + 1/2 Li_2S_5 −> 1/2 Li_2S + 1/2 Li_2S_4	−40.38	−1.75	−53.22	−2.31
Li + 1/2 Li_2S_5 −> 1/2 Li_2S_2 + 1/2 Li_2S_3	−47.87	−2.08	−60.71	−2.63
Li + 1/4 Li_2S_5 −> 1/2 Li_2S + 1/4 Li_2S_3	−38.45	−1.67	−51.28	−2.22
Li + 1/4 Li_2S_5 −> 1/4 Li_2S + 1/2 Li_2S_2	−41.02	−1.78	−53.85	−2.34
Li + 1/6 Li_2S_5 −> 1/2 Li_2S + 1/6 Li_2S_2	−37.02	−1.61	−49.86	−2.16
Li + 1/8 Li_2S_5 −> 5/8 Li_2S	−35.02	−1.52	−47.86	−2.08

6 reactions

TABLE 8S. Heats of reduction reactions of Li_2S_4

	ΔE_{gas}		ΔE_{solid}	
	kcal/mol	eV	kcal/mol	eV
Li + 1/2 Li_2S_4 −> 1/2 Li_2S + 1/2 Li_2S_3	−36.52	−1.58	−49.35	−2.14
Li + 1/2 Li_2S_4 −> Li_2S_2	−41.66	−1.81	−54.49	−2.36
Li + 1/4 Li_2S_4 −> 1/2 Li_2S + 1/4 Li_2S_2	−35.34	−1.53	−48.18	−2.09
Li + 1/6 Li_2S_4 −> 2/3 Li_2S	−33.24	−1.44	−46.07	−2.00

4 reactions

TABLE 9S. Heats of reduction reactions of Li_2S_3

	ΔE_{gas}		ΔE_{solid}	
	kcal/mol	eV	kcal/mol	eV
Li + 1/2 Li_2S_3 −> 1/2 Li_2S + 1/2 Li_2S_2	−34.17	−1.48	−47.00	−2.04
Li + 1/4 Li_2S_3 −> 3/4 Li_2S	−31.60	−1.37	−44.43	−1.93

2 reactions

TABLE 10S. Heats of reduction reactions of Li_2S_2

	ΔE_{gas}		ΔE_{solid}	
	kcal/mol	eV	kcal/mol	eV
Li + 1/2 Li_2S_2 −> Li_2S	−29.03	−1.26	−41.86	−1.82

1 reaction

TABLE 11S. Heats of oxidation reactions of Li_2S

	ΔE_{gas}		ΔE_{solid}	
	kcal/mol	eV	kcal/mol	eV
Li_2S -> Li + 1/2 Li_2S_2	29.03	1.26	41.86	1.82
3/4 Li_2S -> Li + 1/4 Li_2S_3	31.60	1.37	44.43	1.93
2/3 Li_2S -> Li + 1/6 Li_2S_4	33.24	1.44	46.07	2.00
5/8 Li_2S -> Li + 1/8 Li_2S_5	35.02	1.52	47.86	2.08
3/5 Li_2S -> Li + 1/10 Li_2S_6	36.13	1.57	48.96	2.12
7/12 Li_2S -> Li + 1/12 Li_2S_7	37.14	1.61	49.97	2.17
4/7 Li_2S -> Li + 1/14 Li_2S_8	37.76	1.64	50.60	2.19
1/2 Li_2S -> Li + 1/16 S_8	42.36	1.84	53.72	2.33

< 1.8
1.8 ～ 2.0
2.0 ～ 2.2
2.2 ～ 2.4
2.4 ～ 2.6
2.6 ～ 2.8
2.8 ～ 3.0
3.0 ～ 3.2
3.2 <

8 reactions

TABLE 12S. Heats of oxidation reactions of Li_2S_2

	ΔE_{gas}		ΔE_{solid}	
	kcal/mol	eV	kcal/mol	eV
1/2 Li_2S + 1/2 Li_2S_2 -> Li + 1/2 Li_2S_3	34.17	1.48	47.00	2.04
1/2 Li_2S + 1/4 Li_2S_2 -> Li + 1/4 Li_2S_4	35.34	1.53	48.18	2.09
Li2S_2 -> Li + 1/2 Li_2S_4	41.66	1.81	54.49	2.36
1/2 Li_2S + 1/6 Li_2S_2 -> Li + 1/6 Li_2S_5	37.02	1.61	49.86	2.16
1/4 Li_2S + 1/2 Li_2S_2 -> Li + 1/4 Li_2S_5	41.02	1.78	53.85	2.34
1/2 Li_2S + 1/8 Li_2S_2 -> Li + 1/8 Li_2S_6	37.90	1.64	50.73	2.20
1/3 Li_2S + 1/3 Li_2S_2 -> Li + 1/6 Li_2S_6	40.86	1.77	53.69	2.33
3/4 Li_2S_2 -> Li + 1/4 Li_2S_6	46.77	2.03	59.61	2.58
1/2 Li_2S + 1/10 Li_2S_2 -> Li + 1/10 Li_2S_7	38.76	1.68	51.60	2.24
3/8 Li_2S + 1/4 Li_2S_2 -> Li + 1/8 Li_2S_7	41.20	1.79	54.03	2.34
1/6 Li_2S + 1/2 Li_2S_2 -> Li + 1/6 Li_2S_7	45.25	1.96	58.09	2.52
1/2 Li_2S + 1/12 Li_2S_2 -> Li + 1/12 Li_2S_8	39.22	1.70	52.05	2.26
2/5 Li_2S + 1/5 Li_2S_2 -> Li + 1/10 Li_2S_8	41.26	1.79	54.09	2.35
1/4 Li_2S + 3/8 Li_2S_2 -> Li + 1/8 Li_2S_8	44.32	1.92	57.15	2.48
2/3 Li_2S2 -> Li + 1/6Li_2 S_8	49.41	2.14	62.25	2.70
3/7 Li_2S + 1/14 Li_2S_2 -> Li + 1/14 S_8	44.27	1.92	55.42	2.40
1/3 Li_2S + 1/6 Li_2S_2 -> Li + 1/12 S_8	46.81	2.03	57.68	2.50
1/5 Li_2S + 3/10 Li_2S_2 -> Li + 1/10 S_8	50.36	2.18	60.84	2.64
1/2 Li_2S_2 -> Li + 1/8 S_8	55.70	2.42	65.58	2.84

19 reactions

TABLE 13S. Heats of oxidation reactions of Li_2S_3

	ΔE_{gas}		ΔE_{solid}	
	kcal/mol	eV	kcal/mol	eV
1/2 Li_2S + 1/2 Li_2S_3 -> Li + 1/2 Li_2S_4	36.52	1.58	49.35	2.14
1/2 Li_2S + 1/4 Li_2S_3 -> Li + 1/4 Li_2S_5	38.45	1.67	51.28	2.22
1/2 Li_2S_2 + 1/2 Li_2S_3 -> Li + 1/2 Li_2S_5	47.87	2.08	60.71	2.63
1/2 Li_2S + 1/6 Li_2S_3 -> Li + 1/6 Li_2S_6	39.15	1.70	51.98	2.25
1/4 Li_2S + 1/4 Li_2S_2 + 1/4 Li_2S_3 -> Li + 1/4 Li_2S_6	44.21	1.92	57.04	2.47
Li_2S_3 -> Li + 1/2 Li_2S_6	54.25	2.35	67.08	2.91
1/2 Li_2S + 1/8 Li_2S_3 -> Li + 1/8 Li_2S_7	39.91	1.73	52.75	2.29
1/3 Li_2S + 1/6 Li_2S_2 + 1/6 Li_2S_3 -> Li + 1/6 Li_2S_7	43.54	1.89	56.37	2.44
1/2 Li_2S_2 + 1/4 Li_2S_3 -> Li + 1/4 Li_2S_7	50.80	2.20	63.63	2.76
1/4 Li_2S + 1/2 Li_2S_3 -> Li + 1/4 Li_2S_7	48.23	2.09	61.06	2.65
1/2 Li_2S + 1/10 Li_2S_3 -> Li + 1/10 Li_2S_8	40.23	1.74	53.06	2.30
3/8 Li_2S + 1/8 Li_2S_2 + 1/8 Li_2S_3 -> Li + 1/8 Li_2S_8	43.03	1.87	55.87	2.42
1/6 Li_2S +1/ 3Li_2S_2 + 1/6 Li_2S_3 -> Li + 1/6 Li_2S_8	47.70	2.07	60.53	2.63
1/3 Li_2S + 1/3 Li_2S_3 -> Li + 1/6 Li_2S_8	45.99	1.99	58.82	2.55
1/4 Li_2S_2 + 1/2 Li_2S_3 -> Li + 1/4 Li_2S_8	54.47	2.36	67.30	2.92
5/12 Li_2S + 1/12 Li_2S_3 -> Li + 1/12 S_8	45.95	1.99	56.82	2.46
3/10 Li_2S + 1/10 Li_2S_2 + 1/10 Li_2S_3 -> Li + 1/10 S_8	49.33	2.14	59.81	2.59
1/8 Li_2S + 1/4 Li_2S_2 + 1/8 Li_2S_3 -> Li + 1/8 S_8	54.41	2.36	64.30	2.79
1/4 Li_2S + 1/4 Li_2S_3 -> Li + 1/8 S_8	53.13	2.30	63.01	2.73
1/6 Li_2S_2 + 1/3 Li_2S_3 -> Li + 1/6 S_8	61.16	2.65	70.06	3.04

20 reactions

TABLE 14S. Heats of oxidation reactions of Li_2S_4

	ΔE_{gas}		ΔE_{solid}	
	kcal/mol	eV	kcal/mol	eV
1/2 Li_2S + 1/2 Li_2S_4 -> Li + 1/2 Li_2S_5	40.38	1.75	53.22	2.31
1/2 Li_2S + 1/4 Li_2S_4 -> Li + 1/4 Li_2S_6	40.46	1.75	53.29	2.31
1/2 Li_2S_2 + 1/2 Li_2S_4 -> Li + 1/2 Li_2S_6	51.89	2.25	64.73	2.81
1/2 Li_2S + 1/6 Li_2S_4 -> Li + 1/6 Li_2S_7	41.04	1.78	53.88	2.34
1/4 Li_2S + 1/4 Li_2S_2+ 1/4 Li_2S_4 -> Li + 1/4 Li_2S_7	47.05	2.04	59.88	2.60
1/2 Li_2S_3 + 1/2 Li_2S_4 -> Li + 1/2 Li_2S_7	59.94	2.60	72.77	3.16
1/2 Li_2S + 1/8 Li_2S_4 -> Li + 1/8 Li_2S_8	41.16	1.78	53.99	2.34
1/3 Li_2S + 1/6 Li_2S_2 + 1/6 Li_2S_4 -> Li + 1/6 Li_2S_8	45.20	1.96	58.04	2.52
1/2 Li_2S_2 + 1/4 Li_2S_4 -> Li + 1/4 Li_2S_8	53.29	2.31	66.13	2.87
1/4 Li_2S + 1/4 Li_2S_3 + 1/4 Li_2S_4 -> Li + 1/4 Li_2S_8	50.72	2.20	63.56	2.76
2/5 Li_2S + 1/10 Li_2S_4 -> Li + 1/10 S_8	47.84	2.07	58.31	2.53
1/4 Li_2S + 1/8 Li_2S_2 + 1/8 Li_2S_4 -> Li + 1/8 S_8	52.54	2.28	62.43	2.71
Li_2S_4 -> Li + 1/2 Li_2S_8	64.93	2.82	77.76	3.37
1/3 Li_2S_2 + 1/6 Li_2S_4 -> Li + 1/6 S_8	60.38	2.62	69.28	3.00
1/6 Li_2S + 1/6 Li_2S_3 + 1/6 Li_2S_4 -> Li + 1/6 S_8	58.66	2.54	67.57	2.93
1/2 Li_2S_4 -> Li + 1/4 S_8	69.74	3.02	76.67	3.33

16 reactions

TABLE 15S. Heats of oxidation reactions of Li_2S_5

	ΔE_{gas}		ΔE_{solid}	
	kcal/mol	eV	kcal/mol	eV
1/2 Li_2S + 1/2 Li_2S_5 -> Li + 1/2 Li_2S_6	40.54	1.76	53.37	2.31
1/2 Li_2S + 1/4 Li_2S_5 -> Li + 1/4 Li_2S_7	41.37	1.79	54.21	2.35
1/2 Li_2S_2 + 1/2 Li_2S_5 -> Li + 1/2 Li_2S_7	53.72	2.33	66.55	2.89
1/2 Li_2S + 1/6 Li_2S_5 -> Li + 1/6 Li_2S_8	41.42	1.80	54.25	2.35
1/4 Li_2S + 1/4 Li_2S_2 + 1/4 Li_2S_5 -> Li + 1/4 Li_2S_8	47.61	2.06	60.45	2.62
1/2 Li_2S_3 + 1/2 Li_2S_5 -> Li +1/2 Li_2S_8	61.06	2.65	73.90	3.20
3/8 Li_2S + 1/8 Li_2S_5 -> Li + 1/8 S_8	49.70	2.16	59.59	2.58
1/6 Li_2S + 1/6 Li_2S_2 + 1/6 Li_2S_5 -> Li + 1/6 S_8	56.59	2.45	65.49	2.84
1/4 Li_2S_3 + 1/4 Li_2S_5 -> Li + 1/4 S_8	67.80	2.94	74.74	3.24

9 reactions

TABLE 16S. Heats of oxidation reactions of Li_2S_6

	ΔE_{gas}		ΔE_{solid}	
	kcal/mol	eV	kcal/mol	eV
1/2 Li_2S + 1/2 Li_2S_6 -> Li + 1/2 Li_2S_7	42.21	1.83	55.04	2.39
1/2 Li_2S + 1/4 Li_2S_6 -> Li + 1/4 Li_2S_8	41.86	1.82	54.69	2.37
1/2 Li_2S_2 + 1/2 Li_2S_6 -> Li +1/2 Li_2S_8	54.69	2.37	67.53	2.93
1/3 Li_2S + 1/6 Li_2S_6 -> Li + 1/6 S_8	52.75	2.29	61.66	2.67
1/4 Li_2S_2 + 1/4 Li_2S_6 -> Li + 1/4 S_8	64.62	2.80	71.56	3.10

5 reactions

TABLE 17S. Heats of oxidation reactions of Li_2S_7

	ΔE_{gas}		ΔE_{solid}	
	kcal/mol	eV	kcal/mol	eV
1/2 Li_2S + 1/2 Li_2S_7 -> Li +1/2 Li_2S_8	41.51	1.80	54.34	2.36
1/4 Li_2S + 1/4 Li_2S_7 -> Li + 1/4 S_8	58.03	2.52	64.97	2.82

2 reactions

TABLE 18S. Heats of oxidation reactions of Li_2S_8

	ΔE_{gas}		ΔE_{solid}	
	kcal/mol	eV	kcal/mol	eV
1/2 Li_2S_8 -> Li + 1/2 S_8	74.54	3.23	75.59	3.28

1 reaction

TABLE 19S. Heat of reduction reactions for formation of Li_2S_2 from S_8 or Li_2S_n with Li[a]

	ΔE_{gas}	ΔE_{solid}
Li + 1/4 S_8 -> 1/4 Li_2S_2 + 1/4 Li_2S_6	−2.80	−3.10
Li + 1/6 S_8 -> 1/6 Li_2S + 1/6 Li_2S_2 + 1/6 Li_2S_5	−2.45	−2.84
Li + 1/6 S_8 -> 1/3 Li_2S_2 + 1/6 Li_2S_4	−2.62	−3.00
Li + 1/6 S_8 -> 1/6 Li_2S_2 + 1/3 Li_2S_3	−2.65	−3.04
Li + 1/8 S_8 -> 1/4 Li_2S + 1/8 Li_2S_2 + 1/8 Li_2S_4	−2.28	−2.71
Li + 1/8 S_8 -> 1/8 Li_2S + 1/4 Li_2S_2 + 1/8 Li_2S_3	−2.36	−2.79
Li + 1/8 S_8 -> 1/2 Li_2S_2	−2.42	−2.84
Li + 1/10 S_8 -> 3/10 Li_2S + 1/10 Li_2S_2 + 1/10 Li_2S_3	−2.14	−2.59
Li + 1/10 S_8 -> 1/5Li_2S + 3/10 Li_2S_2	−2.18	−2.64
Li + 1/12 S_8 -> 1/3 Li_2S + 1/6 Li_2S_2	−2.03	−2.50
Li + 1/14 S_8 -> 3/7 Li_2S + 1/14 Li_2S_2	−1.92	−2.40
Li +1/2 Li_2S_8 -> 1/2 Li_2S_2 + 1/2 Li_2S_6	−2.37	−2.93
Li + 1/4 Li_2S_8 -> 1/4 Li_2S + 1/4 Li_2S_2 + 1/4 Li_2S_5	−2.06	−2.62
Li + 1/4 Li_2S_8 -> 1/2 Li_2S_2 + 1/4 Li_2S_4	−2.31	−2.87
Li + 1/4 Li_2S_8 -> 1/4 Li_2S_2 + 1/2 Li_2S_3	−2.36	−2.92
Li + 1/6 Li_2S_8 -> 1/3 Li_2S + 1/6 Li_2S_2 + 1/6 Li_2S_4	−1.96	−2.52
Li + 1/6 Li_2S_8 -> 1/6 Li_2S +1/3 Li_2S_2 + 1/6 Li_2S_3	−2.07	−2.63
Li + 1/6 Li_2S_8 -> 2/3 Li_2S_2	−2.14	−2.70
Li + 1/8 Li_2S_8 -> 3/8 Li_2S + 1/8 Li_2S_2 + 1/8 Li_2S_3	−1.87	−2.42
Li + 1/8 Li_2S_8 -> 1/4 Li_2S + 3/8 Li_2S_2	−1.92	−2.48
Li + 1/10 Li_2S_8 -> 2/5 Li_2S + 1/5 Li_2S_2	−1.79	−2.35
Li + 1/12 Li_2S_8 -> 1/2 Li_2S + 1/12 Li_2S_2	−1.70	−2.26
Li + 1/2 Li_2S_7 -> 1/2 Li_2S_2 + 1/2 Li2S_5	−2.33	−2.89
Li + 1/4 Li_2S_7 -> 1/4 Li_2S + 1/4 Li_2S_2 + 1/4 Li_2S_4	−2.04	−2.60
Li + 1/4 Li_2S_7 -> 1/2 Li_2S_2 + 1/4 Li_2S_3	−2.20	−2.76
Li + 1/6 Li_2S_7 -> 1/3 Li_2S + 1/6 Li_2S_2 + 1/6 Li_2S_3	−1.89	−2.44
Li + 1/6 Li_2S_7 -> 1/6 Li_2S + 1/2 Li_2S_2	−1.96	−2.52
Li + 1/8 Li_2S_7 -> 3/8 Li_2S + 1/4 Li_2S_2	−1.79	−2.34
Li + 1/10 Li_2S_7 -> 1/2 Li_2S + 1/10 Li_2S_2	−1.68	−2.24
Li + 1/2 Li_2S_6 -> 1/2 Li_2S_2 + 1/2 Li_2S_4	−2.25	−2.81
Li + 1/4 Li_2S_6 -> 1/4 Li_2S + 1/4 Li_2S_2 + 1/4 Li_2S_3	−1.92	−2.47
Li + 1/4 Li_2S_6 -> 3/4 Li_2S_2	−2.03	−2.58
Li + 1/6 Li_2S_6 -> 1/3 Li_2S + 1/3 Li_2S_2	−1.77	−2.33
Li + 1/8 Li_2S_6 -> 1/2 Li_2S + 1/8 Li_2S_2	−1.64	−2.20
Li + 1/2 Li_2S_5 -> 1/2 Li_2S_2 + 1/2 Li_2S_3	−2.08	−2.63
Li + 1/4 Li_2S_5 -> 1/4 Li_2S + 1/2 Li_2S_2	−1.78	−2.34
Li + 1/6 Li_2S_5 -> 1/2 Li_2S + 1/6 Li_2S_2	−1.61	−2.16
Li + 1/2 Li_2S_4 -> Li_2S_2	−1.81	−2.36
Li + 1/4 Li_2S_4 -> 1/2 Li_2S + 1/4 Li_2S_2	−1.53	−2.09
Li + 1/2 Li_2S_3 -> 1/2 Li_2S + 1/2 Li_2S_2	−1.48	−2.04

40 reaction

[a] Heats of reactions are normalized as one electron reactions. Energies in eV.

TABLE 20S. Solvation energies in sulfolane calculated for S_8 and S_n^{2-} (n = 1-8) in kcal/mol.

	E_{solv}
S_8 (8a)	−1.4
S^{2-} (17)	−277.7
S_2^{2-} (18)	−235.2
S_3^{2-} (19a)	−209.5
S_4^{2-} (20a)	−190.8
S_5^{2-} (21a)	−175.9
S_6^{2-} (22a)	−164.3
S_7^{2-} (23a)	−154.9
S_8^{2-} (24a)	−147.1

3a 0.0 **3b** 64.2 (TS)

Figure 1S. Optimized geometries for isomers of S_3 and their relative energies in kcal/mol. **3b** is a transition state.

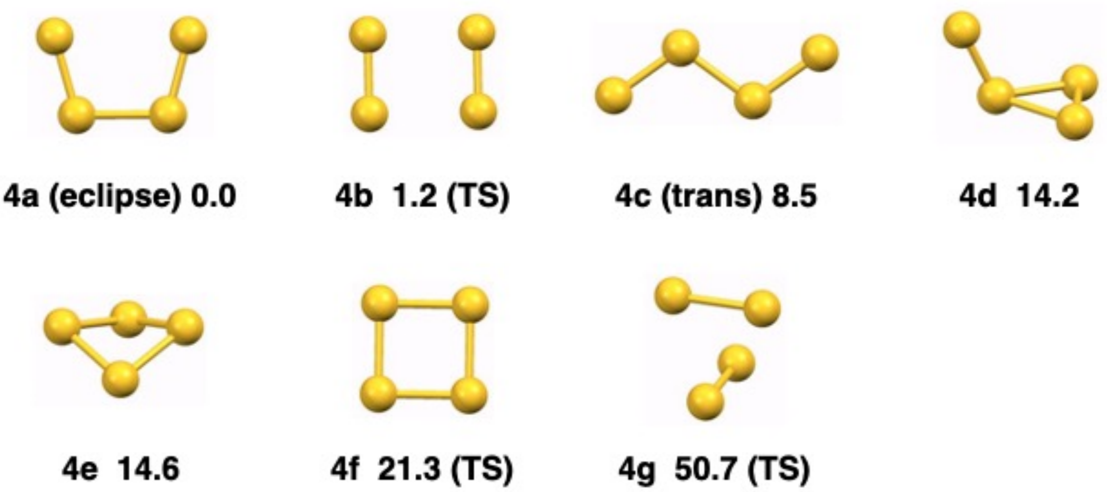


Figure 2S. Optimized geometries for isomers of S_4 and their relative energies in kcal/mol. **4b**, **4f** and **4g** are transition states.

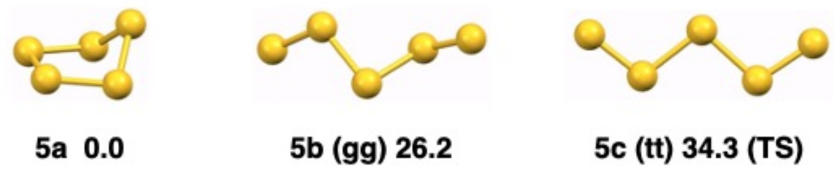


Figure 3S. Optimized geometries for isomers of S_5 and their relative energies in kcal/mol. **5c** is a transition state.

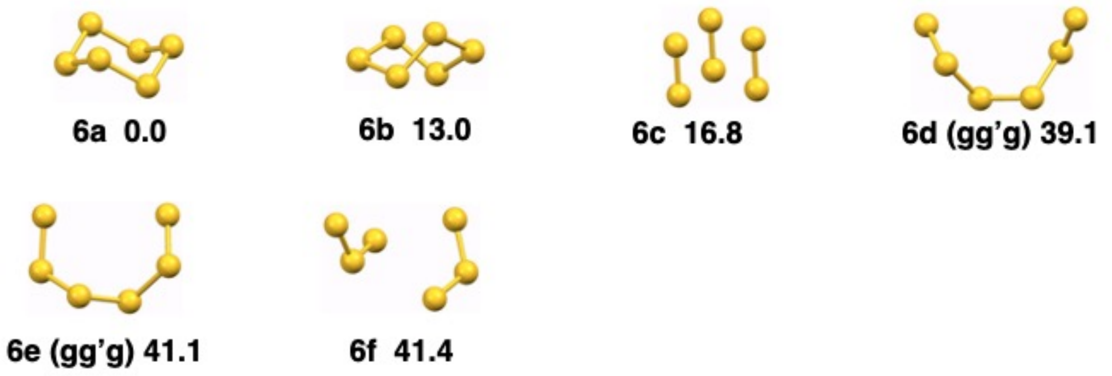


Figure 4S. Optimized geometries for isomers of S_6 and their relative energies in kcal/mol.

7a 0.0 **7b** (tttt) 66.51

Figure 5S. Optimized geometries for isomers of S_7 and their relative energies in kcal/mol.

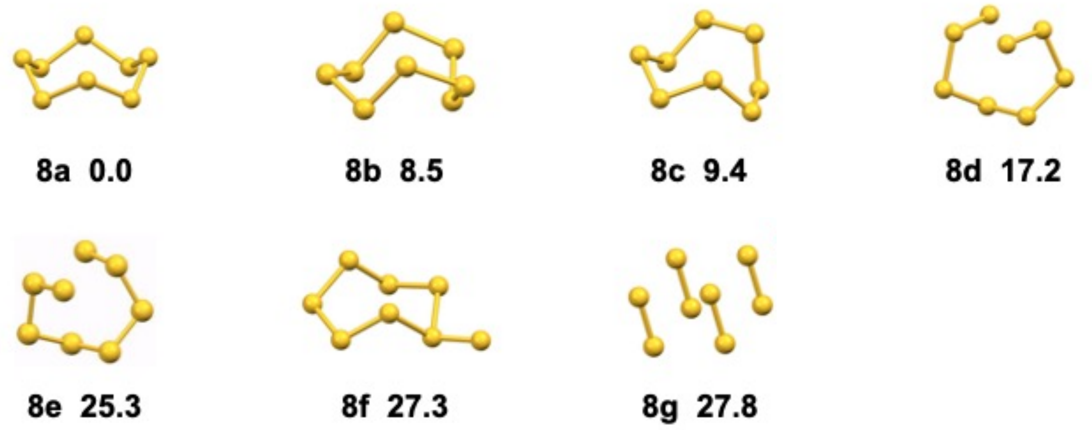


Figure 6S. Optimized geometries for isomers of S_8 and their relative energies in kcal/mol.

Figure 7S. Optimized geometries for isomers of $S_3^{\cdot-}$ and their relative energies in kcal/mol. **11b** is a transition state.

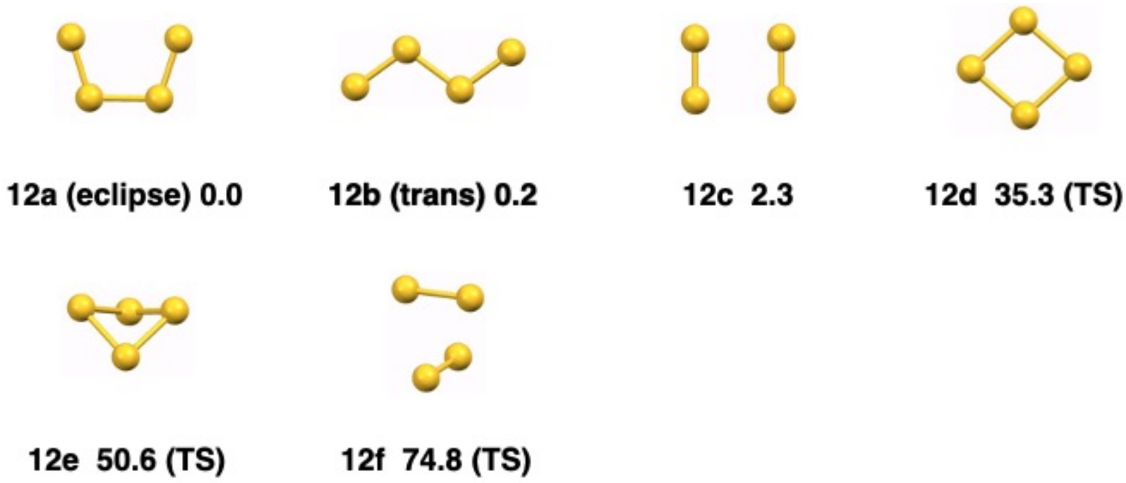


Figure 8S. Optimized geometries for isomers of $S_4^{\cdot-}$ and their relative energies in kcal/mol. **12d**, **12e** and **12f** are transition states.

13a (gg') 0.0 **13b (gg) 1.7** **13c (tg) 1.8** **13d (tt) 7.9 (TS)**

Figure 9S. Optimized geometries for isomers of $S_5^{\cdot -}$ and their relative energies in kcal/mol. **13d** is a transition state.

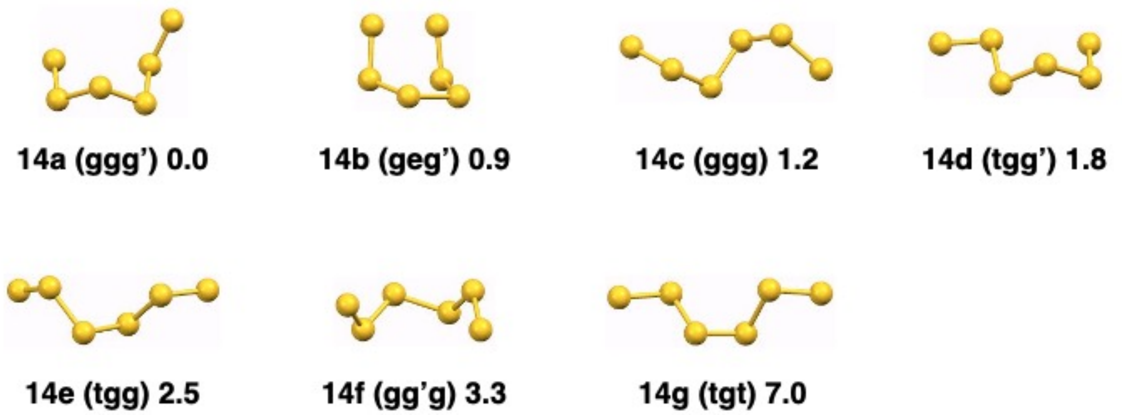


Figure 10S. Optimized geometries for isomers of $S_6^{\cdot -}$ and their relative energies in kcal/mol.

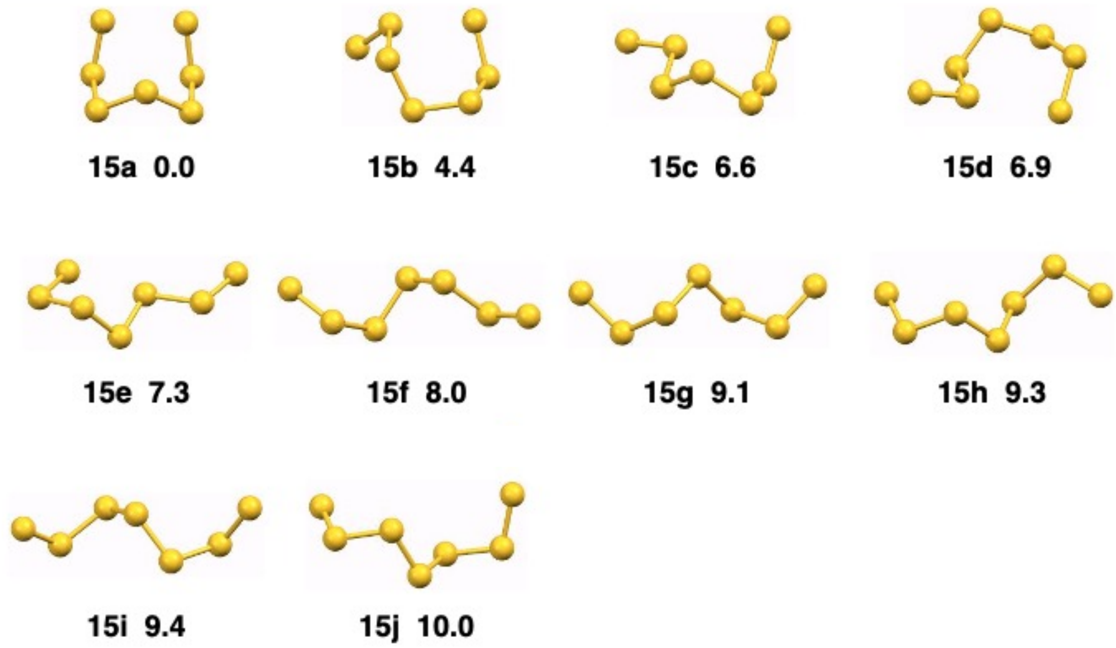


Figure 11S. Optimized geometries for isomers of $S_7^{\cdot -}$ and their relative energies in kcal/mol.

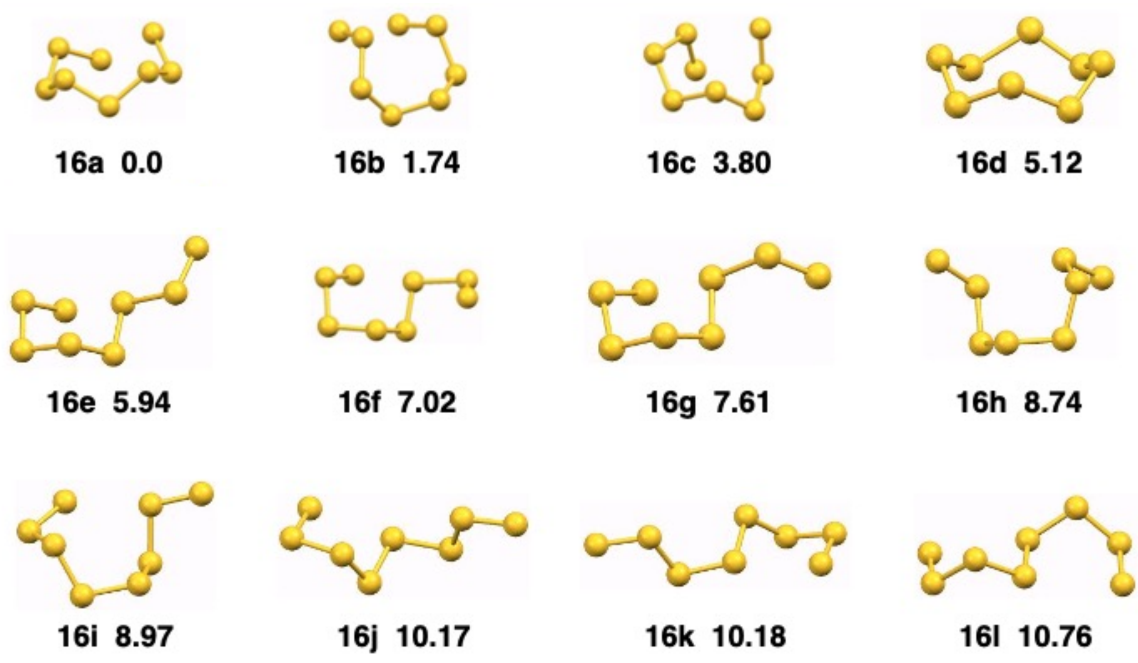


Figure 12S. Optimized geometries for isomers of $S_8^{\cdot -}$ and their relative energies in kcal/mol.

19a 0.0

19b 43.3 (TS)

Figure 13S. Optimized geometries for isomers of S_3^{2-} and their relative energies in kcal/mol. **19b** is a transition state.

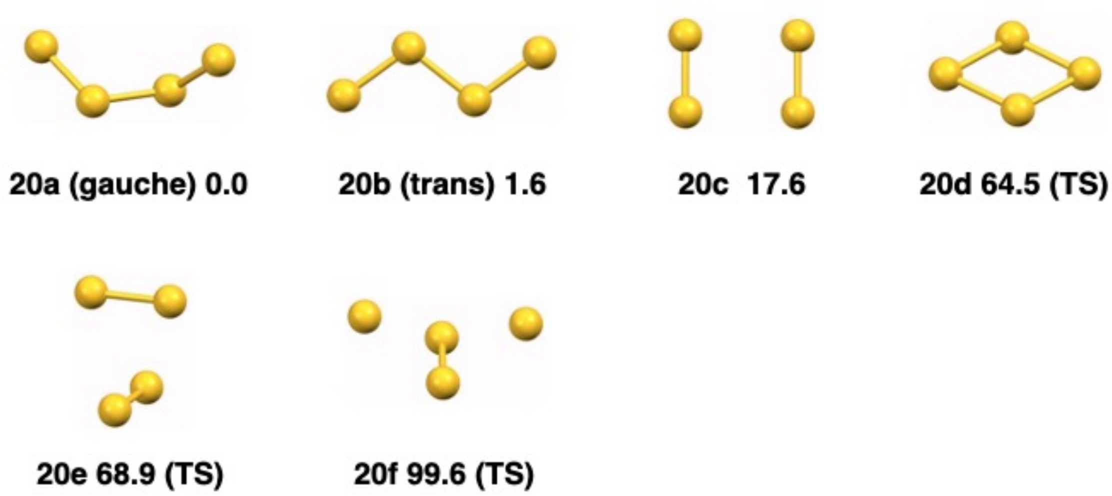


Figure 14S. Optimized geometries for isomers of S_4^{2-} and their relative energies in kcal/mol. **20d**, **20e** and **20f** are transition states.

21a (gg) 0.0 **21b (gg') 3.0** **21c (tt) 8.4 (TS)**

Figure 15S. Optimized geometries for isomers of S_5^{2-} and their relative energies in kcal/mol. **21c** is a transition state.

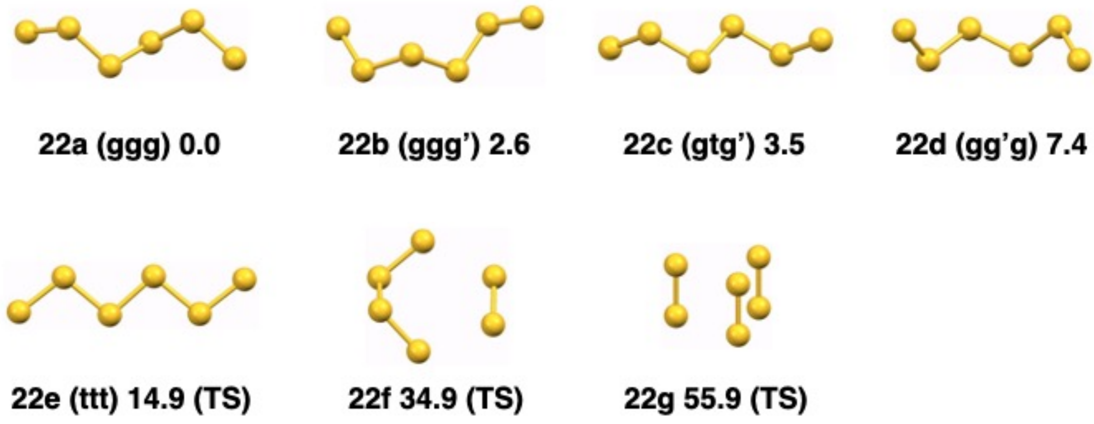
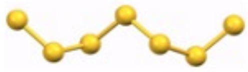


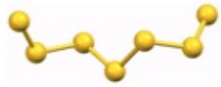
Figure 16S. Optimized geometries for isomers of S_6^{2-} and their relative energies in kcal/mol. **22e**, **22f** and **22g** are transition states.



23a (gggg) 0.0

23b (gggg') 2.1

23c (ggg'g') 3.1



23d (gg'g'g) 4.3

23e (ggg'g) 6.2

Figure 17S. Optimized geometries for isomers of S_7^{2-} and their relative energies in kcal/mol.

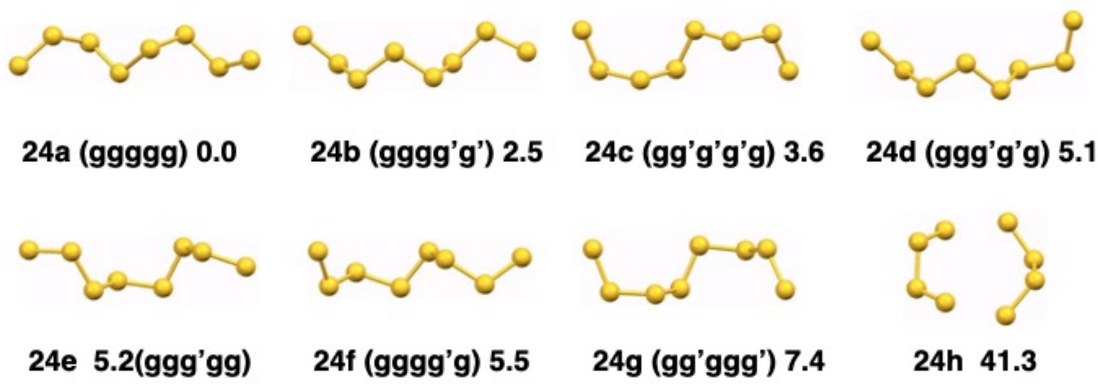


Figure 18S. Optimized geometries for isomers of S_8^{2-} and their relative energies in kcal/mol.

25

Figure 19S. Optimized geometry for $[LiS]^-$.

26a 0.0 **26b 33.2**

Figure 20S. Optimized geometries for isomers of $[LiS_2]^-$ and their relative energies in kcal/mol.

27a 0.0 **27b (TS) 33.1**

Figure 21S. Optimized geometries for isomers of $[LiS_3]^-$ and their relative energies in kcal/mol. **27b** is a transition state.

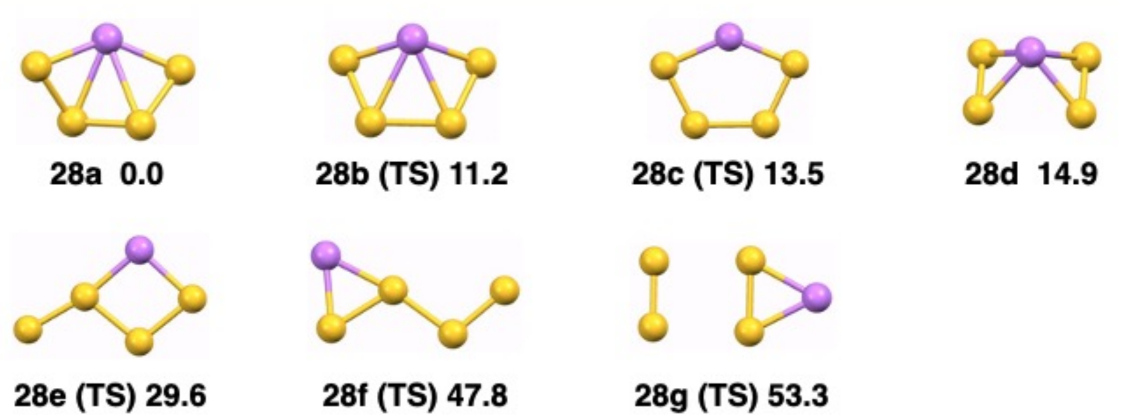


Figure 22S. Optimized geometries for isomers of $[LiS_4]^-$ and their relative energies in kcal/mol. **28b**, **28c**, **28e**, **28f**, **28g** are transition states.

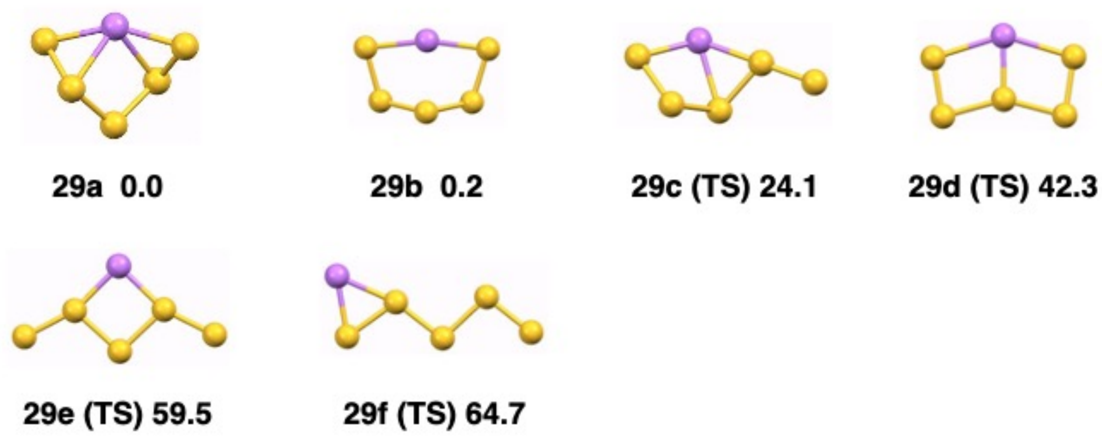
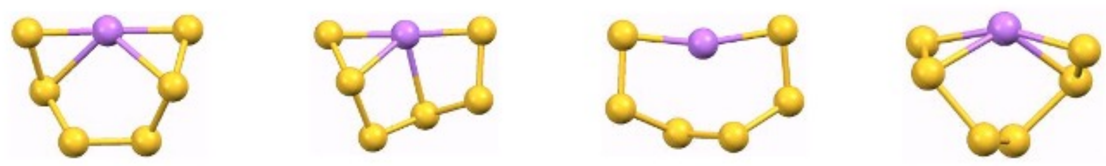


Figure 23S. Optimized geometries for isomers of $[LiS_5]^-$ and their relative energies in kcal/mol. **29c**, **29d**, **29e**, **29f** are transition stat



30a 0.0 30b 0.0 30c 0.9 30d 10.1

Figure 24S. Optimized geometries for isomers of $[LiS_6]^-$ and their relative energies in kcal/mol.

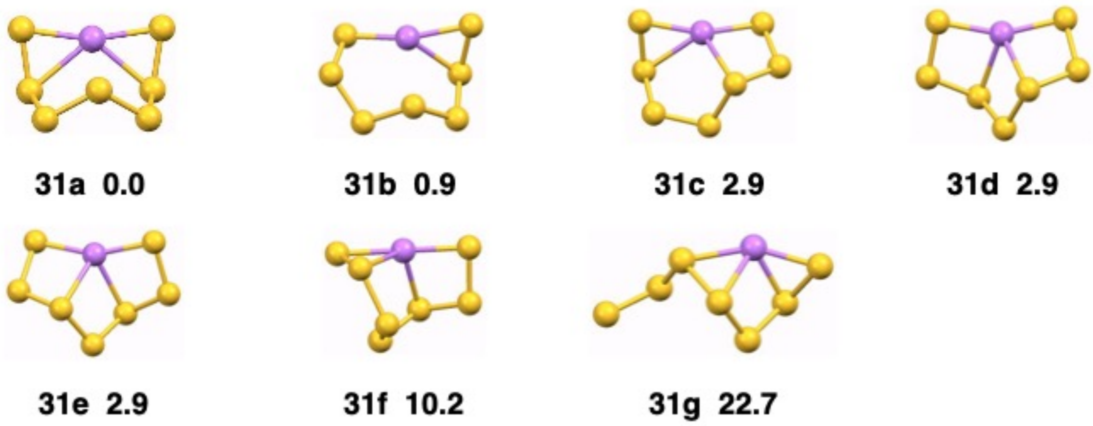


Figure 25S. Optimized geometries for isomers of $[LiS_7]^-$ and their relative energies in kcal/mol.

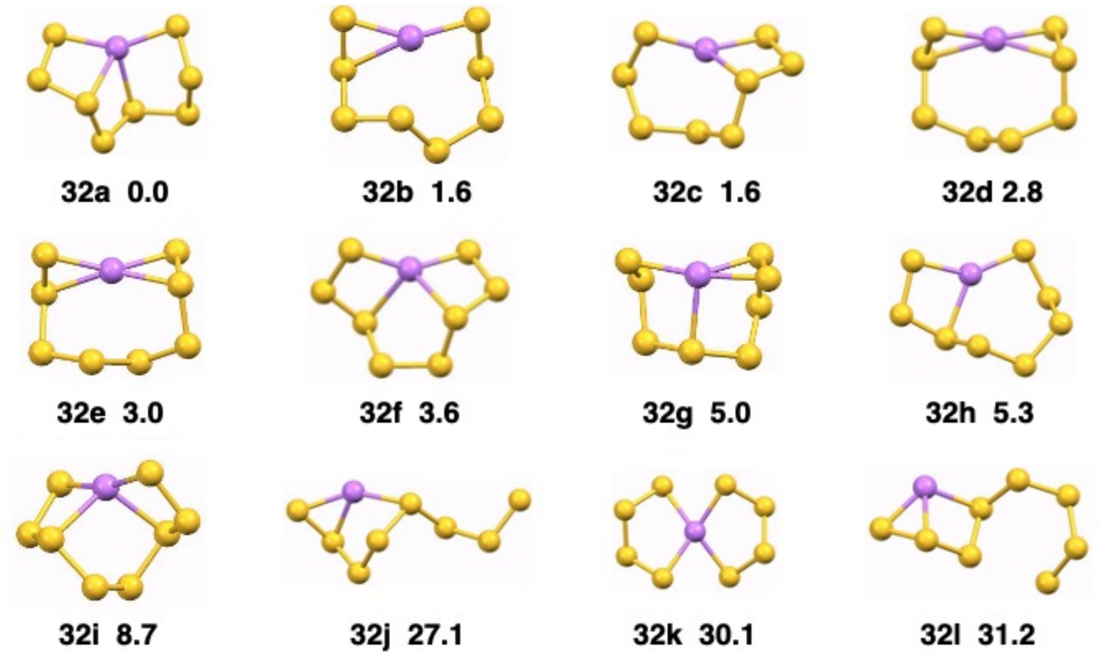
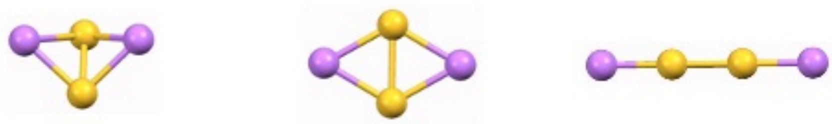


Figure 26S. Optimized geometries for isomers of $[LiS_8]^-$ and their relative energies in kcal/mol.

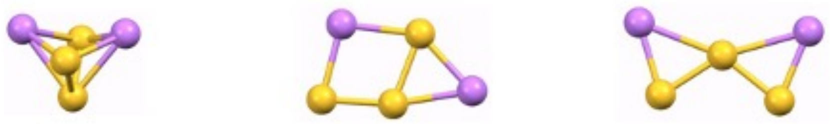
33a 0.0 **33b (TS) 0.1**

Figure 27S. Optimized geometries for isomers of Li_2S and their relative energies in kcal/mol. **33b** is a transition state.



34a 0.0 **34b (TS) 2.3** **34c (TS) 51.6**

Figure 28S. Optimized geometries for isomers of Li_2S_2 and their relative energies in kcal/mol. **34b** and **34c** are transition states.



35a 0.0 **35b (TS) 22.7** **35c (TS) 48.3**

Figure 29S. Optimized geometries for isomers of Li_2S_3 and their relative energies in kcal/mol. **35b** and **35c** are transition states.

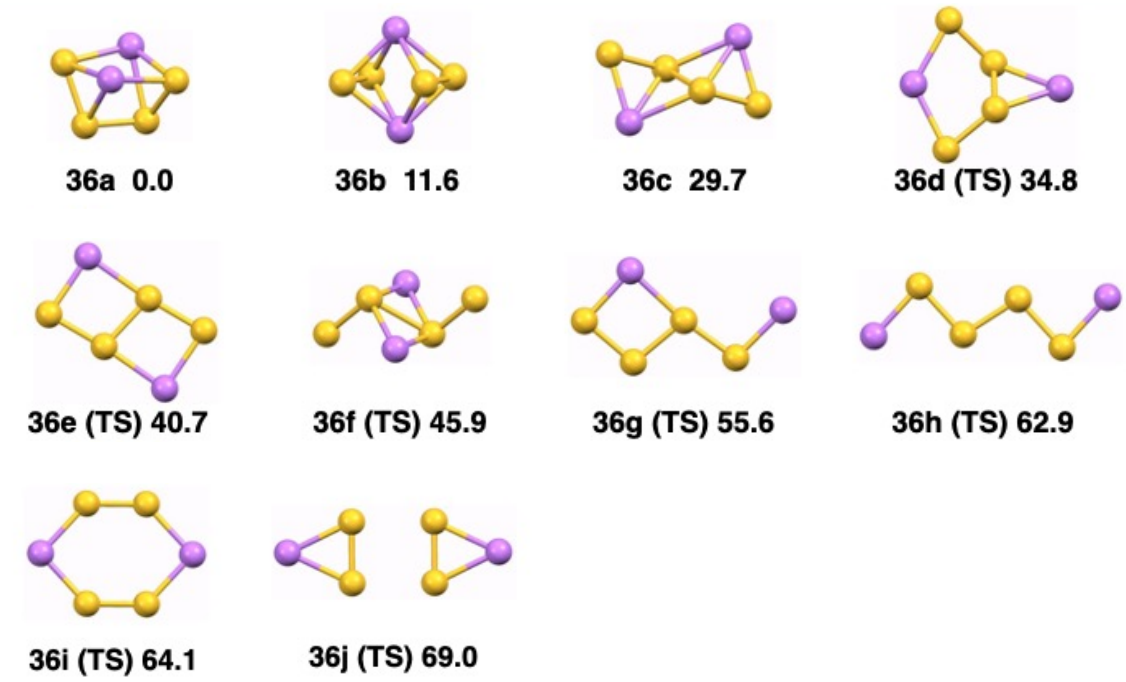


Figure 30S. Optimized geometries for isomers of Li_2S_4 and their relative energies in kcal/mol. **36d, 36e**, **36f, 36g, 36h, 36i** and **36j** are transition states.

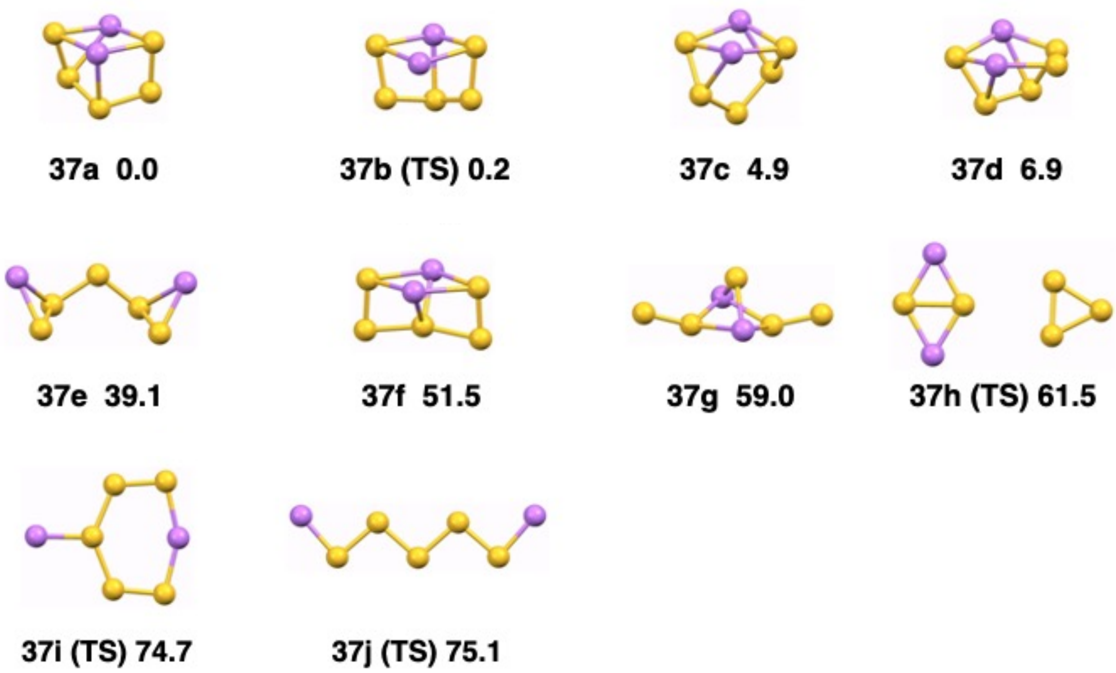
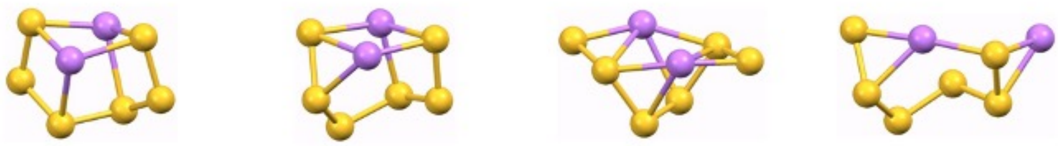
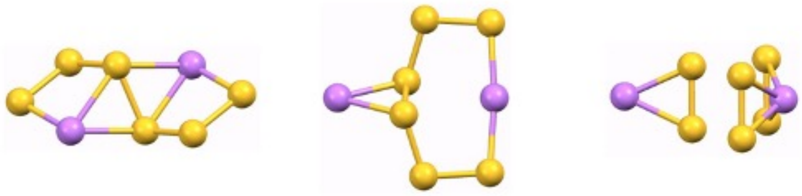


Figure 31S. Optimized geometries for isomers of Li_2S_5 and their relative energies in kcal/mol. **37b**, **37h, 37i** and **37j** are transition states.



38a 0.0 **38b 0.8** **38c 17.4** **38d 20.2**



38e 32.1 **38f 39.7** **38g 44.6**

Figure 32S. Optimized geometries for isomers of Li_2S_6 and their relative energies in kcal/mol.

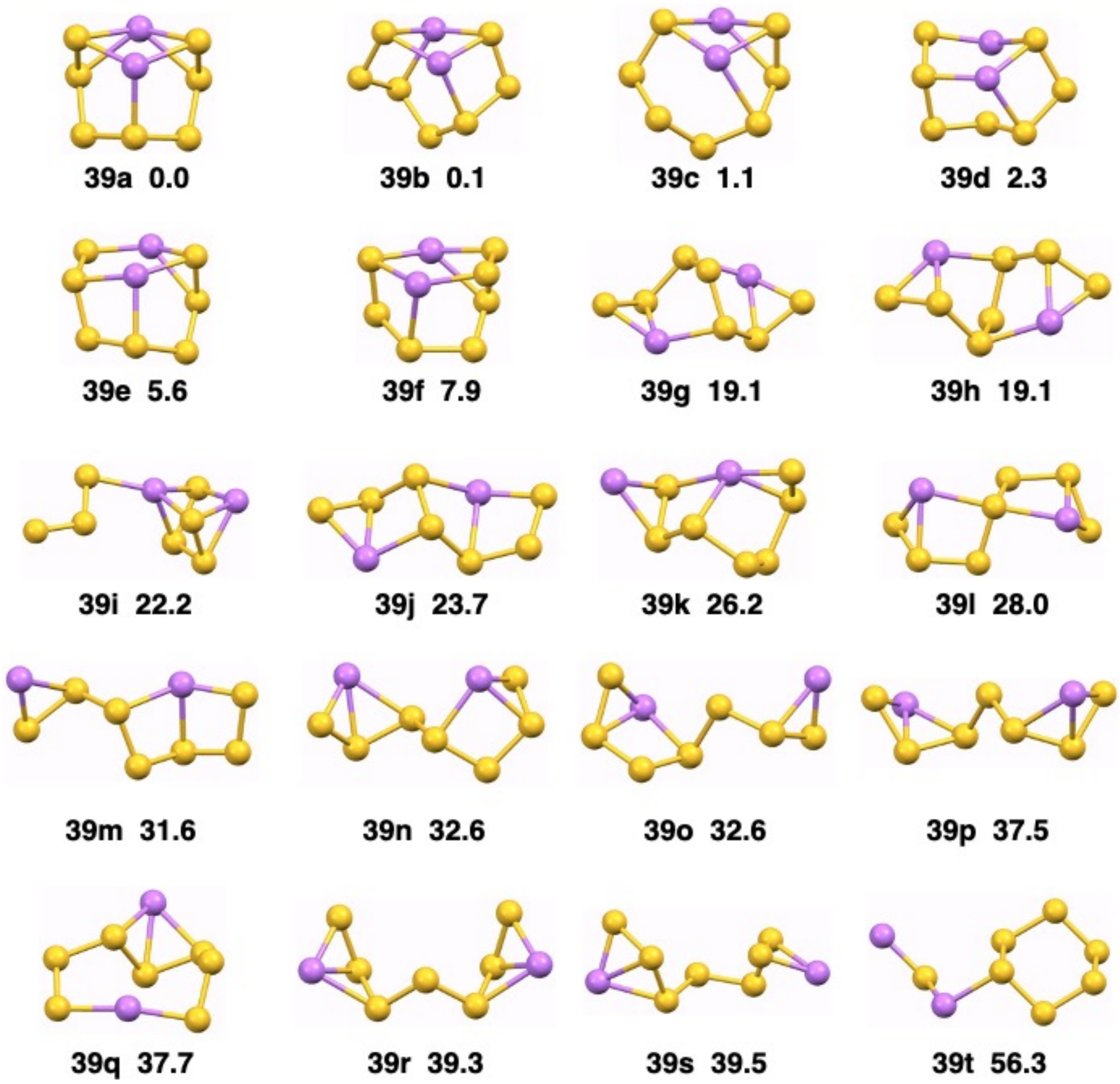


Figure 33S. Optimized geometries for isomers of Li_2S_7 and their relative energies in kcal/mol.

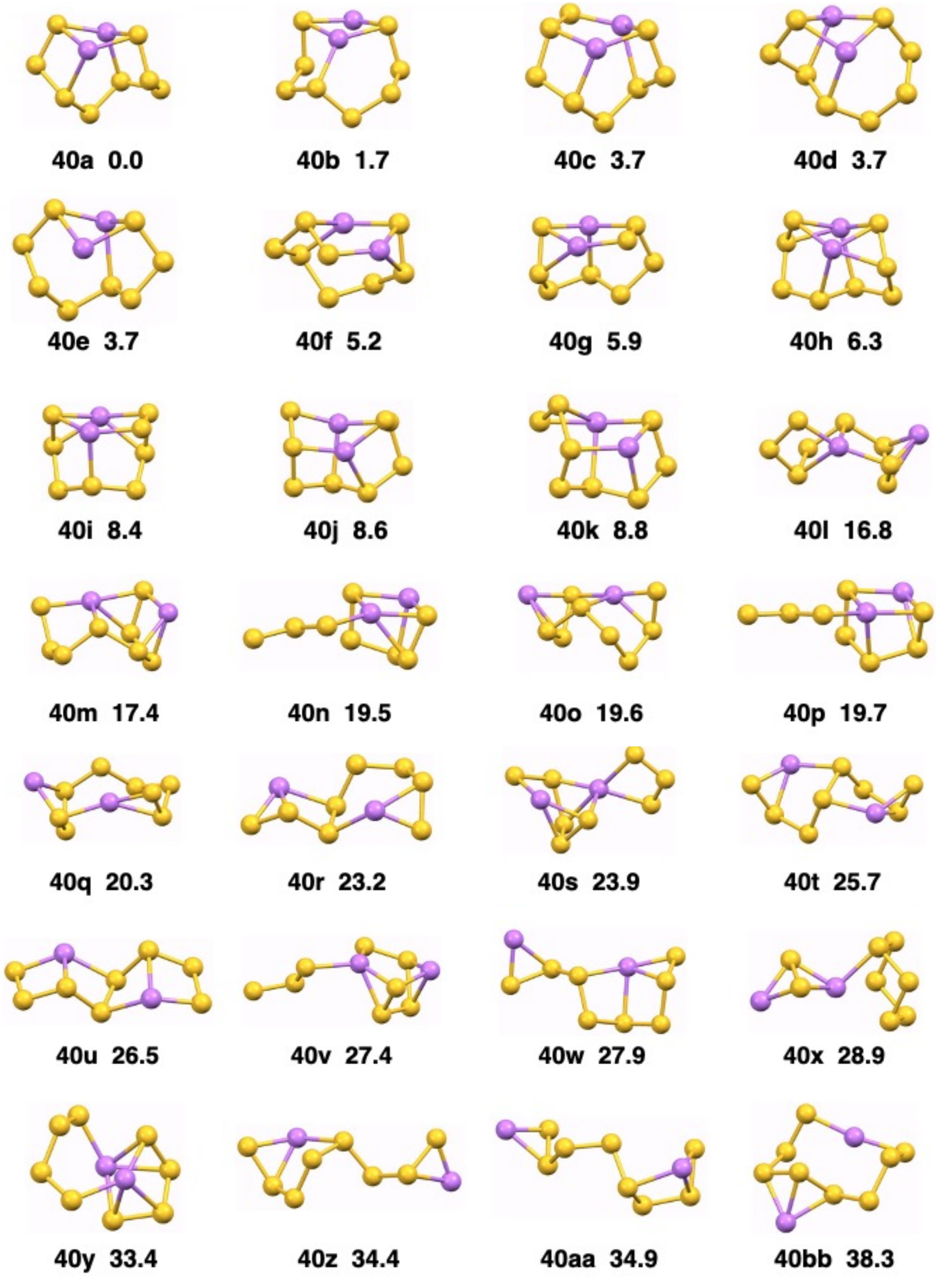


Figure 34S. Optimized geometries for isomers of Li_2S_8 and their relative energies in kcal/mol.

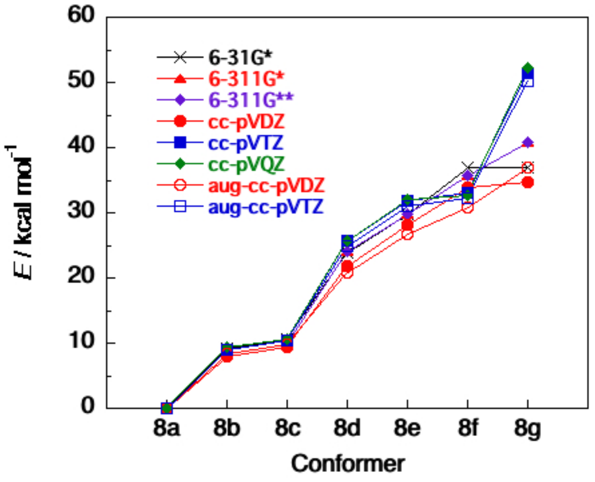


Figure 35S. Relative energies calculated for seven isomers of S_8 (**8a-8g**) at the MP3 level using several basis sets. Geometries of isomers are shown in Figure 6S.

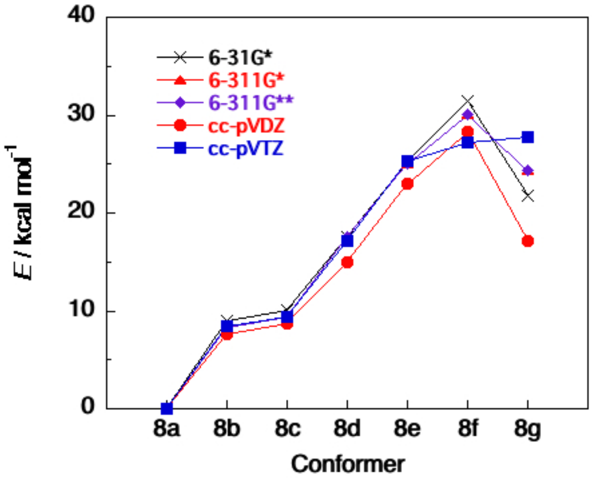


Figure 36S. Relative energies calculated for seven isomers of S_8 (**8a-8g**) at the CCSD(T) level using several basis sets. Geometries of isomers are shown in Figure 6S.

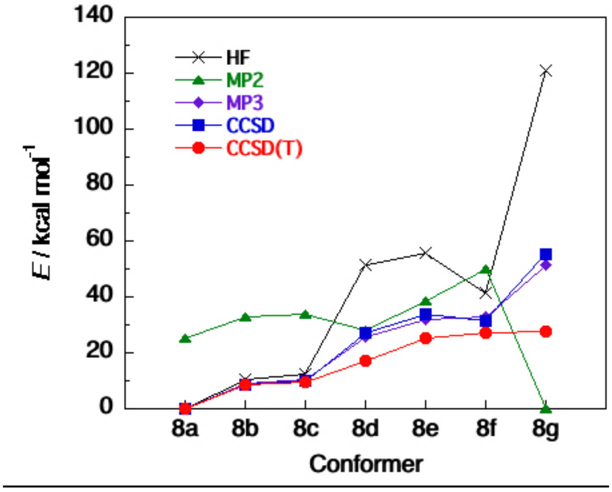


Figure 37S. Relative energies calculated for seven isomers of S_8 (**8a-8g**) with several electron correlation correction methods using cc-pVTZ basis set. Geometries of isomers are shown in Figure 6S.

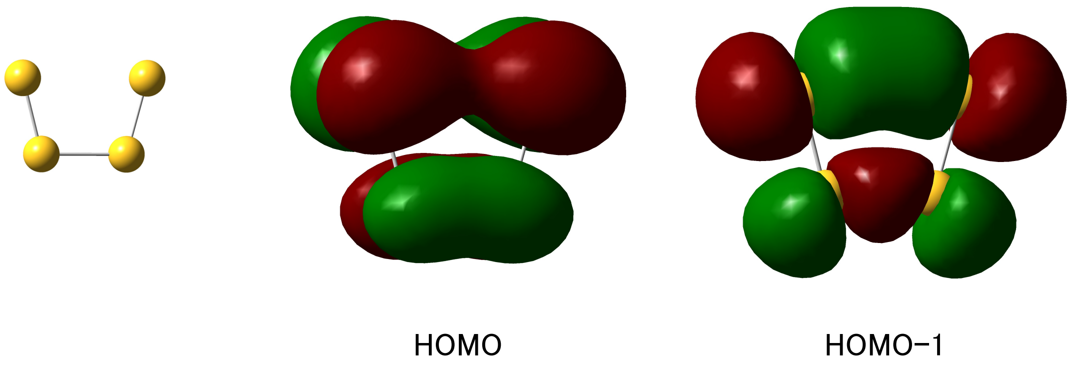
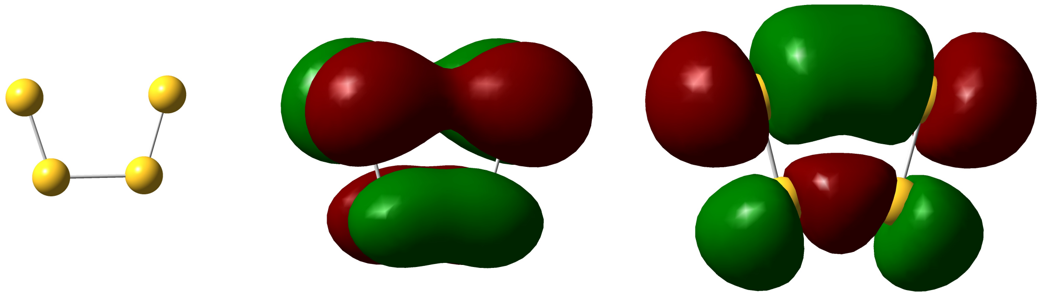


Figure 38S. Molecular orbitals calculated for S_4 (**4a**).



HOMO HOMO−1

Figure 39S. Molecular orbitals calculated for $S_4^{\cdot -}$ (**12a**).

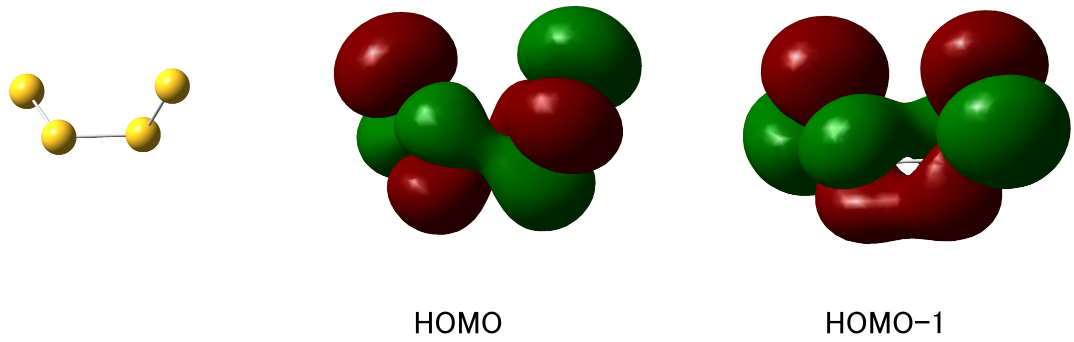


Figure 40S. Molecular orbitals calculated for S_4^{2-} (**20a**).