Supporting Information

Aromatisation of fulvene by complexation with lithium

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Table S1. Calculated properties of the Li-fulvene complex as functions of approach distance. Headings: *d*(Li-fulv), distance from the Li nucleus to the ring centre; *E*(B3LYP), total energy at the B3LYP/6-31G(d,p) level of theory; ΔE(B3LYP), energy relative to complex at d = 5Å (-239.68326 Hartree); *q*(Li), Natural Charge on Li; pEDA(F), ring population descriptor; HOMA, ring geometry aromaticity descriptor; NICS(0), magnetic aromaticity index, *R*(C1-C6), *exo* bond length.

d(Li-fulv) [Å]	*E*(B3LYP) [Hartree]	ΔE [kcal/mol]	*q*(Li) [e]	pEDA(F) [e]	HOMA index	NICS(0) index	*R*(C1-C6) [Å]
1.0	-239.61719	48.312	0.903	0.871	-1.261	-12.675	1.403
1.1	-239.65817	22.591	0.910	0.862	-0.537	-13.341	1.408
1.2	-239.69142	1.728	0.914	0.851	-0.111	-13.651	1.412
1.3	-239.71687	-14.244	0.917	0.839	0.152	-13.656	1.414
1.4	-239.73522	-25.756	0.917	0.826	0.323	-13.418	1.415
1.5	-239.74745	-33.432	0.916	0.814	0.433	-13.002	1.416
1.6	-239.75458	-37.903	0.915	0.802	0.490	-12.473	1.416
1.7	-239.75759	-39.791	0.912	0.792	0.517	-11.884	1.416
1.8	-239.75741	-39.678	0.910	0.784	0.534	-11.267	1.416
1.9	-239.75482	-38.057	0.907	0.776	0.554	-10.639	1.416
2.0	-239.75048	-35.332	0.902	0.767	0.550	-10.003	1.415
2.1	-239.74489	-31.823	0.897	0.758	0.550	-9.356	1.415
2.2	-239.73845	-27.782	0.889	0.746	0.551	-8.687	1.414
2.3	-239.73147	-23.405	0.879	0.733	0.551	-7.958	1.413
2.4	-239.72423	-18.857	0.862	0.716	0.547	-7.000	1.412
2.5	-239.71715	-14.417	0.752	0.636	0.511	-4.428	1.403
2.6	-239.71144	-10.836	0.587	0.518	0.417	-1.677	1.390
2.7	-239.70696	-8.025	0.466	0.428	0.324	0.171	1.380
2.8	-239.70346	-5.827	0.363	0.352	0.215	1.504	1.372
2.9	-239.70079	-4.150	0.272	0.284	0.126	2.403	1.366
3.0	-239.69882	-2.916	0.191	0.224	0.028	2.926	1.360
3.1	-239.69744	-2.049	0.121	0.172	-0.064	3.103	1.355
3.2	-239.69652	-1.472	0.062	0.128	-0.147	2.925	1.351
3.3	-239.69594	-1.107	0.019	0.097	-0.202	2.395	1.348
3.4	-239.69556	-0.868	-0.002	0.080	-0.243	1.740	1.347
3.5	-239.69527	-0.685	-0.009	0.073	-0.267	1.302	1.346
3.6	-239.69501	-0.525	-0.011	0.070	-0.267	1.078	1.345
3.7	-239.69478	-0.380	-0.011	0.068	-0.267	0.961	1.345
3.8	-239.69457	-0.245	-0.011	0.067	-0.292	0.899	1.345
3.9	-239.69436	-0.118	-0.010	0.066	-0.292	0.864	1.345
4.0	-239.69418	0.000	-0.009	0.065	-0.292	0.843	1.345

Table S2. Natural Energy Decomposition Analysis (NEDA) for the interaction energy as Li approaches fulvene. Calculations were performed at the B3LYP/6-31G(d,p) level.
Key: EL:electric, CT: charge transfer, CORE: Pauli repulsion , TOTAL: total interaction. Energies are in kcal/mol and distances in Å. Values for equilibrium structure are in bold.

d(Li-Fulv)	EL	CT	CORE	TOTAL
1	-135.26	-178.81	350.23	36.17
1.1	-128.93	-162.82	304.92	13.17
1.2	-121.18	-148.26	263.25	-6.19
1.3	-112.53	-134.89	226.03	-21.4
1.4	-103.61	-122.59	193.69	-32.51
1.5	-95.03	-111.37	166.45	-39.96
1.6	-87.44	-101.4	144.52	-44.32
1.69	-81.96	-93.66	129.55	-46.08
1.74	**-79.30**	**-89.50**	**122.86**	**-47.00**
1.8	-76.96	-85.47	116.37	-46.06
1.9	-72.57	-78.32	106.44	-44.45
2	-66.99	-70.38	95.63	-41.74
2.1	-58.88	-62.14	82.78	-38.24
2.2	-50.07	-55.27	71.15	-34.18
2.3	-42.39	-49.75	62.37	-29.78
2.4	-36.1	-44.72	55.77	-25.06
2.5	-31.31	-35.9	48.25	-18.96
2.6	-27.73	-26.3	40.69	-13.34
2.7	-24.37	-19.85	34.81	-9.41
2.8	-21.33	-15.12	29.97	-6.49
2.9	-18.61	-11.66	25.92	-4.35
3	-16.17	-9.16	22.51	-2.83
3.09	-14.16	-7.54	19.83	-1.87
3.2	-11.96	-6.19	16.99	-1.16
3.3	-10.21	-5.34	14.75	-0.8
3.4	-8.72	-4.68	12.79	-0.61
3.5	-7.45	-4.11	11.07	-0.49
3.6	-6.35	-3.62	9.57	-0.4
3.7	-5.4	-3.18	8.26	-0.32
3.8	-4.57	-2.8	7.11	-0.26
3.9	-3.86	-2.46	6.11	-0.21
4	-3.25	-2.17	5.25	-0.16

Table S3. Cartesian coordinates in [Å] of the B3LYP/6-311++G** optimized Li-Fulvene complex.

Atom type	Cartesian coordinates		
	X	Y	Z
Li	0.75186305	0.96809447	-1.74840018
C	0.00000000	0.00000000	0.00000000
C	1.44264725	0.00000000	0.00000000
C	1.89545555	1.33627728	0.00000000
C	0.75592793	2.19242046	-0.01597279
C	-0.40138080	1.38544486	-0.02584780
H	2.06302963	-0.88532189	0.04066622
H	2.92723230	1.65860473	0.03601429
H	0.77776335	3.27353177	0.00589854
H	-1.42493754	1.73522428	-0.00822991
C	-0.84881098	-1.12982647	-0.00285768
H	-0.44319886	-2.13299883	0.03639401
H	-1.92576210	-1.01913607	0.01564267