Power Law Distribution Concerning Absolute Free Energies of Linear Sulfur Chains, Polythiazyls, Poly-isoprenes, Linear *trans*-Polyenes, and Polyynes

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Supporting Information

Table S-1. Linear diradicalic sulfur chains $^{(\bullet)}S_n^{(\bullet)}$ **1**, at the triplet state. Absolute free energies, G_n at the B3LYP/6-311++G(2df,p) level of theory in ideal gas (n = number of S-atoms per molecule).

$$^{\bullet}S-(S)_{n-2}-S^{\bullet}$$ **1**

n	G_n (au)	G_n/n (au)	$\delta G = G_n/n - G_{(n-1)}/(n-1)$ (kcal mol^{-1})	$G_n/(n) - G_8/8$ (kcal mol^{-1})
8	–3185.831 550	–398.228 944	–	0.00
9	–3584.064 072	–398.229 341	–0.249	–0.249
10	–3982.296 377	–398.229 638	–0.186	–0.435
11	–4380.528 514	–398.229 865	–0.142	–0.578
12	–4778.761 190	–398.230 099	–0.147	–0.725
13	–5176.993 194	–398.230 246	–0.092	–0.817
14	–5575.226 085	–398.230 435	–0.118	–0.936
15	–5973.458 369	–398.230 558	–0.077	–1.013
16	–6371.690 529	–398.230 658	–0.063	–1.076
17	–6769.923 072	–398.230 769	–0.070	–1.145
18	–7168.155 424	–398.230 857	–0.055	–1.200
19	–7566.387 362	–398.230 914	–0.036	–1.236
20	–7964.620 606	–398.231 030	–0.073	–1.309
21	–8362.852 789	–398.231 085	–0.034	–1.343
22	–8761.084 569	–398.231 117	–0.020	–1.363
23	–9159.316 889	–398.231 169	–0.033	–1.396
24	–9557.548 722	–398.231 197	–0.017	–1.414
25	–9955.780 041	–398.231 202	–0.003	–1.417
26	–10354.012 142	–398.231 236	–0.021	–1.438
27	–10752.243 516	–398.231 241	–0.003	–1.441
28	–11150.476 125	–398.231 290	–0.029	–1.472
29	–11548.708 776	–398.231 337	–0.082	–1.502
30	–11946.944 058	–398.231 469	–0.082	–1.584
31	–12345.171 072	–398.231 325	0.09	–1.494
32	–12743.404 681	–398.231 396	–0.044	–1.538
33	–13141.634 467	–398.231 347	0.030	–1.508

Table S-2. Linear diradicalic sulfur chains $^{(\bullet)}S_n^{(\bullet)}$ **1**, at the triplet state. Absolute energies, E_n at the B3LYP/6-311++G(2df,p) level of theory in ideal gas (n = number of S-atoms per molecule).

$$^{\bullet}S-(S)_{n-2}-S^{\bullet}$$ **1**

n	E_n (au)	E_n/n (au)	$\delta E = E_n/n - E_{(n-1)}/(n-1)$ (kcal mol^{-1})	$E_n/(n) - E_8/8$ (kcal mol^{-1})
8	–3185.797 081	–398.224 635	–	0.00
9	–3584.025 291	–398.225 032	–0.249	–0.249
10	–3982.257 320	–398.225 732	–0.439	–0.688
11	–4380.487 492	–398.226 136	–0.254	–0.942
12	–4778.718 533	–398.226 544	–0.256	–1.198
13	–5176.947 508	–398.226 731	–0.117	–1.315
14	–5575.179 033	–398.227 074	–0.215	–1.530
15	–5973.409 006	–398.227 267	–0.121	–1.651
16	–6371.639 981	–398.227 500	–0.146	–1.798
17	–6769.871 327	–398.227 725	–0.142	–1.939
18	–7168.100 658	–398.227 814	–0.056	–1.995
19	–7566.333 409	–398.228 074	–0.163	–2.158
20	–7964.565 285	–398.228 264	–0.119	–2.277
21	–8362.795 819	–398.228 372	–0.067	–2.345
22	–8761.025 309	–398.228 423	–0.032	–2.377
23	–9159.256 028	–398.228 523	–0.063	–2.440
24	–9557.486 839	–398.228 618	–0.060	–2.499
25	–9955.717 259	–398.228 690	–0.045	–2.544
26	–10353.946 943	–398.228 728	–0.024	–2.568
27	–10752.176 681	–398.228 766	–0.023	–2.592
28	–11150.408 215	–398.228 865	–0.062	–2.654
29	–11548.637 396	–398.228 876	–0.007	–2.661
30	–11946.872 118	–398.229 071	–0.122	–2.784
31	–12345.098 686	–398.228 990	–0.050	–2.733
32	–12743.327 888	–398.228 996	–0.004	–2.736
33	–13141.558 056	–398.229 032	–0.022	–2.759
34	–13539.788 303	–398.229 068	–0.022	–2.782
35	–13938.018 932	–398.229 112	–0.028	–2.809
36	–14336.249 739	–398.229 159	–0.029	–2.839

37	–14734.479 404	–398.229 173	–0.008	–2.848
38	–15132.712 767	–398.229 283	–0.069	–2.917
39	–15530.944 630	–398.229 349	–0.041	–2.958
40	–15929.177 782	–398.229 444	–0.059	–3.017

Table S-3. Linear radical-cation sulfur chains $S_n^{(\bullet,+)}$ **2**. Absolute energies, G_n, at the B3LYP/6-311++G(2df,p) level of theory in ideal gas (n = number of S-atoms per molecule).

$$(S-(S)_{n-2}-S)^{\bullet,+}$$ **2**

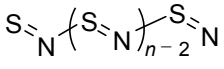
n	G_n (au)	G_n/n (au)	$\delta G = G_n/n - G_{(n-1)}/(n-1)$ (kcal mol^{-1})	$G_n/(n) - G_8/8$ (kcal mol^{-1})
8	–3185.538 681	–398.192 335	–	–
9	–3583.770 423	–398.196 714	–2.75	–2.75
10	–3982.005 351	–398.200 535	–2.40	–5.15
11	–4380.241 144	–398.203 740	–2.01	–7.16
12	–4778.473 439	–398.206 120	–1.49	–8.65
13	–5176.706 884	–398.208 222	–1.32	–9.97
14	–5574.941 185	–398.210 085	–1.17	–11.14
15	–5973.171 428	–398.211 428	–0.84	–11.98
16	–6371.402 697	–398.212 669	–0.78	–12.76
17	–6769.642 335	–398.214 255	–0.99	–13.75
18	–7167.873 643	–398.215 202	–0.59	–14.35
19	–7566.107 786	–398.216 199	–0.62	–14.97
20	–7964.341 063	–398.217 053	–0.54	–15.51
21	–8362.573 809	–398.217 800	–0.47	–15.98
22	–8760.805 023	–398.218 410	–0.38	–16.36
23	–9159.037 537	–398.219 023	–0.38	–16.75
24	–9557.271 183	–398.219 633	–0.77	–17.13
25	–9955.503 213	–398.220 128	–0.31	–17.44
26	–10353.735 599	–398.220 600	–0.30	–17.74
27	–10751.967 672	–398.221 025	–0.27	–18.00
28	–11150.201 448	–398.221 480	–0.28	–18.29
29	–11548.434 423	–398.221 877	–0.25	–18.54
30	–11946.669 433	–398.222 314	–0.27	–18.81
31	–12344.896 283	–398.222 461	–0.09	–18.90
32	–12743.130 836	–398.222 839	–0.24	–19.14
33	–13141.365 781	–398.223 205	0.23	–19.37

Table S-4. Linear radical cation sulfur chains $S_n^{(\bullet,+)}$ **2**. Absolute energies, E_n, at the B3LYP/6-311++G(2df,p) level of theory in ideal gas (n = number of S-atoms per molecule).

$$(S-(S)_{n-2}-S)^{\bullet,+}$$ **2**

n	E_n (au)	E_n/n (au)	$\delta E = E_n/n - E_{(n-1)}/(n-1)$ (kcal mol^{-1})	$E_n/(n) - E_8/8$ (kcal mol^{-1})
8	–3185.505 337	–398.188 167	–	–
9	–3583.734 891	–398.192 766	–2.88	–2.88
10	–3981.967 874	–398.196 787	–2.53	–5.41
11	–4380.202 348	–398.200 213	–2.15	–7.56
12	–4778.432 176	–398.202 681	–1.55	–9.11
13	–5176.662 948	–398.204 842	–1.35	–10.46
14	–5574.895 959	–398.206 854	–1.26	–11.73
15	–5973.124 726	–398.208 315	–0.92	–12.64
16	–6371.351 720	–398.209 482	–0.73	–13.37
17	–6769.592 239	–398.211 308	–1.14	–14.52
18	–7167.822 926	–398.212 385	–0.67	–15.20
19	–7566.053 775	–398.213 357	–0.32	–15.81
20	–7964.286 850	–398.214 342	–0.62	–16.42
21	–8362.517 755	–398.215 131	–0.49	–16.92
22	–8760.745 720	–398.215 714	–0.37	–17.29
23	–9158.970 968	–398.216 129	–0.26	–17.55
24	–9557.209 665	–398.217 069	–0.59	–18.14
25	–9955.441 170	–398.217 647	–0.36	–18.50
26	–10353.672 143	–398.218 159	–0.32	–18.82
27	–10751.901 832	–398.218 586	–0.27	–19.09
28	–11150.127 216	–398.218 829	–0.15	–19.24
29	–11548.356 831	–398.219 201	–0.23	–19.47
30	–11946.594 999	–398.219 833	–0.40	–19.87
31	–12344.824 949	–398.220 160	–0.20	–20.07
32	–12743.053 147	–398.220 411	–0.16	–20.23
33	–13141.289 005	–398.220 880	–0.29	–20.53
34	–13539.515 133	–398.221 033	–0.1	–20.62

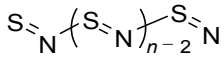
Table S-5. $(SN)_n$ **3**. Absolute free energies, G_n, at the B3LYP/6-311++G(3df,p) level of theory in ideal gas (Singlet state) (n = number of S-atoms per molecule).



3

n	G_n (au)	G_n/n (au)	$\delta G = G_n/n - G_{(n-1)}/(n-1)$ (kcal mol^{-1})	$G_n/(n) - G_2/2$ (kcal mol^{-1})
2	–905.864 492	–452.932 246	–	–
3	–1358.839 354	–452.946 451	–8.91	–8.91
4	–1811.789 421	–452.947 355	–0.57	–9.48
5	–2264.740 811	–452.948 162	–0.51	–9.99
6	–2717.691 493	–452.948 582	–0.26	–10.25
7	–3170.650 968	–452.950 138	–0.98	–11.23
8	–3623.599 443	–452.949 930	0.13	–11.10
9	–4076.561 552	–452.951 283	–0.85	–11.95
10	–4529.517 426	–452.951 743	–0.29	–12.23
11	–4982.476 629	–452.952 421	–0.42	–12.66
12	–5435.423 430	–452.951 952	0.29	–12.37
13	–5888.396 458	–452.953 574	–1.02	–13.38
14	–6341.358 023	–452.954 144	–0.36	–13.74
15	–6794.311 926	–452.954 128	0.01	–13.73

Table S-6. $(SN)_n$ **3**. Absolute energies, E_n, at the B3LYP/6-311++G(3df,p) level of theory in ideal gas (Singlet state) (n = number of S-atoms per molecule).



3

n	E_n (au)	E_n/n (au)	$\delta E = E_n/n - E_{(n-1)}/(n-1)$ (kcal mol^{-1})	$E_n/(n) - E_2/2$ (kcal mol^{-1})
2	–905.842 210	–452.921 105	–	–
3	–1358.819 172	–452.939 724	–11.68	–11.68
4	–1811.769 904	–452.942 476	–1.73	–13.41
5	–2264.720 979	–452.944 196	–1.08	–14.49
6	–2717.672 555	–452.945 426	–0.77	–15.26
7	–3170.631 698	–452.947 385	–1.23	–16.49
8	–3623.581 116	–452.947 639	–0.16	–16.65
9	–4076.542 260	–452.949 140	–0.94	–17.59
10	–4529.500 253	–452.950 025	–0.55	–18.15
11	–4982.459 083	–452.950 826	–0.50	–18.65
12	–5435.407 555	–452.950 63	0.12	–18.53
13	–5888.379 767	–452.952 290	–1.04	–19.57
14	–6341.345 479	–452.953 248	–0.60	–20.17
15	–6794.296 126	–452.953 075	0.11	–20.06

Table S-7. $MeS_n^{(-)}$ **4**. Absolute free energies, G_n at the B3LYP/6-311++G(2df,p) level of theory in ideal gas (n = number of S-atoms per molecule) and linear relationship (1a).

$Me-(S)_n^{(-)}$

4

n	G_n (au)	G_n (kcal mol^{-1})	$G = -249895.156113n - 25079.46$ (1a) (kcal mol^{-1})	δG_{calc} = (kcal mol^{-1})
1	–438.160 649	–274 949.97	–274 974.6	24.69
2	–836.412 197	–524 856.60	–524 869.8	13.21
3	–1 234.657 495	–774 759.31	–774 765.0	5.69
4	–1 632.898 910	–1 024 659.58	–1 024 660.1	0.54
5	–2 031.139 299	–1 274 559.21	–1 274 555.3	–3.92
6	–2 429.375 525	–1 524 456.22	–1 524 450.4	–5.82
7	–2 827.607 520	–1 774 350.58	–1 774 345.6	–4.98
8	–3 225.842 345	–2 024 246.72	–2 024 240.7	–5.97
9	–3 624.074 934	–2 274 141.45	–2 274 135.9	–5.55
10	–4 022.308 623	–2 524 036.87	–2 524 031.1	–5.77
11	–4 420.539 769	–2 773 930.70	–2 773 926.2	–4.50
12	–4 818.773 386	–3 023 826.08	–3 023 821.4	–4.68
13	–5 217.005 009	–3 273 720.20	–3 273 716.5	–3.70
14	–5 615.239 200	–3 523 615.94	–3 523 611.7	–4.24
15	–6 013.471 261	–3 773 510.34	–3 773 506.8	–3.54
16	–6411.703 165	–4 023 404.65	–4 023 402.0	–2.65
17	–6809.937 540	–4 273 300.50	–4 273 297.2	–3.30
18	–7208.169 580	–4 523 194.89	–4 523 192.3	–2.59
19	–7606.402 293	–4 773 089.70	–4 773 087.5	–2.20
20	–8004.635 074	–5 022 984.55	–5 022 982.6	–1.95
21	–8402.868 143	–5 272 879.59	–5 272 877.8	–1.79
22	–8801.096 324	–5 522 771.55	–5 522 772.9	1.35
23	–9199.332 486	–5 772 668.53	–5 772 668.1	–0.43
24	–9597.565 049	–6 022 563.25	–6 022 563.2	–0.04
25	–9995.798 954	–6 272 458.80	–6 272 458.4	–0.40
26	–1 0394.032 401	–6 522 354.07	–6 522 353.6	–0.47
27	–1 0792.260 069	–6 772 245.72	–6 772 248.7	2.98
28	–1 1190.495 173	–7 022 142.03	–7 022 143.9	1.87

29	–11 588.724 074	–7 272 034.45	–7 272 039.0	4.55
30	–11 986.958 238	–7 521 930.17	–7 521 934.2	4.03
31	–12 385.189 799	–7 771 824.26	–7 771 829.3	5.04
32	–12 783.421 899	–8 021 718.68	–8 021 724.5	5.81

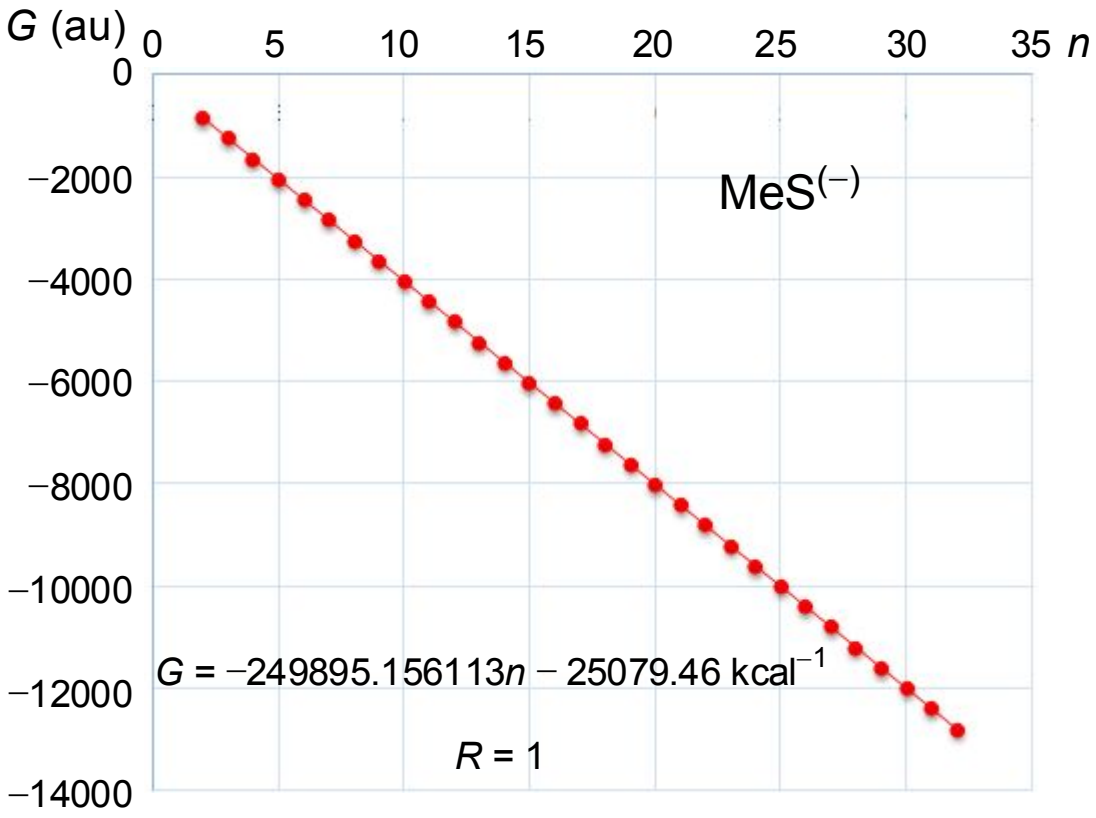


Fig. S-1. G_n values of $MeS_n^{(-)}$ as a function of n (n = number of chain sulfur atoms) at the B3LYP/6.311++G(2df,p) level of theory in ideal gas (1a) (see Table S-7).

Table S-8. $MeS_n^{(-)}$ **4**. Variations of absolute free energies, G_n at the B3LYP/6-311++G(2df,p) level of theory in ideal gas (n = number of S-atoms per molecule).

$Me-(S)_n^{(-)}$

4

n	G_n (au)	G_n/n (au)	$\delta G = G_n/n - G_{(n-1)}/(n-1)$ (kcal mol^{-1})	$\delta G_{calc} = 33\,411 / n^{2.076}$ (kcal mol^{-1})
1	–438.160 649	–438.160 649	–	–
2	–836.412 197	–418.206 098	12 521.67	7 924.1
3	–1 234.657 495	–411.552 498	4 175.20	3 415.0
4	–1 632.898 910	–408.224 727	2 088.21	1 879.4
5	–2 031.139 299	–406.227 860	1 253.05	1 182.6
6	–2 429.375 525	–404.895 921	835.80	809.9
7	–2 827.607 520	–403.943 931	597.38	588.1
8	–3 225.842 345	–403.230 293	447.81	445.7
9	–3 624.074 934	–402.674 993	348.46	349.0
10	–4 022.308 623	–402.230 862	278.70	280.4
11	–4 420.539 769	–401.867 252	228.17	230.1
12	–4 818.773 386	–401.564 449	190.01	192.1
13	–5 217.005 009	–401.308 078	160.87	162.6
14	–5 615.239 200	–401.088 514	137.78	139.4
15	–6 013.471 261	–400.898 084	119.50	120.8
16	–6 411.703 165	–400.731 448	104.57	105.7
17	–6 809.937 540	–400.584 561	92.17	93.2
18	–7 208.169 580	–400.453 866	82.01	82.8
19	–7 606.402 293	–400.336 963	73.36	74.0
20	–8 004.635 074	–400.231 754	66.02	66.5
21	–8 402.868 143	–400.136 578	59.72	60.1
22	–8 801.096 324	–400.049 833	54.43	54.6
23	–9 199.332 486	–399.970 978	49.48	49.8
24	–9 597.565 049	–399.898 544	45.45	45.5
25	–9 995.798 954	–399.831 958	41.78	41.8
26	–10 394.032 401	–399.770 477	38.58	38.6
27	–10 792.260 069	–399.713 336	35.86	35.7
28	–11 190.495 173	–399.660 542	33.13	33.1
29	–11 588.724 074	–399.611 175	30.98	30.8

30	–11 986.958 238	–399.565 275	28.80	28.7
31	–12 385.189 799	–399.522 252	27.00	26.8
32	–127 83.421 899	–399.481 934	25.30	25.0

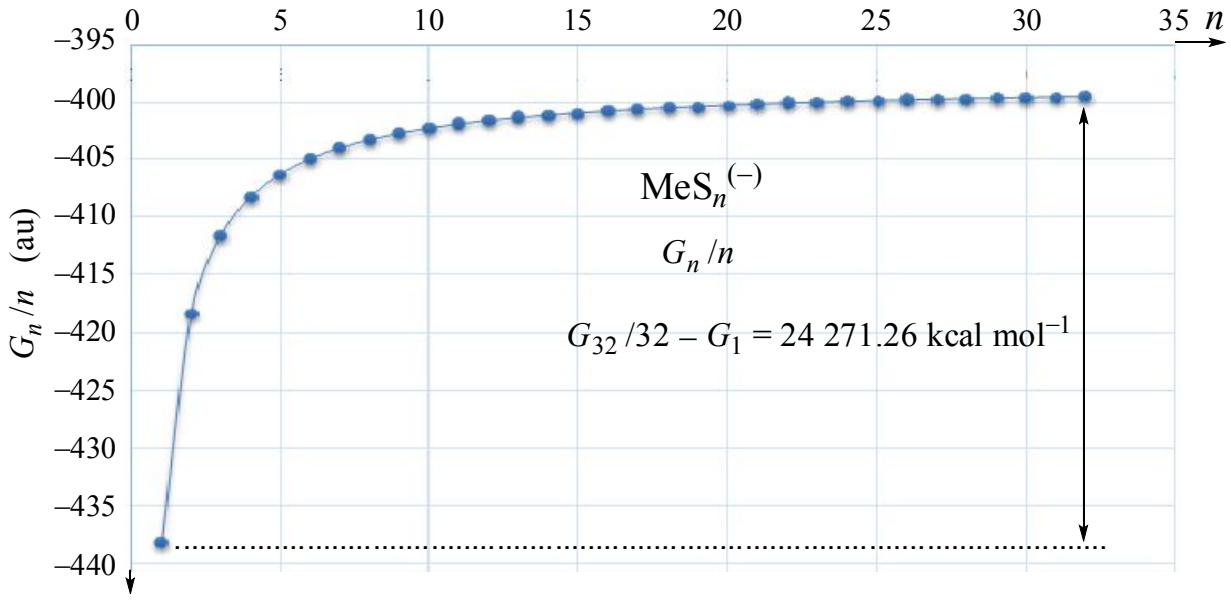


Fig. S-2. Variations of G_n /n values of $MeS_n^{(-)}$ as a function of n (n = number of chain sulfur atoms) at the B3LYP/6.311++G(2df,p) level of theory in ideal gas (see Table S-8).

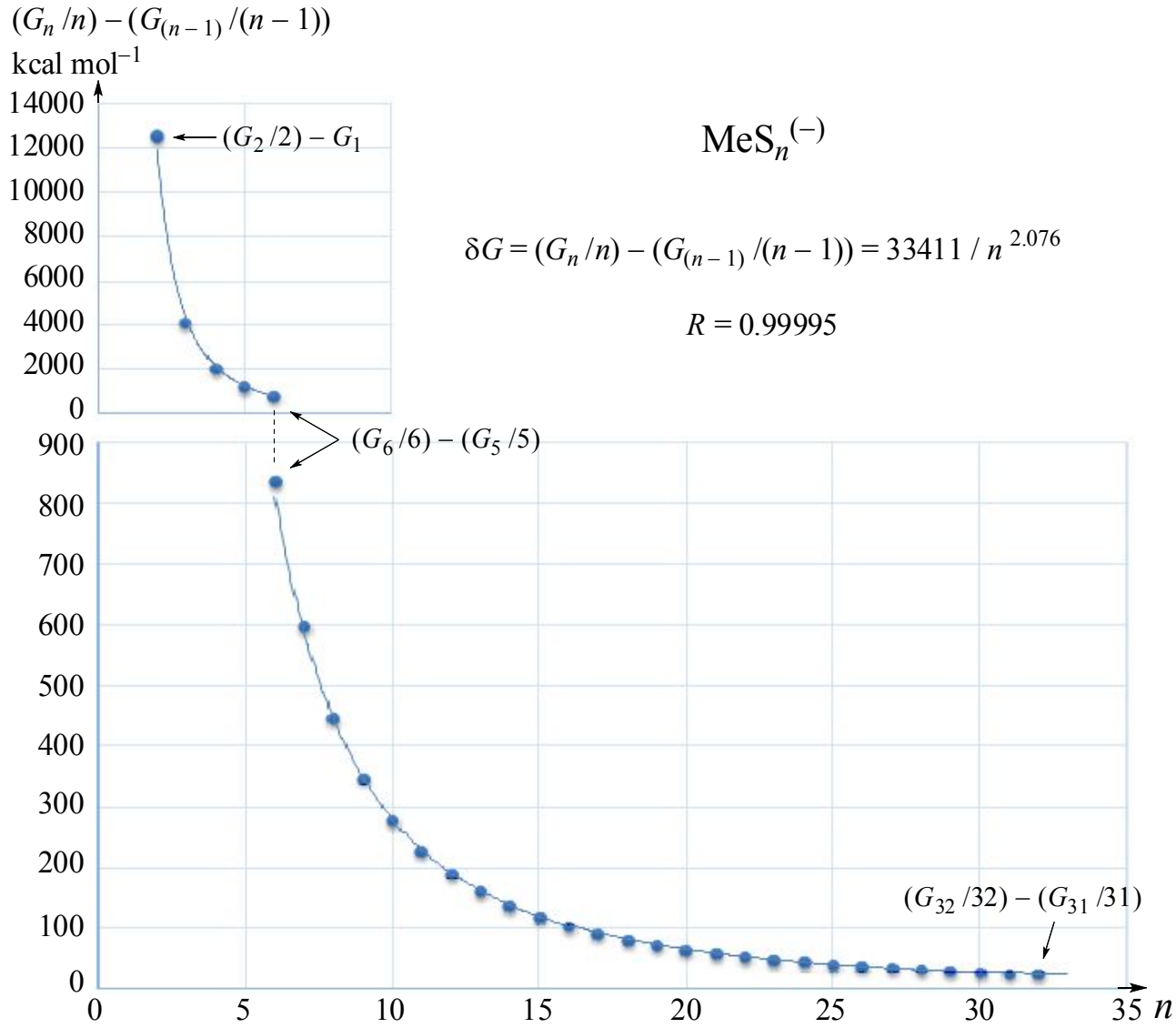


Fig. S-3. Power law (2a): variations of δG values of $MeS_n^{(-)}$ as a function of n (n = number of chain sulfur atoms) at the B3LYP/6-311++G(2df,p) level of theory in ideal gas (see Table S-7).

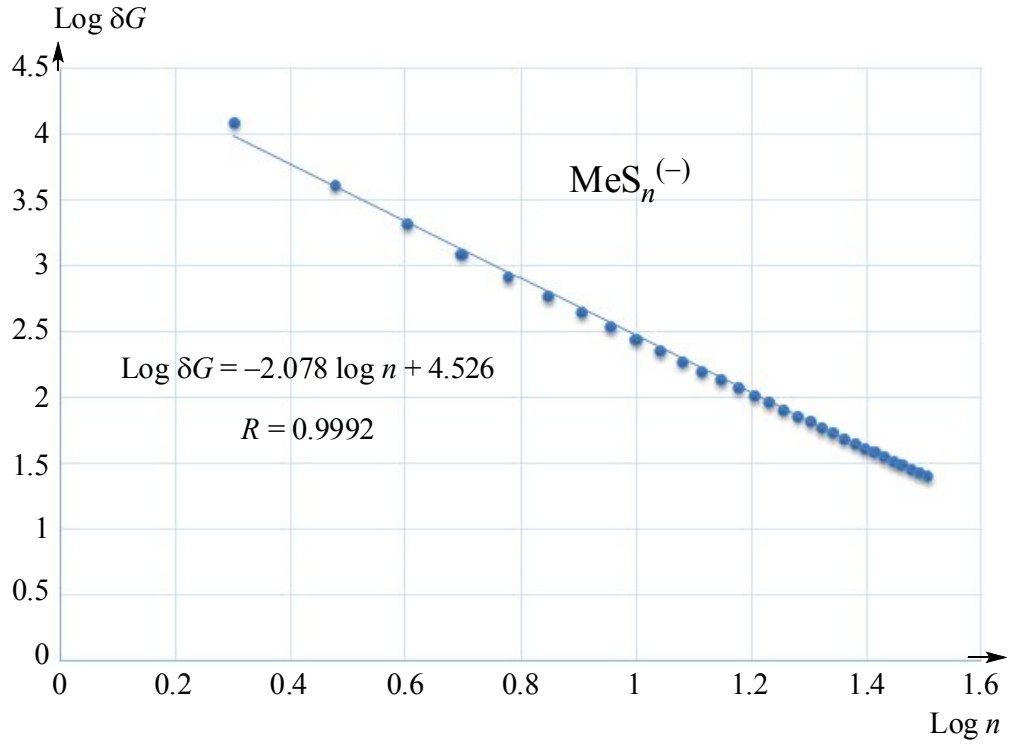


Fig. S-4. $MeS_n^{(-)}$ **4**. Plot of $\log\delta G = \log[G_n/n - G_{(n-1)}/(n-1)]$ *vs* $\log n$, (*signature* of the power law relationship (2a) from manuscript).

Power law (2a): $\delta G_{calc} = 33411 / n^{2.076}$.

Table S-9. $MeS_n^{(-)}$ **4**. Absolute energies, E_n, at the B3LYP/6-311++G(2df,p) level of theory in ideal gas (n = number of S-atoms per molecule).

$Me-(S)_n^{(-)}$ **4**

n	E_n (au)	E_n/n (au)	$\delta E = E_n/n - E_{(n-1)}/(n-1)$ (kcal mol^{-1})	$\delta E_{calc} = 33\,468 / n^{2.077}$ (kcal mol^{-1})
1	–438.172 777	–438.172 777	–	–
2	–836.423 050	–418.211 525	12 525.87	7932.1
3	–1 234.666 534	–411.555 511	4 176.71	3417.0
4	–1 632.906 285	–408.226 571	2 088.94	1880.0
5	–2 031.146 474	–406.229 295	1 253.31	1182.7
6	–2 429.378 280	–404.896 380	836.42	809.9
7	–2 827.610 486	–403.944 355	597.40	588.0
8	–3 225.843 073	–403.230 384	448.02	445.6
9	–3 624.072 900	–402.674 767	348.66	348.9
10	–4 022.305 751	–402.230 575	278.73	280.3
11	–4 420.534 441	–401.866 767	228.29	230.0
12	–4 818.765 817	–401.563 818	190.10	191.9
13	–5 216.996 276	–401.307 406	160.90	162.5
14	–5 615.228 315	–401.087 737	137.84	139.3
15	–6 013.458 920	–400.897 261	119.52	120.7
16	–6 411.689 116	–400.730 570	104.60	105.6
17	–6 809.926 694	–400.583 923	92.02	93.1
18	–7 208.153 205	–400.452 956	82.18	82.7
19	–7 606.390 102	–400.336 321	73.19	73.9
20	–8 004.613 363	–400.230 668	66.30	66.4
21	–8 402.852 908	–400.135 853	59.50	60.0
22	–8 801.075 834	–400.048 901	54.56	54.5
23	–9 199.306 636	–399.969 854	49.60	49.7
24	–9 597.543 753	–399.897 656	45.30	45.5
25	–9 995.778 491	–399.831 140	41.74	41.8
26	–10 393.998 489	–399.769 173	38.88	38.5
27	–10 792.237 973	–399.712 517	35.55	35.6
28	–11 190.469 649	–399.659 630	33.19	33.0
29	–11 588.698 076	–399.610 278	30.97	30.7

30	–11 986.928 408	–399.564 280	28.86	28.6
31	–12 385.151 157	–399.521 005	27.16	26.7
32	–12 783.381 925	–399.480 685	25.30	25.0
33	–13 181.613 136	–399.442 822	23.76	23.5
34	–13 579.855 345	–399.407 419	22.22	22.1

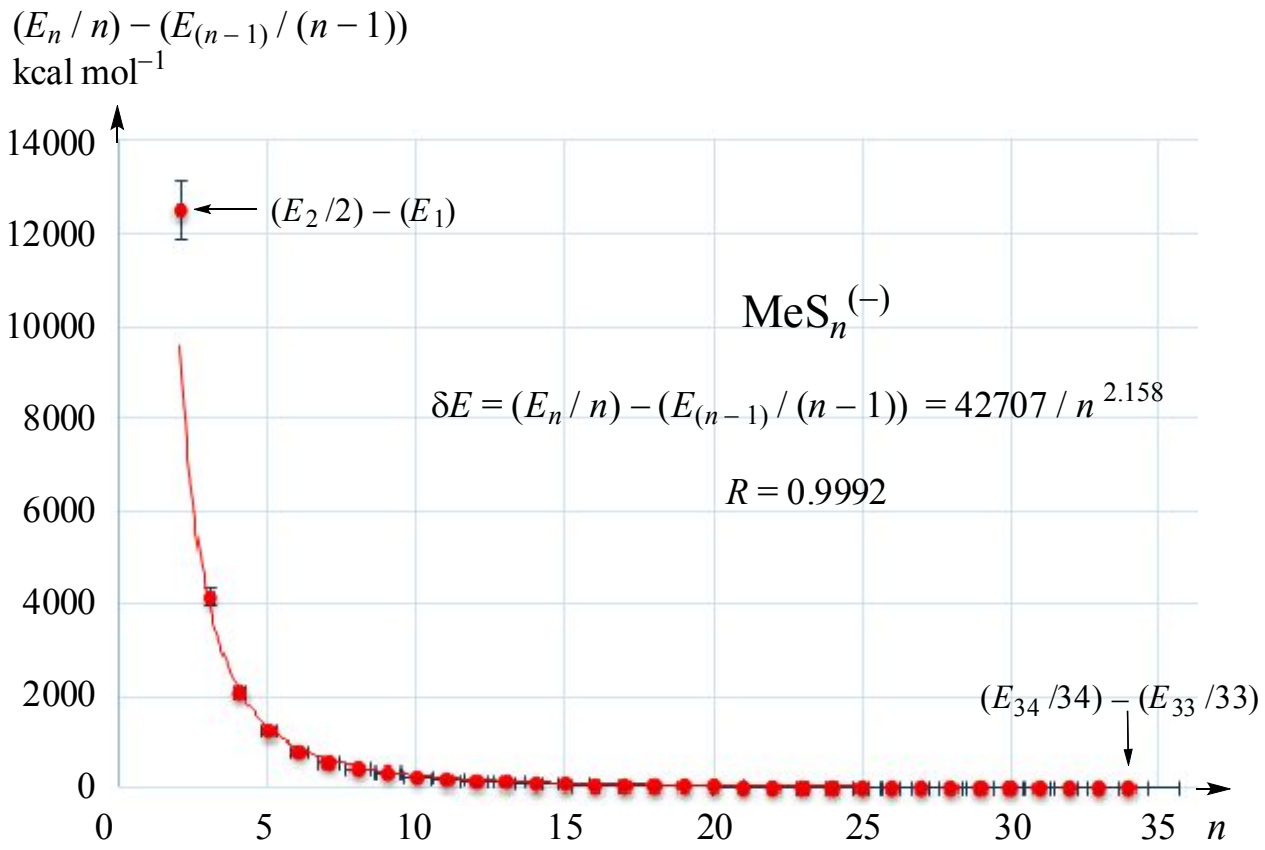


Fig. S-5. Power law (2b): variations of δE values of $MeS_n^{(-)}$ as a function of n (n = number of chain sulfur atoms) at the B3LYP/6-311++G(2df,p) level of theory in ideal gas (error bars given for 95% confidence interval) (see Table S-9).

Table S-10. $MeS_n^{(-)}$ **4**. Absolute free energies, G_n at the B3LYP/6-311++G(2df,p) level of theory in water as solvent (n = number of S-atoms per molecule).

$Me-(S)_n^{(-)}$ **4**

n	G_n (au)	G_n/n (au)	$\delta G = G_n/n - G_{(n-1)}/(n-1)$ (kcal mol^{-1})	$\delta G_{calc} = 33\,997 / n^{2.083}$ (kcal mol^{-1})
1	–438.264 618	–438.264 618	–	–
2	–836.507 714	–418.253 857	12 556.94	8024.08
3	–1 234.746 559	–411.582 186	4 186.54	3448.25
4	–1 632.982 457	–408.245 614	2 093.73	1893.87
5	–2 031.217 381	–406.243 476	1 256.36	1189.83
6	–2 429.450 632	–404.908 439	837.75	813.86
7	–2 827.683 625	–403.954 804	598.41	590.34
8	–3 225.916 982	–403.239 623	448.78	447.0
9	–3 624.150 110	–402.683 346	349.07	349.75
10	–4 022.383 036	–402.238 304	279.27	280.83
11	–4 420.614 896	–401.874 081	228.55	230.26
12	–4 818.847 385	–401.570 615	190.43	192.09
13	–5 217.079 945	–401.313 842	161.13	162.6
14	–5 615.313 426	–401.093 816	138.07	139.3
15	–6 013.545 491	–400.903 033	119.72	120.68
16	–6 411.775 574	–400.735 973	104.83	105.50
17	–6 810.010 397	–400.588 847	92.32	92.98
18	–7 208.243 073	–400.457 948	82.14	82.55
19	–7 606.473 938	–400.340 733	73.55	73.75
20	–8 004.709 348	–400.235 467	66.06	66.28
21	–8 402.940 344	–400.140 016	59.90	59.87
22	–8 801.172 705	–400.053 305	54.41	54.35
23	–9 199.404 821	–399.974 123	49.69	49.54
24	–9 597.638 940	–399.901 622	45.49	45.34
25	–9 995.869 767	–399.834 791	41.94	41.64
26	–10 394.103 236	–399.773 201	38.65	38.37
27	–10 792.333 806	–399.716 069	35.85	35.47
28	–11 190.565 863	–399.663 066	33.26	32.88
29	–11 588.797 588	–399.613 710	30.97	30.57

30	–11 987.031 138	–399.567 770	28.87	28.48
31	–12 385.263 497	–399.524 629	27.07	26.60
32	–12 783.495 945	399.484 248	25.34	24.90

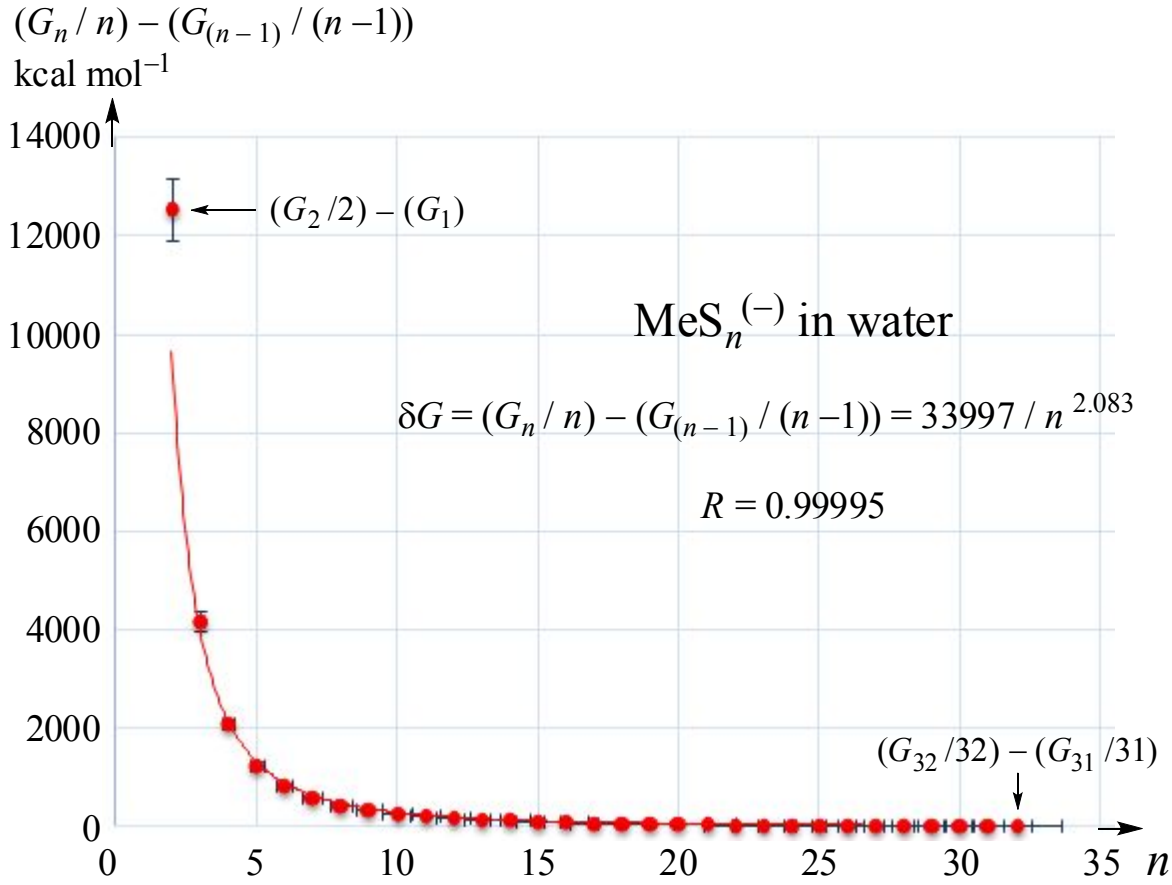


Fig. S-6. Power law (2c): variations of δG values of $MeS_n^{(-)}$ using water as solvent as a function of n (n = number of chain sulfur atoms) at the B3LYP/6-311++G(2df,p) level of theory in water as solvent (error bars given for 95% confidence interval) (see Table S-10).

Table S-11. $MeS_n^{(-)}$ **4**. Absolute energies, E_n at the B3LYP/6-311++G(2df,p) level of theory in water as solvent (n = number of S-atoms per molecule).

$Me-(S)_n^{(-)}$ **4**

n	E_n (au)	E_n/n (au)	$\delta E = E_n/n - E_{(n-1)}/(n-1)$ (kcal mol^{-1})	$\delta E_{calc} = 33\,761 / n^{2.079}$ (kcal mol^{-1})
1	–438.277 383	–438.277 383	–	–
2	–836.518 937	–418.259 468	12 521.4	7924.1
3	–1 234.756 120	–411.585 373	4 188.0	3415.0
4	–1 632.990 237	–408.247 559	2 094.5	1879.4
5	–2 031.224 420	–406.244 884	1 256.7	1182.6
6	–2 429.455 664	–404.909 277	838.10	809.9
7	–2 827.686 958	–403.955 280	598.64	588.1
8	–3 225.918 177	–403.239 772	449.0	445.7
9	–3 624.149 039	–402.683 226	349.24	349.0
10	–4 022.380 224	–402.238 022	279.37	280.4
11	–4 420.611 140	–401.873 740	228.59	230.1
12	–4 818.841 926	–401.570 160	190.50	192.1
13	–5 217.072 616	–401.313 278	161.20	162.6
14	–5 615.303 536	–401.093 110	138.5	139.4
15	–6 013.534 542	–400.902 303	119.73	120.8
16	–6 411.763 830	–400.735 239	104.83	105.7
17	–6 809.996 598	–400.588 035	92.37	93.2
18	–7 208.227 539	–400.457 085	82.17	82.8
19	–7 606.458 502	–400.339 921	73.52	74.0
20	–8 004.689 253	–400.234 463	66.18	66.5
21	–8 402.920 285	–400.139 061	59.86	60.1
22	–8 801.150 906	–400.052 314	54.43	54.6
23	–9 199.381 929	–399.973 127	49.69	49.8
24	–9 597.612 845	–399.900 535	45.55	45.5
25	–9 995.843 101	–399.833 724	41.92	41.8
26	–10 394.075 415	–399.772 131	38.65	38.6
27	–10 792.304 778	–399.714 992	35.86	35.7
28	–11 190.537 883	–399.662 067	33.21	33.1
29	–11 588.766 513	–399.612 638	31.02	30.8

30	–11 986.996 954	–399.566 565	28.91	28.7
31	–12 385.228 745	–399.523 508	27.02	26.8
32	–12 783.459 720	399.483 116	25.35	25.0

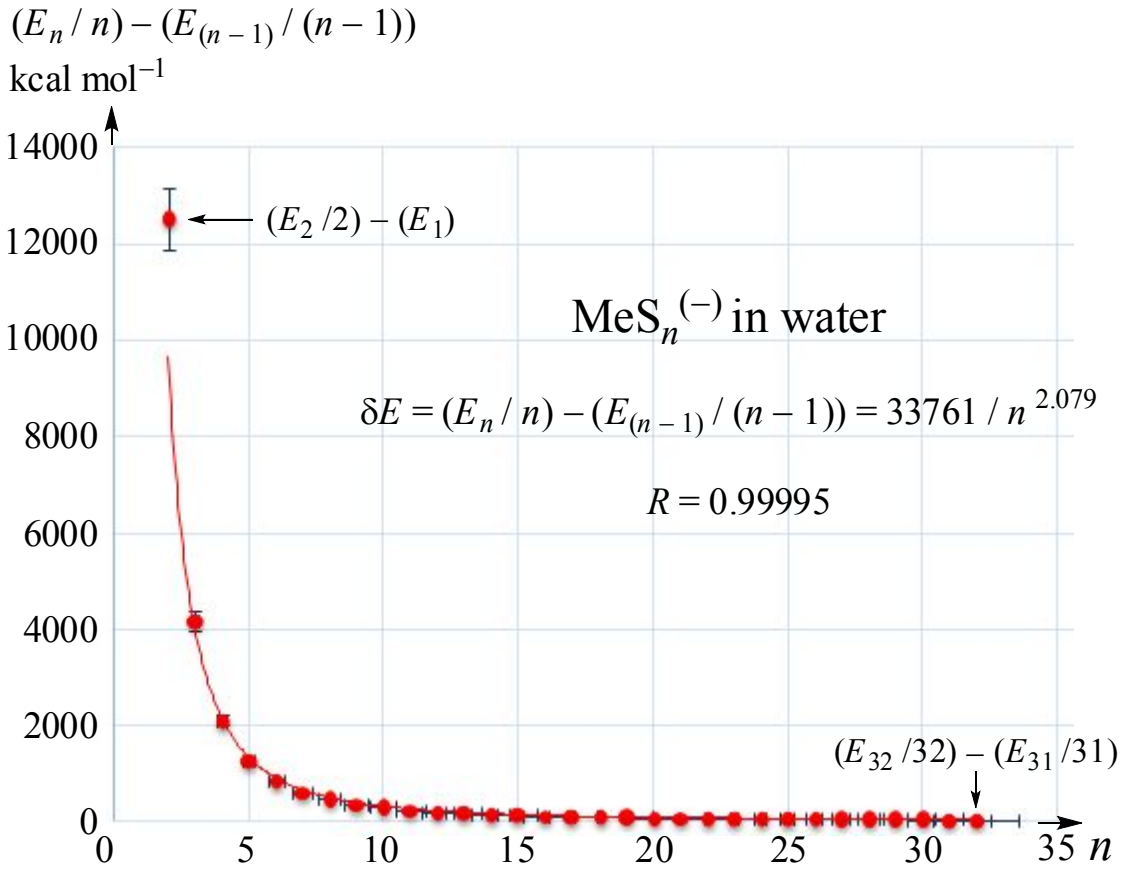


Fig. S-7. Power law (2d): variations of δE values of $MeS_n^{(-)}$ using water as solvent as a function of n (n = number of chain sulfur atoms) at the B3LYP/6-311++G(2df,p) level of theory using water as solvent (error bars given for 95% confidence interval) (see Table S-11).

Table S-12. $MeS_n^{(\bullet)}$ **5**. Absolute free energies, G_n at the B3LYP/6-311++G(2df,p) level of theory in ideal gas (n = number of S-atoms per molecule) and linear relationship (1b).

$Me-(S)_n^{(\bullet)}$

5

n	G_n (au)	G_n (kcal mol^{-1})	$G = -249894.626977n - 25027.13$ (1b) (kcal mol^{-1})	δG (kcal mol^{-1})
1	–438.095 828*	–274 909.294	–274 921.73	12.43
2	–836.351 187	–524 818.315	–524 816.38	–1.93
3	–1 234.581 831	–774 711.827	–774 711.00	–0.83
4	–1 632.815 119	–1024 607.00	–1 024 605.64	–1.36
5	–2 031.046 570	–1 274 501.02	–1 274 500.3	–0.72
6	–2 429.278 723	–1 524 395.48	–1 524 394.89	–0.59
7	–2 827.511 330	–1 774 290.22	–1 774 289.52	–0.70
8	–3 225.743 661	–2 024 184.79	–2 024 184.15	–0.64
9	–3 623.976 708	–2 274 079.81	–2 274 078.77	–1.04
10	–4 022.208 713	–2 523 974.18	–2 523 973.4	–0.78
11	–4 420.441 816	–2 773 869.23	–2 773 868.03	–1.20
12	–4 818.673 839	–3 023 763.61	–3 023 762.65	–0.96
13	–5 216.906 584	–3 273 658.44	–3 273 657.28	–1.16
14	–5 615.139 334	– 3523 553.28	–3 523 551.91	–1.36
15	–6 013.368 867	–3 773 446.09	–3 773 446.53	0.44
16	–6 411.602 230	–4 023 341.31	–4 023 341.16	–0.15
17	–6 809.835 502	–4 273 236.47	–4 273 235.79	–0.686
18	–7 208.068 528	–4 523 131.48	–4 523 130.42	–1.06
19	–7 606.301 254	–4 773 026.3	–4 773 025.04	–1.26
20	–8 004.533 460	–5 022 920.79	–5 022 919.67	–1.12
21	–8 402.765 794	–5 272 815.36	–5 272 814.3	–1.06
22	–8 800.997 869	–5 522 709.77	–5 522 708.92	–0.85
23	–9 199.231 951	–5 772 605.44	–5 772 603.55	–1.89
24	–9 597.462 182	–6 022 498.7	–6 022 498.18	–0.51
25	–9 995.691 816	–6 272 391.57	–6 272 392.8	1.22
26	–10 393.928 045	–6 522 288.59	–6 522 287.43	–1.16
27	–10 792.154 758	–6 772 179.64	–6 772 182.06	2.42
28	–11 190.389 113	–7 022 075.48	–7 022 076.7	1.22

29	–11 588.621 053	–7 271 969.8	–7 271 971.31	1.50
30	–11 986.853 587	–7 521 864.5	–7 521 865.94	–1.43
31	–12 385.085 803	–7 771 759.00	–7 771 760.6	1.60
32	–12 783.319 247	–8 021 654.27	–8 021 655.19	0.92

* 1 imaginary frequency ignored (i–596.8434 cm^{-1}).

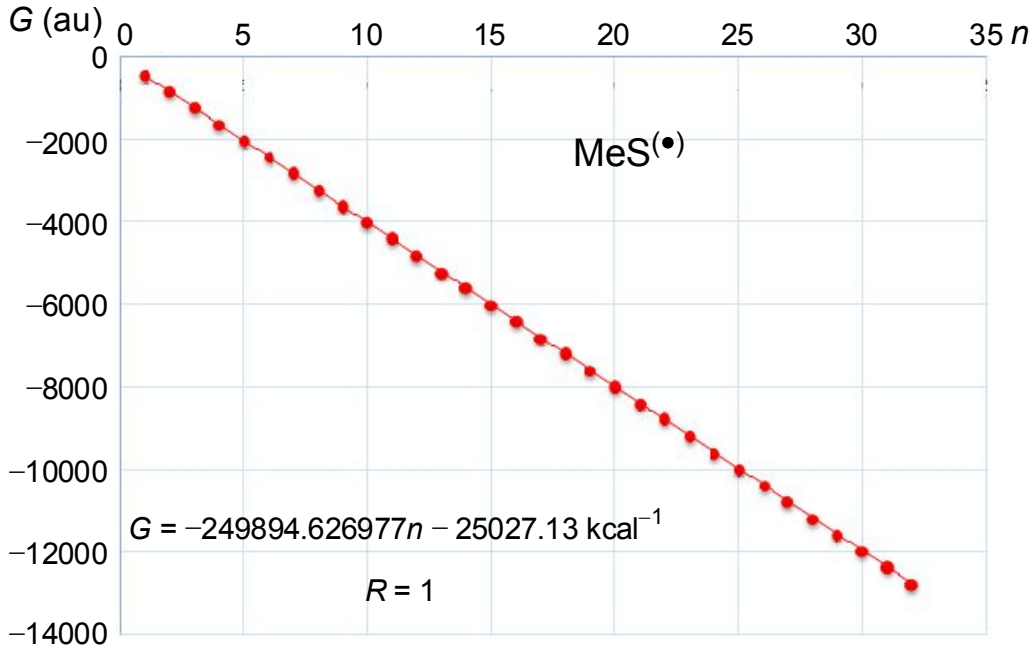


Fig. S-8. G_n values of $MeS_n^{(\bullet)}$ as a function of n (n = number of chain sulfur atoms) at the B3LYP/6.311++G(2df,p) level of theory in ideal gas (1b) (see Table S-12).

Table S-13. $MeS_n^{(\bullet)}$ **5**. Absolute free energies, G_n at the B3LYP/6-311++G(2df,p) level of theory in ideal gas (n = number of S-atoms per molecule).

$Me{-}(S)_n^{(\bullet)}$ **5**

n	G_n (au)	G_n/n (au)	$\delta G = G_n/n - G_{(n-1)}/(n-1)$ (kcal mol^{-1})	$\delta G_{calc} = 33\,596 / n^{2.079}$ (kcal mol^{-1})
1	–438.095 828*	–438.095 828	–	–
2	–836.351 187	–418.175 593	12 500.14	7951.5
3	–1 234.581 831	–411.527 277	4 171.88	3422.5
4	–1 632.815 119	–408.203 780	2 085.53	1881.9
5	–2 031.046 570	–406.209 314	1 251.55	1183.4
6	–2 429.278 723	–404.879 787	834.29	810.0
7	–2 827.511 330	–403.930 190	595.88	587.9
8	–3 225.743 661	–403.217 958	446.93	445.4
9	–3 623.976 708	–402.664 079	347.56	348.6
10	–4 022.208 713	–402.220 871	278.12	280.1
11	–4420.441 816	–401.858 347	227.49	229.7
12	–4 818.673 839	–401.556 153	189.63	191.7
13	–5 216.906 584	–401.300 506	160.42	162.3
14	–5 615.139 334	–401.081 381	137.50	139.1
15	–6 013.368 867	–400.891 258	119.30	120.5
16	–6 411.602 230	–400.725 139	104.24	105.4
17	–6 809.835 502	–400.578 559	91.98	92.9
18	–7 208.068 528	–400.448 252	81.77	82.5
19	–7 606.301 254	–400.331 645	73.17	73.7
20	–8 004.533 460	–400.226 673	65.87	66.2
21	–8 402.765 794	–400.131 704	59.59	59.9
22	–8800.997 869	–400.045 358	54.18	54.3
23	–9 199.231 951	–399.966 606	49.42	49.5
24	–9 597.462 182	–399.894 258	45.40	45.4
25	–9 995.691 816	–399.827 673	41.78	41.7
26	–10 393.928 045	–399.766 463	38.41	38.4
27	–10 792.154 758	–399.709 435	35.78	35.5
28	–11 190.389 113	–399.656 754	33.06	32.9

29	–11 588.621 053	–399.607 622	30.83	30.6
30	–11 986.853 587	–399.561 786	28.76	28.5
31	–12 385.085 803	–399.518 911	26.90	26.7
32	–12 783.319 247	–399.478 726	25.22	25.0

* 1 imaginary frequency ignored (i–596.8434 cm^{-1}).

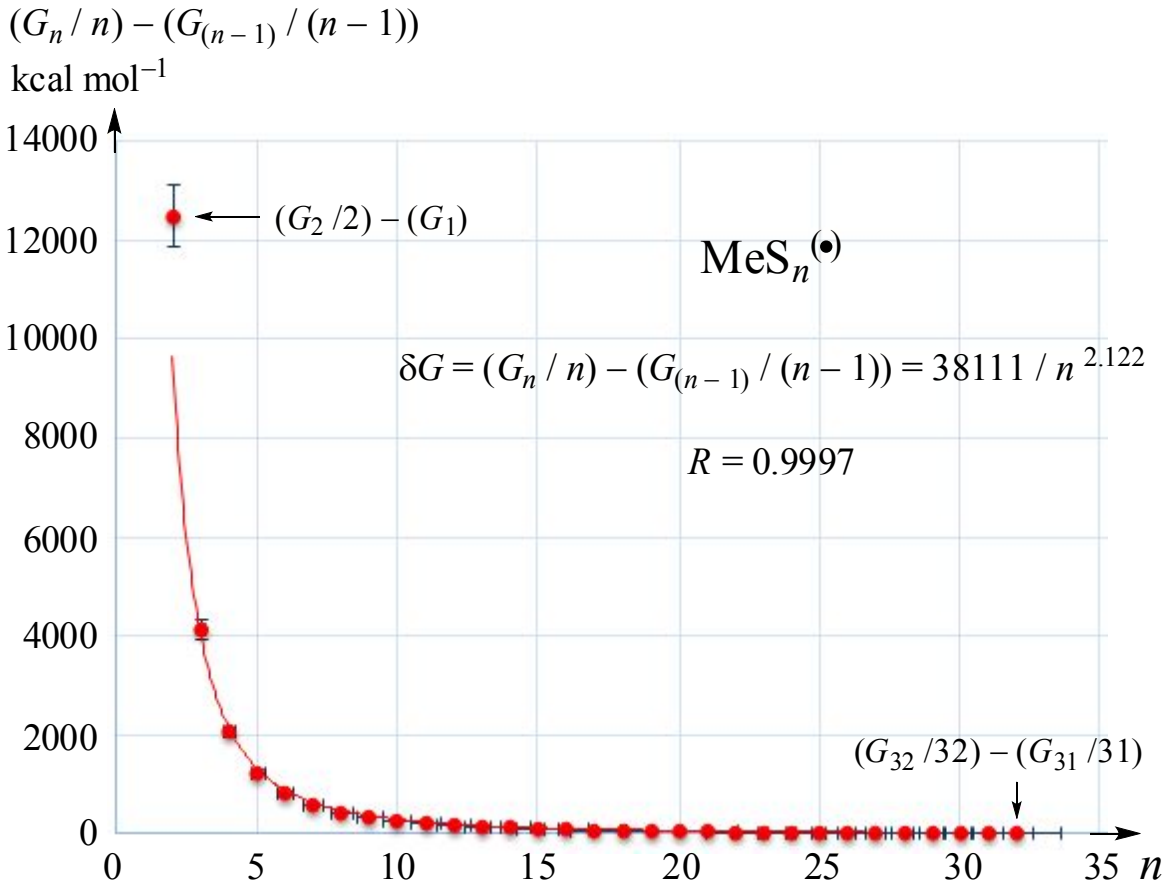


Fig. S-9. Power law (2e): variations of δG values of MeS$_n^{(\bullet)}$ as a function of n (n = number of chain sulfur atoms) at the B3LYP/6-311++G(2df,p) level of theory in ideal gas (error bars given for 95% confidence interval) (see Table S-13).

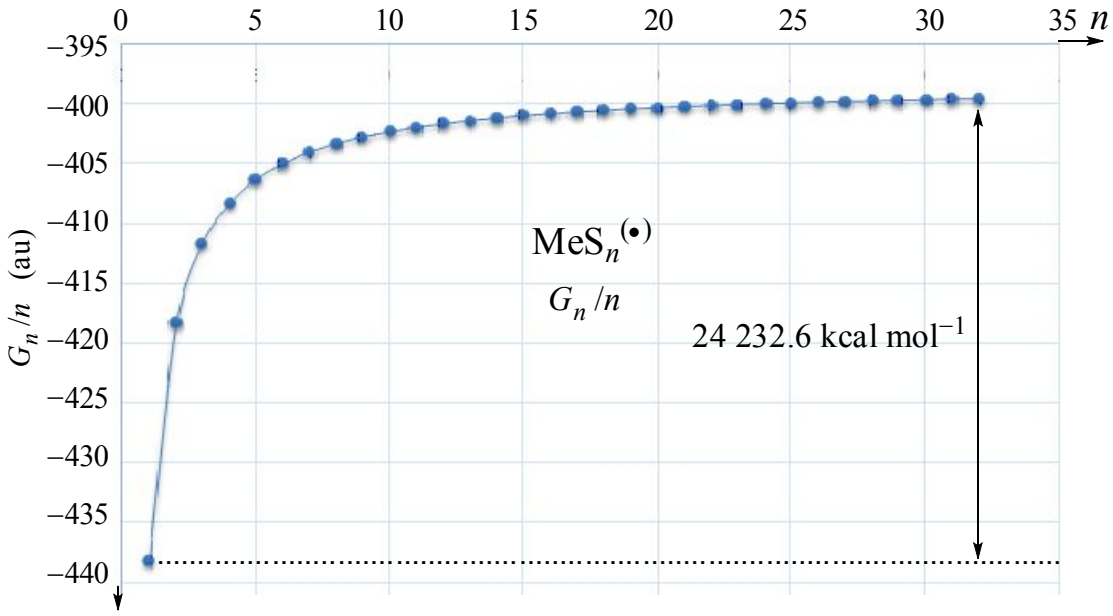


Fig. S-10. Variations of G_n/n values of $MeS_n^{(\bullet)}$ as a function of n (n = number of chain sulfur atoms) at the B3LYP/6-311++G(2df,p) level of theory in ideal gas (see Table S-11).

Table S-14. $MeS_n^{(\bullet)}$ **5**. Energies, E_n, at the B3LYP/6-311++G(2df,p) level of theory in ideal gas (n = number of S-atoms per molecule).

$Me{-}(S)_n^{(\bullet)}$ **5**

n	E_n (au)	E_n/n (au)	$\delta E = E_n/n - E_{(n-1)}/(n-1)$ (kcal mol^{-1})	$\delta E_{calc} = 33\ 110 / n^{2.074}$ (kcal mol^{-1})
1	–438.105 934	–438.105 934	–	
2	–836.361 980	–418.180 990	12 503.09	7863.6
3	–1 234.590.482	–411.530 161	4 173.46	3391.6
4	–1 632.821 915	–408.205 479	2 086.27	1867.6
5	–2 031.051 842	–406.210 368	1 251.95	1175.7
6	–2 429.282 530	–404.880 422	834.55	805.5
7	–2 827.514 175	–403.930 596	596.02	585.1
8	–3 225.744 914	–403.218 114	447.09	443.6
9	–3 623.975 604	–402.663 956	347.74	347.4
10	–4 022.206 465	–402.220 646	278.18	279.2
11	–4 420.436 532	–401.857 866	227.65	229.1
12	–4 818.667 492	–401.555 624	189.66	191.3
13	–5 216.898 223	–401.299 863	160.49	162.0
14	–5 615.128 047	–401.080 575	137.60	138.9
15	–6 013.358 180	–400.890 545	119.24	120.4
16	–6 411.588 004	–400.724 250	104.35	105.3
17	–6 809.820 216	–400.577 660	91.99	92.9
18	–7 208.051 216	–400.447 290	81.81	82.5
19	–7 606.282 955	–400.330 682	73.17	73.7
20	–8 004.512 763	–400.225 638	65.92	66.3
21	–8 402.743 823	–400.130 658	59.60	59.9
22	–8 800.973 758	–400.044 262	54.21	54.4
23	–9 199.204 108	–399.965 396	49.49	49.6
24	–9 597.435 758	–399.893 157	45.33	45.4
25	–9 995.664 965	–399.826 599	41.77	41.7
26	–10 393.897 750	–399.765 298	38.47	38.5
27	–10 792.125 198	–399.708 341	35.74	35.6
28	–11 190.357 368	–399.655 620	33.08	33.0

29	–11 588.586 997	–399.606 448	30.86	30.7
30	–11 986.817 674	–399.560 589	28.78	28.6
31	–12 385.048 224	–399.517 685	26.92	26.7
32	–12 783.279 118	–399.477 472	25.23	25.0
33	–13 181.509 701	–399.439 688	23.71	23.5
34	–13 579.741 653	–399.404 166	22.29	22.1
35	–13 977.967 070	–399.370 488	21.13	20.8
36	–14 376.203 741	–399.338 993	19.76	19.6

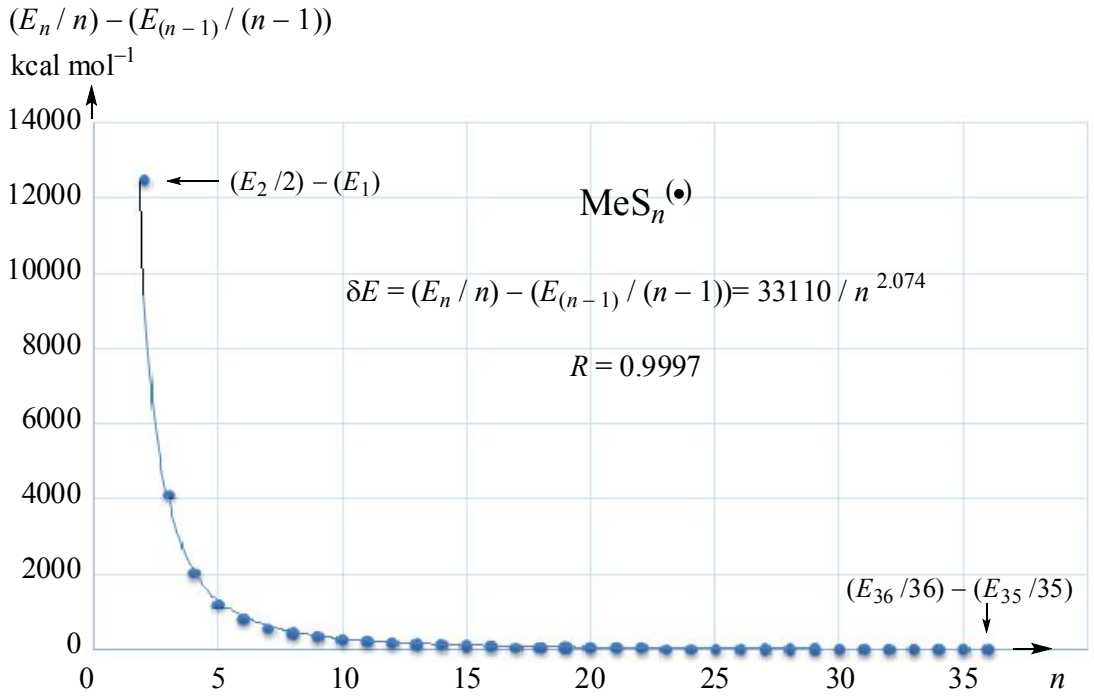
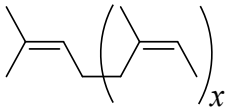


Fig. S-11. Power law (2f): variations of δE values of $MeS_n^{(\bullet)}$ as a function of n (n = number of chain sulfur atoms) at the B3LYP/6-311++G(2df,p) level of theory in ideal gas (see Table S-12).

Table S-15. Poly-(*Z*)-isoprenes **6**. Absolute energies, E_n, at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (*n* is the number of carbon atoms per molecule) and linear relationship (1c).



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x	*n* = 5*x* + 5	E_n (au)	E_n (kcal mol^{-1})	$E_n = -24523.7872n - 755.10$ (1c) (kcal mol^{-1})	δE_{calc} (kcal mol^{-1})
0	5	–196.614 354	–123 377.374 97	–123 374.0	–3.33
1	10	–392.007 964	–245 988.721 49	–245 993.0	4.28
2	15	–587.420 635	–368 612.028 96	–368 611.9	–0.13
3	20	–782.830 779	–491 233.750 71	–491 230.8	–2.95
4	25	–978.227 011	–613 846.742 56	–613 849.8	3.06
5	30	–1 173.634 898	–736 466.734 27	–736 468.7	1.97
6	35	–1 369.047 848	–859 090.530 57	–859 087.6	–2.93

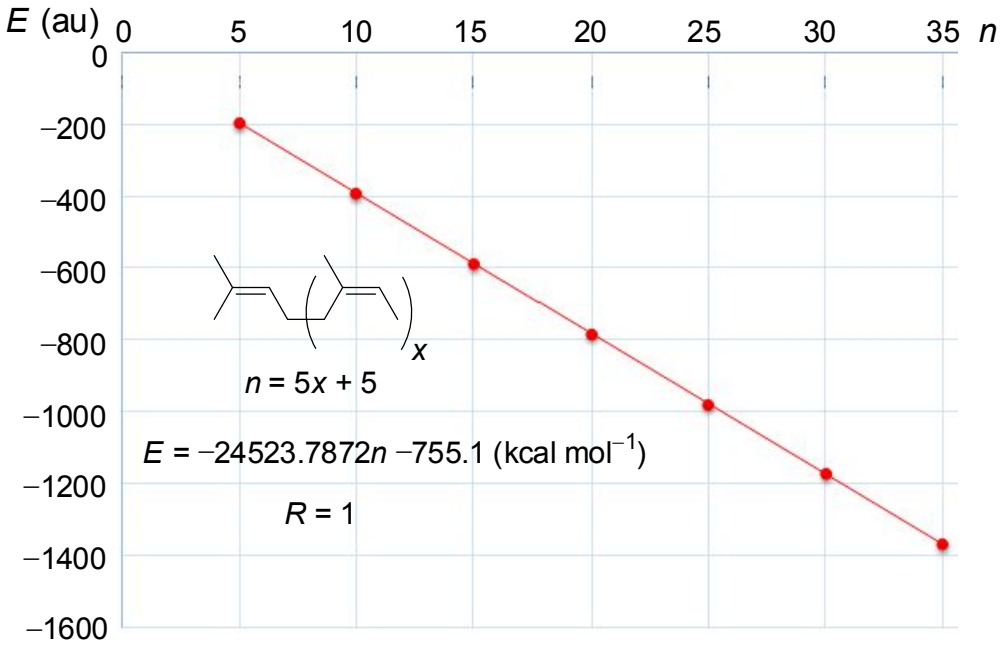
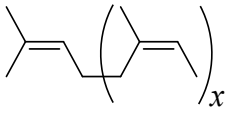


Fig. S-12. E_n values of poly-(*Z*)-isoprenes **6** as a function of *n* (*n* = number of carbon atoms) at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (1c) (see Table S-15).

Table S-16. Poly-(*Z*)-isoprenes **6**. Absolute energies, E_n, at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (*n* is the number of carbon atoms per molecule, $n = 5x + 5$).



6

x	$n = 5x + 5$	E_n (au)	E_n/n (au)	$\delta E = E_n/n - E_{(n-1)}/(n-1)$ (kcal mol^{-1})	$\delta E_{calc} = 19\,753 / n^{2.441}$ (kcal mol^{-1})
0	5	–196.614 354	–39.322 871	–	–
1	10	–392.007 964	–39.200 796	76.60	71.55
2	15	–587.420 635	–39.161 376	24.74	26.59
3	20	–782.830 779	–39.141 539	12.48	13.18
4	25	–978.227 011	–39.129 080	7.82	7.64
5	30	–1 173.634 898	–39.121 163	4.97	4.90
6	35	–1 369.047 848	–39.115 653	3.46	3.36

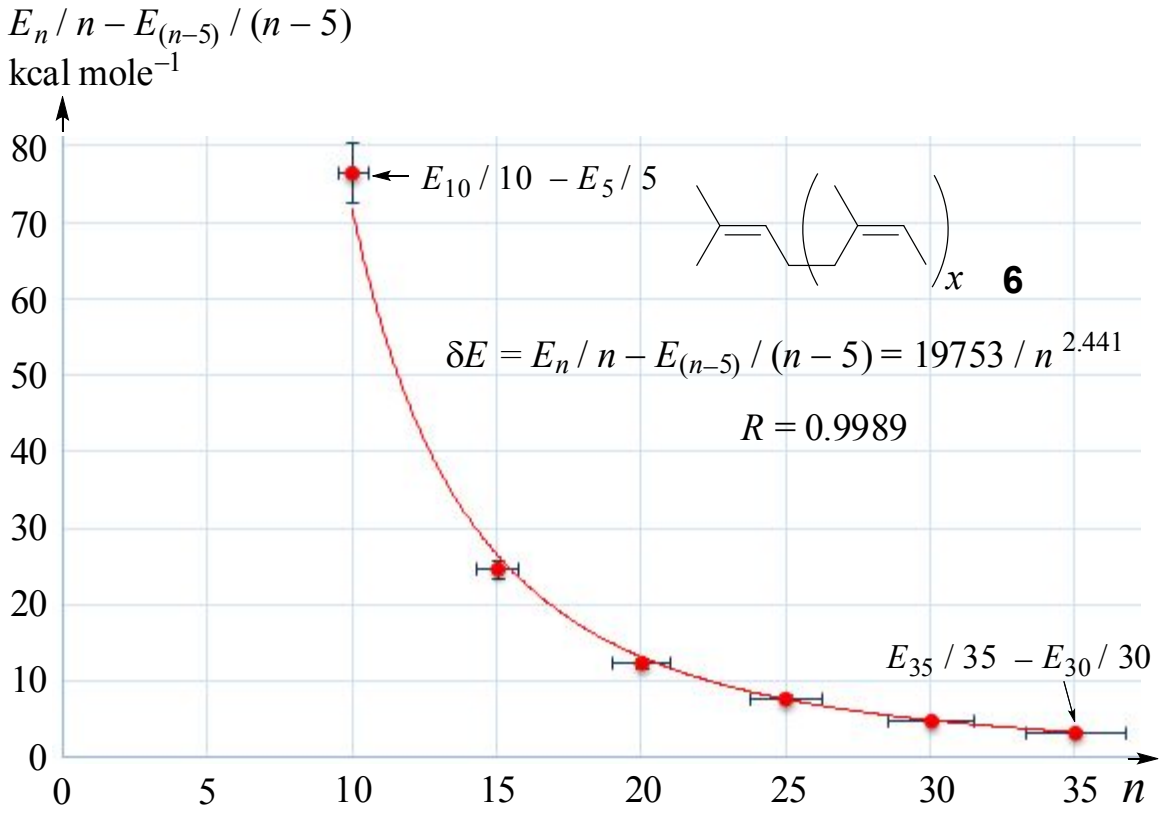


Fig. S-13. Power law (2g): variations of δE values of (*Z*)-polyisoprenes **6** as a function of *n* (*n* = number of carbon atoms) at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (error bars given for 95% confidence interval) (see Table S-16).

Table S-17. Poly-(*Z*)-isoprenes **6**. Absolute free energies, G_n, at the B3LYP/6-311G(d,p) level of theory in ideal gas (*n* is the number of carbon atoms per molecule, $n = 5x + 5$) and linear relationship (1d).

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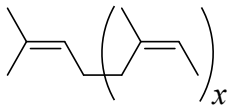


6

x	*n*	G_n (au)	G_n (kcal mol^{-1})	$G = -24508.219133n - 759.7$ (1d) (kcal mol^{-1})	δG (kcal mol^{-1})
0	5	–196.491 966	–123 300.575	–123 300.8	0.22
1	10	–391.777036	–245 843.81	–245 841.9	–1.91
2	15	–587.052 679	–368 381.133	–368 383.0	1.86
3	20	–782.339 481	–490 925.457	–490 924.1	–1.35
4	25	–977.612 205	–613 460.946	–613 465.2	4.25
5	30	–1 172.897 281	–736 004.186	–736 006.3	2.11
6	35	–1 368.186 249	–858 549.869	–858 547.4	–2.47
7	40	–1 563.466 165	–981 089.871	–981 088.5	–1.37
8	45	–1 758.748 227	–1 103 631.22	–1 103 629.6	–1.62
9	50	–1 954.030 368	–1 226 172.62	–1 226 170.7	–1.92
10	55	–2 149.311 034	–1 348 713.09	–1 348 711.8	–1.29
11	60	–2 344.586 613	–1 471 250.37	–1 471 252.8	2.43
12	65	–2 539.871 863	–1 593 793.72	–1 593 793.9	0.18
13	70	–2 735.153 111	–1 716 334.56	–1 716 335.0	0.44
14	75	–2 930.434 644	–1 838 875.58	–1 838 876.1	0.52

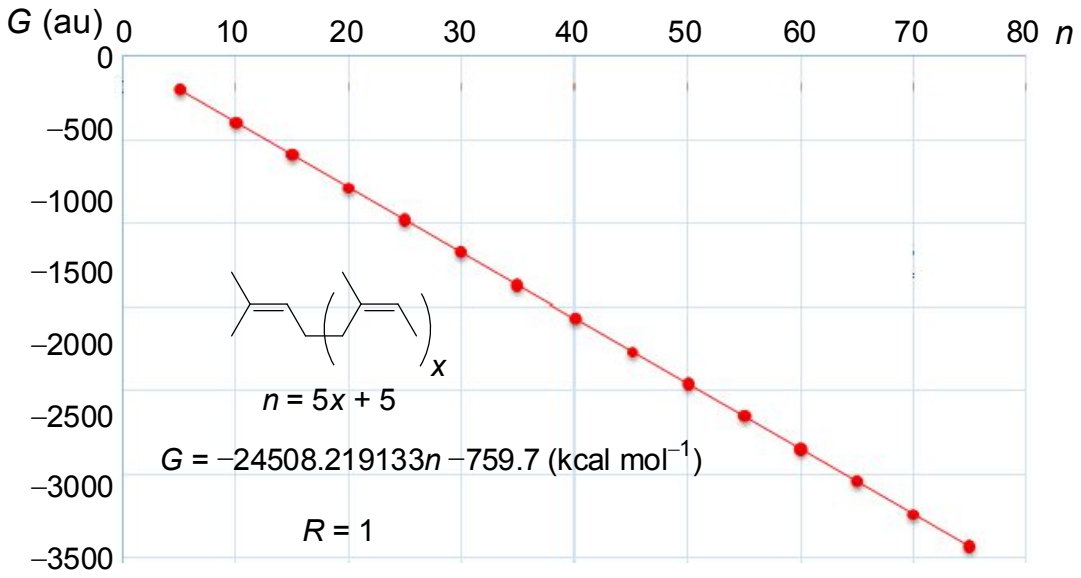
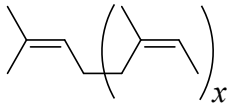


Fig. S-14. G_n values of poly-(*Z*)-isoprenes **6** as a function of *n* (*n* = number of carbon atoms) at the B3LYP/6-311G(d,p) level of theory in ideal gas (1d) (see Table S-17).

Table S-18. Poly-(*Z*)-isoprenes **6**. Absolute free energies, G_n, at the B3LYP/6-311G(d,p) level of theory in ideal gas (*n* is the number of carbon atoms per molecule, $n = 5x + 5$).



6

x	*n*	G_n (au)	G_n/n (au)	G_n/n (kcal mol^{-1})	$\delta G = G_n/n - G_{(n-5)}/(n-5)$ (kcal mol^{-1})	$\delta G_{calc} = 11\,620 / n^{2.257}$ (kcal mol^{-1})
0	5	–196.491 966	–39.298 715	–24 660.32	–	–
1	10	–391.777036	–39.177704	–24 584.38	75.94	64.30
2	15	–587.052 679	–39.136 845	–24 558.74	24.59	25.75
3	20	–782.339 481	–39.116 974	–24 546.27	12.47	13.45
4	25	–977.612 205	–39.104 488	–24 538.44	7.83	8.13
5	30	–1 172.897 281	–39.096 576	–24 533.47	4.96	5.38
6	35	–1 368.186 249	–39.091 036	–24 530.00	3.47	3.80
7	40	–1 563.466 165	–39.086 654	–24 527.25	2.75	2.81
8	45	–1 758.748 227	–39.083 294	–24 525.14	2.11	2.16
9	50	–1 954.030 368	–39.080 607	–24 523.45	1.68	1.70
10	55	–2 149.311 034	–39.078 382	–24 522.06	1.40	1.37
11	60	–2 344.586 613	–39.076 443	–24 520.84	1.22	1.13
12	65	–2 539.871 863	–39.074 952	–24 519.90	0.94	0.94
13	70	–2 735.153 111	–39.073 616	–24 519.06	0.84	0.80
14	75	–2 930.434 644	–39.072 462	–24 518.34	0.72	0.68

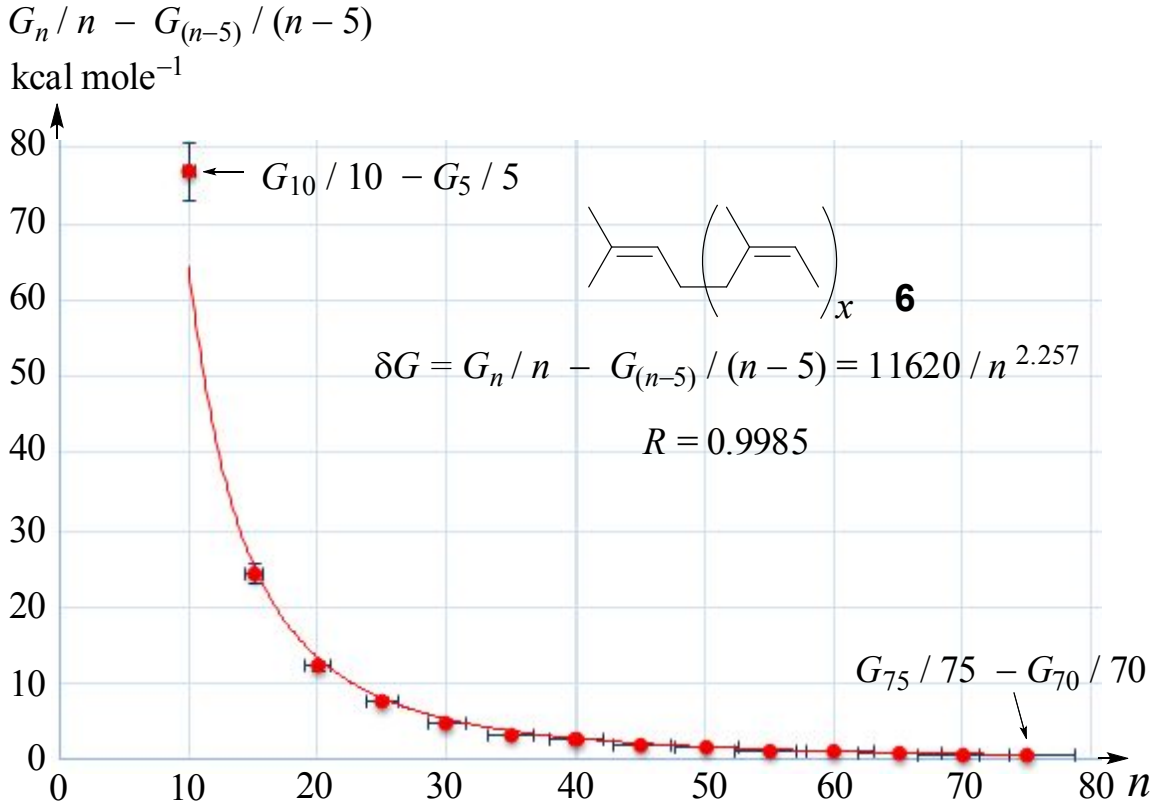


Fig. S-15. Power law (2h): variations of δG values of (*Z*)-polyisoprenes **6** as a function of n (n = number of carbon atoms) at the B3LYP/6-311G(d,p) level of theory in ideal gas (error bars given for 95% confidence interval) (see Table S-18).

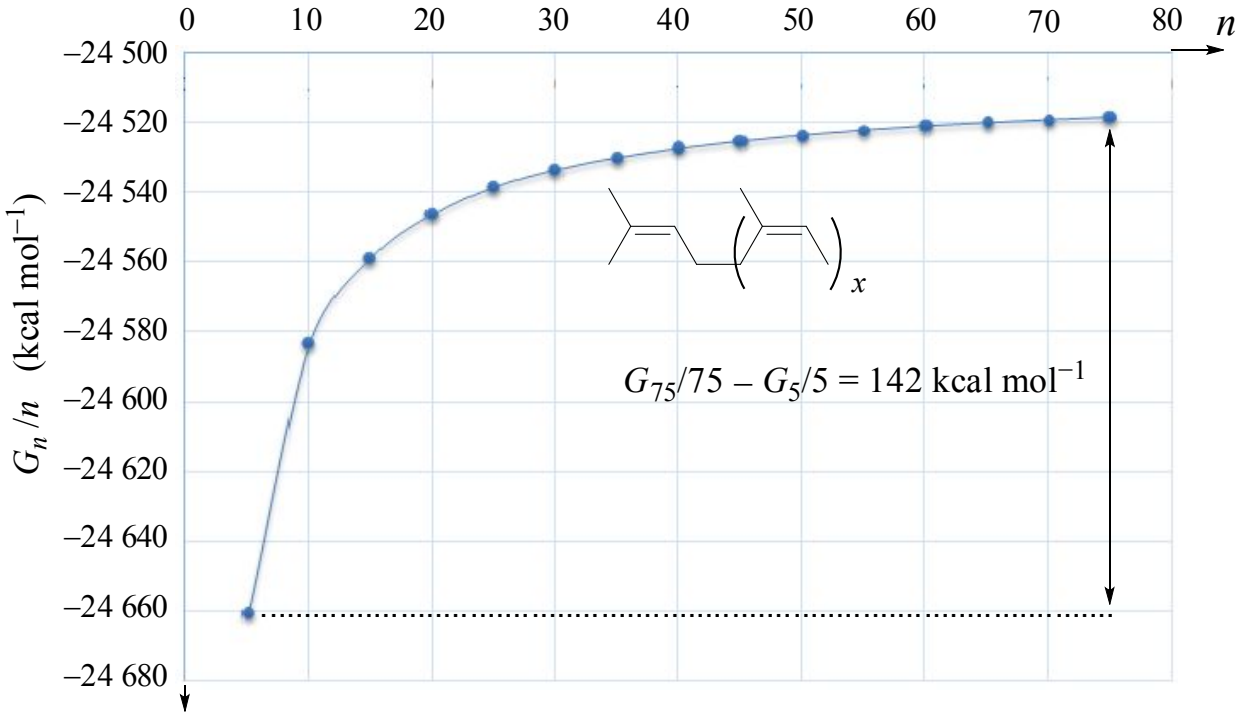
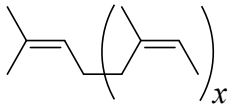


Fig. S-16. Variations of G_n /n values of poly-(*Z*)-isoprenes **6** as a function of n (n = number of carbon atoms) at the B3LYP/6-311G(d,p) level of theory in ideal gas (see Table S-18).

Table S-19. Poly-(*Z*)-isoprenes **6**. Absolute free energies, G_n, at the TPSS-TSS/6-311++G(df,pd) level of theory in ideal gas (*n* is the number of carbon atoms per molecule) and linear relationship (1e).



6

x	*n* = 5*x* + 5	G_n (au)	G_n (kcal mol^{-1})	G = –24513.20486*n* – 753.6 (1e) (kcal mol^{-1})	δG_{calc} (kcal mol^{-1})
0	5	–196.527 734	–123 323.02	–123 324.37	1.35
1	10	–391.834 746	–245 890.717	–245 889.9	–0.82
2	15	–587.166 114	–368 455.886	–368 455.43	–0.46
3	20	–782.491 953	–491 021.08	–491 020.96	–0.12
4	25	–977.801 909	–613 584.188	–613 586.49	2.30
5	30	–1 173.126 414	–736 152.196	–736 152.0	–0.20
6	35	–1 368.455 410	–858 719.861	–858 717.55	–2.31
7	40	–1 563.774 787	–981 283.503	–981 283.07	–0.43
8	45	–1 759.093 127	–1 103 849.07	–1 103 848.6	–0.47
9	50	–1 954.416 009	–1 226 415.94	–1 226 414.13	–1.8
10	55	–2 149.733 140	–1 348 977.85	–1 348 979.7	1.84

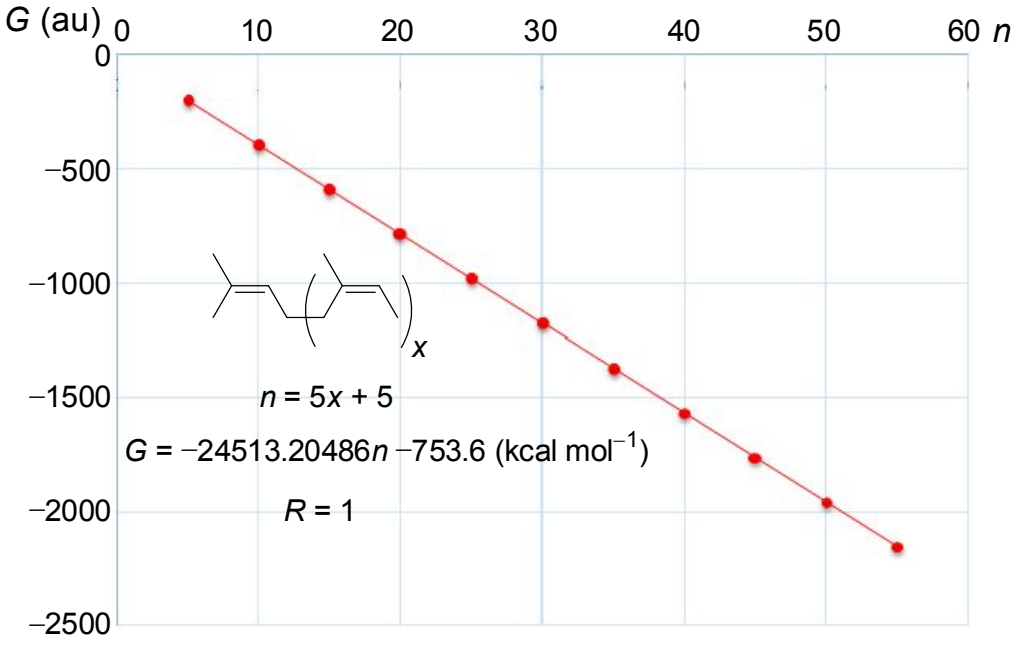
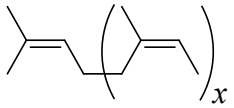


Fig. S-17. G_n values of poly-(*Z*)-isoprenes **6** as a function of *n* (*n* = number of carbon atoms) at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (1e) (see Table S-19).

Table S-20. Poly-(*Z*)-isoprenes **6**. Absolute free energies, G_n, at the TPSS-TSS/6-311++G(df,pd) level of theory in ideal gas (*n* is the number of carbon atoms per molecule).



6

x	*n* = 5*x* + 5	G_n (au)	G_n/n (au)	$\delta G = G_n/n - G_{(n-5)}/(n-5)$ (kcal mol^{-1})	$\delta G_{calc} = 13\,591 / n^{2.31}$ (kcal mol^{-1})
0	5	–196.527 734	–39.305 547	–	–
1	10	–391.834 746	–39.183 475	76.60	66.57
2	15	–587.166 114	–39.144 407	24.52	26.09
3	20	–782.491 953	–39.124 598	12.43	13.42
4	25	–977.801 909	–39.112 076	7.86	8.02
5	30	–1 173.126 414	–39.104 214	4.93	5.26
6	35	–1 368.455 410	–39.098 726	3.44	3.68
7	40	–1 563.774 787	–39.094 370	2.73	2.71
8	45	–1 759.093 127	–39.090 958	2.15	2.06
9	50	–1 954.416 009	–39.088 320	1.66	1.62
10	55	–2 149.733 140	–39.086 057	1.42	1.30

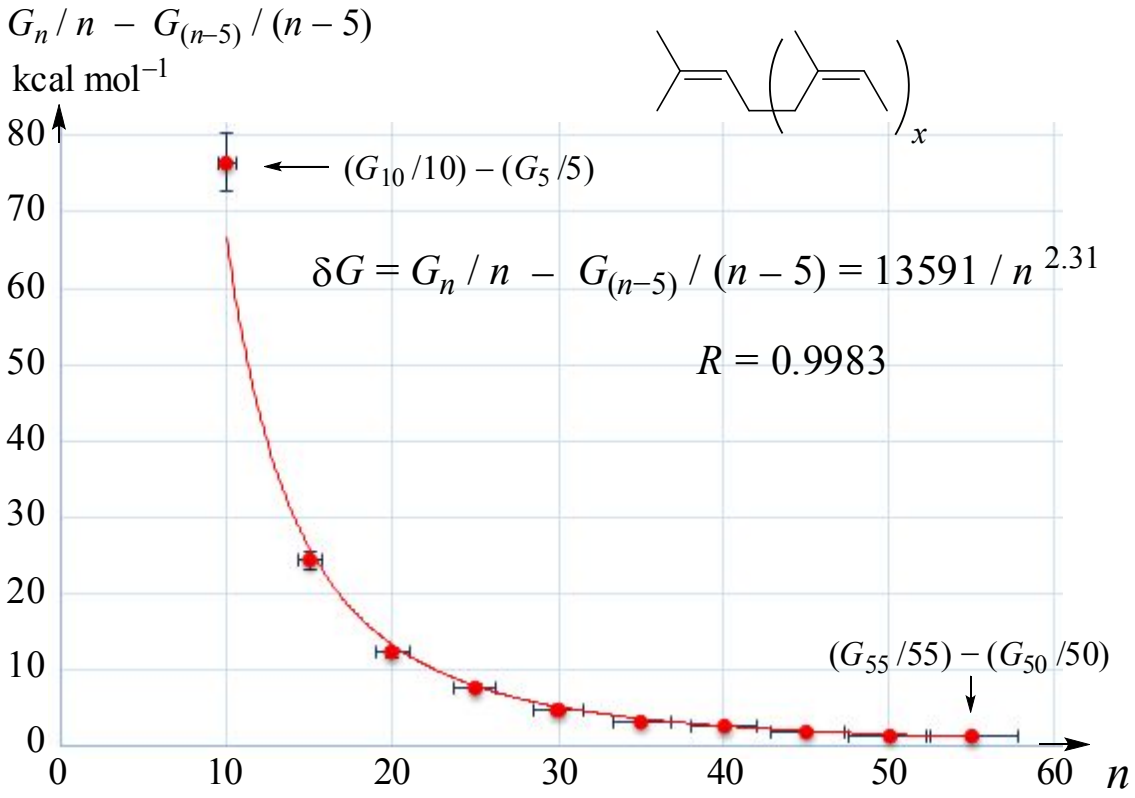
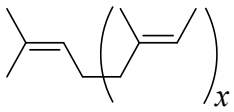


Fig. S-18. Power law (2i): variations of δG values of (*Z*)-polyisoprenes **6** as a function of n (n = number of carbon atoms) at the TPSS-TSS/6-311++G(df,pd) level of theory in ideal gas (error bars given for 95% confidence interval) (see Table S-20).

Table S-21. Poly-(*E*)-isoprenes **7**. Absolute free energies, G_n, at the B3LYP/6-311G(d,p) level of theory in ideal gas (*n* is the number of carbon atoms per molecule, $n = 5x + 5$) and linear relationship (1f).



7

x	*n*	G_n (au)	G_n (kcal mol^{-1})	$G = -24508.241398n - 761.17$ (1f) (kcal mol^{-1})	δG (kcal mol^{-1})
0	5	–196.491 966	–123 300.57	–123 299.6	–0.93
1	10	–391.780 610	–245 846.05	–245 841.1	4.95
2	15	–587.058 904	–368 385.04	–368 382.6	–2.44
3	20	–782.339 975	–490 925.77	–490 924.1	–1.66
4	25	–977.617 807	–613 464.46	–613 465.5	1.04
5	30	–1 172.903 745	–736 008.24	–736 007.0	–1.24
6	35	–1 368.186 519	–858 550.04	–858 548.5	–1.54
7	40	–1 563.470 047	–981 092.31	–981 090.0	–2.31
8	45	–1 758.751 540	–1 103 633.30	–1 103 631.5	–1.80
9	50	–1 954.033 578	–1 226 174.63	–1 226 173.0	–1.63
10	55	–2 149.312 642	–1 348 714.10	–1 348 714.4	0.30
11	60	–2 344.592 418	–1 471 254.02	– 1471 255.9	1.88
12	65	–2 539.877 085	–1 593 797.00	–1 593 797.4	0.40
13	70	–2 735.158 194	–1 716 337.75	–1 716 338.8	1.05
14	75	–2 930.440 335	–1 838 879.15	–1 838 880.3	1.15

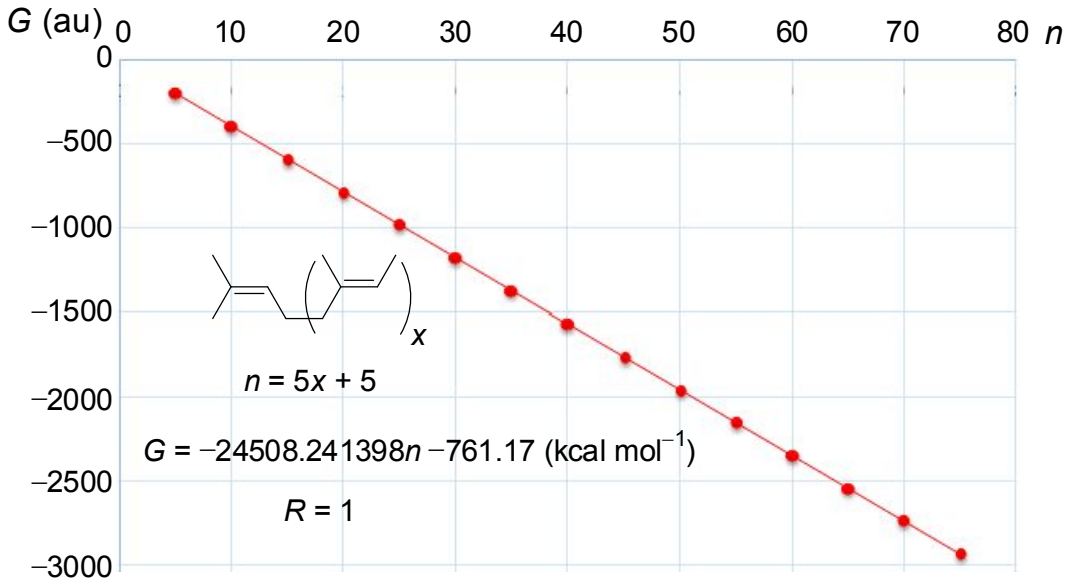
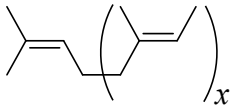


Fig. S-19. G_n values of poly-(*E*)-isoprenes **7** as a function of n (n = number of carbon atoms) at the B3LYP/6-311G(d,p) level of theory in ideal gas (1f) (see Table S-21).

Table S-22. Poly-(*E*)-isoprenes **7**. Absolute free energies, G_n, at the B3LYP/6-311G(d,p) level of theory in ideal gas (*n* is the number of carbon atoms per molecule, $n = 5x + 5$).



7

x	*n*	G_n (au)	G_n/n (au)	$\delta G = G_n/n - G_{(n-5)}/(n-5)$ (kcal mol^{-1})	$\delta G_{calc} = 11\,650 / n^{2.258}$ (kcal mol^{-1})
0	5	–196.491 966	–39.298 393	–	–
1	10	–391.780 610	–39.178 061	75.50	64.32
2	15	–587.058 904	–39.137 260	24.34	25.75
3	20	–782.339 975	–39.116 999	12.71	13.44
4	25	–977.617 807	–39.104 712	7.71	8.12
5	30	–1 172.903 745	–39.096 791	4.97	5.38
6	35	–1 368.186 519	–39.091 043	3.61	3.80
7	40	–1 563.470 047	–39.086 751	2.69	2.81
8	45	–1 758.751 540	–39.083 368	2.12	2.15
9	50	–1 954.033 578	–39.080 672	1.69	1.70
10	55	–2 149.312 642	–39.078 412	1.42	1.37
11	60	–2 344.592 418	–39.076 540	1.17	1.13
12	65	–2 539.877 085	–39.075 032	0.95	0.94
13	70	–2 735.158 194	–39.073 688	0.84	0.79
14	75	–2 930.440 335	–39.072 538	0.72	0.68

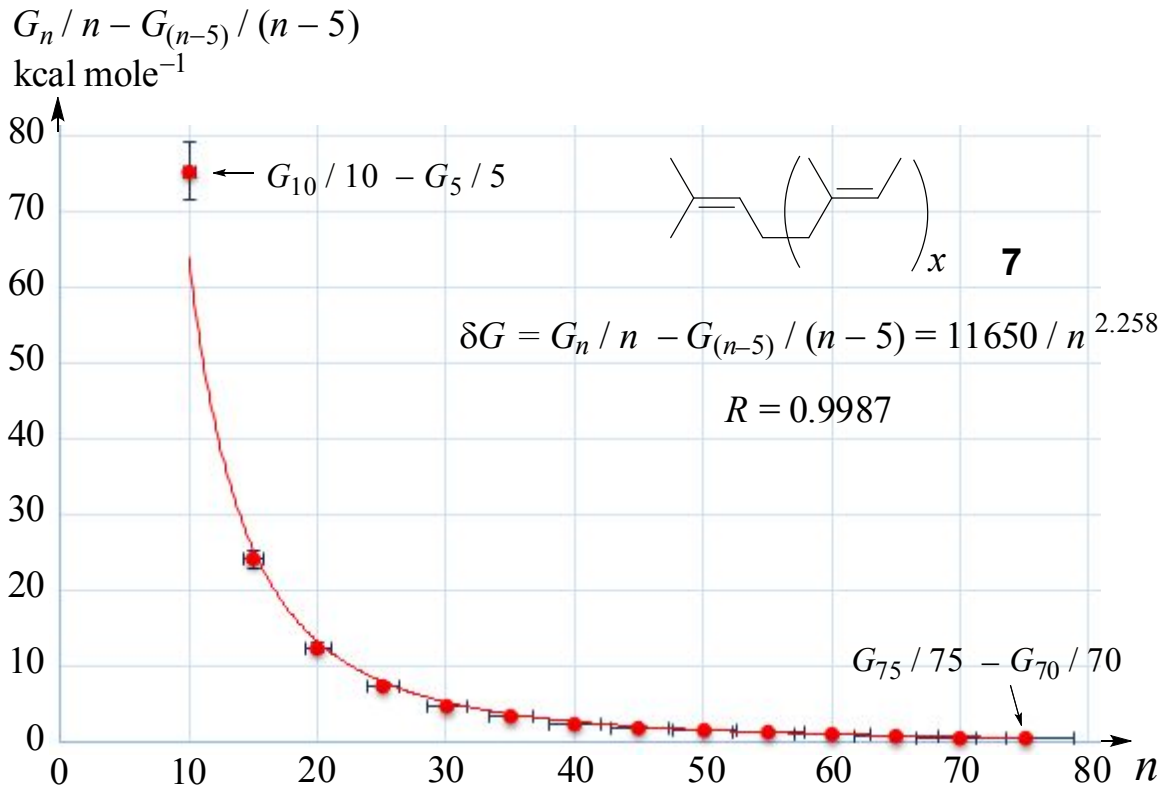
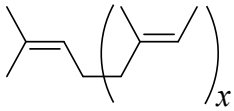


Fig. S-20. Power law (2j): variations of δG values of (*E*)-polyisoprenes as a function of n (n = number of carbon atoms) at the B3LYP/6-311G(d,p) level of theory in ideal gas (error bars given for 95% confidence interval) (see Table S-22).

Table S-23. Poly-(*E*)-isoprenes **7**. Absolute free energies, G_n, at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (*n* is the number of carbon atoms per molecule, $n = 5x + 5$) and linear relationship (1g).



7

x	*n*	G_n (au)	G_n (kcal mol^{-1})	$G = -24513.105885n - 758.84$ (1g) (kcal mol^{-1})	δG (kcal mol^{-1})
0	5	–196.527 734	–123 323.02	–123 324.37	1.35
1	10	–391.851 784	–245 890.72	–245 889.90	–0.82
2	15	–587.171 805	–368 455.89	–368 455.43	–0.45
3	20	–782.491 867	–491 021.08	–491 020.96	–0.12
4	25	–977.808 604	–613 584.19	–613 586.49	2.30
5	30	–1 173.133 149	–736 152.19	–736 152.00	–0.20
6	35	–1 368.457 149	–858 719.86	–858 717.55	–2.31
7	40	–1 563.774 737	–981 283.50	–981 283.07	–0.43
8	45	–1 759.095 398	–1 103 849.07	–1 103 848.60	–0.47
9	50	–1 954.418 131	–1 226 415.94	–1 226 414.13	–1.8
10	55	–2 149.732 958	–1 348 977.85	–1 348 979.70	1.84
11	60	–2 345.054 598	–1 471 544.04	–1 471 545.20	1.16

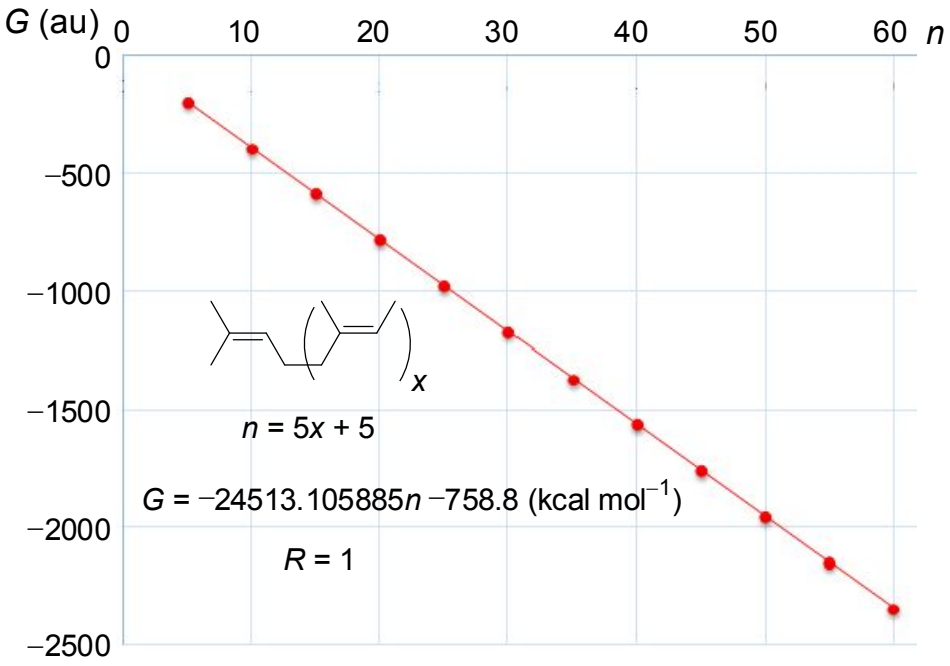
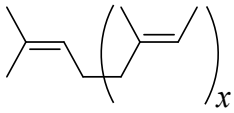


Fig. S-21. G_n values of poly-(*E*)-isoprenes **7** as a function of *n* (*n* = number of carbon atoms) at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (1g) (see Table S-23).

Table S-24. Poly-(*E*)-isoprenes **7**. Absolute free energies, G_n, at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (*n* is the number of carbon atoms per molecule, $n = 5x + 5$).



7

x	*n*	G_n (au)	G_n/n (au)	$\delta G = G_n/n - G_{(n-5)}/(n-5)$ (kcal mol^{-1})	$\delta G_{calc} = 12\,895 / n^{2.29}$ (kcal mol^{-1})
0	5	–196.527 734	–39.305 547	–	–
1	10	–391.851 784	–39.185 178	75.53	66.13
2	15	–587.171 805	–39.144 787	25.34	26.13
3	20	–782.491 867	–39.124 593	12.67	13.52
4	25	–977.808 604	–39.112 344	7.69	8.11
5	30	–1 173.133 149	–39.104 438	4.96	5.34
6	35	–1 368.457 149	–39.098 776	3.55	3.75
7	40	–1 563.774 737	–39.094 368	2.77	2.77
8	45	–1 759.095 398	–39.091 009	2.11	2.11
9	50	–1 954.418 131	–39.088 363	1.72	1.66
10	55	–2 149.732 958	–39.086 054	1.45	1.33
11	60	–2 345.054 598	–39.084 243	1.14	1.09

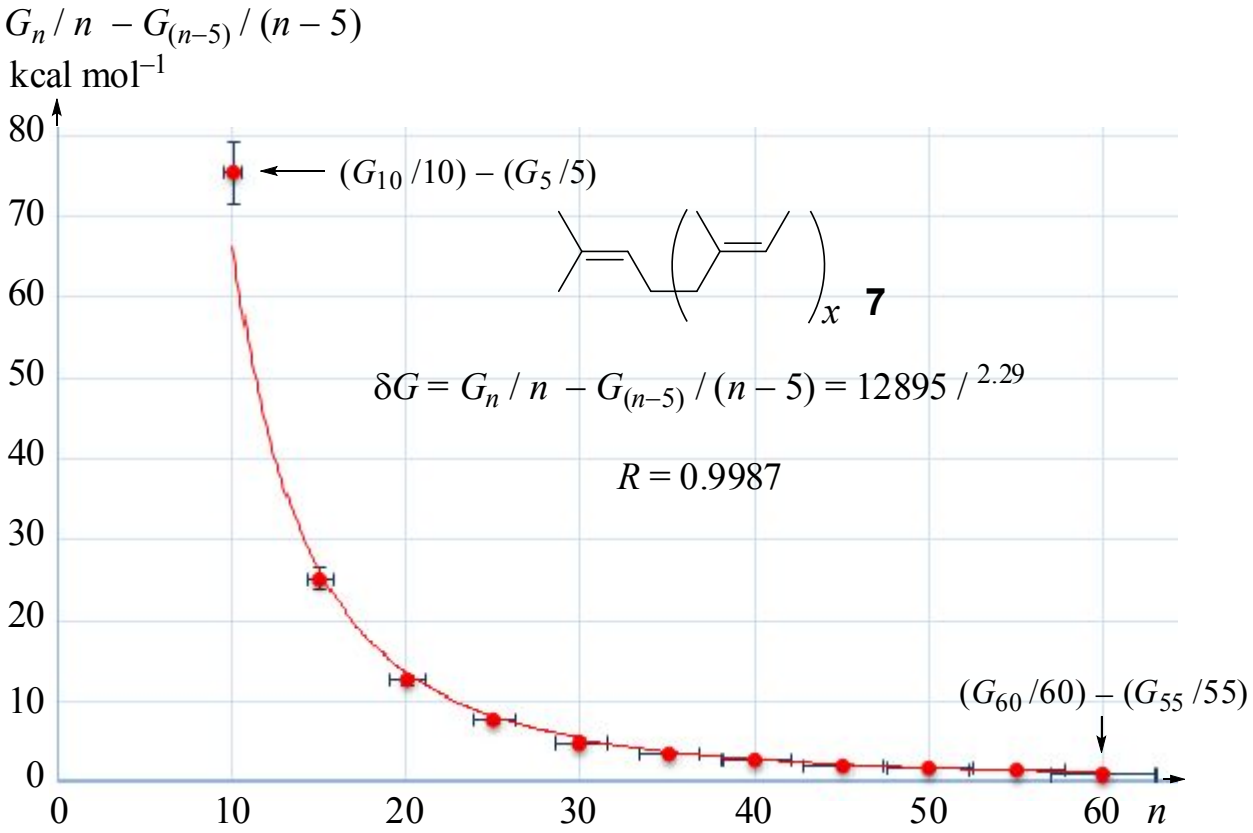
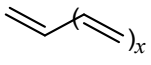


Fig. S-22. Power law (2k): variations of δ*G* values of (*E*)-polyisoprenes as a function of *n* (*n* = number of carbon atoms) at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (error bars given for 95% confidence interval) (see Table S-24).

Table S-25. Linear *trans*-polyenes **8**. Absolute free energies, G_n, at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (*n* is the number of carbon atoms per molecule, $n = 2x + 2$) and linear relationship (1h).



8

x	*n*	G_n (au)	G_n (kcal mol^{-1})	$G = -24285.87898n - 744.63$ (1h) (kcal mol^{-1})	δG_{calc} (kcal mol^{-1})
0	2	–78.593 366	–49 318.0838	–49 316.3931	–1.69
1	4	–155.995 006	–97 888.3482	–97 888.1511	–0.20
2	6	–233.398 134	–146 459.546	–146 459.909	0.36
3	8	–310.801 860	–195 031.12	–195 031.667	0.55
4	10	–388.205 829	–243 602.846	–243 603.525	0.68
5	12	–465.609 923	–292 174.65	–292 175.183	0.53
6	14	–543.014 073	–340 746.489	–340 746.941	0.45
7	16	–620.418 232	–389 318.335	–389 318.699	0.36
8	18	–697.822 496	–437 890.246	–437 890.457	0.21
9	20	–775.226 797	–486 462.18	–486 462.215	0.03
10	22	–852.631 018	–535 034.064	–535 033.973	–0.09
11	24	–930.035 256	–583 605.958	–583 605.731	–0.23
12	26	–1 007.439 486	–632 177.848	–632 177.489	–0.36
13	28	–1 084.843 825	–680 749.806	–680 749.247	–0.56
14	30	–1 162.246 885	–729 320.962	–729 321.005	0.043

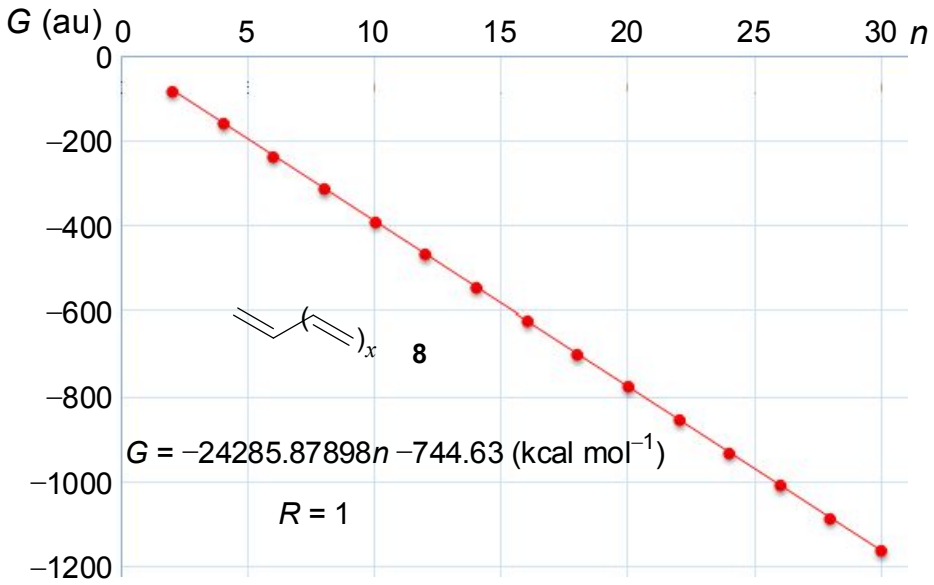
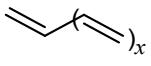


Fig. S-23. G_n values of linear *trans*-polyenes **8** as a function of n (n = number of carbon atoms) at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (1h) (see Table S-25).

Table S-26. Linear *trans*-polyenes **8**. Absolute free energies, G_n, at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (n is the number of carbon atoms per molecule, $n = 2x + 2$).



8

x	n	G_n (au)	G_n/n (au)	$\delta G = G_n/n - G_{(n-2)}/(n-2)$ (kcal mol^{-1})	$\delta G_{calc} = 3\ 645.8 / n^{2.262}$ (kcal mol^{-1})
0	2	–78.593 366	–39.296 683	–	–
1	4	–155.995 006	–38.998 751	186.95	158.46
2	6	–233.398 134	–38.899 689	62.16	63.33
3	8	–310.801 860	–38.850 232	31.03	33.04
4	10	–388.205 829	–38.820 583	18.60	19.94
5	12	–465.609 923	–38.800 827	12.40	13.20
6	14	–543.014 073	–38.786 719	8.85	9.31
7	16	–620.418 232	–38.776 139	6.64	6.89
8	18	–697.822 496	–38.767 916	5.16	5.28
9	20	–775.226 797	–38.761 340	4.13	4.16
10	22	–852.631 018	–38.755 955	3.38	3.35
11	24	–930.035 256	–38.751 469	2.81	2.75
12	26	–1 007.439 486	–38.747 672	2.38	2.30
13	28	–1 084.843 825	–38.744 422	2.04	1.94
14	30	–1 162.246 885	–38.741 563	1.79	1.66

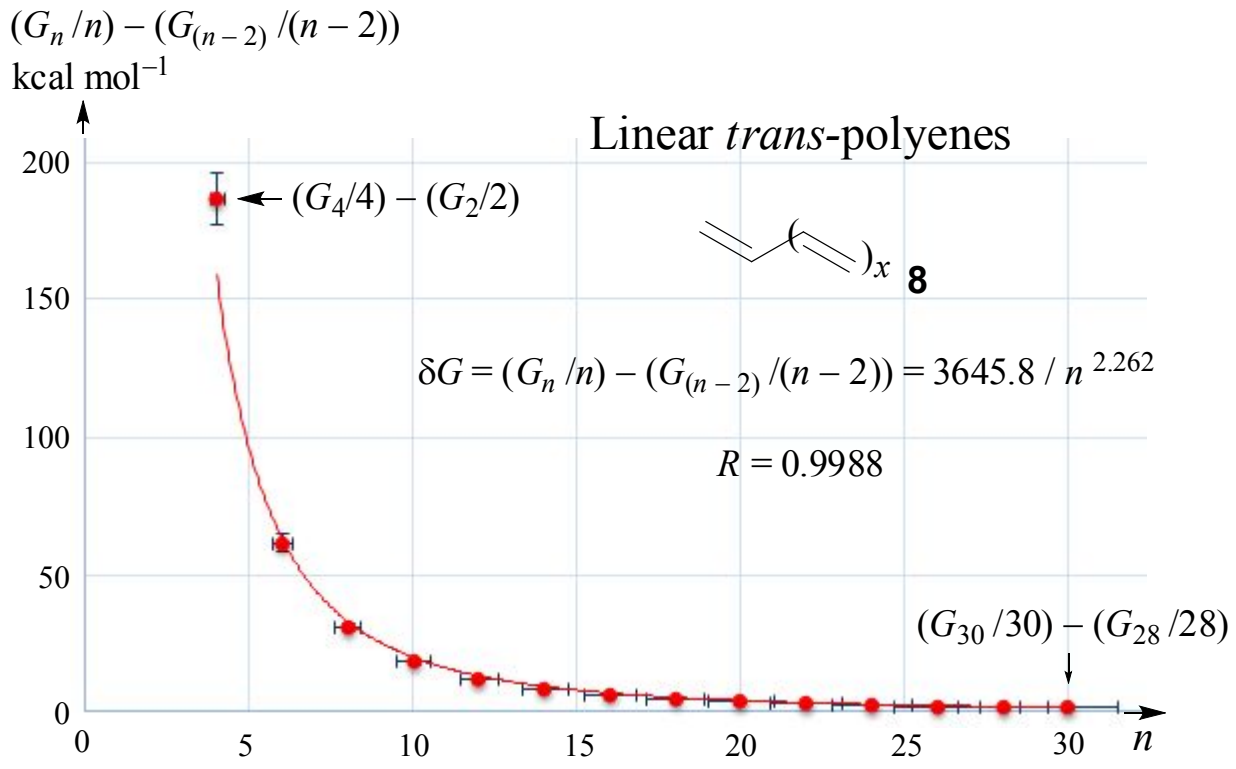
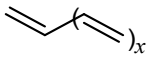


Fig. S-24. Power law (2l): variations of δ*G* values of linear *trans*-polyenes as a function of *n* (*n* = number of carbon atoms) at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (error bars given for 95% confidence interval) (see Table S-26).

Table S-27. Linear *trans*-polyenes **8**. Absolute energies, G_n, at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (*n* is the number of carbon atoms per molecule, $n = x + 2$) and linear relationship (1i).



8

x	*n*	G_n (au)	G_n (kcal mol^{-1})	$G = -24289.49726n - 738.60$ (1i) (kcal mol^{-1})	δG (kcal mol^{-1})
0	2	–78.599 411	–49 321.8771	–49 317.6	–4.28
1	4	–156.011 135	–97 898.4693	–97 896.6	–1.87
2	6	–233.424 857	–146 476.315	–146 475.5	–0.81
3	8	–310.839 403	–195 054.678	–195 054.597	–0.08
4	10	–388.254 327	–243 633.279	–243 633.57	0.29
5	12	–465.669 462	–292 212.011	–292 212.57	0.56
6	14	–543.084 699	–340 790.808	–340 791.56	0.75
7	16	–620.499 999	–389 369.644	–389 370.56	0.92
8	18	–697.915 301	–437 948.482	–437 949.55	1.07
9	20	–775.330 845	–486 527.471	–486 528.54	1.07
10	22	–852.746 429	–535 106.485	–535 107.54	1.05
11	24	–930.161 914	–583 685.438	–583 686.53	1.09
12	26	–1 007.577 379	–632 264.377	–632 265.53	1.15
13	28	–1 084.992 990	–680 843.409	–680 844.52	1.11
14	30	–1 162.409 426	–729 422.958	–729 423.52	0.56
15	32	–1 239.825 225	–778 002.107	–778 002.51	0.40
16	34	–1 317.240 938	–826 581.202	–826 581.5	0.30
17	36	–1 394.655 601	–875 159.639	–875 160.5	0.86
18	38	–1 472.072 249	–923 739.321	–923 739.5	0.18
19	40	–1 549.487 922	–972 318.391	–972 318.5	0.11
20	42	–1 626.903 557	–1 020 897.44	–1 020 897.48	0.04
21	44	–1 704.319 302	–1 069 476.55	–1 069 476.48	–0.07
22	46	–1 781.735 016	–1 118 055.65	–1 118 055.47	–0.18
23	48	–1 859.150 840	–1 166 634.81	–1 166 634.47	–0.34
24	50	–1 936.566 475	–1 215 213.86	–1 215 213.46	–0.40
25	52	–2 013.982 169	–1 263 792.94	–1 263 792.46	–0.48

26	54	–2 091.397 870	–1 312 372.03	–1 312 371.45	–0.58
27	56	–2 168.813 548	–1 360 951.11	–1 360 950.45	–0.65
28	58	–2 246.229 346	–1 409 530.25	–1 409 529.44	–0.81
29	60	–2 323.645 203	–1 458 109.44	–1 458 108.45	–0.99

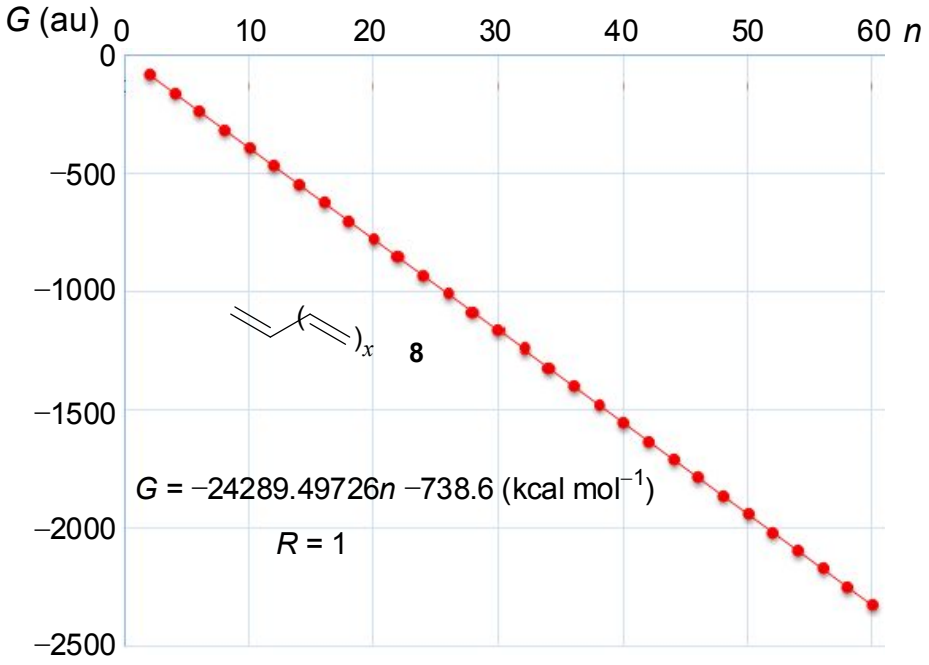
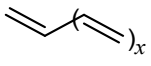


Fig. S-25. G_n values of linear *trans*-polyenes **8** as a function of n (n = number of carbon atoms) at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (1i) (see Table S-27).

Table S-28. Linear *trans*-polyenes **8**. Absolute free energies, G_n, at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (n is the number of carbon atoms per molecule, $n = x + 2$).



8

x	n	G_n (au)	G_n/n (au)	G_n/n (kcal mol^{-1})	$\delta G = G_n/n - G_{(n-2)}/(n-2)$ (kcal mol^{-1})	$\delta G_{calc} = 2961.5 / n^{2.178}$ (kcal mol^{-1})
0	2	–78.599 411	–39.299 705	–24 660.94	–	–
1	4	–156.011 135	–39.002 784	–24 474.62	186.32	144.62
2	6	–233.424 857	–38.904 143	–24 412.72	61.90	59.80
3	8	–310.839 403	–38.854 925	–24 381.83	30.88	31.95
4	10	–388.254 327	–38.825 433	–24 363.33	18.51	19.66
5	12	–465.669 462	–38.805 788	–24 351.00	12.33	13.2
6	14	–543.084 699	–38.791 764	–24 342.20	8.80	9.45
7	16	–620.499 999	–38.781 250	–24 335.60	6.60	7.06
8	18	–697.915 301	–38.773 072	–24 330.47	5.13	5.46
9	20	–775.330 845	–38.766 542	–24 326.37	4.10	4.3
10	22	–852.746 429	–38.761 201	–24 323.02	3.35	3.53
11	24	–930.161 914	–38.756 746	–24 320.23	2.79	2.92
12	26	–1 007.577 379	–38.752 976	–24 317.86	2.36	2.45
13	28	–1 084.992 990	–38.749 750	–24 315.84	2.02	2.09
14	30	–1 162.409 426	–38.746 981	–24 314.10	1.74	1.80
15	32	–1 239.825 225	–38.744 538	–24 312.56	1.53	1.56
16	34	–1 317.240 938	–38.742 380	–24 311.21	1.35	1.37
17	36	–1 394.655 601	–38.740 461	–24 310.01	1.20	1.21
18	38	–1 472.072 249	–38.738 743	–24 308.93	1.08	1.07
19	40	–1 549.487 922	–38.737 198	–24 307.96	0.97	0.96
20	42	–1 626.903 557	–38.735 800	–24 307.08	0.88	0.86
21	44	–1 704.319 302	–38.734 530	–24 306.28	0.80	0.78
22	46	–1 781.735 016	–38.733 370	–24 305.56	0.73	0.71
23	48	–1 859.150 840	–38.732 309	–24 304.89	0.64	0.64
24	50	–1 936.566 475	–38.731 329	–24 304.28	0.61	0.59
25	52	–2 013.982 169	–38.730 426	–24 303.71	0.57	0.54

26	54	–2 091.397 870	–38.729 590	–24 303.18	0.52	0.50
27	56	–2 168.813 548	–38.728 813	–24 302.70	0.49	0.46
28	58	–2 246.229 346	–38.728 092	–24 302.25	0.45	0.43
29	60	–2 323.645 203	–38.727 420	–24 301.82	0.42	0.40

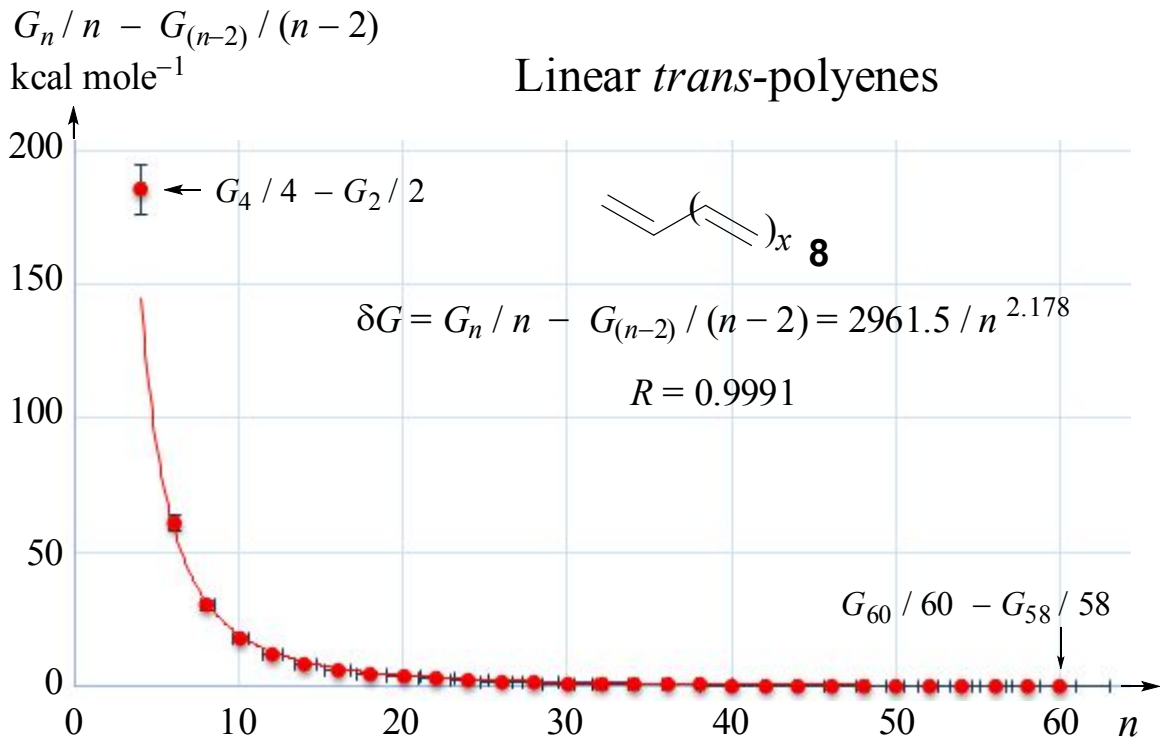


Fig. S-26. Power law (2m): variations of δ*G* values of linear *trans*-polyenes **8** as a function of *n* (*n* = number of carbon atoms) at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (error bars given for 95% confidence interval) (see Table S-28).

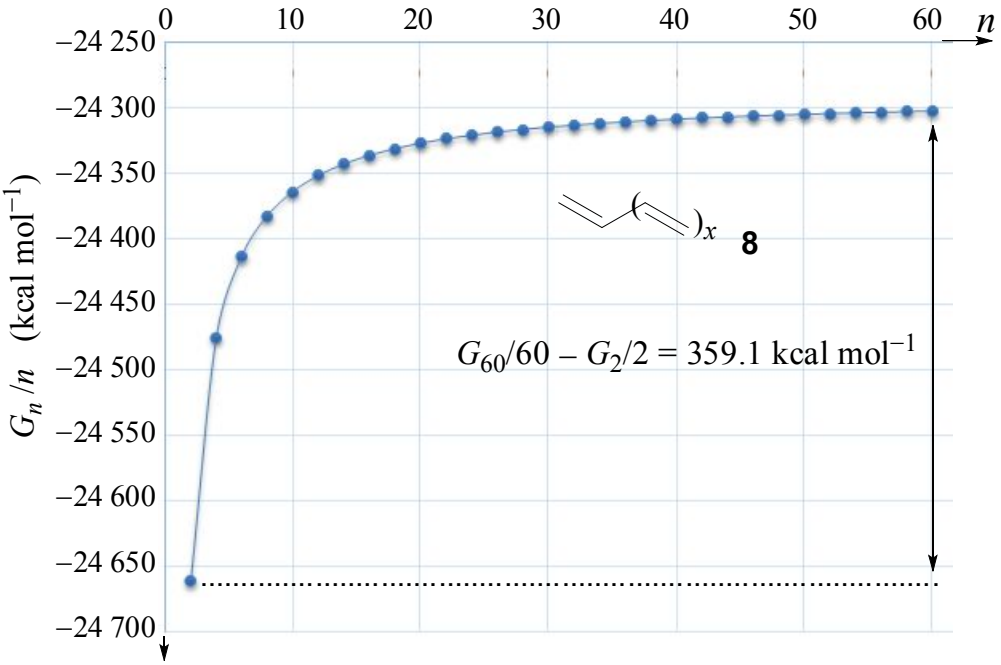


Fig. S-27. Variations of G_n /n values of linear *trans*-polyenes **8** as a function of n (n = number of carbon atoms) at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (see Table S-28).

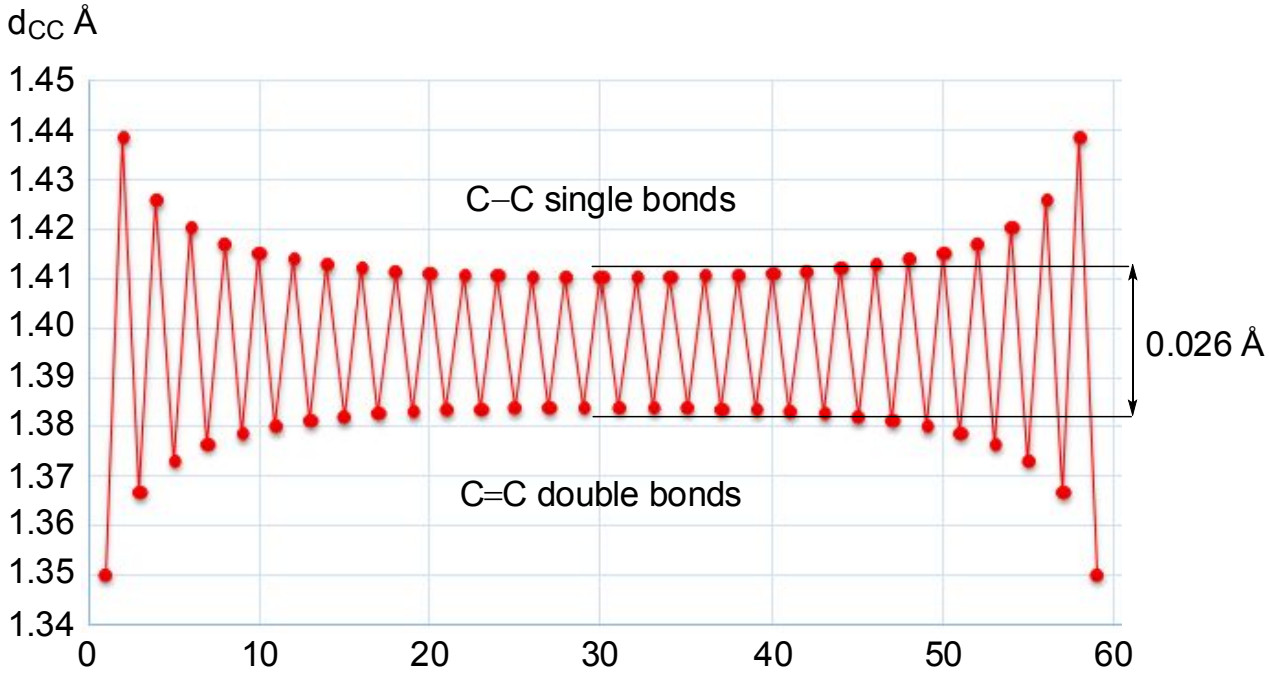


Figure S-28. Variations of the C–C bond lengths (from d(C_1)–(C_2) to d(C_{59})–(C_{60})) for the *trans*-polyene $C_{60}H_{62}$.

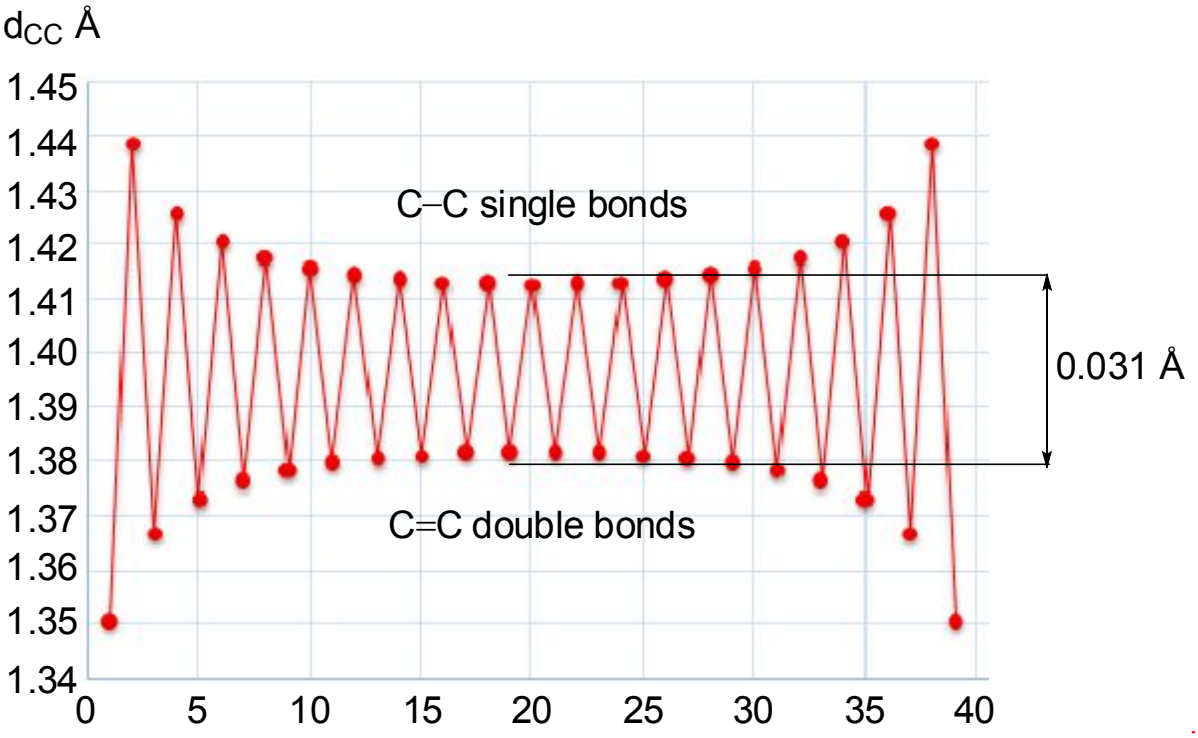


Figure S-29. Variations of the C–C bond lengths (from d(C_1)–(C_2) to d(C_{39})–(C_{40})) for the *trans*-polyene $C_{40}H_{42}$.

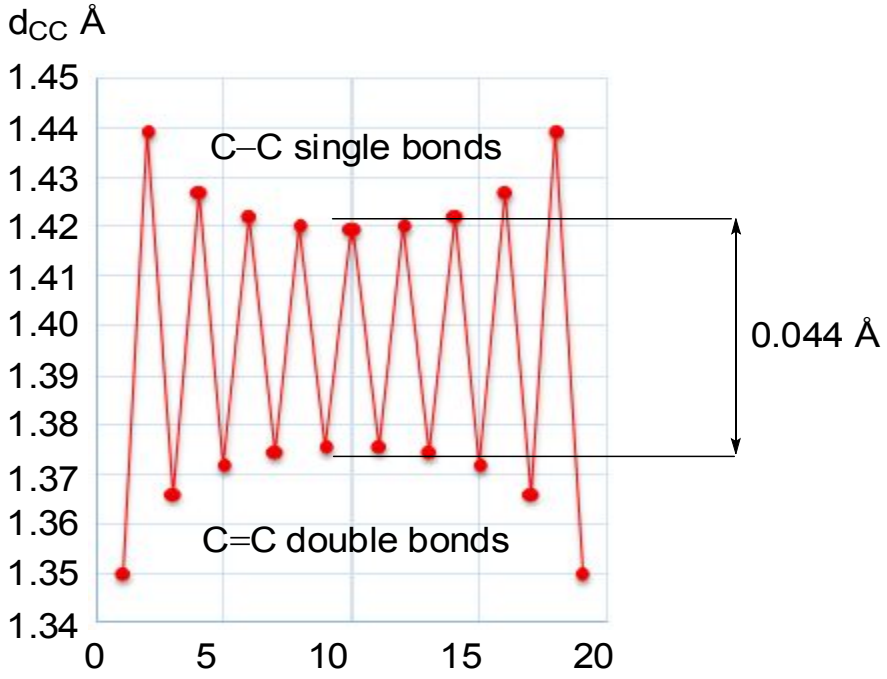
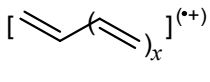


Figure S-30. Variations of the C–C bond lengths (from d(C_1)–(C_2) to d(C_{19})–(C_{20})) for the *trans*-polyene $C_{20}H_{22}$.

Table S-29. Linear *trans*-polyene radical cations **9**. Absolute free energies, G_n, at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (*n* is the number of carbon atoms per molecule, $n = x + 2$) and linear relationship (1j).



9

x	*n* =	G_n (au)	G_n (kcal mol^{-1})	$G = -24289.2725n - 537.84$ (1j) (kcal mol^{-1})	δG (kcal mol^{-1})
0	2	–78.214 321	–49 080.2295	–49 116.3905	36.16
1	4	–155.674 721	–97 687.3663	–97 694.9355	7.57
2	6	–233.109 680	–146 278.539	–14 6273.481	–5.06
3	8	–310.533 970	–194 863.016	–194 852.026	–11.0
4	10	–387.952 532	–243 443.899	–243 430.571	–13.33
5	12	–465.367 593	–292 022.586	–292 009.116	–13.47
6	14	–542.780 351	–340 599.827	–340 587.661	–12.17
7	16	–620.191 449	–389 176.026	–389 166.206	–9.82
8	18	–697.601 474	–437 751.552	–437 744.751	–6.80
9	20	–775.010 581	–486 326.502	–486 323.296	–3.21
10	22	–852.418 910	–534 900.964	–534 901.841	0.87
11	24	–929.826 693	–583 475.083	–583 480.386	5.30
12	26	–1 007.234 022	–632 048.918	–632 058.931	10.01
13	28	–1 084.641 044	–680 622.559	–680 637.476	14.92

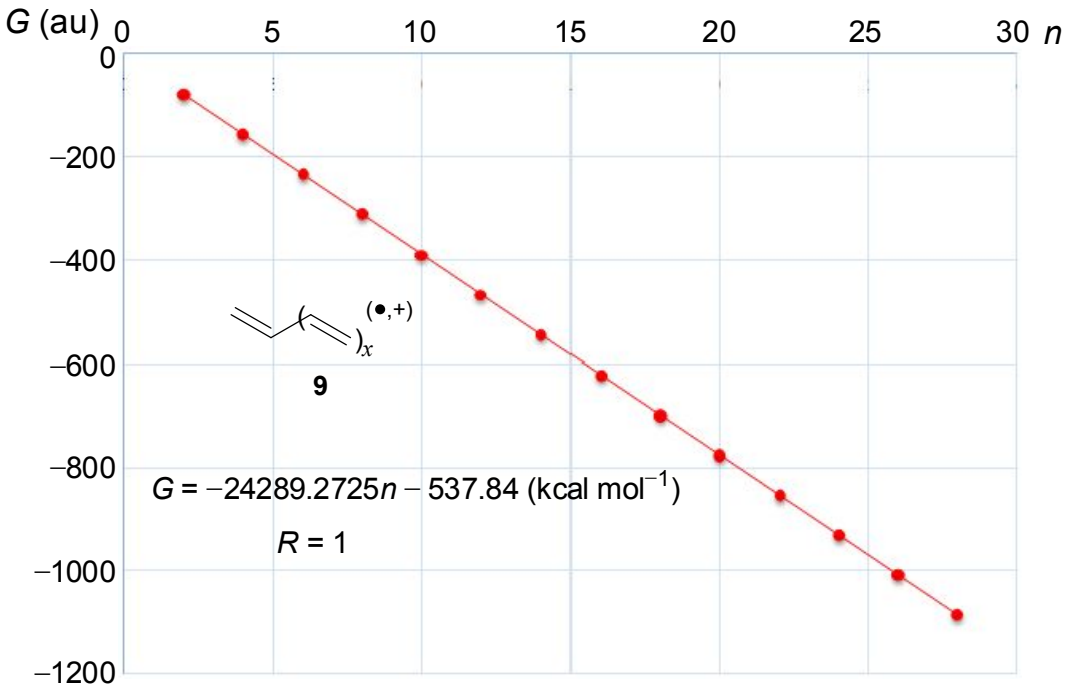
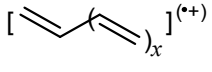


Fig. S-31. G_n values of radical cations **9** as a function of n (n = number of carbon atoms) at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (1j) (see Table S-29).

Table S-30. Linear *trans*-polyene radical cations **9**. Absolute free energies, G_n, at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (*n* is the number of carbon atoms per molecule, $n = x + 2$)



9

x	*n* =	G_n (au)	G_n/n (au)	$\delta G = G_n/n - G_{(n-2)}/(n-2)$ (kcal mol^{-1})	$\delta G_{calc} = 2\,086.7 / n^{2.164}$ (kcal mol^{-1})
0	2	–78.214 321	–39.107 160	–	–
1	4	–155.674 721	–38.918 680	118.27	100.56
2	6	–233.109 680	–38.851 613	42.08	41.82
3	8	–310.533 970	–38.816 746	21.88	22.43
4	10	–387.952 532	–38.795 253	13.49	13.84
5	12	–465.367 593	–38.780 633	9.17	9.33
6	14	–542.780 351	–38.770 025	6.66	6.68
7	16	–620.191 449	–38.761 966	5.06	5.01
8	18	–697.601 474	–38.755 637	3.97	3.88
9	20	–775.010 581	–38.750 529	3.20	3.09
10	22	–852.418 910	–38.746 314	2.64	2.51
11	24	–929.826 693	–38.742 779	2.22	2.08
12	26	–1 007.234 022	–38.739 770	1.89	1.75
13	28	– 1 084.641 044	–38.737 180	1.62	1.49

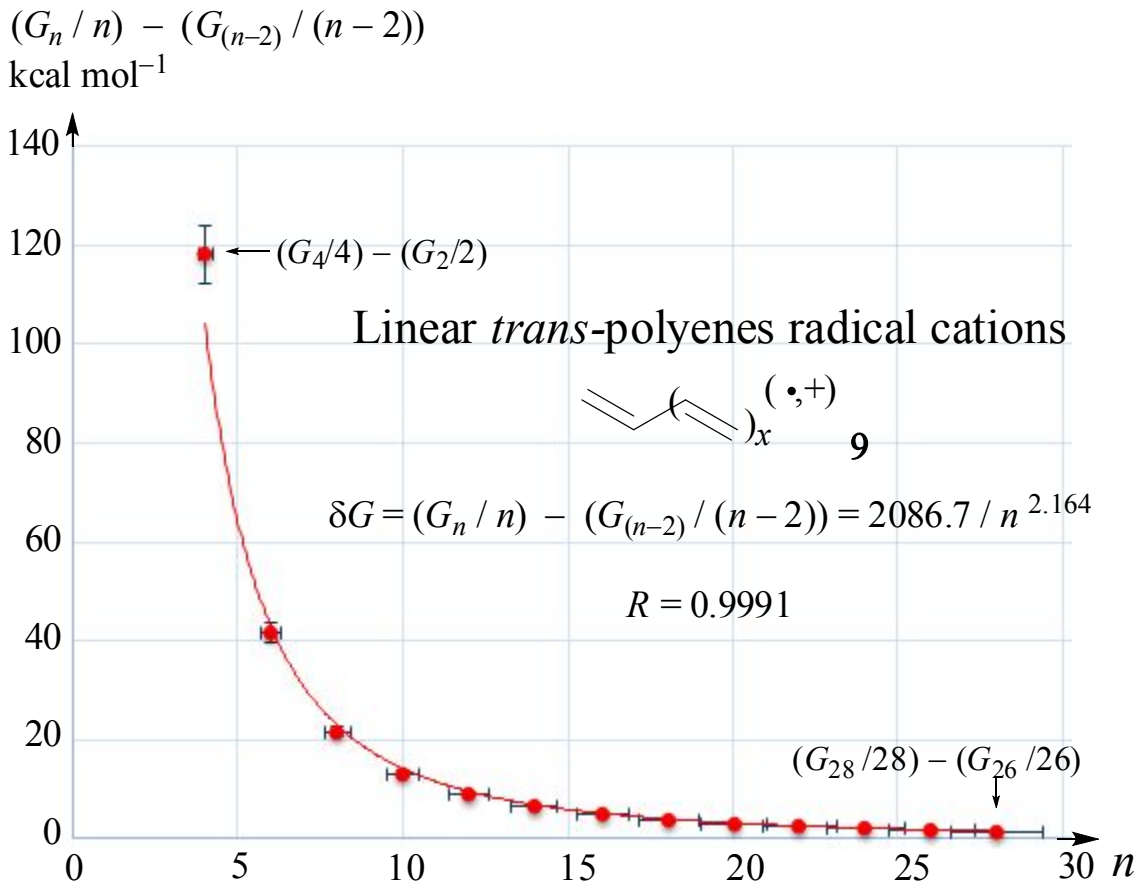
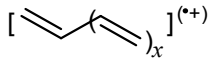


Fig. S-32. Power law (2n): variations of δ*G* values of linear *trans*-polyenes radical cations as a function of *n* (*n* = number of carbon atoms) at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (error bars given for 95% confidence interval) (see Table S-30).

Table S-31. Linear *trans*-polyene radical cations **9**. Absolute free energies, G_n, at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (n is the number of carbon atoms per molecule, $n = x + 2$) and linear relationship (1k).



9

x	n	G_n (au)	G_n (kcal mol^{-1})	$G = 24290.847652n - 564.61$ (1k) (kcal mol^{-1})	δG (kcal mol^{-1})
0	2	–78.224 891	–49 086.86	–49 146.31	59.45
1	4	–155.695 786	–97 700.58	–97 728.00	27.42
2	6	–233.141 426	–146 298.4597	–146 309.7	11.24
3	8	–310.576 649	–194 889.7977	–194 891.396	1.60
4	10	–388.006 263	–243 477.6161	–243 473.091	–4.52
5	12	–465.432 482	–292 063.3041	–292 054.787	–8.52
6	14	–542.856 443	–340 647.5751	–340 636.482	–11.09
7	16	–620.278 822	–389 230.8535	–389 218.177	–12.68
8	18	–697.700 203	–437 813.5055	–437 799.873	–13.63
9	20	–775.120 524	–486 395.4925	–486 381.568	–13.92
10	22	–852.540 330	–534 977.1562	–534 963.264	–13.89
11	24	–929.959 500	–583 558.4209	–583 544.959	–13.46
12	26	–1 007.376 315	–632 138.2077	–632 126.654	–11.55
13	28	–1 084.796 546	–680 720.1382	–680 708.35	–11.79
14	30	–1 162.215 644	–729 301.3577	–729 290.045	–11.31
15	32	–1 239.633 783	–777 881.9754	–777 871.741	–10.23
16	34	–1 317.051 575	–826 462.3753	–826 453.436	–8.94
17	36	–1 394.469 151	–875 042.6397	–875 035.131	–7.51
18	38	–1 471.886 544	–923 622.7893	–923 616.827	–5.96
19	40	–1 549.303 848	–972 202.883	–972 198.522	–4.36
20	42	–1 626.720 973	–1 020 782.864	–1 020 780.22	–2.65
21	44	–1 704.138 081	–1 069 362.835	–1 069 361.91	–0.92
22	46	–1 781.555 114	–1 117 942.759	–1 117 943.61	0.85
23	48	–1 858.972 203	–1 166 522.718	–1 166 525.3	2.59
24	50	–1 936.389 076	–1 215 102.541	–1 215 107.00	4.46
25	52	–2 013.808 390	–1 263 683.896	–1 263 688.69	4.80
26	54	–2 091.221 918	–1 312 261.62	–1 312 270.39	8.77

27	56	–2 168.634 949	–1360 839.033	–1 360 852.09	13.05
28	58	–2 246.050 710	–1 409 418.158	–1 409 433.78	15.62
29	60	–2 323.468 125	–1 457 998.321	–1 458 015.48	17.15

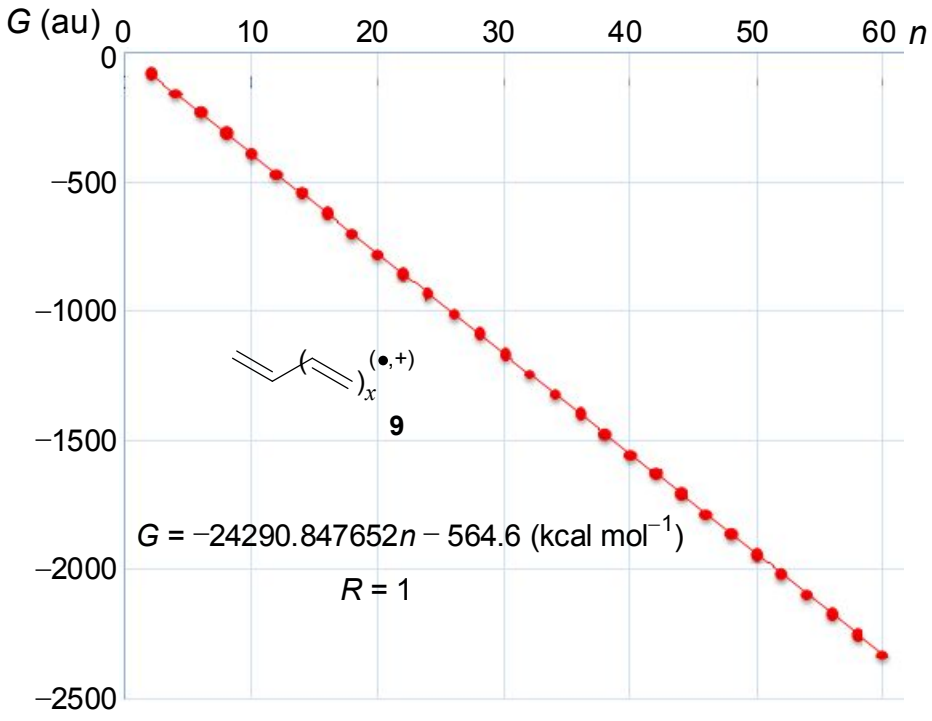


Fig. S-33. G_n values of linear *trans*-radical cations **9** as a function of n (n = number of carbon atoms) at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (1k) (see Table S-31).

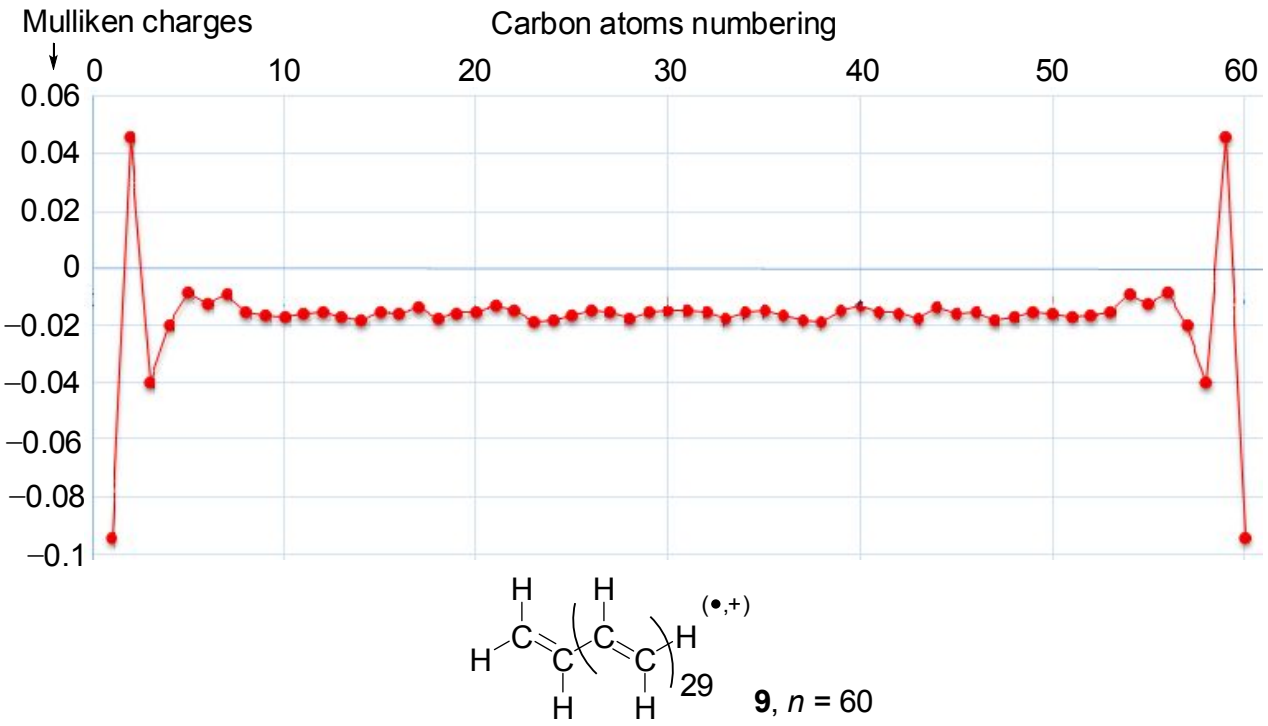


Fig. S-34. Mulliken charges of linear *trans*-radical cations **9** (n = 60) as a function of the numbering of carbon atoms at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (see Table S-31).

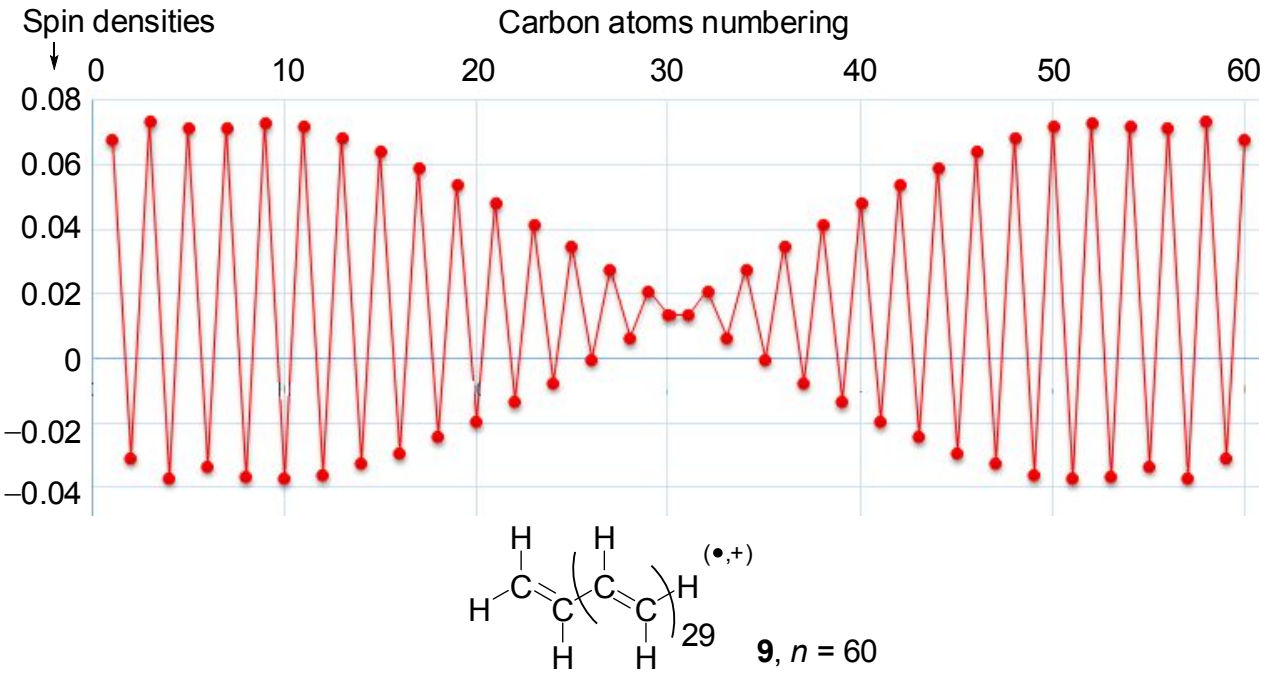
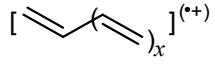


Fig. S-35. Spin densities of linear *trans*-radical cations **9** (n = 60) as a function of the numbering of carbon atoms at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (see Table S-31).

Table S-32. Linear *trans*-polyene radical cations **9**. Absolute free energies, G_n, at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (n is the number of carbon atoms per molecule, $n = x + 2$)



9

x	n	G_n (au)	G_n/n (au)	G_n/n (kcal mol^{-1})	$\delta G = G_n/n - G_{(n-2)}/(n-2)$ (kcal mol^{-1})	$\delta G_{calc} = 1718.5 / n^{2.084}$ (kcal mol^{-1})
0	2	–78.224 891	–39.112 445	–24 543.43	–	–
1	4	–155.695 786	–38.923 946	–24 425.15	118.28	95.60
2	6	–233.141 426	–38.856 904	–24 383.08	42.07	41.07
3	8	–310.576 649	–38.822 081	–24 361.22	21.85	22.55
4	10	–388.006 263	–38.800 626	–24 347.76	13.46	14.16
5	12	–465.432 482	–38.786 040	–24 338.61	9.15	9.69
6	14	–542.856 443	–38.775 460	–24 331.97	6.64	7.02
7	16	–620.278 822	–38.767 426	–24 326.93	5.04	5.32
8	18	–697.700 203	–38.761 122	–24 322.97	3.96	4.16
9	20	–775.120 524	–38.756 026	–24 319.77	3.20	3.34
10	22	–852.540 330	–38.751 833	–24 317.14	2.63	2.74
11	24	–929.959 500	–38.748 312	–24 314.93	2.21	2.28
12	26	–1 007.376 315	–38.745 243	–24 313.01	1.93	1.93
13	28	–1 084.796 546	–38.742 734	–24 311.43	1.57	1.66
14	30	–1 162.215 644	–38.740 521	–24 310.04	1.39	1.43
15	32	–1 239.633 783	–38.738 556	–24 308.81	1.23	1.25
16	34	–1 317.051 575	–38.736 811	–24 307.72	1.09	1.11
17	36	–1 394.469 151	–38.735 254	–24 306.74	0.98	0.98
18	38	–1 471.886 544	–38.733 856	–24 305.86	0.88	0.88
19	40	–1 549.303 848	–38.732 596	–24 305.07	0.79	0.79
20	42	–1 626.720 973	–38.731 452	–24 304.35	0.72	0.71
21	44	–1 704.138 081	–38.730 411	–24 303.70	0.65	0.65
22	46	–1 781.555 114	–38.729 459	–24 303.10	0.60	0.59
23	48	–1 858.972 203	–38.728 586	–24 302.56	0.51	0.54
24	50	–1 936.389 076	–38.727 781	–24 302.05	0.50	0.49
25	52	–2 013.808 390	–38.727 084	–24 301.61	0.50	0.46
26	54	–2 091.221 918	–38.726 332	–24 301.14	0.44	0.42

27	56	–2 168.634 949	–38.725 624	–24 300.70	0.44	0.39
28	58	–2 246.050 710	–38.725 012	–24 300.32	0.38	0.36
29	60	–2 323.468 125	–38.724 469	–24 299.97	0.34	0.34

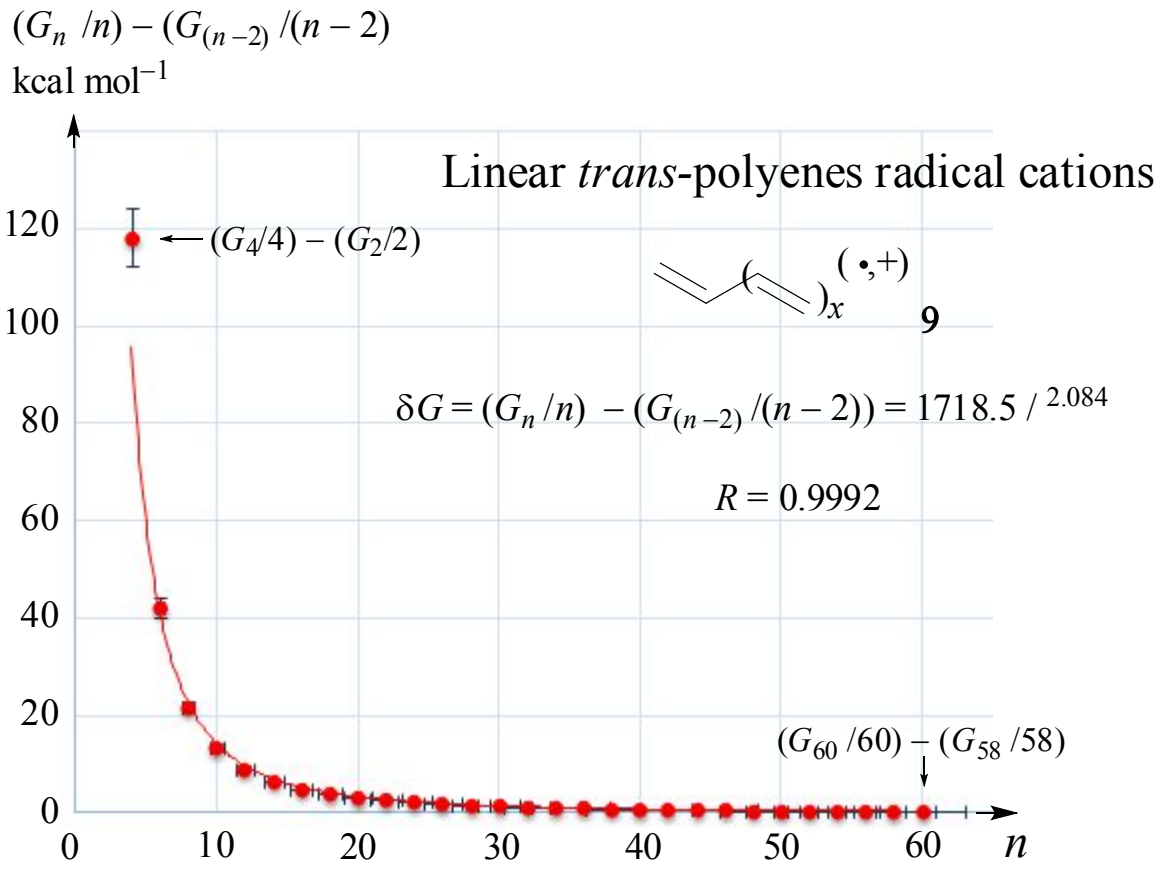


Fig. S-36. Power law (2o): variations of δ*G* values of linear *trans*-polyenes radical cations as a function of *n* (*n* = number of carbon atoms) at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (error bars given for 95% confidence interval) (see Table S-32).

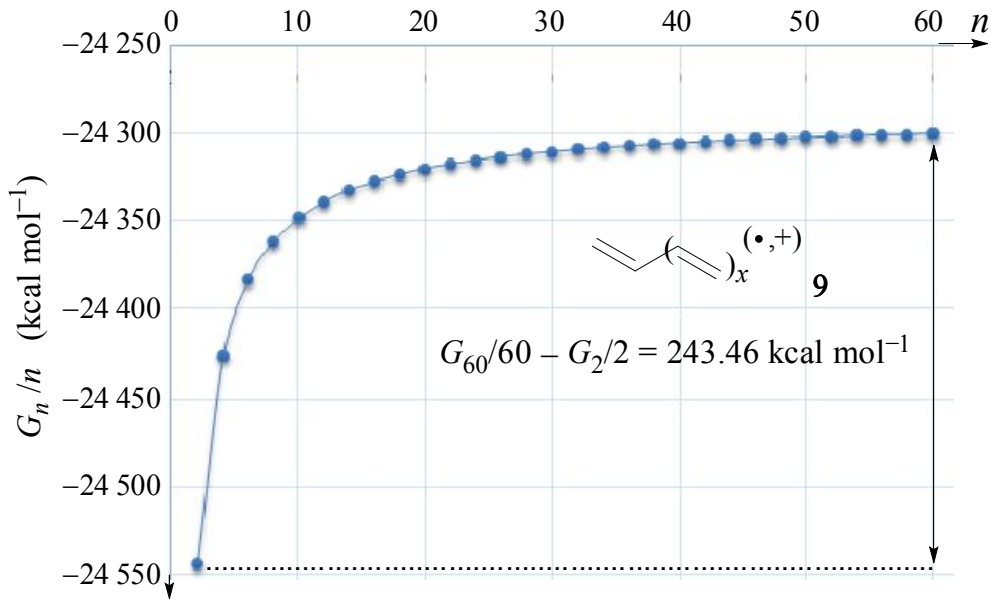
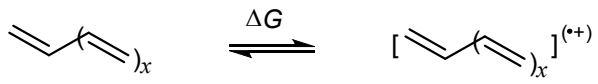


Fig. S-37. Variations of G_n /n values of linear *trans*-polyenes radical cations **9** as a function of n (n = number of carbon atoms) at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (see Table S-32).

Table S-33. Differences between values of absolute free energies, G_n, of *trans*-polyenes **8** and those of the corresponding *trans*-polyene radical cations **9** at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas.



8 **9**

x	$n = x + 2$	**8** G_n (au)	**9** G_n (au)	ΔG_{calc} (kcal mol^{-1})
0	2	–78.599 411	–78.224 891	235.015
1	4	–156.011 135	–155.695 786	197.88
2	6	–233.424 857	–233.141 426	177.85
3	8	–310.839 403	–310.576 649	164.88
4	10	–388.254 327	–388.006 263	155.66
5	12	–465.669 462	–465.432 482	148.71
6	14	–543.084 699	–542.856 443	143.23
7	16	–620.499 999	–620.278 822	138.79
8	18	–697.915 301	–697.700 203	134.98
9	20	–775.330 845	–775.120 524	131.98
10	22	–852.746 429	–852.540 330	129.33
11	24	–930.161 914	–929.959 500	127.02
12	26	–1 007.577 379	–1 007.376 315	126.17
13	28	–1 084.992 990	–1 084.796 546	123.27
14	30	–1 162.409 426	–1 162.215 644	121.60
15	32	–1 239.825 225	–1 239.633 783	120.13
16	34	–1 317.240 938	–1 317.051 575	118.83
17	36	–1 394.655 601	–1 394.469 151	117.00
18	38	–1 472.072 249	–1 471.886 544	116.53
19	40	–1 549.487 922	–1 549.303 848	115.51
20	42	–1 626.903 557	–1 626.720 973	114.57
21	44	–1 704.319 302	–1 704.138 081	113.72
22	46	–1 781.735 016	–1 781.552 097	113.46
23	48	–1 859.150 840	–1 858.972 203	112.10
24	50	–1 936.566 475	–1 936.389 076	111.32
25	52	–2 013.982 169	–2 013.808 390	109.05

26	54	–2 091.397 870	–2 091.221 918	110.41
27	56	–2 168.813 548	–2 168.634 908	112.10
28	58	–2 246.229 346	–2 246.050 710	112.09
29	60	–2 323.645 203	–2 323.468 125	111.12

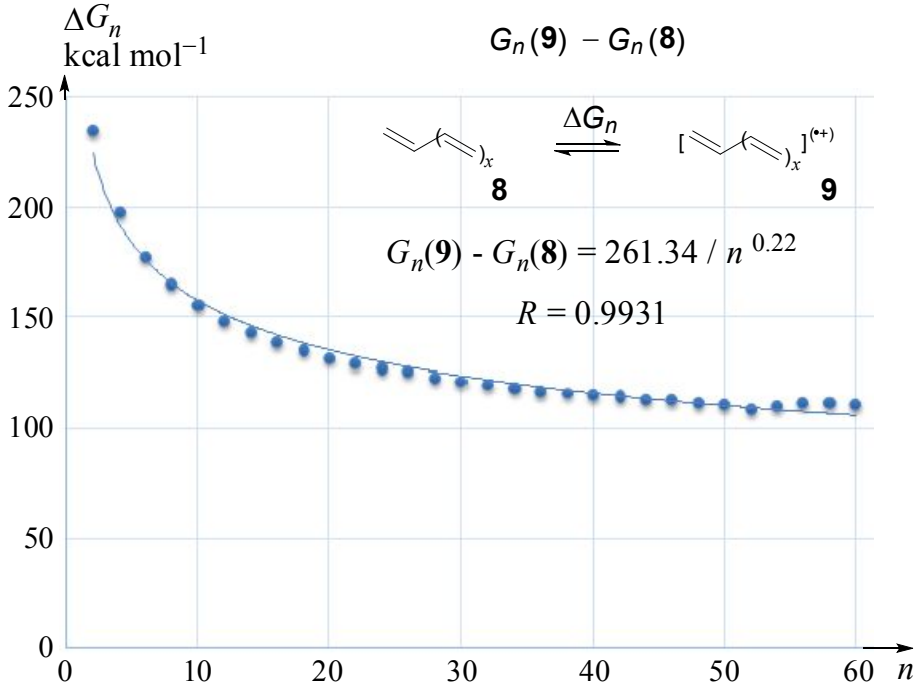
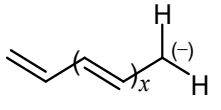


Fig. S-38. Power law (2p): differences between δ*G* values of linear *trans*-polyenes and those of the corresponding of linear *trans*-polyene radical cations as a function of *n* (*n* = number of carbon atoms) at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (see Table S-33).

Table S-34. Linear odd *trans*-polyene anions **10**. Absolute free energies, G_n, at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (*n* is the number of carbon atoms per molecule, $n = 2x + 3$) and linear relationship (1l).



10

x	*n*	G_n (au)	G_n (kcal mol^{-1})	$G = -24287.67787\ n - 752.4$ (1l) (kcal mol^{-1})	δG (kcal mol^{-1})
0	3	–117.285 436	–73 597.7253	–73 615.40	17.67
1	5	–194.712 977	–122 184.243	–122 190.76	6.52
2	7	–272.133 135	–170 766.127	–170 766.11	–0.02
3	9	–349.548 987	–219 345.31	–219 341.47	–3.84
4	11	–426.962 106	–267 922.778	–267 916.83	–5.95
5	13	–504.373 348	–316 499.067	–316 492.18	–6.89
6	15	–581.783 222	–365 074.499	–365 067.54	–6.96
7	17	–659.192 136	–413 649.328	–413 642.89	–6.44
8	19	–736.600 334	–462 223.707	–462 218.25	–5.46
9	21	–814.008 016	–510 797.763	–510 793.60	–4.16
10	23	–891.415 198	–559 371.505	–559 368.96	–2.54
11	25	–968.822031	–607 945.028	–607 944.32	–0.70
12	27	–1 046.228 536	–656 518.346	–656 519.67	1.32
13	29	–1 123.634 865	–705 091.552	–705 095.03	3.48
14	31	–1 201.040 990	–753 664.631	–753 670.38	5.75
15	33	–1 278.446 900	–802 237.575	–802 245.74	8.16

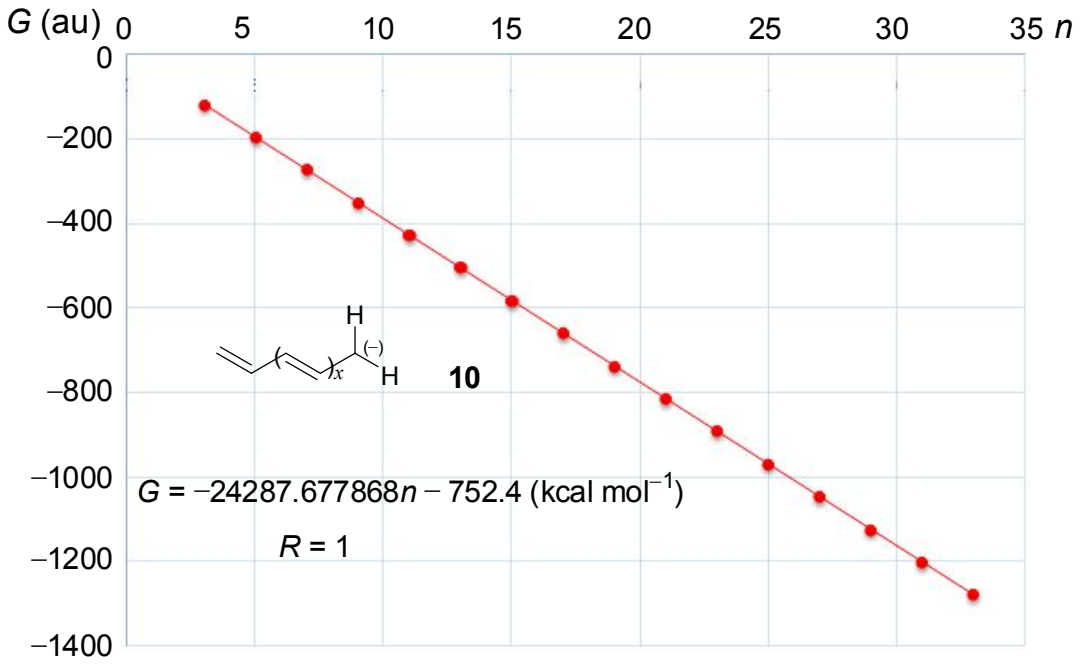
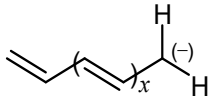


Fig. S-39. G_n values of linear odd *trans*-polyene anions **10** as a function of n (n = number of carbon atoms) at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (1l) (see Table S-34).

Table S-35. Linear odd *trans*-polyene anions **10**. Absolute free energies, G_n, at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (n is the number of carbon atoms per molecule, $n = 2x + 3$).



10

x	n	G_n (au)	G_n/n (au)	$\delta G = G_n/n - G_{(n-2)}/(n-2)$ (kcal mol^{-1})	$\delta G_{calc} = 2790 / n^{2.159}$ (kcal mol^{-1})
0	3	–117.285 436	–39.095 145	–	–
1	5	–194.712 977	–38.942 595	95.73	86.40
2	7	–272.133 135	–38.876 162	41.69	41.79
3	9	–349.548 987	–38.838 776	23.46	24.29
4	11	–426.962 106	–38.814 739	15.08	15.75
5	13	–504.373 348	–38.797 950	10.53	10.98
6	15	–581.783 222	–38.785 548	7.78	8.06
7	17	–659.192 136	–38.776 008	5.99	6.15
8	19	–736.600 334	–38.768 439	4.75	4.84
9	21	–814.008 016	–38.762 286	3.86	3.90
10	23	–891.415 198	–38.757 183	3.20	3.20
11	25	–968.822031	–38.752 881	2.70	2.67
12	27	–1 046.228 536	–38.749 205	2.31	2.27
13	29	–1 123.634 865	–38.746 030	1.99	1.94
14	31	–1 201.040 990	–38.743 258	1.74	1.68
15	33	–1 278.446 900	–38.740 815	1.53	1.47

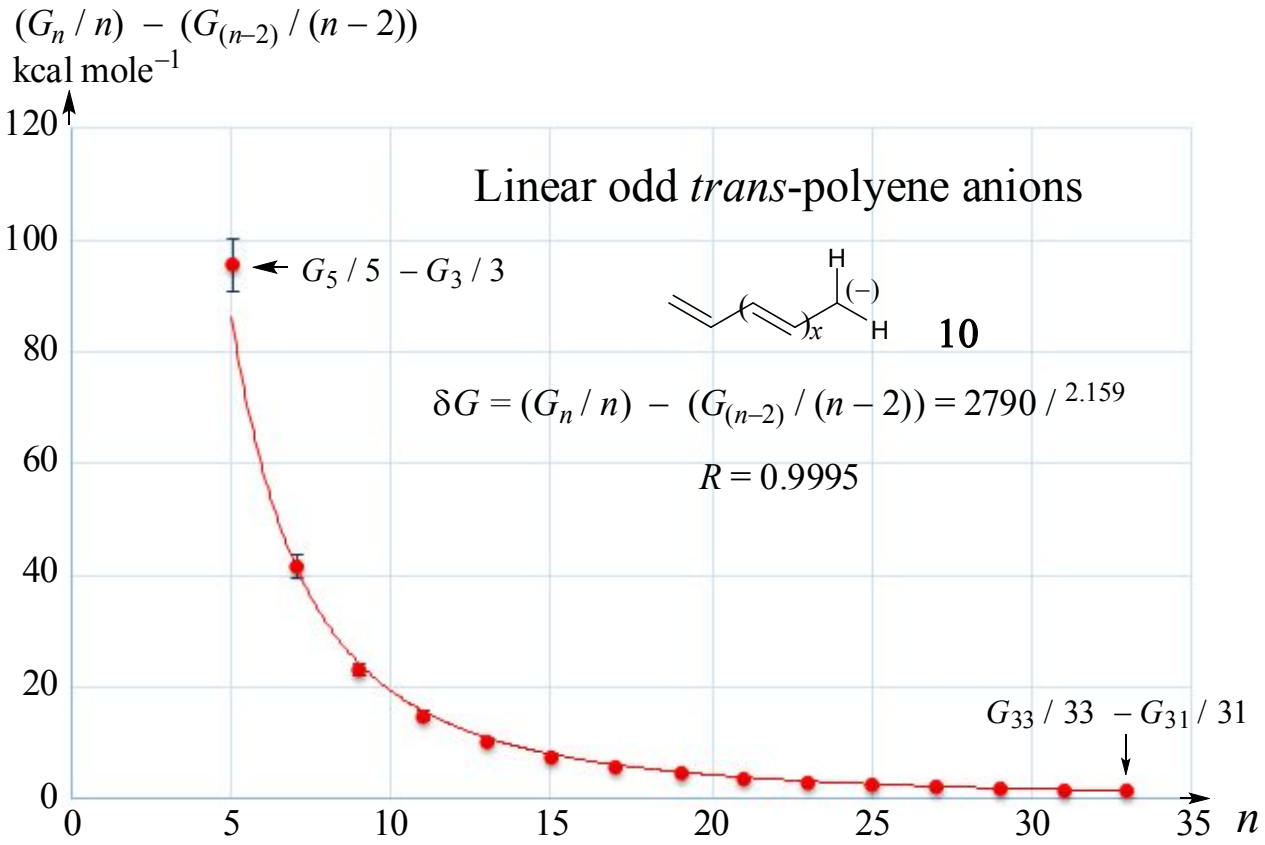
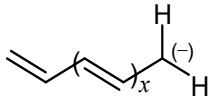


Fig. S-40. Power law (2q): variations of δ*G* values of linear odd *trans*-polyene anions as a function of *n* (*n* = number of carbon atoms) at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (error bars given for 95% confidence interval) (see Table S-35).

Table S-36. Linear odd *trans*-polyene anions **10**. Absolute energies, E_n, at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (n is the number of carbon atoms per molecule, $n = 2x + 3$).



10

x	n	E_n (au)	E_n/n (au)	$\delta E = G_n/n - G_{(n-2)}/(n-2)$ (kcal mol^{-1})	$\delta E_{calc} = 2\,717.8 / n^{2.15}$ (kcal mol^{-1})
0	3	–117.324 016	–39.108 005	–	–
1	5	–194.782 144	–38.956 429	95.11	85.40
2	7	–272.232 562	–38.890 366	41.46	41.42
3	9	–349.678 675	–38.853 186	23.33	24.13
4	11	–427.122 041	–38.829 276	15.00	15.67
5	13	–504.563 553	–38.812 581	10.48	10.94
6	15	–582.003 731	–38.800 249	7.74	8.04
7	17	–659.442 927	–38.790 760	5.95	6.14
8	19	–736.881 366	–38.783 230	4.73	4.84
9	21	–814.319 200	–38.777 105	3.84	3.90
10	23	–891.756 573	–38.772 025	3.19	3.20
11	25	–969.193 568	–38.767 743	2.69	2.68
12	27	–1 046.630 247	–38.764 083	2.30	2.27
13	29	–1 124.066 648	–38.760 919	1.98	1.95
14	31	–1 201.502 809	–38.758 155	1.73	1.69
15	33	–1 278.938 808	–38.755 721	1.53	1.48
16	35	–1 356.374 623	–38.753 561	1.36	1.30

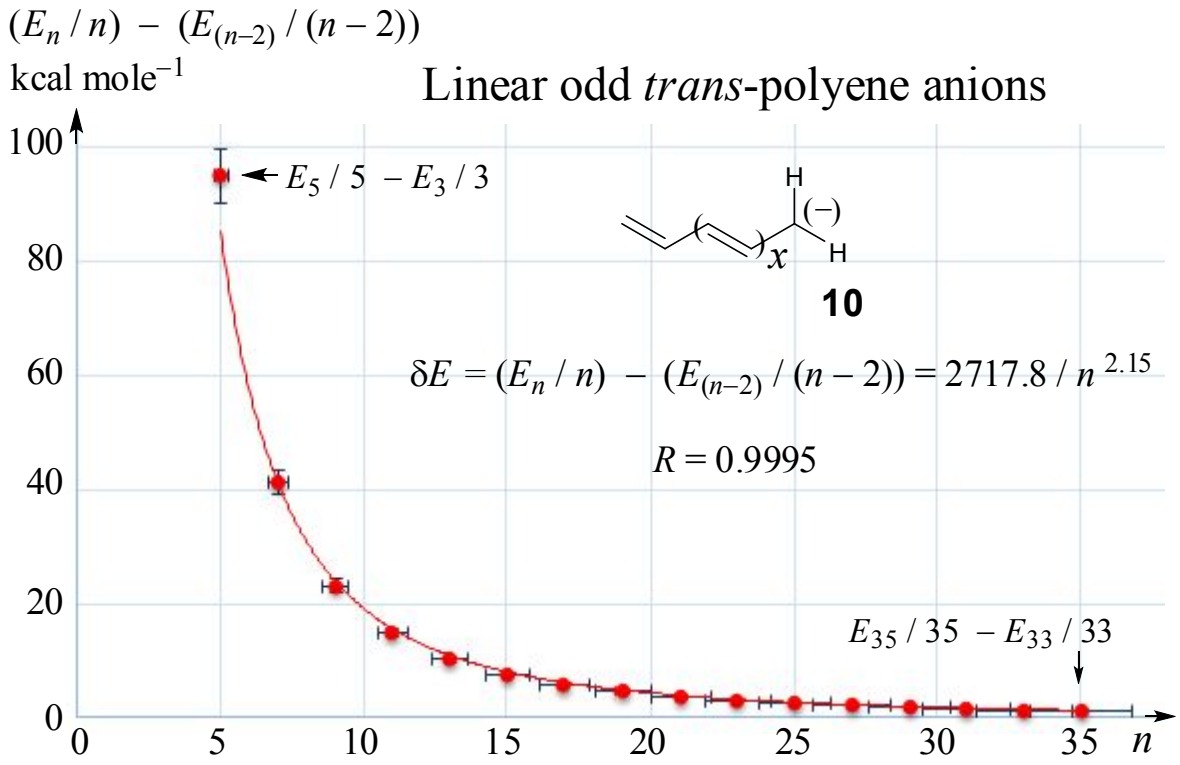
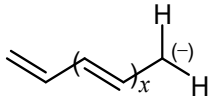


Fig. S-41. Power law (2r): variations of δ*E* values of linear odd *trans*-polyene anions **10** as a function of *n* (*n* = number of carbon atoms) at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (error bars given for 95% confidence interval) (see Table S-36).

Table S-37. Linear odd *trans*-polyene anions **10**. Absolute energies, E_n, at the HF/6-311++G(3df,3pd) level of theory in ideal gas (n is the number of carbon atoms per molecule, $n = 2x + 3$).



10

x	n	G_n (au)	G_n/n (au)	$\delta G = G_n/n - G_{(n-1)}/(n-1)$ (kcal mol^{-1})	$\delta G_{calc} = 2\,574.6 / n^{2.155}$ (kcal mol^{-1})
0	3	–116.465 393	–38.821 798	–	–
1	5	–193.401 280	–38.680 256	88.82	80.25
2	7	–270.329 203	–38.618 457	38.78	38.86
3	9	–347.252 729	–38.583 636	21.85	22.61
4	11	–424.173 473	–38.561 225	14.06	14.67
5	13	–501.092 374	–38.545 567	9.83	10.24
6	15	–578.009 972	–38.533 998	7.26	7.52
7	17	–654.926 642	–38.525 097	5.58	5.74
8	19	–731.842 618	–38.518 032	4.43	4.52
9	21	–808.758 072	–38.512 289	3.60	3.64
10	23	–885.673 137	–38.507 528	2.99	2.99
11	25	–962.587 922	–38.503 517	2.52	2.50
12	27	–1 039.502 473	–38.500 092	2.15	2.12
13	29	–1 116.416 808	–38.497 131	1.86	1.82
14	31	–1 193.331 084	–38.494 551	1.58	1.57
15	33	–1 270.242 586	–38.492 200	1.48	1.37
16	35	–1 347.159 306	–38.490 266	1.21	1.21

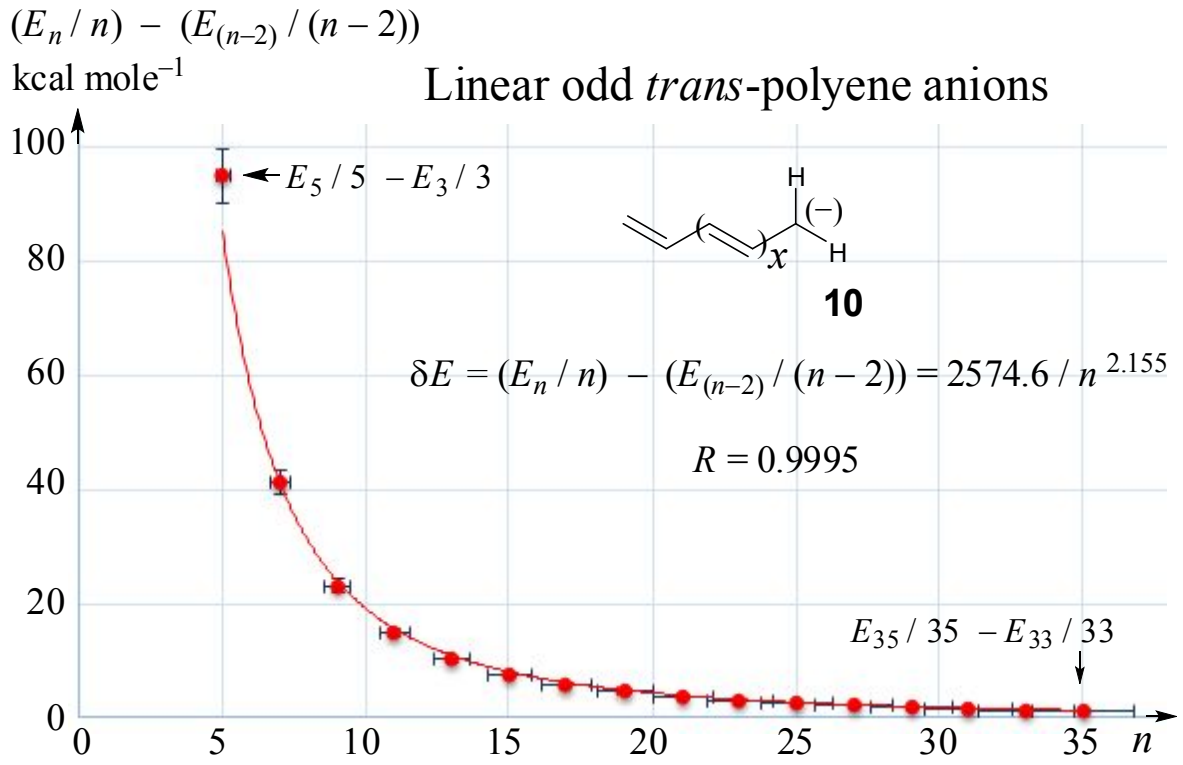
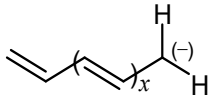


Fig. S-42. Power law (2s): variations of δ*G* values of linear odd *trans*-polyene anions **10** as a function of *n* (*n* = number of carbon atoms) at the HF/6-311++G(3df,3pd) level of theory in ideal gas (error bars given for 95% confidence interval) (see Table S-37).

Table S-38. Linear odd *trans*-polyene anions **10**. Absolute free energies, G_n, at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (n is the number of carbon atoms per molecule, $n = 2x + 3$) and linear relationship (1m).



10

x	n	G_n (au)	G_n (kcal mol^{-1})	$G = -24290.329880n - 765.49$ (1m) (kcal mol^{-1})	δG (kcal mol^{-1})
0	3	–117.293 738	–73 602.9349	–	–
1	5	–194.732 190	–122 196.30	–122 217.14	20.84
2	7	–272.164 590	–170 785.866	–170 797.8	11.93
3	9	–349.591 953	–219 372.272	–219 378.46	6.19
4	11	–427.016 705	–267 957.039	–267 959.12	2.08
5	13	–504.439 573	–316 540.624	–316 539.78	–0.84
6	15	–581.861 159	–365 123.405	–365 120.44	–2.96
7	17	–659.281 786	–413 705.584	–413 701.1	–4.48
8	19	–736.701 728	–462 287.333	–462 281.76	–5.57
9	21	–814.121 171	–510 868.769	–510 862.42	–6.35
10	23	–891.540 327	–559 450.025	–559 443.08	–6.94
11	25	–968.959 282	–608 031.155	–608 023.74	–7.41
12	27	–1 046.373 544	–656 609.339	–656 604.40	–4.94
13	29	–1 123.791 344	–705 189.744	–705 185.06	–4.68
14	31	–1 201.208 921	–753 770.009	–753 765.71	–4.30
15	33	–1 278.626 384	–802 350.203	–802 346.37	–3.83
16	35	–1 356.043 827	–850 930.384	–850 927.03	–3.35
17	37	–1 433.464 542	–899 512.618	–899 507.69	–4.93
18	39	–1 510.882 713	–948 093.256	–948 088.35	–4.90
19	41	–1 588.297 786	–996 671.95	–996 669.01	–2.94
20	43	–1 665.714 487	–1 045251.66	–1 045 249.67	–1.99
21	45	–1 743.128 549	–1 093 829.72	–1 093 830.33	0.60
22	47	–1 820.547 999	–1 142 411.16	–1 142 411.00	–0.16
23	49	–1 897.964 572	–1 190 990.80	–1190 991.65	0.85
24	51	–1 975.381 061	–1 239 570.38	–1 239 572.31	1.93
25	53	–2 052.797 664	–1 288 150.04	–1 288 152.97	2.93

26	55	–2 130.213 986	–1 336 729.51	–1 336 733.63	4.11
27	57	–2 207.630 352	–1 385 309.02	–1 385 314.29	5.27
28	59	–2 285.046 755	–1 433 888.55	–1 433 894.95	6.40
29	61	–2 362.463 270	–1 482 468.15	–1 482 475.61	7.46

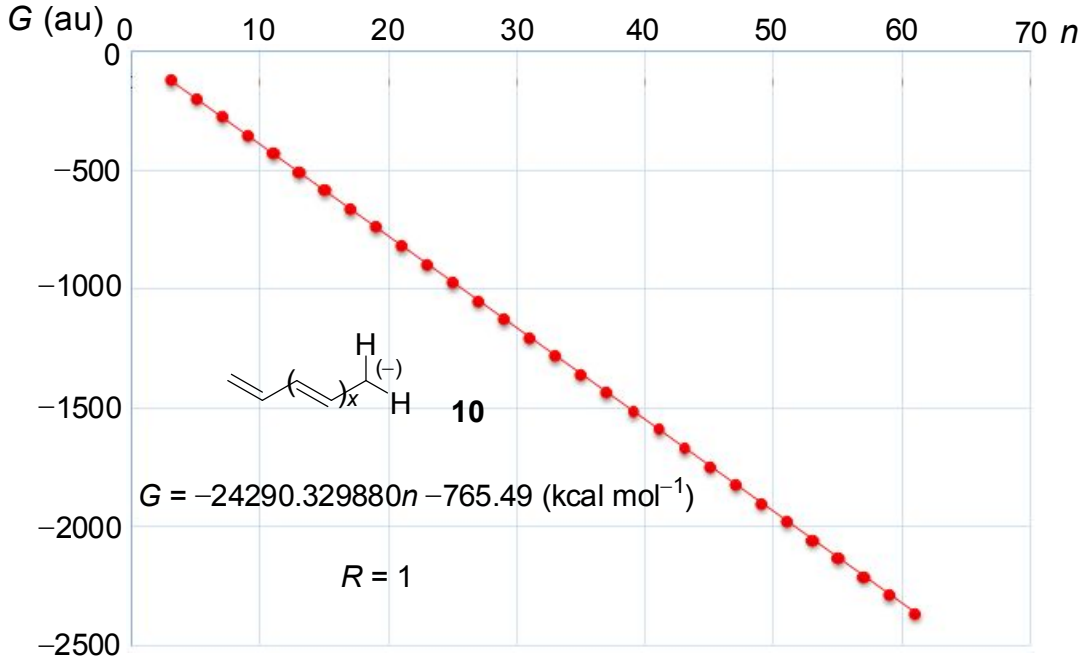
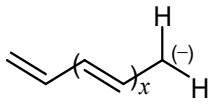


Fig. S-43. G_n values of linear odd *trans*-polyene anions **10** as a function of n (n = number of carbon atoms) at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (1m) (see Table S-38).

Table S-39. Linear odd *trans*-polyene anions **10**. Absolute free energies, G_n, at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (n is the number of carbon atoms per molecule, $n = 2x + 3$).



10

x	n	G_n (au)	G_n/n (au)	G_n/n (kcal mol^{-1})	$\delta G = G_n/n - G_{(n-2)}/(n-2)$ (kcal mol^{-1})	$\delta G_{calc} = 2353.6 / n^{2.097}$ (kcal mol^{-1})
0	3	–117.293 738	–39.097 913	–24 534.31	–	–
1	5	–194.732 190	–38.946 438	–24 439.26	95.05	80.54
2	7	–272.164 590	–38.880 656	–24 397.98	38.00	39.77
3	9	–349.591 953	–38.843 550	–24 374.70	23.28	23.48
4	11	–427.016 705	–38.819 700	–24 359.73	14.97	15.41
5	13	–504.439 573	–38.803 044	–24 349.28	10.45	10.86
6	15	–581.861 159	–38.790 744	–24 341.56	7.72	8.04
7	17	–659.281 786	–38.781 281	–24 335.62	5.94	6.19
8	19	–736.701 728	–38.773 775	–24 330.91	4.71	4.90
9	21	–814.121 171	–38.767 675	–24 327.08	3.83	3.97
10	23	–891.540 327	–38.762 623	–24 323.91	3.17	3.28
11	25	–968.959 282	–38.758 371	–24 321.25	2.67	2.76
12	27	–1 046.373 544	–38.754 576	–24 318.86	2.38	2.35
13	29	–1 123.791 344	–38.751 426	–24 316.89	1.98	2.02
14	31	–1 201.208 921	–38.748 675	–24 315.16	1.73	1.76
15	33	–1 278.626 384	–38.746 254	–24 313.64	1.52	1.54
16	35	–1 356.043 827	–38.744 109	–24 312.30	1.35	1.36
17	37	–1 433.464 542	–38.742 285	–24 311.15	1.14	1.21
18	39	–1 510.882 713	–38.740 582	–24 310.08	1.07	1.08
19	41	–1 588.297 786	–38.738 970	–24 309.07	1.01	0.98
20	43	–1 665.714 487	–38.737 546	–24 308.18	0.89	0.88
21	45	–1 743.128 549	–38.736 190	–24 307.33	0.85	0.80
22	47	–1 820.547 999	–38.735 064	–24 306.62	0.71	0.73
23	49	–1 897.964 572	–38.733 971	–24 305.93	0.69	0.67
24	51	–1 975.381 061	–38.732 962	–24 305.30	0.63	0.62
25	53	–2 052.797 664	–38.732 031	–24 304.72	0.58	0.57
26	55	–2 130.213 986	–38.731 163	–24 304.17	0.54	0.53

27	57	–2 207.630 352	–38.730 357	–24 303.67	0.51	0.49
28	59	–2 285.046 755	–38.729 606	–24 303.20	0.47	0.45
29	61	–2 362.463 270	–38.728 906	–24 302.76	0.44	0.42

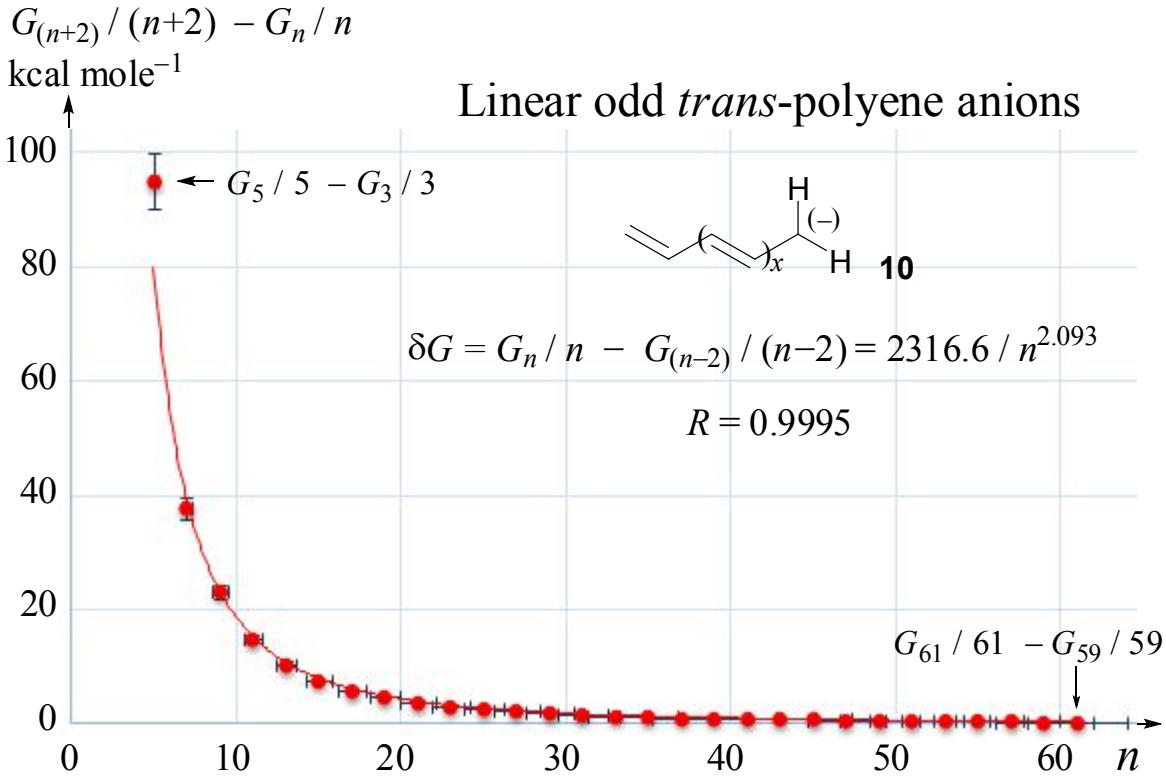


Fig. S-44. Power law (2t): variations of δ*G* values of linear odd *trans*-polyene anions **10** as a function of *n* (*n* = number of carbon atoms) at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (error bars given for 95% confidence interval) (see Table S-39).

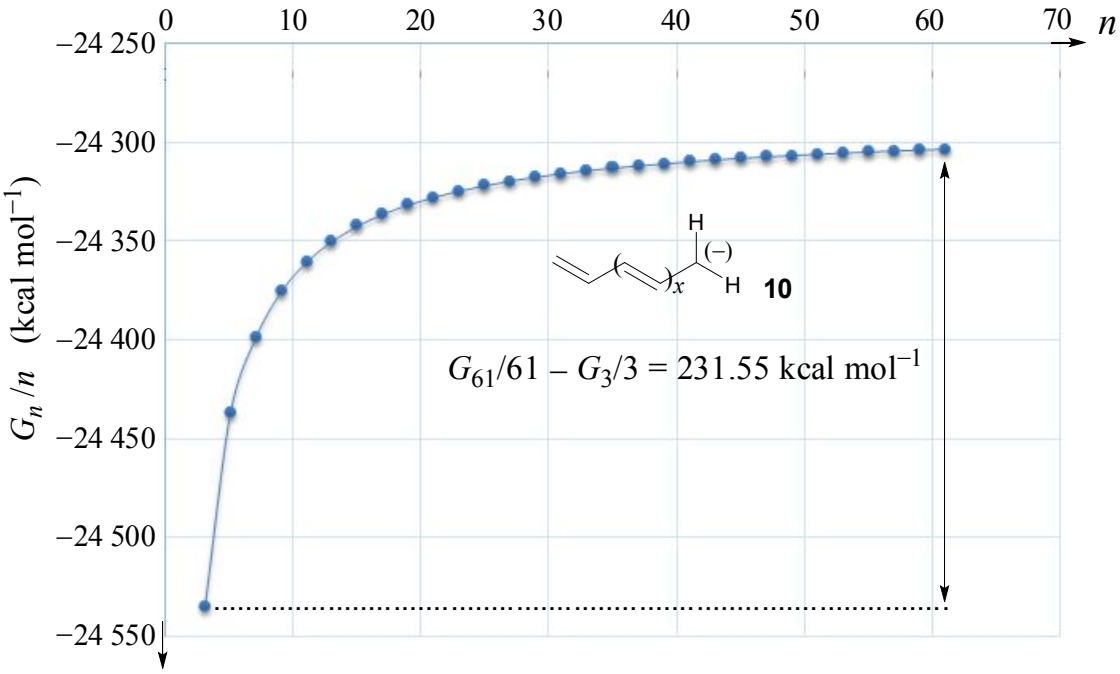
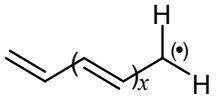


Fig. S-45. Variations of G_n/n values of linear odd *trans*-polyene anions **10** as a function of n (n = number of carbon atoms) at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (see Table S-39).

Table S-40. Linear odd *trans*-polyene radicals **11**. Absolute free energies, G_n, at the uB3LYP/6-311++G(3df,3pd) level of theory in ideal gas (*n* is the number of carbon atoms per molecule) and linear relationship (1n).



11

x	*n* = 2*x* + 3	G_n (au)	G_n (kcal mol^{-1})	G = –24286.413605*n* – 730.88 (1n) (kcal mol^{-1})	δG (kcal mol^{-1})
0	3	–117.266 783	–73 586.0204	–73 590.12	4.10
1	5	–194.677 747	–122 162.136	–122 162.95	0.81
2	7	–272.085 866	–170 736.466	–170 735.78	–0.68
3	9	–349.492 704	–219 309.992	–219 308.61	–1.38
4	11	–426.898 842	–267 883.079	–267 881.43	–1.65
5	13	–504.304 533	–316 455.885	–316 454.26	–1.62
6	15	–581.709 898	–365 028.487	–365 027.09	–1.40
7	17	–659.115 101	–413 600.987	–413 599.92	–1.07
8	19	–736.520 161	–462 173.398	–462 172.74	–0.66
9	21	–813.925 016	–510 745.68	–510 745.57	–0.11
10	23	–891.329 746	–559 317.883	–559 318.4	0.52
11	25	–968.734 392	–607 890.034	–607 891.23	1.20
12	27	–1 046.138 932	–656 462.118	–656 464.05	1.93

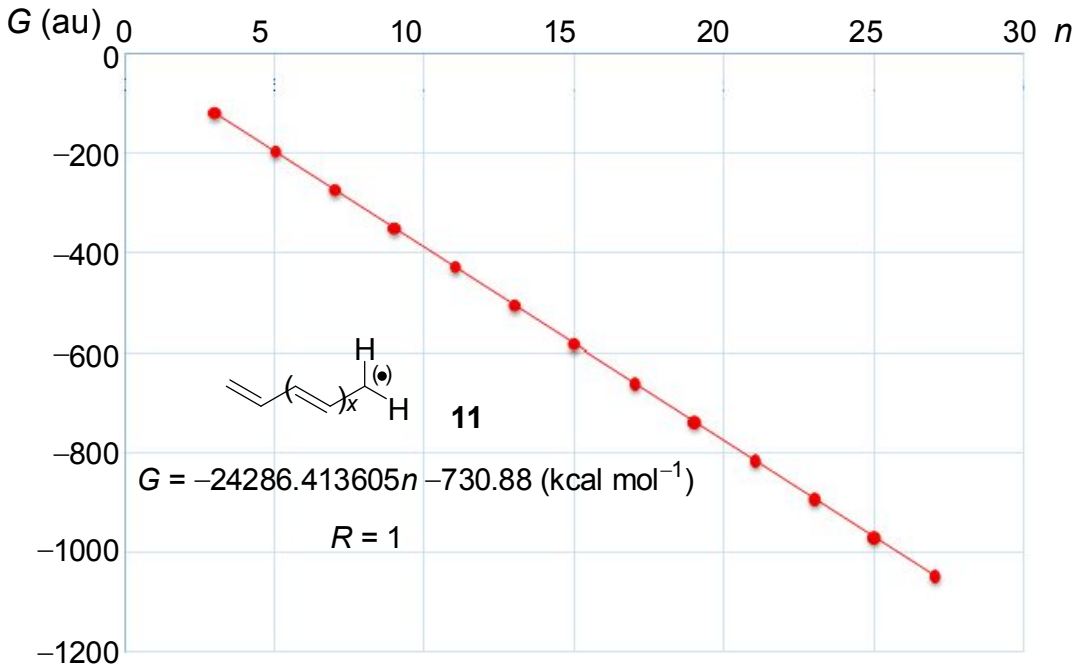
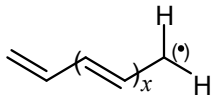


Fig. S-46. G_n values of linear odd *trans*-polyene radicals **11** as a function of n (n = number of carbon atoms) at the uB3LYP/6-311++G(3df,3pd) level of theory in ideal gas (1n) (see Table S-40).

Table S-41. Linear odd *trans*-polyene radicals **11**. Absolute free energies, G_n, at the uB3LYP/6-311++G(3df,3pd) level of theory in ideal gas (*n* is the number of carbon atoms per molecule).



11

x	*n* = 2*x* + 3	G_n (au)	G_n/n (au)	$\delta G = G_n/n - G_{(n-2)} / (n-2)$ (kcal mol^{-1})	$\delta G_{calc} = 3\ 146.2 / n^{2.218}$ (kcal mol^{-1})
0	3	–117.266 783	–39.088 928	–	–
1	5	–194.677 747	–38.935 549	96.25	88.60
2	7	–272.085 866	–38.869 409	41.50	42.01
3	9	–349.492 704	–38.832 523	23.15	24.06
4	11	–426.898 842	–38.808 986	14.77	15.41
5	13	–504.304 533	–38.792 656	10.25	10.64
6	15	–581.709 898	–38.780 660	7.53	7.75
7	17	–659.115 101	–38.771 476	5.76	5.87
8	19	–736.520 161	–38.764 219	4.55	4.58
9	21	–813.925 016	–38.758 334	3.69	3.67
10	23	–891.329 746	–38.753 467	3.05	3.00
11	25	–968.734 392	–38.749 376	2.57	2.50
12	27	–1 046.138 932	–38.745 886	2.19	2.10

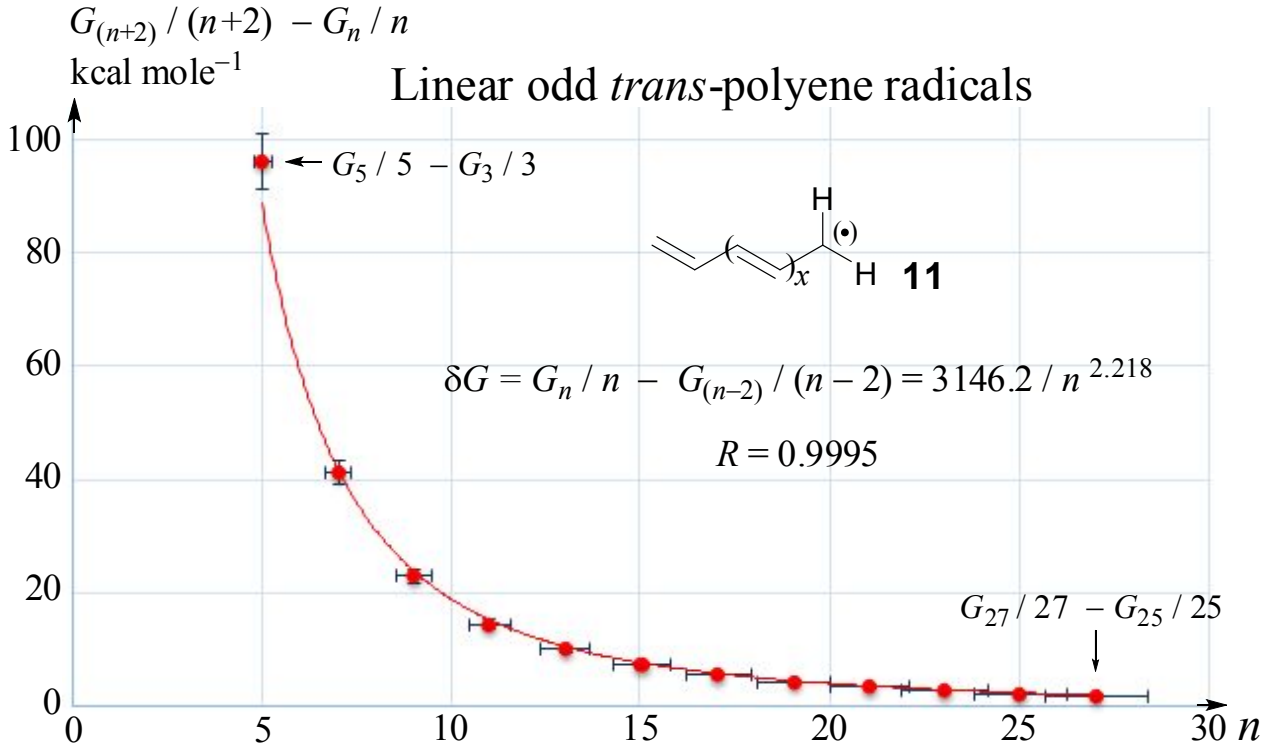
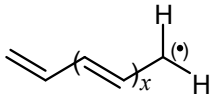


Fig. S-47. Power law (2u): variations of δ*G* values of linear odd *trans*-polyene radicals **11** as a function of *n* (*n* = number of carbon atoms) at the uB3LYP/6-311++G(3df,3pd) level of theory in ideal gas (error bars given for 95% confidence interval) (see Table S-41).

Table S-42. Linear odd *trans*-polyene radicals **11**. Absolute energies, E_n, at the uB3LYP/6-311++G(3df,3pd) level of theory in ideal gas (*n* is the number of carbon atoms per molecule).



11

x	*n* = 2*x* + 3	E_n (au)	E_n/n (au)	$\delta E = E_n/n - E_{(n-1)}/(n-1)$ (kcal mol^{-1})	$\delta E_{calc} = 2\,862.6 / n^{2.18}$ (kcal mol^{-1})
0	3	–117.307 680	–39.102 560	–	–
1	5	–194.748 826	–38.949 765	95.88	85.80
2	7	–272.186 978	–38.883 854	41.36	41.19
3	9	–349.623 808	–38.847 090	23.07	23.81
4	11	–427.059 908	–38.823 628	14.72	15.37
5	13	–504.495 573	–38.807 352	10.21	10.68
6	15	–581.930 948	–38.795 396	7.50	7.81
7	17	–659.366 102	–38.786 241	5.74	5.94
8	19	–736.801 093	–38.779 005	4.54	4.66
9	21	–814.235 998	–38.773 143	3.68	3.75
10	23	–891.670 808	–38.768 296	3.04	3.07
11	25	–969.105 554	–38.764 222	2.55	2.56
12	27	–1 046.540 248	–38.760 750	2.18	2.17
13	29	–1 123.974 854	–38.757 754	1.88	1.85
14	31	–1 201.409 405	–38.755 142	1.64	1.60
15	33	–1 278.844 036	–38.752 837	1.45	1.40
16	35	–1 356.278 583	–38.750 817	1.27	1.23
17	37	–1 433.713 120	–38.749 003	1.14	1.09

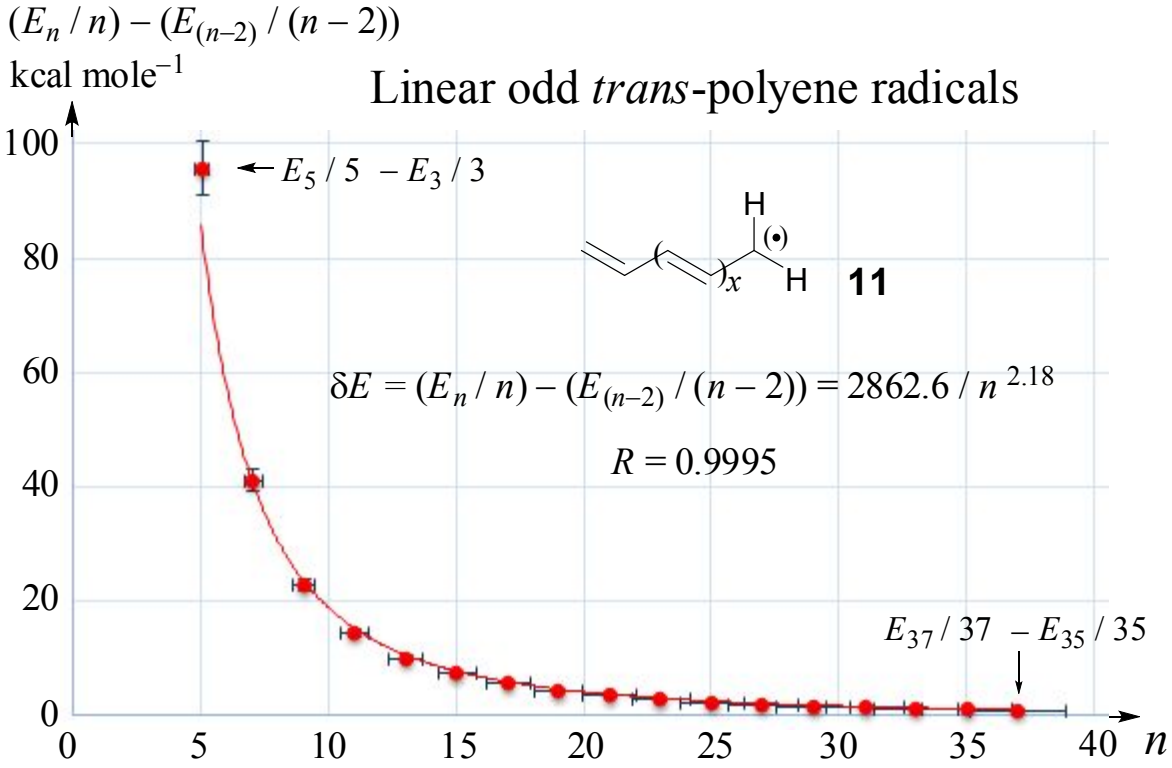


Fig. S-48. Power law (2v): variations of δ*E* values of linear odd *trans*-polyene radicals **11** as a function of *n* (*n* = number of carbon atoms) at the uB3LYP/6-311++G(3df,3pd) level of theory in ideal gas (error bars given for 95% confidence interval) (see Table S-42).

Table S-43. Linear odd *trans*-polyene radicals **11**. Absolute free energies, G_n, at the uTPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (n is the number of carbon atoms per molecule, $n = 2x + 3$) and linear relationship (1o).

x	n	G_n (au)	G_n (kcal mol^{-1})	$G = -24289.609002n - 731.40$ (1o) (kcal mol^{-1})	δG (kcal mol^{-1})
0	3	–117.279 111	–73 593.7563	–73 600.23	6.47
1	5	–194.699 507	–122 175.79	–122 177.38	1.59
2	7	–272.118 810	–170 757.138	–170 758.66	1.52
3	9	–349.536 275	–219 337.333	–219 337.88	0.55
4	11	–426.953 425	–267 917.33	–267 917.10	–0.23
5	13	–504.369 843	–316 496.868	–316 496.32	–0.55
6	15	–581.786 523	–365 076.57	–365 075.54	–1.03
7	17	–659.202 779	–413 656.006	–413 654.75	–1.25
8	19	–736.619 065	–462 235.461	–462 233.97	–1.49
9	21	–814.034 609	–510 814.45	–510 813.19	–1.26
10	23	–891.450 495	–559 393.654	–559 392.41	–1.24
11	25	–968.867 411	–607 973.505	–607 971.63	–1.87
12	27	–1046.283 354	–656 552.744	–656 550.84	–1.90
13	29	–1123.699 336	–705 132.008	–705 130.06	–1.95
14	31	–1201.115 232	–753 711.219	–753 709.28	–1.94
15	33	–1278.531 335	–802 290.559	–802 288.50	–2.06
16	35	–1355.947 474	–850 869.921	–850 867.72	–2.20
17	37	–1 433.363 533	–899 449.234	–899 446.93	–2.30
18	39	–1 510.779 779	–948 028.664	–948 026.15	–2.51
19	41	–1 588.191 540	–996 605.279	–996 605.37	0.09
20	43	–1 665.606 316	–1 045 183.79	–1 045 184.59	0.79
21	45	–1 743.022 502	–1 093 763.18	–1 093 763.80	0.62
22	47	–1 820.438 028	–1 142 342.16	–1 142 343.02	0.86
23	49	–1 897.853 754	–1 190 921.26	–1 190 922.24	0.98
24	51	–1 975.269 492	–1 239 500.37	–1 239 501.50	1.13
25	53	–2 052.685 229	–1 288 079.48	–1 288 080.68	1.20
26	55	–2 130.100 926	–1 336 658.57	–1 336 659.89	1.32
27	57	–2 207.516 653	–1 385 237.67	–1 385 239.11	1.44

28	59	–2 284.932 402	–1 433 816.79	–1 433 818.33	1.54
29	61	–2 362.348 199	–1 482 395.94	–1 482 397.55	1.61

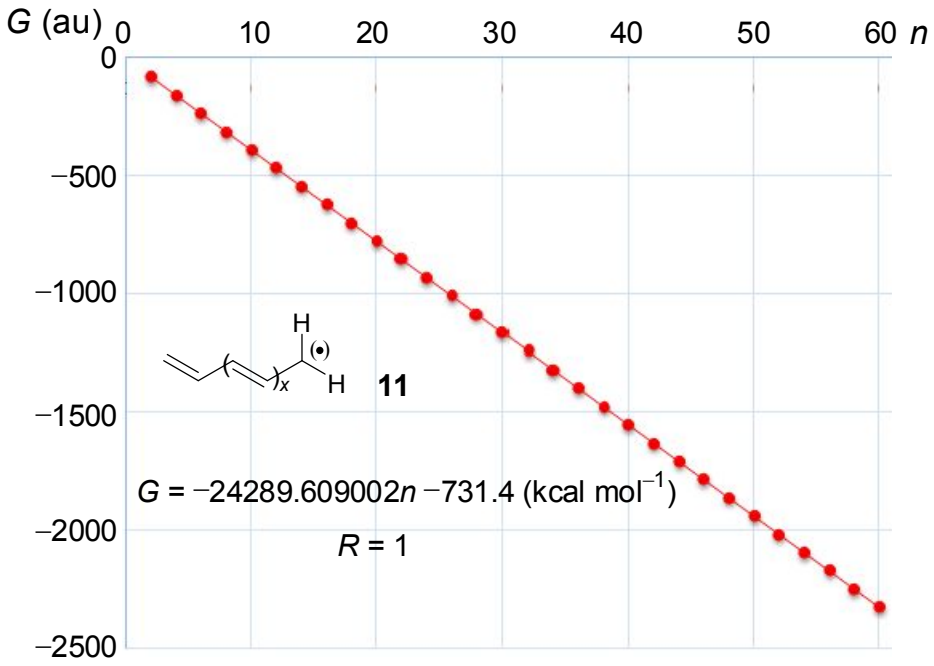


Fig. S-49. G_n values of linear odd *trans*-polyene radicals **11** as a function of n (n = number of carbon atoms) at the uTPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (1o) (see Table S-43).

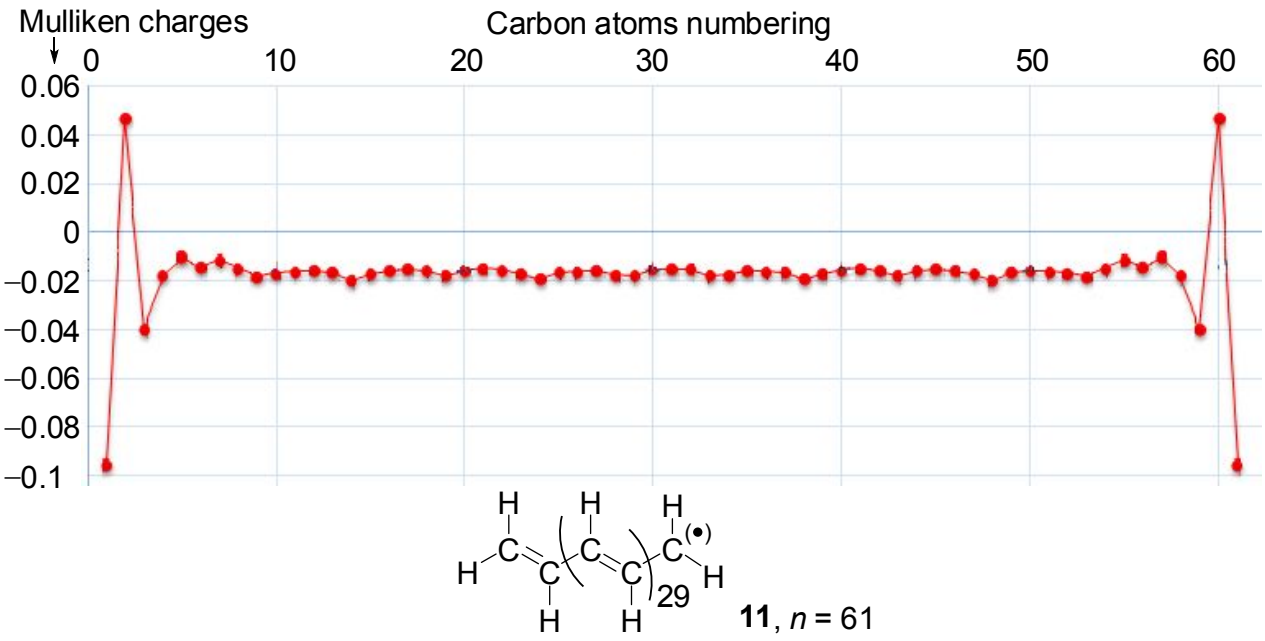


Fig. S-50. Mulliken charges of *trans*-polyenyl radicals **11** (n = 61) as a function of the numbering of carbon atoms at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (see Table S-43).

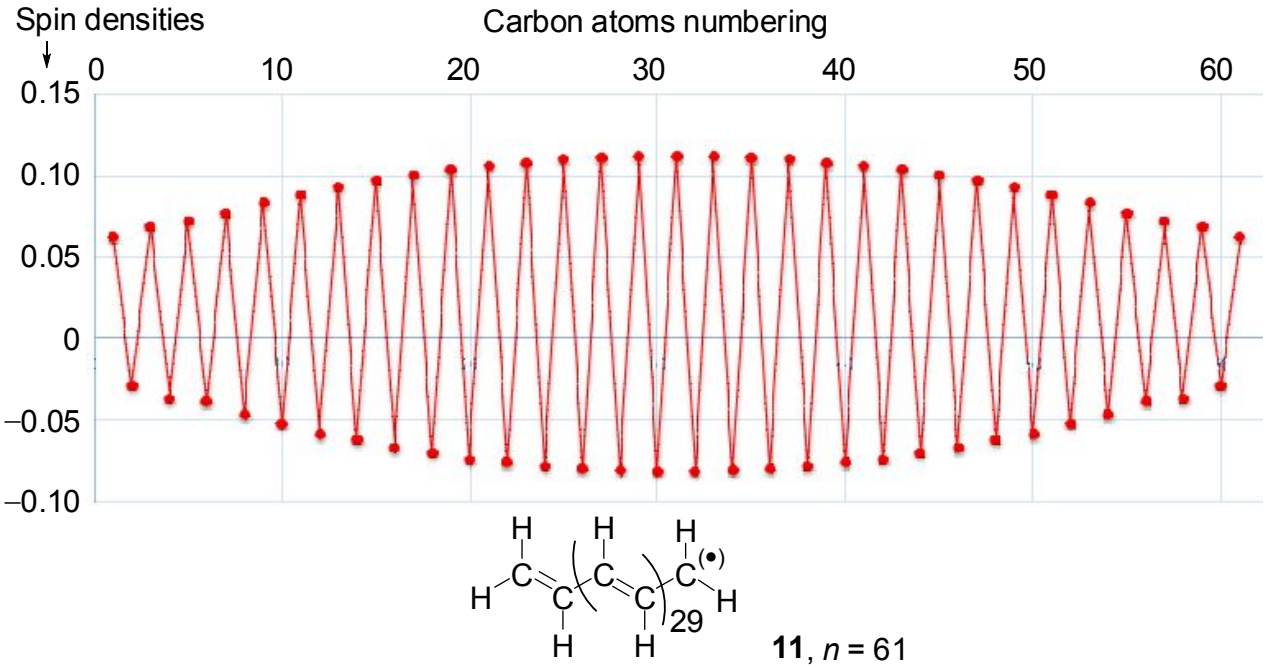
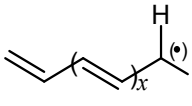


Fig. S-51. . Spin densities of *trans*-polyenyl radicals **11** (n = 61) as a function of the numbering of carbon atoms at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (see Table S-43).

Table S-44. Linear odd *trans*-polyene radicals **11**. Absolute free energies, G_n, at the uTPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (n is the number of carbon atoms per molecule, $n = 2x + 3$).



11

x	n	G_n (au)	G_n/n (au)	G_n/n (kcal mol^{-1})	$\delta G = G_n/n - G_{(n-2)}/(n-2)$ (kcal mol^{-1})	$\delta G_{calc} = 2481.9 / n^{2.128}$ (kcal mol^{-1})
0	3	–117.279 111	–39.093 037	–24 531.25	–	–
1	5	–194.670 866	–38.934 173	–24 431.56	99.69	80.79
2	7	–272.118 810	–38.874 116	–24 393.88	37.69	39.48
3	9	–349.536 275	–38.837 364	–24 370.81	23.06	23.13
4	11	–426.953 425	–38.813 948	–24 356.12	14.69	15.09
5	13	–504.369 843	–38.797 680	–24 345.91	10.21	10.58
6	15	–581.786 523	–38.785 768	–24 338.44	7.47	7.80
7	17	–659.202 779	–38.776 634	–24 332.71	5.73	5.97
8	19	–736.619 065	–38.769 424	–24 328.18	4.52	4.72
9	21	–814.034 609	–38.763 553	–24 324.50	3.68	3.81
10	23	–891.450 495	–38.758 717	–24 321.46	3.03	3.14
11	25	–968.867 411	–38.754 696	–24 318.94	2.52	2.63
12	27	–1046.283 354	–38.751 235	–24 316.77	2.17	2.23
13	29	–1123.699 336	–38.748 253	–24 314.90	1.87	1.92
14	31	–1201.115 232	–38.745 653	–24 313.26	1.63	1.66
15	33	–1278.531 335	–38.743 374	–24 311.83	1.43	1.46
16	35	–1355.947 474	–38.741 356	–24 310.57	1.27	1.28
17	37	–1 433.363 533	–38.739 555	–24 309.44	1.13	1.14
18	39	–1 510.779 779	–38.737 943	–24 308.43	1.01	1.02
19	41	–1 588.191 540	–38.736 379	–24 307.44	0.98	0.92
20	43	–1 665.606 316	–38.735 031	–24 306.60	0.85	0.83
21	45	–1 743.022 502	–38.733 833	–24 305.85	0.75	0.75
22	47	–1 820.438 028	–38.732 724	–24 305.15	0.70	0.69
23	49	–1 897.853 754	–38.731 709	–24 304.51	0.64	0.63
24	51	–1 975.269 492	–38.730 774	–24 303.93	0.59	0.58
25	53	–2 052.685 229	–38.729 910	–24 303.39	0.54	0.53
26	55	–2 130.100 926	–38.729 108	–24 302.88	0.50	0.49
27	57	–2 207.516 653	–38.728 362	–24 302.41	0.47	0.46

28	59	–2 284.932 402	–38.727 668	–24 301.98	0.44	0.42
29	61	–2 362.348 199	–38.727 020	–24 301.57	0.41	0.39

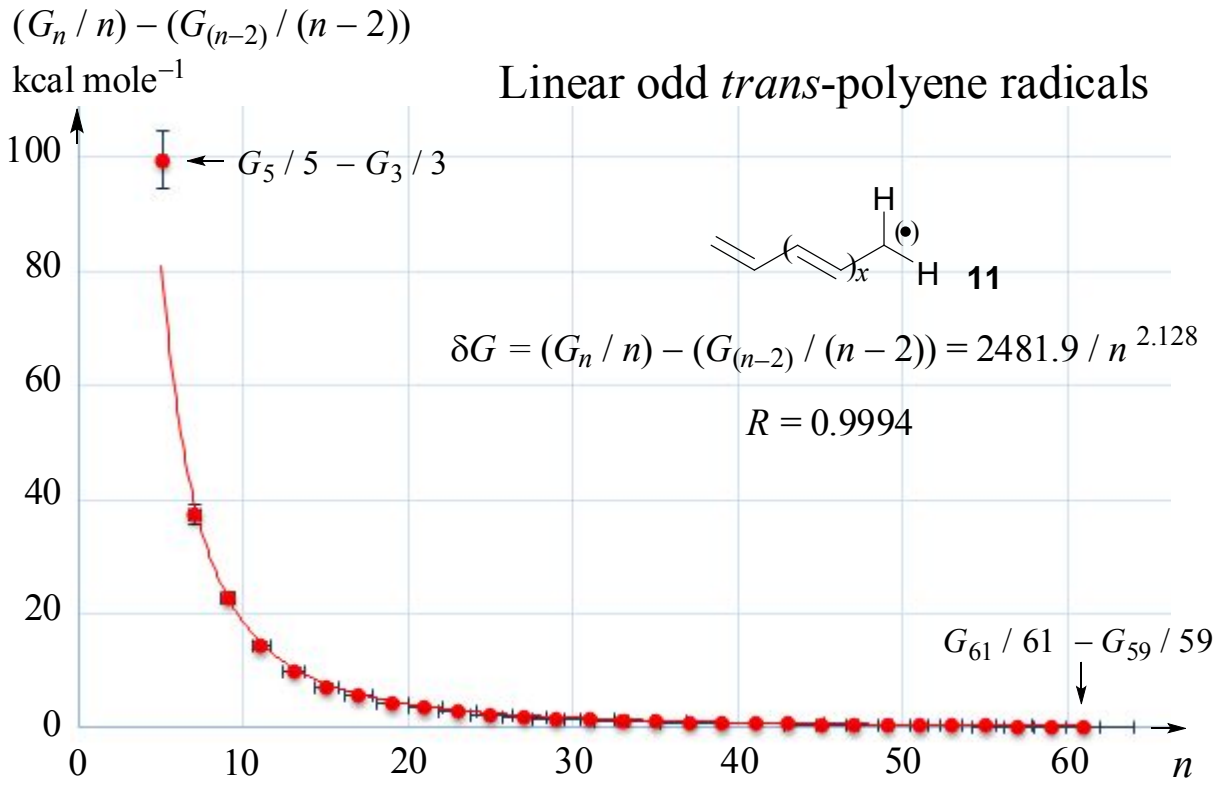


Fig. S-52. Power law (2w): variations of δ*G* values of linear odd *trans*-polyene radicals **11** as a function of *n* (*n* = number of carbon atoms) at the uTPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (error bars given for 95% confidence interval) (see Table S-44).

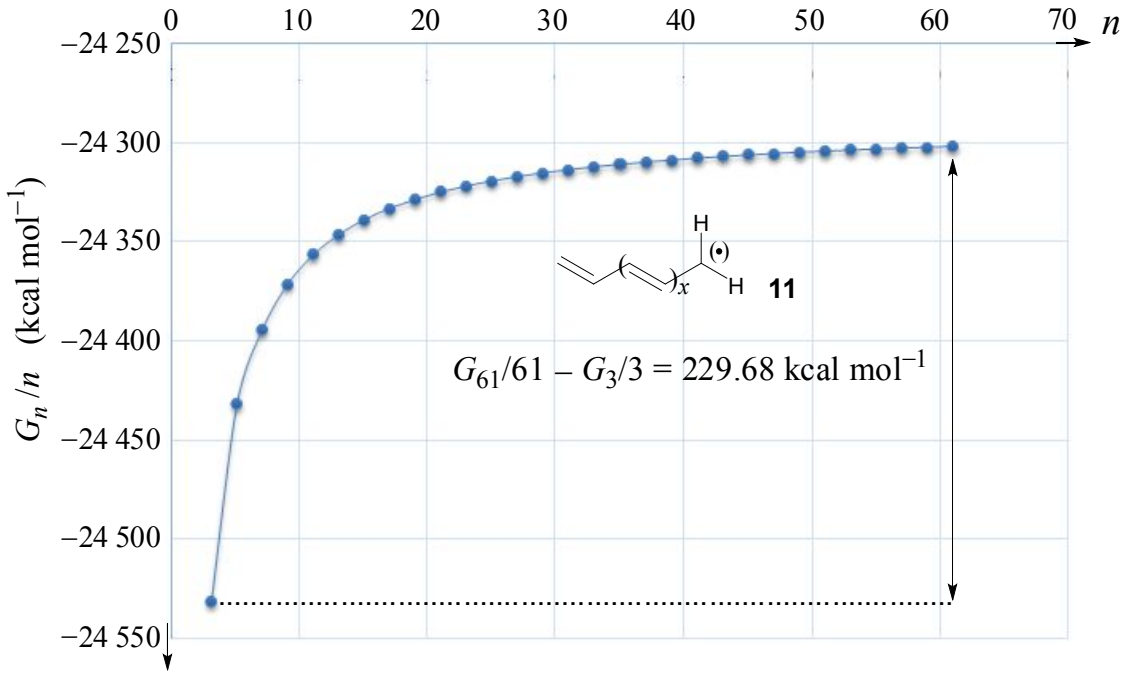
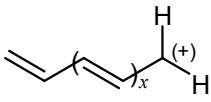


Fig. S-53. Variations of G_n /n values of linear odd *trans*-polyene anions **10** as a function of n (n = number of carbon atoms) at the uTPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (see Table S-44).

Table S-45. Linear odd *trans*-polyene cations **12**. Absolute free energies, G_n, at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (*n* is the number of carbon atoms per molecule) and linear relationship (1p).



12

x	*n* = 2*x* + 3	G_n (au)	G_n (kcal mol^{-1})	G = –24288.212596*n* – 558.48 (1p) (kcal mol^{-1})	δG (kcal mol^{-1})
0	3	–116.967 350	–73 398.1233	–73 423.12	25.00
1	5	–194.406 847	–121 992.143	–121 999.54	7.40
2	7	–271.833 229	–170 577.934	–170 575.97	–1.96
3	9	–349.252 155	–219 159.045	–219 152.39	–6.65
4	11	–426.667 202	–267 737.723	–267 728.82	–8.90
5	13	–504.079 736	–316 314.823	–316 305.24	–9.58
6	15	–581.490 520	–364 890.825	–364 881.67	–9.15
7	17	–658.900 150	–413 466.104	–413 458.09	–8.01
8	19	–736.308 868	–462 040.81	–462 034.52	–6.29
9	21	–813.716 850	–510 615.054	–510 610.94	–4.11
10	23	–891.124 290	–559 188.958	–559 187.37	–1.59
11	25	–968.531 322	–607 762.606	–607 763.79	1.18
12	27	–1 045.937 977	–656 336.017	–656 340.22	4.20
13	29	–1 123.344 480	–704 909.333	–704 916.64	7.31
14	31	–1 200.749 942	–753 481.996	–753 493.07	11.07

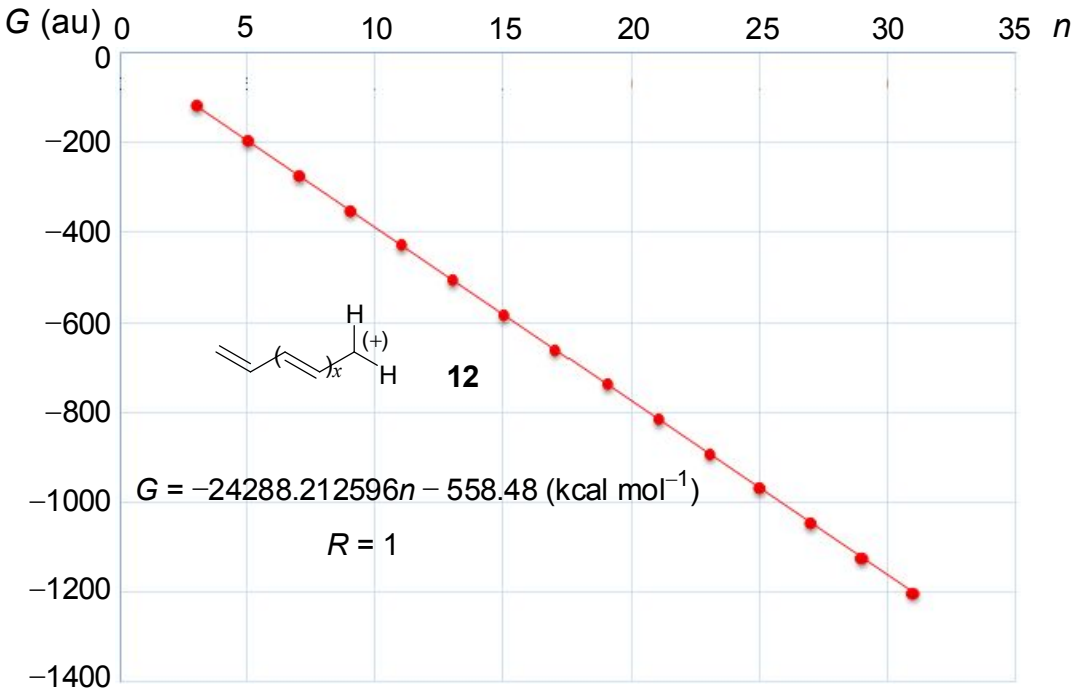
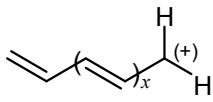


Fig. S-54. G_n values of linear odd *trans*-polyene cations **12** as a function of n (n = number of carbon atoms) at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (1p) (see Table S-45).

Table S-46. Linear odd *trans*-polyene cations **12**. Absolute free energies, G_n, at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (*n* is the number of carbon atoms per molecule).



12

x	$n = 2x + 3$	G_n (au)	G_n/n (au)	$\delta G = G_n/n - G_{(n-2)}/(n-2)$ (kcal mol^{-1})	$\delta G_{calc} = 1\,889.6 / n^{2.123}$ (kcal mol^{-1})
0	3	–116.967 350	–38.989 117	–	–
1	5	–194.406 847	–38.881 369	67.61	62.00
2	7	–271.833 229	–38.833 318	30.15	30.35
3	9	–349.252 155	–38.805 795	17.27	17.80
4	11	–426.667 202	–38.787 927	11.21	11.63
5	13	–504.079 736	–38.775 364	7.88	8.15
6	15	–581.490 520	–38.766 035	5.85	6.02
7	17	–658.900 150	–38.758 832	4.52	4.61
8	19	–736.308 868	–38.753 098	3.60	3.64
9	21	–813.716 850	–38.748 421	2.93	2.95
10	23	–891.124 290	–38.744 534	2.44	2.43
11	25	–968.531 322	–38.741 253	2.06	2.03
12	27	–1 045.937 977	–38.738 444	1.76	1.73
13	29	–1 123.344 480	–38.736 016	1.52	1.48
14	31	–1 200.749 942	–38.733 869	1.35	1.29

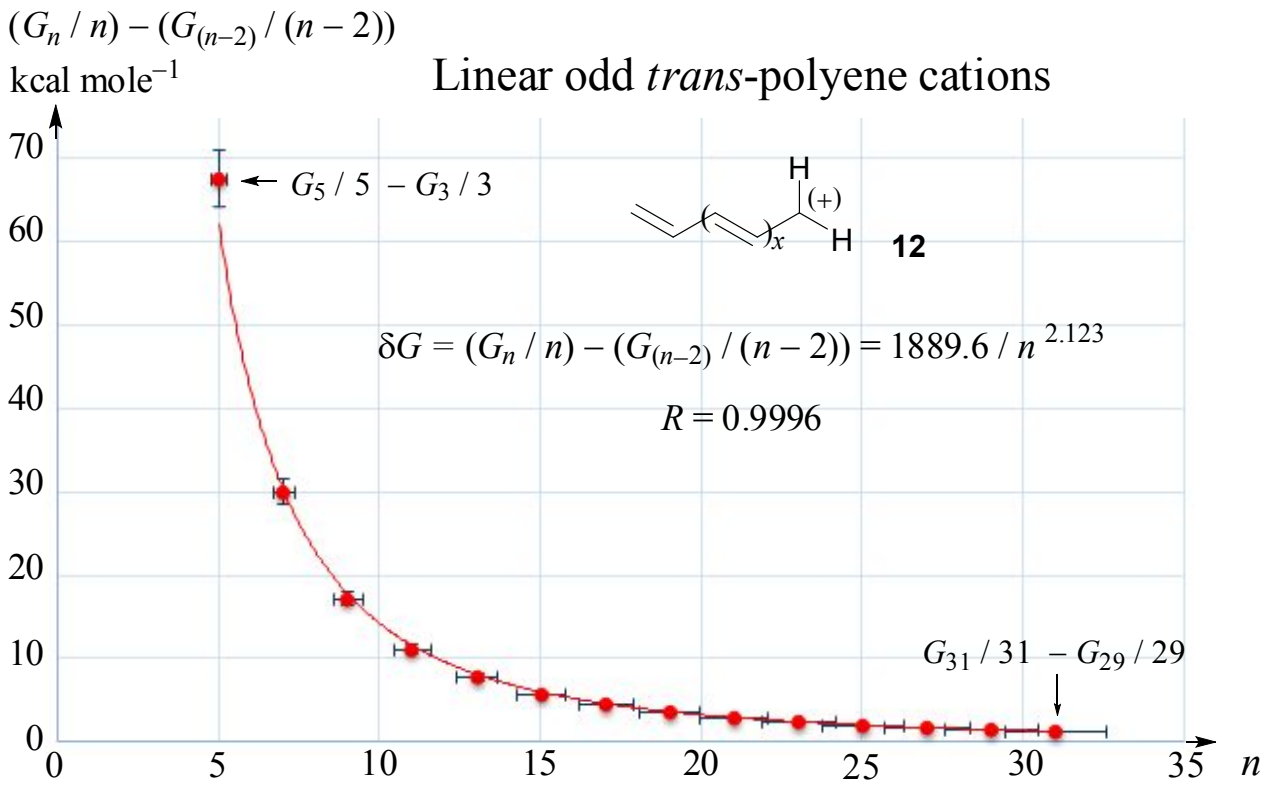
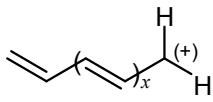


Fig. S-55. Power law (2x): variations of δG values of linear odd *trans*-polyene cations **12** as a function of n (n = number of carbon atoms) at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (error bars given for 95% confidence interval) (see Table S-46).

Table S-47. Linear odd *trans*-polyene cations **12**. Absolute energies, E_n, at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (*n* is the number of carbon atoms per molecule).



12

x	*n* = 2*x* + 3	E_n (au)	E_n/n (au)	$\delta E = E_n/n - E_{(n-2)}/(n-2)$ (kcal mol^{-1})	$\delta E_{calc} = 1\,845.3 / n^{2.113}$ (kcal mol^{-1})
0	3	–117.011 015	–39.003 672		–
1	5	–194.481 921	–38.896 384	67.32	61.54
2	7	–271.938 083	–38.848 297	30.17	30.22
3	9	–349.387 341	–38.820 816	17.24	17.77
4	11	–426.832 663	–38.802 969	11.20	11.63
5	13	–504.275 499	–38.790 423	7.87	8.17
6	15	–581.716 645	–38.781 110	5.84	6.04
7	17	–659.156 545	–38.773 914	4.52	4.63
8	19	–736.595 523	–38.768 185	3.59	3.66
9	21	–814.033 825	–38.763 515	2.93	2.96
10	23	–891.471 562	–38.759 633	2.44	2.45
11	25	–968.908 858	–38.756 354	2.06	2.05
12	27	–1 046.345 787	–38.753 548	1.76	1.74
13	29	–1 123.782 382	–38.751 117	1.53	1.50
14	31	–1 201.218 751	–38.748 992	1.33	1.30
15	33	–1 278.654 803	–38.747 016	1.24	1.14
16	35	–1 356.090 877	–38.745 454	0.98	1.01

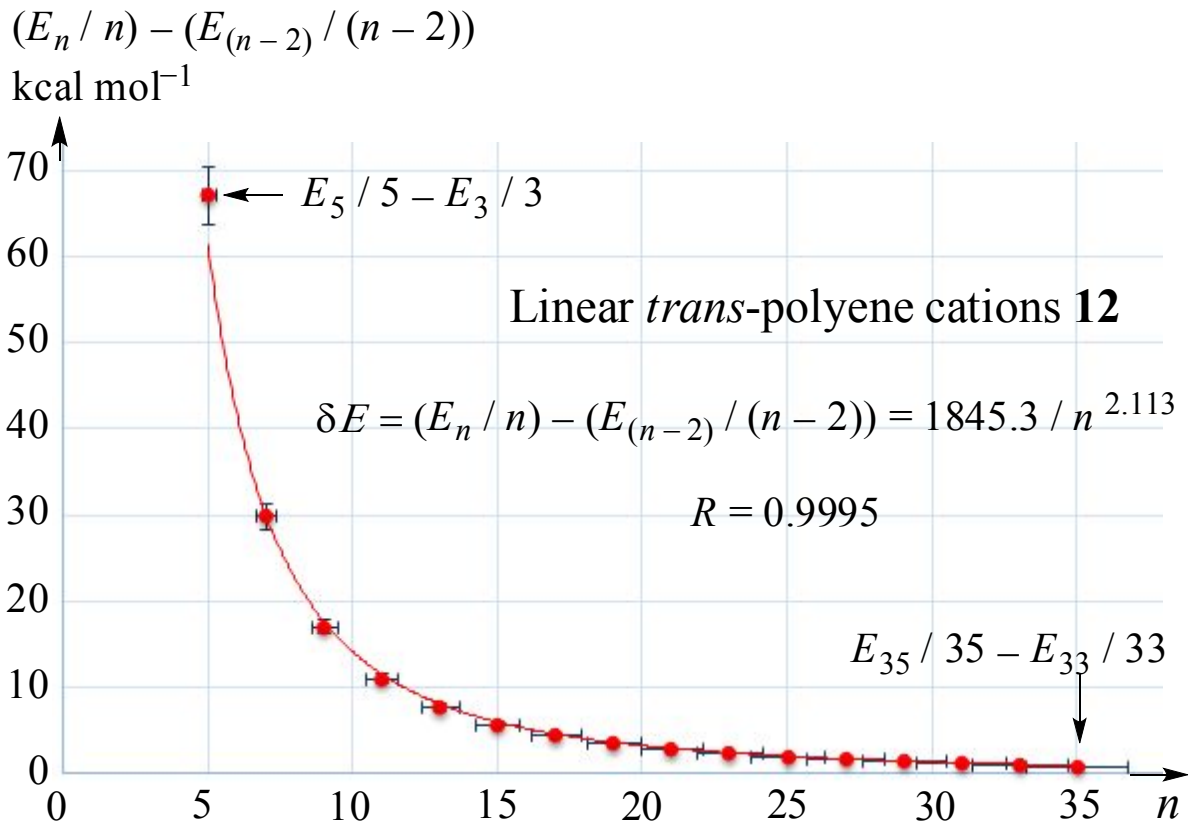
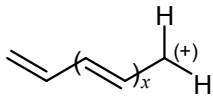


Fig. S-56. Power law (2y): variations of δ*E* values of linear odd *trans*-polyene cations **12** as a function of *n* (*n* = number of carbon atoms) at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (error bars given for 95% confidence interval) (see Table S-47).

Table S-48. Linear odd *trans*-polyene cations **12**. Absolute free energies, G_n, at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (n is the number of carbon atoms per molecule, $n = 2x + 3$) and linear relationship (1q).



12

x	n	G_n (au)	G_n (kcal mol^{-1})	$G = -24290.62735n - 573.47$ (1q) (kcal mol^{-1})	δG (kcal mol^{-1})
0	3	–116.982 098	–73 407.3778	–73 445.35	37.97
1	5	–194.399 531	–121 987.552	–122 026.61	39.06
2	7	–271.870 329	–170 601.214	–170 607.86	6.64
3	9	–349.300 534	–219 189.403	–219 189.12	–0.28
4	11	–426.726 984	–267 775.236	–267 770.37	–4.87
5	13	–504.150 961	–316 359.517	–316 351.62	–7.90
6	15	–581.573 345	–364 942.799	–364 932.88	–9.92
7	17	–658.994 496	–413 525.307	–413 514.13	–11.18
8	19	–736.415 009	–462 107.414	–462 095.39	–12.02
9	21	–813.834 875	–510 689.115	–510 676.64	–12.47
10	23	–891.254 165	–559 270.455	–559 257.9	–12.55
11	25	–968.673 206	–607 851.639	–607 839.15	–12.49
12	27	–1 046.087 680	–656 429.957	–656 420.41	–9.55
13	29	–1 123.505 635	–705 010.459	–705 001.66	–8.80
14	31	–1 200.923 342	–753 590.806	–753 582.92	–7.88
15	33	–1 278.341 005	–802 171.125	–802 164.17	–6.95
16	35	–1 355.758 540	–850 751.364	–850 745.43	–5.93
17	37	–1 433.175 754	–899 331.401	–899 326.68	–4.72
18	39	–1 510.592 847	–947 911.362	–947 907.94	–3.42
19	41	–1 588.009 599	–996 491.109	–996 489.19	–1.92
20	43	–1 665.429 556	–1 045 072.87	–1 045 070.45	–2.42
21	45	–1 742.843 690	–1 093 650.97	–1 093 651.70	0.73
22	47	–1 820.263 138	–1 142 232.41	–1 142 232.96	0.55
23	49	–1 897.679 717	–1 190 812.05	–1 190 814.21	2.16
24	51	–1 975.096 274	–1 239 391.68	–1 239 395.46	3.78

25	53	–2 052.512 786	–1 287 971.27	–1 287 976.72	5.45
26	55	–2 129.929 216	–1 336 550.82	–1 336 557.97	7.15
27	57	–2 207.345 630	–1 385 130.35	–1 385 139.23	8.88
28	59	–2 284.762 074	–1 433 709.91	–1 433 720.48	10.57
29	61	–2 362.178 608	–1 482 289.52	–1 482 301.74	12.22

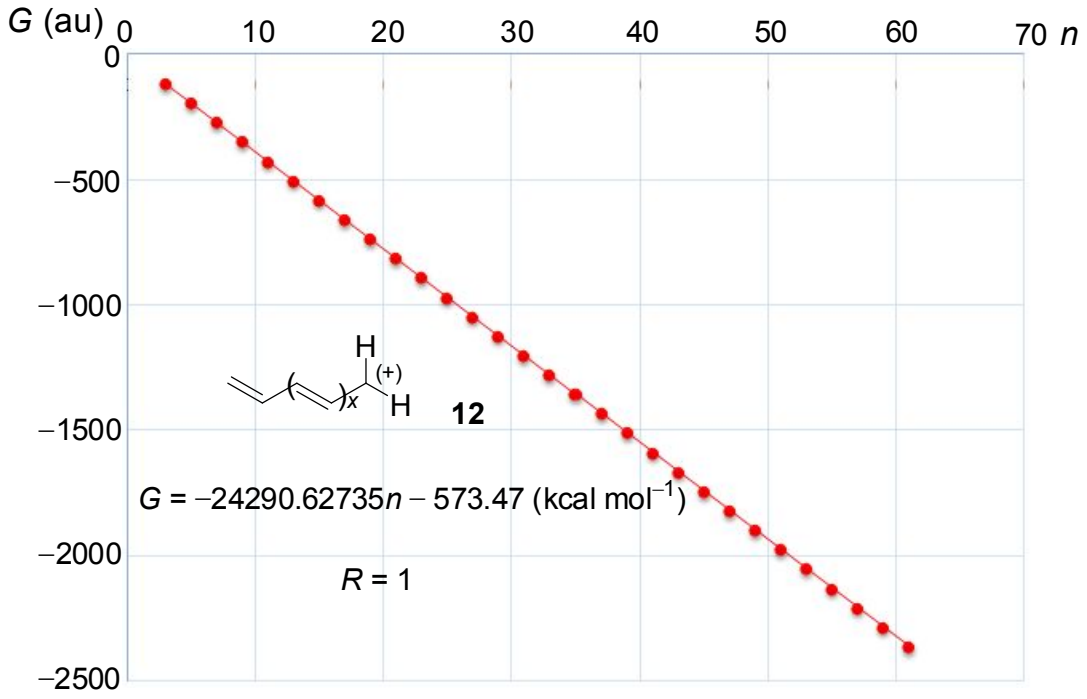
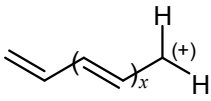


Fig. S-57. G_n values of linear odd *trans*-polyene cations **12** as a function of n (n = number of carbon atoms) at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (1q) (see Table S-48).

Table S-49. Linear odd *trans*-polyene cations **12**. Absolute free energies, G_n, at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (*n* is the number of carbon atoms per molecule, $n = 2x + 3$).



12

x	*n*	G_n (au)	G_n/n (au)	G_n/n (kcal mol^{-1})	$\delta G = G_n/n - G_{(n-2)}/(n-2)$ (kcal mol^{-1})	$\delta G_{calc} = 1625.9 / n^{2.068}$ (kcal mol^{-1})
0	3	–116.982 098	–38.994 033	–24 469.13	–	–
1	5	–194.399 531	–38.879 906	–24 397.51	71.62	58.29
2	7	–271.870 329	–38.838 618	–24 370.60	25.91	29.07
3	9	–349.300 534	–38.811 170	–24 354.38	17.22	17.29
4	11	–426.726 984	–38.793 362	–24 343.20	11.17	11.42
5	13	–504.150 961	–38.780 843	–24 335.35	7.86	8.08
6	15	–581.573 345	–38.771 556	–24 329.52	5.83	6.01
7	17	–658.994 496	–38.764 382	–24 325.02	4.50	4.64
8	19	–736.415 009	–38.758 685	–24 321.44	3.57	3.69
9	21	–813.834 875	–38.754 042	–24 318.53	2.91	3.00
10	23	–891.254 165	–38.750 181	–24 316.11	2.42	2.48
11	25	–968.673 206	–38.746 928	–24 314.06	2.04	2.09
12	27	–1 046.087 680	–38.743 988	–24 312.22	1.84	1.78
13	29	–1 123.505 635	–38.741 574	–24 310.71	1.51	1.54
14	31	–1 200.923 342	–38.739 463	–24 309.38	1.32	1.34
15	33	–1 278.341 005	–38.737 606	–24 308.22	1.16	1.18
16	35	–1 355.758 540	–38. 735 958	–24 307.18	1.03	1.04
17	37	–1 433.175 754	–38.734 480	–24 306.25	0.93	0.93
18	39	–1 510.592 847	–38.733 150	–24 305.42	0.83	0.83
19	41	–1 588.009 599	–38.731 941	–24 304.66	0.76	0.75
20	43	–1 665.429 556	–38.730 920	–24 304.02	0.64	0.68
21	45	–1 742.843 690	–38.729 860	–24 303.35	0.66	0.62
22	47	–1 820.263 138	–38.729 003	–24 302.82	0.54	0.57
23	49	–1 897.679 717	–38.728 157	–24 302.29	0.53	0.52
24	51	–1 975.096 274	–38.727 378	–24 301.80	0.49	0.48
25	53	–2 052.512 786	–38.726 656	–24 301.34	0.45	0.44

26	55	–2 129.929 216	–38.725 986	–24 300.92	0.42	0.41
27	57	–2 207.345 630	–38.725 362	–24 300.53	0.39	0.38
28	59	–2 284.762 074	–38.724 781	–24 300.17	0.36	0.35
29	61	–2 362.178 608	–38.724 239	–24 299.83	0.34	0.33

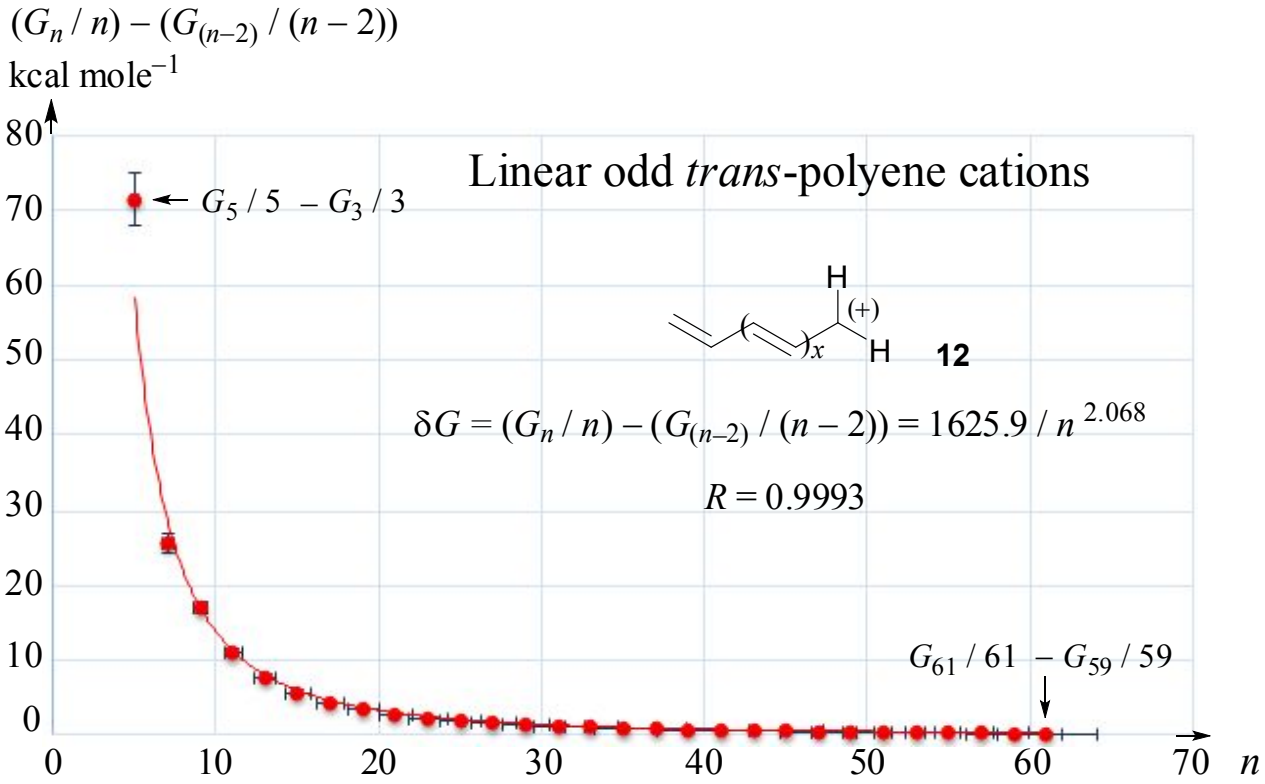


Fig. S-58. Power law (2z): variations of δ*G* values of linear odd *trans*-polyene cations **12** as a function of *n* (*n* = number of carbon atoms) at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (error bars given for 95% confidence interval) (see Table S-49).

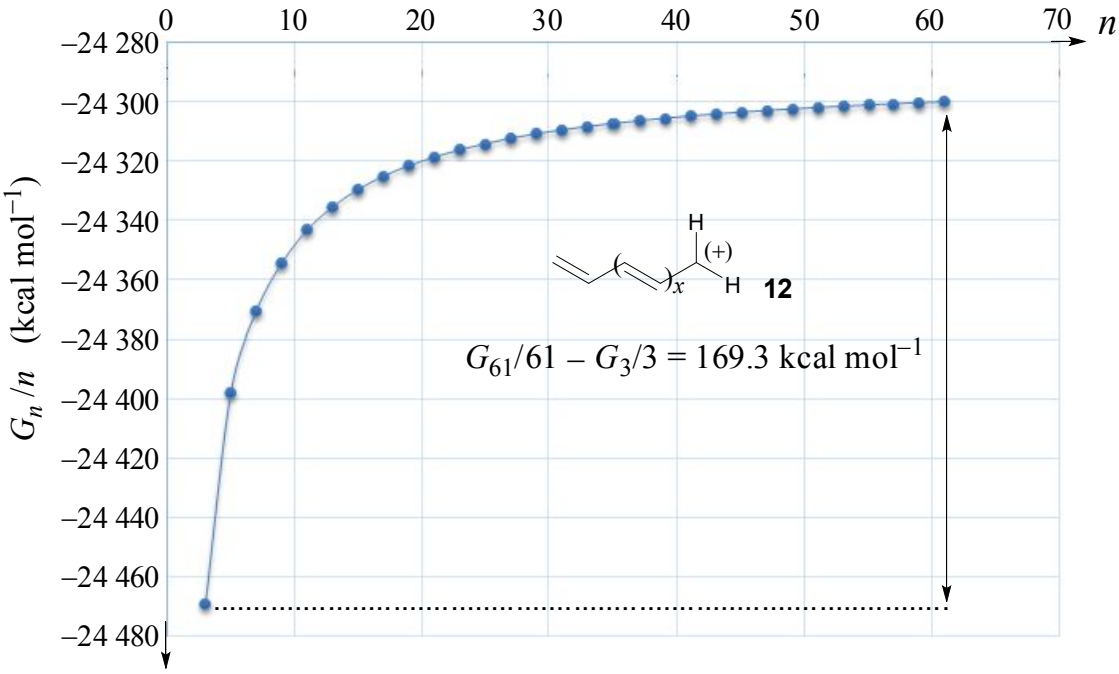
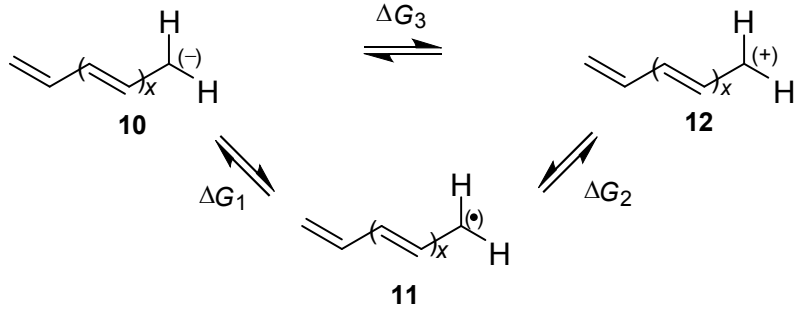


Fig. S-59. Variations of G_n/n values of linear odd *trans*-polyene cations **12** as a function of n (n = number of carbon atoms) at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (see Table S-49).

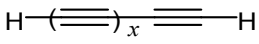
Table S-50. Differences between values of absolute free energies of linear odd *trans*-polyene anions **10**, and those of the corresponding linear odd *trans*-polyene radical **11** or linear odd *trans*-polyene cations **12** at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (*n* is the number of carbon atoms per molecule)



x	*n* = 2*x* + 3	**10** G_n (au)	**11** G_n (au)	**12** G_n (au)	ΔG_1 (kcal mol^{-1})	ΔG_2 (kcal mol^{-1})	ΔG_3 (kcal mol^{-1})
0	3	–117.293 738	–117.279 111	–116.982 098	9.18	186.38	195.56
1	5	–194.706 036	–194.670 866	–194.399 531	22.07	170.26	192.33
2	7	–272.164 590	–272.118 810	–271.870 329	28.73	155.92	184.65
3	9	–349.591 953	–349.536 275	–349.300 534	34.94	147.93	182.87
4	11	–427.016 705	–426.953 425	–426.726 984	39.71	142.09	181.80
5	13	–504.439 573	–504.369 843	–504.150 961	43.76	137.35	181.11
6	15	–581.861 159	–581.786 523	–581.573 345	46.83	133.77	180.60
7	17	–659.281 786	–659.202 779	–658.994 496	49.58	130.70	180.28
8	19	–736.701 728	–736.619 065	–736.415 009	51.87	128.05	179.92
9	21	–814.121 171	–814.034 609	–813.834 875	54.32	125.33	179.65
10	23	–891.540 327	–891.450 495	–891.254 165	56.37	123.20	179.57
11	25	–968.959 282	–968.867 411	–968.673 206	57.65	121.86	179.51
12	27	–1 046.373 544	–1046.283 354	–1 046.087 680	57.00	122.79	179.79
13	29	–1 123.791 344	–1123.699 336	–1 123.505 635	57.74	121.55	179.29
14	31	–1 201.208 920	–1201.115 232	–1 200.923 342	58.79	120.41	179.20
15	33	–1 278.626 382	–1 278.529 024	–1 278.341 005	61.09	117.98	179.07
16	35	–1 356.043 824	–1355.947 404	–1 355.758 540	60.50	118.51	179.01
17	37	–1 433.464 542	–1 433.363 533	–1 433.175 754	63.38	117.83	181.22
18	39	–1 510.882 713	–1 510.779 779	–1 510.592 847	64.59	117.30	181.89
19	41	–1 588.297 786	–1 588.191 540	–1 588.009 599	66.67	114.17	180.84
20	43	–1 665.714 487	–1 665.606 316	–1 665.429 556	67.87	110.92	178.79
21	45	–1 743.128 549	–1 743.022 502	–1 742.843 690	66.54	112.21	178.75

22	47	–1 820.547 999	–1 820.438 028	–1 820.263 138	69.01	109.75	178.76
23	49	–1 897.964 572	–1897.853 754	–1 897.679 717	69.54	109.21	178.75
24	51	–1 975.381 061	–1975.269 492	–1 975.096 274	70.01	108.70	178.71
25	53	–2 052.797 664	–2052.685 229	–2 052.512 786	70.55	108.21	178.76
26	55	–2 130.213 986	–2130.100 926	–2129.929 216	70.95	107.75	178.70
27	57	–2 207.630 352	–2207.516 653	–2 207.345 630	71.35	107.32	178.67
28	59	–2 285.046 755	–2284.932 402	–2 284.762 074	71.76	106.88	178.64
29	61	–2 362.463 270	–2 362.348 199	–2 362.178 608	72.21	106.42	178.63

Table S-51. Polyynes **13**. Absolute free energies, G_n, at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (n is the number of carbon atoms per molecule) and linear relationship (1r).



13

x	$n = 2x + 2$	G_n (au)	G_n (kcal mol^{-1})	$G = -23901.203617n - 735.64$ (1r) (kcal mol^{-1})	δG (kcal mol^{-1})
0	2	–77.355 015	–48 541.0068	–48 538.05	–2.96
1	4	–153.528 201	–96 340.4046	–96 340.45	0.046
2	6	–229.704 939	–144 142.031	–144 142.86	0.83
3	8	–305.882 657	–191 944.273	–191 945.27	1.00
4	10	–382.060 842	–239 746.808	–239 747.68	0.87
5	12	–458.239 117	–287 549.399	–287 550.08	0.68
6	14	–534.417 439	–335 352.02	–335 352.49	0.47
7	16	–610.595 319	–383 154.363	–383 154.90	0.54
8	18	–686.773 695	–430 957.018	–430 957.30	0.28
9	20	–762.951 962	–478 759.604	–478 759.71	0.11
10	22	–839.130 337	–526 562.258	–526 562.12	–0.14
11	24	–915.308 977	–574 365.079	–574 364.53	–0.55
12	26	–991.487 912	–622 168.084	–622 166.93	–1.15

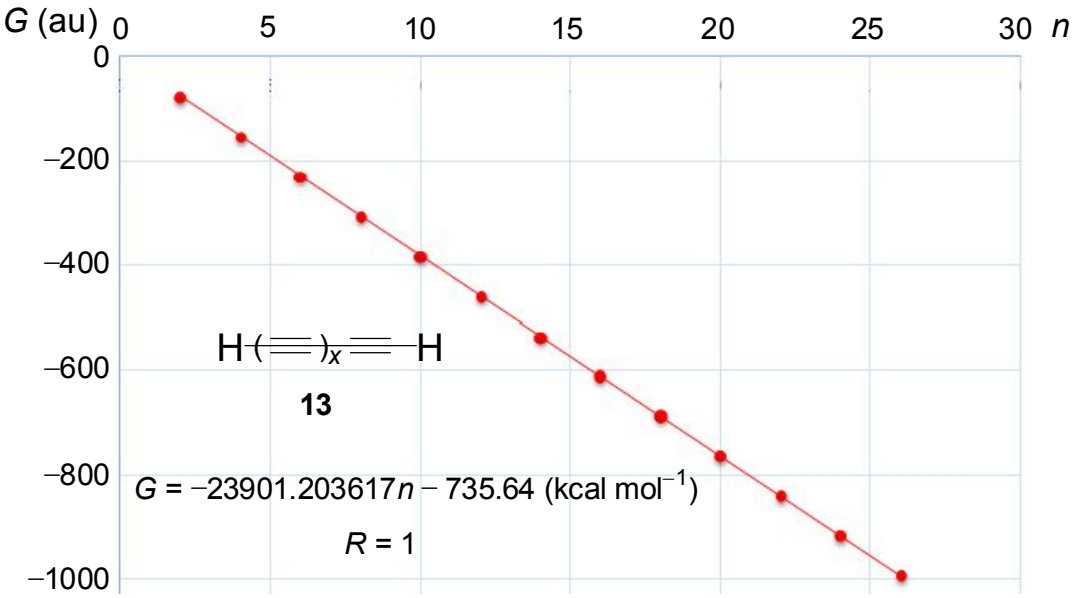
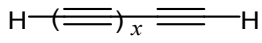


Fig. S-60. G_n values of linear odd polyynes **13** as a function of n (n = number of carbon atoms) at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (1r) (see Table S-51).

Table S-52. Polyynes **13**. Absolute free energies, G_n, at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (n is the number of carbon atoms per molecule).



13

x	$n = 2x + 2$	G_n (au)	G_n/n (au)	$\delta G = G_n/n - G_{(n-2)}/(n-2)$ (kcal mol^{-1})	$\delta G_{calc} = 3\,868.9 / n^{2.294}$ (kcal mol^{-1})
0	2	–77.355 015	–38.677 507	–	–
1	4	–153.528 201	–38.382 050	185.40	160.86
2	6	–229.704 939	–38.284 156	61.43	63.46
3	8	–305.882 657	–38.235 332	30.64	32.80
4	10	–382.060 842	–38.206 084	18.35	19.66
5	12	–458.239 117	–38.186 593	12.23	12.94
6	14	–534.417 439	–38.172 674	8.73	9.08
7	16	–610.595 319	–38.162 207	6.57	6.69
8	18	–686.773 695	–38.154 094	5.09	5.10
9	20	–762.951 962	–38.147 598	4.08	4.01
10	22	–839.130 337	–38.142 288	3.33	3.22
11	24	–915.308 977	–38.137 874	2.77	2.64
12	26	–991.487 912	–38.134 150	2.33	2.20

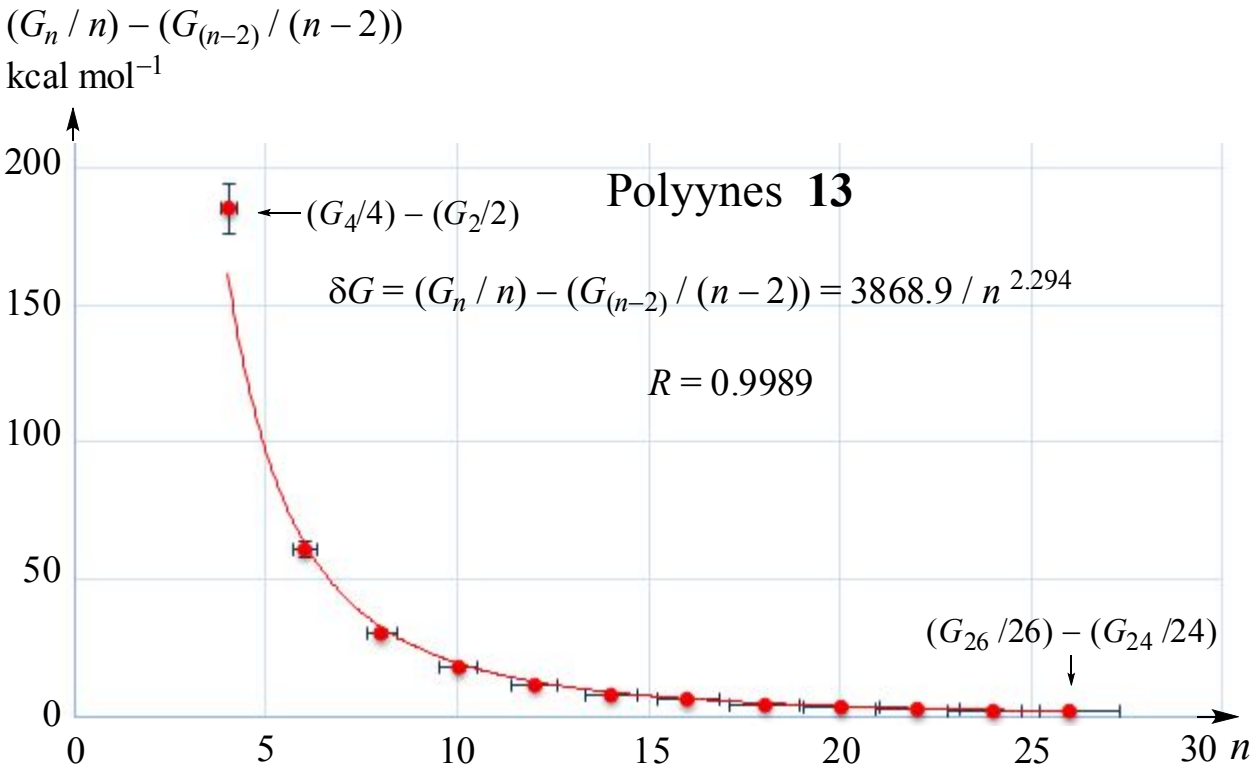
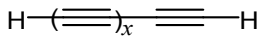


Fig. S-61. Power law (2aa): variations of δG values of polyynes **13** as a function of n (n = number of carbon atoms) at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (error bars given for 95% confidence interval) (see Table S-52).

Table S-53. Polyynes **13**. Absolute energies, E_n, at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (n is the number of carbon atoms per molecule).



13

x	$n = 2x + 2$	E_n (au)	E_n/n (au)	$\delta E = E_n/n - E_{(n-2)}/(n-2)$ (kcal mol^{-1})	$\delta G_{calc} = 3\,860 / n^{2.293}$ (kcal mol^{-1})
0	2	–77.362 337	–38.681 168	–	–
1	4	–153.542 623	–38.385 656	185.44	160.72
2	6	–229.726 321	–38.287 720	61.45	63.42
3	8	–305.911 150	–38.238 894	30.64	32.79
4	10	–382.096 484	–38.209 648	18.35	19.66
5	12	–458.282 047	–38.190 171	12.22	12.94
6	14	–534.467 740	–38.176 267	8.72	9.09
7	16	–610.653 486	–38.165 843	6.54	6.69
8	18	–686.839 276	–38.157 737	5.09	5.11
9	20	–763.025 096	–38.151 255	4.07	4.01
10	22	–839.210 928	–38.145 951	3.33	3.22
11	24	–915.396 738	–38.141 531	2.77	2.64
12	26	–991.582 568	–38.137 791	2.35	2.20

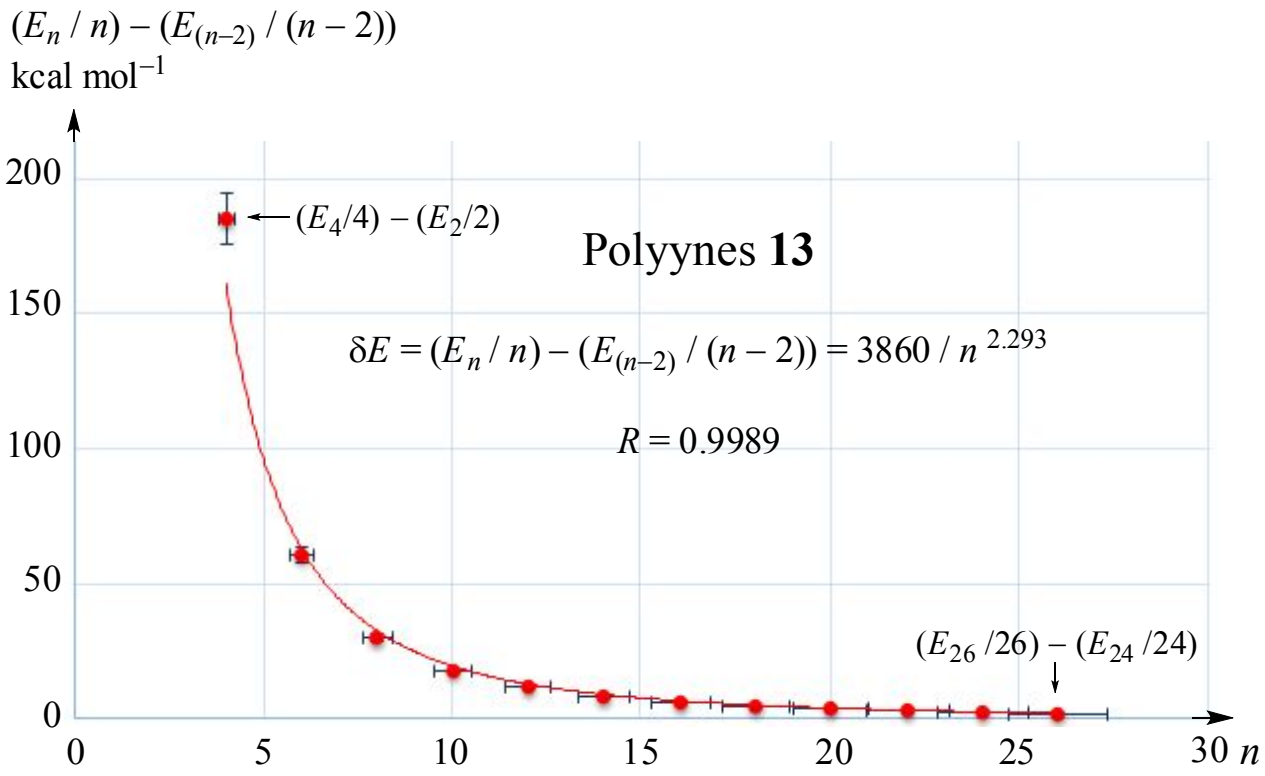
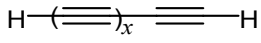


Fig. S-62. Power law (2ab): variations of δE values of polyynes **13** as a function of n (n = number of carbon atoms) at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (error bars given for 95% confidence interval) (see Table S-53).

Table S-54. Polyynes **13**. Absolute free energies, G_n, at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (n is the number of carbon atoms per molecule, $n = 2x + 2$) and linear relationship (1s).



13

x	n	G_n (au)	G_n (kcal mol^{-1})	$G = -23906.64925n - 721.56$ (1s) (kcal mol^{-1})	δG (kcal mol^{-1})
0	2	–77.361 367	–48 544.9927	–48 534.86	–10.13
1	4	–153.546 940	–96 352.1635	–96 348.16	–4.00
2	6	–229.736 807	–144 162.029	–144 161.46	–0.57
3	8	–305.929 837	–191 973.879	–191 974.75	0.87
4	10	–382.125 244	–239 787.221	–239 788.05	0.83
5	12	–458.321 189	–287 600.90	–287 601.35	0.45
6	14	–534.515 791	–335 413.737	–335 414.65	0.91
7	16	–610. 706 543	–383 224.157	–383 227.95	3.79
8	18	–686.903 890	–431 038.717	–431 041.25	2.53
9	20	–763.103 072	–478 854.427	–478 854.54	0.11
10	22	–839.296 282	–526 666.39	–526 667.84	1.45
11	24	–915.489 051	–574 478.077	–574 481.14	3.06
12	26	–991.686 281	–622 292.562	–622 294.44	1.88
13	28	–1 067.883 003	–670 106.729	–670 107.74	1.01
14	30	–1 144.076 903	–717 919.125	–717 921.04	1.91
15	32	–1 220.270 861	–765 731.558	–765 734.34	2.78
16	34	–1 296.470 695	–813 547.678	–813 547.63	-0.05
17	36	–1 372.665 420	–861 360.591	–861 360.93	0.34
18	38	–1 448.855 940	–909 170.866	–909 174.23	3.36
19	40	–1 525.056 649	–956 987.535	–956 987.53	–0.005
20	42	–1 601.252 931	–1 004 801.43	–1 004 800.83	–0.6
21	44	–1 677.449 113	–1 052 615.25	–1 052 614.13	–1.12
22	46	–1 753.640 430	–1 100 426.03	–1 100 427.43	1.40
23	48	–1 829.837 885	–1 148 240.66	–1 148 240.76	0.10
24	50	–1 906.037 242	–1 196 056.48	–1 196 054.02	–2.46
25	52	–1 982.233 086	–1 243 870.09	–1 243 867.32	–2.77
26	54	–2 058.424 083	–1 291 680.67	–1 291 680.62	–0.05

27	56	–2 134.621 886	–1 339 495.51	–1 339 493.92	–1.59
28	58	–2 210.817 382	–1 387 308.91	–1 387 307.22	–1.69
30	60	–2 287.012 882	–1 435 122.31	–1 435 120.52	–1.79

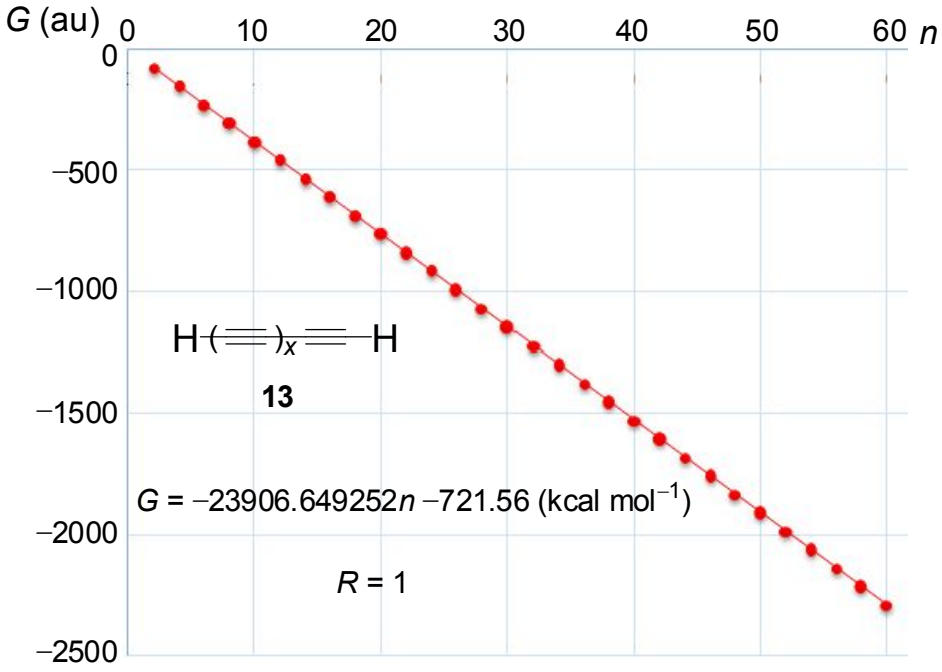


Fig. S-63. G_n values of polyynes **13** as a function of n (n = number of carbon atoms) at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (1s) (see Table S-54).

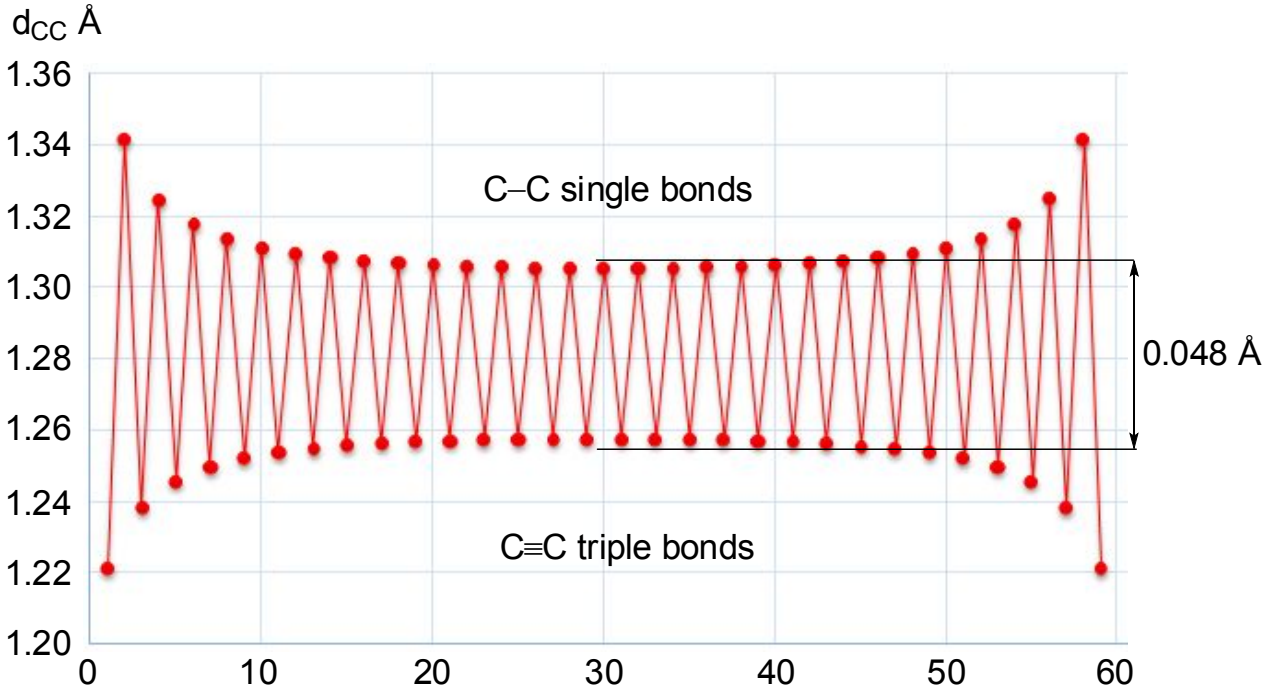


Fig. S-64. Variations of the C–C bond lengths (from d(C_1)–(C_2) to d(C_{59})–(C_{60})) for the polyyne $C_{60}H_2$.

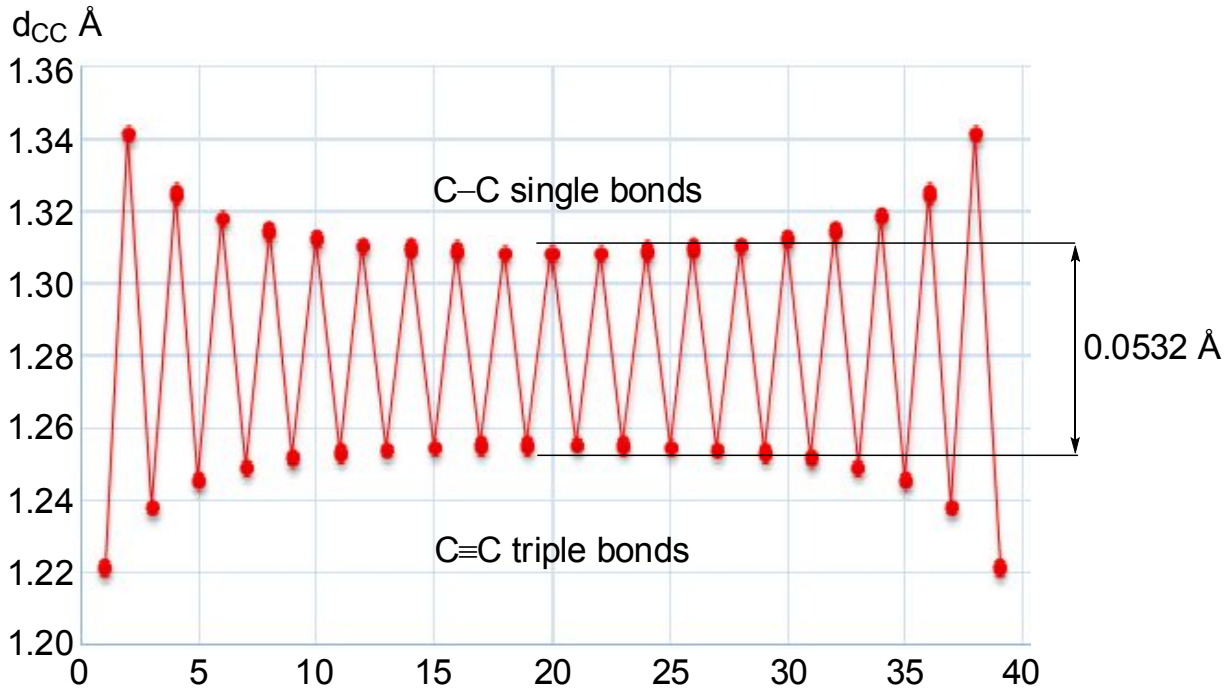


Fig. S-65. Variations of the C–C bond lengths (from d(C_1)–(C_2) to d(C_{39})–(C_{40})) for the polyyne $C_{40}H_2$.

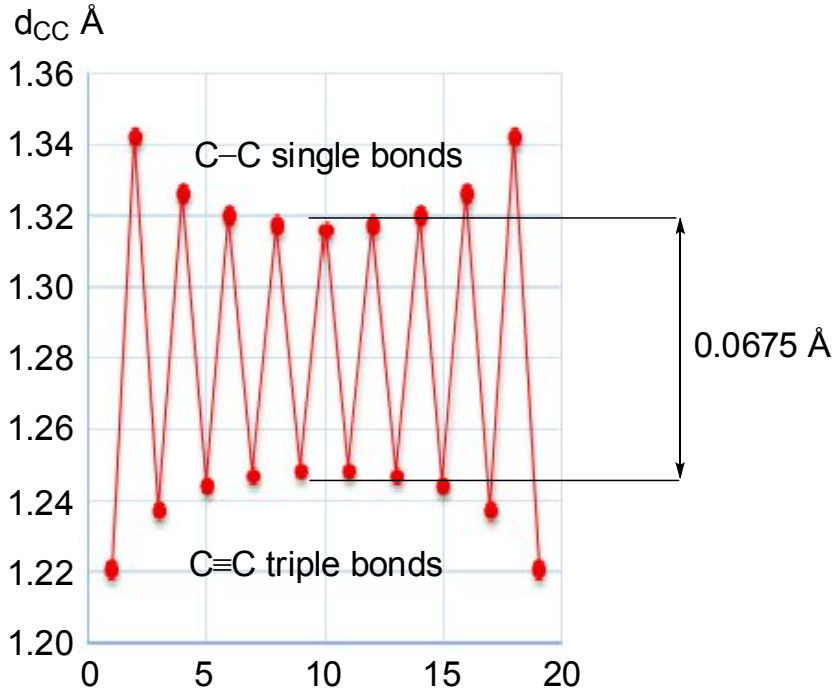
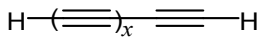


Fig. S-66. Variations of the C–C bond lengths (from d(C_1)–(C_2) to d(C_{19})–(C_{20})) for the polyyne $C_{20}H_2$.

Table S-55. Polyynes **13**. Absolute free energies, G_n, at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (n is the number of carbon atoms per molecule, $n = 2x + 2$).



13

x	n	G_n (au)	G_n/n (au)	G_n/n (kcal mol^{-1})	$\delta G = G_n/n - G_{(n-2)}/(n-2)$ (kcal mol^{-1})	$\delta G_{calc} = 3002.2 / n^{2.192}$ (kcal mol^{-1})
0	2	–77.361 367	–38.680 683	–24 272.50	–	–
1	4	–153.546 940	–38.386 735	–24 088.04	184.45	143.79
2	6	–229.736 807	–38.289 468	–24 027.00	61.04	59.12
3	8	–305.929 837	–38.241 123	–23 996.67	30.27	31.47
4	10	–382.125 244	–38.212 524	–23 978.72	17.95	19.29
5	12	–458.321 189	–38.193 432	–23 966.74	11.98	12.94
6	14	–534.515 791	–38.179 699	–23 958.12	8.62	9.23
7	16	–610. 706 543	–38.169 159	–23 951.51	6.61	6.89
8	18	–686.903 890	–38.161 327	–23 946.59	4.91	5.32
9	20	–763.103 072	–38.155 154	–23 942.72	3.87	4.22
10	22	–839.296 282	–38.149 831	–23 939.38	3.34	3.43
11	24	–915.489 051	–38.145 377	–23 936.59	2.79	2.83
12	26	–991.686 281	–38.141 780	–23 934.33	2.26	2.37
13	28	–1 067.883 003	–38.138 679	–23 932.38	1.95	2.02
14	30	–1 144.076 903	–38.135 897	–23 930.64	1.74	1.74
15	32	–1 220.270 861	–38.133 464	–23 929.11	1.53	1.51
16	34	–1 296.470 695	–38.131 491	–23 927.87	1.24	1.32
17	36	–1 372.665 420	–38.129 595	–23 926.68	1.19	1.16
18	38	–1 448.855 940	–38.127 788	–23 925.55	1.13	1.03
19	40	–1 525.056 649	–38.126 416	–23 924.69	0.86	0.92
20	42	–1 601.252 931	–38.125 070	–23 923.84	0.84	0.83
21	44	–1 677.449 113	–38.123 843	–23 923.07	0.77	0.75
22	46	–1 753.640 430	–38.122 618	–23 922.30	0.77	0.68
23	48	–1 829.837 885	–38.121 623	–23 921.68	0.62	0.62
24	50	–1 906.037 242	–38.120 745	–23 921.13	0.55	0.57
25	52	–1 982.233 086	–38.119 867	–23 920.58	0.55	0.52
26	54	–2 058.424 083	–38.118 964	–23 920.01	0.56	0.48

27	56	–2 134.621 886	–38.118 248	–23 919.56	0.45	0.44
28	58	–2 210.817 382	–38.117 541	–23 919.12	0.44	0.41
30	60	–2 287.012 882	–38.116 881	–23 918.70	0.41	0.38

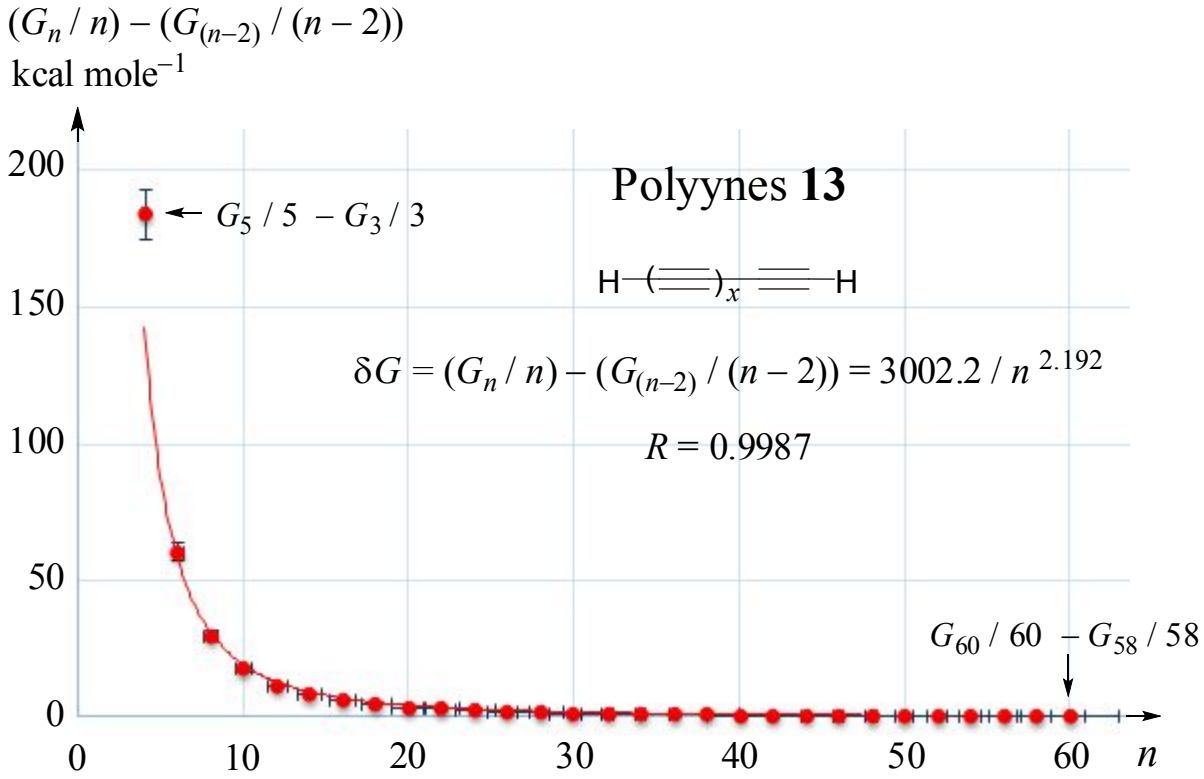


Fig. S-67. Power law (2ac): variations of δ*G* values of polyynes **13** as a function of *n* (*n* = number of carbon atoms) at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (error bars given for 95% confidence interval) (*n* is the number of carbon atoms per molecule) (see Table S-55).

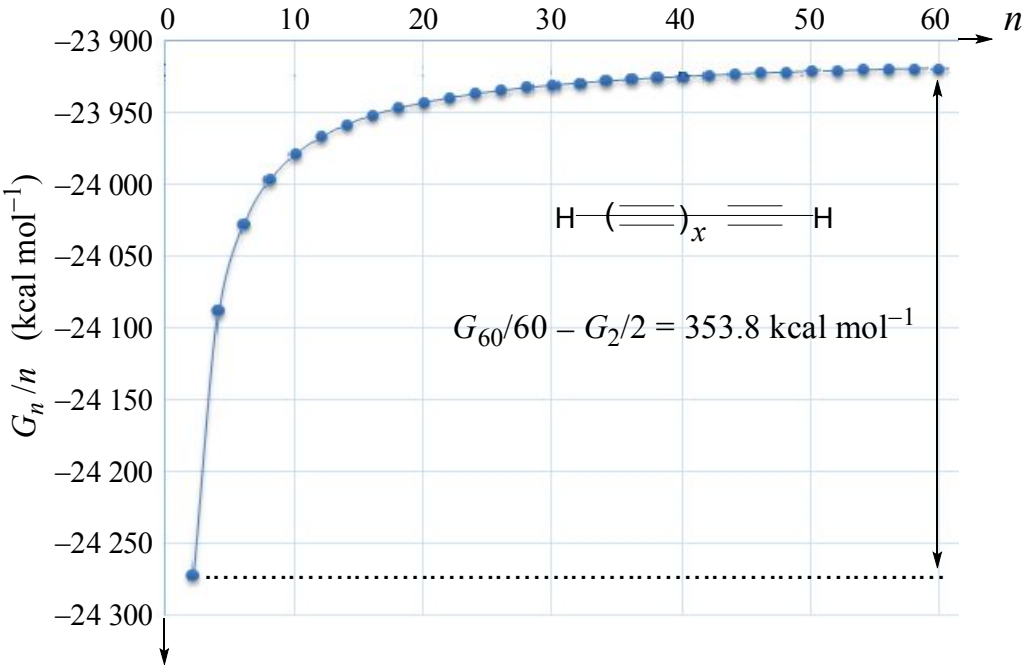
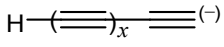


Fig. S-68. Variations of G_n /n values of polyacetylenes **13** as a function of n (n = number of carbon atoms) at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (see Table S-55).

Table S-56. Polyyne anions **14**. Absolute free energies, G_n, at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (n is the number of carbon atoms per molecule) and linear relationship (1t).



14

x	$n = 2x + 2$	G_n (au)	G_n (kcal mol^{-1})	$G = -23903.040516n - 369.43$ (1t) (kcal mol^{-1})	δG (kcal mol^{-1})
0	2	–76.755 447	–48 164.7722	–48 175.51	10.74
1	4	–152.952 159	–95 978.9328	–95 981.59	2.66
2	6	–229.143 124	–143 789.487	–143 787.67	–1.82
3	8	–305.330 630	–191 597.871	–191 593.75	–4.12
4	10	–381.515 878	–239 404.838	–239 399.83	–5.01
5	12	–457.699 600	–287 210.847	–287 205.92	–4.93
6	14	–533.882 344	–335 016.243	–335 012.00	–4.24
7	16	–610.064 201	–382 821.082	–382 818.08	–3.00
8	18	–686.244 975	–430 625.241	–430 624.16	–1.08
9	20	–762.425 566	–478 429.286	–478 430.24	0.95
10	22	–838.605 005	–526 232.607	–526 236.32	3.71
11	24	–914.784 996	–574 036.275	–574 042.40	6.12

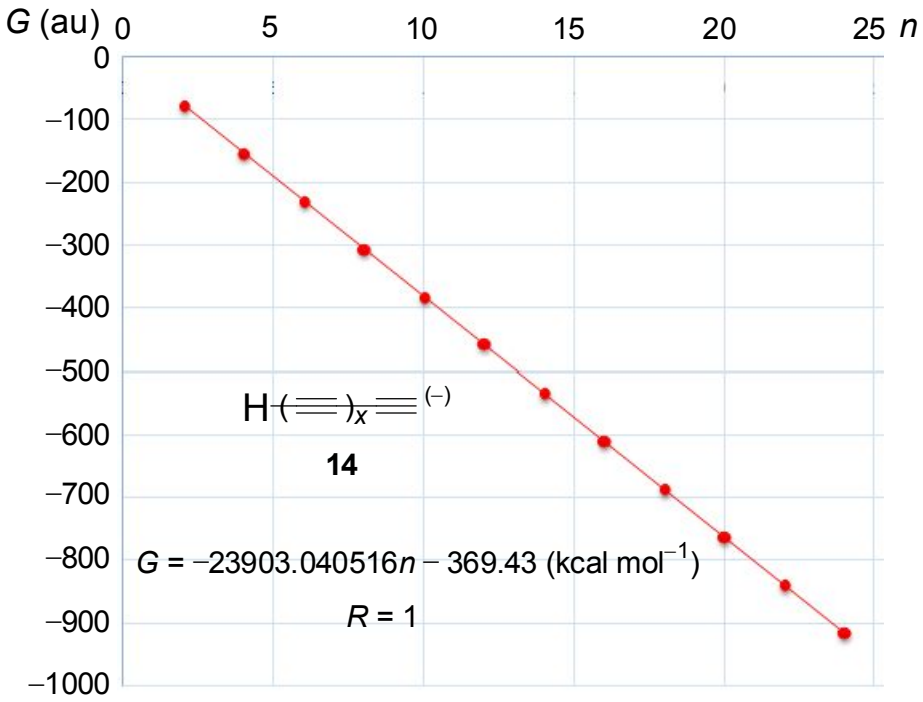
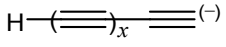


Fig. S-69. G_n values of polyyne anions **14** as a function of n (n = number of carbon atoms) at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (1t) (see Table S-56)

Table S-57. Polyyne Anions **14**. Absolute free energies, G_n, at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (n is the number of carbon atoms per molecule).



14

x	$n = 2x + 2$	G_n (au)	G_n/n (au)	$\delta G = G_n/n - G_{(n-2)}/(n-2)$ (kcal mol^{-1})	$\delta G_{calc} = 1\,686.9 / n^{2.231}$ (kcal mol^{-1})
0	2	–76.755 447	–38.377 723	–	–
1	4	–152.952 159	–38.238 040	87.65	76.54
2	6	–229.143 124	–38.190 521	29.82	30.98
3	8	–305.330 630	–38.166 329	15.18	16.30
4	10	–381.515 878	–38.151 588	9.25	9.91
5	12	–457.699 600	–38.141 633	6.25	6.60
6	14	–533.882 344	–38.134 453	4.50	4.68
7	16	–610.064 201	–38.129 126	3.41	3.47
8	18	–686.244 975	–38.124 721	2.76	2.67
9	20	–762.425 566	–38.121 278	2.16	2.11
10	22	–838.605 005	–38.118 409	1.80	1.71
11	24	–914.784 996	–38.116 041	1.48	1.41

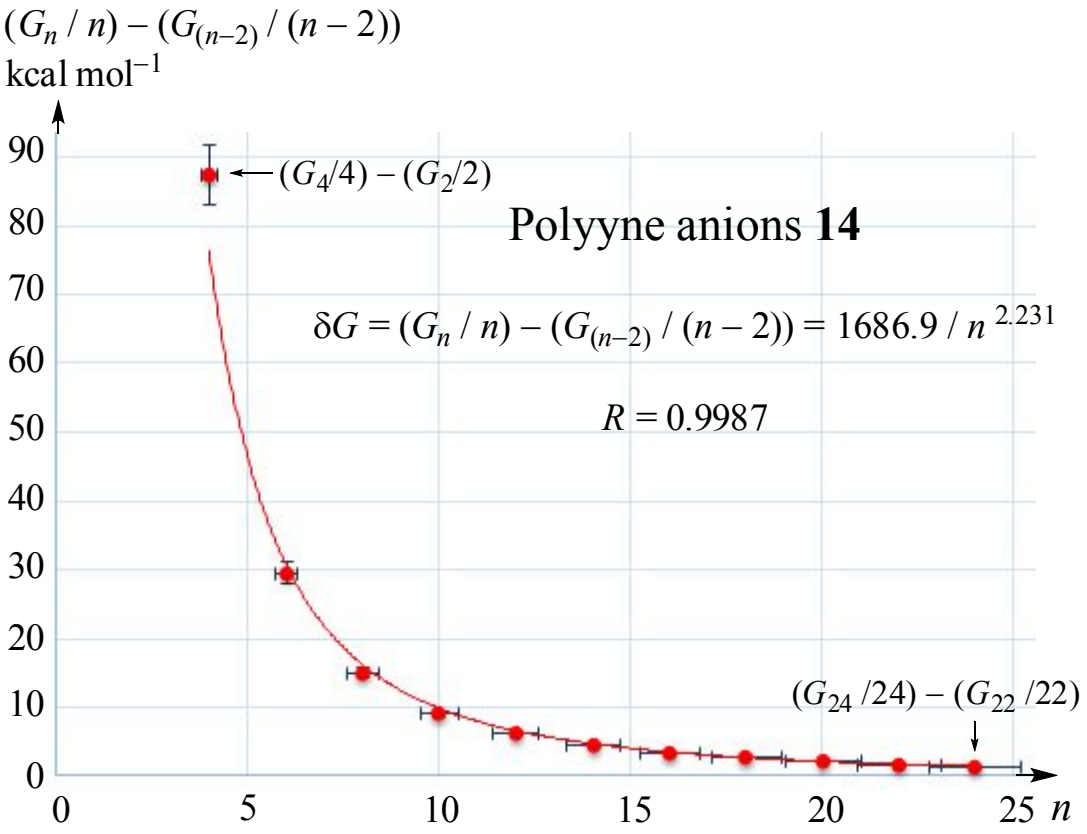
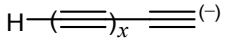


Fig. S-70. Power law (2ad): variations of δG values of polyyne anions **14** as a function of n (n = number of carbon atoms) at the at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (n is the number of carbon atoms per molecule) (error bars given for 95% confidence interval) (see Table S-57).

Table S-58. Polyyne Anions **14**. Absolute energies, E_n, at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (n is the number of carbon atoms per molecule).



14

x	$n = 2x + 2$	E_n (au)	E_n/n (au)	$\delta E = E_n/n - E_{(n-2)}/(n-2)$ (kcal mol^{-1})	$\delta E_{calc} = 1\,653.2 / n^{2.221}$ (kcal mol^{-1})
0	2	–76.750 473	–38.375 236	–	–
1	4	–152.953 821	–38.238 455	85.83	76.06
2	6	–229.151 878	–38.191 980	29.16	30.91
3	8	–305.346 415	–38.168 302	14.86	16.31
4	10	–381.538 776	–38.153 877	9.05	9.94
5	12	–457.729 630	–38.144 136	6.11	6.63
6	14	–533.919 442	–38.137 103	4.41	4.70
7	16	–610.108 468	–38.131 779	3.34	3.50
8	18	–686.296 874	–38.127 604	2.62	2.69
9	20	–762.484 869	–38.124 243	2.11	2.13
10	22	–838.672 509	–38.121 478	1.74	1.73
11	24	–914.859 814	–38.119 159	1.46	1.42
12	26	–991.046 876	–38.117 187	1.24	1.19

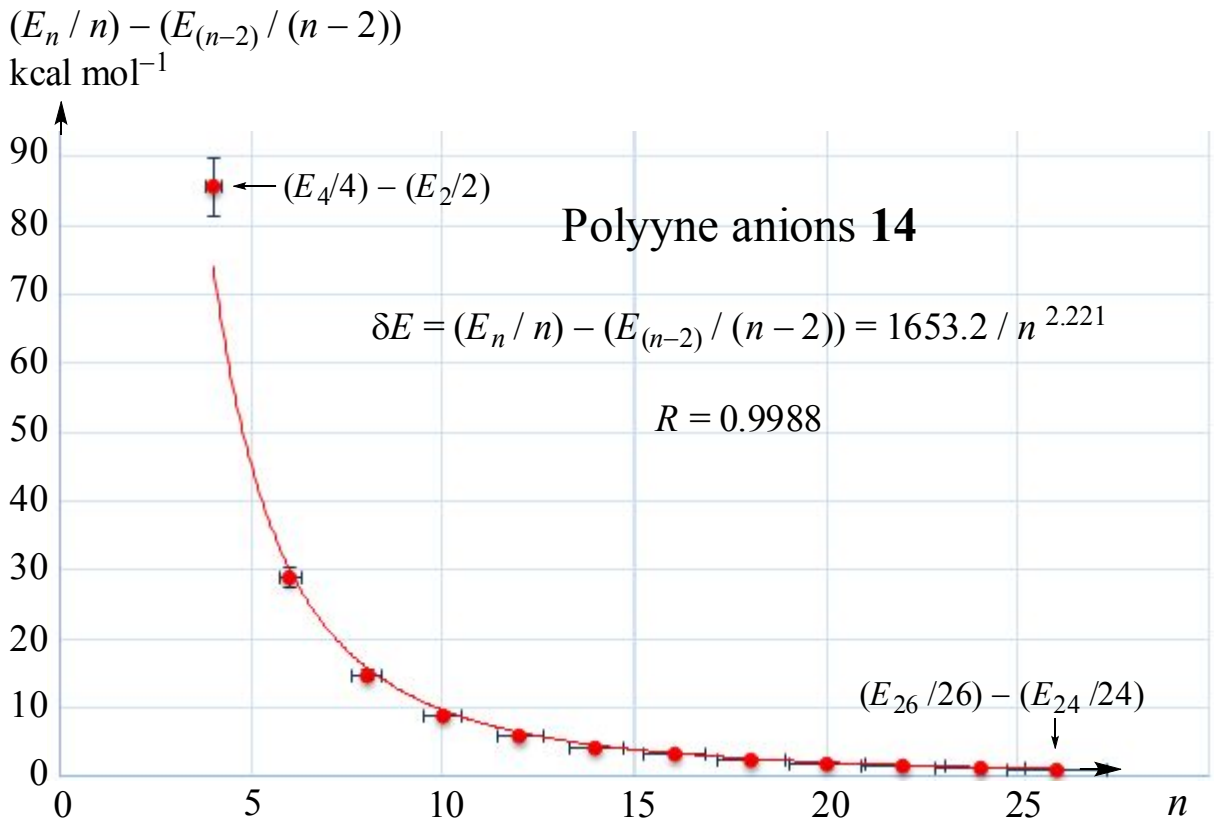
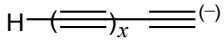


Fig. S-71. Power law (2ae): variations of δE values of polyyne anions **14** as a function of n (n = number of carbon atoms) at the at the B3LYP/6-311++G(3df,3pd) level of theory in ideal gas (n is the number of carbon atoms per molecule) (error bars given for 95% confidence interval) (see Table S-58).

Table S-59. Polyyne Anions **14**. Absolute free energies, G_n, at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (n is the number of carbon atoms per molecule, $n = 2x + 2$) and linear relationship (1u).



14

x	n	G_n (au)	G_n (kcal mol^{-1})	$G = -23907.39063n - 371.7$ (1u) (kcal mol^{-1})	δG (kcal mol^{-1})
0	2	–76.760 036	–48 167.6518	–48 186.48	18.82
2	6	–229.175 321	–95 990.2543	–96 001.26	11.00
3	8	–305.379 195	–143 809.691	–143 816.04	6.35
4	10	–381.581 349	–191 628.346	–191 630.82	2.47
5	12	–457.784 279	–239 445.922	–239 445.60	–0.32
6	14	–533.983 143	–287 263.984	–287 260.39	–3.59
7	16	–610.179 141	–335 079.495	–335 075.17	–4.32
8	18	–686.378 843	–382 893.208	–382 889.95	–3.26
9	20	–762.579 763	–430 709.245	–430 704.73	–4.51
10	22	–838.777 524	–478 526.046	–478 519.51	–6.53
11	24	–914.971 287	–526 340.865	–526 334.30	–6.56
12	26	–991.170 580	–574 153.175	–574 149.07	–4.10
13	28	–1 067.369 08	–621 968.955	–621 963.86	–5.09
14	30	–1 143.567 750	–669 784.238	–669 778.64	–5.60
15	32	–1 219.759 846	–717 599.627	–717 593.42	–6.21
16	34	–1 295.960 518	–765 410.891	–765 408.20	–2.69
17	36	–1 372.156 934	–813 227.537	–813 223.00	–4.54
18	38	–1 448.347 849	–861 041.512	–861 037.76	–3.75
19	40	–1 524.549 200	–908 852.035	–908 852.54	0.50
20	42	–1 600.749 802	–956 669.106	–956 667.32	–1.79
21	44	–1 676.943 822	–1 004 485.71	–1 004 482.10	–3.61
22	46	–1 753.135 817	–1 052 298.18	–1 052 296.90	–1.28
23	48	–1 829.334 220	–1 100 109.38	–1 100 111.70	2.32
24	50	–1 905.533 582	–1 147 924.6	–1 147 926.45	1.85
25	52	–1 981.730 261	–1 195 740.43	–1 195 741.23	0.80
26	54	–2 057.922 266	–1 243 554.57	–1 243 556.00	1.43

27	56	–2 134.120 445	–1 291 365.77	–1 291 370.79	5.02
28	58	–2 210.316 266	–1 339 180.85	–1 339 185.57	4.72
29	60	–2 286.512 685	–1 386 994.45	–1 387 000.30	5.84

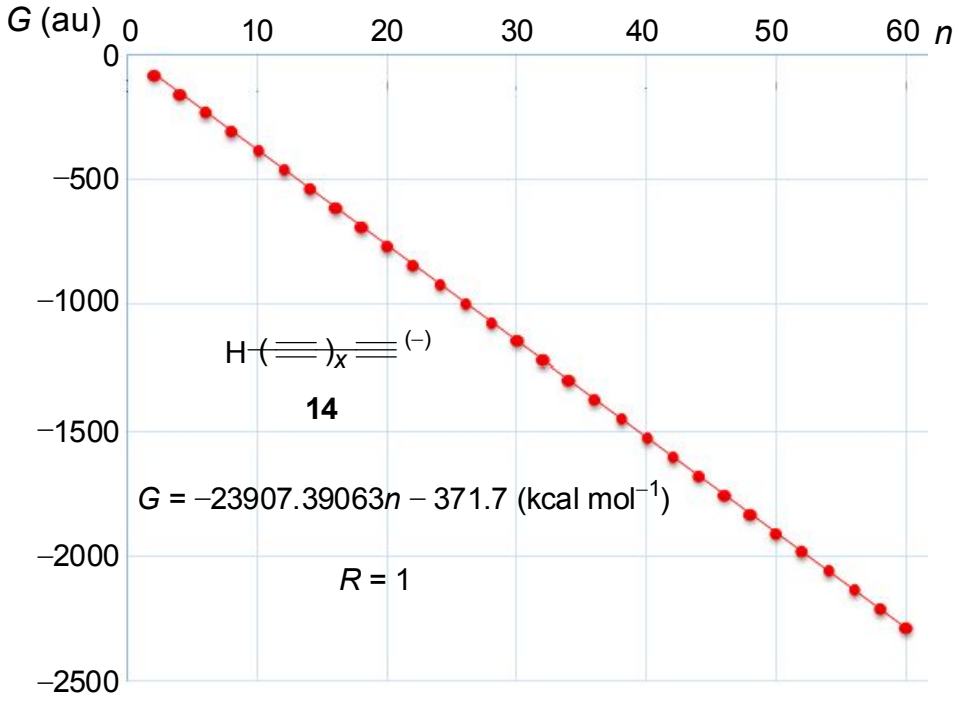
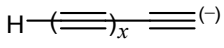


Fig. S-72. G_n values of polyyne anions **14** as a function of n (n = number of carbon atoms) at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (1u) (see Table S-59)

Table S-60. Polyyne Anions **14**. Absolute free energies, G_n, at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (n is the number of carbon atoms per molecule, $n = 2x + 2$).



14

x	n	G_n (au)	G_n/n (au)	G_n/n (kcal mol^{-1})	$\delta G = G_n/n - G_{(n-2)}/(n-2)$ (kcal mol^{-1})	$\delta G_{calc} = 1\,271.2 / n^{2.124}$ (kcal mol^{-1})
0	2	–76.760 036	–38.380 018	–24 083.82	–	–
1	4	–152.970 201	–38.242 550	–23 997.56	86.26	66.90
2	6	–229.175 321	–38.195 886	–23 968.28	29.28	28.27
3	8	–305.379 195	–38.172 399	–23 953.54	14.74	15.35
4	10	–381.581 349	–38.158 135	–23 944.59	8.95	9.55
5	12	–457.784 279	–38.148 690	–23 938.66	5.93	6.49
6	14	–533.983 143	–38.141 653	–23 934.25	4.42	4.67
7	16	–610.179 141	–38.136 196	–23 930.83	3.42	3.52
8	18	–686.378 843	–38.132 158	–23 928.29	2.53	2.7
9	20	–762.579 763	–38.128 988	–23 926.30	1.98	2.19
10	22	–838.777 524	–38.126 251	–23 924.58	1.72	1.79
11	24	–914.971 287	–38.123 804	–23 923.05	1.53	1.49
12	26	–991.170 580	–38.121 953	–23 921.89	1.16	1.25
13	28	–1 067.369 08	–38.120 324	–23 920.86	1.02	1.07
14	30	–1 143.567 750	–38.118 925	–23 919.99	0.88	0.93
15	32	–1 219.759 846	–38.117 495	–23 919.09	0.90	0.81
16	34	–1 295.960 518	–38.116 486	–23 918.46	0.63	0.71
17	36	–1 372.156 934	–38.115 470	–23 917.82	0.64	0.63
18	38	–1 448.347 849	–38.114 417	–23 917.16	0.66	0.56
19	40	–1 524.549 200	–38.113 730	–23 916.73	0.43	0.50
20	42	–1 600.749 802	–38.113 090	–23 916.33	0.40	0.45
21	44	–1 676.943 822	–38.112 360	–23 915.87	0.45	0.41
22	46	–1 753.135 817	–38.111 648	–23 915.42	0.45	0.37
23	48	–1 829.334 220	–38.111 130	–23 915.10	0.33	0.34
24	50	–1 905.533 582	–38.110 672	–23 914.81	0.29	0.31
25	52	–1 981.730 261	–38.110 197	–23 914.51	0.30	0.29
26	54	–2 057.922 266	–38.109 671	–23 914.18	0.33	0.27
27	56	–2 134.120 445	–38.109 293	–23 913.94	0.24	0.25
28	58	–2 210.316 266	–38.108 901	–23 913.70	0.24	0.23

29	60	–2 286.512 685	–38.108 544	–23 913.47	0.22	0.21

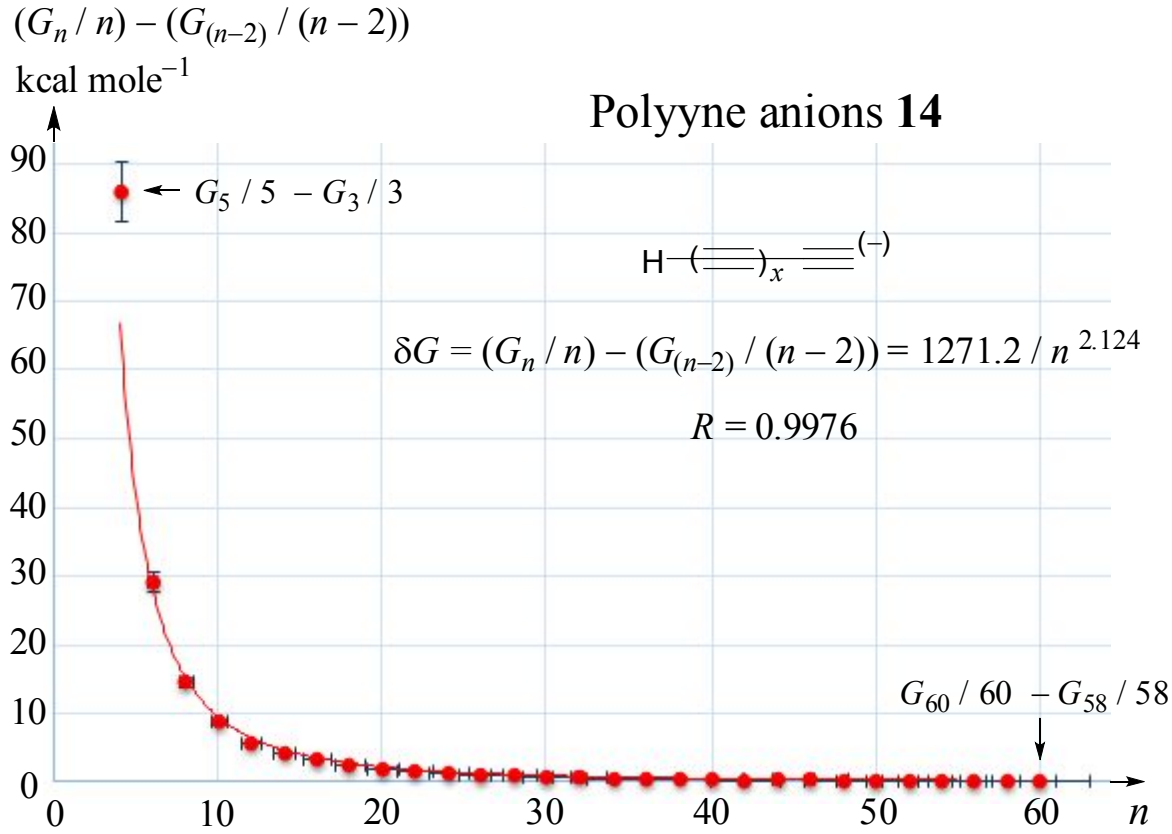


Fig. S-73. Power law (2af): variations of δ*G* values of polyyne anions **14** as a function of *n* (*n* = number of carbon atoms) at the at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (error bars given for 95% confidence interval) (see Table S-60).

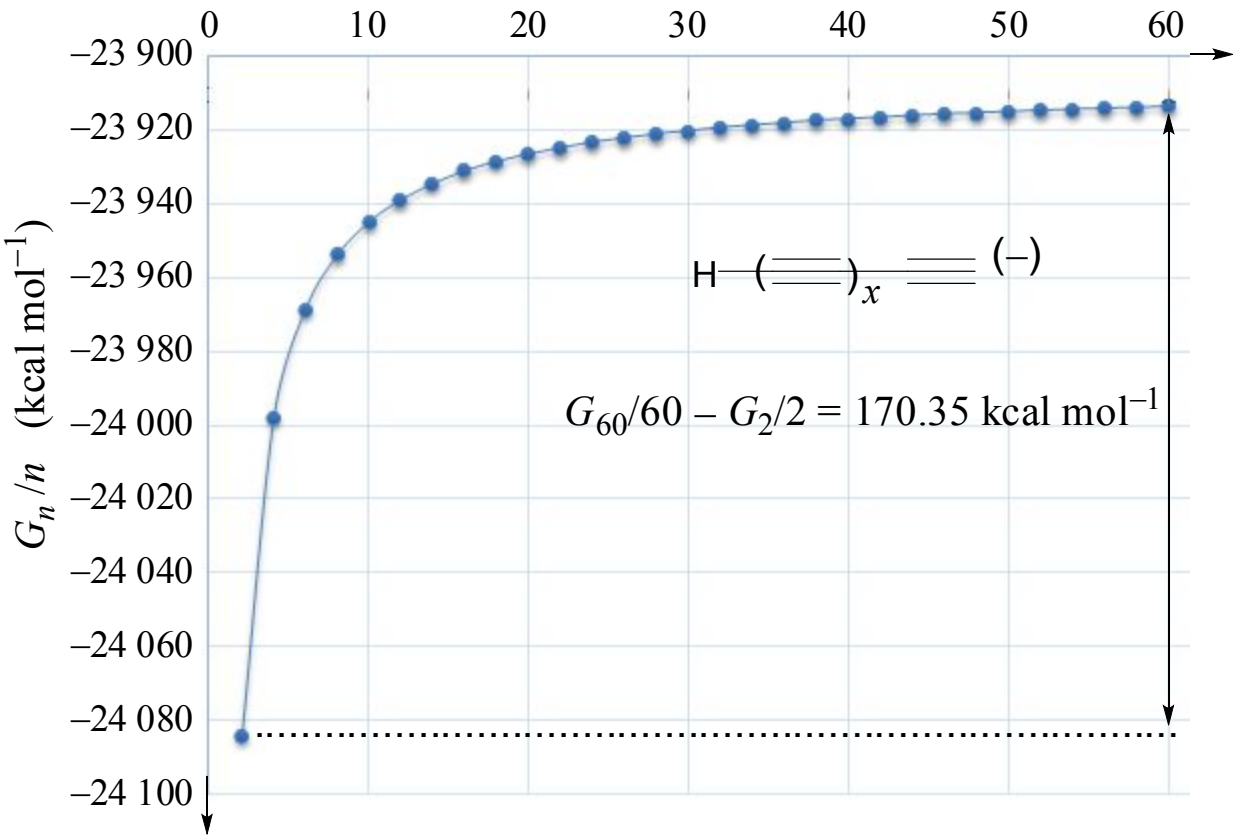


Fig. S-74. Variations of G_n /n values of polyacetylene anions **14** as a function of n (n = number of carbon atoms) at the TPSS-TPSS/6-311++G(df,pd) level of theory in ideal gas (see Table S-60).

Table S-61. Relative stability of various hydrocarbons derivatives in accordance with the lengthening of the chain.

Hydrocarbons	First compound G_n / n (au)	Last compound G_n / n (au)	Differences (au)	Differences (kcal mol^{-1})
n-Alkanes C_1–C_{60} (Ref. 1)	–40.511 040 / 1 = –40.511 040	–2 359.507 857 / 60 = –39.325 131	1.185 909	744.17
(*Z*)-Isoprenes **6**	–196.527 734 / 5 = –39.305 547	–2 345.056 484/ 60 = –39.084 274	0.221 273	138.85
(*E*)-Isoprenes **7**	–196.527 734 / 5 = –39.305 547	–2 345.056 666 / 60 = –39.084 278	0.221 269	138.85
trans-Polyenes **8**	–78.599 411 / 2 = –39.299 705	–2 323.645 203 / 60 = –38.727 420	0.572 285	359.11
trans-Polyene cations **9**	–78.224 891 / 2 = –39.112 445	–2 323.468 125 / 60 = –38.724 469	0.387 976	243.46
odd *trans*-Polyene anions **10**	–117.293 738 / 3 = –39.097 913	–2 362.463 270 / 61 = –38.728 906	0.369 007	231.55
odd *trans*-Polyene radicals **11**	–117.279 111 / 3 = –39.093 037	–2 362.348 199 / 61 = –38.727 020	0.366 017	229.68
odd *trans*-Polyene cations **12**	–116.982 098 / 3 = –38.994 033	–2 362.178 608 / 61 = –38.724 439	0.269 793	169.30
Polyynes **13**	–77.361 367 / 2 = –38.680 683	–2 287.012 882 / 60 = –38.116 881	0.563 802	353.79
Polyyne anions **14**	–76.760 036 / 2 = –38.380 018	–2 286.512 685 / 60 = –38.108 545	0.271 473	170.35