Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

On the diatropic perimeter of iterated *altan*-molecules

G. Monaco

Electronic Supporting Information

Figure ESI1. Orbital energy levels for *altan*^{2}-[10]annulene. In order to compare the HLPM energies with the ab initio ones, the β parameter has been estimated as 0.2377 au, matching the HOMO-LUMO gap of benzene (2β) to the value computed at the HF/6-31G**//B3LYP/6-31G* level (0.47543 au).

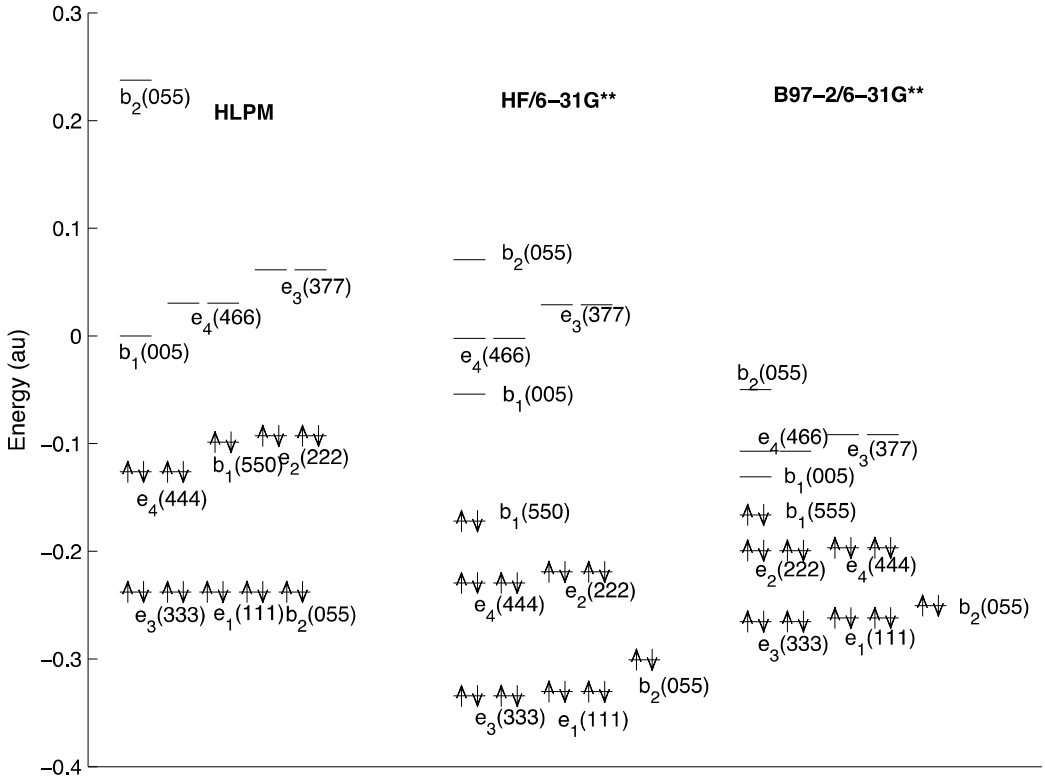
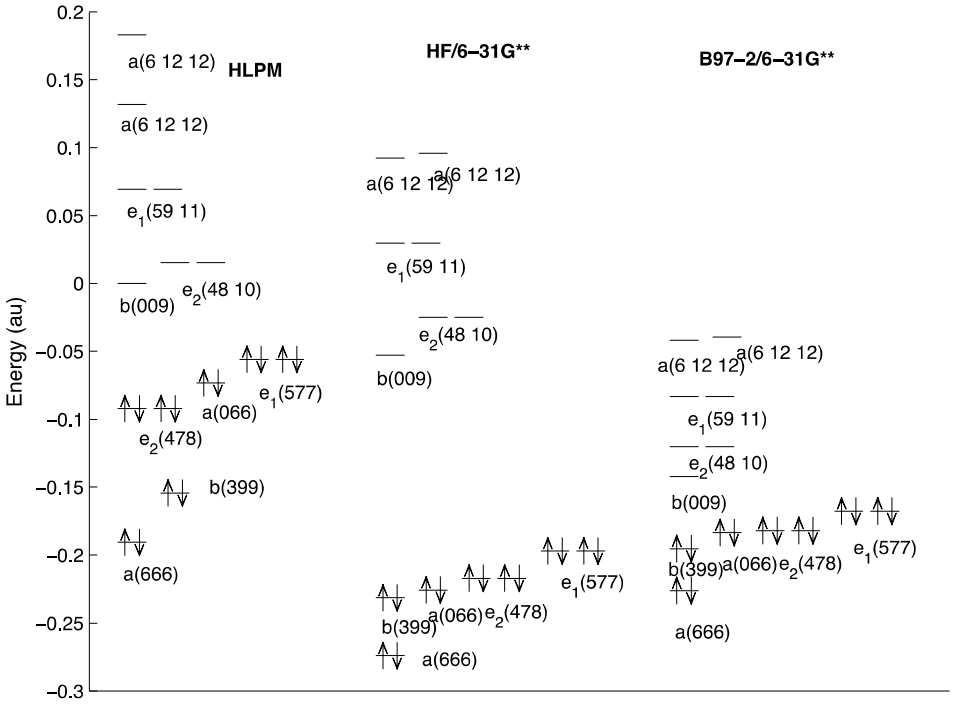


Figure ESI2. Orbital energy levels for *altan*-kekulene. In order to compare the HLPM energies with the ab initio ones, the β parameter has been estimated as 0.2377 au, matching the HOMO-LUMO gap of benzene (2β) to the value computed at the HF/6-31G**//B3LYP/6-31G* level (0.47543 au).



Full reference 18

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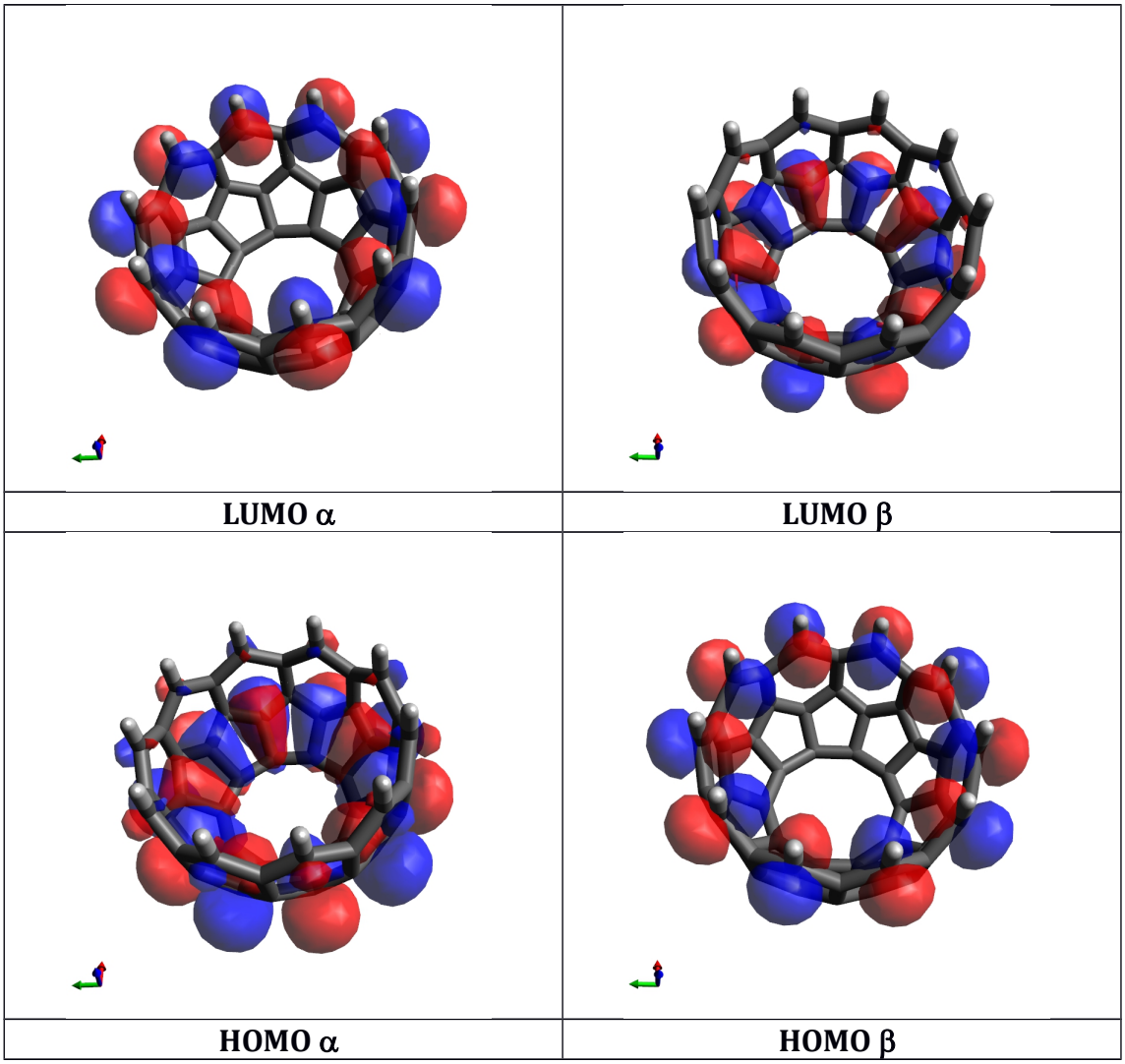
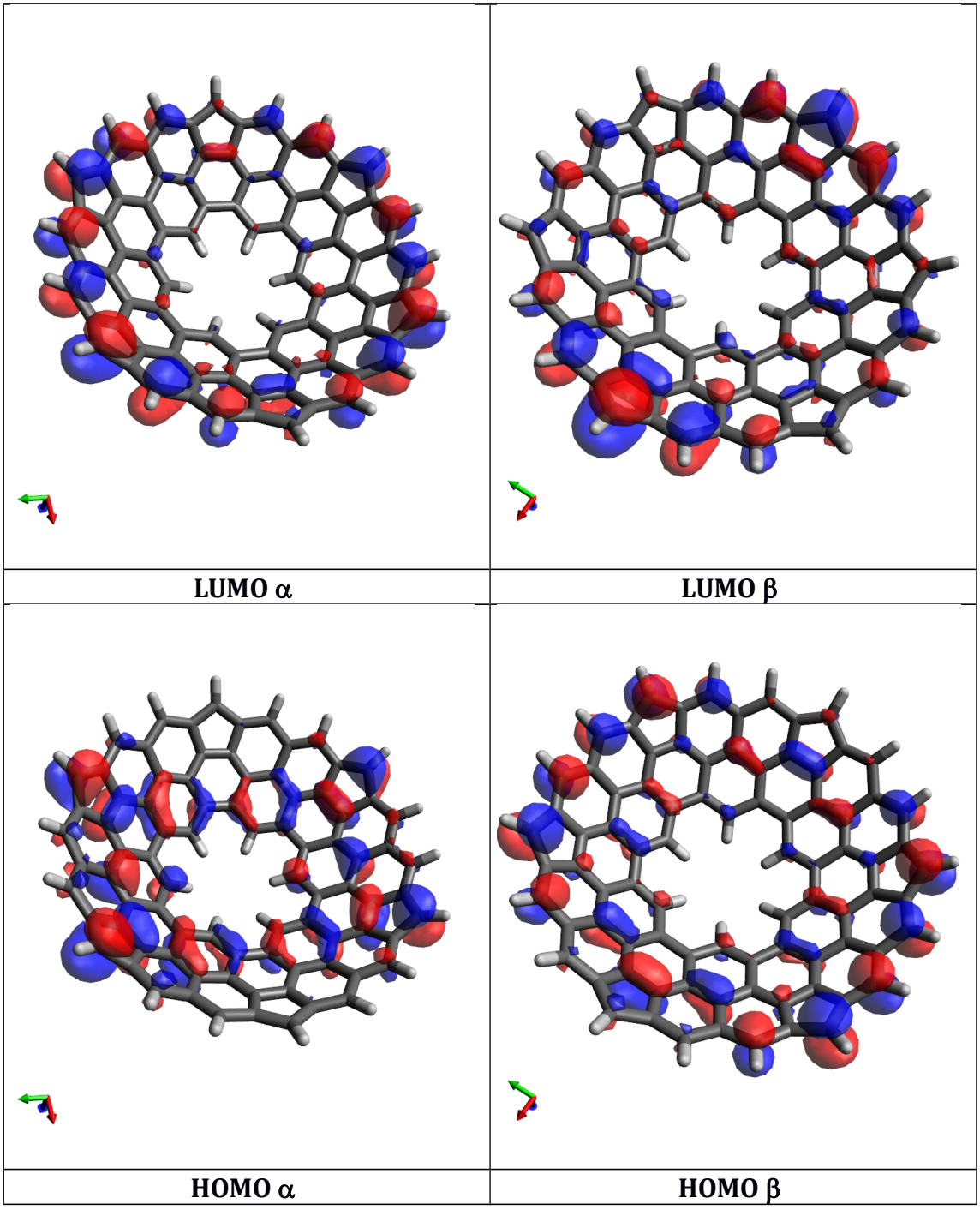
Figure ESI3. Frontier orbitals of *altan*^{2}-[10]annulene at the UB3LYP/6-31G* level



LUMO α	LUMO β
HOMO α	HOMO β

Figure ESI4. Frontier orbitals of *altan*-kekulene at the UB3LYP/6-31G* level



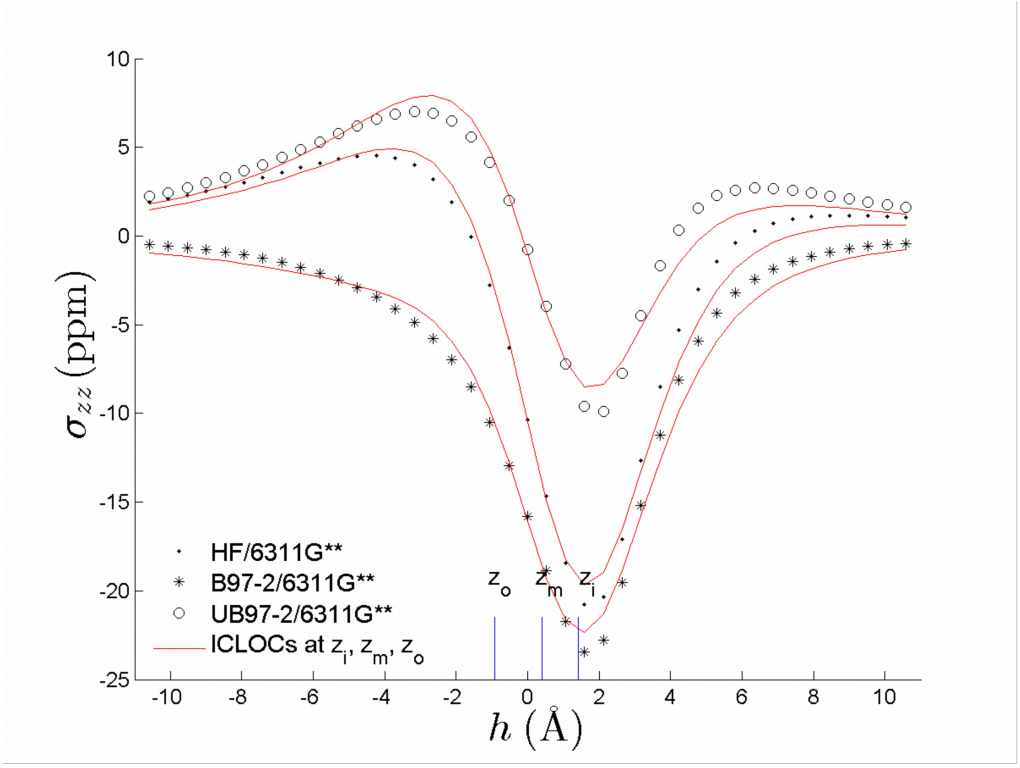
LUMO α	LUMO β
HOMO α	**HOMO β**

Table ESI1. Absolute values of the energies discussed in the paper and Natural Orbital Occupation Numbers (NOONs).

Species	Method	Job	Symm	Energy (au)	NOONs
2 Singlet	UB3LYP/6-31G*	Opt.	C_2	-3215.4869918	2.00 1.99 1.96 1.86 1.37 / 0.63 0.14 0.04 0.01 0.00
2 Triplet	CAS(10,10)/STO-3G //UB3LYP/6-31G*	Single Point	C_2	-3156.1202856	
2 Singlet	CAS(10,10)/STO-3G //UB3LYP/6-31G*	Single Point	C_2	-3156.1113149	1.92 1.92 1.58 1.55 1.50 / 0.53 0.44 0.42 0.08 0.07
2 Singlet	B3LYP/6-31G*	Opt.	C_6	-3215.4820715	
2 Triplet	CAS(10,10)/STO-3G //B3LYP/6-31G*	Single Point	C_6	-3156.0926224	
2 Singlet	CAS(10,10)/STO-3G //B3LYP/6-31G*	Single Point	C_6	-3156.123765	1.94 1.90 1.86 1.80 1.79 / 0.25 0.19 0.14 0.08 0.07
2 Singlet	CAS(10,10)/6-31G* //B3LYP/6-31G*	Single Point	C_6	-3194.9702666	1.95 1.93 1.90 1.87 1.87 / 0.16 0.12 0.09 0.06 0.05
3 Singlet	B3LYP/6-31G*	Opt.	C_{10v}	-1910.827023	
3 Singlet	UB3LYP/6-31G*	Opt.	C_{10v}	-1910.8411170	1.98 1.98 1.861.86 1.29 / 0.71 0.14 0.14 0.02 0.02
3 Triplet	CAS(10,10)/STO-3G //B3LYP/6-31G*	Single Point	C_{10v}	-1875.4321369	
3 Singlet	CAS(10,10)/STO-3G //B3LYP/6-31G*	Single Point	C_{10v}	-1875.4466025	1.91 1.91 1.80 1.80 1.02 / 0.98 0.20 0.20 0.09 0.09
3 Singlet	CAS(10,10)/6-31G* //B3LYP/6-31G*	Single Point	C_{10v}	-1898.627727	1.92 1.92 1.84 1.84 1.36 / 0.64 0.16 0.16 0.08 0.08

Figure ESI5. Comparison of σ_{zz} scans computed for **2** and **3** at the HF/6-311G**, B972/6-31G** and UB972/6-311G** level. Lines are obtained from a fit with 3 ICLOCs with parameters given in Tables ESI2 and ESI3.

2



3

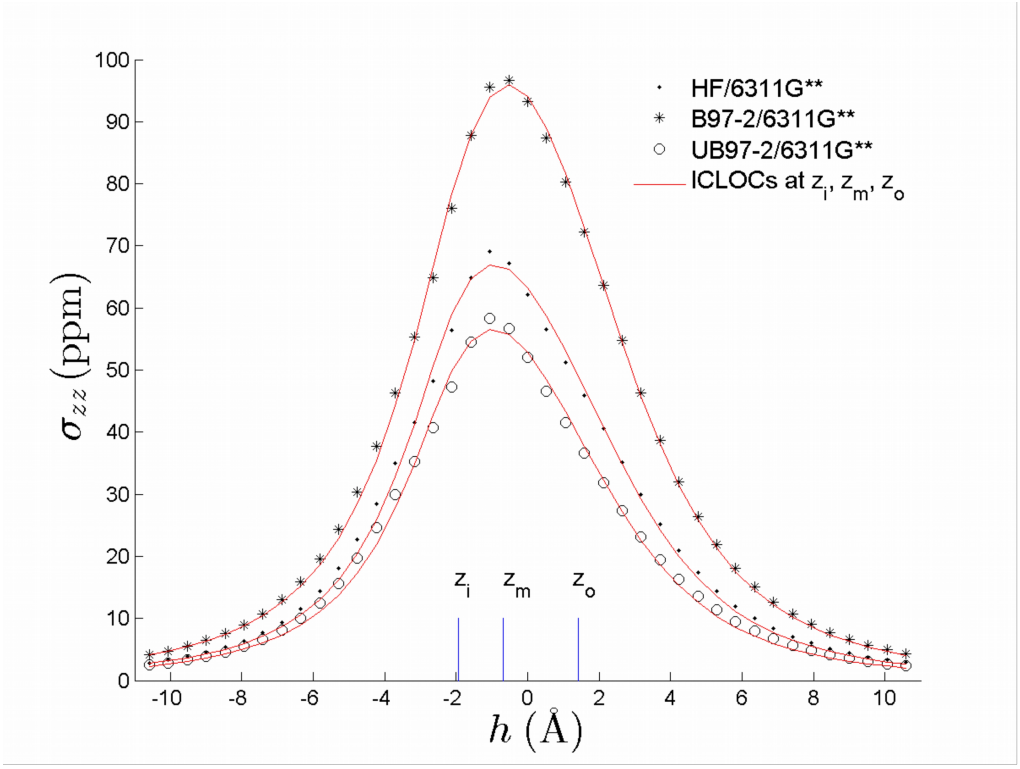


Table ESI2. Best-fit parameters of the 3 ICLOCs used in fitting the σ_{zz} scans for **2** displayed in Fig. ESI5. The scans have been computed, at the HF, B972 and UB972 level, using always the 6-311G** basis set. Each ICLOC model is defined in terms of current strength *I*, ring radius *s*, and ring height *z* (see ref. 45). Calculated (non-relative) current strengths are averages of the appropriate bong current strengths from Fig. 5 of ref. 6. The heights *z* of the loops above the centre of mass along the symmetry axis, and the radii *s* of the loops have been determined geometrically and have not been fitted. Fitted value are expected to be significantly larger than calculated ring current strengths because the fir is affected by the 6 H atoms pointing inwards, which give a strong paramagnetic contribution to the chemical shielding.

Loop	*I* (nA T^{-1})					
	HF scan	Calc.	B972 scan	UB972 scan	*s* (Å)	*z* (Å)
inner	22.6	10.7	18.8	17.4	3.56	1.41
middle	–16.2	–8.7	–17.5	–18.7	5.53	0.40
outer	–4.0	–1.4	10.7	–3.0	7.17	–0.93
Total	2.4	0.6	12.0	–4.3		

Table ESI3. Best-fit parameters of the 3 ICLOCs used in fitting the σ_{zz} scans for **3** displayed in Fig. ESI5. The scans have been computed, at the HF, B972 or UB972 level, using always the 6-311G** basis set. Each ICLOC model is defined in terms of current strength *I*, ring radius *s*, and ring height *z* (see ref. 45). Calculated (non-relative) current strengths are from this paper (Table 1). The heights *z* of the loops above the centre of mass along the symmetry axis, and the radii *s* of the loops have been determined geometrically and have not been fitted.

Loop	*I* (nA T^{-1})						
	HF scan	Calc.	B972 Scan	Calc.	UB972 Scan	*s* (Å)	*z* (Å)
inner	–6.3	–17.7	–3.9	–17.8	–5.2	2.34	–1.94
middle	–25.2	–9.4	–40.6	–23.0	–22.6	3.71	–0.68
outer	–11.5	–13.1	–18.5	–25.1	–7.5	4.07	1.42
Total	–43.0	–40.2	–63.0	–65.9			

B3LYP/6-31G* optimized geometry of C_6 *altan*-kekulene (1 of 3 pages)

6	1.234525	3.616164	1.293861
6	2.514426	2.877232	1.293968
6	-2.514428	2.877212	1.293861
6	3.748969	-0.738941	1.293968
6	-3.748952	-0.738953	1.293861
6	1.234543	-3.616173	1.293968
6	-1.234543	3.616173	1.293968
6	3.748952	0.738953	1.293861
6	-3.748969	0.738941	1.293968
6	2.514428	-2.877212	1.293861
6	-2.514426	-2.877232	1.293968
6	-1.234525	-3.616164	1.293861
6	1.199570	4.914394	0.671057
6	3.656233	3.496078	0.671166
6	-3.656205	3.496055	0.671057
6	4.855809	-1.418352	0.671166
6	1.199575	-4.914430	0.671166
6	-1.199575	4.914430	0.671166
6	4.855775	1.418339	0.671057
6	-4.855809	1.418352	0.671166
6	3.656205	-3.496055	0.671057
6	-1.199570	-4.914394	0.671057
6	0.000000	3.031283	1.628226
6	2.625168	1.515642	1.628226
6	-2.625168	1.515642	1.628226
6	2.625168	-1.515642	1.628226
6	-2.625168	-1.515642	1.628226
6	0.000000	-3.031283	1.628226
6	0.000000	5.559218	0.339107
6	4.814424	2.779610	0.339107
6	-4.814425	2.779609	0.339107
6	4.814425	-2.779609	0.339107
6	0.000000	-5.559218	0.339107
6	2.369320	5.467922	0.147194
6	3.550749	4.785866	0.147239
6	-3.550700	4.785852	0.147194
6	5.920056	-0.682106	0.147239
6	2.369307	-5.467972	0.147239
6	-2.369307	5.467972	0.147239
6	5.920020	0.682070	0.147194
6	-5.920056	0.682106	0.147239
6	3.550700	-4.785852	0.147194
6	-2.369320	-5.467922	0.147194

B3LYP/6-31G* optimized geometry of C_6 *altan*-kekulene (2 of 3 pages)

1	0.000079	2.035514	2.055951
1	1.762846	1.017688	2.055951
1	-1.762767	1.017825	2.055951
1	1.762767	-1.017825	2.055951
1	-1.762846	-1.017688	2.055951
1	-0.000079	-2.035514	2.055951
6	-3.550749	-4.785866	0.147239
6	-5.920020	-0.682070	0.147194
6	-4.855775	-1.418339	0.671057
6	-4.814424	-2.779610	0.339107
6	-3.656233	-3.496078	0.671166
6	5.822766	3.361792	-0.563494
6	5.629779	4.679986	-1.084804
1	6.356336	5.056231	-1.803044
6	4.468791	5.414166	-0.776195
6	3.790828	6.565937	-1.308069
1	4.190512	7.258242	-2.039240
6	2.454412	6.577143	-0.776210
6	6.867839	2.535506	-1.084815
1	7.556996	2.976555	-1.803059
6	6.923178	1.162988	-0.776210
6	7.581682	0.000015	-1.308069
1	8.381078	0.000031	-2.039240
6	6.923201	-1.163003	-0.776195
6	-5.822766	-3.361792	-0.563494
6	-5.629779	-4.679986	-1.084804
1	-6.356336	-5.056231	-1.803044
6	-4.468791	-5.414166	-0.776195
6	-3.790828	-6.565937	-1.308069
1	-4.190512	-7.258242	-2.039240
6	-2.454412	-6.577143	-0.776210
6	-6.867839	-2.535506	-1.084815
1	-7.556996	-2.976555	-1.803059
6	-6.923178	-1.162988	-0.776210
6	-7.581682	-0.000015	-1.308069
1	-8.381078	-0.000031	-2.039240
6	-6.923201	1.163003	-0.776195
6	-6.867876	2.535539	-1.084804
1	-7.556992	2.976633	-1.803044
6	-5.822780	3.361767	-0.563494
6	6.867876	-2.535539	-1.084804
1	7.556992	-2.976633	-1.803044
6	5.822780	-3.361767	-0.563494
6	1.238107	7.215476	-1.084815
1	1.200726	8.032828	-1.803059

B3LYP/6-31G* optimized geometry of C_6 *altan*-kekulene (3 of 3 pages)

6	-0.000015	6.723559	-0.563494
6	-1.238107	-7.215476	-1.084815
1	-1.200726	-8.032828	-1.803059
6	0.000015	-6.723559	-0.563494
6	5.629732	-4.679971	-1.084815
1	6.356270	-5.056273	-1.803059
6	4.468767	-5.414154	-0.776210
6	3.790854	-6.565921	-1.308069
1	4.190566	-7.258211	-2.039240
6	2.454410	-6.577170	-0.776195
6	1.238097	-7.215525	-1.084804
1	1.200656	-8.032864	-1.803044
6	-1.238097	7.215525	-1.084804
1	-1.200656	8.032864	-1.803044
6	-2.454410	6.577170	-0.776195
6	-3.790854	6.565921	-1.308069
1	-4.190566	7.258211	-2.039240
6	-4.468767	5.414154	-0.776210
6	-5.629732	4.679971	-1.084815
1	-6.356270	5.056273	-1.803059

UB3LYP/6-31G* optimized geometry of C_2 *altan*-kekulene (1 of 3 pages)

6	2.510668	-2.881226	1.278430
6	1.233573	-3.617669	1.280664
6	3.738406	0.738757	1.272307
6	-2.510613	-2.881245	1.278491
6	1.233493	3.617673	1.280686
6	-3.738406	0.738705	1.272272
6	3.738406	-0.738705	1.272272
6	-1.233493	-3.617673	1.280686
6	2.510613	2.881245	1.278491
6	-3.738406	-0.738757	1.272307
6	-1.233573	3.617669	1.280664
6	-2.510668	2.881226	1.278430
6	3.653315	-3.503430	0.661655
6	1.199102	-4.922888	0.663419
6	4.846789	1.419587	0.650140
6	-3.653264	-3.503476	0.661760
6	-4.846791	1.419514	0.650062
6	4.846791	-1.419514	0.650062
6	-1.199010	-4.922890	0.663442
6	3.653264	3.503476	0.661760
6	-4.846789	-1.419587	0.650140
6	-3.653315	3.503430	0.661655
6	2.618420	-1.515771	1.606950
6	0.000040	-3.032202	1.615601
6	2.618411	1.515803	1.607030
6	-2.618411	-1.515803	1.607030
6	-0.000040	3.032202	1.615601
6	-2.618420	1.515771	1.606950
6	4.811595	-2.786440	0.323432
6	0.000045	-5.571531	0.336041
6	4.811590	2.786535	0.323574
6	-4.811590	-2.786535	0.323574
6	-4.811595	2.786440	0.323432
6	3.551973	-4.795562	0.147571
6	2.367697	-5.479276	0.147894
6	5.906623	0.687007	0.125823
6	-3.551914	-4.795610	0.147693
6	-5.906614	0.686901	0.125768
6	5.906614	-0.686901	0.125768
6	-2.367612	-5.479298	0.147965
6	3.551914	4.795610	0.147693
6	-5.906623	-0.687007	0.125823
6	-3.551973	4.795562	0.147571
1	1.754174	-1.018732	2.031699
1	0.000045	-2.035867	2.041486

UB3LYP/6-31G* optimized geometry of C_2 *altan*-kekulene (2 of 3 pages)

1	1.754224	1.018746	2.031885
1	-1.754224	-1.018746	2.031885
1	-0.000045	2.035867	2.041486
1	-1.754174	1.018732	2.031699
6	-2.367697	5.479276	0.147894
6	2.367612	5.479298	0.147965
6	1.199010	4.922890	0.663442
6	-0.000045	5.571531	0.336041
6	-1.199102	4.922888	0.663419
6	0.000038	-6.748918	-0.549567
6	1.241037	-7.247432	-1.057860
1	1.206945	-8.076332	-1.762697
6	2.456761	-6.601684	-0.758122
6	3.796267	-6.595440	-1.279290
1	4.200673	-7.294801	-2.001134
6	4.474780	-5.430988	-0.760581
6	-1.240993	-7.247490	-1.057764
1	-1.206915	-8.076402	-1.762586
6	-2.456697	-6.601757	-0.757973
6	-3.796258	-6.595574	-1.279042
1	-4.200703	-7.294983	-2.000817
6	-4.474779	-5.431105	-0.760327
6	-0.000038	6.748918	-0.549567
6	-1.241037	7.247432	-1.057860
1	-1.206945	8.076332	-1.762697
6	-2.456761	6.601684	-0.758122
6	-3.796267	6.595440	-1.279290
1	-4.200673	7.294801	-2.001134
6	-4.474780	5.430988	-0.760581
6	1.240993	7.247490	-1.057764
1	1.206915	8.076402	-1.762586
6	2.456697	6.601757	-0.757973
6	3.796258	6.595574	-1.279042
1	4.200703	7.294983	-2.000817
6	4.474779	5.431105	-0.760327
6	5.636006	4.700683	-1.068815
1	6.367827	5.083336	-1.777936
6	5.823731	3.373157	-0.562778
6	-5.636006	-4.700683	-1.068815
1	-6.367827	-5.083336	-1.777936
6	-5.823731	-3.373157	-0.562778
6	5.635960	-4.700501	-1.069116
1	6.367745	-5.083096	-1.778307
6	5.823702	-3.373011	-0.563017
6	-5.635960	4.700501	-1.069116

UB3LYP/6-31G* optimized geometry of C_2 *altan*-kekulene (3 of 3 pages)

1	-6.367745	5.083096	-1.778307
6	-5.823702	3.373011	-0.563017
6	-6.875640	-2.544059	-1.074929
1	-7.576605	-2.985946	-1.780545
6	-6.919751	-1.172928	-0.771830
6	-7.588797	-0.000088	-1.291760
1	-8.397545	-0.000115	-2.012982
6	-6.919722	1.172770	-0.771948
6	-6.875583	2.543881	-1.075155
1	-7.576516	2.985719	-1.780831
6	6.875583	-2.543881	-1.075155
1	7.576516	-2.985719	-1.780831
6	6.919722	-1.172770	-0.771948
6	7.588797	0.000088	-1.291760
1	8.397545	0.000115	-2.012982
6	6.919751	1.172928	-0.771830
6	6.875640	2.544059	-1.074929
1	7.576605	2.985946	-1.780545

B3LYP/6-31G* optimized geometry of C_{10v} *altan*$_2$-[10]annulene (1 of 2 pages)

6	0.722636	2.224046	-1.939032
6	-0.722636	2.224046	-1.939032
6	-1.891886	1.374536	-1.939032
6	-2.338500	0.000000	-1.939032
6	-1.891886	-1.374536	-1.939032
6	-0.722636	-2.224046	-1.939032
6	0.722636	-2.224046	-1.939032
6	1.891886	-1.374536	-1.939032
6	2.338500	0.000000	-1.939032
6	1.891886	1.374536	-1.939032
6	1.091757	3.360083	-1.016032
6	-1.091757	3.360083	-1.016032
6	-2.858257	2.076645	-1.016032
6	-3.533000	0.000000	-1.016032
6	-2.858257	-2.076645	-1.016032
6	-1.091757	-3.360083	-1.016032
6	1.091757	-3.360083	-1.016032
6	2.858257	-2.076645	-1.016032
6	3.533000	0.000000	-1.016032
6	2.858257	2.076645	-1.016032
6	0.000000	3.885500	-0.356032
6	-2.283840	3.143436	-0.356032
6	-3.695330	1.200686	-0.356032
6	-3.695330	-1.200686	-0.356032
6	-2.283840	-3.143436	-0.356032
6	0.000000	-3.885500	-0.356032
6	2.283840	-3.143436	-0.356032
6	3.695330	-1.200686	-0.356032
6	3.695330	1.200686	-0.356032
6	2.283840	3.143436	-0.356032
6	0.000000	4.063500	1.086968
6	-2.388465	3.287441	1.086968
6	-3.864618	1.255691	1.086968
6	-3.864618	-1.255691	1.086968
6	-2.388465	-3.287441	1.086968
6	0.000000	-4.063500	1.086968
6	2.388465	-3.287441	1.086968
6	3.864618	-1.255691	1.086968
6	3.864618	1.255691	1.086968
6	2.388465	3.287441	1.086968
6	1.254300	3.860338	1.750968
6	-1.254300	3.860338	1.750968
6	-3.283800	2.385820	1.750968
6	-4.059000	0.000000	1.750968

B3LYP/6-31G* optimized geometry of C_{10v} *altan*$_2$-[10]annulene (2 of 2 pages)

6	-3.283800	-2.385820	1.750968
6	-1.254300	-3.860338	1.750968
6	1.254300	-3.860338	1.750968
6	3.283800	-2.385820	1.750968
6	4.059000	0.000000	1.750968
6	3.283800	2.385820	1.750968
1	1.252909	3.856059	2.838968
1	-1.252909	3.856059	2.838968
1	-3.280160	2.383175	2.838968
1	-4.054500	0.000000	2.838968
1	-3.280160	-2.383175	2.838968
1	-1.252909	-3.856059	2.838968
1	1.252909	-3.856059	2.838968
1	3.280160	-2.383175	2.838968
1	4.054500	0.000000	2.838968
1	3.280160	2.383175	2.838968