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

Supporting Information

Stepwise Deprotonation of Sumanene: Electronic Structures, Energetics and Aromaticity Alterations

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Calculation Details

Geometry optimizations were performed with help of hybrid correlation-exchange functional PBE0.[1] All atoms were described at the triple-ζ level using correlation-consistent basis sets (cc-pVTZ). No symmetry restrictions were applied in all cases. All calculated structures are local minima on corresponding potential energy surfaces. Subsequent calculations of the Hessian matrix followed by evaluation of frequencies in the harmonic approximation revealed no imaginary frequency (*i.e.* no negative elements in the Hessian matrix). All these calculations were done with help of Firefly program package (version 8.1.0).[2]

The process of bowl-to-bowl inversion was studied at the PBE0/cc-pVTZ level of theory with help of highly-efficient resolution-of-identity (RI) algorithm, applied using the chain-of-sphere approach (RIJCOSX[3] in terminology of ORCA program,[4] version 3.1.0). All transition states were found to possess only one negative element in calculated Hessian (and, as consequence, one imaginary frequency) clearly corresponding to the transition between reactants and products intended. The nature of transition states was probed through IRC (intrinsic reaction coordinate) technique that led directly to target products or reactants. IRC calculations were performed with help of Firefly program.[2]

Converged PBE0/cc-pVTZ wavefunction was then used for getting insight into the electronic structure of target systems in terms of Natural Bond Orbital (NBO) techniques.[5] The Wiberg bond indexes[6] were used to evaluate the bond orders as it is incorporated in the NBO analysis. All computations were carried out using NBO 6.0 program.[7]

In order to get more reliable evaluation of energetics, single-point calculations (for DFT-optimized geometries) were performed for all minimum structures and transition states with help of highly-accurate single-reference correlated method DLPNO-CCSD(T) (domain-based local pair natural orbitals coupled-cluster with single, double and perturbative triple corrections[8]) with the same basis sets. This method was recently proposed by the group of

Neese and found to be very accurate,[9] providing accuracy comparable with that of CCSD(T), which has reputation of serving as benchmarking method. All these high-level calculations were carried out by using ORCA program.[4] These calculations were performed using RIJCOSX acceleration technique.[3] Also, the same set of single-point calculations was carried out using recently developed double-hybrid DFT functional xDH-PBE0.[10] This functional was proved to provide high accuracy in energy estimations, also very close to that of CCSD(T) method. Calculations at the xDH-PBE0/cc-pVTZ level of theory were performed with Firefly program.[2]

Aromaticity descriptors. Using PBE0/cc-pVTZ-optimized geometries, a set of theoretical descriptors/indexes of aromaticity was calculated. This set includes : (*i*) structure-based Harmonic Oscillator Model of Aromaticity (HOMA, as defined by Kruszewski and Krygowski[11]), (*ii*) Nuclear Independent Chemical Shift (NICS, introduced by von Rague Schleyer *et al.*[12]), and (*iii*) descriptors based on topological Quantum Theory of Atom in Molecule (QTAIM)[13] approach such as Para-Delocalized Index (PDI[14]) and Aromatic Fluctuation Index (FLU[15]). In the latter, two types of atomic spaces were tested, namely, AIM, using Bader's atomic basin definition[16] and Fuzzy atomic space, using Becke atomic space definition.[17] The correlation between the results calculated in fuzzy atomic space and in AIM atomic space was previously reported to be excellent.[18] All QTAIM calculations were carried out by Multiwfn 3.3.7 program.[19] Calculations of NICS values were performed using Gauge Independent Atomic Orbitals (GIAO) approach with help of Gaussian 09 program[20] at the PBE0/cc-pVTZ level of theory. The set of descriptors was augmented by detailed consideration of magnetic induced ring current on target systems using Anisotropy of the Induced Current Density (ACID) approach.[21] The applied magnetic field is perpendicular to the five-membered ring. To obtain induced current vectors and plot map, ACID 2.0.0

program uses the current density tensors, calculated by Continuous Set of Gauge Transformations (CSGT) method[22] implemented in Gaussian 09 package.[20]

Table S1. NBO charges in the neutral sumanene, $C_{21}H_{12}^{0}$, optimized at the PBE0/cc-pVTZ level of theory.

Atom No	Natural Charge	Natural Population: Core	Valence	Rydberg	Total
C 1	-0.03097	1.99883	4.01328	0.01887	6.03097
C 2	-0.03101	1.99883	4.01331	0.01887	6.03101
C 3	-0.03087	1.99883	4.01318	0.01887	6.03087
C 4	0.01957	1.99896	3.96458	0.01689	5.98043
C 5	0.01953	1.99896	3.96462	0.01689	5.98047
C 6	-0.03098	1.99883	4.01329	0.01887	6.03098
C 7	-0.03107	1.99883	4.01337	0.01887	6.03107
C 8	0.01950	1.99896	3.96465	0.01689	5.98050
C 9	0.01958	1.99896	3.96457	0.01689	5.98042
C 10	-0.03094	1.99883	4.01324	0.01887	6.03094
C 11	0.01944	1.99896	3.96471	0.01690	5.98056
C 12	0.01962	1.99896	3.96453	0.01689	5.98038
C 13	-0.20958	1.99913	4.19505	0.01540	6.20958
C 14	-0.20956	1.99913	4.19502	0.01541	6.20956
C 15	-0.20953	1.99913	4.19500	0.01540	6.20953
C 16	-0.20954	1.99913	4.19502	0.01540	6.20954
C 17	-0.20955	1.99913	4.19502	0.01540	6.20955
C 18	-0.20958	1.99913	4.19505	0.01541	6.20958
C 19	-0.43847	1.99929	4.42666	0.01251	6.43847
C 20	-0.43843	1.99929	4.42662	0.01251	6.43843
C 21	-0.43853	1.99929	4.42672	0.01252	6.43853
H 22	0.22838	0.00000	0.76936	0.00226	0.77162
H 23	0.23552	0.00000	0.76227	0.00221	0.76448
H 24	0.22840	0.00000	0.76934	0.00226	0.77160
H 25	0.23552	0.00000	0.76226	0.00221	0.76448
H 26	0.22841	0.00000	0.76933	0.00226	0.77159
H 27	0.23552	0.00000	0.76227	0.00221	0.76448
H 28	0.20826	0.00000	0.78967	0.00207	0.79174
H 29	0.20828	0.00000	0.78966	0.00207	0.79172
H 30	0.20828	0.00000	0.78966	0.00206	0.79172
H 31	0.20827	0.00000	0.78967	0.00207	0.79173
H 32	0.20828	0.00000	0.78966	0.00207	0.79172
H 33	0.20827	0.00000	0.78967	0.00207	0.79173
* Total *	0.00000	41.97935	95.65030	0.37035	138.00000

Table S2. NBO charges in the mono-anionic $C_{21}H_{11}^{-1}$, optimized at the PBE0/cc-pVTZ level of theory.

Atom No	Natural Charge	Natural Population: Core	Valence	Rydberg	Total
C 1	-0.02396	1.99884	4.00561	0.01951	6.02396
C 2	-0.06649	1.99882	4.04786	0.01981	6.06649
C 3	-0.03176	1.99884	4.01329	0.01963	6.03176
C 4	-0.04139	1.99907	4.02363	0.01868	6.04139
C 5	0.01266	1.99896	3.97100	0.01738	5.98734
C 6	-0.06655	1.99882	4.04792	0.01980	6.06655
C 7	-0.03184	1.99884	4.01337	0.01963	6.03184
C 8	-0.04138	1.99907	4.02362	0.01868	6.04138
C 9	0.01262	1.99896	3.97104	0.01738	5.98738
C 10	-0.02384	1.99884	4.00548	0.01951	6.02384
C 11	-0.07863	1.99892	4.06104	0.01867	6.07863
C 12	-0.07847	1.99892	4.06088	0.01867	6.07847
C 13	-0.23811	1.99913	4.22306	0.01592	6.23811
C 14	-0.23816	1.99913	4.22311	0.01592	6.23816
C 15	-0.24445	1.99916	4.22883	0.01646	6.24445
C 16	-0.23624	1.99916	4.22065	0.01643	6.23624
C 17	-0.24446	1.99916	4.22885	0.01646	6.24446
C 18	-0.23633	1.99916	4.22074	0.01644	6.23633
C 19	-0.37045	1.99908	4.35426	0.01710	6.37045
C 20	-0.42635	1.99931	4.41430	0.01274	6.42635
C 21	-0.42641	1.99931	4.41436	0.01274	6.42641
H 22	0.20714	0.00000	0.78991	0.00295	0.79286

H 23	0.20482	0.00000	0.79236	0.00282	0.79518
H 24	0.20716	0.00000	0.78989	0.00295	0.79284
H 25	0.20480	0.00000	0.79238	0.00282	0.79520
H 26	0.18701	0.00000	0.81042	0.00257	0.81299
H 27	0.18214	0.00000	0.81536	0.00250	0.81786
H 28	0.18310	0.00000	0.81425	0.00265	0.81690
H 29	0.18213	0.00000	0.81537	0.00250	0.81787
H 30	0.18310	0.00000	0.81424	0.00265	0.81690
H 31	0.18929	0.00000	0.80826	0.00245	0.81071
H 32	0.18930	0.00000	0.80825	0.00245	0.81070
* Total *	-1.00000	41.97950	95.62360	0.39690	138.00000

Table S3. NBO charges in the di-anionic $C_{21}H_{10}^{-2}$, optimized at the PBE0/cc-pVTZ level of theory.

		Natural Population			
Atom No	Natural Charge	Core	Valence	Rydberg	Total
C 1	-0.01759	1.99887	3.99865	0.02007	6.01759
C 2	-0.08161	1.99883	4.06246	0.02032	6.08161
C 3	-0.01755	1.99887	3.99861	0.02007	6.01755
C 4	-0.05951	1.99907	4.04080	0.01964	6.05951
C 5	-0.10942	1.99892	4.09069	0.01982	6.10942
C 6	-0.06873	1.99884	4.05022	0.01967	6.06873
C 7	-0.08162	1.99883	4.06247	0.02032	6.08162
C 8	-0.08131	1.99903	4.06268	0.01961	6.08131
C 9	-0.05954	1.99907	4.04083	0.01964	6.05954
C 10	-0.06871	1.99884	4.05020	0.01967	6.06871
C 11	-0.08138	1.99903	4.06274	0.01961	6.08138
C 12	-0.10937	1.99892	4.09063	0.01982	6.10937
C 13	-0.28312	1.99916	4.26643	0.01753	6.28312
C 14	-0.25303	1.99916	4.23673	0.01715	6.25303
C 15	-0.25721	1.99916	4.24106	0.01699	6.25721
C 16	-0.25715	1.99916	4.24100	0.01698	6.25715
C 17	-0.28315	1.99916	4.26645	0.01753	6.28315
C 18	-0.25305	1.99916	4.23674	0.01715	6.25305
C 19	-0.41039	1.99909	4.39277	0.01853	6.41039
C 20	-0.41037	1.99909	4.39275	0.01853	6.41037
C 21	-0.41345	1.99932	4.40115	0.01298	6.41345
H 22	0.18691	0.00000	0.80935	0.00374	0.81309
H 23	0.17470	0.00000	0.82180	0.00350	0.82530
H 24	0.16556	0.00000	0.83121	0.00323	0.83444
H 25	0.16559	0.00000	0.83118	0.00323	0.83441
H 26	0.16091	0.00000	0.83595	0.00314	0.83909
H 27	0.16181	0.00000	0.83484	0.00335	0.83819
H 28	0.15953	0.00000	0.83719	0.00328	0.84047
H 29	0.15956	0.00000	0.83716	0.00327	0.84044
H 30	0.16179	0.00000	0.83486	0.00335	0.83821
H 31	0.16092	0.00000	0.83594	0.00314	0.83908
* Total *	-2.00000	41.97961	95.59553	0.42486	138.00000

Table S4. NBO charges in the tri-anionic $C_{21}H_9^{-3}$, optimized at the PBE0/cc-pVTZ level of theory.

		Natural Population			
Atom No	Natural Charge	Core	Valence	Rydberg	Total
C 1	-0.07114	1.99887	4.05208	0.02019	6.07114
C 2	-0.07107	1.99887	4.05201	0.02020	6.07107
C 3	-0.07108	1.99887	4.05202	0.02019	6.07108
C 4	-0.11707	1.99903	4.09696	0.02107	6.11707
C 5	-0.11704	1.99903	4.09693	0.02108	6.11704
C 6	-0.07114	1.99887	4.05209	0.02019	6.07114
C 7	-0.07107	1.99887	4.05200	0.02020	6.07107
C 8	-0.11714	1.99903	4.09702	0.02108	6.11714
C 9	-0.11710	1.99903	4.09700	0.02107	6.11710
C 10	-0.07112	1.99887	4.05206	0.02019	6.07112

C 11	-0.11714	1.99903	4.09703	0.02108	6.11714
C 12	-0.11695	1.99903	4.09684	0.02108	6.11695
C 13	-0.28890	1.99917	4.27158	0.01816	6.28890
C 14	-0.28884	1.99917	4.27151	0.01816	6.28884
C 15	-0.28872	1.99917	4.27138	0.01817	6.28872
C 16	-0.28872	1.99917	4.27139	0.01816	6.28872
C 17	-0.28894	1.99917	4.27161	0.01816	6.28894
C 18	-0.28882	1.99917	4.27149	0.01816	6.28882
C 19	-0.46015	1.99912	4.44065	0.02038	6.46015
C 20	-0.46013	1.99912	4.44064	0.02038	6.46013
C 21	-0.46023	1.99912	4.44073	0.02038	6.46023
H 22	0.14268	0.00000	0.85309	0.00423	0.85732
H 23	0.14268	0.00000	0.85309	0.00424	0.85732
H 24	0.14268	0.00000	0.85308	0.00424	0.85732
H 25	0.13577	0.00000	0.85985	0.00438	0.86423
H 26	0.13575	0.00000	0.85987	0.00438	0.86425
H 27	0.13573	0.00000	0.85988	0.00438	0.86427
H 28	0.13575	0.00000	0.85987	0.00438	0.86425
H 29	0.13575	0.00000	0.85987	0.00438	0.86425
H 30	0.13575	0.00000	0.85987	0.00438	0.86425
* Total *	-3.00000	41.97979	95.56349	0.45672	138.00000

Table S5. Cartesian coordinates for the neutral sumanene, $C_{21}H_{12}^{0}$, optimized at the PBE0/cc-pVTZ level of theory.

C	0.071928328	-1.399255788	-0.898028113
C	-1.161097182	-0.784546753	-0.897072498
C	1.260033889	-0.612920946	-0.897636737
C	-2.270260144	-1.344179468	-0.273334426
C	2.299354150	-1.294400798	-0.274735289
C	-1.247903834	0.637405737	-0.896921627
C	1.176128620	0.762291548	-0.896939427
C	-2.417578815	1.057580180	-0.274496296
C	2.124715879	1.564714241	-0.273420192
C	-0.098923968	1.398022151	-0.896305954
C	-0.028916569	2.638298748	-0.272861227
C	0.293027992	-2.622388979	-0.275471138
C	3.240383578	0.909601140	0.237296745
C	3.326895192	-0.509037833	0.236682451
C	-2.409171926	2.351741500	0.234993782
C	-1.223884840	3.135971722	0.236103239
C	-2.103188613	-2.627137927	0.237347960
C	-0.831387317	-3.261436186	0.236049804
C	-3.268674213	-0.199847080	-0.019674865
C	1.461257532	2.930807113	-0.019384252
C	1.807554776	-2.731143188	-0.021526455
H	2.022059818	-3.056357565	0.998341724
H	2.285778777	-3.452960337	-0.692791728
H	1.636546756	3.280985074	0.999741251
H	1.846736112	3.704784751	-0.692237368
H	-3.657378904	-0.223044782	1.000265055
H	-4.133023867	-0.253527282	-0.690639749
H	-0.742488331	-4.203611320	0.766168057
H	-2.908074186	-3.123639716	0.768752045
H	-1.251909248	4.082425536	0.765332954
H	-3.270266387	2.747432921	0.762858980
H	4.012471235	1.456451428	0.767871695
H	4.159265709	-0.959087841	0.767071599

Table S6. Cartesian coordinates for the mono-anionic $C_{21}H_{11}^{-1}$, optimized at the PBE0/cc-pVTZ level of theory.

C	0.061715222	-1.408779714	-0.889460479
C	-1.167559601	-0.773751296	-0.885644577
C	1.247190781	-0.614612923	-0.891547363
C	-2.282538670	-1.299283721	-0.168703719
C	2.299902996	-1.293864687	-0.285285101
C	-1.253012671	0.625536565	-0.885895394
C	1.163065724	0.762113948	-0.891458376
C	-2.423800813	1.011373449	-0.169347047

C	2.125183248	1.564552506	-0.285270695
C	-0.110279725	1.405998653	-0.888998315
C	-0.026304349	2.655333494	-0.301166081
C	0.297516007	-2.638661673	-0.301565645
C	3.249261209	0.911782796	0.209976522
C	3.336199339	-0.509186231	0.209811840
C	-2.402241485	2.363154446	0.280816372
C	-1.235753554	3.143582097	0.236764688
C	-2.095800228	-2.638104364	0.282244562
C	-0.842958827	-3.270527426	0.237461765
C	-3.118057372	-0.190595099	0.178010654
C	1.464580947	2.933435535	-0.025255507
C	1.811307355	-2.733283607	-0.026319537
H	2.018314171	-3.030439414	1.006631857
H	2.326001854	-3.460004033	-0.669503037
H	1.633867248	3.252374392	1.008025764
H	1.887136741	3.718245775	-0.667404769
H	-4.018106672	-0.245329972	0.776775049
H	-0.756144398	-4.237366343	0.728221054
H	-2.889740221	-3.149316081	0.820881512
H	-1.267978961	4.114007250	0.727155649
H	-3.252865526	2.773858392	0.818877828
H	4.027608433	1.461197033	0.732169416
H	4.175521798	-0.959949745	0.731951108

Table S7. Cartesian coordinates for the di-anionic $C_{21}H_{10}^{-2}$, optimized at the PBE0/cc-pVTZ level of theory.

C	0.061030013	-1.390265020	-0.852399302
C	-1.173804020	-0.765489343	-0.868753886
C	1.255220175	-0.599816658	-0.852144411
C	-2.310057669	-1.309126833	-0.179660249
C	2.316727318	-1.300095753	-0.297965492
C	-1.259769743	0.632882511	-0.866352408
C	1.162279106	0.780920216	-0.869269846
C	-2.434829360	1.013292783	-0.182799636
C	2.106666049	1.614965827	-0.180994024
C	-0.091485742	1.406544494	-0.866680068
C	0.017348451	2.637004905	-0.183763031
C	0.291040846	-2.641112957	-0.298693814
C	3.285937385	0.913295441	0.226768788
C	3.365009023	-0.491713104	0.196934218
C	-2.402219627	2.357589914	0.302348489
C	-1.232899433	3.131831720	0.301787380
C	-2.124843716	-2.669044090	0.227261929
C	-0.862439142	-3.290745280	0.196099786
C	-3.147925308	-0.208938816	0.155063954
C	1.421287222	2.816209422	0.153181092
C	1.804296640	-2.726665771	0.003523790
H	1.974864675	-2.984766473	1.056985871
H	2.318539931	-3.503446111	-0.587059595
H	1.827264403	3.635727683	0.737583438
H	-4.059015625	-0.262135753	0.742610078
H	-0.785207766	-4.276064862	0.658303388
H	-2.927393988	-3.207012655	0.732293663
H	-1.276142264	4.088708460	0.824282057
H	-3.265671379	2.770930248	0.825849977
H	4.094281571	1.442107659	0.732127817
H	4.241371973	-0.947171803	0.660790042

Table S8. Cartesian coordinates for the tri-anionic $C_{21}H_{9}^{-3}$, optimized at the PBE0/cc-pVTZ level of theory.

C	0.059094747	-1.362187114	-0.923895170
C	-1.190706244	-0.740168020	-0.864331186
C	1.229242086	-0.587755234	-0.924308082
C	-2.326209333	-1.308012033	-0.223060150
C	2.291556785	-1.339934514	-0.350909233
C	-1.275565360	0.659270589	-0.806084421
C	1.144819079	0.805726627	-0.865104407
C	-2.468215628	1.030235056	-0.125758470

C	2.111669462	1.629219513	-0.224734497
C	-0.110162448	1.430733519	-0.806055935
C	0.014769489	2.673452575	-0.125724765
C	0.336527645	-2.633604497	-0.349859081
C	3.295803414	0.900185100	0.135210450
C	3.380893403	-0.506794552	0.075667650
C	-2.424932441	2.384301629	0.351283775
C	-1.248568333	3.162791066	0.351368605
C	-2.117578240	-2.682733543	0.137578701
C	-0.855780660	-3.310674287	0.077837039
C	-3.179672267	-0.200397821	0.159891862
C	1.425682153	2.847580795	0.158803164
C	1.759743618	-2.660056976	-0.074846448
H	2.286892375	-3.456597357	0.449904927
H	1.855752434	3.654855302	0.751127887
H	-4.090363182	-0.280317285	0.753081029
H	-0.793535480	-4.316027659	0.509831120
H	-2.922712063	-3.257001123	0.610094291
H	-1.306584481	4.128034123	0.867421072
H	-3.290559175	2.814790188	0.867632272
H	4.139205738	1.416936247	0.607278368
H	4.282442908	-0.956600313	0.507259634

Table S9. Cartesian coordinates for transition state for bowl-to-bowl inversion in the neutral sumanene, $C_{21}H_{12}^{0}$, optimized at the PBE0/cc-pVTZ level of theory (using RIJCOSX approximation).

C	1.962002000	2.981552000	0.000001000
C	-3.177681000	1.627944000	-0.000008000
C	2.977736000	1.956771000	-0.000004000
C	2.673134000	0.580371000	0.000010000
C	1.320866000	0.374762000	0.000018000
C	3.278798000	-0.878302000	-0.000005000
C	-1.832974000	2.052785000	0.000003000
C	1.578923000	-3.170899000	-0.000002000
C	-0.870117000	3.307612000	0.000003000
C	-3.558022000	0.235279000	-0.000006000
C	-2.615284000	-0.812152000	0.000001000
C	0.583006000	2.689059000	0.000007000
C	0.365454000	1.338656000	0.000019000
C	2.015509000	-1.830007000	0.000001000
C	0.954427000	-0.967663000	0.000008000
C	-0.980201000	0.984004000	0.000019000
C	0.182902000	-3.538889000	0.000002000
C	-2.421969000	-2.379857000	0.000001000
C	-1.337706000	-0.325358000	0.000010000
C	-0.856070000	-2.586882000	0.000006000
C	-0.358033000	-1.313739000	0.000014000
H	2.326534000	4.003412000	-0.000014000
H	-3.997234000	2.338374000	-0.000021000
H	4.002730000	2.312372000	-0.000012000
H	3.908739000	-1.052070000	-0.875873000
H	3.908756000	-1.052081000	0.875849000
H	2.282182000	-3.996630000	-0.000009000
H	-1.038417000	3.939011000	-0.875883000
H	-1.038418000	3.939014000	0.875887000
H	-4.625475000	0.039676000	-0.000016000
H	-0.022303000	-4.604512000	-0.000005000
H	-2.886501000	-2.840333000	-0.875172000
H	-2.886520000	-2.840321000	0.875170000

Table S10. Cartesian coordinates for transition state for bowl-to-bowl inversion in the mono-anionic $C_{21}H_{11}^{-1}$, optimized at the PBE0/cc-pVTZ level of theory (using RIJCOSX approximation).

C	3.329382000	-1.245251000	0.000001000
C	0.811423000	3.457350000	0.000007000
C	2.570998000	-2.463614000	-0.000008000

C	1.128293000	-2.520862000	-0.000002000
C	0.655259000	-1.205192000	-0.000004000
C	-0.086233000	-3.339125000	-0.000010000
C	1.541182000	2.250800000	0.000011000
C	-2.693409000	-2.328522000	-0.000007000
C	2.992914000	1.614445000	0.000018000
C	-0.634251000	3.493313000	0.000000000
C	-1.423526000	2.325202000	0.000004000
C	2.740206000	0.052238000	0.000006000
C	1.380043000	-0.059357000	0.000000000
C	-1.255603000	-2.459523000	-0.000006000
C	-0.715203000	-1.170510000	-0.000008000
C	0.710583000	1.162143000	0.000010000
C	-3.389552000	-1.073731000	-0.000005000
C	-2.905576000	1.764798000	0.000011000
C	-0.649583000	1.196021000	0.000007000
C	-2.733682000	0.192000000	-0.000002000
C	-1.380979000	0.010037000	-0.000002000
H	4.409963000	-1.372462000	-0.000006000
H	1.309428000	4.423512000	0.000000000
H	3.168093000	-3.372744000	-0.000012000
H	-3.335800000	-3.206156000	-0.000002000
H	3.561996000	1.945307000	-0.875455000
H	3.561983000	1.945295000	0.875504000
H	-1.083082000	4.483294000	-0.000009000
H	-4.475395000	-1.144798000	-0.000005000
H	-3.456753000	2.124612000	-0.875454000
H	-3.456713000	2.124592000	0.875509000
H	-0.114786000	-4.421544000	0.000027000

Table S11. Cartesian coordinates for transition state for bowl-to-bowl inversion in the di-anionic $C_{21}H_{10}^{-2}$, optimized at the PBE0/cc-pVTZ level of theory (using RIJCOSX approximation).

C	1.946882000	2.963924000	-0.000197000
C	-3.169398000	1.656285000	0.000161000
C	2.960193000	1.941288000	-0.000241000
C	2.695789000	0.521015000	-0.000014000
C	1.315161000	0.365001000	0.000528000
C	3.213673000	-0.879731000	-0.000150000
C	-1.798173000	2.123772000	0.000188000
C	1.606142000	-3.162848000	0.000107000
C	-0.871552000	3.243200000	0.000026000
C	-3.551386000	0.269244000	0.000050000
C	-2.622097000	-0.810502000	0.000218000
C	0.524266000	2.712516000	0.000096000
C	0.355590000	1.333378000	0.000576000
C	2.085994000	-1.795932000	0.000089000
C	0.954093000	-0.958861000	0.000643000
C	-0.971504000	0.984233000	0.000706000
C	0.215631000	-3.532245000	0.000037000
C	-2.426154000	-2.383035000	-0.000164000
C	-1.341155000	-0.321888000	0.000604000
C	-0.855530000	-2.593129000	0.000222000
C	-0.355310000	-1.316790000	0.000584000
H	2.337033000	3.984049000	-0.000498000
H	-4.003852000	2.359052000	-0.000074000
H	3.983814000	2.322153000	-0.000598000
H	2.301395000	-4.003588000	-0.000148000
H	-4.628142000	0.089766000	-0.000135000
H	0.026177000	-4.607265000	-0.000126000
H	-2.896308000	-2.848987000	-0.876648000
H	-2.897064000	-2.849712000	0.875516000
H	4.260424000	-1.167181000	-0.000784000
H	-1.149363000	4.292560000	-0.000762000

Table S12. Cartesian coordinates for transition state for bowl-to-bowl inversion in the tri-anionic $C_{21}H_9^{-3}$, optimized at the PBE0/cc-pVTZ level of theory (using RIJCOSX approximation).

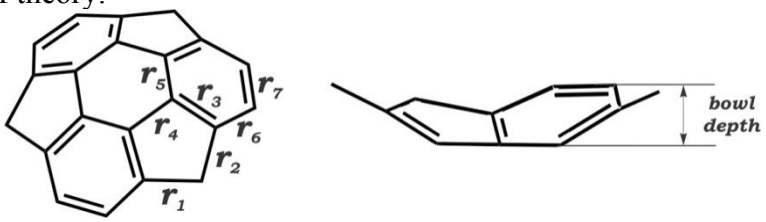
C	1.952308000	2.975006000	-0.015141000
C	-3.165649000	1.628083000	-0.007774000
C	2.971427000	1.946804000	-0.015135000
C	2.714058000	0.522874000	-0.001666000
C	1.320357000	0.368976000	0.005202000
C	3.230352000	-0.868812000	-0.031040000
C	-1.803593000	2.114874000	0.002290000
C	1.579486000	-3.158952000	-0.007967000
C	-0.860835000	3.258916000	-0.031463000
C	-3.547081000	0.230914000	0.006122000
C	-2.621377000	-0.880583000	0.003632000
C	0.526154000	2.730267000	-0.001867000
C	0.359887000	1.338012000	0.005289000
C	2.078183000	-1.801285000	0.002429000
C	0.956597000	-0.961027000	0.006118000
C	-0.973292000	0.985875000	0.006102000
C	0.178953000	-3.528174000	0.005921000
C	-2.386375000	-2.344654000	0.036166000
C	-1.332841000	-0.329963000	0.004511000
C	-0.924388000	-2.592711000	0.003534000
C	-0.362327000	-1.309173000	0.004522000
H	2.350042000	3.997542000	-0.021181000
H	-4.013226000	2.324000000	-0.009717000
H	3.997418000	2.335533000	-0.020712000
H	2.268069000	-4.012533000	-0.010085000
H	-4.631636000	0.064736000	-0.000865000
H	0.003368000	-4.611214000	-0.001319000
H	4.276418000	-1.159289000	0.067201000
H	-1.141853000	4.307479000	0.067695000
H	-3.157561000	-3.109051000	-0.051071000

Table S13. Absolute energies for all systems under consideration at different levels of theory (in a.u.).

System	Energy, a.u.		
	PBE0/cc-pVTZ	xDH-PBE0/cc-pVTZ	DLPNO-CCSD(T)/cc-pVTZ*
$C_{21}H_{12}^0$	-806.745511003338	-806.7320854481	-805.890722407894
bowl-to-bowl-TS* ($C_{21}H_{12}^0$)	-806.715017999489	-806.7043904814	-805.858065692394
$C_{21}H_{11}^{-1}$	-806.171444973922	-806.1545725906	-805.311421927127
bowl-to-bowl-TS* ($C_{21}H_{11}^{-1}$)	-806.137993034072	-806.1239987536	-805.276628996426
$C_{21}H_{10}^{-2}$	-805.463096410587	-805.4426412769	-804.598941742606
bowl-to-bowl-TS* ($C_{21}H_{10}^{-2}$)	-805.430241127185	-805.4122515749	-804.563472742968
$C_{21}H_9^{-3}$	-804.615204255029	-804.5904644651	-803.747451660347
bowl-to-bowl-TS* ($C_{21}H_9^{-3}$)	-804.588132075300	-804.5654981471	-803.718865137106

* Calculations were performed with help of RIJCOSX acceleration technique[3] using ORCA software.[4]

Table S14. Selected geometrical parameters for systems $C_{21}H_{12}^{0}$ and $C_{21}H_{9}^{-3}$, optimized at different levels of theory.



Parameter	Compound							
	$C_{21}H_{12}^{0}$				$C_{21}H_{9}^{-3}$			
	PBE0/cc-pVTZ	PBE0-D/cc-pVTZ	PBE0/aug-cc-pVTZ	PBE0-D/aug-cc-pVTZ	PBE0/cc-pVTZ	PBE0-D/cc-pVTZ	PBE0/aug-cc-pVTZ	PBE0-D/aug-cc-pVTZ
r_1	1.540	1.539	1.539	1.539	(1.450)	1.449	1.448	1.448
r_2	1.540	1.539	1.539	1.539	(1.450)	1.449	1.448	1.448
r_3	1.390	1.391	1.390	1.391	(1.422)	1.423	1.422	1.423
r_4	1.425	1.425	1.425	1.425	(1.403)	1.404	1.403	1.403
r_5	1.378	1.378	1.378	1.379	(1.397)	1.398	1.398	1.399
r_6	1.391	1.390	1.391	1.390	(1.436)	1.436	1.437	1.436
r_7	1.421	1.421	1.422	1.421	(1.411)	1.410	1.412	1.411
bowl depth	1.133	1.141	1.134	1.143	1.054	1.070	1.058	1.065

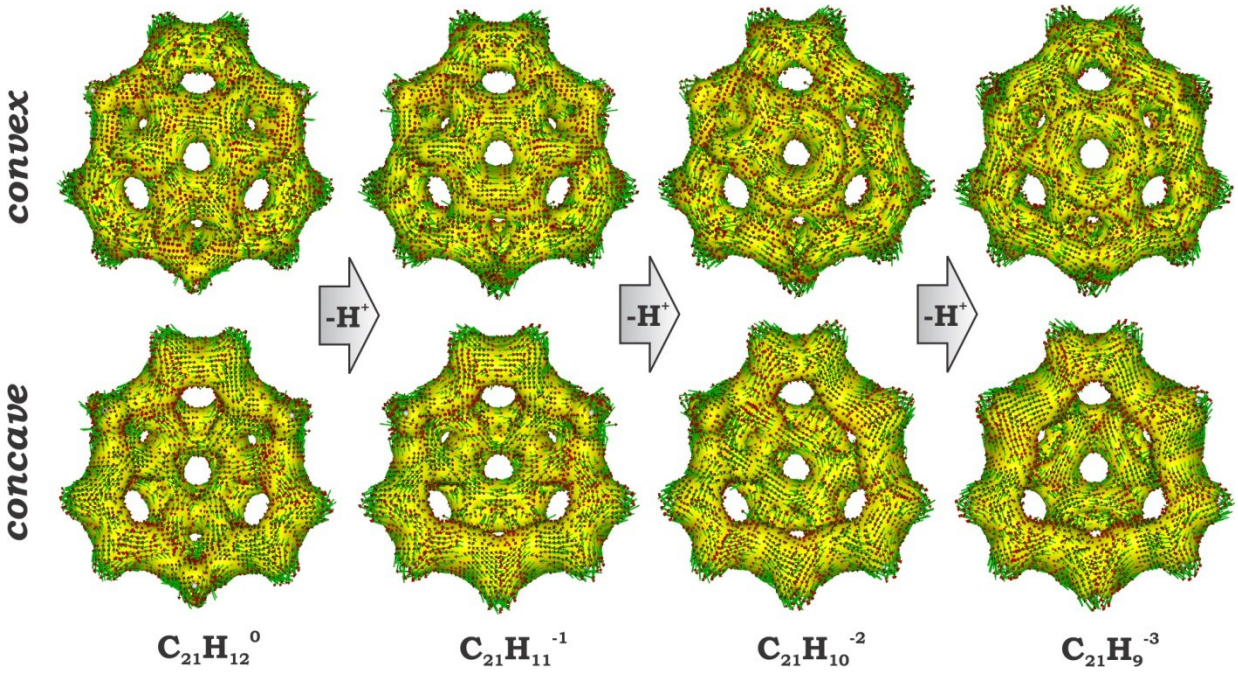


Figure S1. ACID isosurfaces for the neutral sumanene and its deprotonated anions.

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