Supplementary Material for the article:

Experimental electron density of sumanene, a bowl-shaped fullerene fragment; comparison with the related corannulene hydrocarbon

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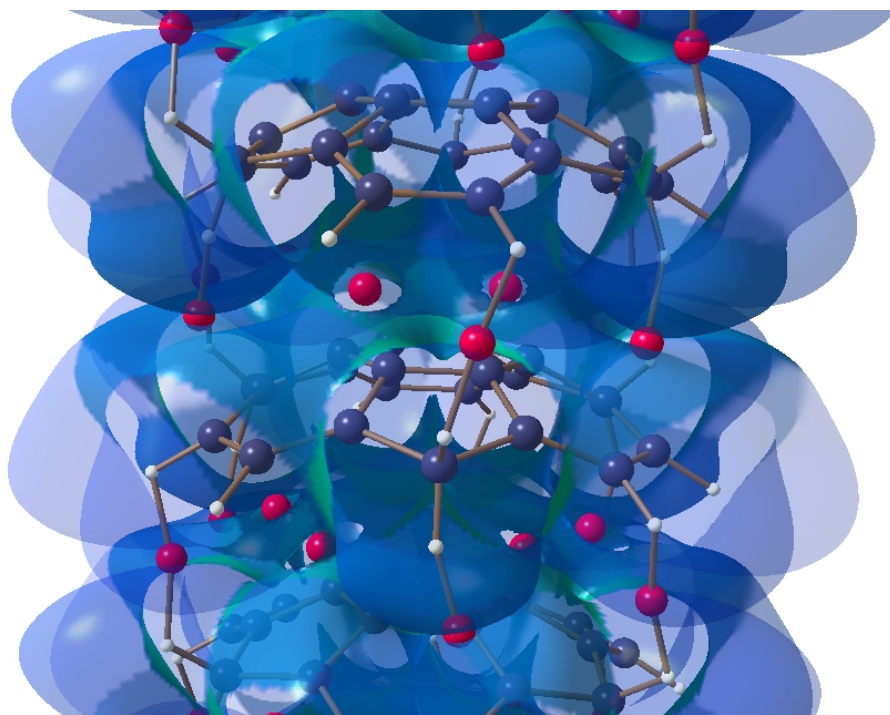
Figure S1. ELI-D of the sumanene packing scheme at an iso-value of $\gamma = 0.55$. Intermolecular saddle points are given as red balls.
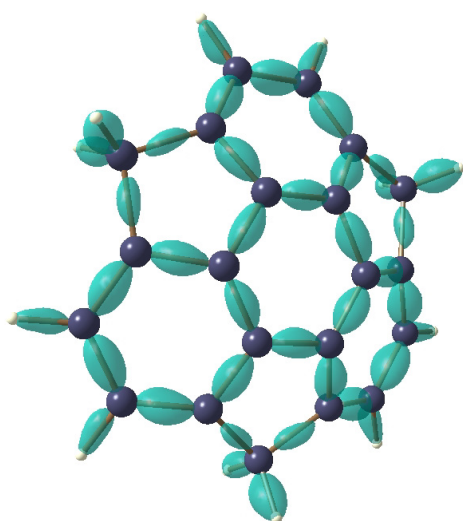

Figure S2. Three-dimensional representation of the static deformation density in sumanene at an iso-surface of 0.30 eÅ^{-3}. MOLISO representation (ref. [5])

Table S1 Topological properties at the bond critical points [$\rho(\mathbf{r}_{bcp})$]. The four entries for each bond are: bond path exp. (1st line); bond length exp. (2nd line); bond path theor.[18] (3rd line); bond length theor. (4th line).

Type	bond path (Å)	$\rho(\mathbf{r}_{bcp})$ (eÅ^{-3})	$\nabla^2\rho(\mathbf{r}_{bcp})$ (eÅ^{-5})	ε	n_b
C1-C2	1.3851	2.23(1)	-22.64(5)	0.18	1.82
(h66)	1.3829(2)				
	1.3853	2.12	-21.65	0.17	1.62
	1.3851				
C1-C2'	1.4300	2.16(1)	-22.23(4)	0.23	1.69
(h56)	1.4292(2)				
	1.4334	1.96	-18.73	0.12	1.38
	1.4325				
C1-C6	1.3964	2.26(3)	-24.14(8)	0.06	1.87
(s)	1.3956(2)				
	1.3975	2.10	-21.06	0.19	1.59
	1.3973				
C2-C3	1.3962	2.26(2)	-24.15(7)	0.06	1.87
(s)	1.3954(2)				
	1.3976	2.10	-21.06	0.19	1.59
	1.3973				
C3-C4	1.3997	2.23(2)	-20.59(7)	0.15	1.82
(f6)	1.3991(3)				
	1.3978	2.05	-19.67	0.23	1.51
	1.3972				
C5-C6	1.4003	2.23(2)	-20.55(7)	0.15	1.82
(f6)	1.3997(3)				
	1.3978	2.05	-19.67	0.23	1.51
	1.3972				
C6-C7	1.5495	1.69(2)	-12.01(5)	0.03	1.05
(f5)	1.5482(3)				
	1.5530	1.55	-11.73	0.04	0.91
	1.5523				
C7-C3'	1.5484	1.68(3)	-12.01(5)	0.04	1.04
(f5)	1.5473(3)				
	1.5530	1.55	-11.73	0.04	0.91
	1.5524				
C4-C5	1.4316	2.16(1)	-18.10(5)	0.21	1.69
(r)	1.4316(3)				
	1.4300	1.93	-17.59	0.21	1.34
	1.4296				

The topological bond order n_B was calculated from an exponential relation given by Bader [19] after

$$n_B = \exp[C_1(\rho(\mathbf{r}_{bcp})-C_2)]$$

where the parameters $C_1 = 1.02289$ and $C_2 = 1.64585$ were derived from an earlier theoretical calculation (P. Luger, M. Messerschmidt, S. Scheins, A. Wagner, Acta Cryst. A, 2004, 60, 390-396)

Table S2 Experimental Bader volumes V_{tot} and charges q (in Å^3 and e) for sumanene and for comparison for corannulene.

Type*	V_{tot}	q	N^{xx}	molecule
H	8.95(4)	0.019(1)	2	sumanene
S	10.27(15)	-0.060(1)	2	sumanene
R6	13.79(25)	-0.394(4)	2	sumanene
R5	9.51	-0.151	1	sumanene
Hydrogen	6.3(7)	0.25(7)	4	sumanene
H	9.1(9)	-0.030(4)	10	corannulene
S	9.7(4)	0.029(4)	10	corannulene
R	12.4(8)	-0.092(6)	17	corannulene
Hydrogen	6.6(14)	0.109(3)	17	corannulene

*Although 7 crystallographically independent carbon atoms exist in sumanene, the two H type atoms C1 and C2 are chemically equivalent, which holds also for the S type atoms C3 and C6 and the R-type atoms (R6) C4 and C5 of the outer six-membered ring. In corannulene only 3 chemically different atom types exist[17].
xxNo. of contributing data.

Table S3. Topological bond and ring descriptors of the bonds and rings in corannulene (cor), sumanene (sum) from optimized gas phase structures and a calculated packing scheme of sumanene (sum_pck). Data listed here were used in the diagrams of Fig.4 and 5. (*). Bond notation as used in the main text.

cor bond	d1 (Å)	d2 (Å)	λ_3 (eÅ⁻⁵)	ε	ρ (eÅ⁻³)	$\nabla^2\rho$ (eÅ⁻⁵)	G/r (he⁻¹)	H/r (he⁻¹)	zfs (eÅ⁻¹)	$\delta(x,y)$	VELI (Å³)	NELI (e)	ELImaxγ	eccnt (Å)
h	0.708	0.708	8.14	0.14	2.02	-19.7	0.30	-0.99	1.31	1.17	4.8	2.45	1.89	0.107
s	0.692	0.691	7.73	0.19	2.15	-22.2	0.33	-1.05	1.42	1.32	7.8	2.77	1.85	0.052
f	0.727	0.720	8.31	0.14	1.89	-17.2	0.28	-0.92	1.28	1.20	5.9	2.46	1.90	0.051
r	0.693	0.693	7.64	0.27	2.09	-20.3	0.35	-1.03	1.42	1.54	12.1	3.10	1.81	0.179
R-H	0.695	0.390	12.55	0.02	1.90	-23.2	0.14	-0.99	0.96	0.96	11.5	2.13	6.49	-
5-ring	1.205	1.205			0.34	7.6	1.48	0.07						
6-ring	1.375	1.460			0.15	3.7	1.45	0.33						

sum bond	d1 (Å)	d2 (Å)	λ_3 (eÅ⁻⁵)	ε	ρ (eÅ⁻³)	$\nabla^2\rho$ (eÅ⁻⁵)	G/r (he⁻¹)	H/r (he⁻¹)	zfs (eÅ⁻¹)	$\delta(x,y)$	VELI (Å³)	NELI (e)	ELImaxγ	eccnt (Å)
h66	0.693	0.693	7.66	0.17	2.12	-21.7	0.33	-1.04	1.38	1.29	6.4	2.69	1.86	0.117
r	0.715	0.715	8.11	0.21	1.93	-17.6	0.31	-0.95	1.32	1.34	7.7	2.67	1.85	0.093
s	0.702	0.695	8.01	0.19	2.10	-21.1	0.33	-1.03	1.38	1.28	6.7	2.66	1.85	0.067
f6	0.692	0.705	7.79	0.23	2.05	-19.7	0.33	-1.01	1.40	1.41	10.7	2.96	1.82	0.074
f5	0.784	0.769	8.52	0.04	1.55	-11.7	0.23	-0.76	1.08	0.98	3.4	1.98	1.97	0.071
h56	0.717	0.717	8.29	0.11	1.96	-18.7	0.29	-0.96	1.28		4.3	2.34	1.92	0.112
R6-H	0.694	0.391	12.45	0.02	1.89	-23.1	0.14	-0.99	0.96	0.97	11.5	2.13	6.47	-
R5-H	0.700	0.395	12.30	0.01	1.85	-21.9	0.15	-0.97	0.95	0.94	10.6	1.98	6.44	-
5-ring	1.242	1.252			0.29	6.5	1.45	0.12						
6-ring (out)	1.385	1.438			0.15	3.9	1.47	0.33						
6-ring (in)	1.410	1.410			0.15	3.7	1.43	0.33						

| sum_pck bond	d1 (Å)	d2 (Å)	λ_3 (eÅ⁻⁵)	ε	ρ (eÅ⁻³)	$\nabla^2\rho$ (eÅ⁻⁵)	G/r (he⁻¹)	H/r (he⁻¹)	zfs (eÅ⁻¹)	$\delta(x,y)$	VELI (Å³)	NELI (e)	ELImaxγ	eccnt (Å)
h66	0.692	0.692	7.76	0.17	2.12	-21.7	0.33	-1.04			6.9	2.72	1.88	0.119
r	0.716	0.717	8.22	0.21	1.92	-17.3	0.31	-0.94			7.6	2.69	1.86	0.092
s	0.702	0.696	8.14	0.19	2.10	-21.0	0.32	-1.02			5.7	2.66	1.87	0.069
f6	0.696	0.706	7.95	0.23	2.03	-19.3	0.33	-1.00			9.3	2.94	1.84	0.070
f5	0.783	0.767	8.50	0.04	1.56	-11.8	0.23	-0.76			3.6	2.00	1.98	0.075
h56	0.716	0.716	8.36	0.11	1.96	-18.8	0.29	-0.96			4.8	2.36	1.94	0.111
R6-H	0.692	0.391	12.56	0.02	1.90	-23.3	0.14	-1.00			11.5	2.14	6.48	-
R5-H	0.699	0.394	12.49	0.02	1.85	-21.4	0.16	-0.98			10.2	1.99	6.37	-
5-ring	1.242	1.252			0.29	6.5	1.43	0.11						
6-ring (out)	1.384	1.440			0.15	3.8	1.44	0.31						
6-ring (in)	1.409	1.409			0.15	3.7	1.39	0.29						

(*) d1 and d2 are the distances from the first/second atom to the bcp; λ_3 is the curvature of $\rho(\mathbf{r}_{bcp})$ along the bond path; ε is the bond ellipticity; ρ and $\nabla^2\rho$ are the ED values and Laplacians at the corresponding $\mathbf{r}_{bcp}/\mathbf{r}_{rcp}$; G/ρ and H/ρ are the kinetic and total energy density ratios over $\rho(\mathbf{r}_{bcp}/\mathbf{r}_{rcp})$; zfs is the integrated number of electrons within the zero flux surface; $\delta(x,y)$ is the localization index of atoms x and y; VELI is the corresponding volume cut at an ED value of 0.001 au; $\text{ELI}_{max}\gamma$ is the corresponding ELI-D value at the attractor position; eccnt is the distance of the attractor position perpendicular to the xy axis.

Table S4. AIM atomic volumes V_{001} (in $Å^3$) and charges q (in e), analyzed with AIM2000 (F. Biegler-König, J. Schönbohm, D. Bayles. AIM2000 – A program to Analyse and Visualize Atoms in Molecules.). *J. Comput. Chem.* 2001, **22**, 545-559.) Atom notation as used in the main text.

cor			sum			sum_pck		
atom	V001	q	atom	V001	q	atom	V001	q
H	9.2	0.00	H	9.3	0.00	H	9.0	0.00
S	10.7	0.00	R6	12.8	-0.01	R6	11.5	0.00
R	12.6	-0.01	S	11.0	-0.02	S	10.0	-0.02
			R5	9.7	0.04	R5	9.1	0.07
R-H	7.4	0.03	H(R6)	7.5	0.02	H(R6)	7.5	-0.01
			H(R5)	7.3	0.03	H(R5)	7.2	-0.01

Figure S3. Topological bifurcation diagram of the ELI-D for the valence electrons of corannulene and sumanene. H, H5 and H6 correspond to the protonated valence basins. For both molecules the separation into hub and spoke bonds on the one side and rim and flank bonds on the other side is visible. For sumanene the early separation of the five-membered ring parts (h56, f5, H5) is also visible, see also Figure S4.
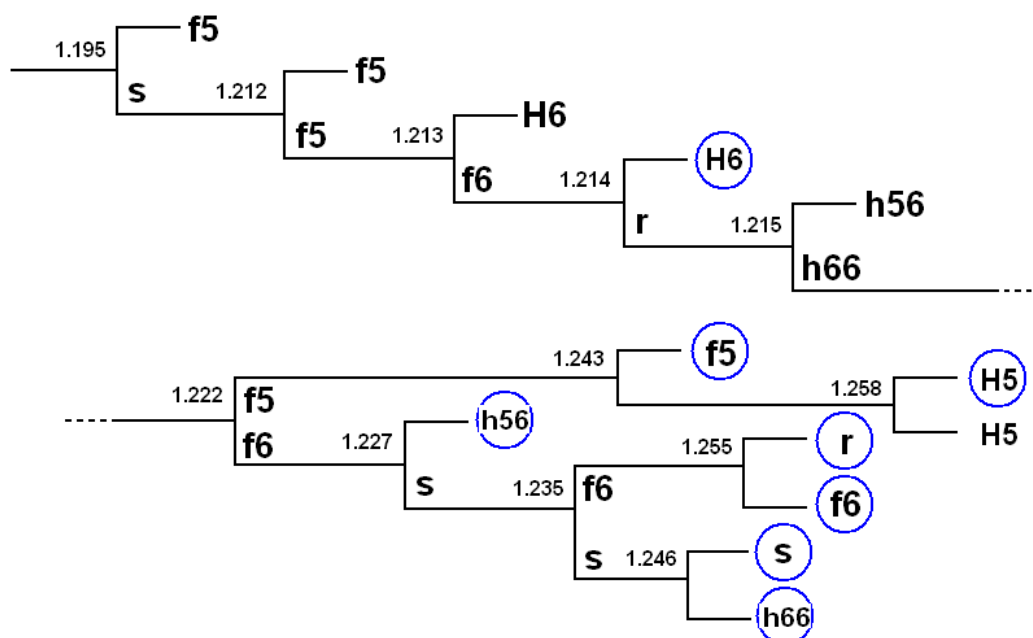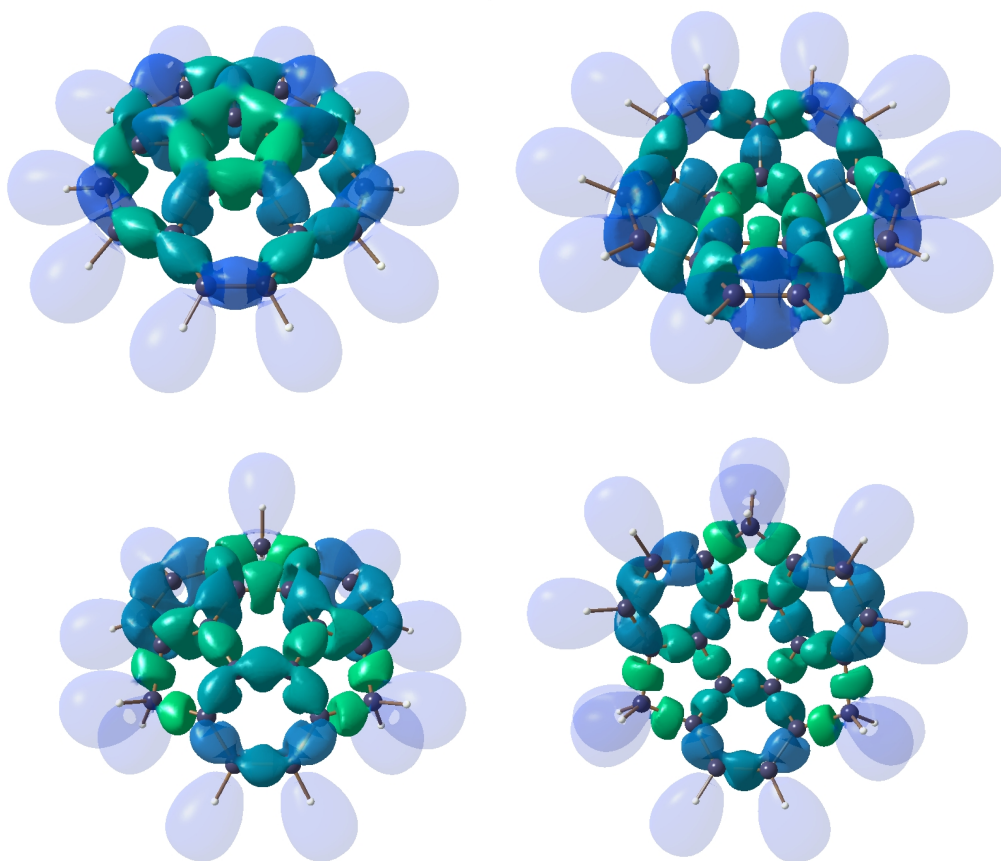
Corannulene
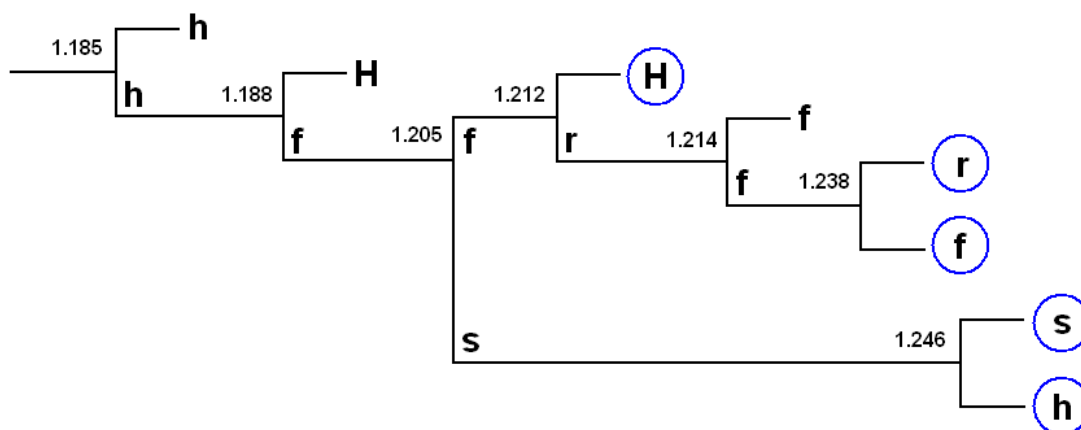
Sumanene

Figure S4. First line: Top and bottom view of the ELI-D at $\gamma = 1.21$ for corannulene; second line: corrsponding figures for sumanene at $\gamma=1.24$. Whereas inside the bowls most basin types are already separated from each other, at these iso values they are still connected at the outer side.
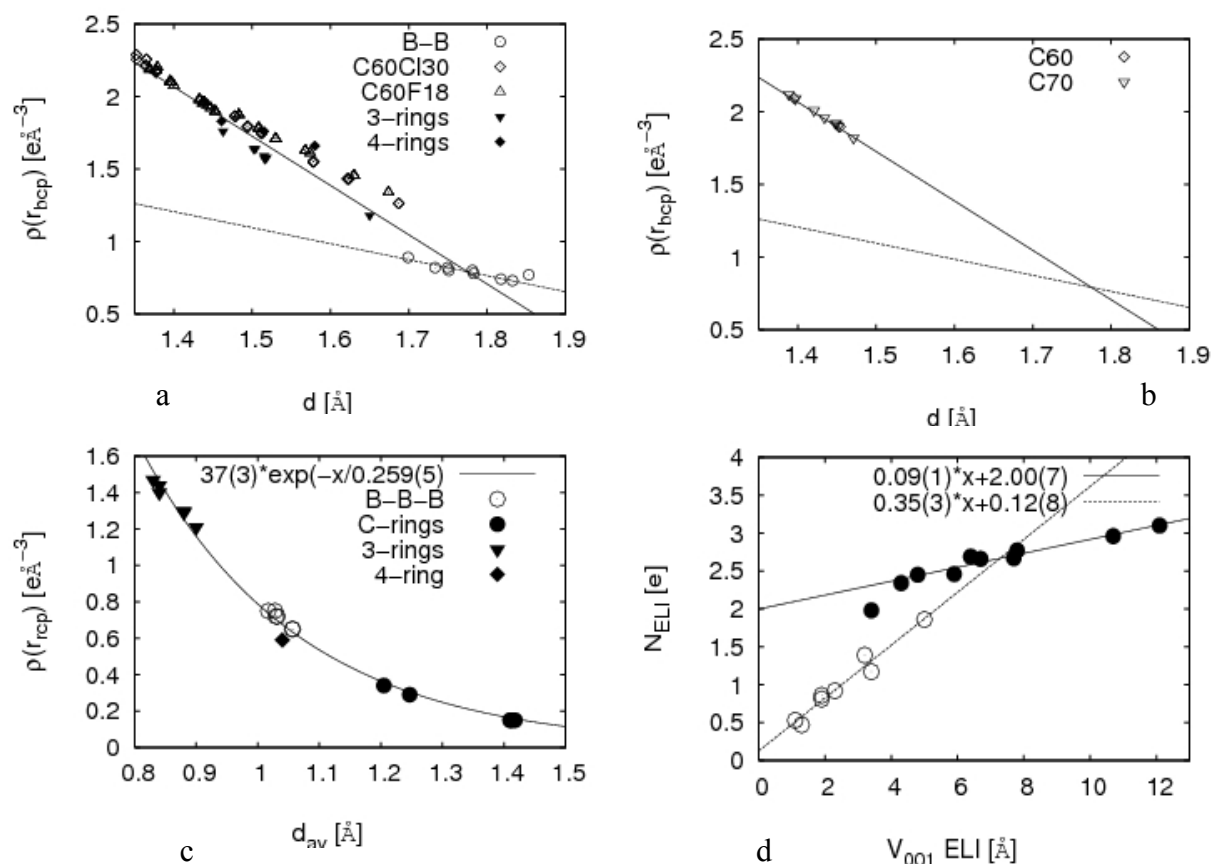
Figure S5. a) Theoretically calculated $\rho(r_{bcp})$ of C-C bonds in 3- and 4-membered rings (cyclopropanes and -butanes, epoxides), 5- and 6-membered C-rings of deformed C_{60}-fullerenes, and B-B bonds of 3-membered B-rings in borane cages are plotted against C-C and B-B bond distances. The solid line is the best-fit line of $\rho(r_{bcp})$ vs. d. The dotted line is the best-fit from reference (S. Mebs, R. Kalinowski, S. Grabowsky, D. Förster, R. Kickbusch, E. Justus, W. Morgenroth, C. Paulmann, P. Luger, D. Gabel and D. Lentz, *Inorg. Chem.*, 2011, 50, 90-103). b) Corresponding results for the C-C bonds in C60 and C70. c). $\rho(r_{rcp})$ plotted against d_{av} (average distance between rcp and ring atoms) for C-rings (black triangles, square, and circles) and 3-membered B-rings (white circles). The exponential relation was calculated under exclusion of the partially fluorinated cyclobutane (black square, D. Lentz, M. Patzschke, A. Bach, St. Scheins, P. Luger, *Org. Biomol. Chem.* 2003, 1, 409- 414). d) N(ELI) plotted against V_{001}(ELI) for sumanene and corannulene (black circles) and boranes of reference (S. Mebs, R. Kalinowski, S. Grabowsky, D. Förster, R. Kickbusch, E. Justus, W. Morgenroth, C. Paulmann, P. Luger, D. Gabel and D. Lentz, *Inorg. Chem.*, 2011, 50, 90-103.) (white circles).

Figures 5a-c display relations between ED and bond distances, Figure S5d compares ELI-populations and -volumes between corannulene and summanene on the one hand and borane cages on the other.

Figure S5a reveals that all C-C bonds of the deformed fullerenes, which are not directly connected to a halogen atom, also match the solid best-fit line very well (bond distances up to ca. 1.5 Å). All C-C bonds, on the other hand, which are directly connected to one or two halogen atoms, are not only significanly enlongated (up to ca. 1.7 A), but show slightly more ED at the bcp than one would expect. The same is true for the partially halogenated cyclobutane (black squares). Only the $\rho(r_{bcp})$ values of the C-C bonds in the 3-membered (hetero) rings (black triangles) lie below the best-fit line, since they are not substituted by halogen atoms.

The slope of the borane best-fit line is considerably less steep in accordance with the electron deficiency in the borane cages. However, these differences are not seen for the corresponding ring critical points (rcp), see Figure S5c. $\rho(r_{rcp})$ is plotted versus the average distances d_{av} of all ring atoms to an rcp. One finds an exponential relation which is matched almost perfectly by all 3- to 6-membered C-rings as well as by the 3-membered B-rings. The results presented here partially disprove the common statement that the low $\rho(r_{bcp})$-value of the B-B bonds and the high $\rho(r_{rcp})$-value of the B-B-B triangles in principle distinguishes borane chemistry from hydrocarbon chemistry because the topological ED-properties seem to be in a quite simple fashion related to the molecular geometries.

In Figure S5d N(ELI) is plotted against the volumes V_{001} of the ELI-D bonding basins. The white circles correspond to the borane cages. The best-fit line for corannulene/sumanene (solid line) was calculated under exclusion of the f5-bond in sumanene which is a single bond. As expected, the electron populations within the B-B bonding basins are even smaller compared to the C-C bonds in corannulene and sumanene if both occupy the same volume. This is a clear distinction between both bond types.