Electronic Supplementary Information

Table S1 Nozzle-to-film distances / mm, weighting functions / nm^{-1}, scale factors, correlation parameters and electron wavelengths / pm used in the electron diffraction study of 1-SB_9H_9.

Nozzle-to-film distance	Δs	s_{min}	sw_1	sw_2	s_{max}	Scale factor[b]	Correlation parameter	Electron wavelength[a]
498.68	2	18	38	132	154	0.764(5)	0.482	5.846
248.73	2	60	80	258	300	0.828(11)	0.496	5.846

[a] Determined by reference to the scattering pattern of benzene. [b] Values in parentheses are the estimated standard deviations.

Table S2 Interatomic distances (r_a / pm), refined and calculated amplitudes of vibration (u_{h1} / pm) and perpendicular corrections (k_{h1} / pm) for the SARACEN-restrained GED structure of 1-SB_9H_9.[a]

	Atom pair	r_a	u_{h1}(exp.)[b]	k_{h1}	u_{h1}(calc.)
u_1	B(10)–H(10)	120.6(5)	8.6(tied to u_2)	0.4	8.2
u_2	B(2)–H(2)	121.0(4)	8.6(6)	0.4	8.2
u_3	B(6)–H(6)	121.3(4)	8.7(tied to u_2)	0.4	8.3
u_4	B(6)–B(10)	172.8(3)	6.8(tied to u_8)	0.5	6.3
u_5	B(2)–B(7)	178.8(2)	7.6(tied to u_8)	0.2	7.0
u_6	B(6)–B(7)	185.6(3)	7.7(tied to u_8)	0.2	7.1
u_8	S(1)–B(2)	193.9(1)	7.3(2)	0.3	6.7
u_7	B(2)–B(5)	194.4(2)	8.9(tied to u_8)	0.3	8.2
u_9	B(10)...H(6)	254.2(12)	13.7(tied to u_{18})	-0.2	12.2
u_{10}	B(2)...H(9)	257.5(9)	14.2(tied to u_{18})	-0.3	12.7
u_{11}	S(1)...H(3)	261.5(14)	13.8(tied to u_{18})	-0.4	12.3
u_{12}	B(9)...B(7)	262.7(4)	7.4(tied to u_{18})	0.2	6.6
u_{13}	B(9)...H(5)	265.8(9)	13.7(tied to u_{18})	-0.5	12.2
u_{14}	B(9)...H(2)	266.0(9)	13.7(tied to u_{18})	-0.3	12.2
u_{15}	B(2)...B(4)	275.0(2)	8.3(tied to u_{18})	0.2	7.4
u_{16}	B(6)...H(9)	280.2(5)	13.6(tied to u_{18})	-0.6	12.1
u_{17}	B(2)...H(5)	286.6(5)	14.5(tied to u_{18})	-0.6	12.9
u_{18}	B(2)...B(7)	288.1(2)	8.1(2)	0.0	7.2
u_{19}	B(3)...B(10)	292.4(3)	7.7(tied to u_{18})	0.0	6.9
u_{20}	H(3)...H(7)	302.2(16)	19.7(fixed)	-0.7	19.7
u_{21}	H(6)...H(10)	309.4(18)	19.4(fixed)	-0.1	19.4
u_{22}	S(1)...B(6)	311.7(1)	7.7(2)	0.0	6.8
u_{23}	H(9)...H(6)	345.0(12)	18.5(fixed)	-0.9	18.5
u_{24}	H(4)...H(5)	348.5(13)	19.2(fixed)	-1.1	19.2
u_{25}	B(9)...H(7)	377.8(7)	13.0(tied to u_{28})	-0.8	10.5
u_{26}	B(2)...H(4)	387.3(7)	13.5(tied to u_{28})	-0.9	11.0
u_{28}	S(1)...B(10)	394.4(4)	7.7(2)	-0.3	6.2
u_{27}	B(10)...H(2)	394.5(9)	14.6(tied to u_{28})	-0.7	11.8
u_{31}	B(2)...H(7)	401.3(4)	13.6(tied to u_{28})	-1.1	11.1
u_{30}	B(2)...H(8)	401.5(4)	13.6(tied to u_{28})	-0.9	11.1
u_{29}	B(2)...H(10)	402.1(6)	13.8(tied to u_{28})	-0.6	11.2
u_{32}	B(9)...H(4)	402.7(4)	13.5(tied to u_{28})	-1.0	11.0
u_{33}	S(1)...H(8)	405.4(9)	14.9(tied to u_{28})	-1.2	12.1
u_{34}	H(9)...H(7)	488.5(16)	13.9(fixed)	-1.8	13.9
u_{35}	H(2)...H(7)	511.7(5)	14.3(fixed)	-2.2	14.3
u_{36}	S(1)...H(10)	513.9(7)	9.9(fixed)	-1.6	9.9

[a] Estimated standard deviations, as obtained in the least squares refinement, are given in parentheses. [b] Amplitudes not refined were fixed at the values obtained using the force field calculated at the B3LYP/ aug-cc-pVTZ level.

Table S3 Least-squares correlation matrix (×100) for 1-SB_9H_9.[a]

	p_3	p_4	u_8	u_{22}	k_1	k_2
p_1	60					
p_2	–52					
p_3		–57	–56			
u_8					53	53
u_{18}				59		
k_1						52

[a] Only elements with absolute values ≥ 50% are shown. k_1 and k_2 are scale factors.

Table S4 GED Cartesian coordinates (in Å) for 1-SB_9H_9.

Atom	*x*	*y*	*z*
S(1)	0.0000	0.0000	1.3663
B(2)	0.0000	1.3753	0.0000
B(3)	1.3753	0.0000	0.0000
B(4)	0.0000	–1.3753	0.0000
B(5)	–1.3753	0.0000	0.0000
B(6)	0.9286	0.9286	–1.4631
B(7)	0.9286	–0.9286	–1.4631
B(8)	–0.9286	–0.9286	–1.4631
B(9)	–0.9286	0.9286	–1.4631
B(10)	0.0000	0.0000	–2.5823
H(2)	0.0000	2.4792	0.5017
H(3)	2.4792	0.0000	0.5017
H(4)	0.0000	–2.4792	0.5017
H(5)	–2.4792	0.0000	0.5017
H(6)	1.7348	1.7348	–1.8830
H(7)	1.7348	–1.7348	–1.8830
H(8)	–1.7348	–1.7348	–1.8830
H(9)	–1.7348	1.7348	–1.8830
H(10)	0.0000	0.0000	–3.7906

Table S5 Calculated Cartesian coordinates [MP2(full)/6-311++G**] (in Å) for 1-SB_9H_9.

Atom	*x*	*y*	*z*
S(1)	0.0000	0.0000	1.3194
B(2)	0.0000	1.3588	–0.0576
B(3)	1.3588	0.0000	–0.0576
B(4)	0.0000	–1.3588	–0.0576
B(5)	–1.3588	0.0000	–0.0576
B(6)	0.9254	0.9254	–1.5147
B(7)	0.9254	–0.9254	–1.5147
B(8)	–0.9254	–0.9254	–1.5147
B(9)	–0.9254	0.9254	–1.5147
B(10)	0.0000	0.0000	–2.6267
H(2)	0.0000	2.4393	0.4242
H(3)	2.4393	0.0000	0.4242
H(4)	0.0000	–2.4393	0.4242
H(5)	–2.4393	0.0000	0.4242
H(6)	1.7166	1.7166	–1.9082
H(7)	1.7166	–1.7166	–1.9082
H(8)	–1.7166	–1.7166	–1.9082
H(9)	–1.7166	1.7166	–1.9082
H(10)	0.0000	0.0000	–3.8076

Energy = –626.35454 Hartrees (not corrected for ZPE).

Figure S1 Experimental and difference (experimental minus theoretical) molecular-scattering intensities for 1-SB_9H_9.