The gaseous structure of *closo*-9,12-$(SH)_2$-1,2-$C_2B_{10}H_{10}$, a modifier of gold surfaces, as determined using electron diffraction and computational methods

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Electronic Supplementary Information

Table S1 Nozzle-to-film distances / mm, weighting points / nm^{-1}, scale factors, correlation parameters and electron wavelengths / pm used in the electron diffraction study of *closo*-9,12-$(SH)_2$-1,2-$C_2B_{10}H_{10}$.

Nozzle-to-film distance	Δs	s_{min}	sw_1	sw_2	s_{max}	Scale factor[b]	Correlation parameter	Electron wavelength[a]
252.2	1	20	40	129	150	0.808(7)	0.486	6.18
92.3	2	80	100	276	320	0.859(15)	0.465	6.18

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

Model description

The model consisted of 20 refinable parameters: eleven distances, seven angles and two torsions. The heavy atom structure was modelled using eleven parameters: three angles and eight distances which were used to define the lengths of the eight unique heavy atom to heavy atom bond lengths, namely: C(1)−C(2), C(1)−B(3), B(5)−B(9), B(3)−B(4), B(4)−B(8), B(9)−B(12), B(8)−B(9) and B−S, see Figure 1 for atom numbering. This was done by taking the weighted average and defining seven differences; the formal definitions of p_1-p_8 are as follows:

p_1 = {[C(1)−C(2)] + 4[C(1)−B(3)] + 4[B(5)−B(9)] + 4[B(3)−B(4)] + 4[B(4)−B(8)] + [B(9)−B(12)] + 4[B(8)−B(9)] + 2[B−S]}/24

p_2 = [B−S] − {[C(1)−C(2)] + 4[C(1)−B(3)] + 4[B(5)−B(9)] + 4[B(3)−B(4)] + 4[B(4)−B(8)] + [B(9)−B(12)] + 4[B(8)−B(9)]}/22

p_3 = [C(1) −C(2)] − {4[C(1)−B(3)] + 4[B(5)−B(9)] + 4[B(3)−B(4)] + 4[B(4)−B(8)] + [B(9)−B(12)] + 4[B(8)−B(9)]}/21

p_4 = [C(1)−B(3)] − {4[B(5)−B(9)] + 4[B(3)−B(4)] + 4[B(4)−B(8)] + [B(9)−B(12)] + 4[B(8)−B(9)]}/17

p_5 = [B(9)−B(12)] − {4[B(5)−B(9)] + 4[B(3)−B(4)] + 4[B(4)−B(8)] + 4[B(8)−B(9)]}/16

p_6 = {[B(5)−B(9)] + [B(3)−B(4)]}/2 − {[B(4)−B(8)] + 4[B(8)−B(9)]}/2

p_7 = [B(5)−B(9)] − [B(3)−B(4)]

p_8 = [B(4)−B(8)] − [B(8)−B(9)]

The eight bond lengths were then defined using p_1-p_8:

C(1)−C(2) = $p_1 - p_2/12 + 21p_3/22$

C(1)−B(3) = $p_1 - p_2/12 - p_3/22 + 17p_4/21$

B(5)–B(9) = $p_1 - p_2/12 - p_3/22 - 4p_4/21 - p_5/17 + p_6/2 + p_7/2$

B(3)–B(4) = $p_1 - p_2/12 - p_3/22 - 4p_4/21 - p_5/17 + p_6/2 - p_7/2$

B(4)–B(8) = $p_1 - p_2/12 - p_3/22 - 4p_4/21 - p_5/17 - p_6/2 + p_8/2$

B(9)–B(12) = $p_1 - p_2/12 - p_3/22 - 4p_4/21 + 16p_5/17$

B(8)–B(9) = $p_1 - p_2/12 - p_3/22 - 4p_4/21 - p_5/17 - p_6/2 - p_8/2$

B–S = $p_1 + 11p_2/12$

To complete the cage structure the angle B(12)−B(9)−B(5) was also used.

The sulfur atoms on B(9) and B(12) were positioned using the angles B(12)−B(9)−S(13) and B(9)−B(12)−S(14) respectively. A single S−H distance was used as the MP2/6-311++G(3df,3pd) calculations showed that the distances differed by less than 0.3 pm. The hydrogens on S(13) and S(14) were positioned using the angles B(12)−S(14)−H(14) and B(9)−S(13)−H(13) and the torsions B(9)−B(12)−S(14)−H(14) and B(12)−B(9)−S(13)−H(13).

A single B–H distance was used, as the MP2(full)/6-311++G(3df,3pd) calculations showed that the distances differed by less than 0.5 pm. The B–H and C–H distances were described using two parameters, a weighted average and a difference, defined as:

p_9 = {2[C−H] + 8[B−H]}/10

p_{10} = [B−H] − [C−H]

The bond lengths were then defined in terms of these parameters as:

B−H = $p_9 + p_{10}/5$

C−H = $p_9 - 4p_{10}/5$

The hydrogens on C(1) and C(2) were positioned using the angle C−C−H and the hydrogens on B(4), B(5), B(7) and B(11) were positioned using the angles B(4)−B(5)−H and X−B(5)−H where X is defined as the centre of B(4), B(5), B(7) and B(11).

Table S2 Experimental and theoretical geometric parameters for *closo*-9,12-$(SH)_2$-1,2-$C_2B_{10}H_{10}$.

Parameter	Description	GED value (r_{h1})	Restraint uncertainty	MP2(full)/ 6-311++G(3df,3pd)
Independent				
p_1	*r*CC/*r*BC/*r*BB/*r*BS average	177.8(2)	—	176.6
p_2	*r*CC/*r*BC/*r*BB/*r*BS diff 1	7.4(7)	2.0	8.8
p_3	*r*CC/*r*BC/*r*BB/*r*BS diff 2	–14.3(5)	0.5	–14.4
p_4	*r*CC/*r*BC/*r*BB/*r*BS diff 3	–8.1(5)	2.3	–9.3
p_5	*r*CC/*r*BC/*r*BB/*r*BS diff 4	2.2(6)	1.1	1.1
p_6	*r*CC/*r*BC/*r*BB/*r*BS diff 5	2.1(5)	0.8	0.8
p_7	*r*CC/*r*BC/*r*BB/*r*BS diff 6	0.4(6)	0.6	0.6
p_8	*r*CC/*r*BC/*r*BB/*r*BS diff 7	1.3(11)	1.1	2.0
p_9	*r*BH/*r*CH average	118.2(6)	1.2	116.0
p_{10}	*r*BH/*r*CH diff	9.9(3)	0.3	9.9
p_{11}	*r*SH	135.7(13)	1.9	133.8
p_{12}	∠B(12)B(9)B(5)	107.6(2)	0.3	107.3
p_{13}	∠B(9)B(12)S(14)	122.5(6)	0.6	121.9
p_{14}	∠B(12)B(9)S(13)	126.3(8)	1.4	123.1
p_{15}	∠BSH	95.4(14)	1.4	94.7
p_{16}	∠CCH	116.3(6)	0.6	116.1
p_{17}	∠BBH	119.6(4)	0.4	119.5
p_{18}	∠XBH [c]	7.2(7)	0.7	8.0
p_{19}	ϕB(9)B(12)S(14)H(14)	86.1(189)	18.7	81.5
p_{20}	ϕB(12)B(9)S(13)H(13)	6.2(104)	10.3	7.7
Dependent				
d_1	*r*C(1)C(2)	163.6(5)	—	162.1
d_2	*r*C(1)B(4)	171.3(5)	—	169.0
d_3	*r*B(5)B(9)	178.4(5)	—	178.1
d_4	*r*B(3)B(4)	178.0(4)	—	177.6
d_5	*r*B(4)B(8)	179.5(5)	—	177.6
d_6	*r*B(9)B(12)	181.4(7)	—	179.3
d_7	*r*B(8)B(9)	181.0(6)	—	180.0
d_8	*r*B(9)S(13)	184.5(6)	—	184.3
d_9	*r*C(1)H(1)	110.2(6)	—	108.0
d_{10}	*r*B(3)H(3)	120.6(6)	—	117.8
d_{11}	*r*S(13)H(13)	135.7(13)	—	134.0

[a] All distances in picometres, angles in degrees. See Figure 1 for atom numbering. [b] Restraint uncertainties derived from the degree of convergence of calculations are shown in parentheses. [c] X refers to the midpoint of B(4), B(5), B(7) and B(11).

Table S3 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 *closo*-9,12-$(SH)_2$-1,2-$C_2B_{10}H_{10}$.

	Atom pair	r_a	u_{h1} (GED) [c]	k_{h1}	u_{h1}
u_1	C(1)-H(1)	109.8(6)	9.1(tied to u_3)	0.4	7.5
u_2	B(3)-H(3)	119.8(6)	9.9(tied to u_3)	0.4	8.2
u_4	B(8)-H(8)	119.8(6)	10.0(tied to u_3)	0.4	8.2
u_3	B(7)-H(7)	119.8(6)	9.9(7)	0.4	8.2
u_5	S(14)-H(14)	135.5(13)	7.7(8)	0.3	8.4
u_6	S(13)-H(13)	135.6(13)	7.4(tied to u_5)	0.3	8.1
u_7	C(1)-C(2)	163.4(5)	7.8(tied to u_9)	0.2	7.1
u_8	C(1)-B(4)	171.2(5)	7.8(tied to u_9)	0.2	7.1
u_9	C(2)-B(3)	171.6(5)	8.0(2)	0.3	7.3
u_{10}	B(6)-B(10)	177.4(14)	7.7(tied to u_9)	0.3	7.0
u_{11}	B(3)-B(7)	178.0(4)	7.6(tied to u_9)	0.4	7.0
u_{13}	B(5)-B(9)	178.3(5)	7.9(tied to u_9)	0.3	7.2
u_{12}	B(10)-B(11)	179.4(5)	7.8(tied to u_9)	0.3	7.1
u_{14}	B(4)-B(5)	179.7(7)	7.7(tied to u_9)	0.3	7.1
u_{15}	B(8)-B(12)	180.8(6)	8.1(tied to u_9)	0.2	7.4
u_{16}	B(9)-B(12)	181.3(7)	8.0(tied to u_9)	0.2	7.4
u_{17}	B(9)-S(13)	184.6(6)	6.5(tied to u_9)	0.2	5.9
u_{18}	B(12)-S(14)	184.6(6)	6.5(tied to u_9)	0.3	6.0
u_{25}	C(2)···H(3)	230.2(9)	9.9(9)	-0.4	12.5
u_{19}	C(2)···H(1)	233.5(10)	9.1(tied to u_{25})	-0.3	11.5
u_{21}	B(9)···H(13)	239.2(26)	11.4(tied to u_{25})	0.6	14.4
u_{20}	B(3)···H(2)	240.7(8)	9.5(tied to u_{25})	-0.3	12.0
u_{22}	B(12)···H(14)	242.1(26)	12.1(tied to u_{25})	3.6	15.3
u_{23}	B(4)···H(1)	247.0(9)	9.3(tied to u_{25})	-0.3	11.8
u_{36}	H(2)···H(3)	247.0(9)	19.4(fixed)	-0.3	19.4
u_{24}	C(1)···H(4)	251.2(10)	9.8(tied to u_{25})	-0.4	12.4
u_{26}	B(6)···H(11)	258.3(10)	10.2(tied to u_{25})	-0.3	12.9
u_{29}	H(1)···H(2)	259.5(21)	17.9(fixed)	-0.3	17.9
u_{28}	B(11)···H(7)	259.8(10)	10.2(tied to u_{25})	-0.4	12.8
u_{27}	B(6)···H(10)	261.7(13)	10.1(tied to u_{25})	-0.4	12.8
u_{30}	B(4)···H(8)	263.1(9)	10.2(tied to u_{25})	-0.4	12.8
u_{31}	B(12)···H(10)	264.1(9)	10.1(tied to u_{25})	-0.4	12.8
u_{32}	B(11)···H(6)	265.8(8)	9.9(tied to u_{25})	-0.3	12.4
u_{34}	B(9)···H(5)	267.9(11)	14.9(tied to u_{37})	-0.4	12.4
u_{33}	B(8)···H(7)	268.3(9)	14.9(tied to u_{37})	-0.4	12.4
u_{38}	C(1)···B(9)	275.7(7)	8.5(tied to u_{37})	0.0	7.1
u_{39}	C(1)···B(7)	276.8(7)	9.1(tied to u_{37})	0.1	7.5
u_{37}	C(1)···B(8)	277.4(10)	8.5(3)	0.1	7.1
u_{35}	B(10)···H(6)	285.0(14)	14.5(tied to u_{37})	-0.4	12.1
u_{40}	H(1)···H(5)	285.4(15)	19.1(fixed)	-0.4	19.1
u_{42}	B(6)···B(12)	288.0(9)	9.0(tied to u_{37})	0.1	7.5
u_{47}	B(3)···B(6)	288.9(13)	10.2(tied to u_{37})	0.2	8.5

u_{44}	B(3)···B(11)	289.0(7)	9.5(tied to u_{37})	0.2	7.9
u_{41}	B(4)···B(7)	289.5(15)	9.0(tied to u_{37})	0.2	7.5
u_{43}	B(5)···B(12)	290.3(8)	9.2(tied to u_{37})	0.1	7.7
u_{45}	B(7)···B(10)	291.2(6)	9.3(tied to u_{37})	0.1	7.8
u_{46}	B(8)···B(10)	293.2(16)	9.3(tied to u_{37})	0.2	7.7
u_{50}	H(7)···H(11)	295.6(17)	20.7(fixed)	-0.5	20.7
u_{48}	H(10)···H(14)	299.4(106)	47.0(fixed)	29.2	47.0
u_{52}	B(12)···H(13)	302.1(38)	30.9(tied to u_{37})	9.6	25.7
u_{51}	H(5)···H(6)	307.9(13)	20.3(fixed)	-0.4	20.3
u_{56}	B(7)···S(14)	310.9(10)	10.0(tied to u_{59})	-0.3	11.5
u_{53}	B(10)···H(14)	312.4(57)	27.6(tied to u_{59})	17.8	31.8
u_{54}	H(4)···H(8)	314.3(12)	20.1(fixed)	-0.5	20.1
u_{49}	S(14)···H(13)	314.6(47)	33.0(tied to u_{59})	20.6	38.0
u_{59}	B(8)···S(13)	318.6(4)	9.5(4)	-0.3	10.9
u_{61}	B(12)···S(13)	320.2(8)	9.1(tied to u_{59})	-0.4	10.5
u_{57}	B(8)···S(14)	320.2(5)	10.1(tied to u_{59})	-0.3	11.6
u_{62}	B(11)···H(14)	322.2(194)	37.7(tied to u_{59})	9.7	43.5
u_{67}	H(11)···H(14)	324.8(328)	68.4(fixed)	11.4	68.4
u_{60}	C(1)···B(12)	325.1(6)	6.3(tied to u_{59})	-0.1	7.3
u_{63}	H(13)···H(14)	325.7(425)	77.1(fixed)	14.9	77.1
u_{58}	B(9)···S(14)	325.9(12)	9.2(tied to u_{59})	-0.4	10.6
u_{64}	B(8)···H(13)	331.9(109)	31.0(tied to u_{59})	2.3	35.8
u_{69}	H(8)···H(13)	332.2(180)	55.4(fixed)	2.6	55.4
u_{65}	B(5)···B(7)	340.7(13)	8.4(6)	0.1	7.7
u_{70}	B(10)···H(13)	340.8(112)	40.1(tied to u_{65})	0.5	36.5
u_{66}	B(6)···B(8)	340.9(12)	6.6(tied to u_{59})	0.1	7.7
u_{55}	H(6)···H(10)	343.7(15)	19.6(fixed)	-0.5	19.6
u_{71}	H(8)···S(13)	343.8(6)	22.4(tied to u_{65})	-0.5	20.4
u_{73}	H(7)···S(14)	343.8(21)	22.4(tied to u_{65})	-0.4	20.4
u_{68}	H(8)···S(14)	346.5(8)	23.3(tied to u_{65})	-0.5	21.3
u_{74}	H(10)···H(13)	350.3(181)	55.7(fixed)	-0.4	55.7
u_{72}	H(4)···S(13)	351.5(17)	22.2(tied to u_{65})	-0.4	20.3
u_{75}	B(9)···H(14)	353.9(186)	50.3(tied to u_{65})	0.7	45.8
u_{82}	B(3)···H(6)	365.7(15)	12.6(fixed)	-0.8	12.6
u_{76}	B(11)···H(1)	368.9(10)	11.6(tied to u_{81})	-0.8	11.2
u_{77}	B(10)···H(1)	374.2(11)	11.2(tied to u_{81})	-0.8	10.8
u_{78}	B(9)···H(1)	375.6(10)	11.0(tied to u_{81})	-0.9	10.7
u_{85}	B(7)···H(14)	376.8(144)	35.3(tied to u_{81})	-5.8	34.2
u_{79}	C(2)···H(4)	379.2(11)	12.2(tied to u_{81})	-0.9	11.8
u_{84}	B(11)···H(3)	380.5(10)	12.4(tied to u_{81})	-0.8	12.0
u_{80}	C(1)···H(8)	385.3(11)	11.7(tied to u_{81})	-0.9	11.4
u_{89}	B(4)···H(13)	388.1(68)	23.3(tied to u_{81})	-5.6	22.6
u_{81}	S(13)···S(14)	388.1(19)	20.1(7)	-0.7	19.5
u_{83}	B(3)···H(11)	390.0(10)	12.6(tied to u_{81})	-0.9	12.2
u_{95}	S(13)···H(14)	391.4(357)	83.6(tied to u_{81})	-4.3	80.9
u_{93}	B(5)···H(13)	394.2(53)	21.2(tied to u_{81})	-6.3	20.6

u_{86}	B(7)···H(4)	396.7(16)	12.1(tied to u_{81})	-0.9	11.7
u_{87}	B(11)···H(8)	397.4(8)	12.2(tied to u_{81})	-0.9	11.8
u_{88}	B(10)···H(7)	398.6(9)	12.2(tied to u_{81})	-0.9	11.8
u_{90}	B(10)···H(8)	399.1(16)	12.2(tied to u_{81})	-0.9	11.8
u_{94}	B(8)···H(14)	399.3(60)	19.0(tied to u_{81})	-8.9	18.3
u_{92}	B(12)···H(5)	401.9(12)	11.9(tied to u_{81})	-1.0	11.5
u_{91}	B(12)···H(6)	402.7(11)	11.7(tied to u_{81})	-1.0	11.4
u_{113}	H(3)···H(6)	413.5(18)	17.4(fixed)	-1.7	17.4
u_{97}	H(7)···H(14)	415.2(221)	54.0(fixed)	-11.2	54.0
u_{96}	B(12)···H(1)	433.7(10)	12.5(tied to u_{102})	-1.1	10.2
u_{100}	H(4)···H(13)	439.5(97)	33.2(fixed)	-9.2	33.2
u_{99}	C(2)···S(14)	439.8(10)	11.6(tied to u_{102})	-0.7	9.4
u_{107}	H(8)···H(14)	442.6(94)	27.8(fixed)	-15.5	27.8
u_{98}	C(1)···S(13)	443.8(8)	11.8(tied to u_{102})	-0.7	9.6
u_{106}	H(5)···H(13)	448.6(71)	29.6(fixed)	-10.2	29.6
u_{105}	B(8)···H(6)	450.0(13)	13.4(tied to u_{102})	-1.1	10.9
u_{102}	B(3)···S(14)	452.9(9)	12.6(3)	-0.7	10.3
u_{103}	B(6)···H(14)	453.6(81)	33.0(tied to u_{102})	11.6	26.9
u_{108}	B(7)···H(13)	454.4(54)	32.8(tied to u_{102})	4.6	26.8
u_{111}	B(7)···S(13)	457.3(6)	11.8(tied to u_{102})	-0.8	9.7
u_{101}	H(2)···H(4)	458.4(16)	15.8(fixed)	-1.7	15.8
u_{104}	B(7)···H(5)	458.8(15)	13.4(tied to u_{102})	-1.1	10.9
u_{112}	B(11)···H(13)	459.0(65)	34.6(tied to u_{102})	3.7	28.2
u_{110}	B(6)···H(8)	459.6(13)	13.4(tied to u_{102})	-1.1	10.9
u_{109}	B(4)···S(14)	460.2(8)	12.6(tied to u_{102})	-0.8	10.3
u_{116}	H(3)···H(11)	466.2(13)	16.7(fixed)	-1.8	16.7
u_{115}	B(5)···H(14)	468.1(100)	43.0(tied to u_{102})	6.9	35.0
u_{117}	C(2)···H(14)	472.9(149)	41.2(tied to u_{102})	1.0	33.6
u_{114}	H(1)···H(10)	473.0(13)	15.1(fixed)	-1.8	15.1
u_{121}	B(3)···H(13)	491.5(80)	30.8(tied to u_{123})	-2.1	27.7
u_{118}	H(4)···H(7)	494.6(20)	16.0(fixed)	-1.9	16.0
u_{120}	H(8)···H(10)	494.9(19)	16.0(fixed)	-2.0	16.0
u_{119}	H(7)···H(10)	495.5(13)	16.0(fixed)	-1.9	16.0
u_{122}	B(6)···H(13)	499.0(74)	30.0(tied to u_{123})	-3.1	26.9
u_{125}	C(1)···H(13)	508.4(28)	18.0(tied to u_{123})	-5.6	16.1
u_{123}	C(1)···S(14)	508.5(4)	9.1(4)	-1.0	8.2
u_{126}	B(4)···H(14)	508.7(100)	31.4(tied to u_{123})	-4.0	28.2
u_{124}	C(2)···S(13)	508.8(4)	9.1(tied to u_{123})	-0.9	8.1
u_{128}	B(3)···H(14)	517.2(54)	20.4(tied to u_{123})	-6.9	18.3
u_{129}	H(2)···S(14)	526.1(16)	13.9(fixed)	-1.6	13.9
u_{127}	H(1)···S(13)	531.7(12)	15.7(tied to u_{123})	-1.5	14.1
u_{132}	C(2)···H(13)	538.8(32)	21.6(tied to u_{123})	-0.8	19.4
u_{131}	H(7)···H(13)	538.9(69)	33.1(fixed)	5.6	33.1
u_{134}	C(1)···H(14)	540.4(36)	21.9(tied to u_{123})	1.4	19.6
u_{133}	H(11)	545.3(85)	35.1(fixed)	4.3	35.1
u_{130}	H(6)···H(14)	554.1(118)	33.5(fixed)	13.8	33.5

u_{140}	H(2)···H(14)	555.8(204)	44.9(fixed)	-0.7	44.9
u_{138}	H(5)···H(14)	557.4(141)	45.1(fixed)	7.6	45.1
u_{139}	H(7)···S(13)	557.5(11)	17.2(11)	-1.9	14.5
u_{135}	H(3)···S(14)	560.4(12)	18.1(tied to u_{139})	-1.7	15.2
u_{137}	H(4)···S(14)	561.6(12)	18.0(tied to u_{139})	-1.8	15.1
u_{136}	H(3)···S(13)	562.9(10)	17.8(tied to u_{139})	-1.7	14.9
u_{142}	H(6)···H(8)	568.4(16)	13.4(fixed)	-2.4	13.4
u_{141}	H(5)···H(7)	576.4(18)	13.5(fixed)	-2.5	13.5
u_{143}	H(3)···H(13)	604.2(93)	34.7(fixed)	-4.2	34.7
u_{145}	H(1)···H(13)	606.2(29)	18.1(fixed)	-8.5	18.1
u_{148}	H(4)···H(14)	611.8(139)	36.5(fixed)	-7.8	36.5
u_{144}	H(6)···H(13)	612.7(83)	33.3(fixed)	-5.7	33.3
u_{146}	H(1)···S(14)	616.7(8)	11.7(11)	-2.1	10.9
u_{147}	H(2)···S(13)	617.3(8)	11.7(tied to u_{146})	-2.1	10.9
u_{149}	H(3)···H(14)	625.5(82)	23.1(fixed)	-11.1	23.1
u_{151}	H(1)···H(14)	646.0(43)	21.5(fixed)	0.0	21.5
u_{150}	H(2)···H(13)	646.6(32)	21.0(fixed)	-2.4	21.0

[a] Estimated standard deviations, as obtained in the least-squares refinement, are given in parentheses. [b] See Figure 1 for atom numbering. [c] Amplitudes not refined were fixed at the values obtained using the force field calculated at the B3LYP/6-311++G(d,p) level.

Table S4 Least-squares correlation matrix (×100) for the refinement of *closo*-9,12-$(SH)_2$-1,2-$C_2B_{10}H_{10}$.

	p_2	p_5	p_{12}	u_{59}	k_2
p_1	-57				
p_2	100	-56			
p_5		100	-59		
p_{14}				-70	
u_9					53

[a] Only elements with absolute values ≥ 50% are shown. k_2 is a scale factor.

Table S5 GED Cartesian coordinates (in pm) for *closo*-9,12-$(SH)_2$-1,2-$C_2B_{10}H_{10}$.[a]

Atom	*x*	*y*	*z*
C(1)	81.8	0.0	-131.5
C(2)	-81.8	0.0	-131.5
B(3)	0.0	-144.5	-87.9
B(4)	144.8	-89.8	0.0
B(5)	144.8	89.8	0.0
B(6)	0.0	144.5	-87.9
B(7)	-144.8	-89.8	0.0
B(8)	0.0	-146.7	89.5
B(9)	90.7	0.0	144.4
B(10)	0.0	146.7	89.5
B(11)	-144.8	89.8	0.0
B(12)	-90.7	0.0	144.4
S(13)	189.9	0.0	300.0
S(14)	-199.9	0.0	293.2
H(1)	130.5	0.0	-230.3
H(2)	-130.5	0.0	-230.3
H(3)	0.0	-208.0	-189.9
H(4)	248.5	-148.7	-15.0
H(5)	248.5	148.7	-15.0
H(6)	0.0	208.0	-189.9
H(7)	-248.5	-148.7	-15.0
H(8)	0.0	-248.7	153.0
H(10)	0.0	248.7	153.0
H(11)	-248.5	148.7	-15.0
H(13)	83.5	-14.5	382.9
H(14)	-200.1	134.7	308.8

[a] Atom numbering corresponds to that in Figure 1.

Table S6 Calculated Cartesian coordinates [MP2(full)/6-311++G(3df,3pd); pm] for *closo*-9,12-$(SH)_2$-1,2-$C_2B_{10}H_{10}$.[a]

Atom	*x*	*y*	*z*
C(1)	–220.40	79.70	0.34
C(2)	–219.87	–82.43	0.07
B(3)	–179.00	–1.63	–145.29
B(4)	–92.36	143.36	–89.07
B(5)	–91.72	142.84	89.82
B(6)	–178.77	–2.25	145.58
B(7)	–89.97	–144.07	–89.39
B(8)	–2.95	0.49	–145.03
B(9)	52.46	91.15	0.04
B(10)	–2.72	–0.76	144.96
B(11)	–90.31	–144.67	88.97
B(12)	53.96	–88.15	–0.04
S(13)	206.09	192.99	0.53
S(14)	211.73	–184.62	–7.55
H(1)	–317.73	126.52	0.66
H(2)	–316.65	–130.41	–0.10
H(3)	–258.56	–1.74	–232.10
H(4)	–109.47	244.56	–147.14
H(5)	–108.73	243.61	148.71
H(6)	–258.08	–2.53	232.64
H(7)	–104.62	–245.70	–147.39
H(8)	57.97	1.23	–246.23
H(10)	58.34	–0.39	246.14
H(11)	–104.94	–246.64	146.36
H(13)	286.47	87.21	–17.15
H(14)	239.40	–174.82	122.75

Energy = –1126.7116295 Hartrees (not corrected for ZPE)

[a] Atom numbering corresponds to that in Figure 1.

Figure S1 Experimental and weighted difference (experimental – theoretical) molecular scattering intensities for *closo*-9,12-$(SH)_2$-1,2-$C_2B_{10}H_{10}$.