

Unusual chalcogen-boron ring compounds: the molecular structure of 1,4-B₄S₂(NMe₂)₄ determined by gas-phase electron diffraction and related molecules by quantum chemical calculations

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Electronic Supplementary Information

Table S1. Nozzle-to-film distances / mm, sample and nozzle temperatures / K, weighting functions / nm⁻¹, scale factors, correlation parameters and electron wavelengths / pm used in the electron diffraction study of 1,4-B₄S₂(NMe₂)₄.

Nozzle-to-film distance ^a	253.6	92.7
Sample temperature	415	433
Nozzle temperature	428	453
Δs	1	2
s _{min}	20	90
sw ₁	40	110
sw ₂	112	310
s _{max}	120	320
Scale factor ^b	0.924(5)	0.842(25)
Correlation parameter	0.497	0.346
Electron wavelength	6.18	6.18

^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 / pm) and distance corrections ($r_a - r_e$) for the SARACEN-restrained GED structure of 1,4-B₄S₂(NMe₂)₄.^a

	Atom pair	r_a	$u(\text{exp.})^b$	$r_a - r_e$	$u(\text{calc.})$	Restraint
u_2	C(12)–H(23)	110.1(3)	8.9(1)	0.4	7.4	
u_1	C(11)–H(20)	110.1(3)	8.9(3)	0.4	7.4	7.4(7)
u_5	C(11)–H(21)	110.1(3)	9.1(tied to u_1)	0.4	7.5	—
u_6	C(12)–H(24)	110.1(3)	9.1(tied to u_1)	0.4	7.5	—
u_3	C(12)–H(22)	110.1(3)	9.1(tied to u_1)	0.4	7.5	—
u_4	C(11)–H(19)	110.1(3)	9.1(tied to u_1)	0.4	7.5	—
u_7	B(3)–N(7)	140.9(5)	5.4(tied to u_9)	0.1	4.5	—
u_8	N(7)–C(12)	146.4(2)	5.7(tied to u_9)	0.1	4.7	—
u_9	N(7)–C(11)	146.4(2)	5.7(2)	0.1	4.7	4.7(5)
u_{10}	B(3)–B(4)	173.6(8)	6.3(6)	0.3	5.9	5.9(6)
u_{15}	H(20)...H(21)	178.2(8)	11.9(fixed)	0.0	11.9	—
u_{14}	H(19)...H(21)	178.2(8)	11.9(fixed)	0.0	11.9	—
u_{13}	H(19)...H(20)	178.2(8)	11.9(fixed)	0.0	11.9	—
u_{11}	H(22)...H(23)	178.2(8)	11.9(fixed)	0.0	11.9	—
u_{16}	H(23)...H(24)	178.2(8)	11.9(fixed)	0.0	11.9	—
u_{12}	H(22)...H(24)	178.3(8)	11.9(fixed)	0.1	11.9	—
u_{17}	S(1)–B(4)	186.0(2)	5.8(2)	0.1	5.6	
u_{19}	N(7)...H(22)	211.1(7)	12.0(1)	–0.1	9.9	
u_{23}	N(7)...H(24)	211.1(7)	12.0(5)	–0.1	9.9	9.9(10)
u_{22}	N(7)...H(20)	211.1(7)	12.0(tied to u_{23})	–0.1	10.0	—
u_{20}	N(7)...H(23)	211.1(7)	12.0(tied to u_{23})	–0.1	10.0	—
u_{21}	N(7)...H(21)	211.1(7)	12.1(tied to u_{23})	–0.1	10.1	—
u_{18}	N(7)...H(19)	211.1(7)	12.1(tied to u_{23})	–0.1	10.0	—
u_{25}	H(19)...H(22)	239.0(42)	27.9(1)	5.2	27.9	—
u_{24}	C(11)...C(12)	240.6(4)	5.5(7)	–0.7	6.9	—
u_{27}	B(3)...C(12)	250.0(4)	5.3(tied to u_{24})	–0.3	6.6	—
u_{28}	B(3)...C(11)	255.8(6)	5.1(tied to u_{24})	–0.4	6.4	—
u_{29}	B(3)...H(23)	260.5(12)	18.8(tied to u_{40})	2.0	14.2	—
u_{32}	C(12)...H(19)	260.9(21)	26.8(tied to u_{40})	0.1	20.2	—
u_{33}	C(11)...H(22)	262.2(21)	23.3(tied to u_{40})	–0.4	17.6	—
u_{26}	H(21)...H(24)	263.7(38)	29.3(fixed)	4.4	29.3	—
u_{30}	B(3)...H(25)	265.9(26)	25.8(tied to u_{40})	5.5	19.5	—
u_{34}	B(3)...H(20)	271.4(13)	19.1(tied to u_{40})	3.2	14.4	—
u_{36}	C(11)...H(24)	271.7(17)	23.8(tied to u_{40})	–0.5	18.0	—
u_{31}	S(1)...H(29)	273.8(12)	27.8(tied to u_{40})	10.0	21.0	—
u_{35}	C(12)...H(21)	273.9(18)	16.9(tied to u_{24})	–0.3	21.2	—
u_{38}	B(3)...N(8)	279.4(13)	10.1(tied to u_{40})	–0.3	7.7	—
u_{42}	B(3)...B(6)	279.7(11)	12.4(tied to u_{40})	–2.0	9.4	—
u_{40}	S(1)...N(8)	282.3(5)	9.3(3)	0.1	7.0	—
u_{37}	H(23)...H(25)	283.8(63)	41.5(fixed)	3.6	41.5	—
u_{39}	N(7)...H(25)	286.2(27)	34.8(1)	6.0	26.3	—
u_{44}	H(19)...H(24)	298.7(23)	36.5(fixed)	–2.5	36.5	—

<i>u</i> ₄₈	B(3)...B(5)	302.8(19)	15.6(tied to <i>u</i> ₄₉)	−1.6	13.5	—
<i>u</i> ₄₆	S(1)...B(3)	302.8(7)	11.5(tied to <i>u</i> ₄₀)	−0.4	8.7	—
<i>u</i> ₄₁	H(23)...H(27)	303.2(32)	49.7(fixed)	5.1	49.7	—
<i>u</i> ₄₅	H(21)...H(22)	304.1(22)	36.9(fixed)	−2.7	36.9	—
<i>u</i> ₄₃	C(12)...H(25)	305.8(42)	45.3(tied to <i>u</i> ₄₀)	3.7	34.2	—
<i>u</i> ₅₀	B(3)...H(22)	317.7(10)	17.4(1)	−1.8	15.1	—
<i>u</i> ₄₇	B(3)...C(13)	318.7(19)	13.7(tied to <i>u</i> ₄₉)	0.0	11.8	—
<i>u</i> ₄₉	S(1)...C(14)	322.3(8)	12.7(4)	0.4	11.0	11.0(11)
<i>u</i> ₅₂	B(3)...H(19)	322.9(11)	21.8(tied to <i>u</i> ₄₀)	−2.4	16.4	—
<i>u</i> ₅₁	B(3)...H(24)	323.0(9)	17.0(tied to <i>u</i> ₄₉)	−1.7	14.7	—
<i>u</i> ₅₃	B(3)...H(21)	326.0(10)	21.4(tied to <i>u</i> ₇₅)	−2.4	16.4	—
<i>u</i> ₅₄	C(12)...H(20)	333.2(7)	13.5(tied to <i>u</i> ₇₅)	−3.3	10.3	—
<i>u</i> ₅₅	C(11)...H(23)	334.3(6)	13.1(tied to <i>u</i> ₇₅)	−2.4	10.0	—
<i>u</i> ₅₆	H(24)...H(27)	349.7(54)	61.6(fixed)	4.2	61.6	—
<i>u</i> ₅₉	N(7)...N(8)	355.1(13)	16.0(tied to <i>u</i> ₇₅)	−0.8	12.3	—
<i>u</i> ₆₂	H(20)...H(22)	356.2(27)	19.2(fixed)	−4.2	19.2	—
<i>u</i> ₆₁	H(19)...H(23)	357.9(26)	19.5(fixed)	−2.5	19.5	—
<i>u</i> ₅₇	C(12)...C(13)	358.0(26)	34.1(tied to <i>u</i> ₇₅)	0.3	26.1	—
<i>u</i> ₆₀	N(7)...C(13)	359.0(17)	24.5(tied to <i>u</i> ₇₅)	−0.1	18.8	—
<i>u</i> ₅₈	C(12)...H(27)	363.0(32)	60.3(tied to <i>u</i> ₆₇)	1.4	45.7	—
<i>u</i> ₆₄	H(20)...H(24)	370.2(20)	19.1(fixed)	−4.4	19.1	—
<i>u</i> ₆₃	H(21)...H(23)	372.3(21)	20.1(fixed)	−3.0	20.1	—
<i>u</i> ₆₆	S(1)...H(23)	380.3(18)	35.7(tied to <i>u</i> ₇₅)	4.8	27.4	—
<i>u</i> ₇₁	S(1)...H(30)	387.7(23)	37.9(tied to <i>u</i> ₇₅)	−3.1	29.1	—
<i>u</i> ₆₇	S(1)...S(2)	388.6(9)	12.4(7)	−1.3	9.4	9.4(9)
<i>u</i> ₇₀	B(3)...H(26)	389.6(34)	30.9(tied to <i>u</i> ₆₇)	−2.3	23.4	—
<i>u</i> ₆₉	B(3)...H(27)	390.9(15)	30.4(tied to <i>u</i> ₇₅)	−2.2	23.3	—
<i>u</i> ₇₂	S(1)...H(28)	396.4(16)	36.9(tied to <i>u</i> ₇₅)	−3.8	28.3	—
<i>u</i> ₆₈	C(11)...H(25)	398.0(22)	39.9(tied to <i>u</i> ₇₅)	5.6	30.5	—
<i>u</i> ₇₃	N(7)...H(27)	402.2(25)	45.9(tied to <i>u</i> ₇₅)	−1.2	35.1	—
<i>u</i> ₆₅	H(21)...H(25)	402.3(29)	40.8(fixed)	9.0	40.8	—
<i>u</i> ₇₈	B(3)...N(10)	407.7(6)	14.9(tied to <i>u</i> ₇₅)	−3.2	11.4	—
<i>u</i> ₇₅	S(1)...N(7)	408.4(12)	18.4(4)	−1.1	14.1	14.1(14)
<i>u</i> ₇₄	H(22)...H(25)	410.8(43)	35.1(fixed)	−0.6	35.1	—
<i>u</i> ₇₇	H(20)...H(23)	415.9(14)	13.4(fixed)	−3.7	13.4	—
<i>u</i> ₇₆	B(3)...C(14)	416.6(12)	10.5(tied to <i>u</i> ₇₅)	−1.3	8.1	—
<i>u</i> ₈₁	B(3)...N(9)	417.9(13)	28.2(tied to <i>u</i> ₇₅)	−2.6	21.6	—
<i>u</i> ₇₉	S(1)...C(13)	419.3(5)	9.8(tied to <i>u</i> ₇₅)	−1.2	7.5	—
<i>u</i> ₈₂	B(3)...H(41)	432.8(21)	33.5(tied to <i>u</i> ₇₅)	4.4	25.7	—
<i>u</i> ₈₆	S(1)...C(12)	439.6(12)	26.4(tied to <i>u</i> ₇₅)	−0.7	20.2	—
<i>u</i> ₈₀	H(20)...H(25)	440.9(33)	37.2(fixed)	5.8	37.2	—
<i>u</i> ₈₃	B(3)...H(29)	442.1(17)	19.2(tied to <i>u</i> ₇₅)	0.9	14.7	—
<i>u</i> ₈₅	S(1)...H(25)	443.8(12)	18.6(tied to <i>u</i> ₇₅)	0.2	14.2	—
<i>u</i> ₈₄	N(7)...H(26)	444.1(25)	32.1(tied to <i>u</i> ₇₅)	−3.5	24.6	—
<i>u</i> ₈₇	H(22)...H(27)	457.8(31)	48.8(fixed)	−2.6	48.8	—
<i>u</i> ₈₈	C(12)...H(26)	458.4(29)	36.2(tied to <i>u</i> ₇₅)	−4.0	27.7	—

u_{89}	B(3)...H(28)	472.2(25)	22.2(tied to u_{75})	-3.0	17.0	—
u_{99}	B(3)...H(32)	472.7(25)	30.6(fixed)	-0.1	30.6	—
u_{96}	B(3)...C(18)	474.8(9)	15.0(tied to u_{93})	-3.6	15.9	—
u_{98}	S(1)...H(22)	476.0(33)	49.3(0)	-1.9	38.3	—
u_{94}	S(1)...H(26)	476.5(9)	15.2(tied to u_{93})	-2.7	16.1	—
u_{91}	B(3)...H(30)	478.2(12)	15.5(tied to u_{93})	-3.1	16.4	—
u_{90}	H(19)...H(25)	479.9(25)	32.1(fixed)	0.6	32.1	—
u_{95}	S(1)...H(27)	480.2(9)	15.7(fixed)	-2.4	15.7	—
u_{101}	B(3)...H(34)	484.8(37)	44.2(tied to u_{112})	2.5	34.3	—
u_{93}	C(11)...C(13)	485.0(15)	22.4(11)	-1.2	23.7	—
u_{100}	N(7)...C(14)	496.4(11)	12.8(tied to u_{93})	-2.2	13.6	—
u_{103}	B(3)...C(15)	496.6(15)	24.5(tied to u_{93})	-3.5	26.0	—
u_{97}	C(12)...H(30)	497.0(26)	46.0(tied to u_{112})	1.6	35.6	—
u_{105}	B(3)...C(16)	503.3(17)	33.7(tied to u_{112})	-3.0	26.1	—
u_{92}	H(20)...H(41)	504.9(37)	36.7(fixed)	14.2	36.7	—
u_{107}	N(7)...N(9)	512.9(22)	46.2(tied to u_{112})	-3.8	35.9	—
u_{108}	B(3)...H(38)	515.1(17)	25.8(tied to u_{112})	-1.3	20.0	—
u_{111}	B(3)...C(17)	521.2(8)	17.1(tied to u_{112})	-4.3	13.2	—
u_{117}	B(3)...H(31)	523.8(22)	55.0(tied to u_{112})	-3.9	42.7	—
u_{104}	C(11)...H(27)	525.2(27)	37.1(tied to u_{93})	-2.5	39.4	—
u_{102}	H(21)...H(27)	527.3(38)	48.0(fixed)	1.5	48.0	—
u_{106}	C(12)...H(29)	529.5(26)	38.9(tied to u_{112})	-1.2	30.1	—
u_{114}	B(3)...H(42)	530.1(20)	46.4(tied to u_{112})	-6.4	36.0	—
u_{115}	S(1)...H(24)	530.3(14)	30.0(tied to u_{112})	-4.3	23.3	—
u_{112}	S(1)...C(11)	531.0(19)	22.0(7)	-2.5	17.0	17.0(17)
u_{119}	B(3)...H(35)	533.0(24)	57.3(tied to u_{112})	-3.3	44.5	—
u_{110}	N(7)...H(29)	534.7(17)	23.8(tied to u_{112})	-1.2	18.5	—
u_{116}	N(7)...N(10)	534.9(6)	12.8(tied to u_{112})	-5.2	9.9	—
u_{120}	H(20)...H(32)	535.7(45)	61.3(fixed)	6.8	61.3	—
u_{109}	N(7)...H(30)	535.9(19)	31.4(tied to u_{112})	-2.1	24.4	—
u_{113}	N(7)...H(41)	537.9(19)	32.9(0)	3.3	25.5	—
u_{118}	S(1)...H(20)	545.3(32)	29.0(tied to u_{137})	0.1	24.2	—
u_{127}	B(3)...H(40)	552.8(19)	31.3(tied to u_{137})	-8.3	26.2	—
u_{129}	N(7)...H(34)	555.3(47)	59.6(tied to u_{137})	1.3	49.8	—
u_{126}	N(7)...H(28)	558.3(21)	19.6(tied to u_{137})	-4.8	16.4	—
u_{125}	C(12)...H(28)	559.5(18)	29.7(tied to u_{137})	-5.2	24.8	—
u_{124}	H(22)...H(26)	559.7(32)	28.8(fixed)	-9.0	28.8	—
u_{123}	C(11)...H(26)	561.2(26)	38.2(tied to u_{137})	-4.6	32.0	—
u_{128}	S(1)...H(19)	562.2(33)	38.3(tied to u_{137})	-2.6	32.0	—
u_{135}	H(20)...H(31)	563.5(64)	78.8(fixed)	2.9	78.8	—
u_{131}	N(7)...H(32)	565.4(24)	56.9(tied to u_{112})	-2.3	44.2	—
u_{121}	H(21)...H(26)	567.4(30)	44.5(fixed)	-1.5	44.5	—
u_{122}	C(11)...H(41)	569.5(26)	34.3(tied to u_{137})	3.8	28.7	—
u_{132}	B(3)...H(37)	569.6(15)	32.5(tied to u_{137})	-5.7	27.2	—
u_{138}	C(12)...H(34)	576.1(46)	74.4(tied to u_{160})	2.0	60.0	—
u_{136}	N(7)...C(16)	579.0(30)	51.8(tied to u_{137})	-4.1	43.3	—

u_{139}	N(7)...C(15)	584.0(20)	51.1(tied to u_{137})	-5.2	42.7	—
u_{130}	H(20)...H(27)	584.7(30)	51.7(tied to u_{112})	-4.8	40.1	—
u_{141}	N(7)...H(35)	588.2(45)	75.7(1)	-2.8	63.3	—
u_{143}	N(7)...H(31)	589.2(34)	76.0(tied to u_{160})	-4.3	61.2	—
u_{134}	H(19)...H(27)	589.9(33)	44.0(fixed)	-5.5	44.0	—
u_{142}	B(3)...H(33)	591.5(18)	29.7(tied to u_{137})	-7.4	24.8	—
u_{137}	N(7)...C(18)	592.0(10)	17.7(9)	-5.8	14.8	—
u_{145}	C(11)...H(32)	592.7(27)	65.7(tied to u_{137})	-2.0	55.0	—
u_{133}	H(20)...H(26)	593.8(41)	41.9(fixed)	-3.5	41.9	—
u_{146}	B(3)...H(36)	594.8(19)	31.7(tied to u_{137})	-8.6	26.5	—
u_{148}	H(19)...H(31)	597.5(58)	94.5(fixed)	-0.1	94.5	—
u_{144}	B(3)...H(39)	599.3(13)	20.1(tied to u_{137})	-7.1	16.8	—
u_{153}	C(11)...H(31)	607.1(46)	91.5(tied to u_{160})	-3.3	73.8	—
u_{149}	H(19)...H(32)	610.6(32)	75.9(fixed)	-3.3	75.9	—
u_{147}	S(1)...H(21)	611.6(14)	21.6(tied to u_{160})	-6.4	17.4	—
u_{140}	H(20)...H(40)	613.4(40)	47.2(fixed)	1.4	47.2	—
u_{156}	H(19)...H(35)	616.8(94)	89.8(fixed)	4.2	89.8	—
u_{155}	C(11)...C(15)	620.3(26)	66.5(tied to u_{160})	-5.0	53.6	—
u_{157}	C(12)...H(35)	625.8(39)	94.1(tied to u_{160})	-4.1	75.9	—
u_{161}	H(19)...H(34)	632.4(94)	73.2(fixed)	1.5	73.2	—
u_{150}	C(11)...C(18)	633.3(20)	23.5(tied to u_{160})	-6.2	19.0	—
u_{151}	C(11)...C(14)	638.8(11)	17.6(tied to u_{160})	-4.0	14.2	—
u_{164}	C(11)...H(35)	639.9(75)	88.4(tied to u_{160})	-1.6	71.2	—
u_{162}	C(11)...H(34)	641.0(78)	54.6(tied to u_{192})	-1.1	56.3	—
u_{154}	H(19)...H(26)	643.2(24)	30.5(fixed)	-10.0	30.5	—
u_{158}	N(7)...H(38)	645.2(15)	26.6(tied to u_{160})	-3.6	21.4	—
u_{169}	H(20)...H(34)	648.4(99)	58.7(fixed)	0.5	58.7	—
u_{152}	H(19)...H(41)	648.6(34)	40.1(fixed)	-2.9	40.1	—
u_{168}	C(11)...C(16)	648.8(58)	63.9(tied to u_{160})	-4.6	51.5	—
u_{159}	N(7)...H(42)	652.0(16)	45.2(tied to u_{160})	-9.7	36.4	—
u_{160}	N(7)...C(17)	652.6(6)	15.4(7)	-6.8	12.4	12.4(12)
u_{171}	H(22)...H(31)	660.2(41)	85.7(fixed)	-3.6	85.7	—
u_{167}	N(7)...H(40)	662.5(25)	29.4(tied to u_{192})	-10.4	30.3	—
u_{165}	C(12)...H(41)	669.2(22)	27.1(1)	0.7	27.9	—
u_{173}	C(12)...H(32)	672.4(27)	59.0(tied to u_{160})	-5.2	47.6	—
u_{175}	C(12)...C(15)	673.6(20)	47.6(tied to u_{192})	-7.2	49.1	—
u_{178}	C(12)...H(31)	674.0(28)	66.0(tied to u_{192})	-6.3	68.1	—
u_{166}	C(11)...H(29)	676.4(17)	22.0(tied to u_{160})	-3.3	17.8	—
u_{179}	N(7)...H(36)	677.2(28)	40.6(tied to u_{192})	-10.9	41.9	—
u_{163}	C(11)...H(30)	678.4(22)	24.4(tied to u_{192})	-4.2	25.2	—
u_{183}	H(20)...H(33)	678.9(44)	59.4(fixed)	-3.2	59.4	—
u_{177}	H(23)...H(32)	679.0(39)	45.1(fixed)	-3.4	45.1	—
u_{170}	H(20)...H(38)	680.4(34)	33.4(fixed)	2.0	33.4	—
u_{184}	H(22)...H(32)	683.8(27)	64.0(fixed)	-5.5	64.0	—
u_{182}	N(7)...H(33)	684.4(19)	39.3(tied to u_{192})	-9.8	40.5	—
u_{185}	H(21)...H(32)	685.2(33)	55.1(fixed)	-8.9	55.1	—

<i>u</i> ₁₇₂	C(11)...H(40)	687.3(36)	38.3(tied to <i>u</i> ₁₉₂)	−9.8	39.5	—
<i>u</i> ₁₇₄	C(11)...H(28)	695.6(17)	18.5(tied to <i>u</i> ₁₉₂)	−6.4	19.0	—
<i>u</i> ₁₈₇	N(7)...H(37)	704.9(14)	24.0(tied to <i>u</i> ₁₉₂)	−9.0	24.7	—
<i>u</i> ₁₈₁	C(11)...H(42)	705.4(24)	44.2(tied to <i>u</i> ₁₆₀)	−11.7	35.6	—
<i>u</i> ₁₉₆	H(21)...H(31)	706.1(48)	74.1(fixed)	−11.6	74.1	—
<i>u</i> ₁₈₀	H(20)...H(29)	707.5(28)	20.0(fixed)	−1.7	20.0	—
<i>u</i> ₁₉₁	H(23)...H(38)	709.1(32)	32.7(1)	−0.2	32.7	—
<i>u</i> ₁₇₆	H(21)...H(30)	711.9(43)	33.0(fixed)	−3.3	33.0	—
<i>u</i> ₁₈₆	H(20)...H(39)	717.0(30)	37.8(fixed)	0.1	37.8	—
<i>u</i> ₁₉₇	C(12)...H(36)	718.1(27)	51.3(tied to <i>u</i> ₁₉₂)	−12.6	52.9	—
<i>u</i> ₁₉₂	C(11)...C(17)	719.1(9)	16.8(15)	−7.8	17.3	—
<i>u</i> ₁₉₃	C(11)...H(38)	720.9(19)	24.3(tied to <i>u</i> ₁₉₂)	−5.1	25.1	—
<i>u</i> ₁₉₈	C(11)...H(33)	724.1(25)	51.0(tied to <i>u</i> ₁₉₂)	−10.4	52.6	—
<i>u</i> ₁₉₄	N(7)...H(39)	724.5(11)	19.8(tied to <i>u</i> ₁₉₂)	−9.5	20.4	—
<i>u</i> ₁₉₀	H(19)...H(29)	726.0(27)	26.1(fixed)	−4.6	26.1	—
<i>u</i> ₁₈₉	H(19)...H(30)	728.0(23)	31.7(fixed)	−5.8	31.7	—
<i>u</i> ₁₈₈	H(20)...H(30)	728.3(24)	24.4(fixed)	−5.9	24.4	—
<i>u</i> ₂₀₂	H(19)...H(33)	729.3(41)	76.5(fixed)	−9.9	76.5	—
<i>u</i> ₁₉₅	H(20)...H(37)	735.8(21)	27.3(fixed)	−2.5	27.3	—
<i>u</i> ₂₀₃	H(20)...H(36)	737.0(70)	55.8(fixed)	−7.3	55.8	—
<i>u</i> ₁₉₉	C(12)...H(38)	737.5(20)	25.0(tied to <i>u</i> ₁₉₂)	−4.7	25.7	—
<i>u</i> ₂₀₆	H(19)...H(36)	740.4(73)	72.3(fixed)	−9.8	72.3	—
<i>u</i> ₂₀₀	H(21)...H(40)	741.6(61)	51.6(fixed)	−14.5	51.6	—
<i>u</i> ₂₀₈	C(11)...H(36)	748.3(53)	49.1(tied to <i>u</i> ₁₉₂)	−11.9	50.6	—
<i>u</i> ₂₀₁	H(19)...H(40)	754.1(25)	54.1(fixed)	−14.4	54.1	—
<i>u</i> ₂₀₅	C(12)...C(17)	757.9(12)	16.0(tied to <i>u</i> ₁₉₂)	−8.7	16.5	—
<i>u</i> ₂₀₄	H(19)...H(28)	761.7(28)	19.8(fixed)	−10.7	19.8	—
<i>u</i> ₂₁₀	H(23)...H(33)	763.1(28)	46.0(fixed)	−9.0	46.0	—
<i>u</i> ₂₀₇	H(19)...H(38)	763.2(34)	46.5(fixed)	−7.1	46.5	—
<i>u</i> ₂₁₄	C(12)...H(33)	770.7(20)	45.8(tied to <i>u</i> ₁₉₂)	−12.0	47.2	—
<i>u</i> ₂₁₆	H(22)...H(33)	771.0(33)	68.3(fixed)	−11.5	68.3	—
<i>u</i> ₂₀₉	C(12)...H(42)	771.0(20)	39.4(tied to <i>u</i> ₁₉₂)	−11.2	40.7	—
<i>u</i> ₂₁₅	H(22)...H(38)	776.1(33)	41.0(fixed)	−5.9	41.0	—
<i>u</i> ₂₁₂	C(11)...H(39)	776.3(16)	28.0(tied to <i>u</i> ₁₉₂)	−9.6	28.9	—
<i>u</i> ₂₁₃	C(11)...H(37)	781.1(11)	20.1(tied to <i>u</i> ₁₉₂)	−10.7	20.8	—
<i>u</i> ₂₁₁	H(19)...H(42)	781.9(34)	41.6(fixed)	−18.2	41.6	—
<i>u</i> ₂₁₇	C(12)...H(40)	794.6(22)	27.9(tied to <i>u</i> ₁₉₂)	−13.2	28.8	—
<i>u</i> ₂₁₈	H(21)...H(38)	803.6(23)	29.8(fixed)	−11.2	29.8	—
<i>u</i> ₂₁₉	C(12)...H(37)	804.7(22)	30.3(tied to <i>u</i> ₁₉₂)	−10.7	31.3	—
<i>u</i> ₂₂₄	H(21)...H(33)	821.2(26)	51.6(fixed)	−18.3	51.6	—
<i>u</i> ₂₂₁	H(23)...H(39)	822.9(24)	27.4(fixed)	−9.0	27.4	—
<i>u</i> ₂₂₀	H(19)...H(39)	823.8(22)	52.0(fixed)	−12.7	52.0	—
<i>u</i> ₂₂₂	C(12)...H(39)	836.1(14)	21.5(tied to <i>u</i> ₁₉₂)	−12.1	22.1	—
<i>u</i> ₂₂₃	H(19)...H(37)	840.1(23)	37.5(fixed)	−15.4	37.5	—
<i>u</i> ₂₂₇	H(21)...H(36)	847.4(49)	49.1(fixed)	−19.6	49.1	—
<i>u</i> ₂₂₅	H(21)...H(37)	850.1(24)	35.4(fixed)	−15.1	35.4	—

u_{226}	H(21)...H(39)	852.8(29)	35.5(fixed)	-15.7	35.5	—
u_{228}	H(22)...H(37)	860.2(38)	36.5(fixed)	-13.9	36.5	—
u_{229}	H(24)...H(33)	868.5(21)	44.8(fixed)	-17.2	44.8	—
u_{230}	H(22)...H(39)	877.1(16)	38.9(fixed)	-13.6	38.9	—
u_{231}	H(24)...H(39)	915.1(19)	23.3(fixed)	-15.9	23.3	—

^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 RHF/6-31G* level.

Table S3. Least-squares correlation matrix ($\times 100$) for 1,4-B₄S₂(NM_e)₄.^a

	p_4	p_6	p_8	p_{10}	p_{11}	p_{12}	p_{13}	u_9	u_{24}	u_{40}	k_2
p_1				-64							
p_3	-84	-59	-64					68			
p_4	100							-52			
p_6		100	57	56	-70				57	-57	
p_7			-56			53					
p_{10}				100	-79		-83				
p_{11}					100	-56	90			61	
p_{13}							100			52	
u_9								100			73

^a Only elements with absolute values $\geq 50\%$ are shown.

Table S4. GED coordinates (in Å) for 1,4-B₄S₂(NMe₂)₄.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
S(1)	0.000	0.000	−1.949
S(2)	0.000	0.000	1.949
B(3)	1.332	0.458	0.736
B(4)	1.332	−0.458	−0.736
B(5)	−1.332	0.458	−0.736
B(6)	−1.332	−0.458	0.736
N(7)	2.324	1.376	1.129
N(8)	2.324	−1.376	−1.129
N(9)	−2.324	1.376	−1.129
N(10)	−2.324	−1.376	1.129
C(11)	2.299	2.222	2.321
C(12)	3.397	1.775	0.219
C(13)	3.397	−1.775	−0.219
C(14)	2.299	−2.222	−2.321
C(15)	−3.397	1.775	−0.219
C(16)	−2.299	2.222	−2.321
C(17)	−3.397	−1.775	0.219
C(18)	−2.299	−2.222	2.321
H(19)	2.288	3.282	2.036
H(20)	1.404	2.012	2.920
H(21)	3.186	2.036	2.940
H(22)	3.319	2.843	−0.017
H(23)	3.336	1.204	−0.716
H(24)	4.376	1.589	0.679
H(25)	3.336	−1.204	0.716
H(26)	3.319	−2.843	0.017
H(27)	4.376	−1.589	−0.679
H(28)	2.288	−3.282	−2.036
H(29)	1.404	−2.012	−2.920
H(30)	3.186	−2.036	−2.940
H(31)	−3.319	2.843	0.017
H(32)	−3.336	1.204	0.716
H(33)	−4.376	1.589	−0.679
H(34)	−1.404	2.012	−2.920
H(35)	−2.288	3.282	−2.036
H(36)	−3.186	2.036	−2.940
H(37)	−3.319	−2.843	−0.017
H(38)	−3.336	−1.204	−0.716
H(39)	−4.376	−1.589	0.679
H(40)	−3.186	−2.036	2.940
H(41)	−1.404	−2.012	2.920
H(42)	−2.288	−3.282	2.036

Table S5. Calculated coordinates [MP2(full)/6-311++G**] for 1,4-B₄S₂(NMe₂)₄.

Atom	x	y	z
S(1)	0.000	0.000	-1.956
S(2)	0.000	0.000	1.956
B(3)	1.336	0.415	0.742
B(4)	1.336	-0.415	-0.742
B(5)	-1.336	0.415	-0.742
B(6)	-1.336	-0.415	0.742
N(7)	2.317	1.356	1.101
N(8)	2.317	-1.356	-1.101
N(9)	-2.317	1.356	-1.101
N(10)	-2.317	-1.356	1.101
C(11)	2.367	2.097	2.353
C(12)	3.420	1.700	0.216
C(13)	3.420	-1.700	-0.216
C(14)	2.367	-2.097	-2.353
C(15)	-3.420	1.700	-0.216
C(16)	-2.367	2.097	-2.353
C(17)	-3.420	-1.700	0.216
C(18)	-2.367	-2.097	2.353
H(19)	2.415	3.174	2.150
H(20)	1.479	1.890	2.950
H(21)	3.259	1.819	2.930
H(22)	3.418	2.778	0.009
H(23)	3.323	1.162	-0.728
H(24)	4.384	1.445	0.676
H(25)	3.323	-1.162	0.728
H(26)	3.418	-2.778	-0.009
H(27)	4.384	-1.445	-0.676
H(28)	2.415	-3.174	-2.150
H(29)	1.479	-1.890	-2.950
H(30)	3.259	-1.819	-2.930
H(31)	-3.418	2.778	-0.009
H(32)	-3.323	1.162	0.728
H(33)	-4.384	1.445	-0.676
H(34)	-1.479	1.890	-2.950
H(35)	-2.415	3.174	-2.150
H(36)	-3.259	1.819	-2.930
H(37)	-3.418	-2.778	0.009
H(38)	-3.323	-1.162	-0.728
H(39)	-4.384	-1.445	0.676
H(40)	-3.259	-1.819	2.930
H(41)	-1.479	-1.890	2.950
H(42)	-2.415	-3.174	2.150

Energy = -1432.02121 Hartrees (corrected for ZPE).

Figure S1. Experimental and difference (experimental minus theoretical) molecular-scattering intensities for 1,4-B₄S₂(NMe₂)₄.

