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Unusual chalcogen-boron ring compounds: the gas-phase structures of 1,4-B₄S₂(NMe₂)₄ and related molecules†

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The structure of 1,4-B₄S₂(NMe₂)₄ has been determined by gas-phase electron diffraction and quantum chemical calculations and is compared with the known solid-state structure. While these structures are similar, with a twisted ring geometry [the dihedral angle S–B–B–S from electron diffraction is 75.4(16)°], they are strikingly different to the solid-state structure of 1,4-B₄O₂(OH)₄, which is planar. Using quantum chemical calculations, the combinations of O or S in the ring and OH or NMe₂ as the substituent have been studied and it has been shown that there are two separate causes of the twisted ring. Since the calculated (and observed) structure of 1,4-B₄O₂(OH)₄ is planar but that of 1,4-B₄S₂(OH)₄ is twisted, it is concluded that the inclusion of sulfur in the ring twists the structure by approximately 40°. By comparing the structures of 1,4-B₄S₂(OH)₄ and 1,4-B₄S₂(NMe₂)₄ it has been determined that the twist caused by the NMe₂ groups is around 30°.

Introduction

The compound 1,4-B₄S₂(NMe₂)₄ (**1**) was first described in 1964 by Malhotra,[1] who synthesised it in greater than 90% yield from the reaction between B₂(NMe₂)₄[2] and excess H₂S in Et₂O. Addition of HCl was necessary to remove HNMe₂ as [NH₂Me₂]Cl, as shown in eqn (1), although HCl addition was not required when B₂(NMe₂)₄ and H₂S were reacted under pressure in an autoclave. Sublimable colourless crystals of **1** were obtained from benzene and were characterised by elemental analysis, melting point, molecular weight, and ¹¹B NMR and infrared spectroscopies.

$$2 \text{ B}_2(\text{NMe}_2)_4 + 2 \text{ H}_2\text{S} + 4 \text{ HCl} \rightarrow \text{B}_4\text{S}_2(\text{NMe}_2)_4 \text{ (1)}$$
$$+ 4 \text{ [NH}_2\text{Me}_2]\text{Cl} \qquad (1)$$

1
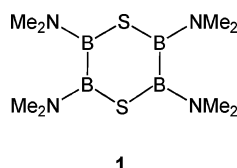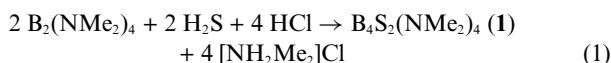
The same compound was subsequently prepared by Nöth and coworkers[3] from the reaction between B₂Cl₂(NMe₂)₂ and the siladithiadiborolane species B₂(NMe₂)₂S₂SiMe₂, and in that study, the solid-state X-ray structure of **1** was also reported. Compound **1** is the only example of its type containing a B₄S₂ ring, although examples in which a B₄O₂ ring is present have been characterised and include B₄O₂(OH)₄[4] and B₄O₂(NR₂)₄ (R = alkyl).[5] Here we report the structure of **1** as determined by gas-phase electron diffraction, and compare it with the previously described solid-state structure. Also presented are the results of quantum chemical

calculations which shed light on the observed differences in ring conformation exhibited by molecules containing sulfur as opposed to oxygen.

Experimental

Synthesis

A sample of compound **1** for use in the gas-phase electron diffraction experiment was prepared by a slight modification of the published methods.[1,3] Excess H₂S was bubbled though a stirred solution of B₂(NMe₂)₄ (1.2 cm³, 5.1 mmol) in hexanes (30 cm³) for 2 hours at room temperature, during which time some colourless precipitate formed. The supernatant liquid was separated and combined with hexane extracts from the remaining solid and then concentrated by vacuum and cooled to 5 °C, affording colourless crystals of **1** (637 mg, 88% yield). NMR (CDCl₃): ¹¹B δ 43.5; ¹H δ 2.7, (d, 24H, N*Me₂*). Anal. Calc. for B₄N₄S₂C₈H₂₄: C, 33.85; H, 8.55; N, 19.75; Found: C, 33.55; H, 8.70; N, 19.80.

Gas-phase electron diffraction (GED)

Data were collected for **1** using the Edinburgh gas-phase electron diffraction (GED) apparatus.[6] An accelerating voltage of 40 kV was used, resulting in an electron wavelength of approximately 6.0 pm. Scattering intensities were recorded on Kodak Electron Image films at two nozzle-to-film distances to maximise the scattering angle over which data were collected. In order to obtain suitable vapour pressures, and to prevent condensation in the nozzle, the sample and nozzle were heated to temperatures listed in Table S1.† The photographic films were scanned using an Epson Expression 1680 Pro flatbed scanner as part of a method that is now used routinely in Edinburgh and described elsewhere.[7] Data-reduction and least-squares refinement processes were carried out using the ed@ed v2.4 program[8] employing the scattering factors of Ross *et al.*[9] The weighting points for the off-diagonal weight

matrices, correlation parameters and scale factors are given in Table S1.†

Computational methods

All calculations were performed using the resources of the NSCCS[10] and the EaStCHEM Research Computing Facility[11] running the Gaussian 03 suite of programs.[12] Imagining the B_4S_2 ring in **1** to have structural similarities to a C_6 saturated ring, several possible geometries were investigated. Real structures were obtained for both a chair conformer (C_s symmetry) and for a conformer with a twisted ring structure (D_2 symmetry). In both the C_s- and D_2-symmetric structures the sums of the angles around N and B atoms indicate that these fragments are planar. This greatly reduces the complexity of determining the geometries as there is no distinction between axial and equatorial conformations. With symmetry fixed, geometries were optimised first at the spin-restricted Hartree–Fock (RHF) level of theory with the 3-21G* basis set[13] on all atoms followed by the 6-31G* basis set[14] and then using MP2(full)[15] to include the energy due to electron correlation. At this level the 6-311G* and 6-311++G** basis sets[16] were also used. Force constants calculated at the RHF/6-31G* level were subsequently used along with the program SHRINK[17] to obtain initial amplitudes of vibration, and third derivatives of the energy (giving cubic anharmonicity terms) were used to give curvilinear perpendicular distance correction terms for use in the GED refinement. The structure obtained from the refinement is thus of the type $r_{a3,1}$. For a full discussion of the a3,1 nomenclature see reference 18.

Results and discussion

Calculations

Two conformers of **1** were studied, the C_s-symmetric chair structure and the D_2-symmetric twisted structure. Although both structures were real, at the RHF/6-31G* level, the twisted structure was more than 38 kJ mol^{-1} lower in energy and so for this reason no further calculations were performed for the C_s conformer. Table 1 contains parameters calculated at the MP2(full)/6-311++G** level.

GED study

Although *ab initio* calculations for the D_2-symmetric twisted structure showed the sums of the angles around N and B to be exactly 360°, the model for the GED refinement included parameters that allowed these groups to become pyramidal. The atom numbering used in the descriptions of the parameters is shown in Fig. 1.

Five distance parameters were required, namely $rS\cdots S$, rS–B, rB–N, rC–N and rC–H (p_{1-5}). Five bond angle parameters were also employed. These included $\angle S$–B–N (p_6), $\angle B(3)$–N(7)–C(11) and $\angle B(3)$–N(7)–C(12) (p_{7-8}), which together create the basic heavy-atom structure of the molecule. As they describe very similar angles, parameters 7 and 8 could have been, but were not, included in the model as the average of the two parameters and the difference between them. However, if when performing the refinement these parameters appear to be very closely correlated, a

Table 1 Refined ($r_{a3,1}$) and calculated (r_e) geometric parameters for 1,4-$B_4S_2(NMe_2)_4$ (**1**) from the GED study[a]

Parameter		$r_{a3,1}$	r_e[b]	Restraint
Independent				
p_1	$rS\cdots S$	389.9(9)	391.2	—
p_2	rS–B	185.9(2)	185.2	—
p_3	rB–N	140.7(5)	140.6	—
p_4	rC–N mean	146.3(2)	145.5	—
p_5	rC–H mean	109.7(3)	109.5	109.5(5)
p_6	$\angle S$–B–N	118.9(5)	119.0	—
p_7	$\angle B(3)$–N(7)–C(11)	126.4(4)	125.8	—
p_8	$\angle B(3)$–N(7)–C(12)	121.4(4)	122.1	—
p_9	$\angle C$–C–H mean	110.3(5)	110.2	110.2(10)
p_{10}	$\angle B$–S–B	98.4(3)	98.1	—
p_{11}	ϕN–B–S$\cdots$S	153.7(16)	150.3	150.3(20)
p_{12}	$\phi C(11)$–N–B–S	−12.4(22)	−2.3	—
p_{13}	$\phi B(3)$–S$\cdots$S–B(4)	37.9(10)	34.5	—
p_{14}	ϕH–C(11)–N–B(3)	−4.6(11)	−5.2	−5.2(10)
p_{15}	ϕH–C(12)–N–B(3)	2.9(11)	2.4	2.4(10)
Dependent				
p_{16}	$rB(3)$–B(4)	173.3(8)	170.0	—
p_{17}	$\angle B(3)$–B(4)–N(8)	125.6(6)	123.3	—
p_{18}	$\angle S(2)$–B(3)–B(4)	115.1(5)	117.6	—
p_{19}	$\phi B(5)$–S(1)–B(4)–B(3)	33.5(5)	31.7	—
p_{20}	$\phi S(2)$–B(3)–B(4)–S(1)	75.4(16)	71.1	—

[a] Distances (r) are in pm, angles ($\angle$) and dihedral angles (ϕ) in degrees. See text for parameter definitions and Fig. 1 for the atom numbering. The figures in parentheses are the estimated standard deviations of the last digits. [b] Refers to an MP2(full)/6-311++G** calculation.

restraint can then be applied to the difference between them, which would reduce or remove the correlation. The methyl groups were calculated to have approximate C_{3v} symmetry and this symmetry was retained in the model by using a single C–C–H angle (p_9) to position the hydrogen atoms. The final bond-angle used in the model was $\angle B$–S–B (p_{10}), which creates the angle at the sulfur atoms. ϕN–B–S$\cdots$S (p_{11}) defines the position of the NMe$_2$ group, where a value of 180° would mean that the N(7)B(3)S(2)B(6)N(10) moiety was planar and w-shaped. $\phi C(11)$–N–B–S (p_{12}) dictates the degree of pyramidality of the BNMe$_2$ group by moving one methyl group. A negative value for p_{12} moves the methyl group away from the B_4S_2 ring. $\phi B(3)$–S–S–B(4) (p_{13}) controls the degree to which the ring is twisted. Finally, each of the symmetry-unique methyl groups has a torsion angle associated with it (p_{14-15}). For both C(11)H$_3$ and C(12)H$_3$ a value of 0° represents one C–H bond eclipsing the B–N bond. In both cases a positive value relates to an anticlockwise rotation of the group about the C–N bond when viewed from the methyl group. All independent geometric parameters were refined by least-squares and restraints were applied, using the SARACEN method,[19] to parameters that could otherwise not be refined (Table 1). The restraints were based on values calculated at the MP2(full)/6-311++G** level and the uncertainties were derived from the changes in value of each parameter during the series of calculations that were performed. Additionally, 15 amplitudes or groups of amplitudes of vibration were refined. (See Table S2 in the supplementary material for a list of amplitudes of vibration.†) The success of the refinement can be assessed numerically using the final R factor, which was $R_G = 0.092$ ($R_D = 0.050$), and visually using the goodness of fit of the radial-distribution and difference curves as seen in Fig. 2, and the molecular-scattering intensity curves (Fig. S1†). The least-squares

(a)

(b)
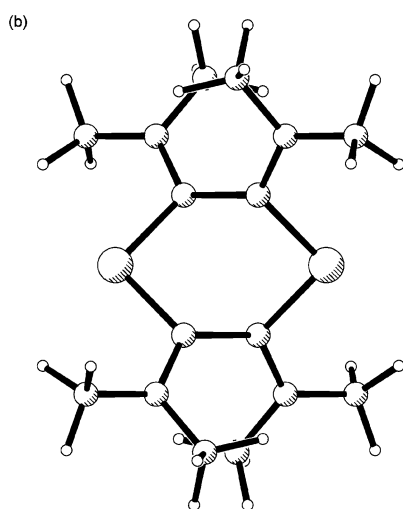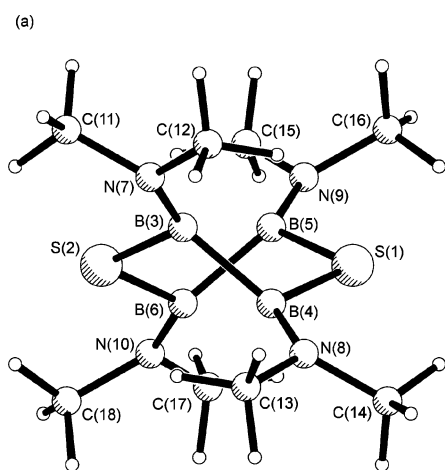
Fig. 1 (a) The twisted molecular structure, including numbering scheme, of 1,4-$B_4S_2(NMe_2)_4$ (**1**) and (b) a view of the same molecule from above the ring.
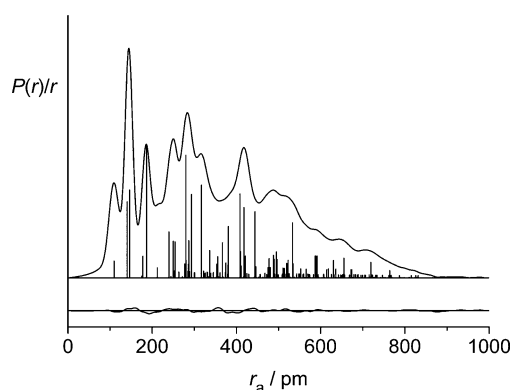
correlation matrix is given in Table S3 and coordinates for the final GED structure and for the calculated structure [MP2(full)/6-311++G**] are in Tables S4 and S5, respectively.†

Fig. 2 Experimental and theoretical-minus-experimental difference radial-distribution curves for 1,4-$B_4S_2(NMe_2)_4$, (**1**). Before Fourier inversion, the data were multiplied by $s \cdot \exp(-0.00002s^2)/(Z_C - f_C)(Z_S - f_S)$, and theoretical intensity values were added below $s = 20$ nm^{-1}.

Comparison of structures

Comparison of the structures of **1** in the gas and solid[3] phases reveals that they are very similar. Table 2 contains selected parameters for the gas-phase experimental and calculated structures [MP2(full)/6-311++G**] and for the crystal structure of **1**, as well as for the crystal structures of $B_4O_2(OH)_4$[4] and $B_4O_2(N^iPr_2)_4$,[5] and for the calculated single molecules of $B_4O_2(OH)_4$, $B_4O_2(NMe_2)_4$ and $B_4S_2(OH)_4$.

The first obvious point of note is that $B_4O_2(OH)_4$ is planar both in the solid state[4] and in the calculated gas-phase structure. In order to identify the cause of the twisting in some of the molecules studied it was then pertinent to compare the calculated structure of $B_4O_2(OH)_4$ with that of the sulfur derivative $B_4S_2(OH)_4$, whereupon it was observed that the B_4Y_2 ring twists by 40.7° for the case when Y is sulfur. This twisting is probably due to the increased propensity of the atomic orbitals on sulfur to form sp³-hybridised orbitals, while those on oxygen will form sp² hybrids.

It is notable, however, that in the solid state, the structure of the amido derivative $B_4O_2(N^iPr_2)_4$[5] is twisted in contrast to the planar $B_4O_2(OH)_4$.[4] To investigate whether this is a consequence of the different substituents on the boron atoms, and whether the same is true for isolated molecules as for those in the solid state, the calculated structures of $B_4O_2(OH)_4$ and $B_4O_2(NMe_2)_4$ were compared with the structures of $B_4S_2(OH)_4$ and $B_4S_2(NMe_2)_4$. [$B_4O_2(NMe_2)_4$ was chosen instead of $B_4O_2(N^iPr_2)_4$ because of the

Table 2 Selected B_4Y_2 geometric ring parameters for the GED, calculated and crystal structures of **1** (Y = S), the calculated structures of $B_4S_2(OH)_4$ (Y = S) and $B_4O_2(NMe_2)_4$ (Y = O), the crystal and calculated structures of $B_4O_2(OH)_4$ (Y = O) and the crystal structure of $B_4O_2(N^iPr_2)_4$ (Y = O)[a]

	$B_4S_2(NMe_2)_4$ (**1**)			$B_4S_2(OH)_4$	$B_4O_2(NMe_2)_4$	$B_4O_2(OH)_4$		$B_4O_2(N^iPr_2)_4$
	GED	MP2[b]	X-Ray[c]	MP2[b]	MP2[b]	X-Ray[d]	MP2[b]	X-Ray[e]
rB–B	173.3(8)	170.0	166.2(14), 169.7(12)	171.1	172.9	173.2(3)	172.2	172.9(4)
rB–Y	185.9(2)	185.2	185.4(9), 186.1(11)	183.4	141.5	137.8(3)–138.5(3)	139.3	140.8(3) mean
∠Y–B–B	115.1(5)	117.6	117.25(62)–118.16(62)	124.8	113.7	120.0(2)–119.1(2)	120.1	112.2(2)
∠B–Y–B	98.4(3)	98.1	100.50(43), 100.77(45)	102.5	124.8	120.5(2)	119.8	117.3(3) mean
ϕB–Y–B–B	33.5(5)	31.7	30.8[f]	18.6	16.8	3.8[f]	0.0	24.5[f]
ϕY–B–B–Y	75.4(16)	71.1	66.6[f]	40.7	36.1	3.8[f]	0.0	55.9[f]

[a] Distances (r) are in pm, angles (∠) and dihedral angles (ϕ) in degrees. The figures in parentheses are the estimated standard deviations of the last digits. [b] MP2(full)/6-311++G**. [c] Reference 3. [d] Reference 4. [e] Reference 5. [f] ESDs unknown.

complications caused by numerous conformers of $B_4O_2(N^iPr_2)_4$ produced by rotation of the isopropyl groups.] On replacing the OH groups with NMe_2 groups in the B_4O_2 species it can be seen that the degree of twist (as measured by the O–B–B–O dihedral angle) increases from 0 to 36.1°. The twisting observed for B_4S_2 species is also more pronounced when the substituents on boron are NMe_2. In this case the increase in the twist dihedral angle is 30.4°, perhaps slightly less than in the previous example because the molecule was already twisted due to the presence of sulfur atoms in the ring. That these rings are twisted when there are amino groups on the boron atoms most probably arises as a consequence of achieving maximum overlap of the nitrogen lone pairs of electrons with the boron p orbitals, *i.e.* the adjacent nitrogen and boron trigonal planes need to be coplanar causing unfavourable steric interactions between methyl groups which are relieved by twisting.

Conclusions

In conclusion, we have shown that there is little apparent difference in the solid and observed or calculated structures of compounds containing the B_4S_2 ring and that the same is true for B_4O_2 compounds. It has further been demonstrated that, in the absence of significant intramolecular steric interactions, B_4O_2 rings are planar whereas B_4S_2 rings are twisted. B_4O_2 rings adopt twisted conformations when amido substituents are placed on the boron atoms and B_4S_2 rings twist even more.

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