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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 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. Excess H₂S was bubbled though a stirred solution of B₂(NMe₂)₄ (1.2 cm³, 5.1 mmol) 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.

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

The same compound was subsequently prepared by Nöth and coworkers from the reaction between B₂Cl₂(NMe₂)₂ and the siladithiadiborolane species B₂(NMe₂)₄SiMe₂, 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 and B₄O₂(NR₂)₄ (R = alkyl). 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.

Gas-phase electron diffraction (GED)

Data were collected for 1 using the Edinburgh gas-phase electron diffraction (GED) apparatus. 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. Data-reduction and least-squares refinement processes were carried out using the ed@ed v2.4 program† employing the scattering factors of Ross et al. 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® and the EaStCHEM Research Computing Facility10 running the Gaussian 03 suite of programs.14 Imagining the B₅S₉ ring in 1 to have structural similarities to a Cₓ saturated ring, several possible geometries were investigated. Real structures were obtained for both a chair conformer (C₁ symmetry) and for a conformer with a twisted ring structure (D₂ symmetry). In both the Cᵥ and D₂-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 set12 on all atoms followed by the 6-31G* basis set14 and then using MP2(full)15 to include the energy due to electron correlation. At this level the 6-31G* and 6-31++G** basis sets16 were also used. Force constants calculated at the RHF/6-31G* level were subsequently used along with the program SHRINK17 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 rₓ,₁. For a full discussion of the a₃,₁ nomenclature see reference 18.

Results and Discussion

Calculations

Two conformers of 1 were studied, the Cᵥ-symmetric chair structure and the D₂-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 Cᵥ conformer. Table 1 contains parameters calculated at the MP2(full)/6-311++G** level.

GED study

Although ab initio calculations for the D₂-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 ρS···S, ρS-B, ρB-N, ρC-N and ρC-H (ρᵢ,j). Five bond angle parameters were also employed. These included ∠S-B-N (ρᵢ,j), ∠B(3)–N(7)–C(11) and ∠B(3)–N(7)–C(12) (ρᵢ,j), 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 restraint can then be applied to the difference between them, which would reduce or remove the correlation. The methyl groups were all calculated to have approximate Cᵥ symmetry and this symmetry was retained in the model by using a single C–C–H angle (ρᵢ,j) to position the hydrogen atoms. The final bond-angle used in the model was ∠B–S–B (ρᵢ,j), which creates the angle at the sulfur atoms. ρN–B···S (ρᵢ,j) defines the position of the NMe₂ 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. ρC(11)–N–B···S (ρᵢ,j) dictates the degree of pyramidalization of the BNMe₂ group by moving one methyl group. A negative value for ρᵢ,j moves the methyl group away from the B₅S₉ ring. ρB(3)–S···S–B(4) (ρᵢ,j) controls the degree to which the ring is twisted. Finally, each of the symmetry-unique methyl groups has a torsion angle associated with it (ρᵢ,j). For both C(11)H₃ and C(12)H₃ 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)/6-31++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. (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 R₀ = 0.092 (Rₑ = 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. S17). The least-squares

<table>
<thead>
<tr>
<th>Parameter</th>
<th>rₓ,₁</th>
<th>rᵢ,j</th>
<th>Restraint</th>
</tr>
</thead>
<tbody>
<tr>
<td>p₁</td>
<td>rS···S</td>
<td>389.9(9)</td>
<td>391.2</td>
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<tr>
<td>p₂</td>
<td>rS-B</td>
<td>185.9(2)</td>
<td>185.2</td>
</tr>
<tr>
<td>p₃</td>
<td>rB-N</td>
<td>140.7(5)</td>
<td>140.6</td>
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<tr>
<td>p₄</td>
<td>rC-N</td>
<td>146.3(2)</td>
<td>145.5</td>
</tr>
<tr>
<td>p₅</td>
<td>rC-H</td>
<td>109.7(3)</td>
<td>109.5</td>
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<tr>
<td>p₆</td>
<td>∠S-B-N</td>
<td>118.9(5)</td>
<td>119.0</td>
</tr>
<tr>
<td>p₇</td>
<td>∠B(3)-N(7)-C(11)</td>
<td>126.4(4)</td>
<td>125.8</td>
</tr>
<tr>
<td>p₈</td>
<td>∠B(3)-N(7)-C(12)</td>
<td>121.4(4)</td>
<td>121.2</td>
</tr>
<tr>
<td>p₉</td>
<td>∠C-C-H</td>
<td>110.3(5)</td>
<td>110.2</td>
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<tr>
<td>p₁₀</td>
<td>∠B-S-B</td>
<td>98.4(3)</td>
<td>98.1</td>
</tr>
<tr>
<td>p₁₁</td>
<td>ϕN-B···S-S</td>
<td>153.7(16)</td>
<td>150.3</td>
</tr>
<tr>
<td>p₁₂</td>
<td>ϕC(11)-N-B-S</td>
<td>-12.4(22)</td>
<td>-2.3</td>
</tr>
<tr>
<td>p₁₃</td>
<td>ϕB(3)-S···S-B(4)</td>
<td>37.9(10)</td>
<td>34.5</td>
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<tr>
<td>p₁₄</td>
<td>ϕH-C(11)-N-B(3)</td>
<td>-4.6(11)</td>
<td>-5.2</td>
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<tr>
<td>p₁₅</td>
<td>ϕH-C(12)-N-B(3)</td>
<td>2.9(11)</td>
<td>2.4</td>
</tr>
</tbody>
</table>

*Distances (r) are in pm, angles (∠) 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. † Refers to an MP2(full)/6-311++G** calculation.

Table 1 Refined (rₓ,₁) and calculated (rᵢ,j) geometric parameters for 1,4-B₅S₉(NMe₂)₃ (1) from the GED study.
Fig. 1  (a) The twisted molecular structure, including numbering scheme, of 1,4-B₄S₂(NMe₂)₄ (I) 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-B₄S₂(NMe₂)₄ (I). 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 I in the gas and solid 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 I, as well as for the crystal structures of B₄O₂(OH)₄ and B₄O₂(NMe₂)₄ and for the calculated single molecules of B₄O₂(OH)₄, B₄O₂(NMe₂)₄ and B₄S₂(OH)₄.

The first obvious point of note is that B₄O₂(OH)₄ is planar both in the solid state 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 B₄O₂(OH)₄ with that of the sulfur derivative B₄S₂(OH)₄, whereupon it was observed that the B₄Y₂ 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 B₄O₂(NiPr₂)₄ is twisted in contrast to the planar B₄O₂(OH)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 B₄O₂(OH)₄ and B₄O₂(NMe₂)₄ were compared with the structures of B₄S₂(OH)₄ and B₄S₂(NMe₂)₄. [B₄O₂(NMe₂)₄ was chosen instead of B₄O₂(NiPr₂)₄ because of the

Table 2  Selected B₄Y₂ geometric ring parameters for the GED, calculated and crystal structures of I (Y = S), the calculated structures of B₄S₂(OH)₄ (Y = O), the crystal and calculated structures of B₄O₂(OH)₄ (Y = O) and the crystal structure of B₄O₂(NPr₂)₄ (Y = O)

<table>
<thead>
<tr>
<th></th>
<th>B₄S₂(NMe₂)₄ (I)</th>
<th>B₄S₂(OH)₄</th>
<th>B₄O₂(NMe₂)₄</th>
<th>B₄O₂(OH)₄</th>
<th>B₄O₂(NPr₂)₄</th>
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<tr>
<td></td>
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<td>MP2</td>
<td>X-Ray</td>
<td>MP2</td>
<td>X-Ray</td>
</tr>
<tr>
<td>rB–B</td>
<td>173.3(8)</td>
<td>170.0</td>
<td>166.2(14), 169.7(12)</td>
<td>171.1</td>
<td>172.9</td>
</tr>
<tr>
<td>rB–Y</td>
<td>185.9(2)</td>
<td>185.2</td>
<td>185.4(9), 186.1(11)</td>
<td>183.4</td>
<td>141.5</td>
</tr>
<tr>
<td>∠Z–B–B</td>
<td>115.1(5)</td>
<td>117.6</td>
<td>117.25(62)–118.16(62)</td>
<td>124.8</td>
<td>113.7</td>
</tr>
<tr>
<td>∠Z–B–Y</td>
<td>98.4(3)</td>
<td>98.1</td>
<td>100.50(43), 100.77(45)</td>
<td>102.5</td>
<td>124.8</td>
</tr>
<tr>
<td>φB–Y–B–Y</td>
<td>33.5(5)</td>
<td>31.7</td>
<td>30.8(8)</td>
<td>40.7</td>
<td>36.1</td>
</tr>
</tbody>
</table>

* 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.  
* MP2(full)/6-311++G**. † Reference 3. ‡ Reference 4. § Reference 5. ¶ ESDs unknown.
complications caused by numerous conformers of B$_2$O$_2$(NPr$_2$)$_4$, produced by rotation of the isopropyl groups. On replacing the OH groups with NMe$_3$ groups in the B$_2$O$_3$ 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$^\circ$. The twisting observed for B$_2$S$_2$ species is also more pronounced when the substituents on boron are NMe$_3$. In this case the increase in the twist dihedral angle is 30.4$^\circ$, 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$_2$S$_2$ ring and that the same is true for B$_2$O$_3$ compounds. It has further been demonstrated that, in the absence of significant intramolecular steric interactions, B$_2$O$_3$ rings are planar whereas B$_2$S$_2$ rings are twisted. B$_2$O$_3$ rings adopt twisted conformations when amido substituents are placed on the boron atoms and B$_2$S$_2$ rings twist even more.

Acknowledgements

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References

10 National Service for Computational Chemistry Software (NSCCS), URL http://www.nsccs.ac.uk.
11 EaStCHEM Research Computing Facility (http://www.eastchem.ac.uk). This facility is partially supported by the eDIKT initiative (http://www.edikt.org).