Short Communications

On the Barrier to Internal Rotation in H₂BSSH₂. An ab initio Study

O. GROOPEN

Institute of Mathematical and Physical Sciences, Department of Chemistry, University of Tromsø, Tromsø, Norway

Electron diffraction studies have shown that the B–S arrangements are planar in a number of compounds.¹ These results give strong evidence for considerable π-bond orders in the B–S bonds. This conclusion is supported by ab initio calculations on H₂BSH.¹ Recently, bis(dimethylboronyl)disulfane was studied by electron diffraction.³ As in related compounds the B–S arrangement is planar. The obtained torsional angle (120° from the syn form) is somewhat larger than the corresponding angle found in the compounds XSSH, and the S–S bond distance was found to be almost identical to the similar bond in dimethyl-1,2,4-trithia-3,5-diborolane (2.076 Å).³ These rather long S–S bonds (2.05 Å in H₂S₄) and large deviation from the anti form give no indication of delocalization in the π-system, but do not exclude a conjugation in the planar state either. In a previous semiempirical calculation rather high bond orders were found in trithiadiborolanes.⁴ The best way to clarify the properties of the S–S bonds in these molecules seems to be by ab initio calculations. The bis(boryl)disulfane molecule was chosen as a reasonable test system (see fig. 1). The potential curve for rotation around the S–S bond has been calculated.

Table 1. Calculated total energies in a.u. and energy differences in kcal/mol.

<table>
<thead>
<tr>
<th>Dihedral angle (°)</th>
<th>Total energy</th>
<th>Energy differences</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>-845.768687</td>
<td>0</td>
</tr>
<tr>
<td>150</td>
<td>-845.768830</td>
<td>-0.0866</td>
</tr>
<tr>
<td>120</td>
<td>-845.768442</td>
<td>-0.4739</td>
</tr>
<tr>
<td>90</td>
<td>-845.769428</td>
<td>-0.4641</td>
</tr>
<tr>
<td>0</td>
<td>-845.739385</td>
<td>+18.3723</td>
</tr>
</tbody>
</table>

The calculations were performed using the program MOLECULE⁸ which solves the Root-Haen-Hall equations for a Gaussian type of basis. A (10,6,1/7,3/4) basis set contracted to double zeta was applied, and no geometry optimization was performed during the rotation around the disulfide bond. The geometry parameters were put equal to the observed values for bis(dimethylboronyl)disulfane, except for the B–H bond length and the angles around boron where the values 1.20 Å and 120° were chosen, respectively.

The total energy was calculated for both syn and anti form together with 150, 120, and 90° for the dihedral angle (syn chosen equal to 0°). The following potential E=α₁+α₂cos ϕ+α₃cos 2ϕ+α₄cos 3ϕ+α₅cos 4ϕ was fitted to the obtained results.

The calculated total energies together with energy differences are presented in Table 1 and the potential curve drawn in Fig. 2. The energy minimum is presented to be at a dihedral angle of 102°, and the barriers to internal rotation around the S–S bond are estimated to 18.1 and 0.7 kcal/mol for syn and anti, respectively. The syn barrier is probably much too high as geometry optimization is important in this form. The anti barrier, however, should be fairly reliable. Taking the differences of the compounds into consideration the agreement with the observed value for the dihedral angle in bis(dimethylboronyl)disulfane (120°) is rather good, and the shallow minimum and low barrier are consistent with results obtained in the electron diffraction investigation. The energy minimum and the anti barrier were also determined excluding the calculated value for the syn form and using only four terms. The obtained anti barrier and dihedral angle were

Fig. 1. Geometry of BH₄S₂BH₄ and definition of the angle ϕ.

Crystal Structure of Methyl 2,3-O-Isopropylidene-β-D-allo-hept-6-ynofuranoside

P. GROTH

Department of Chemistry, University of Oslo, Oslo 3, Norway

Methods for the synthesis and separation of epimeric uronic acids have been studied by Kjelberg et al.¹ One of the methods used for chain extention has been the ethnylation reaction described by Jones et al.² Reaction between methyl 2,3-O-isopropylidene-β-D-ribo-1,5-di-dallopentofuranoside and ethynyl-magnesium bromide gave two isomers (C-5 epimers) in approximately equal amounts.³ Since configurational assignments based on spectroscopic data were somewhat uncertain, an X-ray crystallographic investigation of the isomer which was supposed to be the methyl-2,3-O-isopropylidene-β-D-allo-hept-6-ynofuranoside has been carried out.

The crystals of C₆H₁₂O₆ are orthorhombic with cell dimensions \( a = 5.865(2) \) Å, \( b = 11.555(3) \) Å, \( c = 18.174(3) \) Å and four molecules in the unit cell \( (D_x = 1.23 \text{ g/cm}^3) \). The space group is \( P21_121_2 \). The structure was solved by direct methods⁴ and refined by full-matrix least squares technique⁵ to an \( R \)-value of 3.4 % \( (R_w = 4.1 \%) \) for 971 reflections observed on an automatic four circle diffractometer at room temperature. Anisotropic temperature factors were introduced for oxygen and carbon atoms. The hydroxyl and methyl hydrogen atoms were found in the difference Fourier map. Positional parameters for the remaining hydrogen atoms were calculated. Weights for least squares refinement were obtained from the standard deviations in intensities, \( \sigma(I) \), taken as

\[
\sigma(I) = [C_T + (0.02C_N)^{1/2}]
\]

where \( C_T \) is the total number of counts and \( C_N \) the net count.

Final fractional coordinates and thermal parameters with estimated standard deviations are given in Table 1. The principal axes of thermal vibration ellipsoids for carbon atoms were calculated from the temperature parameters of Table 1. Maximum r.m.s. amplitudes range from 0.220 to 0.331 Å (corresponding 8-values 3.80 and 8.63 Å²).

Bond distances and angles are listed in Table 2. Fig. 1 is a schematic drawing of the molecule (viewed along [100]) which shows that it has the D-allo configuration.

---

¹ All programs used (except those for phase determination) are included in this reference.