Short Communications

On the Barrier to Internal Rotation in H₂BSSBH₂. An *ab initio* Study

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Electron diffraction studies have shown that the B−S arrangements are planar in a number of compounds.[1] These results give strong evidences for considerable π-bond orders in the B−S bonds. This conclusion is supported by *ab initio* calculations on H_2BSH.[1] Recently, bis(dimethylboryl)disulfane was studied by electron diffraction.[2] 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 XSSX, 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 H_2S_2) 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 semi-empirical 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.
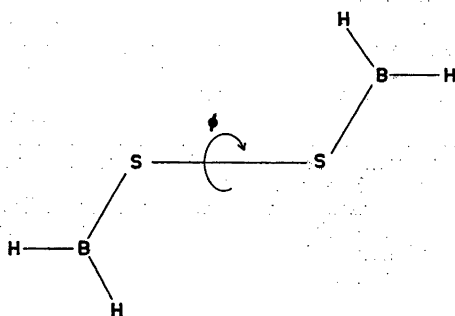

Fig. 1. Geometry of $BH_2S_2BH_2$ and definition of the angle ϕ.

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

Dihedral angle (°)	Total energy	Energy differences
180	− 845.768687	0
150	− 845.768830	− 0.08966
120	− 845.769442	− 0.47339
90	− 845.769428	− 0.46461
0	− 845.739385	+ 18.37235

The calculations were performed using the program MOLECULE[5] which solves the Root-haan-Hall equations for a Gaussian type of basis. A (10,6,1/7,3/4) basis[6] 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(dimethylboryl)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 $E = a_0 + a_1 \cos \phi + a_2 \cos 2\phi + a_3 \cos 3\phi + a_4 \cos 4\phi$ 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 predicted to be at a dihedral angle of 102°, and the barriers to internal rotation around the S−S bond are estimated to 19.1 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(dimethylboryl)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
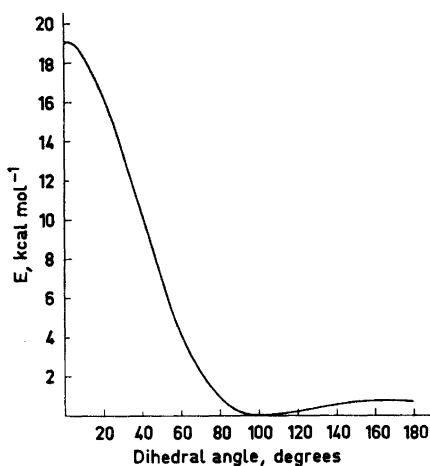
Fig. 2. The total energy as a function of the dihedral angle ϕ.

then found to be 0.6 kcal/mol and 103°, respectively. Compared with hydrogen disulfide the dihedral angle is increased from 90 to 102°, and the *anti* barrier reduced from 4.2 (calculated with same type of basis)[7] to 0.69 kcal/mol.

These reductions of the *anti* barrier and the very shallow minimum compared to hydrogen disulfide supply strong arguments for considerable delocalization in the planar form.

This conjugation is, however, not strong enough to give a planar equilibrium conformation, and with dihedral angle close to 90° the delocalization will not influence the S−S bond length to any extent.

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

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Methods for the synthesis and separation of epimeric uronic acids have been studied by Kjølberg *et al.*[1] One of the methods used for chain extention has been the ethynylation reaction described by Jones *et al.*[2] Reaction between methyl 2,3-O-isopropylidene-β-D-ribo-1,5-dialdopentofuranoside 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 $C_{11}O_5H_{16}$ are orthorhombic with cell dimensions $a = 5.855(2)$ Å, $b = 11.555(3)$ Å, $c = 18.174(3)$ Å and four molecules in the unit cell ($D_x = 1.23$ g/cm³). The space group is $P2_12_12_1$. The structure was solved by direct methods[4] and refined by full-matrix least squares technique *[5] 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

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

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 *B*-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.

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