Redetermination of the crystal structure of 1,4-dithiane, at 200 K – Analysis of intermolecular forces, $C_4H_8S_2$

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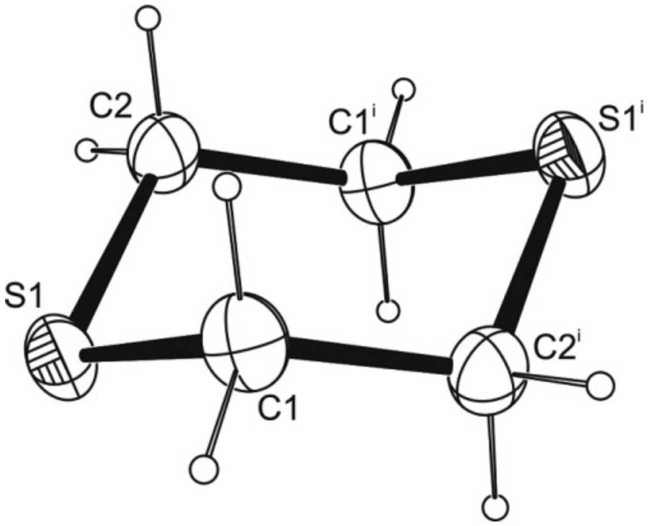

Abstract

$C_4H_8S_2$, monoclinic, $P2/c$ (no. 14), $a = 6.7630(3)$ Å, $b = 5.4100(2)$ Å, $c = 10.0272(4)$ Å, $\beta = 129.660(2)°$, $V = 282.4$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0182$, $wR_{ref}(F^2) = 0.0510$, $T = 200$ K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.116×0.236×0.273 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	7.90 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2495, 647
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 607
$N(param)_{refined}$:	45
Programs:	SHELX [14], ORTEP-3 [15], MERCURY [16], PLATON [17]

Source of material

The compound was obtained commercially (Aldrich). Crystals suitable for the diffraction study were obtained upon storing a freshly molten sample at room temperature over a time span of several months upon which sublimed crystals of high quality could be obtained.

Experimental details

All H atoms were located in a difference map and refined freely.

Discussion

Chelate ligands play a major role in coordination chemistry due to the enhanced thermodynamic stability of their coordination compounds in relation to similar compounds derived from comparable monodentate ligands. Incorporating two donor atoms into a cyclic compound offers an additional level of confinement that might give rise to interesting coordination patterns. 1,4-Dichalcogeno derivatives of cyclohexane appeared as interesting bonding partners as the variation in conformation could easily turn them from mono- into bidentate ligands. 1,4-Dithiane was chosen to act as a starting point in an upcoming study about the coordination behaviour of the aforementioned compounds as it has been found to realize a variety of coordination modes: it has been found to act as a purely monodentate ligand [1], as a monodentate, μ_1 bridging ligand [2], as a monodentate, μ_2 bridging ligand [3] and as bidentate chelating ligand [4]. Its crystal structure has been reported earlier, however, at room temperature only with [5] and without [6] hydrogen atom positions localized or as a private communication at low temperature [7] so that no discussion of metrical parameters is at hand for these latter conditions. The present study is intended to close this gap and to enable the comparison of metrical parameters in envisioned coordination compounds whose structures will be determined at low temperature as well. As the quality of the diffraction data is very high, all hydrogen atoms were located on a DFM and refined freely. Furthermore, the structure of the title compound has also been determined by means of electron diffraction in the gas phase [8] as well as by spectroscopic and quantummechanical methods [9]. The asymmetric unit contains half a molecule. C–S bond lengths vary only slightly with values of 1.8059(10) and 1.8106(11) Å, the latter values invariably bigger than the ones found at room temperature [5] but shorter than available for the data deposited at 100 K [7]. A slightly deviating behaviour is found for the C–S–C angle measured at 99.91(5)° that invariably slightly exceeds both its counterparts, the one at room temperature [5] as well as the one at 100 K [7]. The two S–C–C angles of 113.16(7)° and 113.30(7)° are nearly identical in value. They both exceed the corresponding values deductable from the deposited data obtained at 100 K [7], however, they entirely lie in between the two values reported for the structure determination conducted at room temperature [5]. The intracyclic S···S distance of 3.4731(5) Å is in between a shorter value reported at room temperature [5] and a slightly longer value that can be derived for the data obtained at 100 K [7]. In comparison to the values obtained by structural characterization methods based on electron diffraction studies in the gas phase [8], the length of the C–S bond as well as the C–S–C angle found in the present study deviate to smaller values while both S–C–C angles exceed the ones deduced from the electron diffraction experiments [8]. No data is available from the electron diffraction studies for the intracyclic distance between the two sulfur atoms. A puckering analysis [10] shows the six-membered ring to adopt a $^1C_4$ chair conformation according to [11]. The latter finding is

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corroborated by projections of the structure along the C–S bonds showing nearly ideal staggered conformations for all methylene groups, the relevant C–S–C–C dihedral angles measuring 59.23(9) and 59.34(9)°. An investigation of intra- and intermolecular interactions in the crystal structure of the title compound revealed an interesting picture. Not only are there no interactions whose range falls below the sum of van-der-Waals radii of atoms but – additionally – there are no intermolecular contacts shorter than the sum of van-der-Waals radii plus at least 0.1 Å. Although the hydrogen atoms were located unambigously on a DFM and refined freely in the current study, Xray diffractometry is inherently susceptive for introducing errors into the correct localization of this element. Therefore, the cell constants were compared as these allow for quantifying the shortest centroidal distances between the individual molecules. It is found that these continuously shrink with lowering the temperature during the data collection experiment as the reported shortest cell length decreases from 5.453(5) Å at room temperature [5] over 5.4100(2) Å in the present study at 200 K down to 5.383(1) Å as reported for the study conducted at 100 K [7]. In this context it is noteworthy that the stepwise substitution of the sulfur atoms for its heavier homologue, selenium, gradually increases the dimension of the shortest cell length gradually from 5.464(5) Å for 1,4-dithiane over 5.552(10) Å for 1,4-selenothiane to 5.62(2) Å for 1,4-diselenane [5, 12, 13]. This marked absence of pronounced intermolecular interactions in the crystalline state is in agreement with the surprisingly high volatility and ability of the title compound to sublime despite its high melting point of more than 100 °C. However, the latter is – in turn – not so easy to rationalize given exactly this lack of intermolecular interactions.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(11)	4*e*	0.251(3)	0.429(3)	0.250(2)	0.033(3)
H(12)	4*e*	0.294(3)	0.145(2)	0.301(2)	0.034(3)
H(21)	4*e*	0.919(3)	0.676(2)	0.611(2)	0.040(4)
H(22)	4*e*	0.635(3)	0.758(3)	0.441(2)	0.042(4)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	4*e*	0.68062(4)	0.33676(5)	0.46182(3)	0.0285(2)	0.0272(2)	0.0333(2)	0.00181(8)	0.0223(1)	−0.00329(9)
C(1)	4*e*	0.3386(2)	0.3113(2)	0.3443(1)	0.0269(5)	0.0300(5)	0.0260(5)	−0.0033(4)	0.0160(4)	−0.0070(4)
C(2)	4*e*	0.7346(2)	0.6492(2)	0.5420(2)	0.0286(5)	0.0264(5)	0.0351(5)	−0.0049(4)	0.0228(5)	−0.0040(4)

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