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Crystal Structure Analysis of 3,4-Dimethyl-2,5-dihydrothiophen-1,1-dioxide

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The geometry of 3,4-dimethyl-2,5-dihydrothiophen-1,1-dioxide was determined by X-ray diffraction: cell dimensions are reported together with bond lengths and bond angles. While bond lengths are smaller than those for the homologue 3-methyl-2,5-dihydrothiophen-1,1-dioxide, bond angles are similar. The Me-C_3-C_4-Me torsion angle is $5.1 \pm 0.5°$. These results are consistent with its relatively slow rate of decomposition.

(Keywords: X-Ray analysis)

Kristallstrukturanalyse von 3,4-Dimethyl-2,5-dihydrothiophen-1,1-dioxid

Die Geometrie von 3,4-Dimethyl-2,5-dihydrothiophen-1,1-dioxid wurde mittels Röntgendiffraktion bestimmt. Es werden die Dimensionen der Einheitszelle zusammen mit Bindungslängen und Bindungswinkeln berichtet. Die Bindungswinkel sind sehr ähnlich denen des homologen 3-Methyl-2,5-dihydrothiophen-1,1-dioxids, die Bindungslängen sind jedoch kürzer. Der Me-C 3-C 4-Me Torsionswinkel ist $5.1 \pm 0.5°$. Diese Ergebnisse sind mit der relativ langsamen Zersetzungsgeschwindigkeit im Einklang.

Introduction

The reactions of 1,3-dienes with sulphur dioxide to form 2,5-dihydrothiophen-1,1-dioxides, and the retrogression of the latter compounds at high temperatures is known for more than seventy years[1].

These reactions are potentially useful in the purification of dienes since these compounds are mostly white crystalline solids, easily handled and purified, and stable at room temperature. This makes them a useful form in which to store dienes, avoiding polymerization. It has been found that the decomposition of these 2,5-dihydrothiophen-1,1-dioxides is highly stereospecific[2]. From the synthetic point of view sulphur dioxide addition may act in a protective capacity, permitting the modification of the diene moiety without undesirable side reaction[3,4]. 3,4-Dimethyl-2,5-dihydrothiophen-1,1-dioxide (**2**) was used as a starting material to synthesise 3,4-dimethylenepyrrolidines, the latter compounds have been used to biuld up hydroisoindole systems by subsequent *Diels-Alder* reaction[5,6].

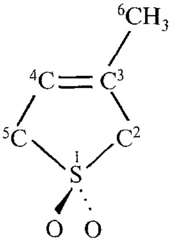
The structures of several of the 2,5-dihydrothiophendioxides have been investigated and cell dimensions have been reported[7—10]. Bond lengths and bond angles have been determined only for 3-methyl-2,5-dihydrothiophen-1,1-dioxide using the *Fourier* technique[11]. An X-ray diffraction study of **2** would add more information on the precise geometry of this dehydrothiophen dioxide and would account for its rate of thermolysis.

Results and Discussion

An X-ray diffraction analysis of a single crystal was carried out by recording 667 reflections on 3,4-dimethyl-2,5-dihydrothiophen-1,1-dioxide. The precise geometry of this compound was also determined.

Crystallographic data for this 2,5-dihydrothiophendioxide: Orthorhombic, 4 molecules to the unit cell with the dimensions $a = 7.613$ Å, $b = 12.419$ Å, $c = 7.797$ Å, and $\alpha = \beta = \gamma = 90°$; space group P_n2_{1a}.

These cell dimensions are in greement with the previously reported data[10]. The results of this investigation show that the molecular structure can be represented as shown for **2**.



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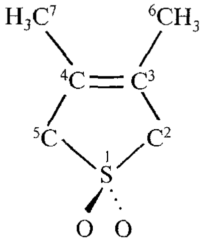


2

Bond lengths and bond angles together with the corresponding values for 3-methyl-2,5-dihydrothiophen-1,1-dioxide (**1**) are collected in Table 1. **1** is the only other analogue which was examined crystallographically[11].

The bond lengths for 3,4-dimethyl-2,5-dihydrothiophen-1,1-dioxide (**2**) are greater than those for **1** (0.05 Å) except for the C_3—C_4 double bond which is less by 0.03 Å. For example the C—C single bonds in **2** are longer by 0.04–0.05 Å. The

Table 1. *Refinement of the crystal structure analysis of 3-methyl-2,5-dihydrothiophen-1,1-dioxide* (**1**) *and 3,4-dimethyl-2,5-dihydrothiophen-1,1-dioxide* (**2**)

	1	**2**
Bond length (Å)		(± 0.02)
$\mathrm{S{-}O}$	1.43	1.45
$\mathrm{S{-}C_2}$	1.75	1.79
$\mathrm{S{-}C_5}$	1.74	1.79
$\mathrm{C_3{-}C_4}$	1.37	1.34
$\mathrm{C_2{-}C_3\ (C_4{-}C_5)}$	1.47	1.51
$\mathrm{C_3{-}C_6}$	1.52	1.53
$\mathrm{C_4{-}C_7}$	—	1.53
Angle (°)		(± 0.5)
$\mathrm{C_2{-}S{-}C_5}$	98.3	98.1
$\mathrm{S{-}C_2{-}C_3}$	104.2	104.8
$\mathrm{S{-}C_5{-}C_4}$	106.3	103.3
$\mathrm{C_2{-}C_3{-}C_4}$	117.0	116.5
$\mathrm{C_3{-}C_4{-}C_5}$	114.1	116.5
$\mathrm{C_4{-}C_3{-}C_6}$	124.5	121.2
$\mathrm{C_2{-}C_3{-}C_6}$	121.0	121.2
$\mathrm{C_5{-}C_4{-}C_7}$	—	121.4
$\mathrm{C_3{-}C_4{-}C_7}$	—	121.4
$\mathrm{O{-}S{-}O}$	—	116.1
$\mathrm{O{-}S{-}C_2\,(C_5)}$	—	110.3
$\mathrm{C_6{-}C_3{-}C_4{-}C_7}$	—	−5.1

Table 2. *Relative rates for the thermolysis of 2,5-dihydrothiophen-1,1-dioxides with different substituents at* C 3 *and* C 4 *(in diphenyl ether)*

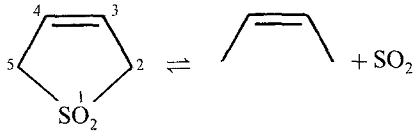
R^3	R^4	K rel. (388.16 K)	corr. coeff. r
H	H	1.00	0.9999
H	CH_3	0.59	0.999
CH_3	CH_3	0.18	0.9997
CH_3	CH_2Br	0.061	0.9994
CH_2Br	CH_2Br	0.054	0.99999

bond angles are similar within the standard error but while the $\mathrm{C_3{-}C_4{-}CH_3}$ angle in **2** is 121.2° it was found to be 124.5° in **1**. On the other hand, the angle of $\mathrm{S{-}C_5{-}C_4}$ was found to be less than the angle in **1** by 3°.

The refinement of the structure of **2** was complicated due to a pseudo-mirror plane through the molecule and accurate molecular dimensions could not be obtained.

From the refinement we conclude that the maximum value for the $CH_3—C_3—C_4—CH_3$ torsion angle is —5.1 ± 0.5 but it may be less than this value. It is clear that while the fivemembered ring is essentially planar, the 3,4-methyls lie out of the plane with a dihedral angle of 5–6°, thus relieving to some extent eclipsing interaction between the methyl groups and no doubt reducing the strain energy.

Further confirmation for the presented structure comes from the kinetic data for the 2,5-dihydrothiophene dioxides[12].



From the study of the structural effects on the rate of decomposition it seems that substituents at both C_3 and C_4 cause a decrease in rate relative to a single substituent compared with the parent 2,5-dihydrothiophen-1,1-dioxide (Table 2), **2** decomposes about six times slower than the parent compound while the rate for **1** is only about two times slower.

Substituents (3-CH_2Br, 4-CH_3) and (3-CH_2Br, 4-CH_2Br) cause a decrease in the rate of 16- to 19-fold, respectively. The origin of the steric effect is not obvious. Repulsive interactions between groups attached to C_3 and C_4 in a planar system are already at the maximum except during ring opening with the two further approaching each other. A *Van der Waals* scale diagram of **2** and the corresponding diene system indicates a closer approach of two methyl groups of only about 1 pm during the whole course of the reaction provided that coplanarity is maintained[12]—an amount hardly commensurate with the observed rate effect. It seems probable, however, that much less bond angle strain would exist in the homologue **1**. This is in agreement with its structure and indicates that (3-CH_3, 4-H) are essentially coplanar with the five membered ring. Apparently in (3-CH_3, 4-CH_3) the methyl groups prefer to be twisted out of the plane of the ring.

Experimental

Preparation of 3,4-Dimethyl-2,5-dihydrothiophen-1,1-dioxide (**2**)[13]

A mixture of 2,3-dimethylbuta-1,3-diene (5 g, 0.061 mol), liquid sulphur dioxide (4 g, 0.062 mol) and pyrogallol (0.06 g) was allowed to stand at room temperature for 15 h in a sealed outoclave. The crude product was dissolved in ethanol, the polymeric material removed by filtration and after decolourization with charcoal and recrystalllization from ethanol 7.6 g (86%) of **2** were obtained as white crystals; m.p. 135 °C, Lit. m.p. 135 °C[13]. Its analytical and spectroscopic data were in agreement with the structure.

MS (*m*/e), rel. int.: 146 (22, M^+), 83 (4.4), 82 (83.8), 81 (14.7), 67 (100), 64 (25). ^{1}H-NMR: 8.2 (s, 6, H-CH_3), 6.42 (s, 4, H-C_2, C_5).

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