

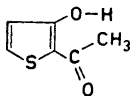
Direct Determination of the Crystal Structure of Thioisomaltol, C₆H₆O₂S

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The crystal structure of thioisomaltol (2-acetyl-3-hydroxy thiophene), C₆H₆O₂S has been determined by the symbolic addition method. The space group is $P2_1/c$. $a=9.749$ Å, $b=5.055$ Å, $c=12.870$ Å, $\beta=96.66^\circ$. The crystal was twinned. Least squares analysis of geometric parameters and anisotropic temperature factors was performed, final R -value 10 %. There are four molecules in the unit cell and the molecules are connected by hydrogen bonds to chains.

This analysis was made to clarify the extent of hydrogen-bonding in the solid phase of thioisomaltol (2-acetyl-3-hydroxy thiophene).



A discussion of the various types of hydrogen bonds in the liquid phase is given in Ref. 1. The possible bonds in the solid phase are also discussed in Ref. 1 where the preparation of the compound is described. Discussions of the possibilities in isomaltol is given in Ref. 4. The present work shows that there is hydrogen bonding between the hydroxyl group in one molecule and the oxygen atom in the carbonyl group in the neighbouring molecule and so on. In this way chains of molecules are formed. There is no indication of other hydrogen bonds.

EXPERIMENTAL

The crystals were kindly supplied by H. J. Jakobsen, Department of Organic Chemistry, Aarhus University. They were needle-like, being elongated in the [010] direction, and were twinned. A crystal was mounted with the needle axis in direction of the rotation axis. It was lined up on a Weissenberg camera, and Rimsky-retigraph photographs were taken of the layers $h0l$, $h1l$, $h2l$, using $MoK\alpha$ radiation. The crystal was transferred to a Hilger and Watts linear diffractometer and intensities of $h0l-h6l$ were recorded

using MoK α radiation selected with balanced filters and pulse height discrimination with a scintillation counter. 1518 independent reflexions were measured. Data reduction and correction for Lorentz-polarization factors were carried out by the GIER-algol program G4, written by R. G. Hazell.² Reflexions of the type $h,k,6n$ from one of the twins overlapped with the reflexions $-h-n,k,6n$ from the other twin. The remaining reflexions could be measured independently. Corrections for the twin effect was performed by a GIER-algol program written by F. R. Poulsen.³ However, the accuracy of the resolved overlapped reflexions is still rather bad. No correction was made for extinction or absorption.

STRUCTURE DETERMINATION

The crystal is monoclinic with the dimensions: $a=9.749 \text{ \AA}$, $b=5.055 \text{ \AA}$, $c=12.870 \text{ \AA}$, $\beta=96.66^\circ$. The following reflexions were systematically absent: $h0l$ for $l=2n+1$ and $0k0$ for $k=2n+1$. Thus the space group is $P2_1/c$. The calculated density (1.50) has a reasonable value if it is supposed that there are 4 molecules of $C_6H_6O_2S$ per unit cell. The normalized structure factors were calculated by a GIER-algol program¹³ using the method described by Karle and Karle.⁵ The calculated average values, $\langle |E^2| \rangle$, $\langle |E| \rangle$, $\langle |E^2-1| \rangle$, are shown in Table 1 together with the theoretical values for centrosymmetric

Table 1. Comparison of theoretical and experimental statistics.

	Noncentrosymmetry	Thioisomaltol	Centrosymmetry
$\langle E^2 \rangle$	1.000	1.069	1.000
$\langle E \rangle$	0.886	0.834	0.798
$\langle E^2-1 \rangle$	0.736	0.969	0.968

and non-centrosymmetric structures with infinitely many atoms per unit cell.

The symbolic addition procedure⁵ was used to find a basic set of signs. 10 of the largest reflexions were selected and given the symbols a—j. After some unsuccessful attempts to find the signs for the symbols, the intensity material was checked and it was found that 3 of the largest reflexions were

Table 2. The 10 basic reflexions.

h	k	l	E	Symbol
2	1	8	2.86	a
5	2	-8	2.73	b
1	5	5	2.56	c
1	1	14	2.91	d
4	2	-2	3.14	e
3	6	5	2.09	f
3	3	-7	2.07	g
2	5	-1	2.06	h
7	1	-8	2.45	i
1	1	4	2.10	j

measured too great by mistake. After having removed these reflexions from the basis and including 3 new reflexions, the structure could be solved. The 10 basic reflexions are given in Table 2.

These reflexions were now combined to give 23 new reflexions using the fact that $h_1+h_2+h_3=0$ implies $S_{h_1}\cdot S_{h_2}\cdot S_{h_3}=1$ with great probability. By choosing $a=+1$, $c=+1$, $d=+1$, values could be found for all the symbols. The program ML4, written by Lehmann,⁶ was now used to combine these 33 reflexions. 16 new signs resulted and these were again combined to give 21 new signs. All 70 signs were later shown to be correct. A combination of 70 reflexions gave totally 482 signs, 54 of these appeared later to be wrong. A Fourier synthesis⁷ showed 4 peaks which were much higher than the other peaks. Calculations of the R -value were performed by the GIER-algol program D445⁸ for each of the four possible cases with a sulphur atom in one of the four peaks. The resulting R -values were 66 %, 55 %, 65 %, 64 %. The position which gave 55 % was chosen as sulphur position and the light atoms were placed in the highest of the remaining peaks.

Successive Fourier syntheses and R -value calculations were made and gave after a few cycles approximate parameters. The D445 program was now used to refine the geometric parameters by the method of Bhuiya and Stanley.⁹ Later on full matrix least squares refinement on 4 scale factors, 27 geometric parameters, and 54 temperature parameters was performed by the ORFLS

Table 3. Final atomic positions in fractions of the cell edges.

	x	$10^4 \times \sigma(x)$	y	$10^4 \times \sigma(y)$	z	$10^4 \times \sigma(z)$
S	0.3739	2	0.2776	4	0.2377	1
O ₁	0.1592	5	0.7996	11	0.3657	3
O ₂	0.2241	6	0.5345	13	0.0599	3
C ₂	0.2543	7	0.5297	12	0.2401	4
C ₃	0.2421	6	0.6096	13	0.3412	4
C ₄	0.3319	7	0.4637	16	0.4162	5
C ₅	0.4067	8	0.2806	16	0.3711	5
C ₆	0.1880	7	0.6259	14	0.1418	4
C ₇	0.0760	8	0.8213	18	0.1379	6

Table 4. Final anisotropic parameters.

Temperature factor expressed as

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}h^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}khl^*c^* + 2U_{13}lhc^*a^* + 2U_{12}hka^*b^*)]$$

	U_{11}	$\sigma(U_{11})$	U_{22}	$\sigma(U_{22})$	U_{33}	$\sigma(U_{33})$	U_{12}	$\sigma(U_{12})$	U_{13}	$\sigma(U_{13})$	U_{23}	$\sigma(U_{23})$
S	0.043	0.001	0.043	0.001	0.038	0.001	0.004	0.001	0.002	0.001	0.004	0.001
O ₁	0.044	0.002	0.064	0.003	0.025	0.002	0.011	0.002	0.006	0.002	-0.002	0.002
O ₂	0.087	0.004	0.068	0.004	0.023	0.002	0.022	0.003	0.009	0.002	0.007	0.002
C ₂	0.043	0.003	0.034	0.003	0.020	0.002	-0.003	0.002	0.002	0.002	0.004	0.002
C ₃	0.033	0.003	0.044	0.003	0.016	0.002	-0.009	0.002	0.001	0.002	0.000	0.002
C ₄	0.045	0.003	0.054	0.004	0.026	0.003	0.000	0.003	-0.002	0.002	0.003	0.003
C ₅	0.047	0.004	0.059	0.004	0.030	0.003	-0.001	0.003	0.004	0.003	0.006	0.003
C ₆	0.049	0.004	0.041	0.003	0.023	0.002	-0.003	0.003	0.006	0.002	0.001	0.002
C ₇	0.051	0.004	0.060	0.005	0.039	0.003	0.016	0.003	0.001	0.003	0.003	0.003

program in the X-RAY-63 system.¹⁰ The IBM 7090 machine at NEUCC in Copenhagen was used. Before the refinement all reflexions with $I_h < 2\sigma(I_h)$ were excluded as insignificant. The reflexions near the b -axis were excluded as the LP-correction here is rather inaccurate and the diffractometer is in a badly defined position. Atomic scattering factors were taken from Vol. III of *Intern. Tables*.¹¹ The final R -value is 10 % calculated on the 1161 significant reflexions. The final geometric parameters and temperature factor parameters are shown in Tables 3 and 4, respectively. A drawing of the molecule is shown in Fig. 1.

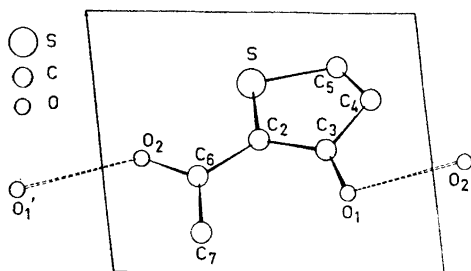


Fig. 1. Thioisomaltol viewed along [010].

DISCUSSION

Because of the poor data there is no attempt to interpret the temperature factors or to locate the hydrogen atoms. The bond lengths and the bond angles were calculated by the BONDLA program.¹⁰ In Tables 5 and 6 are shown the calculated values together with the values found for thiophene by microwave spectroscopy.¹² None of the lengths or values deviates significantly from the values expected. The 5-membered ring is nearly planar. A least

Table 5. Bond lengths in Ångström for thioisomaltol and thiophene.

	Thioisomaltol		Thiophene ¹²
	Distance	σ	Distance
S — C ₂	1.730	0.007	1.7140 ± 0.0014
S — C ₅	1.710	0.007	
C ₂ — C ₃	1.381	0.008	
C ₃ — C ₄	1.431	0.009	
C ₄ — C ₅	1.351	0.011	
C ₂ — C ₆	1.437	0.008	
C ₆ — C ₇	1.469	0.011	
C ₆ — O ₂	1.238	0.008	
C ₃ — O ₁	1.317	0.008	
O ₁ — O ₂ '	2.643	0.007	
O ₁ — O ₂	4.274	0.007	
C ₇ — O ₁	2.952	0.008	

Table 6. Bond angles in degrees for thioisomaltol and thiophene.

	Thioisomaltol angle	σ	Thiophene ¹² angle
C ₅ -S-C ₂	91.35	0.33	92.17 ± 0.10
S-C ₂ -C ₃	111.36	0.42	111.47 ± 0.23
C ₂ -C ₃ -C ₄	111.88	0.56	112.45 ± 0.18
C ₃ -C ₄ -C ₅	112.43	0.54	112.45 ± 0.18
C ₄ -C ₅ -S	112.98	0.53	111.47 ± 0.23
S-C ₂ -C ₆	117.95	0.45	
C ₃ -C ₂ -C ₆	130.67	0.59	
C ₂ -C ₆ -C ₇	120.93	0.57	
C ₂ -C ₆ -O ₂	118.69	0.63	
C ₇ -C ₆ -O ₂	120.34	0.58	
C ₂ -C ₃ -O ₁	124.13	0.50	
C ₄ -C ₃ -O ₁	123.99	0.50	

squares plane for the 5 atoms was calculated by the program LSQPL.¹⁰ The equation for the plane is:

$$7.1627x + 3.4158y - 1.8638z = 3.1825$$

The deviations of all the atoms from the plane is shown in Table 7.

Table 7. Deviations from the least squares plane.

Atom	Deviation in Å	Atom	Deviation in Å
S	-0.0009	C ₆	-0.0382
C ₂	-0.0007	C ₇	0.08942
C ₃	0.0022	O ₁	-0.00760
C ₄	-0.0030	O ₂	-0.13676
C ₅	0.0024		

The two oxygens in the same molecule are not bound together as the distance is too long, 4.274 Å. The distance between the hydroxyl in one molecule and the carbonyl oxygen in a neighbouring molecule is 2.643 Å, indicating a hydrogen bond involving these atoms. The carbonyl oxygen in the first molecule is in the same way by symmetry bound to a hydroxyl group in a third molecule. In that way the chains of hydrogen bonded molecules are formed.

Acknowledgement. I thank Professor S. E. Rasmussen for help with the data collection and cand. polyt. R. G. Hazell, cand. scient. M. S. Lehmann and stud. scient. F. R. Poulsen for the programs they have made available. I am grateful to *Carlsbergfondet* for having supplied the laboratory with the linear diffractometer.

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Received December 17, 1968.