Crystal Structure of *trans*-3-(7-Dihydrothiazolo[2,3-e]-1,2,3-triazolyl)propenal

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The crystals are triclinic, space group $P\bar{1}$, with cell dimensions $a = 10.740(4)$ Å; $b = 4.055(1)$ Å; $c = 9.847(3)$ Å; $\alpha = 81.45(2)°$; $\beta = 75.66(3)°$; $\gamma = 72.85(3)°$, and two molecules in the unit cell. The structure was solved by the use of the program assembly MULTAN and refined by full-matrix least squares methods to an R-value of 0.054 (1697 reflections with $\sin \theta/\lambda$ larger than 0.3, recorded by counter techniques). Estimated standard deviations are $0.002 - 0.003$ Å in distances and $0.2 - 0.3°$ in angles not involving hydrogen atoms.

The propenal side chain has a planar *trans* configuration. The atoms of the triazole ring are coplanar and the three substituent atoms are also situated near the ring plane. The dihydrothiazole ring has an envelope conformation with one carbon atom 0.4 Å out of the plane through the other ring atoms. The two $S - C$ bond lengths are 1.729(2) and 1.840(2) Å, respectively.

Hagen, Ulsaker and Undheim have studied the nitro and diazonium activation in reactions of pyridinium derivatives.[1] Diazotisation of the 8-amino derivative of dihydrothiazolo[3,2-a]-pyridine
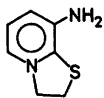
is followed by addition of a hydroxyl ion to the diazonium salt with subsequent re-arrangement to a product with the composition $C_7H_7N_3SO$. In order to identify this compound an X-ray structure determination was undertaken.

EXPERIMENTAL AND STRUCTURE DETERMINATION

The crystals are triclinic with space group $P\bar{1}$. The cell dimensions were determined from diffractometer measurements on 15 general reflections using Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å) $a = 10.740(4)$ Å; $b = 4.055(1)$ Å; $c = 9.847(3)$ Å; $\alpha = 81.45(2)°$; $\beta = 75.66(3)°$; $\gamma = 72.85(3)°$ The volume of the unit cell, which contains two molecules, is 395.7(2) Å^3 giving a calculated density of 1.521 g cm^{-3}.

2347 reflections with $\sin \theta/\lambda < 0.7$ were measured with the use of an automatic four-circle diffractometer using Mo$K\alpha$ radiation (graphite monochromator) and $\omega - 2\theta$ scan technique. 1899 reflections were recorded as observed, the intensities being larger than 2.5 times their standard deviations. The data set was corrected for Lorentz and polarization effects; no corrections for absorption or secondary extinction have been applied.

The structure was solved by the program assembly MULTAN[2] and refined by full-matrix least-squares techniques.[3] Anisotropic temperature factor parameters were introduced for all non-hydrogen atoms. For hydrogen atoms positional parameters (calculated from stereochemical considerations) and isotropic thermal parameters were refined. The final least squares refinement included only reflections with $\sin \theta/\lambda > 0.3$; the function minimized was $\sum w \Delta F^2$. The weights were obtained from the variance in the intensities taken as $C_T + (0.05C_N)^2$ where C_T is the total number of counts and C_N the net count (peak minus background). The atomic form factors were those of Doyle and Turner[4] for carbon, nitrogen, oxygen, and sulfur and of Stewart et al.[5] for hydrogen.

The refinement converged to a final conventional R-factor of 0.054 for 1697 reflections ($R_W = 0.067$). The corresponding atomic parameters are listed in Tables 1 and 2. The structure factor list may be obtained from the author upon request. A rigid-body analysis showed that the thermal motion of the molecule could to a

Table 1. Fractional atomic coordinates and thermal parameters ($\times 10^4$) with estimated standard deviations. The temperature factor is given by $\exp -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	2854(1)	4374(1)	1156(1)	82(1)	677(5)	68(1)	−172(2)	−49(7)	113(2)
O	8206(2)	698(6)	1498(2)	82(2)	1149(19)	125(2)	−234(9)	−18(3)	22(10)
N1	1688(2)	1390(5)	3387(2)	69(2)	659(15)	68(2)	−140(7)	−37(2)	56(7)
N2	1747(2)	−777(6)	4566(2)	86(2)	834(15)	78(2)	−181(8)	−36(3)	155(8)
N3	3003(2)	−1919(6)	4619(2)	87(2)	811(15)	76(2)	−193(8)	−51(3)	135(8)
C1	2894(2)	1664(5)	2685(2)	70(2)	542(12)	59(2)	−126(7)	−35(3)	10(7)
C2	1106(2)	4412(7)	1317(2)	88(2)	712(17)	84(2)	−132(10)	−76(3)	68(10)
C3	529(2)	3559(7)	2863(2)	68(2)	713(16)	95(2)	−130(9)	−50(3)	52(10)
C4	3759(2)	−476(5)	3480(2)	75(2)	592(13)	62(2)	−128(8)	−46(3)	44(7)
C5	7398(2)	−625(7)	2292(3)	74(2)	787(17)	94(2)	−103(9)	−42(3)	−20(10)
C6	5184(2)	−1214(6)	3295(2)	77(2)	613(13)	71(2)	−102(8)	−58(3)	24(8)
C7	5984(2)	303(6)	2308(2)	75(2)	675(15)	81(2)	−113(8)	−50(3)	31(9)

Table 2. Fractional atomic coordinates ($\times 10^3$) and isotropic thermal parameters with estimated standard deviations for hydrogen atoms.

Atom	x	y	z	B
H1C2	106(5)	291(12)	78(5)	3.9(8)
H2C2	69(5)	631(13)	109(5)	5.2(8)
H1C3	14(3)	562(8)	340(3)	3.0(5)
H2C3	−9(4)	225(10)	305(4)	4.4(6)
HC5	770(4)	−256(10)	296(4)	4.9(7)
HC6	558(3)	−285(8)	398(3)	3.5(5)
HC7	565(4)	184(10)	163(4)	4.5(7)

Table 3. Selected interatomic distances and angles. For numbering of atoms, see Fig. 1.

Distance	Å	Corr.	Distance	Å	Corr.	Distance	Å
S−C1	1.729(2)	1.734	N3−C4	1.376(3)	1.379	C2−H2C2	0.80(5)
S−C2	1.840(2)	1.843	C1−C4	1.383(3)	1.386	C3−H1C3	0.98(3)
C2−C3	1.524(3)	1.529	C4−C6	1.439(3)	1.441	C3−H2C3	0.95(4)
C3−N1	1.458(3)	1.460	C6−C7	1.335(3)	1.339	C6−H6	0.96(3)
N1−C1	1.337(3)	1.340	C7−C5	1.450(3)	1.451	C7−HC7	0.91(4)
N1−N2	1.351(2)	1.354	C5−O	1.211(3)	1.213	C5−HC5	0.98(4)
N2−N3	1.302(3)	1.304	C2−H1C2	0.89(5)			

Angle	(°)	Angle	(°)	Angle	(°)
C1−S−C2	89.5(1)	C1−N1−N2	112.1(2)	C1−C4−C6	131.1(2)
S−C2−C3	107.7(1)	N1−N2−N3	106.4(2)	N3−C4−C6	121.6(2)
C2−C3−N1	103.4(2)	N2−N3−C4	109.8(2)	C4−C6−C7	126.0(2)
C3−N1−C1	118.0(2)	N3−C4−N1	107.3(2)	C6−C7−C5	119.5(2)
N1−C1−S	113.3(1)	N1−C1−C4	104.4(2)	C7−C5−O	125.4(2)
C3−N1−N2	129.7(2)	S−C1−C4	142.4(2)		

Atomic deviations (Å) from a plane through the 1,2,3-triazole ring.

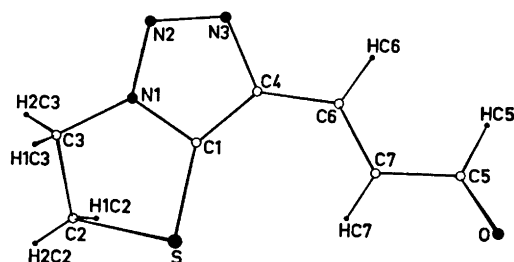|							
N1	−0.001	C1	0.000	C2	−0.413	C7	0.173
N2	0.002	C4	0.002	C3	0.092	C5	0.245
N3	−0.002	S	−0.029	C6	0.036	O	0.438

Fig. 1. Schematical drawing of the molecule as viewed normal to the 1,2,3-triazole ring.

fair approximation be interpreted in terms of translational and librational oscillations (r.m.s.- $\Delta U = 0.0017$ Å^2).

Bond lengths corrected for thermal libration are also listed. Standard deviations are calculated from the correlation matrix. The numbering of atoms may be seen from Fig. 1.

DISCUSSION

The structure of the molecule formed by re-arrangement of the diazonium salt is visualized in Fig. 1. The addition of a hydroxyl ion to the carbon atom next to the ring nitrogen atom in the pyridyl diazonium part has been followed by a ring opening and the formation of a 1,2,3-triazole ring with a propenal side chain; the thiazole moiety remains unaltered. The reaction is discussed in some detail by Hagen, Ulsaker and Undheim.[1]

The 1,2,3-triazole ring is planar (*cf.* Table 3). The bond lengths indicate a high degree of aromaticity in this part of the molecule. The $C1-N1$ bond length (1.340 Å) is the same as that found in pyridine.[6] The lengths of the $C1-C4$ and $N2-N3$ bonds (1.386 and 1.304 Å, respectively) indicate only a slightly higher double bond character than that expected for an aromatic compound; the $N1-N2$ and $N3-C4$ bonds (1.354 and 1.379 Å, respectively) have correspondingly only slightly less double bond character than the aromatic value.[7]

In the thiazole ring four of the atoms are situated close to the plane of the 1,2,3-triazole ring whereas C2 is by 0.4 Å out of this plane. The geometry of the ring is comparable to that found for other thiazole compounds and of tetrahydrothiophene.[8]

The propenal side chain has the planar *trans* configuration with normal bond lengths and

angles. The dihedral angles along the chain are as follows: $C1-C4-C6-C7$ $-5.2°$; $C4-C6-C7-C5$ $182.5°$; $C6-C7-C5-O$ $175.9°$. The external angle $C1-C4-C6$ at C4 is large, probably to relieve strain caused by the small $S-HC7$ separation (3.01 Å).

The intermolecular separations in the crystal are those to be expected for a packing determined by normal van der Waals' interactions.

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