

## Crystal Structure Determinations of 4-(Anilinomethylene)-tetrahydrothiophene-3-one and *N*-Phenyl-2,5-dihydrothiophene-3-carboxamide

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Cycloaddition between phenyl azide and 3,6-dihydro-2*H*-thiopyran-3-one gives the two novel compounds 4-(anilinomethylene)tetrahydrothiophene-3-one (I) and *N*-phenyl-2,5-dihydrothiophene-3-carboxamide(II). In the present publication are reported the crystal structure determinations of these two compounds. I crystallizes in space group  $P2_1/c$  with  $a=6.405(2)$  Å,  $b=20.762(6)$  Å,  $c=7.640(2)$  Å and  $\beta=98.39(2)$ . The five-membered ring has an envelope conformation with the sulfur out of the plane. II crystallizes in space group  $Pna2_1$  with  $a=8.369(4)$  Å,  $b=5.222(3)$  Å and  $c=22.517(7)$  Å. The five-membered ring is planar.

Cycloaddition between phenyl azide and 3,6-dihydro-2*H*-thiopyran-3-one is succeeded by carbonoid rearrangements of the adduct to two new products assigned the structures I and II. In order to prove these assignments and obtain structural data for these new compounds X-ray structure determinations were carried out. We herein report the investigations of the rearrangement products.

### EXPERIMENTAL

The compounds were recrystallized from chloroform (I) and hexane–tetrahydrofuran (5:1) (II). Space groups were determined by use of oscillation and Weissenberg diagrams. The systematic absences for compound II were those of the space groups  $Pnma$  and  $Pna2_1$ . On the basis of the unit cell volume, which implied 4 molecules per unit cell, and the axial lengths, the centrosymmetric space group  $Pnma$  could be excluded. The X-ray experiments were performed on a Syntex P1 diffractometer using  $MoK\alpha$  radiation (graphite mono-

chromator). The temperature was maintained at  $19\pm 1$  °C. Cell dimensions were determined from diffractometer measurements on 15 general reflections with  $2\theta$  values between 20 and 37°, the results are given together with space group data below.

Intensity data were collected using the  $\omega-2\theta$  scan technique with scan speeds of  $2-6^\circ \text{ min}^{-1}$  (I) and  $2-12^\circ \text{ min}^{-1}$  (II), depending on the peak intensity. The estimate of the standard deviation of the intensity was based on counting statistics with an additional term of 2% of the net intensity. Reflections with intensity larger than twice their e.s.d.'s were regarded as observed and used for the structure determinations. The data sets were corrected for Lorentz and polarization effects. The numbers of observed reflections were 996 (I,  $2\theta_{\text{max}}=45^\circ$ , 1381 measured) and 893 (II,  $2\theta_{\text{max}}=60^\circ$ , 1377 measured).

Description of the computer programs applied for the structure analyses are given in Ref. 1. Atomic form factors used were those of Doyle and Turner<sup>2</sup> for sulfur, oxygen, nitrogen and carbon, and of Stewart, Davidson and Simpson<sup>3</sup> for hydrogen.

### CRYSTAL DATA

*Compound I.* 4-(Anilinomethylene)tetrahydrothiophene-3-one  $C_{11}H_{11}NOS$ ,  $M=205.28$ ; space group  $P2_1/c$ ;  $a=6.405(2)$  Å,  $b=20.762(6)$  Å,  $c=7.640(2)$  Å,  $\beta=98.39(2)^\circ$ ,  $V=1005.2(4)$  Å<sup>3</sup>;  $Z=4$ ,  $D_{\text{calc}}=1.356 \text{ g cm}^{-3}$ ,  $F(000)=432$ .

*Compound II.* *N*-Phenyl-2,5-dihydrothiophene-3-carboxamide  $C_{11}H_{11}NOS$ ,  $M=205.28$ ; space group  $Pna2_1$ ;  $a=8.369(4)$  Å,  $b=5.222(3)$  Å,  $c=22.517(7)$  Å,  $V=984.1(7)$  Å<sup>3</sup>;  $Z=4$ ,  $D_{\text{calc}}=1.385 \text{ g cm}^{-3}$ ,  $F(000)=432$ .

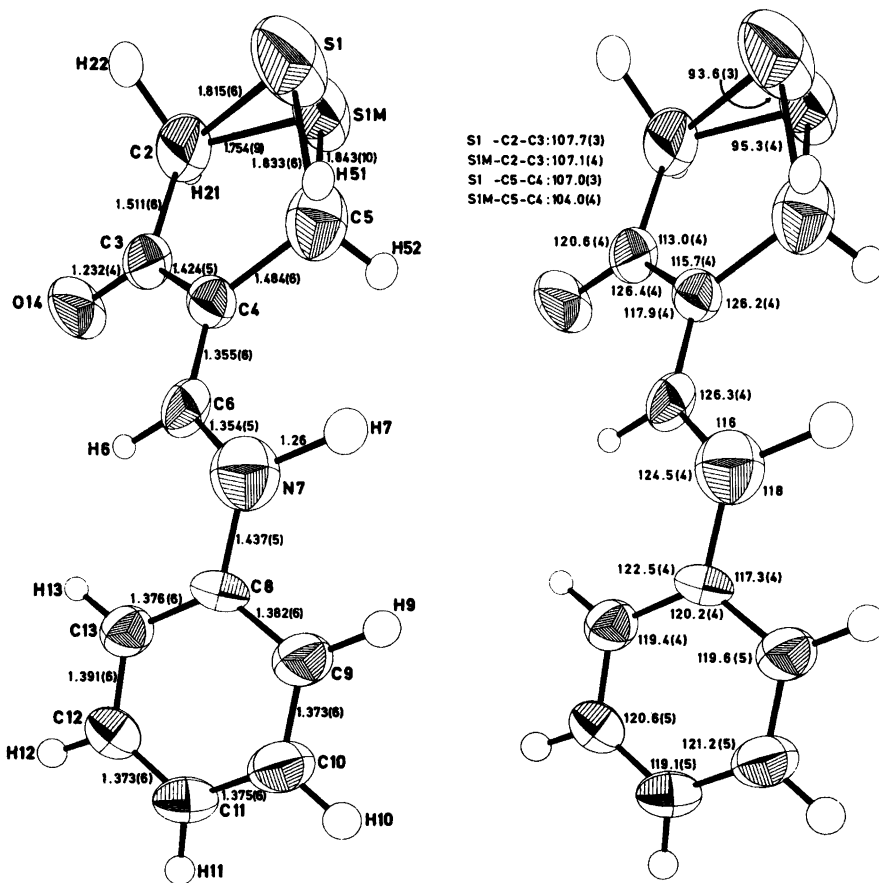


Fig. 1. Bond lengths (Å) and bond angles (°) in I.

## STRUCTURE DETERMINATION

*Compound I.* The phase problem was solved by use of the program assembly MULTAN 77.<sup>4</sup> The structure model was refined to an  $R$  of 0.21. Introduction of anisotropic thermal parameters and full matrix least-squares refinement lowered  $R$  to 0.12. H7 was found in a difference Fourier synthesis and the positions for the other hydrogen atoms were calculated. Refinements of all positional parameters, anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for hydrogen atoms yielded an  $R$  of 0.09.

A difference Fourier synthesis revealed disorder of the sulfur atom. The densities in a Fourier synthesis indicated approximate relative weights of 0.7 (S1) and 0.3 (S1M) with the sulfur distributed on both sides of the plane through the other four

ring atoms. These weights were refined such that the combined weights were equal to 1, together with the positional and isotropic thermal parameters of the two sulfurs and all other positional and thermal parameters. The final weights were not refined further.

Introduction of anisotropic thermal parameters for the sulfur atoms and refinement of all parameters showed that the three hydrogens H22, H51 and H7 could not be refined, probably as a result of the disorder. The positions for these three hydrogens were found in a difference Fourier synthesis and included in the structure factor calculations. Final refinements of all positional and thermal parameters (except those involving H22, H51 and H7) converged to an  $R$  of 0.051 and an  $R_w$  of 0.054. Disorder

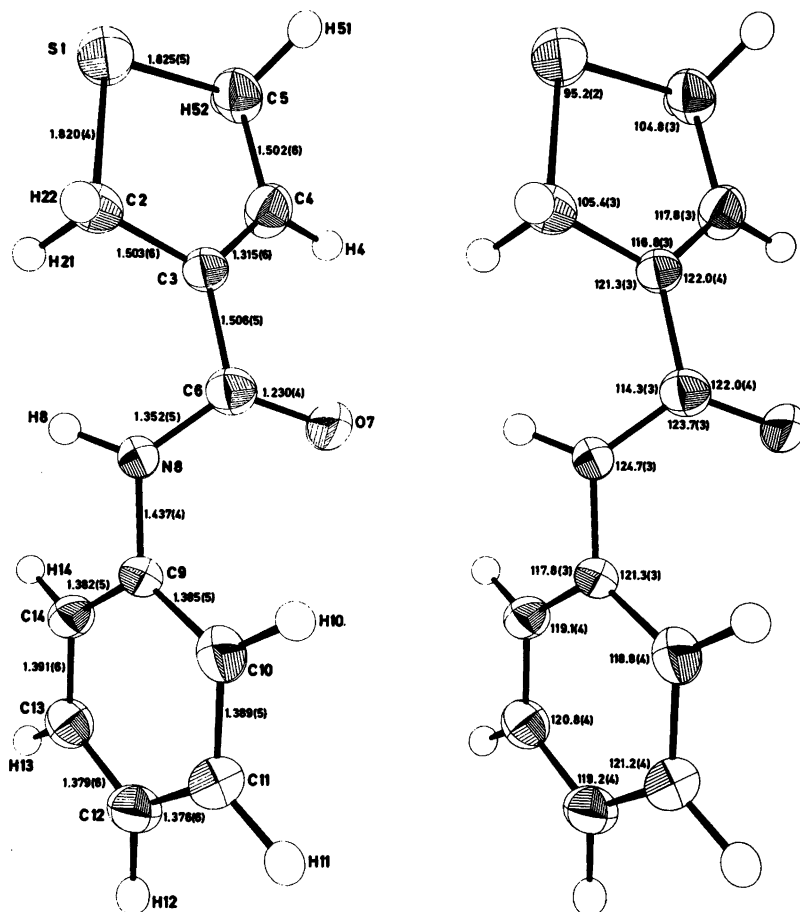


Fig. 2. Bond lengths (Å) and bond angles (°) in II.

is probably the reason for the large thermal parameters obtained for N7, O14, C2 and C5. A difference Fourier synthesis showed only small spurious peaks.

Final atomic parameters are listed in Table 1. The experimental data may be obtained from the authors upon request.

**Compound II.** The phase problem was solved by the program assembly MULTAN 77.<sup>4</sup> The positions for 10 of the 14 non-hydrogen atoms were found from the *E*-map and the other four were found by successive Fourier refinements. The structure model was refined to an *R* of 0.10. Introduction of anisotropic thermal parameters and least-squares refinement lowered *R* to 0.06. The position of H8 was found in a Fourier difference synthesis and positions for other hydrogen atoms were calculated.

These were included in the structure factor calculations with an isotropic thermal parameter of  $3.0 \text{ \AA}^2$ . Full-matrix least-squares refinement of all parameters involving non-hydrogen atoms converged to an *R* of 0.042 and an *R<sub>w</sub>* of 0.035. A difference Fourier synthesis showed only small spurious peaks.

Final atomic parameters are given in Table 1. The experimental data may be obtained from the authors upon request.

## DESCRIPTIONS OF THE STRUCTURES

The molecular geometries may be seen from Figs. 1 and 2, where the numbering of the atoms, bond lengths and bond angles are listed. The bond

Table 1. Fractional atomic coordinates and thermal parameters with estimated standard deviations. The anisotropic temperature factor is given by:  $\exp -2\pi^2(u_{11}(a^*h)^2 + \dots + 2u_{23}b^*c^*kl)$ .

Atom	x	y	z	$u_{11}(B)$	$u_{22}$	$u_{33}$	$u_{12}$	$u_{13}$	$u_{23}$
Compound I									
C1	.9484(6)	.6468(2)	.0008(4)	.0518(13)	.0483(18)	.0766(22)	.0023(12)	.0106(17)	-.0199(15)
C2	1.1839(7)	.6209(2)	-.0858(7)	.0471(27)	.0522(30)	.0522(31)	-.0065(23)	.0034(25)	-.0032(25)
C3	1.1343(6)	.5575(2)	-.1798(6)	.0380(25)	.0427(26)	.0547(30)	.0022(21)	.0089(22)	.0064(23)
C4	.9143(6)	.5435(2)	-.2107(5)	.0370(24)	.0343(24)	.0447(26)	.0018(19)	.0049(20)	-.0003(20)
C5	.7759(7)	.5911(2)	-.1393(7)	.0471(27)	.0610(32)	.0683(37)	.0020(24)	.0083(27)	-.0014(27)
C6	.8529(6)	.4866(2)	-.2884(6)	.0260(24)	.0523(30)	.0565(31)	-.0019(22)	.0074(22)	.0077(24)
N7	.6534(5)	.4633(2)	-.3180(4)	.0672(22)	.0784(24)	.0820(27)	.0053(19)	.0091(19)	.0001(19)
C8	.5979(6)	.3996(2)	-.3820(5)	.0494(26)	.0252(22)	.0433(27)	.0002(20)	-.0041(21)	-.0028(19)
C9	.3990(7)	.3774(2)	-.3634(6)	.0438(27)	.0493(30)	.0724(36)	-.0037(25)	.0064(25)	-.0053(26)
C10	.3400(8)	.3163(2)	-.4189(7)	.0517(31)	.0544(35)	.0871(41)	-.0083(26)	.0038(29)	-.0057(29)
C11	.4748(8)	.2769(2)	-.4942(7)	.0656(33)	.0383(29)	.0719(36)	-.0063(26)	.0010(28)	.0003(26)
C12	.6728(8)	.2991(2)	-.5116(6)	.0642(33)	.0501(32)	.0607(35)	.0055(27)	.0101(27)	-.0081(26)
C 3	.7359(7)	.3607(2)	-.4554(6)	.0440(27)	.0508(31)	.0623(33)	-.0028(24)	.0091(25)	-.0006(25)
O14	1.2769(4)	.5234(1)	-.2209(5)	.0435(18)	.0584(21)	.1144(30)	.0038(16)	.0246(19)	-.0162(20)
S1M	.9448(13)	.6627(4)	-.0932(10)	.0581(32)	.0503(43)	.1278(73)	.0016(27)	.0085(52)	-.0273(45)
H21	1.268(7)	.614(2)	.004(6)	3.6(16)					
H6	.955(6)	.457(2)	-.331(5)	3.0(9)					
H10	.196(7)	.299(2)	-.404(6)	7.3(13)					
H12	.772(6)	.273(2)	-.568(6)	5.6(12)					
H22	1.251	.654	-.174	6.0					
H7	.515	.496	-.258	8.0					
H52	.689(7)	.574(2)	-.057(6)	4.7(12)					
H9	.296(7)	.407(2)	-.315(5)	6.0(13)					
H11	.426(6)	.232(2)	-.524(5)	5.4(11)					
H13	.871(7)	.375(2)	-.470(5)	3.2(11)					
H51	.727	.608	-.204	4.0					
Compound II									
S1	-.0881(2)	.2958(2)	.0224(0)	.0590(6)	.0415(5)	.0330(5)	-.0041(6)	-.0103(7)	-.0019(7)
C2	-.0414(5)	.3158(8)	.1012(2)	.0546(28)	.0425(24)	.0259(18)	-.0043(23)	-.0062(19)	.0040(19)
C3	.0647(5)	.5464(7)	.1076(2)	.0389(26)	.0305(19)	.0236(17)	.0014(20)	.0000(17)	-.0011(16)
C4	.1003(5)	.6709(8)	.0586(2)	.0522(32)	.0365(22)	.0354(20)	-.0036(23)	.0046(24)	.0009(19)
C5	.0330(6)	.5716(8)	.0012(2)	.0598(30)	.0403(23)	.0235(18)	.0030(22)	-.0005(19)	.0048(18)
C6	.1239(5)	.6325(8)	.1675(2)	.0420(30)	.0379(23)	.0302(20)	.0016(21)	.0031(19)	.0001(18)
O7	.1581(5)	.8573(6)	.1777(1)	.0945(29)	.0268(15)	.0369(16)	-.0097(17)	-.0114(18)	.0004(14)
N8	.1387(4)	.4419(6)	.2078(1)	.0483(23)	.0251(15)	.0260(14)	-.0005(16)	-.0006(15)	.0009(14)
C9	.1945(5)	.4757(7)	.2676(2)	.0374(24)	.0294(21)	.0234(16)	-.0027(20)	.0010(18)	.0014(16)
C10	.1405(5)	.6761(8)	.3025(2)	.0487(28)	.0304(22)	.0370(23)	.0052(21)	.0013(19)	.0034(18)
C11	.1927(5)	.6925(8)	.3609(2)	.0539(30)	.0354(24)	.0300(20)	-.0005(23)	.0027(19)	-.0060(20)
C12	.2977(5)	.5158(8)	.3841(2)	.0481(29)	.0458(26)	.0263(17)	-.0060(24)	-.0013(20)	.0007(20)
C13	.3508(6)	.3181(10)	.3486(2)	.0483(28)	.0397(27)	.0362(18)	.0064(24)	-.0078(22)	.0067(18)
C14	.2986(5)	.2950(8)	.2902(2)	.0414(24)	.0350(21)	.0318(17)	.0044(21)	.0033(20)	-.0041(20)
H8	.135	.262	.196	3.0					
H22	-.141	.336	.126	3.0					
H51	-.036	.710	-.018	3.0					
H10	.064	.809	.286	3.0					
H12	.333	.534	.427	3.0					
H14	.337	.150	.264	3.0					
H21	.017	.157	.115	3.0					
H4	.177	.823	.059	3.0					
H52	.119	.524	-.028	3.0					
H11	.153	.835	.387	3.0					
H13	.432	.186	.364	3.0					

Table 3. Selected torsional angles ( $^{\circ}$ ). The angles are positive in a right-hand screw.

I	Angle ( $^{\circ}$ )	II	Angle ( $^{\circ}$ )
C2-S1-C5-C4	14.7(4)	C2-C3-C6-N8	28.4(5)
C2-S1M-C5-C4	-20.4(5)	C2-C3-C6-O7	-152.8(4)
C4-C3-C2-S1	13.6(5)	C3-C6-N8-C9	179.3(4)
C4-C3-C2-S1M	-13.0(5)	C6-N8-C9-C10	44.6(6)
C3-C4-C5-S1	-9.4(5)		
C3-C4-C5-S1M	16.1(5)		
C3-C4-C6-N7	175.6(4)		
C4-C6-N7-C8	-172.4(4)		
C6-N7-C8-C9	164.1(4)		

Table 2. Deviations from least-squares planes ( $\text{\AA} \times 10^3$ ). Deviations for those atoms used to define a plane are marked with \*.

Atom	I.A	I.B	Atom	II.A	II.B
S1	-384		S1	6*	
S1M	401		C2	-14*	
C2	1*		C3	6*	449
C3	9*		C4	8*	
C4	33*		C5	-15*	
C5	-19*	-509	C6	51	679
C6	-8*	-332	O7	544	1489
N7	-80	-24	N8	-516	-54
C8	-277	2*	C9	-610	2*
C9		1*	C10		4*
C10		-4*	C11		-5*
C11		4*	C12		1*
C12		-1*	C13		5*
C13		-2*	C14		-6*
O14	-11*				

the moiety C3-C6(O7)-N8-C9 as is usually found for amides. The torsional angle C3-C6-N8-C9 is 179.3 $^{\circ}$ (4). The angle between planes II.A and II.B is 71.1 $^{\circ}$ .

Apart from the hydrogen bonds the shortest intermolecular distances in the crystals are compatible with normal van der Waals' contacts.

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lengths and angles are normal. In I the lengths indicate resonance stabilization over O14-C3-C4-C6-N7, whereas in II the amide linkage (N8-C6-O7) is resonance stabilized. These conjugations are probably enhanced by the formation of hydrogen bonds N-H $\cdots$ O:

I: N $\cdots$ O (in position:  $-1+x,y,z$ ) 2.906(4)  $\text{\AA}$ ;

II: N $\cdots$ O (in position:  $x,-1+y,z$ ) 3.131(4)  $\text{\AA}$ .

Deviations from planarity are given in Table 2 and some torsional angles in Table 3. The five-membered ring in I has an envelope conformation with the sulfur atom out of the plane, S1: -0.384  $\text{\AA}$  and S1M: 0.401  $\text{\AA}$ . The torsional angle (I) C3-C4-C6-N7 is 175.6 $^{\circ}$ (4), close to planar arrangement in agreement with the high degree of conjugation. The angle between the two planes I.A and I.B is 16.1 $^{\circ}$ . In II the five-membered ring is planar and so is