

REACTION OF 5,5-DIPHENYL-2-THIOHYDANTOIN WITH 1,2-DIBROMOETHANE.  
CRYSTAL AND MOLECULAR STRUCTURES OF 2,3-DIHYDRO-6,6-DIPHENYLMIMI-  
DAZO-[2,1-b]-THIAZOL-5(6H)-ONE AND 2,3-DIHYDRO-5,5-DIPHENYLMIMI-  
DAZO-[2,1-b]-THIAZOL-6(5H)-ONE AND THEIR REACTIVITY

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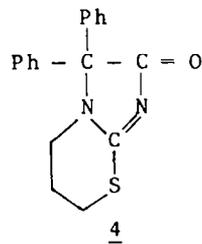
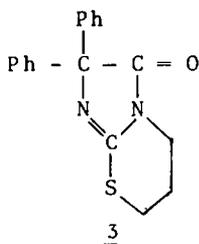
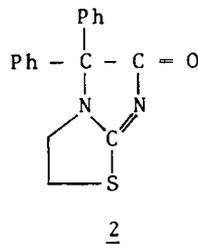
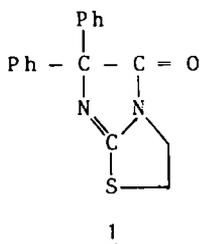
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Abstract - The crystal and molecular structures of the title isomeric compounds 1 and 2, obtained by intramolecular N,5-dialkylation of 5,5-diphenyl-2-thiohydantoin with 1,2-dibromoethane, have been determined from X-ray diffractometer data. 2,3-Dihydro-6,6-diphenylimidazo-[2,1-b]-thiazol-5(6H)-one (1) crystallizes in space group  $P2_12_12_1$  with  $a=11.376(3)$ ,  $b=12.255(5)$ ,  $c=8.434(3)$  Å and  $Z=4$ . Crystals of 2, containing one molecule of benzene, are monoclinic, space group  $P2_1/c$  with  $a=11.539(6)$ ,  $b=10.242(3)$ ,  $c=16.353(5)$  Å,  $\beta=95.45(5)^\circ$  and  $Z=4$ . In both cases a planar geometry of the two fused five-membered heterocyclic rings was found. The selected bond lengths in 1 and 2, as well as those analogous imidazothiazinones 3 and 4, were used to calculate EHOSE (Harmonic Oscillation Stabilization Energy). The problem of stability and chemical reactivity of compounds 1 to 4 is also discussed.

In continuation of our studies<sup>1,2</sup> on the reactivity and structure of cyclic dialkylation products of 5,5-diphenyl-2-thiohydantoin we have focused our attention on two isomeric compounds: 2,3-dihydro-6,6-diphenylimidazo-[2,1-b]-thiazol-5(6H)-one (1) and 2,3-dihydro-5,5-diphenylimidazo-[2,1-b]-thiazol-6(5H)-one (2). The synthesis of both compounds 1 and 2 was already reported<sup>3</sup> and their correct structures were established by Driscoll et al.<sup>4</sup> on the basis of chemical transformations and spectral analysis. The recent paper by Cameron<sup>5</sup>

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on the X-ray analysis of 2 prompts us to report our work with 1 and 2 which include: (a) the synthesis and X-ray analysis of both compounds, (b) the reaction of 1 and 2 with primary amines, and (c) application of the HOSE-model<sup>6,7</sup> for calculating  $\pi$ -electron stabilization energies to 1 and 2 (as well as to 3 and 4).

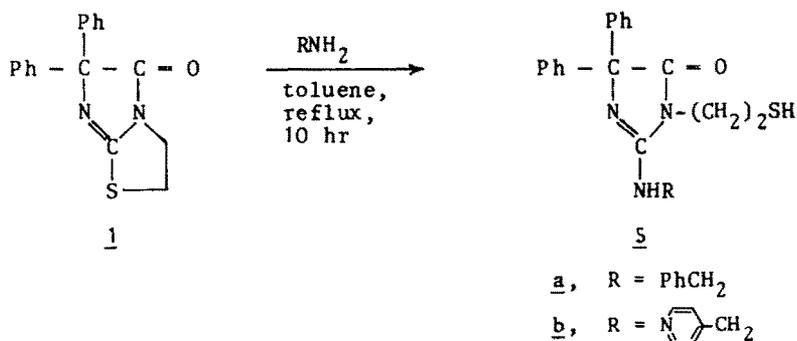
## RESULTS AND DISCUSSION

### Synthesis and Aminolysis of 1 and 2.

A mixture of isomeric diphenylimidazothiazolones 1 and 2 was obtained in a 74.5% yield by treatment of 5,5-diphenyl-2-thiohydantoin with 1,2-dibromoethane in an ethanol-water solution in the presence of equimolar amounts of sodium hydroxide. Each pure isomer (1 and 2) originally present in a 1:7 ratio, was obtained after column chromatography and recrystallization from ethanol (mp 199-201°C and 179-181°C, respectively). Their spectral properties were practically identical with those reported in the literature<sup>4</sup>. It is interesting to note that recrystallization of 2 from benzene resulted in the formation of a crystalline inclusion complex containing one molecule of the solvent.

A mixture of 1 and 2 was also obtained by alkylation of 5,5-diphenyl-2-thiohydantoin with 1,2-dibromoethane under phase transfer catalytic conditions applied by us<sup>2</sup> in the synthesis of compounds 3 and 4. Under such conditions the ratio between 1 and 2 was 1:4 and the total yield of both compounds was 81%. In this context we should note that the use of 1,2-dibromoethane as alkylating agent instead of 1-chloro-2-bromoethane (applied by Driscoll) results in much better yield of the isomeric mixture of 1 and 2.

The chemical behaviour of the isomeric diphenylimidazothiazolones 1 and 2 toward nucleophilic reagents is analogous to that of the related diphenylimidazothiazinones 3 and 4. Thus, isomer 1 is more reactive and shows a typical reactivity for the isothioureia grouping<sup>8</sup>. For example, 1 reacts with primary amines (benzylamine,  $\gamma$ -picolylamine) in refluxing toluene (10 hr) to give the corresponding 3(2-mercaptoethyl)-2-amino-5,5-diphenylhydantoin 5a and 5b. Under the same reaction conditions isomer 2 does not react even if after refluxing for 30 hr.



The present results together with our previous observations on the chemical behaviour of the isomeric diphenylimidazothiazinines 3 and 4 allow a qualitative comparison of the chemical reactivity and stability between these two pairs of isomeric compounds. Generally, thiazinones 3 and 4 are more reactive than thiazolones 1 and 2. For instance, whereas 3 undergoes hydrolysis in an ethanol-water solution, 1 is stable in this medium. Similarly, 4 reacts with primary amines while 2 is completely resistant to their action.

Crystal Structures of 2,3-Dihydro-6,6-diphenylimidazo-[2,1-b]-thiazol-5(6H)-one (1) and 2,3-Dihydro-5,5-diphenylimidazo-[2,1-b]-thiazol-6(5H)-one (2).

X-Ray analysis of both isomers 1 and 2 was undertaken not only to confirm their molecular structures but mainly to determine the molecular geometry and structural parameters of 1 and 2 for a more exact comparison of their stability and reactivity through HOSE calculations.

The solid state structures of 1 and 2 (containing one molecule of benzene) with the atom-numbering system are shown in Fig.1 and 2, respectively. The corresponding bond lengths and angles are listed in Table 1 and 2. It was found that the two five-membered heterocyclic rings in each investigated compound are essentially coplanar. More detailed information about the geometry of these two fused rings is given in Table 3. Two planar benzene rings bonded to C(3) form with the best plane of the thiohydantoin ring in 1 the angles 61° and 65° while in 2 the corresponding angles are 72.2° and 68.5°.

X-Ray analysis of 2 was conducted on the 1:1 inclusion complex of 2 with benzene. Therefore, there are some differences between our structure and that of 2 reported by Cameron et al.<sup>5</sup> First of all, we found a significant difference in the sum of angles around the nitrogen atom N(1).

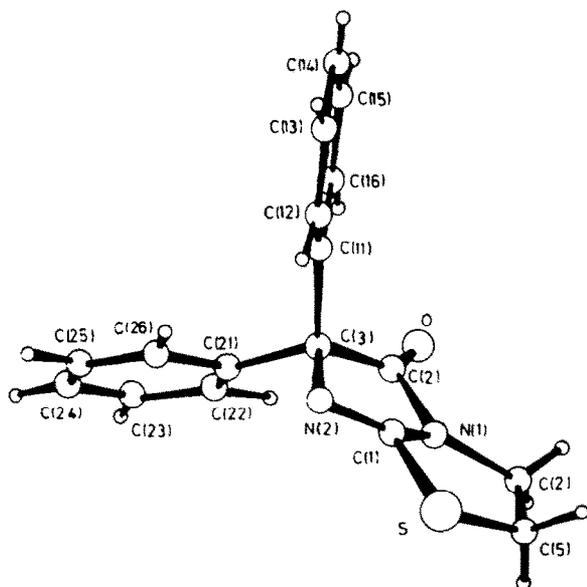


Fig.1. A perspective view of the molecule of 1 with the atom-numbering scheme.

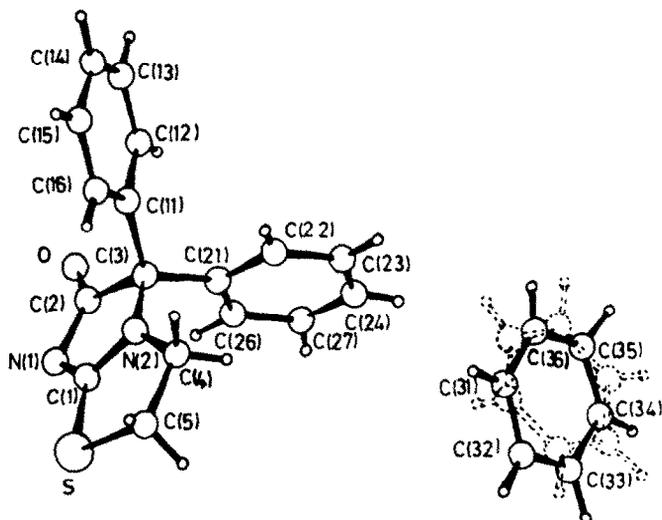


Fig. 2. A perspective view of the molecule of 2 (with molecule of benzene) showing the atom-numbering scheme

In our case this value is  $358.0^\circ$  which agrees well with the  $sp^2$ -hybridization and planarity of this nitrogen atom. The corresponding value found by Cameron *et al.* is smaller and equal to  $346.0^\circ$ . Secondly, the N(2)-C(1) and S-C(1) bonds of 1.326(4) and 1.705(3) Å, respectively, in our structure are slightly shorter than those found by Cameron *et al.* [1.340(2) and 1.723(2) Å]. Due to these differences the five-membered dihydrothiazole ring is flatter in our structure.

Table 1. Bond lengths (Å)

a) 2,3-Dihydro-6,6-diphenylimidazo-[2,1-b]-thiazol-5(6H)-one (1)

C(1) -S	1.733(9)	C(5) -S	1.833(12)
C(2) -O	1.185(11)	C(1) -N(1)	1.364(12)
C(2) -N(1)	1.385(11)	C(1) -N(2)	1.293(12)
C(3) -N(2)	1.529(10)	C(4) -N(1)	1.515(12)
C(3) -C(2)	1.503(11)	C(11)-C(3)	1.513(11)
C(21)-C(3)	1.563(12)	C(5) -C(4)	1.528(15)

The average values of the C-C bonds for the phenyl rings are 1.389(8) and 1.380(26) Å

b) 2,3-Dihydro-5,5-diphenylimidazo-[2,1-b]-thiazol-6(5H)-one (2)

C(1) -S	1.705(4)	C(5) -S	1.803(4)
C(2) -O	1.210(4)	C(1) -N(1)	1.314(4)
C(2) -N(2)	1.374(4)	C(1) -N(2)	1.326(4)
C(3) -N(2)	1.462(4)	C(4) -N(2)	1.448(5)
C(3) -C(2)	1.566(4)	C(11)-C(3)	1.524(4)
C(21)-C(3)	1.515(4)	C(5) -C(4)	1.519(6)

The average values of the C-C bonds for the phenyl rings are 1.374(4) and 1.373(6) Å; for the included benzene ring 1.364(10) and 1.395(13), respectively, for s.o.f 0.75 and 0.25.

Table 2. Bond angles ( $^{\circ}$ )

## a) 2,3-dihydro-6,6-diphenylimidazo-[2,1-b]-thiazol-5(6H)-one (1)

C(5) -S -C(1)	88.6(5)	C(2) -N(1) -C(1)	107.3(7)
C(4) -N(1) -C(1)	124.6(8)	C(4) -N(1) -C(2)	128.1(8)
C(3) -N(2) -C(1)	101.2(6)	N(2) -C(1) -S	128.2(7)
N(1) -C(1) -S	111.9(7)	N(1) -C(1) -N(2)	119.9(8)
N(1) -C(2) -O	123.6(9)	C(3) -C(2) -O	131.3(8)
C(3) -C(2) -N(1)	105.0(7)	C(2) -C(3) -N(2)	106.4(6)
C(21) -C(3) -N(2)	10(.9(6)	C(21) -C(3) -C(2)	113.0(6)
C(11) -C(3) -N(2)	110.5(6)	C(11) -C(3) -C(2)	109.9(7)
C(11) -C(3) -C(21)	110.0(6)	C(5) -C(4) -N(1)	96.4(8)
C(4) -C(5) -S	118.5(8)	C(12) -C(11) -C(3)	120.3(7)
C(16) -C(11) -C(3)	120.0(7)	C(22) -C(21) -C(3)	121.0(8)
C(26) -C(21) -C(3)	117.3(8)		

The average angles for the phenyl rings are  $119.9(9)^{\circ}$  and  $120(1)^{\circ}$ .

## b) 2,3-dihydro-5,5-diphenylimidazo-[2,1-b]-thiazol-6(5H)-one (2)

C(5) -S -C(1)	92.0(2)	C(2) -N(1) -C(1)	104.8(3)
C(3) -N(2) -C(1)	108.3(2)	C(4) -N(2) -C(1)	118.1(3)
C(4) -N(2) -C(3)	131.6(3)	N(1) -C(1) -S	128.4(3)
N(2) -C(1) -S	113.6(2)	N(2) -C(1) -N(1)	118.0(3)
N(1) -C(2) -O	126.3(3)	C(3) -C(2) -O	123.5(3)
C(3) -C(2) -N(1)	110.3(3)	C(2) -C(3) -N(2)	98.5(2)
C(11) -C(3) -N(2)	113.2(2)	C(11) -C(3) -C(2)	108.5(2)
C(21) -C(3) -N(2)	109.9(2)	C(21) -C(3) -C(2)	112.4(3)
C(21) -C(3) -C(11)	113.2(2)	C(5) -C(4) -N(2)	106.4(3)
C(4) -C(5) -S	109.3(3)	C(12) -C(11) -C(3)	118.8(3)
C(16) -C(11) -C(3)	122.7(3)	C(22) -C(21) -C(3)	119.1(3)
C(26) -C(21) -C(3)	122.3(3)		

The average angles for the phenyl rings are  $120.0(6)^{\circ}$  and  $119.8(7)^{\circ}$ ; for the included benzene ring  $120.0(6)^{\circ}$  and  $120.0(9)^{\circ}$ , respectively, for s.o.f. 0.75 and 0.25

Table 3. The least-squares planes for five-membered rings.

## a) structure 1

Plane 1	Plane 2
N(1) - 0.006(7)	S 0.006(3)
N(2) 0.027(6)	N(1) 0.012(7)
C(1) - 0.015(10)	C(1) - 0.012(10)
C(2) 0.022(9)	C(4) - 0.005(10)
C(3) - 0.028(8)	C(5) - 0.001(13)

$$\text{Plane 1 } 0.0971X + 0.5517Y + 0.8284Z = 1.6915$$

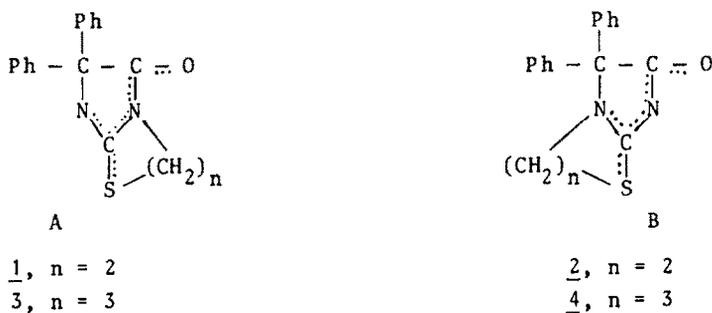
$$\text{Plane 2 } 0.1037X + 0.5601Y + 0.8219Z = 1.7417$$

b) structure 2

Plane 1	Plane 2
N(1) - 0.009(5)	S - 0.016(4)
N(2) - 0.023(5)	N(2) - 0.047(5)
C(1) - 0.022(6)	C(1) 0.040(6)
C(2) - 0.005(5)	C(4) 0.027(7)
C(3) 0.015(7)	C(5) - 0.004(6)
Plane 1 0.5577X - 0.3924Y + 0.7315Z = 14.8310	
Plane 2 0.5801X - 0.4924Y + 0.6563Z = 14.0451	

Application of the HOSE-Model to Estimation of Relative Stabilities of Isomeric Diphenylimidazothiazolones 1 and 2 and Diphenylimidazothiazinones 3 and 4

The experimental data presented above point to a markedly higher reactivity (lower stability) of the compounds 1 and 3 (pair A) in comparison with 2 and 4 (pair B). Since the reactive centre in all these compounds is the carbon atom C-2 incorporated in a system of conjugated bonds of the thiohydantoin moiety, it is quite reasonable to expect that a difference in chemical reactivity between the A and B pairs results mainly from a different extent of  $\pi$ -electron conjugation. The systems of conjugated bonds in both pairs of compounds A and B, which differ in the contribution of some bonds to the  $\pi$ -electron system formed, are depicted below.



It is proposed here that the local  $\pi$ -electron fragments in compounds 1 to 4 can be employed to account for the differences in their stability and hence in reactivity. To this end the HOSE model<sup>6,7</sup> was used to calculate the stabilization energy of the  $\pi$ -electron fragments of the molecules under discussion. The method proposed, based on elements of molecular mechanics, is particularly convenient for our purpose because of simplicity of calculations and the possibility of using X-ray data (bond lengths) for a more extensive analysis of the differences between the related  $\pi$ -electron systems.

According to the definition of  $E_{\text{HOSE}}$  (Harmonic Oscillation Stabilization Energy - it is the negative value of the energy required to transform a real molecule into its *i*-th resonance structures) the more stable, i.e. less reactive, compound will be the one for which the calculated stabilization energy of the  $\pi$ -electron system is numerically greater. The  $E_{\text{HOSE}}$ -values for the compounds under discussion were calculated according to the procedure described in detail by one of us (J.K-W)<sup>10</sup> in the study on the  $\pi$ -electron  $\gamma$ -delocalized thiourea system. They are shown together with the bond lengths required for calculations in Table 4. It should be noted that because of the large e.s.d.'s ( $\delta > 0.006 \text{ \AA}$ ) for the bond lengths in 1 the energy calculated for it can only be treated as approximate.

Table 4. The calculated  $E_{\text{HOSE}}$ -values for 1, 2, 3 and 4 and the bond distances taken for calculations

Compounds	Bond distances [ $\overset{\text{O}}{\text{Å}}$ ]					$E_{\text{HOSE}}$ [kJ·mol <sup>-1</sup> ]
	N(2)-C(1)	C(1)-N(1)	C(1)-S	N(1)-C(2)	C(2)-O	
<u>1</u>	1.293(12)	1.364(12)	1.733(9)	1.385(11)	1.185(11)	46(10)
<u>2</u>	1.326(4)	1.314(4)	1.705(3)	1.374(4)	1.210(4)	85(4)
<u>3</u>	1.290(4)	1.387(4)	1.736(3)	1.376(4)	1.209(4)	36(2)
<u>4</u>	1.330(4)	1.333(3)	1.717(3)	1.363(4)	1.216(4)	88(4)

An inspection of the results in Table 4 reveals that the  $E_{\text{HOSE}}$ -values for the compounds 2 and 4 (pair B) are significantly higher than those for the compounds 1 and 3 (pair A), indicating a higher stability for the former pair. Thus, the results of calculations are in full agreement with our experimental data concerning hydrolysis and aminolysis of the compounds investigated. It is clear that the model employed does not allow a distinction to be made for reactivity difference within each pair. This is because the thiazine and thiazolidine rings are not conjugated  $\pi$ -electron systems, there being no significant effect on the system of conjugated bonds of the thiohydantoin moiety.

## EXPERIMENTAL SECTION

2,3-Dihydro-6,6-diphenylimidazo-[2,1-b]-thiazol-5(6H)-one (1) and 2,3-dihydro-5,5-diphenylimidazo-[2,1-b]-thiazol-6(5H)-one (2)

A boiling solution of 5,5-diphenyl-2-thiohydantoin (5.36 g, 0.02 mole) in 96% ethanol (40 ml) was treated with 1,2-dibromoethane (3.74 g, 0.02 mole) and then dropwise during 1 hr with a solution of sodium hydroxide (0.8 g, 0.02 mole) in 50% ethanol (40 ml). The reaction mixture was refluxed for 2 hr, concentrated in vacuum and cooled. After cooling, 5.1 g of a solid product, consisting of unreacted thiohydantoin and two isomeric dialkylation products 1 and 2 (TLC analysis, ethyl acetate: chloroform, 1:1) was obtained. This product was chromatographed on silica gel (100/200 mesh). The first fraction separated with benzene elution (300 ml) contained 5,5-diphenyl-2-thiohydantoin (0.41 g, 7.5%,  $R_f$  0.88).

Elution with chloroform (300 ml) gave a second fraction containing 1. Evaporation of the solvent and recrystallization from ethanol gave 2,3-dihydro-6,6-diphenylimidazo-[2,1-b]-thiazol-5(6H)-one (1) 0.55 g, 9.5%, mp. 199-201°C,  $R_f$  0.74 <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 3.57 (m, 4H, CH<sub>2</sub>-CH<sub>2</sub>), 7.15 and 7.29 (m, 10H, aromatic H); <sup>13</sup>C-NMR (CD<sub>3</sub>SOCD<sub>3</sub>): 33.93 (C<sub>3</sub>), 39.98 (C<sub>2</sub>), 86.72 (C<sub>6</sub>), 126.56, 127.60, 128.25 and 140.28 (aromatic carbons), 167.19 (C(=N)S), 176.23 (C=O); UV (EtOH): 217 nm (log  $\epsilon$  = 4.32) 244 (log  $\epsilon$  = 3.97).

The third fraction obtained by further elution with chloroform (300 ml) was found to contain 2,3-dihydro-5,5-diphenylimidazo-[2,1-b]-thiazol-6(5H)-one (2) which was isolated and recrystallized from ethanol to give 3.86 g (65%) of white crystals, mp 179-181°C,  $R_f$  0.47. <sup>1</sup>H-NMR (CD<sub>3</sub>SOCD<sub>3</sub>): 3.50 (t, 3H, CH<sub>3</sub>) 3.72 (t, 2H, CH<sub>2</sub>), 7.35 (m, 10H, aromatic); <sup>13</sup>C-NMR (CD<sub>3</sub>SOCD<sub>3</sub>): 31.07 (C<sub>3</sub>), 46.02 (C<sub>2</sub>), 77.49 (C<sub>5</sub>) 127.47, 128.38, 128.77 and 137.03 (aromatic carbons), 189.81 and 189.94 (C=O and C(=N)S); UV (EtOH): 241 nm (log  $\epsilon$  = 4.03), 267 nm (log  $\epsilon$  = 3.98).

3-(2-Mercaptoethyl)-2-benzylamino-5,5-diphenylhydantoin (5a)

A solution of 1 (0.3 g, 1.02 mmole) and benzylamine (0.2 g, 1.87 mmole) in toluene (10 ml) was refluxed for 10 hr. The precipitated solid was filtered and recrystallized from methanol to give the analytically pure 5a, 0.3 g (75%), mp. 259-261°C. IR (KBr): 3300, 3100, 1675, 1590, 1490, 1440, 1390, 1335, 1255, 1200, 1060, 1040, 960, 920, 740, 690  $\text{cm}^{-1}$ ; MS(70eV): 401( $\text{M}^+$ , 15), 365 (11), 295 (7), 294 (30), 266(14), 265(14), 180(6), 165(40), 135(23), 107(14), 106(30), 104(20), 91(100), 77(26). Anal.Calc. for  $\text{C}_{24}\text{H}_{23}\text{N}_3\text{OS}$ : C, 71.78; H, 5.78; N, 10.46. Found: C, 72.08; H, 5.68; N, 10.33%.

3-(2-Mercaptoethyl)-2-( $\gamma$ -picolylamino)-5,5-diphenylhydantoin (5b)

A solution of 1 (0.3 g, 1.02 mmole) and  $\gamma$ -picolylamine (0.2 g, 1.85 mmole) in toluene (10 ml) was refluxed for 10 hr. After cooling two layers were formed. Separation of the solvent (upper layer) and recrystallization of the residue from methanol gave the analytically pure title compound 5b, 0.25 g (62%), mp 242-244°C. IR (KBr): 3430, 3280, 3080, 1690, 1595, 1510, 1470, 1415, 1355, 1315, 1265, 1210, 1080, 1060, 1030, 990, 970, 770, 745, 700  $\text{cm}^{-1}$ ; MS(70 eV): 402 ( $\text{M}^+$ , 13), 295(14), 294(61), 266(29), 265(26), 180(5), 165(52), 135(40), 104(15), 92(43), 80(100). Anal.Calc. for  $\text{C}_{23}\text{H}_{22}\text{N}_4\text{OS}$ : C 68.62; H, 5.51; N, 13.92; S, 7.98. Found: C, 68.77; H, 5.55; N, 14.13; S, 7.86%.

X-Ray structure determination of 1

Crystal data:  $\text{C}_{17}\text{H}_{14}\text{ON}_2\text{S}$ .  $M = 294.39$ . Orthorhombic,  $a = 11.376(3)$ ,  $b = 12.255(5)$ ,  $c = 8.434(3)$  Å,  $V = 1463.64$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.344$   $\text{g}\cdot\text{cm}^{-3}$ ,  $D_m = 1.320$   $\text{g}\cdot\text{cm}^{-3}$ , space group  $P2_12_12_1$ .

The compound 1 was crystallized from dimethyl sulphoxide. The intensity data were collected on a Syntex  $P2_1$  diffractometer using Cu-K $\alpha$  radiation. The intensity of 1449 reflections was corrected for the Lorentz polarization effect but not for absorption ( $\mu_{\text{Cu-K}\alpha} = 18.44$   $\text{cm}^{-1}$ ). After application of the criterion  $F > 2\sigma(F)$ , 1256 unique reflections were considered to be observed.

The structure was solved by direct methods (MULTAN-76) and from the E-map 10 non-hydrogen atoms were located. The refinement was carried out by a blocked full-matrix least-squares procedure. All H-atoms were located from difference syntheses calculated during the anisotropic refinement of the non-hydrogen atoms. The positional parameters of the H-atoms were not refined. The final conventional R-value was 0.105 with unit weight. The refinement was stopped at this stage since the largest parameter shift was less than 0.2 of its standard deviation and the highest residual electron density in the final difference map was 0.5  $\text{e}\text{\AA}^{-3}$ . The atomic parameters for the non-hydrogen atoms are collected in Table 5.

X-Ray structure determination of 2

Crystal data:  $\text{C}_{17}\text{H}_{14}\text{ON}_2\text{S}\cdot\text{C}_6\text{H}_6$ .  $M = 372.48$ . Monoclinic,  $a = 11.539(6)$ ,  $b = 10.242(3)$ ,  $c = 16.353(5)$  Å,  $\beta = 95.45(5)^\circ$ ,  $V = 1923.79$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.294$   $\text{g}\cdot\text{cm}^{-3}$ ,  $D_m = 1.271$   $\text{g}\cdot\text{cm}^{-3}$ , space group  $P2_1/c$ .

The compound 2 was crystallized from benzene as its inclusion complex with one molecule of solvent. The crystals were sealed into a Lindemann glass capillary tube. The intensity data were collected on a Stoe STADI-4 four-circle diffractometer with graphite monochromated Mo-K $\alpha$  radiation in the  $\theta$ - $2\theta$  mode ( $2\theta \leq 55^\circ$ ). A Lorentz polarization correction but no absorption correction ( $\mu_{\text{Mo-K}\alpha} = 1.43$   $\text{cm}^{-1}$ ) was applied. Of 2710 reflections measured, 2069 reflections, for which  $F > 5\sigma(F)$ , were used for solving and refinement of the structure.

The structure was solved by direct methods. The initial coordinates for 9 atoms were obtained from the E-map calculated from phases developed by weighted multisolution tangent (SHELX 76). Several difference syntheses were carried out to find the positions of other non-hydrogen atoms ( $R = 0.164$ ). The included benze-

ne molecule was found to be disordered. The site occupation factors were established between 0.75 and 0.25. The refinement by a blocked full-matrix least-squares with anisotropic temperature factors for all non-hydrogen atoms converged at  $R = 0.098$ . The benzene molecule with the site occupation factor of 0.25 was refined as a rigid group with joint isotropic temperature factors for all C and H atoms. The positions of the remaining hydrogens were located from a difference map. During the process of refinement  $R$  was reduced to 0.053 ( $R_w = 0.048$ ,  $w = 1.439/[\sigma^2(F_o) + 0.0003F^2]$ ). The atomic parameters for all non-hydrogen atoms of 2 are listed in Table 5.

Table 5. Positional parameters ( $\times 10^4$ ) and  $U_{eq} = (U_{11} \cdot U_{22} \cdot U_{33})^{1/3}$  for non H atoms

a) 2,3-dihydro-6,6-diphenylimidazo-[2,1-b]-thiazol-5(6H)-one (1)

	X	Y	Z	$U_{eq}$
S	7744(3)	401(2)	709(5)	95
O	11712(6)	-653(5)	1399(9)	93
N(1)	9905(7)	-84(4)	945(9)	67
N(2)	8656(6)	-1004(4)	2297(8)	64
C(1)	8801(7)	-324(6)	1398(12)	67
C(2)	1068(7)	-684(6)	1588(11)	61
C(3)	9917(6)	-134(4)	2429(9)	44
C(4)	10182(9)	703(5)	-94(13)	92
C(5)	8916(7)	1023(7)	-267(18)	113
C(11)	10029(7)	-2228(5)	1643(9)	51
C(12)	9029(8)	-2682(5)	1154(11)	59
C(13)	9154(9)	-3496(6)	401(13)	75
C(14)	10257(10)	-3870(6)	261(12)	75
C(15)	11254(8)	-3440(6)	787(13)	71
C(16)	11113(7)	-2617(6)	1500(11)	64
C(21)	10202(8)	-1418(5)	4236(10)	59
C(22)	11189(9)	-1052(7)	4854(11)	70
C(23)	11415(11)	-1165(9)	6485(15)	105
C(24)	10646(15)	-1621(9)	7416(14)	101
C(25)	9673(11)	-1999(8)	6810(14)	87
C(26)	9445(8)	-1875(7)	5139(11)	70

b) 2,3-dihydro-5,5-diphenylimidazo-[2,1-b]-thiazol-6(5H)-one (2)

	X	Y	Z	$U_{eq}$
S	9813(1)	2163(1)	8632(1)	67
O	12118(2)	-103(2)	6662(2)	61
N(1)	10796(2)	608(3)	7537(2)	51
N(2)	11563(2)	2604(2)	7837(2)	41
C(1)	10764(3)	1707(3)	7948(2)	45
C(2)	11770(3)	707(3)	7118(2)	46
C(3)	12383(2)	2054(3)	7300(2)	39
C(4)	11644(3)	3726(4)	8378(2)	51
C(5)	10610(3)	3646(4)	8885(3)	54
C(11)	12405(3)	2793(3)	6493(2)	39
C(12)	13199(3)	2426(3)	5958(2)	50
C(13)	13235(3)	3042(4)	5216(2)	59
C(14)	12478(4)	4032(4)	4993(2)	64
C(15)	11669(3)	4394(4)	5509(2)	64
C(16)	11636(3)	3777(4)	6260(2)	53

Table 5 continued

C(21)	13574(3)	1914(3)	7768(2)	40
C(22)	14275(3)	3004(4)	7887(2)	49
C(23)	15332(3)	2923(5)	8342(2)	59
C(24)	15695(4)	1762(5)	8684(3)	67
C(25)	15027(4)	671(5)	8574(2)	55
C(26)	13961(3)	752(4)	8116(2)	53
C(31)	16496(5)	3365(6)	11378(4)	72*
C(32)	17383(5)	2683(5)	11768(3)	63*
C(33)	18395(5)	2449(5)	11397(3)	69*
C(34)	18481(7)	2924(7)	10632(4)	80*
C(35)	17578(8)	3608(8)	10234(4)	87*
C(36)	16588(7)	3828(7)	10601(4)	93*
C(31)'	18110(8)	3504(10)	10268(5)	67(4)**
C(32)'	17012(8)	4080(10)	10246(5)	68(4)**
C(33)'	16318(8)	3870(10)	10887(5)	68(4)**
C(34)'	16722(8)	3083(10)	11550(5)	92(6)**
C(35)'	17820(8)	2506(10)	11572(5)	72(4)**
C(36)'	18514(8)	2717(10)	10931(5)	100(6)**

\* The atoms of the included benzene molecule with s.o.f. 0.75

\*\* The atoms of the included benzene molecule with s.o.f. 0.25 and  $U_{iso}$

## REFERENCES AND NOTES

1. K.Kiec-Kononowicz, A.Zejc, M.Mikołajczyk, A.Zatorski, J.Karolak-Wojciechowska and M.W.Wieczorek, *Tetrahedron*, **36**, 1079 (1980).
2. K.Kiec-Kononowicz, A.Zejc, M.Mikołajczyk, A.Zatorski, J.Karolak-Wojciechowska and M.W.Wieczorek, *Tetrahedron*, **37**, 409 (1981).
3. Z.Cichon and A.Zejc, *Pol.J.Pharmacol.Pharm.*, **25**, 187, 263 (1973).
4. K.Okada, J.A.Kelley and J.S.Driscoll, *J.Org.Chem.*, **42**, 2594 (1977).
5. A.F.Cameron, I.R.Cameron and F.D.Duncanson, *J.Chem.Soc.Perkin II*, 789 (1981).
6. T.Wieckowski and T.M.Krygowski, *Can.J.Chem.*, **39**, 1622 (1981).
7. T.M.Krygowski, R.Anulewicz and J.Kruszewski, *Acta Cryst.*, **B-39**, 732 (1983).
8. It is interesting that the oxygen analogue of **1** shows different reactivity. The reaction of 2,3-dihydro-6,6-diphenylimidazo-[2,1-b]-oxazol-5(6H)-one with ethanoloamine takes place at the carbon atom  $C_4$  affording 3-[2(N-8-hydroxyethyl)aminoethyl]-5,5-diphenylhydantoin<sup>9</sup>.
9. G.Peng, V.E.Marquez and J.S.Driscoll, *J.Med.Chem.*, **18**, 846 (1975).
10. J.Karolak-Wojciechowska, *Phosphorus and Sulfur*, in press.
11. The positional parameters for H-atoms, anisotropic temperature factors and structure factors for **1** and **2** are deposited with the British Library Lending Division as supplementary publication.