# MOLECULAR AND CRYSTAL STRUCTURE OF 1-PHENYL-3-METHYL-5-(o-HYDROXYPHENYL)-1,2,4-TRIAZOLE

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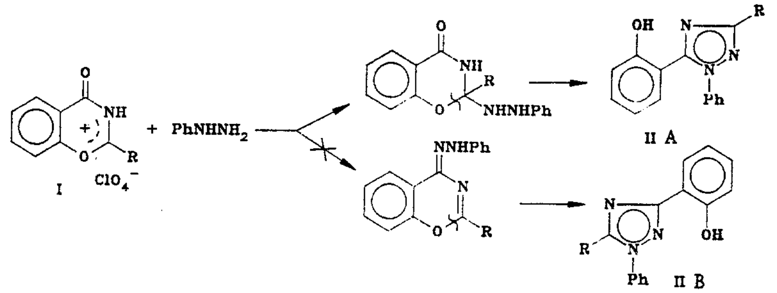
A choice between the possible mechanisms of the recyclization of 4-oxo-1,3-benzoxazine salts due to reaction with phenylhydrazine was made based on the x-ray structure of 1-phenyl-3-methyl-5-(o-hydroxyphenyl)-1,2,4-triazole.

The recyclization of 4-oxo-1,3-benzoxazine salts due to reaction with phenylhydrazine leads to the formation of o-hydroxyphenyl-1,2,4-triazoles in 65-100% yield [1, 2].

Quantum mechanical calculations of the model cation 4-oxo-1,3-benzoxazine (I, R = H) show that the positive charge in salts of I is localized mainly on atoms $C_{(2)}$ and $C_{(4)}$ of the heterocycle. It is assumed that position 2 of the ring is the most electron-deficient and consequently more susceptible to nucleophilic attack, although the less-hindered position 4 may turn out to be such. In this regard, the formation of one of the isomeric triazoles IIA or IIB is possible upon reaction of phenylhydrazine with salts of benzoxazinone.



The choice between the possible isomers, and consequently between the mechanisms of the recyclization reaction, was made based on the x-ray study of the triazole obtained by reaction of 2-methyl-4-oxo-1,3-benzoxazine (I, R = $CH_3$) perchlorate with phenylhydrazine.

The compound studied is shown to be 1-phenyl-3-methyl-5-(o-hydroxyphenyl)-1,2,4-triazole (IIA) (Fig. 1, Table 1).

TABLE 1. Bond Angles in the Triazole IIA

| Angle | ω° | Angle | ω° | Angle | ω° |
|---|---|---|---|---|---|
| $N_{(2)}N_{(1)}C_{(5)}$ | 109,9(2) | $N_{(1)}C_{(5)}C_{(6)}$ | 128,7(2) | $C_{(8)}C_{(9)}C_{(10)}$ | 120,4(3) |
| $N_{(2)}N_{(1)}C_{(13)}$ | 117,4(2) | $N_{(4)}C_{(5)}C_{(6)}$ | 122,4(2) | $C_{(9)}C_{(10)}C_{(11)}$ | 119,9(3) |
| $C_{(5)}N_{(1)}C_{(13)}$ | 132,7(2) | $C_{(5)}C_{(6)}C_{(7)}$ | 118,4(2) | $C_{(6)}C_{(11)}C_{(10)}$ | 121,5(3) |
| $N_{(1)}N_{(2)}C_{(3)}$ | 102,6(2) | $C_{(5)}C_{(6)}C_{(11)}$ | 123,9(2) | $N_{(1)}C_{(13)}C_{(14)}$ | 119,0(2) |
| $N_{(2)}C_{(3)}N_{(4)}$ | 114,4(2) | $C_{(7)}C_{(6)}C_{(11)}$ | 117,7(2) | $C_{(14)}C_{(13)}C_{(14')}$* | 121,9(3) |
| $N_{(2)}C_{(3)}C_{(12)}$ | 122,6(3) | $C_{(6)}C_{(7)}O$ | 122,9(2) | $C_{(13)}C_{(14)}C_{(15)}$ | 117,5(3) |
| $N_{(4)}C_{(3)}C_{(12)}$ | 123,1(3) | $C_{(6)}C_{(7)}C_{(8)}$ | 120,0(3) | $C_{(14)}C_{(15)}C_{(16)}$ | 122,2(4) |
| $C_{(3)}N_{(4)}C_{(5)}$ | 104,2(2) | $C_{(8)}C_{(7)}O$ | 117,1(2) | $C_{(15)}C_{(16)}C_{(15')}$* | 118,8(4) |
| $N_{(1)}C_{(5)}N_{(4)}$ | 108,9(2) | $C_{(7)}C_{(8)}C_{(9)}$ | 120,5(3) | | |

*Atoms related by a symmetry plane are denoted by a prime.

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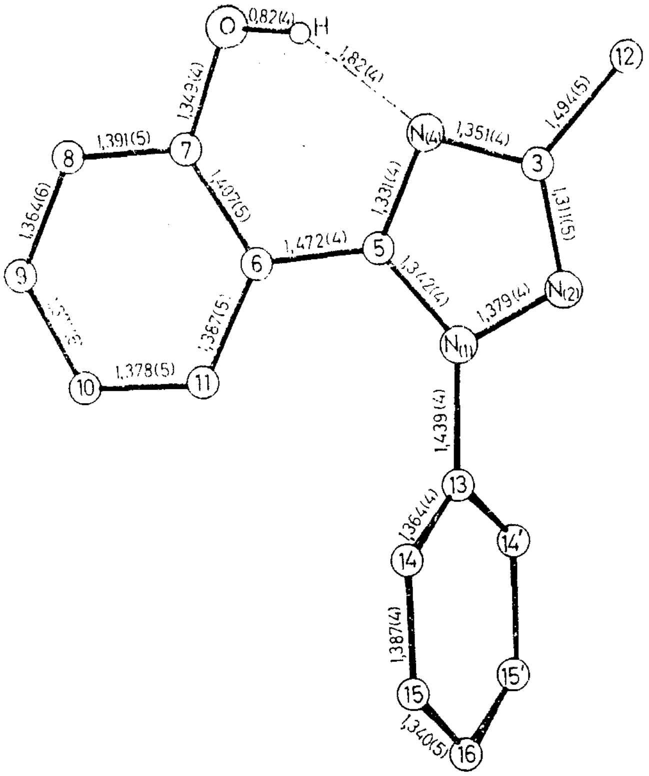

Fig. 1. Structure of IIA in the crystal.

TABLE 2. Atomic Coordinates (× $10^4$, for H, × $10^3$)

| Atom | x | y | z | Atom | x | y | z |
|---|---|---|---|---|---|---|---|
| O | 5375(1) | 6594(2) | 1/4 | $C_{(14)}$ | 3990(2) | 1341(3) | 831(5) |
| $N_{(1)}$ | 3911(2) | 3386(3) | 1/4 | $C_{(15)}$ | 4024(2) | −10(3) | 885(7) |
| $N_{(2)}$ | 3190(2) | 3911(3) | 1/4 | $C_{(16)}$ | 4036(3) | −675(4) | 1/4 |
| $C_{(3)}$ | 3325(2) | 5170(4) | 1/4 | $H_{(0)}$ | 491(2) | 655(4) | 262(5) |
| $N_{(4)}$ | 4073(2) | 5489(3) | 1/4 | $H_{(8)}$ | 678(2) | 616(4) | 1/4 |
| $C_{(5)}$ | 4430(3) | 4345(3) | 1/4 | $H_{(9)}$ | 736(2) | 405(3) | 1/4 |
| $C_{(6)}$ | 5264(2) | 4240(3) | 1/4 | $H_{(10)}$ | 666(2) | 223(4) | 1/4 |
| $C_{(7)}$ | 5694(2) | 5397(3) | 1/4 | $H_{(11)}$ | 538(2) | 227(3) | 1/4 |
| $C_{(8)}$ | 6483(2) | 5337(4) | 1/4 | $H_{(12,1)}$ | 223(2) | 575(4) | 1/4 |
| $C_{(9)}$ | 6846(2) | 4162(4) | 1/4 | $H_{(12\cdot2)}$ | 274(1) | 667(2) | 142(4) |
| $C_{(10)}$ | 6437(3) | 3024(4) | 1/4 | $H_{(14)}$ | 400(1) | 181(2) | −27(4) |
| $C_{(11)}$ | 5654(3) | 3066(3) | 1/4 | $H_{(15)}$ | 404(1) | 234(2) | −24(4) |
| $C_{(12)}$ | 2704(2) | 6163(4) | 1/4 | $H_{(16)}$ | 409(3) | 841(5) | 1/4 |
| $C_{(13)}$ | 3974(2) | 1986(3) | 1/4 | | | | |

The molecule is located in a special position, on a symmetry plane, which coincides with the plane of the heterocycle and the o-hydroxyphenyl substituent and bisects the N-phenyl substituent perpendicular to its plane. The insignificant differences in the bond distances and angles in IIA and 1,2,4-triazoles studied earlier [3-5] demonstrates the small dependence of the geometry of these heterocycles on the position and nature of the substituents [3]. The increase in the endocyclic angle at atom $N_{(4)}$ to 104.2(3)° which is small by comparison with angles of other 1,2,4-triazoles (equal to 101.4-103.2° [3-5]), is apparently explained by the participation of this atom in an intramolecular hydrogen bond (IMB) O—H...$N_{(4)}$ [distances O...$N_{(4)}$, 2.557(4); O—H, 0.82(3); H...$N_{(4)}$, 1.83(4) Å; angle O—H...$N_{(4)}$, 145(2)°].

The data obtained indicate a substantial effect of the IMB on the conformation of the molecule. The formation of a strong IMB causes a twisting of the o-hydroxyphenyl substituent into the plane of the triazole ring and gives a quasiaromatic character to the 6-membered ring thus formed. As a result the molecule becomes planar and all atoms lie in one plane,* coin-

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*In a difference map, the atom $H_{(0)}$ is divided into two "half-atoms," related by the symmetry plane (Table 2). However, the separation is small enough that the hydrogen bond formed is in fact planar.

ciding with the plane of symmetry (except for atoms $C_{(14)}$, $C_{(14')}$, $C_{(15)}$, and $C_{(15')}$ of the N-phenyl ring, which due to steric interactions with the o-hydroxyphenyl ring rotates by 90° around the $N_{(1)}$—$C_{(13)}$ bond). However, this rotation does not completely destroy the spatial difficulties arising from formation of a planar tricyclic system as reflected in the distorted exocyclic angles around atoms $N_{(1)}$ [$N_{(2)}N_{(1)}C_{(13)}$, 117.4(2)° and $C_{(5)}N_{(1)}C_{(13)}$, 132.7(2)°], $C_{(5)}$ [$N_{(4)}C_{(5)}C_{(6)}$, 122.4(2)° and $N_{(1)}C_{(5)}C_{(6)}$, 128.7(2)°], and $C_{(6)}$ [$C_{(5)}C_{(6)}$-$C_{(7)}$, 118.4(2)° and $C_{(5)}C_{(6)}C_{(11)}$, 123.9(2)°].

## EXPERIMENTAL

Crystals of IIA ($C_{15}H_{13}N_3O$) are rhombic, at 20°C: $a$ = 17.606(1), b = 10.252(1), c = 7.143(5) Å, V = 1289.3(2) Å$^3$, Z = 4, $d_{calc}$ = 1.30 g/cm$^3$, space group Pnam. Cell constants and intensities of 1098 independent reflections were measured on a Hilger—Watts automatic 4-circle diffractometer ($\lambda_{MoK_\alpha}$, 0/20 scanning, $2° \leq \theta \leq 30°$).

The structure was solved by direct methods using MULTAN and 758 independent reflections with $I \geq 2\sigma$ and was refined by block diagonal anisotropic least squares of 750 reflections with $|F| > 4\sigma$ using the weighting scheme $1/w = \sigma(F)^2 + (0.01F_{mea})^2$. Hydrogen atoms were located by temperature factors. Final agreement factors were R = 0.050 ($R_w$ = 0.051). All calculations were carried out on an IBM EKLIPS S/200 using programs INEXTL [6]. Atomic coordinates are given in Table 2.

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# SYNTHESIS OF 5-AMINO-1,2,3-THIADIAZOLE

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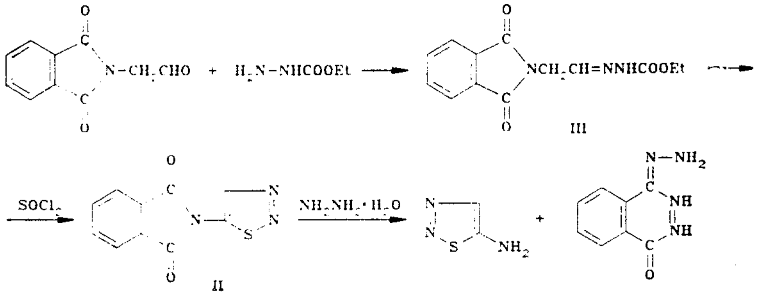
A convenient method is proposed for the synthesis of ethyl phthalimidoethylideneaminocarbamate, an intermediate in the synthesis of 5-amino-1,2,3-thiadiazole.

5-Amino-1,2,3-thiadiazole (I) is used as an intermediate in the synthesis of 1,2,3-thiadiazol-5-yl ureas having pesticidal action. One of the methods for the preparation of thiadiazole I is the reaction of ethoxycarbonylhydrazine with phthalimidoacetaldehyde, sub-



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