# The Crystal and Molecular Structure of 1-Phenyl-3-methyl-4-phenyl-hydrazono-pyrazole-5-thione

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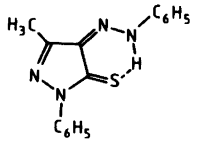
1-Phenyl-3-methyl-4-phenylhydrazono-pyrazole-5-thione is a potential reagent for nonferrous and noble metals[1-3] and in comparison with usual *o*-mercaptoarylazo compounds it has a remarkable stability against oxydation, caused by structural properties. $^1$H- and $^{13}$C–NMR investigations[1] favour the structure being the hydrazo form *1*; other authors[2] assume from UV and NMR data the azo form *2*. To determine these propositions an X-ray structure analysis was performed.

*Structure determination.* The synthesis of the compound has been described by Michaelis *et al.*[4] Suitable crystals could be prepared by slow crystallization from a solution with ethanol.[1] The X-ray measurements were carried out on a computer-controlled Enraf-Nonius CAD 4 diffractometer using graphite monochromatized Mo$K\alpha$ radiation ($\lambda$=0.71069 Å). The unit cell dimensions were determined by a least-squares calculation from the $2\theta$ values of 25 high order reflections measured at 20 °C.



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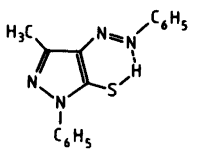

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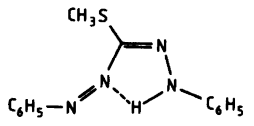

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*Table 1.* Atomic coordinates and equivalent isotropic temperature parameters $U_{eq}$ (Å$^2$·10$^4$) for non-hydrogen atoms. $U_{eq}$=1/3 ($U_{11}$+$U_{22}$+$U_{33}$).

| Atom | *X* | *Y* | *Z* | $U_{eq}$ |
|---|---|---|---|---|
| S | .04494(2) | .34117(12) | .17753(4) | 718(5) |
| N(1) | .11863(6) | .3299(3) | .05843(12) | 494(11) |
| N(2) | .12595(7) | .2865(3) | −.03421(12) | 552(13) |
| N(3) | .00088(7) | .2258(3) | −.03363(13) | 536(12) |
| N(4) | −.03119(7) | .2438(3) | .02798(14) | 559(13) |
| C(1) | .08387(9) | .2453(3) | −.07325(15) | 540(14) |
| C(2) | .04703(8) | .2597(3) | −.00872(15) | 500(13) |
| C(3) | .07101(8) | .3138(3) | .07742(15) | 498(13) |
| C(4) | .07706(15) | .1919(6) | −.17210(20) | 761(23) |
| C(5) | −.08078(9) | .2113(3) | .00304(17) | 545(15) |
| C(6) | −.09620(10) | .1419(4) | −.08188(18) | 619(17) |
| C(7) | −.14486(11) | .1102(4) | −.10180(21) | 723(20) |
| C(8) | −.17773(11) | .1497(5) | −.03787(25) | 755(21) |
| C(9) | −.16226(11) | .2186(4) | .04601(26) | 768(21) |
| C(10) | −.11335(10) | .2508(4) | .06802(21) | 679(19) |
| C(11) | .16008(8) | .3828(3) | .11504(16) | 509(14) |
| C(12) | .15645(10) | .4618(4) | .20047(18) | 619(17) |
| C(13) | .19775(10) | .5177(4) | .25173(21) | 693(19) |
| C(14) | .24275(10) | .4975(4) | .21810(23) | 698(20) |
| C(15) | .24628(10) | .4173(4) | .13372(23) | 724(20) |
| C(16) | .20580(9) | .3595(4) | .08197(20) | 636(17) |

0302-4377/84 $2.50

*Table 2.* Atomic coordinates and temperature parameters $U$ (Å$^2$) for the hydrogen atoms. The temperature factor is $\exp[-8\pi^2 U(\sin^2\theta/\lambda^2)]$. The $U$'s have been multiplied by $10^3$.

| Atom | $X$ | $Y$ | $Z$ | $U$ |
|---|---|---|---|---|
| H(1) | −.0156(9) | .283(3) | .0999(17) | 88(8) |
| H(41) | .1100(12) | .179(5) | −.1949(23) | 138(14) |
| H(42) | .0590(12) | .276(5) | −.2086(22) | 122(13) |
| H(43) | .0598(11) | .082(4) | −.1775(20) | 111(13) |
| H(6) | −.0761(9) | .108(4) | −.1228(16) | 87(10) |
| H(7) | −.1577(9) | .053(4) | −.1647(18) | 87(9) |
| H(8) | −.2091(9) | .135(4) | −.0530(17) | 85(9) |
| H(9) | −.1831(11) | .241(4) | .0908(19) | 110(12) |
| H(10) | −.1008(9) | .296(3) | .1298(18) | 84(9) |
| H(12) | .1253(8) | .478(3) | .2210(14) | 59(7) |
| H(13) | .1926(8) | .571(4) | .3097(17) | 77(9) |
| H(14) | .2698(8) | .536(3) | .2579(16) | 71(8) |
| H(15) | .2777(9) | .397(3) | .1074(16) | 79(8) |
| H(16) | .2070(9) | .308(3) | .0210(17) | 83(9) |

*Crystal data.* $C_{16}H_{14}N_4S$ F.W.=294.4 monoclinic, space group $C2/c$ red needles. $a$=27.642(6) Å, $b$=7.329(3) Å, $c$=14.528(3) Å, $\beta$=93.87(17)°, $V$=2936.5 Å$^3$, $D_c$=1.33 g cm$^{-3}$, $D_m$=1.35 g cm$^{-3}$ (flotation) $Z$=8, $\mu$=1.10 cm$^{-1}$ (Mo$K\alpha$).

Intensity data for 3138 reflections were collected at 20 °C within $2\theta \leq 55°$ by the $\omega-2\theta$ scan technique. After data reduction, including Lp-correction but no absorption correction, 2124 reflections with net intensity $I>2\sigma(I)$, were regarded as observed. The structure was solved by direct methods[5] (MULTAN). Structure refinement was carried out by means of CRYLSQ of the X-RAY 76 program system.[6] The hydrogen positions found from difference maps were included in the refinement and the final $R$-factor is 0.039.

Final coordinates and temperature parameters for the non-hydrogen atoms are listed in Table 1; for the hydrogen atoms in Table 2. Lists of structure factors and anisotropic thermal parameters are available on request from the authors (L.K.H.). Scattering factors given by Cromer and Mann were used for sulfur, nitrogen and carbon.[7] For hydrogen the scattering factor curve given by Stewart *et al.*[8] was used. The numbering of atoms is shown in Fig. 1.

*Discussion.* The molecular structure of the title compound is shown in Fig. 2. Bond lengths and angles are given in Tables 3 and 4. The structure

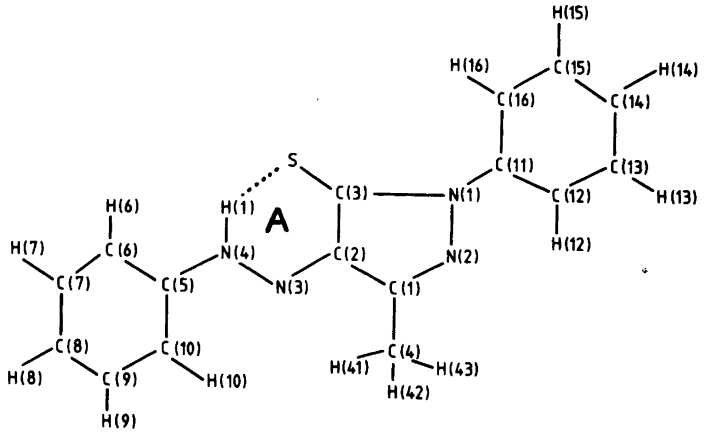


*Fig. 1.* The numbering of atoms in the molecule 1-Phenyl-3-methyl-4-phenylhydrazono-pyrazole-5-thione.

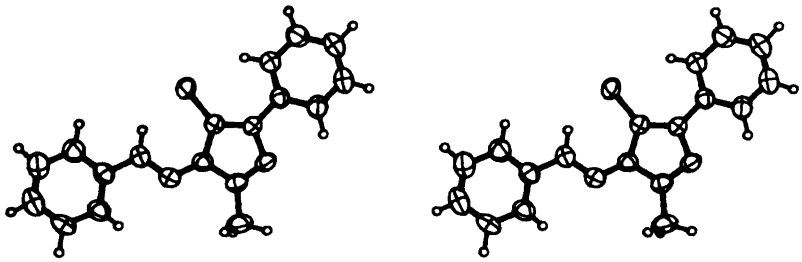

*Fig. 2.* The molecular structure of the title compound.

analysis proves unambiguously that the molecule exists in the hydrazo form *1*.

From a difference map the hydrogen atom H(1) could be localized. It is bonded to the nitrogen atom N(4) with a distance of 1.14 Å. In this way a six membered ring (ring A, *cf.* Fig. 1) including the atoms S, C(3), C(2), N(3), N(4) and H(1) is formed. The ring is nearly planar. The greatest deviations from a least-squares plane through the ring are found for the atoms C(3) with 0.025 Å and S with −0.022 Å. The intramolecular distance H(1)···S is 2.00 Å, the N(4)···S distance is 3.01 Å with an angle N(4)−H(1)···S=145°. In the similar ring system of monothiodibenzoylmethane[9] a S···H distance of 1.91 Å has been found.

For the single N(3)−N(4) bond (1.308 Å) a comparison with the same type of bond in *S*-methyldithizone (*3*) is very interesting.[10] In this compound values of 1.34 and 1.27 Å have been determined for the N−N single bond and the N−N double bond, respectively. The bond

*Table 3.* Bond lengths (Å) in 1-Phenyl-3-methyl-4-phenylhydrazono-pyrazole-5-thione.

| | |
|---|---|
| S−C(3) | 1.678(2) |
| N(1)−N(2) | 1.411(3) |
| N(1)−C(3) | 1.368(3) |
| N(1)−C(11) | 1.419(3) |
| N(2)−C(1) | 1.295(3) |
| N(3)−N(4) | 1.308(3) |
| N(3)−C(2) | 1.326(3) |
| N(4)−C(5) | 1.414(3) |
| C(1)−C(2) | 1.434(3) |
| C(1)−C(4) | 1.488(4) |
| C(2)−C(3) | 1.432(3) |
| C(5)−C(6) | 1.375(4) |
| C(5)−C(10) | 1.379(4) |
| C(6)−C(7) | 1.376(4) |
| C(7)−C(8) | 1.373(5) |
| C(8)−C(9) | 1.361(5) |
| C(9)−C(10) | 1.388(4) |
| C(11)−C(12) | 1.379(4) |
| C(11)−C(16) | 1.392(3) |
| C(12)−C(13) | 1.382(4) |
| C(13)−C(14) | 1.375(4) |
| C(14)−C(15) | 1.369(5) |
| C(15)−C(16) | 1.372(4) |

*Table 4.* Bond angles (°) in 1-Phenyl-3-methyl-4-phenylhydrazono-pyrazole-5-thione.

| | |
|---|---|
| S−C(3)−N(1) | 129.78(17) |
| S−C(3)−C(2) | 126.15(18) |
| N(2)−N(1)−C(3) | 112.02(17) |
| N(2)−N(1)−C(11) | 116.90(18) |
| N(1)−N(2)−C(1) | 106.73(19) |
| C(3)−N(1)−C(11) | 131.07(19) |
| N(1)−C(3)−C(2) | 104.03(19) |
| N(1)−C(11)−C(12) | 122.11(22) |
| N(1)−C(11)−C(16) | 118.87(22) |
| N(2)−C(1)−C(2) | 110.68(20) |
| N(2)−C(1)−C(4) | 122.37(26) |
| N(4)−C(3)−C(2) | 118.58(19) |
| N(3)−N(4)−C(5) | 119.84(20) |
| N(3)−C(2)−C(1) | 121.37(20) |
| N(3)−C(2)−C(3) | 132.10(22) |
| N(4)−C(5)−C(6) | 121.91(24) |
| N(4)−C(5)−C(10) | 117.10(23) |
| C(2)−C(1)−C(4) | 126.95(25) |
| C(1)−C(2)−C(3) | 106.52(20) |
| C(6)−C(5)−C(10) | 120.99(25) |
| C(5)−C(6)−C(7) | 119.36(27) |
| C(5)−C(10)−C(9) | 118.52(28) |
| C(6)−C(7)−C(8) | 120.26(28) |
| C(7)−C(8)−C(9) | 120.10(29) |
| C(8)−C(9)−C(10) | 120.76(30) |
| C(12)−C(11)−C(16) | 118.99(23) |
| C(11)−C(12)−C(13) | 120.10(26) |
| C(11)−C(16)−C(15) | 119.92(27) |
| C(12)−C(13)−C(14) | 120.72(29) |
| C(13)−C(14)−C(15) | 119.03(27) |
| C(14)−C(15)−C(16) | 121.22(28) |

lengths between the exocyclic N(3)–N(4)-group and the adjacent carbon atoms of phenyl ring C(5) and the pyrazole ring C(2) are significantly different. The bond length C(2)–N(3) is 1.326 Å and corresponds to a C–N double bond (expected value: 1.30 Å[11]). The C(5)–N(4) bond has a value of 1.414 Å and comes near to a single bond (expected value: 1.47 Å[11]). The same value for a single C–N bond has been found in the structure analysis of an *o*-mercaptoarylazo-compound (1.42 and 1.43 Å[12]).

The C(3)-S distance of 1.678 Å comes near to a C–S double bond (expected value : 1.61 Å[13]). The bond distances in ring A show that there is a considerable resonance over the ring. The pyrazole ring and the two phenyl rings are exactly planar. The greatest deviations from least squares planes through the rings are less than 0.01 Å.

The angles between the planes of the pyrazole ring and the phenyl rings (C(5) to C(10) and C(11) to C(16) are 7.4 and 11.9°, respectively. The pyrazole ring and ring A are nearly co-planar and form an angle of 1.6°. There are no intermolecular distances shorter than the van der Waals distances.

The structure determination confirms the conclusions from the NMR investigations by Hinsche *et al.*[1]

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