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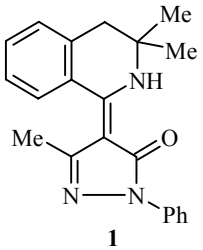
SYNTHESIS, CRYSTALLINE STRUCTURE, AND SPECTRA OF 3,3-DIMETHYL-1-(3-METHYL-1-PHENYLPYRAZOL-5-ONYLIDENE-4)-1,2,3,4-TETRAHYDROISOQUINOLINE

V. I. Sokol[1], O. A. Yakimenko[2], V. V. Davydov[2], Yu. V. Shklyaev[3], V. S. Sergienko[1], and M. A. Ryabov[2]

3,3-Dimethyl-1-(3-methyl-1-phenylpyrazol-5-onylidene-4)-1,2,3,4-tetrahydroisoquinoline has been synthesized and its crystalline and molecular structures determined. It was found by IR and electronic absorption spectroscopic methods that the structure of this compound is not changed in solutions.

Keywords: antipyrine derivatives, isoquinoline derivatives, crystalline structure, spectroscopic investigation.

3,3-Dimethyl-3,4-dihydro- and 3,3-dimethyl-1,2,3,4-tetrahydroisoquinoline derivatives [1, 2] as well as antipyrine (2,3-dimethyl-1-phenylpyrazol-5-one) and its 4-amino derivatives [3] are known for their pharmacological activity. In a search for novel, efficient preparations which affect hemostasis it was of interest to obtain a derivative of 3,3-dimethyl-3,4-dihydroisoquinoline which contained a pyrazolone fragment as the substituent in position 1. This work is concerned with the synthesis of 3,3-dimethyl-1-(3-methyl-1-phenylpyrazol-5-onylidene-4)-1,2,3,4-tetrahydroisoquinoline (**1**) and a study of its structure using X-ray structural analysis, IR, and electronic spectroscopy as well as quantum-chemical calculations using the PPP approximation.



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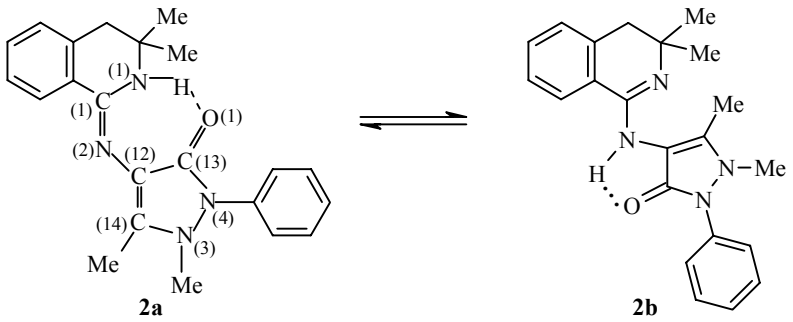
To some degree, compound **1** is an analog of the previously studied 3,3-dimethyl-1-N-(2,3-dimethyl-5-oxo-1-phenyl-3-pyrazolin-4-yl)imino-1,2,3,4-tetrahydroisoquinoline (**2**) [4]. The structural difference between the molecules **1** and **2** lies in the method of linking of the tetrahydroisoquinoline and pyrazolone fragments: in compound **1** they are directly bound by a C–C bond and in compound **2** *via* the bridging $N_{(2)}$ atom.

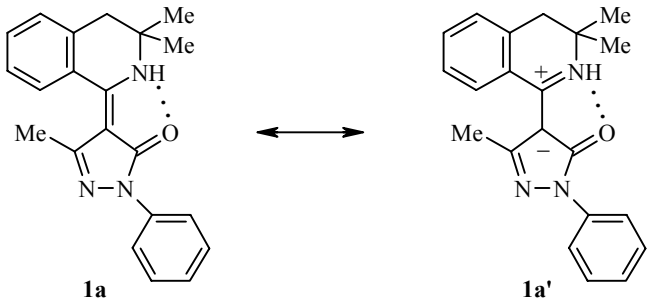
[1] N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow 117907, Russia; e-mail: sokol@ionchran.rinet.ru. [2] Russian University of Peoples' Friendship, Moscow 117198, Russia; e-mail: vdavidov@sci.pfu.edu.ru. [3] Institute of Technical Chemistry, Ural Section, Russian Academy of Sciences, Perm' 614000, Russia. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1696-1703, December, 2002. Original article submitted April 10, 2000.



This leads to a significant difference in the structures of the molecules **1** and **2**, although they have similar features also.

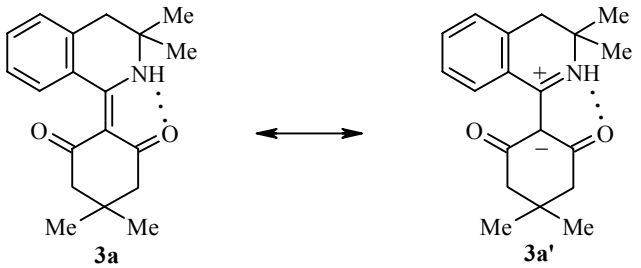
Like **2**, compound **1** crystallizes in the enamino ketone form **1a**, stabilized by the intramolecular $N_{(1)}$–$HN_{(1)}\cdots O_{(1)}$ hydrogen bond.

In both molecules **1** and **2** the "mobile" hydrogen atom is localized on the $N_{(1)}$ atom of the tetrahydroisoquinoline fragment. However, the nature of the distribution of π-electron density along the C–N and C–C bonds between the fragments differs markedly in the molecules **1** and **2**. In the molecule **1** a significant delocalization of the π-interaction is observed along the $N_{(1)}$–$C_{(1)}$–$C_{(12)}$ bonds and this leads one to consider the contribution of a saturated bipolar structure **1a'** to the structure of isomer **1a**.

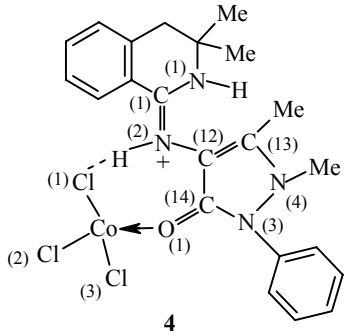


In fact, the $N_{(1)}$–$C_{(1)}$ bond length of 1.331(4) Å in compound **1** is intermediate between the lengths of a standard $N(sp^2)=C(sp^2)$ double bond (1.311-1.324, mean 1.316 Å) and an $N(sp^2)$–$C(sp^2)$ single bond (1.363-1.382, mean 1.371 Å) [5]. The exocyclic $C_{(1)}$–$C_{(12)}$ bond (1.409(4) Å) also corresponds not to a double but to a standard sesqui $C(sp^2)\approx C(sp^2)$ bond (1.380 Å).

A similar delocalization of the π-interaction along the $N_{(1)}$–$C_{(1)}$ and $C_{(1)}$–$C_{(12)}$ bonds not fitting the strict description of the structure of molecule **1** *via* the formula **1a** is seen to an even greater degree in the dimedone derivatives of 3,4-dihydroisoquinoline: 3,3-dimethyl-1-(4,4-dimethylcyclohexa-2,6-dion-1-ylidene)-1,2,3,4-tetrahydroisoquinoline (**3**) [6] and other derivatives. From the data for the seven structurally characterized compounds of this type [6-12] it is evident that the length of the intracyclic $N_{(1)}$–$C_{(1)}$ bond in the indicated compounds (1.289-1.319 Å) is typical for an $N(sp^2)=C(sp^2)$ double bond. The actual distance for the $C_{(1)}$–$C_{(12)}$ (1.435-1.470 Å) approximates not even to a sesquibond but to a single $C(sp^2)$–$C(sp^2)$ bond (1.463-1.480, mean 1.470 Å) [5]. Thus, in these cases, the shift from the "pure" enamino diketone form **3a** to the bipolar **3a'** is expressed to an even greater degree than for the structure **1**.



In compound **2**, similar deviations in the distribution of the π-electron density along the N–C bonds from isomer **2a** are not observed. The intracyclic $N_{(1)}$–$C_{(1)}$ bond (1.349 Å) is significantly longer than the exocyclic $N_{(2)}$–$C_{(12)}$ (1.290 Å). However, the protonation of molecule **2** at atom $N_{(2)}$ is achieved in the 1:1 acetone solvate of 3,3-dimethyl-1-{[N-(2,3-dimethyl-5-oxo-1-phenyl-Δ^3-pyrazolin-4-yl)]imino}-1,2,3,4-tetrahydro-isoquinolinium trichlorocobaltate (**4**) [13] and this results in a significant delocalization of π-electron density along the $N_{(1)}$–$C_{(1)}$ and $N_{(2)}$–$C_{(1)}$ bonds making both approximately equal. In structure **4**, compared with **2**, the $N_{(1)}$–$C_{(1)}$ bond is shortened by 0.034 Å to 1.315 Å while the $N_{(2)}$–$C_{(1)}$ bond is lengthened to the same degree (by 0.037 Å) to 1.327 Å.



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Thus in the structure **4**, as in the structures of **1** and dimedone derivatives of hydroisoquinoline, the effect of separating the charges in the molecule on the distribution of the π-electron interaction through the C–C and C–N bonds appears.

In the hydroisoquinoline fragment of structure **1**, as in other analogous compounds, the $N_{(1)}$–$C_{(9)}$ bond (1.477(4) Å) is significantly longer than $N_{(1)}$–$C_{(1)}$ bond (1.331(4) Å). The C–C bonds in this fragment have usual values and its conformation resembles that found in all other compounds of this type studied. The atoms $N_{(1)}$, $C_{(9)}$, and $O_{(1)}$ are displaced to one side from the plane of benzene ring and that of the atoms $C_{(1)}$ and $C_{(8)}$ conjugated to it (in the different compounds only the value of these shifts vary). In structure **1**, the $N_{(1)}$, $C_{(9)}$, and $O_{(1)}$ atoms deviate from the indicated plane by 0.529, 1.028, and 0.150 Å respectively.

As in compounds **2**, **3**, and **4**, in the molecule **1** an $N_{(1)}$–$HN_{(1)}\cdots O_{(1)}$ hydrogen bond exists between the hydroisoquinoline and pyrazolone fragments forming an almost planar six-membered pseudocycle. In its geometric parameters (N–H 0.88, N···O 2.649, O···H 1.90 Å. NHO angle 142°) this bond is similar to the H-bond in molecule **3** (in compounds **2** and **4** the formation of the intramolecular H-bond closes seven-membered rings). The participation of the oxygen atoms in the H-bond formation in compounds **1**, **2**, and **3** leads to some increase in the C=O distance (to 1.256(2), 1.232, and 1.236 Å respectively) when compared with the C=O distance in molecule **3** for the second carbonyl group which does not take part in hydrogen bonding (1.227 Å).

It should be noted that there are significant angular distortions at the points of contact of the hydroisoquinoline and pyrazolone fragments in the molecule **1** (the $C_{(1)}$ and $C_{(12)}$ atoms). In particular, we observed an increase in the value of the exocyclic angles $C_{(2)}C_{(1)}C_{(12)}$ 127.0(3)° and $C_{(1)}C_{(12)}C_{(13)}$ 134.7(3)°, possibly because of steric strain or the repulsion of the O and N(NH) atom unshared electron pairs.

Moreover, the linkages associated with the atoms $C_{(1)}$, $C_{(12)}$, $N_{(1)}$, and $N_{(3)}$ are almost planar: the sum of angles for them being 359.9, 359.8, 359.6, and 359.9° respectively.

The geometric parameters for the pyrazolone ring in structures **1** and **2** differ in agreement with the possible tautomeric forms (**1**, **1a**, and **2a**). In structure **2** the N–C bonds are equalized (1.391 and 1.395 Å) while in the molecule **1** they are significantly different: the bond $N_{(2)}$–$C_{(13)}$ being by 0.065 Å shorter than $N_{(3)}$–$C_{(14)}$ bond (respectively 1.311(4) and 1.376(4) Å). On the other hand, the C–C bonds ($C_{(12)}$–$C_{(13)}$ 1.436(4) and $C_{(12)}$–$C_{(14)}$ 1.442(4) Å) in structure **1** are equivalent while in the molecule **2** they differ by 0.114Å (1.335 and 1.449 Å). Hence in the structure **1** the double bond is localized between the atoms $N_{(2)}$=$C_{(13)}$ and in molecule **2** between the atoms $C_{(12)}$=$C_{(13)}$. The N–N distances in structures **1** and **2** are similar (1.399(4) and 1.406 Å respectively).

The $N_{(3)}$–$C_{(16)}$ bond between the pyrazolone and phenyl rings in compound **1** (1.417(4) Å) is somewhat longer than a standard C(sp^2)–N(sp^2) bond (1.380 Å) and close to the length of the analogous bond in structure **2** (1.423 Å). The phenyl ring lies in a plane almost parallel to the benzene ring of hydroisoquinoline (the angle between them being 1.5°). Relative to the plane of the pyrazolone ring, the phenyl ring is twisted by 33.6°. The angle between the mean $C_{(1)}$–$C_{(8)}$ planes of hydroisoquinoline and pyrazolone (35°) is close to that found in compound **3** (32°).

The IR spectra of polycrystalline samples of compound **1** (in KBr tablets or as suspensions in nujol) show the presence of an intramolecular N–H···O=C type H-bond which is characterized by a low-frequency shift of the strong ν (C=O) band to 1621 cm^{-1} region when compared with 1662 cm^{-1} in the spectrum of antipyrine [14]. The NH stretching vibrations appear as a broad (diffuse), low-intensity band in the region of approximately 3500-2700 cm^{-1}.

Six bands are observed for the stretching vibrations of the C=O, C=N, and C=C bands and for δ (NH) in the region of 1621-1500 cm^{-1} with maxima at 1621, 1604, 1594, 1561, 1521, and 1501 cm^{-1}.

In the electronic absorption spectrum of the polycrystalline sample the noted above π-conjugation between the three cyclic fragments of molecule **1** leads to the appearance of a band with maximum at 402 nm which is absent in the spectra of 1,3,3-trimethyl-3,4-dihydroisoquinoline and antipyrine [15, 16]. It should be noted that an analogous band is observed in the spectrum of compound **2** [4]. The observed spectroscopic parameters are the basis for a discussion of the structure of compound **1** in solutions.

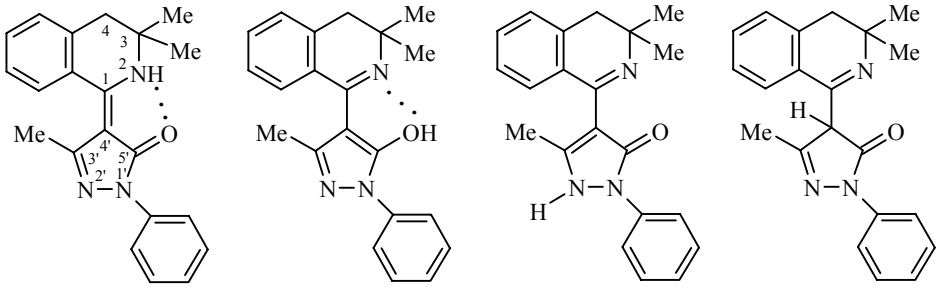
According to IR and electron spectroscopic data, the form **1a** of compound **1**, the conformation of the molecule, and the intramolecular H-bond that were found in the crystal of compound **1** are, as a whole, retained in solutions in aprotic solvents. In fact, in the IR spectrum of compound **1** in CCl_4 the position and the form of the ν (C=O) and ν (NH) bands are the same as in the spectra of the solid samples and are unchanged with dilution of the solution and this points to a retention of the intramolecular H-bond. In the electronic absorption spectrum of compound **1** in ethanol and in MeCN, the band characterizing the conjugation between the cyclic fragments of the molecule is preserved. An observed hypsochromic shift of this band when compared with the spectrum in the polycrystalline state (337 and 402 nm respectively) is due, as in compound **2**, to some decrease in the conjugation between hydroisoquinoline and antipyrine fragments of the molecule as a result of a decrease in their coplanarity.

The results of PPP type quantum-chemical calculations for the planar model of compound **1**, in which the atoms not containing π-electrons were absent, were in a satisfactory agreement with experimental data. Thus a calculation of the atomization energy ΔH_{at} for the series of possible isomers of compound **1** has shown that the maximum atomization energy is characteristic, in fact, of the enamino ketone isomer **1a**

Calculations have also confirmed the proposal stated above concerning the contribution of the bipolar structure **1a'** in the structure of compound **1**. The calculated overall π-charge values for the atoms of the tetrahydroisoquinoline ring amount to +0.52 e and on the atoms of the pyrazolone ring to -0.41 e. Electronic absorption spectra, calculated for the planar model of compound **1**, satisfactorily agree with experimental. In

TABLE 1. Bond Lengths (*d*) and Bond Angles (ω) in Structure **1**

Bond	*d*, Å	Angle	ω, deg	Angle	ω, deg
$O_{(1)}$–$C_{(14)}$	1.256(3)	$C_{(1)}$–$N_{(1)}$–$C_{(9)}$	125.4(3)	$O_{(1)}$–$C_{(14)}$–$C_{(12)}$	130.4(3)
$N_{(1)}$–$C_{(1)}$	1.331(4)	$C_{(13)}$–$N_{(2)}$–$N_{(3)}$	106.3(2)	$N_{(3)}$–$C_{(14)}$–$C_{(12)}$	104.8(3)
$N_{(1)}$–$C_{(9)}$	1.477(4)	$C_{(14)}$–$N_{(3)}$–$N_{(2)}$	112.2(2)	$C_{(17)}$–$C_{(16)}$–$C_{(21)}$	120.2(3)
$N_{(2)}$–$C_{(13)}$	1.311(4)	$C_{(14)}$–$N_{(3)}$–$C_{(16)}$	128.9(3)	$C_{(17)}$–$C_{(16)}$–$N_{(3)}$	121.1(3)
$N_{(2)}$–$N_{(3)}$	1.393(3)	$N_{(2)}$–$N_{(3)}$–$C_{(16)}$	118.8(2)	$C_{(21)}$–$C_{(16)}$–$N_{(3)}$	118.7(3)
$N_{(3)}$–$C_{(14)}$	1.376(4)	$N_{(1)}$–$C_{(1)}$–$C_{(12)}$	117.5(3)	$C_{(16)}$–$C_{(17)}$–$C_{(18)}$	119.2(3)
$N_{(3)}$–$C_{(16)}$	1.417(4)	$N_{(1)}$–$C_{(1)}$–$C_{(2)}$	115.4(3)	$C_{(19)}$–$C_{(18)}$–$C_{(17)}$	120.7(3)
$C_{(1)}$–$C_{(12)}$	1.409(4)	$C_{(12)}$–$C_{(1)}$–$C_{(2)}$	127.0(3)	$C_{(20)}$–$C_{(19)}$–$C_{(18)}$	119.7(3)
$C_{(12)}$–$C_{(13)}$	1.436(4)	$N_{(1)}$–$C_{(9)}$–$C_{(10)}$	105.8(2)	$C_{(19)}$–$C_{(20)}$–$C_{(21)}$	120.6(3)
$C_{(12)}$–$C_{(14)}$	1.442(4)	$N_{(1)}$–$C_{(9)}$–$C_{(11)}$	110.7(3)	$C_{(20)}$–$C_{(21)}$–$C_{(16)}$	119.6(6)
$C_{(16)}$–$C_{(17)}$	1.385(4)	$N_{(1)}$–$C_{(9)}$–$C_{(8)}$	106.3(2)		
$C_{(16)}$–$C_{(21)}$	1.386(4)	$C_{(1)}$–$C_{(12)}$–$C_{(13)}$	134.7(3)		
$C_{(17)}$–$C_{(18)}$	1.383(5)	$C_{(1)}$–$C_{(12)}$–$C_{(14)}$	120.2(3)		
$C_{(18)}$–$C_{(19)}$	1.381(5)	$C_{(13)}$–$C_{(12)}$–$C_{(14)}$	104.9(3)		
$C_{(19)}$–$C_{(20)}$	1.371(5)	$N_{(2)}$–$C_{(13)}$–$C_{(12)}$	111.6(3)		
$C_{(20)}$–$C_{(21)}$	1.382(5)	$N_{(2)}$–$C_{(13)}$–$C_{(15)}$	116.2(3)		
$N_{(1)}$–$H_{(1)}$–(N1)	0.88(5)	$O_{(1)}$–$C_{(14)}$–$N_{(3)}$	124.9(3)		



1a **1b** **1c** **1d**

particular, the long-wavelength bands are observed in the spectra at 400 and 330 nm and this agrees well with the conclusions made previously regarding the presence of the conjugation between the tetrahydroisoquinoline and pyrazolone fragments.

Hence the set of data obtained allows us to conclude that compound **1**, both in solutions and in the crystal, exists only in the form **1a**.

EXPERIMENTAL

IR spectra of the crystalline samples (in KBr tablets or as suspensions in nujol) or in CCl_4 solution at concentrations of 1×10^{-2} to 1×10^{-3} M were recorded on a Specord IR-75 spectrometer. Electronic absorption spectra of samples in the solid state (as suspensions in Nujol) and in solutions at concentrations of 5×10^{-5} to 1×10^{-3} M were obtained on a Specord UV-vis spectrophotometer. Quantum-chemical calculations were carried out using the PPP method with optimization of interatomic distances using a minimum of heats of atomization [17].

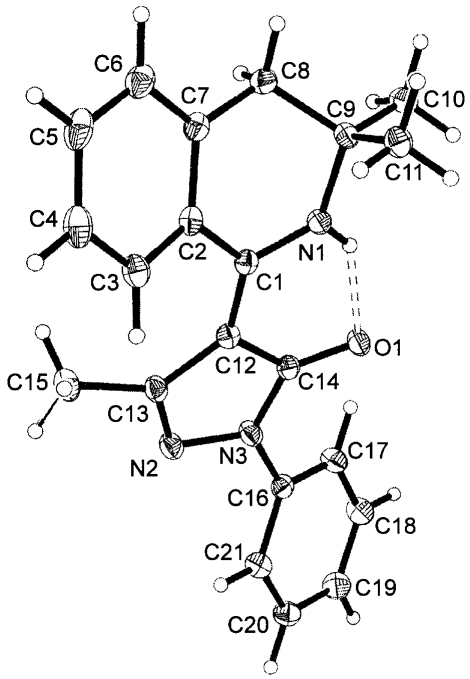


Fig. 1. Structure of molecule **1**.

X-ray Crystallographic Analysis. Crystals of compound **1**, $C_{21}H_{21}N_3O$ are obtained as light yellow colored prisms assigned to the monoclinic crystal system. The unit cell parameters are: a = 9.617(2), b = 9.810(2), c = 18.668(4) Å; β = 102.19(3)°; V = 1721.5(6) Å^3; $\rho_{(calc)}$ = 1.279 g/cm^3; μ_{Mo} = 0.80 cm^{-1}; F(000) = 704; M = 331.41; Z = 4; space group $P2_1/c$.

Experimental data were obtained for an edged crystal (0.48×0.45×0.32 mm) on an Enraf-Nonius CAD-4, automatic, four-circle diffractometer (MoKα radiation, graphite monochromator, ω-scanning, $2\theta_{max}$ = 55.8°). In all, 1713 reflections were recorded of which 1657 were independent (R_{int} = 0.016); in the calculations 1641 reflexes were used with I ≥ 2σ (I).

The structure was solved by a direct method (SHELXS-86 [18]) and refined by an F^2 least-squares method in the full-matrix, anisotropic approximation for non-hydrogen atoms (SHELX-93 [19]).

The $HN_{(1)}$ hydrogen atom was localized by difference Fourier synthesis and refined isotropically, the remaining H atoms being calculated geometrically and included in the refinement in fixed positions (U_j = 0.08 Å^2).

The final parameters for the refinement were: $R1$ = 0.045, ω$R2$ = 0.108, GOOF = 1.041 for 1641 reflections with $I \geq 2\sigma$ (I) (231 refined parameters), $R1$ = 0.048, ω$R2$ = 0.113 for all 1657 reflections. Extinction coefficient 0.006 (2), $\Delta\rho_{max}$ = 0.205, $\Delta\rho_{min}$ = 0.190 e·Å^{-3}.

Table 1 shows the bond lengths and bond angles for structure **1** and the numbering of the atoms is given in Fig. 1.

3,3,-Dimethyl-1-(3-methyl-1-phenylpyrazol-5-onylidene-4)-1,2,3,4-tetrahydroisoquinoline (1). Solution of 3,3-dimethyl-1-methylthio-3,4-dihydroisoquinoline (2.05 g, 10 mmol) and 1-phenyl-3-methylpyrazol-5-one (1.74 g, 10 mmol) in glacial acetic acid (10 ml) was heated for 3 h, the reaction mixture was poured into water (100 ml), and after 30 min it was filtered and the filtrate was alkalized to pH 7. The precipitate formed was separated, dried, and crystallized from a minimum amount of ethanol or ethyl acetate. Yield 62%. Found, %: C 76.00; H 6.25; N 12.40. $C_{21}H_{21}N_3O$. Calculated, %: C 76.10; H 6.39; N 12.68.

The monocrystals used for the X-ray analysis were obtained by crystallization of compound **1** from acetone.

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