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The structure of 1-phenyl-3-methyl-4-benzoylpyrazol-2-in-5-selenone and its derivatives

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Abstract

It is shown that 1-phenyl-3-methyl-4-benzoylpyrazol-2-in-5-selenone exists in a SeH-tautomeric form in the solid phase. Crystal and molecular structure of bis(1-phenyl-3-methyl-4-benzoylpyrazolyl-5)selenide as a supplementary product of the synthesis of selenopyrazolone and di(1-phenyl-3-methyl-4-benzoylselenopyrazolyl-5)diselenide as the product of oxidation of the latter were characterised by X-ray single crystal diffraction.

Keywords: Selenopyrazolones and pyrazolones; Tautomerism; X-ray single crystal diffraction

1. Introduction

Unlike a great number of publications devoted to synthesis, structure and reactivity of pyrazol-2-in-5-ones, widely used in pharmacology, dyeing industry, and in metal extracting processes, chemistry of their chalcogen containing analogues is hardly explored. Although the first representatives of thio and selenopyrazolones were synthesised by German chemists as far back as in the beginning of the century [1,2], their structure remained unknown until recently. There were only few publications concerning tautomerism, acid–base and other properties of chalcogenopyrazolones [3–8]. Judging by the results of our theoretical works [9–11], thio and selenopyrazolones must perceptibly differ from their oxygen analogues by the stability of their tautomeric forms and inclination to the processes of proton and electron transfer, etc. Experimental reliability of the theoretical predictions was recently confirmed by us for thiopyrazolones [12,13].

The aim of the present work was to study the structure of 1-phenyl-3-methyl-4-benzoylpyrazol-2-in-5-selenone (**I**), hereafter referred to as selenopyrazolone, in comparison with the structure of its oxo and thio analogues studied earlier [12,14–18]. First of all, we were interested in the stability of the tautomeric forms of selenopyrazolone (**I**) and the possibility of

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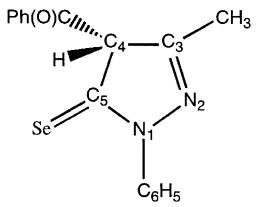
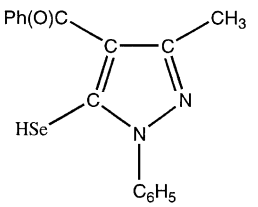
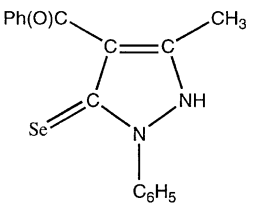


CH-(I)



SeH-(I)



NH-(I)

their stabilisation in various aggregation states due to intra- and intermolecular H-bonding, solvation effects, etc.

2. Experimental

2.1. General procedures

All the experiments were carried out in inert atmosphere of argon with the use of absolute solvents and freshly distilled reagents.

IR spectra were recorded on a Specord M80 spectrometer at intervals of 600–4000 cm^{-1} in the solid state (in Nujol) and in solutions (in chloroform, the concentration of substances was 0.1 mol/l, the thickness of cell was $d = 0.1 - 0.12$ mm). The measurement accuracy is ± 1 cm^{-1}.

^{1}H NMR spectra were obtained on a Unity-300 ('Varian') spectrometer at 300 MHz and 25°C with deuterochloroform taken as the internal standard.

Thin-layer chromatography was performed using Silufol UV-254 plates, processed in an iodide camera and fixed in water. Acetone–toluene 1:6 mixture was used as the eluent.

2.2. X-ray structure determination

The X-ray data for crystals (**II**) and (**III**) were collected on a CAD4 Enraf–Nonius automatic diffractometer at 20°C. The stability of the crystal and of experimental conditions was checked every 2 h using three control reflections, while the orientation was monitored every 200 reflections by centring three standards. Decay corrections were not necessary. Corrections for Lorentz and polarisation effects were applied. Twenty-five centred reflections were used to determine the unit cell dimensions.

Crystals (**II**), $C_{34}H_{26}N_4O_2Se_2$, $M = 680.53$, $F(000) = 1368$, orthorhombic, $a = 20.947(9)$, $b = 8.883(4)$, $c = 15.783(9)$ Å, $V = 2937(3)$ Å^3, $d_{calc.} = 1.54$ g/cm^3, $Z = 4$, space group *Pbcn* (a molecule in a special position on a 2 axis). A total of 4485 unique reflections were measured in the range $2° \le \theta \le 57°$ using graphite monochromated λ CuK_α radiation and $\omega/2\theta$-scan mode, of which 3952 were with $I < 3\sigma$. Empirical absorption correction was applied ($\mu Cu = 35.23$ cm^{-1}) based on ψ-scans using seven reflections with $\chi \ge 80°$.

Crystals (**III**), $C_{34}H_{26}N_4O_2Se$, $M = 601.57$, $F(000) = 1232$, triclinic, $a = 10.932(2)$, $b = 11.024(2)$, $c = 25.582(6)$ Å, $\alpha = 91.52(2)$, $\beta = 101.66(2)$, $\gamma = 106.32(2)°$, $V = 2886(1)$ Å^3, $d_{calc.} = 1.38$ g/cm^3, $Z = 4$, *P1*. A total of 8991 unique reflections were measured in the range of $2° \le \theta \le 26°$ using graphite monochromated λ MoK_α radiation and ω-scan mode, of which 3808 were with $I < 3\sigma$. Absorption correction was not necessary ($\mu Mo = 3.22$ cm^{-1}).

The structures were solved by direct methods and difference Fourier syntheses using SIR program [19] and MolEN package [20]. All non-hydrogen atoms were refined anisotropically; H-atoms, located in ΔF maps for both crystals, were included for the structure factor calculations with fixed positional and thermal parameters for crystal (**II**) and refined isotropically for crystal (**III**). The final agreement factors are $R = 0.047$, $R_w = 0.078$ for crystal (**II**) based on 3604 reflections with $F^2 \ge 3\sigma$ and $R = 0.043$, $R_w = 0.045$ for crystal (**III**) based on 4168 reflections with $F^2 \ge 3\sigma$.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC 151195 and 1511194 (**II** and **III**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk).

2.3. Syntheses

1-Phenyl-3-methyl-4-benzoyl-5-chloropyrazole was synthesised according to the method described in Ref. [21], followed by recrystallisation from ethanol. M.p. = 88–90°C (m.p. = 88°C), thin-layer chromatography, $R_f = 0.55$. IR (Nujol): ν (cm^{-1}) = 1625 (C=6;O); 1583, 1520 (C=6;C and C=6;N). ^1H NMR ($CDCl_3$): δ (ppm) = 2.36 (s, 3H, CH_3), 7.40–7.85 (m, 10H, C_6H_5).

1-Phenyl-3-methyl-4-benzoylpyrazol-2-in-5-selenone (**I**) was synthesised according to modified method outlined in Ref. [22].

In a round-bottom flask supplied with return refrigerator an alcohol solution of 4.35 g (0.015 mol) of 1-phenyl-3-methyl-4-benzoyl-5-chloropyrazole with the saturated alcohol solution of 3.5 g (0.03 mol) of potassium hydroselenide was heated for an hour. In the reaction, we used a double excess of KSeH in comparison with the stoichiometric quantity. Potassium hydroselenide, used as the selenation reagent, was obtained in situ by saturating bubbling of hydrogen selenide with a 20% alcohol solution of potassium hydrate. Hydrogen selenide was obtained by heating thoroughly mixed selenium, paraffin and asbestos in a round flask.

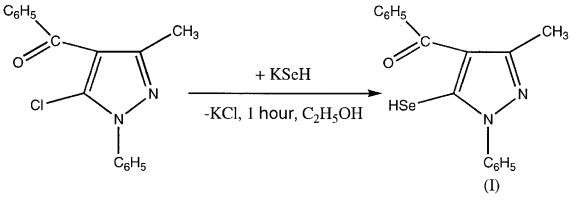
Reaction mixture was left over the night, filtered with precipitated potassium chloride and a transparent red filtrate was evacuated on a water-jet pump (without heating and in an inert atmosphere). Residue obtained after topping (evaporation) of ethanol was treated with water, the main part of the product being dissolved in water (it is a turbid solution A); and the insoluble part solidified as a bright-yellow oil (product B). Product B was dried and dissolved in ethanol. While cooling the ethanol solution a yellow crystalline sediment fell out, m.p. = 214–216°C, assigned to bis(1-phenyl-3-methyl-4-benzoylpyrazolyl-5)selenide (**III**). Found, %: C 67.95; H 5.11. Calculated for $C_{34}H_{26}N_4SeO_2$, %: C 67.89; H 4.36.

Solution A was filtered out from the impurities of solid yellow sediment. Yellow transparent filtrate (pH = 13) was acidified with a dilute solution of hydrochloric (muriatic) acid until the red sediment fell out. This sediment was then filtered, washed in water and dried. The product was purified twice by reprecipitation: red sediment was dissolved in an alkaline solution and slowly with intense mixing was acidified with a dilute solution of hydrochloric acid to pH = 1–2. We have thus obtained a bright-red powdered sediment of compound (**I**), m.p. = 94–96°C (m.p. = 96°C [22]). Yield 56%. Found, %: C 56.53; H 4.73. Calculated for $C_{17}H_{14}N_2OSe$, %: C 59.82; H 4.11.

With the recrystallisation of 1-phenyl-3-methyl-4-benzoylpyrazol-2-in-5-selenone (**I**) from ethanol di(1-phenyl-3-methyl-4-benzoylselenopyrazolyl-5)diselenide (**II**) is isolated as a red crystal, m.p. = 139–140°C (m.p. = 141°C [22]).

3. Results and discussion

Selenopyrazolone (**I**) was obtained by following a modified method [22] described in Section 2 by the reaction of potassium hydroselenide and 1-phenyl-3-methyl-4-benzoyl-5-chloropyrazole in an alcohol solution:



(I)

Compound (**I**) isolated from the reaction mixture was a bright-red powdered sediment, which was further purified by the reprecipitation of alkaline solutions with dilute hydrochloric acid. In IR spectra of compound (**I**) in Nujol there are narrow intense absorption bands at 1648 and 1628 cm^{-1}, assigned to the carbonyl group of the benzoyl substituent; bands in the range of 1600 and 1502 cm^{-1} are characteristic of phenyl groups; at 1580 and 1550 cm^{-1} — signals of the pyrazole ring; and additionally a broad weak absorption band of the SeH-group in the range of 2450 cm^{-1}. The bands of stretching vibrations of NH-group in the range of ~2550 cm^{-1}, characteristic of the NH tautomeric forms of the known pyrazolones and thiopyrazolones, were absent in IR spectra.

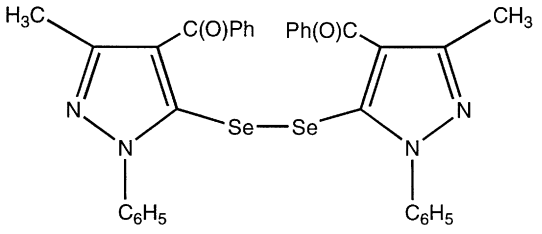
The set of obtained spectral characteristics allowed us to assign the structure of SeH-tautomeric form to the obtained compound apparently stabilised by weak intramolecular hydrogen bond with the carbonyl group of benzoyl substituents, as evident from the

formation of a band in the range of 2450 cm^{-1} (ν_{Se-H}). Probably two signals of the carbonyl group in IR spectra belong to different conformers like it was observed in the solid phase for oxo and thioanalogues in their XH-forms [12,16–18].

Unfortunately, numerous attempts to obtain single crystals of selenopyrazolone (**I**) suitable for X-ray structure determination were not successful. The product of oxidation of selenopyrazolone (**I**) — di(1-phenyl-3-methyl-4-benzoylselenopyrazolyl-5) diselenide (**II**) was obtained from different solvents, while accomplishing the purification in darkness and blowing by argon. The structure of the latter was proved by X-ray single crystal diffraction and IR spectroscopy.

The analysis of solutions of compound (**I**) revealed the presence of compound (**I**) as well as of compound (**II**). Therefore, in the ^1H NMR spectrum of deuterochloroform there are: two signals of methyl groups — 1.97 ppm (**I**) and 2.21 ppm (**II**); no signals of a proton at the saturated carbon C_4 (~3.50 ppm); and a low-field signal of a proton at the N_2 atom indicative of the CH- and (or) NH-tautomeric forms of compound (**I**). In the IR spectrum in chloroform, there is a strong band at the carbonyl group at 1650 cm^{-1}, two bands at 1600 and 1502 cm^{-1} assigned to $\nu_{C=C}$ of the aromatic ring and the bands characteristic of enol forms of pyrazolones (1580, 1550 for $\nu_{C=C}$, $\nu_{C=N}$, respectively), as well as weak broad band ν_{Se-H} in the range of 2400–2440 cm^{-1}. In the thin layer chromatography, there are two spots with $R_f = 0.58$ (**I**) and $R_f = 0.36$ (**II**).

The molecule of diselenide (Fig. 1) consists of two identical parts as the molecule is in a special position on a 2 axis ($-x$, y, 1/2-z):

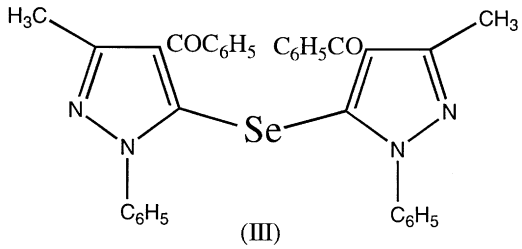


(II)

The torsion angle along the central Se–Se bond is equal to −64.1(1)° in contrast to orthogonal conformations observed in disulfides and in dialkyl or diaryldiselenides. The pyrazole cycles in the molecule are planar within 0.006 Å, and the phenyl group is twisted from the pyrazole plane by 60.8(2)°. The benzoyl group is not planar with the dihedral angle between the phenyl plane and carbonyl group equal to 34.3(4)°. The carbonyl group is *syn* to the selenium atom, and such orientation results in a short non-covalent contact O13···Se1 3.122(2) Å. The possibility of the Se···O attractive interaction in selenoiminoquinones was shown by Barton et al. [23]. In diselenide (**II**), this interaction is weaker, but it is still attractive, as we can judge by the geometry of the Se1–C5C4–C13–Ph fragment.

The geometry of the heterocyclic fragment is similar to that of the structure of bis(pyrazolyl)selenide (**III**) to be discussed further.

Besides the main product in synthesis of selenopyrazolone (**I**) a supplementary product was obtained, which is bis(1-phenyl-3-methyl-4-benzoylpyrazolyl-5)selenide (**III**) according to X-ray single crystal diffraction and IR and ^1H NMR spectroscopy:



(III)

In the IR spectrum of compound (**III**) in Nujol there are narrow strong absorption bands in the range of 1640 cm^{-1} ($\nu_{C=O}$), 1596 and 1504 cm^{-1} ($\nu_{C=C\ arom}$), 1578 cm^{-1}

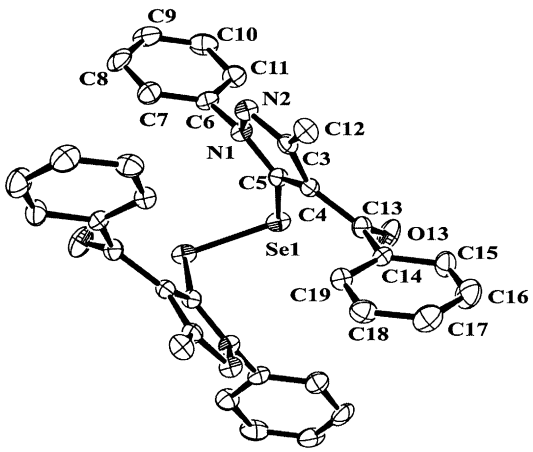


Fig. 1. Molecular structure of and di(1-phenyl-3-methyl-4-benzoyl-selenopyrazolyl-5)diselenide (**II**).

($\nu_{C=C}$). There is a singlet of methyl protons at 2.05 ppm and a multiplet of phenyl protons at 7.26–7.60 ppm.

Selenide (**III**) has two independent molecules in an asymmetric part of the unit cell; both molecules have similar conformations with *anti*-orientation of the carbonyl groups respective to the selenium atom (Fig. 2) unlike the *syn*-orientation in the molecule of diselenide (**II**). All pyrazole and aromatic cycles in selenide (**III**) are planar within 0.01 Å and the sums of the valence angles at N1 atoms are not smaller than 359.9°. Phenyl groups at N1 atoms are twisted by 42.8(3)–61.5(4)°, these deviations from the pyrazole plane are naturally larger than in a molecule of 1-Ph–3-Me–4–PhC(O)-thiopyrazolone (**IV**) (−42.7°) and in its oxygen analogue (**V**) (30.6 and 35.2° in two conformers).

In both the independent molecules of selenide (**III**) the selenium atoms are symmetrically shielded by phenyl groups of the benzoyl substituents, the corresponding C…Se contacts being equal to 3.097(7)–3.235(6) Å, which is significantly shorter than the sum of the Van der Waals radii of carbon and selenium (Fig. 2).

The formation of selenide (**III**) can be explained by the formation of K_2Se salt in the reaction mixture when obtaining potassium hydroselenide. The interaction of the latter with 1-phenyl-3-methyl-4-benzoyl-5-chloropyrazole led to bispyrazolylselenide (**III**) formation.

Diselenide (**II**) and selenide (**III**) are derivatives of the enol tautomeric form (SeH) which is the most stable in the crystalline phase like the corresponding enol form (SH) of 1-phenyl-3-methyl-4-benzoylpyrazol-2-in-5-thione (**IV**). It predominates in solutions of thiopyrazolone (**IV**) [12]. All three tautomeric forms [12,13,16–18,24] were obtained for the oxoanalogue 1-phenyl-3-methyl-4-benzoylpyrazol-2-in-5-one (**V**) in the crystalline phase. In solutions of pyrazolone (**V**) mainly OH- and NH-forms are realised depending on solvents [13–15], the enol (OH) form being stabilised exclusively by the intramolecular hydrogen bonding and the keton (NH) form by the intermolecular hydrogen bonds with the participation of the solvent. Apparently keto-forms (CH- and NH-) of chalcogenopyrazolones are less stable because of the lower energy of C=S and C=Se bonds in comparison with the C=O bond [25]. The only selenopyrazolones of the keto type with a mobile hydrogen characterised reliably are the 1-phenyl-3-methyl-4-aminomethyleneheteropyrazolones [3,5–8], stabilised

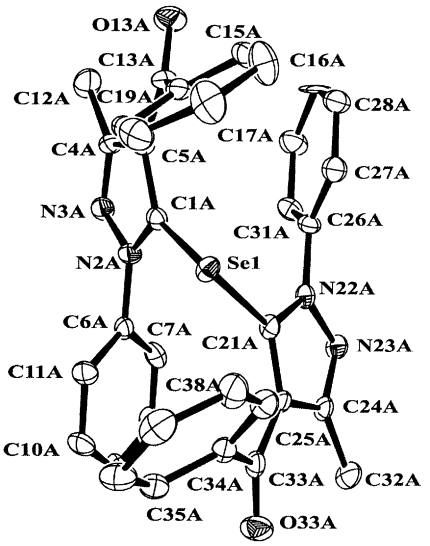
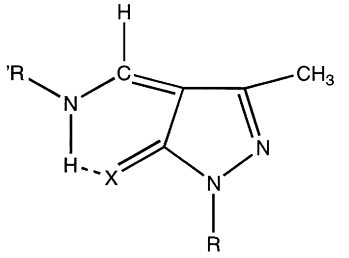


Fig. 2. Molecular structure of bis(1-phenyl-3-methyl-4-benzoylpyrazolyl-5)selenide (**III**).

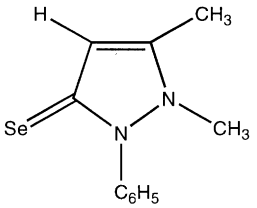
by strong N–H…X hydrogen bonds



X = S, Se;
R = C_6H_5, CH_3;
R' = H, CH_3, C_2H_5, iso-C_3H_7 tert-C_4H_9, C_6H_5 etc.

We also tried to synthesise 1-phenyl-3-methylpyrazol-2-in-5-selenone (**VI**) to estimate the stability of its tautomeric forms in the absence of the 4-benzoyl substituent stabilising the SeH-form. For the synthesis of selenopyrazolone (**VI**), we used the above mentioned method — the treatment of 1-phenyl-3-methyl-5-chloropyrazole by potassium hydroselenide and the transformation of the carbonyl group into the selenocarbonyl group with the help of phenylselenophosphonic dichloride [$PhP(Se)Cl_2$] [26,27]. In spite of numerous attempts to change the reaction conditions, varying the reagent ratio, carrying out

experiments in darkness and in an inert atmosphere we did not succeed in isolating the desirable product. Elementary selenium was always precipitated from the reaction mixture. Apparently the instability of compound (**VI**) is connected with the presence of two 'acidic' hydrogen atoms in position 4. This supposition seems reasonable because selenopyrine (**VII**), which has no mobile hydrogen atoms is a stable compound [2]:



(VII)

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