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Short Note

3-Methyl-1-phenyl-4-thioacetylpyrazol-5-one

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Abstract: The novel compound 3-methyl-1-phenyl-4-thioacetylpyrazol-5-one is obtained in excellent yield via a thionation of the corresponding oxygen analogue. The product is isolated in pure form using column chromatography and is characterised using 1D and 2D NMR experiments, ATR IR and HRMS spectra, and single-crystal XRD.

Keywords: 3-methyl-1-phenyl-4-thioacetylpyrazol-5-one; acylpyrazolone; NMR; single-crystal XRD

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1. Introduction

The isolation and separation of metal ions, especially critical ones, both from natural raw materials and from industrial waste, are among the main priorities of the world economy [1–3]. One of the most powerful tools in this direction is extraction processes [4–12]. The correct selection of ligands for each specific object is a major factor in achieving high efficiency and, therefore, the efforts of a huge number of scientific groups are directed towards the development of new effective organic molecules [13–18]. β-Dicarbonyl compounds are amongst the most widely used chelating extractants due to their excellent coordination properties [19–24]. A leading role inside the group belongs to acylpyrazolones because of the remarkable effectiveness displayed [25–30]. From the other side, sulphur-containing ligands possess spectacular coordination abilities [31–34] with extraordinarily broad applications [35–43].

As a part of our study on the development of effective ligands for metal isolation and separation [44–50], we focused our efforts towards the preparation of sulphur analogues of acylpyrazolones. The direct thioacylation is restricted by the very limited variety of reagents available on the market. However, numerous protocols for the direct construction of thioligands and for oxygen replacement in already-built molecules are developed [51–54], with the use of Lawesson's reagent being amongst the most exploited in the latter [55–61]. Thiopyrazolones, in particular, are very poorly studied. To the best of our knowledge, there are only a few records in the literature including the C-thionation of pyrazolones [62], oxygen replacement leading to thiopyrazolones [63–66], and the preparation of thioacetyl pyrazolones through the direct acylation of a pyrazolone [67] or the thionation of 4-benzoyl-5-chloro-pyrazole [63].

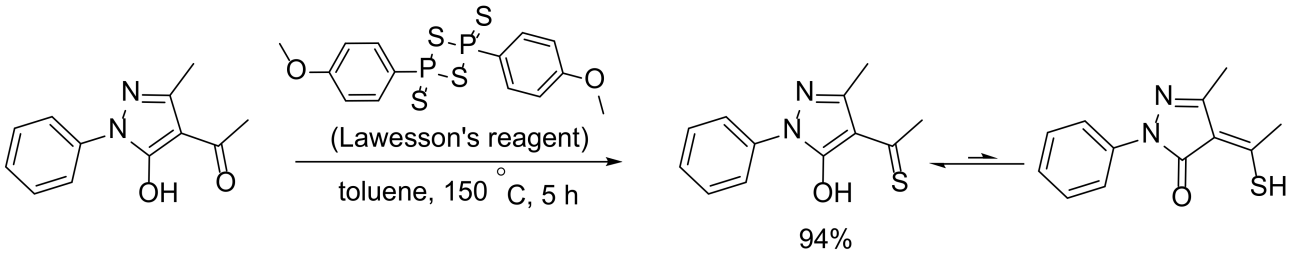
Herein, we report on the synthesis of a novel ligand, 3-methyl-1-phenyl-4-thioacetylpyrazol-2-one, and its characterization with NMR and HRMS spectra in solution and by an ATR IR spectrum and single-crystal XRD in the solid state.

2. Results and Discussion

2.1. Synthesis

The novel compound 3-methyl-1-phenyl-4-thioacetylpyrazol-5-one was obtained via the thionation of the corresponding acylpyrazolone, as shown in Scheme 1. The replacement of the acyl group oxygen by sulphur was carried out by using Lawesson's reagent.

The solvent, temperature, reaction prolongation, and reagent proportions were varied and the best conversion was obtained in toluene at 150 °C in a closed vessel. The pure product was isolated using column chromatography in 94% yield. It has to be noted that the monothionated compound was the only reaction product even when the transformation was performed by using an equimolar reagens ratio. The latter indicates that the tautomeric hydroxyl oxygen in 4-acetyl-3-methyl-1-phenyl-pyrazol-5-one cannot be replaced by sulphur in these particular conditions.



Scheme 1. Synthesis of 3-methyl-1-phenyl-4-thioacetylpyrazol-5-one.

The structure of the product was assigned using 1D and 2D NMR spectra (see Supporting Information). The ^{1}H spectrum in $CDCl_3$ showed characteristic signals for a phenyl group, two singlets for methyl groups, and a singlet for tautomeric OH in the low field. The ^{13}C spectrum displayed signals for a phenyl group CH, two methyl groups, and five quaternary carbons. The latter were assigned by analysing the specific correlations in the HMBC experiment, namely, C_q-4, i-Ph, C_q-3, C_q-5, and *C*=S at 114.75, 137.04, 147.06, 160.59, and 216.85 ppm, respectively. The assignment of the signals for both methyl groups, CH_3-3 at 2.563 and 17.48 and CH_3-CS at 2.946 and 36.34 ppm, was based on the observed CH_3-3/C_q-3, CH_3-3/C_q-4, CH_3-CS/C_q-4, and CH_3-CS/*C*=S interactions. The structure of the product was confirmed using a high-resolution electrospray mass spectrum.

2.2. Crystallography

The synthesized 3-methyl-1-phenyl-4-thioacetylpyrazol-5-one crystallized as orange-coloured crystals in a block shape, obtained using slow evaporation from iso-propanol. The title compound crystallized in the monoclinic *C2/c* space group with cell parameters a = 17.9610 (6) Å, b = 4.9709 (2) Å, c = 26.2901 (8) Å and β = 102.357 (2)° (Table S1). The unit cell contained a total of eight molecules (Z = 8, Z′ = 1), occupying a volume of 2292.86 (14) Å^3. A close inspection of the molecular features of the 3-methyl-1-phenyl-4-thioacetylpyrazol-5-one molecule revealed that it was almost planar with an RMSD of 0.035 Å, i.e., the conjugation was extremely pronounced (Figure 1). The planarity and molecular geometry were further stabilized by two intramolecular interactions (Table S2) C10-H10 ... O1 and O1-H1 ... S1. The three-dimensional packing of the 3-methyl-1-phenyl-4-thioacetylpyrazol-5-one molecules was stabilized by CH_3 ... π and C-H ... S interactions (Figure 2).

A search in the CSD (2022.3) for the thioacetylpyrazol-5-one moiety disclosed one similar structure (OCEGEJ, private communication), namely 3-methyl-1-phenyl-4-thiobenzoylpyrazol-5-one. The bond length values S1–C6, C5–O1, C4–C5, C4–C6, and C3–C4, of OCEGEJ and the title compound were comparable: 1.680 vs. 1.662 (2); 1.312 vs. 1.315 (2); 1.409 vs. 1.407 (3); 1.412 vs. 1.412 (3); and 1.443 vs. 1.437 (3) Å, respectively. The observed CS bond length in similar compounds is usually longer, e.g., 1.729 and 1.724 Å for UZIYIN and EZIXOC, respectively.

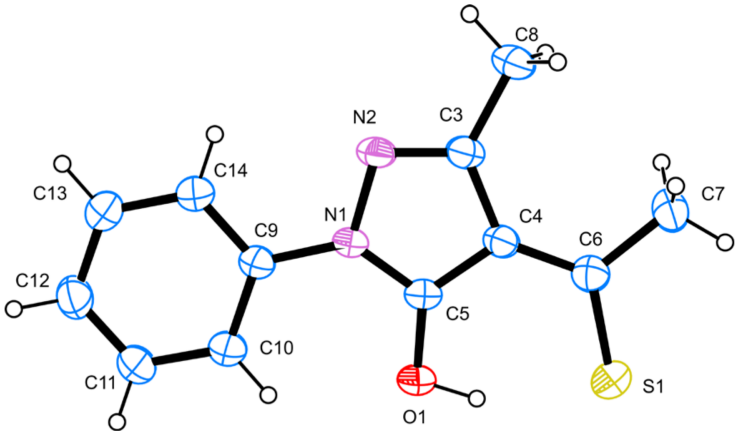


Figure 1. A representation of the 3-methyl-1-phenyl-4-thioacetylpyrazol-5-one molecule present in the asymmetric unit with employed numbering scheme; atomic displacement parameters (ADP) are at 50%, and hydrogen atoms are shown as small spheres with arbitrary radii.

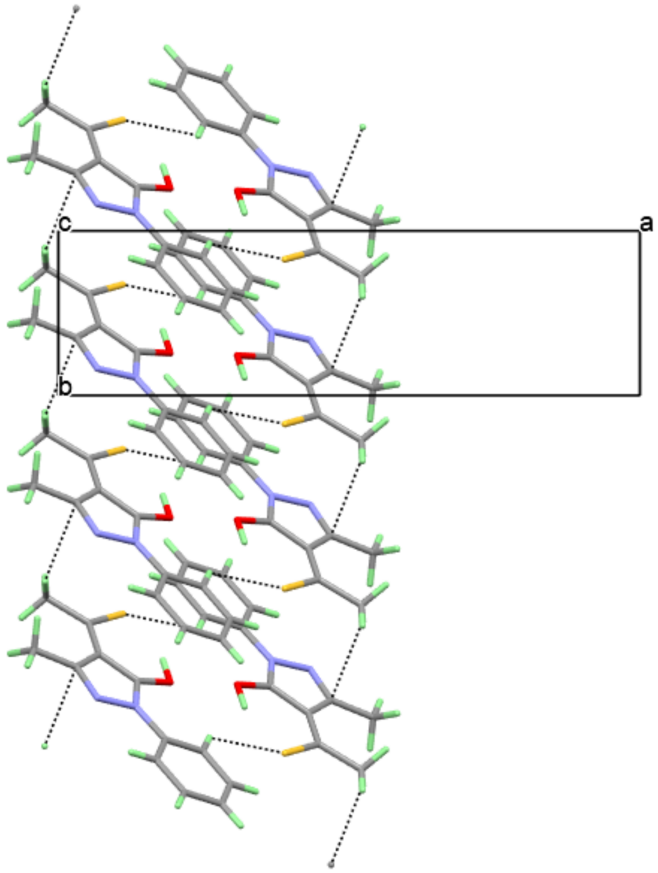


Figure 2. Observed weak C-H3 ... π, C-H2 and C-H ... S interactions which stabilize the crystal packing of 3-methyl-1-phenyl-4-thioacetylpyrazol-5-one.

3. Materials and Methods

3.1. General

All reagents were purchased from Aldrich, Merck, and Fluka and were used without any further purification. The deuterated chloroform was purchased from Deutero GmbH (Kastellaun, Germany). Fluka silica gel (TLC-cards 60778 with fluorescent indicator 254 nm) plates were used for TLC chromatography and R_f-value determination. Merck Silica gel 60 (0.040–0.063 mm) was used for the flash chromatography purification of the

product. The melting point was determined in a capillary tube on an SRS MPA100 OptiMelt (Sunnyvale, CA, USA) automated melting point system with a heating rate of 1 °C per min. The NMR spectra were recorded on a Bruker Avance NEO 400 spectrometer (Rheinstetten, Germany) in $CDCl_3$; the chemical shifts were quoted in ppm in δ-values against tetramethylsilane (TMS) as an internal standard and the coupling constants were calculated in Hz. The assignment of the signals was confirmed by applying two-dimensional HSQC and HMBC techniques. The spectra were processed with the Topspin 3.6.3 program. The IR spectrum was measured on a Shimadzu IR Spirit FT-IR spectrometer (Shimadzu Corporation, Columbia, MD, USA) using QATR-S as a single-reflection ATR measurement attachment. The mass spectrum was recorded in positive mode on Q Exactive Plus Hybrid Quadrupole-Orbitrap Mass Spectrometer Thermo Scientific (ESI HR-MS) The spectrum was processed with the Xcalibur Free Style program version 4.5 (Thermo Fisher Scientific Inc., Waltham, MA, USA).

3.2. Synthesis of 3-methyl-1-phenyl-4-thioacetylpyrazol-5-one

A solution of 3-methyl-1-phenyl-4-acetylpyrazol-5-one (2 mmol) and Lawesson's reagent (1 mmol) in toluene (15 mL) was stirred at 150 °C in a closed vessel for 5 h. The solvent was evaporated in vacuo and the crude product was purified using column chromatography on silica gel by using DCM as a mobile phase to give the pure product: 94% yield; R_f 0.67 (1% acetone in DCM); orange solid; m. p. 61.8–62.1 °C; ^{1}H NMR 2.563 (s, 3H, CH_3-3), 2.946 (s, 3H, CH_3-CS), 7.326 (t, 1H, J 7.3, p-Ph), 7.471 (dd, 2H, J 7.7, 7.4, m-Ph), 7.848 (d, 2H, J 7.7, o-Ph), 14.440 (s, 1H, OH); ^{13}C NMR 17.48 (CH_3-3), 36.34 (CH_3-CS), 114.75 (C_q-4), 121.41 (o-Ph), 127.11 (p-Ph), 129.14 (m-Ph), 137.04 (i-Ph), 147.06 (C_q-3), 160.59 (C_q-5), 216.85 (*C*=S); IR (ATR) 1592, 1563, 1522, 1483, 1456, 1406, 1386, 1359, 1328, 1117, 1041, 1028, 1013, 871, 824, 776, 750, 705, 683, 606, 505 cm^{-1}; HRMS (ESI^+) *m*/*z* calcd. for $C_{12}H_{13}N_2OS^+$ $[M + H]^+$ 233.0743, found 233.0741, Δ = −0.2 mDa.

3.3. Crystallography

Orange-coloured crystal blocks from the titled compound were obtained through recrystallization from iso-propanol. A suitable crystal with an appropriate size (0.25 × 0.2 × 0.1 mm^3) was mounted on a nylon loop using cryoprotective Paratone oil. Diffraction data were collected on a Bruker D8 Venture diffractometer equipped with a IμS micro-focus sealed X-ray source (MoKα radiation, λ = 0.71073 Å) and a PHOTON II CPAD detector. Diffraction data were processed in the APEX4 software package [68]; the peaks were integrated with the Bruker SAINT software (ver. 2016/2) [69] using a narrow-frame algorithm. The intensities were scaled and the data were corrected for absorption effects using the multi-scan method (SADABS) [69]. The structure was solved with the intrinsic phasing method and refined with the full-matrix least-squares method on F^2 (ShelxT and ShelxL program packages [70,71]) using OLEX—ver. 1.5 software [72]. All non-hydrogen atoms were located successfully from the Fourier map and were refined anisotropically. The hydroxyl hydrogen atom (H1) was located from the Fourier map and refined isotropically. The remaining hydrogen atoms were placed on calculated positions riding on the parent carbon atoms using the following scheme: Ueq = 1.2 for $C\text{-}H_{aromatic}$ = 0.93 Å and $C\text{-}H_{methyl}$ = 0.96 Å. ORTEP-3v2 software [73] was used to illustrate the molecule present in the asymmetric unit. A three-dimensional packing visualization of the molecules was made using CCDC Mercury [74]. The most important data collection and crystallographic refinement parameters for 3-methyl-1-phenyl-4-thioacetylpyrazol-5-one are given in Table S1. Complete crystallographic data for the reported structure have been deposited in the CIF format with the Cambridge Crystallographic Data Center as 2239465. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, deposited on 2 February 2023 (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +441223336033; E-mail: depos-it@ccdc.cam.ac.uk).

4. Conclusions

3-Methyl-1-phenyl-4-thioacetylpyrazol-5-one was obtained in excellent yield through the thionation of the corresponding acylpyrazolone by using Lawesson's reagent. It was found that only acetyl oxygen was replaced by sulphur regardless of the reagent's proportions. The product was isolated with column chromatography and characterized with 1D and 2D NMR, IR, and HRMS spectra. The single-crystal XRD revealed that 3-methyl-1-phenyl-4-thioacetylpyrazol-2-one crystallized in the monoclinic C2/c space group.

Supplementary Materials: ^{13}C, HSQC and HMBC NMR, ATR IR and ESI HR-MS spectra, Tables S1 and S2, CIF and checkcif report for the title compound.

Author Contributions: The synthetic experiments and NMR analyses were carried out by V.K. The ESI HR-MS spectrum was conducted by Z.P. The single-crystal XRD was performed by R.R. and B.S. All authors contributed to the discussion of the results and to writing the manuscript. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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