

Short Note

1-(2,4-Dinitrophenyl)-2-((Z)-2-((E)-4-fluorobenzylidene)-3,4-dihydronaphthalen-1(2H)-ylidene)hydrazine

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Abstract: The reaction of (*E*)-2-(4-fluorobenzylidene)-3,4-dihydronaphthalen-1(2*H*)-one and (2,4-dinitrophenyl)hydrazine in boiling ethanol containing hydrochloric acid (0.2 mL; 37%) for 1.5 h gave 1-(2,4-dinitrophenyl)-2-((*Z*)-2-((*E*)-4-fluorobenzylidene)-3,4-dihydronaphthalen-1(2*H*)-ylidene)hydrazine in a 90% yield. Various spectral analyses, including NMR, and X-ray crystallography established the structure of the newly synthesized hydrazone.

Keywords: 3,4-dihydronaphthalen-1(2*H*)-one; chalcones; hydrazones; X-ray crystal structure; heterocycles; synthesis



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1. Introduction

Hydrazones and their derivatives are significantly important compounds in the pharmaceutical industry. They show activities against various conditions such as inflammation, leishmaniasis, cancer, and Alzheimer's [1–4]. Hydrazone derivatives are used as drugs in the treatment of illnesses (e.g., leprosy, tuberculosis, and mental disorders) and as fungicides [5,6]. The use of hydrazones enables improvement in drug delivery through site-specific drug release, including to areas such as tumor tissue or thrombosis [7–9].

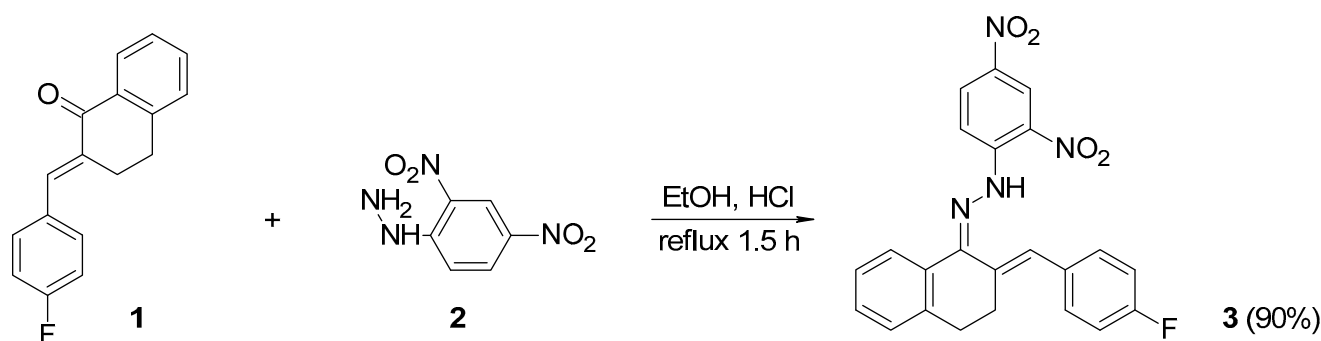
Substituted hydrazones also possess properties that make them useful as metal-extracting agents [10]. Schiff base hydrazones have a variety of applications in analytical chemistry, including the selective extraction of certain transition metals and their use in spectroscopic determination [11,12]. Additionally, hydrazones are versatile compounds that can be used in the construction of sensor materials for detecting fluoride ions, cyanide ions, heavy metals, and poisonous fumes [13–17].

Recently, the synthesis and structure elucidation of a range of new heterocycles have been explored [18–20]. The title compound was synthesized in continuation of this work. Dinitrobenzenes display significant biological activities [21] and the dihydronaphthalene group has been investigated for its medicinal properties [22]. The aim of this work was to generate a composite hydrazone containing 2,4-dinitrobenzene and 3,4-dihydronaphthalene moieties using a simple procedure.

2. Results and Discussion

2.1. Synthesis of 3

The reaction of (*E*)-2-(4-fluorobenzylidene)-3,4-dihydronaphthalen-1(2*H*)-one (**1**) and (2,4-dinitrophenyl)hydrazine (**2**) in ethanol (EtOH) containing hydrochloric acid (HCl; 0.2 mL, 37%) as a catalyst for 1.5 h gave 1-(2,4-dinitrophenyl)-2-((*Z*)-2-((*E*)-4-fluorobenzylidene)-3,4-dihydronaphthalen-1(2*H*)-ylidene)hydrazine (**3**) (Scheme 1). The crude product was recrystallized from dimethylformamide (DMF) to give **3** in a 90% yield.



Scheme 1. Synthesis of hydrazone 3.

2.2. IR and NMR Spectroscopy of 3

The IR spectrum of hydrazone 3 showed an absorption band at 3297 cm^{-1} due to the NH group. The absorption bands for the C=N and the C=C in aromatic moieties appeared at 1612 and 1589 cm^{-1} , respectively.

The ^1H NMR spectrum of 3 showed two multiplets at high field (2.76 and 2.92 ppm), each with 2H. These multiplets were attributed to the $\text{CH}_2\text{--CH}_2$ protons of the tetralin moiety. The NH proton appeared at a very high field (11.92 ppm).

In the ^{13}C NMR spectrum of 3, the carbon at the 4-position of the 4-fluorophenyl group was observed at a very low field (161.7 ppm) as a doublet with a large coupling constant of 243.8 Hz. The doublet was due to the coupling between the fluorine atom and the C atom. The C2/C6 of the 4-fluorophenyl group appeared at 130.8 ppm as a doublet with a small coupling constant of 8.3 Hz. Additionally, the C3/C5 of the 4-fluorophenyl group appeared at 115.5 ppm as a doublet with a coupling constant of 21.8 Hz. Furthermore, the C=N carbon appeared at 149.7 ppm, while the $\text{CH}_2\text{--CH}_2$ carbons of tetralin moiety appeared at very high field (26.8 and 30.4 ppm). The spectrum showed all other carbons within the range of the expected chemical shifts (See Supplementary Materials for the spectra).

2.3. Crystal Structure of 3

The asymmetric unit is one molecule of the title compound (Figure 1). The molecule comprises five fragments, namely fluoromethylbenzene (**fmbenz**, C1–C7, F1), tetrahydronaphthalene (**thnaph**, C8–C17), phenyldiazene (**phdiaz**, C18–C23, N1, N2), and two nitro groups [(**nitr1**, N3, O1, O2) and (**nitr2**, N4, O3, O4)].

In the tetrahydronaphthalene group, the nonhydrogen atoms are coplanar, apart from C9, which is offset from the least-squares plane of the rest of the atoms by 0.75 (1) Å. The plane of the fluoromethylbenzene group deviates from the planar part of the tetrahydronaphthalene group by an **fmbenz**/**thnaph** twist angle of $15.10 (10)^\circ$. The ring centroid of the fluoromethylbenzene group also deviates from the plane through the planar part of the tetrahydronaphthalene group by 0.94 Å. This deviation accounts for the configuration of the imine double bond as it gives the least hindered arrangement. The alternative configuration of the imine double bond would lead to an overlap of hydrogen atoms. A similar deviation is also observed in the structure of 2-(4-chlorobenzylidene)-3,4-dihydronaphthalen-1(2H) [23], in which the chlorobenzene group is twisted and offset from the tetrahydronaphthalene group.

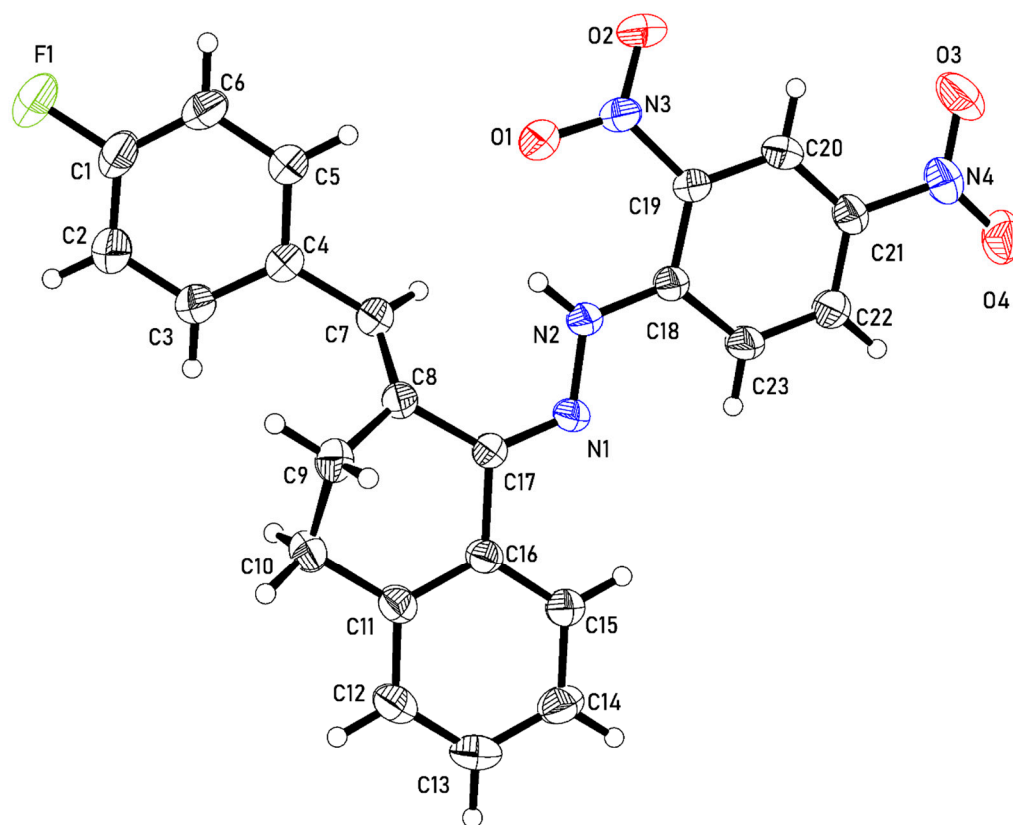


Figure 1. Ortep representation of **3** showing 50% probability atomic displacement ellipsoids.

The tetrahydronaphthalene and phenyldiazene groups are coplanar with a **thnaph/phdiaz** twist angle of $4.16(9)^\circ$. The planes of the nitro groups are close to that of the phenyldiazene, with **nitr1/phdiaz** and **nitr2/phdiaz** twist angles of $8.8(3)^\circ$ and $1.9(3)^\circ$, respectively. The near-coplanarity of the tetrahydronaphthalene, phenyldiazene, and nitro groups is also observed in the structure of 1-(2,4-dinitrophenyl)-2-(1,2,3,4-tetrahydronaphthalen-1-ylidene)hydrazine [24].

Intramolecular N–H...O hydrogen bonding occurs in the molecule, with a N2...O1 distance of $2.617(2)$ Å and N2–H2A...O1 angle of 128.3° (Figure 2a) and graph set geometry S(6). In the crystal, pairs of molecules related by inversion symmetry are linked by two intermolecular C–H...O contacts, with a C6...O2 distance of $3.388(3)$ Å and C6–H6...O2 angle of 146.1° . The molecules are arranged with their molecular planes parallel to the (123) plane in the crystal (Figure 2b).

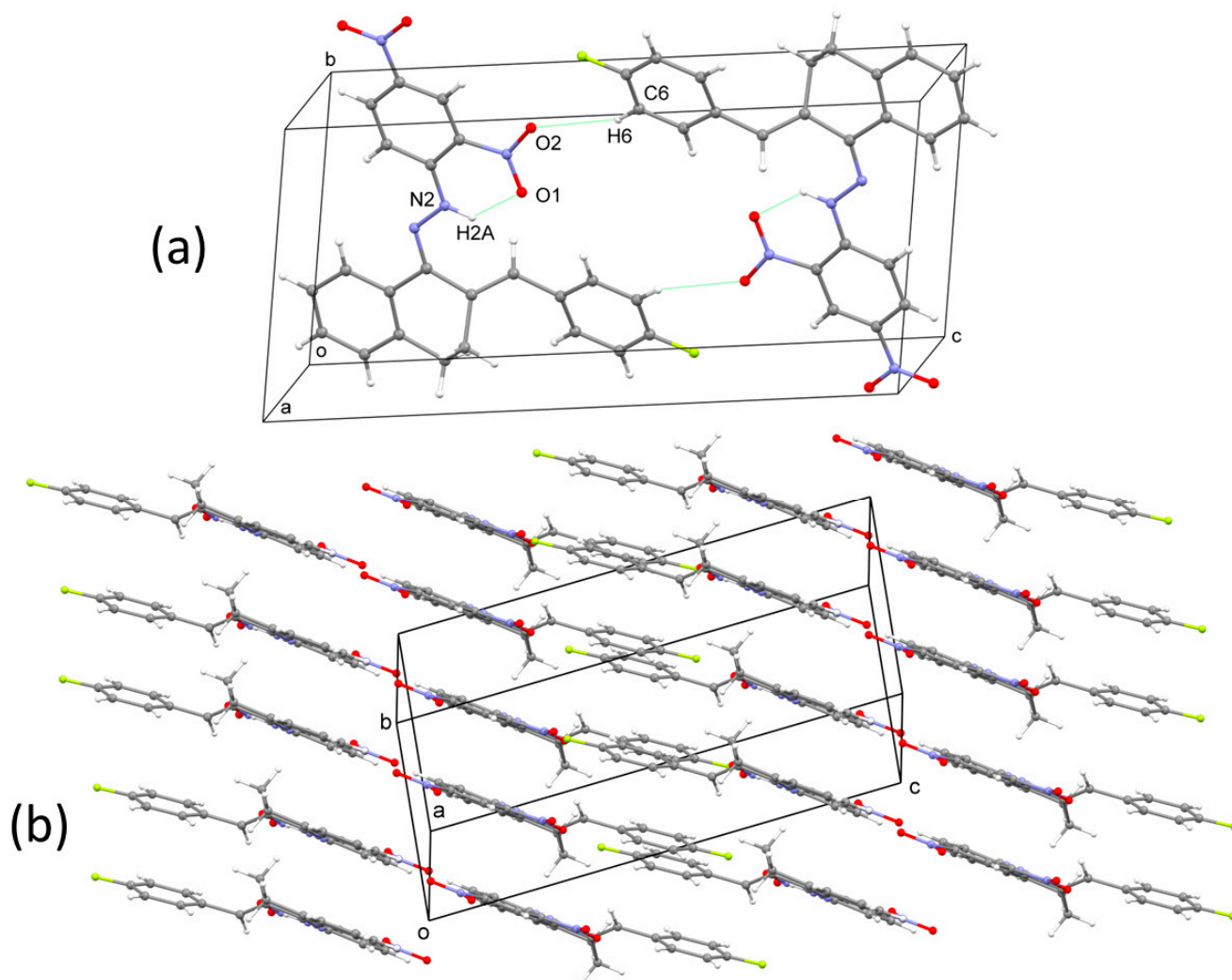


Figure 2. (a) A segment of the crystal structure of **3** showing intra- and intermolecular contacts and (b) crystal packing viewed along the molecular plane.

3. Materials and Methods

3.1. General

Chemicals, reagents, and analytical solvents were obtained from Merck. The IR spectrum of the title heterocycle was recorded on a Bruker Vertex 80 ATR-FTIR spectrometer ($400\text{--}4000\text{ cm}^{-1}$). The NMR spectra, at 300 MHz for the ^1H and 75 MHz for ^{13}C were recorded in deuterated dimethyl sulfoxide ($\text{DMSO-}d_6$) using a Varian Mercury 300 VX spectrometer. The chemical shift (δ) was reported in ppm and the coupling constant (J) was measured in Hz. Compound **1** was produced using a reported procedure [25].

3.2. Synthesis of **3**

A mixture of **1** (1.26 g, 5.0 mmol) and **2** (1.00 g, 5.0 mmol) in EtOH (15 mL) containing HCl (0.2 mL; 37%) was refluxed for 1.5 h. The mixture was left to cool to $20\text{ }^\circ\text{C}$ and the red solid obtained was removed by filtration. The solid was washed with EtOH, dried, and recrystallized from DMF to give **3** in a 90% yield. Mp $220\text{--}222\text{ }^\circ\text{C}$. IR (KBr): $3297, 3107, 1612, 1589\text{ cm}^{-1}$. ^1H NMR: 2.76 (m, 2H, H4 of tetralinyl), 2.92 (m, 2H, H3 of tetralinyl), 7.16 (s, 1H, CH), 7.23–7.48 (m, 8H, 4-fluorophenyl and tetralinyl), 8.09 (m, 1H, H6 of 2,4-dinitrophenyl), 8.31 (dd, $J = 3, 9\text{ Hz}$, 1H, H5 of 2,4-dinitrophenyl), 8.72 (d, $J = 3\text{ Hz}$, 1H, H3 of 2,4-dinitrophenyl), 11.92 (s, 1H, NH). ^{13}C NMR: 26.8 (C3 of tetralinyl), 30.4 (C4 of tetralinyl), 115.5 ($J = 21.8\text{ Hz}$, C3/C5 of 4-fluorophenyl), 116.2 (C6 of 2,4-dinitrophenyl), 122.7 (C8a of tetralinyl), 124.3 (C3 of 2,4-dinitrophenyl), 126.5 (C8 of tetralinyl), 128.9

(C7 of tetralinyl), 129.3 (C5 of tetralinyl), 129.8 (C2 of 2,4-dinitrophenyl), 129.9 (C1 of 4-fluorophenyl), 130.8 ($J = 8.3$ Hz, C2/C6 of 4-fluorophenyl), 131.2 (C5 of 2,4-dinitrophenyl), 131.3 (C6 of tetralinyl), 132.0 (C2 of tetralinyl), 132.3 (CH), 137.1 (C4a of tetralinyl), 138.7 (C4 of 2,4-dinitrophenyl), 144.1 (C1 of 2,4-dinitrophenyl), 149.7 (C1 of tetralinyl), 161.7 ($J = 243.8$ Hz, C-4 of 4-fluorophenyl). Anal. Calcd. for $C_{23}H_{17}FN_4O_4$ (432.12): C, 63.89; H, 3.96; N, 12.96. Found: C, 64.02; H, 4.18; N, 13.13%.

3.3. Crystal Structure Determination

Data collection was conducted on an Agilent SuperNova Dual Atlas diffractometer using mirror monochromated $MoK\alpha$ radiation. The structure was solved with direct methods using SHELXS [26] and refined with SHELXL [27] using full-matrix least-squares methods on F^2 . $C_{23}H_{17}FN_4O_4$, FW = 432.40, T = 296 (2) K, $\lambda = 0.71073$ Å, triclinic, $P\bar{1}$, a = 6.1729(3) Å, b = 8.7289(4) Å, c = 18.6407(9) Å, $\alpha = 79.228(4)^\circ$, $\beta = 88.765(4)^\circ$, $\gamma = 88.813(4)^\circ$, V = 986.34(8) Å³, Z = 2, calculated density = 1.456 Mg/m³, absorption coefficient = 0.108 mm^{−1}, F (000) = 448, crystal size = 0.290 × 0.180 × 0.120 mm³, reflections collected = 8997, independent reflections = 4654, R (int) = 0.0237, parameters = 289, goodness-of-fit on $F^2 = 1.068$, R1 = 0.0567, wR2 = 0.1323 for (I > 2σ (I)), R1 = 0.0941, wR2 = 0.1582 for all data, and largest difference peak and hole = 0.204 and −0.249 e.Å^{−3}. The X-ray crystallographic data for heterocycle 3 have been deposited in the Cambridge Crystallographic Data Center with CCDC reference number 2333117.

4. Conclusions

A novel 2,4-dinitrophenylhydrazone containing the 3,4-dihydronaphthalene moiety has been synthesized. The procedure used was simple and the yield obtained was high. The structure of the synthesized hydrazone was established using both nuclear magnetic resonance and X-ray diffraction.

Supplementary Materials: Figure S1: IR spectrum of heterocycle 3, Figure S2: ¹H NMR spectrum of heterocycle 3, Figure S3: ¹³C NMR spectrum of heterocycle 3, CIF of heterocycle 3, and CheckCIF report of 3.

Author Contributions: Conceptualization: G.A.E.-H. and B.M.K.; methodology: B.F.A.-W., B.M.K. and G.A.E.-H.; X-ray crystal structures: B.M.K.; investigation: B.F.A.-W., H.A.M., B.M.K. and G.A.E.-H.; writing—original draft preparation: B.F.A.-W., H.A.M., B.M.K. and G.A.E.-H.; writing—review and editing: B.F.A.-W., H.A.M., B.M.K. and G.A.E.-H. All authors have read and agreed to the published version of the manuscript.

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