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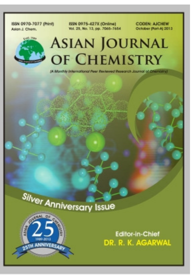

# Crystal Structure and Properties of N-Phenyl-N'-(2-nitrobenzoyl)thiourea

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N-phenyl-N'-(2-nitrobenzoyl)thiourea has been synthesized in high yield under PEG-400 as the phase-transfer catalyst. The structure of the synthesized substituted thiourea was determined by single crystal X-ray diffraction. In DMSO solutions, **L1** exhibited selective recognition for $F^-$, $OAc^-$ and $H_2PO_4^-$. In addition, the compound is also a considerable plant-growth regulator.

**Key Words: Aroylthiourea, Anion recognition, Crystal structure, Biological activity.**

## INTRODUCTION

The development of selective optical signaling systems for anions has received considerable attention in recent decades due to their important roles in biological and environmental processes[1]. Since the first synthetic sensor for inorganic anions was reported in 1968[2], great progress has been made[3-5]. Recently, thiourea and its derivatives as neutral receptors have been growing in the field of host-guest chemistry[6,7]. Among a variety of possible H-bond donor groups, systems employing thiourea moieties have been proven to be very efficient in the design of neutral anion binding receptors[8]. We synthesized a anion sensor bearing NH groups, in addition, in order to achieve colorimetric recognition, we induced nitrophenyl group as signal report group. The results show that it can be used as anion sensor in DMSO, at the same time, by investigating the biological activity of the title compound, we found that the compound has high plant growth regulating activity at low concentration.

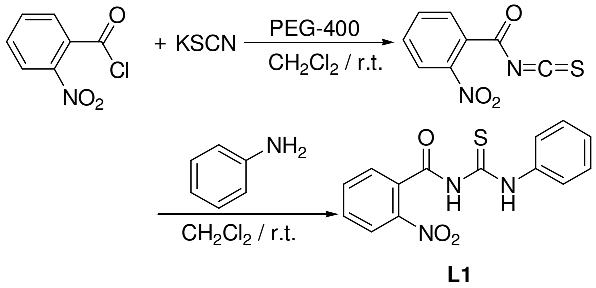
## EXPERIMENTAL

All reagents for synthesis were analytical grade, commercially and were used without further purification. All the anions were added in the form of tetrabutylammonium (TBA) salts, which were purchased form Sigma-Aldrich Chemical, stored in a vacuum desiccator.

Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). The infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer. UV-VIS spectra were recorded on a Shimadzu UV-2550 spectrometer. $^1$H NMR spectra were recorded on a Varian Mercury Plus-400 MHz spectrometer with DMSO-$d_6$ as solvent and TMS as an internal reference. Electrospray ionization mass spectra (ESI-MS) were measured on an Agilent 1100 LC-MSD-Trap-VLsystem. Elemental analyses were performed by Thermo Scientific Flash 2000 organic elemental analyzer.

All the UV-visible experiments were carried out in DMSO on a Shimadzu UV-2550 spectrometer. Any changes in the UV-visible spectra of sensor **L1** were recorded upon the addition of tetrabutylammonium salts while keeping the concentration of sensor **L1** constant in all experiments. The solution of the sensor **L1** ($2.0 \times 10^{-4}$ M) in DMSO was prepared and stored in dry atmosphere. The solution was used for all spectroscopic studies after appropriate dilution. Solutions of $1.0 \times 10^{-2}$ mol $L^{-1}$ tetrabutylammonium salts of the respective anions were prepared.

**Synthesis:** N-Phenyl-N'-(2-nitrobenzoyl)thiourea was synthesized in high yield was shown in **Scheme-I:** powdered potassium thiocyanate (7.5 mmol) 2-nitrobenzoyl chloride (5 mmol), PEG-400 (3 % with respect to ammonium thiocyanate) and dichloromethane 20 mL were placed in a dried round-bottomed flask containing a magnetic stirrer bar and stirred at room temperature for 1 h, then aniline (5 mmol) was added and the mixture were stirred for additional 0.5 h. The corresponding thiourea precipitates immediately. The product was filtered, washed with water to remove inorganic salts, dried and recrystallized from DMF-EtOH-$H_2O$ to give the title compound. Yield, 78 %; m.p. 179-181 ºC; $^1$H NMR ($CDCl_3$, 400 MHz) δ: 12.28 (s, 1H, NH), 11.62 (s, H, NH), 7.24-8.14 (m, 9H, Ar-H); $^{13}$C NMR ($CDCl_3$, 400 MHz) δ: 124.25, 124.94, 127.09, 128.27, 128.86, 130.03, 131.93, 134.27, 137.18, 145.80, 166.68, 177.88; ESI-MS: 301.7 (*m/z* + 1). IR (KBr,



**Scheme-I:** Synthetic route of **L1**

$\nu_{max}$, cm$^{-1}$): 3169, 3028 (NH), 1691 (C=O), 1258(C=S); anal. calcd. (%) for $C_{14}H_{11}N_3SO_3$: C: 55.80, H: 3.68, N: 13.95; Found C: 55.77, H: 3.70, N: 13.97.

**Structure determination:** The crystal structure of the title compound atom scheme-labeling was shown in Fig. 1. The crystal data and structure refinement details for $C_{14}H_{11}N_3O_3S$ are summarized in Table-1, selected bond distances and angles are listed in Tables 2 and 3.

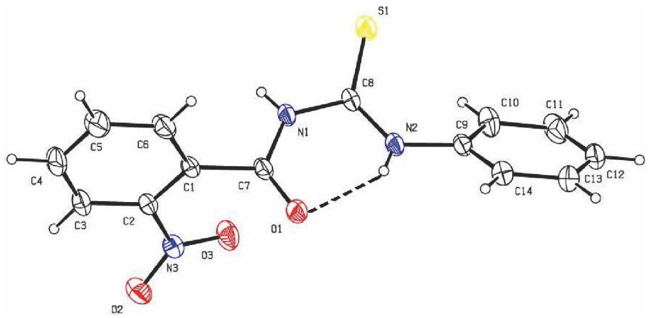


Fig. 1. Crystal structure of the title compound

TABLE-1
CRYSTAL DATA OF THE TITLE COMPOUND

| | |
|---|---|
| Formula | $C_{14}H_{11}N_3O_3S$ |
| f.w. | 301.32 |
| Crystal system, | Triclinic |
| Space group | $P_{-1}$ |
| a (Å) | 6.2013(4) |
| b (Å) | 9.9667(6) |
| c (Å) | 11.9444(8) |
| α (º) | 74.188(3) |
| β (º) | 85.421(3) |
| γ (º) | 83.191(3) |
| V (Å$^3$), Z | 704.42(8), 2 |
| $F_{(000)}$ | 312 |
| Reflections collected/unique ($R_{int}$) | 4293/2993 [$R_{(int)}$ = 0.0096] |
| Obsd reflns [I ≥ 2σ(I)] | 2993 |
| data/restraints/parameter | 2993/0/198 |
| $D_c$ (Mg m$^{-3}$) | 1.421 |
| μ (mm$^{-1}$) | 0.243 |
| Goodness-of-fit on F$^2$ | 1.051 |
| $R_1$,$^a$ w$R_2$$^b$ [I ≥ 2σ(I)] | 0.0471, 0.1381 |

**Crystal structure:** The structure of the N-phenyl-N′-(2-nitrobenzoyl)thiourea is shown in Fig. 1, the intramolecular N-H···O (2.135 Å) hydrogen bonding between the amide-N and benzoyl-O atoms completes a nearly planar six-membered ring in the central part of the molecule. This group makes dihedral angles of 34.98 (1) and 76.39(1)º with the *o*-nitrobenzoyl and other phenyl rings, respectively.

TABLE-2
SELECTED BOND DISTANCES (nm) AND
BOND ANGLES (°) FOR THE COMPOUND

| Bond lengths | | | |
|---|---|---|---|
| S(1)-C(8) | 1.650(2) | C(1)-C(7) | 1.508(3) |
| C(2)-N(3) | 1.458(3) | C(7)-O(1) | 1.206(3) |
| C(7)-N(1) | 1.367(3) | C(8)-N(2) | 1.316(3) |
| C(8)-N(1) | 1.394(2) | C(9)-N(2) | 1.422(2) |
| **Bond angles** | | | |
| C(3)-C(2)-N(3) | 117.53(19) | C(1)-C(2)-N(3) | 120.15(17) |
| C(7)-N(1)-C(8) | 128.70(19) | C(8)-N(2)-C(9) | 129.25(19) |

TABLE-3
DATA OF HYDROGEN BOND (nm)
AND ANGLE (°) OF TITLE COMPOUND

| D-H···A | D-H (nm) | H···A (nm) | D···A (nm) | D-H···A (º) | Symmetry code |
|---|---|---|---|---|---|
| N2-H2N···O1 | – | – | 2.698(6) | 144. 8 | -x+1, -y+1, -z+2 |

Fig. 2 showed that the crystals were linked to one-dimensional chain-like superamolecular through the intermolecular hydrogen bonds, which form a eight-membered ring with C8A, N1A, H1NA, S1C, C8C, N1C, H1NC, S1A. Moreover, it is found that the supramolecular are connected by intermolecular hydrogen bond of N(1C)-H(1NC)···S(1A) along the *oc*-axis direction and parallel packing along the *oa*-axis direction. As shown in Fig. 2, we can find the parallel packing of the phenyl rings in the crystal of the compound; however, the distance between the centers of two parallel phenyl rings is 0.6201 nm, which is out of the accepted range of the intermolecular π-π interaction[9].

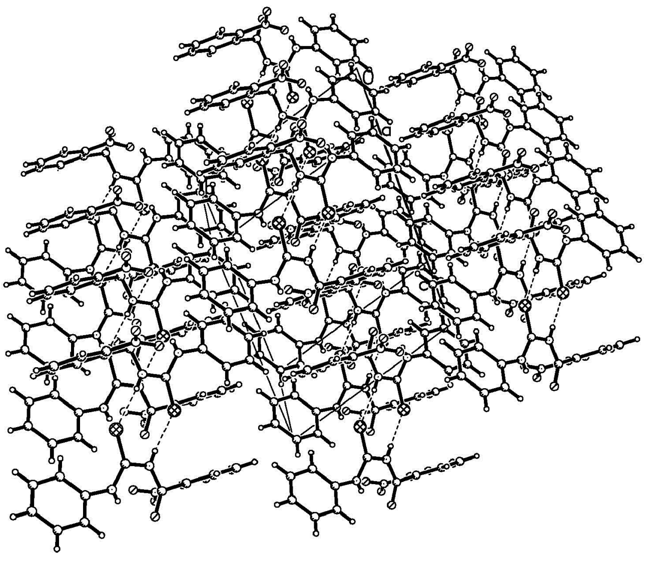


Fig. 2. Packing diagram of the title compound

## RESULTS AND DISCUSSION

**Anion recognition properties:** Compound **L1** (2 × 10$^{-5}$ M) exhibited strong absorption at 303 nm in DMSO solution. When adding 50 equiv of $F^-$, $OAc^-$, $H_2PO_4^-$ to the DMSO solution of **L1** (Fig. 3), it indicated that the receptor **L1** exhibited selective recognition for $F^-$, $OAc^-$ and $H_2PO_4^-$ in DMSO. The same test were applied to $Cl^-$, $Br^-$, $I^-$, $HSO_4^-$, $ClO_4^-$, no obvious changes were observed.

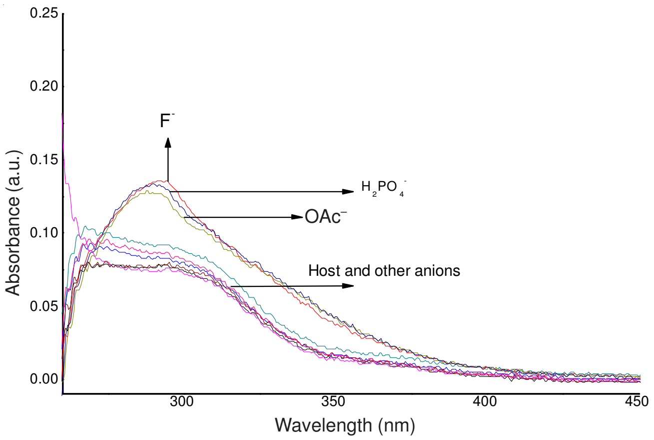


Fig. 3. UV-visible absorption of sensor **L1** (c = $2.0 \times 10^{-5}$ M) in the presence of 50 equiv. various anions in DMSO

UV-visible titrations were carried out in DMSO at a concentration of $2.0 \times 10^{-5}$ mol $L^{-1}$ with the addition of tetrabutylammonium $OAc^-$, the spectra are shown in (Fig. 4). The plot gives a 1:1 stoichiometric ratio between $OAc^-$ and **L1** in (Fig. 5), by the association constants $K_a$ of the sensor[10] **L1** toward $OAc^-$ was obtained as $1.5 \times 10^5$ $M^{-1}$.

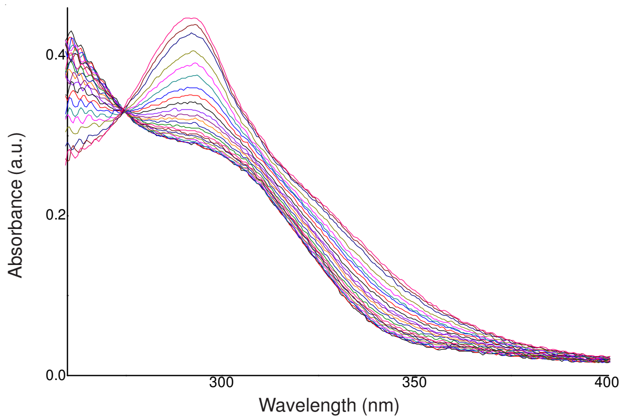


Fig. 4. UV-visible spectral titration of sensor **L1** with $OAc^-$

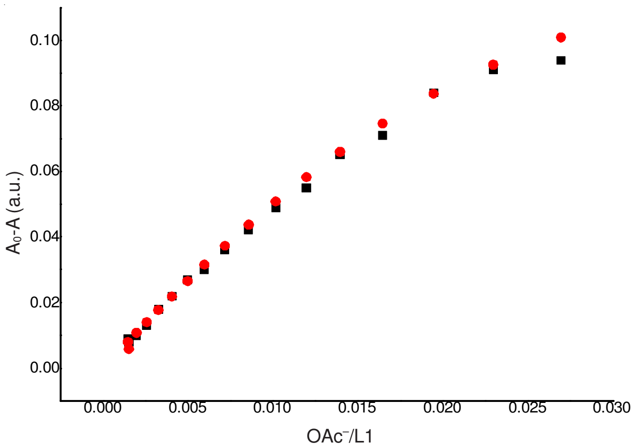
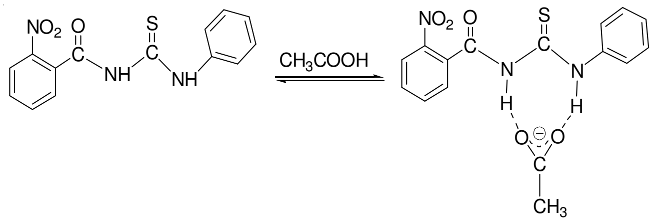


Fig. 5. Plot of the absorbance at 303 nm *vs*. equivalents of $OAc^-$ in DMSO. C (**L1**) = $2 \times 10^{-5}$ M, the correlation coefficient is 0.998

The whole reaction process was shown in **Scheme-II**. This phenomenon may be attributed to its basicity and geometry configuration to converge the two -NH groups at a point *via* -NH- anions hydrogen binding[11].



**Scheme-II:** Proposed binding mode of **L1** with $OAc^-$ in DMSO

**Biological activity:** We also investigated plant growth regulation activity. Here, we adopted the method of plate culture. The compound was collected to the solutions in concentration of 100, 10, 1, 0.1, 0.01 and 0.001 ppm and rape seeds were cultured in a 10 cm petri-dish with 10 mL different solutions and a circular filter paper. After growing at room temperature for 4 days, the root length was gained and the percentage plant growth activity was calculated according to the following equation:

$$\text{Percentage plant growth activity} = \frac{(N - N_1)}{N_1} \times 100\ \%$$

In the equation, N is the root length cultured in compound solutions and $N_1$ is the root length cultured in the distilled water under the same condition. The data are shown in Table-4.

TABLE-4
PLANT GROWTH REGULATING ACTIVITY DATA (RAPE)

| Compound | Plant growth activity (%)[a] | | | | | |
|---|---|---|---|---|---|---|
| | 100 ppm | 10 ppm | 1 ppm | 0.1 ppm | 0.01 ppm | 0.001 ppm |
| L1 | -100 | -22.1 | 67.4 | 68.2 | 49.6 | 16.3 |
| Heteroauxing | -100 | -92.5 | -91.2 | -80.2 | -28.9 | -10.7 |

[a]Solution was prepared in the proportion of $H_2O$:DMF = 99.5:0.5 and 0.1 g Tween-80 was added to promote the compound to dissolved.

From the results summarized in Table-4, compared with heteroauxing, the compound exhibited root elongation activity and with the concentration was decreased from 100-0.001 ppm, the root elongation activity becomes strengthener gradually. It was obvious that the compound shown excellent plant-growth regulation activity in the concentration of 0.1 ppm, which the growth activity was reached to 68.2 %.

## Conclusion

In summary, we have synthesized N-phenyl-N′-(2-nitrobenzoyl)thiourea in high yield. The crystal structure show that the intramolecular N-H···O hydrogen bonding between the amide-N and benzoyl-O atoms completes a nearly planar six-membered ring in the central part of the molecule, moreover, in the crystals, the moleculars of **L1** were linked to one-dimensional chain-like superamolecular through the intermolecular hydrogen bonds. The anion-binding properties of **L1** has been studied by UV-visible, which is shown to be capable of strongly binding for $OAc^-$ through hydrogen bonding interaction in DMSO and formed a 1:1 stoichiometry complex. In addition, investigation of biological activity shows the compound show good plant-growth regulation activity.

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