INTRODUCTION

Thiourea derivatives are widely used as building blocks in numerous organic synthesis such as in the synthesis of heterocyclic compounds. Many thiourea derivatives also act as versatile ligands in numerous applications due to their ability to coordinate with various transition metal ions as monodentate or bidentate ligands. Furthermore, the nucleophilic nature of the sulphur atom and the presence of N-H donor groups make thiourea derivatives enable to form extensive intra- and intermolecular hydrogen bonds. These interactive properties of thiourea compounds make them broadly used in numerous fields such as pharmaceutical, environmental, electrochemical and also agrochemical industry.

Carbonyl thiourea, one kind of thiourea derivatives, has been extensively explored in recent years. Most of carbonyl thioureas have been synthesized from the reaction of carbonyl isothiocyanate with amine compound in acetone. Only a few of them have been synthesized from diamine compound to produce bis-carbonyl thioureas.

SYNTHESIS AND X-RAY CRYSTALLOGRAPHIC STUDY OF \( \text{N,N}' - \text{bis}(2-, 3-, \text{and} 4\text{-methoxybenzamidothiocarbonyl}) \text{Hydrazines} \)

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ABSTRACT

Introduction: Most of carbonyl thioureas have been synthesized from the reaction of carbonyl isothiocyanate with amine compound in acetone. Only a few of them have been synthesized from diamine compound to produce bis-carbonyl thioureas.

Objective: To investigate the one-pot reaction of 2, 3, and 4-methoxybenzoyl chloride with ammonium thiocyanate and hydrazine in acetone by reflux condition.

Methods: Each of the crystal compounds was analysed by X-ray crystallography.

Result: Three compound of bis-thiourea derivatives, namely \( \text{N, N}' - \text{bis} \) (2-methoxy-benzamidothiocarbonyl) hydrazine (1), \( \text{N, N}' - \text{bis} \) (3-methoxybenzamidothiocarbonyl) - hydrazine (2), and \( \text{N, N}' - \text{bis} \) (4-methoxybenzamidothiocarbonyl) hydrazine (3) were successfully synthesised by the reaction of each 2, 3, and 4-methoxybenzoyl chloride with ammonium thiocyanate and hydrazine in acetone. The structure of these compounds was studied by chemical crystallography.

Conclusion: Compound 1 and 3 were crystallized in the triclinic crystal system while compound 2 was crystallized in the monoclinic crystal system. The thiourea moiety in all compounds have trans geometry and each of the hydrogens of the amide group is trans to the carbonyl group.

Key Words: Bis-carbonyl thiourea; bis-thiourea; carbonyl thiourea; \( \text{N, N}' - \text{bis} \) (benzamidothiocarbonyl) hydrazine derivatives; X-ray Crystallography

Figure 1: Chemical Structures of Reported Bis-carbonyl Thioureas with Hydrazine Linker.
In this paper, we reported a one-pot reaction of 2, 3, and 4-methoxybenzoyl chloride with ammonium thiocyanate and hydrazine in acetone by reflux condition. Each reaction produced N, N'-bis (methoxybenzamidothiocarbonyl) hydrazine isomer in moderate yield. Each of the crystal compounds was analysed by X-ray crystallography.

**Materials and Methods**

**Synthesis Method**

The synthesis of bis(benzamidothiocarbonyl)hydrazine derivatives followed the previous report by using 2-, 3-, and 4-methoxybenzoylchlorides as the substrates.

**N,N'-bis(o-methoxybenzamidothiocarbonyl) hydrazine (1)**

Yield 16%; Yellow solid, m.p 327.3-327.9 °C. IR (KBr, cm⁻¹): ν(N-H)3407; ν(C=O)1661; δ(N-H)1610; ν(C-N)1240; ν(C-S)1090; ν(C=O-Me) Asym. 1305; sym. 1014. ¹H-NMR (DMSO-d₆, 400 MHz): δ 3.88 (s, 3H); 7.06-7.63 (m, 13H). Anal. Calc. For C₁₈H₁₈N₄O₄S₂: C, 51.66; H, 4.34; N, 15.29; S, 15.32. Found: C, 52.23; H, 4.81; N, 15.93; S, 15.04. λmax 302.5 nm, ε 18,850.17 L.mol⁻¹.cm⁻¹. MS exact mass 418.08; m/z 417.06 (M-1)⁻ (10%).

**N,N'-bis(m-methoxybenzamidothiocarbonyl) hydrazine (2)**

Yield 72%; colourless solid, m.p 327.3-327.9 °C. IR (KBr, cm⁻¹): ν(N-H)3401; ν(C=O)1678; δ(N-H)1611; ν(C-N)1230; ν(C=O-Me) Asym. 1324; sym. 1034. ¹H-NMR (DMSO-d₆, 400 MHz): δ 3.86 (s, 3H); 7.22-7.61 (m, 14H); 12.16 (s, 1H). ¹³C-NMR (DMSO-d₆, 100 MHz): δ 159.6; 133.3; 130.2; 121.7; 120.3; 113.8; 56.0. Anal. Calc. For C₁₈H₁₈N₄O₄S₂: C, 51.66; H, 4.34; N, 15.29; S, 15.32. Found: C, 52.54; H, 4.96; N, 14.17; S, 16.20. λmax 301.5 nm, ε 21,577.73 L.mol⁻¹.cm⁻¹. MS exact mass 441.03; m/z 441.05 (MNa)⁻ (41%).

**N,N'-bis(p-methoxybenzamidothiocarbonyl) hydrazine (3)**

Yield 42%; colourless solid, m.p 327.3-327.9 °C. IR (KBr, cm⁻¹): ν(N-H)3319; ν(C=O)1656; δ(N-H)1599; ν(C-N)1212; ν(C=S)1076; ν(C=O-Me) Asym. 1311; sym. 1018. ¹H-NMR (DMSO-d₆, 400 MHz): δ 3.86 (s, 3H); 7.22-7.61 (m, 14H); 12.16 (s, 1H). ¹³C-NMR (DMSO-d₆, 100 MHz): δ 56.0; Anal. Calc. For C₁₈H₁₈N₄O₄S₂: C, 51.66; H, 4.34; N, 15.29; S, 15.32. Found: C, 51.69; H, 4.89; N, 13.91; S, 16.01. λmax 336 nm, ε 21,577.73 L.mol⁻¹.cm⁻¹. MS exact mass 441.08; m/z 441.03 (MNa)⁻ (41%).

**X-ray Crystallographic Study**

Compound 1, 2 and 3 were crystallized in a different type of solvent. Crystal of compound 1 was recrystallized in CHCl₃, while compound 2 was obtained in DMSO. In the other hand, compound 3 crystalized in DMF. All of the crystals were treated by using the method. Single crystal data were collected by using Bruker SMART APEX CCD Diffractometer with graphite monochromatic Mo Kα radiation source. Crystal structures were solved by the SHELXS-97 program and refined by SHELXL-97 program.

**Results and Discussion**

**Synthesis**

The synthesis of bis(methoxybenzoylthiourea)hydrazine is followed the previous method which the X substituent is o-, m-, and p-methoxy for compound 1, 2, and 3 (Figure 2), respectively, as shown in Figure 2. The mixture of methoxybenzoyl chloride and ammonium thiocyanate in acetone gave white precipitate, indicated that ammonium chloride, as well as methoxybenzoyl isothiocyanate, were produced. The addition of hydrazine gave precipitate after the mixture was refluxed for around 30 minutes.

**X-Ray Crystallographic Study**

Both 1 and 3 crystallized in the triclinic crystal system with a space group of P. In the other hand, compound 2 crystallized in the monoclinic crystal system, and the space group is C2/m. The crystal system of all compounds, as well as the refinement parameters, are shown in Table 1.

Molecule 2 is highly disordered. One of the hydrogen atoms attached to C7 is symmetryally generated. The DMSO C11 is disordered. Furthermore, C10 is also symmetryally generated. Therefore, no attempt to treat the disordered was pursued.

The asymmetric unit of the three isomers consists of half molecule. Molecule 1 and 3 possess a centre of inversion at N2-N2A bond and molecule 2 is centrosymmetric at the midpoint of N2-N2A bond. Molecule 1 and 3 contain one solvated molecule of chloroform and DMSO, respectively.
Table 1: Crystal Data and Structure Refinement of 1, 2, and 3

| Data | Compound |  |  |
|------|----------|---|---|
| **Empirical formula** | C_{18}H_{18}N_{4}O_{4}S_{2}·2(CHCl) | C_{18}H_{18}N_{4}O_{4}S_{2}·2(C_{4}H_{9}O) | C_{18}H_{18}N_{4}O_{4}S_{2}·2(C_{4}H_{9}O) |
| **Formula weight** | 657.24 | 604.85 | 314.34 |
| **Temperature** | 301(2) K | 300(2) K | 301(2) K |
| **Wavelength** | 0.71073 Å | 0.71073 Å | 0.71073 Å |
| **Crystal system, space group** | Triclinic, P\(_{1}\) | Monoclinic, C 2/m | Triclinic, P\(_{1}\) |
| **Unit cell dimensions** | a = 8.6332(12) Å, α= 102.424(4)° | a = 19.0998(14) Å, α = 90° | a = 6.4304(4) Å, α = 88.8555(17)° |
| **Volume, Z** | b = 9.318(13) Å, β = 107.682(3)° | b = 6.7421(5) Å, β = 91.507(2)° | b = 8.2379(5) Å, β = 76.4842(18)° |
| **Density (calculated)** | c = 9.9351(13) Å, γ = 104.5139(4)° | c = 10.9230(8) Å, γ = 90° | c = 9.6961(6) Å, γ = 67.1326(18)° |
| **Absorption coefficient** | 699.46(17) Å\(^{-1}\), 1 | 1406.10(18) Å\(^{-1}\), 4 | |
| **F(000)** | 1.560 Mg/m\(^3\) | 1.485 Mg/m\(^3\) | 471.63(3) Å\(^3\), 1 |
| **Crystal size** | 0.798 mm\(^3\) | 0.396 mm\(^3\) | 1.473 Mg/m\(^3\) |
| **Theta range for data collection** | 334 | 648 | 0.307 mm\(^3\) |
| **Index ranges** | 0.260 x 0.250 x 0.250 mm\(^3\) | 0.320 x 0.160 x 0.150 mm\(^3\) | 218 |
| **Reflections collected** | 2.888 to 25.999° | 2.871 to 25.999° | 0.440 x 0.140 x 0.090 mm\(^3\) |
| **Independent reflections** | -10<=h<=10, -11<=k<=11, -12<=l<=12 | -23<=h<=23, -8<=k<=8, -13<=l<=13 | 3.286 to 25.999°. |
| **Completeness to theta = 25.242°** | 15640 | 15683 | |
| **Refinement method** | 2756 [R(int) = 0.1200] | 1512 [R(int) = 0.0600] | 25980 |
| **Data / restraints / parameters** | Full-matrix least-squares on F\(^{2}\) | 99.8 % | 3537 [R(int) = 0.0560] |
| **Goodness-of-fit on F\(^{2}\)** | 2756 / 0 / 164 | 1512 / 1 / 118 | 99.9 % |
| **Final R indices [I>2sigma(I)]** | 1.029 | 1.069 | Full-matrix least-squares on F\(^{2}\) |
| **R indices (all data)** | R\(_{1}\) = 0.0562, wR\(_{2}\) = 0.0835 | R\(_{1}\) = 0.0857, wR\(_{2}\) = 0.2298 | 3537 / 3 / 271 |
| **Largest diff. peak and hole** | R\(_{1}\) = 0.1315, wR\(_{2}\) = 0.1011 | R\(_{1}\) = 0.1113, wR\(_{2}\) = 0.2524 | R\(_{1}\) = 0.0407, wR\(_{2}\) = 0.0901 |
|  | 0.200 and -0.241 e.Å\(^{-3}\) | 1.177 and -0.471 e.Å\(^{-3}\) | 0.216 and -0.302 e.Å\(^{-3}\) |
Molecule 1 possesses four pseudo-six-membered rings \{(C8/N1/C9/N2/H2A\ldots O2), (C8A/N1A/C9A/N2A/H2AA\ldots O2A), (C1/C6/C8/N1/H1\ldots O1), (C1A/C6A/C8A/N1A/H1A\ldots O1A)\} by N2-H2A\ldots O2, N2A-H2AA\ldots O2A, N1-H1\ldots O1, and N1A-H1A\ldots O1A intramolecular hydrogen bonds, and two pseudo-five-membered rings \{(C9/N2/H2AA\ldots S1) and (C9A/N2A/H2AA\ldots S1A)\} by N2-H2A\ldots S1A and N2A-H2AA\ldots S1 intramolecular hydrogen bonds (Figure 3).

Similarly, molecule 3 also has two pseudo-six-membered rings \{(C8/N1/C9/N2/H2A\ldots O1) and (C8A/N1A/C9A/N2A/H2AA\ldots O1A)\} by N2-H2A\ldots O2 and N2A-H2AA\ldots O2A intramolecular hydrogen bonds, and two pseudo-five-membered rings \{(C9/N2/H2AA\ldots S1) and (C9A/N2A/H2AA\ldots S1A)\} by N2-H2A\ldots S1A and N2A-H2AA\ldots S1 intramolecular hydrogen bonds (Figure 3).

Figure 3: The molecular structure of \textit{N}, \textit{N}'-bis(2-methoxybenzamido-thiocarbonyl)hydrazine 1 drawn at 50\% probability displacement ellipsoid. The hydrogen bonds are illustrated by the dashes lines.

Compound 2 has two pseudo-six-membered rings \{(C8/N1/C9/N2/H2A\ldots O1) and (C8A/N1A/C9A/N2A/H2AA\ldots O1A)\} by N2-H2A\ldots O2 and N2A-H2AA\ldots O2A intramolecular hydrogen bonds, and two pseudo-five-membered rings \{(C9/N2/H2AA\ldots S1) and (C9A/N2A/H2AA\ldots S1A)\} by N2-H2A\ldots S1A and N2A-H2AA\ldots S1 intramolecular hydrogen bonds (Figure 3).

Figure 4: The molecular structure of \textit{N}, \textit{N}'-bis(3-methoxybenzamido-thiocarbonyl)hydrazine 2 drawn at 50\% probability displacement ellipsoid. The hydrogen bonds are illustrated by the dashes lines. Compound 2 has two pseudo-six-membered rings \{(C8/N1/C9/N2/H2A\ldots O1) and (C8A/N1A/C9A/N2A/H2AA\ldots O1A)\} by N2-H2A\ldots O2 and N2A-H2AA\ldots O2A intramolecular hydrogen bonds, and two pseudo-five-membered rings \{(C9/N2/H2AA\ldots S1) and (C9A/N2A/H2AA\ldots S1A)\} by N2-H2A\ldots S1A and N2A-H2AA\ldots S1 intramolecular hydrogen bonds (Figure 3).

Molecular packing of 1 shows the connection of the main molecule to two chloroform solvent molecules through C10-H10\ldots O2 intermolecular hydrogen bond. They are arranged along the bc face (Figure 5).

Similarly, molecule 3 also has two pseudo-six-membered rings \{(C8/N1/C9/N2/H2A\ldots O1) and (C8A/N1A/C9A/N2A/H2AA\ldots O1A)\} by N2-H2A\ldots O2 and N2A-H2AA\ldots O2A intramolecular hydrogen bonds, and two pseudo-five-membered rings \{(C9/N2/H2AA\ldots S1) and (C9A/N2A/H2AA\ldots S1A)\} by N2-H2A\ldots S1A and N2A-H2AA\ldots S1 intramolecular hydrogen bonds (Figure 3).

Figure 5: The molecular structure of \textit{N}, \textit{N}'-bis(4-methoxybenzamido-thiocarbonyl)hydrazine 3 drawn at 50\% probability displacement ellipsoid. The hydrogen bonds are illustrated by the dashes lines. The packing of the \textit{meta} isomer 2 is slightly different. The molecules are connected by C3-H3A\ldots O1 intermolecular hydrogen bond and form one dimensional chain along the a-axis. At the same time, the DMSO solvent molecule is connected to two thiourea molecules by N1-H1a\ldots O3, C5-H5a\ldots O3 and C10-H10a\ldots O2 intermolecular hydrogen bonds (Figure 6).

Figure 6: Molecular packing of compound 1 viewed down b axis. The hydrogen bonds are illustrated by the dashes lines.
bonds and form a polymeric chain. Overall, the arrangement of the molecules is a 2-dimensional network along a and c axis (Figure 6).

Molecule 3 also forms a 2-dimensional network but slightly different when compared to compound 2. It has no solvent molecules. Each of the centrosymmetric molecules is connected to four other molecules by N1-H1A···S1, N1A-H1AA···S1A, C7-H7A···O1 and C7A-H7AA···O1A intermolecular hydrogen bonds (Figure 7, 8). The symmetry codes of all three isomers are shown in Table 2,3,4.

**Table 2: Hydrogen bonds geometry of N, N'-bis(2-methoxybenzamido-thiocarbonyl) hydrazine 1 (Å and °)**

| D-H···A     | d(D-H) | d(H···A) | d(D···A)   | <(DHA) |
|------------|--------|---------|------------|--------|
| N1-H1···O1   | 0.86   | 1.91    | 2.625(4)   | 139    |
| N2-H2A···O2  | 0.86   | 1.89    | 2.568(4)   | 134    |
| N2-H2A···S1  | 0.86   | 2.56    | 2.933(3)   | 107    |
| C5-H5···O2#2 | 0.93   | 2.38    | 2.722(5)   | 101    |
| C10-H10···O2#3 | 0.98   | 2.34    | 3.171(4)   | 142    |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+2  #2 x,y,z  #3 x,y,z-1

**Table 3: Hydrogen bonds geometry of N,N'-bis(3-methoxybenzamido-thiocarbonyl) hydrazine 2 (Å and °)**

| D-H···A     | d(D-H) | d(H···A) | d(D···A)   | <(DHA) |
|------------|--------|---------|------------|--------|
| N1-H1a···O3#3 | 0.82(3)| 2.21(3) | 3.017(6)   | 170(5) |
| N2-H2a···O2  | 0.65(6)| 2.08(6) | 2.547(5)   | 131(7) |
| N2-H2a···S1  | 0.65(6)| 2.56(6) | 2.933(6)   | 120(6) |
| C1-H1b···O2#4 | 0.93   | 2.42    | 2.746(7)   | 101    |
| C3-H3a···O1#6 | 0.93   | 2.50    | 3.433(8)   | 178    |
| C5-H5a···O3#3 | 0.93   | 2.17    | 3.103(7)   | 177    |
| C10-H10a···O2#7 | 0.96   | 2.48    | 3.389(10)  | 158    |

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y,-z+1     #2 x,-y+2,z     #3 x,-y,z     #4 x,y,z
#5 -x+1,y,-z+1    #6 -x,y,-z+1    #7 x,-y+1,z+1

**Figure 7:** Molecular packing of compound 2 viewed down b axis. The hydrogen bonds are illustrated by the dashes lines.

**Figure 8:** Molecular packing of crystal 3 viewed down b axis. The hydrogen bonds are illustrated by the dashes lines.
Table 4: Hydrogen bonds geometry of N,N'-bis(4-methoxybenzamido-thiocarbonyl) hydrazine 3 (Å and °)

| D-H···A     | d(D-H)   | d(H···A)  | d(D···A)   | <(DHA)  |
|------------|----------|----------|-----------|---------|
| N1-H1A···S1#2 | 0.861(18) | 2.867(15) | 3.6219(17) | 147(2)  |
| N2-H2A···O2  | 0.86(2)  | 1.91(2)  | 2.566(3)  | 133(2)  |
| N2-H2A···S1  | 0.86(2)  | 2.55(2)  | 2.9412(18) | 109(2)  |
| C1-H1B···O2#3 | 0.93     | 2.43     | 2.756(3)  | 101     |
| C7-H7A···O1#4 | 0.98     | 2.50     | 3.397(3)  | 155     |

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z    #2 -x,-y+2,-z    #3 x,y,z    #4 -x+2,-y+2,-z+1

The bond lengths and angles of compound 1, 2 and 3 are presented in Table 5 and 6. All bond lengths and angles are in normal ranges.23

Table 5: Selected bond lengths of 1, 2, and 3

| Bond Length | 1       | 2       | 3       |
|-------------|---------|---------|---------|
| S1 – C9     | 1.651(3) | 1.668(5) | 1.622(2) |
| N2 – N2A    | 1.368(4) | 1.375(9) | 1.376(3) |
| N2 – C9     | 1.325(3) | 1.313(7) | 1.326(3) |
| N1 – C9     | 1.384(4) | 1.386(6) | 1.387(2) |
| N1 – C8     | 1.366(4) | 1.379(6) | 1.379(2) |
| O2 – C8     | 1.223(3) | 1.220(6) | 1.221(2) |
| C7 – O1     | 1.431(3) | 1.440(10)| 1.427(3) |

Table 6: Selected bond angles of 1, 2, and 3

| Bond Angle | 1       | 2       | 3       |
|------------|---------|---------|---------|
| O2 – C8 – C6 | 120.9(3) | 121.1(5) | 122.02(18) |
| C6 – C8 – N1 | 117.9(2) | 118.0(4) | 116.97(17) |
| O2 – C8 – N1 | 121.2(3) | 120.9(5) | 121.01(17) |
| N1 – C9 – N2 | 114.6(3) | 115.8(5) | 115.16(17) |
| N2 – C9 – S1 | 124.2(2) | 122.8(4) | 124.03(14) |
| C9 – N2 – N2A | 119.5(3) | 121.0(6) | 119.6(2) |

CONCLUSION

As a conclusion, three isomers of N, N'-bis (methoxybenzamidothiocarbonyl) hydrazines have been synthesized from 2, 3, and 4-methoxybenzoyl chloride, ammonium thiocyanate and hydrazine hydrate in room temperature and reflux conditions. Crystal of compound 2 crystallized in the monoclinic system, while 1 and 3 crystallized in the triclinic crystal system. All thiourea moieties of these three crystals revealed trans geometry.

ACKNOWLEDGEMENT

Authors thank School of Chemical Science and Food Technology, Faculty of Science and Technology, National University of Malaysia (UKM) as well as The Centre for Research and Instrumentation (CRIM) UKM for all the facilities. We also thank Indonesia Endowment Fund for Education (LPDP) of the Indonesian Ministry of Finance for the scholarship, and Publication Management Centre of Hasanuddin University for the publication support.

Source(s) of Funding: No funding is involved.

Conflicting Interest: The authors declare no conflicting interest.

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