

**CHARACTERIZATION AND MECHANISTIC  
STUDIES ON THE SYNTHESIS OF 1,3,4-  
THIADIAZOLE DERIVATIVES**

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The versatile compound of thiourea and a highly biological potential of *S*-benzylthiocarbamate (SBDTC) compound have inspired the production of hybrid compounds which contained both moieties which are thiourea and dithiocarbamate. For this reason, a reaction between acyl chloride, ammonium thiocyanate and SBDTC were reacted to produce the desired thiourea-dithiocarbamate derivatives. However, the desired compound did not obtained from the reaction but gives a heterocyclic compound namely 1,3,4-thiadiazole derivatives. The same outcome occurred when the SBDTC is substituted by 4-phenylthiosemicarbazide. Six novel compounds of 1,3,4-thiadiazole derivatives were yield from both reactions. They have been confirmed through characterization using the spectroscopic methods such as Fourier Transform Infrared (FTIR) and  $^1\text{H}$  and  $^{13}\text{C}$  Nuclear Magnetic Resonance (NMR). Compounds A1 and B1 were obtained as single crystals and suitable to be analyzed using Single Crystal X-ray Diffractometer. IR spectra showed three important stretching bands for functional groups  $\nu(\text{C-S})$ ,  $\nu(\text{C=N})$  and  $\nu(\text{C=O})$  in the range of  $600\text{ cm}^{-1}$ ,  $1400\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$ . The absorption band in the range of  $3200\text{ cm}^{-1}$  is identified for  $\nu(\text{N-H})$  and only can be seen in the IR spectra for compounds derived from the reaction of 4-phenylthiosemicarbazide. The value of  $^1\text{H}$  and  $^{13}\text{C}$  in their spectra shows a continuation in the determination of the atomic positions in the compounds. The chemical shift for aromatic protons can be seen at around  $\delta_{\text{H}} 7.00\text{ ppm}$  whereas the alkyl protons appeared at the upfield area at around  $\delta_{\text{H}} 3.00\text{ ppm}$ . The peak appears at a chemical shift around  $\delta_{\text{C}} 170\text{ ppm}$  in the  $^{13}\text{C}$  spectra indicates the carbon of carbonyl group ( $\text{C=O}$ ). The molecular structure of compound A1 and B1 are revealed by single crystal X-ray diffraction analysis. The bond lengths and angles are in the normal ranges. Both compounds of A1 and B1 are discrete and contain two intramolecular hydrogen bonding at ( $\text{C14-H14B}\cdots\text{N1}$  &  $\text{C15-H15B}\cdots\text{N1}$ ) and ( $\text{C15-H15A}\cdots\text{N2}$  &  $\text{C17-H17A}\cdots\text{O}$ ) and forming a pseudo-six membered ring respectively. The molecules in compound A1 and B1 are linked by intermolecular hydrogen bonds  $\text{C-H}\cdots\text{O}$  and  $\text{N-H}\cdots\text{O}$ . Two mechanisms have been proposed to explain the synthetic routes of formation of these compounds. Consequently, a simple way to synthesis 1,3,4-thiadiazole derivatives is suggested.

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## PENCIRIAN DAN KAJIAN MEKANISME PENGHASILAN TERBITAN 1,3,4-TIADIAZOL

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Ciri unik dan potensi biologi yang terdapat pada sebatian tiourea dan *S*-benzilditiokarbamat (SBDTC) telah memberikan idea kepada penghasilan sebatian hibrid yang mengandungi kedua-dua moiety iaitu ditiokarbamat dan tiourea. Satu tindak balas telah dilakukan di antara asil klorida, ammonium tiosianat dan SBDTC untuk menghasilkan sebatian hibrid tersebut. Walaubagaimanapun, sebatian yang dikehendaki tidak terhasil daripada tindak balas tersebut tetapi memberikan sebatian heterosiklik iaitu terbitan 1,3,4-tiadiazol. Hasil yang sama telah diperolehi apabila SBDTC ditukarganti dengan 4-feniltiosemikarbamid. Enam sebatian novel terbitan 1,3,4-tiadiazol telah terhasil daripada kedua-dua tindak balas. Sebatian tersebut telah disahkan melalui pencirian menggunakan kaedah spektroskopi seperti Inframerah Transformasi Fourier (FTIR) dan  $^1\text{H}$  dan  $^{13}\text{C}$  Resonan Magnetik Nukleus (RMN). Sebatian **A1** dan **B1** diperolehi dalam bentuk hablur tunggal dan sesuai untuk analisis pembelauan hablur tunggal kristalografi sinar-X. Spektra FTIR menunjukkan tiga regangan penting bagi kumpulan berfungsi  $\nu(\text{C-S})$ ,  $\nu(\text{C=N})$  dan  $\nu(\text{C=O})$  masing-masing pada lingkungan  $600\text{ cm}^{-1}$ ,  $1400\text{ cm}^{-1}$  dan  $1600\text{ cm}^{-1}$ . Serapan pada lingkungan  $3200\text{ cm}^{-1}$  telah dikenalpasti sebagai serapan untuk  $\nu(\text{N-H})$  dan hanya dapat dilihat pada spektra IR bagi sebatian terbitan dari tindak balas 4-feniltiosemikarbamid. Nilai yang ditunjukkan pada  $^1\text{H}$  dan  $^{13}\text{C}$  menunjukkan terdapat kesinambungan dalam penentuan kedudukan atom di dalam sebatian. Proton aromatik dapat dilihat pada anjakan kimia sekitar  $\delta_{\text{H}} 7.00$  ppm manakala proton alkil berada pada kawasan medan tinggi iaitu sekitar  $\delta_{\text{H}} 3.00$  ppm. Puncak yang muncul pada anjakan kimia sekitar  $\delta_{\text{C}} 170$  ppm dalam spektra  $^{13}\text{C}$  merujuk kepada karbon bagi kumpulan karbonil (C=O). Panjang dan sudut ikatan molekul adalah dalam julat yang normal. Kedua-dua sebatian A1 dan B1 adalah diskret dan mengandungi dua ikatan hidrogen intramolekul iaitu masing-masing pada (C14-H14B...N1 & C15-H15B...N1) dan (C15-H15A...N2 & C17-H17A...O) yang membentuk gelang pseudo enam ahli. Molekul A1 dan B1 masing-masing dihubungkan melalui ikatan hidrogen intermolekul C-H...O dan N-H...O. Dua mekanisma tindak balas pembentukan telah dicadangkan bagi menerangkan laluan sintetik bagi sebatian tersebut. Satu kaedah mudah untuk mensintesis sebatian 1,3,4-tiadiazol telah dicadangkan.