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MOLECULAR PROPERTIES, SPECTRA AND COMPLEX FORMATION OF METHYLBENZOYLTHIOUREA DERIVATIVES THROUGH EXPERIMENTAL AND AB INITIO CALCULATION STUDIES

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DEDICATION

This thesis is dedicated to my beloved parents

For their endless love, support and encouragement

Abstract of thesis presented to the Senate of Universiti Malaysia Terengganu in fulfillment of the requirement for the degree of Master of Science

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This thesis describes the comparison between the experimental study and ab initio calculation of methylbenzoylthiourea derivatives based on their molecular properties, spectra and complex formation. For the experimental study, thirteen molecules of methylbenzoylthiourea derivatives (L1-L13) were synthesized and successfully characterized using FTIR and NMR spectroscopy, while the crystal structures of these molecules were analyzed using single crystal X-ray diffraction analysis. For the theoretical study, Gaussian 09 software package at the theoretical level of DFT/B3LYP with three different basis set 6-31G(d,p), 6-31+G(d,p) and 6-311G(d,p) were employed to evaluate the optimized molecular geometry, vibrational frequencies and isotropic chemical shift analysis. The physical parameters such as total electronic energy, dipole moment, entropy, zero-point vibrational energy, specific heat capacity and thermal energy of these molecules were assessed at the same theoretical level. The results on the calculation of vibrational frequencies, isotropic chemical shift analysis and optimized molecular geometry were compared with the experimental value obtained from FTIR, NMR, X-ray, respectively. Interestingly, the optimized molecular geometry on the bond parameter studies for all molecules shows in good agreement with the data obtained from X-ray crystallography. The vibrational frequencies of these molecules are focused on several distinctive peaks such as ν(N-H), ν(C=O), ν(C-N) and ν(C=S) groups. The results on calculated values of basis set 6-31G(d,p) showed excellent consistencies data which is 99.82% compared to the other basis set such as [6-31+G(d,p) (99.76%)] and [6-311G(d,p) (99.79%)]. This means that the calculated data on vibrational frequencies of ν(N-H), ν(C=O), ν(C-N) and ν(C=S) using basis set 6-31G(d,p) is more consistent and systematic compared to the other basis set. Gauge Independent Atomic Orbital (GIAO) method were applied to predict the ^{1}H and ^{13}C NMR calculation of $\delta_{(C-H)}$, $\delta_{(N-H)}$, $\delta_{(C=O)}$ and

$\delta(_{C=S})$, respectively. The ratio of the experimental and theoretical values on the evaluation of $\delta(_{C=S})$ showed that the basis set 6-311G(d,p) produced good ratio which is 0.9364-0.9628. The study on the electronic properties of these molecules was investigated using the calculation on HOMO-LUMO energy and HOMO-LUMO band gap. The electronic studies showed that observed transition from HOMO to LUMO in methylbenzoylthiourea derivatives is $\pi \rightarrow \pi^*$. The results showed that these molecules have higher energy band gap which is 3.8773-4.3274 eV. This means that these molecules are not suitable to be used as electrical transport materials. Further studies on the possibility complex formation of ligand in interest with copper chloride were also employed using Gaussian 09 software package at the theoretical level of DFT/B3LYP with basis set LANL2DZ. From the results, thirteen complexes exhibit energy stabilization at calculated value of -157.3221 kJ/Mol to -183.1611 kJ/Mol. Hence, these methylbenzoythiourea derivatives ligands were suitable to form complex with copper chloride.

Abstrak tesis yang dikemukakan kepada Senat Universiti Malaysia Terengganu sebagai memilih keperluan untuk ijazah Sarjana Sains

KAJIAN SECARA EKPERIMEN DAN PENGIRAAN AB INITIO TERHADAP SIFAT MOLEKUL, SPEKTRA DAN PEMBENTUKAN KOMPLEKS TERBITAN METILBENZOILTIOUREA

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Tesis ini menerangkan tentang perbezaan antara kajian eksperimen dan pengiraan *ab initio* bagi sebatian terbitan metilbenzoiltiourea berdasarkan kepada sifat molekul, spektra dan pembentukan kompleks. Bagi kajian eksperimen, tiga belas molekul terbitan metilbenzoiltiourea telah disintesis dan telah berjaya dicirikan menggunakan spektroskopi Infra Merah Transformasi Fourier (FTIR) dan Resonans Magnetik Nukleus (NMR), manakala struktur hablur bagi semua molekul dianalisis menggunakan kaedah kristallografi Hablur Tunggal. Bagi kajian teori, pakej perisian *Gaussian 09* pada tahap teori *DFT/B3LYP* dengan tiga set asas yang berlainan iaitu 6-31G(d,p), 6-31+G(d,p) dan 6-311G(d,p) telah digunakan untuk menilai pengoptimuman geometri molekul, frekuensi getaran dan analisis anjakan kimia isotropik. Parameter fizikal seperti jumlah tenaga elektronik, momen dwikutub, entropi, titik sifar tenaga getaran, muatan haba tentu dan tenaga haba molekul ini telah dikira di peringkat teori yang sama. Keputusan pengiraan frekuensi getaran, analisis anjakan kimia isotropik dan geometri molekul yang dioptimumkan dibandingkan dengan nilai eksperimen dari FTIR, NMR, X-ray. Menariknya, pengoptimuman geometri molekul pada kajian parameter ikatan bagi semua molekul menunjukkan data yang baik dengan nilai ekperimen. Kajian frekuensi getaran bagi semua molekul memfokuskan empat regangan yang utama iaitu ν(N-H), ν(C=O), ν(C-N) dan ν(C=S). Set asas 6-31G(d,p) menunjukkan data yang sangat konsisten bagi semua molekul iaitu mencapai 99.82% berbanding set asas yang lain iaitu [6-31+G(d,p) (99.76%)] dan [6-311G(d,p) (99.79%)]. Ini bermakna data yang dikira pada frekuensi getaran ν(N-H), ν(C=O), ν(C-N) dan ν(C=S) menggunakan set asas 6-31G(d,p) adalah lebih sistematik berbanding set asas lain. Kaedah *Gauge Independent Atomic Orbital* (GIAO) telah digunakan untuk meramal pengiraan proton (^{1}H) dan karbon (^{13}C) NMR pada anjakan kimia $\delta_{(C-H)}$, $\delta_{(N-H)}$, $\delta_{(C=O)}$ dan $\delta_{(C=S)}$. Berdasarkan keputusan set asas 6-311G(d,p) yang diperolehi, nisbah nilai experimen dan teori pada anjakan kimia karbon tiol $\delta_{(C=S)}$ adalah sangat baik iaitu 0.9364-0.9628. Kajian ke atas sifat-sifat elektronik pada semua molekul ini telah dijalankan menggunakan pengiraan tenaga HOMO-LUMO dan jurang tenaga HOMO-LUMO. Sifat-sifat elektronik menunjukkan berlakunya

peralihan elektron daripada tenaga HOMO kepada tenaga LUMO pada molekul terbitan metilbenzoiltiourea iaitu $\pi \rightarrow \pi^*$. Berdasarkan keputusan yang diperolehi, semua molekul terbitan metilbenzoiltiourea mempunyai nilai jurang tenaga yang lebih tinggi iaitu 3.8773-4.3274 eV. Ini menunjukkan bahawa semua molekul ini tidak sesuai untuk digunakan sebagai bahan pengangkut elektrik. Kajian kebolehsesuaian pembentukan komplek kuprum klorida dengan semua ligan terbitan metilbenzoiltiourea juga dilakukan menggunakan pakej perisian *Gaussian 09* pada peringkat teori *DFT/B3LYP* dengan set asas *LANL2DZ*. Berdasarkan keputusan yang diperolehi, kesemua molekul ini menunjukkan tenaga kompleks yang stabil iaitu -157.3221 kJ/Mol hingga -183.1611 kJ/Mol. Oleh itu, semua ligan terbitan metilbenzoiltiourea ini sangat sesuai membentuk kompleks dengan kuprum klorida.