THEORETICAL STUDIES ON THE CONFORMATIONAL FLEXIBILITY AND STABILITY, ELECTRONIC PROPERTIES AND REACTION PATHWAY OF *N*-BENZOYL-*N'*-PYRIDYLTHIOUREA DERIVATIVES

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THEORETICAL STUDIES ON THE CONFORMATIONAL FLEXIBILITY AND STABILITY, ELECTRONIC PROPERTIES AND REACTION MECHANISM PATHWAY OF *N*-BENZOYL-*N'*-PYRIDYLTHIOUREA DERIVATIVES

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Two conformers of a single molecule of N-benzoyl-N'-(2-pyridyl)thiourea (M1), N-benzoyl-N'-(6-methyl-2-pyridyl)thiourea (M2), N-benzoyl-N'-(4-methyl-2-pyridyl)thiourea (M3), N-benzoyl-N'-(5-methyl-2-pyridyl)thiourea (M4), N-benzoyl-N'-(3-methyl-2-pyridyl)thiourea (M5) which are anti-syn and syn-anti were investigated through B3LYP and M06 method with 6-31G and G-311G(d,p) basis set are made for conformation analysis, atomic changer analysis, NBO, spectral study and reaction mechanism. It was found that anti-syn conformation is slightly stable compared to syn-anti conformation in all compounds. The stabilization of both conformers is attributed to the formation of intramolecular hydrogen bond, where compound M2 is the most stable. Conformational analysis has shown that energy barrier occurs at dihedral = 180° for all compound M1 – M5. NBO analysis of syn-anti conformation found that only compound M2 has hyperconjugation of methyl group with pseudo six-membered ring with the stabilization energy of 3.04 kJ/mol. Vibrational analysis also indicates that vibration of methyl group appeared only in syn-anti conformation at 1363 cm^{-1} and 1501 cm^{-1}(M2), 1425 $cm^{-1}$and 1515 cm^{-1}(M3), 1416 cm^{-1}(M4), 1447 cm^{-1} and 1508 cm^{-1}(M5) indicating polarity. Mulliken change analysis shows the increase of electron density of pseudo six-membered ring in syn-anti conformation and M2 is the highest. The sulphur atom of compound M2 has stronger ability to form intermolecular hydrogen bond to form bimolecular compound. Anti-syn conformers of compound M1 – M5 were suggested to form via two phases, which are nucleophilic addition reaction followed by conformational change. Potential energy surface scan indicating that M2 is harder to change from syn-anti to anti-syn conformation with an energy barrier of 68.30 kJ/mol in salvation. The appropriate position of methyl in compound M2 could form extra intra-molecular interaction with a benzene ring in syn-anti conformation.

By these findings, it's may give the explanation why compound crystallized in rare syn-anti conformation.

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KAJIAN SECARA TEORI TERHADAP KEBOLEHLENTURAN DAN KESTABILAN KONFORMASI, SIFAT – SIFAT ELEKTRON DAN LALUAN MEKANISME TINDAK BALAS BAGI SEBATIAN *N*-BENZOIL-*N'*-PIRIDILTIOUREA DAN TERBITANNYA

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Dua konformasi molekul tunggal untuk sebatian N-benzoil-N'-2-piridiltiourea (M1), N-benzoil-N'-(6-metil-2-piridil)tiourea (M2), N-benzoil-N'-(4-metil-2-piridil)tiourea (M3), N-benzoil-N'-(5-metil-2-piridil)tiourea (M4), N-benzoil-N'-(3-metil-2-piridil)tiourea (M5) iaitu anti-sin dan sin-anti telah dikaji menggunakan kaedah B3LYP dan M06 berserta dengan basis set 6-31G dan G-311G(d,p). Kajian tersebut di buat keatas konformasi molekul,taburan cas atom, NBO, analisis spektroskopi dan mekanisma tindak balas. Didapati bahawa konformasi anti-sin adalah lebih stabil daripada konformasi sin-anti bagi semua sebatian tersebut. Kestabilan kedua-dua konformasi itu disebabkan oleh pembentukan ikatan hidrogen intramolekul dan sebatian M2 adalah yang paling stabil. Hasil daripada analisis konformasi mendapati sawar tenaga berlaku pada konfomasi dihedral = 180° untuk semua sebatian M1 – M5. Analisis NBO pula mendapati pada konformasisin-anti, hanya gegelang enam ahli pada sebatian M2 yang mampu melakukan hiperkojugas idengan kumpulan metil yang mana tenaga penstabilannya adalah 3.04 kJ/mol. Analisis spektrum IR mendapati munculnya puncak bagi getaran kumpulan metil untuk konformasi sin-anti pada 1363 cm^{-1} dan 1501 cm^{-1} (M2), 1425 cm^{-1} dan 1515 cm^{-1} (M3), 1416 cm^{-1} (M4), 1447 cm^{-1} dan 1508 cm^{-1} (M5) ini memberi makna bahawa kumpulan metil itu mempunyai sifat kekutuban. Analisis cas Mulliken pula menujukkan berlaku peningkatan ketumpatan elektron pada gegelang enam ahli untuk konformasi syn-anti dan sebatian M2 menunjukkan peningkatan yang tertinggi, Atom sulfur pula untuk sebatian M2 mempunyai keupayaan yang lebih tinggi untuk membentuk ikatan hidrogen antara molekul bagi membentuk sebatian dwi-molekul. Konformasi anti-sin bagi sebation M1 – M5 dicadangkan terbentuk

melalui dua fasa iaitu tindak balas penambahan nukleofilik diikuti dengan transformasi konformasi. Imbasan permukaan tenaga keupayaan pula menunjukkan bahawa sebatian M2 lebih sukar untuk berubah konformasinya dari sin-anti kepada anti-sin dengan sawar tenaga adalah 68.30 kJ/mol dalam keadaan keterlarutan.Ini bermakna kedudukan yang sesuai bagi kumpulan penukar ganti metil membentuk interaksi antara molekul dengan gelang benzena pada konformasi sin-anti untuk sebatian M2. Penemuan ini dapat memberi gambaran kenapa sebatian M2 terhablur dalam konformasi sin-anti yang jarang-jarang berlaku.