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Vibrational and NMR studies on diethyl 2–(ter–butylimino)–2,5–dihydro–5–ox0–1–phenyl–1H–pyrrole–3,4–dicarboxylate using DFT calculations

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Abstract: Synthesis of diethyl–2–(ter–butylimino)–2,5–dihydro–5–oxo–1–phenyl–1H–pyrrole–3,4–dicarboxylate, 1, was carried out and characterized by FT–IR,^{1}HNMR, ^{13}CNMR spectroscopy. The structures were confirmed by ^{1}H and ^{13}C nuclear magnetic resonance and FT-IR. The experimental results were compared with by performing DFT calculations in geometries, vibrational frequencies and proton and carbon shieldings constants using 6–311G++(d,p) basis set with B3LYP and PBE1PBE methods. The wavelength frequencies were calculated for **1** and compared with experimental data.The DFT calculations indicated that for wavelength frequencies,the B3LYP method give more accurate results. The ^{13}C NMR and ^{1}H NMR chemical shifts of **1** calculated and compared with available experimental data of the molecules.

Keywords: Diethyl-2–(tert–butylimino)–2,5–dihydro–5–ox0–1–phenyl–1H–pyrrole–3,4–dicarboxylate, DFT, FT–IR, NMR chemical shifts.

Introduction

Pyrrole derivatives are heterocyclic compounds that have great interest during the last few years because of their biological activity which they applied in synthesis of the natural and non–natural products [1, 2]. Multicomponent reactions based on isocyanide, typically lead to the formation cyclic and acyclic useful compounds. These reactions are attracted in chemistry because these reactions increase the efficiency by combining several steps without any isolation of intermediates or changes of the conditions [3–7]. Isocyanides have nucleophilic character towards dimethyl acetylenedicarboxylate (DMAD) [8,9]. In these reactions isocyanides reacted with carbon–carbon triple bonds in a one–pot through a zwitterionic intermediate [10].

In this study, we report a three component reaction due to synthesis of diethyl2–(ter–butylimino)–2,5–dihydro–5–oxo–1–phenyl–1H–pyrrole–3,4–dicarboxylate, **1** (Schemes **1**) [11-20]. The DFT study on the geometrical parameters, vibrational analysis, proton or carbon chemical shifts of **1**preformed and theoretical results compared with the experimental data.

Results and Discussion

A proposed reaction mechanism indicates that three–component reactions between three compounds which presents in Scheme **2**.

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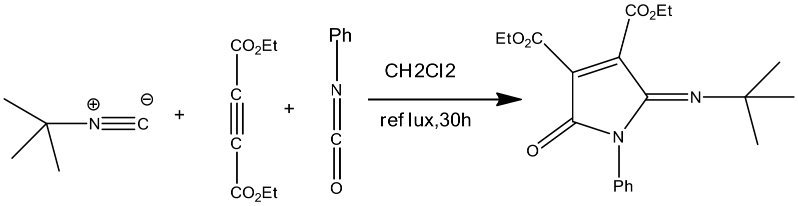
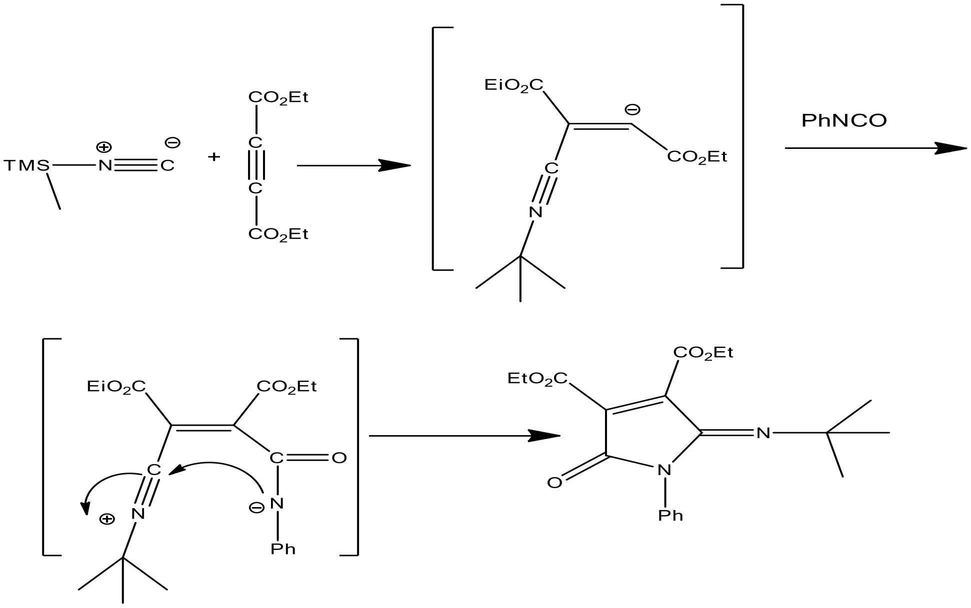
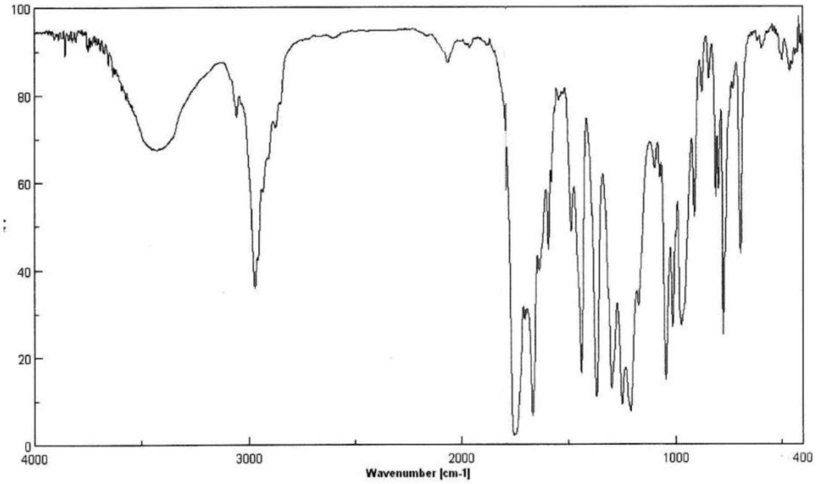


Scheme 1. Diethyl 2-(ter-butylimino)-2,5-dihydro-5-ox0-1-phenyl-1H-pyrrole-3,4-carboxylate



Scheme 2. A proposed mechanism for synthesis of **1**.



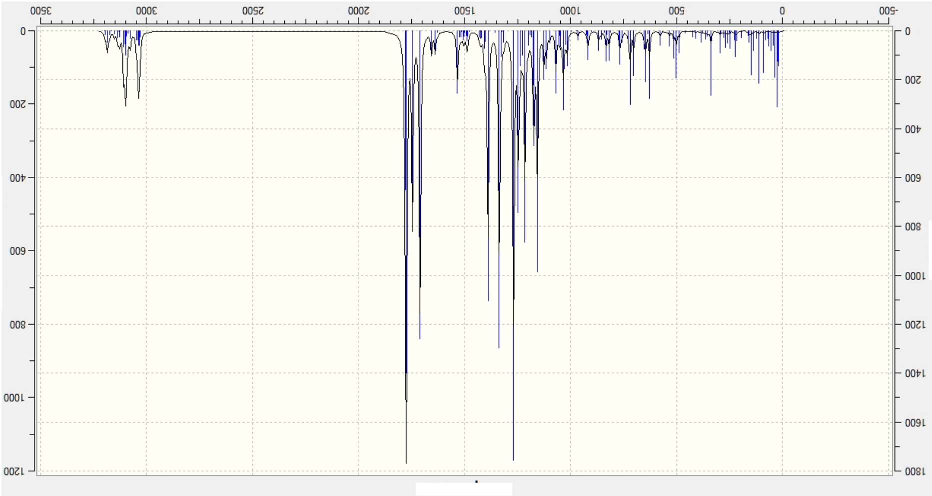


Figure 1. Experimental and calculated IR spectra for **1**.

Vibrational assignments

The experimental and calculated FT–IR spectra of **1** were shown in Fig. 1.The studied molecule consists of 51 atoms. The number of vibration normal modes of 1 were 147 normal vibrational modes including 111 in–plane (A') vibrations modes and 36 out–of–plane (A '') modes. Total of these vibration were sum of A' and A'' (Γvib= 111A' +36A'').

C–H vibrations

The C–H stretching vibration in alkanes, alkenes and aromatic structure are in the regions of 2850–3000 cm$^{–1}$, 3010–3100cm$^{–1}$ and 3000–3100cm$^{–1}$, respectively [25, 26]. InFT–IRspectrum,the C–H stretching vibration was observed for alkane and phenyl group at 2970 and 3056cm$^{–1}$,respectively.The calculated C–H stretching vibrations appear at 2933 and 3053 cm$^{–1}$ using the B3LYP/6–311++G(d,p) level which was in good agreement with experimental data. The calculated C–H stretching vibrations appear at 3032 and 3161 cm$^{–1}$ by the PBE1PBE/6–311++G(d,p) level.

C=C vibrations

The C=C stretching vibrations in alkenes and aromatic compounds normally occur in the region of 1620–1680 cm$^{–1}$and 1400–1600 cm$^{–1}$, respectively [25, 26]. The C=C stretching vibrations in pyrrole ring observed at 1592 cm$^{–1}$. The calculated C=C stretching vibration appears at 1576cm$^{–1}$ using the B3LYP/6–311++G(d,p) level which was in good agreement with experimental data. The calculated C=C stretching vibration appears at 1646 cm$^{–1}$ by the PBE1PBE/6–311++G(d,p) level.

C=O vibrations

The C=O bond in esters and amides assigned in the region of 1730–1750 and 1630–1690cm$^{–1}$, respectively [25, 26]. For title compound, the C=O bond assigned at 1744, 1721 cm$^{–1}$ for two esters and 1668 cm$^{–1}$for amide functional group. The calculated C=O stretching vibration appears at 1722 and 1718 cm$^{–1}$for two esters and 1691 cm$^{–1}$for amide functional groupusing the B3LYP/6–311++G(d,p) level which was closer to experimental data. The calculated C=O stretching vibration appears at 1812 and 1808 cm$^{–1}$ for ester and 1777cm$^{–1}$ for amide by the PBE1PBE/6–311++G(d,p) level.

C=N vibrations

The stretching absorption of C=N appears in the region of 1640–1690 cm$^{–1}$[25, 26]. In this structure, the C=N bond experimentally assigned at 1635 cm$^{–1}$.The calculated C=N stretching vibration appears at 1656 cm$^{–1}$ using the B3LYP/6–311++G(d,p) and at 1740 cm$^{–1}$ by the PBE1PBE/6–311++G(d,p) level. Relationship between the experimental and computed wavelength number of **1** obtained by B3LYP and PBE1PBE which presented in Fig. 2. The computed vibrational frequency of **1** were in good agreement with the experimental values at the B3LYP level (R^2=0.9991) which in contrast with PBE1PBE level (R^2=0.9988) (Figure **2**). This graph shows that the calculated frequencies at the B3LYP method were closer to experimental data.

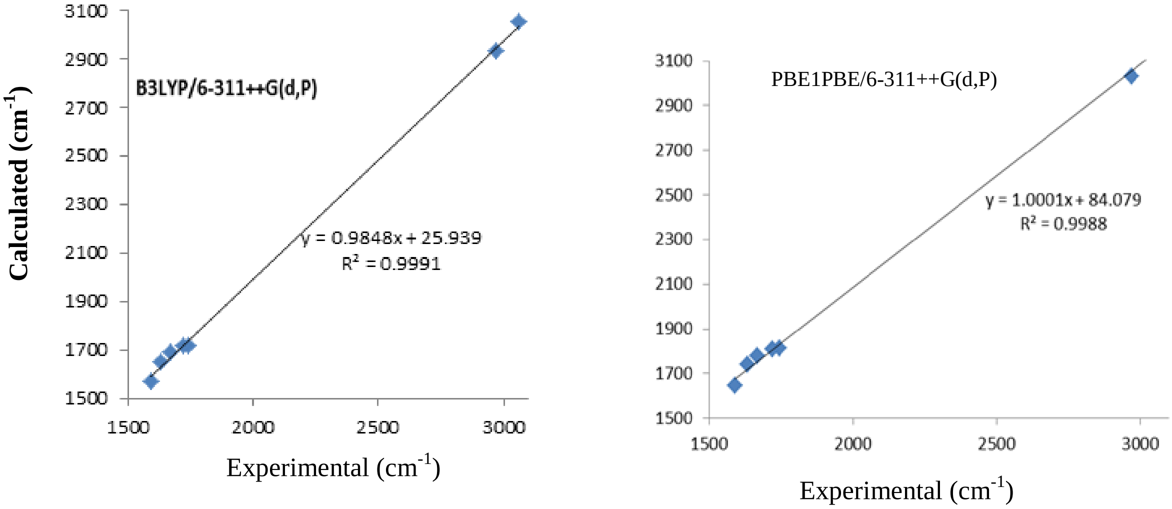
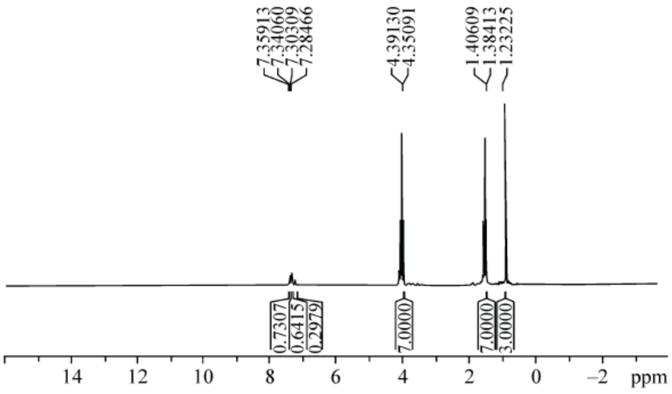


Figure 2. Relationship between the experimental and computed frequencies of **1**.

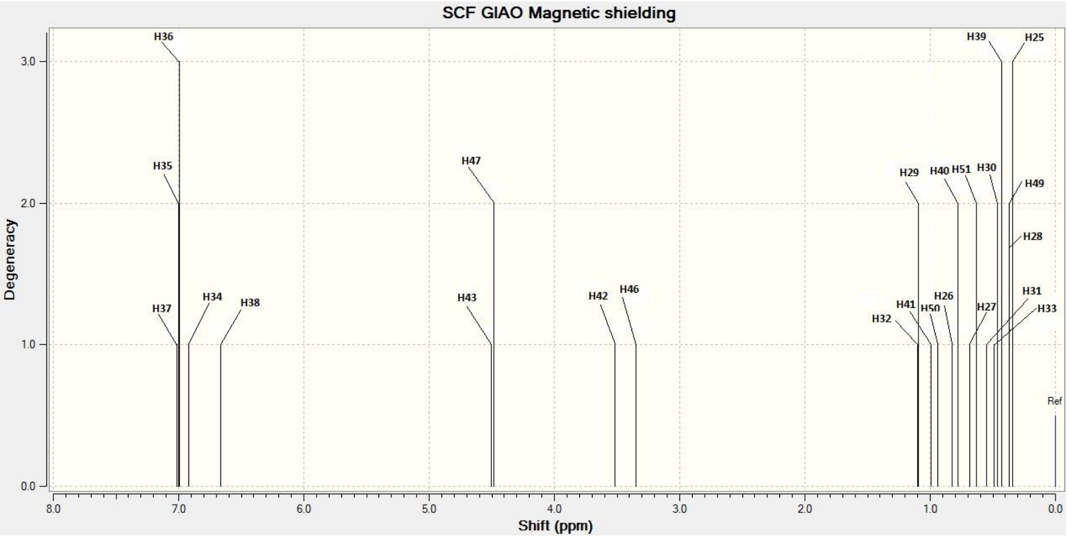
Chemical Shift Analysis

Proton Chemical Shift Analysis, ^{1}H NMR

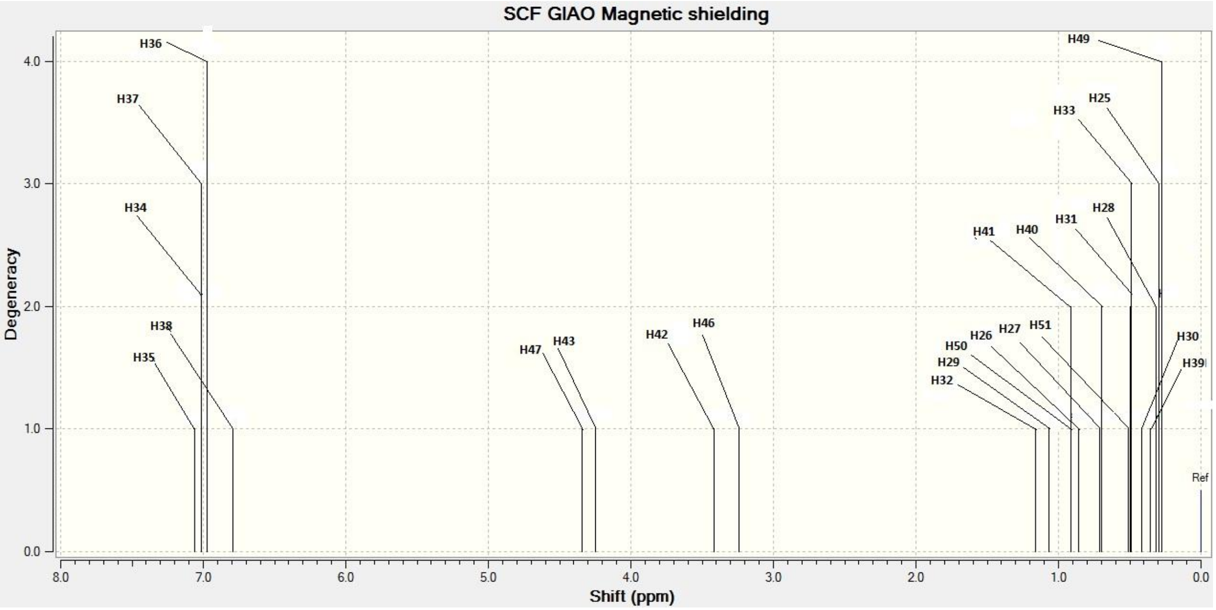
Experimental and theoretically simulation of ^{1}H NMR spectra were performed by GaussView software which was shown in Figure **3**.The ^{1}H chemical shift values (with respect to TMS) occur at 0.64-6.92 ppm and 0.56-6.97 ppm by the B3LYP and PBE1PBE levels, respectively, whereas the experimental shifts are observed at 1.28-7.31 ppm. The methyl protons ($H_{25–27}$, $H_{28–30}$ and $H_{31–33}$) experimentally resonate at 1.28 ppm as a singlet which these chemical shifts theoretically predict resonate at 0.67 ppm and 0.64 at the B3LYP and PBE1PBE levels of theory, respectively. The methyl protons of the ethyl groups ($H_{39–41}$ and $H_{49–51}$) experimentally resonate at 1.38 and 1.40 ppm as a triplet which those chemical shifts theoretically predict in the range of 0.64-0.73 ppm and 0.56-0.65 at the B3LYP and PBE1PBE levels of theory, respectively. The signals at 4.37 ppm was assigned to the methylene protons which experimentally resonate in the range of 3.96 and 3.81 at the B3LYP and PBE1PBE levels of theory, respectively ($H_{42,43}$and $H_{46,47}$). The multiplet at 7.31 ppm corresponds to the aromatic protons ($H_{34–38}$) that calculated at 6.92 and 6.97 ppm by the B3LYP and PBE1PBE, respectively.



Experimental ^{1}H NMR



Calculated ^{1}H NMR(B3LYP)

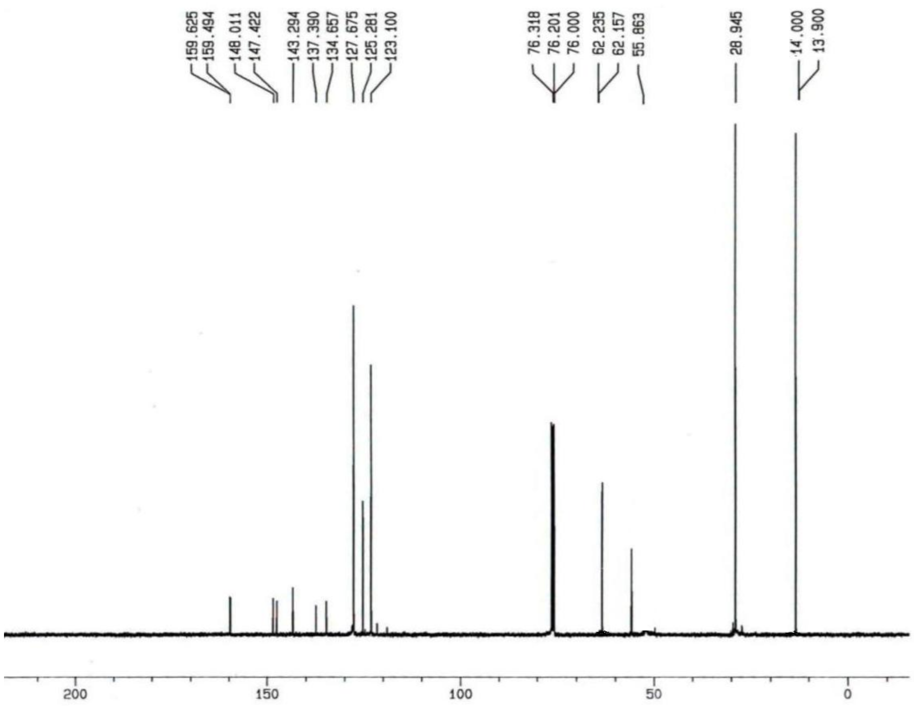


Calculated ^{1}H NMR(PBE1PBE)

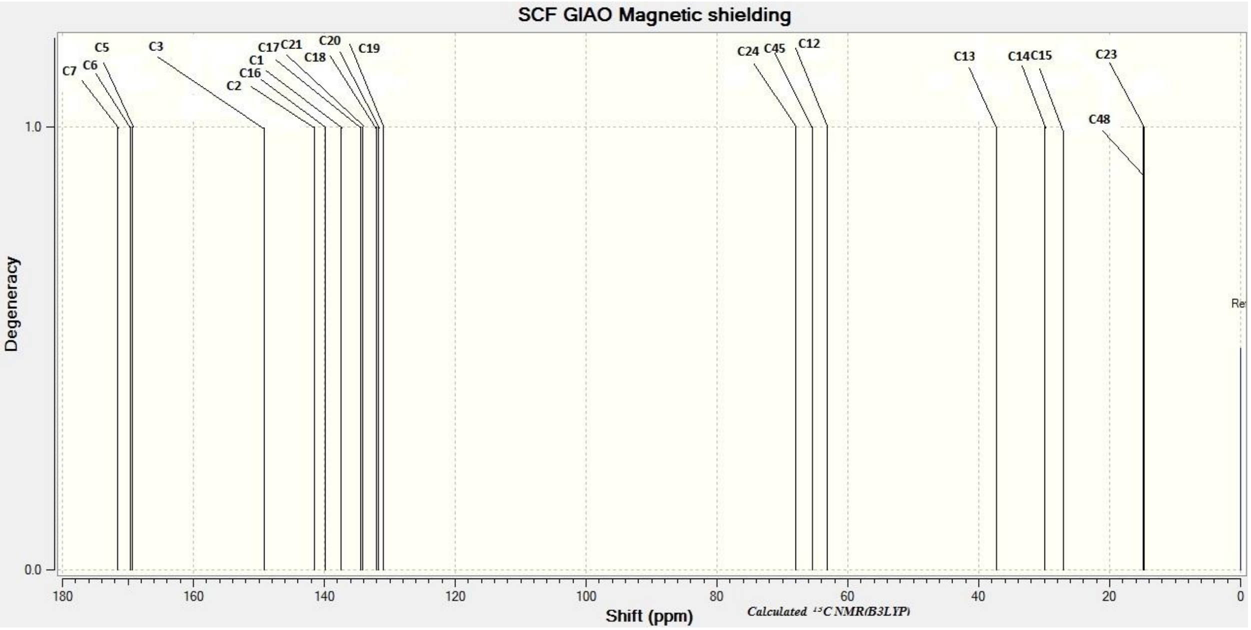
Figure 3. Experimental and calculated ^{1}H NMR.

Carbon Chemical Shift Analysis, ^{13}CNMR

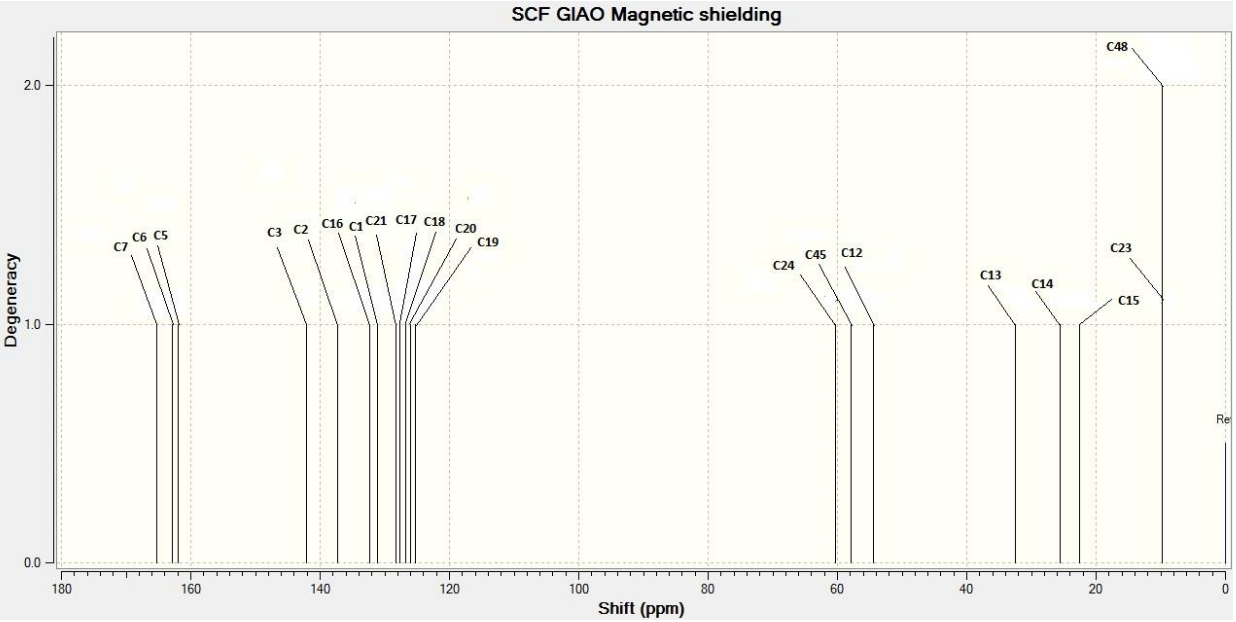
Experimental and theoretically simulation of ^{1}H NMR spectra were performed by GaussView software which was shown in Figure **4**. The ^{13}C chemical shift values (with respect to TMS) assigned in the range of 10.40-165.79and 9.81–163.34 ppm by B3LYP and PBE1PBE, respectively while the experimental results were located in the range of 13.95–155.71 ppm. The chemical shift values of for the ethyl group,experimentally were observed at 13.95 and 62.15 ppm. The theoretically chemical shift values of thatgroup assigned at 10.4 ($|\delta_{exp}–\delta_{B3LYP}|=3.55$), 62.37 ($|\delta_{exp}–\delta_{B3LYP}|=–0.11$) at the B3LYP, and 9.81 ($|\delta_{exp}–\delta_{PBE1PBE}|=4.19$), 59.10($|\delta_{exp}–\delta_{PBE1PBE}|=3.05$)at PBE1PBE levels, respectively. The chemical shift value of carbonyl groups experimentally were observed at 155.71 ppm. The theoretically chemical shift values of that group assigned at 165.79($|\delta_{exp}–\delta_{B3LYP}|=-10.09$), at the B3LYP, and 163.34 ($|\delta_{exp}–\delta_{PBE1PBE}|=-7.64$) at PBE1PBE level, respectively.



Experimental ^{13}C NMR



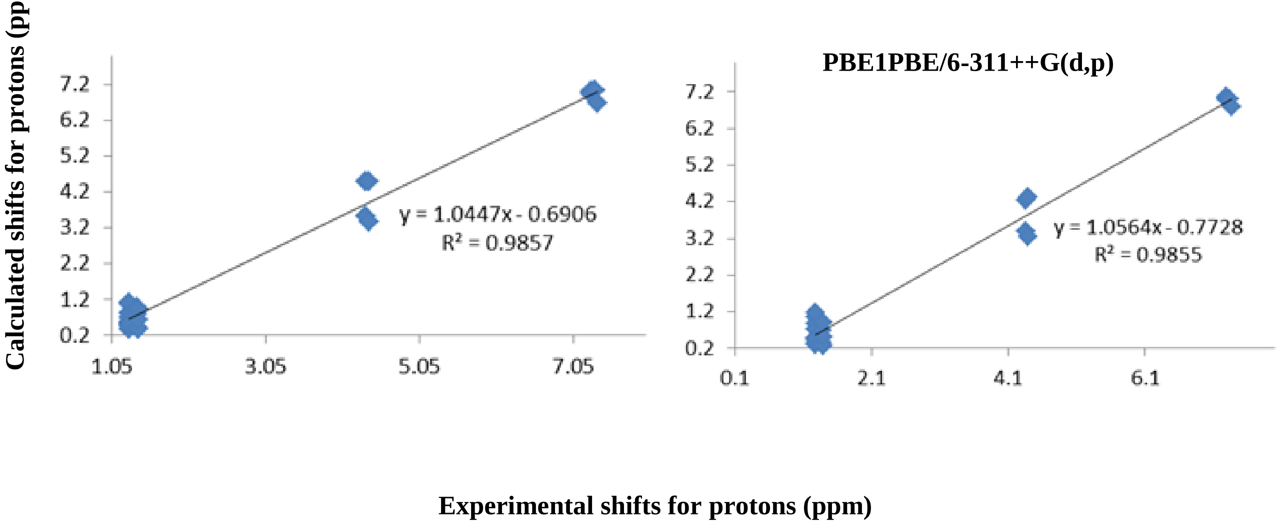
Calculated ^{13}C NMR (B3LYP)



Calculated ^{13}C NMR (PBE1PBE)

Figure 4. Experimental and calculated ***^{13}CNMR***.

Relationship between the experimental and calculated chemical shift of ^{1}H and ^{13}CNMR for 1 is shown in Figure **5**. The B3LYP values of the chemical shift for ^{1}H and ^{13}C correlation (R^2_{1HNMR}=0.9857 and R^2_{13CNMR}=0.9942) were found to be in good agreement with the experimental values while the PBE1PBE values (R^2_{1HNMR}=0.9855 and R^2_{13CNMR}=0.9949) were found to be in good agreement with the experimental values for ^{13}CNMR.



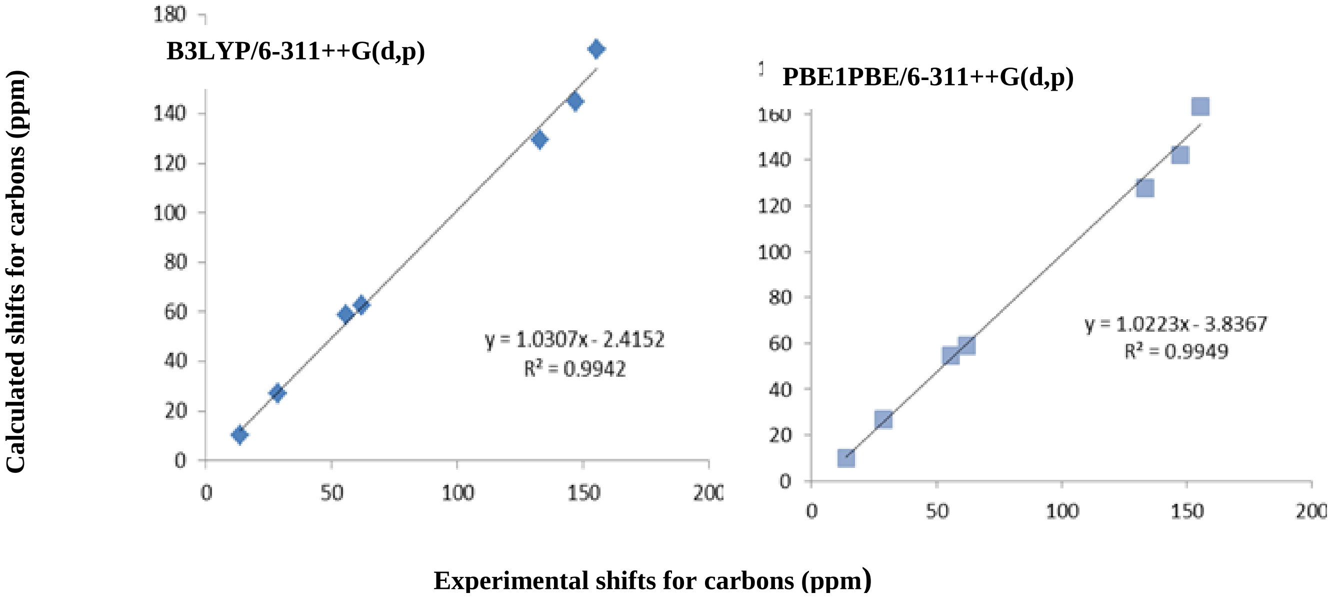


Figure 5: Relationship between the experimental and calculated chemical shift for ^{1}H and ^{13}C NMR of **1**.

Conclusion

The studied compound in this work, diethyl 2–(ter–butylimino)–2,5–dihydro–5–oxo–1–phenyl–1H–pyrrole–3,4–dicarboxylate, 1, has been produced via one–pot three components, between, t–butyl isocyanides, diethyl acetylenedicarboxylate and phenyl isocyanate in this reaction. The structure of 1 was determined and characterized by elemental analysis, FT–IR,^{1}H and ^{13}CNMR. Comparison between the calculated and experimental values of the vibrational wavenumbers and chemical shift for ^{1}HNMR calculation of **1** indicates that the B3LYP level is better than PBE1PBE level of theory. Comparisons between the calculated chemical shift for ^{13}CNMR shows that the PBE1PBE/6–311++G(d,p) level found to be in good agreement with the experimental values.

Experimental

Synthesis and mechanism of the reaction

Starting materials and solvents were obtained from Merck (Germany) and Fluka (Switzerland) and were used without further purification. Three components in this reaction are t–butyl isocyanides, diethylacetylenedicarboxylate and phenyl isocyante. This one–pot synthesis proceeded spontaneously at 35 ^{0}C in CH_2C_{l2} and leads to diethyl 2–(ter–butylimino)–2,5–dihydro–5–oxo–1–phenyl–1H–pyrrole–3,4–dicarboxylate, **1** (Scheme **1**)[21].The solution of t–butyl isocyanides (0.1 g, 1 mmol) in dry CH_2Cl_2 (5 ml) solvent was slowly added dropwise to a mixture of phenyl isocyanate (0.1 g, 0.8 mmol) and DEAD (0.13 g, 0.8 mmol) in 25 mL of CH_2Cl_2 solvent for 5 min. After the addition, the mixture was allowed to warm to room temperature and was refluxed at 35 ºC for 30 h. Then, the solvent was removed under reduced pressure. Then, the solvent was removed under reduced pressure, and the yellow powder product washed with mixture of cold diethyl ether and n–hexane with 1: 3 ratio (2×3 mL). The liquid phase was filtered off and residual recrystallized in diethyl ether. The progress of the reactions monitored by TLC and NMR techniques, which indicated that there were no side products. The IR spectra measured on a Perkin–Elmer RXI and FT–IR spectrometer. The ^{1}H and ^{13}C NMR spectra ($CDCl_3$) recorded on a BrukerAvance Spectrometer at 250.0 and 62.9 MHz, respectively.

Diethyl-2–(tert–butylimino)–2,5–dihydro–5–ox0–1–phenyl–1H–pyrrole–3,4–dicarboxylate

Yellow crystals; yield 82%, 0.31 g, mp 63–65 ° C; IR (KBr) (νmax, cm^{-1}): 1744 and 1721 (2C=O of ester), 1668 (C=O). ^{1}H NMR (400.1 MHz, $CDCl_3$): δH 1.28 (9H, s, CMe_3), 1.38 and 1.40 (6H, 2t, $2CH_3$), 4.35 and 4.39 (4H, 2q, $2OCH_2$), 7.28–7.36 (5H, m, Ar–H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δC 13.9 and 14.0

($2CH_3$), 28.9 (CMe_3), 55.7 (N–CMe_3), 62.1 and 62.2 ($2OCH_2$), 123.1, 125.3, 127.7, 134.6, 137.4, 143.3 (C_{arom} and C=$C_{pyrrole\ ring}$), 147.4 (C=N), 148.0 (C=O), 159.5 and 159.6 (2C=O of ester).

In present work, we carried out the theoretical investigation on **1** using B3LYP and PBE1PBE methods with 6–311++G(d,p). All the calculations were done using Gaussian 09 program [22]. The chemical shifts were calculated based on GIAO approach and applied to the optimized molecule [23]. The chemical shifts (δ) were calculated by subtracting the appropriate isotopic part of the shielding tensor σ from that of TMS σ_{TMS}: $\delta = \sigma_{TMS} - \sigma$ (ppm). Furthermore, ^1H and ^{13}C chemical shifts were simulated using GaussView software [24].

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