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# Spectroscopic and DFT Investigations on Some New Aryl (trichloroacetyl)carbamate Derivatives

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A two-component reaction between phenol or naphthol derivatives and trichloroacetyl isocyanate in $CH_2Cl_2$ was performed smoothly and cleanly at room temperature and aryl (trichloroacetyl)carbamate derivatives were formed in excellent yields and no side reactions were observed. The structures of the products were confirmed by IR, $^1$H NMR, $^{13}$C NMR and elemental analyses. The data from IR spectra and $^1$H and $^{13}$C NMR chemical shifts computations of the aryl (trichloroacetyl)carbamate derivatives in the ground state were calculated using density functional theory. The correlation graphic for compounds by the B3LYP method associated with the 6-311++G** basis set in gas phase and $CH_2Cl_2$ solvent are presented. There was an excellent agreement between the experimental and theoretical results.

**Keywords:** Trichloroacetyl isocyanate, Carbamate, Density functional theory

## INTTRODUCTION

Carbamates (urethanes) widely provide useful properties in the agrochemicals industry as herbicides [1], fungicides [2] and pesticides [3], in the pharmaceuticals industry [4], in the synthesis of polyurethane [5], in protection of amino groups in peptide chemistry [6] and in combinatorial chemistry as linkers [7]. The role of carbamate linkage has been fundamentally investigated in structurally different molecules against different diseases such as cancer, bacterial and fungal diseases, malaria, viral diseases, HIV, estrogenic, progestational and osteoporosis diseases, inflammatory, filarial, and tubercular maladies, diabetes, obesity, convulsion, helminths and Alzheimer's disease [8-11]. Carbamates are usually produced as a result of the reaction between amines, alcohols, and phosgene, which is a toxic and flammable carbonylation reagent [12-14]. Safer compounds such as 1,1,1-trichloromethylformate (diphosgene) [15] and bis-(1,1,1-trichloromethyl) carbonate (triphosgene) have been suggested as alternatives to phosgene [16] and have been extensively used recently.

Other methods for the synthesis of carbamate derivatives include the reaction between substituted ureas and organic carbonates in the presence of a catalyst [17], the reaction of an amine, $CO_2$ and alkyl halides in the presence of $Cs_2CO_3$ and tetrabutylammonium iodide [18], the reaction of amines with chloroformates using catalytic amounts of Yttria-Zirconium [19], and the reaction of aromatic oximes with alcohols using methyltrioxorhenium and urea-hydrogen peroxide [20].

Computational chemistry is defined as the application of computer simulation to predict or interpret chemical reactivities. Computational organic chemistry has been also introduced as an important area in determining the mechanisms of chemical reactions [21], especially catalysis [22], structural determination of organic compounds [23], prediction of spectroscopic data such as $^1$H NMR and $^{13}$C NMR chemical shifts [24], calculating properties of organic molecules [25] and the interaction of a substrate with an enzyme [26].

In recent years, density functional theory (DFT) has become very popular among computational chemists. The basic premise of DFT is that the energy of a molecule can be determined from its electron density instead of a wave

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*Corresponding author. E-mail: shajari_nahid@yahoo.com function. This theory is originated from the Hoenburg-Kohn theorem [27]. A practical application of this theory was developed by Kohn and Sham (Kohn-Sham method) [28].

In line with our recent interest in trichloroacetyl isocyanate chemistry [31] and computational chemistry [30], herein, a two-component reaction of phenol or naphthol derivatives (1) with trichloroacetyl isocyanate (2) to produce aryl (trichloroacetyl)carbamate derivatives (3) is reported. Also, the IR spectra data, $^{1}$H and $^{13}$C NMR chemical shifts computations, the thermodynamic and electronic properties of the aryl (trichloroacetyl) carbamate derivatives are studied using density functional theory (DFT).

## RESULTS AND DISCUSSION

The two-component reaction of phenol or naphthol derivatives (1) with trichloroacetyl isocyanate (2) occurred in a 1:1 ratio in $CH_2Cl_2$ at room temperature, and the aryl (trichloroacetyl)carbamate derivatives (3a-d) were afforded in high yields, and fairly mild reaction conditions (Fig. 1 and Table 1). A mechanistic rationalization proposed for this reaction is provided in Fig. 2. The structures of the products were deduced from their $^{1}$H NMR, $^{13}$C NMR, IR spectra, and elemental analysis. For example, the $^{1}$H NMR spectrum of 3a exhibited distinct signals at $\delta_H$ 7.18-7.45 ppm (5H, *m*) arising from the aromatic CH groups and at $\delta_H$ 8.87 ppm (1H, *s*) for the NH group. The $^{13}$C NMR spectrum of 3a showed 7 distinct resonances arising from the $CCl_3$ group ($\delta$c 91.57 ppm), aromatic carbons ($\delta$c 121.08, 126.79, 129.72 and 149.59 ppm) and 2C=O ($\delta$c 148.15 and 157.87 ppm).

## EXPERIMENTAL

All starting materials and solvents were purchased from Merck (Germany) and Fluka (Switzerland) and were used without further purification. The melting points were measured using an electrothermal 9100 apparatus and were uncorrected. The IR spectra were recorded on a Jasco FT-IR 6300 spectrometer. The $^{1}$H and $^{13}$C NMR spectra were measured ($CDCl_3$ solution) with a Bruker DRX-250 Avance spectrometer at 250.13 and 62.90 MHz, respectively. The elemental analyses were realized using a Heraeus CHN-O-rapid analyzer.

### General Procedure for the Synthesis of 3a-d

To a magnetically stirred solution of trichloroacetyl isocyanate (2, 1 mmol) in $CH_2Cl_2$ (5 ml) was added phenol or naphthol derivatives (1, 1 mmol) at -10 °C. The mixture was stirred at room temperature for 1-2 h. Then, the mixture was filtrated, and the products 3a-d were obtained.

**Phenyl (trichloroacetyl)carbamate (3a).** White solid, yield: 98%; m. p.: 79.9-81.8 °C; Anal. Calcd. for $C_9H_6Cl_3NO_3$ (282.51): C, 38.26; H, 2.14; N, 4.96. Found: C, 38.34; H, 2.10; N, 5.01; IR (KBr, cm$^{-1}$): 3376 (NH), 1736 (C=O), 1667 (C=O), 1459 (C-N), 1203 (C-O), 849 (C-Cl, Str.), 499 (C-Cl, bending); $^{1}$H NMR (250.13 MHz, $CDCl_3$, $\delta$/ppm): 7.18-7.21 (2H, *m*, aromatic C*H*), 7.29- 7.32 (1H, *m*, aromatic C*H*), 7.39- 7.45 (2H, *m*, aromatic C*H*), 8.87 (1H, *s*, NH); $^{13}$C NMR (62.90 MHz, $CDCl_3$, $\delta$/ ppm): 91.57 ($CCl_3$), 121.08, 126.79 and 129.72 (5*C*H, aromatic), 149.59 (C, aromatic), 148.15 and 157.87 (2C=O).

**4-*Tert*-butylphenyl (trichloroacetyl)carbamate (3b).** White solid, yield: 98%; m. p.: 100.4-102.3 °C; Anal. Calcd. for $C_{13}H_{14}Cl_3NO_3$ (338.61): C, 46.11; H, 4.17; N, 4.14. Found: C, 46.18; H, 4.12; N, 4.21; IR (KBr, cm$^{-1}$): 3371 (NH), 1789 (C=O), 1726 (C=O), 1253 (C-O), 861 (C-Cl, Str.), 471 (C-Cl, bending); $^{1}$H NMR (250.13 MHz, $CDCl_3$, $\delta$/ppm): 1.32 (9H, *s*, *Me*$_3$C), 7.11 (2H, *d*, $^{3}J_{HH}$ = 8.5 Hz, aromatic C*H*), 7.42 (2H, *d*, $^{3}J_{HH}$ = 8.5 Hz, aromatic C*H*), 8.85 (1H, *s*, NH); $^{13}$C NMR (62.90 MHz, $CDCl_3$, $\delta$/ppm): 31.37 (*Me*$_3$C), 34.57 (Me$_3$*C*), 91.61 ($CCl_3$), 120.39 and 126.60 (4*C*H, aromatic), 147.29 and 149.74 (2C, aromatic), 148.30 and 157.85 (2C=O).

**Naphtalen-1-yl (trichloroacetyl)carbamate (3c).** White solid, yield: 96%; m. p.: 142.2-144.9 °C; Anal. Calcd. for $C_{13}H_8Cl_3NO_3$ (332.57): C, 46.95; H, 2.42; N, 4.21. Found: C, 46.92; H, 2.45; N, 4.28; IR (KBr, cm$^{-1}$): 3292 (NH), 1792 (C=O), 1507, 1246 (C-O), 830 (C-Cl, Str.), 430 (C-Cl, bending); $^{1}$H NMR (250.13 MHz, $CDCl_3$, $\delta$/ppm): 7.38-7.57 (4H, *m*, aromatic C*H*), 7.79- 7.98 (3H, *m* , aromatic C*H*), 9.02 (1H, *s*, NH); $^{13}$C NMR (62.90 MHz, $CDCl_3$, $\delta$/ppm): 91.65 ($CCl_3$), 117.85, 120.74, 125.25, 126.84, 127.01 and 128.12 (7*C*H, aromatic), 126.23, 134.66 and 145.41 (3C, aromatic), 148.36 and 157.88 (2C=O).

**Naphtalen-2-yl (trichloroacetyl)carbamate (3d).**

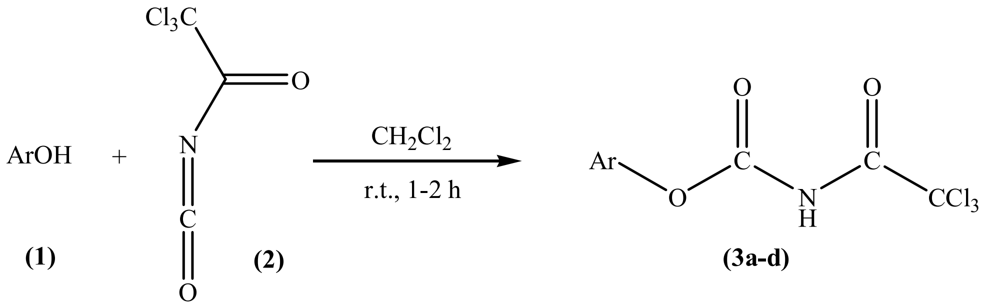
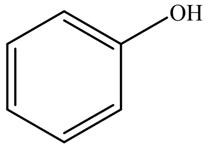
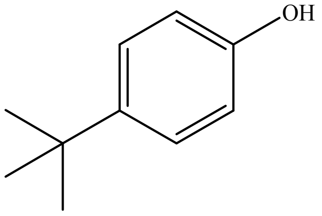
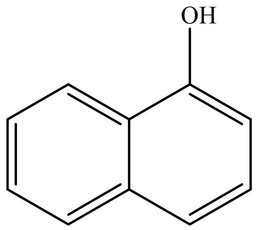
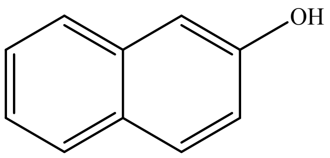


**Fig. 1.** Two-component reaction of trichloroacetyl isocyanate with phenol or naphthol derivatives (3a-d).

**Table 1.** Synthesis of Aryl (trichloroacetyl)carbamate Derivatives (3a-d)

| Entry | Compounds | ArOH | Yield (%) |
|---|---|---|---|
| 1 | 3a |  | 98 |
| 2 | 3b |  | 98 |
| 3 | 3c |  | 96 |
| 4 | 3d |  | 95 |

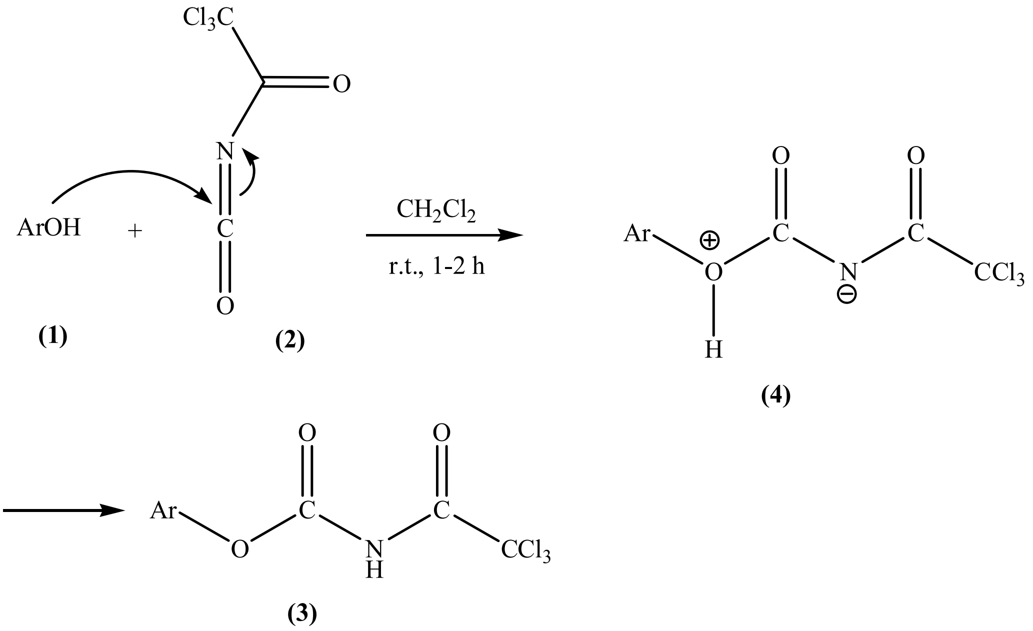


**Fig. 2.** A proposed mechanism for the formation of (3).

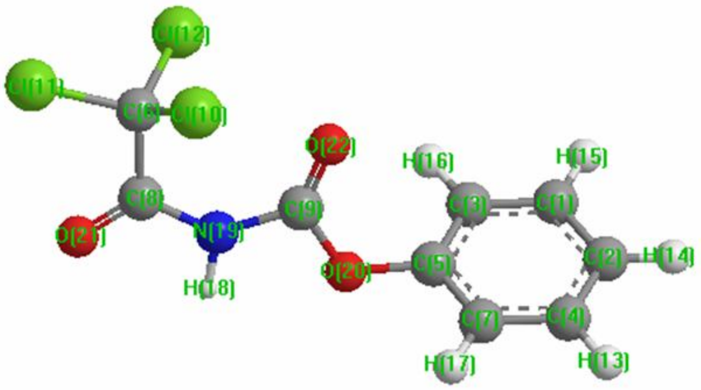


**Fig. 3.** The theoretical geometric structure of compound (3a) (optimized at the B3LYP/6-311++G** level).

White solid, yield: 95%; m. p.: 139.2-140.5 °C; Anal. Calcd. for $C_{13}H_8Cl_3NO_3$ (332.57): C, 46.95; H, 2.42; N, 4.21. Found: C, 46.93; H, 2.46; N, 4.17; IR (KBr, $cm^{-1}$): 3292 (NH), 1792 (C=O), 1507, 1246 (C-O), 830 (C-Cl, Str.), 438 (C-Cl, bending); $^1H$ NMR (250.13 MHz, $CDCl_3$, $\delta$/ppm): 2.28-7.35 (1H, *m*, aromatic C*H*), 7.48-7.56 (2H, *m*, aromatic C*H*), 7.66-7.72 (1H, *m*, aromatic C*H*), 7.81-7.91 (3H, *m*, aromatic C*H*), 8.84 (1H, *s*, NH); $^{13}C$ NMR (62.90 MHz, $CDCl_3$, $\delta$/ppm): 91.60 ($CCl_3$), 118.41, 120.10, 126.31, 126.98, 127.79, 127.85 and 129.86 (7*C*H, aromatic), 131.77, 133.53 and 147.17 (3C, aromatic), 148.18 and 157.79 (2C=O).

## COMPUTATIONAL METHODS

All the calculations were carried out using the Gaussian

**Table 2.** The Comparison of Observed and Calculated Vibrational Wavenumbers (cm$^{-1}$) for (3a)

| Experimental wavenumbers by FT-IR (cm$^{-1}$) | | | Calculated vibrational wavenumbers by DFT method (cm$^{-1}$) | | | |
|---|---|---|---|---|---|---|
| | | | B3LYP (Gas phase) | | B3LYP ($CH_2Cl_2$) | |
| | | | 6-31+G* | 6-311++G** | 6-31+G* | 6-311++G** |
| Assignments | NH | 3376 | 3375.23 | 3360.56 | 3389.31 | 3385.75 |
| | C=O | 1736 | 1792.88 | 1781.86 | 1799.09 | 1796.21 |
| | C-O | 1203 | 1217.77 | 1200.08 | 1230.77 | 1228.11 |
| | C-Cl, Str. | 849 | 860.79 | 867.35 | 860.27 | 867.03 |
| | C-Cl, bending | 499 | 501.26 | 500.90 | 504.46 | 503.29 |

**Table 3.** The Comparison of Observed and Calculated Vibrational Wavenumbers (cm$^{-1}$) for (3b)

| Experimental wavenumbers by FT-IR (cm$^{-1}$) | | | Calculated vibrational wavenumbers by DFT method (cm$^{-1}$) | | | |
|---|---|---|---|---|---|---|
| | | | B3LYP (Gas phase) | | B3LYP ($CH_2Cl_2$) | |
| | | | 6-31+G* | 6-311++G** | 6-31+G* | 6-311++G** |
| Assigments | NH | 3371 | 3375.76 | 3370.11 | 3380.36 | 3378.29 |
| | C=O | 1789 | 1778.30 | 1788.25 | 1791.26 | 1791.01 |
| | C-O | 1253 | 1270.84 | 1255.21 | 1269.45 | 1257.11 |
| | C-Cl, Str. | 861 | 871.80 | 860.25 | 870.43 | 868.54 |
| | C-Cl, bending | 471 | 472.9142 | 470.25 | 472.9142 | 470.25 |

03 package of programs. Geometry optimizations were performed with B3LYP/6-31+G*, and B3LYP/6-311++G** methods in gas phase and $CH_2Cl_2$ solvent. The DFT technique employed the Becke3 exchange functional supplemented with Lee, Yang, Parr (LYP) correlation functional [31]. Molecular geometries were fully optimized by Berny's optimization algorithm. Atomic charges were visualized using GaussView 03 program.

## IR SPECTROSCOPY

Geometry optimizations were performed using B3LYP/6-31+G*, and B3LYP/6-311++G** methods in gas phase and $CH_2Cl_2$ phase. The theoretical geometric structure of compound (3a) with B3LYP/6-311++G** level has been demonstrated in Fig. 3.

The wavenumbers of aryl (trichloroacetyl)carbamate

**Table 4.** The Comparison of Observed and Calculated Vibrational Wavenumbers ($cm^{-1}$) for (3c)

| Experimental wavenumbers by FT-IR ($cm^{-1}$) | | | Calculated vibrational wavenumbers by DFT method ($cm^{-1}$) | | | |
|---|---|---|---|---|---|---|
| | | | B3LYP (Gas phase) | | B3LYP ($CH_2Cl_2$) | |
| | | | 6-31+G* | 6-311++G** | 6-31+G* | 6-311++G** |
| Assignments | NH | 3292 | 3223.42 | 3203.08 | 3226.24 | 3301.78 |
| | C=O | 1792 | 1819.72 | 1813.83 | 1832.23 | 1831.30 |
| | C-O | 1246 | 1247.52 | 1251.19 | 1296.87 | 1287.62 |
| | C-Cl, Str. | 830 | 838.85 | 837.54 | 839.11 | 838.14 |
| | C-Cl, bending | 430 | 429.48 | 425.69 | 436.12 | 433.38 |

**Table 5.** The Comparison of Observed and Calculated Vibrational Wavenumbers ($cm^{-1}$) for (3d)

| Experimental wavenumbers by FT-IR ($cm^{-1}$) | | | Calculated vibrational wavenumbers by DFT method ($cm^{-1}$) | | | |
|---|---|---|---|---|---|---|
| | | | B3LYP (Gas phase) | | B3LYP ($CH_2Cl_2$) | |
| | | | 6-31+G* | 6-311++G** | 6-31+G* | 6-311++G** |
| Assignments | NH | 3292 | 3226.65 | 3204.98 | 3276.52 | 3299.98 |
| | C=O | 1792 | 1818.32 | 1812.26 | 1805.11 | 1801.26 |
| | C-O | 1246 | 1250.56 | 1239.43 | 1270.67 | 1245.43 |
| | C-Cl, Str. | 830 | 836.27 | 834.27 | 835.31 | 839.27 |
| | C-Cl, bending | 438 | 445.40 | 446.70 | 440.52 | 448.98 |

**Table 6.** The Correlation Value ($R^2$) for the Calculated and Experimental Vibrational Wavenumbers for Compounds 3a-d

| Compounds | B3LYP/6-31+G* | B3LYP/6-311++G** | B3LYP/6-31+G* | B3LYP/6-311++G** |
|---|---|---|---|---|
| | Gas phase | | $CH_2Cl_2$ solvent | |
| 3a | 0.9975 | 0.9992 | 0.9989 | 0.9996 |
| 3b | 0.9986 | 0.9999 | 0.9981 | 0.9999 |
| 3c | 0.9996 | 0.9995 | 0.9991 | 0.9991 |
| 3d | 0.9996 | 0.9995 | 0.9993 | 0.9989 |

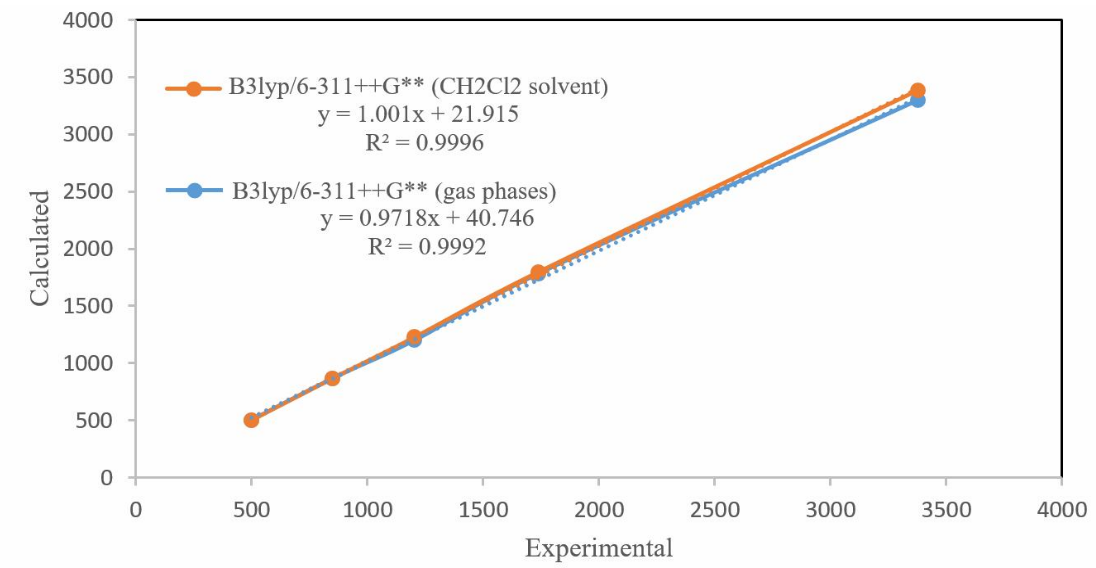


**Fig. 4.** The correlation graphic of calculated and experimental vibrational wavenumbers for (3a) (using B3LYP/6-311++G** in gas phase and $CH_2Cl_2$ solvent).

**Table 7.** The Experimental and Calculated $^1$H NMR and $^{13}$C NMR Chemical Shifts (ppm) for Phenyl (trichloroacetyl)carbamate (3a)

| H atoms | Experimental $\delta_H$ ($CDCl_3$) | Computed $\delta_H$ by B3LYP/6-311++G** (gas phase) | Computed $\delta_H$ by B3LYP/6-311++G** ($CH_2Cl_2$ phase) |
|---|---|---|---|
| Aromatic CH | 7.18-7.45 | 7.14-7.54 | 6.36-7.82 |
| NH | 8.87 | 7.54 | 8.68 |
| C atoms | Experimental $\delta_C$ ($CDCl_3$) | Computed $\delta_H$ by B3LYP/6-311++G** (Gas phase) | Computed $\delta_H$ by B3LYP/6-311++G** ($CH_2Cl_2$ phase) |
| *C*$Cl_3$ | 91.57 | - | 99.73 |
| Aromatic carbons | 121.08 | 125.4 | 128.11 |
| | 126.79 | 125.5 | 131.02 |
| | 129.72 | 127.53 | 133.42 |
| | 149.59 | 133.96 | 151.90 |
| 2C=O | 157.87 | 157.63 | 163.21 |

**Table 8.** The Experimental and Calculated $^1$H NMR and $^{13}$C NMR Chemical Shifts (ppm) for 4-*Tert*-butylphenyl (trichloroacetyl)carbamate (3b)

| H atoms | Experimental $\delta_H$ ($CDCl_3$) | Computed $\delta_H$ by B3LYP/6-311++G** (Gas phase) | Computed $\delta_H$ by B3LYP/6-311++G** ($CH_2Cl_2$ phase) |
|---|---|---|---|
| Me$_3$C | 1.32 | 1.24 | 2.38 |
|  | 7.11 | 7.18 | 7.37 |
| Aromatic CH | 7.42 | 7.42 | 7.62 |
| NH | 8.85 | 7.53 | 8.11 |
| C atoms | Experimental $\delta_C$ ($CDCl_3$) | Computed $\delta_H$ by B3LYP/6-311++G** (Gas phase) | Computed $\delta_H$ by B3LYP/6-311++G** ($CH_2Cl_2$ phase) |
| *Me*$_3$C | 31.37 | 33.19 | 33.09 |
| Me$_3$*C* | 34.57 | 33.30 | 35.14 |
| *C*Cl$_3$ | 91.61 | - | 98.84 |
|  | 120.39 | 124.48 | 129.11 |
|  | 126.60 | 125.96 | 131.27 |
|  | 147.29 | 154.6 | 156.13 |
| Aromatic carbons | 149.74 | 155.28 | 157.99 |
|  | 148.30 | 155.96 | 159.21 |
| 2C=O | 157.85 | 160.18 | 161.11 |

derivatives in the ground state were calculated using density functional theory (DFT) at the 6-31+G* and 6-311++G** basis set levels in gas phase and $CH_2Cl_2$ phase. The observed FT-IR bands and calculated wavenumbers and assignments are provided in Tables 2-6. Based on our calculations and experimental infrared spectra, we made a reliable one-to-one correspondence between our fundamentals and any of our wavenumbers calculated by B3LYP method in gas phase and $CH_2Cl_2$ phase. For the title compound (3a), the strong band at 3376 cm$^{-1}$ in the FT-IR spectrum is assigned as the $\nu_{NH}$ mode. The calculated values for this mode were 3375, 3360, 3389 and 3385 cm$^{-1}$ for B3LYP/6-31+G*, B3LYP/6-311++G** in gas phase, B3LYP/6-31+G* and B3LYP/6-311++G** levels in $CH_2Cl_2$, respectively.

There was an excellent agreement between experimental and theoretical results for all the methods used. To examine this agreement, the correlation graphic based on the theoretical and experimental data was investigated. For example, the correlation graphic of the calculated and experimental frequencies for 3a at B3LYP/6-311++G** in gas phase and $CH_2Cl_2$ solvent is depicted in Fig. 4. The

**Table 9.** The Experimental and Calculated $^1$H NMR and $^{13}$C NMR Chemical Shifts (ppm) for Naphtalen-1-yl (trichloroacetyl)carbamate (3c)

| H atoms | Experimental $\delta_H$ ($CDCl_3$) | Computed $\delta_H$ by B3LYP/6-311++G** (Gas phase) | Computed $\delta_H$ by B3LYP/6-311++G** ($CH_2Cl_2$ phase) |
|---|---|---|---|
| Aromatic CH | 7.38-7.98 | 7.42-7.97 | 7.46-8.11 |
| NH | 9.02 | 8.13 | 8.83 |
| C atoms | Experimental $\delta_C$ ($CDCl_3$) | Computed $\delta_H$ by B3LYP/6-311++G** (Gas phase) | Computed $\delta_H$ by B3LYP/6-311++G** ($CH_2Cl_2$ phase) |
| $CCl_3$ | 91.65 | - | 96.92 |
| | 117.85 | 123.56 | 124.14 |
| | 120.74 | 125.24 | 129.03 |
| | 125.25 | 127.17 | 130.17 |
| | 126.23 | 129.48 | 132.91 |
| | 126.84 | 130.7 | 135.44 |
| | 127.01 | 131.13 | 137.76 |
| | 128.12 | 131.61 | 139.11 |
| | 134.66 | 132.36 | 140.27 |
| Aomatic carbons | 145.41 | 133.13 | 143.21 |
| | 148.36 | 151.58 | 152.09 |
| 2C=O | 157.88 | 152.04 | 158.11 |

correlation value ($R^2$) for the compounds (3a-d) at B3LYP/6-311++G** in gas phase and $CH_2Cl_2$ solvent are shown in Table 6. A small difference between the experimental and calculated vibrational modes was observed. The results of the gas phase and the dichloromethane solvent are significantly consistent.

## NMR PARAMETERS

The $^1$H NMR and $^{13}$C NMR chemical shifts of aryl (trichloroacetyl)carbamate derivatives (3a-d) were computed at the B3LYP/6-311++G** level in gas phase and $CH_2Cl_2$ solvent. The experimental and calculated values of $^1$H and $^{13}$C NMR chemical shifts of aryl (trichloroacetyl)carbamate derivatives (3a-d) are given in Tables 7-10. Based on calculations and experimental infrared spectra, we examined a reliable one-to-one correspondence between experimental data and the wavelengths derived from the B3LYP methods in gas phase and $CH_2Cl_2$ solvent. For the compound titled (3a), the

**Table 10.** The Experimental and Calculated $^1$H NMR and $^{13}$C NMR Chemical Shifts (ppm) for Naphtalen-2-yl (trichloroacetyl)carbamate (3d)

| H atoms | Experimental $\delta_H$ ($CDCl_3$) | Computed $\delta_H$ by B3LYP/6-311++G** (Gas phase) | Computed $\delta_H$ by B3LYP/6-311++G** ($CH_2Cl_2$ phase) |
|---|---|---|---|
| Aromatic CH | 7.28-7.91 | 7.50-8.01 | 7.61-8.11 |
| NH | 8.84 | 8.12 | 8.92 |
| C atoms | Experimental $\delta_C$ ($CDCl_3$) | Computed $\delta_H$ by B3LYP/6-311++G** (Gas phase) | Computed $\delta_H$ by B3LYP/6-311++G** ($CH_2Cl_2$ phase) |
| $CCl_3$ | 91.60 | - | 97.71 |
|  | 118.41 | 123.47 | 124.13 |
|  | 120.10 | 126.07 | 128.02 |
|  | 126.31 | 127.13 | 129.77 |
|  | 126.98 | 130.64 | 131.54 |
|  | 127.79 | 131.27 | 133.29 |
|  | 127.85 | 132.69 | 135.11 |
|  | 129.86 | 132.78 | 139.83 |
|  | 131.77 | 134.19 | 141.36 |
| Aromatic carbons | 133.53 | 137.45 | 144.75 |
| 2C=O | 148.36 | 151.70 | 152.99 |

aromatic CH protons appeared at $\delta_H$ 7.18-7.45 ppm and the calculated amounts at B3LYP/6-311++G** basis set levels in gas phase and $CH_2Cl_2$ solvent were at 7.14-7.54 and 6.36-7.82 ppm, respectively. The NH proton appeared at $\delta_H$ 8.87 ppm, the calculated amounts at the B3LYP/6-311++G** level in the gas phase and $CH_2Cl_2$ solvent were at 7.54 and 8.68, respectively.

In order to understand this agreement, the correlation graphic based on the theoretical and experimental data was investigated. The correlation value ($R^2$) for the calculated $^1$H NMR and $^{13}$C NMR chemical shifts of 3a-d by the B3LYP method at the 6-311++G** level in gas phase and $CH_2Cl_2$ solvent are represented in Table 11. The correlation graphic for 3a by the B3LYP method at the 6-311++G** level in the gas phase and $CH_2Cl_2$ solvent are depicted in Fig. 5. There was an excellent agreement between the experimental and theoretical results.

In summary, there was a good agreement between the experimental and calculated $^1$H and $^{13}$C NMR chemical shifts for aryl (trichloroacetyl)carbamate derivatives and they support each other.

**Table 11.** The Correlation Value ($R^2$) for the Calculated $^1$H NMR and $^{13}$C NMR for 3a-3d (Using the B3LYP/6-311++G**) in Gas Phase and $CH_2Cl_2$ Phase

| Compounds | Computed $\delta_H$ by B3LYP/6-311++G** (Gas phase) | Computed $\delta_H$ by B3LYP/6-311++G** ($CH_2Cl_2$ phase) |
|---|---|---|
| 3a | 0.9776 | 0.9887 |
| 3b | 0.9990 | 0.9893 |
| 3c | 0.9890 | 0.9961 |
| 3d | 0.9992 | 0.9969 |

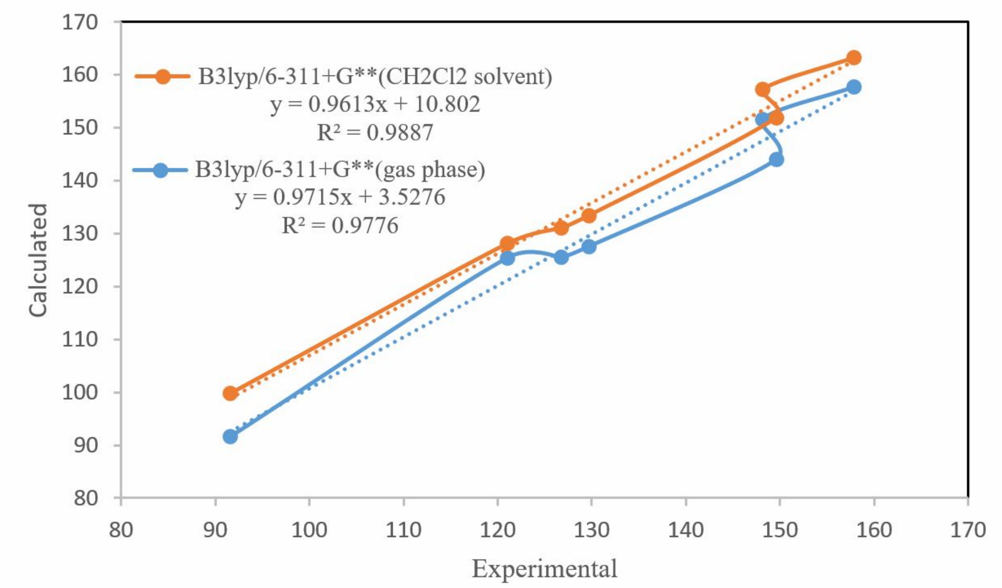


**Fig. 5.** The correlation graphic for 3a caculated at the B3LYP level in gas phase and $CH_2Cl_2$ solvent at the 6-311++G** level.

## CONCLUSIONS

In the present study, a two-component reaction is reported between phenol or naphthol derivatives and trichloroacetyl isocyanate to produce aryl (trichloroacetyl) carbamate derivatives. The reported method offers a simple and efficient procedure with high yield and available stating materials in a short time for the synthesis of these compounds. The products were characterized by IR, $^1$H NMR, $^{13}$C NMR, and elemental analyses. The IR spectra and $^1$H NMR and $^{13}$C NMR chemical shifts computations were performed for the compounds in the ground state . An excellent agreement was observed between the experimental and theoretical results.

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## REFERENCES

[1] Yemets, A.; Stelmakh, O.; Blume, Y. B., Effects of the herbicide isopropyl-*N*-phenyl carbamate on microtubules and MTOCs in lines of nicotiana sylvestris resistant and sensitive to its action. *Cell Biol. Int.* **2008**, *32*, 623-629, DOI: 10.1016/ j.cellbi.2008.01.012.

[2] Atamaniuk, T. M.; Kubrak, O. I.; Husak, V. V.; Storey, K. B.; Lushchak, V. I., The mancozeb-containing carbamate fungicide tattoo induces mild oxidative stress in goldfish brain, liver, and kidney. *Environ. Toxicol.* **2014**, *29*, 1227-1235, DOI: 10.1002/tox.21853.

[3] Riondel, A.; Caubère, P., A high yield method for preparation of potential pesticides: Syntheses of 1-alkoxy-ethyl-*N*,*N*-dialkyl carbamates. *Synth. Commun.* **1987**, *17*, 1467-1475, DOI: 10.1080/ 00397918708057773.

[4] Martin, L. L.; Davis, L.; Klein, J. T.; Nemoto, P.; Olsen, G. E.; Bores, G. M.; Camacho, F.; Petko, W. W.; Rush, D. K.; Selk, D.; Smith, C. P.; Vargas, H. M.; Wilson, J. T.; Effland, R. C.; Fink, D. M., Synthesis and preliminary structure-activity relationships of 1-[(3-fluoro-4-pyridinyl)amino]-3-methyl-1*H*-indol-5-yl methyl carbamate (P10358), a novel acetylcholinesterase inhibitor. *Bioorg. Med. Chem. Lett.* **1997**, *7*, 157- 162, DOI: 10.1016/S0960-894X(96)00592-6.

[5] Feldman, D.; Barbalata, A., Synthetic Polymers, Technology, Properties, Applications; Chapman and Hall: London, 1996.

[6] Kim, J. - G.; Jang, D. O., Indium-catalyzed reaction for the synthesis of carbamates and carbonates: selective protection of amino groups. *Tetrahedron Lett.* **2009**, *50*, 2688-2692, DOI: 10.1016/ j.tetlet.2009.03.143.

[7] Dressman, B. A.; Spangle, L. A.; Kaldor, S.W., Solid phase synthesis of hydantoins using a carbamate linker and a novel cyclization/cleavage step. *Tetrahedron Lett.* **1996**, *37*, 937-940, DOI: 10.1016/ 0040-4039(95)02395-X.

[8] a) Giannessi, F.; Pessotto, P.; Tassoni, E.; Chiodi, P.; Conte, R.; Angeles, F. D.; Uomo, N. D.; Catini, R.; Deias, R.; Tinti, M. O.; Carminate, P.; Ardnini, A., Discovery of a long-chain carbamoyl aminocarnitine derivative, a reversible carnitine palmitoyltransferase inhibitor with antiketotic and antidiabetic activity. *J. Med. Chem.* **2003**, *46*, 303-309, DOI: 10.1021/ jm020979u; b) Ouellet, R.; Rousseau, J.; Brasseur, N.; Lier, J. E.; Doksic, M.; Westera, G., Synthesis, receptor binding, and target-tissue uptake of carbon-11 labeled carbamate derivatives of estradiol and hexestrol. *J. Med. Chem.* **1984**, *27*, 509-513, DOI: 10.1021/jm00370a013.

[9] Kuznetsova, L.; Chen, J.; Sun, L.; Wu, X.; Pepe, A.; Veith, J. M.; Pera, P.; Bernacki, R. J.; Ojima, I., Syntheses and evaluation of novel fatty acid-second-generation taxoid conjugates as promising anticancer agents. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 974-977, DOI: 10.1016/j.bmcl.2005.10.089.

[10] Takaoka, K.; Tatsu, Y.; Yumoto, N.; Nakajima, T.; Shimamoto, K., Synthesis of carbamate-type caged derivatives of a novel glutamate transporter blocker. *Bioorg. Med. Chem.* **2004**, *12*, 3687-3694, DOI: 10.1016/j.bmc.2004.04.011.

[11] Ray, S.; Pathak, S. R.; Chaturvedi, D., Organic carbamates in drug development. Part II: antimicrobial agents-Recent reports. *Drugs Future,* **2005**, *30*, 161-180, DOI: 10.1358/ dof.2005.030.02.869228.

[12] Gupte, S. P.; Shivarkar, A. B.; Chaudhari, R. V., Carbamate synthesis by solid-base catalyzed reaction of disubstituted ureas and carbonates. *Chem. Commun.* **2001**, 2620-2621, DOI: 10.1039/B107947F.

[13] Mindl, J.; Hrabík, O.; Stěrba, V.; Kaválek, J., Cyclization of substituted phenyl *N*-(2-hydroxybenzyl)carbamates in aprotic solvents. Synthesis of 4*H*-1,3-benzoxazin-2(3*H*)-ones. *Collect. Czech. Chem. Commun.* **2000**, *65*, 1262-1272, DOI: 10.1135/cccc20001262.

[14] Motolcsy, G.; Nadasy, M.; Andriska, V., Pesticide Chemistry; Academiai Kiado: Budapest, 1988, pp. 90.

[15] Katakai, R.; Lizuka, Y., An improved rapid method for the synthesis of *N*-carboxy .alpha.-amino acid anhydrides using trichloromethyl chloroformate. *J. Org. Chem.* **1985**, *50*, 715-716, DOI: 10.1021/jo00205a039.

[16] Cotarka, L.; Delgu, P.; Mardelli, A.; Sunjuc, V., Bis(trichloromethyl) carbonate in organic synthesis. *Synthesis,* **1996**, 553-576, DOI: 10.1055/s-1996-4273.

[17] Shivarkar, A. B.; Gupte, S. P.; Chaudhari, R. V., Carbamate synthesis via transfunctionalization of substituted ureas and carbonates. *J. Mol. Catal. A: Chem.* **2004**, *223*, 85-92, DOI: 10.1016/j.molcata.2003.09.041.

[18] Salvatore, R. N.; Shin, S II.; Nagle, A. S.; Jung, K. W., Efficient carbamate synthesis *via* a three-component coupling of an amine, $CO_2$, and alkyl halides in the presence of $Cs_2CO_3$ and tetrabutylammonium iodide. *J. Org. Chem.* **2001**, *66*, 1035-1037, DOI: 10.1021/jo001140u.

[19] Pandey, R. K.; Dagade, S. P.; Dongare, M. K.; Kumar, P., Synthesis of carbamates using yttria-zirconia based lewis acid catalyst. Synth. Commun. 2003, 33, 4019-4027, DOI: 10.1081/SCC-120026337.

[20] Cardona, F.; Soldaini, G.; Goti, A., Methyltrioxorhenium-catalyzed oxidation of aromatic aldoximes. *Synlett,* **2004**, 1553-1556, DOI: 10.1055/s-2004-829088.

[21] a) Dixit, S.; Patil, M.; Agarwal, N., Ferrocene catalysed heteroarylation of BODIPy and reaction mechanism studies by EPR and DFT methods. *RSC Adv.* **2016**, *6*, 47491-47497, DOI: 10.1039/C6RA03705D; b) Zheng, L.; Qiao, Y.; Lu, M.; Chang, J., Theoretical investigations of the reaction between 1,4-dithiane-2,5-diol and azomethine imines: mechanisms and diastereoselectivity. *Org. Biomol. Chem.* **2015**, *13*, 7558-7569, DOI: 10.1039/C5OB00807G.

[22] a) Bekhradnia, A.; Norrby, P. O., New insights into the mechanism of iron-catalyzed cross-coupling reactions. *Dalton Trans.* **2015**, *44*, 3959-3962. DOI: 10.1039/C4DT03491K; b) Duca, D.; Manna, G. L.; Russo, M. R., Computational studies on surface reaction mechanisms: ethylene hydrogenation on platinum catalysts. *Phys. Chem. Chem. Phys.* **1999**, *1*, 1375-1382, DOI: 10.1039/A808634F.

[23] a) Smith, S. G.; Goodman, J. M., Assigning stereochemistry to single diastereoisomers by GIAO NMR calculation: The DP4 probability. *J. Am. Chem. Soc.* **2010**, *132*, 12946-12959, DOI: 10.1021/ja105035r; b) Yang, Z.; Yu, P.; Houk, K. N., Molecular dynamics of dimethyldioxirane C-H oxidation. *J. Am. Chem. Soc.* **2016**, *138*, 4237-4242, DOI: 10.1021/jacs.6b01028.

[24] a) Hansen, P. E.; Spanget-Larsen, J., Structural studies on mannich bases of 2-hydroxy-3,4,5,6-tetrachlorobenzene. An UV, IR, NMR and DFT study. *A Mini-Review. J. Mol. Struct.* **2016**, *1119*, 235-239, DOI: 10.1016/j.molstruc.2016.04.075; b) Demir, S.; Sarioğlu, A. O.; Güler, S.; Dege, N.; Sönmez, M., Synthesis, crystal structure analysis, spectral IR, NMR UV-Vis investigations, NBO and NLO of 2-benzoyl-*N*-(4-chlorophenyl)-3-oxo-3-phenylpropanamide with use of X-ray diffractions studies along with DFT calculations. *J. Mol. Struct.* **2016**, *1118*, 316-324, DOI: 10.1016/j.molstruc.2016.04.042.

[25] a) Saha, S. Kr.; Hens, A.; Murmu, N. C.; Banerjee, P., A comparative density functional theory and molecular dynamics simulation studies of the corrosion inhibitory action of two novel *N*-heterocyclic organic compounds along with a few others over steel surface. *J. Mol. Liq.* **2016**, *215*, 486-495, DOI: 10.1016/j.molliq.2016.01.024; b) Anderson, G. M.; Cameron, I.; Murphy, J. A.; Tuttle, T., Predicting the reducing power of organic super electron donors. *RSC Adv.* **2016**, *6*, 11335-11343, DOI: 10.1039/C5RA26483A.

[26] Kellie, J. L.; Wetmore, S. D., Selecting DFT methods for use in optimizations of enzyme active sites: applications to ONIOM treatments of DNA glycosylases. *Can. J. Chem.* **2013**, *91*, 559-572, DOI: 10.1139/cjc-2012-0506.

[27] Hohenberg, P.; Kohn, W., Inhomogeneous electron gas. *Phys. Rev.* **1964**, *136*, 864-871, DOI: 10.1103/PhysRev.136.B864.

[28] Kohn, W.; Sham, L. J., Self-consistent equations including exchange and correlation effects. *Phys. Rev. A,* **1965**, *140*, 1133-1138, DOI: 10.1103/PhysRev.140.A1133.

[29] a) Shajari, N.; Kazemizadeh, A. R.; Ramazani, A., Synthesis of 5-aryl-*N*-(trichloroacetyl)-1,3,4-oxadiazole-2-carboxamide *via* three-component reaction of trichloroacetyl isocyanate, (*N*-isocyanimino)triphenylphosphorane, and benzoic acid derivatives. *Turk. J. Chem.* **2015**, *39*, 874-879, DOI: 10.3906/kim-1501-43; b) Shajari, N.; Kazemizadeh, A. R.; Ramazani, A.; Joo, S. W.; Ślepokura, K.; Lis, T.; Souldozi, A., Facile synthesis and crystal structure of 1,5-dimethyl-6-thioxo-1,3,5-triazinane-2,4-diones. *J. Struct. Chem.* **2015**, *56*, 806-810, DOI: 10.1134/S0022476615040332.

[30] a) Shoaei, S. M.; Kazemizadeh, A. R.; Ramazani, A., Synthesis and chemical shifts calculation of α-acyloxycarboxamides derived from indane-1,2,3-trione by DFT and HF methods. *Chinese, J. Struct. Chem.* **2011**, *30*, 568-574; b) Yahyaei, H.; Kazemizadeh, A. R.; Ramazani, A., Synthesis and chemical shifts calculation of α-acyloxycarboxamides derived from indane-1,2,3-trione by DFT and HF methods. *Chinese, J. Struct. Chem.* **2011**, *31*, 1346-1356.

[31] a) Becke, A. D., Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A,* **1988**, *38*, 3098-3100, DOI: 10.1103/PhysRevA.38.3098; b) Lee, C.; Yang, W.; Parr, R. G., Development of the colle-salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B,* **1988**, *37*, 785-789, DOI: 10.1103/PhysRevB.37.785.