

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, ^1H NMR, ^{13}C NMR and elemental analyses. The data from IR spectra and ^1H 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

INTRODUCTION

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 ^1H 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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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, ^1H 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 ^1H NMR, ^{13}C NMR, IR spectra, and elemental analysis. For example, the ^1H NMR spectrum of 3a exhibited distinct signals at δ_{H} 7.18-7.45 ppm (5H, *m*) arising from the aromatic CH groups and at δ_{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 (δ_{C} 91.57 ppm), aromatic carbons (δ_{C} 121.08, 126.79, 129.72 and 149.59 ppm) and $2\text{C}=\text{O}$ (δ_{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 ^1H 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 $-10\text{ }^\circ\text{C}$. 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.: $79.9\text{-}81.8\text{ }^\circ\text{C}$; Anal. Calcd. for $\text{C}_9\text{H}_6\text{Cl}_3\text{NO}_3$ (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); ^1H NMR (250.13 MHz, CDCl_3 , δ/ppm): 7.18-7.21 (2H, *m*, aromatic CH), 7.29- 7.32 (1H, *m*, aromatic CH), 7.39- 7.45 (2H, *m*, aromatic CH), 8.87 (1H, *s*, NH); ^{13}C NMR (62.90 MHz, CDCl_3 , δ/ppm): 91.57 (CCl_3), 121.08, 126.79 and 129.72 (5CH, aromatic), 149.59 (C, aromatic), 148.15 and 157.87 ($2\text{C}=\text{O}$).

4-Tert-butylphenyl (trichloroacetyl)carbamate (3b). White solid, yield: 98%; m. p.: $100.4\text{-}102.3\text{ }^\circ\text{C}$; Anal. Calcd. for $\text{C}_{13}\text{H}_{14}\text{Cl}_3\text{NO}_3$ (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); ^1H NMR (250.13 MHz, CDCl_3 , δ/ppm): 1.32 (9H, *s*, Me_3C), 7.11 (2H, *d*, $^3J_{\text{HH}} = 8.5\text{ Hz}$, aromatic CH), 7.42 (2H, *d*, $^3J_{\text{HH}} = 8.5\text{ Hz}$, aromatic CH), 8.85 (1H, *s*, NH); ^{13}C NMR (62.90 MHz, CDCl_3 , δ/ppm): 31.37 (Me_3C), 34.57 (Me_3C), 91.61 (CCl_3), 120.39 and 126.60 (4CH, aromatic), 147.29 and 149.74 (2C, aromatic), 148.30 and 157.85 ($2\text{C}=\text{O}$).

Naphtalen-1-yl (trichloroacetyl)carbamate (3c). White solid, yield: 96%; m. p.: $142.2\text{-}144.9\text{ }^\circ\text{C}$; Anal. Calcd. for $\text{C}_{13}\text{H}_8\text{Cl}_3\text{NO}_3$ (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); ^1H NMR (250.13 MHz, CDCl_3 , δ/ppm): 7.38-7.57 (4H, *m*, aromatic CH), 7.79- 7.98 (3H, *m*, aromatic CH), 9.02 (1H, *s*, NH); ^{13}C NMR (62.90 MHz, CDCl_3 , δ/ppm): 91.65 (CCl_3), 117.85, 120.74, 125.25, 126.84, 127.01 and 128.12 (7CH, aromatic), 126.23, 134.66 and 145.41 (3C, aromatic), 148.36 and 157.88 ($2\text{C}=\text{O}$).

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

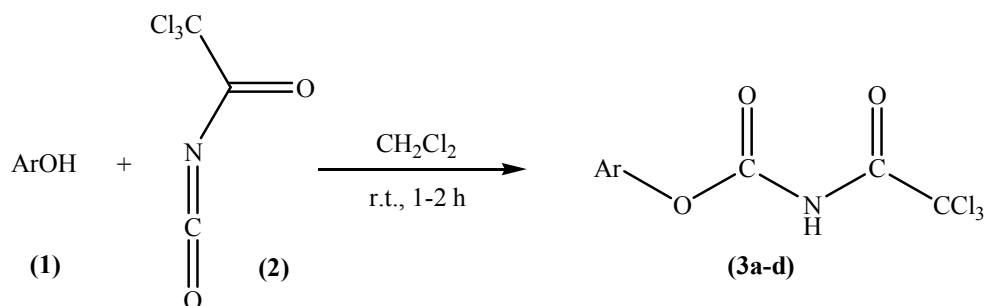


Fig. 1. Two-component reaction of trichloroacetyl isocyanate with phenol or naphthol derivatives (3a-d).

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

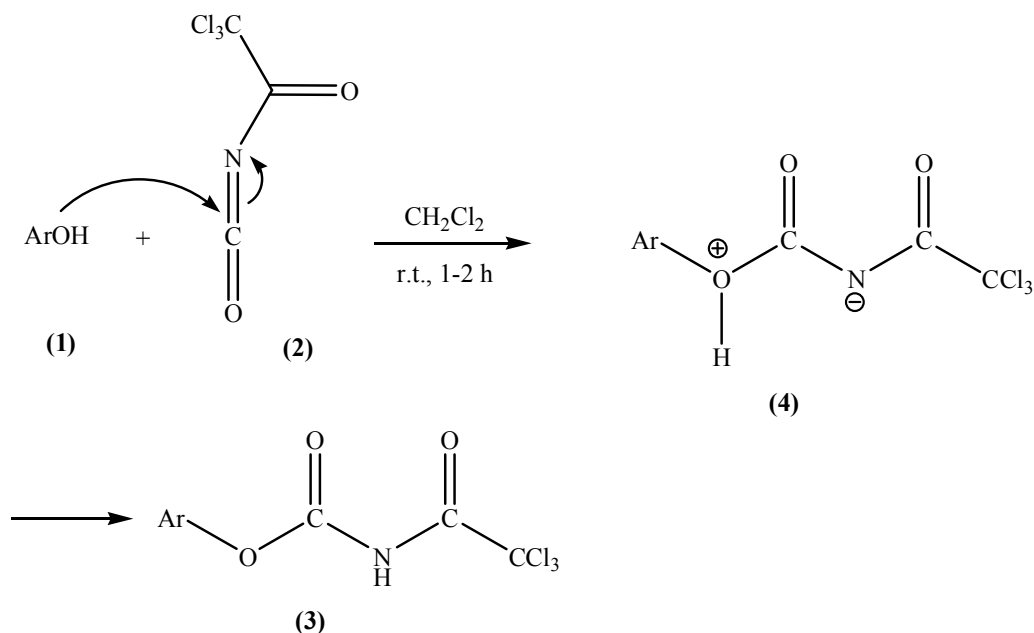


Fig. 2. A proposed mechanism for the formation of (3).

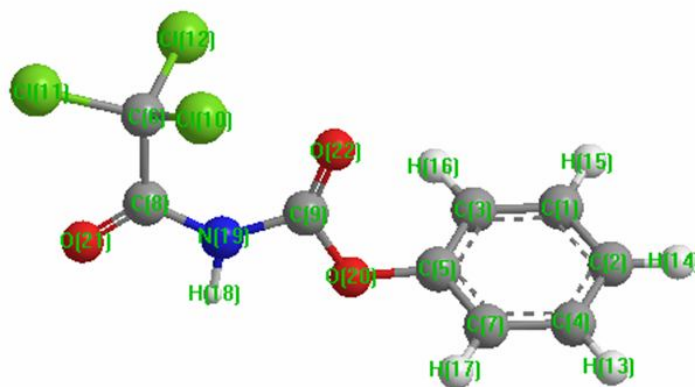


Fig. 3. The theoretical geometric structure of compound (3a) (optimized at the B3LYP/6-311++G** level).

White solid, yield: 95%; m. p.: 139.2-140.5 °C; Anal. Calcd. for C₁₃H₈Cl₃NO₃ (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, CDCl₃, δ/ppm): 2.28-7.35 (1H, *m*, aromatic CH), 7.48-7.56 (2H, *m*, aromatic CH), 7.66-7.72 (1H, *m*, aromatic CH), 7.81-7.91 (3H, *m*, aromatic CH), 8.84 (1H, *s*, NH); ¹³C NMR (62.90

MHz, CDCl₃, δ/ppm): 91.60 (CCl₃), 118.41, 120.10, 126.31, 126.98, 127.79, 127.85 and 129.86 (7CH, 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**
Assignments	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

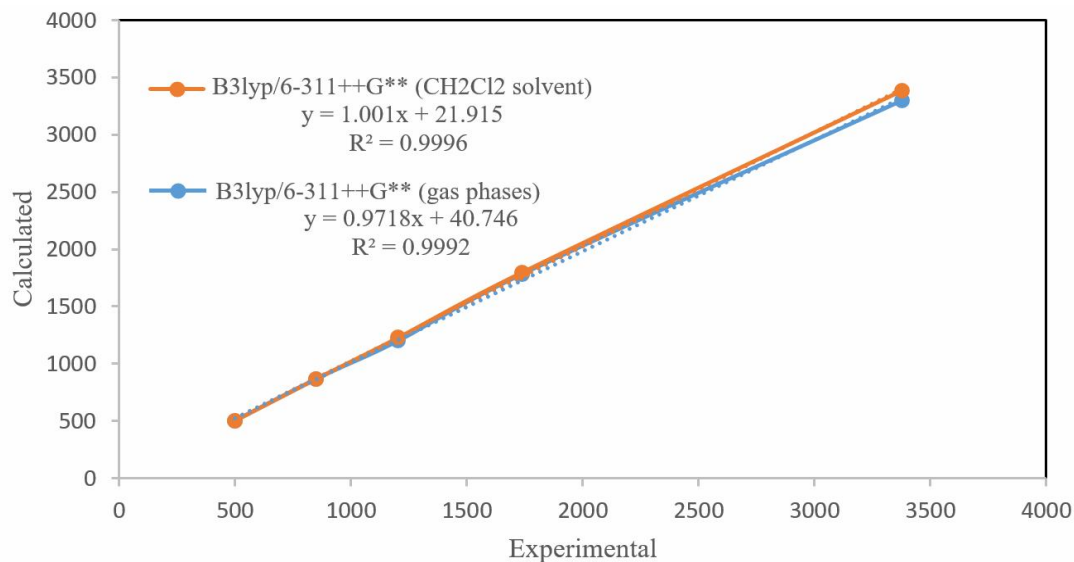


Fig. 4. The correlation graphic of calculated and experimental vibrational wavenumbers for (3a) (using B3LYP/6-311++G** in gas phase and CH₂Cl₂ solvent).

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

H atoms	Experimental	Computed δ_H by	Computed δ_H by
	δ_H (CDCl ₃)	B3LYP/6-311++G** (gas phase)	B3LYP/6-311++G** (CH ₂ Cl 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	Computed δ_H by	Computed δ_H by
	δ_C (CDCl ₃)	B3LYP/6-311++G** (Gas phase)	B3LYP/6-311++G** (CH ₂ Cl ₂ phase)
CCl ₃	91.57	-	99.73
	121.08	125.4	128.11
Aromatic carbons	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 ^1H NMR and ^{13}C NMR Chemical Shifts (ppm) for 4-*Tert*-butylphenyl (trichloroacetyl)carbamate (3b)

H atoms	Experimental	Computed δ_{H} by	Computed δ_{H} by
	δ_{H} (CDCl_3)	B3LYP/6-311++G** (Gas phase)	B3LYP/6-311++G** (CH_2Cl_2 phase)
Me_3C	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	Computed δ_{H} by	Computed δ_{H} by
	δ_{C} (CDCl_3)	B3LYP/6-311++G** (Gas phase)	B3LYP/6-311++G** (CH_2Cl_2 phase)
Me_3C	31.37	33.19	33.09
Me_3C	34.57	33.30	35.14
CCl_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
$2\text{C}=\text{O}$	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 ν_{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 ^1H NMR and ^{13}C NMR Chemical Shifts (ppm) for Naphtalen-1-yl (trichloroacetyl)carbamate (3c)

H atoms	Experimental δ_{H} (CDCl_3)	Computed δ_{H} by B3LYP/6-311++G** (Gas phase)	Computed δ_{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 δ_{C} (CDCl_3)	Computed δ_{H} by B3LYP/6-311++G** (Gas phase)	Computed δ_{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
Aromatic carbons	145.41	133.13	143.21
	148.36	151.58	152.09
$2\text{C}=\text{O}$	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 ^1H 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 ^1H 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 ^1H NMR and ^{13}C NMR Chemical Shifts (ppm) for Naphtalen-2-yl (trichloroacetyl)carbamate (3d)

H atoms	Experimental	Computed δ_{H} by	Computed δ_{H} by
	δ_{H} (CDCl_3)	B3LYP/6-311++G** (Gas phase)	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 δ_{C} (CDCl_3)	Computed δ_{H} by	Computed δ_{H} by
		B3LYP/6-311++G** (Gas phase)	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
$2\text{C}=\text{O}$	148.36	151.70	152.99

aromatic CH protons appeared at δ_{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 δ_{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.

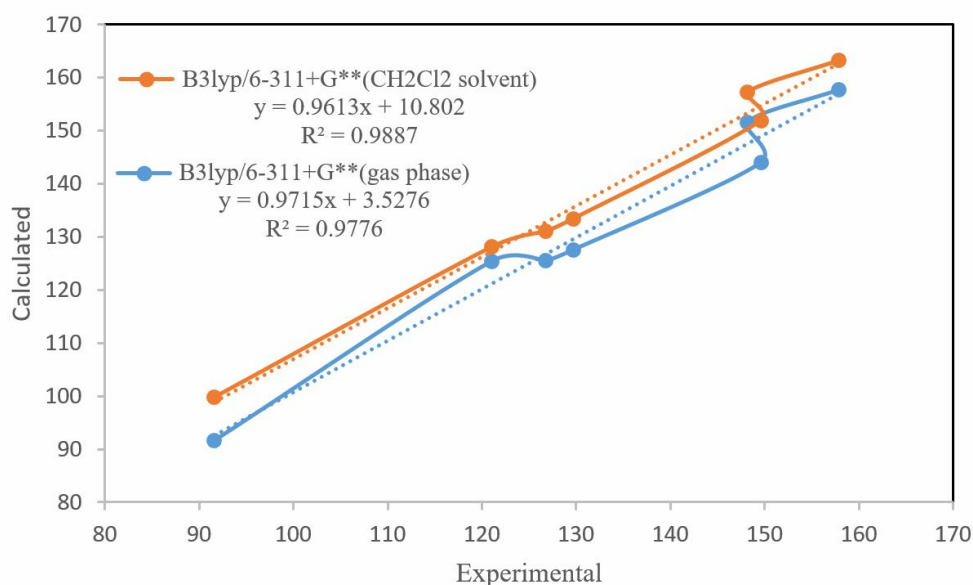
In order to understand this agreement, the correlation graphic based on the theoretical and experimental data was investigated. The correlation value (R^2) for the calculated ^1H NMR and ^{13}C NMR chemical shifts of 3a-d by the

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 ^1H 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 ^1H NMR and ^{13}C NMR for 3a-3d (Using the B3LYP/6-311++G**) in Gas Phase and CH_2Cl_2 Phase

Compounds	Computed δ_{H} by	Computed δ_{H} by
	B3LYP/6-311++G** (Gas phase)	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 calculated 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

starting materials in a short time for the synthesis of these compounds. The products were characterized by IR, ^1H NMR, ^{13}C NMR, and elemental analyses. The IR spectra and ^1H 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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