

Preparation, Investigation, Correlation Analysis and Theoretical Study of Bromoacetamide and Bis (2-Bromo Acetamide) Derivatives

*Hanan A. Alhazam, Nahid H. Al-Haidery
and Amjed A. Ahmed

Dept. of Chemistry, Science College, Basrah University, Basrah, Iraq
**Corresponding Author E-mail: hananalhazam1965@yahoo.com*

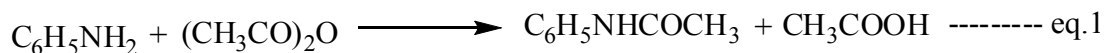
Abstract

new compounds of bromoacetamide and bis (bromo acetamide) derivatives have been prepared and investigated by FT-IR, theoretical study and correlation analysis with mono substituent parameter (MSP) and dual substituent parameter (DSP) .

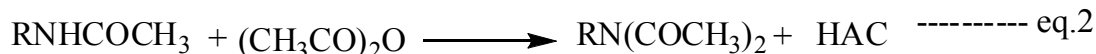
Keywords: bromoacetamide, correlation analysis, MSP, DSP

Introduction

Acetyl derivative of aromatic amine may be prepared either with acetic acid or acetic anhydride or with a mixture of both reagents. Primary amine reacts readily upon warming with acetic anhydride to yield the first instance, the mono acetyl derivative [1, 2] eq.1.



If the heating be prolonged and excess of acetic anhydride is employed, variable amount of diacetyl derivative are formed^[2] eq.2



Acylating agent such as chloro acetyl chloride, bromo acetyl chloride, iodoa cetyl chloride (XCH_2COCL); ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) is a versatile reagent and has been extensively used in organic synthesis.

Acylation of carbon functionalities using acylating reagent generally fall in to tow categories: acylation under Friedel-Craft condition and under an ionic condition [3, 4].

N-acylation of nitrogen groups in organic compound is the most frequently used in organic synthesis [5].

Primary and secondary amine reacts readily with XCH_2COCl to form amide [6-8]. In the case of diamines both nitrogen atoms can be acylated.

The aim of this paper is to prepare tow types of compound: mono acetyl and bis acetyl compounds from bromoacetyl chloride. Physical properties, IR, NMR spectra, theoretical study and correlation analysis were also reported.

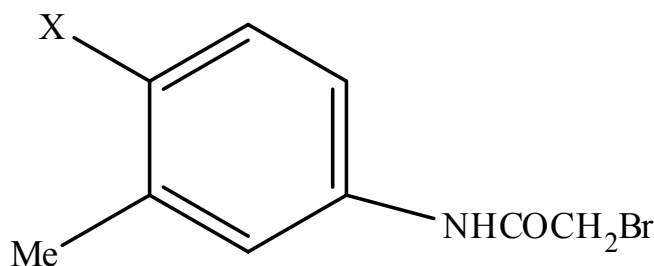
Experimental Work

Preparation

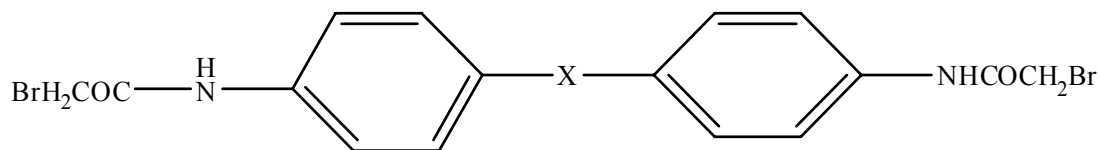
In general, mono amine or diamine (0.2 moles) was suspended in toluene used as asolvent and bromoacetyl chloride (0.8 moles) was gradually added with stirring. The mixture was allowed for refluxing for 2 hours. After the completion of reaction, cotent was cooled to room temperature and poured over crushed ice, the solid product was separated and dried re-crystallized in chloroform to obtain the new compounds as described in Table 1.

Table 1: Characteristic of compounds

Comp. no.	X	Molecular. weight	Molecular formula	m.P ⁰ c	% Yield
1	H	227	C ₉ H ₁₀ NOBr	172	65
2	Me	257	C ₉ H ₁₂ NOBr	177	70
3	OMe	273	C ₉ H ₁₂ NO ₂ Br	173	60
4	Cl	261	C ₉ H ₉ NOBrCl	166	65
5	Br	305	C ₉ H ₉ NOBr ₂	165	65
6	O=CMe	296	C ₁₁ H ₁₂ NO ₂ Br	167	65

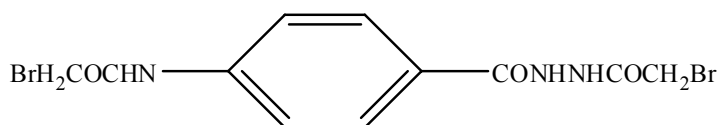


X = H , Me , OMe , Br , Cl , O=CMe



Comp.no.	X	M.weight	M.formuler	M.P c	% Yiled
7	O	440	C ₁₆ H ₄ N ₂ OBr ₂	160	65
8	CH ₂	438	C ₁₇ H ₁₂ N ₂ Br ₂	172	65
9	SO ₂	588	C ₁₆ H ₄ N ₂ SO ₄ Br ₂	185	60
10	*	391	C ₁₁ H ₁₁ N ₃ O ₃ Br ₂	177	60

*The structure of compound no.10 was:



Physical Measurements

IR Spectra were recorded on a SHADZU 8400 FT-IR spectrophotometer. Melting points were measured in a Gallen Kamp melting point apparatus were uncorrected

Theoretical Calculation

All theoretical computation were preformed in a Pentium IV.PC. The AM₁ semiempirical method in the program hyper chem. 6.01 was utilized to compute the heat of formation (ΔH). CS .Chem. draw program 4.5 was used to compute theoretical

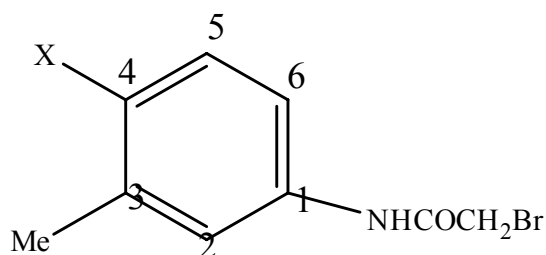
Result and discussion

¹³C NMR

The prepared compounds (1-6) are characterized depending on the additive method by using CS. Chem draw program. The values of peaks position are show in table 2 depending also upon references [9,10].

Table 2: Band of ¹³CNMR spectra of these compounds

no	X	CH2Br	C=O	C 1	C2	C 3	C 4	C 5	C 6	Me
1	H	28.3	166.2	136.7	131.6	130.7	129.3	125.9	125.0	17.3
2	Me	28.3	168.2	133.2	134.2	131.1	142.2	126.2	114.7	17.6
3	OMe	28.3	168.2	128.5	135.0	120.8	156.1	111.5	110.9	17.6
4	Cl	28.3	168.2	134.3	135.7	132.5	129.8	126.0	110.7	55.8
5	Br	28.3	168.2	135.2	136.5	134.0	118.6	128.8	123.7	16.8
6	COCH ₃	28.3	166.2	140.1	134.2	129.2	134.7	126.0	108.8	26.6



FT-IR

The IR spectra of all compounds were performed by the KBr disc method.

The spectra of these compounds, depending on references [11,12], show that all compounds have common peaks such as C-N stretching as strong peak emerged at $1480-1475\text{ cm}^{-1}$ and N-H stretching at $3400-3200\text{ cm}^{-1}$. Absorption bands exist near $1608-1720\text{ cm}^{-1}$ which belongs to C=O stretching gave good evidence to the formation amid derivatives. Out of plane N-H wagging is responsible for broad band of medium intensity in $800-650\text{ cm}^{-1}$ region. C-Br stretching appears at $500-700\text{ cm}^{-1}$. In addition to these absorption peaks, there is a number of characterized absorption bands of substituted benzene such as C-Br and C-Cl stretching at 750 and 850 cm^{-1} respectively. C-H bending of CH_3 at 1620 cm^{-1} and asymmetrical and symmetrical C-H stretching for methyl group at 2930 and respectively.

The spectra of compound number 10; 2-bromo-N(4-(2-(2-bromoacetyl)hydrazine carbonyl)acetamide); showed three position of N-H stretching at (3424 , 3346 , 3234) cm^{-1} due to the presence three different type of N-H while C=O stretching appeared as strong and broad at 1600cm^{-1} due to three type of C=O stretching.

Electronic properties

Some molecular information about the system considered is given in table 3. The AM_1 geometry optimizations yield a planar as the stable form of the studied molecules. Fig .1.

Heat of formation (ΔH) of amid and imides are calculated for all prepared compounds. Imidic forms produce from the mobility of N-H proton to oxygen of carbonyl group. Fig .2.

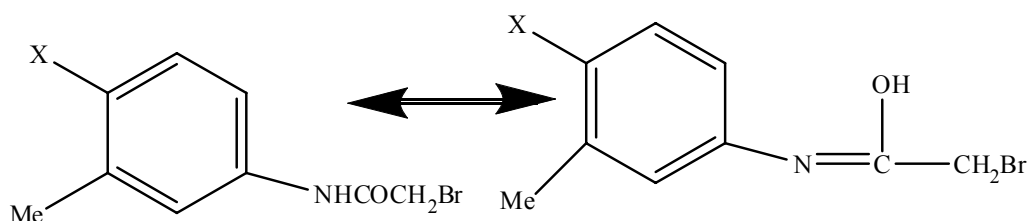


Figure 2: equilibrium between amid and imidic form.

ΔH of amid is more stable than imidic form because ΔH of amid is smaller than ΔH of imidic form, this results is agreed with these results of FT-IR spectra because the absorption C=N and OH does not reveal in all spectra of these compounds.

Table 3: Some of the molecular information about the compounds studied

Comp. no.	X	No. of electron	No. of occupied level	Total orbital	ΔH Kcal/mol amid	ΔH Kcal/mol amidic
1	X	64	32	58	104	106
2	H	70	35	64	112	120
3	Me	76	38	68	118	124
4	OMe	70	35	61	120	126
5	Cl	70	35	61	127	132
6	Br	76	38	68	122	127
7	COCH ₃	120	60	106	198	200
8		120	60	108	90	99
9		120	60	106	50	66
10		102	61	87	43	54

Correlation Analysis

Correlation analysis of ¹³C-nuclear magnetic resonance shift ($\delta^{13}\text{C}$) for compounds (1-6) with mono substituent parameter (MSP), σ^{13} model [13] and dual substituent parameter (DSP) model (Reynolds [14], Swains [15] and Taft's model [16] are studied. It is found that only $\delta^{13}\text{C}$ of C1 atom does correlate significantly with σ^{13} as show in eq.3

$$\delta^{13}\text{C} = 135 + 6.9 \sigma^{13}$$

$$s = 1.3 \quad n = 6 \quad R = 90$$

σ^{13} model is measure of polar (electronic) effect, in principle, independent of the nature of the reaction. The reaction constant (6.9) is a measure of the susceptibility of the reaction of ¹³C-NMR to the influence of polar substituent's and it depends, on the nature of the reaction and other condition such as solvent and temperature [14, 15]. $\delta^{13}\text{C}$ of C1 gave an excellent correlation with Swains model as show in eq.4 and failed with Reynolds and Taft's model.

$$\delta^{13}\text{C} = 136 - 1.22 F + 4.66 R$$

$$S = 0.91 \quad n = 6 \quad R = 97$$

It is may be due to the separation of transmission for resonance and inductive field effect. This is particularly important in studies of chemical shifts because the relative transmission of these two effects can change markedly from one site to another [17].

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