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Synthesis, NMR analysis, and DFT calculation studies on 2*H*-quinolizine derivative under solvent-free conditions

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Abstract: Computational studies have been carried out at DFT-B3LYP/6-31G and 6-31++G** level of theory on the structural and spectroscopic properties of 2H-quinolizines. 2H-quinolizines obtain from four-component reaction of the zwitterion generated from pyridine and dialkylcarbodiimide with electron-deficient dialkyl acetylenedicarboxylat. The optimized geometry of these compounds and their bonding characteristics, and NMR Spectra as well as charge have been calculated and analyzed. The influence of the bulk solvent was investigated at the B3LYP/ 6-31++G** level using polarizable continume model. The results of this study show that the **4d** is more stable than the **11** in the gas and solvent phase, due to intra molecular hydrogen bonding. Also, natural bond orbital (NBO) analysis shows that there is long π-electron delocalization in compound **4d** in comparison to compound **11,** which leads to the stabilization of the compound **4d** inrelative to compound **11**. There is a good agreement between the experimental and calculated chemical shifts in ^{13}C and ^{1}H-NMR.

Keywords: 2H-Quinolizine; Multi-component reaction; Zwitterion;solvent-free conditions; Characterization; Quantum chemical calculation.

Introduction

Quinolizines are of considerable interest due to their widespread occurrence in natural products, particularly in the field of alkaloids [1]. Although many routes to the basic ring systems are known, new general synthetic approaches are still highly desirable.A large variety of nitrogen heterocycles are known to form zwitterionic species on addition of activated olefins or acetylenes. Pyridine deserves special mention owing to the variety of transformations that it mediates. The earliest work in the area was reported by Diels and Alder, and their study [2] and subsequently the structure elucidation of Acheson [3] showed that pyridine reacts smoothly with dimethyl acetylenedicarboxylate (DMAD) to form 4*H*-quinolizine.

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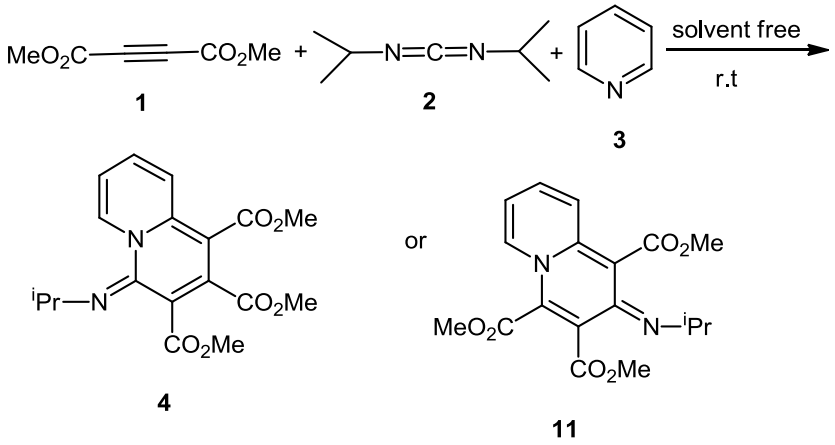
Intermolecular trapping of the 1,4-dipole with carbon dioxide [4], hexachloroacetone [5],phenyl isocyanide [6], isocyanates [7], benzoyl cyanide [8], electrophilic styrenes [9] and various strong C–H acids [10] are also noteworthy. However, only an isolated example of the addition of a 1,4-zwitterionic intermediate to carbonyl groups has been described [11].Recently, Nair [12], Shi [13] and Shaabani [14] have reported the trapping of the 1,4-zwitterionic intermediate generated from pyridine and DMAD with arylaldehydes, N-sulfonated imines, *N*-tosyl imines, arylmethylidene malononitriles and tetracyanoethylene (TCNE).

Modern computational chemistry methods, especially DFT, have proven to be excellent tools for determining molecular structures. Recently, such capabilities have been broadened to span spectroscopic properties such as NMR chemical shifts and couplings. DFT calculations can predict ^{13}C and ^{1}H-NMR chemical shifts to a degree of accuracy that has enabled researchers to sort out many issues in the

structural elucidation of complex organic molecules such as natural products [15-18].

Results and discussion

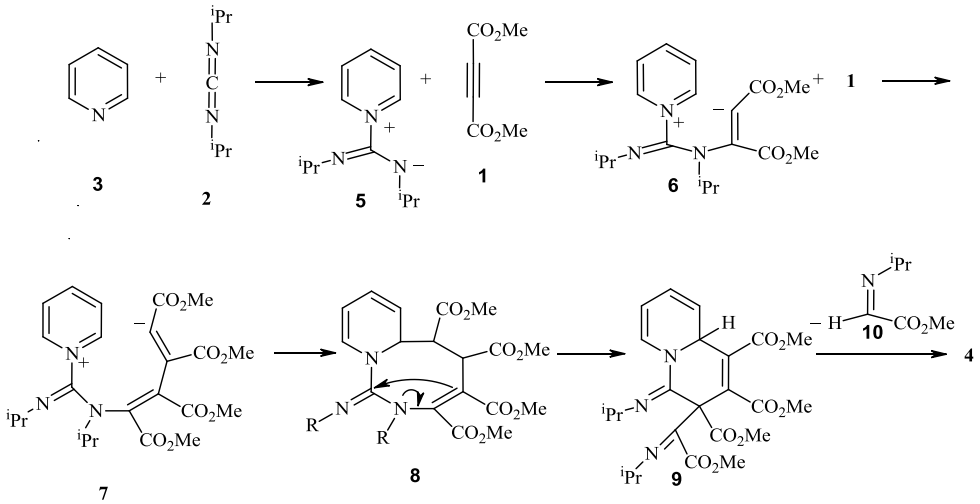
In continuation of our previous works in field of synthesis of heterocyclic compound via multicomponent reactions [23-24], herein we reporta four-component one-pot synthesis of 4*H*-quinolizine derivative **4**, by using of DMAD **1**, diisopropylcarbodiimde **2** in presence of pyridine **3**under solvent free reaction conditions (Scheme **1**).



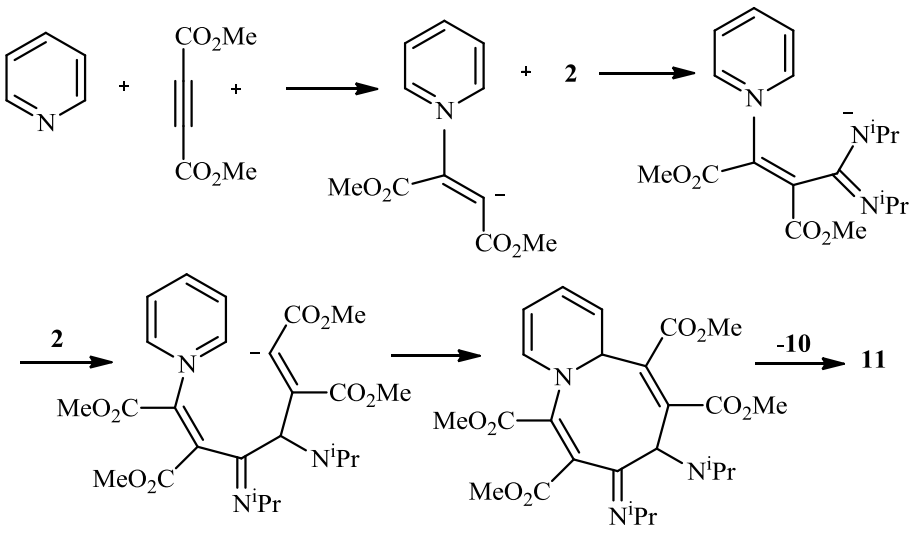
Scheme 1: Synthesis of 4.

A plausible rationalization may be advanced to explain the product formation. Presumably, the zwitterion **5** formed from pyridine and thedicyclocarbodiimide, adds totheacetyleniccompoundto furnish intermediate **6**, which then adds to another molecule of acetylenic ester to produce **7**. This intermediate undergoes cyclization to furnish the fused structure **8**. Intermediate **8** is converted to **9** by recyclization and then by elimination of **10**, the product **4** is produced (Scheme **2**).

An alternative possible mechanism, which leads to produce the other product **11** is shown in Scheme **3**, too.



Scheme 2: The proposed mechanism for structure of 4.



Scheme 3: The proposed mechanism for structure of 11.

For a more-detailed insight and to accurate characterization of structures, in this paper, we synthesized and performed theoretical investigation on compounds **4** and proposed product trialkyl 4-(isopropylimino)-4*H*-quinolizine-1,2,3-tricarboxylates **11** respectively.

The density functional theory is performed at 6-31G and 6-31++G** basis sets. Optimized geometry and NMR parameters are carried out by theoretical methods, and compared with the experimental values.

The 6-31G basis set was utilized as a minimal basis set, since calculation at this level of theory has been shown to give accurate results from geometry, energy and spin evaluation points of view even in biomolecules[25, 26]**.** Due to the zwitterion character of **4** and **11**, all the calculations were redone at the 6-31++G** which include polarized and diffuse functions on all elements (Figure **1**).

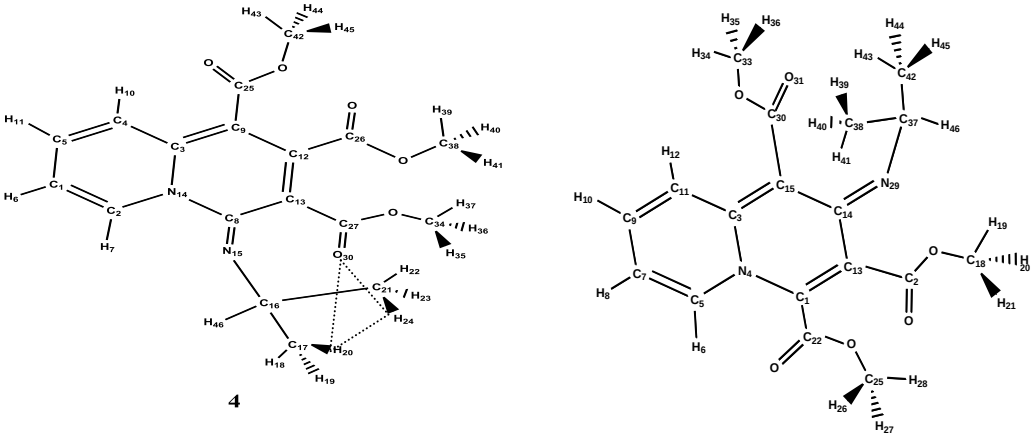


Figure 1: Moleculae structure of Compounds 4d and 11.[11]

Thermo chemical analysis is done for **4** and **11.** The values of electronic energies, Gibbs free energies and Enthalpyin gas and solvent phase at room temperature are reported in Table **1-3**.

The calculations of the vibrational frequencies were performed on full optimized geometries of **4** and **11**at B3LYP levels with the 6-31++G** basis set. The influence of the solvent on the relative stability of **4** and **11** was studied by means of the Onsager approach.

According to calculated electronic energies (Table **1**), at these two basis sets, compound **4** is more stable than compound **11**[at 6-31G **4** is (about 18 kcal.mol^{-1}) more stable than **11**and at the 6-31++G** **4** is (about 17 kcal.mol^{-1}in gas phase and 15.7 kcal.mol^{-1} in solvent phase) more stable than **11**. The Calculated Gibbs free energies (Table **2**) confirm the stability of the compound **4** in comparison with **11**[at 6-31G **4** is (about 17 kcal.mol^{-1})more stable than **11**and at the 6-31++G** **4** is (about 14.5 kcal.mol^{-1} in gas phase and 15 kcal.mol^{-1}) more stable than **11**.

Table 1. Calculated stabilization electronic energies and relative energies at B3LYP/6-31G andB3LYP/6-31++G** level.

Compounds	**Eenergy stabilization (kcal.mol^{-1})**			**ΔE(kcal.mol^{-1})**		
	6-31G	6-31++G**[a]	6-31++G**[b]	6-31G	6-31++G**[a]	6-31++G**[b]
4	-789659.52	-789947.40	-789955.86	0.00	-287.88	-296.34
11	-789641.40	-789930.28	-789940.13	18.12	-270.76	-280.61

[a]optimization in gas phase

[b]optimization in solvent phase

The Calculated Gibbs free energies(Table **2**) confirm the stability of the compound 4 in comparison with 11[at 6-31G 4 is (about 17 kcal.mol-1)more stable than 11and at the 6-31++G** 4 is (about 14.5 kcal.mol-1 in gas phase and 15 kcal.mol-1) more stable than 11].

Table 2. Calculated Gibbs free energies at B3LYP/6-31G and B3LYP/6-31++G** level.

Compounds	**Gibss Free Eenergy (kcal.mol^{-1})**			**ΔG(kcal.mol^{-1})**		
	6-31G	6-31++G**[a]	6-31++G**[b]	6-31G	6-31++G**[a]	6-31++G**[b]
4	-789465.83	-789755.23	-789763.75	0.00	-287.4	-297.92
11	-789448.41	-789738.73	-789748.74	17.42	-272.9	-282.91

[a]optimization in gas phase

[b]optimization in solvent phase

We can see these stability in calculated enthalpy (Table **3**) [at 6-31G **4** is (about 18kcal.mol^{-1}) more stable than **11**and at the 6-31++G**,**4** is (about 17kcal.mol^{-1} in gas phase and 15.6 kcal.mol^{-1}) more stable than **11**].

Table 3. Calculated Enthalpy at B3LYP/6-31G and B3LYP/6-31++G** level.

Compounds	**Enthalpy (kcal.mol^{-1})**			**ΔH(kcal.mol^{-1})**		
	6-31G	6-31++G**[a]	6-31++G**[b]	6-31G	6-31++G**[a]	6-31++G**[b]
4	-789413.17	-789702.49	-789711.23	0.00	-289.32	-298.06
11	-789395.28	-789685.57	-789695.64	17.89	-272.4	-282.47

[a]optimization in gas phase
[b]optimization in solvent phase

Chloroform as solvent has considerable effect in stabilization energy of both compound **4** and **11**. The solvent effect results stabilization of compound **4**by about 8.5kcal.mol^{-1} and compound **11**by about 9.9 kcal.mol^{-1}.

We found that the Gibbs free energies (ΔG) of the compound **4** and **11** in solution are smaller than when in the gas phase, because interactions in solution are stronger than in the gas phase (The stabilization for the compound **4**is about 10.5kcal.mol^{-1} and the compound **11** is about 10 kcal.mol^{-1}).

The calculated enthalpy confirms the strong interaction in solvent phase in compared to gas phase (The stabilization for the compound **4**is about 8.74kcal.mol^{-1} and the compound **11** is about 10.1 kcal.mol^{-1}).

Structural analysis of compound **4** (Table **4**) shows a triangular that was made by hydrogen bonding between two hydrogen atom of two methyl groups and oxygen atom of ester group (Figure **1**).

Table 4. Selected structural details of optimized structures at B3LYP/6-31++G** levelin chloroform solvent, bond distances (Å) and bond and dihedral angles (º).

Structure	**Compound 4**	**Structure**	**Compound 11**
Bond distance(A^0)		**Bond distance(A^0)**	
C1=C2	1.36	C7=C9	1.42
C1=C5	1.41	C7=C5	1.36
C2-N14	1.37	C5-N4	1.36
C8-N14	1.47	C1-N4	1.42
C8=N15	1.26	C1-C22	1.49
C16-N15	1.46	C22=O	1.21
C16-C17	1.53	C22-O	1.35
C25=O	1.22	C14=N29	1.28
C25-O	1.36	C37-C42	1.54
O30-H20	2.69	O31-H39	2.35
O30-H24	2.35	O31-H43	2.55
C2-H7	1.08	C5-H6	1.08
C16-H46	1.09	C25-H26	1.09
C17-H20	1.09	C37-H46	1.10
Bond Angle(^{0})		**Bond Angle(^{0})**	
C5-C1-C2	118.11	C9-C7-C5	118.44
C2-N14-C8	117.21	C5-N4-C1	119.85
C2-N14-C3	122.70	C5-N4-C3	121.27
N14-C8-N15	113.73	C1-C13-C14	119.67
C8-N15-C16	130.21	C14-N29-C37	130.08
C17-C16-C21	112.69	C38-C37-C42	112.63
C27-O-C34	116.03	C2-O-C18	115.42
Dihedral Angle (^{0})		**Dihedral Angle (^{0})**	
N14-C8-N15-C16	174.18	C15-C14-N29-C37	9.76
C13-C8-N15-C16	-4.6		

The involvement of oxygen between two hydrogen atoms gives stability to this form of product.Natural bond orbital (NBO) analysis of products, calculated muliken charges of atoms (Table **5**) and structural parameters (Table **2**) show that there is long π-electron delocalization in the compound **4** in comparison to compound **11** which leads to the stabilization of the compound **4** inrelative to compound**11.**

The effect of solvent on stability of compound **4**in solvent and calculated muliken charges of atoms confirmed that this product is a polar molecule. It is like a zwitterion, because the charge of the most positive atom (C12) is about +1 C and the charge of the most negative atom (C8) is about -1.48 C. Charge separation in this molecule causes high interaction between solute and solvent.

Table 5. Calculated muliken and NBO net charges of atoms (in atomic units) at B3LYP/6-31++G** level in chloroform solvent.

Atoms	Compound 4		Atoms	Compound 11	
	Muliken Charge	NBO Charge		Muliken Charge	NBO Charge
C1	-0.13	-0.29	**C1**	0.11	0.03
C2	0.37	0.06	**C2**	-0.20	0.82
C3	0.35	0.28	**C3**	0.54	0.23
C4	-0.47	-0.24	**C5**	0.27	0.05
C5	-0.78	-0.17	**C7**	-0.12	-0.30
N14	0.54	-0.36	**C9**	-0.59	-0.19
C8	-1.48	0.46	**C11**	-0.57	-0.23
C9	-0.26	-0.28	**C13**	0.28	-0.00
N15	-0.12	-0.47	**C14**	-0.42	0.23
C12	0.99	0.04	**C15**	-0.06	-0.07
C13	0.64	-0.27	**C18**	-0.17	-0.30
C16	0.24	-0.08	**C22**	0.08	0.22
C17	-0.54	-0.67	**C30**	0.09	0.78
C25	0.22	0.80	**C37**	0.33	-0.09
C26	-0.19	0.82	**C38**	-0.59	-0.65
C27	0.13	0.79	**N4**	0.37	-0.36
C34	-0.17	-0.29	**N29**	0.01	-0.42
O30	-0.41	-0.62	**O31**	-0.45	-0.63
O33	-0.21	-0.55	**O32**	-0.27	-0.57

DFT calculations of ^{13}C and ^{1}H-NMR chemical shifts were done on the compound **4** and **11**in gas and solvent phases (Table **6, 7**). There is a good agreement between the experimental and theoretical chemical shifts of the compound **4** in compared to the compound **11** in ^{13}C and ^{1}H-NMR.

In Figure **2** we show the correlation between experimentaland calculated ^{13}C chemical shifts obtained for the truestructure of compound **4**. We note that this structure has a very good correlation with the experimental chemical shifts values of the product.

Because of π-delocalization system in structure **4**, we expect that carbon atoms C9 and C13 are shielded than C3 and C12. As it has shown in Table **6**, there is good agreement between calculated and experimental chemical shifts of these carbon atoms (carbon atoms C9 and C13 were observed at δ = 104 and 109 ppm, respectively, and carbon atoms C3 and C12 were observed in the downfield region of the spectrum, δ = 145 and 146 ppm).

In structure **11**, we expect that carbon atoms C15 and C13 were observed at high field region ,because of resonance between lone-pair electrons of Nitrogen atom with double bond, but atom C15 was observed at δ = 148 ppm instead of δ = 109 ppm in calculation.

Also in structure **4**, two Carbonyl groups C25 and C27 must be appeared in lower chemical shift than C26, since there is high electron density at carbon atoms C9 and C13.

There is a difference between calculated and experimental chemical shifts of C8. This atom is sp^2-hybridazation and also has attached to two electronegative atoms (N), therefore, we expect it appears at lower field than atom C12. The high interaction between two Nitrogen atoms with solvent in solution may cause this disagreement.

In figure 3, there were three chemical shifts that belong to hydrogen atoms of two methyl groups (C17, C21). One of them belongs to hydrogen atoms of C21 and the second one belongs to hydrogen atoms of C17, the third one belongs to H24.This splitting between hydrogen atoms of C21 is because of hydrogen bonding interaction between H24 and O30. This interaction is expected because the H24 is the nearest atom to O30 along other hydrogen atoms. There are about 1ppm disagreement between calculated and

experimental chemical shifts of H24 and H46. High interaction between the solute molecules and between the solute and solvent cause these disagreements.

Table 6. Representation of some experimental and theoretical chemical shifts (ppm) of compound 4.

^{13}C	CALC[a]	^{13}C	CALC[b]	EXP	^{1}H	CALC[a]	^{1}H	CALC[b]	EXP
C21	17.70	**C21**	17.57	23.4	**H18**	1.02 (1.15)[c]	**H18**	0.93(1.16)[c]	1.15
C17	21.02	**C17**	20.85	29.68	**H20**	1.22(1.15)	**H19**	1.26(1.16)	1.15
C42	52.045	**C42**	51.43	52.7	**H19**	1.23(1.15)	**H20**	1.28(1.16)	1.15
C38	53.45	**C38**	52.86	52.94	**H22**	1.39(1.14)	**H22**	1.36(1.09)	1.13
C34	53.51	**C34**	53.06	53.2	**H23**	0.89(1.14)	**H23**	0.81(1.09)	1.13
C16	59.04	**C16**	59.10	59.1	**H24**	2.30	**H24**	2.47	1.25
C9	95.88	**C9**	96.19	104.42	**H35**	3.72(3.79)	**H35**	3.73(3.74)	3.91
C13	103.45	**C13**	103.70	109.1	**H36**	3.97(3.79)	**H36**	3.92(3.74)	3.91
C1	113.94	**C1**	110.92	119.29	**H37**	3.68(3.79)	**H37**	3.56(3.74)	3.91
C4	121.04	**C4**	121.00	125.31	**H43**	3.76(3.83)	**H43**	3.57(3.78)	3.91
C2	132.08	**C5**	130.86	130.07	**H44**	3.94(3.83)	**H44**	3.95(3.78)	3.91
C5	134.28	**C2**	131.74	138.54	**H45**	3.81(3.83)	**H45**	3.82(3.78)	3.91
C8	142.50	**C8**	141.85	157.13	**H39**	4.13(4.03)	**H39**	4.19(3.98)	3.97
C3	145.34	**C3**	144.89	146.28	**H40**	4.17(4.03)	**H40**	4.11(3.98)	3.97
C12	146.90	**C12**	147.51	145.85	**H41**	3.81(4.03)	**H41**	3.64(3.98)	3.97
C27	161.13	**C27**	160.28	164.39	**H46**	4.77	**H46**	4.64	3.84
C25	162.67	**C25**	161.15	164.96	**H6**	7.29	**H6**	6.78	7.51
C26	166.67	**C26**	164.33	166.37	**H11**	7.96	**H11**	7.45	8.01
					H10	8.70	**H10**	8.63	8.82
					H7	9.00	**H7**	8.91	9.44

[a]The calculated chemical shift in chloroform as solvent phase.
[b]The calculated chemical shift in gas phase.
[c]The calculated protons chemical shift's average in parentheses

Table 7. Representation of some experimental and theoretical chemical shifts (ppm) of compound 11.

^{13}C	CALC[a]	^{13}C	CALC[b]	EXP	^{1}H	CALC[a]	^{1}H	CALC[b]	EXP
C38	18.71	**C38**	18.41	23.4	**H45**	0.71(0.86)[c]	**H45**	0.67(0.84)[c]	1.15
C42	21.29	**C42**	21.27	29.68	**H44**	0.87(0.86)	**H44**	0.84(0.84)	1.15
C33	52.30	**C33**	51.82	52.7	**H43**	1.00(0.86)	**H43**	1.01(0.84)	1.15
C18	53.77	**C25**	52.92	52.94	**H40**	0.7662(1.07)	**H40**	0.72(1.08)	1.13
C25	53.82	**C18**	53.07	53.2	**H41**	1.3677(1.07)	**H41**	1.44(1.08)	1.13
C37	62.57	**C37**	62.62	59.1	**H39**	2.31	**H39**	2.41	1.25
C15	101.85	**C15**	102.77	104.42	**H26**	3.80(3.88)	**H26**	3.61(3.79)	3.91
C7	107.95	**C7**	105.38	119.29	**H27**	3.81((3.88)	**H27**	3.79(3.79)	3.91
C11	122.24	**C11**	122.90	125.3	**H28**	4.02(3.88)	**H28**	3.97(3.79)	3.91
C1	126.84	**C1**	124.76	146.3	**H34**	3.80(3.85)	**H34**	3.62(3.79)	3.91
C9	131.24	**C9**	127.70	130.1	**H35**	3.91(3.85)	**H35**	3.92(3.79)	3.91
C5	135.98	**C5**	134.80	138.54	**H36**	3.83(3.85)	**H36**	3.84(3.79)	3.91
C3	147.93	**C14**	146.81	145.85	**H19**	3.73(3.91)	**H19**	3.53(3.84)	3.97
C13	148.35	**C3**	146.97	109.1	**H20**	3.99(3.91)	**H20**	3.99(3.84)	3.97
C14	148.36	**C13**	150.97	157.13	**H21**	4.01(3.91)	**H21**	3.99(3.84)	3.97
C22	159.58	**C22**	157.91	164.39	**H46**	4.79	**H46**	4.78	3.84
C2	161.79	**C2**	158.96	164.96	**H8**	6.79	**H8**	6.27	7.51
C30	162.31	**C30**	161.08	166.37	**H10**	7.58	**H10**	7.07	8.01
					H6	8.03	**H6**	7.71	8.82

					H12	8.53	**H12**	8.46	9.44

[a]The calculated chemical shift in chloroform as solvent phase.
[b]The calculated chemical shift in gas phase.
[c]The calculated protons chemical shift's average in parentheses

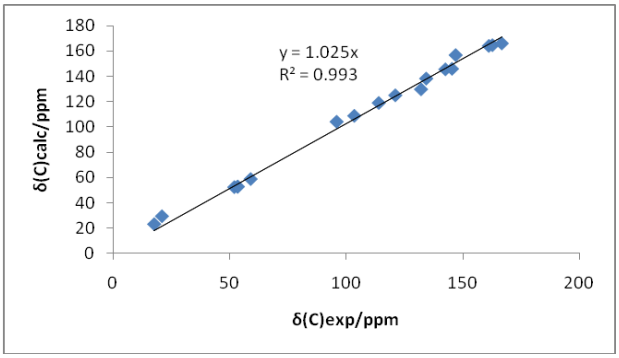


Figure 2. Correlation between experimental and calculated 13C chemical shifts of compound 4.

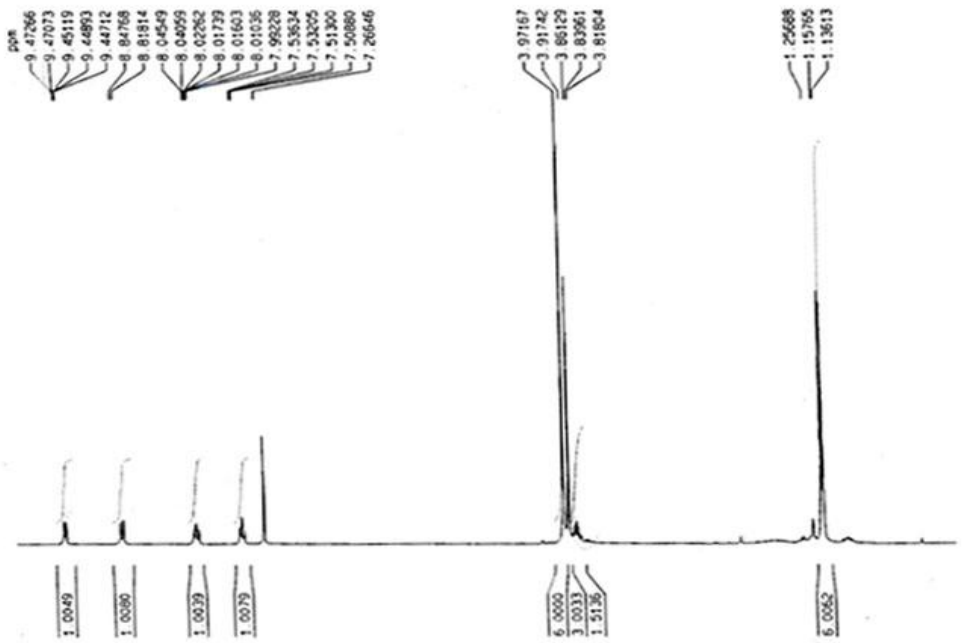


Figure 3. The experimental 1H-NMR of compound 4 in chloroform solvent.

Experimental

Chemicals were purchased from Fluka and used without further purification. Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses for C, H and N were performed using a Heraeus CHN-O-Rapid analyzer and the results agreed favorably with the calculated values. Mass spectra were recorded on a Finnigan MAT 8430 spectrometer operating at an ionization potential of 70 eV. IR spectra were measured on a Shimadzu IR-460 spectrometer. ^{1}H and ^{13}C NMR spectra were measured on a BrukerAvance DRX-

300 spectrometer using $CDCl_3$ as applied solvent and TMS as internal standard at 300 and 75 MHz, respectively. A mixture of diisopropyl acetylenedicarboxylate (0.78 mL, 4 mmol), pyridine (0.16 g, 2 mmol) and dicyclocarbodiimide (DCC) (0.41 g, 2 mmol) was stirred at room temperature for appropriate time. After completion of the reaction, monitored by TLC, the residual products were purified by recrystallized from diethyl etheras yellow powder; yield: 0.41 g (57%), mp 143-145 °C. IR (KBr) (ν_{max}/cm^{-1}): 1739, 1715 and 1686 (3 C=O), 1625

(C=N), ^{1}H NMR (300 MHz, $CDCl_3$):δ= 1.14 (d, 6H, J = 6.4 Hz, $2CH_3$), 3.84 (sept, 1H, J = 6.4 Hz, CH), 3.91 (s, 3H, OCH_3), 3.97 (s, 6H, $2OCH_3$), 7.51 (t, 1H, J = 7.2 Hz, CH), 8.01 (t, 1H, J = 6.9 Hz, CH), 8.82 (d, 1H, J = 8.8 Hz, CH), 9.44 (d, 1H, J = 7.1, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$):δ = 23.4 and 29.68 ($2CH_3$), 59.1 (CHN), 52.7, 52.9, and53.2 ($3OCH_3$), 104.4 (C), 109.1 (C), 119.3 (CH), 125.3 (CH), 130.1 (CH), 138.5 (CH), 145.8 (C), 146.3 (C), 157.1 (N-C=N), 164.4 (C=O), 165.0 (C=O), 166.4 (C=O) ppm. Anal. Calcd for $C_{18}H_{20}N_2O_6$ (360): C, 59.99; H, 5.59; N, 7.77; Found: C, 60.19; H, 5.92; N, 7.46 %.

COMPUTATIONAL METHOD

Quantum mechanical calculations were carried out with the GAUSSIAN program series 2003 [19]. The optimization of the geometry was performed employing a hybrid Hartree–Fock density-functional scheme, that is, the Becke three-parameter with Lee–Yang–Parr (B3LYP) functional of density functional theory (DFT) [20] with two standard basis sets, 6-31G and 6-31++ G**. Full optimizations were performed without any symmetry constraints, in gas phase and in solvent. The solvent effect is taken into account via the self-consistent reaction field (SCRF) method. This method is based on Onsager reaction field theory of electrostatic solvation. In this model, the solvent is considered as a uniform dielectric with a given dielectric constant (ε). The solute is placed into a cavity within the solvent. SCRF approaches differently in how they define the cavity and the reaction field [21]. The solvent effects on the stabilization of products have been investigated with the SCRF=IEFPCM Keyword [22] at the B3LYP/6-31++G** level with chloroform (ε = 4.9) as a solvent. Natural bonding orbital of atoms (NBO) was done for better characterization of atoms of molecules and for analysis of atomic net charges. For thermochemical properties, The vibrational frequency calculation in room temperature has been doneon full optimized geometries of 4*H*-quinolizine derivatives with 6-31G and 6-31++ G **, and the stabilization energies, enthalpies, Gibbs free energies, entropies, and other thermo chemical properties with special prominence of solvent effect on them were obtained. Ourresults were compared with those obtained for the gas phase as well; the effect of the permittivity of solvents on the steadiness of this structure was explored and discussed. NMR computations of absolute shielding were performed using the gauge including atomic orbital (GIAO) method [22] on the DFT-optimized structure in gas phase and in the presence of chloroform as solvent. The ^{1}H and ^{13}C chemical shifts were calculated as $\delta = \sigma_{ref} - \sigma$, where σ_{ref} is the shielding constant of $(CH_3)_4Si$ calculated at the same level of theory and at the same solvent (σ_{ref}(C) = 192.97 ppm, σ_{ref}(H) = 31.67 ppm) (Table **2**).

Conclusion

Theoreticalstudyofstructures **4**and**11** indicated:

1. Thermo chemical studies (electronic, Gibbs free energies and enthalpy) confirm the stability of the compound **4** in compared to the compound **11**.
2. The solvent effect shows stabilization of compound **4** than compound **11**.This effect and calculated muliken charges of atoms confirmed that product **11** is a nonpolar molecule.
3. Structural analysis of compound **4** shows hydrogen bonding between two hydrogen atom of two methyl groups and oxygen atom of ester group.
4. There is long π-electron delocalization in the compound **4** in comparison to compound **11** which leads to the stabilization of the compound **4** inrelative to compound **11.**
5. There was a good agreement between experimental and theoretical of ^{13}CNMR and ^{1}HNMR of the compound **4**in compared to **11**.

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