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Research Article

Density Functional Theory Study on Conformers of Benzoylcholine Chloride

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The optimized molecular structures and vibrational frequencies and also gauge including atomic orbital (GIAO) ^{1}H and ^{13}C NMR shift values of benzoylcholine chloride [(2-benzoyloxyethyl) trimethyl ammonium chloride] have been calculated using density functional theory (B3LYP) method with 6-31++G(d) basis set. The comparison of the experimental and calculated infrared (IR), Raman, and nuclear magnetic resonance (NMR) spectra has indicated that the experimental spectra are formed from the superposition of the spectra of two lowest energy conformers of the compound. So, it was concluded that the compound simultaneously exists in two optimized conformers in the ground state. Also the natural bond orbital (NBO) analysis has supported the simultaneous exiting of two conformers in the ground state. The calculated optimized geometric parameters (bond lengths and bond angles) and vibrational frequencies for both the lowest energy conformers were seen to be in a well agreement with the corresponding experimental data.

1. Introduction

The determination of the minimum energy conformers of acetylcholine has been subject by many theoretical works [1–3]. Marino et al. have investigated the conformational behavior and molecular motion of acetylcholine in vacuum and aqueous solution [4]. They have calculated five low lying conformers by molecular mechanics computing. The ab initio data of acetylcholine has indicated that the most stable conformer is the transgauche arrangement of the two essential torsion angles (τ_1; C-C-O-C and τ_2; N-C-C-O) [5, 6]. The observed conformer of acetylcholine is transgauche ($\tau_1 = -166.9$ and $\tau_2 = 84.7^\circ$) in the crystal of its chloride [7, 8], gauche-gauche ($\tau_1 = 78.9$ and $\tau_2 = 78.4^\circ$) in the crystal of its bromide [9], and gauche-gauche ($\tau_1 = \pm 83$ and $\tau_2 = \pm 89^\circ$) in the crystal of its iodide [10].

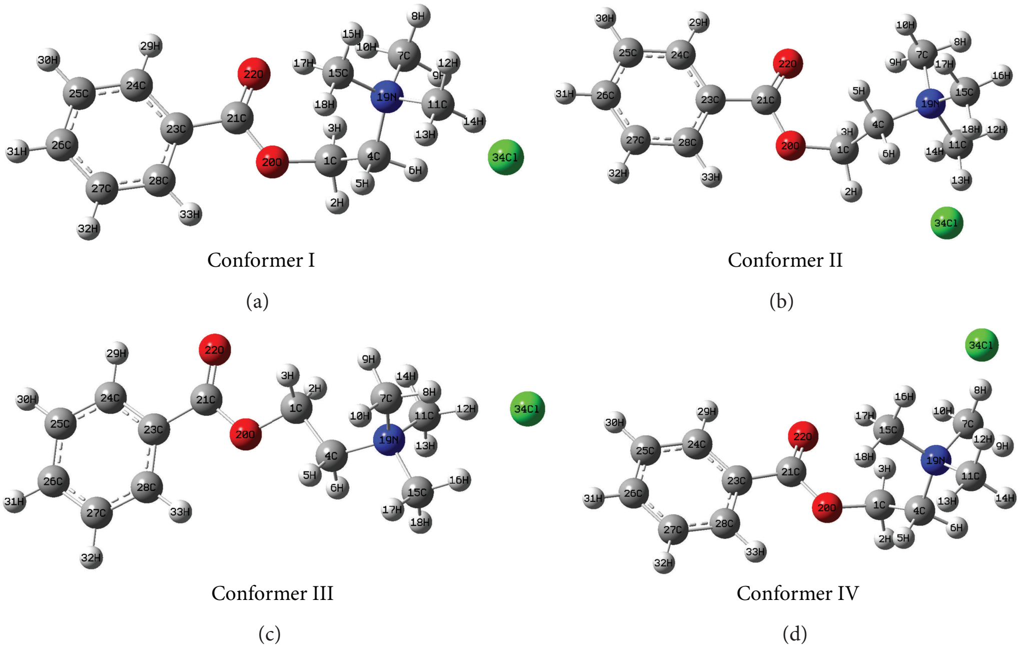
In this study we wish to report the IR, Raman (R), NMR, and NBO analysis of benzoylcholine chloride (BzChCl) to obtain the lowest energy conformer in the ground state by means of density functional theory (B3LYP) method.

2. Computational Details

The optimized structure parameters and vibrational frequencies of BzChCl were calculated by density functional theory B3LYP method at 6-31++G(d) basis set level. All the computations were performed by using Gaussian 03 package [11] and Gauss-View molecular visualization programs [12] on the personal computer. The calculated vibration frequencies have been scaled with a scale factor of 0.9614 [13]. The chemical shifts of ^{1}H and ^{13}C NMR in vacuum for all the conformers of the compound were calculated by GIAO method [14] using the same set level of the theory which is routinely used for NMR chemical shift calculations on fairly large molecules [15, 16]. In the chemical shift calculations tetramethylsilane (TMS) was used as reference molecule.

3. Results and Discussion

3.1. Ground State Conformers. The molecular structures of all the calculated optimized conformers of BzChCl can be



Conformer I

(a)

Conformer II

(b)

Conformer III

(c)

Conformer IV

(d)

Figure 1: Optimized molecular structures of four conformers of BzChCl.

Table 1: Five essential torsion angles for all the conformers of BzChCl.

Torsion Angles (°)	Exp. [6]	Conformer I	Conformer II	Conformer III	Conformer IV
τ_1[C(21)-O(20)-C(1)-C(4)]	167.9	115.02	83.64	−179.64	136.13
τ_2[O(20)-C(1)-C(4)-N(19)]	84.7	−81.83	−153.87	−179.83	−87.70
τ_3[C(1)-C(4)-N(19)-C(11)]	171.4	−172.97	−49.28	−61.10	174.13
τ_4[C(1)-C(4)-N(19)-Cl(34)]	—	−112.83	−105.05	−179.75	−166.48
τ_5[O(22)-C(21)-O(20)-C(1)]	5.2	−9.68	−0.87	0.00	−3.70

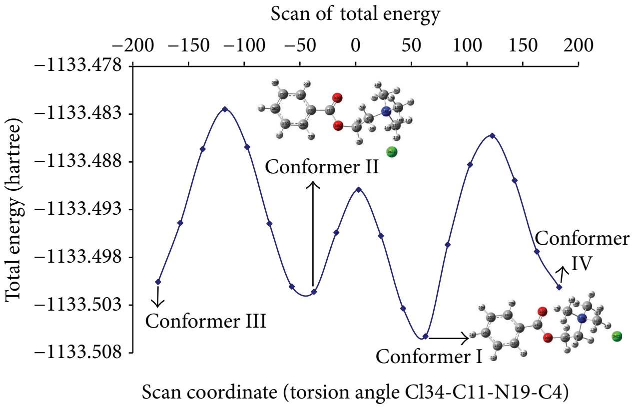


Figure 2: Potential energy surface (PES) scan of BzChCl.

seen in Figure 1. In calculations firstly the potential energy surface (PES) of the compound was scanned around the torsion angle of Cl(34)-C(11)-N(19)-C(4) from −180° to 180° at increments of 20° with an Cl⋯N distance of around 3.60 Å at B3LYP/6-31 G(d,p). The PES showed four minimum-energy structures (Figure 2). The barrier height between the conformer I and II is 9.6 kcal/mol while those between the conformer I and III or I and IV is bigger than 13 kcal/mol. These structures were chosen as initial geometry to obtain the further ones. The conformers of the compound are defined by five essential torsion angles as given in Table 1. For comparison, the experimental data being available for a similar molecule, acetylcholine chloride, are also shown in the table.

The electronic energies, relative energies, and mean vibrational deviations for all the conformers of the compound are given in Table 2. The relative energy values and calculated mean vibrational deviations in the table are respect to the lowest energy conformer I of the compound. As seen the mean vibrational deviation increases while the relative energy increases. Therefore, we state that the more different the molecular structures of the two conformers are the higher the relative energy is between them, and so, a bigger mean vibrational deviation occurs. This comment has also been given for pyridine carboxaldehyde and difluorobenzaldehyde molecules in our previous studies [17, 18]. From Table 2 we also see that the relative energies and mean vibrational

Table 2: Electronic energies, and relative energies and mean calculated vibrational deviations between the conformers of BzChCl.

	Conformer I	Conformer II	Conformer III	Conformer IV
Energy (Hartree/part.)	−1133.243575	−1133.242015	−1133.239145	−1133.238584
Relative energy (kcal/mol)	0.00	0.978	2.778	3.130
Vib. deviations $\|\Delta\nu\|_{\text{ave}}$	0.00	6.219688	9.875208	6.393542

Table 3: Experimental and calculated vibrational frequencies of two lower-energy conformers of BzChCl. ν shows stretching, δ bending, γ out of plane bending, ρ_r rocking, t twisting, τ torsion, and w wagging modes.

Mode no.	Assignments	Experimental frequencies (cm^{-1}) BzChCl [19]		Calculated frequencies (cm^{-1}) B3LYP 6-31++G(d)	
		IR	R	Conformer I	Conformer II
96	Ring $\nu(\text{CH})_{\text{sym}}$			3107	3109
95	Ring $\nu(\text{CH})_{\text{sym}}$		3091vw	3100	3098
94	Ring $\nu(\text{CH})_{\text{asym}}$			3086	3086
93	Ring $\nu(\text{CH})_{\text{asym}}$			3085	3078
92	$\nu(\text{CH}_3)_{\text{asym}}$		3073s	3077	3076
91	Ring $\nu(\text{CH})_{\text{asym}}$		3068sh	3066	3065
90	$\nu(\text{CH}_3)_{\text{asym}}$	3065w		3065	3058
89	$\nu(\text{CH}_3)_{\text{asym}}$			3053	3053
88	$\nu(\text{CH}_3)_{\text{asym}}$			3050	3048
87	$\nu(\text{CH}_3)_{\text{asym}} + \nu(\text{CH}_2)_{\text{asym}}$		3037w	3046	3044
86	$\nu(\text{CH}_2)_{\text{asym}} + \nu(\text{CH}_3)_{\text{asym}}$	3034vw	3023m	3026	3024
85	$\nu(\text{CH}_3)_{\text{asym}} + \nu(\text{CH}_2)_{\text{asym}}$			3018	3018
84	$\nu(\text{CH}_2)_{\text{asym}}$	2994sh	2997m	2998	3015
83	$\nu(\text{CH}_3)_{\text{sym}} + \nu(\text{CH}_2)_{\text{sym}}$		2979m	2988	2980
82	$\nu(\text{CH}_2)_{\text{sym}} + \nu(\text{CH}_3)_{\text{sym}}$	2956.2927vs	2951m	2972	2975
81	$\nu(\text{CH}_3)_{\text{sym}} + \nu(\text{CH}_2)_{\text{sym}}$		2932m	2919	2920
80	$\nu(\text{CH}_3)_{\text{sym}} + \nu(\text{CH}_2)_{\text{sym}}$	2871sh	2892w	2906	2904
79	$\nu(\text{CH}_2)_{\text{sym}} + \nu(\text{CH}_3)_{\text{sym}}$	2855vs	2836vw	2809	2887
78	ν (C=O)	1725vs	1726vs	1687	1688
77	Ring ν (C=C) + Ring δ(CH)	1598m	1601s	1588	1589
76	Ring ν (C=C) + Ring δ(CH)	1583w	1584w	1569	1569
75	$\gamma(\text{CH}_3) + \delta(\text{CH}_2)$			1498	1493
74	$\gamma(\text{CH}_3) + \delta(\text{CH}_2)$	1486m	1489vw	1485	1479
73	$\delta(\text{CH}_2) + \gamma(\text{CH}_3)$ + Ring δ(CCH)			1481	1476
72	Ring δ(CCH) + $\delta(\text{CH}_2) + \gamma(\text{CH}_3)$		1471sh	1475	1474
71	$\gamma(\text{CH}_3) + \delta(\text{CH}_2)$			1466	1464
70	$\gamma(\text{CH}_3) + \delta(\text{CH}_2)$			1464	1458
69	$\delta(\text{CH}_3) + \delta(\text{CH}_2)$	1459, 1451s	1455m	1458	1455
68	Ring δ(CH) + $\gamma(\text{CH}_3) + \delta(\text{C–CH}_2) + \delta(\text{CH}_2)$		1443w	1445	1448
67	$\delta(\text{CH}_2) + \gamma(\text{CH}_3)$			1437	1444
66	$\gamma(\text{CH}_3) + \delta(\text{CH}_3)$			1435	1434
65	Ring δ(CH) + ν(Ring) + δ(CCC)	1434sh		1434	1434
64	$\delta(\text{CH}_3) + \delta(\text{C–CH}_2)$	1411w	1413vw	1413	1412
63	$\delta(\text{CH}_3) + \delta(\text{C–CH}_2)$		1404vw	1402	1402
62	$\delta(\text{CH}_3) + \delta(\text{C–CH}_2)$		1385vw	1394	1391
61	$\delta(\text{C–CH}_2) + \delta(\text{CH}_3)$	1381ms		1374	1362
60	$\delta(\text{C–CH}_2) + \delta(\text{CH}_3)$ + δ(CH) + ν(Ring)	1341w	1346w	1338	1319
59	$\delta(\text{C–CH}_2) + \delta(\text{CH}_3)$ + δ(CH)	1311m	1311w	1314	1314
58	δ(CH) + δ(CCC)		1283m	1299	1300
57	$\delta(\text{N–CH}_3) + \delta(\text{C–CH}_2) + \nu(\text{N–CH}_2)$	1280.1261s	1269sh	1272	1281

Table 3: Continued.

Mode no.	Assignments	Experimental frequencies ($\mathrm{cm^{-1}}$) BzChCl [19]		Calculated frequencies ($\mathrm{cm^{-1}}$) B3LYP 6-31++G(d)	
		IR	R	Conformer I	Conformer II
56	δ(C–CH$_2$) + δ(N–CH$_3$)	1249sh	1261m	1259	1262
55	δ(C–CH$_2$) + δ(CH) + ν(C–O) + Ring ν(C–C) + δ(CC=O)		1249sh	1239	1246
54	δ(N–CH$_3$) + δ(C–CH$_2$) + ν(N–CH$_3$)	1219vw	1221w	1231	1227
53	δ(N–CH$_3$) + δ(C–CH$_2$)			1206	1209
52	δ(CH)	1172m	1163m	1160	1162
51	δ(CH)	1161w	1143vw	1148	1148
50	δ(NCH)	1141vw		1135	1139
49	δ(NCH)	1118s	1121vw	1115	1119
48	δ(CCC) + ν(CO) + δ(NCH)	1103w	1089vw	1093	1094
47	δ(CCH)	1076m		1067	1066
46	τ(HCCH) + δ(NCH)	1041vw		1058	1060
45	δ(NCH)	1033w	1042w	1055	1051
44	δ(NCH) + Ring ν(CC)	1018m		1011	1026
43	δ(CCH) + ν(O–C)		1002s	1003	1012
42	δ(Ring) + ν(O–CH$_2$) + δ(NCH)		992vw	983	979
41	τ(HCCH)			979	978
40	τ(HCCH)			978	976
39	τ(HCCH)	951ms	959, 953w	961	961
38	ν(N–CH$_3$) + δ(NCH)			929	940
37	τ(Ring)			927	927
36	δ(CCH) + ν(N–CH$_3$)	902m	903w	906	924
35	ν(N–CH$_3$) + δ(NCH)	869w	871w	861	883
34	Ring γ(CH)		836m	835	835
33	δ(N–CH$_3$) + δ(Ring) + δ(OC=O)	812vw	811vw	828	825
32	τ(HCCH) + Ring γ(CH) + γ(OC=O)			793	788
31	τ(HCCH) + Ring γ(CH) + γ(OCC)			785	778
30	Breathing (choline)	714s	724m	698	717
29	Ring γ(CH) + γ(CC=O)	688vw	680m	673	699
28	γ(Ring)	679w		671	670
27	δ(Ring) + δ(COC)			657	663
26	δ(Ring)	619vw	619m	606	606
25	δ(N–CH$_3$) + δ(NCC) + δ(OCC)	544w	544vw	526	516
24	δ(N–CH$_3$) + δ(NCC) + δ(OCC)	474w	495vw	471	465
23	δ(N–CH$_3$) + δ(N–CH$_2$)		476w	454	459
22	δ(N–CH$_3$)		455vw	440	441
21	γ(Ring) + γ(OC=O)		423w	431	434
20	γ(Ring)			409	399
19	δ(N–CH$_3$)			399	390
18	δ(N–CH$_3$) + ρ_r (CH$_2$)		369w	369	374
17	ρ_r (CH$_2$) + ρ_r (CH$_3$)			356	357
16	ρ_r (CH$_3$) out of plane			344	329
15	ρ_r (CH$_3$) out of plane			324	322
14	w(CH$_3$)			303	293
13	ρ_r (CH$_3$) out of plane		261w	266	266
12	ρ_r (Ring) + w(CH$_3$)			255	236
11	ρ_r (CH$_2$) + w(Ring)		209m	236	226

Table 3: Continued.

Mode no.	Assignments	Experimental frequencies (cm^{-1}) BzChCl [19] IR	R	Calculated frequencies (cm^{-1}) B3LYP 6-31++G(d) Conformer I	Conformer II
10	ν(N–Cl) + ρ_r (CH_3) out of plane			185	177
9	w(Ring) + ν(N–Cl)		166w	166	161
8	ρ_r (CH_3) + ρ_r (CH_2)			138	149
7	ρ_r (CH_2) + w(Ring)			132	130
6	ρ_r (CH_2) + ρ_r (CH_3)		111w	106	114
5	w(CH_2) + w(C=O)			84	72
4	ρ_r (Ring) + w(CH_2) + ρ_r (CH_3)			63	54
3	w(Ring) + w(C=O) + w(Cl)			38	33
2	w(Ring) + ρ_r (CH_3) out of plane			25	26
1	ρ_r (Ring) out of plane + w(CH_3)			19	20
			R^2	0.9998	0.9998
			RMSE	12.8726	12.6161
			MAE	8.8888	9.6111

w: weak, m: medium, s: strong, v: very, sh: shoulder, and br: broad.

deviations between the conformers I and II are fairly low while the others are fairly high. Therefore, we take into account only the conformers I and II after this part of the study.

3.2. Vibrational Frequencies. The calculated vibrational frequencies and proposed vibrational assignments for the two lowest energy conformers I and II of BzChCl are given in Table 3. In the table are also given the experimental vibrational frequencies (IR and R) of the compound [19]. The linear correlation coefficients (R^2), mean absolute error (MAE) and the root mean square errors (RMSE) were also given in the last lines of the table. The RMSE is defined by the following

$$\mathrm{RMSE}\left(w_i\right) = \sqrt{\sum \frac{\left(\delta_i^{\mathrm{calc}} - \delta_i^{\mathrm{exp}}\right)^2}{n}}, \tag{1}$$

where δ_i^{calc} and δ_i^{exp} are the calculated and experimental chemical shifts of atom i, respectively, and n denotes the number of atoms. According to these values it can be stated that the calculated vibrational frequencies are in a good agreement with the experiment data. The calculated vibrational frequencies are slightly higher than the observable values for the majority of the normal modes. Two factors may be responsible for this discrepancy. The first is the environmental change of the molecule in the experimental medium and the second is that the calculated frequencies are harmonic while the experimental ones are anharmonic.

The assignments in the table are similar those done for a choline derivative molecule, acetylcholine bromide, which is available in literature [21].

3.3. Geometric Structures. BzChCl consists of a benzene ring and a choline group. The calculated optimized structure parameters for the lowest energy conformers I and II of BzChCl are summarized in Table 4, in accordance with the atom numbers in Figure 1. Since the X-ray analysis of the compound could not be reached the theoretical optimized structures were compared with those of acetylcholine chloride for which the crystal structure has been solved [5]. The R^2, MEA, and RMSE values between the calculated and experimental geometric parameters are given in the last lines of the table and they show a well agreement for the two conformers.

3.4. Chemical Shifts. The experimental and calculated ^1H and ^{13}C NMR chemical shifts (with respect to TMS) for the lowest energy conformers I and II of BzChCl are given in Table 5. The experimental chemical shifts have been obtained from Spectral Database for Organic Compounds Web Page [20]. Since the experimental ^1H chemical shift values of individual hydrogens are not available we have found the average values of ^1H chemical shifts for the CH_2 and CH_3 hydrogen atoms. These are shown as bold in the table. For comparison the average chemical shift values of the two conformers are also given in the table. The R^2, MEA, and RMSE values between the experimental and theoretical chemical shifts are obtained, and given in the last two lines of Table 5. According to these values one important observation is that the calculated results for the average chemical shifts values of the two conformers have a better agreement with the experimental data relative to the individual conformers.

3.5. NBO Analysis. The role of hyperconjugative interactions in the stabilization of the conformers of the compound was investigated by NBO analysis [22–25]. Here, the hyperconjugative represents the transfer of an electron from the lone pair (LP Cl) to an antibonding orbital since the molecular structures of the conformers are only changed by the location

Table 4: Calculated optimized geometric parameters for two lower-energy conformers of BzChCl.

Parameters	Experimental [6]		Calculated B3LYP [6-31++G(d)]	
Bond lengths (Å)			Conformer I	Conformer II
N(19)-C(7)	1.52		1.513	1.500
N(19)-C(11)	1.50		1.514	1.513
N(19)-C(15)	1.49		1.499	1.512
N(19)-C(4)	1.49		1.532	1.528
C(1)-C(4)	1.47		1.516	1.535
C(1)-O(20)	1.45		1.451	1.439
O(20)···N(19)	3.26		3.324	3.760
O(20)···C(15)	3.17		3.252	4.862
C(21)-C(23)	1.49		1.487	1.486
C(21)-O(20)	1.38		1.356	1.358
C(21)-O(22)	1.18		1.221	1.221
C(11)-H(12)	—		1.092	1.092
C(11)-H(13)	—		1.092	1.100
C(11)-H(14)	—		1.097	1.091
C(7)-H(8)	—		1.092	1.092
C(7)-H(9)	—		1.097	1.089
C(7)-H(10)	—		1.090	1.091
C(15)-H(16)	—		1.092	1.092
C(15)-H(17)	—		1.089	1.092
C(15)-H(18)	—		1.092	1.097
C(1)-H(2)	—		1.093	1.091
C(1)-H(3)	—		1.090	1.093
C(4)-H(5)	—		1.094	1.092
C(4)-H(6)	—		1.105	1.098
C(23)-C(24)	—		1.404	1.404
C(23)-C(28)	—		1.404	1.404
Cl(34)···N(19)	—		3.616	3.593
Cl(34)···C(4)	—		3.317	3.33850
Cl(34)···H(6)	—		2.281	—
Cl(34)···H(9)	—		2.467	—
Cl(34)···H(14)	—		2.463	—
Cl(34)···H(6)	—		—	2.377
Cl(34)···H(13)	—		—	2.381
Cl(34)···H(18)	—		—	2.486
		R^2	0.999	0.9414
		RMSE	0.0397	0.5327
		MAE	0.0303	0.2207
C(7)-N(19)-C(11)	109		108.2	110.2
C(7)-N(19)-C(15)	108		109.8	109.5
C(4)-N(19)-C(7)	111		110.8	110.9
C(4)-N(19)-C(11)	111		106.2	111.0
C(4)-N(19)-C(15)	107		112.4	107.1
N(19)-C(4)-C(1)	119		118.2	114.3
N(19)-C(7)-H(9)	—		107.3	109.9
C(1)-O(20)-C(21)	115		118.5	116.4
C(11)-N(19)-C(15)	111		109.3	108.1
O(20)-C(21)-O(22)	123		122.9	122.4
O(22)-C(21)-C(23)	129		124.4	124.9
O(20)-C(1)-C(4)	111		113.8	109.2

Table 4: Continued.

Parameters Bond lengths (Å)	Experimental [6]	Calculated B3LYP [6-31++G(d)] Conformer I	 Conformer II
O(20)-C(21)-C(23)	108	112.8	112.8
H(2)-C(1)-H(3)	—	108.4	110.2
H(6)-C(4)-H(5)	—	110.0	111.3
H(6)-C(4)-N(19)	—	104.0	105.4
H(14)-C(11)-N(19)	—	107.5	109.0
H(13)-C(11)-N(19)	—	108.4	107.3
H(12)-C(11)-N(19)	—	108.2	107.9
H(12)-C(11)-H(13)	—	110.1	111.1
H(12)-C(11)-H(14)	—	111.3	109.6
H(16)-C(15)-H(17)	—	109.5	110.2
H(8)-C(7)-H(9)	—	110.8	110.3
H(8)-C(7)-N(19)	—	107.6	108.5
N(19)-C(7)-H(10)	—	108.8	108.9
N(19)-C(15)-H(16)	—	108.4	108.3
H(17)-C(15)-H(18)	—	110.7	111.1
C(4)-C(1)-H(3)	—	113.5	113.4
O(20)-C(1)-H(2)	—	104.9	104.9
C(21)-C(23)-C(24)	—	117.9	118.0
C(21)-C(23)-C(28)	—	122.2	122.1
C(23)-C(24)-H(29)	—	119.0	119.0
C(23)-C(28)-H(33)	—	119.8	119.8
C(23)-C(24)-C(25)	—	120.1	120.0
C(23)-C(28)-C(27)	—	119.9	119.8
	R^2	0.7623	0.8597
	RMSE	3.2139	2.5758
	MAE	2.6083	1.9333

of the Cl anion. Table 6 consists of hyperconjugative interactions (kcal mol^{-1}) for the two lowest energy conformers of the compound calculated by using the B3LYP/LANL2DZ method. As seen the total hyperconjugative energies determined relative to only the location of the Cl anion for the two conformers are very near. This supports that the two conformers of the compound should have close optimized energies.

3.6. Spectral Analysis. The calculated IR and R spectra of the lowest energy conformers I and II of the compound are given in Figures 3(a) and 3(b), respectively. The powder experimental spectra of the compound are also given in the figures, as labeled (d). As seen the experimental IR or R spectrum does fit well to none of the calculated spectra for the two conformers, individually. The experimental spectra show the peaks splinted doublets or triplets, and thus, have more spectral lines than the calculated ones. Since the relative energy values and barrier height between the two conformers of the compound are very low we think that the spectra of these two conformers can simultaneously exist in one experimental spectrum. So, we have drawn the sum of the calculated spectra (IR or R) of these conformers, and obtained the spectra in Figure 3(c). By confronting them to the experimental ones (Figure 3(d)) it can be seen that they fit very well to each other. Therefore, we state that the title compound simultaneously contain these two optimized lowest energy conformers of the compound in the ground state.

When we investigate the relationship of the experimental and calculated chemical shifts by taking into consideration the R^2, MAE, and RMSE values we see from Table 5 the agreement between them are better for the average chemical shift values of the two conformers. This also confirms the simultaneous presence of the two conformers, regarding one experimental NMR spectrum for the two conformers since of their fast motions in the solution phase. Since of these, we state that the title compound simultaneously contains the two optimized energy conformers in the ground state. This is maybe because of highly deliquescent of choline compounds.

4. Conclusion

The optimized molecular structures (bond lengths and bond angles), vibrational frequencies, and chemical shifts of all the conformers of benzoylcholine chloride have been calculated using B3LYP method at 6-31++G(d) basis set level. The comparison of the experimental and calculated IR, R, and NMR

Table 5: Theoretical and experimental ^{13}C and ^{1}H isotropic chemical shift (with respect to TMS, all values in ppm) for two lower-energy conformers of BzChCl.

Atom	Experimental (ppm) (in DMSO-d_6) [20]	Calculated B3LYP/6-31++G(d) GIAO		
		Conformer I	Conformer II	Average
C1	58.680	60.411	58.651	59.531
C4	63.810	64.922	59.722	62.322
C7	52.810	47.663	52.414	50.039
C11	52.810	54.922	48.123	51.523
C15	52.810	51.758	53.989	52.874
C21	165.100	163.479	163.453	163.466
C23		126.700	123.718	125.209
C24	129.270	127.056	126.633	126.845
C28	129.270	124.849	126.745	125.797
C25	128.750	125.041	122.853	123.947
C27	128.750	124.475	123.381	123.928
C26	133.540	127.651	128.555	128.103
	R^2	0.9967	0.9973	0.9985
	RMSE	3.4388	3.6272	3.1446
	MAE	3.0257	3.0399	2.6414
H2		4.013	4.612	4.313
H3		5.452	4.477	4.965
H(O–CH_2)	4.752	4.733	4.545	4.639
H5		2.491	2.123	2.307
H6		7.794	7.291	7.543
H(N–CH_2)	3.973	5.142	4.707	4.925
H8		2.011	2.328	2.170
H9		6.254	3.733	4.994
H10		3.113	2.535	2.824
H(N–CH_3)	3.309	3.793	2.865	3.329
H12		1.930	1.820	1.875
H13		2.071	6.906	4.489
H14		6.429	1.981	4.205
H(N–CH_3)	3.309	3.477	3.569	3.523
H16		2.140	1.991	2.066
H17		2.887	2.100	2.494
H18		2.152	6.384	4.268
H(N–CH_3)	3.309	2.393	3.492	2.943
H29		8.373	8.257	8.315
H33		8.140	8.230	8.185
H(Benzene)	8.037	8.257	8.244	8.251
H30		7.458	7.468	7.463
H32		7.435	7.482	7.459
H(Benzene)	7.578	7.447	7.475	7.461
H31		7.761	7.554	7.658
H(Benzene)	7.711	7.761	7.554	7.658
	R^2	0.9290	0.9713	0.9665
	RMSE	0.5631	0.3460	0.3810
	MAE	0.3946	0.2869	0.2561

Table 6: Calculated hyperconjugative interactions (kcal mol^{-1}) for two lower-energy conformers of BzChCl.

Donor NBO	Acceptor NBO	Calculated B3LYP/6-31++G(d)	
		Conformer I	Conformer II
LP (Cl)	σ^* C_1–H_2	—	0.09
	σ^* C_4–H_5	0.12	0.20
	σ^* C_4–H_6	15.03	10.26
	σ^* C_7–H_9	7.54	—
	σ^* C_{11}–H_{13}	—	10.07
	σ^* C_{11}–H_{14}	7.51	—
	σ^* C_{11}–N_{19}	—	0.08
	σ^* C_{15}–H_{18}	—	6.92
	Total	30.20	27.62
	Relative energy	2.58	0.00

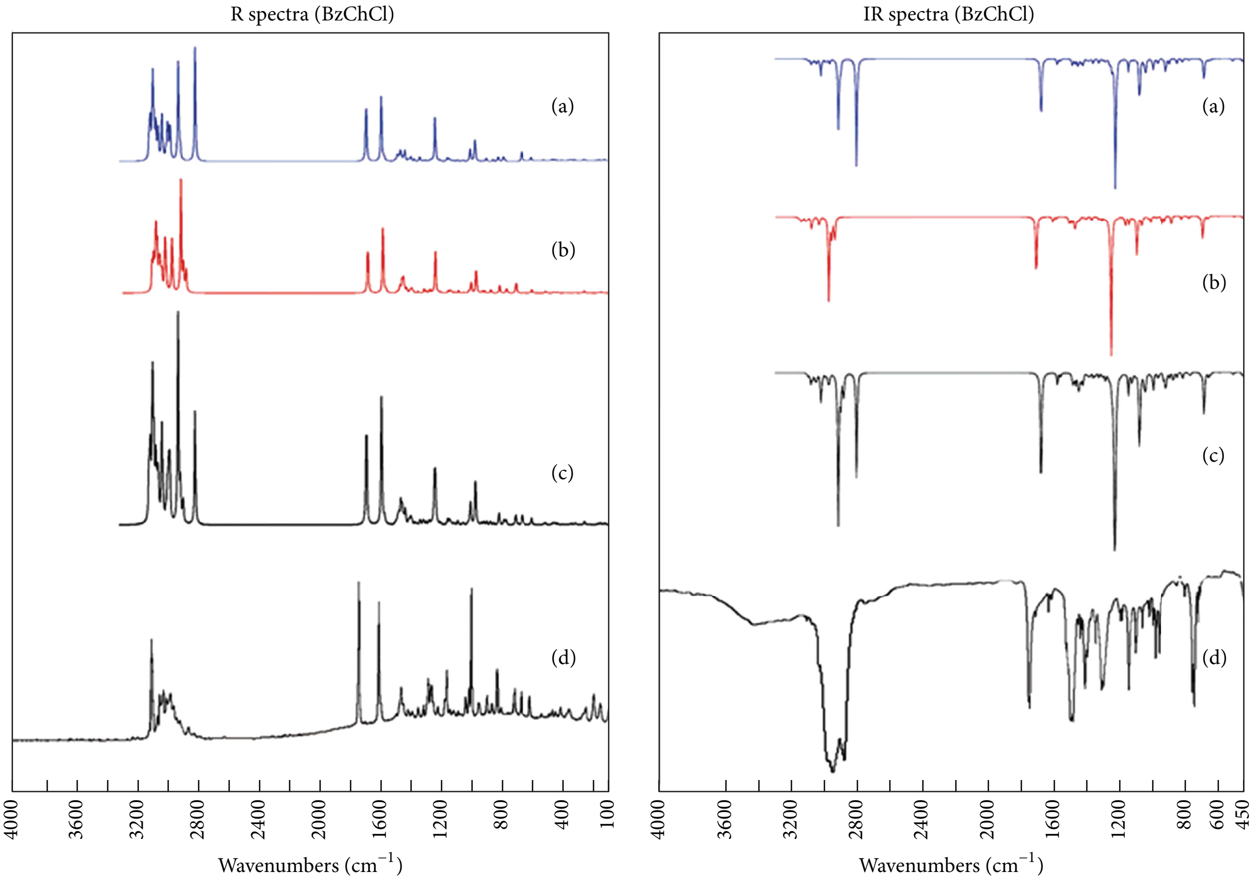


Figure 3: Calculated IR and R spectra of conformers I and II of BzChCl as labeled (a) and (b), respectively. (c) shows the sum of (a) and (b); (d) shows experimental spectrum [19].

spectra of the compound have shown that the experimental spectra are formed from the superposition of the spectra of two optimized energy conformers of the compound. So it was concluded the compound simultaneously exits in two optimized energy conformers in the ground state.

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