Original Research article

Computational NQR–NBO Parameters and DFT Calculations of Ampicillin and Zwitterion (Monomer and Dimer Structures)

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ARTICLE INFORMATION

ABSTRACT

Density functional theory (DFT) was used to analyze the structure and Nuclear quadrupole coupling constants (NQCC), χ, and asymmetry parameters, η, of ^{14}N nuclei have been calculated for the antimicrobial ampicillin in monomeric and their dimers using B3LYP/6-311G(d) method on the differences between the structural parameters in monomeric and their dimers states in the gas phase. For this purpose, electric field gradient (EFG) at the sites of quadrupole nuclei and resonance interactions have been calculated and evaluated for each compound. Additionally, it could be observed that the factor of resonance interaction which is not the only effective factor on values and trend of NQR parameters changes by passing of monomeric state to other ones. It was also found that conformation plays a very effective role in the determination of the values of the calculated NQCC parameters. Sensitivity of the NQR parameters to the changes in the conformational structure is significantly greater than that of the changes in the other structural parameters such as bond lengths.

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Graphical Abstract

(b)

(a)

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H^+
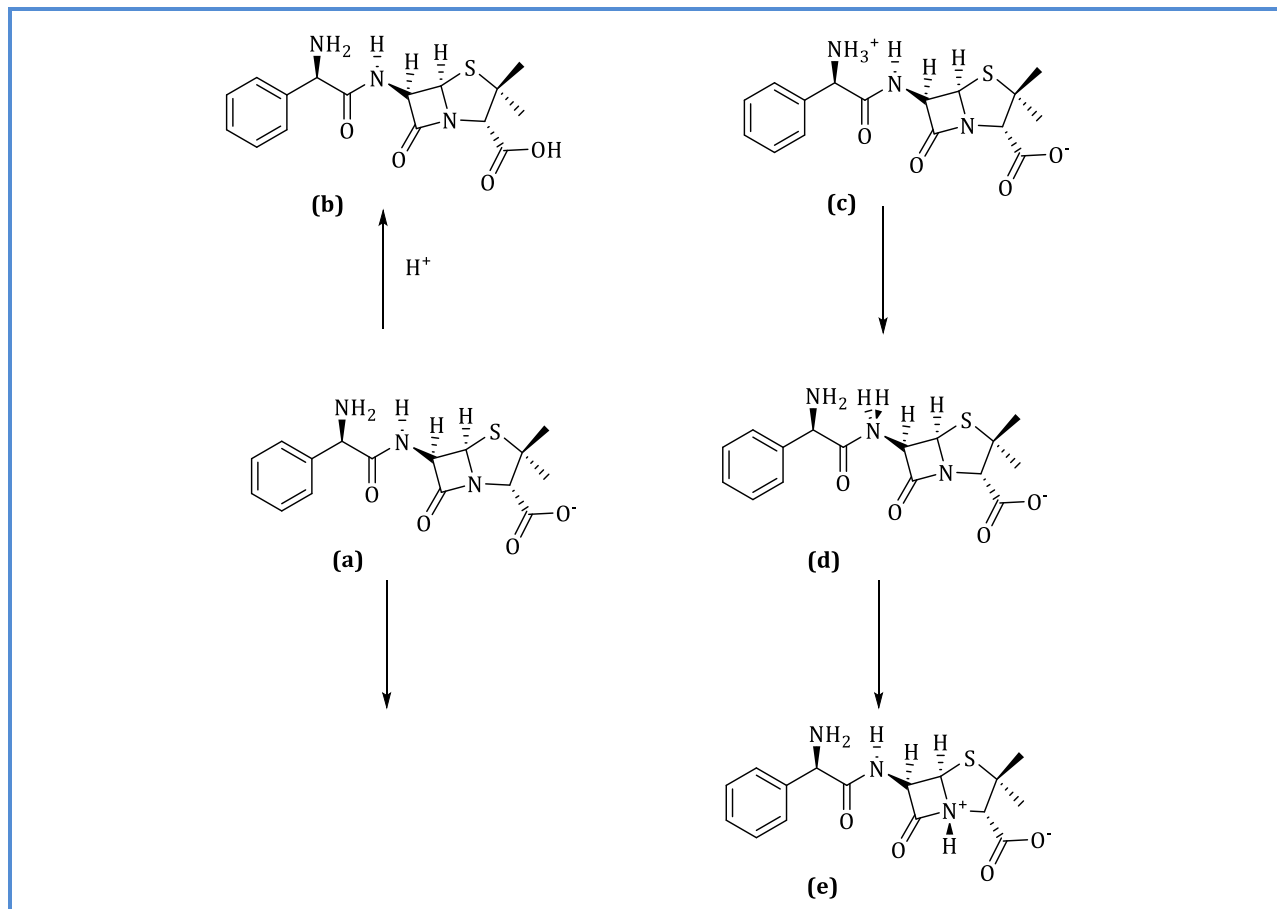
Introduction

Ampicillin (6-[2-amino-2-phenylacetamido] penicillin acid) was first prepared by Doyle et al. [1] in 1961. After extensive antimicrobial and pharmacological evaluations, this antibiotic was shown to be very acid stable [2]. The penicillin and cephalosporin have widely been used in the treatment of bacterial diseases due to their broad spectrum and low toxicity [3]. Ampicillin apparently owes its activity and stability to the presence of the free amino group at the or-position of the N-acyl side chain of the penicillin nucleus, since when this group is substituted or derivatives are made, the activity [1] obviously, the A-amino group plays an important role in the broader activity, due to an ability to cross cell wall barriers. Addition of an amino group to the benzyl penicillin (Penicillin G) molecule resulted in the creation of ampicillin, a drug with a broadened spectrum of activity [4]. The basic structure of penicillin (6-aminopenicillanic acid) consists of three components: a thiazolidine ring, an attached β-lactam ring, and a side chain. Both ampicillin and amoxicillin have an amino group added to the basic benzyl penicillin molecule [4]. The reactive β-lactam ring is the

most important structural feature contributing to the antibacterial activity of the penicillin group which requires (i) a ring of sufficient strain, (ii) possibilities for electron delocalization outside the lactam ring, and (iii) some conformational requirements [3]. Therefore, the reactivity of the β-lactam ring was linked to the lack of resonance of the amide end cyclic system caused by the pronounced pyramidal character of the β-lactam nitrogen atom. However, this factor seems not to be the only molecular parameter that it is necessary to consider in the interpretation of the biological activities, and 3D aspects should play an important role. Most of what is known about ampicillin conformation has been interpreted as an evidence for the biological relevance of this conformation. Many such penicillin are relatively easy to crystallize and therefore can also be studied by X-ray diffraction methods. The X-ray structures available in the Cambridge Structural Database (CSD) reveal that the majority of penicillin (80%) are in the axial conformation. This conformational preference of penicillin in the solid state has been ascribed to the stabilizing effect of the intramolecular N—H- - -S and C—H- - -O contacts [5-7]. Experimental approaches such as nuclear magnetic resonance (NMR), nuclear quadrupole resonance (NQR) and Raman spectroscopies allow us to complement the information obtained from X-ray crystallographic studies. NMR has been used for some 45 years to study atomic arrangement, chemical bonding and structural grouping in crystalline forms [8]. Solid-state nuclear magnetic resonance has had a major role in the elucidation of antibiotics compositions [9].

NQR spectroscopy has more recently increased the resolution and accuracy of the experimental results obtained in the measurements on antibiotics. The parameters are the NQR frequency (υ_Q) and nuclear quadrupole coupling constant (NQCC). In NQR spectroscopy, the interaction between nuclear electric quadrupole moments of quadrupolar nuclei (having spin $I>1/2$) with the local molecular electric field gradient (EFG) has the characteristic role [10, 11]. The EFG at a nucleus in molecular environment is a one-electron property and can be obtained with a reasonable effort using ab initio computations. Since, it involves only the ground state wave function, calculation of the EFG should be easier and faster than the calculation of the NMR chemical shifts. Therefore, theoretical efforts needed to devote to the interpretation of NQR spectroscopy are less than that of NMR spectroscopy [12, 13]. In the study of small protein fragments reported by Torrent et al., the ^{14}N NQCC values and their asymmetry parameters were calculated theoretically to distinguish between the two secondary structures, a-helix and h-sheet, of proteins. In this work, it has been stated that the calculated NQCC value or the ^{14}N atom of the peptide bond in proteins depends on the specific conformation of the backbone. This parameter is observably different between a-helices

and h-sheets. Hence, protein conformation may be identified through analysis of the ^{14}N NQR parameter [14].

The components of the EFG tensor are defined in its principal axis system and are ordered as follows: $|q_{zz}|>|q_{yy}|>|q_{xx}|$; Also, the principal components of the EFG tensor, q_{ii}, are computed in atomic unit (1 a.u.=9.717365×10^{21} Vm^{-2}). The nuclear quadrupole coupling constant, abbreviated as NQCC and denoted by χ, of a given quadrupolar nucleus is given by $\chi=e^2 Qq_{zz}h^{-1}$ [15]. Where e is the charge of electron, Q is the nuclear electric quadrupole moment of the nucleus and h is the Plank's constant [16]. The NQCC parameter is a measure of the interaction between the nuclear quadrupole moment and the EFG at the quadrupole nucleus site due to the no spherical and no cylindrical (anisotropic) charge distribution in the system. Such interaction can be measured either in the gas phase (using microwave spectroscopy) or in the solid phase (mostly by NQR spectroscopy). Asymmetry parameter, g, which is a measure of the deviation of the charge distribution from axial symmetry, is defined as $\eta_Q=|(q_{yy}-q_{xx})/q_{zz}|$, $(0<\eta_Q<1)$ [17].

Monomeric and dimeric states were extracted from the crystallographic structure obtained by Cambridge Structure Data (CSD). In this work, penicillin (Ampicillin, Zwitterion) and their dimers (Zwitterion- Zwitterion) are studied as benchmarks for the study of antibiotics (Figure 1). We try to examine the ability of the NQR, as a reliable method, to distinguish different positions of a specific β-lactam ring (for example Ampicillin) in the penicillin structures. Which might appear identical or similar in the other spectroscopic methods. In this line, variation of the ^{14}N NQR parameters in the selected β-lactam ring and their dimers has been studied.
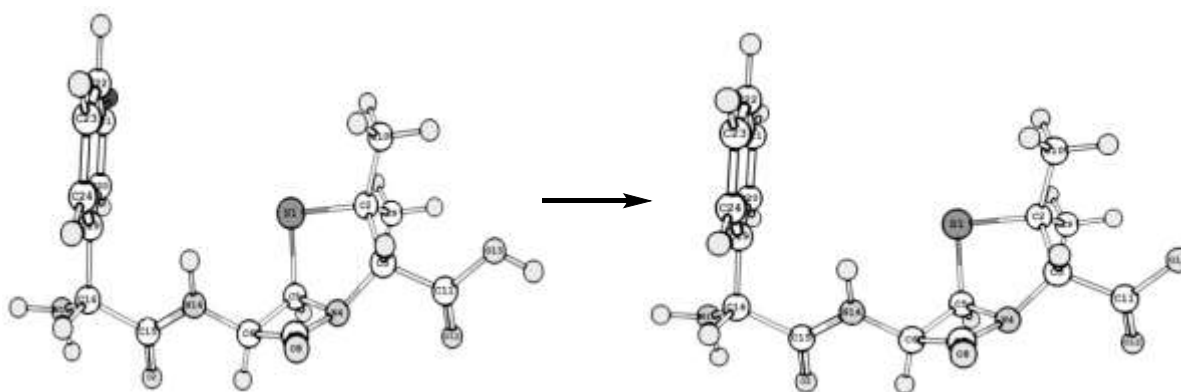
Figure 1. The chemical structure of monomeric state of ampicillin and zwitterion

Experimental

The geometrical parameters for the most stable conformer ampicillin (or zwitterion) of monomer and dimer structure in the ground state were optimized at B3LYP of theory level [18, 19] using the

6-311G(d) basis set. Afterwards, NBO analysis [20, 21] and EFG tensors at the sites of ^{14}N nuclei calculations were performed on the optimized structures at B3LYP/6-311G** of theory level in the gas phase all calculations were performed by using the GAUSSIAN03 [22] package of programs, and the results are summarized in Table 1.

Table 1. Bond lengths (Å) and bond angles (°) experimental and optimized of monomer and dimer conformer of ampicillin and zwitterion at the B3LYP/6-311G(d) of theory level in the gas phase

Parameters	Experimental X-ray	Monomer (Ampicillin)	Monomer (Zwitterion)	Dimer (Zwitterion)
Bond lengths (Å)				
S1- C2	1.85	1.89	1.93	1.85
C2-C3	1.56	1.59	1.56	1.56
C3-N4	1.47	1.45	1.46	1.47
N4-C5	1.47	1.47	1.48	1.47
C5-C6	1.53	1.57	1.56	1.53
C6-C7	1.53	1.55	1.55	1.53
C7-N4	1.38	1.40	1.34	1.38
C7-O8	1.18	1.20	1.24	1.18
C3-C11	1.57	1.53	1.61	1.57
C11-O12	1.26	1.20	1.24	1.26
C11-O13	1.19	1.36	1.25	1.19
C6-N14	1.43	1.43	1.46	1.43
N14-C15	1.34	1.37	1.36	1.34
C15-O17	1.21	1.22	1.23	1.21
C15-C16	1.55	1.55	1.55	1.55
C16-N18	1.51	1.46	1.54	1.51
C16-C19	1.50	1.52	1.51	1.50
C3-H25	1.27	1.10	1.10	1.27
C5-H26	0.98	1.09	1.10	0.10
C6-H27	1.05	1.09	1.10	1.10
Bond angle (°)				
S1-C2-C3	103.16	104.26	105.76	103.17
C2-C3-N4	105.97	108.10	105.65	105.97
C3-N4-C5	117.97	117.91	120.14	117.97
C3-C11-O12	115.60	126.37	114.58	115.60
C3-C11-O13	119.35	110.29	111.38	119.36
N4-C5-C6	88.55	88.50	87.79	88.55
C5-C6-C7	85.75	83.96	83.60	85.75
C6-C7-O8	138.13	136.75	133.04	138.13
N4-C7-O8	130.21	131.36	132.41	130.21
C5-C6- N14	120.31	120.79	117.04	120.31
C6-N14-C15	122.47	121.86	115.32	122.47
N14-C15-O17	124.96	122.93	124.46	124.96
O17-C15-C16	119.87	120.53	118.32	119.87
C15-C16-N18	105.94	106.53	99.00	105.94
N18-C16-C19	111.78	111.86	111.49	111.78

Results and discussion

Geometrical structure

The crystal structure of the studied molecule is available; therefore, the optimized structures were compared with the crystal structurally similar molecules as following discussions. The atomic numbering scheme of all the 2 conformers and dimer structure of the title compound are shown in Figures 1 and 2. Bond lengths and bond angles for monomer of the ampicillin and dimer structures of the zwitterion conformer are listed in Table 1. The molecular conformation when starting with a zwitterion form, proton transfer occurs during the optimization procedure Figure 1. In the electronic structure theories of atoms and molecules, based on the developing density functional theory (DFT), the electron correlation is one of the most important concepts. The central issue in quantum chemical computations is how to take electron−electron correlation into consideration. The bond lengths of the dimer molecule are thiazolidine ring, an attached β-lactam ring, and a side chain (except little difference) equal to for experimental values. The bond lengths were observed for monomer of ampicillin and zwitterion more than experimental values. However, there is seen increasing for bond lengths, this can be the effect of proton transfer, the bond length of N_{14}-H was observed at 1.01211 Å for ampicillin, these values are lower than experimental values but monomer of zwitterion are bigger than experimental values.
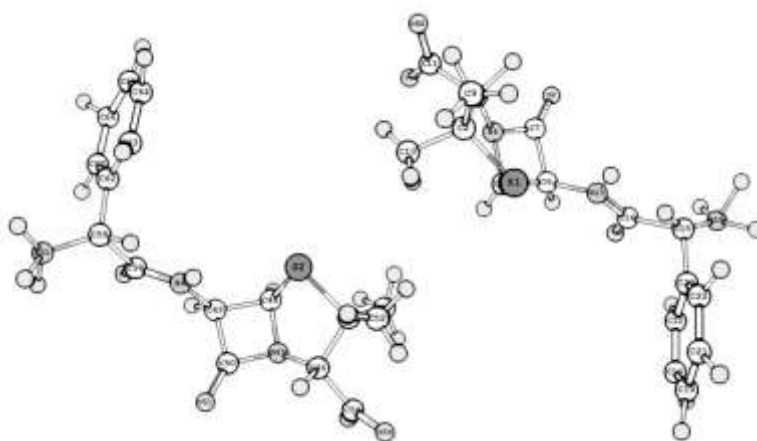
Figure 2. The chemical structure of dimeric state of zwitterion

The bond angles of the ring

The bond angles of the ring are observed in the range of 103.16−119.35 for thiazolidine and 88.55−120.31. In this study, the bond angle X-ray from normal value is same as the dimer of zwitterion. The other bond angles of the studied molecule are listed in Table 1. The bond angles

showed the small difference between the experimental values for monomer of ampicillin and zwitterion. this can be due to calculation belongs to gas phase and experimental results belong to solid phase. One can quite easily see from Table 1.

All the calculations of bond angles are in very consistency with the compared experimental values.

NBO (natural bond orbital analysis)

NBO analysis provides the most accurate possible natural Lewis structure picture of φ, because all orbital details are mathematically chosen to include the highest possible percentage of the electron density. A useful aspect of the NBO method is that it gives information about interactions in both filled and virtual orbital spaces that could enhance the analysis of intra and intermolecular interactions. The second-order Fock matrix was carried out to evaluate the donor–acceptor interactions in the NBO analysis. NBO analysis has been carried out to explain the charge transfer or delocalization of charge due to the intra-molecular inter action among bonds, and also provides a convenient basis for investigating charge transfer or conjugative interaction in molecular systems. Some electron donor orbital, acceptor orbital and the interacting stabilization energy resulting from the second-order micro disturbance theory is reported [23]. The larger the stabilization energy value, the more intensive is the interaction between electron donors and electron acceptors, i.e. the more donating tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally, unoccupied (anti bond or Rydberg) non-Lewis NBO orbitals correspond to a stabilizing donor–acceptor interaction. NBO calculation is performed by using Gaussian 03 package program at the DFT/B3LYP method in order to understand various second-order interactions between the filled orbitals of one sub system and vacant orbitals of another subsystem, which is a measure of the delocalization. The corresponding results have been tabulated in Tables 2. The NBO data indicated that occupancy and resonance energy values for LP (Ns) $\rightarrow \sigma^*$ and π^* delocalizations of the monomer structure for ampicillin, thiazolidine ring are less and more than they are for LP (Ns) $\rightarrow \sigma^*$ and π^* ones of the structure's β-lactam ring. On the other hand, the comparison of monomer and dimer structures for zwitterion that occupancy and resonance energy values for LP (^{14}N) $\rightarrow \sigma^*$ and π^* of the monomer structure in the thiazolidine ring are more and less than dimer structures. The interaction energy is observed as increase in (C−O) antibonding orbital that weakens the respective bonds in the all of structures. In dimeric state extracted from CSD file, there is an interaction between 2 structures. The results showed that the dimeric one, interaction energy values of (C_7−O_8) in LP (N_4 and N_{47}) increase while they decrease LP

(N_{14} and N_{60}). The intramolecular hyperconjugative interaction of the LP (N_{14} and N_{60}) distribute to π^* (C_7–O_8) leads to less stabilization of 0.78 kJ/mol. This enhanced further conjugate with antibonding orbital of π^* (C_{15}–O_{17}) of LP (1) N_{14} in the monomer of ampicillin and monomer or dimer structures for zwitterion which leads to strong delocalization of 49.44, 43.37, 80.86 and 81.20kJ/mol, respectively. This enhanced π^* (C_{15}–O_{17}) resulting in an enormous stabilization energy 81.20 kJ/mol, as shown in Tables 2.

Table 2. NBO results showing formation of Lewis and non-Lewis orbitals for monomer and dimer conformer of ampicillin and zw*i*tterion at the B3LYP/6-311G(d) of theory level in the gas phase

Structures	Lewis-type NBOs		Non-Lewis NBOs	Interaction energy E2	Σ E(2)
	Type	Type	Type		
Monomer (Ampicillin)	LP (1) N_4	1.73231	BD*(1) C15 –C5	4.94	57.35
			BD*(1) C20 –C 5	0.64	
			BD*(1) C11 –C15	1.89	
			BD*(1) C 3 –H 35	1.65	
			BD*(1) C 5 –H 36	3.08	
			BD*(1) C 5 –S 1	6.99	
			BD*(2) C 7 –O 8	38.16	
	LP (1) N_{14}	1.69461	BD*(1) C 15 –O 17	2.05	66.87
			BD*(2) C 15 –O 17	49.44	
			BD*(1) C 5 –C 6	9.37	
			BD*(1) C 6 –C 7	6.01	
	LP (1) N_{18}	1.95374	BD*(1) C 16 –C 19	2.33	10.63
			BD*(1) C 16 –H 29	7.72	
			BD*(1) C 20 –H 28	0.58	
Monomer (Zwitterion)	LP (1) N_4 LP (1) N_{14}	a	---	--	---
		---	BD*(1) C15 –C 16	2.92	57.45
		1.70995	BD*(1) C15 –O 17	1.41	
			BD*(2) C 15 –O 17	43.37	
			BD*(1) C 6 –C 7	6.87	
			BD*(1) C 6 –H 27	1.31	
			BD*(2) C 7 –O 8	1.57	
	LP (1) N_{18}	---	---	---	---
Dimer (Zwitterion)	LP (1) N_4	1.68837	BD*(1) C 11 –C 3	3.96	63.66
			BD*(1) C 2 –C 3	0.60	
			BD*(1) C 3 –H 35	4.56	
			BD*(1) C 5 –H 36	3.85	
			BD*(1) C 5 –S 1	5.36	
			BD*(2) C 7 –O 8	45.33	
	LP (1) N_{14}	1.62529	BD*(2) C 15 –O17	80.86	93.02
			BD*(1) C 5 –C 14	4.33	
			BD*(1) C14 –C 6	7.05	
			BD*(2) C 7 –O 8	0.78	
	LP (1) N_{18}	1.63166	BD*(1) C 16 –C19	1.54	42.93
			BD*(1) C 16 –H 29	5.99	
			BD*(1) H43 –N 18	13.54	
			BD*(1) H 42 –N 18	21.86	
	LP (1) N_{47}	1.68809	BD*(1) C 46 –C 54	3.96	63.7

			BD*(1) C 45 –C 46	0.59	
			BD*(1) C 46–H 81	4.55	
			BD*(1) C 48 –H 82	\3.89	
			BD*(1) S 44–C45	5.28	
			BD*(2) C 50 –O 51	45.43	
	LP (1) N_{57}	1.62412	BD*(2) C 58–O 60	81.20	93.35
			BD*(1) C 48 –C 49	4.32	
			BD*(1) C 49 –C 50	7.05	
			BD*(2) C 50 –O51	0.78	
	LP (1) N_{61}	1.63184	BD*(1) C 59 –C 61	1.55	42.76
			BD*(1) C 59 –H 72	5.99	
			BD*(1) H 73 –N	13.21	
			61	22.01	
			BD*(1) H 74 –N 61		

[a] There are no data for the lone pair of nitrogens in the output files

NQR (nuclear quadrupole resonance)

EFG calculations were carried out on the B3LYP/6-311G(d) optimized structures of the selected nitrogen atoms in the most stable the monomer of ampicillin and monomer or dimer structures for zwitterion. The results are reported in Table 3. As mentioned previously, our aim is to determine the effect of structure on the NQCC parameters. It should be noted here that in this work, it is not intended to put emphasis on the calculated values of NQCC parameters. It is rather intended to develop a methodology by which the measured NQCC values can be used to refine the structures already obtained by other techniques. A detailed analysis of the calculated values of EFG has been carried out and the results: We observed the following changes by passing of the monomeric structure of ampicillin state to zwitterion one:

– NQCC and principal axis such as q_{zz} values of N_4, N_{14} and N_{18} nitrogens decrease while they decrease for asymmetry parameters and field gradient tensor from axial symmetry such as ν_+ and resonance energy value of LP (N) →σ* and π* delocalizations for nitrogens decrease. The proton transfers from O_{13} to N_{18} in the state of natural molecule ampicillin to zwitterion is considered by decreasing NQCC and q_{zz} at N_4, N_{14} and N_{18}. Occupancy of the N_{14} increases with decreasing Bond length of N_{14}-C_{15} and Bond angles of C_5-C_6-N_{14} and C_6-N_{14}-C_{15}. We observed the following changes by passing of the monomeric structure of zwitterion to dimeric structure of zwitterion:

– NQCC and principal axis such as q_{zz} values N_4 and N_{18} nitrogens increase while they decrease N_{14} and asymmetry parameters and field gradient tensor from axial symmetry such as ν_+ values of N_4 and N_{18} nitrogens increase and its value of N_{14} almost decrease. On the other hand, resonance energy value for LP (N_{14}) →σ* and π* delocalization's increase while it decreases occupancies.

– NQCC, principal axis such as q_{zz} and field gradient tensor from axial symmetry such as ν_+ values of thiazolidine ring decrease. On the other hand, resonance energy value for LP (N_{14}) and π^* delocalization's increase while it decreases occupancies.

Table 3. Calculated EFG tensors, the NQR parameters and related frequencies of ^{14}N nuclei for the monomeric and dimeric states of ampicillin at the B3LYP/6-311G(d) of theory level in the gas phase

	Nuclei	q_{xx} (vm^{-2})	q_{yy} (vm^{-2})	q_{zz} $(v\,m^{-2})$	$e^2\,q_{zz}\,Q/h$ (MHZ)	η_Q	ν_+ (MHZ)	ν_- (MHZ)	ν_0 (MHZ)
Monomer (Ampicillin)	N_4	-3.51788	-5.26045	8.778327	4.338574	0.198508	3.469241	3.03862	0.43062
	N_{14}	-3.33968	-5.24401	8.583698	4.242381	0.221854	3.417084	2.946488	0.470596
	N_{18}	-6.22679	-3.70781	9.934597	4.910045	0.253557	3.993778	3.37129	0.622488
Monomer (Zwitterion)	N_4	-2.19447	-4.02912	6.223593	3.07593	0.294789	2.533635	2.08026	0.453376
	N_{14}	-3.33479	-4.81775	8.152539	4.029286	0.181902	3.205199	2.83873	0.366469
	N_{18}	-0.95553	-2.04009	2.995621	1.480547	0.36205	1.244418	0.976402	0.268016
Dimer (Zwitterion)	N_4	-2.87107	-5.40079	8.271858	4.088258	0.305821	3.378763	2.753625	0.625139
	N_{14}	-2.93324	-4.73658	7.669829	3.790713	0.235121	3.065854	2.620216	0.445638
	N_{18}	-1.07091	-3.06621	4.13711	2.044713	0.482292	1.780072	1.286997	0.493074
	N_{47}	-2.86961	-5.38705	8.25666	4.080747	0.304899	3.371614	2.749506	0.622108
	N_{57}	-2.93315	-4.69755	7.630697	3.771373	0.231224	3.046538	2.610521	0.436016
	N_{61}	-1.08717	-3.05628	4.143446	2.047844	0.475234	1.779185	1.292582	0.486603

Conclusion

The above reported DFT calculations provide a reasonable scheme from the effects of inter-intra molecular interactions on the structure and NQR tensors of monomeric to dimeric states of the nitrogen atom on the ampicillin and zwitterion**.** The results showed that, The NBO analysis showed that increasing order of the total resonance between LP(N) and non-Lewis type NBOs (σ^* or π^*) is in parallel with trend the electronic energy obtained from geometry optimization. In each one of monomeric states, the NQR tensors of nitrogen nuclei are different each other and are strongly affected by chemical environment and molecular interactions however, nitrogens of thiazolidine ring (N_{18}) have more NQCC and q_{zz} values than β-lactam ring (N_4). On the other hand, the NBO data indicated that resonance energy values for LP (Ns)→σ^* and π^* delocalization's of the structure's thiazolidine ring is more than they are for LP (Ns) →σ^* and π^* ones of the structure's β-lactam ring. The factor of resonance interaction isn't the only effective factor on values and trend of NQR parameters changes by passing of monomeric state to dimer one and the nuclear quadrupole coupling constant (NQCC) values are controlled by decreasing bond length of N_{14}-C_{15} and bond angles of C_5-C_6-N_{14} and C_6-N_{14}-$C_{15\,by}$ increasing on nitrogen nuclei their NQCC values increase.

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