Conformational Analysis of Chloromethylenimine and its Hydrogen-Bonded Dimers with Water from the Study of Nuclear Quadrupole Interactions *

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A molecular conformation study on N-Chloromethylenimine and its 1 : 1 dimeric form with water has been carried out using the ab-initio method at 6-31 G and 6-31 G* basis set. We consider the two most stable conformers of the N-chloromethylenimine – water binary mixture involving double hydrogen bonds. In all cases the proton affinity has been calculated. Each system considered in this work has the nuclear quadrupole interactions of the nitrogen and chlorine resonant nuclei which have been calculated and compared. It is found that the nuclear quadrupole coupling constant for the nitrogen nucleus increases in the hydrogen bonded complexes and decreases for the chlorine nucleus compared to the monomeric values. The influence of proton affinity is reflected in the nuclear quadrupole coupling constant.

Key words: N-Chloromethylenimine, Water, Hydrogen bond, Nuclear Quadrupole Coupling Constant, Proton Affinity, Ab-initio.

Introduction

Molecular conformation studies can be carried out by estimating molecular parameters such as the total energy, binding energy, charge distribution, etc. In the present work, nuclear quadrupole coupling constants (NQCCs) have been calculated for resonant nuclei such as nitrogen ^{14}N and chlorine ^{35}Cl, which have spin $I = 1$ and 3/2, respectively. The systems considered are N-chloromethylenimine as a monomer [1] and its two most stable conformers [2] of 1 : 1 dimeric form with water, having a double hydrogen bond (HB). In addition, proton affinity calculations have been carried out for these structures to investigate their influence on the NQCC.

Method of Calculation

To calculate the nuclear quadrupole coupling constants we adopt the method due to Kaplansky and Whitehead [3]. In their procedure it is shown that the NQCC is related to the population density matrix corresponding to the wavefunctions of electrons surrounding the resonant nucleus. If we know the principal axes of the electric field gradient (EFG) tensor at the site of the resonant nucleus, it can be used to obtain precise information on the electron distribution and its location. Hence for any molecular system with a chosen geometry, by running self consistent field molecular orbital (SCF-MO) calculations both on semi-empirical and ab-initio levels, one has to diagonalize the population submatrix associated with the *p*-orbitals of the resonant nucleus. At this stage, the EFG matrix is related to the population density submatrix in the following way [4]:

$$q_{zz} = \left[P_{zz} - \frac{1}{2}(P_{xx} + P_{yy}) \right] q_{zz}^{p_z} . \qquad (1)$$

In (1) $q_{zz}^{p_z}$ denotes the EFG corresponding to the single electron in the p_z atomic orbital of the free atom. The off-diagonal elements of the EFG matrix becomes zero when the population submatrix is diagonalized. Here we used the values of $q_{zz}^{p_z}$ for the nitrogen and chlorine nucleus as in [4].

The NQR frequencies are calculated using the relations

$$\nu_{\pm} = \frac{3}{4} e Q q \left(1 \pm \frac{\eta}{3} \right), \qquad (2)$$

$$\nu_0 = \frac{1}{2} \eta e Q q , \qquad (3)$$

where η is the asymmetry parameter.

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The geometries are taken from [2], and the ab-initio calculations at 6-31 G and 6-31 G * basis set level have been carried out using the Berny gradient optimization technique with GAUSSIAN-92W [5] version. The Kaplansky and Whitehead [3] method is used for the minimal basis set calculations, where the population submatrix corresponding to the resonant nuclei is of the order of 3 × 3. But in the case of extended basis sets, the population submatrix corresponding to the *p*-orbital of the resonant nuclei is of the order 6 × 6. Here the population submatrix corresponding to the *p* and *p'* orbitals centered on both ^{14}N and ^{35}Cl nuclei is diagonalized [6].

Results and Discussion

Figure 1 shows the molecular structures of N-chloromethylenimine (a) and its HB complexes (b, c) along with the protonated systems (d, e, f). Out of the two HB systems, structure (b) is found to be more stable than structure (c) on the basis of minimal energy [2]. In the case of protonated dimers, structure (e) is found to be more stable than structure (f) on the basis of total energy of the systems [2]. NQCCs for all the systems considered in this study are collected in Tables 1 and 2, in which it is evident that the calculated NQCC value for ^{35}Cl of structure (a) is found to be −63.67 MHz at 6-31 G basis level and −65.22 MHz at 6-31 G * basis level, and the experimental [1] value is −72.7(4) MHz. Thus the monomeric values obtained using the polarized basis set (6-31 G*) are found to be in close agreement with the experimental results [1]. Hereafter we discuss this work using polarized basis set values in all the cases.

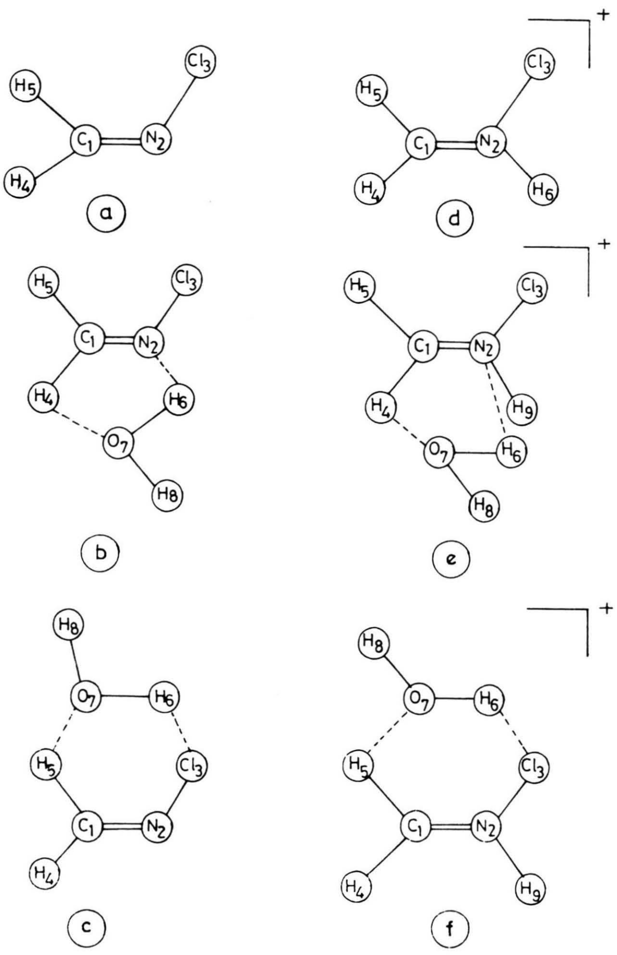

Fig. 1. a) The structure of N-Chloromethylenimine; b) the structure of N-chloromethylenimine with water forming the hydrogen bonded 1:1 binary mixture involving the nitrogen atom; c) the structure of N-chloromethylenimine with water forming the hydrogen bonded 1:1 binary mixture involving the chlorine atom; d) the structure of protonated monomer N-chloromethylenimine; e) the structure of protonated dimer (b); f) the structure of protonated dimer (c).

The NQCCs are found to decrease in case of ^{35}Cl for the HB dimers and increase in case of ^{14}N HB dimers over the monomer. For the protonated dimeric systems, NQCCs are found to be not in any order and an experimental proof is needed to confirm the stable structure. In the case of HB dimers the ^{14}N NQCC values are found to be in increasing order, as was found in the case of formamide-water and formamide-methanol HB systems [7]. Hence it is found that the stable structure has a maximum NQCC value, and in this case it is found that structure (b) is more stable than the structure (c). The ^{35}Cl NQCC values for the HB dimers are found to be in decreasing order from structure (c) to structure (b), and the stable conformer has a minimum NQCC value. The NQCC values for the protonated monomer are very low compared to the corresponding monomeric values in the chlorine system, while the reverse is observed in the nitrogen system. As such the observed trend indicates that the NQCC is not a sensitive parameter to decide the stable conformer on both nitrogen and chlorine systems. The same trend is observed in the case of the NQR frequencies. It may be due to the breaking of HB as reported in [2]. Since no imaginary harmonic frequencies are observed, all the systems considered should have stable conformers.

Table 1. Nuclear quadrupole coupling constants (NQCCs) in MHz, and the asymmetry parameter η.

Structure	^{14}N		^{35}Cl		Asymmetry parameter η			
					^{14}N		^{35}Cl	
	6-31 G	6-31 G*	6-31 G	6-31 G*	6-31 G	6-31 G*	6-31 G	6-31 G*
a	−3.17	−3.35	−63.67	−65.22	0.75	0.62	0.23	0.23
b	−1.51	−1.24	−76.78	−76.74	0.68	0.20	0.04	0.06
c	−0.77	−3.29	−57.48	−74.72	1.00	0.87	0.29	0.04
d	−1.05	−1.43	−96.88	−90.92	0.20	0.72	0.20	0.21
e	−1.65	−0.87	−30.22	−34.91	1.38	0.01	2.68	2.03
f	−1.32	−1.62	−60.46	−102.77	1.50	0.23	0.89	0.06

Table 2. Nuclear Quadrupole Resonance (NQR) frequencies in MHz.

Structure	Nitrogen nucleus ^{14}N						Chlorine nucleus ^{35}Cl					
	ν_+		ν_-		ν_0		ν_+		ν_-		ν_0	
	6-31 G	6-31 G*	6-31 G	6-31 G*	6-31 G	6-31 G*	6-31 G	6-31 G*	6-31 G	6-31 G*	6-31 G	6-31 G*
a	−2.96	−3.06	−1.78	−1.97	−1.19	−1.08	−51.48	−52.58	−44.02	−45.26	−7.46	−7.32
b	−1.39	−0.99	−0.88	−0.87	−0.52	−0.12	−58.43	−58.72	−56.73	−56.39	−1.70	−2.33
c	−0.77	−3.18	−0.39	−1.75	−0.39	−1.43	−47.23	−56.85	−38.99	−55.23	−8.24	−1.63
d	−0.84	−1.33	−0.73	−0.82	−0.10	−0.51	−77.61	−72.84	−67.71	−63.54	−9.90	−9.31
e	−1.81	−0.65	−0.67	−0.64	−1.14	−0.01	−42.91	−43.90	−2.42	−8.47	−40.5	−35.43
f	−1.48	−1.31	−0.49	−1.13	−0.99	−0.18	−58.86	−78.51	−31.83	−75.65	−27.0	−2.86

Conclusion

The Kaplansky and Whitehead method is found to be good both in the case of chlorine and nitrogen systems. The structure (b) is found to be more stable than the structure (c) of the hydrogen bonded system on the basis of the NQCC. In the case of protonated structures further study is needed to find the stable conformer on the basis of the NQCC.

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