Nuclear Quadrupole Coupling Constant and Conformational Studies*

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A molecular conformation study on three 3-monosubstituted derivatives of propene has been carried out by evaluating the EFG at the site of the halogen nucleus using a semi-empirical LCAO-MO-SCF method. Calculations are performed on several conformers at INDO and CNDO level, using "sp" and "spd" valence basis sets, with Slater type orbitals as the basis functions. The results obtained for various conformers indicate that the nuclear quadrupole coupling constant is practically independent of the orientation of the CH_2X group ($X = Cl$, Br and I) (Figure 1). The mean value of $e^2 Q q_{zz}/h$ (averaged over all conformers) in each system matches favourably with the experimental value, despite the severe approximations that are inherent in the semi-empirical theory as well as in its application in the evaluation of the EFG.

Introduction

The nuclear quadrupole coupling constant (NQCC) is essentially a one electron property, which can be used as a sensitive parameter for checking the correct charge distribution in any polyatomic molecular system [1]. In an earlier attempt [2] the molecular dipole moment was used as a test parameter to arrive at the correct equilibrium configuration of the systems chosen in the current study. The principal nuclei of interest in the present study are ^{35}Cl ($I = 3/2$), ^{79}Br ($I = 3/2$), and ^{127}I ($I = 5/2$). Experimental investigations of the NQR are usually done on crystalline powders or single crystals. The theoretical investigation carried out here, however, is done on isolated molecules.

Method of Calculation

Our procedure is based on the method due to Kaplansky and Whitehead [3] in which it has been shown that, provided the principal axes of the electric field gradient (EFG) tensor at the resonant nuclear site are known and also they can be related to the density matrix corresponding to the wave functions of electrons surrounding it, one can gather much information on the electron distribution at the site of the quadrupolar nucleus. Thus, having run the self consistent field-molecular orbital (SCF-MO) calculation for any molecular system with a chosen geometry, one has to diagonalize the population sub-matrix related to the p-orbitals of the resonant nucleus. On doing so, the EFG matrix in its simplest diagonal form is related to the population matrix, which is also in the diagonal form, in the following way:

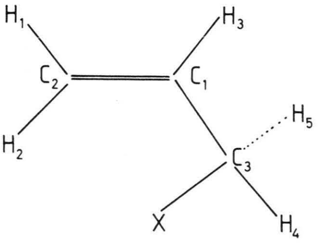

Fig. 1.

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

Here $q_{zz}^{p_z}$ is the EFG corresponding to a single electron in the p_z atomic orbital of the free atom.

The off-diagonal element of the EFG matrix disappear automatically, when once the population matrix is diagonalized, because of the relation:

$$q_{xy} = (8\pi/5)\, P_{xy}\, q_{zz}^{p_z}. \qquad (2)$$

For carrying out SCF-MO calculations, geometries of the systems are generated using bond

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lengths and bond angles taken from the compilation volume of Sutton [4] and only tetrahedral and trigonal bond angles are used. Calculations at intermediate (complete) neglect of differential overlap (INDO, CNDO) levels are performed with both "sp" and "spd" basis sets for ten conformations in each system. All computations are carried out using Pople's [5] original programme with little modification required for including bromine and iodine in the picture. The programme was run on a computer IBM 370 at I.I.T., Madras, India.

Table 1. Nuclear quadrupole coupling constants in MHz.

Calculated mean value				Experimental value or value obtained from empirical relation
INDO sp	INDO spd	CNDO sp	CNDO spd	
3-Chloropropene				
77.56	93.07	83.93	99.73	67.50
3-Bromopropene				
573.19	702.24	622.70	749.85	506.25
3-Iodopropene				
1905.74	2315.83	2048.06	2498.54	1620.00

Results and Discussion

Results of the various calculations performed on several conformers in each system indicate clearly that the NQCC is almost independent of the orientation of the CH_2X group. The mean value of the coupling constant averaged over all conformers in each system is given in Table 1. Comparison with the experimental data shows that the results obtained by the INDO method with "sp" basis set fall much closer to the experimental values. Calculation with "spd" basis set overestimates the coupling in all cases. Inclusion of the "d" orbitals in the basis set is generally expected to improve the accuracy of the calculation at the loss of a simple pictorial description of the molecular orbitals [6]. Many authors [7–10] have also realized the need for explicit inclusion of such polarization functions into the basis set for better prediction of molecular properties. The reason for the overestimation of the coupling constants in our calculations is two fold. Firstly, although we are increasing the size of the basis set by including the d-orbitals, the empirical parameters used in such an extension scheme are rather uncertain. Secondly, the effective electronegativity of the halogen atom is raised when once d-orbitals are included in the basis set. This results in a greater charge transfer to the quadrupolar nucleus and a consequent increase in the elements of the density matrix that determine the magnitude of the coupling constants.

As pointed out earlier, the EFG at the site of the resonant nucleus and hence the NQCC are almost independent of the orientation of the CH_2X group with respect to the rigid C=C structure. This is, in fact, an expected results, because the change in the orientation of the CH_2X group does not at all alter the distance of the resonant nucleus from the carbon atom to which it is bonded nor the distances of the resonant atom from the methyl group protons. The minor changes observed are obviously due to the change in the disposition of the resonant atom with respect to the C=C bond. Also the differences between the energies of various conformers in each system are quite small, and therefore the CH_2X group is as such a freely rotating one. Hence one cannot expect much change in the value of the EFG when the CH_2X group changes its orientation. Since no experimental data on 3-bromopropene and 3-iodopropene are as such available for comparison with our theoretical values, the following empirical relations [11] have been used

$$^{127}\mathrm{I}\,(e^2 Q\, q_{zz}/h)/^{79}\mathrm{Br}\,(e^2 Q\, q_{zz}/h) = 3.2 \pm 0.3,$$
$$^{79}\mathrm{Br}\,(e^2 Q\, q_{zz}/h)/^{35}\mathrm{Cl}\,(e^2 Q\, q_{zz}/h) = 7.5 \pm 0.5. \qquad (3)$$

In all, there is a general overall agreement between our theoretical values and the experimental solid state values (or anticipated values from empirical relations) despite the inherent assumptions in both the semi-empirical SCF-MO scheme and in its application to calculating EFG's.

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