

Molecular polarizability of substituted pyridine

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ABSTRACT

Lippincott's ' δ ' function model of chemical binding has been applied to evaluate the mean molecular polarizabilities of hetero nuclear ring compounds. The results obtained are compared with the experimental values reported earlier and are discussed in terms of contributions from π and σ bonds. The relative merits of the present method compared with that of Lippincott and Stutman are also discussed.

Keywords : Molecular Polarizability, 4-hydroxy-3-nitro Pyridine.

INTRODUCTION

The specification of molecular polarizability ellipsoid is one of the physical methods used in stereo chemical analysis. Such studies require a knowledge of the mean polarizability of the molecule which is usually determined from experiments on refractivity measurements a few theoretical methods¹⁻³ of evaluation of mean molecular polarizabilities are also developed. The one-dimensional δ -function potential model developed by Frost⁴ and improved by Lippincott is one of the most useful method suggested in studying the spectroscopic parameters like vibrational frequencies and anharmonicities. It is also useful in considering polarizability as an effective criterion in judging the proximity of wavelength to real situations. According to this model the potential energy of an n -electron system is the sum of the single electron δ -function potentials. The space integral of this function is definite and is known as ' δ -function strength'.

This semi-empirical model was used by Lippincott and Stutman⁵ and others⁶⁻¹⁰ for the calculation of the molecular polarizabilities of some

systems. Rao & Murthy^{3,2} have used this model to evaluate the mean polarizabilities of some substituted pyridines. In this paper, the method is extended to the calculations of mean polarizability of 4-hydroxy-3-nitro pyridine.

Method of Evaluation

Molecular polarizability is calculated by using semi-empirical delta function model suggested by Lippincott and Stutman⁵. In this model the coulombic potentials in Schrodinger equation of the molecular system are replaced by the delta function potential. The molecular functions are constructed from the linear combination of atomic delta function wave function⁸.

Molecular polarizability is contributed by the parallel and perpendicular components of the constituent bond polarizability. The bond parallel component is taken to be sum of the bonding electron contribution and the contribution from the valence shell non-bonding electrons in each atom of the bond. The bonding electron contribution is calculated by using a linear combination of atomic delta function wave function representing the nuclei involved in the bond *i.e.* the expectation value of

the electron position squared ($\bar{x}^2$) along the bond axis is calculated and this in turn is used to obtain the bond parallel component of the polarizability from the equation.

$$\alpha_{11b} = 4nA_{12} \frac{[\bar{x}^2]^2}{a_0}$$

$$\text{Where } \bar{x}^2 = \frac{R^2}{4} + \frac{1}{2C_{12}^2}, \quad A_{12} = (A_1 A_2)^{1/2}$$

n is the bond order, R is inter-nuclear distance at the equilibrium position and

$$C_{12} = [n_1 n_2 N_1 N_2]^{1/4} [A_1 A_2]^{1/2}$$

Here n_i and N_i ($i=1,2$) are the principal quantum number, In case the bond is of heteronuclear type, the bond parallel component of the polarizability must be corrected to account for the charge density introduced by the electro negativity difference of the bonding atoms. Here the charge density in the bond region should then be related to the percent covalent character σ believed to exist in the form.

$$\sigma = \exp \left[-\frac{(\chi_1 - \chi_2)^2}{4} \right]$$

Where χ_1 and χ_2 are the electro-negativities of atom 1 and 2 forming the bond on pauling scale⁹ taking into account the polarity correction is given by:

$$\alpha_{11p} = \sigma \alpha_{11b}$$

The contribution of the non-bonded region electrons to the parallel component of the polarizability written as:

$$\alpha_{11n} = \sum_i f_i \alpha_i$$

where f_j is the fraction of the valence electrons in the j^{th} atom not participating in bonding and α_i is the atomic polarizability of the j^{th} atom. The sum of perpendicular components of the bond polarizability is given by

$$\sum 2\alpha_{\perp i} = n_{df} \sum_i \frac{\gamma_i^2 \alpha_i}{\chi_i^2}$$

where $n_{df} = 3N - 2n_b$ is the residual atomic polarizability degrees of freedom. This is obtained by taking into account the symmetry and geometry of molecules. The average molecular polarizability with polarity correction can be expressed as:

$$\alpha_M = \frac{1/3[\sum_i \alpha_i + \sum_j f_j \alpha_j + n_{df} \sum_i \chi_i^2 \alpha_i]}{\sum_i \chi_i^2}$$

The summation subscript 'i' refers to bonds and 'j' refers to atoms.

For the atoms involved in molecules of present study, the delta function strengths in atomic units, the parameter values in atomic units, the atomic polarizability and electro-negativities are collected in Table-1. The molecular structural data employed in the present computation are taken from literature⁹⁻¹⁴

RESULTS AND DISCUSSION

Molecular structure of 4-Hydroxy-3nitro pyridine (abbreviated as 4, 3-HNP) is shown in Fig.1.

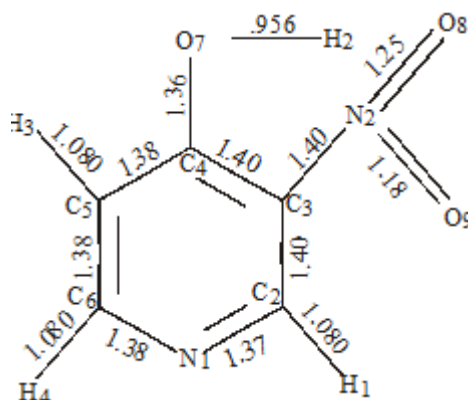


Fig. - 1: Molecular Structure of 4, 3-HNP

Table - 1: Delta function strength, parameter, atomic polarizability and Electro-negativities of some elements

Element	Delta Function Strength 'A' (in atomic mass units)	Parameter 'C' in atomic mass Unit	Atomic Polarizability α (in 10^{-25} cm^3)	Electro Negativities X
H	1.000	1.414	5.920	2.1
C	0.846	3.334	9.780	2.5
N	0.927	4.146	7.430	3.0
O	1.000	4.899	5.92	3.5

In the present study the residual atomic polarizability degree of freedom are included in the table-2. The sum of bond perpendicular components, bond parallel components, contribution of non-bond region electron and mean molecular polarizability for the molecules under present investigation are given in the Table-2.

The bond parallel components of the different bonds are compared with the experimental values and the values calculated by other workers in Table-3, it is apparent that some of the computed values are in reasonable agreement with the experimental data which shows the soundness of

Table - 2: Bond and molecular polarizability (in 10^{-25} cm^3) for 4-Hydroxy-3-nitro pyridine

n_{df}	$\Sigma 2 \alpha_{\perp}$	$\Sigma 2 \alpha_{11b}$	$\Sigma \alpha_{11n}$	$2 \alpha_m$
18	132.845	274.275	17.784	141.635

Table - 3: Bond Parallel Components of Polarizability for individual bonds (in 10^{-25} cm^3)

Bond	Bond Length Å	α_{11b}
C-H	1.080	20.6311
C-H	1.080	20.6311
C-N	1.38	14.855
C-N	1.37	14.425
C-C	1.40	16.107
C-C	1.38	15.244
C-O	1.36	12.002
O-H	0.956	2.8625
C-N	1.40	15.699
N=O	1.25	10.799
N=O	1.18	8.612

these calculation. The parallel components of inter nuclear distance. however in cases where the distances are identical in different molecules are transferable as evident by inspection of table-3. The

bond perpendicular component is independent of inter-nuclear distance and hence it may be transferred from one molecular system to another for the same pairs of atoms.

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