

Bond and molecular polarizabilities of α - and β -halogenonaphthalenes

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The semi-empirical delta-function model of chemical binding proposed by Lippincott and Stutman has been employed to calculate the bond region electron contributions and nonbond region electron contributions to the bond parallel component of the polarizability, the bond perpendicular component of the polarizability and the average molecular polarizability of α - and β -halogenonaphthalenes using delta-function electronic wavefunctions. The atomic polarizability degrees of freedom (n_{eff}) for these system has been determined by the same approach as in J. Phys. Chem. 77 (1973) 2552. The calculated results are found to be in good agreement with experimental values of molecular polarizabilities reported by LeFevre *et al.*

1. INTRODUCTION

Various methods¹⁻¹² based on the quantum mechanical models have been adopted to calculate the atomic and molecular polarizabilities of many ions, atoms and simple diatomic molecules. These investigations were limited to simple atoms ions and diatomic molecules and were not applicable to triatomic or even simple polyatomic molecules. Lippincott and Stutman¹³ applied the semi-empirical delta-function potential model in calculation of bond and molecular polarizabilities for various diatomic and polyatomic molecules with the assumption that in a polyatomic molecule each bond behaves as if it were a simple diatomic molecule and the contributions of all the bonds in the entire molecular system can be added up to obtain the average or mean molecular polarizability. This model has been successfully applied to simple polyatomic molecules by Lippincott et al¹⁴, Nagarajan¹⁵, Sanyal et al^{16,17} and Beran and Kevan¹⁸. Further, Sanyal et al¹⁹ successfully extended this model for the evaluation of molecular polarizabilities of substituted hydrocarbons with ring and chain structures. In all these investigations, it was assumed that every bond of a polyatomic molecule is a pure diatomic molecule. This assumption does not lead to any significant deviation from the correct value of mean or average molecular polarizability of a simple polyatomic molecule but it will not be applicable in the case of heavier and highly complex

molecules. It is because the $C = C$ bond in ethylene cannot be considered as a pure diatomic molecule as the delta function strength of the carbon atom in ethylene is smaller than in a pure diatomic molecule. The main reason for this is that there is a greater distribution of polarizability along the bonds from the carbon atom of ethylene than from the carbon atom of a pure diatomic molecule. Nagarjan²⁰ has computed the delta function strengths, atomic polarizabilities and average molecular polarizabilities for few simple polyatomic molecules on an improved model. This improved approach has been extended by Sanyal and Ahmad²¹ for some condensed hydrocarbons and the results were found in reasonable agreement with the experimental values.

In the present paper, we have calculated the bond and molecular polarizabilities of α - and β -halogenonaphthalenes. The calculated results are discussed in terms various characteristic bonds and the configuration of molecular systems.

2. THEORETICAL CONSIDERATIONS

The delta-function potential model can be explained by considering an electron in a diatomic molecule moving in a potential field consisting of two finite potential wells, one about each nucleus, the width of each potential well is allowed to shrink and the height is at the same time allowed to increase without limit in such a way that the area remains finite and constant. The potential about each nucleus then becomes a delta function. The integral of the potential over all space, however, is finite and equal to a parameter, called, *delta-function strength* or *reduced electronegativity*.

The potential energy for the n -electron problem is considered to be the sum of the single delta-function potentials, each having the following form for a diatomic system—

$$V = - [A_1 g \delta(x - \frac{1}{2} a) + A_2 g \delta(x + \frac{1}{2} a)] \quad (1)$$

where x is the coordinate of the motion along the inter-nuclear axis, a is the delta-function spacing, A_1 and A_2 are the delta function strengths for nuclei 1 and 2 respectively g is the unit delta-function strength (the value for the hydrogen atom) and $\delta(x)$ a delta-function whose properties are—

$$\begin{aligned} \delta(x) &= 0 && \text{when } x \neq 0 \\ \delta(x) &= \infty && \text{when } x = 0 \end{aligned} \quad (2)$$

and $\int_{-\infty}^{+\infty} \delta(x) dx = 1$

Substituting this potential function in Schrodinger wave equation and adopting the variational treatment²² first introduced by Hylleraas²³ and Hasse¹, one get the parallel component of bond polarizability in bond region as

$$\alpha_{\parallel b} = \frac{4b A_{12}}{a_0} (X^{-2})^2 \quad (3)$$

where b is the bond order, a_0 is the radius of first Bohr orbit and

$$\bar{x}^2 = \frac{1}{4} R^2 + \frac{\dots}{2C_{R12}^2} \quad (4)$$

in which R is the internuclear distance at the equilibrium configuration and $C_{R12} = (n_1 n_2 N_1 N_2)^{1/4} (A_1 A_2)^{1/2}$. Here n_1 , N_1 and n_2 , N_2 represent the principal quantum number and number of electrons making the contribution to the bonding in atoms 1 and 2 respectively. A_{12} is the geometric mean of A_1 and A_2 . The delta-function strength for an atom having a bonding with another is different from that of the same having two or more bondings with other atoms, because of the difference in the electronic distributions. The value of A for an atom in the bond of a diatomic molecule and that of an atom in a bond of polyatomic molecule can be obtained from the equations

$$A = \left[\frac{X}{2.6n - 1.7p - 0.8D + 3.0F} \right]^{1/2} \quad (5)$$

$$\text{and } (A^*)^2 = A^2 \left[\frac{(n-3)}{(n-1)} \right] \text{ respectively.}$$

X is the electronegativity of the atom on Pauling Scale²⁴ n is the principal quantum number, p is 1 for an atom with p electrons in the valence shell. D is the total number of completed p and shells and F is the total number of completed f shells in the atom.

In the heteronuclear type of bond, the bond parallel component of the polarizability must be corrected to allow for a charge density not in the bond region by virtue of the polarity induced by the electronegativity difference of the atoms. Thus, the bond parallel component of polarizability with the polarity correction is given by

$$\alpha_{\parallel p} = \alpha_{\parallel b} \cdot \exp[-\frac{1}{4} (X_1 - X_2)^2] \quad (6)$$

The contribution of non-bonded electrons to the bond parallel component

$$\sum \alpha_{||n} = \sum_j \alpha_{||b} f_j \dots\dots (7)$$

of polarizability is expressed as where f_j is the fraction of the valence electrons in the j th atom not involved in the bonding and α is the atomic polarizability of the j th atom.

The bond perpendicular component of polarizability is calculated by an empirical approach made by Lippincott and Stutman¹³ which is expressed as

$$\sum 2\alpha_{\perp} = n_{df} \sum x_j^2 \alpha_j \dots\dots (8)$$

where n_{df} is the residual atomic polarizability degrees of freedom obtained from the considerations of symmetry and geometry of the molecule (as in ref. 19).

Thus the average molecular polarizability with bond polarity corrections can be expressed as

$$\bar{\alpha} = \frac{1}{3} \left[\sum \alpha_{||n} + \sum \alpha_{||b} + n_{df} \sum_j \frac{x_j^2 \alpha_j}{x_j^2} \right] \dots\dots (9)$$

3. RESULTS AND DISCUSSION

Table 1 presents the delta-function strength A in atomic units and atomic polarizabilities in 10^{-25} cm³ of hydrogen, carbon, fluorine, chlorine, bromine and iodine atoms for the bonds of diatomic and polyatomic systems. Calculated values of average molecular polarizabilities of α -halogeno-naphthalenes have been given in table 2, alongwith the experimental values. Molecular polarizabilities of these molecules have also been calculated by assuming the molecule as made up of pure diatomic molecules. These values have also been presented in same table (indicated by asteriks). Internuclear distances were taken from the work of Sutton²⁵: It is evident from the table that the values indicated by asteriks are lesser than experimental values²⁷ while the calculated values (with A and α for polyatomic molecules) are greater than experimental values and these values are much closer to experimental values when substituent atoms are heavier.

Table 1. Delta-function strengths in atomic units and atomic polarizability in 10^{-25} cm³ of some elements for bond of diatomic and polyatomic systems

Element	A	A ¹	α_A	α_A^1
Hydrogen	1.000	—	5.92	—
Carbon	0.846	0.757	9.78	13.70
Fluorine	1.065	0.953	4.90	6.87
Chlorine	0.753	0.715	13.88	16.26
Bromine	0.633	0.612	19.41	25.93
Iodine	0.584	0.565	29.72	32.82

¹The values for the bonds of polyatomic molecules.

Table 2. Molecular polarizabilities of substituted naphthalenes in 10^{-25} cm³)

Molecule	$\Sigma \alpha_{ p}$	$\Sigma \alpha_{ n}$	$\Sigma 2\alpha_{\perp}$	α_M (cal)	α_M (obs)	Ref.
Naphthalene	277.699	0.000	283.215	186.971	174.8	26
	307.307*	0.000	184.520*	163.942*	164.6	27
					176.8	28
α -Fluoronaphthalene	282.659	5.899	231.108	173.218	163.667	27
	308.944*	4.200*	175.485*	162.876*		
α -Chloronaphthalene	303.878	13.937	254.738	190.851	186.333	27
	331.681*	11.8972	197.482*	180.353*		
α -Bromonaphthalene	313.545	22.226	270.038	201.937	193.667	27
	341.806*	16.630*	205.670*	188.035*		
α -Iodonaphthalene	331.305	28.129	274.749	211.394	211.333	27
	361.001*	25.470*	216.367*	200.946*		

*See text (Results and discussion).

It is also concluded that the C-C and C-H bond polarizability is characteristic one and can be easily transferred from one system to another similar system. The internuclear distances in all the α - and β -halafeno-naphthalenes are not known. But the experimental values²⁷ of average molecular polarizabilities are same for α - and β -substitutions. In the delta-function model the parallel component of polarizability depends upon the fourth power of internuclear distances and perpendicular component depends upon the number of atoms. Hence it can be concluded that from α - to β -substitution either there is no change in internuclear distances or the algebraic sum of the changes in similar bonds is zero.

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