ABSTRACT

The molecular polarizabilities of 20 cobaltocene derivatives have been calculated using a new empirical approach based on the square of the sum of the atomic hybrid components (ahc), namely \( \alpha (\text{ahc}) = \frac{4}{N} (\sum A \tau_A) (\text{Å})^3 \). Where the summation proceeds over all atoms \( A=1,2,3, \ldots \), and \( N \) is the total number of electrons in the molecule. Common trends and patterns of behaviour are recognised and discussed. The results have been compared with those calculated by using Lippincott & Stutman’s method.
(3.1) INTRODUCTION:

In the previous chapter we have used Lippincott Stutman’s method for computing polarizability. Here a new empirical method is used which is most successful to the calculation of molecular polarizabilities including the environment through atomic hybridization about the central atom or with the atoms defining a bond or groups. Miller and Savchik\(^1\) were the first to propose the method that features atom hybridization (ah) in which each atom is characterised by its state of atomic hybridization. They used a functional form

\[
\alpha(\text{ahc}) = \frac{4}{N} \left[ \sum A \tau_A(\text{ahc}) \right]^2
\]  

(3.1)

Where \(\tau_A\) is an atomic hybrid component (ahc) for each atom A in a given state of hybridization, and N is the total number of electrons. This formula was based on a theoretical interpretation of variational perturbation result\(^1\text{--}^4\) and interpreted with molecular orbital theory. Their optimized atomic hybrid components, \(\tau_A(\text{ahc})\) reproduced to 1-3% and within experimental error for most of the molecules studied. They wrote the average atomic polarizability as

\[
\alpha^*_A(\text{ahc}) = \frac{4}{N_A} \tau_A^2
\]  

(3.2)

using the set of \(\tau_A\) from the ahc optimization, where \(N_A\) is the number of electron in atom A. \(\alpha^*_A(\text{ahc})\) will be referred to as the conjugate atomic hybrid component polarizability.
\[ \alpha^* \text{(ahc)} = \sum_A \alpha^*_A \text{(ahc)} \] (3.3)

Lang and John\textsuperscript{5,6} refined the atomic polarizabilities to obtain an optimum set of atomic hybrid polarizabilities, which reproduce the molecular polarizability.

\[ \alpha \text{(ahp)} = \sum_A \alpha_A \text{(ahp)} \] (3.4)

It will be convenient to define a conjugate (*) ahc parameter

\[ \tau^*_A \text{(ahp)} = \left[ N_A \alpha_A \text{(ahp)}/4 \right]^{1/2} \] (3.5)

Calculated with the optimum parameters \( \alpha_A \text{(ahp)} \) from which the conjugate (*) ahp molecular polarizability becomes

\[ \alpha^* \text{(ahp)} = (4/N) \left[ \sum_A \tau^*_A \text{(ahp)} \right]^2 \] (3.6)

to relate equations (3.4) and (3.6) through eq. (3.5)

Comparisons between the ahc and ahp methods of eqs. (3.1) and (3.4) calculated with newly optimized \( \tau_A \text{(ahc)} \) and \( \alpha_A \text{(ahp)} \) and the conjugate methods of eqs. (3.3) and (3.6) will be made to examine the interchangeability the equivalence of the two methods of partitioning the molecular polarizability and the atomic size.

The simplicity of the ahc and ahp atomic hybrid methods is understood by noting that the molecular polarizability cannot be written as a sum of atomic polarizabilities\textsuperscript{7,8} when atoms are defined only by the atomic number. Eisenlohr\textsuperscript{8,9} and more recently Vogel\textsuperscript{10} setup an extensive system of atomic refractions\textsuperscript{11} that have been supplemented by Batsanov\textsuperscript{12} in which each atom must be assigned polarizability depending on the atoms to which it is bonded.
Silberstein pointed out that atomic polarizabilities are not additive unless the atomic environment is considered in great detail. The methods that consider atoms in atomic hybrid states eliminate the need to develop an extensive set of rules that consider the specific atoms involved in bonding.

This method of calculating molecular polarizability originated with the early work by Von Steiger, Smyth, and Denbigh, who demonstrated additivity of bond polarizabilities (bp)

\[ \alpha_{(bp)} = \sum_b \alpha_b \text{(bp)} \]  

(3.7)

Where the sum is over all bonds B in the molecule. Denbigh and Vickery obtained a set of \( \alpha_b \) (bp) that reproduce \( \alpha(bp) \) to 1-2% of 52 molecules, and Vogel et al., have obtained the most refined set of bond polarizabilities. This method has been used very successfully. It introduces the environment into the parameterization through bonds linking pairs indirectly incorporates atomic hybridization.

In this chapter optimum sets of ahc and ahp parameters will be presented and the bp and gp methods will be related to the ahp method. Unlike the atomic hybrid methods in which parameter is required for each of M atoms or types, the method requires M(M-1)/2 bond parameters, and a bond distinction between carbon atoms in aromatic, naphthalenic etc bonds is made. The results by our method are compared with those calculated by Semwal & Balodi using Lippincott and Stutman’s method and interpreted the results in terms of observations of Waite & Papadopoulos and others.
(3.2) RATIONALIZATION OF THE EMPIRICAL APPROACH:

The Functional form of the empirical formula proposed in this investigation can be rationalized with the variational-perturbation approach proposed by Hylleraas and Hasse. The $xx$ component of molecular polarizability is expressed in the form:

$$\alpha_{xx} = \frac{4N}{a_0} \left[ (x_1 - \bar{x})^2 - (N-1)(x_1 - \bar{x})(x_2 - \bar{x})^2 \right]$$

(3.8)

Where $N$ is the no. of electrons, $\bar{x}$ is the average position of an electron in the $x$-direction, $(x_1 - \bar{x})^2$ is the mean square deviation of an electron from its average position, and $(x_1 - \bar{x})(x_2 - \bar{x})$ is the average correlation between two electrons in the $x$-direction. The average value of the operator $q$,

$$\overline{q} = \int \Psi^* q \Psi \, d\tau$$

(3.9)

is calculated with the zeroth-order wave function $\Psi$ obtained from perturbation theory. If the term in brackets in eq (3.8) is rewritten to include a summation over all electrons $i,j, = 1,2,3$ ----- $N$, then

$$\alpha_{xx} = \frac{4}{N a_0} \left[ \sum_{ij} (x_i - \bar{x}_i)(x_j - \bar{x}_j) \right]^2$$

(3.10)

$$= \frac{4}{N a_0} \left[ L_{xx} \right]^2$$

(3.11)

The term in brackets in eq. (3.10) and (3.11) reduces to.

$$L_{xx} = \left[ \sum_{ij} (x_i - \bar{x}_i) - (\sum_i \bar{x}_i) \right]^2$$

(3.12)

For closed shell systems the Zeroth order wave function may be approximated by an antisymmetrized product of molecular orbital $\Psi_\mu, \mu = 1, 2, 3$
and spin function $\eta$ and $\bar{\eta}$ with z components equal to $\pm \frac{1}{2}$.

$$\Psi = (N!)^{\frac{1}{2}} A \{ \Psi_1 (1) \eta (1) \Psi_1 (2) \bar{\eta} (2) \ldots \}$$  \hspace{1cm} (3.13)

substituting eq (3.13) into eq (3.12) yields.

$$L_{xx} = -2 \sum_{\mu} \sum_{\nu} \int \Psi_\mu^* \chi_{\nu} \Psi_\nu^* \chi_\mu \, d\tau + 2 \sum_{\mu} [\Psi_\mu^* \chi^2 \Psi_\mu] \, d\tau$$  \hspace{1cm} (3.14)

where $\mu$ and $\nu$ refer to the occupied molecular orbitals. The molecular orbitals are expanded as a linear combination of atomic orbitals $\chi_{At}$:

$$\Psi_\mu = \sum_A \sum_t C_{At}^\mu \chi_{At}$$  \hspace{1cm} (3.15)

where ‘t’ may refer $S$, $P_x$, $P_y$, and $P_z$ atomic orbitals or to hybrid atomic orbitals on atoms $A = 1, 2, 3 \ldots$ substituting eq (3.15) into eq (3.14) and using the zero differential overlap approximation yields,

$$L_{xx} = \sum a_0^{\frac{1}{2}} \tau_{Axx}$$  \hspace{1cm} (3.16)

Where

$$\sqrt{a_0} \tau_{Axx} = -2 \sum_{uv} \sum_{wz} \sum_{vz} C_{Auv}^* C_{Auv} C_{Bvz}^* C_{Bvz}$$

$$x \int \chi_{At}^* x \chi_{Au} d\tau \int \chi_{Bv}^* x \chi_{Bw} d\tau + 2 \sum_{t} \sum_{u} \sum_{\mu} C_{Atu}^* C_{Au\mu}$$

$$x \int \chi_{At}^* x^2 \chi_{Au} d\tau$$  \hspace{1cm} (3.17)

provides the link between the proposed empirical formula,

$$\alpha_{abc} = \frac{4}{N} \frac{[\sum_A \tau_A]^2 \text{Å}^3}{\text{Å}^3}$$  \hspace{1cm} (3.18)
and a molecular orbital model. Atomic orbitals, t, u, v, and W are centered on atoms A and B in At, Au, Bv and Bw. It is convenient to assume that $\Psi_\mu, \Psi = 1, 2, 3 \ldots$ are the localized molecular orbitals studied extensively by England et al.$^{23-24}$, their orbitals, confined to the region of a chemical bond, are written as a sum of hybrid atomic or $\pi$-orbitals. For acyclic hydrocarbons two center localized molecular orbitals are found, whereas for condensed hydrocarbons two-to four center localized molecular orbitals connected through a set of adjacent atoms are obtained.

To complete the rationalization of the formula $\alpha_{(ah, c)} = \frac{4}{N} [\Sigma_A \tau_A]^2 \text{Å}^3$ the components of polarizability $\alpha_{xx}$ obtained with eq (3.8) and similarly $\alpha_{yy}$ and $\alpha_{zz}$, are assumed to be calculated with XYZ coordinate system oriented along the principal axes of the polarization ellipsoid. Then the average molecular polarizability.

$$\alpha_M = \frac{1}{3} [\alpha_{xx} + \alpha_{yy} + \alpha_{zz}]$$

is obtained from,

$$\alpha = \frac{4}{N} [\Sigma_A \tau_A]^2 \quad (3.19)$$
(3.3) RESULTS AND DISCUSSION:

The calculated values of average molecular polarizabilities of 20 cobaltocene are given in table 3.1 along with the values obtained by using Lippioncott & Stutman’s method\textsuperscript{17-18}. The empirical approach proposed with $\alpha(\text{ahc}) = \frac{4}{N} (\sum \tau_A)^2 \text{Å}^3$ resulted from an attempt to obtain molecular polarizabilities for atoms in various hybrid states. The empirical approach proposed in this investigation appears to have several advantages over other methods like:

(i) Fewer parameters are required.

(ii) $\tau_A$ does not depend on atoms to which atom A is bounded, but rather bonding is contained implicitly in the choice of atomic hybrid component $\tau_A$.

(iii) Only one component $\tau_A$ is needed for each atomic hybrid configuration. For each atom A, one value of $\tau_A$ is needed for each type of bond as well as lone pairs are automatically incorporated into a parameter $\tau_A$ by the hybrid state of each atom. In the determination of $\tau_A$, for example, from the average polarizability of H$_2$, one obtains $(\alpha_H/8)^2 = \tau_H = 0.314 \text{ Å}^{3/2}$ and then from $\alpha_{\text{CH}_4}, \tau_c = [\sqrt{\frac{10}{4} \alpha_C - 4 \tau_H}] = 1.294 \text{ Å}^{3/2}$, for carbon in the tetrahedral hybrid configuration $\tau_c$ (te te te te). Then ethylene ($\tau_C = 1.436 \text{ Å}^{3/2}$) and benzene ($\tau_C = 1.428 \text{ Å}^{3/2}$) for the hybrid state C (tr tr tr $\pi$), finally acetylene yields $\tau_c = 1.393 \text{ Å}^{3/2}$ for C (di di $\pi\pi$). Using the same method we have determined the value of $\tau_{\text{Co}} = 3.917 \text{ Å}^{3/2}$. 
The $\alpha_m$ value for cobaltocene is $189.7 \times 10^{-25}$ cm$^3$ where as our theoretical value of $\alpha_m$ is $190.41 \times 10^{-25}$ cm$^3$, a close agreement. The small difference may be caused due to several reasons of the mechanism of its structural interpretations i.e. the complex mechanisms of distribution of the nine valence electron pairs of cobaltocene among 10 (Co-C) and 10 (C-C) bonds. The (Co-C) bonds show very small ionic character and treating the molecule on the basis of electroneutrality principle, there are many compatible structures. The order of polarizability of different substituent in cobaltocene derivatives is found to be as follows :

$\text{NH}_2 < \text{CHO} < \text{Cl} < \text{CN} < \text{CH}_3 < \text{-C} \equiv \text{CH} < \text{CH} = \text{CH}_2 < \text{-CoCH}_3 < \text{CH}_2 \text{Cl} < \text{CH Cl}_2 < \text{CH}_2 \text{I} < \text{CHI}_2$

The trend specified above is a consequence of the important role of the delocalized $\pi$-electrons, which is common in these substrates. The main contributions connected with the cobalt atom and the interacting associated with it are considerably smaller. In the case of the cobaltocenes, $\pi$-electrons delocalization through the cobaltocene unit is not as effective as we observe a linear conjugated structures. For most of the molecules, our calculated values are in reasonable agreement with the experimental values. This indicates the wide applicability of the Miller’s method to complicated molecular systems and complex metal carbonyls.
Table 3.1
Molecular Polarizabilities of Cobaltocene and Some derivatives (10^{-25} \text{ cm}^3)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compound</th>
<th>(a_M) Lippincott &amp; stutman’s method</th>
<th>(a_M) Miller’s method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>((C_5H_5)_2) Co</td>
<td>206.254</td>
<td>192.42</td>
</tr>
<tr>
<td>2.</td>
<td>Co-NH$_2$</td>
<td>195.08</td>
<td>200.51</td>
</tr>
<tr>
<td>3.</td>
<td>Co-CHO</td>
<td>209.53</td>
<td>204.53</td>
</tr>
<tr>
<td>4.</td>
<td>Co-CN</td>
<td>213.62</td>
<td>210.34</td>
</tr>
<tr>
<td>5.</td>
<td>Co-CH$_3$</td>
<td>212.57</td>
<td>210.14</td>
</tr>
<tr>
<td>6.</td>
<td>Co-Cl</td>
<td>215.13</td>
<td>211.03</td>
</tr>
<tr>
<td>7.</td>
<td>Co-CC ≡ H</td>
<td>216.32</td>
<td>215.18</td>
</tr>
<tr>
<td>8.</td>
<td>Co-CH = CH$_2$</td>
<td>219.53</td>
<td>221.18</td>
</tr>
<tr>
<td>9.</td>
<td>CHO - Co - CHO</td>
<td>225.92</td>
<td>224.69</td>
</tr>
<tr>
<td>10.</td>
<td>Co-C-CH$_3$</td>
<td>221.81</td>
<td>226.17</td>
</tr>
<tr>
<td>11.</td>
<td>Co-CH$_2$ Cl</td>
<td>227.16</td>
<td>228.93</td>
</tr>
<tr>
<td>12.</td>
<td>Co-I</td>
<td>234.73</td>
<td>238.26</td>
</tr>
<tr>
<td>13.</td>
<td>Co-CHCl$_2$</td>
<td>241.38</td>
<td>248.41</td>
</tr>
<tr>
<td>14.</td>
<td>Co-CH$_2$I</td>
<td>243.40</td>
<td>256.82</td>
</tr>
<tr>
<td>15.</td>
<td>Co-CHI$_2$</td>
<td>275.67</td>
<td>305.21</td>
</tr>
<tr>
<td>16.</td>
<td>Co-CH=CH-Ar</td>
<td>346.19</td>
<td>306.28</td>
</tr>
<tr>
<td>17.</td>
<td>CHO-Co-CH=CH-Ar</td>
<td>408.17</td>
<td>329.09</td>
</tr>
<tr>
<td>18.</td>
<td>Ar-CH=CH-Co-CH=CH-Ar</td>
<td>490.54</td>
<td>404.44</td>
</tr>
<tr>
<td>19.</td>
<td>Co-CH=CH-Ar-NO$_2$</td>
<td>349.46</td>
<td>411.53</td>
</tr>
<tr>
<td>20.</td>
<td>Co-H=CH-Ar-CH=CH-Co</td>
<td>569.16</td>
<td>329.78</td>
</tr>
</tbody>
</table>
(3.4) CONCLUSIONS:

The work reported here provides the following important conclusions:

(i) Organometallic systems in general offer additional structural flexibility to design non-linear molecular materials.

(ii) They offer a rich variety of excited states to investigate the relative contributions of these states to optical non-linearity.

(iii) In case of structures involving cobaltocene, $\pi$-electron delocalization through the cobaltocene unit is not as effective as in linear conjugated structures.

(iv) The d-d transition of the metal does not make significant contribution to optical non-linearity compared to the $\pi-\pi^*$ transitions.
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