CHAPTER V

Purine

Nucleoside and Nucleotide Systems
5.1. Molecular Polarizability

5.1.1. Introduction

Levene and Jacob's\(^1\) isolated the first nucleoside, guanosine along with adenosine. Among the nucleosides isolated from natural sources adenine thio-methyl pentoside is a constituent of yeast and is present in tissues of many animals. The term nucleotide was introduced by Levene and Mandel\(^2\) in 1908 to denote the products isolated from acidic digests of thymus nucleic acid. The first nucleotide inosinic acid (muscle fibre) was isolated from beef extract by Liebig\(^3\) as early as in 1847. Since then many mononucleotides usually 5'-phosphates (though adenosine-3'-phosphate is present in the venom of tiger snakes) have been isolated by direct extraction of tissue or organism\(^4\). Adenosine-5'-phosphate, inosine-5'-phosphate, Guanosine-5'-phosphate, Xanthosine-3'-phosphate and deoxy adenosine-5'-phosphate are all purine nucleotides. Uridine-2'-phosphate, Cytidine-3'-phosphate and Thymidine-3'-phosphate are pyrimidine nucleotides. Pyrimidine and purine nucleotides are major energy carriers, subunits of DNA and RNA and precursors for the synthesis of nucleotide cofactors such as NAD and SAM. Purine nucleotides have multifunctional role in cellular metabolism. They function as regulators of many allosteric enzymes and are involved in aggregation of platelets. They participate in dehydrogenase reactions as part of the NAD, NADP molecules. Thus they are critical for virtually every aspect of cellular life. Puromycin is an antibiotic produced by 'Streptomyces Albomiger'. Medical applications of these purine nucleosides and nucleotides are given in the beautiful reviews of Suhadolnik\(^5\), Cheng\(^6,7\), Doran\(^8\), Montgomery\(^9\) and Hitching\(^10\) and one can consult these reviews for further in depth studies.

The purine ring is the result of fusion of \(\pi\)-electron deficient pyrimidine ring with \(\pi\)-electron rich imidazole nucleus and hence presents very interesting theoretical studies. A variety of physical and chemical techniques have appeared in literature to study these effects. Bond and molecular polarizabilities are chosen here to understand this peculiar structure. Molecular polarizability can be estimated from molar refraction studies. But the inner details of the structure of the molecule cannot be understood by this average value. As such bond polarizabilities from molecular vibration parameters are expected to allow the electronic structure. In the light of this,
bond and molecular polarizabilities are evaluated by the two theoretical methods presented in chapter II. For the reasons quoted in the earlier chapter, diamagnetic susceptibility and electron ionization cross-section for Adenosine, Guanosine and a few of their nucleotides are presented in this chapter.

5.1.2. Lippincott-δ-function Potential model

This method of evaluation is based on the following steps:
1. The parallel component of polarizability of each bond.
2. The non-bond region electron contribution to parallel component of polarizability.
3. The estimation of perpendicular components of polarizability from atomic polarizabilities, knowing the number of degrees of freedom, and
4. The determination of molecular polarizability from the above three components.


The parallel, non-bond region electron contribution to parallel component and the perpendicular components are estimated from the appropriate relations and tabulated as follows.

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>TABLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adenosine and its nucleosides and nucleotides</td>
<td>5.1</td>
</tr>
<tr>
<td>Guanosine and its nucleosides and nucleotides</td>
<td>5.2</td>
</tr>
</tbody>
</table>

From these values the molecular polarizability is estimated using the expression

\[
\alpha_{\text{m}} = \frac{1}{3} \left( \sum \alpha_{\text{lp}} + \sum \alpha_{\text{ln}} + \sum 2\alpha_{\perp} \right) \]

------ (2.18)
### TABLE-5.1

Molecular polarizabilities of Adenosine and its derivatives

Lippincott method $\alpha \times 10^{23}$ cm$^3$

<table>
<thead>
<tr>
<th>S.No</th>
<th>MOLECULE</th>
<th>$\Sigma \alpha_{lp}$</th>
<th>$\Sigma \alpha_{lm}$</th>
<th>$\Sigma 2\alpha_L$</th>
<th>$\alpha_M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Adenosine</td>
<td>4.474</td>
<td>0.305</td>
<td>2.138</td>
<td>2.306</td>
</tr>
<tr>
<td>2</td>
<td>Sodium salt of Deoxyadenosine-5'-Phosphate Hexahydrate</td>
<td>5.998</td>
<td>0.395</td>
<td>2.330</td>
<td>2.907</td>
</tr>
<tr>
<td>3</td>
<td>Adenosine-5'-methyl Phosphonate Hemi hydrate</td>
<td>6.467</td>
<td>0.385</td>
<td>2.621</td>
<td>3.158</td>
</tr>
<tr>
<td>4</td>
<td>Adenosine-5'-O-methyl phosphate</td>
<td>6.156</td>
<td>0.419</td>
<td>2.671</td>
<td>3.202</td>
</tr>
<tr>
<td>5</td>
<td>Adenosine-3'-phosphate Dihydrate</td>
<td>6.139</td>
<td>0.424</td>
<td>2.446</td>
<td>3.003</td>
</tr>
<tr>
<td>6</td>
<td>8-[(2-Aminoethyl) amino] adenosine cyclic5', 5'- Monophosphate Tetra hydrate</td>
<td>7.408</td>
<td>0.439</td>
<td>2.485</td>
<td>3.564</td>
</tr>
<tr>
<td>7</td>
<td>8,2'-Anhydro-8-mercapto-9-β-D-arabinofuranosyladenine-5'-mono phosphate Tri hydrate</td>
<td>6.616</td>
<td>0.506</td>
<td>2.272</td>
<td>3.132</td>
</tr>
<tr>
<td>8</td>
<td>β-Adenosine-2'-β-Uridine-5'-Phosphoric Acid</td>
<td>10.283</td>
<td>0.681</td>
<td>4.047</td>
<td>5.004</td>
</tr>
<tr>
<td>9</td>
<td>2', 3'-Dideoxy-2', 3'-didehydroadenosine</td>
<td>4.340</td>
<td>0.227</td>
<td>1.831</td>
<td>2.133</td>
</tr>
<tr>
<td>10</td>
<td>Cordycepin</td>
<td>4.622</td>
<td>0.267</td>
<td>2.012</td>
<td>2.300</td>
</tr>
<tr>
<td>11</td>
<td>2'-O-Methyladenosine</td>
<td>5.116</td>
<td>0.306</td>
<td>2.286</td>
<td>2.570</td>
</tr>
</tbody>
</table>
TABLE-5.2

Molecular polarizabilities of Guanosine and its derivatives

Lippincott method \( \alpha \times 10^{23} \text{ cm}^3 \)

<table>
<thead>
<tr>
<th>S.No</th>
<th>MOLECULE</th>
<th>( \Sigma \alpha_{\text{Ip}} )</th>
<th>( \Sigma \alpha_{\text{Ham}} )</th>
<th>( \Sigma 2\alpha_\perp )</th>
<th>( \alpha_M )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Guanosine</td>
<td>4.475</td>
<td>0.346</td>
<td>2.332</td>
<td>2.384</td>
</tr>
<tr>
<td>2</td>
<td>Guanosine 3',5'-cyclic monophosphate sodium Tetrahydrate</td>
<td>6.003</td>
<td>0.424</td>
<td>2.322</td>
<td>2.916</td>
</tr>
<tr>
<td>3</td>
<td>Disodium deoxyguanosine-5'-phosphate Tetrahydrate</td>
<td>5.85</td>
<td>0.484</td>
<td>2.322</td>
<td>2.885</td>
</tr>
<tr>
<td>4</td>
<td>8-Methylguanosine Trihydrate</td>
<td>5.198</td>
<td>0.345</td>
<td>2.336</td>
<td>2.627</td>
</tr>
<tr>
<td>5</td>
<td>7-Methyl-8-oxo-7,8-dihydroguanosine Monohydrate</td>
<td>5.337</td>
<td>0.385</td>
<td>2.387</td>
<td>2.703</td>
</tr>
<tr>
<td>6</td>
<td>5-aza-7-deaza-2'-deoxyguanosine</td>
<td>4.869</td>
<td>0.306</td>
<td>2.062</td>
<td>2.412</td>
</tr>
<tr>
<td>7</td>
<td>2'-Deoxy-6-thioguanosine Monohydrate</td>
<td>5.217</td>
<td>0.388</td>
<td>2.183</td>
<td>2.596</td>
</tr>
<tr>
<td>8</td>
<td>2',3'-O-Isopropylidene guanosine Hemihydrat</td>
<td>6.081</td>
<td>0.346</td>
<td>2.507</td>
<td>2.978</td>
</tr>
<tr>
<td>9</td>
<td>2',3',5'-Tri-O-acetylguanosine</td>
<td>6.932</td>
<td>0.464</td>
<td>3.216</td>
<td>3.537</td>
</tr>
<tr>
<td>10</td>
<td>Disodium Guanosine 5'-Phosphate Heptahydrate</td>
<td>6.073</td>
<td>0.484</td>
<td>2.366</td>
<td>2.974</td>
</tr>
</tbody>
</table>
5.1.3. Molecular Dynamics Method

This method relates the bond polarizability coefficients to the force field constant and mean amplitude of vibration of the bond under consideration. A detailed description of the method is given in chapter II section 2. The bond polarizabilities of each bond are obtained by solving the expressions (2.28) and (2.30).

\[ b_L - b_T = A \left( (x_1 x_2)^{1/2} \left( \frac{aN}{K - b} \right)^{2/3} \right) \]  \hspace{1cm} \text{------ (2.28)}

and

\[ b_L + 2b_T = C_{p^{1/2}} J^{2/3} \]  \hspace{1cm} \text{------ (2.30)}

The significance of the various symbols is explained in chapter II. The stretching force constants of the purine ring in the two nucleosides are evaluated following the methods of Ladd, Orvilli-Thomas and Cox\textsuperscript{33}; Dicius\textsuperscript{34}; and Susi and Ard\textsuperscript{35}. These data are presented along with the bond polarizability coefficients. IR and Raman Frequency data appropriate to the present work are reported by Angell\textsuperscript{36}, Lord and Thomson\textsuperscript{37}, Lee et al\textsuperscript{38}, Mohan and Ilangovan\textsuperscript{39} and Vidyasagar\textsuperscript{40}. The consolidated results on the longitudinal (b\textsubscript{L}) and transverse (b\textsubscript{T}) bond polarizability coefficients for these systems are presented in tables as shown:

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>TABLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adenosine nucleosides and nucleotides</td>
<td>5.3</td>
</tr>
<tr>
<td>Guanosine nucleosides and nucleotides</td>
<td>5.4</td>
</tr>
</tbody>
</table>

The mean polarizability is given by the expression (2.31)

\[ \alpha_M = \sum_i \frac{n_i (b_T + 2b_T)}{3} \]  \hspace{1cm} \text{------ (2.31)}
where $n_i$ is the number of bonds of type $i$. These values are compared with those obtained by the $8$-function model values and the results obtained by summing the Le Fevre bond polarizability coefficients in tables as shown:

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>TABLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adenosine and its derivatives</td>
<td>5.5</td>
</tr>
<tr>
<td>Guanosine and its derivatives</td>
<td>5.6</td>
</tr>
</tbody>
</table>
**TABLE-5.3**

Force field data and bond polarizability coefficients of Adenosine and its derivatives

Molecular Dynamics Method  $b \times 10^{23}$ Cm$^3$

<table>
<thead>
<tr>
<th>BOND</th>
<th>FORCE CONSTANT 'K' m dyne/A$^0$</th>
<th>$b_L$</th>
<th>$b_T$</th>
<th>$(b_L+2b_T)/3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-N</td>
<td>7.190</td>
<td>0.195</td>
<td>0.074</td>
<td>0.115</td>
</tr>
<tr>
<td>C-N</td>
<td>7.607</td>
<td>0.178</td>
<td>0.081</td>
<td>0.113</td>
</tr>
<tr>
<td>C-C</td>
<td>6.572</td>
<td>0.144</td>
<td>0.046</td>
<td>0.079</td>
</tr>
<tr>
<td>C-C</td>
<td>7.459</td>
<td>0.201</td>
<td>0.120</td>
<td>0.147</td>
</tr>
<tr>
<td>N-H</td>
<td>5.382</td>
<td>0.093</td>
<td>0.084</td>
<td>0.087</td>
</tr>
<tr>
<td>C-H</td>
<td>5.253</td>
<td>0.074</td>
<td>0.062</td>
<td>0.066</td>
</tr>
<tr>
<td>N-C'</td>
<td>2.480</td>
<td>0.203</td>
<td>0.128</td>
<td>0.153</td>
</tr>
<tr>
<td>C'-C'</td>
<td>3.761</td>
<td>0.179</td>
<td>0.047</td>
<td>0.091</td>
</tr>
<tr>
<td>C'-O</td>
<td>6.227</td>
<td>0.185</td>
<td>0.054</td>
<td>0.098</td>
</tr>
<tr>
<td>O-H</td>
<td>6.282</td>
<td>0.180</td>
<td>0.049</td>
<td>0.093</td>
</tr>
<tr>
<td>C'-H</td>
<td>4.681</td>
<td>0.076</td>
<td>0.064</td>
<td>0.068</td>
</tr>
<tr>
<td>P-O</td>
<td>5.698</td>
<td>0.138</td>
<td>0.067</td>
<td>0.090</td>
</tr>
<tr>
<td>P=O</td>
<td>5.698</td>
<td>0.127</td>
<td>0.072</td>
<td>0.090</td>
</tr>
<tr>
<td>P-C</td>
<td>7.964</td>
<td>0.177</td>
<td>0.118</td>
<td>0.138</td>
</tr>
<tr>
<td>C-S</td>
<td>4.100</td>
<td>0.246</td>
<td>0.032</td>
<td>0.103</td>
</tr>
<tr>
<td>C'=C' (deoxyribose)</td>
<td>9.637</td>
<td>0.131</td>
<td>0.042</td>
<td>0.072</td>
</tr>
<tr>
<td>C-H (methyl)</td>
<td>4.889</td>
<td>0.075</td>
<td>0.064</td>
<td>0.067</td>
</tr>
</tbody>
</table>
### TABLE-5.4

Force field data and bond polarizability coefficients of Guanosine and its derivatives

<table>
<thead>
<tr>
<th>BOND</th>
<th>FORCE CONSTANT $K$ m dyne/A$^0$</th>
<th>$b_L$</th>
<th>$b_T$</th>
<th>$(b_L+2b_T)/3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-N</td>
<td>7.268</td>
<td>0.196</td>
<td>0.074</td>
<td>0.115</td>
</tr>
<tr>
<td>C=N</td>
<td>7.607</td>
<td>0.178</td>
<td>0.081</td>
<td>0.113</td>
</tr>
<tr>
<td>C-C</td>
<td>6.572</td>
<td>0.144</td>
<td>0.046</td>
<td>0.079</td>
</tr>
<tr>
<td>C=C</td>
<td>7.459</td>
<td>0.201</td>
<td>0.120</td>
<td>0.147</td>
</tr>
<tr>
<td>C=O</td>
<td>10.264</td>
<td>0.169</td>
<td>0.044</td>
<td>0.086</td>
</tr>
<tr>
<td>N-H</td>
<td>5.382</td>
<td>0.093</td>
<td>0.084</td>
<td>0.087</td>
</tr>
<tr>
<td>C-H</td>
<td>5.160</td>
<td>0.075</td>
<td>0.063</td>
<td>0.067</td>
</tr>
<tr>
<td>N-H (amino)</td>
<td>6.002</td>
<td>0.091</td>
<td>0.081</td>
<td>0.085</td>
</tr>
<tr>
<td>N-C'</td>
<td>2.480</td>
<td>0.203</td>
<td>0.128</td>
<td>0.153</td>
</tr>
<tr>
<td>C-H (methyl)</td>
<td>4.626</td>
<td>0.076</td>
<td>0.065</td>
<td>0.068</td>
</tr>
<tr>
<td>C'-C'</td>
<td>3.761</td>
<td>0.179</td>
<td>0.047</td>
<td>0.091</td>
</tr>
<tr>
<td>C'-O</td>
<td>6.227</td>
<td>0.185</td>
<td>0.054</td>
<td>0.098</td>
</tr>
<tr>
<td>C'=C' (in deoxyribose)</td>
<td>9.637</td>
<td>0.131</td>
<td>0.042</td>
<td>0.072</td>
</tr>
<tr>
<td>O-H</td>
<td>6.282</td>
<td>0.180</td>
<td>0.049</td>
<td>0.093</td>
</tr>
<tr>
<td>C'-H</td>
<td>4.681</td>
<td>0.076</td>
<td>0.064</td>
<td>0.068</td>
</tr>
<tr>
<td>P-O</td>
<td>5.698</td>
<td>0.138</td>
<td>0.066</td>
<td>0.090</td>
</tr>
<tr>
<td>P=O</td>
<td>5.698</td>
<td>0.127</td>
<td>0.072</td>
<td>0.090</td>
</tr>
<tr>
<td>C=S</td>
<td>3.950</td>
<td>0.197</td>
<td>0.058</td>
<td>0.104</td>
</tr>
</tbody>
</table>
# TABLE-5.5

Molecular polarizabilities of Adenosine and its derivatives

\[ \alpha_M \times 10^{-23} \text{ cm}^3 \]

<table>
<thead>
<tr>
<th>S.No</th>
<th>MOLECULE</th>
<th>( \alpha_M ) LIPP</th>
<th>( \alpha_M ) MDM</th>
<th>( \alpha_M ) LEFEVRE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Adenosine</td>
<td>2.306</td>
<td>2.791</td>
<td>2.412</td>
</tr>
<tr>
<td>2</td>
<td>Sodium salt of Deoxyadenosine-5' Phosphate Hexahydrate</td>
<td>2.907</td>
<td>3.165</td>
<td>3.281</td>
</tr>
<tr>
<td>3</td>
<td>Adenosine-5'-methyl Phosphonate Hemi hydrate</td>
<td>3.150</td>
<td>3.610</td>
<td>3.581</td>
</tr>
<tr>
<td>4</td>
<td>Adenosine-5’-O'-methyl phosphate</td>
<td>3.202</td>
<td>3.640</td>
<td>3.692</td>
</tr>
<tr>
<td>5</td>
<td>Adenosine-3'-phosphate Dihydrate</td>
<td>3.003</td>
<td>3.490</td>
<td>3.515</td>
</tr>
<tr>
<td>6</td>
<td>8'- [(2-Aminoethyl) amino] adenosine cyclic3',5'- Monophosphate Tetra hydrate</td>
<td>3.564</td>
<td>4.090</td>
<td>4.147</td>
</tr>
<tr>
<td>7</td>
<td>8',2'-Anhydro-8-mercapto-9-β-D-arabinofuranosyladenine-5' mono phosphate Tri hydrate</td>
<td>3.132</td>
<td>3.446</td>
<td>3.602</td>
</tr>
<tr>
<td>8</td>
<td>β-Adenosine-2'-β-Uridine-5'-Phosphoric Acid</td>
<td>5.004</td>
<td>6.109</td>
<td>5.850</td>
</tr>
<tr>
<td>9</td>
<td>2',3'-Dideoxy-2',3'-didehydroadenosine</td>
<td>2.133</td>
<td>2.790</td>
<td>2.646</td>
</tr>
<tr>
<td>10</td>
<td>Cordycepin</td>
<td>2.300</td>
<td>3.075</td>
<td>2.815</td>
</tr>
<tr>
<td>11</td>
<td>2'- O-Methyladenosine</td>
<td>2.570</td>
<td>3.404</td>
<td>3.139</td>
</tr>
</tbody>
</table>

* Denotes present experimental value.
### TABLE-5.6

Molecular Polarizabilities of guanosine and its derivatives

\[
\alpha_M \times 10^{23} \text{cm}^3
\]

<table>
<thead>
<tr>
<th>S.No</th>
<th>MOLECULE</th>
<th>(\alpha_M) LIPP</th>
<th>(\alpha_M) MDM</th>
<th>(\alpha_M) LE FEVRE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Guanosine</td>
<td>2.384</td>
<td>2.839</td>
<td>2.811</td>
</tr>
<tr>
<td>2</td>
<td>Guanosine 3', 5'-cyclic monophosphate sodium tetrahydrate</td>
<td>2.916</td>
<td>3.471</td>
<td>3.328</td>
</tr>
<tr>
<td>3</td>
<td>Disodium deoxyguanosine-5'-phosphate tetrahydrate</td>
<td>2.885</td>
<td>3.541</td>
<td>3.394</td>
</tr>
<tr>
<td>4</td>
<td>8-Methylguanosine trihydrate</td>
<td>2.627</td>
<td>3.527</td>
<td>3.288</td>
</tr>
<tr>
<td>5</td>
<td>7-Methyl-8-oxo-7, 8-dihydroguanosine monohydrate</td>
<td>2.703</td>
<td>3.689</td>
<td>3.392</td>
</tr>
<tr>
<td>6</td>
<td>5-aza-7-deaza-2'-deoxyguanosine</td>
<td>2.412</td>
<td>3.197</td>
<td>2.921</td>
</tr>
<tr>
<td>7</td>
<td>2'-deoxy-6-thioguanosine monohydrate</td>
<td>2.596</td>
<td>3.199</td>
<td>2.893</td>
</tr>
<tr>
<td>8</td>
<td>2', 3'-O-Isopropylidene guanosine hemihydrate</td>
<td>2.978</td>
<td>3.897</td>
<td>3.543</td>
</tr>
<tr>
<td>9</td>
<td>2', 3', 5'-Tri-O-acetylguanosine</td>
<td>3.537</td>
<td>4.448</td>
<td>4.113</td>
</tr>
<tr>
<td>10</td>
<td>Disodium guanosine 5'-phosphate heptahydrate</td>
<td>2.974</td>
<td>3.571</td>
<td>3.428</td>
</tr>
</tbody>
</table>

* Denotes present experimental value.
5.2. Diamagnetic Susceptibility

5.2.1. Introduction

As pointed out earlier, since it is difficult to estimate diamagnetic susceptibility of polyatomic molecules by Vanvleck’s theory\(^4\) based on quantum mechanical concepts, approximate methods have been developed. Among these methods, the Pascal’s method\(^2\) and the Rao et al’s method\(^3\) are discussed in detail in chapters II and IV. Following these methods the susceptibilities of purine nucleosides and nucleotides have been estimated in this section.

5.2.2. Pascal’s Method\(^2\)

The details of the Pascal’s atomic increment system of determining the molar diamagnetic susceptibility have been described in chapter II section 3. According to this method, the molar diamagnetic susceptibility is given by the expression.

\[
\chi_M = \sum_i n_i \chi_{ai} + \sum_i \lambda_i \quad \text{(2.37)}
\]

Where \(\chi_a\) is the atomic susceptibility and \(\lambda_i\) is the constitutive correction for a system of molecules. The various Pascal’s atomic and bond increments and the constituent corrections appropriate for the present study have been reported in tables 2.1-2.3. Using these constants, the molar diamagnetic susceptibilities for all molecules are evaluated and presented in tables 5.7 and 5.8.

5.2.3. Rao et al’s Method\(^3\)

It is based on the linear relationship between polarizability and diamagnetic susceptibility. Rao and Murthy developed this method, the details of which are given in chapter II. The expression reads as

\[
-\chi_M = \left(\mu_0\sigma'\right)\alpha_M \quad \text{(2.38)}
\]

where \(\sigma'\) is the degree of covalence factor estimated from Pauling’s electronegativities \(\gamma\) is the saturation factor, \(\alpha_M\) is the polarizability.
Using these covalence factors and the molecular polarizability values estimated by molecular dynamics method, the diamagnetic susceptibilities are estimated and presented in tables 5.7 and 5.8.


**TABLE-5.7**

Diamagnetic susceptibilities of Adenosine and its derivatives

$-\chi_M \times 10^6 \text{ CGS emu mol}^{-1}$

<table>
<thead>
<tr>
<th>S.No</th>
<th>MOLECULE</th>
<th>PASCAL METHOD</th>
<th>RAO et al METHOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Adenosine</td>
<td>141.60</td>
<td>134.36</td>
</tr>
<tr>
<td>2</td>
<td>Sodium salt of Deoxyadenosine $-5'$-Phosphate Hexahydrate</td>
<td>141.16</td>
<td>139.67</td>
</tr>
<tr>
<td>3</td>
<td>Adenosine-$5'$-methyl Phosphonate Hemi hydrate</td>
<td>156.80</td>
<td>159.31</td>
</tr>
<tr>
<td>4</td>
<td>Adenosine-$5'$-O-methyl phosphate</td>
<td>161.41</td>
<td>160.63</td>
</tr>
<tr>
<td>5</td>
<td>Adenosine- $3'$-phosphate Dihydrate</td>
<td>148.70</td>
<td>154.01</td>
</tr>
<tr>
<td>6</td>
<td>8-[(2-Aminoethyl) amino] adenosine cyclic$3'$,$5'$-Monophosphate Tetra hydrate</td>
<td>179.19</td>
<td>180.49</td>
</tr>
<tr>
<td>7</td>
<td>8,2'$'$-Anhydro-8-mercapto $-9'$-$\beta$-$D$-arabinofuranosyladenine-5'$'$-mono phosphatetrihydrate</td>
<td>153.23</td>
<td>151.95</td>
</tr>
<tr>
<td>8</td>
<td>$\beta$-Adenosine-2'$'$-$\beta$-Uridine-5'$'$-Phosphoric Acid</td>
<td>252.55</td>
<td>257.90</td>
</tr>
<tr>
<td>9</td>
<td>2'$'$,3'$'$-Dideoxy-2'$'$,3'$'$-didehydroadenosine</td>
<td>116.52</td>
<td>121.02</td>
</tr>
<tr>
<td>10</td>
<td>Cordycepin</td>
<td>126.99</td>
<td>133.38</td>
</tr>
<tr>
<td>11</td>
<td>2'$'$-O-Methyladenosine</td>
<td>144.31</td>
<td>147.65</td>
</tr>
</tbody>
</table>
### TABLE-5.8

Diamagnetic susceptibilities of Guanosine and its derivatives

$\chi_M \times 10^6$ CGS emu mol$^{-1}$

<table>
<thead>
<tr>
<th>S.No.</th>
<th>MOLECULE</th>
<th>PASCAL METHOD</th>
<th>Rao et al METHOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Guanosine</td>
<td>138.70</td>
<td>137.40</td>
</tr>
<tr>
<td>2</td>
<td>Guanosine $3', 5'$-cyclic monophosphate sodium tetrahydrate</td>
<td>133.81</td>
<td>135.51</td>
</tr>
<tr>
<td>3</td>
<td>Disodium deoxyguanosine-$5'$-phosphate tetrahydrate</td>
<td>139.43</td>
<td>138.25</td>
</tr>
<tr>
<td>4</td>
<td>8-Methylguanosine trihydrate</td>
<td>142.58</td>
<td>153.0</td>
</tr>
<tr>
<td>5</td>
<td>7-Methyl-8-oxo-7,8-dihygroguanosine monohydrate</td>
<td>140.85</td>
<td>160.01</td>
</tr>
<tr>
<td>6</td>
<td>5-aza-7-deaza-2'-deoxyguanosine</td>
<td>125.26</td>
<td>138.67</td>
</tr>
<tr>
<td>7</td>
<td>2'-deoxy-6-thioguanosine monohydrate</td>
<td>141.99</td>
<td>138.76</td>
</tr>
<tr>
<td>8</td>
<td>2', 3'-O- Isopropylidene guanosine hemihydrate</td>
<td>160.20</td>
<td>169.04</td>
</tr>
<tr>
<td>9</td>
<td>2', 3', 5'-Tri-O-acetylguanosine</td>
<td>178.26</td>
<td>176.15</td>
</tr>
<tr>
<td>10</td>
<td>Disodium guanosine $5'$-phosphate heptahydrate</td>
<td>141.11</td>
<td>139.42</td>
</tr>
</tbody>
</table>
5.3. Molecular Electron Ionization cross-sections

5.3.1. Introduction

The subject of molecular electron ionization cross-section has been introduced in chapter II. Beran and Kevan\textsuperscript{44} developed semi-empirical relations between ionization cross-sections and the related parameters; polarizability and susceptibility of the molecules. Their relations are extended in the present work to study the adenosine and guanosine nucleoside and nucleotide systems.

5.3.2. Polarizability and susceptibility correlations

Beran and Kevan evaluated the polarizabilities and susceptibilities of various systems of molecules and measured the ionization cross-sections at 70eV. From these they proposed the correlations presented in chapter II, section 4.1. The modified correlation appropriate to the present work reads as

\[
Q_{\text{exp}} = \frac{1}{5.6 \times 10^{-6} \text{ cm}} \left[ \alpha_M - 4.2 (n_C + 2) + (n_N + 2) \right] \quad \text{------ (2.39)}
\]

where \( Q \) is the ionization cross-section and \( \alpha_M \) is the polarizability. Using the polarizability values estimated by molecular dynamics method, the cross-sections are calculated and presented in tables 5.9 and 5.10.

The susceptibility correlation reads as

\[
Q \left( \times 10^6 \text{ cm}^2 \right) = 0.278 \chi_M \quad \text{------ (2.40)}
\]

where \( \chi_M \) is the diamagnetic susceptibility of the molecule. \( \chi_M \) estimated by Rao et al.’s method is used to evaluate cross-sections and the results are tabulated in the same tables 5.9 and 5.10.

5.3.3. Atomic correlation

This correlation is based on the additivity concept of atomic cross-sections. Taking into consideration Mann’s atomic electron ionization cross-section the atomic correlation of Beran and Kevan has been extended to the purine nucleosides and nucleotides. The relation which reads as:
The correlation of Beran and Kevan has been extended to the purine nucleosides and nucleotides. The relation which reads as:

$$Q \times 10^{16} \text{ cm}^2 = 1.34 \times 10^6 n_C + 1.77 n_N + 0.30 n_H + 1.68 n_O + 5.37 n_P + 5.24 n_S \times 0.71 \text{ for purines}$$

(2.41)

The results obtained by this correlation are tabulated in the tables 5.9 and 5.10 along with the results obtained by polarizability and susceptibility correlations. Discussion of the results is given in the next chapter.
TABLE-5.9

Molecular Electron Ionization Cross-Sections of Adenosine and its derivatives

\[ Q \times 10^{16} \text{ cm}^2 \]

<table>
<thead>
<tr>
<th>S.No</th>
<th>MOLECULE</th>
<th>FROM ( \alpha_M )</th>
<th>FROM ( \chi_M )</th>
<th>ATOMIC CORRELATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Adenosine</td>
<td>42.34</td>
<td>37.35</td>
<td>39.55</td>
</tr>
<tr>
<td>2</td>
<td>Sodium salt of Deoxyadenosine - 5'-Phosphate Hexahydrate</td>
<td>42.27</td>
<td>38.82</td>
<td>47.85</td>
</tr>
<tr>
<td>3</td>
<td>Adenosine-5'-methyl Phosphonate Hemi hydrate</td>
<td>49.47</td>
<td>44.28</td>
<td>50.81</td>
</tr>
<tr>
<td>4</td>
<td>Adenosine-5'-O'-methyl phosphate</td>
<td>50.00</td>
<td>44.65</td>
<td>52.41</td>
</tr>
<tr>
<td>5</td>
<td>Adenosine- 3'-phosphate Dihydrate</td>
<td>48.07</td>
<td>42.81</td>
<td>49.73</td>
</tr>
<tr>
<td>6</td>
<td>8- [(2-Aminoethyl) amino] adenosine cyclic3',5'- Monophosphate Tetra hydrate</td>
<td>55.79</td>
<td>50.17</td>
<td>56.85</td>
</tr>
<tr>
<td>7</td>
<td>8,2'-Anhydro-8-mercaptop-9-ß-D-arabino-furanosyladenine-5'- mono phosphate Tri hydrate</td>
<td>47.29</td>
<td>42.24</td>
<td>52.55</td>
</tr>
<tr>
<td>8</td>
<td>ß-Adenosine-2'-ß-Uridine-5'-Phosphoric Acid</td>
<td>86.44</td>
<td>71.69</td>
<td>82.87</td>
</tr>
<tr>
<td>9</td>
<td>2',3'-Dideoxy-2',3'-didehydroadenosine</td>
<td>35.57</td>
<td>33.64</td>
<td>35.78</td>
</tr>
<tr>
<td>10</td>
<td>Cordycepin</td>
<td>40.66</td>
<td>37.07</td>
<td>37.95</td>
</tr>
<tr>
<td>11</td>
<td>2'- O-Methyladenosine</td>
<td>45.79</td>
<td>41.04</td>
<td>42.22</td>
</tr>
</tbody>
</table>
**TABLE-5.10**

Molecular Electron Ionization Cross-Sections of guanosine and its derivatives

$Q \times 10^{16}$ cm$^2$

<table>
<thead>
<tr>
<th>S.No</th>
<th>MOLECULE</th>
<th>FROM $\sigma_M$</th>
<th>FROM $\chi_M$</th>
<th>ATOMIC CORRELATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Guanosine</td>
<td>43.19</td>
<td>32.97</td>
<td>39.55</td>
</tr>
<tr>
<td>2</td>
<td>Guanosine $3',5'$-cyclic monophosphate sodium tetrahydrate</td>
<td>47.73</td>
<td>37.67</td>
<td>48.88</td>
</tr>
<tr>
<td>3</td>
<td>Disodium deoxyguanosine-$5'$-phosphate tetrahydrate</td>
<td>48.98</td>
<td>38.43</td>
<td>49.45</td>
</tr>
<tr>
<td>4</td>
<td>8-Methylguanosine trihydrate</td>
<td>47.98</td>
<td>42.53</td>
<td>43.82</td>
</tr>
<tr>
<td>5</td>
<td>7-Methyl-8-oxo-7,8-dihydroguanosine monohydrate</td>
<td>50.88</td>
<td>44.48</td>
<td>45.41</td>
</tr>
<tr>
<td>6</td>
<td>2',3',5'-Tri-0-acetylguanosine</td>
<td>42.84</td>
<td>38.55</td>
<td>39.54</td>
</tr>
<tr>
<td>7</td>
<td>2'-deoxy-6-thioguanosine monohydrate</td>
<td>42.88</td>
<td>38.57</td>
<td>42.93</td>
</tr>
<tr>
<td>8</td>
<td>2',3'-O- Isopropylidene guanosine hemihydrate</td>
<td>53.09</td>
<td>46.99</td>
<td>48.59</td>
</tr>
<tr>
<td>9</td>
<td>2',3',5'-Tri-O-acetylguanosine</td>
<td>60.68</td>
<td>48.96</td>
<td>60.27</td>
</tr>
<tr>
<td>10</td>
<td>Disodium guanosine $5'$-phosphate heptahydrate</td>
<td>49.52</td>
<td>38.75</td>
<td>50.76</td>
</tr>
</tbody>
</table>
References