CHAPTER - 1

A GENERAL REVIEW ON SPACERS
1.1. INTRODUCTION:

According to Seebach "the primary motivation that once induced chemists to undertake natural products syntheses no longer exist and now chemists are drawn to supramolecular chemistry". The development of new synthetic methods in the area of host-guest chemistry, studies on molecular and ionic recognition, supramolecular catalysis, self organization, aggregation, signal transfer, allosteric effects etc. form a new branch of study called supramolecular chemistry. Macrocyclic molecules like synthetic crown ethers, cryptands, spherands, cyclophanes, natural cyclodextrins, tectons, calixarenes etc. also form interesting class of compounds in this branch.

The work of Disenhofer, Hüber and Mitchel on the photosynthetic apparatus of a bacterium have laid strong emphasis on carrying out work in distant effect for electron/energy transfer. Distant effect is not only discernible in chemical and biological system but also visible in sociological and political framework. For this effect to operate in any background, an organization is necessary. Attempts have been made to understand distant effect in a molecular system by studying the behaviour of molecules with spacer. The spacers act as the insulator and
give a quantitative measure of distant effect. The spacers by their rigidity or flexibility affect the properties. Therefore, the influence of spacer in various properties like equilibria, computer simulation studies, photochemical properties, reactivities have been reviewed.

1.2. FLEXIBLE MOLECULES IN FLUID PHASES:

Flexibility in molecules is interesting because of their diversity in behaviour. There is a very broad scope to study the structural, dynamic and rheological behaviour of flexible molecules in liquids and dense polymers. Fig. 1.1 shows a schematic representation of a long chain alkane molecule showing both intermolecular and intramolecular (excluded volume) interactions. To understand the

Fig.1.1. Schematic representation of an ideal chain molecule.
flexibility of the long chain, polybutane built from butane united-atom \((\text{CH}_2)_4\) sequences can be taken as the simplest long chain molecule which has torsional and bond bending degrees of freedom. The C-C bonds are often considered to be rigid.\(^{11}\) This type of model has been originally developed for liquid n-alkane simulations. However, in solid phases, where molecular conformations are more restricted than in the liquid phase, an all atom description like methylene groups with explicit hydrogen atom is required.\(^{12}\) Klein\(^{13}\) has made computer simulation molecular dynamic calculations to illustrate the diverse behaviour like self assembled monolayers composed of long-chain molecules, surfactant micelles in aqueous solution, soap films, model membranes and membrane-bound protein exhibited by n-alkane crystals.

Another simple flexible molecule is ethylene glycol in which both intra and intermolecular interactions have been considered for molecular dynamics simulations.\(^{14}\) Comparison of the behaviour of ethylene glycol molecules in water and in xenon solution has shown a small population of trans-conformer in the later indicating the existence of folding due to internal hydrogen bond formation.

The internal motion of flexible and semiflexible molecules can be described in terms of dynamic correlations between the rigid groups. For large flexible molecules intramolecular dynamic correlations and their dependence on the nature and properties of the surrounding liquid is considered. In such cases the random perturbations arise from interactions with the solvent molecules as well as from
the rest of the molecules. It is known that in polymer-like molecules the motion of monomers within a short time period becomes increasingly uncorrelated with increasing distance along the chain. 15-18

Dörf Müller et al. 19,20 have taken some anthroate derivatives with flexible and semiflexible links. They have tried to describe the internal motion of these molecules (1, 2, 3) in terms of dynamic correlation between rigid groups. Study of molecules having one scattering group and a long alkyl chain (1) shows that the dynamic correlation between

\[ R = -(CH_2)_n - CH_3 \ (n = 0, 1, 2, 3, 5, 7, 11), -C(CH_3)_3 \]

1

2

3

\( n = 2, 8 \)
the head group and the methylene groups of the chain is quite large and decreases only slightly with distance from the head group. The groups separated by more than five or six methylene groups, however, move in an increasingly uncorrelated way. The molecules with two scattering groups with rigid link (2) and flexible link (3) behave differently as shown in Fig. 1.2 which displays the geometry of two molecules. In case of (2) reorientation of the molecules can be observed taking the molecule as a whole, whereas, for a flexible link (3) between two groups there is some internal reorientation due to non-parallel configuration of the vectors \( Y_1 \) and \( Y_2 \).

Fig. 1.2: Schematic representation of the alkanediyl dianthroates.
The chord model of flexible alkane solute ordering in the nematic phase is extended to dimer molecules. Dimers are interesting as they provide opportunity to evaluate molecular flexibility in a well defined system by systematic variation of molecular topology. Molecular flexibility depends upon a set of conformations that the molecule can assume and affects the ordering of the molecules in nematic medium. Photinos et al have examined the effect of linkage between the mesogenic core and flexible spacer on the ordering properties of the dimers by studying the homologous series of cyanobiphenyl (CB) ethers, \( \text{CBO-} \{ \text{CH}_2 \}_n \text{-OCB,} \{ n = 2-10 \} \) (Fig.1.3) with different primary structural topologies, i.e. with para-, meta-, ortho-, linkages. In case of these dimers, molecular conformations are generated by internal rotations about (i) the bond of the spacer chain, (ii) the bond linking the spacer chain to the cyanobiphenyl cores and (iii) the biphenyl para-axis (in the case of CBO-DN dimers). In order to explore the effect of the linkage topology on the orientational ordering of the chain, the order parameters of the chord segments of the spacer chain of the three CBO dimer families (\( \alpha-, \beta-, \gamma- \)) with even and odd spacer chains (\( n = 2-10 \)) have been calculated. From the results of these calculations it is observed that the chord ordering decreases towards the middle of the \( \beta- \) linked spacer chain, whereas it increases in case of the \( \alpha- \) linked spacer and remains essentially constant along the \( \beta- \) linked spacer.
Fig 1.3: Schematic representation of dimer molecules with para, meta and ortho linkages of the core to the spacer chain, showing structural differences associated with the topology of the core chain linkage and the parity of the spacer chain (even and odd number of atoms).
Dimer mesogens, where a hydrocarbon spacer chain links two mesogenic cores are technologically important because they provide liquid crystalline system. Introduction of flexibility in several oxetane derivatives (4) carrying azobenzene moiety also creates a liquid crystalline system. Azobenzene moiety anchored to a flexible main chain can move more smoothly in the polymer matrices to create a liquid crystalline system than the mesogenic groups anchored to a rigid main chain.

\[
\text{R} = \text{CH}_3\text{O}^-, \text{H}, \text{nC}_4\text{H}_9\text{O}^-, \text{nC}_6\text{H}_{13}\text{O}^-, \\
n = 0, 1, 2. m = 4, 5, 6.
\]

1.3. EQUILIBRIA:
1.3.1. Acidity and basicity:

The \( pK_a \) values of dibasic acids\(^\text{25} \) are found to increase with increase in the chain length of the spacer which act as insulator (Table-1.1).
Table 1.1. $pK_a$ values of some dibasic acids, chloroacids and aminoacids.

<table>
<thead>
<tr>
<th>Acid</th>
<th>n</th>
<th>$pK_a$</th>
<th>$\Delta pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: HOOC ((CH_2)_n) COOH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>1.25</td>
<td>3.81</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2.05</td>
<td>5.70</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4.21</td>
<td>5.64</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4.32</td>
<td>5.42</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4.41</td>
<td>5.41</td>
</tr>
<tr>
<td>B: Cl((CH_2)_n) COOH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2.86</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4.52</td>
<td></td>
</tr>
<tr>
<td>C: NH$_3^+$ (CH$_2$)$_n$ COOH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2.34</td>
<td>9.60</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3.60</td>
<td>10.20</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4.23</td>
<td>10.43</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4.27</td>
<td>10.79</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>4.43</td>
<td>10.79</td>
</tr>
</tbody>
</table>
The relationship of $pK_a$ value with the spacers can be correlated to the inductive effect operating in the molecule. In case of chloroacids \cite{26} and aminoacids \cite{27} ionization constant values have been observed to be decreasing with the increase in inductive effect arising out of decrease in the length of the spacer group.

The $pK_a$ values of a homologous series of diacidic bases are given in table 1.2. \cite{28} The effect of one ionized amino group upon the other amino group falls off with increasing spacer chain in the molecule.

Table 1.2. $pK_a$ values of some diacidic bases, $\text{NH}_2(\text{CH}_2)^n\text{NH}_2$.

<table>
<thead>
<tr>
<th>Value of 'n'</th>
<th>$pK_a$</th>
<th>$\Delta pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>9.92</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.86</td>
<td>3.06</td>
</tr>
<tr>
<td>3</td>
<td>10.55</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.88</td>
<td>1.67</td>
</tr>
<tr>
<td>4</td>
<td>10.80</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.63</td>
<td>1.17</td>
</tr>
<tr>
<td>8</td>
<td>11.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.10</td>
<td>0.90</td>
</tr>
</tbody>
</table>

The $\Delta pK_a$ values in each class of compounds decrease asymptotically with increase in spacer chain.

Inductive effect is a through bond effect whereas field effect operates through space. In the compounds 5 and
6, the inductive effect of the chlorine atoms on the dissociation of COOH and hence on the acidity should be same, but the lower pK$_a$ values of 5 as compound to that of 6 may be ascribed to the distant effect in space because the chlorine atom is closer in space to the COOH in isomer 5 than it is in 6.\textsuperscript{29}

\begin{align*}
\text{pK}_a &= 5.67 \\
\text{pK}_a &= 6.07
\end{align*}

It is also observed that the presence of insulating environment between two sites alters the properties as compared to a situation where conducting environment is available. This is suitably illustrated from the ratio of dissociation constant values of malonic acid (7) and diethyl malonic acid (8).\textsuperscript{30} In 7, the COOH groups are solvated by water molecules, as a result, the field effect due to a COO\textsuperscript{−} is experienced by the COOH group, whereas in 8, the presence of hydrophobic ethyl groups insulate the field effect.

\begin{align*}
\frac{k_1}{k_2} &= 700 \\
\frac{k_1}{k_2} &= 120,000
\end{align*}
1.3.2. Stacking:

Due to n-frame work aromatic rings stack with appropriate orientation and change the molecular characteristics. There are many evidences put forth for stabilization of arene dimers with stacked and "T-Shaped" configurations. Masnovi et al. have investigated the crystal structures and reactivities in solution of dicarbazolyl alkanes (9) in which two carbazole rings are linked at nitrogen by a polymethylene spacer of varying chain length. The nature of interchromophoric interaction influence the delocalization of charge and spin upon oxidation of these compounds to the respective radical cations $[M]^+$. (10).

\[ N \cdots (CH_2)_n \cdots N \]

\[(X = H, NO_2; n = 1-5)\]

\[ (R' = -(CH_2)_n \cdots N \cdots R') \]

\[ [M]^{\cdots} \]

\[ (R = -(CH_2)_n \cdots N \cdots R') \]
Specifically, interaction between two carbazole rings has been found to be stabilizing for [M]⁺⁺ when n = 3 in which "sandwich" stabilization is observed. For n = 4, a "non-sandwich" parallel planar interaction is possible which is less stabilizing. No stabilization has been evident for [M]⁺⁺ with n = 2 and n = 5, for which only non-planar interactions are accessible. The carbazole groups of n = 1 also are prohibited from being parallel, although they are constrained to lie together.

Itahara et al.⁴⁶ have reported the synthesis of some heterocycles containing spacer chain with a view to see the effect of spacer on stacking of heterocyclic rings. They have synthesized three compounds (11, 12, 13) by treatment of theophylline, theobromine and 3-methyl uracil with dibromoalkanes X(CH₂)ₙ X (X = Br or I, n = 1-12). The difference in chemical shift values of H₉ in D₂O for 11 (n = 3) and 11 (n = 10) at 27°C and 70°C is 0.22 and 0.17 ppm respectively, whereas that for 12 (n = 3) and 12 (n = 10), 13 (n = 3) and 13 (n = 10) are 0.02 and 0.01 ppm respectively.

![Chemical structure](image)

\((n = 1 - 12)\)

11

13
These results indicate stacking between the purine rings in 11 only. Though 11 and 12 are structural isomers, 12 does not show any stacking. It is also observed that the chemical shift of $H_g$ is upfield for $n=1$ and changes to a downfield shift for $n=2$ for 11 and 13 but no such change occurs for 12. Subsequent increase in carbon chain does alter the chemical shift values by a small margin. The polymethylene chain of 11 may aggregate in $D_2O$ as a result of which the purine ring may stack (Scheme-1.1). Such a situation may also occur in 12 and 13 but the positive charges on nitrogen (scheme-1.2) do not allow such a stacking process to occur.
1.3.3. Binding:

Cyclodextrins are cyclic oligomers of 1-4 linked α-D glucose monomers. The inner cavity of a cyclodextrin (CD) is hydrophobic in character, allowing the formation of inclusion complexes with a wide variety of organic molecules α-, β- and γ-Cyclodextrins having six, seven and eight glucopyranose units respectively can form strong host-guest complexes with ferrocene in aqueous as well as in organic media. To study the effect of spacer on binding constants,
cyclodextrins attached to a ferrocene moiety through a spacer have been used. Osa et al. have reported the synthesis of some ferrocene appended cyclodextrins (14) and have studied the effect of spacer length on binding constants of the host-guest complexation.

(a) \( \chi = \beta-CD, n=0 \)
(b) \( \chi = \gamma-CD, n=0 \)
(c) \( \chi = \beta-CD, n=3 \)
(d) \( \chi = \gamma-CD, n=3 \)
(e) \( \beta-CD \)
(f) \( \gamma-CD \)

The host-guest binding constants \((K)\) of 14a-14d (Table-1.3) for several guests like 1-borneol, 1-adamantanol etc. are markedly small compared to the \(K\) values of corresponding native cyclodextrins. This result indicates that the ferrocene moiety itself acts as an intramolecular inhibitor for host-guest complexation. The presence of spacer chain in ferrocene moiety further lowers the binding constant values. This occurs due to increase in the freedom of the movement of ferrocene moiety attached to a long alkyl chain, thus forming intramolecular cyclodextrin-ferrocene complexes.
Table 1.3: Host-guest binding constants ($K$) of cyclodextrins for several guests in 20% ethylene glycol aqueous solutions at 25°C.

<table>
<thead>
<tr>
<th>Guest</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Borneol</td>
<td>2630±50</td>
<td>591±3</td>
<td>225±5</td>
<td>191±5</td>
<td>8500</td>
<td>3700</td>
</tr>
<tr>
<td>1-Adamantanol</td>
<td>2880±10</td>
<td>405±3</td>
<td>223±5</td>
<td>172±5</td>
<td>14500</td>
<td>5160</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>893±7</td>
<td>1070±20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1-Menthol</td>
<td>255±5</td>
<td>129±5</td>
<td>-</td>
<td>-</td>
<td>3980</td>
<td>1260</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>58.5±2.5</td>
<td>6.9±0.1</td>
<td>45.3±4.7</td>
<td>-</td>
<td>930</td>
<td>-</td>
</tr>
</tbody>
</table>

Vicens et al\(^\text{15}\) have synthesized some calixarene Schiff base (15) and have observed that metal ion binding by these calix [4] arenes depends on the length of the bridge. They have noticed that the ligand containing a bridge of three carbon atoms form stable complexes. The stability of the complexes is found to decrease for the longer bridged ligand and also for rigid aromatic ligand.
Reinhoudt et al.\textsuperscript{49} have synthesized some metallocliefs (16,18,19) and metallomacrocycles (17) possessing a Lewis acidic uranyl cation and have studied host-guest complexation behaviour of these molecules.

\begin{align*}
(R = \text{a: } & -(\text{CH}_2)_3-, \text{b: } -(\text{CH}_2)_4, \\
& \text{c: } -\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-)
\end{align*}

\begin{align*}
(R = & \text{H, OMe})
\end{align*}
In the metallomacrocycles (17) rotations around the -O-CH$_2$- and -CH$_2$-C$_6$H$_5$- bonds are restricted by connecting the two aromatic rings of the original cleft (16) by a spacer and are more organized than 16. In metalloclefts (18) the only conformational freedom is the rotation of the phenyl group of the biphenyl unit. All these compounds (16-19) form complexes with guests like pyridine and its derivatives, aniline, isoquinoline, benzylamine, benzonitrile, benzamide, N-phenylurea etc. The metallocycles (17) with an extended cleft forms more stable complexes. The maximal stability has been observed for 17b benzylamine complex. This is because in this case the distance between the benzyl groups of the cleft (17b) is 6.8-6.9 Å which is the optimal distance of aromatic rings for π-π stacking.

"Molecular tweezers" are interesting because of their capability to bind or trap organic molecules of different sizes. Chen and Whitlock have synthesized several bifunctional derivatives of caffeine with spacers. The compounds (20-23) possess following characteristic features to enhance complexation of aromatic molecules in aqueous solution.
of the two caffeine moieties and
(ii) The caffeine-caffeine distance in the syn-conformation is 7Å° which is optimum for insertion of a π - system between the rings.

They have shown that molecules with rigid diyne spacer can associate strongly with 1,3-dihydroxy-2 naphthoate (DHNA) whereas compounds with flexible spacer are less capable to associate.

Zimmerman et al.\textsuperscript{51-53} have synthesized some compounds with aromatic chromophores with spacers (24,25) and referred these molecules as "molecular tweezers". These compounds possess an interchromophoric distance of 7Å° and can form complexes with guest molecules of unrestricted
length and width provided they have the thickness of a single aromatic ring.

Mishra et al. have attempted to synthesize tweezer like compounds with styryl chromophores having nonabsorbing flexible spacers.

They have studied the spectral properties of these compounds. The 4-styryl dyes having electron donating groups suffer from bathochromic shift with decrease in spacer length.
length whereas the reverse effect takes place with electron withdrawing groups.

They have also observed the adsorption behaviour of 26 on silica surface. The area of coverage per molecule on the silica surface are found to increase with increase in spacer length. This result implies that the two chromophoric groups sit on the silica surface with methylene bridge and thereby increase the area of coverage values.

Wuest et al. have devised small complementary molecules that can act as autocatalytically effective template for their own replication. It has been observed that the flexible templates do not have constraints of self association and hence are able to recognize their constituent parts, bind them and accommodate the transition state of reaction that joins them together. In contrast, rigid templates can be designed to be perfectly self complementary and to orient the subunits in close juxtaposition. But these type of templates have been found to be ineffective promoters of the coupling step because of their high degree of self association. For example, pyridones can be linked by spacer to create self complementary molecules known as dipyridones that are able to form strong duplexes (28) and triplexes (29) joined by multiple hydrogen bonds. Despite its structural simplicity these compounds have been found to encode little chemical information to control its own replication.
Gemini surfactants are a class of self assembling molecules possessing in sequence, a long hydrocarbon chain, an ionic group, a spacer, a second ionic group and another hydrocarbon tail (fig-1.4). This class of surfactants have a higher critical micellar concentration and form small micelles despite the potential to grow, polymer-like, into extended strands. Menger and Littau have investigated aggregation of geminis (30-32) by surface tension, film-balance.

Fig.1.4. Schematic representation of gemini surfactants.

- □ = spacer, ● = ion, — = hydrocarbon

30

31
methods, dynamic scattering $^1\text{H}$ and $^{23}\text{Na}$ NMR and spectral changes in adsorbed dye.

Recently Rosen and Song$^{59}$ have investigated the effect of spacer on dynamic properties of gemini surfactants. Liu$^{60}$ has observed the interaction of some diquarternary gemini surfactants with anionic surfactants.

Menger and Littau$^{61}$ have reported that the surfactants such as octadecyl phosphate form micelles in which the chains extend inwardly within the spherical aggregates. However, surfactants having two chains such as dioctadecyl phosphate (33) form bilayers due to pairing of

$$\text{CH}_3\text{(CH}_2\text{)}_{15}\text{-O-P-O-Ph-CH=CH-Ph-O-P-O-(CH}_2\text{)}_{15}\text{-CH}_3$$

chains. A rigid spacer prevents the pairing of the chain. They have further observed that this class of surfactants have some unusual properties e.g. they cannot form aggregates without exposing hydrocarbon tails to the water in contrast to conventional surfactants.
1.4. CONFORMATIONAL STUDIES:

Metacyclophanes (MCP) are important both synthetically and stereochemically and therefore have aroused interest for the past two decades with particular attention paid to [2,2] metacyclophanes since it possess anti-stepped conformation. Krois and Lehner have reported that in [3,3] MCP, the aromatic rings adopt the syn-arrangement (34), its lower and higher homologues i.e. [3,2], [4,2] and [4,3] MCPs have the mobile-anti conformation (35). The ring inversion barrier (eq-1.1) for the higher [m,n] MCPs is found to increase with decreasing length of the spacer (Table-1.4).

![Diagram](image)

Table 1.4: Coalescence temperature (Tc) and energy barriers \( \Delta G_c \) for \([m,n]\) MCPs with \( n = 2, 3, 4 \).

<table>
<thead>
<tr>
<th>No. of methylene carbons ( n ) in the MCP (34)</th>
<th>Tc ( (^\circ C) )</th>
<th>( \Delta G_c ) ( \text{(kcal/mol)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>&gt;190</td>
<td>&gt;27</td>
</tr>
<tr>
<td>3</td>
<td>90</td>
<td>17.5</td>
</tr>
<tr>
<td>4</td>
<td>35</td>
<td>14.3</td>
</tr>
</tbody>
</table>
By substituting methyl groups in the benzene nucleus, Yamato et al. have studied some \([m,n]\) metacyclophanes (MCP) higher than \([4,2]\) MCP (36, 37, 38).

\[
\begin{align*}
\text{36: } X &= S \\
\text{37: } X &= S\text{O}_2 \\
\text{38: } X &= -
\end{align*}
\]

Chemical shift values (\(\delta\)) of internal methyl protons of 2-thia \([3,n]\) metacyclophanes, 2-thia \([3,n]\) metacyclophane dioxide and \([n,2]\) metacyclophane are given in table-1.5.

**Table 1.5: Chemical shift (\(\delta\)) of internal methyl protons of 2-thia \([3,n]\) MCPs (36), 2-thia \([3,n]\) MCP (37) dioxide and \([n,2]\) MCPs (38).**

<table>
<thead>
<tr>
<th>No. of methylene carbons (n) in MCPs</th>
<th>(\delta) -values</th>
<th>36</th>
<th>37</th>
<th>38</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.84</td>
<td></td>
<td></td>
<td>0.55</td>
</tr>
<tr>
<td>3</td>
<td>1.12</td>
<td>1.12</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.28</td>
<td>1.24</td>
<td>0.86</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.47</td>
<td>1.23</td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1.49</td>
<td>1.39</td>
<td>1.25</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1.80</td>
<td>1.70</td>
<td>1.47</td>
<td></td>
</tr>
</tbody>
</table>
It is seen that the chemical shift values are highly dependent on the number of methylene carbons. Change in $\delta$ value between $n = 2$ to 8 is 0.966 for 36 and 0.926 for 38. These chemical shift values provide information regarding any conformational change. The conformation of these compounds have been found to be sensitive to the length of the spacer. In this case also the ring inversion barrier (eq-1.2) decreases with increasing length of the spacer (Table-1.6).

Table 1.6: Coalescence Temperature ($T_c$) and energy barriers ($\Delta G_c$) of 2-thia [3, n] MCPs, 2-thia [3, n] MCP dioxides and [n, 2] MCPs.

<table>
<thead>
<tr>
<th>No. of carbon (n) in MCPs</th>
<th>$T_c(\Delta G_c)$</th>
<th>$T_c(\Delta G_c)$</th>
<th>$T_c(\Delta G_c)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$&gt;150$</td>
<td>$&gt;150$</td>
<td>$&gt;150$</td>
</tr>
<tr>
<td>6</td>
<td>90(16.6)</td>
<td>120(18.9)</td>
<td>$&gt;150$</td>
</tr>
<tr>
<td>8</td>
<td>$&lt;-60$</td>
<td>$-50(10.3)$</td>
<td>140(20.5)</td>
</tr>
</tbody>
</table>

Synthesis and structural analysis of dimethoxy derivatives of cyclobutane fused [n, 2] metacyclopahnes (39) having cyclobutane ring bridge and methoxyl groups at para positions have been reported. These compounds ($n = 6, 8, 10$).
and 12) have only syn-conformation as confirmed by $^1$H NMR spectrum. Table 1.7 shows that Δδ values are small and nearly zero. This implies that due to existence of steric repulsion between methoxyl groups and methylene groups of alkyl bridge, formation of syn-conformer dominates the reaction. The strain energy of the compounds (Table-1.8) gradually increases from n = 6 to n = 12 in the range of 10 kcal/mol thus showing that increasing spacer length decreases the stability of the compound.

![Diagram](attachment:image.png)

( n = 6,8,10,12)

Table 1.7. Conformational Analysis of cyclophanes(39):

<table>
<thead>
<tr>
<th>Compound</th>
<th>Hα (δ)</th>
<th>Hβ (δ)</th>
<th>Δδ</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 6</td>
<td>6.79</td>
<td>6.61</td>
<td>0.18</td>
<td>syn</td>
</tr>
<tr>
<td>n = 8</td>
<td>6.73</td>
<td>6.64</td>
<td>0.09</td>
<td>syn</td>
</tr>
<tr>
<td>n = 10</td>
<td>6.67</td>
<td>6.63</td>
<td>0.04</td>
<td>syn</td>
</tr>
<tr>
<td>n = 12</td>
<td>6.67</td>
<td>6.62</td>
<td>0.05</td>
<td>syn</td>
</tr>
</tbody>
</table>
Table 1.8: Strain energy (SE) and strain energy difference (ΔSE) of cyclophanes (39).

<table>
<thead>
<tr>
<th>No. of methylene groups (n)</th>
<th>SE (kcal/mol)</th>
<th>ΔSE (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>54.4</td>
<td>25.7</td>
</tr>
<tr>
<td>8</td>
<td>54.6</td>
<td>25.9</td>
</tr>
<tr>
<td>10</td>
<td>58.8</td>
<td>30.1</td>
</tr>
<tr>
<td>12</td>
<td>64.7</td>
<td>36.0</td>
</tr>
</tbody>
</table>

Bates et al. have prepared some metacyclophanes (40, 41) and have discussed the preferred conformation of these cyclophanes. They have reported two types of structure for dimers. One type has methoxyls on opposite side of the large ring (where \( n \) = even), other type has methoxyl on the same side of the ring (where \( n \) = odd). The change from a tight loop in small rings to loose loop in large ones comes at the 18 membered ring (\( n = 15 \)) for monomeric compounds (40). For dimeric compounds (41) this change comes at 16-18 membered ring (\( n = 5-6 \)) compounds. From NMR study they have also shown that the compound with \( n = 9 \) is the most stable which is further confirmed by X-ray analysis.
The conformational flexibility and the intramolecular hydrogen bonding of a series of \([n,3,3] \) propylenediols and related compounds (42-49) has been studied by Khot et al.\(^6\) They have shown that the preferred conformation of the bicyclo [3,3,0] octyl portion of these molecules depends on spacer length. For compounds with no spacer and with the larger and flexible spacer down-down-hydrogen bonded (DDH) form dominates along with significant amount of up-down (UD) form. Intermediate compounds i.e. 44, 45, 46 prefer DDH, up-up (UU) and UD forms respectively.

A change in chemical shift values of carbazolyl protons (\(H_a, H_b, H_c\)) due to change in spacer in \(1, n\) dicarbazoylalkanes (9) has been reported by Masnovi et al\(^4\) (Table-1.9).
Table: 1.9: Chemical shift values ($\delta$) for $H_a$, $H_b$ and $H_c$ protons of 1,8 dicarbazolylalkanes:

<table>
<thead>
<tr>
<th>No. of methylene Carbons (n) in (9)</th>
<th>$\delta$ for $H_a$</th>
<th>$\delta$ for $H_b$</th>
<th>$\delta$ for $H_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.00</td>
<td>8.11</td>
<td>8.31</td>
</tr>
<tr>
<td>2</td>
<td>8.82</td>
<td>8.00</td>
<td>8.07</td>
</tr>
<tr>
<td>3</td>
<td>8.99</td>
<td>8.14</td>
<td>8.25</td>
</tr>
<tr>
<td>4</td>
<td>8.98</td>
<td>8.12</td>
<td>8.28</td>
</tr>
<tr>
<td>5</td>
<td>8.99</td>
<td>8.12</td>
<td>8.29</td>
</tr>
</tbody>
</table>

It is noticed from Table 1.9 that the spacer plays a role in the chemical shift values of the protons. In this case also the compound with $n = 1$ shows an upfield shift whereas the same compound with $n = 2$ shows a downfield shift. With increasing spacer chain length, the progressive upfield shift is noticed.

Behera et al.\(^8\) have synthesized a series of schiff bases with spacers (50,51) and have observed that the chemical shift values of the protons of the alkyl chain change with the change in the number of carbon atoms in the spacer.

\[ \text{(o-e, X = -(CH}_2)_n \text{, where } n = 0,2,3,4 \\& 6 \text{ resp.}} \]

50 51

31
The structures of isomeric compounds of different stereochemistry can be elucidated by utilizing Nuclear Overhauser Effect (NDE), where interaction of different magnetic nuclei occurs through space. The NDE is only noticeable over short distances, generally 2-4 Å, falling off rapidly as the inverse sixth power of the distance between the nuclei. The structure of oxindole has been established to be 52 and not 53 on the basis of NMR studies.

In 52, the distance between H₅ and H₇a is small, as a result of which a mutual interaction becomes possible. This is, however, not possible in 53.

Hoffmann and coworkers in 1968 have proposed that through bond interactions are relatively large in magnitude and strongly dependent upon the orientation of the intervening bonds. Subsequently, Grob, Cookson et al., Hudec have carried out various investigations on the structural effect on chemical characteristic and UV spectra. Paulson et al. have used charge transfer rates to investigate the structural dependence of through bond coupling on spacer structure. In consistence with Hoffman's
prediction they have also noticed that the rates suggest the following relationship.

1 trans-chain \[ \cong \] 2 gauche chains \[ \cong \] 3 (or 4) cis' chains

i.e. gauche \[ \cong \] 1/2 trans, cis \[ \cong \] 1/3 (or 1/4) trans.

1.5. PHOTOCHEMISTRY:
1.5.1. Reaction:

Mutai et al\textsuperscript{76} have reported the photochemical behaviour of some bichromophoric chain molecules (54) with an electron acceptor (A) and an electron donor (D) at the terminal ends. They have shown that the reactivity of a homologous series of compounds (54, \(n = 2-10, 12\) and 16) depends on the spacer length. The compounds having \(n = 2-6\) undergo nucleophilic rearrangement to give \(\omega\)-(p-nitrophenyl) amino alkanol (eq - 1.3) while the compounds with \(n \geq 8\) undergo an intramolecular photoredox reaction to give \(\omega\)-(p-nitrosophenoxy) alkanol and aniline (eq-1.4). The compound with \(n = 7\) does not exhibit any of

\[
\text{O}_2\text{N} - \text{O} - (\text{CH}_2)_n \text{NH} \quad \text{hv} \quad \overset{n=2-6}{\longrightarrow} \quad \text{O}_2\text{N} - \text{N} - (\text{CH}_2)_n \text{OH}
\]

... 1.3

\[
\text{O}_2\text{N} - \text{O} - (\text{CH}_2)_n \text{NH} \quad \overset{n=8-16}{\longrightarrow} \quad \text{ON} - \text{O} - (\text{CH}_2)_n \text{CHO} + \quad \overset{\text{H}_2\text{N}}{\text{H}_2\text{N}}
\]

... 1.4
these two types of photoreactions. Variation in the nature of the product can be explained as follows.

Photoredox reaction requires abstraction of H-atom from an active methylene group which is possible when a cyclic transient conformation occurs due to relative disposition of the two terminal aromatic rings to give a head-to-tail geometry (55). This is impossible in case of lower homologues because of the limit of the short polymethylene spacer chains. Lower homologues can only possess head-to-head type conformation (56) which leads to a rearranged product. Photoinduced intramolecular electron transfer to generate a radical ion pair is observed for all homologues and the quantum yield is found to decrease with increasing chain length.

Fluorocarbon molecules are more hydrophobic than hydrocarbons and form aggregates in aqueous organic solvents which provide models for molecular assemblies having valuable application in various disciplines of Chemistry. Tung et al have taken fluorinated alkyl 2-naphthoates \( \text{NpCOOC}_2 \text{F}_{2n+1} \) (\( \text{NpFC}_n \), \( n = 4, 7, 12; \text{Np = 2 naphthyl} \)) and 9-anthrylmethyl perfluoroalkanoates.
investigate the emission spectra and photodimerisation of these compounds. Addition of long chain fluorocarbon compounds to the solution results in reduction in the excimer emission and an enhancement of monomer emission.

Selective excitation of the naphthalene moiety in the mixture solution of NpFC\textsubscript{n} and AnFC\textsubscript{n} leads to a strong emission from AnFC\textsubscript{n}. Photoirradiation of NpFC\textsubscript{n} (57) yields a 'cubane like' photodimer (58) with 100% quantum yield (Scheme-1.3). All these observations suggest that hydrophobic interactions force molecules with long fluorocarbon chains to form aggregates in aqueous organic binary mixtures.
1.5.2. Synthesis:

The photochemistry of aromatic azides is of interest due to its application in photoresist systems and in biochemical photo-affinity labelling.\textsuperscript{81-84} Tomioka et al.\textsuperscript{85} have examined the photochemistry of 2-(ω-phenyl alkyl) phenyl azides (59, n = 1-4) to investigate the reaction of a photolytically generated aryl nitrene with an intramolecular C-H bond. Irradiation of a solution of azide (n = 1-4) in cyclohexane shows that product distribution is dependent on the chain length of the spacer group at the 2-position. 2-Azidodiphenyl methane (59a) in cyclohexane on irradiation gives a mixture of the corresponding azobenzene (60) and the aniline (61) both of which are considered to be products of the triplet state of nitrene. No evidence for the intramolecular CH insertion of the photolytically generated nitrenes could be detected. In contrast, the photolysis of 2-(2-phenyl ethyl) phenyl azide (59b) gives 2-phenyl indoline (62) exclusively due to intramolecular insertion of

![Image of chemical structures](image.png)
the nitrene into a $\beta$-CH bond of the 2-phenyl ethyl group. For photolysis of 2-(3-phenyl propyl) phenyl azide (59c) intramolecular insertion into a $\gamma$-CH bond occurs which gives 2-phenyl-1,2,3,4-tetrahydroquinoline with only 10% yield. A major photoreaction product is corresponding azobenzene. Further elongation of the methylene chain ($n = 4$) at the 2-position resulted in a considerable decrease (Yield = 2%) in the formation of intramolecular CH insertion products (63d) and gives corresponding azobenzene almost exclusively. The variation of product distribution as dependent on the chain length of the spacer can be explained as follows.

In the nitrene generated from benzylic $\beta$-hydrogens can be located close to the nitrenic centre, assuming a free rotation of 2-nitrenophenyli group around the $C_{\text{Ar}} - C_{\alpha}$ bond. Therefore, the intramolecular CH insertion can occur smoothly to give 2-phenyl indoline (62). However, for 1,3-disubstituted propanes, the nitrene generated from this compound prefer a trans-trans conformation about the $C_{\alpha} - C_{\beta}$ and $C_{\beta} - C_{\gamma}$ bonds respectively, such that the nitrene cannot interact with reactive benzylic $\gamma$-hydrocarbons (scheme-1.4) and as a result only trace amounts of 2-benzyl indole (63c) are obtained. These observations imply that the rate of reaction with an unreactive $\beta$-CH bond is considerably reduced so that the dimerization of the triplet nitrene to give the azobenzene predominates. Thus, the 2-phenyl tetrahydroquinoline (62c) species obtained would originate from the nitrene with a less stable gauche-trans
conformation. This explanation accounts for a low yield of the intramolecular CH insertion products in the photolysis of 2- (3-phenyl propyl) phenyl azide.

1.5.3. EMISSION:

The influence of microenvironment on the quenching of zinc phthalocyanine excited states by viologens has been studied by Jixiang et al.\textsuperscript{86} The fluorescence quenching and laser photolysis studies indicate that the functional surfactants are solubilized at different sites in micelles, the process depends upon chain length and exerts great influence on the quenching of zinc phthalocyanine excited states.

In a recent study zinc tetraphenyl porphyrin (ZnP, 64) complex containing four substituted amphiphilic chains has been embedded in liposomes. The distance from the porphynin plane to the outer aqueous phase has been varied
by changing the alkyl chain length (i.e. \(-\text{CH}_2\)^n, n = 4, 6, 10 and 18). Thus the distance from the embedded ZnP to the outer phase has been changed from 9 to 27\(\text{Å}^0\). In the study of electron transfer reaction from the excited complex to an acceptor in the outer aqueous phase Kaneko has shown that in presence of the methyl viologen (MV\(^{2+}\)) quencher, the electron transfer occurs at a distance of less than 12\(\text{Å}^0\). This is in agreement with the report that electron transfer processes occur at a distance of less than 13\(\text{Å}^0\) in biological system.

Behera et al. have synthesized some O-alkyl derivatives of naphthols (ROR') having long hydrophobic chain (65) and (methylene)\(^n\) bis-\(\gamma\)-picolinium salts (66) with \(n = 1, 2, 4, 6\). Fluorescence quenching studies of naphthols and alkyl naphthols have been done with \(\text{CCl}_4\) and \(\gamma\)-picolinium salt in microemulsion media. It has been
observed that radii of the quenching sphere of action does not alter for all the alkyl derivatives when CCl₄ is taken as the quencher. The coefficient of relative diffusion of CCl₄ towards excited alkyl naphthols has been found to have no significant relation with the chain length of ROR'.

\[ R' = \text{CH}_3, \text{C}_9\text{H}_{19}, \text{C}_{12}\text{H}_{25}, \text{C}_{16}\text{H}_{33}, \text{C}_{18}\text{H}_{37} \]

However, transient quenching constant (\(K_T\)) values show variation when \(\gamma\)-picolinium salts are taken as quencher. The \(K_T\) values remain same with change in spacer length of salts for \(\alpha\)- and \(\beta\)-naphthols whereas these values decrease with increase in spacer length for alkyl naphthols. These results have been explained on the basis of locational and orientational behavior of both fluorophores and quenchers at the interface of microemulsion media.
1.6: SPECTRAL BEHAVIOUR:

Reversal in solvatochromism by some cyanine dyes (67) has been observed by Behera et al ⁹⁰. Two sets of solvents like acetone, DMF, DMSO, CH₃CN, pyridine (HBA type) and water, methanol, ethanol, 2-propanol, 1-butanol and t-butanol have been taken for study. The reversion in solvatochromism is found to be independent of the nature of spacers and occurs at almost a constant $E^*(30)$ value (49.8).

![Chemical structure](image)

However, they have observed that the sensitivity of $E^*(30)$ values towards $\lambda_{max}$ values in case of solvents like 2-propanol, isobutanol and tertiary butanol changes with the nature of the spacer.

Spectral behaviour of some Schiff bases (50,51) are studied in microemulsion media and in organic solvents by Behera et al ⁹¹. The compounds (50) show a peak at 221 nm in hexane. The $\varepsilon_{max}$ values for the 221 nm peak are found to increase with increasing the length of the spacer. A plot of $\varepsilon_{max}$ values versus the number of carbon atoms obeys eqn-1.5.

$$\varepsilon_{max}(221) = \varepsilon_0 + 0.61n \quad ...1.5$$

where $n$ is the number of carbon atoms in the spacer. The
spectra of these compounds are found to show a hypsochromic shift in w/o to o/w microemulsion as the spacer becomes more and more hydrophobic. This is due to a greater pulling effect of the compound towards the hydrophobic region of microemulsion.

1.7. BIOLOGICAL SYSTEM:

Spacers also play an important role in biological processes like cloning of genes, elastic stability of DNA trajectories in chromatin fibres, photosynthesis etc.

Geralds\textsuperscript{92} has studied the elastic stability of the trajectory of DNA in the solenoid model for the 30 nm chromatin fibre as extended by McGhese et al to visualise both internucleosomal (spacer) DNA and DNA bound to core histones.

In photosynthesis,\textsuperscript{93} the light induced charge separation has been achieved through spatial arrangement of the pigments and elements of the electron transport chain in the thylakoid membrane. Photooxidation of water to oxygen (eq-1.6) accompanied by photoreduction to formaldehyde (eq-1.7) are connected through electron transport chain.

\begin{align*}
2\text{H}_2\text{O} & \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- & \ldots 1.6 \\
\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- & \rightarrow (\text{CH}_2\text{O}) + \text{H}_2\text{O} & \ldots 1.7 \\
\end{align*}

To mimic photosynthesis or to develop photosynthetic units artificially, the following conditions are required.
(a) A photo-antennae involving organized dyes such that a bathochromic shift in the organized system is observed. These organized dyes act as donor.

(b) The electron transfer from the donor to an acceptor should have a distance effect such that the thermal back electron-transfer leading to degradation of light energy to thermal energy is avoided.

(c) A potential energy barrier between the donor and acceptor should be there.

(d) Since solution reactions are almost single electron transfer events, there should be an organization for multi electron transfer.

Deisenhoffer, Höber and Mitchel have worked out the photosynthetic apparatus of a bacterium. Since then the work on distant effect has gained ground.

Mamalian tachykinins function as neuropeptides through their own endogenous receptors named Neurokinin (Nk) -1, -2, and -3 respectively. Dimers of Nk-A and Nk-B interact very strongly with these receptors. Matsumoto et al. have synthesized a series of dimeric analogs of NkB -10 namely succinyl bis[(Gly)$_n$-Asp-Ser-Phe-Val-Gly-Leu-Met-NH$_2$] when $n = 0 - 4$. They have shown that the reactivity of these dimers in guinea pig ileum (GPI) containing all of Nk-1, 2 and 3 receptors is highest when the cross linking spacer with oligoglycine of $n = 2$, and decreased sharply for dimers with shorter and longer chain length ($n = 0$ and 1; 3 and 4).

The presence of spacer can influence the biological activity of a drug. In case of antimalarial
drug, primaquine (68), the activity is greater for compounds with even number of spacer group. Thus, the proper binding of a side chain to the receptor is governed by the size and shape of the side chain.

Several models for oxygen binding to heme group have been proposed by different workers. In 1977, Bayer and coworkers synthesized a heme group embedded in a polyene network (Fig. 1.5) from polyethylene glycol bis(glycine ester) and polyurethanes. The close proximity of the porphyrin system to certain residues of the peptide chain in hemoglobin requires flexibility of peptide chains. This model describes a good application of flexible peptide chain in biological system.

Fig. 1.5 Bayer's model for a hemopolymer
Carboxypeptidase A is a zinc dependent enzyme which catalyses the hydrolysis of C-terminal amino acid residues of peptides and proteins and the hydrolysis of the corresponding esters. The only Zn atom is situated in the centre of the molecule and is coordinated by His-69, Glu-12, His-196 and a water molecule. This coordination is possible due to the presence of long peptide chains which enable the different groups to come closer and form bonds with Zn atom.

Fig. 1.6. A model for Zn$^{+2}$ binding site of carboxypeptidase-A.

1.8. REACTIVITY:

Intramolecular catalysis is greatly affected by the nature of intervening spacer between the reactive and catalytic groups. From the relative rate of hydrolysis of aryl esters$^{98-101}$ (Table 1.10) in aqueous medium it is observed that the rate of hydrolysis is dependent on the spacer group intervening the ester group and the catalytic group. The catalytic efficiency of the carboxylate group is reduced by a factor of 200 on increasing the intervening
methylene group by one.

Table 1.10: The relative rate constant of hydrolysis of various aryl esters.

<table>
<thead>
<tr>
<th>Ester</th>
<th>( k_{rel} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. PhOOCCH(_3)</td>
<td>1.0</td>
</tr>
<tr>
<td>2. PhOOC(CH(_2))(_3)COO(^-)</td>
<td>150.0</td>
</tr>
<tr>
<td>3. PhOOC(CH(_2))(_2)COO(^-)</td>
<td>23000.0</td>
</tr>
<tr>
<td>4. PhOOC(_6)H(_4)COO(^-)(m)</td>
<td>(1.1 \times 10^6)</td>
</tr>
<tr>
<td>5. PhOOC(CH(_2))(_4)NMe(_2)</td>
<td>(10^6)</td>
</tr>
<tr>
<td>6. PhOOC(CH(_2))(_3)NMe(_2)</td>
<td>(2.5 \times 10^6)</td>
</tr>
</tbody>
</table>

The hydrolysis of amino esters (Sl. no.-5,6) also depends on the intervening methylene groups but the increase in rate constant is by 2.5 times only on decreasing the spacer chain from 4 to 3. In both cases a ring intermediate is formed which opens up in the subsequent step to give the product. The five membered ring intermediate appears to be more stable than the six membered one as a result the compounds 3 and 6 undergo hydrolysis faster than 2 and 5 respectively. Hence the role of spacer chain is to provide a structural backbone to form a stable cyclic intermediate.

The total entropy of a molecule is the sum of its translational, rotational and internal entropies. The rate increase found in intramolecular reactions can be attributed
to the restriction of unfavourable rotomer distribution. Bruice \(^{102}\) in 1960, has studied the intramolecular displacement of \(p\)-bromophenol (to form an anhydride intermediate) in a series of compounds and found out that the rate depends on the spacer groups (Table-1.11).

Table 1.11: Relative rate of diacid formation from corresponding ester.

<table>
<thead>
<tr>
<th>Ester</th>
<th>Relative rate of diacid formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{COO} - \text{Br})</td>
<td>1</td>
</tr>
<tr>
<td>(\text{COO}^\ominus)</td>
<td>200</td>
</tr>
<tr>
<td>(\text{COO} - \text{Br})</td>
<td>10,300</td>
</tr>
<tr>
<td>(\text{COO}^\ominus)</td>
<td>53,000</td>
</tr>
</tbody>
</table>

He has shown that the removal of one degree of freedom increases the rate by about 200 times. With the rigid groups the reaction rates are much larger because of proper alignment of the reactive groups. The resulting rate enhancement in these reactions is a direct consequence of the proximity effect or closeness of the reactive groups.
This results in favourable changes in translational and rotational entropies of activation. Bruice has suggested that "freezing" internal rotation of the substrate can affect catalytic efficiency of enzymes plus the entropic effect.

Extensive work has been done to study the effect of magnetic fields on recombination kinetics of the triplet radical ion pair state (RIPS) of the Zn-porphyrin viologen dyads (p-sp-Vi$^{2+}$) in which Zn porphyrin (p) and viologen (Vi$^{2+}$) are linked by a flexible or semi-rigid spacer (sp) (Fig-1.7). Nature of spacer can affect the exchange interaction ($J$) and spin orbit coupling. Shafirovich et al have elucidated the effects of the spacer structure on the recombination kinetics (Scheme-1.5) of the RIPS of the Zn-porphyrin viologen dyads (17) in an external magnetic field.

<table>
<thead>
<tr>
<th>Dyad</th>
<th>Spacer (Sp)</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-(CH$_2$)$_3$Vi$^{2+}$</td>
<td>-(CH$_2$)$_3$</td>
<td>H</td>
</tr>
<tr>
<td>P-(CH$_3$)$_6$Vi$^{2+}$</td>
<td>-(CH$_3$)$_6$</td>
<td>H</td>
</tr>
<tr>
<td>P-Ph-Vi$^{2+}$</td>
<td></td>
<td>H</td>
</tr>
<tr>
<td>P-Ph-Me-Vi$^{2+}$</td>
<td></td>
<td>CH$_3$</td>
</tr>
<tr>
<td>P-(CH$<em>2$)$</em>{10}$Vi$^{2+}$</td>
<td>-(CH$<em>2$)$</em>{10}$</td>
<td>H</td>
</tr>
<tr>
<td>P-BPh-Vi$^{2+}$</td>
<td></td>
<td>H</td>
</tr>
</tbody>
</table>

Fig.1.7. Molecular structure of the dyads and spacers.
Laser photoexcitation of \( p\text{-sp-Vi}^+ \) in acetonitrile results in the appearance of the triplet excited state, \( 3\text{p-sp-Vi}^2+ \) and RIPS \( (p^+\text{-sp-Vi}^-) \). Decay of \( 3\text{p-sp-Vi}^2+ \) is due to intramolecular energy transfer from \( 3\text{p} \) to \( \text{Vi}^2+ \) (eq-1.8).

\[
3\text{p-sp-Vi}^2+ \xrightarrow{k_e} 3\text{p}'^+\text{-sp-Vi}^- \tag{1.8}
\]

Values of \( k_e \) (Table-1.12) remain almost unaltered with nature and length of spacer except for \( 3\text{p-Bph-Vi}^2+ \) where \( k_e \) has the lowest value.
Table 1.12: Effect of the nature of the spacer on the relative yields of the fluorescence of \( p^{\cdot}\text{sp-Vi}^{2+}(\phi_f,\text{rel}) \), \( 3_{p^{\cdot}\text{sp-Vi}^{2+}}(\phi_I,\text{rel}) \), \( 3[p^{\cdot+}\text{sp-Vi}^{+}](\phi_R,\text{rel},\tilde{\phi}_R,\text{rel}) \), and the rate constant of the \( 3p^{\cdot}\text{Sp-Vi}^{2+} \) decay \( (k_e) \) at 20°C.

<table>
<thead>
<tr>
<th>( p^{\cdot}\text{sp-Vi}^{2+} )</th>
<th>( \phi_f,\text{rel} )</th>
<th>( \phi_I,\text{rel} )</th>
<th>( \phi_R,\text{rel} )</th>
<th>( \tilde{\phi}_R,\text{rel} )</th>
<th>( k_e/10^7\text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( p{-\text{CH}<em>2}</em>{10}\text{-Vi}^{2+} )</td>
<td>0.5</td>
<td>0.2</td>
<td>0.3</td>
<td>0.5</td>
<td>5.0</td>
</tr>
<tr>
<td>( p{-\text{BPh-Vi}^{2+} )</td>
<td>0.6</td>
<td>0.3</td>
<td>0.3</td>
<td>0.6</td>
<td>1.2</td>
</tr>
<tr>
<td>( p{-\text{CH}<em>2}</em>{6}\text{-Vi}^{2+} )</td>
<td>0.5</td>
<td>0.2</td>
<td>0.3</td>
<td>0.5</td>
<td>4.8</td>
</tr>
<tr>
<td>( p{-\text{PhMe}_2\text{Vi}^{2+} )</td>
<td>0.4</td>
<td>0.2</td>
<td>0.2</td>
<td>0.4</td>
<td>4.0</td>
</tr>
<tr>
<td>( p{-\text{Ph-Vi}^{2+} )</td>
<td>0.5</td>
<td>0.3</td>
<td>0.2</td>
<td>0.5</td>
<td>4.3</td>
</tr>
<tr>
<td>( p{-\text{CH}<em>2}</em>{3}\text{-Vi}^{2+} )</td>
<td>0.1</td>
<td>0.0</td>
<td>0.1</td>
<td>0.1</td>
<td>-</td>
</tr>
</tbody>
</table>

\[
\frac{k_r}{3[p^{\cdot+}\text{sp-Vi}^{2+}]} \quad \Rightarrow \quad p^{\cdot}\text{Sp-Vi}^{2+} \quad \ldots 1.9
\]

The decay rate for the above reaction (1.9) has been observed in zero magnetic field \((B = 0)\) and in a strong magnetic field \((B = 0.24T)\). The \( k_r \) values are given in Table 1.13 which increases with increase of spacer length when \( B = 0 \) and almost invariant when \( B = 0.24T \). Magnetic field effect \( k_r(B = 0)/k_r(B = 0.24T) \) decreases with decrease of the spacer length. The values of magnetic field effects for flexible molecules are higher than that for semi-rigid spacers.
Table 1.13: Recombination rate constants ($k_r$) of the triplet RIPS of the Zn-porphyrin-viologen dyads at 20°C.

<table>
<thead>
<tr>
<th>$3[p^+-(CH_2)_{10}-Vi^+]$</th>
<th>$k_r/10^6$ s$^{-1}$</th>
<th>$k_r(B=0)/k_r(B=0.24T)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$B=0$</td>
<td>$B_{\text{max}}$</td>
</tr>
<tr>
<td>$3[p^+-(CH_2)_{10}-Vi^+]$</td>
<td>5.9</td>
<td>5.9</td>
</tr>
<tr>
<td>$3[p^+-(CH_2)_{6}-Vi^+]$</td>
<td>3.5</td>
<td>3.7</td>
</tr>
<tr>
<td>$3[p^+-(CH_2)_{6}-Vi^+]$</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>$3[p^+-(Ph-Me)_2-Vi^+]$</td>
<td>1.5</td>
<td>1.6</td>
</tr>
<tr>
<td>$3[p^+-(Ph-Vi^+]$</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>$3[p^+-(CH_2)_{3}-Vi^+]$</td>
<td>0.8</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Brinker et al$^{112}$ have investigated the importance of the spacer chain length between the cyclopropylidene ring and the double bond in the study of intramolecular insertion reaction of N-alkenyl substituted cyclopropylidenes (69) leading to the formation of a spiro compound (70) and an allene (71). They have found that when $n = 3$, the spiro
compound is formed with high yield whereas allene is formed when \( n = 4 \). This effect of spacer has been explained by kinetically and thermodynamically controlled processes.

Behera et al.\(^{113}\) have studied acid catalyzed hydrolysis of Schiff bases in reversed micellar medium. They have proposed a mechanism (Scheme 1.6) where hydrolysis occurs through a carbinolamine intermediate. The rate of hydrolysis decreases with increase in spacer length \(( n = 2 \gg 3 > 4 > 6)\). This change in rate constants with spacers has been attributed to the nature of monolayer structure of Schiff base at the interface because of which the carbinolamine gets differently oriented and affects the rate.

![Chemical Reaction](image)

**Scheme 1.6**

Electrical communication between alcohol dehydrogenase and graphite electrode has been established in a domain of polyacrylic acid thin layer coated on graphite felt in which ferrocynyl amino alkylamine (FC - \( \text{CH}_2\text{NH(CH}_2\text{)}_n\text{NH}_2, n = 2, 4, 6, 8, 10 \) and 12\), NADH, diaphorase and alcohol dehydrogenase have been chemically immobilized.\(^{114}\) The effects of ferrocene derivatives with
different alkyl chain lengths to electromediated oxidations of NADH and alcohol dehydrogenase have been examined and the best result is obtained by the use of the flexible ferrocene derivative with spacers length of $12 \sim 15 \text{ Å}$ (n = 6 $\sim$ 9).
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