CHAPTER-II

Study of 4,8,9,10-tetraaryl-l,3-diazaadamantane-1,3-diazaadamantane-6-ones

INTRODUCTION;

The chemistry of adamantanes and its derivatives particularly nitroadamantanes is of interest for their use as high-density energetic materials. Recent interest in adamantanes has extended into the area of host-guest compounds, combinatorial chemistry, optically active organic molecules and dendritic macromolecules. Tetraaryl substituted cage hydrocarbons with tetrahedral symmetry are potential precursors for energetic materials, dendrimers, star shaped macromolecules and molecules of interest in combinatorial chemistry. 1,3-Diazaadamantane derivatives are of great importance as conformationally rigid analogues of pharmacologically active molecules. As the biological activities are often related to the stereochemistry of the molecules, studies on the stereochemistry of the 4,8,9,10-tetraaryl-l,3-diazaadamantane-6-ones are of interest.

On the basis of $^1$H-NMR, $^3$C-NMR, NOE with spin-lattice relaxation time studies of 4,8,9,10-tetrakis(4-methylphenyl)-1,3-diazaadamantane-6-one and the X-ray analysis of 4,10-diphenyl-8,9-bis(4-methylphenyl)-1,3-diazaadamantane-6-one,
Quast et al. concluded that the two-aryl substituents are in an axial orientation in one piperidone ring and the other two-aryl substituents are in an equatorial orientation in another piperidone ring.

They used the PMR and NOE difference spectra also for the 4,8,9,10-tetrakis(4-methylphenyl)1,3-diazaadamantane and observed a small enhancement of the ortho protons of one pair of aromatic rings on irradiation of the 2-protons and an enhancement of the downfield proton H/7 of the 6-methylene group. With these results they distinguished between the resonances arising from the two sides of the molecules and allows a total assignment of the proton spectrum. Irradiation of bridgehead protons leads to a large enhancement of both set of ortho protons and a very significant negative NOE for the meta protons on both ways. This phenomenon is characteristic of an approximately linear arrangement of the three-proton system, 5H-H^\(\tau f/j_0\)-H(wea) and thus roughly defines the conformation of the 1,3-diequatorially arranged aryl groups. The other pair which is 1,3-diaxially oriented is virtually held in
one conformation for which the arrangement of the three protons also linear.

Sivasubramanian et al.\textsuperscript{10} also studied the stereochemistry of tetraaryl-1,3-diazaadamantan-6-ones. They assigned the bridge head (5,7) positions and C-2 protons by preparing the (5,7\textsuperscript{-2})-4,8,9,10-tetraphenyl-l,3-diazaadamantan-6-one. They observed two different signals for methylene protons with a difference of one ppm and stated that the downfield shift of one proton is due to the anisotropic effect of two syn-axial aryl groups. The axial protons in 2,6-diphenyl-4-piperidones and 2,6-diphenyl piperidine systems appear at upfield than the equatorial protons. On the basis of the above studies, axial and equatorial benzylic protons are assigned. The clear distinction between the axial and equatorial aryls is observed for the 4,8,9,10-tetrapheny 1-l,3-diazaadamantan-6-one, 4,8,9,10-tetraphenyl-l,3-diazaadamantane and 4,8,9,10-tetrakis(4-methylphenyl)-l,3-diazaadamantan-6-one, but in the case of 4,8,9,10-tetrakis(4-methylphenyl)-l,3-diazaadamantane, the aromatic protons do not show any distinction for axial and equatorial aryls. The reduction of 4,8,9,10-tetrakis(4-chlorophenyl)-l,3-diazaadamantan-6-one with NaBH\textsubscript{4} results only one epimer. This may be due to the attack of hydride ion from the less hindered side\textsuperscript{9,15} leads to the thermodynamically more stable alcohol. If the two axial aryls are in one
piperidone ring and the other two aryls are in equatorial in another piperidone ring then these adamantanes should give two epimeric alcohols on reduction with NaBH$_4$ but yields only one epimer. On this basis Sivasubramainan et.al$^{10}$ proposed the structure that each piperidone ring containing one axial and one equatorial group in each ring.

Moreover there is no detailed report about the carbon chemical shift values in the system. In literature also there is no such detailed report available on the uniformly substituted 4,8,9,10-tetraary 1,1,3-diazatricyclo[3.3.1.1]decan-6-ones. This prompted us to undertake an extensive NMR investigation of these compounds 2.1a-e. The 'H-NMR, $^{13}$C-NMR and two-dimensional NMR spectra such as H, H-COSY and C, H-COSY provided unambiguous chemical shift assignments and information on the conformational aspects of these compounds.
RESULTS AND DISCUSSION:

1) Study on 4,8,9,10-tetraaryl-1,3-diazaindicyclo[3.3.1.1]decain-6-ones

\[
\text{Compound} \quad \text{Ar} \quad \text{R} \quad \text{IV} \quad \text{X}
\]
\begin{align*}
2.1a & \quad \text{C}_6\text{H}_5 & \quad \text{H} & \quad \text{H} & \quad \text{0} \\
2.1b & \quad \text{p-CH}_3\text{C}_6\text{H}_5 & \quad \text{H} & \quad \text{H} & \quad \text{0} \\
2.1c & \quad \text{p-CH}_3\text{OC}_6\text{H}_5 & \quad \text{H} & \quad \text{II} & \quad \text{0} \\
2.1d & \quad \text{p-C\text{C}_6\text{H}_5} & \quad \text{H} & \quad \text{H} & \quad \text{0} \\
2.1c & \quad \text{C}_6\text{H}_5 & \quad \text{CH}_3 & \quad \text{II} & \quad \text{0} \\
2.1g & \quad \text{C}_6\text{H}_5 & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
2.1h & \quad /\text{CH}_3\text{C}_6\text{H}_5 & \quad \text{H} & \quad \text{H} & \quad \text{H}
\end{align*}

a) Proton Chemical Shifts:

Assignment of 'H-NMR signals of a representative compound 2.1a is discussed below. The H, H-COSY spectrum shows that the singlet at 4.05 ppm due to H-5,7 with a half width of 5 Hz couples with the singlet at 4.80 ppm as well as with the singlet at 4.90 ppm. The relatively upfield peak at 4.80 ppm couples with the relatively downfield peak at 7.68 ppm in aromatic region, on the other hand the relatively downfield
peak at 4.90 ppm couples with the relatively upfield at 7.10 ppm in aromatic region. It reveals that the two pairs of phenyl rings are in two different environments, i.e. one pair has the axial orientation and the other pair has the equatorial orientation, and hence the benzylic protons are observed at two distinct positions. Moreover these values intuits that the peaks at 4.80, 7.68, 7.45 and 7.36 ppm form one set of protons and the peaks at 4.90, 7.10, 6.96 and 6.80 ppm form another set of protons. The singlet at 4.50 ppm with a half width of 3 Hz couples with the singlet at 4.80 ppm is due to the H-2s and it is also further evidenced by the appearance of triplet for the same in the off resonance decoupled spectrum. The high intense contours and low intense contours between 4.80 ppm and 4.50 ppm are observed in H, H-COSY and ROESY spectra respectively and hence the relatively upfield singlet at 4.80 ppm with a half width of 6 Hz is assigned to the axial oriented at H-8, 9. The downfield singlet at 4.90 ppm with a half width of 3 Hz has the proximity with ortho protons of both set of aryls and doesn't have any coupling with H-2 in ROESY spectrum, assigned to the equatorial at H-4, 10. The protons of two phenyl rings in the axial orientation and the other phenyl rings in the equatorial orientation absorb at different positions, the former phenyl protons appearing upfield relative to those of the latter may be due to the mutual shielding of phenyls to each other. An examination of the
H, H-COSY and ROESY spectra for 2.1a clearly shows that the doublet at 7.68 ppm ($J = 6.5$ Hz) has proximities with peaks at 4.90, 4.80, 4.50 and 7.45 ppm in ROESY spectrum and coupling with the triplet at 7.45 ppm in H, H-COSY spectrum is due to ortho protons (H-o) in equatorially oriented phenyl at 8,9. The triplet at 7.45 ppm (with J values of 6.5, 8.0 Hz) couples with the doublet at 7.68 ppm as well as with the triplet at 7.36 ppm and is due to H-m and the remaining triplet at 7.36 ppm ($J = 8.0$) is assigned to H-p of aryls in equatorial orientation at 8,9. Similarly the doublet at 7.10 ppm (with J value of 8 Hz) has proximity with the peaks at 4.90, 6.98 ppm only in ROESY and couples with the triplet at 6.98 ppm in IT, H-COSY spectrum assigned to the ortho protons (H-o') in axial orientation at 4,10. H, H-COSY spectrum reveals that the multiple! at 6.98 ppm couples with the doublet at 7.10 ppm as well as with the doublet at 6.80 ppm and is assigned to H-m' and the remaining doublet at 6.80 ppm (with $J$ value of 6.5 Hz) is due to H-p'. These observations are in conformity with X-ray crystallographic studies\textsuperscript{12}. The ortho and meta protons of 2.1b and 2.1c are differentiated through the ROSEY spectra. The ortho protons are in proximity with their benzylic protons whereas the meta protons are in proximity with the methyl or methoxyl groups in their aryl rings. The other signals of 2.1b-2.1d are
assigned similarly and lead to the similar conclusions and listed in Table-2.1.

The signals of the compound 2.1e are assigned below. The H, H-COSY spectrum shows that the singlet at 5.55 ppm with a half width of 5 Hz due to IT-7 couples with the singlet at 4.30 ppm with a half width of 6 Hz. The singlet at 4.30 ppm (W|/2 = 6 Hz) assigned to H-8, 10 shows that they are in relatively the same environment. The singlets at 4.45 ppm (W|/2 = 4 Hz) and 4.32 ppm (Wj/? = 5 Hz) are due to the H-4 and H-9, respectively. The singlet at 4.87 ppm with a half width of 12 Hz integrated for two protons are due to the H-2s. An examination of the signals of the aromatic protons reveals that the doublet at 7.75 ppm is due to the o-protons of phenyl at C-4. The doublet at 7.57 ppm is assigned to the o-protons of the phenyl at C-9. The multiplet at 7.35-7.43 ppm integrated for six protons is due to the m and/? protons of the phenyls at C-4 and C-9. The singlet at 7.10 ppm is due to the o-protons of the phenyl at C-10 and the multiplet, which integrated for eight protons, is assigned to the m and p protons of the phenyl at C-10 and the protons of another phenyl at C-8.

b) 13C CHEMICAL SHIFTS

The assignment of benzylic, bridge, bridgehead and the hydrogen bearing aromatic carbons of 2.1a-e have been made on the basis of a C,
H-COSY spectrum. The signal that occurs far downfield has been assigned to the carbonyl carbon. The *ipso* carbons of 2.1a-e are identified through the C, H-COSY since they did not show any contours. The *para* and *ipso* carbons of 2.1b-d are differentiated through COSY studies. The distinction of the *two-ipso* carbons (C-i and C-i’) has been made on the basis of HMBC spectrum and all the chemical shifts have been listed in Table-2.2. An examination of the chemical shift data in Table-2.2 suggests that the signals of the axial phenyl rings and benzylic carbons with axial substituents appear upfield (relative to those of the corresponding carbons of equatorial substituents) as they are in a sterically more crowded environment.

The carbon chemical shift assignments of 2.1a made above have also been corroborated by the correlations disclosed by ID-INADEQUATE spectrum discussed below and is given in Table-2.3. From this spectrum, it is quite clear that carbonyl carbon interacts with CH carbon resonating at 50.05 ppm via \( j(C(=O), C(H)) = 37.6 \) Hz. Further coupling constants are mentioned in the following Table-2.3. In the region of aromatic CH carbons the data cannot be analysed since the signals overlap.

From the \( \text{I}^1J(^{13}C, ^{13}C) \) data in Table-2.3, assignment of the chemical shifts of carbons belonging two independent paths involving carbonyl
carbon are available - (i) 213.5 -(37.6 Hz) -> 50.1-(30.4 Hz) -> 64.2-
(48.7 Hz) ->139.6 and (ii) 213.5-(37.6 Hz) ->50.1 -(28.0 Hz) -> 69.3 -
(47.6 Hz) ->137.9 and isolated CH₂ group. These results confirm the
assignments arrived at using NOESY, I1MQC and I1MBC data.

The bispidones having the carbethoxy group at 5 position with
aryl at 4,8,9,10 are not converted into 1,3-diazaadamantan-6-ones by
adopting the same procedure due to the steric effect. The two NH groups
cannot be linked through -CH₂- group because of steric effect.
Table 2.1: Proton chemical shifts (ppm) and proton-proton coupling constants [Hz] of 4,8,9,10-tetraaryl-1,3-diazatricyclo[3.3.1.1]decan-6-ones and 4,8,9,10-tetraaryl-1,3-diazatricyclo[3.3.1.1]decanes in CDCl₃.

<table>
<thead>
<tr>
<th>Compound</th>
<th>H-5,7</th>
<th>H-4,10</th>
<th>H-8,9</th>
<th>H-2</th>
<th>H-6</th>
<th>Equatorial</th>
<th>Aryl Protons</th>
<th>Axial</th>
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<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>o-H</td>
<td>m-H</td>
<td>p-H</td>
</tr>
<tr>
<td>2.1a</td>
<td>4.05 s</td>
<td>4.90 s</td>
<td>4.80 s</td>
<td>4.50 s</td>
<td>---</td>
<td>7.68 d</td>
<td>7.45 t</td>
<td>7.36 t</td>
</tr>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>[6.5]</td>
<td>[8.0,6.5]</td>
<td>[8.0]</td>
</tr>
<tr>
<td>2.1b</td>
<td>3.90 s</td>
<td>4.84 s</td>
<td>4.64 s</td>
<td>4.39 s</td>
<td>---</td>
<td>7.47 d</td>
<td>7.17 d</td>
<td>---</td>
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<td></td>
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<td></td>
<td></td>
<td>[8.0]</td>
<td>[8.0]</td>
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<tr>
<td>2.1c</td>
<td>3.96 s</td>
<td>4.81 s</td>
<td>4.67 s</td>
<td>4.56 s</td>
<td>---</td>
<td>7.41 d</td>
<td>6.84 d</td>
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<td>3.87 s</td>
<td>4.75 s</td>
<td>4.70 s</td>
<td>4.35 s</td>
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<td>7.53 d</td>
<td>7.42 d</td>
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<tr>
<td>2.1e</td>
<td>5.55 s</td>
<td>4.45 s</td>
<td>4.32 s</td>
<td>4.87 s</td>
<td>---</td>
<td>7.75 d</td>
<td>7.35-7.43 m</td>
<td>---</td>
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<tr>
<td>(H-7)</td>
<td></td>
<td>(H-4)</td>
<td>(H-9)</td>
<td></td>
<td></td>
<td>[6.60]</td>
<td>(6 protons)</td>
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<tr>
<td></td>
<td>4.30 s</td>
<td>4.30 s</td>
<td></td>
<td></td>
<td></td>
<td>at C-4</td>
<td>at C-4 and C-9</td>
<td></td>
</tr>
<tr>
<td>(H-10)</td>
<td></td>
<td>(H-8)</td>
<td></td>
<td></td>
<td></td>
<td>[6.60]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1g</td>
<td>2.81 s</td>
<td>4.29 s</td>
<td>4.56 s</td>
<td>2.40 s</td>
<td>4.38 s</td>
<td>7.24 t</td>
<td>7.39-7.61 t</td>
<td>---</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.39 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1h</td>
<td>2.95 s</td>
<td>4.34 s</td>
<td>4.39 s</td>
<td>3.64 s</td>
<td>4.20 s</td>
<td>7.47 d</td>
<td>7.22 d</td>
<td>---</td>
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<td></td>
<td></td>
<td></td>
<td>3.58 s</td>
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Table 2.2: Carbon-13 chemical shifts [ppm] of 4,8,9,10-tetraaryl-1,3-diazatricyclo[3.3.1.1]decan-6-ones in CDCl₃.

| Compound | C-6 | C-5,7 | C-4,10 | C-8,9 | C-2 |  |  |  |  |  |  |  |  |  |  |  |
|----------|-----|-------|--------|-------|-----|---|---|---|---|---|---|---|---|---|---|
|          |     |       |        |       |     |  |  |  |  |  |  |  |  |  |  |  |
| 2.1a     | 213.54 | 50.23 | 64.32  | 69.48 | 68.63 | 137.90 | 129.13 | 127.35 | 127.55 | —  | 139.60 | 128.14 | 127.00 | 126.40 | —  |
| 2.1b     | 213.90 | 50.40 | 63.90  | 69.30 | 68.20 | 136.90 | 126.80 | 128.00 | 135.10 | 20.70 | —  | 127.30 | 129.60 | 135.50 | 21.00 |
| 2.1c     | 211.85 | 50.39 | 63.48  | 68.89 | 67.82 | 129.97 | 127.99 | 114.28 | 157.67 | 55.39 | 132.31 | 129.08 | 112.81 | 158.76 | 55.07 |
| 2.1d     | 213.83 | 49.83 | 63.61  | 68.66 | 68.23 | 132.89 | 129.41 | 127.58 | 136.01 | —  | 133.72 | 128.26 | 137.64 | —  |
| 2.1e     | 213.51 | 49.54 | 76.22  | 70.86 | 68.60 | 139.40 | 128.32 | 130.51 | 126.95 | —  | 138.51 | 127.41 | 129.04 | 126.81 | 17.35 |
|          | (C-5) | (C-4) | (C-8)  | (C-8) |      |     |     |     |     |     |     |     |     |     |     |
|          | 52.23 | 63.37 | 69.90  |       |      |     |     |     |     |     |     |     |     |     |     |
|          | (C-7) | (C10) | (C-9)  |       |      |     |     |     |     |     |     |     |     |     |     |
| 2.1g     | 27.63 | 26.52 | 60.49  | 58.28 | 66.26 | 141.29 | 125.91 | 126.53 | 141.37 | —  | 141.37 | —  | 128.57 | —  | —  |
| 2.1h     | 35.71 | 28.39 | 63.91  | 63.98 | 57.56 | 69.33 | 138.62 | 126.78 | 129.04 | 138.76 | 20.97 | 143.58 | 126.30 | 128.60 | —  | 21.10 |

* not seen in spectra.

*§ merged with signals of phenyl at C-8.

c-§ merged with signals of phenyl at C-8.
Table-2.3: $^1J(^{13}C, ^{13}C)$ (Hz) coupling constants in 4,8,9,10-tetraphenyl-1,3-diazatricyclo[3.3.1.1]decan-6-one in CDCl$_3$.

<table>
<thead>
<tr>
<th>Carbon</th>
<th>$\delta(^{13}C)$</th>
<th>$^1J(^{13}C, ^{13}C)$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O</td>
<td>213.5</td>
<td>37.6</td>
</tr>
<tr>
<td>C</td>
<td>139.6</td>
<td>48.7 and 58.9 ($C_bC_a$)</td>
</tr>
<tr>
<td>C</td>
<td>137.9</td>
<td>47.6 and 58.9 ($C_bC_a$)</td>
</tr>
<tr>
<td>CH</td>
<td>69.3</td>
<td>47.6 and 28.0</td>
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<tr>
<td>CH$_2$</td>
<td>68.5</td>
<td>-a</td>
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<tr>
<td>CH</td>
<td>64.2</td>
<td>48.7 and 30.4</td>
</tr>
<tr>
<td>CH</td>
<td>50.1</td>
<td>37.6, 30.4 and 28.0</td>
</tr>
</tbody>
</table>

Note: $^a$No signal as expected
2) Spectral study of the 4,8,9,10-tetraaryl-1,3-rfiazatncycIo[3.3JJ] decarases:

When 2.1a and 2.1b are reduced to 2.1g and 2.1h the H-5, 7 are shifted to the upfield due to the conversion of C6 \(sp^2\) carbon to \(sp^3\) carbon upon reduction and hence the bridgehead positions have some flexibility and so the strain along the ring also is relived. The hydrogens at C4, C10, C8, C9 and C2 are also shifted to the upfield (when the strain in the ring increases, the ring throws its electron density to the outer orbitals, i.e. towards the orbitals which have the bond with H-4, 8, 9, 10 and 2 positions). In these adamantane systems, the strain is due to the two factors, one is due to the presence of bulky substituents at 4, 8, 9 and 10 positions and another is due to the \(sp\) carbon at C6. Similarly for 2Jg also the hydrogens at 4, 8, 9, 10 and 2 positions in the system are shifted to the upfield and it is given in the table. For 2.1c and 2.1d the compounds are decomposed when it is reduced. The ring strain is relived when it is reduced. The \(^{13}\text{C}\) chemical shift values are given in Table-2.2.
a) Protosi Cfiemkasi Shifts:

For 4,8,9,10-tetraaryl-1,3-diazatricyclo[3.3.1.1]decanes, 4,8,9,10-tetraphenyl-1,3-diazatricyclo[3.3.1.1]decane is taken as a representative sample and its chemical shift values are assigned as follows. The -CH₂- and -CH- carbons are differentiated by the DEPT method and the chemical shift values of the protons attached to these carbon atoms are identified by the HETCOR spectra. The chemical shift values of two -CH₂- protons are 2.81 ppm and 4.38 ppm. The H, H-COSY spectrum shows that the singlet at 4.38 ppm with a halfwidth of 8 Hz is having the vicinal couplings with the singlet at 4.56 ppm (\( W/2 = 5 \) Hz) and 4.29 ppm (sharp singlet) is due to the hydrogens at C-2 positions. It is also having the vicinal coupling with the ortho and meta protons of the phenyl oriented axially. So it is assigned to the protons at C-2 position. Similarly the singlet at 4.56 ppm couples with ortho protons of aryl also. The singlet at 2.8 ppm couples with both 4.56 ppm and 4.38 ppm as well as with the singlet at 2.40 ppm is assigned for bridgehead protons. The bridge protons at C-6 position couples with the singlet at 2.81 as well as with 4.56 ppm. The aryl protons are not having any distinct peaks for axial and equatorial aryls in H, H-COSY and PMR. Only three types of peaks are available at 7.24 (t) ppm, 7.34 - 7.39 (m) ppm, and 7.61 (t) ppm. In this case 7.61 (t) integrated for eight protons couples with the multiplet at
7.34-7.39 ppm is due to the ortho protons. The multiplet at 7.34-7.39 ppm integrated for eight protons coupled with 7.61 (t) ppm as well as with 7.24 (t) ppm is due to the meta protons of aryls. The triplet at 7.24 integrated for four protons couples with 7.34 -7.39 (m) ppm is due to the para protons. The singlet at 4.56 ppm couples with the ortho protons that is the ortho protons of aryl group and the equatorial hydrogens are in the same plane. Similarly the bridge protons at C-2 positions have the coupling with ortho and meta protons i.e. here also the N-CH2-N and ortho, meta protons are in the same plane. This shows that the aryls at axial and equatorial are perpendicular to each other. The observance of small contours between the ortho protons and benzylic protons at 4,10 positions is due to the vicinal coupling intuits that the concerned hydrogens are in the plane. Similarly the ortho, meta protons of aryls and benzylic at 8,9 positions also be in the same plane is inferred by the low intensity contours observed between these atoms. (Moreover ortho hydrogens of aryls at 4, 10 and benzylic hydrogens at 4,10 are in the same plane. So that it gives the vicinal coupling. Similarly the hydrogens at C-2 position and ortho, meta protons of aryls orienting equatorial are in the same plane and that it gives vicinal coupling.) The coupling is not due to the aryls at axial group because it is away from the
molecular nucleus. In a similar way the proton chemical shift values of other members also assigned and are presented in the Table-2.1.

b) $^3$C-Cfeemkal Shift:

The assignment of benzylic, bridge, bridgeheads and the hydrogen bearing aromatic carbons of 2J.g and 2.lSi have been made on the basis of a C[-II-COSY spectrum and arc given in Table-2.2. The ipso carbons are identified through the C,H-COSY since they did not show any contours for 2.1 g. The para and ipso carbons of 2.1 Hi are differentiated through COSY studies. The distinction of the two ipso carbons C-i and C-i’ has been made tentatively.

3) X-ray CrysteSlographic studies of 4,8,9,10-tetraaryl-1,3-diazatricyclo[3.3.1.1]decan-6-ones:

The 4,8,9,10-tetraaryl-1,3-diazatricyclo[3.3.1.1.]decan-6-ones are prepared using the methods available in the literature\textsuperscript{9,11} and crystallised using benzene, chloroform and acetone mixture in 2:2:1 ratio at room temperature. The melting points of 2.1a-e are lower than that cited in the literature (shown in the scheme-2 ), but the 'H-NMR, $^{13}$C-NMR data of 2.1a-2.1e does not show any significant variation in the chemical shifts. The compounds crystallised from two different mediums were earlier considered as isomers. Since they are indistinguishable from their 'li and $^{13}$C-NMR
spectra, X-ray crystallographic study for 2.1a, 2.1c and 2Je where carried out. There is a remarkable difference in their molecular conformation and crystal packing modes for 2.1a and 2.1e. The X-ray crystallographic study of 2.1c clearly shows that it adsorbs four benzene molecules in the unit cell and whereas 2.1a adsorbs acetone molecule in the unit cell which results in the decrease of melting point. A plane passing through the N1, C2, N3 and carbonyl group bisects the molecule in 2.1c. This is a striking example of retention of crystallographic site symmetry by molecule at the expense of packing efficiency.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ar</th>
<th>R</th>
<th>M.pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1a</td>
<td>C₆H₅</td>
<td>H</td>
<td>204°C [224-228°C]</td>
</tr>
<tr>
<td>2.1b</td>
<td>/?-CH₃C₆H₄</td>
<td>H</td>
<td>186°C [200°C]</td>
</tr>
<tr>
<td>2.1c</td>
<td>/?-CH₃OC₆H₄</td>
<td>H</td>
<td>176°C [185°C]</td>
</tr>
<tr>
<td>2.1d</td>
<td>C₆H₅</td>
<td>CH₃</td>
<td>224° &amp; 238°C [268°C]</td>
</tr>
<tr>
<td>2.1e</td>
<td>P-C1C₆H₄</td>
<td>H</td>
<td>268°C [268°C]</td>
</tr>
</tbody>
</table>

Literature melting points are given in the parenthesis

Scheme-2

55
Common characteristics of molecules 2Ja-e irrespective of entrapped solvent molecule in the unit cell are given below.

1. The two-aryl substituents at axial orientation in one piperidone ring (N3, C4, C5, C6, C7, C10) and the other set of aryl substituents at equatorial orientation in another piperidone ring (N1, C9, C5, C6, C7, C8). Consider the two six member rings consisting of N1, C2, N3, C4, C5, C9 atoms and N1, C2, N3, C10, C7, C8 atoms. There is one axial and one equatorial aryl group for each ring.

2. The distance between the two-aryl groups at C4 and C10 is 3.939 Å for 2.1e, whereas for 2.1a it is 3.613 Å. Since the bulky aryl substituents are at 3-positions, the a-bonds are shorter than the (3-bonds with respect to the carbonyl group.

3. The short C-H bond lengths 0.965 Å and 1.011 Å for 2.1a and similarly 0.95 Å and 0.87 Å evidenced the high * character of the carbons at a-positions with respect to carbonyl group.

4. The angle C8-N1-C9 (107.8) is smaller than the angle C10-N3-C4 (113.6) reveals that the substituents at C4 and C10 have steric repulsion between them.

5. Bond lengths N3-C4 and N3-C10 are longer than N1-C9 and N1-C8.

6. Axially substituted aryls at C4 and C10 are
facing each other and hence there exist steric interaction and 71-71 repulsion between them. To minimize these interactions (a) the corresponding internal angle (C10-N3-C4) and (b) the bond lengths of C4-N3 and N3-C10 bonds are increased and hence the hybridisation of N3 atom has been slightly disturbed. (10) To minimize the steric interaction between the axial aryl groups, the piperidone ring containing axial substituted aryls are flattened along C5-C4 and C7-C10 bonds and consequently the other piperidone ring containing equatorial substituted aryls are inclined more than the normal values.

The effect of steric hindrance on hybridisation:

The 2.1c adsorbs solvent molecule in the unit cell and has perfect symmetry than 2.1la. 2.1e does not have any symmetry so the values of bond angle, bond length, etc., of 2.8c and 2.1c were taken for comparative study. The internal angle around N1 at C2-N1-C8, C2-N1-C9 and C8-N1-C9 for 2.1c and 2.1c are 110°3 ', 110°3 ', 107°8 ' and 109°, 110°9', 109°5' respectively. Similarly the internal angle around N3 at C2-N3-C4, C2-N3-C10 and C4-N3-C10 for 2.1c and 2.1earc 107°2', 107°2', 1 13°6'and 107°3', 106°3' I 14° respectively, 'lllic bond lengths of N3--C4, N3-C10, N1-C9 and N1-C8 are 1.487, 1.487, 1.475 and 1.475 A. for 2.1c. In 2.1e the bond
lengths N3-C4, N3-C10, N1-C9 and N1-C8 are 1.482, 1.487, 1.471 and 1.463 Å, respectively.

The above values reveal that in 2.1c and 2.1c (i) The N3 atom does not have the perfect sp$^3$ hybridisation whereas N1 has. (ii) The angle C8-N1-C9 (107.8) is smaller than the angle C10-N3-C4 (113.6) reveals that the substituents at C4 and C10 have steric repulsion between them, (iii) Bond lengths N3-C4 and N3-C10 are longer than N1-C9 and N1-C8.

Axially substituted aryls at C4 and C10 are facing each other and hence there exist steric interaction and %-%- repulsion between them. Tn order to minimize these interactions (a) the corresponding internal angle (C10-N3-C4) and (b) the bond lengths of C4-N3 and N3-C10 bonds are increased and hence the hybridisation of N3 atom has been slightly disturbed.

In 2.1e the internal angle around C5 at C6-C5-C4, C6-C5-C9, C4-C5-C9, C6-C5-H5, C4-C5-H5, and C9-C5-H5 are 108°0', 106°7', 109°1', 107°0', 1 15°0' and 111°0' respectively. Similarly the internal angle around C7 at C6-C7-C10, C6-C7-C8, C10-C7-C8, C6-C7-H7, C10-C7-H7 and C8-C7-H7 are 111°6', 105°7', 106°8', 111°0', 111°0' and 110°0' respectively. These values reveal that the piperidone ring containing axial substituted aryls are
flattened along C5-C4 and C7-C10 bonds and consequently the other piperidone ring containing equatorial substituted aryls are inclined more than the normal values. This is to minimize the steric interaction between the axial aryl groups. The internal angle values of C5 in the case of 2.1c also reveal the same. In 2.1c due to the molecular symmetry, internal angles around C5 and C7 atoms have the same values. The internal angles around C7 at C6-C7-C10, C6-C7-C8 and C9-C7-C8 are 109°0', 107°2' and 108°8* respectively. The bond lengths of 2.1c and 2.1e are given in Table-2.4 and 2.5. The other internal angles for 2.1c and 2.1© around C4, C8, C9 and C10 are given in Table-2.6 and 2.7.

In the case of 2.1c the internal angles around (A and CIO are same. Similarly for C8 and C9 also have the same angles due to the molecular symmetry, but not in 2.fle. The above given values reveal that all the aryls substituted at 4, 8, 9 and 10 positions are moved away from the molecular cage as much as possible to reduce the steric hindrance in the molecule. It also intuits that the hydrogens at these positions are comparatively nearer to the molecular cage.

Effect of benzene solvent molecule in the unit cell:

Since the molecule 2.1c has molecular symmetry due to the adsorption of four benzene molecules in the unit cell and to understand the
effect of benzene molecule in the unit cell, certain values of the bond length and bond angle of 2.k is compared with the X-ray data of another molecule 2.1c which is not having any solvent molecule in the unit cell. In 2.1e the torsional angle of C2-N3-C4-C41 (ipso carbon at C4) is -172° 07' and that of C2-N3-C10-C101 (ipso carbon at C10) is 164° 06'. It indicates that the aryl substituents at C4 and C10 have the different angle of orientation to minimize there-cloud interaction between them. The N3-C4 bond and N3-C10 bond lengths are different. Similarly the N1-C9 bond and N1-C8 bond lengths are different. This also reveals the loss of molecular symmetry in 2.1e (Fig 2.26). But in 2.1c the angle of orientation of aryl substituent at C4 and C10 are same and similarly the aryls at C8 and C9 also have the same angle of orientation. The bonds N3-C4, N3-C10 and N1-C9, N1-C8 also has the same bond lengths and the molecular symmetry is maintained. The presence of solvent molecules in the unit cell assists the system to overcome the steric hindrance as well as re-re repulsion between the aryl substituent at C4 and C10 (Fig. 2.27). Thus the trapping of the benzene molecule within the crystal lattice of the methoxy-substituted derivative (2.1c) accounts for the retention of molecular symmetry. Presence of solvent molecules in the crystal structure plays a role in optimising packing efficiency within the lattice.
Table 2.4: Bond lengths (Å) for compound 4,8,9,10-tetrakis(4-chloro phenyl)-1,3-diazatricyclo[3.3.1.1]decan-6-one.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Bond length</th>
<th>Atoms</th>
<th>Bond length</th>
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<td>N3-C10</td>
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<td>N1-C9</td>
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<td>C9-C91</td>
<td>1.509</td>
<td>C4-C41</td>
<td>1.526</td>
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<tr>
<td>C8-C81</td>
<td>1.520</td>
<td>C10-C101</td>
<td>1.514</td>
</tr>
<tr>
<td>C8-H81</td>
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<td>C4-H41</td>
<td>0.990</td>
</tr>
<tr>
<td>C9-H91</td>
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<td>C10-H101</td>
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<td>C10-C7</td>
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<td>C5-C6</td>
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<td>C6-O</td>
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Table-2.5: Bond angles involving atoms in the main skeleton for the compound 4,8,9,10-tetrakis(4-chlorophenyl)-1,3-diazatricyclo[3.3.1.1]decan-6-one.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Bond angle (°)</th>
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<td>C2-N3-C4</td>
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<td>N3-C10-C7</td>
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<td>N3-C10-C101</td>
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<td>N3-C10-11101</td>
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<tr>
<td>C81-C8-C7</td>
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<td>C101-C10-C7</td>
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<td>H81-C8-C7</td>
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<td>C7-C10-H101</td>
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</tr>
<tr>
<td>N1-C9-C91</td>
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<td>N3-C4-C41</td>
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<td>N1-C9-C5</td>
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<td>N3-C4-C5</td>
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<td>C41-C4-H41</td>
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</tr>
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<td>C5-C9-H91</td>
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<td>C5-C4-H41</td>
<td>109.00</td>
</tr>
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<td>C6-C7-C10</td>
<td>111.60</td>
</tr>
<tr>
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<td>C6-C7-C8</td>
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</tr>
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Table-2.6: Internal angles for compound 4,8,9,10-tetrakis(4-methoxyphenyl)-1,3-diazatricyclo[3.3.1.1.3]decan-6-one with benzene molecule in the unit cell

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<th>Atoms</th>
<th>Internal angle (degrees)</th>
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<tbody>
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<td>N3-C4-C41 (ipso)</td>
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<td>N3-C10-C101 (ipso)</td>
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<td>N3-10-C7</td>
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<tr>
<td>C41-C4-C5</td>
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<td>C101-10-C7</td>
<td>115.3</td>
</tr>
<tr>
<td>N1-C8-C81 (ipso)</td>
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<td>N1-C9-C91 (ipso)</td>
<td>111.4</td>
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<tr>
<td>N1-C8-C7</td>
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<td>N1-C9-C5</td>
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</tr>
<tr>
<td>C81-C8-C7</td>
<td>114.6</td>
<td>C91-C9-C5</td>
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<td>C2-N3-C4</td>
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<td>C2-N3-C10</td>
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<td>C4-N3-C10</td>
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<td>C9-C5-C4</td>
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Table 2.7: Internal angles for compound 4,8,9,10-tetrakis(4-chlorophenyl)-1,3-diazatricyclo[3.3.1.1]decan-6-one with benzene molecule in the unit cell

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Internal angle (degrees)</th>
<th>Atoms</th>
<th>Internal angle (degrees)</th>
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<tbody>
<tr>
<td>N3-C4-C41 <em>(ipso)</em> 113.3</td>
<td>N3-C10-C101 <em>(ipso)</em> 113.3</td>
<td>N3-C4-C5 110.1</td>
<td>N3-10-C7 109.6</td>
</tr>
<tr>
<td>C41-C4-C5 114.0</td>
<td>C10M0-C7 117.1</td>
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<td></td>
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<tr>
<td>N1-C8-C81 <em>(ipso)</em> 111.7</td>
<td>N1-C9-C91 <em>(ipso)</em> 110.1</td>
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<td></td>
</tr>
<tr>
<td>N1-C8-C7 109.5</td>
<td>N1-C9-C5 108.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C81-C8-C7 114.2</td>
<td>C91-C9-C5 116.4</td>
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<td>C2-N1-C8 110.9</td>
<td>C2-N3-C4 107.3</td>
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<tr>
<td>C2-N1-C9 109.5</td>
<td>C2-N3-C10 106.3</td>
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<tr>
<td>C8-N1-C9 109.0</td>
<td>C4-N3-C10 114.1</td>
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</tr>
<tr>
<td>C6-C7-C10 111.6</td>
<td>C6-C5-C4 108.0</td>
<td></td>
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</tr>
<tr>
<td>C6-C7-C8 105.7</td>
<td>C6-C5-C9 106.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C10-C7-C8 106.8</td>
<td>C9-C5-C4 109.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Adsorption of acetone molecule by 4,8,9,10-tetraaryl-1,3-diazatricyclo[3.3.1.1]decan-6-ones in the unit cell:

This kind of adsorption takes place when the compounds 2.1 are crystallised using the benzene, CHCl₃ and acetone mixture in the temperature range of 0-15°C. The mixture is stirred under the magnetic stirrer for an hour and then allowed to crystallize at the same environment. The compounds 2.1a and 2.1b gave the crystal with adsorption of acetone molecules in the unit cell. The ORTEP diagram of 2.1a shows that in the unit cell two molecules of 2.1a along with one molecule of acetone. So one molecule of 4,8,9,10-tetraphenyl-1,3-diazatricyclo[3.3.1.1]decan-6-one without solvent molecule is named as A and for the another which having the acetone molecule in the vicinity is named as B and its corresponding bond length and bond angles are given in the following Tables-2.10-2.13. The compound 2.1a and 2.1b also crystallised in CHCl₃ and C₆H₆ and does not have any solvent molecule in the unit cell. The bond length, bond angles of this crystal is given in Table-2.8 and 2.9.

The values reveal that it also has the main features like 2.1a without solvent molecule in the unit cell. Acetone molecule imparts some symmetry to the molecule when it is in the unit cell but not as the benzene solvent.
Table 2.8: Bond lengths (in Å) for compound 4,8,9,10-tetraphenyl-1,3-diazatricyclo[3.3.1.1]decan-6-one.

<table>
<thead>
<tr>
<th>Atoms</th>
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<th>Atoms</th>
<th>Bond length</th>
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Table 2.9: Bond angles involving atoms in the main skeleton for the compound 4,8,9,10-tetraphenyl-1,3-diazatricyclo[3.3.1.1]decan-6-one.

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Table-2.10: Bond lengths for the atoms involved in main skeleton of 4,8,9,10-tetraphenyl-1,3-diazatricyclo[3.3.1.1.7]decan-6-one with Acetone in the unit cell. (Molecule A with Acetone).

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Table-2.11: Bond angles involving atoms in the main skeleton for the compound 4,8,9,1 Q-tetraphenyl-1,3-diazatricyclo[3.3.1.1.] decan-6-one with Acetone in the unit cell. (Molecule A with Acetone).

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<th>Atoms</th>
<th>Bond angle (°)</th>
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Table-2.12: Bond lengths for the atoms involved in main skeleton of 4,8,9,10-tetraphenyl-1,3-diazatricyclo[3.3.1.1]decan-6-one with Acetone in the unit cell: (Molecule B).

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Table-2.13: Bond angles involving atoms in the main skeleton for the compound 4,8,9,10-tetraphenyl-1,3-diazatricyclo[3.3.1.1]decan-6-one with Acetone in the unit cell. (Molecule B).

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C7-C6-C5 112.63
EXPERIMENTAL:

All the NMR spectra were measured using a Bruker 360 and a Jeol AMX 400 instruments. The $^1$H-NMR spectra were measured for approximately 0.03 M solutions in CDC$_3$ at either 360 or 400 MHz with TMS as internal reference. Similarly, coupled and decoupled C-NMR spectra were measured for approximately 0.05 M solutions in CDCl$_3$ at 100 MHz with TMS as internal reference.

For $^3$C-NMR spectra, a pulse angle of 37.5° (5 ns), an acquisition time of 0.72 s and a repetition time of 3.72 s were used, collecting 32K data points in the quadrature detection mode for a spectral width of 22700 Hz. The accuracy of the $^1$H and $^13$C chemical shifts is considered to be 0.02 and 0.05 ppm, respectively. H, H-COSY spectra were obtained using the COSY-45 procedure while one-bond H- C correlation's were recorded using the HETCOR pulse sequence over the required frequency ranges.

The two dimensional spectra are acquired with 1024 data points along $t_2$ and 512 data points along $t_1$. These are zero filled to get a two dimensional matrix of 1024 X 1024 points. The time increments used are 0.000112 s with a sweep width of 4464 Hz in double quantum filtered COSY experiment with TPPI as an internal standard. F1 and F2 processing are done in Sine Square weighting function. For ROESY spectra the time
increments used are 0.000136 s with sweep width of 3676.47 Hz in double quantum filtered COSY experiment with TPPI as an internal standard. F1 and F2 processing are done in Sine Square weighting function. Spectra were obtained using the roesytp procedure. Nuclear Overhauser enhancements (NOE) were determined by the difference method using the low-intensity presaturation pulses of 5s before each acquisition pulse. A sequence of eight scans with selected irradiation followed by eight scans with irradiation at a nearby blank position was repeated 12 times. The summed irradiated and blank free-induction decays were subtracted and transformed to give the difference spectra.

The methods available in the literature were adopted with some mod ideation to prepare these compounds. 10 ml of aq. formalin was used to condense 5 grams of 2,4,6,8-tetraaryl-3,7-diazabicyclo[3.3.1]nonan-9-ones into diazaadamantan-6-ones in benzene solvent at room temperature for three days. Two layers were separated and the organic layer was dried with anhydrous CaCL and the excess benzene is distilled out. The remaining residue is washed with acetone and it is filtered, dried and crystallized using benzene chloroform and acetone mixture in 2:2:1 ratio and the melting points are noted.
Fig. 2.01  H, H-COSY spectrum of 4,8,9,10-tetraphenyl-1,3-diazatricyclo[3.3.1.1]decan-6-one.
Fig. 2.02  H, H-COSY enlarged spectrum of 4,8,9,10-tetraphenyl-1,3-diazatricyclo[3.3.1.1]decan-6-one-1.
H, H-COSY enlarged spectrum of 4,8,9,10-tetraphenyl-1,3-diazatricyclo[3.3.1.1]decan-6-one-2.
Fig. 2.05  C, H-COSY enlarged spectrum of 4,8,9,10-tetraphenyl-1,3-diazatricyclo[3.3.1.1]decan-6-one-1.
Fig. 2.06  C, H-COSY enlarged spectrum of 4,8,9,10-tetraphenyl-1,3-diazatricyclo [3.3.1.1]decan-6-one-2.
Fig. 2.07  NOESY spectrum of 4,8,9,10-tetraphenyl-1,3-diazatricyclo[3.3.1.1]decan-6-one.
Fig. 2.08  Proton NMR spectrum of 4,8,9,10-tetrakis(4-methoxy phenyl)-1,3-diazatricyclo[3.3.1.1]decan-6-one.
Fig. 2.09  $^{13}$Carbon NMR spectrum of 4,8,9,10-tetrakis(4-methoxy phenyl)-1,3-diazatricycloc[3.3.1.1]decan-6-one.
Fig. 2.10  C, H-COSY spectrum of 4,8,9,10-tetrakis(4-methoxyphenyl)-1,3-diazatricyclo[3.3.1.1]decan-6-one.
Fig. 2.11  NOESY spectrum of 4,8,9,10-tetrakis(4-methoxyphenyl)-1,3-diazatricyclo[3.3.1.1]decan-6-one.
Fig. 2.12  ROESY spectrum of 4,8,9,10-tetraakis(4-methoxyphenyl)-1,3-diazatricyclo[3.3.1.1]decan-6-one.
Fig. 2.13  Proton NMR spectrum of 4,8,9,10-tetrakis(4-chlorophenyl)-1,3-diazatricyclo[3.3.1.1]decan-6-one.
Fig. 2.14  $^{13}$Carbon NMR spectrum of 4,8,9,10-tetrakis(4-chlorophenyl)-1,3-diazatricyclo[3.3.1.1]decan-6-one.
Fig. 2.15  Proton NMR spectrum of 1-methyl-4,8,9,10-tetraphenyl-1,3-diazatricyclo[3.3.1.1]dec-6-one.
Fig. 2.16 $^{13}$Carbon NMR spectrum of 1-methyl-4,8,9,10-tetraphenyl-1,3-diazatricyclo[3.3.1.1]decan-6-one.
Fig. 2.17 Proton NMR spectrum of 4,8,9,10-tetraphenyl-1,3-diazatricyclo[3.3.1.1]decane.
Fig. 2.18  $^{13}$Carbon NMR spectrum of 4,8,9,10-tetraphenyl-1,3-diazatricyclo[3.3.1.1]decane.
Fig. 2.19  H-H-COSY spectrum of 4,8,9,10-tetraphenyl-1,3-diaza-tricyclo[3.3.1.1]decan
Fig. 2.21  DEPT spectrum of 4,8,9,10-tetraphenyl-1,3-diazatricyclo [3.3.1.1]decane
Fig. 2.22 ORTEP plot of 4,8,9,10-tetraphenyl-1,3-diazatricyclo[3.3.1.1]decan-6-one.
Fig. 2.23 ORTEP plot of 4,8,9,10-tetraphenyl-1,3-diazatricyclo[3.3.1.1]decan-6-one with acetone solvent.
Fig. 2.24 PLUTO view of 4,8,9,10-tetraphenyl-1,3-diazatricyclo[3.3.1.1]decan-6-one.
Fig. 2.25  PLUTO view of 4,8,9,10-tetraphenyl-1,3-diazatricyclo[3.3.1.1]decan-6-one with acetone solvent.
Fig. 2.26 PLUTO view of 4,8,9,10-tetrakis(4-chlorophenyl)-1,3-diaza tricyclo[3.3.1.1]decan-6-one.

Fig. 2.27 PLUTO view of 4,8,9,10-tetrakis(4-methoxyphenyl)-1,3-diazatricyclo[3.3.1.1]decan-6-one.
REFERENCES:


