SUMMARY

Chapter-1

Several of 2,4,6,8-tetraaryl-3,7-diazabicyclo[3.3.1]nonan-9-ones have been prepared using Noller-Baliah synthesis.

The stereochemistry of these compounds has been assigned unambiguously using ¹H-NMR, ¹³C-NMR, H,H-COSY, C,H-COSY, NOE and it is supported by the i) Molecular Modelling Calculations and ii) X-ray studies. The studies reveal that the compounds adopt chair-boat conformation with all the aryl groups in the equatorial orientation at 2,4,6,8. The aryls at 2 and 4 are orthogonal to the aryls at 6 and 8 with an angle of approximately 60°.

2. The chemical shift values of each aryl carbons and aryl hydrogens are also assigned unambiguously.

3. The literature misassignment of chemical shift values for bridgehead and benzylic carbon atoms are corrected using C,H-COSY spectra.

4. The orientation of hydrogen in NH group is fixed as equatorial using trans bands in IR spectra.

5. 1-Carbethoxy-2,4,6,8-tetraaryl-3,7-diazabicyclo[3.3.1]nonan-9-ones are also prepared and its chemical shift values for each hydrogen and
carbon atoms are assigned using the NMR techniques like $^1$H-NMR, $^{13}$C-NMR, H,H-COSY, C,H-CGSY, DEPT methods.

Chapter-II

1 1,3-diazaadamantan-6-ones with various aryl substituents at 4,8,9,10 are prepared and their stereochemistry is fixed using NMR techniques like $^1$H-NMR, $^{13}$C-NMR, H,H-COSY, C,H-COSY, ROESY, HMBC and supported by the X-ray studies. The stereochemistry of the compounds is that the aryls at 4 & 10 are in axial orientation and the aryls at 8 & 9 are in equatorial orientation. Similarly the chemical shift values of hydrogens and carbons of 4,8,9,10-tetraaryl-1,3-diazatricyclo[3.3.1.1]decanes also assigned through the PMR, $^{13}$C-NMR, H,H-COSY, C,H-COSY, DEPT methods.

2 The crystallization has been carried out in various solvent molecules using Benzene, Chloroform and Acetone for some of the 4,8,9,10-tetraaryl-1,3-diazaadamantan-6-ones. It has been observed that the solvent molecules are entrapped in the unit cell during crystallisation. The melting point of the compounds with solvent molecules in the unit cell have lower value than the compounds without solvent molecules in the unit cell. Perfect symmetry is maintained in the first case whereas in the latter case the symmetry is not maintained. The
study using bond lengths, bond angles and torsional angles reveals that the strain produced in the ring due to the axial aryl substituents is larger than the equatorial substituents.

Chapter-III

The ring strain in the compounds containing piperidine skeleton viz; 2,6-diaryl-4-piperidone, 2,4,6,8-tetraaryl-3,7-diazabicyclo[3.3.1]nonan-9-ones and 4,8,9,10-tetraaryl-1,3-diazatricyclo[3.3.1.1]decan-6-ones have been studied through the chemical shift values, C,H-coupling constants, bond angles, bond lengths and torsional angles of carbonyl carbon, a-carbons to the carbonyl carbon and carbonyl stretching frequencies in IR. Effect of sp\(^2\) carbon atoms in the ring, substituents on the main ring also considered. From these studies, it can be concluded that the bulky substituents present in the cyclic systems cause the ring strain. To minimize the effect of ring strain, (i) the hybridisation of the concerned atom is slightly shifted otherwise (ii) the outer orbitals of the ring would get more ‘s’ character. Cyclic ketones with normal valence angle (a) shows \(\gamma_c=0\) between 1698-1705 cm\(^{-1}\) in IR and (b) \(^{13}\)C-NMR of «- between 50-52 ppm. If the
stretching values are increased and its chemical shift values of \( \alpha \)-carbons to the carbonyl group also increased.

Chapter-IV

1. 3-Carbethoxy-2,6-diaryl-4-piperidones and 3-carbethoxy-2,6-(bis-4-methoxyphenyl)piperid-5-en-4-one, 3-carbethoxy-2,6-(bis-4-methylphenyl)piperid-5-en-4-one were prepared. The stereochemistry of these compounds are discussed using NMR techniques like \(^1\text{H-NMR}, \ ^{13}\text{C-NMR}, \ ^{1}H\text{-H-COSY}, \ ^{1}C\text{-H-COSY}, \text{DEPT-135}\) and X-ray methods. The aryls at 2 and 6 positions are in equatorial orientations and both the aryls are having cis relation in saturated cyclic ketones. Similarly the carbethoxy group at C3 is also in equatorial orientation and has trans relation with the aryls at 2 and 6.

2. The 3-carbethoxy substitution in 3-Carbethoxy-2,6-diphenyl-4-piperidone produces the strain in the piperidone ring and hence the ring flattening occurs along the C4 and C5 to minimise the strain.

3. In 3-carbethoxy-2,6-(bis-4-methoxyphenyl)piperid-5-en-4-one and 3-carbethoxy-2,6-(bis-4-methylphenyl)piperid-5-en-4-one, the strain in the ring increases further hence the respective atoms at C4 and C5 in the ring comes to the single plane results the unsaturation at the C4 and C5 positions.
4. The X-ray studies indicate that two molecules are present in the unit cell for 3-carbethoxy-2,6-diphenyl-4-piperidone.

Chapter-V

3-Carbethoxy-2,6-diaryl-4-piperidone (4.11a-c) and 3-carbethoxy-2,6-(bis-4-methoxyphenyl)piperid-5-en-4-one, 3-carbethoxy-2,6-(bis-4-methylphenyl)piperid-5-en-4-one were prepared and these were condensed with hydrazine-hydrate at 15°C yielded the 3,4(3-hydroxypyrazolo)-2,6-diaryl piperid-2-ene, 3,4(3-hydroxypyrazolo)-2,6-(bis-4-methoxyphenyl)piperid-2-ene, 3,4(3-hydroxypyrazolo)-2,6-(bis-4-methylphenyl) piperid-2-ene respectively. The compounds are characterised through IR, 'H-NMR, $^{13}$C-NMR and mass spectrum.