CHAPTER XVIII

COMPARATIVE STUDY ON THE CONFORMATIONAL ASPECTS OF DIAZEPINE DERIVATIVES.

IDHD

DPMU

TTNPHBD
18.1 INTRODUCTION:

The X-ray crystal structure analyses of three heterocyclic organic compounds all belonging to the same family called 'diazepine' are presented in chapters XV to XVII in the thesis. All the three structures have essentially the diazepine ring as the basic skeleton. The structure determination was undertaken in order to study the orientation of the substituent groups and their effect on the geometry of the diazepine ring. The study was also undertaken to know how the conformation of the diazepine ring changes due to the fusion of cyclohexane (DPMU) and benzene (TTNPBHD) ring system with the diazepine ring.

18.2 COMPARISON OF IDHD AND DPMU (CHAPTERS XV AND XVI)

The bond lengths, bond angles and torsion angles of the diazepine ring observed in IDHD and DPMU are summarized in Table 18.1. From the study of this table, we note that the corresponding bond lengths and bond angles of IDHD and DPMU are in close agreement with each other. It is evident from the diazepine ring torsion angles (Fig 18.1) that the chair conformation of IDHD is more distorted (about 1.1 - 10.1°, Table 18.1) compared to DPMU. The phenyl rings are equatorially oriented in both molecules. The isopropyl group in IDHD and the methyl group in DPMU are equatorially oriented. The carboxyl oxygen bond (C=O) is not the same in both molecules (1.228(3) Å in IDHD and 1.267(4) Å in DPMU). The oxygen atom in both the molecules are involved in intermolecular hydrogen bonding. Crystal packing forces may affect the geometry of flexible portions of the molecule. The N1-C2 bond in IDHD (1.489(3) Å) is a single bond and the disposition of bonds is pyramidal at N1. The N4-C5 bond
in IDHD(1.329(3) Å) is shortened by electron delocalization between the nitrogen lone pair and the carbonyl oxygen atom to a length of about half-way between the C-N pure single and double bond values. Similar argument holds good for DPMU also. Thus, we see that the different substituents in IDHD and the diazepine ring in DPMU change the chair conformation of the diazepine ring to a considerable amount.

18.3 COMPARISON OF DPMU AND TTNPHBD (CHAPTERS XVI AND XVII)

The bond lengths, bond angles and torsion angles of the diazepine ring observed in DPMU and TTNPHBD are summarized in Table 18.1. From the study of this table, we note that the bond lengths, bond angles and torsion angles of DPMU and TTNPHBD are different in both the molecules. This is because of the benzo-fusion in TTNPHBD and cyclohexane fusion with the diazepine ring in DPMU. In the seven-membered heterocyclic ring of DPMU there is no formal double bond present, but there is an amide double bond C5-N6(1.302(4) Å). Therefore, due to the trans fusion and different substituents, the diazepine ring adopts a chair conformation in DPMU. In TTNPHBD, the diazepine ring contains one shared aromatic bond. The N-C bond length varies from 1.385(3) Å to 1.479(3) Å in TTNPHBD. The bulky carbamoyl group is in coplanar orientation with reference to C2-N1-C10 plane. The methyl group substituted on the C2 atom is in the equatorial orientation. Therefore, due to the benzofusion and different substituents, the diazepine ring adopts a boat conformation in TTNPHBD.
18.4 CONCLUSION:

From the analysis of the molecules IDHD, DPMU and TTNPHBD, the following conclusions have been drawn:

1. The molecule of the IDHD compound consists of a diazepine ring. The diazepine ring adopts a distorted chair conformation.

2. The molecule of the DPMU compound consists of a cyclohexane ring fused to a diazepine ring. The diazepine ring is in chair conformation. The trans fusion of the cyclohexane ring to the diazepine ring is evident from the present crystal structure analysis.

3. The molecule TTNPHBD consists of a benzene(benzo) ring fused to a diazepine ring. The benzene ring is planar. The diazepine ring adopts a boat conformation.
Fig. 18.1 Conformation of diazepine rings