CHAPTER 2

LITERATURE SURVEY

This chapter describes the extensive studies of the structure, symmetry and conformation of three organic compounds of pharmaceutical importance by the method of single crystal X-ray diffraction.

Fun has done X-ray crystal structure studies of Bis[4-(4-chlorophenyl)-4-hydroxy-piperidinium] dipicrate dimethylsulfoxide solvate. The asymmetric unit of the title salt solvate, 2C₁₁H₁₅ClNO⁺. 2C₆H₅N₃O₇ : C₂H₆OS, contains two crystallographically independent 4-(4-chlorophenyl)-4-hydroxy-piperidinium cations, two picrate anions and a dimethyl sulfoxide solvent molecule. In each cation, the piperidinium ring adopts a chair conformation. In the crystal structure, the cations, anions and solvent molecules are connected by intermolecular O–H–O, N–O and C–H–O hydrogen bonds, forming a three-dimensional network. The title compound crystallizes in a monoclinic space group P₂₁ with a = 8.9207 (4) Å; b = 18.1230 (9) Å; c = 12.9886 (6) Å; α = 90°; β = 98.430 (1)°; γ = 90°; V = 2077.18 (17) Å³; Z = 2; D_cal = 1.533 Mg/m³ at 100K. The structure was solved by direct methods and refined by full-matrix least-squares procedures to final R = 0.029 using 15185 reflections. Fun has done X-ray crystal structure studies of 4-(4-Chlorophenyl)-4-hydroxy-piperidinium.

2-(2-phenylethyl)benzoate, in this title compound, C₁₁H₁₅ClNO⁺.C₁₅H₁₃O₂⁻, the piperidinium ring adopts a chair conformation. In the crystal, cations and anions are connected by intermolecular O–H–O and N–H–O hydrogen bonds, forming two-dimensional networks parallel to the bc plane. Furthermore, the crystal structure is stabilized by weak C–H–π interactions. The title compound crystallizes in a monoclinic space group P₂₁/c with a = 13.1016 (2) Å; b = 10.2963 (2) Å; c = 16.8015 (3) Å; α = 90°; β = 98.234 (1)°; γ = 90°; V = 2243.12 (7) Å³; Z = 4; D_cal = 1.297 Mg/m³ at 100K.
The structure was solved by direct methods and refined by full-matrix least-squares procedures to final $R= 0.042$ using 8207 reflections.

Allen et al. (1987) have studied the electron density function $\rho(r)$ in a crystal determines its diffraction patterns, that is, both the magnitudes and phases of its X-ray diffraction maxima, and conversely. If, however, as is always the case, only magnitudes are available from the diffraction experiment, then the density function $\rho(r)$ cannot be recovered. If one invokes prior structural knowledge, usually that the crystal is composed of discrete atoms of known atomic numbers, then the observed magnitudes are, in general, sufficient to determine the positions of the atoms, that is, the crystal structure.

Bernstein et al. (1995) have studied the “Graph Set Analysis of Hydrogen Bond Motifs” by the method of single crystal X-ray diffraction

Cremer and Pople (1974), have studied a general definition of Ring Puckering Coordinates. Further they revealed that a unique mean plane is defined for a general monocyclic puckered ring. The geometry of the puckering relative to this plane is described by amplitude and phase coordinates which are generalizations of those introduced for cyclopentane by Kilpatrick, Pitzer and Spitzer. Unlike earlier terms based on torsion angles, no mathematical approximations are involved. A short treatment for the four, five and six membered ring demonstrates the usefulness of this concept. Finally as example is given of the analysis of crystallographic structural data in terms of these coordinates.

Ranu and Banerjee (2005) have explored “Ionic Liquid as Catalyst and Reaction Medium”, in Michael Addition of Active Methylene Compounds to Conjugated Ketones, Carboxylic Esters, and Nitriles. Although the addition to $\pi-\pi$ unsaturated ketones proceeds in the usual way, giving the mono addition products, this ionic liquid always drives the reaction of open-chain 1,3-dicarbonyl compounds with $\pi-\pi$ unsaturated esters and nitriles toward bis-addition to produce exclusively bis-adducts in one stroke.

Khan et al. (2008) have made studies on X-ray crystal structure of “3, 5-Dinitrobenzyl methanesulfonate”. The title compound, $C_8H_8N_2O_7S$, an intermediate in the synthesis of N, N-bis (2-hydroxyethyl)-3, 5-dinitroaniline, exist as a discrete molecule; the nitro groups are twisted with respect to the aromatic system [dihedral angles $= 17.0 \text{ (1)}$ and $26.3 \text{ (1)}$]. The title compound crystallizes in a monoclinic space group $P2_1/c$ with $a = 9.3549 \text{ (5) Å}$, $b = 8.7552 \text{ (5) Å}$; $c = 14.1526 \text{ (8) Å}$; $\alpha = 90^\circ$; $\beta = 107.430 \text{ (1)°}$; $\gamma = 90^\circ$; $V = 1105.91 \text{ (11) Å}^3$; $Z$
= 4; \( D_{\text{cal}} = 1.659 \text{ Mg/m}^3 \text{ at } 89 \text{(1)K} \). The structure was solved by direct methods and refined by full-matrix least-squares procedures to final \( R= 0.019 \) using 2233 reflections.

John C Mac Donald and George M. White sides (1994) focused on molecules that form tapes, because these rigid, linear aggregates simplify the packing problem by imposing predictable structural order in crystals. All but one class of diamides they surveyed form tapes. This fact is remarkable considering the range of possible packing patterns. They infer that not surprisingly, many cyclic diamides also form structures other than tapes, including dimers, ribbons, layers, and three-dimensional motifs. While these structures are interesting in their own right as motifs for crystal engineering, the frequency with which tapes occur, and the large number of tapes that form relative to other motifs make tapes the motif of choice for designing crystals based on diamides.

Koch U and Popelier PLA (1995), have shown that the total charge density is a valid source to confirm hydrogen bonding invoking a reference charge density. A set of criteria are proposed based on the theory of “atoms in molecules” to establish hydrogen bonding, even for multiple interactions involving C–H–O hydrogen bonds. These criteria are applied to several Van der Waals complexes. Finally a bifurcated intramolecular C–H–O hydrogen bond is predicted in the anti-AIDS drug AZT, which may highlight a crucial feature of the biological activity of a whole class of anti-drugs.