ABSTRACT

The work reported in this thesis can be divided into four chapters. The first two chapters deal with the crystallographic and spectroscopic studies of six terminal alkynes. The third chapter describes the crystal structure analysis of two natural products. The fourth chapter deals with the structural studies of two organic compounds. The structures were solved by direct methods and refined by full matrix least squares procedure.

Acetylenic compounds are used as anaesthetic, sedative and hypnotic agents. In the first chapter of the thesis the crystal structure analyses of six terminal alkynes, namely (1) 1β - hydroxy - 1α - propargyl - 2β - methyl - 2 (2'- carb-ethoxy - vinyl) - cycloheptane. (2) 2β - hydroxy - 2α - 3 (propargyl) -4’ methyl - spiro (5.5) - undec -3’ - ene -2’ - one. (3) 5β - hydroxy - 5α - (3 -propargyl) - 10β - methyl - Δ19 octalin - 2 - one (4) 5β - hydroxy - 5α - ethynyl - 10β - methyl Δ19 octalin - 2-one. (5) 2α, 4’β - dihydroxy - 2 β, 4’α -diethynyl - spiro (5.5) - undec - 2’-ene. and (6) 1β - hydroxy - 1α - propargyl - 2α -(2’ - carb - ethoxy - vinyl) - 2,4,4’ - trimethyl cyclopentane are presented. These compounds will hereafter be referred to as TA (I), TA (II), TA (III), TA (IV), TA (V), and TA (VI) respectively.

TA (I) : C_{16}H_{24}O_{3}, M_r = 264.35, P2_1/c, a = 11.483 (2)Å, b = 11.615 (1)Å, c = 12.412 (2)Å, β = 111.78 (1)° V = 1537.3 (4)Å^3, Z=4, D_x = 1.142 Mgm^{-3}, CuKα radiation (λ = 1.5418 Å) μ = 0.616 mm^{-1} and T = 293K. R = 0.072 for 1486 reflections with I > 2σ (I). TA (II) : C_{16}H_{20}O_{2},
Mr = 232.31, Pna21, a = 27.700 (3)Å, b = 7.630 (4)Å, c = 12.382 (1)Å, V = 2617.1 (1)Å³, Z = 8, Dx = 1.179 Mgm⁻³, CuKα radiation (λ = 1.5418 Å), μ = 0.571 mm⁻¹ and T = 293K. R = 0.0474 for 1990 reflections with I>2σ(I).

TA (III) : C₁₄H₉₈O₂, Mr = 218.28, Pca₂₁, a = 13.559 (1)Å, b = 7.960 (2)Å, c = 21.748 (3)Å, V = 2347.4 (6)Å³, Z = 8, Dₓ = 1.235 Mgm⁻³, MoKα radiation (λ=0.71073Å) μ=0.081 mm⁻¹, T = 293 K. R = 0.0405 for 1399 reflections with I > 2σ(I).

TA (IV) : C₁₃H₁₆O₂, Mr = 204.26, Pbca, a = 10.244 (7)Å, b = 12.734 (2)Å, c = 17.125 (2)Å, V = 2233.9(2)Å³, Z = 8, Dₓ = 1.215 Mgm⁻³, CuKα radiation (λ = 1.54180Å), μ = 0.640 mm⁻¹, T = 293K. R = 0.0403 for 1379 reflections with I > 2σ(I).

TA (V) : C₁₅H₁₈O₂.₁/₂ H₂O, Mr = 248.31 PFI, a = 6.414 (2)Å b = 6.921 (1) Å, c = 30.760 (1) Å, α = 94.33(5)°, β = 90.20(3)°, γ = 100.59(3)°, V = 1338.18 (2) Å³, Z = 4, Dₓ = 1.185 Mgm⁻³ CuKα radiation (λ = 1.5418Å), μ = 0.630 mm⁻¹, T = 293 K. R = 0.0586 for 3229 reflections with I > 2σ(I).

TA (VI) : C₁₆H₂₄O₃, Mr = 264.35, P2₁/c, a = 8.526 (6)Å, b = 10.815 (5)Å, c = 17.547 (9)Å, β = 90.40(6)°, V = 1617.9(2)Å³, Z = 4, Dₓ = 1.085 Mgm⁻³, CuKα radiation (λ = 1.5418Å), μ = 0.585 mm⁻¹, T = 293K. R = 0.0510 for 2111 reflections with I> 2σ(I).

Terminal alkynes act as an excellent model system for studying the C-H...O hydrogen bonds because of the presence of high acidity - C≡C-H groups. In the second chapter, an attempt has been made to understand the existence of C-H...O hydrogen bonds in terminal alkynes. The analysis is performed using criteria which are customary for the stronger N-H...O and
O-H...O) hydrogen bonds, namely, lengths (D), angles (θ,φ) and effects on crystallographic and spectroscopic properties.

From the results obtained it is concluded that the C-H...O hydrogen bond is weaker in TA(VI) compared with the other five terminal alkynes. A good correlation is noted between the solid state C(sp) - H stretching frequencies and intermolecular C...O distances.

Chapter 3 deals with the structural studies on two natural products, namely, 1. Triterpenoids (Piscidinol C) and 2. Isoflavonoids (Dalspinosin). These compounds will hereafter be referred to as NP(I) and NP(II) respectively.

NP(I) : This compound was extracted from the plant Walnsura Piscidia Roxb. This plant is used in traditional medicine as a stimulant and expectorant. \( C_{32}H_{46}O_8; M_r = 558.69, C222_1, a = 18.985(4)Å, b = 13.092(5)Å, c = 24.690 (7)Å, V = 6136.93(4)Å^3, Z = 8, D_x = 1.209 Mgm^{-3}, MoK\alpha radiation (λ = 0.71073 Å) \mu = 0.090 mm^{-1} \text{ and } T = 293K. R = 0.0580 \text{ for 1668 reflections with } I > 2\sigma(I). \)

NP(II) : This compound was extracted from the plant Dalbergia Spinosas. A spoonful of powdered roots in a tumblerful of water is said to be sufficient to destroy in less than half an hour, the effects of alcohol. \( C_{18}H_{16}O_7; M_r = 344.31, P2_1/c, a = 10.752 (1)Å, b = 8.711 (2) Å, c = 16.646 (1) Å, β = 94.4 (1)°, V = 1554(4)Å^3, Z = 4, D_x = 1.471 Mg m^{-3}, MoK\alpha radiation (λ=0.71073Å), \mu = 0.144 mm^{-1}, \text{ and } T = 293 K. R = 0.0399 \text{ for 2116 reflections with } I>2\sigma(I). \)
In the fourth chapter, the structural studies on two organic compounds are reported. 1. 2-methyl - 2 methyl acrylyl - cyclohexanone - (1,5) - Dioxaspiro mononeopentyl ketal. 2. 3 (1-phenyl methylidine) - 6 - methyl - benzfuran - 2 - one. These compounds will hereafter be referred to as SP (I) and SP (II) respectively.

1. SP(I): Compounds of similar structure have anticonvulsant and antidepressant properties. C\textsubscript{16} H\textsubscript{24} O\textsubscript{5}, Mr = 296.36 P\textsubscript{2}/a, a = 13.049 (1)Å, b=10.411 (1) Å, c = 12.317 (3)Å, β = 105.5(1)°, V = 1612.8 (2) Å\textsuperscript{3}, Z = 4, \(D_{x} = 1.221 \text{ Mgm}^{-3}\), MoK\textsubscript{α} radiation (\(\lambda = 0.71073 \text{ Å}\)), \(\mu = 0.06 \text{mm}^{-1}\) and \(T = 293 \text{ K} \). R = 0.050, for 1641 reflections with I>3σ (I). 2. SP(II): Compounds containing the furan ring system have antibacterial activity. C\textsubscript{17}H\textsubscript{14}O\textsubscript{2}, Mr = 250.3, P\textsubscript{T}, a = 9.890 (5)Å, b = 9.258 (4)Å, c = 8.878 (5)Å, \(\alpha = 108.26 (4)^{\circ}\), \(\beta = 78.48 (4)^{\circ}\), \(\gamma = 67.38 (4)^{\circ}\), V = 663.3 (6) Å\textsuperscript{3}, Z = 2, \(D_{x} = 1.253 \text{ Mgm}^{-3}\), MoK\textsubscript{α} radiation (\(\lambda = 0.71073 \text{ Å}\)), \(\mu = 0.0757 \text{mm}^{-1}\) and \(T = 293 \text{ K} \). R = 0.063, for 913 reflections with I > 3σ (I).