09-Crystallography of Organic Compounds

Single crystal X-ray structural studies are carrying out in order to unequivocally establish the solid state molecular structure, including absolute configurations of the chiral samples, and provide accurate geometrical parameters. Using the X-ray based geometries semiempirical calculations are being applied on the whole series in order to generate structural and energetic conformational parameters.

X-ray solid state geometries and theoretical conformations will be compared and discussed.

Methodology:

— Crystal Structure Determinations:
  Cad4, a6/26, Profile Analysis, Direct Methods, Dinlif, SHELX76, Bijvoet, Parst.

— Conformational Analysis:
  ChemX (Chemical Design Ltd, Oxford, England, UK)

PS-06.02.14 CRYSTAL STRUCTURE OF PROTOPINE HYDROCHLORIDE: By Y. Y. Gong,1,2,* S. D. Lao,3 Y. F. Yang,4 South West Forestry College, Kunming, China; 2 State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Beijing, China; 3 Yunnan Institute of Botany, Chinese Academy of Sciences, Kunming, China; 4 Institute of Multipurpose Utilization of Mineral Resources, Ministry of Geology and Mineral Resources, Chengdu, China.

The crystal structures of protopine and its analogues, well known isoquinolinine type alkaloids with ten-membered heteroring have been determined by Hall (Hall, S. R. et al., 1968), Acta Cryst., B24, 337. It has been reported that the resonance absorptive values of carbonyls of these compounds in IR and C13 NMR are smaller than the corresponding values of a, β-unsaturated acetylene. Therefore, it was inferred that a cross-ring interaction exists between carbon-14 and the N atom of the pyridine ring. Afterward it was discovered that the hydroxy peaks of protopine trichloracetate, hydrochloride and acetate in C13 NMR appeared while the carboxyl peaks about 19 ppm disappeared, implying that some kind of structure changes occurred during the reaction between this type of alkaloide and acids.

Single crystals of protopine hydrochloride were grown from water solution by natural evaporation. The crystallographic parameters by direct methods are the following: monoclinic, P21/a, a = 15.906 Å, b = 17.776(3) Å, c = 6.497(2) Å, β = 104.55°, Z = 4.

PS-06.02.15 (18)ANNULENE C18H18: STRUCTURE, DISORDER AND HUCKEL'S 4e+2 RULE. By M. Kremer, S. Gorter, C. Romers, Chemistry Department, Leiden University, The Netherlands, and D.W.B. Cogdill*, Chemistry Department, UMIST, Manchester, U.K.

The Congress logo by its outer blue part shows the ring structure of C18H18. For over 50 years theoreticians have debated whether, as n increases in large polyenes, C–C bond lengths should alternate or end in equality. The recent 3-1G SCF calculations for (18)annulene by Schulman & Disch (J. Mol. Struct. 1991, 233, 219) reported that a planar D3h structure with bond alternation was more stable than a D6h structure with nearly equal bonds; however when REM2 electron correlation was considered, D6h was favoured.

The X-ray study by Bregman et al. (Acta Cryst., 1965, 19, 227, 235) resulted in an almost planar molecule with twelve inner C–C bonds of mean 1.383(3) Å and six outer bonds of 1.419(4) Å. The 0.03 Å difference was puzzling.

The crystal structure has now been reinvestigated at 111 K, and an unexpected disorder has been discovered. 85.5% of the molecules are in the orientation found by Bregman et al. and 14.5% are rotated by 30° in the mean plane. The twelve outer hydrogens are in essentially the same places in both orientations (30°/12 = 30'). Constrained refinement yields a major molecule of approximate D6h symmetry with means: inner bonds 1.387(1) Å, outer bonds 1.408(1) Å, C–C–C ring re-entrant angles 128.0°. The six inner hydrogens alternate up and down by 0.1 Å from the mean plane; the TDL analysis and molecular packing suggest slight disorder across the plane. The results agree well with the D6h calculations of Schulman & Disch. A 50:50 inversion disorder of D3h molecules can be excluded as their ring diameters are up to 0.20 Å too large. Thus the 4e+2 e-electron molecule [18]annulene is confirmed as having an aromatic structure.