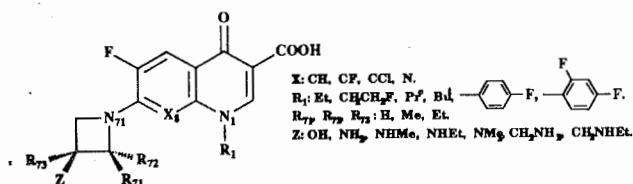


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06-Crystallography of Organic Compounds



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, $\omega/2\theta$, Profile Analysis, Direct Methods, Dirdif, Shelx76, Bijvoet, Parst.

— Conformational Analysis:

ChemX (Chemical Design Ltd, Oxford, England, UK)
 AM1 (M.J.S. Dewar, J. Am. Chem. Soc., 1985, 107, 3902)

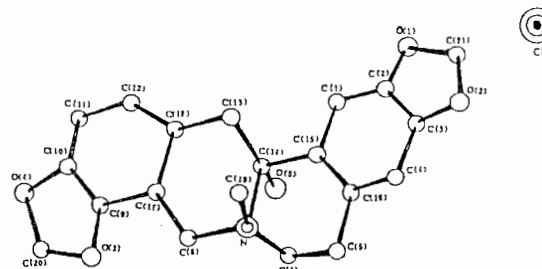
PS-06.02.14 CRYSTAL STRUCTURE OF PROTOPINE HYDROCHLORIDE. By Y. H. Gong^{1,2,*}, S. D. Lao³, Y. F. Yang⁴, ¹South West Forestry College, Kunming, China; ²State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Beijing, China; ³Kunming Institute of Botany, Chinese Academy of Science, Kunming, China; ⁴Institute of Multipurpose Utilization of Mineral Resources, Ministry of Geology and Mineral Resource, Chengdu, China.

The crystal structures of cryptopine and its analogues, well known isoquinolin type alkaloids with ten-membered heterorings 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 α , β -unsaturated acetyry. Therefore, it was inferred that a cross-ring interaction exists between carbon-14 and the N atom (Guinandeau, H. et al; (1982) Lloydia, 45, 237). Afterward it was discovered that the hydroxyl peaks of protopine trichloracetate, hydrochloride and acetate in C13 NMR appeared while the carbonyl peaks about sc of 194 ppm disappeared, implying that some kind of structure changes occurred during the reaction between this type of alkaloid and acids.

Single crystals of protopine hydrochloride were grown from water solution by natural evaporation. The crystallographic parameters are the following: monoclinic, $p21/a$, $a=13.965(4)\text{\AA}$, $b=17.776(5)\text{\AA}$, $c=6.997(2)\text{\AA}$, $\beta=104.35^\circ$, $Z=4$,

$V=1677.96\text{\AA}^3$, $CuKa$ (1.5418\text{\AA}), $\mu=21.95\text{cm}^{-1}$. 3062 independent reflections with $6^\circ \leq 2\theta \leq 130^\circ$ were collected using a PW-1100 diffractometer with graphite monochromator. The structure was solved by direct methods (program RANTAN) and refined by least square techniques (SHELX-76) to a final R of 0.0773 for 2833 reflections with $I \geq 3\sigma(I)$.

The crystal structure shows that the distance between the C-14 and N atom of protopine hydrochloride is 1.587\text{\AA}. (The corresponding value in protopine 2.555\text{\AA}), indicating that a covalent link formed between the two atoms and the structure has changed from ten-membered heteroring to two six-membered condensed heterorings. So it can be considered as a cross-ring structural rearrangement. The reaction leading to this type of structural rearrangement will be reversed if the alkaloid is transferred from an acidic to basic solution. Studies of this tautomerism will be beneficial to the studies of the biological activity, conformation and synthesis of this type of alkaloid.



PS-06.02.15 [18]ANNULENE C₁₈H₁₈: STRUCTURE, DISORDER AND HUCKEL'S 4n+2 RULE. By M. Krever, S. Gorter, C. Romers, Chemistry Department, Leiden University, The Netherlands, and D.W.J. Cruickshank*, 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 tend to equality. The recent 6-31G SCF calculations for [18]annulene by Schulman & Disch (J. Mol. Struct., 1991, 234, 213) reported that a planar D_{3h} structure with bond alternation was more stable than a D_{6h} structure with nearly equal bonds; however when RMP2 electron correlation was considered, D_{6h} 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 1.382(3) \text{\AA} and six outer bonds of 1.419(4) \text{\AA}. The 0.037 \text{\AA} 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 (360°/12 = 30°). Constrained refinement yields a major molecule of approximate D_{6h} symmetry with means: inner bonds 1.387(1) \text{\AA}, outer bonds 1.400(1) \text{\AA}, C-C-C ring re-entrant angles 128.0°. The six inner hydrogens alternate up and down by 0.1 \text{\AA} from the mean plane; the T,L analysis and molecular packing suggest slight disorder across the plane. The new results agree well with the D_{6h} calculations of Schulman & Disch. A 50:50 inversion disorder of D_{3h} molecules can be excluded as their ring diameters are up to 0.20 \text{\AA} too large.

Thus the 4n+2 π -electron molecule [18]annulene is confirmed as having an aromatic structure.