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PS-06.02.10 THE CRYSTAL AND MOLECULAR STRUCTURES OF 2,6-BIS-(N-METHYLENEMORPHOLINO)-4-METHYLPHENOL AND ITS BROMO DERIVATIVE. by G. Shanmugam\*, S. Shanmuga Sundara Raj and M.N. Ponnuswamy, Department of Madras, Guindy Campus, Madras-600 025, INDIA.

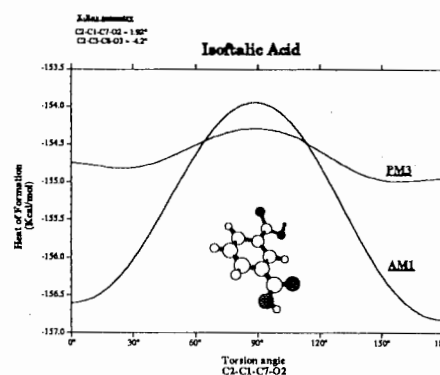
The crystal structures of 2,6-bis(N-methylenemorpholino)-4-methylphenol (MMP) and its bromo derivative (MBP) have the clear application to the design of novel magnetic and electronic solid state materials and play the role of polymetallic sites in biological processes. The crystals are isostructural and crystallize in monoclinic space group  $P2_1/c$  and  $Z=4$ . The crystal data are: NMP,  $C_{17}H_{26}N_2O_3$ ,  $a=10.927(2)$ ,  $b=10.777(2)$ ,  $c=14.197(2)$  Å,  $\beta=94.04(2)^\circ$ ,  $V=1667.7(5)$  Å<sup>3</sup>,  $D_{cal}=1.22$  Mg m<sup>-3</sup>; MBP:  $C_{16}H_{23}N_2O_3Br$ ,  $a=10.955(1)$ ,  $b=10.785(1)$ ,  $c=14.213(1)$  Å,  $\beta=94.54(2)^\circ$ ,  $V=1674.0(4)$  Å<sup>3</sup>,  $D_{cal}=1.48$  Mg m<sup>-3</sup>. Data were collected on a CAD-4 diffractometer at  $T=293$  K using CuK $\alpha$  radiation. The structures were solved using direct methods and refined by full-matrix least-squares methods to a final  $R=0.049$  (MMP) and  $R=0.055$  (MBP) for 3040 and 3123 observed reflections respectively. The two morpholino rings assume perfect chair conformation and orient at an angle of  $50.2(1)^\circ$  (MMP) and  $57.4(1)^\circ$  (MBP) with each other. The structures are stabilized by van der Waals forces.

PS-06.02.11 DIFFUSE SCATTERING IN P-CHLORO-N-(P-METHYLBENZYLIDENE) ANILINE,  $C_{14}H_{12}ClN$ . By T.R. Welberry\* B.D. Butler & A.P. Heerdegen, Research School of Chemistry, Australian National University, GPO Box 4, Canberra City, ACT 0200, Australia.

Detailed diffuse X-ray scattering measurements have been recorded from a sample of p-Chloro-N-(p-methylbenzylidene) aniline,  $C_{14}H_{12}ClN$  (MeCl). The observed scattering has been interpreted by comparison with diffraction patterns of a model system obtained using Monte Carlo computer simulation. Strong diffuse scattering peaks originate from a type of disorder in which the molecule is flipped *end-to-end*, and indicate a tendency for the structure to form a super-lattice with local symmetry  $P2_1/n$  compared to the  $P2_1/a$  symmetry of the reported average structure. A second type of disorder involving *side-to-side* flipping of the molecules appears to occur randomly through the structure with no evidence for short-range ordering. Accompanying these two effects there is strong diffuse scattering which can be satisfactorily modelled assuming rigid-body molecular displacements. This scattering is largely temperature independent and must arise because local relaxational displacements accompany the main disorder.

PS-06.02.12 Crystal structures and conformational analysis of the twelve benzenecarboxylic acids. By S. Garcia-Granda\*, B. Tejerina, and F. Gómez-Beltrán Departamento de Química Física y Analítica, Universidad de Oviedo, Spain.

The crystal structures for the twelve benzenecarboxylic acids have been determined by different authors since 1955 (García-Granda, S. Acta Cryst. 1990, C46, 2399). The solid state conformations show a wide range for relative positions of the carboxylic groups partially affected by the molecular packing as the crystallographic data reveal. Once the crystal structures of the two benzenetetracarboxylic acids were determined (García-Granda, S., Acta Cryst. 1993, C49, 000-000), in order to analyze their solid state preferred conformation and make a comparison between the X-Ray results and those in gas phase, semiempirical calculation has been performed on all members within the series.



Heat of formation is the criteria being used to make a difference among the conformers that belong to the same family and also intramolecular symmetry has been taken into account when possible. Both, AM1 and PM3 semiempirical methods have been used and the results are compared.

Methodology:

— Crystal Structure Determinations:  
Cad4,  $\omega/2\theta$ , Profile Analysis, Direct Methods, Dirdif, Shelx76, Parst.

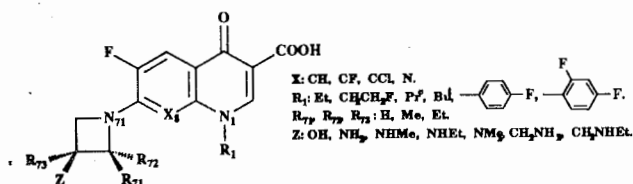
— Conformational Analysis:  
AM1 (M.J.S. Dewar, J. Am. Chem. Soc., 1985, 107, 3902)  
MNDO-PM3 (J.J.P. Stewart, J. Comput. Chem. 1989, 10, 209)

PS-06.02.13 Latest Crystallographic Results on the Structure Antibacterial Activity Relationships in New Quinolones. By S. Garcia-Granda\*, Departamento de Química Física y Analítica, Universidad de Oviedo and J. Frigola, J. Corbera and J. Más, Departamento de Química Médica, Laboratorios Dr. Esteve S.A., Barcelona, Spain.

A family of novel antibacterial quinolones and naphthyridines was prepared (J. Frigola, J. Med. Chem., 1993, 36, 000). Within this series the usual piperazine or aminopyrrolidine groups were replaced by 7-azetidiny substituents. Compounds with outstandingly broad-spectrum activity, particularly against Gram-positive organisms, improved in vitro efficacy in high blood levels were identified among these new azetidinyquinolones. In order to detect the structural trends responsible for the antibacterial activity of these compounds a QSAR study was performed (A. Colombo, Pharmacochemistry Library, 1991, 16, 397-400).

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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)

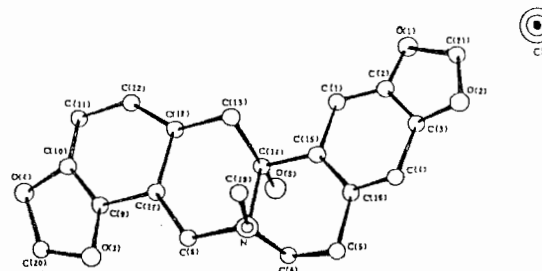
**PS-06.02.14** CRYSTAL STRUCTURE OF PROTOPINE HYDROCHLORIDE. By Y. H. Gong<sup>1,2,\*</sup>, S. D. Lao<sup>3</sup>, Y. F. Yang<sup>4</sup>, <sup>1</sup>South West Forestry College, Kunming, China; <sup>2</sup> State Key Laboratory for Structural Chemistry of Unstable and stable Species, Beijing, China; <sup>3</sup>Kunming Institute of Botany, Chinese Academy of Science, Kunming, China; <sup>4</sup>Institute 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  $\alpha$ ,  $\beta$ -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 trichloroacetate, hydrochloride and acetate in C13 NMR appeared while the carbonyl peaks about  $\delta$  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 C<sub>18</sub>H<sub>18</sub>: 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 C<sub>18</sub>H<sub>18</sub>. 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<sub>3h</sub> structure with bond alternation was more stable than a D<sub>6h</sub> structure with nearly equal bonds; however when RMP2 electron correlation was considered, D<sub>6h</sub> 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<sub>6h</sub> 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<sub>6h</sub> calculations of Schulman & Disch. A 50:50 inversion disorder of D<sub>3h</sub> molecules can be excluded as their ring diameters are up to 0.20  $\text{\AA}$  too large.

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