04-Crystallography of Biological Small Molecules

PS-04.05.03 THE CRYSTAL AND MOLECULAR STRUCTURE OF STYRYL BORONIC ACID: A POTENTIAL WOOD PRESERVATIVE. By C.J. Gainsford* and R.H. Monhold, New Zealand Institute for Industrial Research and Development (Industrial Research Limited), PO Box 31-310, Lower Hutt, New Zealand

A range of organo-boron compounds have been synthesized. 11B and 13C solid state NMR have been used to study the compounds in their natural state and after impregnation into pinus radiata timber. The structure of styryl boronic acid has been determined to provide basic information for its action and polymerization.

The title compound C18H12O2B crystallizes as transparent, extremely thin plates, (~0.01-0.03mm) which are difficult to handle and form intergrowths. Use of polarized light and a microscope on a mounting table with television pickup assisted crystal selection, but even then, over eight crystals were mounted before a satisfactory diffraction pattern was obtained. The crystals are monoclinic with a 19.36(2), b 5.12(8), c 8.159(6)Å and β 100.11(6)*, and space group P2₁/c. A total of 317 reflections were observed (Icut-off=2.3σ(I00)) out of the 1322 reflections measured at low temperature to 2θ of 48° on a Nicolet R3m diffractometer. Final R, R1 values are both 0.055 for the 20 atoms and 99 parameter restrained refinement.

The structure (see Figure) consists of strongly hydrogen bonded (H-O...H-O) molecules with a 26 degree angle between the styryl and boronic acid (H(OH)2) planes. Two types of hydrogen bonds are noted: end-on pairs across the crystallographic centres of symmetry (A), and between adjacent molecules along the short b axis (B). The unexpected nonplanarity of the molecule can be rationalized by the hydrogen bond spatial requirements and may play an important part in any solid state reactions, e.g. polymerisation, which is under investigation.

At the meeting, we will present the structural parameters, reports of continuing studies and any conclusions about viability for wood preservation and solid state reaction mechanisms. The assistance of the Forest Research Institute of New Zealand for the field trials, and the support of the Foundation for Research Science and Technology of New Zealand is gratefully acknowledged.

**Figure**

Selected molecules of styryl boronic acid in the crystal showing hydrogen bonding (see text)

---

PS-34.05.04 X-RAY STUDY OF A SATURATED METHYLENE-BRIDGED IMIDAZO[1,2-a]IMIDAZOLE By A. Kapor, E. B Bíró, G. Stájer, E. Frippörg-Hanss, G. Bernath and P. Engel, *Institute of Physics, Faculty of Sciences, University of Novi Sad, Novi Sad, Yugoslavia, Institute of Pharmaceutical Chemistry, Albert Szent-Györgyi Medical University, Szeged, P.O.B. 121, Hungary, Laboratory for Chemical and Mineralogical Crystallography, University of Bern, Switzerland.

In a continuation of studies on saturated condensed isoimidazoles, phenyl-monomethylated derivatives containing a norbornane moiety instead of a cyclohexane ring have now been synthesized with a view to preparing compounds with acridine activity. The reaction of 3-endo-benzyloxy-8-exo-aminobicyclo[2.2.1]heptane-endo-carboxylic acid and ethylenediamine in toluene yields 6,9-methanof-7,8-dihydro-1H-imidazo[1,2-a]imidazole 1,2-a isocarbostyril-8'-apo C23H14N4O. The crystal belongs to the monoclinic space group P21/n, a 0.5077(4), b 0.2691(4), c 0.2679(4), β 98.95°. Hydrogen parameters were refined by the least-squares fit (SHELXL-76) up to a final R-factor of 26.8% (Rw=24.7, w=0.110, gof=0.99). Hydrogen atoms were isotropically refined except the phenyl hydrogens which were generated from assumed geometry. Fig. 1 shows a perspective view of the molecule. Analysis of the geometry indicates an annellation of the norbornane moiety and the pyridine ring (8.85Å-C3a-C9-C9a). The phenyl group on the carbodiimide cycle is strictly flat (C12-C13-C14-C15=1.5°, C12-C13-C14-C15=1.5°, C9a-C7a-C18a-130.6(2°), while the 9b-phenyl group and the exocyclic 5a,9c conversion is the same for the norbornane and pyridine rings as shown for the five-membered ring (C9-C9a-C12-C13-C12=102.4(4°)). Conformational analysis of the five-membered N1-C2-C3-N4-C10 and pyridine rings N4-C5-C6-C9a-C9b from the values of asymmetry factors [C14.0.012(4)Å, C95.0.010(4)Å, C96.0.015(9)Å, C99.0.015(9)Å, C91.0.012(4)Å, C92.0.012(4)Å, C93.0.012(4)Å, C94.0.012(4)Å] (Kleman, A., Czegler, M. & Simon, K., 1962 Molecular Structure and

---

Fig. 1. Biological Activity, ed. J.P. Griffin & W.L. Dux, pp. 367-376, New York, Elsevier, Biomedical shows that it adopts envelope and half-chair conformations, respectively. The location of the 9b-phenyl group is stabilized by two short intramolecular contacts C13...H6 (2.647(2)Å, 98.7(1°), and C17-H71...N1 (2.927(4)Å, 81.8(18)°).