

04.5-4 OPTICAL RESOLUTION OF BICYCLIC CYANOHYDRINS. THE STRUCTURE OF THE HYDROGEN BONDED BRUCINE - CYANOHYDRIN COMPLEX DERIVED FROM (+)-NORBORNENONE.

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Brucine has been used to resolve tertiary alcohols and aryl substituted cyanohydrins (1). We have successfully used this technique with the cyanohydrins of ( $\pm$ )-oxanorbomenone and have obtained optically pure (+)-oxanorbomenone in better than 20% yield (2). Recently we have extended this to prepare optically pure (+)-norbornenone.

We have determined the structure of the brucine complex with the cyanohydrin derived from (+)-norbornenone in order to determine the nature of the interaction between brucine and the cyanohydrin and to gain insight into the possible generalisation of this technique.

$C_{31}H_{35}N_3O_5$ , orthorhombic,  $a = 12.519(2)$ ,  $b = 14.286(1)$ ,  $c = 14.607(2)$  Å,  $P2_12_12_1$ , 4605 unique reflections (2879

with  $I > 3\sigma$ ), direct methods (RANTAN), full matrix least squares,  $R = 0.038$ .

The complex is formed by hydrogen bonding between the exo -OH group of the cyanohydrin and N(19) of the brucine. The other interactions between these two molecules are not sufficient for chiral recognition. The closest van der Waal's contacts of the cyanohydrin involve two other brucine molecules in the lattice.

1. F. Toda, K. Kanaka, *Tetrahed. Lett.*, **22**, 4669 (1981); *Chem. Lett.*, 661 (1983).
2. K.A. Black, P. Vogel, *Helv. Chim. Acta*, **67**, 1612 (1984).

04.6-1 MAGNESIUM BIS(HYDROGEN MALEATE) HEXAHYDRATE, BY NEUTRON DIFFRACTION AND AB-INITIO CALCULATIONS. By F. Vanhouteghem <sup>a</sup>, A.T.H. Lenstra <sup>a</sup>, H.J. Geise <sup>a</sup> and P. Schweiss <sup>b</sup>, <sup>a</sup> University of Antwerp (UIA), Chemistry Department, Wilrijk, Belgium and <sup>b</sup> Laboratoire Leon Brillouin, CEN, Saclay, France.

Magnesium bis(hydrogen maleate) hexahydrate was investigated at room temperature by neutron diffraction, establishing the H positions and H-bonding scheme with great accuracy. The Mg cation at a center of inversion is surrounded by 6 water molecules, which are rotated over 9°, 28° and 44°, respectively, out of their ideal  $O_h$  planes. A slightly asymmetric intramolecular O(3)-H---O(1) bridge is found in the hydrogen maleate ion, together with an asymmetric crystalline environment of the O atoms involved: O(1) is also an acceptor to an intermolecular H-bridge to the  $Mg(OH_2)_6$  cluster, whereas O(3) is not. Experimental bond lengths and angles are compared to those obtained from geometry relaxed 4-21G ab-initio calculations of the free hydrogen maleate ion. Observed differences are of the same magnitude as those to be expected for crystal field effects. The experimental hydrogen maleate ion is not planar, the carboxyl groups being rotated out of the carbon plane in a disrotatory fashion. Calculations on the free ion show this to be energetically favoured over a conrotatory movement.

04.6-2 THE STEREOCHEMISTRY OF THE HYDROGEN-BONDING OF WATER MOLECULES IN THE CRYSTAL STRUCTURES OF SMALL MOLECULE NUCLEIC ACID COMPONENTS. By G.A. Jeffrey and H. Maluszynska, Department of Crystallography, University of Pittsburgh, Pittsburgh, PA 15260 USA.

The structural environment of the water molecules has been examined in 100 crystal structures of purine, pyrimidine, nucleoside and nucleotide hydrates. Of these, only five were neutron diffraction analyses, the others were the more precise X-ray analyses in classes 44 and 47 of the Cambridge Crystallographic Data Base. Of the 370  $XH---O_W$  and  $O_WH---A$  hydrogen bonds examined, 60 (16%) were three-centered, 1 was four-centered. There were 5 examples of three-centered/bifurcated bonds. The water molecules more commonly accept one bond than two, by a ratio of  $\sim 2:1$ . The direction of this acceptor bond ranges from pyramidal to planar with respect to the  $H_2O$  plane, and  $\pm 30^\circ$  with respect to the  $H_2O$  two-fold axis. There were two examples where the water molecules did not accept a hydrogen bond, but none in which they did not donate two bonds. Twelve different hydrogen-bond configurations are observed, corresponding to between 2 and 8 first neighbour  $O_W---A$  distances within 2.5 to 3.5 Å. The two-center  $O_WH---A$  distances range from 1.60 to 2.25 Å, the three-center distances from 1.81 to 2.95 Å. For the water acceptor bonds, the sequence of mean  $XH---O_W$  bond lengths is  $P-OH < \text{>NH} < COH < \text{>NH} < O_WH < N(H)H$ . For the water donor bonds the sequence of mean  $O_WH---A$  bond lengths is  $O=P < O=C < O=C < O_W \approx N \approx O < C \approx C \approx Br^- < I^- \approx S=C$ . These observed results can serve as a portfolio of observed stereochemistries for interpreting hydrogen-bonding around water molecules in crystal structures where the hydrogen positions cannot be observed.

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