04. ATOMIC SCALE MECHANISMS AND CHEMICAL PROPERTIES

04.6-4 OPTICAL RESOLUTION OF BICYCLIC CYANOHYDRINS.
THE STRUCTURE OF THE HYDROGEN BONDED BRUCINE-CYANOHYDRIN COMPLEX DERIVED FROM (+)-NORBORNENONE.
By A.A. Pinkerton, Department of Chemistry, University of Toledo, Toledo, OH43606, USA and P.-A. Carrupt and P. Vogel, Institut de Chimie Organique, Universite de Lausanne, 1005 Lausanne, Switzerland.

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

We have determined the structure of the brucine complex with the cyanohydrin derived from (+)-norborenone 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. 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—OH and OXH—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 ~2:1. The direction of this acceptor bond ranges from pyramidal to planar with respect to the HO2 plane, and ~30° with respect to the H2O 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—H—A distances within 2.5 to 3.5 Å. The two-center OH—A distances range from 1.60 to 2.25 Å, the three-center distances from 1.81 to 2.39 Å. For the water acceptor bonds, the sequence of mean XH—OH bond lengths is O—H < O—N < O—S < O—C < N—H < N(H)H. For the water donor bonds the sequence of mean OXH—A bond lengths is O—P < O—C < O—S < O—C < C—C < Br—C < I—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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