04.5-4 OPTICAL RESOLUTION OF BICYCLIC CYANOHYDRINS.

THE STRUCTURE OF THE CYANOGEN COMPLEX DERIVED FROM (+)-NORBORNENONE.

By A.A. Pinkerton, Department of Chemistry, University of Toledo, Toledo, OH 43606, USA and P.-A. Currupt 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 (1). We have successfully used this technique with the cyanohydrins of (+)-oxanorbornenone and have obtained optically pure (+)-oxanorbornenone in better than 20% yield (2). 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 better than 2.5% yield. The closest van der Waal’s contacts of the 2-H and 2-Brucine. The other interactions between these molecules are of the same magnitude as those to be expected for crystal field effects. The 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 carbonyl 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.


04.5-5 MAGNESIUM BIS(HYDROGEN MALATE) HEXAHYDRATE, BY NEUTRON DIFFRACTION AND AB-INITIO CALCULATIONS.

By F. Vanhouteghem a), A.T.H. Leenstra a), H.J. Geise a) and G. Schwend b), a) University of Antwerp (UAR), Chemistry Department, Wilrijk, Belgium and b) Laboratoire de Chimie Organique, Universite Paris-Sud, 91405 Orsay, 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 90°, 28° and 46°, respectively, out of their ideal 0° planes. A slightly asymmetric intramolecular O(3)-H--O(1) bridge is found in the hydrogen maleate ion, together with an asymmetric crystallographic environment of the 0 atoms involved: O(1) is also an acceptor to an intermolecular H-bridge to the Mg(OH)2 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 carbonyl 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.

04.6-1 MAGNESIUM BIS(HYDROGEN MALATE) HEXAHYDRATE, BY NEUTRON DIFFRACTION AND AB-INITIO CALCULATIONS.

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04.6-2 MAGNESIUM BIS(HYDROGEN MALATE) HEXAHYDRATE, BY NEUTRON DIFFRACTION AND AB-INITIO CALCULATIONS.

By F. Vanhouteghem a), A.T.H. Leenstra a), H.J. Geise a) and G. Schwend b), a) University of Antwerp (UAR), Chemistry Department, Wilrijk, Belgium and b) Laboratoire de Chimie Organique, Universite Paris-Sud, 91405 Orsay, 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 90°, 28° and 46°, respectively, out of their ideal 0° planes. A slightly asymmetric intramolecular O(3)-H--O(1) bridge is found in the hydrogen maleate ion, together with an asymmetric crystallographic environment of the 0 atoms involved: O(1) is also an acceptor to an intermolecular H-bridge to the Mg(OH)2 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 carbonyl 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.