Single crystals of InMnO$_3$ were prepared from In$_2$O$_3$ (Cerac, 99.99%) and Mn$_2$O$_3$ (Cerac 99.99%) in a Bi$_2$O$_3$ (Cerac 99.9%) flux. Approximately 3 mmol of the binary oxides was ground together and pelletized. The pellet was heated at 950 °C for 3 days in air on platinum foil and quenched to room temperature. Partial melting of the pellet occurred during the heating cycle, and black hexagonal plates were visible on the surface of the pellet. The flux matrix was weakened with concentrated nitric acid, and crystals were mechanically separated.

InMnO$_3$ is a low-temperature structure and decomposes above 1000 °C. The spinel solid solution, In$_{2-x}$Mn$_{1+x}$O$_4$,[20] is the stable In–Mn–O structure above 1000 °C and forms preferentially if a mixture of In$_2$O$_3$ and Mn$_2$O$_3$ is ground together and heated in air. Polycrystalline InMnO$_3$ can be prepared via a nitrate decomposition route, although care must be taken not to exceed 1000 °C, at which point InMnO$_3$ powder decomposes into In$_2$O$_3$ and Mn$_2$O$_3$.

The structure of InMnO$_3$,[21] shown in Figure 1, consists of alternating layers of octahedrally coordinated indium and trigonal bipyramidally coordinated manganese. The manganese and indium coordinations are fixed by symmetry (atomic positions are shown in Table I) and, consequently, have ideal D_{3h} and near-ideal octahedral symmetry, respectively. The structure of InMnO$_3$ may be described as a stuffed delafossite structure,[22] in which an extra oxygen, O(2), has been inserted into the manganese plane; instead of the linear coordination of B found in ABO$_2$ delafossite, manganese is trigonal bipyramidally coordinated. Alternatively, the InMnO$_3$ structure may be described as related to the CdI$_2$ structure,[23] except instead of empty octahedral sites located between a layer of filled sites, an MnO hexagonal net (6,3)[24] has been inserted between slabs of InO$_6$ octahedra in which all octahedral interstices are filled. The trigonal bipyramidally coordinated manganese layers repeat with every second layer. The staggered arrangement of the manganese atoms results in only limited communication between the transition metal oxide planes. It has been shown that transition metal structures with low dimensional units have the potential for interesting magnetic and electronic effects.[25-30] The low dimensional InMnO$_3$ structure, thus, should give rise to strong intralayer manganese–manganese interactions, while oxygen-mediated interlayer interactions are not expected to be significant except at very low temperatures. Preliminary measurements indicate that InMnO$_3$ orders antiferromagnetically with a complex applied magnetic field dependence. We will report on the magnetic properties of InMnO$_3$ at a later date.

The structures of InMnO$_3$ and (RE)AlO$_3$[31,32] (RE = Y, Eu, Gd, Tb, Dy, Ho, Er) are very similar, differing only in the coordination of the indium/RE site. In the case of YAlO$_3$, the yttrium is bound by six oxygen atoms at a distance of 2.274 Å and two additional oxygens, above and below at a distance of 2.63 Å. The higher coordination of the yttrium site causes the unit cell to be compressed in the c-direction, c = 10.52 Å. In the case of InMnO$_3$, on the other hand, indium interacts with O(2) only slightly, if at all. The indium–O(2) distance is 2.869 Å, more than 0.2 Å longer than the yttrium–O(2) distance in YAlO$_3$, even though the ionic radius of indium is 0.1 Å shorter than that of yttrium in octahedral coordination. Consequently, the c-axis in InMnO$_3$, c = 11.47 Å, is almost 1 Å longer than that of YAlO$_3$. This difference is even more pronounced in isostructural InFeO$_3$,[33,34] where the indium–O(2) distance is 3.044 Å and c = 12.175 Å. The structure of InMnO$_3$ is thus unique when compared to the YAlO$_3$ structure since the need of the rare earth atoms for higher coordination creates a shortening of the c-axis and a strong bond with O(2), which is not the case for InMnO$_3$. The difference is also evident in the chemical reactivity of rare earth aluminates, which transform to the perovskite structure above 1000 °C, unlike InMnO$_3$ which decomposes into the binary oxides.

It is unlikely that InMnO$_3$ is the only transition metal indate crystallizing in this structure, and in fact single crystals of the isostructural InFeO$_3$ compound have been prepared.[33] The syntheses of other members of this unusual structural family are in progress.

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Supplementary Material Available: Tables of positional and thermal parameters and crystal data for InMnO$_3$ (3 pages); table of observed and calculated structure factors (1 page). Ordering information is given on any current masthead page.

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(21) Crystal data for InMnO$_3$: Crystals were analyzed by microprobe (JEOL 781), indicating a stoichiometry of In:Mn of 1:1. The space group is $P6_3/mmc$ (No. 194), a = 3.3985 (2) Å, c = 11.4752 (6) Å, V = 114.78 (1) Å^3, Z = 2. Of 778 reflections collected 109 were unique. Data was corrected for absorption empirically, μ = 149.00 mm^{-1}. The secondary extinction coefficient = 0.1829 × 10^{-4}. All atoms were anisotropically refined. R = 3.3% and R_w = 3.5%.

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Absolute Configuration of Isoflurane

P. L. Polavarapu,[*,†] A. L. Cholli,[‡] and G. Vernice[§]

Department of Chemistry, Vanderbilt University
Nashville, Tennessee 37235
The BOC Group, Inc., Technical Center
Murray Hill, New Jersey 07974
Anaquest, Inc., BOC Health Care
Murray Hill, New Jersey 07974

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The enantiomers of chiral anesthetic agent isoflurane (CF$_2$HOCHClCF$_3$)[1-3] have a 2-fold difference in their effectiveness on the anesthetic-activated potassium current and in their inhibition of current mediated by acetylcholine receptors. These differences were attributed to the stereospecific binding between the chiral isoflurane enantiomers and the anesthetic-sensitive proteins in the brain.[4,5] To understand these stereospecific interactions at the molecular level, it is necessary to know the absolute configurations of the isoflurane enantiomers and the conformations in which these isomers exist. Neither the configurational nor the conformational details are available in the lit-

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[†] Vanderbilt University.

[‡] The BOC Group, Inc.

[§] Anaquest, Inc.

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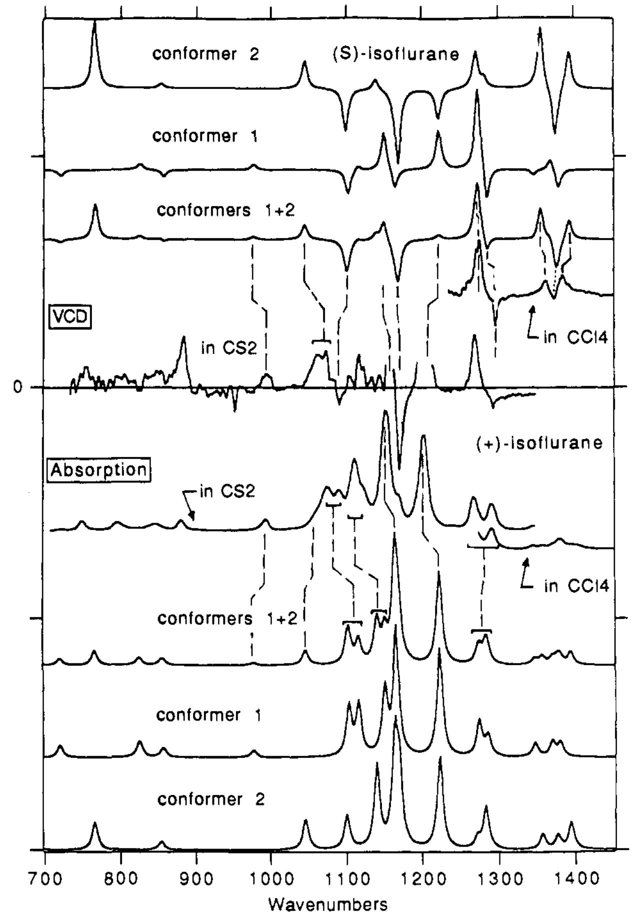

Figure 1. Vibrational absorption (bottom half) and circular dichroism (top half) spectra for isoflurane. The theoretical frequencies obtained with the 6-31G* basis set were multiplied by 0.87 to bring them closer to the experimental values, especially those in the 1200–1400-cm^{-1} region. Experimental spectra are for the (+)-enantiomer, and theoretical spectra are for the (*S*)-configuration. The theoretical VCD bands for the (*R*)-configuration will have signs opposite to those for the (*S*)-configuration. All spectra are presented on arbitrary intensity scales. On the basis of the computed Gibbs energy difference, the populations of conformers 1 and 2 at the 6-31G* level are expected to be ~85% and 15% respectively. However, considering the uncertainties in the energies at the 6-31G* level and considering that equal populations appear to provide a better simulation of the experimental spectra, equal populations were assumed in simulating the theoretical spectrum for the mixture of conformers 1 and 2.

erature for isoflurane, but they can be determined from vibrational optical activity.[6,7] We report the absolute configurations and predominant conformations for the isoflurane enantiomers deduced from vibrational circular dichroism (VCD).

The experimental spectra in the 1600–700-cm^{-1} region were measured on a Fourier transform infrared VCD instrument.[8] To minimize the base-line artifacts, the VCD spectra for the (+)-enantiomer were obtained in the commonly practiced way as one-half the difference between the raw spectra for the (+)- and (−)-enantiomers. The spectra were obtained at 4-cm^{-1} resolution for isoflurane dissolved in CCl_4 (1600–1200-cm^{-1} region) and CS_2 (1350–700-cm^{-1} region) solvents at concentrations of ~0.1 M. The samples were held in a variable path length cell equipped with KBr windows at room temperature (~20 °C). The data collection time was ~1 h per sample. Typical spectra are displayed in Figure 1. The experimental magnitudes for the two VCD bands in the 1150–1200-cm^{-1} range are weak and as shown in Figure 1 have uncertainties resulting from the excessive absorbance at the path lengths employed. The (+)- and (−)-enantiomers used in this study had optical rotations of $[\alpha]^{D}_{25} = +107°$ and −107°, respectively.

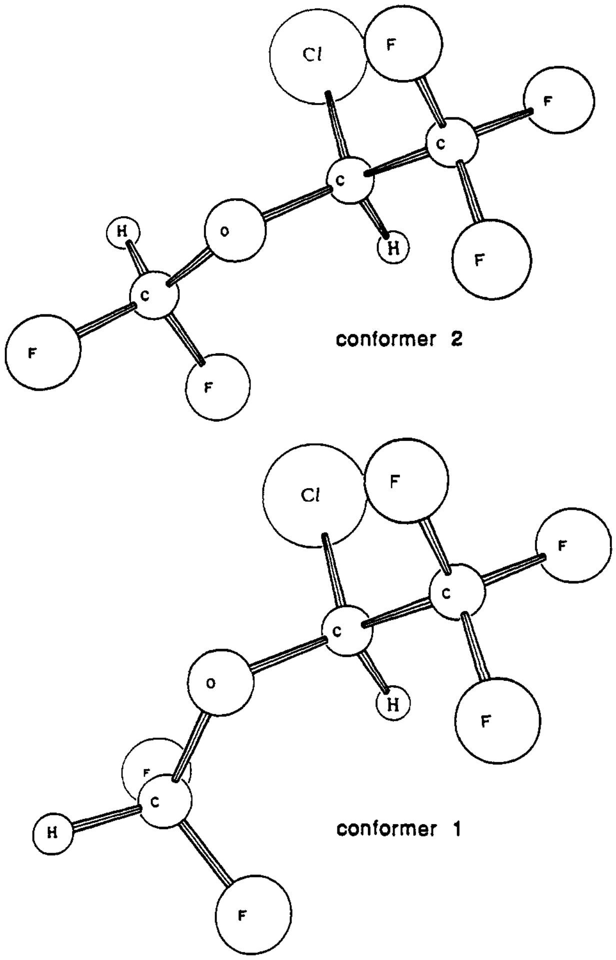

Figure 2. Three-dimensional structures of the two lowest energy conformations for (*S*)-isoflurane obtained with the 6-31G* basis set. The electronic energy of conformer 1 (bottom structure) is −1146.315 252 4, and that of conformer 2 (top structure) is −1146.313 389 8 hartrees. The C–O–C*–C dihedral angles, where C* is the chiral center, are 134° and 164°, respectively, for conformers 1 and 2.

The theoretical spectra were calculated at the fully optimized structures determined from the GAUSSIAN 90[9] or CADPAC[10] programs using the 6-31G* basis set.[11] The VCD spectra were obtained with the localized molecular orbital theory[12] using the ab initio LMOVCD program which has been found[13] to correctly

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predict the absolute configurations in other molecules. This program used the localized orbital centroids obtained from the GAMESS program[14] using Boys's localization scheme.[15] A Cray Y-MP supercomputer and a minisupercomputer were used for the calculations. The theoretical spectra were simulated with Lorentzian band shapes using 5-cm^{-1} half-width at half-height.

Nine different conformations are possible for isoflurane. Rotations around the O–C* bond, the asterisk (*) representing the chiral center, and the C–O bond give rise to nine plausible conformations. However, steric interactions limit rotations around the O–C* bond that lead to gauche orientations of the CF_3 and CF_2H groups. The two lowest energy conformers, which differ in energy by ~1 kcal/mol, are shown in Figure 2. The next lower energy conformer is ~3 kcal/mol higher in energy than the lowest energy conformer shown in Figure 2. The correlation between the experimental and theoretical spectra is indicated by dotted lines in Figure 1. From a comparison of the absorption spectra, the existence of isoflurane in more than one conformation at ambient temperatures becomes unambiguous. The theoretical VCD obtained as a sum of those for the two lowest energy conformers with (*S*)-configurations is found to match well with the experimental VCD obtained for the (+)-enantiomer. As in the absorption spectra, the theoretical spectrum of any one of the two conformers does not satisfactorily reproduce the experimental spectrum and the presence of both conformers is required to match the experimental spectrum. The overall agreement for the sign patterns in the experimental and theoretical VCD spectra leads us to conclude that (+)-isoflurane has the (*S*)-configuration [hence (−)-isoflurane has the (*R*)-configuration] and that isoflurane exists in two conformations (Figure 2) at room temperature.

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$C_2H_4B_2N_2$: A Prediction of Ring and Chain Compounds

Ivan Cernusak,[†,‡] Miroslav Urban,[†,‡] Peter Ertl,[‡] and
Rodney J. Bartlett*[,†]

Quantum Theory Project, University of Florida
Gainesville, Florida 32611
Department of Physical Chemistry and
Chemistry Institute, Faculty of Science
Comenius University, Mlynska Dolina
84215 Bratislava, Czech and Slovak Federative Republic

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Cyanoboranes[1-4] belong to a large variety of molecules which can be derived from hydrocarbons by substituting for CH or CH^+ groups their isoelectronic N and BH analogs. An important group of such compounds are the macrocyclic cyanoboranes,[2] which have been shown to be six- to eight-membered rings. Macrocyclic cyanoboranes serve as starting compounds for further synthesis of boron analogs of amino acids, amine–BH_2CN adducts, etc. which have considerable chemical and biological activity.[5-8] Moreover, polymeric $(BN_2CN)_x$ and similar compounds are pertinent to recent efforts in developing C,B,N thin films which are useful materials in semiconductor technology.[9-13]

Table I. SCF and MBPT(2) Reaction Energies[a]

reaction	SCF	MBPT(2)
boat → $2H_2BCN$	64.1	82.5
boat → $2\mathrm{H\overline{CNB}H}$	203.7	231.3
boat → 2HCN_BH	499.6	565.2
boat → cis	144.9	42.7
boat → trans	150.5	52.1
cis → $2H_2BCN$	−80.8	39.8
cis → $2\mathrm{H\overline{CNB}H}$	58.8	188.6
cis → 2HCN_BH	354.7	522.5
cis → trans	5.6	9.4
H_2BCN → $\mathrm{H\overline{CNB}H}$	69.8	74.4
H_2BCN → HCN_BH	217.7	241.2

[a] In kilojoules/mole. All electrons correlated.

The six-membered-ring structures containing B, C, and N atoms represent an interesting group of compounds because they could be benzene analogs and they contain both electron deficient (BH) and electron rich (N) centers in one skeleton. Benzene analogs which replace a CHCH group by an isoelectronic HNBH group were recently investigated semiempirically (MNDO).[14]

The idea to investigate the six-membered $\overline{\mathrm{CHBHNCHBHN}}$ ring arose from our recent research on the three-membered rings borazirene, $\mathrm{H\overline{CNB}H}$, and isoborazirene and bent-chain molecules HNC_BH and HCN_BH.[15] The last system may be classified as a donor–acceptor complex of HCN and BH with a binding energy of about 162 kJ/mol. Borazirene is a stable, potentially aromatic ring, analogous to the isoelectronic cyclopropenyl cation or, better, the C_3H_2 cyclopropenylene system. Its formation via hydrogen migration from cyanoborane, BH_2CN, the most stable species of our previous study, has been investigated.[15] See also ref 16. The presently suggested six-membered ring may be formally considered as a dimer of either $\mathrm{H\overline{CNB}H}$ or HCN_BH.

Thanks to a considerable development in new methods and computer algorithms, relatively large molecules are now amenable to ab initio treatments that include electron correlation.[17] Gradient techniques as implemented in the ACES II computer program,[18] used in most of the present calculations, are a necessary prerequisite in such treatments.[19]

In order to obtain reasonable starting geometries and Hessians,

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[‡] Comenius University.
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