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.

Acknowledgment. The experimental spectra were obtained on a VCD instrument funded by the NIH, and some of the calculations used an SCS-40 computer that was funded by NSF. We thank Drs. C. G. Huang, L. A. Rozov, and D. F. Halpern for providing the isoflurane enantiomers used in this study, R. Pandurangi for some of the experimental measurements, and A. J. Ellgren and G. Adelstein for their support and encouragement.

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(14) Schmidt, M. W.; Boatz, J. A.; Baldridge, K. K.; Koseki, S.; Gordon, M. S.; Elbert, S. T.; Lam, B. *QCPE Bull.* **1987**, *7*, 115.

(15) Foster, J. M.; Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 300–302.

$C_2H_4B_2N_2$: A Prediction of Ring and Chain Compounds

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Received July 15, 1992

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 → $2H\overline{CNB}H$	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 → $2H\overline{CNB}H$	58.8	188.6
cis → 2HCN_BH	354.7	522.5
cis → trans	5.6	9.4
H_2BCN → $H\overline{CNB}H$	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 $\overline{CHBHNCHBHN}$ ring arose from our recent research on the three-membered rings borazirene, $H\overline{CNB}H$, 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 $H\overline{CNB}H$ 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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(1) Paetzold, P. *Pure Appl. Chem.* **1991**, *63*, 345.

(2) Spielvogel, B. F.; Bratton, R. F.; Moreland, C. G. *J. Am. Chem. Soc.* **1972**, *94*, 8597.

(3) Martin, D. L.; Chiusano, M. A.; Dennyston, M. I.; Dye, D. J.; Martin, E. D.; Pennington, B. T. *J. Inorg. Nucl. Chem.* **1978**, *40*, 9.

(4) Wissian-Neilson, P.; Das, M. K.; Spielvogel, B. F. *Inorg. Chem.* **1978**, *17*, 2327.

(5) Gyorgi, B.; Emri, J.; Feher, I. *J. Organomet. Chem.* **1983**, *17*, 255. Gyorgi, B.; Lasar, I.; Emri, J. *J. Organomet. Chem.* **1988**, *29*, 344.

(6) Spielvogel, B. F.; Ahmed, F. U.; McPhail, A. T. *Synthesis* **1986**, 833.

(7) Charandabi, M. R. M. D.; Feakes, D. A.; Ettel, M. L.; Morse, K. W. *Inorg. Chem.* **1991**, *30*, 2433.

(8) Mittakanti, M.; Morse, K. W. *Inorg. Chem.* **1991**, *30*, 2434.

(9) Maya, L.; Richards, H. L. *J. Am. Ceram. Soc.* **1991**, *74*, 406.

(10) Karnezos, M. Synthesis and Properties of Boron Nitride. *Mater. Sci. Forum* **1990**, *54/55*, 261.

(11) Montasser, K.; Morita, S.; Hattori, S. Synthesis and Properties of Boron Nitride. *Mater. Sci. Forum* **1990**, *54/55*, 295.

(12) Yamaguchi, E. Synthesis and Properties of Boron Nitride. *Mater. Sci. Forum* **1990**, *54/55*, 329.

(13) Gissler, W.; Haupt, J.; Hoffman, A.; Gibson, P. N.; Rickerby, D. G. *Thin Solid Films* **1991**, *199*, 113.

(14) Massey, S. T.; Zoellner, R. W. *Int. J. Quantum Chem.* **1991**, *39*, 787; *Inorg. Chem.* **1991**, *30*, 1063.

(15) Cernusak, I.; Beck, S.; Bartlett, R. J. *J. Phys. Chem.* **1992**, *96*, 10284.

(16) Byun, Y.-G.; Saebo, S.; Pittman, C. U., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 3689.

(17) Bartlett, R. J. *J. Phys. Chem.* **1989**, *93*, 1697.

(18) ACES II (Advanced Concepts in Electronic Structure): an ab initio program system for performing MBPT/CC calculations, including analytical gradients, methods for excited states, and a number of other unique methods. Authors: Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. Quantum Theory Project, University of Florida, Gainesville, FL, 1987.

(19) Bartlett, R. J.; Stanton, J. F.; Watts, J. D. *Advances In Molecular Vibrations and Collision Dynamics*; JAI Press, Inc.: Greenwich, CT, 1991; Vol. 18, pp 139–167. Salter, E. A.; Trucks, G. W.; Bartlett, R. J. *J. Chem. Phys.* **1989**, *90*, 1752. Gauss, J.; Stanton, J. F.; Bartlett, R. J. *J. Chem. Phys.* **1991**, *95*, 2623.

0002-7863/92/1514-10955$03.00/0

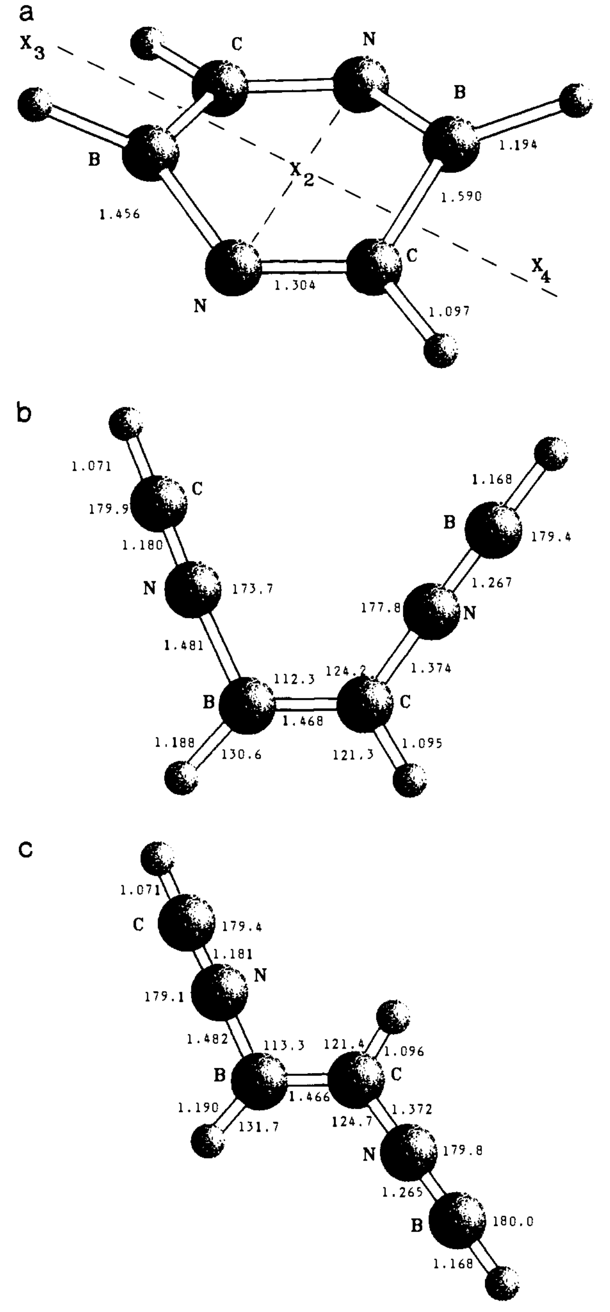

Figure 1. Three MBPT(2)/DZP optimized structures of $C_2H_4B_2N_2$. (a) Boat (C_2). Bond angles (deg): $CNX_2 = 63.5$; $BNX_2 = 56.1$; $HCN = 119.1$; $HBN = 120.7$; $X_3X_2N = 90.0$. Dihedral angles (deg): $CNX_2X_3(X_4) = 172.4$; $BNX_2X_4(X_3) = 156.0$; $HCNX_2 = -158.1$; $HBNX_2 = -144.9$. X_2 is the NN distance midpoint; X_3, X_2, and X_4 are collinear. (b) Cis (C_s). (c) Trans (C_s).

semiempirical AM1 optimizations are first performed, followed by SCF/3-21G and SCF/DZP (double-ζ basis with polarization) evaluation. The DZP basis set is described in ref 15. Note that at the SCF/3-21G level we find both boat and chair ring conformations differing only by a few kilojoules/mole but at the SCF/DZP level the chair minimum disappears. Final refinements are made at the MBPT(2)/DZP (second-order perturbation theory) level. The geometry of the ring molecule $C_2H_4B_2N_2$ is presented in Figure 1a.

We present a selection of reaction energies in Table I. All correlated reaction energies are based on MBPT(2) optimized geometries partly taken from our previous study.[15] As follows from data in Table I, the boat-ring molecule is markedly more stable when compared to two BH_2CN molecules. Comparing the energy of the boat to the two HCN_BH molecules, we can estimate the binding energy in our ring compound to be 565 kJ/mol, which corresponds to the formation of the two B–C bonds in the ring.

Besides the ring $C_2H_4B_2N_2$, we also suggest two nonring "cis" and "trans" molecules (see parts b and c of Figure 1). Both are more stable than two BH_2CN, with the electron correlation contribution being a crucial factor in their stability. The strength of the B–C bond in both chain dimers is pretty high, as is seen from the reaction energies cis(trans) → 2HCN_BH in Table I. This is in accord with the relatively short B–C bond length, which corresponds to a double bond. The shorter of the two BN bond lengths is close to a triple BN bond length typical in iminoboranes,[1] with practically a linear H–B–N–C chain.

Though our suggested molecules have the same molecular formula, $(BH_2CN)_2$, as the experimentally described molecules mentioned above,[2] also shared by the nonclassical cyanoborane, they are completely different. First, the cited authors found at least rings formed from tetramers. Second, and even more important, the bonding in our molecules contains the two- and three-coordinate boron, while in the experimentally described $(BH_2CH)_x$ polymers there is a four-coordinate boron. The three-coordinate boron atoms conform to classical boron compounds; the occurrence of the two-coordinate boron is less typical.[1] Since both boron atoms are three coordinate in the boat-ring structure, with a nearly planar conformation of C, N, and H atoms bonded to B, this would be expected to rationalize its high stability.

The possible polymeric structure is not shown in this paper but may be easily derived from nonring dimers, preferably trans, simply by bending any of the terminal hydrogens and adding the next HCN_BH molecule. In the closed polymer structure, all borons and carbons would be tricoordinate and, thus, further stabilized.

A more detailed description of geometry, vibrational spectra, thermodynamics of pertinent reactions, and bonding analysis will be presented in a forthcoming paper.[20] Since electron correlation is so important in reaction energies, we also extend the MBPT(2) treatment to the more sophisticated coupled-cluster approach.

Acknowledgment. This work has been supported by the U.S. AFOSR under Grant No. AFOSR-F49620-92-J-0141. M.U. thanks Prof. R. J. Bartlett and the QTP staff for the warm hospitality during his stay at the University of Florida.

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(20) Cernusak, I.; Urban, M.; Stanton, J. F.; Bartlett, R. J. In preparation.

The Barium(II) Complex of *p-tert*-Butylcalix[4]arene-crown-5: A Novel Nucleophilic Catalyst with Transacylase Activity

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Received August 7, 1992

In this communication we report that *p-tert*-butylcalix[4]arene-crown-5 (**1**),[1,2] when suitably activated by barium ion under moderately basic conditions, acts as a fairly efficient transacylation catalyst in the methanolysis of *p*-nitrophenyl acetate (pNPOAc)

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(1) (a) Ungaro, R.; Pochini, A.; Andreetti, G. D. *J. Inclusion Phenom.* **1984**, *2*, 199–206. (b) Ghidini, E.; Ugozzoli, F.; Ungaro, R.; Harkema, S.; El-Fadl, A. A.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1990**, *112*, 6979–6985.

(2) Casnati, A.; Pochini, A.; Ungaro, R.; Cacciapaglia, R.; Mandolini, L. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2052–2054.