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operation is designated with the symbol "*".

(b) The plane spanned by atoms 5, 6, 10 (perpendicular to the previous one): The corresponding symmetry operation is denoted with "_". It inverts ring A and inverts and permutates ring B.

These symmetry operations are commutative and both self invert ("**" = " "). C_1 conformations appear 4 times, C_2 or C_s conformations appear twice, and the central C_{2v} conformations are unique.

The nomenclature used for depicting the conformations of the cyclohexane ring is that proposed by Hendrikson[15a,b,c] for "chair" (C), "twist-boat" (TB), "boat" (B), and "planar" (P) and Anderson[1e] for "half-chair" (HC) and "half-boat" (HB). For five-membered rings one generally adheres to the distinction between half-chair (HC) and envelope (E) conformations.[5] However, spiro substitution may be the cause of severe distortions in ring B and the selected label can be somewhat conventional. In conformational sequences such as HC2b the capital letters refer to the conformation of ring A, the number 2 differentiates the nonsymmetrically related members of a given conformational family (Figure 2), and the small letter labels the conformation of ring B (Figure 3). The previously defined symmetry operations act on the parent label to give the equivalent labels (e.g., HC2*b*, $\underline{\text{HC2b}}$, $\underline{\text{HC2*b*}}$).

These notations allow a rapid identification of symmetrically equivalent structures without a detailed analysis of the torsional angles. The symmetry properties of free rings A and B propagate into the labels of **1** or **2**. For example, using the equal symbol for identical (not equivalent) conformations, C = $\underline{\text{C*}}$, $\underline{\text{a}}$ = a* and therefore "_" acts on Ca to give $\underline{\text{C}}$a*. Similarly, TB1 = $\underline{\text{TB1*}}$ and the conformation TB1*a is invariant under the operation "$\underline{*}$".

Acknowledgment. We express our gratitude to Professor E. Osawa (Hokkaido University, Sapporo, Japan) for allowing us to use his MM2 version. Our thanks are also due to Professor J. P. Penot (Université de Pau et des Pays de l'Adour, France) for helpful discussions about the mathematical aspects of the problem. This research was sponsored by the Centre de Calcul Vectoriel pour la Recherche, Ecole Polytechnique, Palaiseau (France), which is gratefully acknowledged.

Supplementary Material Available: Tables including the labeling matrix for **1** and torsional features, energies, and indices for nonsymmetrically related critical points of **1** and **2** and Figures 7 and 8 showing experimental and computed bandshapes of the *gem*-dimethyl group of **1** and **2** at different temperatures (7 pages). Ordering information is given on any current masthead page.

MBPT and Coupled-Cluster Investigation of Isomerization Reactions: $HCN \Leftrightarrow HNC$, $BH_3CN^- \Leftrightarrow BH_3NC^-$, and $HCNBH_3 \Leftrightarrow HNCBH_3$

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Received May 26, 1987

Abstract: Heats of isomerization of title processes and binding energies of BH_3 to HCN, HNC, and CN^- were investigated by the fourth-order many-body perturbation theory (MBPT(4)) and coupled-cluster methods. Correlation effects are essential in the quantitative calculation of reaction heats of isomerization for H(CN) and $H(CN)BH_3$ and in binding energies of BH_3 toward HCN and HNC. Correlation effects are less important in reactions with the CN^- anion. Calculated isomerization energies are 64, 42, and 9 kJ/mol for H(CN), $BH_3(CN^-)$, and $H(CN)BH_3$ isomerizations, respectively. The binding energies of BH_3 to HCN and HNC are 71 and 124 kJ/mol, respectively, and the binding energies of BH_3 to CN^- and NC^- are 250 and 209 kJ/mol, respectively. Geometries of $H(CH)BH_3$ and $BH_3(CN)^-$ isomers were determined by a combination of MBPT(4) and gradient SCF methods.

Organoborates are interesting and important starting compounds in modern synthetic organic chemistry.[1] They are involved in reactions where migration of an organic group (or hydrogen) from boron to the acceptor carbon atom is usually exploited. An exceptional synthetic potential exists for cyanoborates,[2a] which may be regarded as donor-acceptor complexes of organoborane with HCN or HNC. The simplest compound of this type is $HCNBH_3$ and its isocyano isomer $HNCBH_3$. Since cyanoborate processes are usually initiated in salts,[2] BH_3CN^- and BH_3NC^- are of interest as well. In addition, since HNC is not normally available, BH_3CN^- and its subsequent protonated form contribute the source of the synthetically important $HNCBH_3$ molecule.[2]

In general, binding energies of molecules having weak dative bonds have been difficult to ascertain experimentally. This is particularly true for complexes of the transient monoborane species, BH_3, whose very short lifetime does not permit the direct determination of its energy. Although the binding energies of some related compounds, as e.g. BH_3CO, BH_3BH_3, and BH_3NH_3, have been investigated thoroughly both experimentally and theoretically (for a review, see ref 3a), little is known[4-6] about the geometry and the binding energy of HCN (and HNC) to BH_3. Particularly, we found no experimental data on binding energies of BH_3 to HCN, HNC, and CN^-, although all these BH_3 complexes were synthesized in the laboratory.[2] Recent semiempirical[4,5] and ab

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initio[5] SCF calculations were mainly devoted to the investigation of the hydrogen migration from boron to the carbon atom. The binding energy of HNC to BH_3 has been calculated at the 4-31G level,[5] but no information on the cyano–isocyano isomerization is given. Finally, it should be mentioned that the correlation effects account for about half of the total binding energy in BH_3 complexes.[3] Thus, any calculation that does not take this fact into consideration must be regarded only as a preliminary estimate of this quantity. Some previous correlation effects were investigated in calculations of Marynick et al.[6] on BH_3CN^-, BH_3NC^-, and the transition state for their isomerization.

The present investigation is a continuation of the previous work of R.J.B. using many-body methods to study the binding energies of BH_3BH_3, BH_3CO, and BH_3NH_3[3a] and a series of isocyanide isomerizations, namely of HCN, LiCN, BCN,[7] and CH_3CN.[8] In the case of HCN $\Leftrightarrow$ HNC, a prediction of the isomerization energy of 60 ± 8 kJ/mol[7] was later verified by experiment.[9]

Besides our interest in contributing to an understanding of the bonding and isomerization of cyanoborate compounds, one additional aim of the present paper is to collect data on a more extended series of isomerization reactions. This, hopefully, will allow us to infer some general suggestions of methods that must be applied to accurate calculations of reaction heats and activation barriers for reactions of this type. To achieve this goal, methods used in the present paper were extended (in comparison to that used elsewhere[7,8]) to the full fourth order of many-body perturbation theory (MBPT) and, moreover, the coupled-cluster approach with single- and double-excitation operators[10] (CCSD). Although some MBPT results for the HCN $\Leftrightarrow$ HNC reaction overlap with previous ones,[7] we can now analyze the effects of the fourth-order triple excitations (omitted in paper[7]) and also include higher order contributions from single, double, and the disconnected triple and quadruple excitation operators that are recovered by CCSD.

Calculations

A. Methods. The merits of MBPT and CCSD methods in calculations of correlations effects in reaction energies and activation barriers have been thoroughly discussed in ref 11. The advantage of both methods consists mainly in their correct scaling with size; i.e., they are "extensive", which guarantees, among other things, that for closed-shell products $E(BH_3NCH) = E(BH_3) + E(NCH)$ at infinite separation. A related property is their comparatively high computational efficiency for incorporating most of the effect of double and higher than double excitations; and, in the possibility to analyze, transparently, the effects of individual excitations (single, double, triple, and disconnected quadruple excitations in MBPT(4)).

The reliability of fourth-order MBPT in calculations of reaction energies is not entirely clear, because two factors may significantly influence the final result: i.e., the basis set effect and the convergence of MBPT. Both must be examined carefully. It seems that the accuracy of about 4–8 kJ/mol should be generally achievable by fourth-order MBPT provided[12-14] that a rather large basis set is used, with diffuse functions and more than one set of polarization functions (up to f functions for first-row atoms). However, even with such extended basis sets, disagreement with experiment as large as 7 kJ/mol is found[14] for the reaction energy of the process $H_2CO \rightarrow H_2 + CO$.

Residual errors from higher orders of MBPT have been investigated for small molecules[15,16] and found not always negligible. In the present work, we can estimate the importance of at least that part of higher orders that arises from the effect of single (S), double (D), and (disconnected) quadruple (Q) excitation operators by using our CCSD results and comparing them to their fourth-order (MBPT) equivalent, SDQ-MBPT(4), which omits the triple excitations. When the SDQ-MBPT(4) result is close to CCSD, we have good convergence. Furthermore, we also have at our disposal, the CC method in which connected triples are included, namely the CCSDT-n approaches,[17,18] and now full CCSDT,[19] but we decided not to use them in this work. As we shall see later, the observed effect from connected triple excitations is only marginal in our reactions, so that CCSDT results would appear to be an unwarranted use of computer time.

Table I. Examples of Geometry Optimizations at the Different Levels of MBPT (Bond Lengths in 10^{-10} m; Angles in Degrees)

	BH_3NC^-			$HNCBH_3$:
	B–N	ρ[a]	B–H	C–B
SCF/4-31G	1.564	19.0	1.222	1.607
SCF/DZ+P (+Dif)	1.577	18.0	1.228	1.611
D-MBPT(2)/DZ+P (+Dif)	1.560	17.7	1.225	1.573
D-MBPT(4)/DZ+P (+Dif)	1.565	17.7		1.586
SDQ-MBPT(4)/DZ+P (+Dif)	1.566	17.9	1.228	1.589

[a] Out-of-plane angle for the BH_3 group.

B. Basis Sets. In calculations of reaction energies and activation barriers, we use the DZP (i.e. double-ζ + polarization) basis with Dunning's contraction of the Huzinaga (9s5p/4s) set[20,21] and the polarization exponents of Redmon et al.[3a] Choosing this basis, we depend upon our previous finding[22] that for reactions where the bonding situation does not change too much during the reaction (which is the case in isomerization reactions) one can use the DZP basis and fourth-order MBPT successfully. A smaller than DZP basis is not recommended, however, for the simple reason that correlation effects can largely only manifest themselves when polarization functions are present.[23] We employ six polarization d functions for B, C, and N atoms with exponents 0.386, 0.654, and 0.902, which are the same as those used in our previous calculations on isomerization reactions[7,8] and were optimized at the correlated level for related systems.[3a] For anions, this basis set was supplemented by diffuse s functions in geometry optimization and by both diffuse s and p functions in energy calculations. An exponent of 0.07 was optimized[24] for CN^-.

For all hydrogens, the exponent of the p polarization function was 0.7, very close to the optimum values for both BH_3 and HCN.[3a,7]

C. Geometries. For HCN, HNC, and their transition states we use the geometry of Pearson et al.[25] optimized by configuration interaction with single and double excitations (CI-SD).

The complete optimization of our larger systems, BH_3CN^-, BH_3NC^-, and their transition states, by the fourth-order MBPT or CCSD would be expensive, so we chose to use a less precise approach. In the first step we supposed that BH_3CN^- and BH_3NC^- may be investigated as loose complexes of CN^- and BH_3. Therefore, we started with the pointwise optimization of the BC or BN distances and the out-of-plane angle ρ of the BH_3 group, retaining the C_{3v} structure (the isolated BH_3 molecule is planar). This was done at the SDQ-MBPT(4) level. With BC or BN distances and the angle ρ fixed at their optimum SDQ-MBPT(4) values, we subsequently performed a gradient SCF optimization of the CN and BH distances.

The sensitivity of optimized parameters to the quality of the method is demonstrated in Table I with results for BH_3NC^- as an example. The most sensitive is the BN distance, which becomes significantly shorter with the inclusion of correlation effects in comparison to the SCF value. The MBPT(2) energy overcorrects the SCF value, as in many other cases, while higher orders decrease this overcorrection. Usually correlation effects provide longer bond distances in comparison to SCF values.[26] In our case, the shortening of the BX bond resembles what may

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Table II. Energy Components for Molecules That Participate in the Isomerization Reactions $BH_3CN^- \Leftrightarrow BH_3NC^-$ and $HCNBH_3 \Leftrightarrow HNCBH_3$ (Energies in au)

contribution[a]	BH_3CN^-[b]	BH_3NC^-[b]	transitn st[c] $BH_3(CN)^-$	$HCNBH_3$[b]	$HNCBH_3$[b]
SCF	-118.795 111	-118.781 012	-118.733 507	-119.293 920	-119.296 250
D-MBPT(2)	-0.396 808	-0.393 842	-0.392 234	-0.395 143	-0.386 767
D-MBPT(4)	-0.426 815	-0.425 406	-0.423 489	-0.427 716	-0.421 999
SDQ-MBPT(4)	-0.423 188	-0.421 862	-0.419 509	-0.423 663	-0.418 260
SDTQ-MBPT(4)	-0.439 794	-0.438 198	-0.436 889	-0.438 686	-0.433 342
CCSD	-0.422 612	-0.421 357	-0.419 420	-0.423 806	-0.417 967
ZPE,[d] kJ/mol	102.5	101.7	95.0	135.6	135.6

[a] Symbols S, D, T, and Q denote the inclusion of single, double, triple, and quadruple excitations in MBPT. The number in parentheses is the highest order contribution included in the perturbation expansion. Quadruple-excitation terms also incorporate the fourth-order renomalization term. The CCSD term means the coupled-cluster (CC) energy with single- and double-excitation cluster operators. [b] Geometries determined by a combination of SDQ-MBPT(4) and gradient SCF method. [c] Geometry from the gradient SCF optimization. [d] Estimated from SCF/4-31G vibrational frequencies.

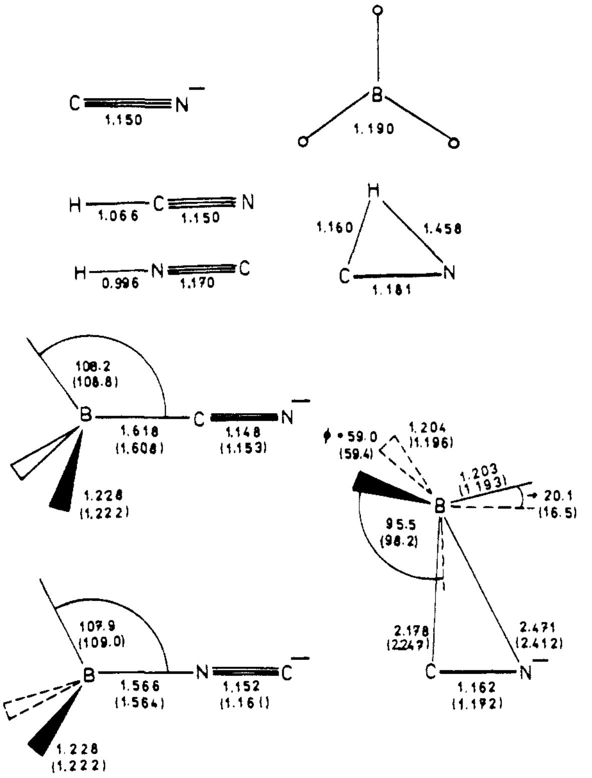

Figure 1. Geometries of CN^-, H(CN), BH_3, and $BH_3(CN^-)$. Bond lengths are in 10^{-10} m; ϕ is the dihedral angle for hydrogens of the BH_3 group related to B, C, and N atoms. The geometry of the transition structure is determined by the gradient technique at the SCF level. Values in parentheses are for the 4-31G basis set.

Table III. Energy Components for Molecules That Participate in the Isomerization Reaction $HCN \Leftrightarrow HNC$ (Energies in au)

	molecule[b]		
contribution[a]	HCN	HNC	transitn st
SCF	-92.889 201	-92.873 404	-92.811 510
D-MBPT(2)	-0.283 790	-0.272 242	-0.278 702
D-MBPT(4)	-0.295 021	-0.287 285	-0.294 580
SDQ-MBPT(4)	-0.292 761	-0.285 608	-0.293 511
SDTQ-MBPT(4)	-0.305 372	-0.297 571	-0.306 530
CCSD	-0.292 666	-0.285 269	-0.294 408

[a] See footnote *a*, Table II. [b] Geometries of Pearson et al.[25] from the CI-SD optimization.

Table IV. Isomerization Energies, ΔE, and Barriers to Isomerization, E_a, for $HCN \Leftrightarrow HNC$ and $BH_3CN^- \Leftrightarrow BH_3NC^-$ and the Isomerization Energy for the $HCNBH \Leftrightarrow HNCBH$ Process (Energies in kJ/mol)

	$HCN \Leftrightarrow HNC$[b]		$BH_3CN^- \Leftrightarrow BH_3NC^-$[c]		$HCNBH_3 \rightleftharpoons HNCBH_3$:[d]
contribution[a]	ΔE	E_a	ΔE[e]	E_a[f]	ΔE[e]
SCF	41.5	204.0	37.0	161.7	-6.1
D-MBPT(2)	32.9	13.4	7.8	12.0	22.0
D-MBPT(4)	20.3	1.2	3.7	8.7	15.0
SDQ-MBPT(4)	18.8	-2.0	3.5	9.7	14.2
SDTQ-MBPT(4)	20.5	-3.0	4.2	7.6	14.0
CCSD	19.4	-4.6	3.3	8.4	15.3
CCSD+T(4)	21.1	-5.6	4.0	6.4	15.2
SCF+SDTQ-MBPT(4)	62.0	200.9	41.2	169.4	7.9
SCF+CCSD+T(4)	62.6	198.3	41.0	168.1	9.1
ZPE	1.8[g]	-16.0[h]	0.8[i]	-7.5[i]	0.0[i]

[a] See footnote, Table II. T(4) is the fourth-order contributions from triple excitations. [b] Energies are measured relative to HCN. [c] Energies are measured relative to BH_3CN^-. [d] Energies are measured relative to $HCNBH_3$. [e] With geometries determined by a combination of SDQ-MBPT(4) and gradient SCF method. [f] With geometries determined by the gradient SCF method. [g] Reference 27. [h] Reference 28. [i] From SCF harmonic frequencies.

Table V. Enthalpy and Entropy Contributions (kJ/mol) to the Equilibria $BH_3CN^- \Leftrightarrow BH_3NC^-$ and $HCNBH_3 \Leftrightarrow HNCBH_3$ and Equilibrium Constants of These Reactions in the Gas Phase[a]

	0 K	298.15 K	500 K	1000 K
$BH_3(CN^-)$				
ΔH	40.2	40.6	40.7	40.7
$T\Delta S$		0.7	1.2	2.5
p*K*		7.0	4.1	2.1
$H(CN)BH_3$				
ΔH	9.0	8.5	8.8	9.5
$T\Delta S$		-1.2	-1.6	-2.2
p*K*		1.7	1.1	0.6

[a] SCF+CCSD+T(4) electronic energies were used in ΔH.

be found in intermolecular interactions. We also examine the influence of the method used for the optimization of the BH bond. With the pointwise optimization we obtain the same value with SDQ-MBPT(4) as with the SCF method, and both these results agree with the final SCF gradient optimized result. The angle ρ is quite insensitive to the method chosen. In the optimization of $HCNBH_3$ and its isomer we proceed similarly as with BH_3CN^-.

First, we optimize the BN and BC distance and the out-of-plane angle ρ at the SDQ-MBPT(4) level. With BN or BC and ρ fixed at their optimum values we similtaneously optimize the CH or NH bond, the CN bond, and the BH bond lengths by gradient optimization at the SCF level. We verified that the optimum structure is C_{3v}. The sensitivity of the optimum BC bond length to the method is demonstrated in the last column in Table I. It is analogous to that in BH_3NC^- or BH_3CN^-. Geometries of all species are collected in Figures 1 and 2.

Second, we also optimize the transition structure for the isomerization of anionic systems. We restrict ourselves to the SCF level and employ the analytical gradient technique. The residual maximum force is less than 5×10^{-4} au, as in all our other gradient optimizations. The resulting structure is presented in Figure 1.

The hypersurface for the isomerization of the neutral system is much more complicated than that of the anionic system. Our preliminary study

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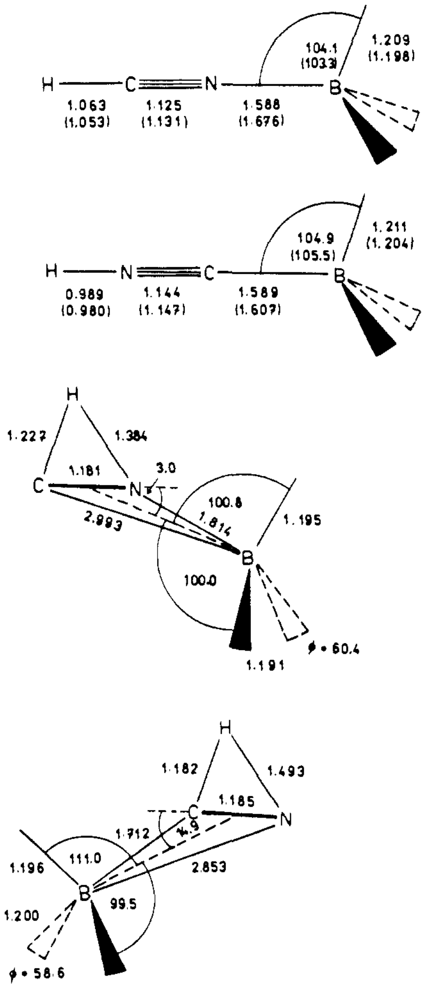

Figure 2. Geometries of $H(CN)BH_3$. Bond lengths are in 10^{-10} m. Values in parentheses are for the 4-31G basis set.

indicates the presence of several transition structures and local minima. These results will be published separately.

Results and Discussion

Energy components for molecules that participate in the isomerization reaction $BH_3CN^- \Leftrightarrow BH_3NC^-$ and $HCNBH_3 \Leftrightarrow HNCBH_3$ are presented in Table II. In Tables III–V we present the energy components for our "bench-mark" HCN ⇔ HNC reaction. In Table IV we collect the isomerization energies, ΔE, for all three of our reactions and barriers to isomerization, E_a, for H(CN) and $BH_3(CN)^-$ reactions. In all cases the inner shell occupied molecular orbitals and the corresponding virtual molecular orbitals are dropped in the MBPT and CCSD calculations.

A. Energies of Isomerization. The inspection of Table IV reveals that in all our reactions the correlation energy reinforces the stability of cyanide compounds over the isocyanide ones, albeit to a very different extent. In HCN the correlation effects are responsible for roughly one-third of ΔE, while in BH_3CN^- their role is not very important, but in $HCNBH_3$ they even change the sign of ΔE. At the SCF level $HCNBH_3$ is less stable than the $HNCBH_3$ isomer, but with correlation effects the order of stability is reversed. The observation that the cyanide has a larger correlation energy than the isocyanide holds not only for our three systems, but also for LiCN, BCN,[7] and CH_3CN.[8] This property is correctly described already by second-order perturbation theory but only qualitatively. In all reactions the second-order energy significantly overestimates the correlation effects in ΔE. This overestimation is compensated primarily by the third-order contribution.

The difference between the SDQ-MBPT(4) and CCSD reaction energies is quite small, so that higher than fourth-order contributions from single, double, and disconnected quadruple excitations to ΔE and E_a are not very important. According to our experience,[19] if this is true for doubles and quadruples, then the same is expected also with triple excitations. While in molecules like HCN and their reactions the good convergence of MBPT might be expected on the basis of previous MBPT and CC calculations;[29,30] this is not so obvious in boron-containing compounds, due to potential problems with quasi-degeneracy.[11] However, extensive comparison of CC results and MBPT(4) for B_2H_6[3b] indicates there is little residual error in MBPT(4). The poorer convergence of MBPT resolves itself primarily within the first four orders of perturbation theory for the individual molecules (see Tables II and ref 11).

It is important from the methodological and practical point of view that our calculations fully confirm the anticipation of Redmon et al.[7,8] that the computationally more difficult triple excitations should be less important in investigations of isomerization reactions. In all cases they contribute less than 2 kJ/mol.

B. HCN ⇔ HNC Reaction. The discussion in the preceding part supports the conclusion that CCSD+T(4) as well as fourth-order MBPT will be good estimates of correlation effects in our isomerization reactions. Relying on the preceding SDQ-MBPT(4) analysis[7] of the basis set effects in the HCN ⇔ HNC isomerization, we might anticipate that our DZP basis set is satisfactory as well. To wit, the extension of the basis set from the DZP to the [6s4p2d/3s2p] set changed the ΔE value no more than by 0.4 kJ/mol (and E_a was lowered by only 3.3 kJ/mol). Since it appears that the inclusion of triple excitations has little effect in our isomerizations and that the convergence of MBPT is quite satisfactory, we can expect that the basis set effects with our CCSD+T(4) energies are also of the same magnitude. Thus, our final value of ΔE = 62.6 kJ/mol should be reliable. The zero-point energy (ZPE) corrections to the equilibrium energy difference are all about 1.8 kJ/mol[27] so that our ΔE = 64.4 kJ/mol is in very good agreement with a recent ion cyclotron resonance experiment,[9] which led to the value of 61.9 ± 8.4 kJ/mol. This result, together with an excellent agreement with experiment for the isomerization energy and the activation barrier of another isomerization reaction, $CH_3NC \Leftrightarrow CH_3CN$, investigated at the SDQ-MBPT(4) level with a DZP basis,[8] provides additional support for the methods used in the present predictions of ΔE and E_a for the isomerizations $BH_3CN^- \Leftrightarrow BH_3NC^-$ and $HCNBH_3 \Leftrightarrow HNCBH_3$.

C. $BH_3CN^- \Leftrightarrow BH_3NC^-$ Reaction. The geometry of $BH_3(CN)^-$ isomers as well as the overall picture of contributions to ΔE resembles to some extent the isomerization of $CH_3(CN)$.[6,8,28,31] In our system, however, the BC and BN bonds are about 0.14 × 10^{-10} m longer than the CC or CN bonds in $CH_3(CN)$.

The isomerization energy, 41 kJ/mol, is substantially smaller for the $BH_3CN^- \Leftrightarrow BH_3NC^-$ reaction than for the $CH_3CH \Leftrightarrow CH_3NC$ case (95 kJ/mol), with cyanide isomers more stable in both cases. In both reactions the correlation effects only slightly increase the SCF values.

Qualitatively, our results agree with limited CI-SD calculations of Marynick et al.[6] In agreement with their findings, the BH_3CN^- isomer is more stable than BH_3NC^- and correlation effects favor binding through the carbon atom. Our ΔE (37 kJ/mol) is, however, significantly lower than theirs (49 kJ/mol) already at the SCF level, and the difference is even larger when the correlation energy is incorporated (41 and 72 kJ/mol, respectively). Since our basis set contains diffuse functions and since our many-body methods incorporate much more correlation effects than in ref 6, our results should be more trustworthy. The reliability of our calculations is also supported by the fact that analogous methods used in the investigation of isomerizations of HCN and CH_3CN[8] led to excellent agreement with experiment.

Using SCF+CCSD+T(4) electronic energies, we present ΔH and $T\Delta S$ contributions to the equilibrium and pertinent equilib-

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Table VI. Binding Energies (kJ/mol) of BH_3 to CN^-, HCN, and HNC

contribution[a]	BH_3 + CN^-	BH_3 + NC^-	HCN + BH_3	HNC + BH_3
SCF	-196.6	-159.6	-30.1	-77.7
D-MBPT(2)	-59.7	-51.9	-46.8	-57.8
D-MBPT(4)	-51.9	-48.0	-39.3	-44.6
SDQ-MBPT(4)	-50.0	-46.5	-37.9	-42.5
SDTQ-MBPT(4)	-55.1	-50.9	-41.7	-48.1
CCSD	-48.2	-44.9	-36.6	-40.7
CCSD+T(4)	-53.3	-49.3	-40.4	-46.4
SCF+SDTQ-MBP-T(4)	-251.7	-210.5	-71.8	-125.9
SCF+CCSD+T(4)	-249.9	-208.9	-70.6	-124.1

[a] See footnote *a*, Table II. T(4) is the fourth-order contribution from triple excitations.

rium constants in Table V. It is clear that the equilibrium is controlled by the energy difference; the change in ZPE as well as the entropy change is negligible. Equilibrium constants are calculated for four temperatures with the rigid rotor and harmonic oscillator approximation. Harmonic vibrational frequencies are calculated at the SCF/4-31G level at corresponding geometries. Although originally intended as preliminary, since the contributions of ZPE and ΔS are shown to be very small, it appears unimportant to go to a higher level.

D. $HCNBH_3 \Leftrightarrow HNCBH_3$ Reaction. The isomerization energy of this process is the lowest of all our reactions. At the SCF level the $HNCBH_3$ isomer is more stable than the $HCNBH_3$ one. The correlation energy changes this order of stability, but total electronic energies of both isomers remain quite similar. Since the change of ZPE is zero and the entropy change during the reaction is very small (see Table V), the equilibrium is controlled solely by the electronic energy difference between $HCNBH_3$ and $HNCBH_3$ isomers. The resulting equilibrium constant at 298.15 K is about 0.02, which is a fairly large value. Consequently, both isomers are thermodynamically allowed, especially at higher temperatures.

Our theoretical geometry of the $HNCBH_3$ isomer is comparable to the experimental geometry of a related compound, CH_3NCBH_3, which was determined from microwave spectra.[32] Our CB bond length is 0.02×10^{-10} m longer, and the CBH angle is 0.8° smaller than observed in the microwave structure of CH_3NCBH_3, implying slightly weaker bonding of BH_3 to HNC than that of BH_3 to CH_3NC. The symmetry is in both cases C_{3v}.

E. Binding Energies of BH_3 to CN^-, HCN, and HNC. CN^- is an ambidentate anion, and thus it may react at both C and N sites. Its bonding to the BH_3 molecule is accompanied by considerable charge reorganization on C and N atoms in both isomers with significant charge transfer from CN^- to the BH_3 group. While in BH_3CN^-, the Mulliken net charges at B, C, and N atoms are, respectively, -0.49, +0.18, and -0.52 e, and in BH_3NC^- they are -0.35, +0.02, and -0.44 for B, N, and C atoms, with the hydrogen charges very slightly negative (-0.06 and -0.08 for BH_3CN^- and BH_3NC^-). The charge transfer is more pronounced in BH_3CN^-, and this fact may contribute to its larger stability in comparison to BH_3NC^- already at the SCF level. The binding energy of BH_3 to CN^- and NC^- is presented in Table VI. The SCF contribution dominates in both B-C and B-N bonds, but correlation contributions are still very high in both cases. The correlation contribution of ~50 kJ/mol is consistent with the correlation effects on binding energies of the isoelectronic charge-transfer complex, BH_3CO.[3a]

The binding energies of BH_3 to HCN and HNC differ considerably from the binding energies of BH_3 to CN^-; see Table VI. The more detailed comparison shows that correlation effects are similar in binding energies of BH_3 to CN^-, HCN, and HNC; but with the CN^- anion, the total binding is much stronger due to the SCF component. The low contribution of the SCF energy to the binding energy in neutral systems makes correlation effects exceptionally important in both HCN + BH_3 and HNC + BH_3 systems. In the former case the correlation contribution even dominates over the SCF ones. This confirms results of previous calculations of BH_3 complexes[3] in that it is senseless to investigate compounds of this kind without considering effects of electron correlation.

The stronger total (SCF + correlation) attraction of HNC to BH_3 than that of HCN to BH_3 (they differ by as much as 53 kJ/mol) has an important chemical consequence. Namely, the total electronic energies of both $HCNBH_3$ and $HNCBH_3$ isomers are quite close to each other, in sharp contrast to their component molecules, HCN and HNC. As a result, the isomerization energy is much lower for the reaction $HCNBH_3 \Leftrightarrow HNCBH_3$ than for the HCN $\Leftrightarrow$ HNC isomerization.

F. Proton Affinities for BH_3CN^- and BH_3NC^-. For relative energies of BH_3CN^-, $HNCBH_3$, BH_3NC^-, and $HNCBH_3$, one may easily arrive at proton affinities for the anionic systems. As expected, they are very high, 1300 and 1350 kJ/mol for BH_3CN and BH_3NC, respectively. Correlation contributions are -16 kJ/mol in the former case and 3 kJ/mol in the latter case and thus unimportant in relation to the total protonization energy.

G. Barriers to Isomerization. The SCF gradient optimized transition structure of $BH_3(CN)^-$ is quite similar to the transition structure of the analogous $CH_3(CN)$ system,[28] also optimized by the SCF gradient technique. In our system, however, the BC and BN bond lengths are substantially longer than analogous bond lengths in $CH_3(CN)$, reflecting weaker bonding of the BH_3 group to CN^-. The in-plane hydrogen of the BH_3 group is oriented toward the nitrogen atom of CN^-, as is the hydrogen of the CH_3 group in $CH_3(CN)$, and in accord with previous SCF/4-31G optimizations[6] of $BH_3(CN)^-$. Comparing 4-31G results with DZP results in Figure 1, we may observe that the influence of the quality of the basis set on the optimized geometry is much more noticeable for the transition structure than for the geometry of the BH_3CN^- and BH_3NC^- isomers.

As Table IV shows, barriers to isomerizations, E_a, for H(CN) and $BH_3(CN)^-$ reactions are very high. Both cases are strictly dominated by SCF energies. Thus, in contrast to ΔE, correlation effects are relatively less important in E_a. Our barrier to isomerization for H(CN) agrees very well with other comparably published results[7,23,25] and need not be discussed in greater detail. The classical barrier to isomerization of $BH_3(CN)^-$, 168 kJ/mol, is slightly lower than the barrier for the isomerization of another related system, CH_3CN, for which it is 191 kJ/mol.[8] The barrier for $BH_3(CN)$ is still sufficiently large, however, so that both BH_3CN^- and BH_3NC^- isomers should exist as noninterconverting entities under conditions where only unimolecular processes occur. Both isomers of $BH_3(CN)^-$ are thus observable in the laboratory,[2] but due to a stronger attraction of BH_3 to the carbon side of CN^-, the equilibrium is shifted to the BH_3CN^- side. After its subsequent protonization, this compound leads to synthetically important $HNCBH_3$.

Similar to the anionic systems, both neutral compounds, $HCNBH_3$ and $HNCBH_3$, seem to be separated by a very high barrier. Our preliminary study so far indicates two structures with a single negative eigenvalue of the Hessian matrix. In both these structures the H, C, and B atoms form a triangle, which resembles the transition structure of the isolated HCN. The BH_3 group is very weakly bonded either to the N-side or to the C-side of this triangle and has a tendency to flatten. The corresponding barrier is about 200 kJ/mol for the C-side structure and 220 kJ/mol for the N-side structure. The ZPE lowers them by about 20 kJ/mol, but the barriers still remain very high. At present, we are searching for alternative transition structures and local minima. Results of these studies for the mechanism of the isomerization of HCNBH will be presented separately.

Quantitatively, we would expect our computed barriers for $H(CN)BH_3$ and $BH_3(CN)^-$ to be, artificially, somewhat high, since we compare MBPT results at SCF transition states with MBPT results at MBPT geometries of the two molecules, but this should have little effect on any qualitative conclusions. Future

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work will employ analytical correlated MBPT(2) first- and second-derivative methods[33] to obtain more quantitative results.

Conclusions

1. We have predicted binding energies of BH_3 to HCN, HNC, and CN^-. The bonding of BH_3 to the carbon atom in HCN and CN^- is strongly preferred over the bonding to the nitrogen atom.

2. We have calculated reaction energies for HCN $\Leftrightarrow$ HNC, $BH_3CN^- \Leftrightarrow BH_3NC^-$, and $HCNBH_3 \Leftrightarrow HNCBH_3$ isomerizations. In all cases cyano isomers (i.e. HCN, BH_3CN, and $HCNBH_3$) are more stable than their isocyano isomers. However, the isomerization energy for $H(CN)BH_3$ is much lower than that for the composite molecule, H(CN) (9 and 63 kJ/mol, respectively). This difference results from the much stronger attraction of BH_3 to HNC than to HCN. The calculated equilibrium constant for $HCNBH_3 \Leftrightarrow HNCBH_3$ is 0.02.

3. Estimated barriers to isomerization are very high in all three reactions (182, 161, and 200 kJ/mol, including ZPE). The calculated barrier for the $H(CN)BH_3$ isomerization is only preliminary. The understanding of the mechanism of this reaction requires a more detailed investigation of the energy hypersurface.

4. The inclusion of effects of electron correlation is inevitable in the quantitative description of the bonding of BH_3 to HCN, HNC, and CN^-. Electron correlation is also very important in the prediction of energies of isomerization but less important in calculations of activation barriers of investigated reactions.

5. We have demonstrated that MBPT methods are suitable for a quantitative prediction of energy characteristics of present isomerization reactions. Higher orders of the wave-function expansion considered in CCSD brought very little change of calculated quantities in comparison to the corresponding SDQ-MBPT(4) values. Even D-MBPT(4), in which only double excitations are taken into account, is quite satisfactory in the present case.

Acknowledgment. M.U. is very grateful for the warm hospitality of Professor R. J. Bartlett and the Quantum Theory Project members during his stay in Gainesville, FL. The authors also thank Professor G. Ryschkewitsch for useful discussions. This work was supported by the USAF Office of Scientific Research.

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Structures and Stabilities of Singly Charged Three-Electron Hemibonded Systems and Their Hydrogen-Bonded Isomers

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Abstract: Ab initio molecular orbital theory has been used in a systematic study of the first- and second-row ion dimers $He_2^{\bullet+}$, $(NH_3)_2^{\bullet+}$, $(H_2O)_2^{\bullet+}$, $(HF)_2^{\bullet+}$, $Ne_2^{\bullet+}$, $(PH_3)_2^{\bullet+}$, $(H_2S)_2^{\bullet+}$, $(HCl)_2^{\bullet+}$, and $Ar_2^{\bullet+}$. With the exception of the inert-gas ion dimers, these can exist in principle either as hydrogen-bonded ions or as hemibonded species, the latter involving binding through heavy atom–heavy atom three-electron bonds. The hydrogen-bonded systems are preferred for all the first-row systems, and the two isomers have comparable energies in the case of the $P_2H_6^{\bullet+}$ system, while, for the remaining second-row systems, the hemibonded isomers are preferred. The barriers to interconversion and to dissociation of the hydrogen-bonded and hemibonded isomers are found in most cases to be sufficiently large that, under appropriate conditions, experimental observation of the individual isomers should be possible. A simple Hückel model of the length and strength of a three-electron hemibond is presented and is shown to give a satisfactory qualitative account of such bonding. It is found, nevertheless, that comparatively high levels of ab initio theory, including in particular electron correlation, are necessary to predict accurately the binding energies of hemibonded systems and, in certain cases, to ensure even a *qualitatively* correct description of their potential energy surfaces.

The emergence as stable entities of systems containing a three-electron bond with a formal bond order of $^1/_2$ is an intriguing recent phenomenon. Numerous experimental papers[1-20] on the subject have now appeared, with the pioneering work of Alder[1-4] on nitrogen-containing systems, of Asmus[5-9] on sulfur-containing molecules, and of Symons[10-15] having particular relevance to our own studies. The first theoretical discussions, by Pauling,[21] date from more than 50 years ago. More recently, we have examined a nitrogen-containing system[22] while Clark[23a-c] has reported elegant

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