C_5H_5BeF also shows dimerization to be disfavored by ~57 kcal/mol, even though dimerization of HBeF through fluorine is favored by ~90 kcal/mol. Both CH_3 and F in the R^t position tend to destabilize the dimers regardless of the bridging group, and BH_4 provides a uniform dimer stabilization. Phenyl bridging is calculated to be highly favorable, suggesting a rich chemistry of molecules of the type $R^tBePh_2BeR^t$.

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Chair–Boat Equilibria in Bicyclo[3.3.1]nonane at 65 and 400 °C Studied by Electron Diffraction and Molecular Mechanics†

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Abstract: Gaseous bicyclo[3.3.1]nonane has been studied by electron diffraction with a new high-temperature nozzle system at a temperature of 400 °C. The structural analysis revealed substantially more (ca. 25%) of the boat–chair conformer than in the previous investigation carried out at a lower temperature (ca. 5% at 65 °C). This result is in excellent agreement with molecular mechanics calculations leading to the value of 2.3 kcal/mol as the energy difference between boat–chair and twin chair conformers. The structural parameters obtained by molecular mechanics calculations are in good agreement with the experimental results, which for both conformers are (with estimated errors of 3σ): C–C = 1.536 (1) Å, C–H = 1.109 (3) Å, H–C–H = 107.6 (3.7)°, C_1–C_9–C_5 = 108.5 (4.2)°, C_2–C_3–C_4 = C_6–C_7–C_8 = 112.8 (4.5)°, θ = 123.4 (1.5)°, ϕ = 44.7 (2.3)°. The amplitudes of vibration were calculated and used in the analysis as fixed values.

Introduction

The potential conformational mobility of the bicyclo[3.3.1]nonane (henceforth BN) rings makes it an interesting system for study. Accordingly, the chemistry of BN has received much attention from both synthetic[1] and theoretical points of view. For BN three conformers CC, BC, and BB are possible by analogy with cyclohexane (C = chair, B = boat). There is, however, one important quantitative difference between BN and cyclohexane due to the serious endo 3,7 hydrogen–hydrogen transannular interaction in the former system, which leads to the relation

CC (C_{2v}) BC (C_s) BB (C_2)

C (D_{3d}) D_2 C_{2v}

$$\Delta E_1 < \Delta E_2 \approx \Delta E$$

The greater accessibility of the boat conformation in BN (ΔE_1 is calculated from 1.5 to 2.5 kcal/mol) than in cyclohexane ($\Delta E \approx$ 5–6 kcal/mol[2]) has been predicted by molecular mechanics calculations[3,4] for BN itself and verified experimentally ($\Delta E_1 \approx$ 2.1–2.7 kcal/mol[5]) for some of its derivatives.[6] This provided the hope that a detectable amount of the BC conformer might be obtained in an appropriate high-temperature experiment. Since no experimental ΔE_1 or ΔE_2 values have been previously reported for BN, we felt that even a rough measurement of this quanity would be worthwhile.[7]

Earlier we studied the geometry of the CC conformer in BN by electron diffraction.[8] It was logical, therefore, to try to use the same method for the detection of the BC conformer, because there already were many successful applications of electron diffraction to the study of conformational problems.[9-14]

It was clear from the outset that it would be a difficult task to identify the BC conformer on the background of CC conformer, since they have a similar distribution of internuclear distances. Bearing in mind the limited accuracy of electron diffraction, two

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† Dedicated to Professor Otto Bastiansen in honor of his sixtieth birthday.

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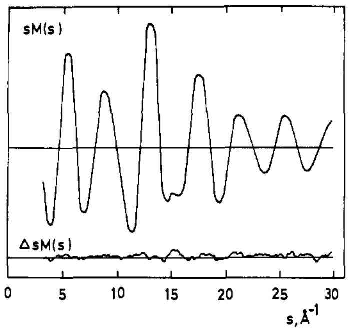

Figure 1. Experimental molecular intensity curve and the difference (experimental minus theoretical) corresponding to the model of Table III.

special points were taken into account: (1) the temperature of the experiment should be carefully selected in order to maximize the amount of BC conformer; (2) the power of electron diffraction is known to increase if it is combined with simultaneous vibrational and conformational calculations[15] which are used as additional information.

Experimental Section

The sample of BN was the same as that used in our previous study.[8] Its thermal stability was checked in the following way. Small portions of BN were placed in an inert atmosphere in ampules which were sealed and transferred to an oven heated to fixed temperatures of 350, 400, and 450 °C. After 5–30 minutes in the oven, the compound was analyzed by GLC. Traces of decomposition (ca. 10% of more volatile compounds) were found only at 450 °C after 30 min; therefore, it was decided to carry out the electron diffraction experiment at 400 °C, the highest temperature at which BN is stable under the experimental conditions.

Since normally electron diffraction equipment is designed to reach temperatures of about 200 °C,[16] a special high-temperature nozzle system was constructed.[17] The gas flow through the nozzle can be regulated by a needle valve, and the temperature of the system can be raised by resistance heating up to about 900 °C. The temperature is measured by a thermocouple situated at the nozzle tip.

Diffraction patterns were recorded at 400 ± 30 °C on the modified EG-100A electron apparatus[18] at Moscow State University using the gas standard (benzene) method recently developed for determination of the wavelength of the electron beam.[19,20] Three photographs for each nozzle-to-plate distance (492.3 and 186.0 nm) were used to cover the range from $s = 3.2$ to $s = 14.2$ Å^{-1} ($\lambda = 0.049216$ Å) and from $s = 11.4$ to $s = 30$ Å^{-1} ($\lambda = 0.049011$ Å), respectively. Optical densities ranged from 0.11 to 0.31 and from 0.18 to 0.32 for the long and short camera length plates, correspondingly. The data were treated in the conventional manner,[21] except that the initial drawing of the background functions was done automatically by splines with the program written by Novikov.[22]

Experimental intensities $I(s)$ are available as supplementary material, and molecular intensities $sM(s)$ are shown in Figure 1.

Data Analysis

Table I. Structural Parameters of BN^a Calculated by Using Force Field MM2[24]

parameter	CC conformer	BC conformer
C_1-C_2	1.540	1.542
C_1-C_6		1.544
C_2-C_3	1.536	1.537
C_6-C_7		1.536
C_1-C_9	1.534	1.537
C-H(av)	1.116	1.116
C_1-C_9-C_5	108.1	108.2
C_2-C_3-C_4	112.9	111.7
C_6-C_7-C_8		112.0
H-C-H(av)	105.7	105.8
θ_1	116.4	115.6
θ_2		120.1
ϕ_1	42.2	50.2
ϕ_2		47.9

^{a} Bond distances are in ångstroms and bond angles are in degrees.

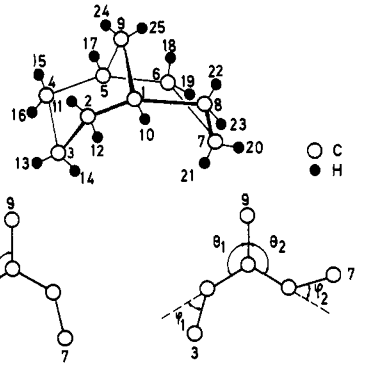

Figure 2. Numbering of atoms in bicyclo[3.3.1]nonane and projections for the CC and BC conformers which show the specified dihedral angles.

The structure determination of the CC conformer of BN was a delicate problem for electron diffraction as was demonstrated elsewhere,[8] and many difficulties were anticipated in the concurrent analysis of a mixture of two conformers. In fact, this problem is too complex for a unique determination of the ratio of conformers, as well as their entire set of geometrical and vibrational parameters, by electron diffraction alone. Therefore, some simplified model was obviously needed.

The first problem was how many independent parameters were necessary to describe adequately the geometries of both conformers. This task was largely overcome by the use of molecular mechanics calculations. Molecular mechanics has become a well-established technique for the prediction of molecular geometry, with an accuracy rivaling that achieved by experimental methods and comparable to or higher than that of the best semi- or nonempirical quantum chemical calculations[4,23] in favorable cases.

The geometrical parameters for both conformers, listed in Table I, were calculated by a recently improved force field, MM2.[24] (Our results are in perfect agreement with the calculation by Ōsawa et al.,[25] who used the same force field; both calculations give exactly the heat of formation of BN, for which the experimental value was later reported.[26] On the basis of these results, 11 independent geometrical parameters can be selected (see Figure 2 for the numbering of atoms) for both conformers: the average bond distances C–C and C–H and bond angles H–C–H, C_1–C_9–C_5, and C_2–C_3–C_4 = C_6–C_7–C_8, as well as the following dihedral angles (for the CC conformer) θ and ϕ and (for BC) θ_1, θ_2, ϕ_1, and ϕ_2. It was assumed that the CH_2 units have local C_{2v}

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Table II. Molecular (Urey-Bradley) Force Field and Calculated Amplitudes of Vibration[a]

$K(C\text{–}C) = 2.304$ $F(C\cdots H) = 0.482$ $H(C\text{–}C\text{–}H) = 0.217$
$K(C\text{–}H) = 4.050$ $F(H\cdots H) = 0.069$ $H(H\text{–}C\text{–}H) = 0.435$
$F(C\cdots C) = 0.200$ $H(C\text{–}C\text{–}C) = 0.320$ $Y = 0.107$

distance	*u*	distance	*u*
C–C(av)	598	$C_2\cdots H_{18}$	1778
C–H(av)	794	$C_2\cdots H_{19}$	2916
$C_1\cdots C_3$, $C_1\cdots C_7$	1030 (908)	$C_2\cdots H_{20}$, $C_6\cdots H_{13}$	2065 (1937)
$C_1\cdots C_4$	1162	$C_2\cdots H_{21}$, $C_6\cdots H_{14}$	3129 (1727)
$C_1\cdots C_5$	915	$C_2\cdots H_{22}$	1373
$C_2\cdots C_4$	1006	$C_2\cdots H_{23}$	2192
$C_2\cdots C_6$	1940	$C_2\cdots H_{24}$	2466
$C_2\cdots C_7$, $C_3\cdots C_6$	1958 (1372)	$C_2\cdots H_{25}$	1266
$C_2\cdots C_8$	1205	$C_3\cdots H_{10}$	1251
$C_2\cdots C_9$	1082	$C_3\cdots H_{18}$, $C_7\cdots H_{11}$	1898 (1521)
$C_3\cdots C_7$	2171 (1662)	$C_3\cdots H_{19}$, $C_7\cdots H_{12}$	3283 (1894)
$C_3\cdots C_9$, $C_7\cdots C_9$	1214 (978)	$C_3\cdots H_{20}$, $C_7\cdots H_{13}$	2486 (2348)
$C_1\cdots H_{11}$	1204	$C_3\cdots H_{21}$, $C_7\cdots H_{14}$	3231 (1792)
$C_1\cdots H_{13}$	1244	$C_3\cdots H_{24}$, $C_7\cdots H_{25}$	2709 (1127)
$C_1\cdots H_{14}$	1947	$C_3\cdots H_{25}$	1320
$C_1\cdots H_{15}$[b]	2043	$C_9\cdots H_{11}$	2112
$C_1\cdots H_{16}$[b]	1508	$C_9\cdots H_{12}$	1269
$C_2\cdots H_{15}$	1974	$C_9\cdots H_{13}$	1564
$C_2\cdots H_{16}$	1249	$C_9\cdots H_{14}$, $C_9\cdots H_{21}$	1761 (1131)

[a] Force constants *K* and *F* are in mdyn·Å^{-1}; *H* and *Y*(torsion) are in mdyn·Å; amplitudes (*u*) are in 10^{-4} Å. The H···H pairs are not listed. The average amplitudes of vibration are given for the distances which are equal or close in both conformers when $\theta = \theta_1 = \theta_2$ and $\phi = \phi_1 = \phi_2$. For those distances which are different in conformers in parentheses are listed the values corresponding to the BC form. [b] In calculation of theoretical *s*M(*s*) function the contributions of close internuclear distances were summed for the following three groups: (1) $C_1\cdots H_{11}$, $C_1\cdots H_{24}$, $C_2\cdots H_{10}$, $C_2\cdots H_{13}$, $C_3\cdots H_{11}$ and $C_9\cdots H_{10}$; (2) $C_1\cdots H_{15}$ and $C_1\cdots H_{17}$; (3) $C_1\cdots H_{16}$, and $C_2\cdots H_{17}$.

Table III. Structural Results (Distances (Å) and Angles (Deg)) for Bicyclo[3.3.1]nonane, Experimental (at 65 and 400 °C) and Calculated by Molecular Mechanics

	exptl		calcd[a]	
parameter	65 °C	400 °C	CC	BC
C–C	1.536 (2)	1.536 (1)	1.537	1.539
C–H	1.107 (7)	1.109 (3)	1.116	1.116
∠H–C–H	106.5 (4.5)	107.6 (3.7)	105.7	105.8
$\angle C_1\text{–}C_9\text{–}C_5$	107.3 (5.6)	108.5 (4.2)	108.1	108.2
$\angle C_2\text{–}C_3\text{–}C_4$	113.0 (4.1)	112.8 (4.5)	112.9	111.9
θ	122.8 (1.7)	123.4 (1.5)	116.5	117.9
ϕ	40.0 (3.0)	44.7 (2.3)	42.2	49.1
α(BC), %	5 (4)	25 (10)		
R factor	0.114	0.049		

[a] If the geometry of BN is fixed at the molecular mechanics calculated values and only the conformational ratio is varied, the following results are obtained by a least-squares fitting to the electron diffraction data: α(BC) = 8 (6)% at 65 °C ($R = 0.144$) and α(BC) = 38 (20)% at 400 °C ($R = 0.085$). The *R* factor of 0.114 was obtained because the experimental data used at 65 °C were taken directly from earlier work. Adjustment of the background function could presumably reduce this quantity but was not attempted, as it was not important for present purposes. It has been generally noticed that such reductions of the *R* factor in electron diffraction by say from 0.11 to 0.05 give almost no change in the refined parameters obtained but only decrease their standard deviations.

symmetry. A special geometrical subroutine was written which permitted the refinement of 11 independent structural parameters and also the composition parameter α, i.e., the percentage of conformers with the restriction that α(CC) + α(BC) + α(BB) = 100%. In order to reduce the complexity of the analysis, we set α(BB) = 0, since with $\Delta E_2 = 5.02$ kcal/mol (from the MM2 calculation), the amount is only about 4% at 400 °C.

It became clear during the initial part of analysis that the number of parameters was excessive (the 3σ values for dihedral angles ϕ and θ were too high: 25 and 10°, respectively) and it was necessary, therefore, to introduce additional constraints in order to reduce the complexity of the model to a manageable number of parameters. Finally, the initial differences in dihedral angles for the two conformers were removed; i.e., it was assumed that $\theta = \theta_1 = \theta_2$ and $\phi = \phi_1 = \phi_2$. (This constraint was partially relaxed, however, as explained below.)

The same geometrical subroutine was used to analyze in parallel our previous data taken at 65 °C and concurrently the data obtained at 400 °C. It was hoped that such a procedure could more objectively show the percentage of BC at different temperatures. This particular part of the analysis was absent in our study of BN at 65 °C, and, accordingly, a short description is given below.

The amplitudes of vibration, calculated with a program written by Stölevik,[27] were employed throughout the analysis as fixed values. In these calculations the Urey-Bradley force field reported for cyclohexane by Takahashi et al.[28] was used. The amplitudes calculated at 65 °C were reported earlier (Table IV, ref 8), while those calculated at 400 °C are listed in Table II. Shrinkage corrections were ignored.

(1) Experiment at 65 °C. The molecular intensity *s*M(*s*) obtained earlier[8] was directly analyzed by the current procedure. Three different starting values for α(BC) were tested: 3, 5, and 50%. (The same values were used later in the subsequent analysis at 400 °C.) All the refinements smoothly converged to the values listed in the first column of Table III. In parentheses are given the 3σ values except for α(BC) = 5 ± 4% where the 1σ value is taken to keep the amount of conformer formally above the significance level for future calculations (see Discussion). We realize that this is rather artificial, but our deductions do not depend on this point. Furthermore, due to the sensitivity of electron diffraction, if the BC conformer were not detected, it would be more reasonable to assume that its quantity is no more than 10% (see, e.g., ref 9a).

An *R* factor (0.058) obtained earlier[8] for the CC conformer with only the average C–C distance was noticeably better, however, than the present value (0.114). This is due to the fact that the amplitudes of vibration fixed in this study were previously used as the refinable variables. The value of α(BC) = 2 ± 3% with *R* = 0.058 was obtained in a special calculation when the refined amplitudes were employed.

(2) Experiment at 400 °C. The refinements with the same starting values for α(BC) as used in the previous section led to the results summarized in the second column of Table III. These are illustrated by the difference radial distribution shown in Figure 3. The curves B, α(BC) = 5%, and C, α(BC) = 50%, have some obvious defects in the conformationally important area of 2.5–4.0 Å, which disappear for the best model, curve A, with α(BC) = 25%.

The MM2 calculations show that the longest carbon–carbon distance for the BB form is 4.21 Å. An inspection of the radial distribution curve in this area reveals no indication of the presence of this conformer, although the expected amount is so small (4% at 400 °C) that is presence cannot be ruled out.

In the course of the analysis, the correlation coefficients were repeatedly calculated. For a number of parameters correlation coefficients were higher than 0.5 (these were −0.55 for θ and

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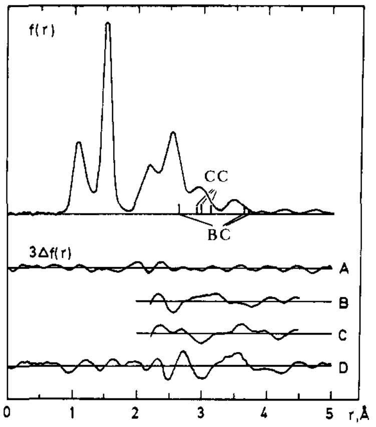


Figure 3. The experimental radial distribution curve of bicyclo[3.3.1]nonane at 400 °C and 3 times the difference (A - D) radial distribution curves. The vertical lines indicate the internuclear C···C distances which most significantly differ in the two conformers. The difference curves correspond to the following theoretical models. Curve A: the best-fit model which gives $\alpha(\mathrm{BC}) = 25\ (10)\%$ ($R = 0.049$); for geometrical parameters, see Table III. Curve B: corresponds to a fixed conformational ratio $\alpha(\mathrm{BC}) = 5\%$ ($R = 0.058$) found at 65 °C. Curve C: conformational ratio is fixed at $\alpha(\mathrm{BC}) = 50\%$ ($R = 0.059$). Curve D: geometrical parameters are fixed at the molecular mechanics calculated values (see Table I), and only the conformational ratio is allowed to vary, leading to $\alpha(\mathrm{BC}) = 38\ (20)\%$ ($R = 0.085$).

C_1–C_9–C_5, 0.62 for ϕ and C_1–C_9–C_5, –0.65 for θ and ϕ, and 0.79 for <H–C–H and C_2–C_3–C_4). Several additional refinements with different starting values for these parameters were performed but no other least-squares minima were found.

In the final stage of analysis, two additional attempts were made to measure the conformation ratio: (a) as an alternative the geometrical results directly obtained by the MM2 calculations were used and (b) a compromise between theoretical and experimental structures to try to remove some of the constraints imposed earlier on the dihedral angles in the two conformers was used.

(a) For this purpose the geometries of the CC and BC conformers (see Table I) were introduced into the analysis and did not vary, but only the conformational ratio was refined. This led to a slightly larger value of $\alpha(\mathrm{BC}) = 38 \pm 20\%$ but still within the limits of experimental error. The corresponding difference radial distribution curve is also shown in Figure 3.

The result of this refinement is included in Table III, but here both conformers are characterized by the corresponding averaged values instead of the precise geometrical parameters collected in Table I in order to facilitate the comparison with an experiment.

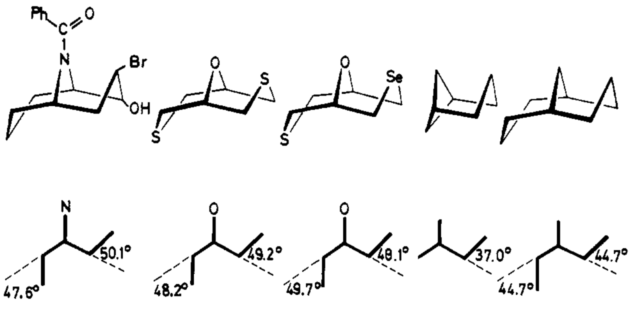
(b) As may be seen from Table I, the theoretical estimates of dihedral angles θ and ϕ are quite different in the two conformers. This encouraged us to test models with nonequivalent dihedral angles, although, as was mentioned above, it proved impossible to find the nonequivalence experimentally. This was done by using the differences themselves taken from molecular mechanics calculations, which meant that the refinements were carried out under the following conditions: $\theta_1 = \theta + 0.83°$, $\theta_2 = \theta + 4.47°$, $\phi_1 = \phi + 8.08°$, and $\phi_2 = \phi + 5.75°$. Interestingly, this version converged to the similar value $\alpha(\mathrm{BC})$ of $23 \pm 11\%$. The other parameters changed slightly but within the reported uncertainties, while for dihedral angles, the following results were obtained: $\theta = 123.3\ (1.8)°$, $\theta_1 = 124.1°$, $\theta_2 = 127.8°$, $\phi = 43.3\ (3.0)°$, $\phi_1 = 51.4°$, and $\phi_2 = 49.1°$.

This refinement gave nearly the same fit with experiment ($R = 0.052$). Therefore, we prefer either to determine the conformational ratio by a more economical model with average dihedral angles (second column, Table III) or to use the purely theoretical geometry (third and fourth columns, Table III). As was mentioned above, the least-squares refinement gives $25 \pm 10\%$, with 3σ as the estimated standard deviations. We think, rather subjectively, that a better representation could be 25 (+20, –10)%. This is partly based on refinements of the theoretical model (Table III) and partly takes into account a slight dependence of the parameters on improvements of the initial background function: at the earlier stages of analysis higher values (up to 40%) of $\alpha(\mathrm{BC})$ were obtained.

Discussion

Molecular Structure. As expected, the values for most of the distances and angles of BN, summarized in Table III, show little or no variation with temperature, in agreement with other studies carried out at different temperatures.[9–11] The largest variation was found for the flap angle ϕ, which increased by 4.7° with the sum of associated errors equal to 5.3°. This difference, if real, is readily interpretable in terms of molecular mechanics calculations. This angle is the only parameter which differs significantly in the two conformers, being larger by 6.9° in BC. Since experimentally the average value of this angle is measured, the increasing fraction of BC conformer with temperature should provoke an apparent opening of this angle.

In our previous study of BN[8] the geometrical parameters of the CC conformer were extensively discussed, comparing them with those measured in other bicyclic hydrocarbons. In addition, a detailed comparison between our experimental and calculated (with the MM2[24] force field) geometries of BN has already been reported by Ōsawa et al.[25] Here we focus only on the bicyclic systems where boat conformations exist. This series includes 3-benzoyl-3α-bromo-2β-hydroxy-9-azabicyclo[3.3.1]nonane (I),[29]



I II III IV BN

9-oxa-7,9-dithiabicyclo[3.3.1]nonane (II),[30] and 9-oxa-3-selena-7-thiabicyclo[3.3.1]nonane (III),[31] which were studied in crystals, and bicyclo[3.1.1]heptane (IV),[32] which was studied in the gas phase. Their dihedral angles are shown on the projections below, in comparison with those estimated here for BN.

Conformational Ratio. The major result of this study is that the experimental data taken at 65 and 400 °C and similarly treated show an increase in the amount of BC conformer as the temperature is raised. This proves the existence of the conformational equilibrium for BN in the gas phase and provides a rough estimate of its thermodynamic parameters.

Our experimental data can serve as a gauge of model force fields employed in molecular mechanics calculations, which show a considerable spread in the energy difference $\Delta E_1 = E_{\mathrm{BC}} - E_{\mathrm{CC}}$, depending on the force field used. As was mentioned in the Introduction, two earlier estimates of 1.5[3] and 2.5[4] kcal/mol were obtained. A more recent calculation by Mikhailov et al.[33] gives the largest value of 3.8 kcal/mol, while calculations in this work using the MM2[24] force field lead to the value of 2.3 kcal/mol.

With these values of ΔE_1, the mole fractions (N) and percentages $\alpha(\mathrm{BC})$ and $\alpha(\mathrm{CC})$ of the two conformers can be calculated by expression 1 for the equilibrium constant, where Q is

$$K = \frac{N_{\mathrm{BC}}}{N_{\mathrm{CC}}} = \frac{\alpha(\mathrm{BC})}{100 - \alpha(\mathrm{BC})} = \frac{Q_{\mathrm{BC}}}{Q_{\mathrm{CC}}} \exp\left(\frac{-\Delta E_1}{RT}\right) \qquad (1)$$

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Table IV. The amount of BC Conformer According to Different Molecular Mechanics Calculations

calcd by	t, °C	Q_{BC}/Q_{CC}	α(BC), % 1.5[a]	2.3[a]	3.8[a]
eq 2	65	2	17.7	6.1	0.7
	400	2	39.5	26.4	10.5
eq 1[b]	65	2.097	18.4	6.4	0.7
	400	2.043	40.0	26.8	10.7
eq 1[c]	65	1.833	16.4	5.6	0.6
	400	1.824	37.3	24.6	9.6

[a] ΔE_1, in kcal/mol. [b] All torsion constants (y) equal 0.107 mdyn·Å. [c] In the chair moiety $Y = 0.107$ while in the boat moiety $Y = 0.02$ mdyn·Å.

the partition function for a given conformer. The vibrational partition functions were calculated from the frequencies derived from the force field listed in Table II. Of special concern were the torsional force constants which can strongly influence the vibrational partition functions.[34] This constant for the chair conformer of cyclohexane was determined[28] to be $Y = 0.107$ mdyn·Å, while for the boat conformer the necessary force constant is unknown. An attempt was additionally made to ascribe more flexibility to BC conformer setting $Y(6-7) = Y(7-8) = 0.02$ mdyn·Å, whereas for the chair moiety, the above mentioned value of 0.107 was retained.[35]

Equation 1 can be simplified by assuming that the vibrational frequencies and moments of inertia of both conformers are equal

$$K = \frac{\alpha(\mathrm{BC})}{100 - \alpha(\mathrm{BC})} = 2 \exp\left(\frac{-\Delta E_1}{RT}\right) \qquad (2)$$

where the factor of 2 is a result of the different symmetry numbers of BC and CC (see later).

The percentages of the BC conformer were calculated at 65 and 400 °C for different reported values of ΔE_1 and by using both eq 1 and 2. These results, collected in Table IV, show that (i) all types of calculations can be adequately presented by the simplest form of eq 2 and (ii) our experimental data ($\alpha(\mathrm{BC}) = 5\%$ at 65 °C and 25% at 400 °C) are in excellent accord with the actually obtained calculated value $\Delta E_1 = 2.3$ kcal/mol. The equally acceptable value of 2.5 kcal/mol[4] gives $\alpha(\mathrm{BC}) = 4.6\%$ at 65 °C and 23.6% at 400 °C, as calculated by eq 2. On the other hand, the values $\Delta E_1 = 1.5$[3] and 3.8 kcal/mol[33,36] can be at least tentatively rejected: the former gives too high a percentage (17.7%) at 65 °C that should have been detected by our experiment, while the latter gives too small an amount of BC conformer at 400 °C (10.5%) to be compared with our experimental results.

Apart from this choice of the reported ΔE_1 values through comparisons between measured and calculated percentages, the energy and entropy differences can be extracted from our data because they give the variation of sample composition with temperature. For this purpose the third version of eq 1 can be employed

$$K = \frac{\alpha(\mathrm{BC})}{100 - \alpha(\mathrm{BC})} = \exp\left(\frac{\Delta S}{R}\right) \exp\left(\frac{-\Delta E_1}{RT}\right) \qquad (3)$$

The results are $\Delta E_1 = 2.48$ kcal/mol and $\Delta S = 1.52$ cal/(mol·deg). These values should be considered as rough estimates of the thermodynamic parameters in question. If statistical error estimates were desired, the experiment would have to be done at a minimum of three temperatures.[11] Nevertheless, the results obtained are consistent with conclusions drawn from an inspection of data collected in Table IV: the entropy contribution in the conformational equilibrium of BN in the gas phase is rather small and the sample composition is governed by the thermodynamic stability of the two conformers, with $\Delta E_1 \approx 2.3$–2.5 kcal/mol. Furthermore, if we make the usual assumption that for conformers the vibrational, rotational, and translational contributions to the entropy are the same, we can predict the relative entropies of the conformers from a consideration of their symmetry properties alone.[2a] These are both single isomers (no optical activity and no entropy of mixing). The CC conformer has a symmetry number of two, while that for the BC is one. Hence the latter should have the more positive entropy by $R \ln 2 = 1.38$ eu, in good agreement with the experimental value (1.52 eu).

We can try to understand the differences ΔE, ΔE_1, and ΔE_2 from the molecular mechanics calculations. Using our definition of strain,[37] we find that the strain in the chair form of cyclohexane is 2.6 kcal/mol and that in the twist and C_{2v} forms of the boat are respectively 8.0 and 9.1 kcal/mol. The strain calculated for the BN molecule is as follows: CC, 12.3; BC, 14.6; BB, 17.3 kcal/mol, respectively. We can look at the difference in strain in BN relative to the two separate cyclohexane rings in the appropriate conformations. These differences in strain amount to 7.1 kcal for CC, 2.9 kcal for BC, and 1.3 kcal for BB. The latter shows relatively little strain beyond that of the two twist–boat conformations. The small excess strain results from the fact that the individual cyclohexane rings are prevented from reaching full twist conformations because of mutual interactions. But interestingly, the BC conformation has 2.9 kcal of excess strain, even after one has allowed for the fact that one of the rings is in the eclipsed boat form. This excess appears to be due mainly to the repulsion between the internal hydrogens at the bow and stern of the boat, and the deformations the molecule undergoes to relieve this repulsion. The distance between the two offending hydrogens is calculated to be 2.28 Å in BN, while it is only 2.33 Å in cyclohexane itself. The fusion of the second ring in BN significantly constrains the ability of the boat form to relax, raising its energy considerably. In CC, the strain is quite large indeed, as a result of the quite serious repulsions between hydrogens on opposite ends of the molecule, and the deformations the molecule undergoes to relieve those repulsions. Thus the strain energies in these conformations are quite different than one might have estimated from simple considerations. The calculations gave correctly (to within experimental error) both the heat of formation of the compound and ΔE_1. No experimental value for ΔE_2 is available, so the value given above is a prediction.

Supplementary Material Available: A tabulation of the experimental data (3 pages). Ordering information is given on any current masthead page.

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(34) S. Rustad and R. Stõlevik, *Acta Chem. Scand., Ser. A*, **A30**, 209 (1976).

(35) It is, however, stressed on the basis of molecular mechanics calculations by Peters et al.[6] and by Ōsawa et al.[25] that in the BC conformer the boat ring is not twisted and only the BB conformer is flexible, having the twisted form.

(36) This value is calculated[33] by using the Dashevskii force field, *Zh. Strukt. Khim.*, **9**, 289 (1968); **11**, 489, 912 (1970).

(37) N. L. Allinger, *Adv. Phys. Org. Chem.*, **13**, 1 (1976). MM2 Operating Manual (see ref 24).