The Conformation and the Ring Inversion of 8,9,10,11-Tetrahydro-7*H*-cycloocta[*de*]naphthalene

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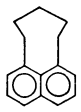
(Received September 12, 1978)

The ^{1}H-NMR spectra of 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene (**1**) and its 8,8,10,10-tetradeuterio derivative have been studied at various temperatures. The NMR parameters of compound **1** were determined accurately by means of computer analysis of the low-temperature spectrum. It was found that the ground-state conformation of **1** is a boat, which is somewhat in a distorted form (puckering) as a result of the steric repulsion between the interior benzyl protons. Activation parameters $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$, for the boat inversion process in the molecule were obtained by the line-shape analysis method as 14.5, 16.1 kcal/mol and 5.4 e.u., respectively. These results are best explained in terms of a conformational interconversion process in which the pseudorotations of the peri bonds are involved. Some discussion is also made on the conformational properties of compound **1** in comparison with those of the structurally analogous benzocyclic compound 6,7,8,9-tetrahydro-5*H*-benzocycloheptene.

Recently, as parts of our studies on the chemistry of pericyclic naphthalenes, we have studied the conformations of several derivatives of the 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene system.[1,2] In the course of these studies, it was found that the eight-membered peri rings in these compounds are rather strained due to the peri interaction inherent in the peri-substituted naphthalenes.[3] In the present paper, in order to determine accurately the effects of the peri strains on the ring geometry of the 8-membered pericyclized naphthalenic compound and to study in detail the ring inversion of this system, a study has been made on the conformation of the parent compound **1**.



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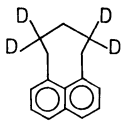

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Since the knowledge of conformational properties of compound **1** is fundamental and very important for studies of the chemistry of the 8-membered pericyclized naphthalene system, it is worthwhile to discuss fully on the conformation and the ring inversion of this molecule based on the accurate and reliable experimental data, though some brief discussion on these points has already been made by Nelsen and Gillespie[4] using the approximate NMR methods (first order approximation and coalescence temperature method).

In this paper, we study the ^{1}H-NMR spectra of compound **1** and its 8,8,10,10-tetradeuterated derivative **2** at various temperatures. The computer analysis of the low-temperature spectrum is performed to determine the accurate NMR parameters of **1**, from which the precise geometry of the stable ground-state conformation of **1** is defined. Further, we report the results of the complete line shape analysis of the temperature-dependent ^{1}H-NMR spectra of **1** by means of the density matrix method, and present the kinetic parameters of the ring inversion process in **1**. We will also discuss about the ^{1}H-NMR result and the conformational properties of **1** by comparing with those of the structurally analogous 6,7,8,9-tetrahydro-5*H*-benzocycloheptene (**3**).

Results

The room-temperature ^{1}H-NMR spectrum of the alkyl portion of 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]-naphthalene-8,8,10,10-d_4 (**2**) in *ca.* 10% solution in the deuteriochloroform consists of a singlet at δ 1.24 for the C_9-protons (2H) and a broad hump centered at δ 3.47 for the C_7- and C_{11}-protons (4H). As the temperature of the sample is progressively lowered each methylene signal broadens and then splits into an AB quartet characterized by the chemical-shift difference ($\Delta\delta$) of 0.314 and 1.035 ppm ($J_{AB}=-14.4$ Hz), respectively. The lower-field signal of the benzylic AB pattern can be assigned to the interior protons (H_{in}) on C_7 and C_{11} positions of the peri ring, since these protons are expected to have a large steric interaction owing to their proximity with each other.[1,2,4]

The aromatic region of the spectrum of **2** consists of three quartets of equal intensities (2H) which show almost no change in their appearence on the variation of temperature. From the peak area and the values of the chemical shifts and coupling constants, these signals can be assigned most reasonably as is shown in Table 2.[1]

The room-temperature ^{1}H-NMR spectrum of the aliphatic region of 8,9,10,11-tetrahydro-7*H*-cycloocta-[*de*]naphthalene (**1**) dissolved (*ca.* 10%) in a mixture of deuteriochloroform and carbon disulfide (3: 1) consists of a broad band at δ 2.6—3.2 for the benzylic protons (4H), a somewhat broad quintet at δ 1.86 (4H, J=*ca.* 6.6 Hz) for the C_8- and C_{10}-protons and a multiplet centered at δ 1.30 for the C_9-protons (2H). As the temperature is decreased the spectrum undergoes a change such that at −44.7 °C the benzyl methylene signals are separated into two distinct absorption bands of equal intensities, consisting of eight lines, whereas the signals centered at δ 1.86 and 1.30 are changed into more complex multiplets resonating at δ 1.6—2.2 and 0.8—1.8, respectively. These signals remained unchanged on further decrease in temperature (*ca.* −100 °C).

Figure 1a shows the low-temperature ^{1}H-NMR spectrum of the benzyl methylene groups of **1**, where

TABLE 1. NMR PARAMETERS OF THE BENZYLIC METHYLENE PROTONS OF **1**

	Chemical shifts (ppm)[a]		Coupling constants (Hz)				
	δ_{7in}[d]	δ_{7ex}	J_{7gem}	$J_{7in,8eq}$	$J_{7ex,8ax}$	$J_{7in,8ax}$	$J_{7ex,8eq}$
1[b]	3.9742	2.9406	−14.23	12.88	1.28	6.49	6.82
2[c]	3.975 (4.8)	2.940 (2.9)	−14.4				

a) δ from internal standard TMS. b) Obtained from the computer simulation of the spectrum of **1** at −44.7 °C. c) Obtained by the first order analysis of the spectrum of **2** at −26.7 °C; the figures in the parentheses are the values of the line widths of the signals (in Hz). d) The numbers refer to the carbon position on the ring and the letters are as follows; in (interior), ex (exterior), eq (equatorial) and ax (axial).

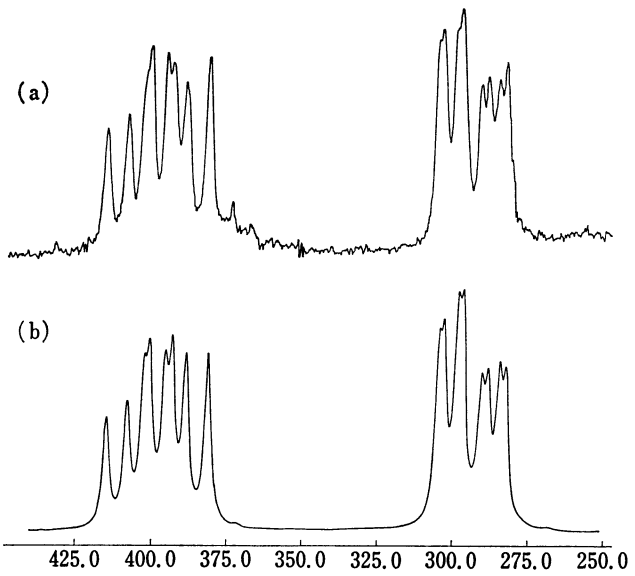


Fig. 1. The observed (a) and the calculated (b) NMR spectra of the benzylic methylene protons of **1** at −44.7 °C.

the low-field signal is assigned to the interior protons and the high-field one to the exterior protons as described above. Analysis of this spectrum as AB part of an ABCD spin system using LAOCOON MBYH program[5] afforded chemical shifts and coupling constants of the benzyl protons of **1** listed in Table 1. The calculated spectrum (Fig. 1b) obtained from these NMR parameters agrees well with the observed one (Fig. 1a). Computer analyses were also attempted for the spectra of the C_8- and C_9-protons but unsuccessful, since these signals are very complex because of their small shift differences.

On the other hand, when the temperature of the sample is elevated, the broad band of the benzylic protons of **1** sharpens and then splits into a triplet (J=6.8 Hz) above 70 °C. The chemical shift (δ=3.45) and coupling constant (J=6.8 Hz) of the benzyl protons of **1** obtained from the high-temperature spectrum are in good agreement with the values (δ=3.46 and J= 6.7 and 7.1 Hz) obtained by averaging the low-temperature data in Table 1.

From the temperature-dependent ^{1}H-NMR spectra of compounds **1** and **2** described above, it is indicated that the 8-membered peri ring of **1** undergoes the conformational change in the temperature range studied, by which the interior and exterior benzyl protons are interchanged. Figure 2a illustrates the gradual spectral changes observed for the benzyl methylene protons of **1** at various temperatures. In order to determine the kinetic parameters for the conformational change of **1**, the complete line shape analysis of the benzyl proton signals of **1** was performed by means of the density

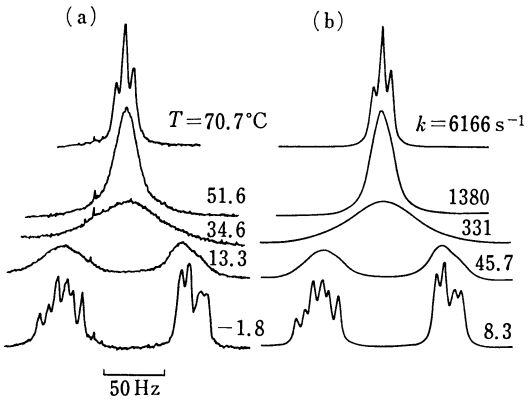


Fig. 2. The observed (a) and the calculated (b) NMR spectra of the benzylic methylene protons of **1** at various temperatures.

TABLE 2. NMR DATA OF THE C_9- AND THE NAPHTHALENE PROTONS OF **1**[a]

	Chemical shifts (ppm)				Coupling constants (Hz)			
δ_{9eq}	δ_{9ax}	$\delta_{1(6)}$	$\delta_{2(5)}$	$\delta_{3(4)}$	J_{9gem}	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$
1.395 (2.8)[b]	1.081 (5.5)	7.186	7.314	7.671	−14.4[c]	7.1	1.9	7.7

a) Obtained from the spectrum of the deuterated derivative **2** at −26.7 °C. b) Values in parentheses are those of the line widths of the peak (in Hz). c) This value is very similar to the value found in the cyclooctane (−14.5 Hz) (Ref. 17) and somewhat larger than the value (−13.9 Hz) observed for the C_7-protons of **3** (Ref. 9).

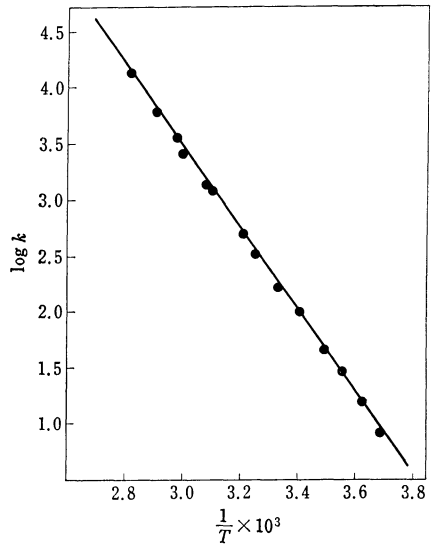


Fig. 3. Arrhenius plot for the ring inversion of **1**.

matrix method[6] using INVERS EX2 program[7] developed by the author (O. Yamamoto) previously. By computer simulation of the temperature-dependent spectra of the benzyl methylene protons, using the NMR parameters given in Table 1, the rate constants (k) for exchanging the benzyl protons of **1** at various temperatures were obtained. Figure 2b shows an example of the best fits between the observed and calculated spectra. The rate constants thus obtained within -10 to 90 °C are then plotted as $\ln k$ *vs.* $1/T$ in Fig. 3, from which the Arrhenius and Eyring activation parameters were calculated through the least-squares method. The results are shown below.

$$E_a = 16.7 \pm 0.5 \text{ kcal/mol}$$
$$\Delta G^{\ddagger} = 14.5 \pm 0.1 \text{ kcal/mol at } 30\,^{\circ}\text{C}$$
$$\Delta H^{\ddagger} = 16.1 \pm 0.5 \text{ kcal/mol}$$
$$\Delta S^{\ddagger} = 5.4 \pm 1.7 \text{ e.u.}$$

Discussion

The relatively simple NMR spectra of 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene (**1**) and its 8,8,10,10-tetradeuterated derivative **2** at low temperatures suggest that, in the ground state, the 8-membered peri ring of compound **1** exists in one conformation, either the boat (**B**) or the chair (**C**), which has a mirror plane (Cs) passing through the C_9 and angular carbon atoms of the naphthalene nucleus.[1] The twist-boat conformation (**TB**) with a C_2 symmetry is excluded from the ground-state conformation of **1**, since the methylene protons on C_9 distinctly show an AB signal in the low-temperature spectrum of **2**.[1]

As can be seen from the Newman projections in Fig. 4, the interior benzyl proton in the boat conformation is situated in a position *trans* to an adjacent equatorial proton, while the exterior proton in the chair has a dihedral angle of about 0° with respect to an adjacent equatrial proton. In light of this and Karplus equation about the dihedral angles and spin coupling constants of

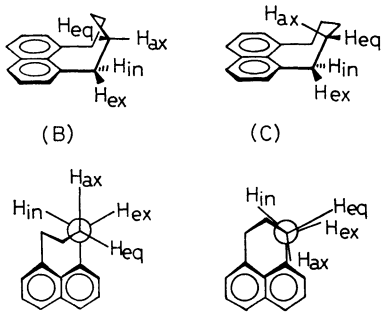
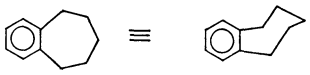


Fig. 4. The boat (**B**) and the chair (**C**) conformations for **1** and their Newman projections about the C_7–C_8 (C_{10}–C_{11}) bonds.

the carbocyclic ring,[8] the fact that the interior benzyl protons of **1** show a considerably large vicinal coupling constant (J=12.88 Hz) clearly suggests that compound **1** assumes the boat (**B**) as the ground-state conformation. This is also indicated from the spectra of the deuterated derivative **2**, where the signal of the interior benzyl proton is much broader (4.8 Hz) than that of the exterior proton (2.9 Hz) in reflection of the strong coupling between the interior proton and the equatorial deuterium which are in *trans* to each other in the boat conformation.

Consequently, the changes in the variable-temperature NMR spectra of **1** are interpreted in terms of the interconverting boat conformations. The predominance of the boat conformation over the chair observed in **1** seems reasonable, since the boat lacks the eclipsing strains about the C_7–C_8 and C_{10}–C_{11} bonds present in the chair.[1,2,4] This is in striking contrast to the case of structurally analogous 6,7,8,9-tetrahydro-5*H*-benzocycloheptene (**3**) which exists only in the chair conformation in the ground state.[9,10]



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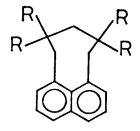
Now that the boat conformation for **1** has been established, the assignment of the C_9–AB signal of **2** is straightforward. That is, the high-field doublet is assigned to the axial proton, H_{9a}, and the low-field one to the equatorial proton, H_{9e}, of the C_9-methylene group of **1**, since the H_{9a}, which lies spatially closer to the naphthalene ring than the H_{9e} proton in the boat conformation, is expected to be more shielded than the H_{9e} proton not only by the effect of the magnetic anisotropies of adjacent C–C bondings but also by the effect of the ring current induced by the naphthalene nucleus.[1] Actually, the H_{9a} proton of **2** resonates at appreciably higher field (δ=1.081) than the corresponding H_{7ax} proton (δ=1.580) on the analogous position of the benzocyclic compound **3**, which exists in the chair conformation.[10] This suggests that the H_{9a} proton of **1** is substantially shielded by the ring current of naphthalene and is a further evidence in

favor of the boat conformation for **1**. The predominance of the boat conformation in **1** is also supported by the line widths of the C_9-protons of **2**, where the signal of the H_{9a} proton is greatly broadened (5.5 Hz) as compared to that of the H_{9e} proton (2.8 Hz) in reflection of the *trans* steric relationship between the H_{9a} and adjacent axial protons (on C_8 and C_{10}) in the boat conformation.

We have already studied the NMR spectra of the boat conformations of several 8,8,10,10-tetrasubstituted 8,9,-10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalenes (**4**).[1]



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Comparing the NMR data of these compounds with those of the unsubstituted compound **1**, the chemical shift of the H_{9a} proton of **1** (δ=1.081) is somewhat larger than those of the substituted compounds (δ=−0.032—1.071).[1] Moreover, the chemical-shift difference ($\Delta\delta$) of the C_9-methylene protons of **1** ($\Delta\delta$=0.314) is small as compared to those of **4** ($\Delta\delta$=0.85—1.2)[1] and also to the $\Delta\delta$ value (1.32—1.92) calculated for the boat conformation of the 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene ring.[1] The shift difference observed between **1** and **4** results possibly from the direct and/or indirect (changes in geometry of the peri ring associated with the introduction of the substituents) effects of the substituting groups, which might cause some differences in the magnetic environments around the C_9-methylene group of the boat conformation between these compounds. Although details are not known at present, the rather large deviation of the $\Delta\delta$ value in **1** from the calculated value might be related partly to the ring distortion inherent in the eight-membered pericyclized naphthalene system as described below.

The chemical shift of the exterior benzyl protons of **1** is almost comparable to those of the benzyl protons (δ=2.827 and 2.721)[10] of the benzocyclic compound **3**, whereas the signal of the interior protons of **1** is shifted markedly (δ=3.9742) to lower field as a result of the steric compression effect. From a calculation similar to that reported by Corey and Sneen,[11] it is revealed that the interatomic distance between the two interior benzyl protons of the boat conformation is 0.652 Å, much smaller than the sum of the van der Waals radii of the two hydrogens (2.4 Å). This suggests that although the boat is the most favored conformation for **1**, it still involves a severe steric repuslion between the two interior protons. Therefore, it is expected that the boat conformation of **1** is somewhat in a distorted form **[B]**, in which the two interior protons are pushed apart mutually to avoid the steric interaction between them. This is strongly supported by the observation that the vicinal coupling constant, $J_{7ex,8ax}$ (1.28 Hz) is very small as compared to the value of $J_{7in,8ax}$ (6.49 Hz), since, as is seen in Fig. 5, these couplings are explained much better by the dihedral angles (H_{7ex}/H_{8ax}; $\theta>60°$, H_{7in}/H_{8ax}; $\theta<60°$) in the distorted molecule **[B]** than by the dihedral angles ($\theta\simeq60°$) in the normal boat conformation (**B**).

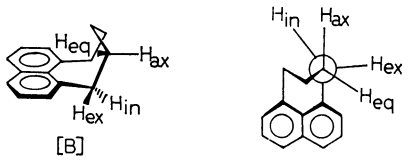


Fig. 5. The distorted boat conformation **[B]** for **1** and its Newman projection about the C_7–C_8 (C_{10}–C_{11}) bond.

Recently, the *R* method has been proposed for the determination of ring geometry in six-membered rings.[12] The *R* value is defined as a ratio of averaged vicinal coupling constants J_{trans}/J_{cis} where $J_{trans}=1/2(J_{aa}+J_{ee})$ and $J_{cis}=1/2(J_{ae}+J_{ea})$ for a $-CH_2CH_2-$ fragment of the ring system. This parameter has not yet been applied or tested for the eight-membered ring.

In order to determine accurately the ring geometry of the 8-membered pericyclic compound **1**, the dihedral arrangement about the C_7–C_8 bond of this molecule was examined by means of the *R* method. For the boat conformation of the 8,9,10,11-tetrahydro-7*H*-cycloocta-[*de*]naphthalene system, the *R* value about the C_7–C_8 bond can be obtained from the expression; $R=J_{trans}/J_{cis}=(J_{7in,8eq}+J_{7ex,8ax})/(J_{7in,8ax}+J_{7ex,8eq})$, using the individual coupling obtained from the low-temperature spectrum. The *R* value can also be obtained from the high-temperature averaged spectrum, where only the time-averaged couplings, $J_{trans}(J_{7in,8eq}\rightleftarrows J_{7ex,8ax})$ and $J_{cis}(J_{7in,8ax}\rightleftarrows J_{7ex,8eq})$ are observed as a result of the rapid boat-boat interconversion.[2]

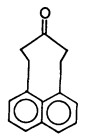
Thus, from the low-temperature data in Table 1, the *R* value for **1** is calculated to be 1.06, while under the condition of the rapid boat inversion it is calculated to be 1.0 ($J_{trans}=J_{cis}$=6.8 Hz). The two *R* values obtained from the two different temperature spectra agree very well with each other. These values are rather small as compared to the value (2.16) obtained for the cyclohexane chair which has an almost perfect staggered conformation.[12] This suggests that the internal dihedral angle (Ψ) about the C_7–C_8 (and C_{10}–C_{11}) bond of the boat conformation of **1** is appreciably decreased as compared to the case of the cyclohexane ring ($\Psi=58°$).[12]

It is considered that the X–CH_2CH_2–Y fragment in the C_7 and C_8 positions of the 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene ring possesses the pseudo-trigonal projection symmetry as in the six-membered rings.[12] Therefore, the dihedral angles around this bond of compound **1** including Ψ can be estimated from the relationship; $\cos\Psi=(3/(2+4R))^{1/2}$.[12] Using R=1.06, the following angles characterizing the structure of **1** are obtained: $\Psi=46°$, $H_{7in}/H_{8ax}=H_{7ex}/H_{8eq}=46°$, $H_{7ex}/H_{8ax}=74°$, and $H_{7in}/H_{8eq}=166°$.

From this it is apparent that compound **1** exists in the distorted boat **[B]** rather than in the normal boat (**B**) as a result of the steric interaction between the interior benzyl protons. Here, it should be noted that this distortion is puckering, not flattening, in sharp contrast to the cases of the previously studied compounds such

as the six-membered rings[12] or seven-membered rings.[10] This is ascribable to the difference in the ring system, and is a unique feature of the 8-membered pericyclized naphthalene system.

The free energy of activation (ΔG^*) for boat inversion of **1** is 14.5 kcal/mol, which is somewhat higher than the ΔG^* value (12.4 kcal/mol)[2] observed for the boat inversion of the ketone **5**. Since it is known that com-



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pounds **1** and **5** have very similar ring structures in their ground states (based on the discussion similar to that described above, it is clear that compound **5** also exists in the puckered boat in the ground state)[2] and both undergo the ring inversions through the same mechanism,[2] the entropy of activation (ΔS^*) obtained for **1** (5.4 e.u.) can be considered to be also characteristic of **5**.[13] It is therefore justifiable to assume that ΔG^* difference observed between **1** and **5** is entirely enthalpic in origin ($\Delta\Delta G^* = \Delta\Delta H^*$).

It has recently been suggested that the boat-to-boat interconversion of the 8,9,10,11-tetrahydro-7*H*-cycloocta-[*de*]naphthalene ring proceeds by pseudorotations of the peri bonds through the twist-boat (**TB**) as an intermediate,[2,4] the highest energy conformation being possibly (**TS**), which effectively contains six coplanar carbon atoms[2] (Fig. 6). This process involves rotations about the C_8–C_9 and C_9–C_{10} bonds in the conversions of (**B**)⇄(**TS**) and (**TS**)*⇄(**B**)*, respectively.

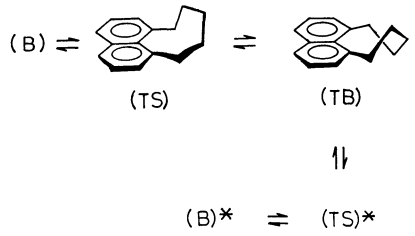

Fig. 6. Pathways for boat inversion of **1** (asterisks* indicate the inverted forms).

Thus, considering the barriers to methyl rotation in propane (3.3 kcal/mol)[14] and acetone (0.8 kcal/mol),[15] it is expected that if the boat inversion of the 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene ring occurs indeed by the pseudorotations of the peri bonds as described above, the energies necessary for reaching the transition states in **5** are smaller than in the case of **1** by the value approximately equal to the difference in the barriers between propane and acetone. Actually, the difference in energy barrier observed between **1** and **5** is almost comparable to that observed in propane and acetone. This strongly supports the idea that the boat inversion is caused by pseudorotations of the peri bonds in the 8-membered pericyclized naphthalene system.

The activation energy for boat inversion of **1** is much higher than the ΔG^* value (10.7 kcal/mol)[16] observed for the chair inversion of **3**. This suggests that although the ground state of **1** is destabilized considerably by the steric interaction between the interior benzyl protons, the transition state of **1** is destabilized to a greater extent because of the peri strains involved.

Experimental

Materials. 8,9,10,11-Tetrahydro-7*H*-cycloocta[*de*]-naphthalene (**1**) was prepared by the Clemmensen reduction of 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalen-9-one (**5**) as described previously.[18] 8,9,10,11-Tetrahydro-7*H*-cycloocta[*de*]naphthalene-8,8,10,10-d_4 (**2**) was prepared from the 8,8,10,10-tetradeuterated derivative of **5** using the procedures described below.

Compound **5** (1.5 g) was refluxed with a solution of potassium carbonate (1.5 g) in deuterium oxide (15 ml) and dioxane (25 ml) for 3 days. The mixture was poured into ice-hydrochloric acid, and the resulting crystalline precipitate was collected by filtration, washed with water and dried *in vacuo*. The above deuterium exchange reaction was repeated twice to afford the completely deuterated ketone, 8,8,10,10-tetradeuterio-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalen-9-one (1.46 g); mp 193.5—195 °C (**5**; mp 195—196 °C[18]), whose structure was evidenced by the complete absence of the NMR signal due to the α protons.[18] The above deuterated ketone (0.93 g) was stirred overnight with excess sodium borohydride in ethanol (120 ml) at room temperature. The reaction mixture was worked up in the same manner as described above to yield 8,8,10,10-tetradeuterio-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalen-9-ol (0.89 g); mp 148—149 °C; IR (Nujol): ν_{max} 3364 and 3284 cm^{-1} due to OH. This alcohol (0.89 g) was then stirred with methanesulfonyl chloride (2.5 ml) in pyridine (9.5 ml) for 4 h at room temperature with an occasional heating on water bath. The mixture was worked up as above to give 9-mesyloxy-8,8,10,10-tetradeuterio-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene (1.2 g); mp 133.5—134.5 °C; IR (Nujol): ν_{max} 1348 and 1173 cm^{-1} (mesyl ester). The mesylate (1.0 g) was then stirred under reflux with lithium aluminum hydride (2.8 g) in ether (250 ml) and benzene (20 ml) for 5 days. The mixture was poured into ice–hydrochloric acid and the mixture was extracted with ethyl acetate. The acetate extracts were worked up as usual to leave a brown paste, which was purified by chromatography on alumina. Elution with hexane gave the hydrocarbon **2** (130 mg), whose structure was confirmed by the TLC (SiO_2–hexane), mp (56.5—57.5 °C, **1**; mp 55—56 °C[4] and 57.5—58 °C[18]) and its spectra (IR, NMR). Further elution with hexane yielded 10,11-dihydro-7*H*-cycloocta[*de*]-naphthalene-8,10,10-d_3 (50 mg; mp 64.5—65.5 °C), details of which will be reported elsewhere. Further elution with ethyl acetate afforded another crystal (104 mg), which, based on the TLC, mp, and IR, was identified to the 8,8,10,10-tetradeuterio-9-ol described above.

Measurements. The IR spectra were determined on a JASCO IR-G spectrometer calibrated with polystyrene. The ^{1}H-NMR spectra were determined on a Varian HA-100D spectrometer (at 100 MHz) in a temperature range between −100—110 °C, using a *ca.* 10% solution in a mixture of deuteriochloroform–carbon disulfide (3:1) (compound **1**) or in deuteriochloroform (compound **2**). The sample temperature was measured by use of the temperature dependent chemical shift of the OH proton of methanol or ethylene glycol.[19] The analysis of the NMR spectra at slow exchange limit and

the calculations of the theoretical line shape were made using a FACOM 270/30 computer.

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