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The Conformations and the Ring Inversions of Some 8- and 10-Methyl-substituted 8,9,10,11-Tetrahydro-7*H*-cycloocta[*de*]naphthalenes and Their 9-Oxo Derivatives

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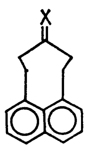
The IR and NMR studies on the conformations of several 8- and 10-methyl-substituted 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalenes (*cis*-8,10-dimethyl (**3a**), *trans*-8,10-dimethyl (**4a**), 8,8-dimethyl (**5a**), 8,8,10-trimethyl (**6a**), and 8,8,10,10-tetramethyl (**7a**)) and their 9-oxo derivatives (**3b**—**7b**) have been described. It was found that compounds **3**—**7** exist exclusively in a boat conformation in the ground state, the peri ring of which is somewhat distorted (puckered) as a result of the steric repulsion between the interior benzyl protons; the molecules of **3a** and **3b** are rather strongly puckered, while those of **7a** and **7b** exist in a less puckered form than the conformations of the other methylated compounds. In the latter case, a novel type of the reflex effect was found arising from the 1,3-synaxial CH_3–CH_3 steric interaction and the interior benzyl H–H interaction. Moreover, it was revealed that free energy barriers ($\Delta G^{\neq}$) to boat inversion for compounds **5a**, **5b**, **7a**, and **7b** are markedly increased ($\Delta\Delta G^{\neq}$ = 4.8—5.9 kcal/mol) as compared with the unmethylated compounds. These results were discussed in terms of the boat-to-boat interconversion process in which the pseudorotations of the peri bonds are involved. Some discussion was also made on the spectral and conformational features of the eight-membered pericyclized naphthalene ring system.

Previously, as parts of our studies on the chemistry of pericyclized naphthalene system, we have studied the conformations of 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene (**1a**)[1] and its 9-oxo compound **1b**.[2] Studies on the conformational equilibria of 8-monomethyl-substituted derivatives of this system **2a**[3] and **2b**[4] have also been reported. In these studies, it was found that the 8-membered peri rings in these compounds are rather strained due to the peri interaction inherent in the peri-substituted naphthalenes.[5] In the present paper, in order to determine the effects of the methyl substituent on the ring geometry and the ring inversion in these 8-membered pericyclized naphthalenic compounds, we have extended our study to more highly methylated compounds of this system, 8- and 10-methyl-substituted 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalenes (*cis*-8,10-dimethyl (**3a**), *trans*-8,10-dimethyl (**4a**), 8,8-dimethyl (**5a**), 8,8,10-trimethyl (**6a**), and 8,8,10,10-tetramethyl (**7a**)) and their 9-oxo derivatives (**3b**—**7b**).



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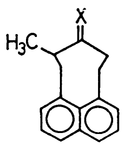

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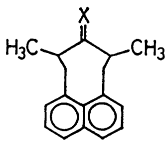

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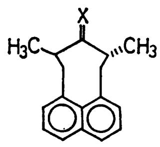

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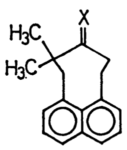

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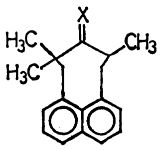

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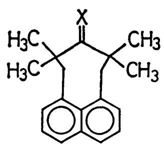

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a: X=H_2
b: X=O

Here, we report the conformations of this series of methyl compounds based on the IR and NMR (^{1}H and ^{13}C) spectra, and discuss about the spectral and conformational features of these methylated compounds in comparison with the parent compounds **1a** and **1b** as well as the monomethyl derivatives **2a** and **2b**. Further we report the activation energies for ring inversions of some of the methylated compounds **3**—**7** by a study of the variable-temperature ^{1}H NMR spectra. Detailed discussion on these points will also be described.

Results and Discussion

The ^{1}H and ^{13}C NMR data of a series of the methylated compounds (**3a**—**7a**) and (**3b**—**7b**) are summarized in Tables 1 and 2. The assignment was made based on the data of the parent compounds **1a**[1] and **1b**[2] and the substituted derivatives **2a**[3] and **2b**,[4] as well as those of the deuterated compounds **3b**-8,10-d_2, **4b**-8,10-d_2, and **6b**-10-*d*. Also off-resonance technique was employed for the assignments of the ^{13}C spectra.

It is shown in the table that all the ^{1}H spectra of these compounds are relatively simple and the splitting patterns of the benzyl methylene protons in the hydrocarbons (**a**) are very similar to those in the corresponding 9-oxo compounds (**b**). This suggests that each methyl compound studied exists in one conformation in its ground state and both hydrocarbons (**a**) and ketones (**b**) assume the same geometry in each class of the methylated compounds.

It has previously been shown[1—4,6,7] that the interior benzyl protons (H_{in}) on C-7 and C-11 in the 8-membered pericyclized naphthalene system resonate at much lower field than the exterior protons (H_{ex}) due to the steric compression effect. In 8,8-dimethyl-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene (**5a**) and its 9-oxo derivative **5b**, the interior proton on C-11 (H_{11in}) is coupled strongly with an adjacent C-10 proton (J=13.3 and 13.1 Hz). This indicates that the peri rings in these compounds exist in the boat form (**5B**) rather than in the chair (**5C**), since, as can

TABLE 1. ^{1}H NMR DATA OF THE METHYL AND BENZYL PROTONS OF 8- AND 10-METHYL-SUBSTITUTED 8,9,10,11-TETRAHYDRO-7*H*-CYCLOOCTA [*de*]NAPHTHALENES (**3a**—**7a**) AND THEIR 9-OXO DERIVATIVES (**3b**—**7b**)[a–d]

Compound	H_{7in}[g]	H_{7ex}	H_{11in}	H_{11ex}	$C\underline{H}_3$			
					8-ax	8-eq	10-ax	10-eq
3a	4.28 J=14.4 6.5	2.63 J=14.4 i)	4.28 J=14.4 6.5	2.63 J=14.4 i)		0.84d J=6.8		0.84d J=6.8
4a[e]	4.17 J=14.5 6.5	2.64 J=14.5 1.4	3.71 J=14.1 12.8	2.90 J=14.1 6.7		0.80d J=6.7	1.22d J=7.0	
5a	3.98 J=14.3	2.51 J=14.3	3.92 J=14.5 13.3 6.3	2.88 J=14.5 6.9 1.6	1.16s (1.6)	0.80s (1.9)		
6a	4.00 J=14.3	2.50 J=14.3	4.21 J=14.3 6.4	2.59 J=14.3 1.5	1.16s	0.81s		0.80d J=6.8
7a	4.09 J=14.3 (2.8)[h]	2.53 J=14.3 (2.5)	4.09 J=14.3 (2.8)	2.53 J=14.3 (2.5)	1.29s (1.7)	0.74s (1.9)	1.29s (1.7)	0.74s (1.9)
3b	4.86 J=14.6 6.4	2.77 J=14.6 2.3	4.86 J=14.6 6.4	2.77 J=14.6 2.3		0.97d J=6.8		0.97d J=6.8
4b[f]	4.79 J=14.8 5.8	2.76 J=14.8 2.2	4.23 J=14.5 11.5	3.03 J=14.5 6.1		0.94d J=6.4	1.45d J=6.5	
5b	4.61 J=14.8 (3.6)	2.69 J=14.8 (3.0)	4.43 J=14.6 13.1 6.1	2.97 J=14.6 6.8 1.7	1.42s (1.8)	0.93s (2.2)		
6b	4.58 J=14.7	2.69 J=14.7	4.73 J=14.7 6.7	2.69 J=14.7 2.2	1.43s (1.4)	0.92s (1.8)		0.99d J=6.8
7b	4.69 J=14.5 (2.9)	2.72 J=14.5 (2.0)	4.69 J=14.5 (2.9)	2.72 J=14.5 (2.0)	1.48s (1.5)	0.92s (2.0)	1.48s (1.5)	0.92s (2.0)

a) All the samples except **4a** and **4b** were measured at 30 °C. b) The chemical shifts are expressed in ppm (δ) downfield from internal standard tetramethylsilane, and the coupling constants (J) are in Hz. c) The chemical shifts of the C-8 and C-10 protons are determined as follows; H_{8ax}: 2.16 (**3a**), 3.18 (**3b**), 3.39 ppm (**4b**), H_{10ax}: 2.15 (**5a**), 2.27 (**6a**), 3.35 (**5b**), 3.48 ppm (**6b**), H_{10eq}: 1.67 (**5a**), 2.82 (**4b**), 2.51 ppm (**5b**). d) The chemical shifts of the C-9 methylene protons are not determined because these signals are buried under the signals of methyl groups. e) Measured at −21.5°C. f) Measured at −65.9 °C. g) The numbers refer to the carbon position on the ring and the letters, in, ex, eq, and ax denote interior, exterior, equatorial, and axial protons, respectively. h) The figures in parentheses denote the line widths of the signals. i) This coupling ($J_{ex,ax}$) is small enough not to be resolved.

TABLE 2. ^{13}C CHEMICAL SHIFTS OF THE METHYL AND THE PERI RING CARBONS OF 8- AND 10-METHYL-SUBSTITUTED 8,9,10,11-TETRAHYDRO-7*H*-CYCLOOCTA[*de*]NAPHTHALENES (**3a**—**7a**) AND THEIR 9-OXO DERIVATIVES (**3b**—**7b**)[a,b]

Compound	C-7	C-8	C-9	C-10	C-11	$\underline{C}H_3$			
						8-eq	8-ax	10-eq	10-ax
3a	42.4	33.4	39.0	33.4	42.4	22.2		22.2	
4a[c]	42.1	27.1	35.4	34.3	43.8	21.8			20.4
5a	49.8	34.7	34.7	26.7	35.8	30.5	28.0		
6a	49.2	34.9	43.6	29.5	41.7	30.7	28.5	22.0	
7a	48.9	36.1	48.3	36.1	48.9	32.6	30.9	32.6	30.9
3b	41.7	45.7	213.2	45.7	41.7	15.0		15.0	
4b[d]	40.5	40.5	217.2	52.1	43.3	14.4			19.0
5b	49.0	48.5	214.8	42.9	34.6	23.5	28.1		
6b	49.6	48.7	215.3	41.0	41.4	23.8	28.1	15.5	
7b	48.7	50.2	218.3	50.2	48.7	27.0	30.1	27.0	30.1

a) All the samples except **4a** and **4b** were measured at room temperature. b) The chemical shifts are expressed in δ (ppm) from internal reference tetramethylsilane and are considered accurate to be ±0.1 ppm. c) Measured at −51.6 °C. d) Measured at −44.0 °C.

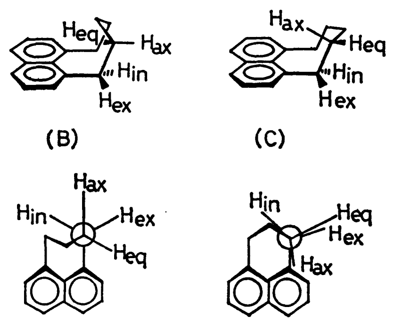
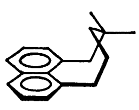
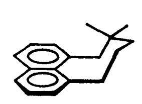


Fig. 1. The boat (**B**) and the chair (**C**) conformations for the 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene ring and their Newman projections about the C_7–C_8 (C_{10}–C_{11}) bonds.



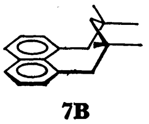
5B



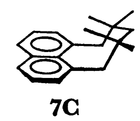
5C

be seen in Fig. 1, the H_{in} proton in the boat conformation is situated in a position *trans* to an adjacent equatorial proton and thus a strong coupling is expected between these two protons. If the chair **5C** would be the predominant conformation for **5a** and **5b**, then the large J_{vic} value could be observed for the H_{ex} proton. Additionally, the splitting patterns of the C-11 interior protons observed in **5a** and **5b** are analogous to those of the parent compounds[1,2] and the monosubstituted derivatives,[3,4] which exist in the boat conformations alone. The **5B** conformation is also suggested from the line widths of the methyl and the benzyl protons. In both **5a** and **5b**, the equatorial methyl group shows somewhat broadened signal (half-width; 1.9 and 2.2 Hz) as compared to that of the axial methyl group (1.6 and 1.8 Hz), while the signal of the C-7 interior proton of **5b** is broader (3.6 Hz) than that of the corresponding exterior proton (3.0 Hz). This arises possibly from the long-range spin coupling of the interior proton with the equatorial methyl group because of their *trans* steric relationship,[7] and is a further evidence in favor of the boat conformation **5B** for **5a** and **5b**.

Similar type of long-range spin coupling is observed in the spectra of 8,8,10,10-tetramethyl compounds **7a** and **7b** (in both compounds, the signals of the interior benzyl proton and the equatorial methyl group are apparently broader than those of the exterior proton and the axial methyl group, respectively; see Table 1). Therefore, these compounds clearly assume a boat form (**7B**). This is strongly supported by the line widths of the exterior benzyl protons; as can be seen in the table, the line widths of the interior benzyl protons are almost equal between the hydrocarbon **7a** (2.8 Hz) and the ketone **7b** (2.9 Hz), while the exterior proton of **7a** clearly shows a broadened signal (2.5 Hz) as compared to that of **7b** (2.0 Hz). This may be reasonably explained in terms of the W-type long-range spin coupling of the exterior proton with the C-9 equatorial proton, which is characteristic of the boat conformation as described before.[7]

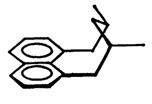


7B

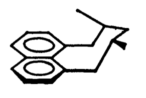


7C

In *trans*-8,10-dimethyl compounds **4a** and **4b**, the value of spin coupling constant between the C-7 interior proton and C-8 methine proton is small (J=6.5 and 5.8 Hz), while it is large between the C-11 interior proton and the C-10 methine proton (J=12.8 and 11.5 Hz). Thus it is clear that **4a** and **4b** exist in a boat (**4B**) in which the C-8 methyl is equatorial and that on C-10 is axial.

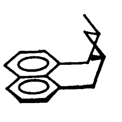


4B

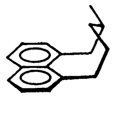


4C

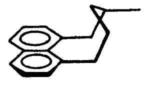
On the other hand, in the *cis*-dimethyl compounds **3a** and **3b**, the small J_{vic} values (6.5 and 6.4 Hz) observed between the interior benzyl proton and the vicinal methine proton suggest that **3a** and **3b** exist either in a boat form (**3B**) or in a chair form (**3C**) bearing equatorial methyl groups. However, in view of the fact that the equatorial isomers of the monomethyl compounds **2a** and **2b** exist exclusively in the boat conformation (**EB**) in their ground states (corresponding chair conformation **EC** is not obtained),[3,4] it seems reasonable to consider that the dimethyl compounds **3a** and **3b** exist in the boat (**3B**) rather than in the chair (**3C**). Actually, the chemical shifts and coupling constants of the benzyl and the methyl protons observed in **3a** and **3b** are very similar to those found for the corresponding protons of the **EB** isomer. Moreover, the equilibration experiment revealed[8] that the *cis*-dimethyl ketone **3b** is much more stable than the *trans* isomer **4b** (**4B** conformation). Thus, considering the fact that the equatorial conformation (**EB**) is more stable than the axial conformation (**AB**),[3,4] it is apparent that the conformation of **3a** and **3b** is the boat form **3B**.



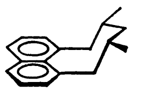
3B



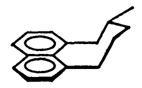
EB



AB

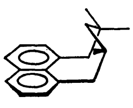


3C

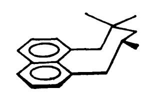


EC

For the same reason, the small J_{vic} values (6.4 and 6.7 Hz) observed between the C-11 interior proton and the C-10 methine proton in the trimethyl compounds **6a** and **6b** suggest that these compounds exist in a boat (**6B**), in which the C-10 methyl group is equatorial. The somewhat broadened signal of the equatorial methyl group on C-8 (half-width; 1.8 Hz) in comparison

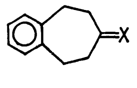


6B

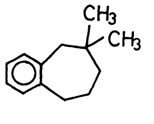


6C

with that of the corresponding axial methyl group (1.4 Hz) observed in **6b** results possibly from the long-range spin coupling of the equatorial methyl group with the C-7 interior proton as observed in **5B** and **7B** conformations.



8a; X=H_2
8b; X=O



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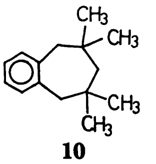

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Consequently, it became clear that all the compounds (**3**—**7**) exist solely in the boat conformations (**3B**—**7B**) in their ground states. This result is in striking contrast to the case of structurally analogous benzocyclic compound, 6,7,8,9-tetrahydro-5*H*-benzocycloheptene system (**8**). It has been reported that 6,6-dimethyl- (**9**)[9] and 6,6,8,8-tetramethylbenzocycloheptene derivatives (**10**)[10] as well as the unsubstituted compounds **8a**[10,11] and **8b**[12] assume only the chair conformations in their ground states. The unusually greater stability of the boat conformation (**3B**—**7B**) over the chair (**3C**—**7C**) observed in **3**—**7** results chiefly from much lower torsional energy about the C_7—C_8 and C_{10}—C_{11} bonds of the boat conformation (staggered) than the chair (eclipsed), which is one of the unique features in the 8-membered pericyclized naphthalene system (Fig. 1). All compounds of this system studied so far, including the parent compounds[1,2,6] as well as the substituted derivatives,[3,4,7] exist solely in the energetically stable boat conformations. In addition, the closeness of the axial methyl group to the naphthalene ring in the chair[7] (**4C**—**7C**) makes this much less stable than the boat conformation (**4B**—**7B**).

The ^{13}C data of **3**—**7** shown in Table 2 fully agree with the boat conformations (**3B**—**7B**) described above. Thus a high-field shift of C-7 signal relative to that of C-11 ($\Delta\delta$=1.7 ppm) in the *trans*-dimethyl compound **4a** is caused by a gauche interaction[3,4] between the equatorial methyl group on C-8 and the peri bond. This interaction is also observed in the spectra of the *cis*-dimethyl (**3a**) and the trimethyl compounds (**6a**), the C-11 carbons of which show chemical shifts approximately equal to the value found in the C-7 carbon of **4a**. On the other hand, the C-8 carbon of **4a** is markedly shielded relative to the C-10 carbons of **3a** and **4a** ($\Delta\delta$=6.3 and 7.2 ppm, respectively) because of the so-called γ-effect.[3,4,13] By the same effect, the C-10 carbon of **6a** shifts to a 3.7 ppm higher field than that of **3a**, while the C-10 carbon of the *gem*-dimethyl compound **5a** is more shielded than the corresponding carbons of the parent compound **1a** and the monomethyl compound **2a** (**EB** conformer) by 3.0 (see footnote in Table 3) and 2.7 ppm,[3] respectively. Moreover, the C-9 carbons of **4a** and **5a** resonate at appreciably higher field than the C-9 carbon of **3a** ($\Delta\delta$=3.6 and 3.3 ppm, respectively) as a result of the γ-effect.

Thus, in compounds **3a**—**7a**, since the axial and the equatorial methyl carbons experience shieldings due to the γ-effect and the gauche interaction, respectively, the shift difference between the axial and the equatorial methyl groups in these compounds is considerably decreased ($\Delta\delta$=1.4—2.2 ppm) as compared with the cyclohexane ring (6.0 ppm).[13] This effect is also reflected in the chemical shifts of the methine carbons; the chemical shift difference between the methine carbon having an axial methyl group (C-10 of **4a**) and that having an equatorial methyl group (C-10 of **3a**) is only 0.9 ppm, much smaller than the value (4.5 ppm)[13] observed in the cyclohexane ring.

Similar spectral features are observed in the ketones (**3b**—**7b**) due to the gauche interaction and the γ-effect (see Table 2). In addition to this, in this series, also the methyl-carbonyl interaction[14,15] is observed as in the case of the monomethyl ketone **2b**.[3,4] Table 4 summarizes the effect of this interaction on the ^{13}C chemical shifts (Δ) of the methyl and the peri ring carbons in each class of the methyl compounds (**3**—**7**), which is obtained from the differences of the carbonyl substituent effects (δ^{ab}) (Table 3) between the methylated compounds (**3**—**7**) and the parent compound **1** ($\Delta=\delta^{ab}$ (**3**—**7**)$-\delta^{ab}$ (**1**); see Tables 3 and 4 and

TABLE 3. EFFECT OF 9-KETO FUNCTION ON THE ^{13}C CHEMICAL SHIFTS OF SOME 8,9,10,11-TETRAHYDRO-7*H*-CYCLOOCTA[*de*]NAPHTHALENES (δ^{ab} in ppm)[a)]

Compound	C-7	C-8	C-9	C-10	C-11	CH_3			
						8-eq	8-ax	10-eq	10-ax
1[b)]	2.5	−16.3	−192.6	−16.3	2.5				
2-EB[c)]	1.9	−12.0	−185.0	−16.4	1.4	7.4			
2-AB[c)]	1.9	−17.9	−190.8	−17.4	2.4		0.9		
3	0.7	−12.3	−174.2	−12.3	0.7	7.2		7.2	
4	1.6	−13.4	−181.8	−17.8	0.5	7.4			1.4
5	0.8	−13.8	−180.1	−16.2	1.2	7.0	−0.1		
6	−0.4	−13.8	−171.7	−11.5	0.3	6.9	0.4	6.5	
7	0.2	−14.1	−170.0	−14.1	0.2	5.6	0.8	5.6	0.8

a) In each compound, $\delta^{ab}=\delta_{Hydrocarbon}-\delta_{Ketone}$; a minus sign indicates a low-field shift. b) Obtained from the chemical shift values; 36.6 (C-7,11), 29.7 (C-8, 10), and 21.3 ppm (C-9) (measured at −66.5 °C) for **1a** (Ref. 26) and from the data (**1b**) in Ref. 2. c) Refs. 3 and 4.

Table 4. Effect of carbonyl-methyl interaction on ^{13}C chemical shifts of compounds (**2**—**7**) (Δ in ppm)[a]

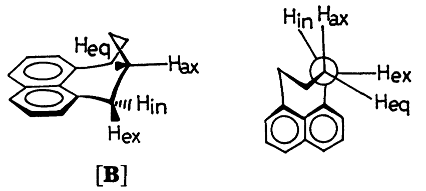
Compound	C-7	C-8	C-9	C-10	C-11	CH_3[b] 8-eq	8-ax	10-eq	10-ax
2-EB	−0.6	4.3	7.6	−0.1	−1.1	7.4			
2-AB	−0.6	−1.6	1.8	−1.1	−0.1		0.9		
3	−1.8	4.0	18.4	4.0	−1.8	7.2		7.2	
4	−0.9	2.9	10.8	−1.5	−2.0	7.4			1.4
5	−1.7	2.5	12.5	0.1	−1.3	7.0	−0.1		
6	−2.9	2.5	20.9	4.8	−2.2	6.9	0.4	6.5	
7	−2.3	2.2	22.6	2.2	−2.3	5.6	0.8	5.6	0.8

a) Obtained from the difference of the carbonyl substituent effect (δ^{ab}) (Table 3) between the methylated compounds (**2**—**7**) and the unsubstituted compound, $\Delta=\delta^{ab}_{(2-7)}-\delta^{ab}_{1}$; a minus sign indicates a low-field shift.
b) Data taken from Table 3.

footnotes therein). From this it is clear that, in all the methyl compounds, the axial methyl groups of the ketones (**b**) give chemical shifts almost comparable to the values found in the corresponding hydrocarbons (**a**), whereas the equatorial methyl groups of the ketones suffer marked shieldings (5.6—7.4 ppm) due to the eclipsed interaction between the carbonyl function and the equatorial methyl group. The carbonyl carbons of **3b**—**7b** ($\Delta\delta$=10.8—22.6 ppm) together with the C-8 (of **3b**—**7b**) and the C-10 (of **3b**, **6b**, and **7b**) carbons, which have the equatorial methyl groups on them ($\Delta\delta$=2.2—4.8 ppm), are also markedly shielded by the effect of this interaction.

The ^1H and ^{13}C data in the table show other spectral and conformational features characteristic of the boat conformation of the peri-eight membered ring. In both hydrocarbons (**a**) and the ketones (**b**), the proton chemical-shift differences between the axial and the equatorial methyl groups in **3**—**7** are greatly increased ($\Delta\delta$=0.35—0.55 ppm for **3a**—**7a** and 0.51—0.56 ppm for **3b**—**7b**) as compared with the cyclohexane system ($\Delta\delta$=0.07 ppm for methylcyclohexane[16] and 0.14 ppm for 2-methylcyclohexanone[17,18]) by the effect of the ring current of naphthalene.[3,7] The C-8 axial proton (H_{8ax}) of **3a** is greatly deshielded (*ca.* 0.8 ppm) relative to the corresponding proton (H_{1ax}) of *cis*-1,3-dimethylcyclohexane,[16] (see footnote in Table 1) since the H_{8ax} proton, which experiences the magnetic anisotropy effect of the adjacent C–C bondings smaller than that of the H_{1ax} proton (H_{8ax} is *trans* to the C_7–C_{6a} peri bond, see Fig. 1), is further deshielded by the ring-current effect of naphthalene ring (a calculation[7,19] reveals that the ring current of naphthalene deshields the axial and the equatorial protons on C-8 (and C-10) by *ca.* 0.52 and 0.37 ppm, respectively). Similar effect is observed for the H_{10ax} proton of **6a**, which is *ca.* 0.7 ppm deshielded relative to the corresponding proton of the cyclohexane ring.[16] On the other hand, marked deshieldings of the axial proton (H_{10ax}) (**3**, **5**, **6**; $\Delta\delta$= 1.02—1.21 ppm) relative to the equatorial proton (H_{10eq}) (**5**; $\Delta\delta$=0.84 ppm) by the effect of the carbonyl function might be caused chiefly by the σ-π bond overlap[20] as observed in the parent ketone **1b**.[2]

In all the compounds (**3**—**7**), whereas the chemical shifts of the exterior benzyl protons (δ=2.5—3.03 ppm) are almost comparable to the values (δ=2.219—2.875 ppm) found for the benzyl protons of the benzocyclic compounds **8**—**10**,[9-11] the interior protons of **3**—**7**, in contrast, are markedly deshielded (δ=3.71—4.86 ppm) due to the steric compression effect (the interatomic distance between the two interior protons has been calculated to be 0.652 Å for **1a**[1] and 0.632 Å for **1b**[3]). Thus it is expected that, as in the case of the parent compounds[1] and the monomethyl derivatives,[3] all the boat conformations (**3B**—**7B**) of compounds **3**—**7** exist in a somewhat distorted (puckered) form, in which the two interior protons are pushed apart mutually to relieve the steric repulsion between them.



[B]

Fig. 2. The distorted (puckered) boat conformation [**B**] and its Newman projection about the C_7–C_8 (C_{10}–C_{11}) bonds.

Recently, the crystal structures of the non-cyclized 1,8-disubstituted naphthalenes have been studied based on the X-ray analyses. This shows that the peri bonds of 1,8-dimethylnaphthalene undergo in-plane bending to give a planar structure,[5,21] while, in the most of the other compounds including 1,8-di-tert-butylnaphthalene,[5,22] the molecules are seriously distorted from planarity due to the out-of-plane bending of the substituting groups. In the present case, since the molecules of **3** and **7** have a C_s symmetry as have been suggested from the NMR spectra, it is reasonable to consider that, as in the case of the parent compound **1**, the peri bonds of **3**—**7** undergo chiefly in-plane bending rather than out-of-plane bending in solution to result in a symmetric (C_s passing through the C-9 and the angular carbon atoms of naphthalene nucleus) peri ring conformation [**B**] (Fig. 2) or a conformation close near to it (the contribution of the out-of-plane deformation, even if it actually existed in **3**—**7**, seems very small, since it would give unsymmetrical conformations).

Actually, the spectra of **3**—**6** show features characteristic of the distorted conformation—*i.e.*, the axial proton (H_{ax}) always couples more strongly with the interior proton (H_{in}) (J_{vic}=5.8—6.7 Hz) than with the exterior proton (H_{in}) (J_{vic}=0—2.3 Hz)—as observed in **1** and **2**. This result may be explained much better by the space arrangement of the distorted conformation [**B**] (the dihedral angle (θ) for the H_{in} and H_{ax} protons is smaller than 60°, while it is larger than 60° for the H_{ex} and H_{ax} protons) than by the space arrangement of the undistorted conformation (**B**) (θ is close to 60°) (see Figs. 1 and 2).

Furthermore, the distortion of peri ring is also indicated from the internal dihedral angles (Ψ) calculated from the vicinal coupling constants about the C_{10}—C_{11} bonds of the *gem*-dimethyl compounds **5a** and **5b** (the calculations were performed using *R*-value method[23] as reported previously[1]). The magnitudes of Ψ obtained for these compounds (Ψ=47° for **5a** (*R* value; 1.1) and 48° for **5b** (*R* value; 1.2)) are approximately equal to the value found in the parent compound **1a** (46°)[1] and much smaller than the value of cyclohexane (58°)[23] which has an almost staggered conformation. Consequently, it seems reasonable to consider that all compounds **3**—**7** exist in the puckered conformation [**B**] rather than in the normal boat conformation (**B**) as a result of the steric repulsion of the interior benzyl protons.

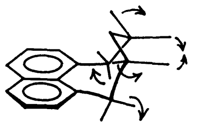


Fig. 3. Reflex effect in the 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene ring.

Examination of molecular models reveals that the puckering of the boat conformation is accompanied by the following geometrical changes of the peri ring. Namely, as can be seen in Fig. 3, (i) the two axial methyl groups on C-8 and C-10 are compressed, (ii) the equatorial groups on these carbons come at a position more distant from the naphthalene nucleus, and (iii) the C–C–C bond angle at C-9 carbon becomes contracted.

Thus it is expected that molecules of the tetramethyl compounds **7a** and **7b** exist in a less distorted (thus more flattened) form than those of the other compounds (**1**—**6**) due to the steric repulsion between the 1,3-synaxial methyl groups (on the other hand, the presence of steric congestions around the C-9 carbon in **7a** and **7b** have been suggested from the difficulties in effecting reactions at this position[8]). This is clearly indicated from the observation that the axial methyl protons of **7a** are 0.13 ppm more deshielded than those of compounds **5a** and **6a** due to the steric compression,[24] while the equatorial methyl protons of **7a**, which come spatially closer to the naphthalene ring than the equatorial methyl protons of **3a**, are 0.10 ppm more shielded than the latter protons by the effect of the ring current of naphthalene (in the cyclohexane system in which the effect of the naphthalene ring is absent, the equatorial methyl protons of the 1,1,3,3-tetramethyl derivative give chemical shift value approximately equal to that (δ=0.88 ppm) found for the equatorial methyl protons of the *cis*-1,3-dimethyl derivative[24]).

Moreover, whereas, in compounds **5** and **6**, the axial methyl protons of the geminal methyl group are more greatly deshielded (0.26 and 0.27 ppm) than the corresponding equatorial methyl protons (0.11 and 0.13 ppm) by the effect of the carbonyl function, in contrast, in the case of the tetramethyl compound **7**, the magnitude of the carbonyl deshielding effect is almost comparable for the axial (0.19 ppm) and the equatorial methyl (0.18 ppm) protons probably due to the flattening of the boat conformation described above (Table 1).

The flattening of the boat in **7** is also suggested from the chemical shifts of the benzyl methylene protons. Table 5 summarizes the chemical shift values of the benzyl methylene protons of compounds **3**—**7** calculated from the chemical shifts of the parent compounds **1a** and **1b** and those of the axial and the equatorial isomers

TABLE 5. CALCULATED ^{1}H CHEMICAL SHIFTS OF THE BENZYL PROTONS OF COMPOUNDS (**3**—**7**) (in ppm)[a,b)]

Compound	H_{7in}	H_{7ex}	H_{11in}	H_{11ex}
3a	4.27(−0.01)	2.64(−0.01)	4.27(−0.01)	2.64(−0.01)
4a	4.15(0.02)	2.60(0.04)	3.69(0.02)	2.88(0.02)
5a	3.95(0.03)	2.60(−0.09)	3.89(0.03)	2.88(0.00)
6a	3.97(0.03)	2.58(0.08)	4.17(0.04)	2.58(0.01)
7a	3.87(0.22)	2.54(−0.01)	3.87(0.22)	2.54(−0.01)
3b	4.77(0.09)	2.70(0.07)	4.77(0.09)	2.70(0.07)
4b	4.77(0.02)	2.70(0.06)	4.19(0.04)	2.98(0.05)
5b	4.56(0.05)	2.75(−0.06)	4.40(0.03)	2.93(0.04)
6b	4.44(0.14)	2.67(0.02)	4.65(0.08)	2.62(0.07)
7b	4.32(0.37)	2.59(0.13)	4.32(0.37)	2.59(0.13)

a) The chemical shifts of compounds (**3a**—**7a**) were calculated from the chemical shifts of the parent compound **1a** (Ref. 1) and the values of the methyl substituent effects obtained from the chemical shifts of the axial (**AB**) and the equatorial isomers (**EB**) of the 8-monomethyl derivative **2a** (Ref. 3); **2a-AB**: −0.30 (H_{7in}), −0.04 (H_{7ex}), −0.10 (H_{11in}), −0.04 ppm (H_{11ex}), **2a-EB** : 0.28 (H_{7in}), −0.30 (H_{7ex}), 0.02 (H_{11in}), −0.02 ppm (H_{11ex}) (a minus sign indicates a high-field shift). Similarly, the chemical shifts of (**3b**—**7b**) were calculated from those of **1b** (Ref. 2) and the values of the methyl substituent effects, obtained from the chemical shifts of the **2b-AB** and **2b-EB** isomers (Ref. 4); **2b-AB**: −0.33 (H_{7in}), −0.03 (H_{7ex}), −0.12 (H_{11in}), −0.08 ppm (H_{11ex}), **2b-EB**: 0.25 (H_{7in}), −0.31 (H_{7ex}), −0.12 (H_{11in}), −0.08 ppm (H_{11ex}). b) Figures in parentheses denote the differences of the chemical shifts between the observed (Table 1) and the calculated values; $\Delta\delta=\delta_{obsd}-\delta_{calcd}$.

of the monomethyl derivatives **2a** and **2b** (see footnotes in Table 5). Comparison of these calculated values with those observed in the spectra of **3**—**7** (Table 1) reveals that the chemical shift values observed in the hydrocarbons (**3a**—**6a**) differ from the calculated values by only —0.09—0.08 ppm, while the value observed for the interior benzyl protons of the tetramethyl compound **7a** is greatly increased (0.22 ppm) relative to the value obtained by the calculation. Similar result is obtained for the ketones (**3b**—**7b**), in which the chemical shift value observed for the interior benzyl protons of the tetramethyl ketone **7b** is larger than the calculated value by 0.37 ppm. The pronounced deshielding of the interior benzyl protons in **7a** and **7b** results possibly from the less puckered conformation of **7** mentioned above, since the distance of the interior protons in such conformation is somewhat shortened relative to that of the other compounds due to the synaxial CH_3–CH_3 interaction and thus the interior protons of **7a** and **7b** are expected to be more greatly compressed than the interior protons of the latter compounds.

The above result is also reflected in the ^{13}C NMR spectra. The methyl carbons (both axial and equatorial) of **7a** are considerably deshielded (2—3 ppm) relative to those of **5a** and **6a** (Table 2), while the carbonyl shielding effect in **7** is rather decreased (equatorial methyl, 5.6 ppm) as compared with the latter compounds (6.9—7.0 ppm) (Table 3). The deshielding of methyl carbons due to the steric compression has also been observed in other ring systems.[25]

In Table 6 are shown the chemical shifts of the peri ring carbons of compounds (**3**—**7**) calculated from the chemical shifts of the parent compounds **1a**[26] and **1b**[2] and the monomethyl compounds **2a**[3] and **2b**[4] (see footnotes in the table). This indicates that, in the hydrocarbons (**3a**—**7a**), the calculated values well agree with the observed data in Table 2 (*ca.* ±1 ppm) for all the positions except the C-8 carbon of the tetramethyl compound **7a**, which resonates at appreciably lower field (4.4 ppm) than the calculated value (the rather large deviations of the observed values for the C-8 and C-10 carbons from those calculated in **5a** might be caused chiefly by the geminal effect as observed in the cyclohexane ring;[13] the observed data of **6a** and **7a** in Table 2 are in better agreement with the calculated values by use of the data of **5a** rather than by use of the data of **2a** alone (this effect is also observed in the ketone **5b**)). Similar result is obtained for the ketones (**3b**—**7b**), where the C-8 carbon of **7b** is markedly deshielded (*ca.* 5 ppm) relative to the value obtained by the calculation (although details are not known at present, the relatively large deviations of the observed data from those calculated for the carbonyl carbons might be attributed chiefly to the alterations in geometry around the carbonyl group, since the magnitude of the carbonyl–methyl shielding effect is highly dependent on the steric arrangement between the two interacting groups[3]).

Consequently, it can be considered that the molecules of **7a** and **7b** are more greatly destabilized than those of **1**—**6** in their ground states due to the steric repulsions arising from the interior benzyl protons as well as the 1,3-synaxial methyl groups. This is a novel type of the "reflex effect" inherent in the 8-membered pericyclized naphthalene system, though the analogous effect is reported for the cyclohexane system.[27] Here, it is interesting that, whereas the interior benzyl protons of **7a** and **7b** are more greatly deshielded relative to those of the other compounds (**1**—**6**) by virtue of the reflex effect (Table 5), the chemical shifts of the benzyl

TABLE 6. CALCULATED ^{13}C CHEMICAL SHIFTS OF THE PERI RING CARBONS OF COMPOUNDS (**3**—**7**) (in ppm)[a,b,c]

Compound	C-7	C-8	C-9	C-10	C-11
3a	41.9(0.5)	32.9(0.5)	37.9(1.1)	32.9(0.5)	41.9(0.5)
4a	42.3(−0.2)	27.9(−0.8)	35.2(0.2)	33.8(0.5)	43.9(−0.1)
5a	50.6(−0.8)	37.6(−2.9)	35.2(−0.5)	24.1(2.6)	35.6(0.2)
6a	49.9(−0.7)	37.3(−2.4)	43.5(0.1)	27.6(1.9)	41.6(0.1)
	[49.1(0.1)	34.4(0.5)	43.0(0.6)	30.2(−0.7)	41.8(−0.1)]
7a	49.6(−0.7)	32.0(4.1)	49.1(−0.8)	32.0(4.1)	49.6(−0.7)
	[49.0(−0.1)	31.7(4.4)	48.1(0.2)	31.7(4.4)	49.0(−0.1)]
3b	41.1(0.6)	45.0(0.7)	215.3(−2.1)	45.0(0.7)	41.1(0.6)
4b	40.5(0.0)	41.0(−0.5)	218.4(−1.2)	51.8(0.3)	43.1(0.2)
5b	49.3(−0.3)	51.2(−2.7)	218.4(−3.6)	41.6(1.3)	34.3(0.3)
6b	49.7(−0.1)	51.0(−2.3)	219.1(−3.8)	40.8(0.2)	40.9(0.5)
	[49.4(0.2)	48.3(0.4)	215.5(−0.2)	42.1(−1.1)	41.2(0.2)]
7b	49.5(−0.8)	46.8(3.4)	222.9(−4.6)	46.8(3.4)	49.5(−0.8)
	[49.5(−0.8)	45.4(4.8)	215.7(2.6)	45.4(4.8)	49.5(−0.8)]

a) The chemical shifts of compounds (**3a**—**7a**) were calculated from the chemical shifts of the parent compound **1a** (see footnote inTabe 3) and the values of the methyl substituent effects, obtained from the chemical shifts of the axial (**AB**) and the equatorial isomers (**EB**) of the 8-monomethyl derivative **2a** (Ref. 3); **2a-AB**: 8.0 (C-7), 4.4 (C-8), 5.6 (C-9), −5.3 (C-10), −0.3 ppm (C-11), **2a-EB**: 6.0 (C-7), 3.5 (C-8), 8.3 (C-9), −0.3 (C-10), −0.7 ppm (C-11) (a minus sign indicates a high-field shift). Similarly, the chemical shifts of **3b**—**7b** were calculated from those of **1b** (Ref. 2) and the values of the methyl substituent effects obtained from the chemical shifts of the **2b-AB** and **2b-EB** isomers (Ref. 4); **2b-AB**: 8.6 (C-7), 6.0 (C-8), 3.8 (C-9), −4.2 (C-10), −0.2 ppm (C-11), **2b-EB**: 6.6 (C-7), −0.8 (C-8), 0.7 (C-9), −0.2 (C-10), 0.4 ppm (C-11). b) Figures in brackets indicate the calculated shift values obtained by use of the observed data of **5a** or **5b** (Table 2). c) Figures in parentheses are the differences of the chemical shifts between the observed (Table 2) and the calculated values; $\Delta\delta=\delta_{obsd}-\delta_{calcd}$.

methylene carbons of **7a** and **7b**, in contrast, are little influenced by the steric compression effect (Table 6). On the other hand, the steric compression of the synaxial methyl groups in **7a** and **7b** is clearly reflected in both proton and carbon chemical shift values of the axial methyl group as described above.

Similar result is obtained from the spectra of the parent compound **1a**. Comparison of the ^{13}C data of **1a** (see footnote in Table 3)[26] with those of the structurally analogous benzocyclic compound **8a** (36.6 (C-5,9), 28.2 (C-6,8), 32.6 ppm (C-7))[28] reveals that, although the interior benzyl protons of **1a** are markedly deshielded ($\Delta\delta=1.1$—1.2 ppm)[1] relative to the benzyl protons of **8a** due to the steric compression, the chemical shift values of the benzyl methylene carbons are quite equal ($\delta=36.6$ ppm) between these two compounds; however, it should be noted here that the C-9 carbon of **1a** which has the gauche steric arrangements with the peri bonds (C_7–C_{6a} and C_{11}–C_{11a} bonds) in the boat conformation (see Newman projection in Fig. 1) is greatly shielded ($\Delta\delta=11.3$ ppm) relative to the C-7 carbon of **8a** which exists in the chair conformation.

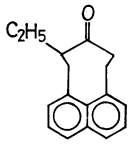
It is seen in Table 1 that in each class of methyl compounds, the interior benzyl protons of the ketones (**b**) are always greatly deshielded ($\Delta\delta=0.51$—0.63 ppm) relative to those of the corresponding hydrocarbons (**a**) (the values of shift difference are only 0.09—0.19 ppm for the corresponding exterior protons). Similar result was obtained for compounds **1** ($\Delta\delta=$*ca.* 0.67 ppm)[1,2] and **2** ($\Delta\delta=0.5$—0.7 ppm).[3,4] This result may be attributed chiefly to the difference in the interatomic distance of the interior benzyl protons. That is, the H_{in} protons of the ketone, the distance of which is shorter than that in the case of the hydrocarbon, are more greatly compressed and more greatly deshielded than the H_{in} protons of the hydrocarbon. However, in view of such large $\Delta\delta$ values found in the ketone, it is probable that the difference of the H_{in} distance between the ketone and the hydrocarbon is, in practice, somewhat larger than the value of 0.02 Å obtained from the calculation[1,3] (see above). Therefore it may be considered that the ketone exists somewhat in a less puckered form than the conformations of the hydrocarbon in each class of compound probably due to the rigid C-9 double (C=O) bond (see Fig. 3).

In the case of compounds **3a** and **3b** which have *cis*-diequatorial methyl groups, the molecules are expected to be more strongly puckered than the other compounds to relieve the steric interaction between the equatorial methyl groups and the naphthalene ring[3,4] (Fig. 3). The small $J_{ex,ax}$ value observed in **3a** (this coupling is small enough not to be resolved) probably reflects this (see Newman projection in Fig. 2).

The distortion of the peri ring is also reflected in the IR spectra. Table 7 shows the carbonyl stretching frequencies ν(C=O) of the methyl ketones (**2b**—**7b**) determined in the chloroform solution. The magnitudes of the ν(C=O) values obtained apparently depend on the orientations of the substituting methyl groups. This may be explained in terms of the inverse relationship between the stretching frequency and the carbonyl angle (>C=O)[27] as follows.

The carbonyl stretching frequency of the ketone **2b** (1706 cm^{-1}) having an equatorial methyl group (in **2b**, the methyl group prefers the equatorial conformation (**EB**) to the axials (**AB**) by 0.07 kcal/mol at room temperature)[4] is 3 cm^{-1} higher than the absorption (1703 cm^{-1})[29] of the unsubstituted ketone **1b**. This arises probably because the molecule of **2b** is more distorted (puckered) than that of **1b** to relieve the methyl-naphthalene interaction, which makes the carbonyl angle of **2b** somewhat smaller than that of **1b** (Fig. 3). This effect is more clearly shown in the spectrum of **3b** which has *cis*-diequatorial methyl groups. The carbonyl frequency of **3b** is increased by 8 cm^{-1} as compared with the parent ketone **1b**.

On the other hand, introduction of an axial methyl group at C-8 or at C-10 position of these compounds (**2b** and **3b**) results in a 5—8 cm^{-1} decrease in the carbonyl frequency (thus, 0—2 cm^{-1} decrease relative to **1b**) as observed in compounds (**4b**—**6b**), because the carbonyl angle in these compounds is, to some extent, expanded (thus the peri ring exists in a less puckered form) relative to that of the ketones **2b** and **3b** due to the 1,3-synaxial CH_3-H steric interactions (the existence of this interaction is also suggested from the observation that the C-8 or C-10 axial protons which have a synaxial steric relationship with a methyl group resonate at *ca.* 0.1—0.3 ppm lower field than the protons without such steric interactions; see footnote in Table 1). This effect is also observed in the axial isomer (**AB**) of 8-ethyl-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalen-9-one (**11**) (in this compound, the axial conformation is preferred to the equatorial conformation by 0.69 kcal/mol at room temperature),[4] where the carbonyl stretching frequency is lowered by 3 cm^{-1} as compared with the parent ketone **1b**.



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The above result is in sharp contrast to the case of the α-methylcyclanones including the cyclohexane system previously reported. In 3-keto steroids,[30] introduction of one methyl group in the 2- or the 4-position causes a 4—7 cm^{-1} decrease in the carbonyl stretching frequencies, irrespective of whether the methyl group is in the axial or in the equatorial conformation; the carbonyl frequencies of the α-*gem*-dimethylated 3-keto steroids, therefore, are more greatly decreased (12—13 cm^{-1}) by the effect of the methyl groups[30] than in the case of the ketones (**4b**—**6b**) (0—2 cm^{-1}) which experience the puckering distortion due to the methyl(eq)–naphthalene steric interaction.

The carbonyl stretching frequency of the fully methylated ketone **7b** is greatly decreased (14 cm^{-1}) as compared with the parent ketone **1b**. Thus it is suggested that the carbonyl angle of **7b** is greatly expanded (thus the peri ring is flattened) relative to that of (**1**—**6**) in excellent agreement with the NMR spectra described above. Analogous effect was

TABLE 7. CARBONYL STRETCHING FREQUENCIES (νC=O) OF THE METHYL KETONES (**2b**—**7b**)[a]

Compound	Frequency ν(cm^{-1})	$\Delta\nu$[b]
Unsubstituted ketone (**1b**)[c]	1703	
8-Monomethyl ketone (**2b**)[d]	1706	+3
cis-8,10-Dimethyl ketone (**3b**)	1711	+8
trans-8,10-Dimethyl ketone (**4b**)	1701	−2
8,8-Dimethyl ketone (**5b**)	1701	−2
8,8,10-Trimethyl ketone (**6b**)	1703	0
8,8,10,10-Tetramethyl ketone (**7b**)	1689	−14
8-Ethyl ketone (**11**)[e]	1700	−3
Cyclooctanone	1694[f]	−9
Cyclohexanone	1708[g]	+5

a) The IR spectra were measured in chloroform (spectro grade) at room temperature, using a 0.1 mm-length KBr cell. The concentration of the samples was *ca.* 0.1 mol/l for all the ketones and the measurements were run twice for each sample. The positions of absorption maxima were obtained from the expanded spectra and calibrated with polystyrene ($\Delta\nu=\pm0.5$ cm^{-1}). b) Frequency shift from the parent ketone **1b**. c) Ref. 29. d) The equatorial isomer (**EB**) is more favored than the axials(**AB**) by 0.07 kcal/mol at 30 °C (Ref. 4). e) The axial conformation is preferred to the equatorial conformation by 0.69 kcal/mol at 30 °C (Ref. 4). f) Shifted to 1705 cm^{-1} in carbon tetrachloride (Lit. 1703 cm^{-1}; Ref. 31). g) Reported to be 1716 cm^{-1} in carbon tetrachloride (Ref. 31).

reported[30] for 2,2,4,4-tetramethylcholestan-3-one, in which the carbonyl frequency is lowered by *ca.* 17 cm^{-1} as compared with the unmethylated compound.

As can be seen in Table 7, the carbonyl frequency of **1b** (1703 cm^{-1})[29] is 9 cm^{-1} higher than that of cyclooctanone and 5 cm^{-1} lower than that of cyclohexanone. Therefore it may be considered that the carbonyl angle of **1b** is probably between that of these two cyclanones, if it could be assumed that the magnitude of the carbonyl frequency depend solely upon the carbonyl angle irrespective of the ring system to which the ketones belong. This is consistent with the NMR result that the internal bond angle at C-9 carbon of the peri-8-membered ring system is, to some extent, contracted as a result of the puckering of the boat conformation (Fig. 3).

Previously, we have studied the ring inversions in compounds **1a**[1] and **1b**.[2] In order to determine the effect of the C-8 and C-10 methyl substituent on the ring inversions in the 8-membered pericyclized naphthalene system, the free energy barriers to boat-to-boat interconversion process were investigated for several methylated compounds (8-methyl (**2a**), *trans*-8,10-dimethyl (**4a**), 8,8-dimethyl (**5a**), and 8,8,10,10-tetramethyl (**7a**)) and their 9-oxo derivatives (**2b**, **4b**, **5b**, and **7b**) by use of the variable-temperature ^{1}H NMR technique. In these conformational changes, three types of ring inversions are observed. In compounds **4** and **7**, a degenerate process occurs in which the conformer exchanges with itself. In compound **5**, the ring inversion process is enantiomeric, while **2** undergoes conformational inversion into its diastereomer. In all of these conformational processes, the methyl group in each compound is interchanged between the axial and the equatorial conformations of equal conformational energies (since the ($-\Delta G^\circ$) values for **2a**[3] and **2b**[4] are very small, the populations of the two isomers in these compounds were assumed to be equal at the temperatures studied).

We therefore examined the ^{1}H NMR spectra of the methyl groups of each compound as a function of the temperature (for **2a**, **2b**, and **4b**, the deuterated derivatives **2a**-8,10,10-d_3,[3] **2b**-8,10,10-d_3,[4] and **4b**-8,10-d_2 were employed, respectively). The methyl signals in all compounds show a change typical of the dynamic exchange processes on varying the temperature—*viz.*, the two separated methyl signals at low temperature broaden, coalesce, and then sharpen as the temperature is increased. From these spectral changes the free energy barrier ($\Delta G^{\neq}$) to boat inversion for each methyl compound is calculated by means of the coalescence temperature (T_c) method (see footnotes in Table 8).[32] The results are summarized in Table 8 together with the data of the parent compounds **1a**[1] and **1b**[2] previously reported.

As can be seen in the table, the free energy barriers ($\Delta G^{\neq}$) for 8-monomethyl derivative **2a** and *trans*-8,10-dimethyl compound **4a** are almost comparable to the value of the parent compound **1a** ($\Delta\Delta G^{\neq}=0.4$ and 0.6 kcal/mol, respectively), whereas barriers for the *gem*-dimethyl compound **5a** and the tetramethyl compound **7a** are markedly increased as compared with **1a** ($\Delta\Delta G^{\neq}=5.4$ and 5.9 kcal/mol, respectively). A similar trend is observed in the $\Delta G^{\neq}$ values of the ketones, where the $\Delta G^{\neq}$ for **5b** and **7b** is much higher than the value of **1b** ($\Delta\Delta G^{\neq}=4.8$ and 5.6 kcal/mol, respectively), whereas that of **2b** and **4b** is approximately equal to the value of **1b** ($\Delta\Delta G^{\neq}=-0.1$ and 0.2 kcal/mol, respectively). The observation of the same trend in $\Delta G^{\neq}$ for the hydrocarbons (**a**) and the ketones (**b**) strongly suggests that the boat conformation of both classes of methyl compounds interconverts through the same pathway. Therefore, it seems reasonable to assume[32] that $\Delta G^{\neq}$ differences in Table 8 ($\Delta\Delta G^{\neq}$) are fair approximations to $\Delta\Delta H^{\neq}$ for all the methylated compounds studied.

Recently, it has been shown that the boat-to-boat interconversion in the 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene ring proceeds by pseudorotations of the peri bonds *via* the twist-boat conformation (**TB**) as an intermediate,[1,6] the transition state for this process being possibly a high-energy conformation (**TS**)[1,2] (see Fig. 4). The $\Delta G^{\neq}$ value of each methyl compound in Table 8 can be adequately explained in terms of the boat inversion mechanism described above.

In **2a** and **2b**, the methyl substituent could produce no serious steric interaction either in the (**TS**) or in the (**TB**) conformation during the ring inversion as is seen in Fig. 5. In these compounds, the transition state of boat inversion may somewhat be elevated as a result of the methyl substitution (which could cause some increase in the torsional barrier for rotation about the C_8–C_9 and C_9–C_{10} bonds in (**TS**)), but the ground state is also elevated due to the transannular synaxial CH$_3$–H interaction or to the eq-CH$_3$–naphthalene gauche

Table 8. Free energy barriers ($\Delta G^{\neq}$) to boat inversion for several 8- and 10-methyl-substituted 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalenes (**a**) and their 9-oxo compounds (**b**)[a,b]

Compound	Signal obsd	$\Delta\nu$/Hz[e]		T_c/°C		$\Delta G^{\neq}$/kcal·mol^{-1} [f]		Difference[g]
		(**a**)	(**b**)	(**a**)	(**b**)	(**a**)	(**b**)	
Unsubstituted (**1**)						14.5[c]	12.4[d]	2.1
8-Monomethyl (**2**)	CH_3	36	50	26.6	−21.3	14.9(0.4)	12.3(−0.1)	2.6
trans-8,10-Dimethyl (**4**)	CH_3	42	51	32.5	−15.0	15.1(0.6)	12.6(0.2)	2.5
8,8-Dimethyl (**5**)	CH_3	36	49	121.5	73.7	19.9(5.4)	17.2(4.8)	2.7
8,8,10,10-Tetramethyl (**7**)	CH_3	55	56	137.9	92.7	20.4(5.9)	18.0(5.6)	2.4

a) Variable-temperature ^{1}H NMR studies were carried out using deuteriochloroform solution for all compounds except **5a** and **7a**, which were measured in *o*-dichlorobenzene. The energy of activation ($\Delta G^{\neq}$) for the boat inversion was calculated from Eqs.; $\Delta G^{\neq}=4.57T_c(10.32-\log k_c+\log T_c)$ and $k_c=\pi\Delta\nu/\sqrt{2}$ (Ref. 32), using the coalescence temperature (T_c) of the methyl signal. b) In each compound, figures in the left column are due to the hydrocarbons (**a**), while those in the right are to the ketones (**b**). c) Obtained by means of the complete line-shape analysis method (Ref. 1); Nelsen and Gillespie reported this value to be 14.0 kcal/mol using the coalescence temperature method (Ref. 6). d) From Ref. 2. e) The chemical-shift difference of the methyl proton signals; data for compounds **4**, **5**, and **7** were taken from Table 1, while those for **2a** and **2b** were taken from Refs. 3 and 4, respectively. f) Figures in parentheses are the values of $\Delta G^{\neq}$ relative to the parent compounds **1a** and **1b**. g) The $\Delta G^{\neq}$ difference between the hydrocarbon (**a**) and the ketone (**b**).

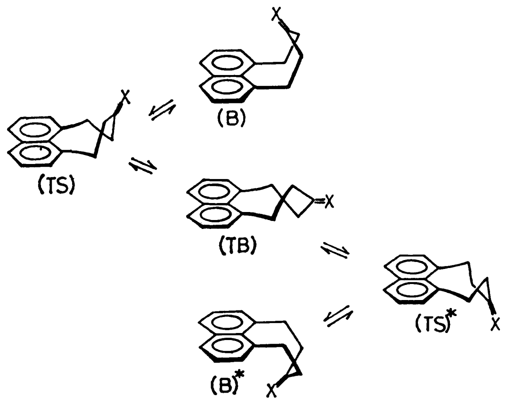
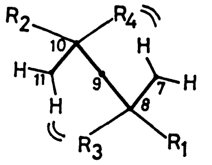


Fig. 4. Pathway for boat inversion of the 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene ring (**a**; X= H_2, **b**; X=O, the signal marked with an asterisk indicates the inverted form).



1; $R_1=R_2=R_3=R_4=H$
2; $R_1=CH_3$, $R_2=R_3=R_4=H$
3; $R_1=R_4=CH_3$, $R_2=R_3=H$
4; $R_1=R_2=CH_3$, $R_3=R_4=H$
5; $R_1=R_3=CH_3$, $R_2=R_4=H$
6; $R_1=R_2=R_3=CH_3$, $R_4=H$
7; $R_1=R_2=R_3=R_4=CH_3$

Fig. 5. Steric interaction in the twist-boat conformation (**TB**)(C_2) of compounds (**1**—**7**) viewed from in front of the C-9 carbon (naphthalene moiety is omitted).

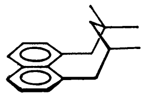
interaction, as the result of which the effect of the methyl group on the barrier to ring inversion seems very small. Similar arguments are also valid for **4a** and **4b** (see Fig. 5). Therefore it is understandable to observe that the $\Delta G^{\neq}$ values for compounds **2a**, **2b**, **4a**, and **4b** are almost comparable to the values for the parent compounds or slightly higher than the values of the latter compounds.

On the other hand, in the case of compounds **5a** and **5b** which have one *gem*-dimethyl group in the C-8 position, the pseudorotations of the peri bonds give rise to a close approach of the methyl substituent to the peri hydrogen (at C-11) in the transition state as well as in the (**TB**) conformation (in compounds **2** and **4** without a *gem*-dimethyl group at C-8, this interaction is avoidable) (Fig. 5). Therefore, it is expected that the (**TS**) of **5a** and **5b** is more greatly elevated relative to **4a** and **4b** by the interaction of these two groups. In view of this together with that the energy of the ground state of **5a** and **5b** is close near to that of **4a** and **4b** (in both cases, the synaxial CH_3–H interaction and the (eq)CH_3–naphthalene interaction are the most important), it is understandable to observe that the $\Delta G^{\neq}$ values of **5a** and **5b** are unusually higher than the values of **4a** and **4b** as well as those of **2a** and **2b**.

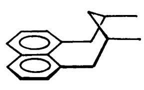
For the same reason, the $\Delta G^{\neq}$ for the tetramethyl compounds **7a** and **7b** is also markedly increased as compared with the parent compounds (see Fig. 5). In this case, the $\Delta G^{\neq}$ value for **7a** and **7b** shows only a small increase ($\Delta\Delta G^{\neq}<1$ kcal/mol) relative to **5a** and **5b**, respectively, though the (**TS**) and (**TB**) of the former compounds are more greatly destabilized than those of the latter compounds (**7a** and **7b** involve twice a steric interaction as that present in **5a** and **5b**; Fig. 5). This arises probably because the ground state of **7** is greatly destabilized by virtue of the reflex effect arising from the the synaxial CH_3–CH_3 steric interaction coupled with the interior benzyl H–H interaction as described above.

The above result is in striking contrast to the case of other ring systems such as the cyclohexane and 6,7,8,9-tetrahydro-5*H*-benzocycloheptene (**8**). The $\Delta G^{\neq}$ value for the chair inversion of 6,6-dimethyl- (**9**) and 6,6,8,8-tetramethylbenzocycloheptene derivatives (**10**) is only slightly increased (**9**; 0.6 kcal/mol) or lowered (**10**; 0.3 kcal/mol) relative to the unmethylated compound **8a**.[9] Similarly, the $\Delta G^{\neq}$ value for the 1,1-dimethyl- and 1,1,3,3-tetramethylcyclohexane derivatives is slightly higher (0.1 kcal/mol) or lower (0.9 kcal/mol), respectively, than the value for the parent cyclohexane.[33]

In each methyl compound, $\Delta G^{\neq}$ for the ketone (**b**) is always lower than the value for the corresponding hydrocarbon (**a**) by 2.4—2.7 kcal/mol. Similar trend has been observed for the parent compounds ($\Delta\Delta G^{\neq}$= 2.1 kcal/mol).[1,2] This result may be adequately explained in terms of the boat inversion mechanism described above. The pseudorotations of the peri bonds in the boat inversion are accompanied by rotations about the C_9–C_{10} and C_8–C_9 bonds in the conversions of $(\mathbf{B})\leftrightarrows(\mathbf{TS})\leftrightarrows(\mathbf{TB})$ and $(\mathbf{TB})\leftrightarrows(\mathbf{TS})^*\leftrightarrows(\mathbf{B})^*$, respectively.[1] Thus, in view of the barriers to methyl rotation in propane (3.3 kcal/mol)[27] and acetone (0.8 kcal/mol),[33] it is expected that energies necessary for reaching the transition states in the ketone (**b**) are smaller than in the case of the hydrocarbon (**a**) by the value close to the difference in the barrier between propane and acetone.[33] Actually, the difference in $\Delta G^{\neq}$ observed between the ketone and the hydrocarbon in each methyl compound is almost comparable to the value observed in propane and acetone. Moreover, in each compound of (**2**—**7**), the effect of the methyl group on $\Delta G^{\neq}$ is always larger for the hydrocarbon than for the ketone by 0.3—0.6 kcal/mol. This might be taken chiefly as a reflection of the difference in the torsional barriers about the C_8–C_9 and/or C_9–C_{10} bonds between the hydrocarbon and the ketone caused by the steric interaction with the methyl group.



6B′



3B′

On the other hand, the ^{1}H NMR spectra of **3b** and **6b** reveals that conformations of **3B** and **6B** are also enough stable at room temperature (these spectra show no change below 90 °C), because another boat (**3B′** and **6B′**) involves steric repulsion due to the synaxial methyl groups and the (**TS**) and (**TB**) states involve the peri-H-CH_3 steric interaction as illustrated in Fig. 5.

All the results presented above provide a strong evidence that the boat inversion is caused by pseudorotations of the peri bonds in the 8-membered pericyclic naphthalene ring system. Consequently, this study reveals that the molecule of the 8-membered pericyclized naphthalenic compounds exists in a steric circumstance very different from that of the cycloalkanes and the benzocyclic compounds not only in the ground state but also in the transition state due to the peri strains involved.

Experimental

The synthesis of 8- and 10-methyl-substituted 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalenes (**3a**—**7a**) and their 9-oxo derivatives (**3b**—**7b**) have been reported previously.[8] The deuterated compounds, *cis*-8,10-dimethyl-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalen-9-one-8,10-d_2 (**3b**-d_2), *trans*-8,10-dimethyl-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalen-9-one-8,10-d_2 (**4b**-d_2), and 8,8,10-trimethyl-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalen-9-one-10-*d* (**6b**-*d*) were obtained from the ketones **3b** and **6b** using the deuterium exchange procedure previously described.[1] Deuteration of **3b** in a boiling mixture of potassium carbonate in dioxane and deuterium oxide gave an equilibration mixture from which **3b**-d_2 and **4b**-d_2 were isolated by recrystallization from ethanol. Similar result was obtained on reaction (boiling with a solution of sodium deuteroxide in dioxane and deuterium oxide) with diethyl 8,10-dimethyl-9-oxo-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene-8,10-dicarboxylate.[8] The structures of the deuterated compounds were confirmed on the basis of the TLC, melting points (**3b**-d_2; 228—229 °C (**3b**; 230—231 °C),[8] **4b**-d_2; 125—126 °C (**4b**; 126—127 °C),[8] **6b**-*d*; 125—126 °C (**6b**; 124.5—125 °C)[8]), and their spectra (IR and NMR).

The ^{1}H NMR spectra were determined on a Varian HA-100D spectrometer at 100 MHz using a *ca.* 10% (w/v) solution of samples in deuteriochloroform (for compound **3b**, a *ca.* 3% solution was employed); the chemical shifts are expressed in ppm (δ) downfield from the internal standard, tetramethylsilane, and the coupling constants (*J*), in Hz with an accuracy of ±0.1 Hz. The variable-temperature ^{1}H NMR studies were carried out using a deuteriochloroform solution for all compounds except **5a** and **7a**, which were measured in *o*-dichlorobenzene. The sample temperature was controlled by passing precooled nitrogen through the sample cavity and measured by a calibrated copper–constantan thermocouple. The ^{13}C NMR spectra were determined on a Varian NV-14 FT NMR spectrometer operating at 15.087 MHz, using deuteriochloform as a solvent and tetramethylsilane as an internal standard (accuracy, ±0.1 ppm). The IR spectra were measured on a JASCO IR-G grating infrared spectrometer using a *ca.* 0.1 mol/l solution of samples in chloroform (spectro grade) with a 0.1 mm-length KBr cell. The measurements were run twice for each compound, and the positions of absorption maxima were calibrated with polystyrene ($\Delta\nu$= ±0.5 cm^{-1}).

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