Conformational Equilibria of 8-Alkyl-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalenes

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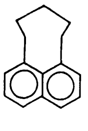
The conformations of 8-methyl (**4**) and 8-ethyl-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalenes (**5**) have been studied on the basis of the NMR spectra. It was found that both compounds exist as an equilibrium mixture of the axial-boat (**ab**) and the equatorial-boat (**eb**) conformers in solution. The ^{1}H spectra revealed that the boat conformations of all these isomers are somewhat in the distorted form due to the steric repulsion between the interior benzyl protons. The free-energy differences ($-\Delta G^\circ$) between the two isomers (**ab**$\rightleftharpoons$**eb**) in **4** and **5** were calculated from the ^{13}C spectra and found to be 0.09 and -0.07 kcal/mol, respectively. These results are discussed in terms of the structural and conformational features of the 8-membered pericyclized naphthalene ring and compared with the cyclohexane ring.

Recently, as a part of our studies on the chemistry of the 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene system (**1**),[1–4] the conformations of 8-alkyl-9-oxo derivatives, **2** and **3**, were reported.[5] In the present paper, we have extended our study to the deoxo compounds **4** and **5** in order to examine in detail the effect of the alkyl substituent on the stability of the peri ring in these pericyclized naphthalene system. Here, we will report the conformational equilibria in these 8-alkylated compounds by a study of the ^{1}H- and ^{13}C-NMR spectra and make some discussion about the conformational and spectral features of the 8-membered pericyclized naphthalene system in comparison with the cyclohexane ring.



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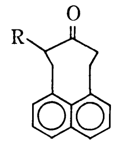
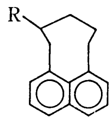


2; R=CH_3
3; R=C_2H_5



4; R=CH_3
5; R=C_2H_5

Results and Discussion

The room-temperature ^{1}H-NMR spectrum of 8-methyl-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene-8,10,10-d_3 (**4**-d_3) in a *ca.* 10% solution in deuteriochloroform shows broad signals for both the methyl and the benzyl protons. As the temperature of the sample is progressively lowered, the methyl signal broadens and then splits into two different lines with a chemical-shift difference of 0.36 ppm, while the benzyl proton signal changes into four sets of AB quartets of different intensities, centered at δ 3.29, 3.38, 3.44, and 3.46 ppm, respectively. The proton-decoupled ^{13}C-NMR spectrum of **4** at 30 °C gives a broad line for each of the peri ring carbons and the methyl group, all of which split into a doublet of different peak heights on lowering the temperature. Similar spectral changes were observed for the ethyl compound **5**.

From these spectra it is apparent that both **4** and **5** assume two different forms interchanging to each other by the inversion of the peri ring. Analysis of the low-temperature spectra of **4** and **5** as well as their 8,10,10-trideuterated derivatives (**4**-d_3, **5**-d_3) affords the ^{1}H- and ^{13}C-data for each conformational isomer of these compounds which are summarized in Tables 1 and 2.

It has previously been shown[1–6] that the interior benzyl protons (H_{in}) in the 8-membered pericyclized naphthalene ring suffer a severe steric interaction and resonate at much lower field than the corresponding exterior protons (H_{ex}). Thus the strong vicinal couplings (J=13 Hz) observed in the lower-field signals of the C-11 methylene groups in all the conformations (Table 1) clearly suggest that only boat conformations are significantly populated in these 8-alkylated compounds, since, as can be seen in Fig. 1, the H_{in} proton of the boat conformation (**B**) is situated in a position trans to an adjacent equatorial proton (H_{eq}), and thus a strong coupling is expected between these two protons.

TABLE 1. ^{1}H-NMR DATA OF CONFORMATIONAL ISOMERS OF **4** AND **5**[a,b]

Conformer	7-C$\underline{H}_2$	11-C$\underline{H}_2$	C$\underline{H}_3$
4-eb	4.25 (J=−14.4, 6.1 Hz)	3.99 (J=−14.3, 13.0, 7.0 Hz)	0.84 *d* (J=6.8 Hz)
	2.64 (J=−14.4, 1.0 Hz)	2.92 (J=−14.3, 6.0 Hz)[d]	
4-ab	3.67 (J=−14.1, 12.7 Hz)	3.87 (J=−14.3, 13.0, 7.0 Hz)	1.20 *d* (J=7.0 Hz)
	2.90 (J=−14.1, 6.0 Hz)	2.90 (J=−14.3, 6.0 Hz)[d]	
5-eb	4.20 (J=−14.6, 6.1 Hz)	3.98 (J=−14.5, 13.0, 7.0 Hz)	*ca.* 1.0[c]
	2.75 (J=−14.6, 1.0 Hz)	2.93 (J=−14.5, 6.0 Hz)[d]	
5-ab	3.57 (J=−14.4, 11.5 Hz)	3.83 (J=−14.3, 13.0, 6.0 Hz)	*ca.* 1.0[c]
	2.89 (J=−14.4, 6.0 Hz)	2.96 (J=−14.3, 6.0 Hz)[d]	

a) At −45.1 °C in $CDCl_3$, δ in ppm from internal TMS. b) Signals due to the C-9 protons are buried under those of the methyl group. c) Because of overlapping of signals splitting of this signal was not observed. d) The coupling ($J_{ex,ax}$) is small enoguh not to be observed.

TABLE 2. CARBON-13 CHEMICAL SHIFTS OF CONFORMATIONAL ISOMERS OF **4** AND **5**[a]

Conformer	C-7	C-8	C-9	C-10	C-11	$\underline{C}H_3$[b]	$\underline{C}H_2$[b]
4-eb	42.6	33.2	29.6	29.4	35.9	22.0	
4-ab	44.6	34.1	26.9	24.4	36.3	20.0	
5-eb	39.5	40.7	26.6	29.2	36.5	12.4	27.7
5-ab	43.2	40.7	23.8	24.6	36.5	12.4	27.7

a) At −56.1 °C in $CDCl_3$, δ in ppm from internal TMS.
b) Carbons due to the alkyl group.

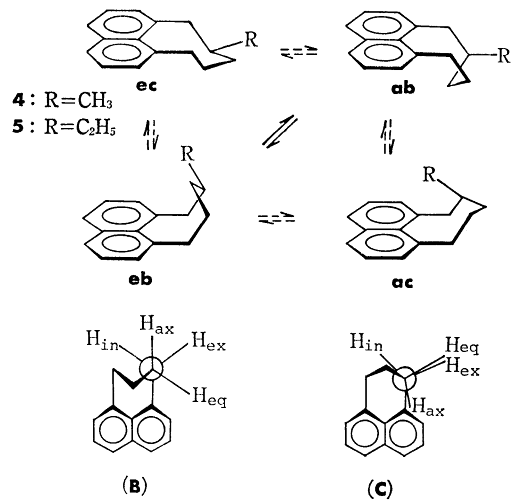
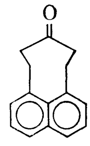


Fig. 1. The boat (**B**) (**eb**, **ab**) and the chair (**C**) (**ec**, **ac**) conformations for **4** and **5**, and their Newman projections about the C_{10}–C_{11} bond.

On the contrary, if the chair (**C**) would be the predominant conformation for **4** and **5**, then the strong vicinal coupling could be observed for the H_{ex} protons (see Newman projections in Fig. 1). The splitting pattern of the C-11 interior proton signal (J=14.3, 13.0, 7.0 Hz) in each conformer of **4** and **5** is analogous to that of the parent compound **1** (J=14.2, 12.9, 6.5 Hz),[4] which exists in the boat conformation alone.

Then the positions of the alkyl group in each conformation can be obtained from the magnitude of the vicinal couplings of the C-7 interior protons. Thus the isomers which have larger values (12.7 Hz in **4** and 11.5 Hz in **5**) have the alkyl groups at axial (**4-ab** and **5-ab**), while the others with smaller values (6.1 Hz in both **4** and **5**) have the equatorial alkyl groups (**4-eb** and **5-eb**).

This result is consistent with the ^{13}C chemical shifts in Table 2. Thus, high-field shifts of the C-7 carbons in the equatorial isomers (**eb**) relative to those in the axials (**ab**) ($\Delta\delta$=2.0—3.7 ppm) are caused by a gauche interaction between the alkyl substituent and the peri bond in the **eb** isomer (see Fig. 1), whereas marked shieldings of the C-9 ($\Delta\delta$=2.7—2.8 ppm) and C-10 carbons ($\Delta\delta$=4.6—5.0 ppm) in the **ab** conformations as compared to those in the **eb** result from the so-called γ-effect.[7] By these effects the chemical-shift differences in the C-8 ($\Delta\delta$=0.0—0.9 ppm) and in the alkyl carbons ($\Delta\delta$=0.0—2.0 ppm) between the axial (**ab**) and the equatorial (**eb**) isomers in these peri-8-membered ring system are rather small as compared to those observed in the cyclohexane system ($\Delta\delta$=4.5 and 6.0 ppm for the α and the methyl carbons, respectively).[7]



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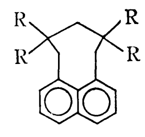

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Consequently, compounds **4** and **5** exist as an equilibrium mixture of the axial-boat (**ab**) and the equatorial-boat (**eb**) conformers in solution. The unusually overwhelming preference of the boat conformations (**ab**, **eb**) over the chair (**ac**, **ec**) observed in these compounds 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 peri-8-membered ring system of naphthalene (Fig. 1). All the other compounds of this ring system studied so far, including the substituted (**2**, **3**,[5] and **7**[1]) and unsubstituted (**1**[4] and **6**[2]) compounds exist solely in the boat conformation, too. The interconversion between **ab**$\rightleftarrows$**eb** in **4** and **5** is likely to proceed by pseudorotations of the peri bonds *via* the twist-boat as in the parent compound **1**.[4,6]

TABLE 3. CONFORMATIONAL EQUILIBRIA BETWEEN **ab** $\rightleftarrows$ **eb** IN **4** AND **5**[a]

	R=CH_3		R=C_2H_5	
	4	**2**	**5**	**3**
K(**eb**/**ab**)	1.27		0.89	
$-\Delta G°$/(kcal/mol)	0.09	0.10[b]	−0.07	−0.59[b]
	1.70[c]	1.6—1.8[d]	1.75[c]	1.1—1.2[d]

a) Obtained from the intensity ratio of the C-7 carbon signal at −56.1 °C. b) Data taken from Ref. 5. c) For the alkylcyclohexane (Ref. 8). d) For the 2-alkylcyclohexanone (Ref. 10).

In order to determine the effect of the naphthalene moiety on the stabilities of isomers in **4** and **5** (the C-8–C-9–C-10 moiety of the boat has a geometry very similar to that of the cyclohexane ring;[1] Fig. 1), the isomer ratios (**eb**/**ab**) in these compounds were then calculated from the C-7 carbon signal intensities of each conformational isomer in the low-temperature ^{13}C spectra. The results are shown in Table 3 together with the corresponding free energy differences ($-\Delta G°$). In **4**, the equatorial methyl group at C-8 is slightly favored *vis-à-vis* the corresponding axial group, by *ca.* 0.09 kcal/mol, while the C-8 ethyl group in **5**, on the contrary, prefers the axial conformation by *ca.* 0.07 kcal/mol at −56.1 °C. This result is in striking contrast with the situation of the cyclohexane system, in which both the methyl and the ethyl substituting groups have a strong preference for the equatorial conformation ($-\Delta G°$=1.7 and 1.75 kcal/mol, respectively).[8]

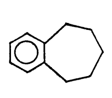
The unusual high stability of the axial isomers (**ab**) observed in these 8-membered pericyclized naphthalenic compounds **4** and **5** as compared to those in the cyclohexane ring may be explained on the basis of molecular models as follows:[5] The axial alkyl group in the **ab** conformation involves one gauche arrangement around the C_9–C_{10} bond and one *syn*-axial hydrogen at C-10 position. This corresponds to only one half of the steric interaction present in the axial isomer of the alkylcyclohexanes.[9] In the case of the equatorial isomer, however, the cyclohexane ring has no significant steric interaction within molecules,[9] while the equatorial alkyl group in the peri-8-ring (**eb**) involves one gauche arrangement with the C-7 peri bond.

Here, it is of interest to note that the bulkiness of the substituting group in the peri-8-ring system can play a more significant role in determining the conformational equilibria than in the cyclohexane ring, since, with increasing the steric bulkiness of the alkyl group, the conformation **eb** additionally suffers a non-bonded interaction between the alkyl group and the naphthalene nucleus, which is absent in the cyclohexane system. Thus, the $\Delta G°$ difference ($\Delta\Delta G° = -0.16$ kcal/mol) on going from the methyl (**4**) to the ethyl (**5**) derivative may be attributed chiefly to the alkyl-naphthalene interaction mentioned above, by which the stability of the **5-eb** conformation is further decreased as compared to that of the equatorial isomer of the alkylcyclohexane ($\Delta\Delta G° = 0.05$ kcal/mol).[8]

We have already studied[5] the NMR spectra of the 8-alkyl-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalen-9-ones (**2** and **3**) and shown that these compounds exist also as an equilibrium mixture of the **ab** and the **eb** conformers in solution. Comparison of the $\Delta G°$ values between the hydrocarbons (**4**, **5**) and the ketones (**2**, **3**) reveals that $-\Delta G°$ value of the methyl compound **4** (0.09 kcal/mol) is almost equal to that of the corresponding ketone **2** (0.10 kcal/mol), whereas in the case of the ethyl derivatives the $-\Delta G°$ value of the ketone **3** is considerably decreased (-0.59 kcal/mol) relative to the value of the deoxo compound **5** (-0.07 kcal/mol) (Table 3). This can be reasonably explained in terms of the so-called "2-alkylketone effect," since the geometry around the C-8–C-9–C-10 moiety of the peri-8-membered ring system is very similar to that of the cyclohexane ring.[1] That is, because of the eclipsed interaction between the equatorial ethyl group and the carbonyl function, the **3-eb** isomer is more destabilized than the **5-eb** isomer by the energy of *ca.* 0.5 kcal/mol, which is almost comparable to the value (0.55—0.65 kcal/mol)[10] found in the cyclohexane system.

The ^{1}H- and ^{13}C-data in the tables show other spectral and conformational features inherent in the 8-membered pericyclized naphthalene ring. The chemical-shift difference between the axial and the equatorial methyl protons in **4** ($\Delta\delta = 0.36$ ppm) is greatly increased relative to the value (0.07 ppm)[11] found in the cyclohexane system. This may be caused chiefly by the ring-current effect of the naphthalene nucleus, since, in the boat conformation of the peri-8-membered ring, the equatorial methyl group on C-8 has a position closer to the naphthalene ring than the corresponding axial methyl group (see Fig. 1). Actually, the magnitude of the shift difference of the two methyl protons observed in the spectrum (0.36 ppm) well agrees with the result of the calculation that the equatorial methyl protons resonate at *ca.* 0.46 ppm higher field than the axial methyl protons by the effect of the ring current of naphthalene.[1]

In all the isomers of **4** and **5**, the chemical shifts of the exterior benzyl protons ($\delta = 2.64$—2.96 ppm) are approximately equal to the values reported for the benzyl protons of 6,7,8,9-tetrahydro-5*H*-benzocycloheptene **8** ($\delta = 2.721$—2.827 ppm),[12] whereas the interior protons of **4** and **5** are deshielded markedly ($\delta = 3.57$—4.25 ppm) as a result of the steric compression effect. The calculation[4] revealed that the interatomic distance between the two interior 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 (**ab**, **eb**) is the most favored conformation for **4** and **5**, it still involves severe steric repulsion between the two interior protons.



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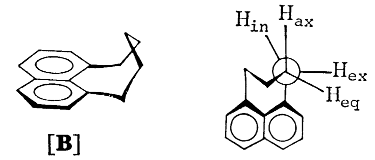
Thus it is expected that as in the case of the parent compound **1**,[4] the boat conformations of **4** and **5** are also in the distorted form [**B**], in which the two interior benzyl protons are pushed apart to relieve the steric repulsion between them. In this case, in view of the fact that the splitting patterns observed in the C-11 protons of **4** and **5** are very similar to those of **1** and **6**, it is reasonable to consider that the peri bonds of **4** and **5** undergo in-plane deformation as in the compounds **1**[4] and **6**[2,4] to result in the symmetric (C_s) conformation [**B**] as is shown in Fig. 2 (in studies on the peri-substituted naphthalenes, it was revealed that the peri bonds of 1,8-dimethylnaphthalene undergo in-plane deformation,[13,14] while, in 1,8-di-*t*-butylnaphthalene,[15,16] the peri bonds undergo out-of-plane deformation). Table 1 shows that in all the isomers the vicinal spin couplings between the C-11 exterior and the C-10 axial protons are very small (splitting is not observed) as compared to the values observed between the C-11 interior and the C-10 axial protons ($J = 6.0$ and 7.0 Hz). Similar trend is observed in the vicinal couplings about the C_7–C_8 bond of the **eb** isomer, where the axial protons are coupled more strongly with the interior benzyl protons ($J = 6.1$ Hz) than with the exterior protons ($J = 1$ Hz). These facts strongly support that all the isomers of **4** and **5** exist in the distorted boat [**B**] rather than in the normal boat (**B**), since as is seen in Fig. 2, the observed couplings are explained much



[**B**]

Fig. 2. The distorted boat conformation [**B**] for the 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene ring and its Newman projection about the C_7–C_8 (C_{10}–C_{11}) bond (see text).

better by the space arrangement in the distorted molecule [**B**] (H_{ex}/H_{ax}; $\theta > 60°$, H_{in}/H_{ax}; $\theta < 60°$) than by the space arrangement in the normal boat conformation (**B**) ($\theta \approx 60°$).

In our previous paper,[5)] we have reported the NMR spectra of **2** and **3**. The interior benzyl protons in these compounds suffer also marked deshieldings (δ=4.22—4.89 ppm) and show splitting patterns (**2**; J=14.8, 13.4, 7.3 Hz, **3**; J=14.7, 13.5, 5.6 Hz) similar to those of the distorted conformations (**6**; J=14.8, 13.0, 5.9 Hz).[2,4)] Thus, taking account of this fact, it is most probable that **2** and **3** also experience the ring distortions as in the deoxo compounds **4** and **5**, though the magnitude of the vicinal splitting ($J_{ex,ax}$) is not known in **2** and **3**. It should be noted here that the interior benzyl protons in the ketones (**2**, **3**) are *ca.* 0.5—0.7 ppm more deshielded than those of **4** and **5**, which makes the chemical-shift differences of the benzyl methylene protons in the former molecule much larger ($\Delta\delta$=1.21—2.11 ppm) than those in the latter molecules ($\Delta\delta$=0.68—1.61 ppm). Similar trend is observed between the unsubstituted compounds **1** and **6** ($\Delta\delta$= 1.03 and 1.55 ppm for **1** and **6**, respectively). This results probably from the differences in the steric interaction of the interior benzyl protons. A calculation reveals that the distance between the interior benzyl protons of the peri-8-ring system is somewhat shortened when the bond of the C-9 carbon changes from the sp^3 (0.652 Å)[4)] into the sp^2 hybrid (0.632 Å). Thus it can be expected that the interior benzyl protons of the ketones (**2**, **3**, and **6**) suffer the steric repulsion larger than that of the hydrocarbons (**4**, **5**, and **1**) and are deshielded more largely than in the case of the latter compounds.

Comparison of the ^{13}C chemical shifts of **4** and **5** with those of the ketones (**2**, **3**) reveals that the axial methyl group in the ketone **2-ab** is only slightly shielded (0.9 ppm) relative to that of the hydrocarbon **4-ab**, whereas the methyl group in the equatorial isomer suffers a marked shielding (7.4 ppm) by introduction of the carbonyl group. Similar trend is observed in the ethyl derivative, where the methylene carbon of the equatorial ethyl group (**eb**) is greatly shielded (6.0 ppm) relative to that of the axial isomer (**ab**) by the effect of the carbonyl group. This chiefly arises from the eclipsed interaction of the carbonyl function and the alkyl group in the equatorial isomer as is noted in the cyclohexane system.[17)] This interaction is also reflected in the chemical shifts of the peri ring carbons of both alkyl compounds, in which the C-8 and the carbonyl carbons of the equatorial isomers are shielded by 5.8—7.1 ppm relative to those of the axial isomers (for the other peri ring carbons, which are remote from the interacting groups, the effects are rather small (0.0—1.0 ppm)). This result is interesting in comparison with the result of the norbornane system previously reported.[18)] In 3-methyl-2-norbornanones, in which the carbonyl group is nearly in the same orientation with respect to the exo- and the endo-methyl groups, the carbonyl substituent effects differ only by 0.9—2.3 ppm between the two isomers.

Table 5 shows the effect of the 8-alkyl group on the chemical shifts of the C-7 benzyl protons. In both hydrocarbon (**4**) and ketone (**2**), the exterior protons are shielded markedly (0.30—0.31 ppm) by the effect of the equatorial methyl group, whereas the interior protons, on the contrary, are markedly deshielded (0.25—0.28 ppm) by the same substituting group. On the other hand, the introduction of an axial methyl group shields both the interior and the exterior protons on C-7, but the effects for the former protons are much larger (0.30 and 0.33 ppm) than those for the latter protons (0.03 and 0.04 ppm). Similar effect was

TABLE 4. EFFECT OF THE CARBONYL GROUP ON THE CARBON-13 CHEMICAL SHIFTS OF 8-ALKYL-8,9,10,11-TETRAHYDRO-7*H*-CYCLOOCTA[*de*]NAPHTHALENES (in ppm)[a)]

R	Isomer	C-7	C-8	C-9	C-10	C-11	$\underline{C}H_3$	$\underline{C}H_2$
Me	**eb**	1.9	−12.0	−185.0	−16.4	1.4	7.4	
	ab	1.9	−17.9	−190.8	−17.4	2.4	0.9	
	$\Delta^{b)}$	0.0	5.9	5.8	1.0	−1.0	6.5	
Et	**eb**	1.7	−11.4	−187.4	−17.1	1.9	0.2	6.8
	ab	2.1	−18.5	−193.2	−17.9	2.5	0.2	0.8
	$\Delta^{b)}$	−0.4	7.1	5.8	0.8	−0.6	0.0	6.0

a) $\Delta\delta = \delta^{\text{Hydrocarbon}} - \delta^{\text{Ketone}}$ (obtained from the data in Table 2 and in Ref. 5). b) Differences of the carbonyl substituent effect between the two isomers ($\Delta = \Delta\delta^{\text{eb}} - \Delta\delta^{\text{ab}}$)

TABLE 5. EFFECT OF 8-ALKYL GROUP ON THE CHEMICAL SHIFTS OF 7-BENZYL PROTONS IN THE 8,9,10,11-TETRAHYDRO-7*H*-CYCLOOCTA[*de*]NAPHTHALENE RING (in ppm)[a)]

Isomer	R	H_{7in}[b)]			H_{7ex}[b)]		
eb	Me	0.28	0.25	(θ=166°)[c)]	−0.30	−0.31	(θ=46°)[c)]
	Et	0.23	0.07		−0.19	−0.17	
ab	Me	−0.30	−0.33	(θ=46°)[c)]	−0.04	−0.03	(θ=74°)[c)]
	Et	−0.40	−0.42		−0.05	−0.08	

a) A minus sign indicates a high-field shift. b) Figures in the left column are due to the hydrocarbons ($\Delta\delta = \delta$(**4**, **5**)$-\delta$(**1**)) (Ref. 4), and those in the right column are to the ketones ($\Delta\delta = \delta$(**2**, **3**)$-\delta$(**6**)) (Refs. 2 and 5). c) Torsional angle between the C_7-benzyl proton and the alkyl group (taken from the data of **1** in Ref. 4).

observed in the cyclohexane ring[11,19] and some theories to explain this were reported.[20,21] In the present case, although details are not known at present, the above results may be interpreted qualitatively in terms of carbon–carbon single-bond anisotropies.[19] Since the peri rings of **4** and **5** have a geometry analogous to that of the parent compound **1**, the torsional angle about the C_7–C_8 bond of **4** and **5** can be estimated from the data of **1** as follows; $H_{7in}/CH_3(ax) = H_{7ex}/CH_3(eq) = 46°$, $H_{7ex}/CH_3(ax) = 74°$ and $H_{7in}/CH_3(eq) = 166°$ (the peri-eight-membered ring of 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene system is more greatly distorted (internal dihedral angle $\Psi = 46°$)[4] than the cyclohexane ring ($\Psi = 58°$),[22] see Fig. 2). These angles could adequately explain the trend of the shift values of the C_7-benzyl protons of **4** described above. For the ethyl compounds (**3**, **5**), almost the same trend is observed except for the H_{7in} proton of the **eb** isomer (see Table 5). The small shift value (0.07 ppm) observed in the ketone **3-eb**, in contrast to the case of the hydrocarbon **5-eb** (0.23 ppm), might be related chiefly to the 2-alkylketone effect described above.

Experimental

The synthesis of 8-methyl-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene (**4**) was reported previously.[3] 8-Ethyl-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene (**5**) was synthesized from diethyl 9-oxo-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene-8,10-dicarboxylate (**9**)[3] as follows.

To a stirred solution of sodium ethoxide in ethanol (obtained by dissolving 1.7 g of sodium into 150 ml of absolute ethanol) was added a solution of 5 g of keto ester **9** in 50 ml of absolute ethanol and 30 ml of dry dimethyl sulfoxide. After 1 h heating, excess ethyl bromide was added and the mixture was refluxed overnight. The mixture was poured into ice–water and the resulting cloudy solution was extracted with ethyl acetate. The organic solution was worked up as usual to leave a brown oil, which then treated with alkaline solution. The solid precipitated was crystallized from ethanol to give 1.2 g of 8-ethyl-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalen-9-one (**3**) as white needles; mp 97—98 °C; Found: C, 85.87; H, 7.83%. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61%. Clemmensen reduction of the ketone **3** gave the hydrocarbon **5**. The product was obtained as white needles after recrystallization from aqueous ethanol; mp 38—39 °C; Found: C, 90.95; H, 8.70%. Calcd for $C_{17}H_{20}$: C, 91.01; H, 8.99%.

8-Methyl-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene-8,10,10-d_3 (**4**-d_3) and 8-ethyl-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene-8,10,10-d_3 (**5**-d_3) were synthesized by Clemmensen reduction of the corresponding 8,10,10-trideuterated derivatives[5] of **2** and **3**, which had been obtained by the deuterium exchange reactions described previously.[4] The structures of the deuterated compounds were confirmed based on TLC, mp (**4**-d_3; 39—40 °C, **4**; 40—41 °C,[3] **5**-d_3; 38—39.5 °C) and their spectra (IR and NMR).

^1H NMR spectra were determined on a Varian HA-100D spectrometer operating at 100 MHz. ^{13}C NMR spectra were determined on a Varian NV-14 spectrometer operating at 15.087 MHz with a Varian 620/L computer (16K) in the pulsed FT mode (pulse flipping angle, 48°; pulse repetition time, 1.3 s). The samples were dissolved in chloroform-*d* (*ca.* 10% (w/v) solution), and tetramethylsilane was used as an internal standard. The temperature was controlled by using cooled nitrogen and measured by calibrated copper–constantan thermocouple.

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