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CONFORMATIONAL PREFERENCE IN 8-ALKYL-8,9,10,11-TETRAHYDRO-7*H*-CYCLOOCTA[*de*]NAPHTHALENE-9-ONES

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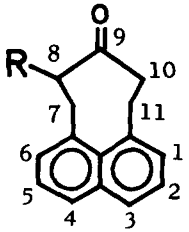
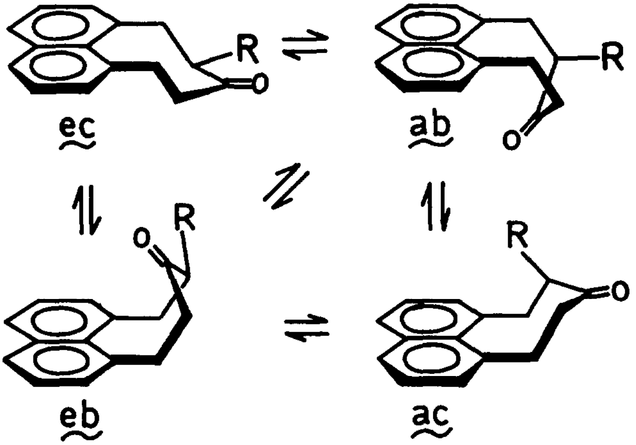
Compared to cycloalkanes, little is known about the stereochemistry of pericyclic naphthalenes, particularly compounds of medium-sized rings.[1-4] During our studies of conformations of the peri-8 ring system[3,4] in some derivatives of 8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalene, the stereochemistry of which is of great interest because they are strained owing to the peri interaction, we have found on the basis of NMR spectra that each of 8-methyl- (**1**)[5] and 8-ethyl-8,9,10,11-tetrahydro-7*H*-cycloocta[*de*]naphthalen-9-ones (**2**)[5] exists in two different conformations, one of which has an axial alkyl group.

At room temperature, the ^{1}H-NMR spectrum of high-field portion of 8,10,10-trideuterated methyl ketone (**1**-*d*$_3$)[5] consists of a singlet due to the methyl group, and a broad signal arising from the C_7- and C_{11}-protons. When the temperature is decreased, the methyl signal is split into a doublet with different peak areas, while the benzyl proton signals appear as three sets of AB quartets with different intensities. Thus, it became clear that **1** assumes two different conformations interconverting to each other at ambient temperature. A similar result was obtained for **2**. Table 1 shows the ^{1}H-NMR data obtained by the first-order analysis of the low-temperature spectra of **1** and **2** as well as their 8,10,10-trideuterated derivatives.

We previously showed that the *interior* benzylic protons in the eight-membered peri ring appear at lower fields than the *exterior* protons do.[3,4] Thus, the strong vicinal couplings observed in the lower-field signals of the C_{11}-methylene groups in all conformations clearly indicate that only boat conformations are significantly populated in these 8-alkyl ketones, because the *interior* benzylic proton of 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.[4] The splitting patterns of the *interior* C_{11}-proton signals in each conformer of **1** and **2** are similar to that of the parent ketone **3**, which exists exclusively in the boat conformation alone.[4] Then the large J-values between the *interior* C_7- and adjacent C_8-protons observed in the conformers of **1** (12.1 Hz)



1, R=Me
2, R=Et
3, R=H



and **2** (12.3 Hz) suggest that the C_8-methine protons are *equatorial* in these conformations. On the other hand, the small J-values (6.4 Hz for **1** and 7.2 Hz for **2**) suggest that the C_8-protons are *axial*. Consequently, **1** and **2** exist as an equilibrium mixture of *equatorial*-boat (**eb**) and *axial*-boat (**ab**) conformers in solution.

The ^{13}C-NMR data in Table 2 agree fully with conformations **eb** and **ab**. Thus high-field shifts of the C-10 signal in the *axial* isomer (**ab**) relative to that in the *equatorials* (**eb**) result from the γ-*gauche* effect.[6] Marked shieldings of C-8 and C-9 as well as the alkyl carbons in **eb** respectively compared to those in **ab** should be caused by some steric interaction between the carbonyl and alkyl groups which are almost *eclipsed* by each other in **eb**.[7] Moreover, C-7 in **eb** resonates at a higher field than that in **ab**, probably because the relationship between the alkyl group and the peri bond is *gauche* in the former, whereas it is *trans* in the latter.[6]

Conformational isomer ratios (**eb**/**ab**) in **1** and **2** are calculated from ^{13}C chemical shifts as well as from ^{13}C signal intensity ratios of the underlined peaks in Table 2, and the results are shown in Table 3 together with the corresponding free energy differences. In **1** the *equatorial* methyl group at C_8 is slightly favored, *vis-à-vis* the corresponding *axial* group, by ca. 0.07 kcal/mol, while the C_8-ethyl group in **2** prefers the *axial* conformation by ca. 0.69 kcal/mol at ambient temperature. This is in sharp contrast to the situation in alkylcyclohexanones which have a strong preference for a chair conformation with the *equatorial* alkyl group.[8]

The rather unusual predominance of the boat conformation (**eb**, **ab**) over the chair (**ec**, **ac**) observed in **1** and **2** seems reasonable, because the boat lacks the eclipsing strains along the C_7-C_8 and C_{10}-C_{11} bonds present in the chair.[2-4]

The interconversion between **eb**$\rightleftharpoons$**ab** in **1** and **2** is likely to proceed through

TABLE 1. ^{1}H-NMR Data of Conformational Isomers of 1 and 2 at -57.6° in CDCl$_3$.[a]

Conformer	C_7-C$\underline{H}_2$	C_{11}-C$\underline{H}_2$	C$\underline{H}_3$
1-eb	4.89 (J= -14.6, 6.4 Hz) 2.78 (J= -14.6 Hz)[b]	4.52 (J= -14.8, 13.4, 7.3 Hz) 3.01 (J= -14.8 Hz)[b]	0.95 (J= 6.8 Hz)
1-ab	4.31 (J= -14.6, 12.1 Hz) 3.06 (J= -14.6 Hz)[b]	4.52 (J= -14.8, 13.4, 7.3 Hz) 3.01 (J= -14.8 Hz)[b]	1.46 (J= 6.8 Hz)
2-eb	4.71 (J=-14.6, 7.2 Hz) 2.92 (J= -14.6 Hz)[b]	4.52 (J=-14.7, 13.5, 5.6 Hz) 3.05 (J= -14,7 Hz)[b]	c
2-ab	4.22 (J= -14.6, 12.3 Hz) 3.01 (J= -14.6 Hz)[b]	4.52 (J= -14.7, 13.5, 5.6 Hz) 3.05 (J= -14.7 Hz)[b]	0.97 (J= 7.1 Hz)

[a] δ values relative to internal TMS. [b] Because of overlapping of signals, vicinal couplings were not obtained for this proton. [c] Signal buried under that of the methyl group of the ab isomer.

TABLE 2. ^{13}C Chemical Shifts[a] of Conformational Isomers of 1[b] and 2[c] in CDCl$_3$.

Conformer	C-7	C-8	C-9	C-10	C-11	$\underline{C}H_3$[d]	$\underline{C}H_2$[d]
1-eb	40.7	45.2	214.6	45.8	34.5	14.6	
1-ab	42.7	52.0	217.7	41.8	33.9	19.1	
2-eb	37.8	52.1	214.0	46.3	34.6	12.2	20.9
2-ab	41.1	59.2	217.0	42.5	34.0	12.2	26.9

[a] δ in ppm from TMS. [b] At -66.5°. [c] At -59.4°. [d] Carbon of an alkyl group.

TABLE 3. Conformational Equilibria at Ambient and Low Temperatures.

	8-Me-ketone (1)		8-Et-ketone (2)	
K (eb/ab)	1.27[a]	1.13[b]	0.25[c]	0.32[b]
$-\Delta G^{o}$[d]	0.10	0.07	-0.59	-0.69

[a] At -66.5°. [b] At 30.0°. [c] At -59.4°. [d] In kcal/mol.

the twist-boat as in the parent ketone **3**[4] rather than through the process in which the chairs (**ec**, **ac**) are involved, because molecular models show that the pseudorotation of the peri bonds in the former process occurs more easily than the wagging of the peri bonds necessary for the chair-boat exchange (**ec**$\rightleftharpoons$**eb**, **ab**$\rightleftharpoons$**ac**) present in the latter process.

It is interesting to note that the *axial* isomers (**ab**) in **1** and **2** are unusually stabilized compared to those in 2-alkylcyclohexanones.[8] The following is the most likely explanation. The *axial* alkyl group in **ab** involves one *gauche* arrangement around the C_9-C_{10} bond and one *syn*-*axial* hydrogen at C_{10}. This corresponds to only one half of the steric interaction present in the *axial* isomer of 2-alkylcyclohexanone.[8] In the case of the *equatorial* isomer, however, the cyclohexane rings have no steric interaction within the molecule,[8] while the *equatorial* alkyl group in the peri-8 rings (**eb**) involves one *gauche* arrangement with the C_7 peri bond.

The increasing stability of the *axial* isomer (**ab**) on going from the methyl (**1**) to the ethyl (**2**) ketones is probably caused mainly by the alkyl ketone effect, as observed in cyclohexanones.[8] In the peri-8 ring system, however, the bulkiness of the alkyl substituent can play a more significant role in determining the conformational equilibria than in the cyclohexane ring, because with increasing bulkiness of the alkyl group, the conformation **eb** may be destabilized not only by the interaction between the alkyl and carbonyl groups but also by the additional interaction between the alkyl group and the naphthalene ring, which is absent in the cyclohexane system. The ΔG^o difference between the methyl and the ethyl ketone ($\Delta\Delta G^o$) in the peri-8 ring is ca. 0.76 kcal/mol, which is somewhat larger than that in a cyclohexane ring (ca. 0.5 kcal/mol).[8] This difference may be attributable to the alkyl-naphthalene interaction mentioned above, which greatly decreases the stability of the **2**-**eb** conformation compared to the *equatorial* isomer of 2-ethylcyclohexanone. Detailed studies on this point as well as the preparations of **1** and **2** will be reported in a full paper.

REFERENCES

(1) V. Balasubramanian, *Chem. Rev*. **66**, 567 (1966).
(2) S. F. Nelsen and J. P. Gillespie, *J. Amer. Chem. Soc*. **95**, 2940 (1973).
(3) T. Kamada, N. Wasada and O. Yamamoto, *Bull. Chem. Soc. Japan* **49**, 275 (1976).
(4) T. Kamada and O. Yamamoto, *Chem. Lett*. 843 (1976).
(5) **1**, mp 158-159°; **2**, mp 97-98°; **1**-8,10,10-*d*$_3$, mp 156.5-157°; **2**-8,10,10-*d*$_3$, mp 96-98°. All compounds gave satisfactory elemental analyses as well as spectral properties consistent with their structure.
(6) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York (1972).
(7) S. H. Grover, J. P. Guthrie, J. B. Stothers and C. T. Tan, *J. Magn. Resonance* **10**, 227 (1973).
(8) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York (1959).