CHEMISTRY LETTERS, pp. 111-114, 1980.

PREFERRED CONFORMATIONS OF 9-MONOSUBSTITUTED DERIVATIVES OF 8,9,10,11-TETRAHYDRO-7H-CYCLOOCTA[de]NAPHTHALENE

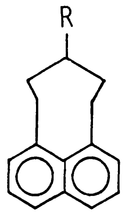
Toshihiro KAMADA* and Osamu YAMAMOTO
National Chemical Laboratory for Industry
1-1 Higashi-Yatabe, Tsukuba, Ibaraki 305

The conformations of 8,9,10,11-tetrahydro-7H-cycloocta[de]naphthalen-9-ol and its esters have been studied based on the NMR spectra. It was found that these compounds assume solely the equatorial-boat (eb) conformations in solution, the peri rings of which are unusually rigid as compared with the conformations previously reported.

Recently, we have studied the conformations of the eight-membered peri rings of the 8,9,10,11-tetrahydro-7H-cycloocta[de]naphthalene system (1),[1,2] the stereochemistry of which is of great interest because it is strained owing to the peri interaction.[3] In our continuing study on the chemistry of the pericyclic naphthalenes, it was found that the peri rings of 8,9,10,11-tetrahydro-7H-cycloocta[de]naphthalen-9-ol (2)[4] and its esters (3 – 6) are unusually stabilized as compared with the compounds previously studied. In this paper, we report the preferred conformations of these 9-monosubstituted compounds by a study of the NMR spectra.

The ^{1}H-NMR spectrum of 8,8,10,10-tetradeuterated derivative of 2 (2-d_4) in $CDCl_3$ gives a singlet (1H) for the C-9 methine proton and a pair of AB quartet (4H) for the benzyl methylene protons. These signals show no change in their appearence on the variation of the sample temperature (from −90 to 190 °C). Thus it is suggested that the molecule of 2 assumes a symmetrical (C_s) conformation, either a boat (eb, ab) or a chair (ec, ac), the peri ring of which is rigid enough not to undergo any conformational change in the temperature range studied (Fig. 1).[5] In the spectrum of the non-deuterated compound 2, the benzyl protons give two complicated absorption bands, each of which consists of eight lines, while the methine proton signal splits into seven lines due to the coupling with the vicinal protons (C-8, C-10). Computer analysis of the spectrum using LAOCOON MBYH program[1] gave the chemical shifts and the coupling constants of these protons which are listed in Table 1.

As can be seen in the table, the interior benzyl proton of 2 is coupled strongly with an adjacent proton (C-8, C-10) (J = 13.30 Hz).[6] This indicates that the peri ring of 2 assumes a boat form in its ground state, because the interior proton in the boat conformation is in trans to an equatorial proton on C-8 (C-10) and such a large J_{vic} value is expected between these two protons.[1,2] The rather broadened signal of the interior benzyl proton (half-width = 5.5 Hz) compared to that of the exterior proton (3.3 Hz) observed in the spectrum of the deuterated compound 2-d_4 is caused by the strong coupling of the interior proton with the equatorial deuterium due to their trans steric arrangement, which strongly supports that 2 exists in the boat conformation (Table 1). Moreover, the splitting patterns of the benzyl protons observed in 2 are also very similar to those of the parent compound 1, which exists in the boat conformation alone.[1] Then the strong vicinal coupling



1; R = H
2; R = OH
3; R = OAc
4; R = OBz
5; R = OTs
6; R = OBs

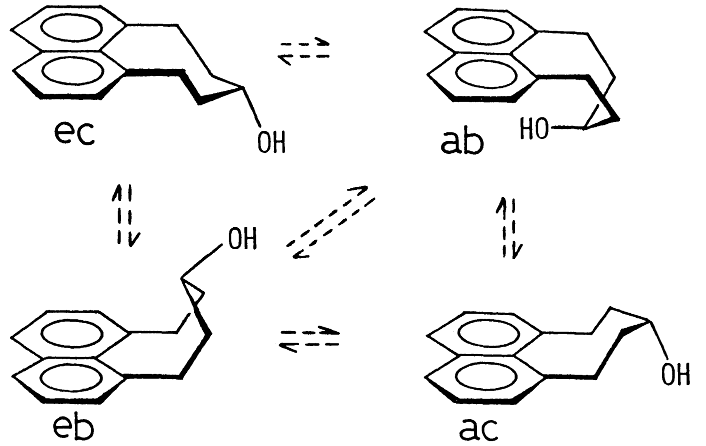


Fig. 1. The boat (eb, ab) and the chair (ec, ac) conformations for compound 2

(J = 11.49 Hz) observed in the C-9 methine proton of 2 is produced by the spin interaction between the diaxial protons on C-9 and C-8 (and C-10),7,8) suggesting that the hydroxyl group on C-9 adopts an equatorial conformation.

Consequently, it is clear that compound 2 exists solely in the equatorial-boat (eb) conformation. This result is consistent with the ^{13}C-NMR spectrum, which is invariant of temperature and contains only three lines for the peri ring carbons of 2 as is shown in Table 2. The chemical shift values obtained for 2 agree very well with the chemical shifts calculated for the eb conformation. Furthermore, it is supported by the experiment using the shift reagent ($Eu(DPM)_3$) — i. e., as can be seen in Table 3, no marked difference is observed in the shift values (Δ_{Eu}) between the axial and the equatorial protons on C-8 (C-10) of 2, which can be adequately explained by the equatorial conformation (eb) as has been suggested by Demarco et al.9) in study on the cyclohexane system.

The unusually greater stability of the boat conformation over the chair observed in 2 results chiefly from much lower torsional energy about the C_7–C_8 (C_{10}–C_{11}) bond of the boat conformation (staggered) than the chair (eclipsed), which is one of the unique features in the 8-membered peri-cyclized naphthalene system.1,2) It is of great interest to find that compound 2 assumes only a single form and the peri ring of 2 is markedly stabilized even at such an elevated (190 °C) temperature. This result is very different from the cases of the other peri-8-membered ring compounds so far studied including the parent compound 11) and 9-oxo derivative 7,2) where the ring inversions readily occur under the usual experimental conditions. This is also in striking contrast to the case of the cyclohexane system, in which the OH substituting group assumes both the axial and the equatorial conformations.10) The marked difference in conformational mobility observed between compounds 2 and 1 (7) could be explained by the fact that the axial-boat (ab) conformation involves a severe steric interaction between the hydroxyl group and the naphthalene nucleus, which come spatially close to each other in the boat conformation.11)

The absence of the ab conformation in 2 is also suggested from the infrared spectrum12)— i. e., the O–H stretching band of 2 measured in highly diluted solution (0.002 mol/l CCl_4) gives an absorption maximum only at 3631 cm^{-1} characteristic of the free hydroxyl group; if the conformation ab actually existed in 2, then the spectrum of 2 would have shown an additional absorption due to the intramolecular interaction between the axial OH group and the π-electrons of the naphthalene nucleus.13)

Then the R-value was calculated from the vicinal couplings about the C_7–C_8 bond given in Table 1 to determine the geometry of the peri-8-membered ring of 2.14) The R-value obtained (1.3) is appreciably smaller than those (2.16) reported for the cyclohexane ring having an almost perfect staggered conformation.15) It is thus considered that the peri ring of 2 is in a somewhat distorted (puckered)

Table 1. ^{1}H-NMR data of the peri ring protons of **2**a)

	Chemical shift δ (ppm)			Coupling constant J (Hz)						
	7ind)	7ex	9ax	7gem	7in,8eq	7in,8ax	7ex,8eq	7ex,8ax	8ax,9ax	8eq,9ax
2b)	4.008	2.957	3.647	−14.83	13.30	5.32	7.05	2.72	11.49	3.75
2-d_4c)	4.01 (5.5)	2.92 (3.3)	3.58 (5.8)	−14.5						

a) The ^{1}H-NMR spectra were measured on a Varian HA-100D spectrometer (at 100 MHz) in chloroform-d (ca. 7 (w/v)%) with TMS as an internal standard. The C-8 (C-10) protons of **2** give an unresolved complex multiplet at δ 1.6 − 2.3, while the hydroxyl proton gives a singlet at δ 1.35 which shifts markedly on the variation of temperature.

b) Obtained from the computer simulation (LAOCOON MBYH program, Ref. 1) of the spectrum of **2**.

c) Obtained by the first-order analysis of the spectrum of **2**-d_4; figures in the parentheses are the values of the line widths of the signals (in Hz).

d) The numbers refer to the carbon positions on the ring and the letters are as follows; in (interior), ex (exterior), eq (equatorial), and ax (axial).

Table 2. ^{13}C chemical shifts of the peri ring carbons of **2**a)

	C-7,11		C-8,10		C-9	
Observed	34.2		38.9		68.4	
Calculatedb)	36.0	30.3	38.3	35.9	65.1	59.7

a) The ^{13}C-NMR spectra were measured on a Varian NV-14 FT NMR spectrometer (at 15.1 MHz) in chloroform-d (ca. 10%); the chemical shifts are expressed in δ (ppm) from internal standard TMS.

b) The calculations were made by use of the data of the parent compound **1** (Ref. 16) and the values of the hydroxyl substituent effect obtained from the data of cis- and trans-4-t-butylcyclohexanols (Ref. 17); figures in the left side are the chemical shifts calculated for the **eb** conformation and those in the right are the values for the **ab** conformation.

Table 3. Effect of the shift reagent (Eu(DPM)$_3$) on the chemical shifts of the peri ring protons of 8,9,10,11-tetrahydro-7H-cycloocta[de]naphthalen-9-ol (**2**) (Δ_{Eu} in ppm)a)

	OH	H_{9ax}	H_{8ax}, H_{8eq}b)	H_{7in}	H_{7ex}
Δ_{Eu}	−44.3	−14.3	−10.2	−4.3	−3.2

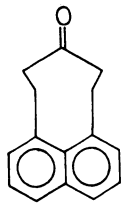
a) The shift values were measured with chloroform-d as a solvent, and the Δ_{Eu} values were calculated according to the method described in the literature (Ref. 9).

b) The C-8 (C-10) methylene signal is not separated by the addition of the shift reagent.

form as a result of the steric repulsion between the interior benzyl protons.

Studies have then been extended to the esters of 2 such as acetate 3 (mp 161.5 – 162 °C), benzoate 4 (mp 121.5 – 122 °C), tosylate 5 (mp 146 – 147 °C(dec.)), and brosylate 6 (mp 123.5 – 124 °C (dec.)). All these compounds showed spectral features similar to those found in the parent alcohol 2. Therefore it is apparent that compounds (3 – 6) also exist in the equatorial-boat (eb) conformations. This gives a further evidence in favor of the eb conformation for the 9-monosubstituted derivatives of 8,9,10,11-tetrahydro-7H-cycloocta[de]naphthalene. Detailed discussion will be reported in a full paper.

References and Notes



7

1) T. Kamada and O. Yamamoto, Bull. Chem. Soc. Jpn., 52, 1159 (1979).
2) T. Kamada and O. Yamamoto, Chem. Lett., 1976, 843.
3) V. Balasubramaniyan, Chem. Rev., 66, 567 (1966).
4) Compound 2 (needles from C_2H_5OH, mp 147.5 – 148 °C) was obtained by the reduction ($NaBH_4$ or $Al(O\text{-}i\text{-}Pr)_3$) of the ketone 7 (Ref. 2); the structure was confirmed by elemental analysis and its spectra.
5) The twist-boat conformation (TB) with a C_2 symmetry is also possible for 2, but it can hardly exist in 2 because it is much more strained than the boat or the chair conformations (Ref. 1).
6) The interior proton of the benzyl methylene group in the 8-membered pericyclized naphthalene system resonates always at lower field than the corresponding exterior proton due to the steric compression effect.
7) The C-8–C-9–C-10 portion of the 8,9,10,11-tetrahydro-7H-cycloocta[de]naphthalene ring has a geometry analogous to that of the cyclohexane system.
8) The C-9 proton of 2 shows the splitting pattern similar to that of the C-1 proton of trans-4-t-butylcyclohexanol (J = 11.1 and 4.3 Hz) having the equatorial OH group; the C-1 proton of the corresponding cis isomer having the axial OH group shows the vicinal couplings of ca. 3.0 and 3.0 Hz (F. A. L. Anet, J. Am. Chem. Soc., 84, 1053 (1962)).
9) P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, J. Am. Chem. Soc., 92, 5734 (1970).
10) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison,"Conformational Analysis," Interscience Publishers, New York (1965).
11) The proximity between the axial group on C-9 and the naphthalene ring in the boat conformation of the 8,9,10,11-tetrahydro-7H-cycloocta[de]naphthalene system is reflected in the NMR spectra of compound 1, where the axial proton on C-9 is appreciably shielded by the effect of the ring current of the naphthalene ring (Ref. 1).
12) The infrared spectrum of 2 was measured on a JASCO IR-G grating infrared spectrometer in carbon tetrachloride with a 50 mm-length quartz cell.
13) M. Ōki, H. Iwamura, T. Onoda, and M. Iwamura, Tetrahedron, 24, 1905 (1968).
14) The calculation was made in the same manner as that described in Ref. 1.
15) J. B. Lambert, Acc. Chem. Res., 4, 87 (1971).
16) T. Kamada and O. Yamamoto, to be published.
17) J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, J. Am. Chem. Soc., 92, 1338 (1970).

(Received November 15, 1979)