CHEMISTRY LETTERS, pp. 843-846, 1976. Published by the Chemical Society of Japan

PROTON MAGNETIC RESONANCE STUDY ON CONFORMATION OF 7,8,10,11-TETRAHYDRO-9*H*-CYCLOOCTA[de]NAPHTHALENE-9-ONE

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The proton magnetic resonance spectra of the title compound (1) have been studied at various temperatures. The changes in variable-temperature PMR spectra of 1 are interpreted in terms of inter-converting boat conformations. The free energy barrier $\Delta G^{\ddagger}$ for the ring inversion was found to be 12.4 kcal/mol. The stereochemical properties inherent in the peri-8 ring in 1 were discussed.

While a number of studies have been reported on the conformation of alicyclic ring systems, little is known about the conformation of pericyclic ring systems of naphthalene, particularly medium-sized ring compounds.[1,2] Recently, we have studied the conformations of peri-8 membered rings in several derivatives of 8,9,10,11-tetrahydro-7*H*-cycloocta[de]naphthalene.[2] These compounds are of much interest in organic stereochemistry, since they involve some strain due to peri-interaction[2,3] and, in contrast to other ring systems, exist only in boat conformations in the ground state.[2] We report here a PMR study on conformation of the title compound (1) which is a novel, 9-oxo-derivative of this peri-8 ring system.[4]

The PMR spectrum[5] for the benzylic (a,b) and 8,10-protons (c,d) of 1 changes markedly with temperature, as shown in Fig. 1. Thus the room-temperature spectrum reveals that molecules of 1 are undergoing ring inversion which results in the exchange between H_a and H_b, and that between H_c and H_d. The benzylic proton signal in the spectrum of 8,8,10,10-tetradeuterated derivative of 1 (1-d_4)[4] changes its appearence from a singlet to an AB quartet with $\Delta\delta$ = 1.55 ppm and J_{AB} = -14.9 Hz on lowering the temperature. The coalescence temperature (T_c) for this spectral change is estimated to be -6.4°C. A first order analysis of the low-temperature spectrum of 1 as an ABCD spin system gives the coupling constant and chemical shift data listed in Table 1.[6]

The relatively simple PMR spectrum of 1 at low temperature indicates that, in the ground state, molecules exist in a conformation which has a mirror plane or two-fold axis passing through C-9 and angular carbon atoms of the naphthalene ring. Molecular model shows that 1 can assume two conformations: boat (B) and chair (C) with a C_s symmetry[7] which are shown in Fig. 2 as well as the changes in geometry associated with interconversion of H_a and H_b, and H_c and H_d. The most likely ground-state conformation of 1 can be determined on the basis of coupling constants. We have previously shown that interior benzylic protons in the peri-8 ring system

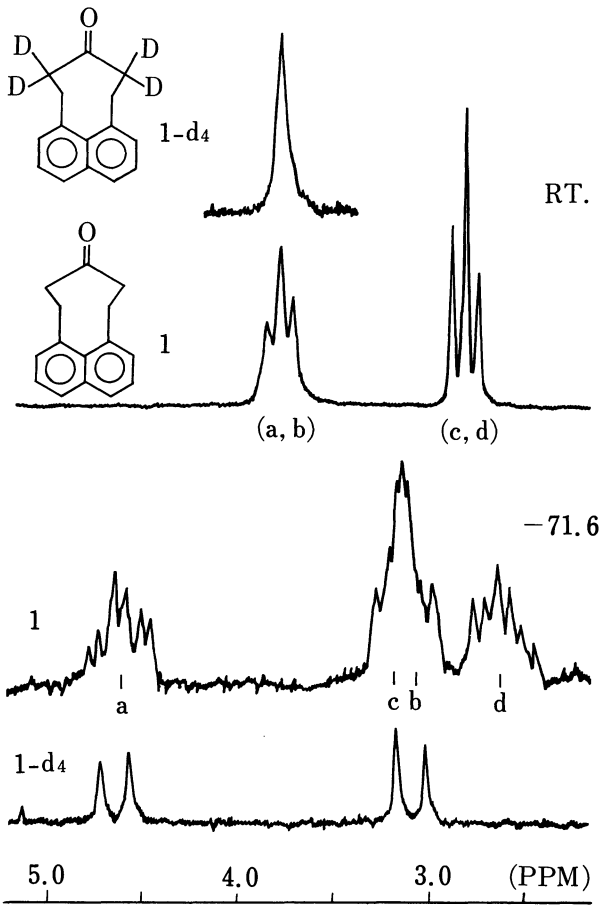


Fig. 1. High (above) and low (below) temperature PMR spectra of aliphatic portion of 1 and its 8,8,10,10-tetra-deuterated derivative (1-d_4).

resonate at lower field than the exterior ccunterparts due to the steric compression effect.[2] As the downfield resonance (H_a) has a large coupling (13 Hz) with a vicinal proton H_d, the dihedral angle for these protons must be close to 0° or 180°. This suggests that the ground-state conformation of 1 is conformation (B), in which the space arrangement of H_a and H_d is trans coplanar.

The predominance of conformation (B) over (C) also seems reasonable, since (B) lacks the eclipsing interactions present in (C), as can be seen in the Newman projections about the C_7-C_8 (or C_{10}-C_{11}) bondings in Fig. 2. The observed coupling constants for 1 are very similar to those for the corresponding positions of the cyclohexanone ring, which is geometrically similar to conformation (B).[8]

Thus, H_d (which is trans to H_a) can be assigned to the equatorial protons alpha to the carbonyl group, and H_c to the axial ones, where the former resonate at higher field than the latter by ca. 0.5 ppm. Although it has already been reported that axial protons alpha to the carbonyl group in several α-substituted cyclanones resonate at lower field than their equatorial counterparts in their epimeric isomers,[9-11] to the best of our knowledge, 1 is the first cyclanone without α-substituent groups, in which axial protons alpha to the carbonyl group are deshielded. This result may be rationalized in terms of σ-π bond overlap,[11] since it is hardly to be expected in the boat conformation of 1 that the chemical shift between H_c and H_d is influenced either by magnetic anisotropies of adjacent C-C bondings, or by the ring current of naphthalene.[12]

Consequently, the spectral changes observed for 1 are interpreted in terms of

Table 1. PMR data of peri ring protons in 1 at −71.6° C (at 100 MHz in $CDCl_3$).

δ_a*	δ_b*	δ_c**	δ_d	J_{ab}*	J_{ac}	J_{ad}	J_{bc}***	J_{bd}	J_{cd}
4.64	3.09	3.17	2.63	-14.8	5.9	13.0	....	7.5	-12.1

* Obtained from the spectra of the deuterated derivative (1-d_4). ** Estimated from the average chemical shift at room temperature and high field shift (δ_d) at a low temperature. *** This coupling constant is small enough not to be resolved.

the interconverting boat conformations. This result is consistent with ^{13}C spectra, which are independent of temperature and consist of only three peaks for the peri ring carbons as shown in Table 2.[13]

Table 2. ^{13}C chemical shifts of 1 at -54.9° C (δ from TMS).

Position	C-1,6	C-2,5	C-3,4	C-3a	C-6a,11a	C-6b	C-7,11	C-8,10	C-9
δ	129.2	129.6	125.5	135.5	136.6	131.2	34.1	46.0	213.9

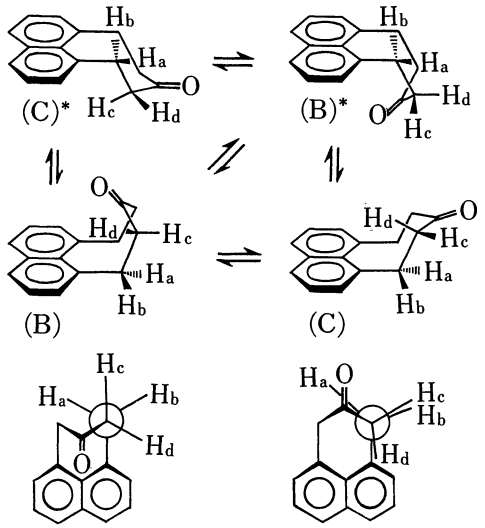
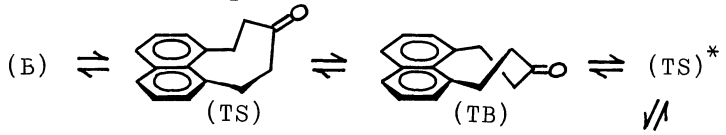


Fig. 2. Conformational changes and Newman projections of boat (B) and chair (C) conformations of 1.

The free energy barrier $\Delta G^{\ddagger}_{Tc}$ for ring inversion is calculated, in the usual manner,[14] from T_c of the AB type benzylic protons in the deuterated derivative (1-d_4), to be 12.4 kcal/mol. Examination of the molecular model shows that the most feasible pathway for the boat inversion in 1 involves pseudorotation of one end of the peri bridge to give the twist-boat conformation (TB) as an intermediate; and here, conformation (C) is not involved.
A possible transition state for this process would be high-energy conformation (TS) in which C-7, -8, -9, and -10 lie essentially in one plane, while C-7, -10, -11, and naphthalene ring lie in another plane.



(* indicates inverted conformations)

It is one of the significant features in the peri-8 ring system of naphthalene that the boat form is the most stable conformation, and this is a unique case which has not yet been observed in other ring systems such as cyclohexanes, where the chair is the predominant conformation. This result is also in striking contrast to the case of structurally analogous 5,6,8,9-tetrahydro-7*H*-cycloheptabenzene-7-one (2), in which the chair predominates over the boat, since the latter is destabilized by steric repulsion between the carbonyl group and benzene ring.[15] It is also noted that the $\Delta G^{\ddagger}$ value for 1 is larger than that for 6,7,8,9-tetrahydro-5*H*-cycloheptabenzene (3) (10.7 kcal/mol).[16] The chemical-shift difference in two benzylic protons in 1 is also much larger than that of the corresponding protons in the latter compound (0.1 ppm) owing to the steric compression effect.[17]

Detailed studies by computer analysis as well as the preparations of 1 will be reported in future.

References and Notes

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4) The syntheses of compound (1, mp 195-196°) and its 8,8,10,10-tetradeuterated derivative (1-d_4, mp 193.5-195°) will be described in full elswhere. All compounds gave satisfactory elemental analyses and spectral properties consistent with their structure.
5) The PMR spectra were recorded on a Varian HA-100D spectrometer at 100 MHz, using $CDCl_3$ as the solvent and TMS as the internal standard.
6) Aromatic region of the spectrum of 1 consists of two temperature-independent multiplets for naphthalene ring protons, which were also analyzed as shown below; $\delta_{1(6)}$ 7.26, $\delta_{2(5)}$ 7.36, $\delta_{3(4)}$ 7.74, $J_{12} = J_{23} = 7.0$, $J_{13} = 2.6$ Hz.
7) Molecular model also shows that 1 can assume the twist-boat conformation (TB) with a C_2 symmetry, but (TB) can hardly exist in the ground state, since it is much more strained than (B) or (C) conformation.
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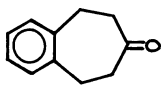
It is shown from the molecular model that the pentamethylene ring of 3 can assume three symmetric conformations; boat and chair (C_s) and twist-boat (C_2), which are geometrically analogous to those of the corresponding conformations in the peri-8 ring system respectively. However, it is reported that most benzo-derivatives including 2 and 3 exist predominantly in the chair.



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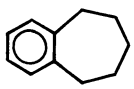

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(Received June 2, 1976)