

RESTRICTED ROTATION INVOLVING THE TETRAHEDRAL CARBON. IV.

RESTRICTED ROTATION OF METHYL GROUPS IN 1-t-BUTYL-1,4-DIHYDRONAPHTHALENE
1,4-ENDOXIDE DERIVATIVES¹

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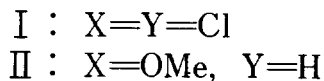
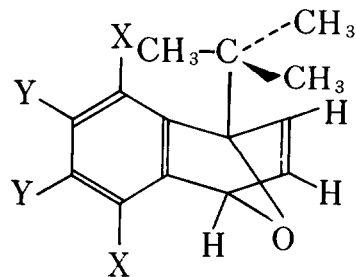
Although there have been ample examples of the restricted rotation, as revealed by the NMR technique, of the t-butyl group², little is known about the restricted rotation of the methyl group in the liquid phase. The only report on the hindered rotation of methyl group seems to us the one by Bartle et al³ which showed the broadening of the methyl signal of 9-methyl-9,9'-bifluorenyl at -60°C. Since the barrier of rotation about the C_{Me}-C_{Bu}^t bond in neopentane is known to be ca. 4.5 Kcal/mole⁴, one may have to lower the temperature very deeply in order to see the restricted rotation in this type of compound by the proton NMR technique in the liquid phase.

During the course of an extension of our study on the restricted rotation of the t-butyl group, we happened to encounter a very interesting phenomenon. Namely, the computer-simulated and observed spectral line shapes⁵ of the t-butyl group in 1-t-butyl-1,4-dihydronaphthalene-1,4-endoxide derivatives agreed well until temperature was lowered to about -60° C, but the agreement became poor when temperature was further lowered. In this paper, we wish to report the experimental results obtained at further lower temperature to present evidence for the restricted rotation of methyl groups, as observed

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by the proton NMR technique.

The compounds I, m.p.95-96°C, and II, m.p. 109-110°C, were prepared by the Diels-Alder reaction between 2-t-butylfuran and 1,2,3,4-tetrachlorobenzene and 1,4-dimethoxybenzene, respectively.⁶ The NMR spectra were recorded on a Varian HA 100D spectrometer and the temperature was measured from the chemical shift difference between the hydroxy proton of methanol and TMS signals and also using a calibrated thermocouple.



The NMR spectrum of the compound I in CS₂-CH₂Cl₂ at room temperature showed a sharp singlet of t-butyl group, whereas that at -60°C showed three sharply separated signals at 1.60, 1.24, and 1.03 ppm from internal TMS for the t-butyl group.⁷ The signals of the methyl group seemed rather broad at -60°C. Therefore the temperature was lowered further to obtain better data of the chemical shifts. To our surprise, however, further broadening of the two methyl signals which were located at the higher field occurred, whereas the line width of the peak at the lowest field little changed

The reasons why the line width of the methyl groups became larger as the temperature was lowered may generally be one or more of the followings

- (1) The rotation of the methyl group is restricted
- (2) The line widths become larger because of the small couplings between the methyl protons and other methine protons, which may be observed when the rotation of the t-butyl group becomes sufficiently slow
- (3) A specific interaction may take place between the solute and the solvent
- (4) Viscosity of the solution is high at lower temperature

If the second reason were the case, the line shapes of the coupled methine protons should have inevitably changed as the peaks of the methyl groups broaden. But actually the line shapes of the three methine protons of the compound I

remain unchanged at all temperatures. Thus the second possibility is ruled out. The third possibility may be neglected, because it is highly improbable to consider the strong interaction between the methyl group and the inert solvent molecules such as carbon disulfide and methylene chloride. The fact that the third peak A remains sharp at the lower temperature may be taken as another piece of evidence supporting the ruling out of this possibility. The fourth reason may also be neglected because of the fairly narrow line widths of the three methine protons and methyl A protons. Therefore, the first reason becomes the choice.

In order to ascertain the possibility of strongly restricted rotation of the methyl groups, the NMR spectra of this compound were measured at further lower temperature using condensed vinyl chloride as a solvent. The results are shown in the Figure. The chemical shift differences among three methyl groups in vinyl chloride are found to be smaller than those in CS_2 - CH_2Cl_2 . Although lower temperature was needed to observe line-broadening with the $\text{CH}_2=\text{CHCl}$ solution than with the CS_2 - CH_2Cl_2 solution, the two peaks B and C became broader as the temperature was lowered and the spectrum at -133°C clearly indicated that the peak C began to separate into some peaks. Thus these spectra at the low temperature clearly suggest that the rotation of the two methyl groups B and C is strongly restricted, although the assignment of the methyl groups is obscure at the present time. The reason for the high barrier to

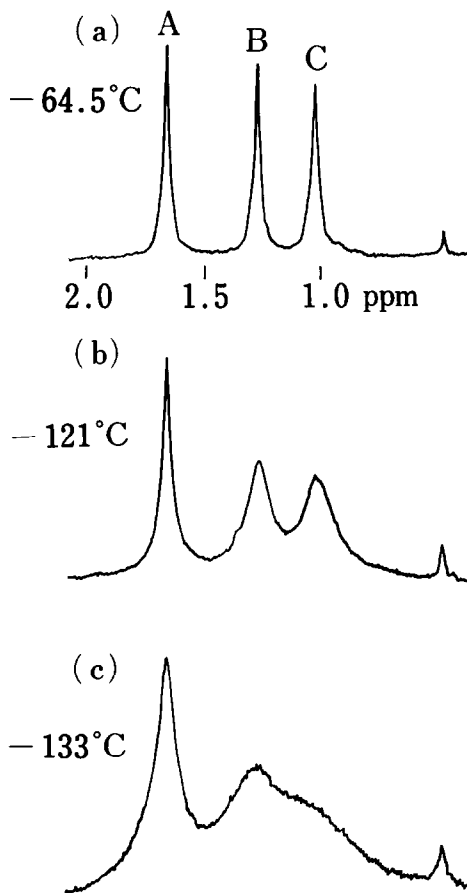


Fig Temperature dependence of the methyl signal of 1-t-butyl-5,6,7,8-tetrachloro-1,4-dihydronaphthalene 1,4-endoxide. A small peak at the extreme right is the ^{13}C satellite of TMS.

rotation must be the severe steric repulsion between the methyl groups and chlorine, etheno, and oxide bridges.

It is evident from the spectra in the figure that the degree in broadening of the two methyl peaks B and C is different from each other, but it cannot be concluded immediately that the rotational barriers of the two methyl groups are different to an appreciable extent, because at present we do not know the chemical shifts of six protons of the two methyl groups.

The NMR spectra of the compound II behave similarly as that of the compound I when the temperature was lowered and thus the rotation of methyl groups of t-butyl part of this compound is also slow at lower temperatures.

We claim that, to the best of our knowledge, these compounds are the first unambiguous examples, in which the slow rotation of a methyl group in the liquid phase is found by the use of proton NMR spectroscopy.

- 1) The preceding paper: M. Ōki and G. Yamamoto, Chem. Lett., 1972, 45.
- 2) a) H. Kessler, Angew. Chem. Internat. Ed., 9, 219 (1970) and references therein. b) M. Ōki and M. Suda, Bull. Chem. Soc. Japan, 44, 1876 (1971). c) J. E. Anderson and H. Pearson, Tetrahedron Lett., 1972, 2779 and references therein. d) C. H. Bushweller, G. U. Rao, W. G. Anderson, and P. E. Stevenson, J. Amer. Chem. Soc., 94, 4734 (1972).
- 3) K. D. Bartle, P. M. G. Bavin, D. W. Jones, and R. L'Amie, Tetrahedron, 26, 911 (1970)
- 4) J. R. During et al reported the barrier to be 4.3 Kcal/mole from the far-infrared studies of the solid (J. Chem. Phys., 52, 2046 (1970), whereas the calculation by Allinger et al showed the barrier in the gas phase to be 4.64 Kcal/mole at 298°K (J. Amer. Chem. Soc., 90, 1199 (1968).
- 5) Presented before the 27th Annual Meeting of the Chemical Society of Japan at Nagoya (October, 1972) and to be published in Bull. Chem. Soc. Japan.
- 6) These compounds gave satisfactory analytical and spectral data.
- 7) Although the relative chemical shifts are different, the spectrum was quite similar to the one shown in the figure.