

Nuclear Magnetic Resonance Study of Exchanging Systems. IX.¹⁾ The Slow Rotation of the Methyl Group in Sterically Overcrowded Compounds

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In order to obtain information about the slow rotation of methyl groups, the ¹H NMR spectra of 9-*t*-butyl-ethenoanthracene and 9-*t*-butyltritycene derivatives were measured at very low temperatures. It was found that the signals of the two methyls of the *t*-butyl group in these compounds show a considerable line broadening at low temperatures, and it was made clear that the rotation of the methyl groups in these compounds is strongly restricted.

A rotation about the sp₃–sp₃ carbon-carbon single bond has for a long time been considered to be free, but recently it was reported²⁾ that, in some sterically overcrowded molecules, the rotation about the sp₃–sp₃ carbon-carbon single bond in bulky groups, such as *t*-butyl and isopropyl groups, is strongly restricted. On the other hand, the rotation of the methyl group, the smallest alkyl group, is especially rapid, and it is well known that the rotation of the methyl group in a quite overcrowded compound, for example, hexamethylbenzene, is not frozen on the NMR time scale at a temperature as low as –150 °C, even in the solid state.³⁾

Most recently, however, the first example of a strongly restricted rotation of a methyl group on the NMR time scale was found in 1-*t*-butyl-1,4-dihydro-1,4-epoxynaphthalene derivatives (1).^{4,5)} Then, in 9-methyltritycene derivatives (2), the methyl rotations were also found to be sufficiently slow and the activation parameters of the rotation were determined from the NMR complete line-shape analyses.^{6,7)} The rotation of a methyl group in the Diels-Alder adduct (3) of 9-methylanthracene with *p*-benzoquinone was also analysed.⁸⁾

In this paper, we will present new examples of the slow rotation of methyl groups in two sterically overcrowded compounds.

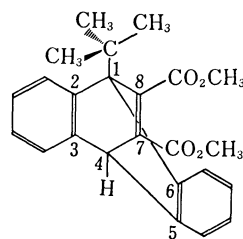
Experimental

Materials. Dimethyl 9-*t*-butyl-9,10-ethenoanthracene-11,12-dicarboxylate (4) was prepared by a Diels-Alder reaction between 9-*t*-butylanthracene and dimethyl acetylenedicarboxylate, heating at 180–200 °C for 10 h in a sealed Pyrex tube. The purification was made by Al₂O₃ column chromatography and three recrystallizations from ethanol. mp 146–148 °C (lit.⁹⁾ mp 182–183 °C).

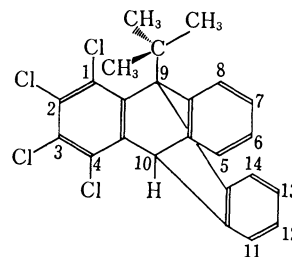
1,2,3,4-Tetrachloro-9-*t*-butyltritycene (5) was prepared by the benzyne reaction of 9-*t*-butylanthracene and 1,2,3,4-tetrachloroanthranilic acid by a method similar to that described in the literature.^{7,10)} mp 277–278 °C. The purification of 5 was done similarly as has been described above.

The purity of these compounds was checked by studying the ¹H NMR spectra.

Measurements. The ¹H NMR spectra of 4 and 5 were recorded on Varian HA-100 D (100.0 MHz) and XL-100-15 A FT (100.1 MHz) spectrometers. The spectra of 4 at 155 and 199 °C were measured by the former spectrometer, using a 5-mmϕ sample tube. The solvent was hexachloro-1,3-butadiene. The measurements at low temperatures were made by means of the latter spectrometer. As the solubility of 4 and 5 is very poor at low temperatures, a 12-mmϕ sample tube was used and a one hundred-fold accumulation was made by means of a pulsed FT method



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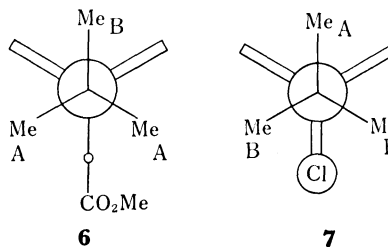


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at very low temperatures. The sample concentration was 0.013 mol/l for 4 and 0.011 mol/l for 5 in the (CS₂+CDCl₃+CD₂Cl₂+CD₃COCD₃+CD₃C₆D₅, 5 : 1 : 2 : 1 : 2) solvent system. The temperature was read by means of a calibrated copper-constantan thermocouple.

Results and Discussion

The ¹H NMR signal of the *t*-butyl group of 4 at room temperature consists of two sharp peaks (δ: 1.733 and 1.874 from TMS), whose intensities are in a 2 : 1 ratio, as is shown in Fig. 1. The higher field peak is assigned to methyl A protons, and the lower to methyl B protons, judging from the line intensities (see the Newman projection 6). This spectrum shows that the rotation of the *t*-butyl group is frozen at this temperature on the NMR time scale. This line shape remains unchanged at temperatures as high as 155 and 199 °C, and no line broadening occurs.* This means that the rotation of the *t*-butyl group of 4 is sufficiently slow at these temperatures.**



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In order to obtain information about the rotation of a methyl group, the spectra of 4 were measured at low temperatures, since the methyl rotation is expected to be strongly restricted by the bulky phenyl and meth-

* Ōki and Suda reported the same result for the spectrum of 4 at 132 °C.⁹⁾

** The activation free energy, ΔG*, of the rotation of the *t*-butyl group in 4 is roughly estimated to be much larger than 30 kcal/mol.

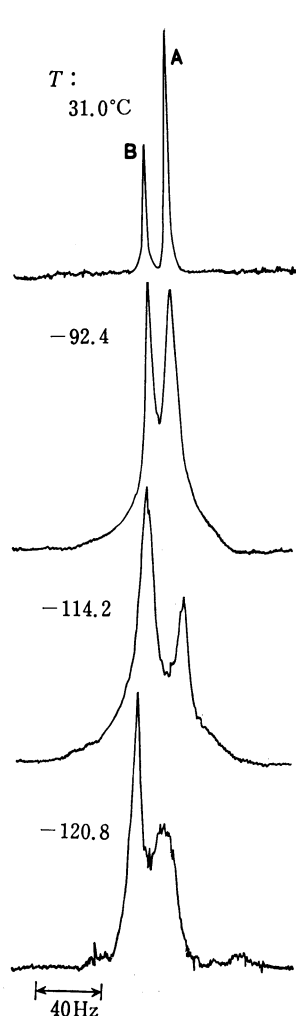


Fig. 1. ^1H NMR spectra of *t*-butyl group in **4** at low temperatures.

oxycarbonyl groups, and since the bicyclo[2.2.2]octatriene skeleton is very rigid. The spectra obtained are given in Fig. 1. Figure 1 clearly shows that the peak height of the higher field signal of methyl A protons is conspicuously reduced as the temperature is decreased. The peak height of the higher field signal of methyl A, which is twice that of the methyl B at room temperature, is almost the same as that of the methyl B at -92.4°C and becomes a half of it at -114.2°C . At -120.4°C , the line width of the A peak is 18 Hz and that of the B peak is 8 Hz. The exceeding peak-height reduction in the signal of the methyl A protons of **4** with the decrease in the temperature clearly shows that the rotation of the methyl A group is strongly restricted at these low temperatures, and that the line-broadening occurs because of the chemical exchange among three *non-equivalent* protons of the methyl group. Figure 1 also shows that the line-broadening in the signal of the methyl B protons occurs to a small extent at such low temperatures. Nevertheless, this fact does not directly indicate a slow rotation of the methyl B group, because the line-broadening in the methoxy protons also occurs and the peak height ratio between the signals of the methyl B and methoxy methyl protons are almost the same at all temperatures. The

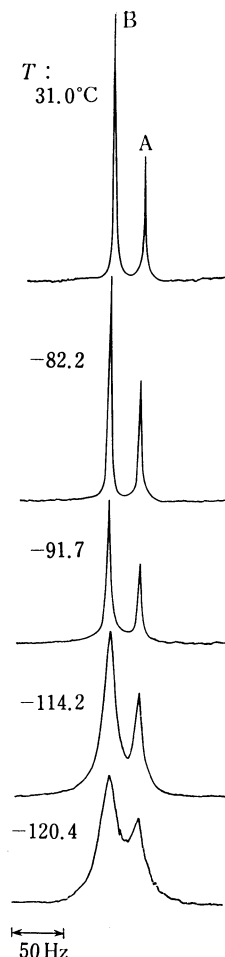


Fig. 2. Temperature-dependent ^1H NMR spectra of *t*-butyl group in **5**.

small line-broadening in the methyl B protons may be due to the high viscosity of the sample and the poor resolution of the NMR measurements at these very low temperatures. The anomalous slow rotation of the methyl A group in **4** indicates that the bis(methoxycarbonyl)etheno bridge is more bulky than the benzo bridge, which is the same conclusion as in the ^{13}C NMR study of the isopropyl analogue.¹⁾

As an extension of the study of the slow rotation of the methyl groups in **4**, the 9-*t*-butyltritycene derivatives (**5**) was also investigated, because the steric hindrance in **5** is expected to be large in the triptycene (tribenzo[b,e,h]bicyclo[2.2.2]octatriene) skeleton.^{6,7,11)} The spectra at low temperatures are shown in Fig. 2. The peak height ratio of the lower-field peak, B, to the higher-field peak, A (the chemical shift δ : 2.296 for B and 2.005 for A from TMS), is 2.0 at 31.0°C , 1.8 at -91.7°C , and 1.4 at -120.4°C . The peak height ratios of the methyl A peak to the bridgehead methine peak (δ : 5.986 from TMS) are almost the same throughout the temperature range from 31.0°C to -114.2°C . These facts mean that the line-broadening due to the chemical exchange occurs at the lower-field methyl signal, which is assigned to the methyl B group surrounded by a phenyl ring and a tetrachlorosubstituted phenyl ring, as is shown in the Newman projection scheme **7**, on the basis of the line intensities.

This result indicates that the rotation of the methyl B group in **5** is also strongly restricted at the low temperatures, although the degree of the restriction seems to be smaller than in the case of **4**, judging from the apparent line shapes.***

Thus, it was made clear that the rotations of the two methyl groups in the *t*-butyl group in **4** and **5** are strongly restricted at low temperatures. It is worth pointing out, from the results in this study, that, in **4** and **5**, the rotation of the methyl groups β -positioned to the bicyclo[2.2.2]octatriene skeleton is severely restricted by the bulky *peri*-substituents, while in the previously reported compounds **2** (e.g., 1,2,3,4-tetrachloro-9-methyltripitycene) and **3**, the rotation of the α -positioned methyl group is restricted also by the *peri*-substituents.⁶⁻⁸⁾ In the case of **1** (e.g., 1-*t*-butyl-5,6,7,8-tetrachloro-1,4-dihydro-1,4-epoxynaphthalene), the rotation of the β -positioned methyl group is restricted by the *oxide bridge* instead of the *peri*-substituent in the 1,4-dihydro-1,4-epoxynaphthalene skeleton.⁵⁾ This interesting difference may be caused by the variety in the geometries of their different skeletons and the

*** Strictly speaking, the comparison between the activation parameters of the rotations of the methyl groups in **4** and **5** is impossible at the present time, because we do not know the exact chemical shifts of the three protons of the methyl groups in question, and so no line-shape analyses can be made.

bonded alkyl groups.

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