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RESTRICTED ROTATION INVOLVING THE TETRAHEDRAL CARBON—VI

SOME DIELS–ALDER ADDUCTS DERIVED FROM 2-t-BUTYLFURAN[1]

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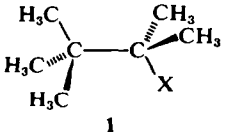
Abstract—1 - t - Butyl - 1, 4 - dihydronaphthalene 1, 4 - endoxide derivatives were prepared by treating 2 - t - butylfuran with some benzynes to see the effect of the bulkiness on the barrier to rotation. The NMR signals of the t-Bu group of these compounds split at low temperature, showing that the rotation about the C_{Bu}–C_t bond was frozen on the NMR time scale. Activation parameters for rotation were obtained by the total line shape analysis. On further lowering of the temperature, the restricted rotation of the Me in t-Bu group was observed. The signals of the Me groups were assigned by taking the chemical shifts and the through-space H-F couplings into consideration.

Barrier to rotation about the C—C single bond of the normal ethan-like molecules are known to be, in general, less than 5 kcal/mole.[2] However, recent reports from various laboratories have revealed that, in hindered case, the barrier to rotation can be as high as 10 kcal/mole.[3] One of the examples is the barriers to rotation of 1, 1, 2, 2 - tetramethylpropyl derivatives (**1**) which were found to be 7 to 11 kcal/mole depending on the substituent X. There are some more papers which report the extraordinarily high barrier to rotation. Brewer *et al.*[5] reported that 1 - t - butyl - 2, 3, 4, 5 - tetrafluorobenzo [b]bicyclo[2. 2. 2]octatriene (**2**) showed two NMR peaks for the t-Bu group with the relative intensities of 2:1 and that these signals coalesced at 120°. Although the barrier to rotation was not mentioned in that literature, the free energy of activation can roughly be estimated as *ca* 20 kcal/mole from the temperature dependent spectra.

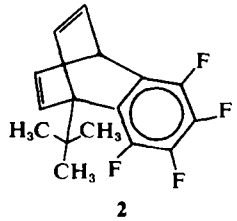
In one of the preceding papers of this series, we showed that the barrier to rotation about the C_{Bu}–C_t bond of dimethyl 1 - t - butyldibenzo [b, e] bicyclo [2. 2. 2] octatriene - 7, 8 - dicarboxylate (**3**) was at least 23 kcal/mole from the fact that two NMR signals for the t-Bu group did not coalesce even at 132°.[6] This estimation has been verified by isolating two rotational isomers of dimethyl 1 - (1 - benzyl - 1 - methylethyl) dibenzo [b, e] bicyclo [2. 2. 2] octatriene - 7, 8 - dicarboxylate (**4**) and finding the Arrhenius activation energy to be 33 kcal/mole.[7]

The extraordinarily high barrier to rotation of the compounds **2**, **3**, and **4** must be attributed to the low potential of the ground state, where three Me groups of the t-Bu group reside comfortably at the apertures made by the three bridges, and the high potential of the transition state, where the three Me groups must come to the fully eclipsed state with the three bridges. At the transition state, the large



1

X = H
F
Cl
Br
I



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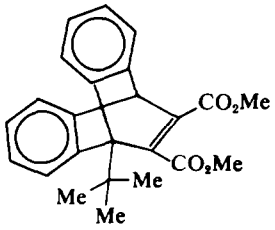

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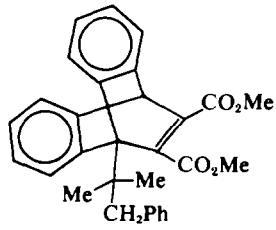

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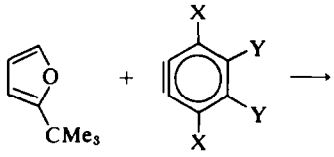
repulsive force may not be relieved to a large extent by changing the bond angles because of the presence of three rigid, bulky bridges in the molecule.

In this connection, it must be interesting to investigate the change in barriers to rotation by changing the bridges to enable the t-Bu group to bend. Replacement of one of the benzo or etheno bridges by oxygen will enable such a case to occur. This paper deals with the results obtained with 1 - t - butyl - 1, 4 - dihydronaphthalene 1, 4 - endoxide derivatives (**5–9**) which are the examples possessing such an oxygen bridge.

EXPERIMENTAL

Syntheses. The 1 - t - butyl - 1, 4 - dihydronaphthalene 1, 4 - endoxides were synthesized by treating **10**[8] with the corresponding benzynes.[9-13]



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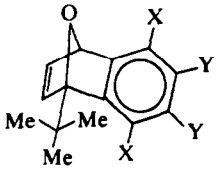


5: X = Y = H
6: X = OCH_3, Y = H
7: X = Y = F
8: X = Y = Cl
9: X = Y = Br.

1 - t - *Butyl* - 1, 4 - *dihydronaphthalene* 1, 4 - *endoxide* **5**. A soln of butyl nitrite (3·11 g; 0·03 mole) and 2 - t - butylfuran (1·87 g; 0·05 mole) in 30 ml ether was refluxed with vigorous stirring and treated with anthranilic acid (1·78 g; 0·013 mole) in 30 ml THF over a period of 3 hr. The mixture was heated for further 3 hr, cooled, and evaporated *in vacuo*. The residue was taken up in hexane, washed with $NaHCO_3$aq and then with NaClaq, and dried over $NaSO_4$. After evaporation, the product was purified by chromatography on alumina. Elution with hexane followed by recrystallization from pentane yielded 1·5 g of pure **5**, m.p. 51·5–52·0°. (Found: C, 83·90; H, 8·04. Calc for $C_{14}H_{16}O$: C, 83·96; H, 8·05%); NMR (CS_2, δ from TMS): 1·21 (9 H, s), 5·40 (1 H, broad s), 6·6–7·3 (6 H, m).

1 - t - *Butyl* - 1, 4 - *dihydro* - 5, 8 - *dimethoxynaphthalene* 1, 4 - *endoxide* (**6**). To a vigorously stirred soln of 1 - chloro - 2, 5 - dimethoxybenzene (3·45 g; 0·02 mole) and 2 - t - butylfuran (3·72 g; 0·03 mole) in 20 ml dry benzene, was added a suspension of phenylsodium (*ca* 2 g; 0·02 mole) in 20 ml benzene over a period of 30 min under N_2. The mixture was stirred for further 5 hr below 20°. Treatment of the product as above gave 2·3 g of colorless crystals, m.p. 109–110°, after recrystallization from hexane. (Found: C, 73·55; H, 7·91. Calc for $C_{16}H_{20}O_3$: C, 73·82; H, 7·44%); NMR (CS_2, δ from TMS): 1·17 (9H, s), 3·72 (3 H, s), 3·75 (3 H, s), 5·60 (1 H, broad s), 6·44 (2 H, s), 6·85 (2 H, broad s).

1 - t - *Butyl* - 1, 4 - *dihydro* - 5, 6, 7, 8 - *tetrafluoronaphthalene* 1, 4 - *endoxide* (**7**) was prepared by treating 2 - t - butylfuran and butyl nitrite in CH_2Cl_2 with tetrafluoroanthranilic acid in purified acetone. This compound was obtained as a liquid after chromatography on alumina. The yield was 55%. (Found: C, 61·40; H, 4·40; F, 28·32. Calc for $C_{14}H_{12}F_4O$: C, 61·77; H, 4·44; F, 27·91%); NMR (CS_2, δ from TMS): 1·18 (9 H, d J = 0·75 Hz), 5·78 (1 H, m), 6·8–7·0 (2 H, m).

1 - t - *Butyl* - 1, 4 - *dihydro* - 5, 6, 7, 8 - *tetrachloronaphthalene* 1, 4 - *endoxide* (**8**), m.p. 95–96°, was similarly prepared by treating 2 - t - butylfuran and butyl nitrite in CH_2Cl_2 with tetrachloroanthranilic acid in purified acetone. The yield was 40%. (Found: C, 49·84; H, 3·50; Cl, 41·79. Calc for $C_{14}H_{12}Cl_4O$: C, 49·74; H, 3·58; Cl, 41·95%); NMR (2:1 CS_2-CH_2Cl_2, δ from TMS): 1·35 (9 H, s), 5·73 (1 H, s), 5·9–6·1 (2 H, m).

1 - t - *Butyl* - 1, 4 - *dihydro* - 5, 6, 7, 8 - *tetrabromonaphthalene* 1, 4 - *endoxide* (**9**), m.p. 128°, was prepared by treating 2 - t - butylfuran and butyl nitrite in CH_2Cl_2 with tetrabromoanthranilic acid in purified acetone. This yield was 35%. (Found: C, 32·69; H, 2·42; Br, 61·98. Calc for $C_{14}H_{12}Br_4O$: C, 32·60; H, 2·34; Br, 61·96%); NMR (CS_2, δ from TMS): 1·33 (9 H, s), 5·72 (1 H, m), 6·8–7·1 (2 H, m).

NMR measurements. NMR spectra at various temps were recorded on a Varian HA-100D spectrometer at 100 MHz. Temperature was determined from the difference in chemical shifts between the signal of the OH proton of MeOH and that of TMS. The temp below −90° was measured using a calibrated copper-constantan thermocouple. The error in temp reading was estimated to be within ±0·5°.[14]

Total line shape analysis. Since the long range coupling between the protons of different Me groups of t-Bu group can be considered to be negligibly small, the calculation of the spectra in the total line shape analysis can be performed using the modified Bloch equations which should be applied to the system without any coupling. The absorption intensity $I(\omega)$ at each frequency is given by the following equation.

$$I(\omega) = \frac{1}{\pi} \mathrm{Re}(-\mathrm{P} \cdot [\mathrm{i}(\Omega - \omega) + \mathrm{D}]^{-1} \cdot 1)$$

where the notation of the matrices (P, Ω, ω, D, 1) refer to the reference of Johnson[14] and Re stands for the real part of the matrices. In the rotation of t-Bu group, the matrix of the probability of the spin transfer is as follows,

$$D = \begin{pmatrix} -\frac{1}{T_2} - \frac{1}{\tau} & \frac{0.5}{\tau} & \frac{0.5}{\tau} \\ \frac{0.5}{\tau} & -\frac{1}{T_2} - \frac{1}{\tau} & \frac{0.5}{\tau} \\ \frac{0.5}{\tau} & \frac{0.5}{\tau} & -\frac{1}{T_2} - \frac{1}{\tau} \end{pmatrix}$$

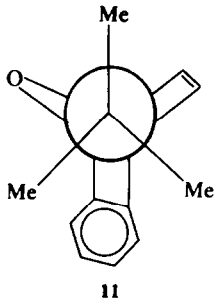
where T_2 and τ are the natural line width and the life time, respectively. The computor program EXNMRO[16] was used in the simulation analysis. The chemical shifts of three non-exchanging methyl groups were found to vary according to the temperature change to some extent. Chemical shifts of t-butyl group of compound **8** were 1·60, 1·24, and 1·03 ppm from the internal TMS at −61·7°, whereas those at −104° were 1·58, 1·21, and 1·01 ppm. Fortunately, however, the important factor which determines the line-shape of the theoretical spectra is not the absolute chemical shifts but the relative ones, the differences in the chemical shifts, which are constant to a good approximation. The natural line width T_2 was included in the calculation, taking advantage of the line width of bridge-head proton of the compounds, or that of the peak of TMS at each temperature.

For a given set of chemical shifts, line width, and life time, theoretical spectra were calculated and plotted in the frequency range involved at the interval of 0·1 Hz and were written by a X-Y plotter. The rotation rate at each temperature was determined by iteration method or by visual fitting of the experimental and theoretical spectra. The agreement between the observed and the calculated spectra was excellent.

RESULTS AND DISCUSSION

The NMR spectrum of **5** in CS_2-CH_2Cl_2 (2:1) at room temperature showed a sharp singlet at 1·20 ppm from the internal TMS, corresponding to nine t-Bu protons. Thus the rotation of the t-Bu group is fast at room temperature on the NMR time scale, making a contrast with the case of **2**. However, the signal became broad as the temperature was lowered and split into two broad signals at −111·1°, the peaks being at 1·10 (6 H) and 1·28 ppm (3 H). Since the bridge head carbon is asymmetric, the t-Bu signal is expected to show three peaks if the rotation is frozen (see **11**). Thus the rotation about the C_{Bu}—C_1 bond in this compound is still taking place on the NMR time scale at this temperature.

The increase in bulkiness of the bridges will result in the increase in repulsive interaction at the transition state: the barrier is expected to increase. Thus methoxy groups are introduced to the benzo group. Compound **6** in CS_2 showed a sharp singlet for the t-Bu group at room temperature, the chemical shift being at 1·17 ppm from the internal TMS. This signal, however, broadened easily when the temperature was lowered and began to split into two signals at −52·0°. Below −61·4°, three Me signals were observed which sharpened on further cooling and observed at 1·42, 1·04, and 0·93 ppm from the TMS. The results indicate that, as expected, introduction of the OMe group increases the barrier to rotation and the rotation in question is now frozen at −76·7° on the NMR time scale.



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In order to obtain further examples of restricted rotation, compounds **7**, **8**, and **9** were prepared. The NMR signals for the t-Bu groups of these compounds in CS_2-CH_2Cl_2 behaved similarly with that of compound **6** when the temperature was varied. Taken **8** as an example, a sharp singlet located at 1·35 ppm from the internal TMS at room temperature began to split into two at −43·7° and three sharply separated signals of almost equal height were observed at 1·60, 1·24, and 1·03 ppm at −61·7° (Fig 1). Computor simulation of the observed curves was carried out using EXNMRO program to see the rate constants of rotation at various temperatures. The results obtained in the case of compound **8** are also shown in Fig 1 for comparison. As for compound **5**, the chemical shifts of three Me groups are unknown. Therefore the chemical shifts were considered as variables in calculation. The best-fit spectra for those observed were obtained when the chemical shifts of 1·48, 1·14, and 1·05 ppm were assumed for the three Me groups.

In the case of **7**, there are spin–spin couplings between Me protons and fluorine nuclei. Therefore, strictly speaking, the total line shape analysis has to be made using density matrix method. Nevertheless, the activation parameters can be approximately estimated using the modified Bloch equation method and setting apparent natural line width to be equal to true natural one plus the line width due to the spin coupling, because a very broad line shape is treated which is caused by the spin exchange in the line-shape analysis and the long range couplings between methyl protons and fluorine nuclei are relatively small (< 1·0 Hz) in **7**.

From the rate constants thus obtained, the Arrhenius' plot yielded a good linear relationship and activation energies were obtained. Putting these data into Eyring's equation gave kinetic parameters as shown in Table 1.

Table 1. Activation parameters for the rotation of the t-Bu group (25°C)

Compound	$\Delta G^{\neq}$ kcal/mole	$\Delta H^{\neq}$ kcal/mole	$\Delta S^{\neq}$ eu	Ea kcal/mole
5	9·9 ± 1·0	7·1 ± 0·6	−9·4 ± 2·3	7·7 ± 0·6
6	11·4 ± 0·8	10·2 ± 0·5	−4·1 ± 1·0	10·8 ± 0·5
7	11·1 ± 1·0	7·6 ± 1·0	−11·8 ± 1·0	8·2 ± 1·0
8	12·0 ± 0·9	10·1 ± 0·6	−6·5 ± 1·0	10·7 ± 0·6
9	11·1 ± 0·8	12·4 ± 0·4	+4·5 ± 1·6	13·0 ± 0·4

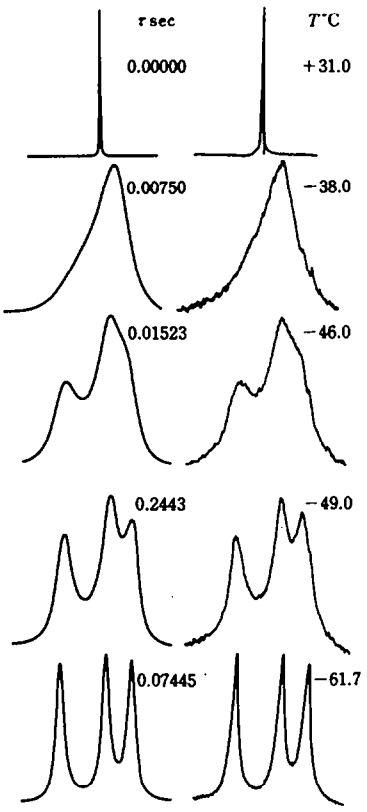


Fig 1. The calculated and observed spectra of compound **8**.

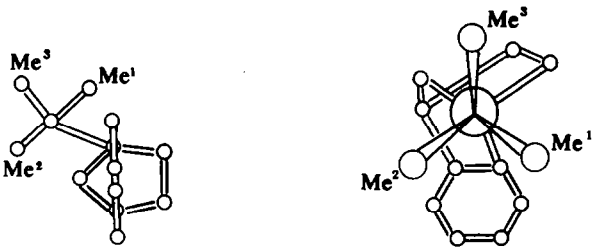
$\Delta H^{\neq}$'s for these compounds are 7 to 12 kcal/mole depending on the substituents at the peri positions and are much smaller than those for compounds **2**, **3**, and **4**. This will mean, as expected, that the t-Bu groups lean over the O atom, the smallest bridge, by changing the bond angles to lower the potential of the transition state. Thus it is now clear that in order to have high barrier to rotation, each of the three bridges must be large in addition to the rigid structure.

The increase in $\Delta H^{\neq}$ on increasing the bulkiness of the substituent at the peri-position is normal in a sense that compounds **5** and **7** give the lowest values and compound **9** the highest. Although, in general, the introduction of a substituent should increase the potentials of both the ground state and the transition state, the effect seems to be greater in the latter as far as the present data concern. On the other hand, the $\Delta G^{\neq}$ values are rather the same except for compound **5**. Therefore, although some compounds give split signals for the t-Bu group at relatively high temperature compared with others, this is so only because the compounds happened to have large difference in chemical shifts among three Me groups. Since the increase and decrease in entoropy of activation may include some systematic errors other than that obtained by the least-square method, it is difficult to present a detailed discussion at the present.

Now the problem remains in assignment of the Me signals. The further importance of assignment arises by finding that two of the three Me signals broadened considerably when the temperature was further lowered. The agreement between the observed and the calculated spectra of the t-Bu group at low temperature was excellent but one point: the observed signal at the highest magnetic field was a little smaller in height than the calculated at very low temperature.* We then assumed that, at still lower temperature, the peak would sharpen, the more accurate chemical shift could be obtained, and the agreement between the observed and the calculated spectra would be better. To our surprise, however, the peak further broadened at the lower temperature, as shown in Fig 3 for the case of compound **8** which is typical. Since the signal at the lowest magnetic field is still sharp, it will not be reasonable to explain the phenomenon by prevention of the isotropic tumbling of the molecules due to the increase in solvent viscosity. Instead, the phenomenon may be attributed to the slow rotation of the Me groups on the NMR time scale.[17]

The chemical shifts of the three Me groups of each compound are listed in Table 2. The molecular model of these compounds, shown in Fig 2, indicate that the C_{Bu}—C_1 bond is tilted by *ca* 20° out of the benzene ring because of the existence of the strained oxygen bridge. As a result one of the Me groups (Me' in Fig 2) comes very close to the planes of both the benzene ring and the etheno bridge. Thus it is predicted that there will be one Me group whose signal appears at a fairly low field compared with other two because of the anisotropic

*Except for the fluorine compound **7**. See the text.



View along the plane of benzene ring View along the C_{Bu}—C_1 axis

Fig 2. Molecular models.

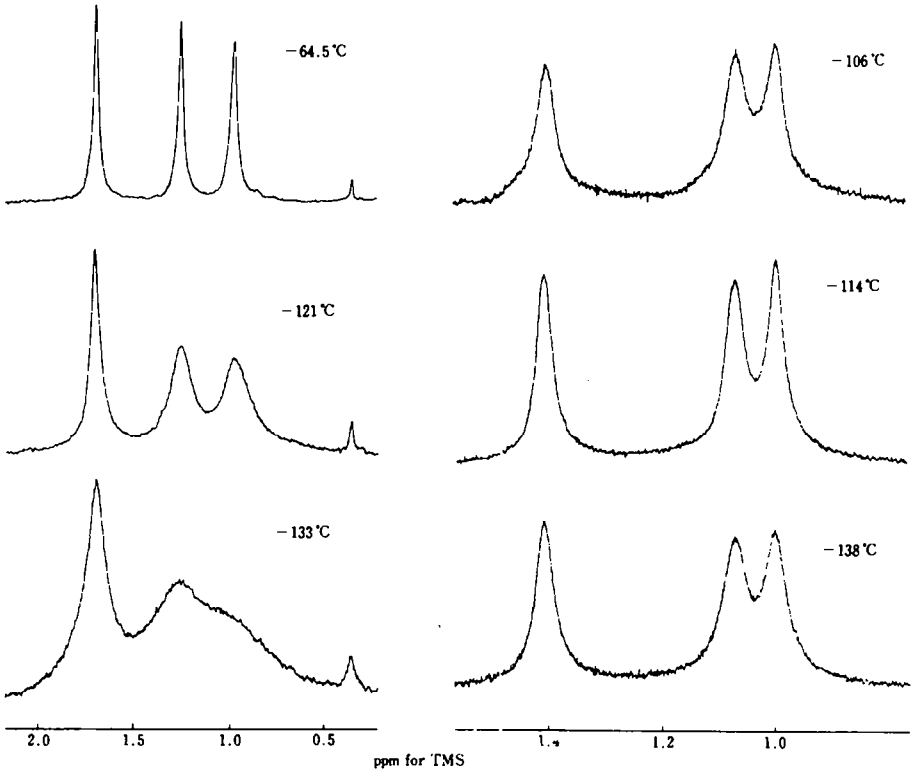


Fig 3. The observed NMR spectra (100 MHz) of t-butyl groups (CH_2:CHCl solution). Right: compound 7. Left: compound 8.

Table 2. Chemical shifts of three methyl groups of 1 - t - Butyl - 1, 4 - dihydronaphthalene 1, 4 - endoxides. (ppm from internal TMS)

Compounds	δ_A	δ_B	δ_C
5	1·48	1·14	1·05
6	1·42	1·04	0·94
7	1·43	1·08	1·03
8	1·60	1·24	1·03
9	1·67	1·28	0·97

effect of those groups. If there is such a signal, that should be assigned to Me^1. In reality compounds have one Me group whose signal appears at the lower field by at least 0·3 ppm than the other two. Thus the signals at δ_A can be assigned to Me^1. The assignment of δ_B and δ_C is much more complicated because the chemical shift differences between δ_B and δ_C are generally small: there are factors to be considered. Since the degree of broadening of the signals at δ_C was largest in every compound examined at very low temperature, the signals at δ_C, and thus those at δ_B, may be assigned to the same

kind of Me group. Inspection of the data in Table 2 reveals that the drift of the chemical shifts of the signals at δ_C is at least, though the substituents on the benzene ring are varied, whereas the signals at δ_A and δ_B move as the substituents vary. The results imply that the signal at the highest magnetic field which is least affected by the substituent may be assigned to the Me group which is located far from the benzene ring. Thus, from the chemical shifts, δ_A, δ_B, and δ_C are assigned to Me^1, Me^2, and Me^3. A support for the above assignment is obtained by considering the long-range ^1H-^{19}F couplings also. At room temperature, the t-butyl signal of **7** showed a doublet due to the coupling with a F nucleus, the coupling constant being 0·75 Hz. Since this coupling constant is the average of three Me groups, those for the Me groups which really show the coupling at the lower temperature are expected to be close to 3/2 of that constant, because one of the Me groups which is located far from the F is not expected to show any appreciable through-space coupling. This is an analogy of the results obtained by Brewer *et al* who reported that, in compound **2**, the coupling constant between the F and the Me groups, which are close to the F, is 2·9 Hz, whereas no visual splitting of the Me, which is far from the F, is observed.[5]

The NMR results of lowering temperature of the solution of **7** are shown in Fig 3 together with those of **8** for comparison. Unfortunately, no splitting due to spin–spin coupling was observed probably because of the viscosity effect of the solution but the following feature of the spectra may be pointed out. At the point of freezing the rotation of the t-Bu group, the height of the signal at the highest magnetic field is the smallest for **8**, whereas that is the largest for **7**. This contrasting feature of the spectra is easily explained when one considers the through-space coupling between ^1H and ^{19}F: the signals at δ_A and δ_B appear short in height because of the presence of unresolvable coupling with F whereas the coupling of the signal at δ_C is negligible. On further lowering of the temperature, the rotation of Me^2 and Me^3 become slow on the NMR time scale to lower the heights of these Me groups in comparison of that of Me^1.

All the data presented above are consistent with the idea that the signals at δ_A, δ_B, and δ_C should be assigned to Me^1, Me^2, and Me^3 in Fig 2. Thus it is concluded that the line broadening of the Me^3 signal occurs at the highest temperature. However, it is not clear yet at the present time whether the rotation of Me^3 is really the slowest or not, because the chemical shifts of the respective hydrogens are unknown.

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