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Barriers to Rotation of Methyl Groups in 4-Methylacridine and Related Compounds. Side-on Steric Bulk of Lone-Pair Electrons

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Rotational barriers of the methyl groups in 1-methylanthracene (**1**), 1-methylanthraquinone (**2**), 1,9-dimethylanthracene (**3**), 4-methylacridine (**4**), 1,4-dimethylanthracene (**5**), and 1,4-dimethylanthraquinone (**6**) were determined from the temperature dependence of the ^{1}H spin–lattice relaxation times in the solids. Correlating the methyl barriers for **1–4** and that for 4-methylphenanthrene (**8**) with the van der Waals radii of the substituents adjacent to the methyl groups yields an estimate of the side-on steric bulk of the lone-pair electrons of the sp^2 nitrogen atom in **4** of 1.1 Å in terms of the van der Waals radius. Close similarity in rotation of the methyl groups in **4** and its HCl salt (**7**) suggests that the hydrogen atom of HCl in **7** does not coordinate tightly to the nitrogen atom in the solid. ^{13}C NMR chemical shifts of the methyl carbon atoms are also investigated from the standpoint of the steric effects of the substituents.

Effective sizes of substituents (typically in terms of the van der Waals radii)[1] in a variety of systems have been obtained from barriers to internal rotation.[2,3] However, studies on the size of the lone-pair electrons of nitrogen reported so far have been mainly concerned with the head-on steric bulk.[2] Therefore, it is of additional interest in connection with the anisotropy[2,4,5] in steric interactions to investigate the side-on steric bulk of the lone-pair electrons.

In the course of our studies on rotation of congested methyl groups, it has been ascertained that barriers to rotation of perimethyl groups in 8-substituted 1-methylnaphthalenes offer a measure of effective sizes of the substituents.[6] In the present work, we have determined barriers to rotation of the 1-methyl groups in 1-methylanthracene (**1**), 1-methylanthraquinone (**2**), 1,9-dimethylanthracene (**3**), 1,4-dimethylanthracene (**5**), and 1,4-dimethylanthraquinone (**6**) from the temperature dependence of the ^{1}H spin–lattice relaxation times (T_1) in the solids in order to elucidate the side-on steric and the buttressing effects on the methyl barriers. Furthermore, by determining barriers to rotation of the methyl groups in 4-methylacridine (**4**) and its HCl salt (**7**), we have estimated the side-on steric bulk of the lone-pair electrons of the sp^2 nitrogen atom in **4**, which are directed parallel to the adjacent C4–CH$_3$ bond in contrast to the 9-hydrogen atom in **1**.

Since the ^{13}C NMR chemical shift is sensitive to steric congestion, it enables us to endorse the relaxation data. In a previous paper,[6] we ascribed the downfield shift of 5.8 ppm for the ^{13}C resonance line of the methyl carbon atoms in 1,8-dimethylnaphthalene (**11**) from that in 1,5-dimethylnaphthalene (**10**) in the solid state to the side-on steric effect or the δ effect in the syn-parallel orientation[7] of the 1,8-dimethyl groups in **11**. The further downfield shift of 1.7 ppm for the ^{13}C resonance signal of the methyl carbon atoms in 1,4,5,8-tetramethylnaphthalene (**12**) compared with that in **11**[6] was ascribed to the remote buttressing effect caused by the steric repulsion between the 4,5-dimethyl groups in **12**. Subsequently, we have also examined the steric effects of the substituents in the present compounds by the ^{13}C NMR chemical shifts of the methyl groups in the solids.

Experimental Section

Compounds **1–6** were prepared and purified by repeated recrystallizations and sublimations. Passing dry HCl through a benzene solution of **4** yielded **7** as yellow precipitates: mp 171.5–174.0 °C (dec). Anal. ($C_{14}H_{12}NCl$) C, H.

Measurements of proton T_1 were performed by using a home-built spectrometer operating at 90.0 or 59.5 MHz described elsewhere.[8] The ^{13}C solid-state NMR spectra for **1–7** and 9-methylanthracene (**9**) were recorded on the same spectrometer operating at 22.6 MHz by using the CPMAS techniques[9] with a mixing time of 5 ms, repetition times of 4–150 s, and a sample-spinning frequency of 3 kHz.

Results

The ^{13}C NMR chemical shifts of the methyl groups in **1–7** and **9** and those of the C9 carbon atoms in **4** and **7** obtained by the present work and the ^{13}C chemical shift of the 4-methyl group in 4-methylphenanthrene (**8**)[10] are given in Figure 1. Experimental T_1 values for **1–4** measured at 90.0 MHz and those for **5** and **6** are plotted against the reciprocal temperature in Figures 2 and 3, respectively. The T_1 values determined at 90.0 and 59.5 MHz for **1** and **3** and those for **4** are plotted against the reciprocal temperature in Figures 4 and 5, respectively. Figure 5 also contains a plot of the T_1 values for **7** obtained at 90.0 MHz.

Discussion

Barriers to Rotation of Methyl Groups. The spin–lattice relaxation rate by a thermally activated reorientation of a methyl group modulating the proton dipolar in-

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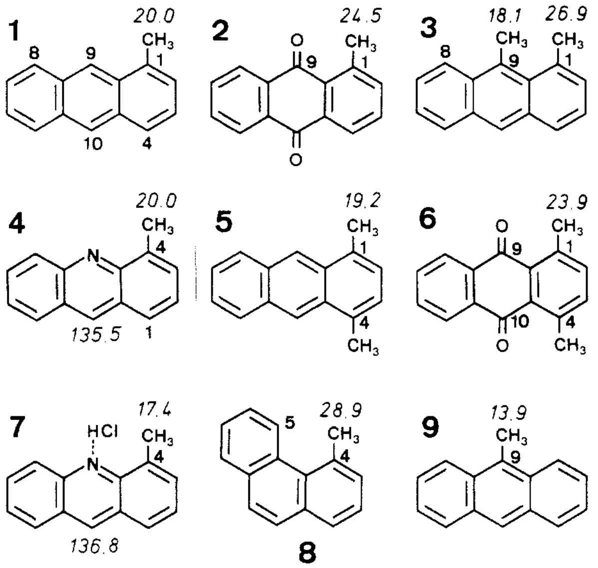

Figure 1. Numbering of atoms in the molecules and ^{13}C solid-state NMR chemical shifts (in ppm) of the methyl carbon atoms for 1–9 and those of the C9 carbon atoms for 4 and 7.

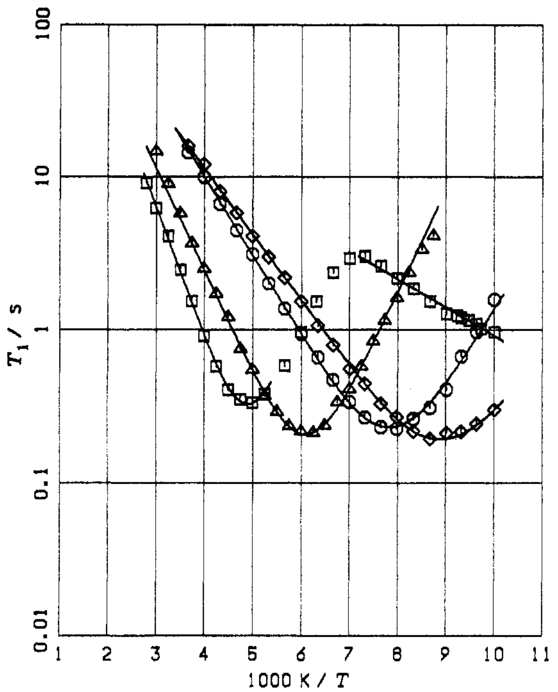

Figure 2. Temperature dependence of the ^1H spin–lattice relaxation times (T_1) at 90.0 MHz for 1-methylanthracene (**1**, ○), 1-methylanthraquinone (**2**, △), 1,9-dimethylanthracene (**3**, □), and 4-methylacridine (**4**, ◇).

teraction with the correlation time τ is given by the Bloembergen–Purcell–Pound (BPP) equations[11]

$$T_1^{-1} = CB(\tau) \tag{1}$$

$$B(\tau) = \frac{\tau}{1 + \omega^2\tau^2} + \frac{4\tau}{1 + 4\omega^2\tau^2} \tag{2}$$

$$C = \frac{N_{\mathrm{Me}}}{N_{\mathrm{all}}} \frac{9}{20} \frac{\gamma^4\hbar^2}{r^6} \tag{3}$$

where ω is the Larmor frequency, r is the intramethyl proton–proton distance, N_{Me} and N_{all} are the numbers of

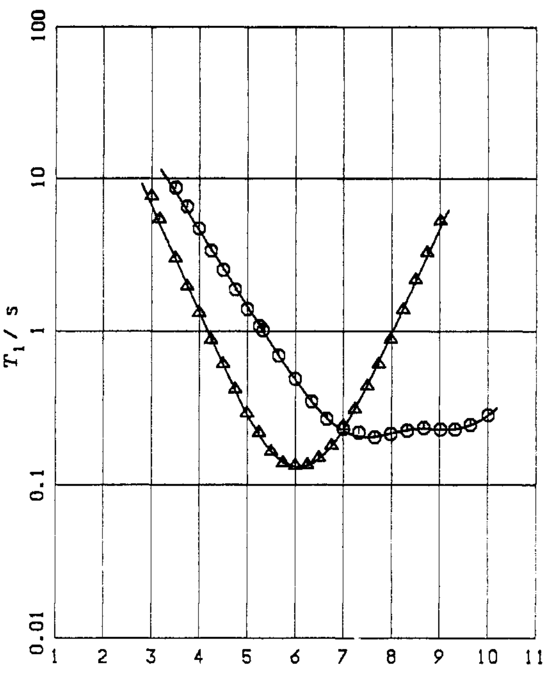

Figure 3. Temperature dependence of the ^1H spin–lattice relaxation times (T_1) at 90.0 MHz for 1,4-dimethylanthracene (**5**, ○) and 1,4-dimethylanthraquinone (**6**, △).

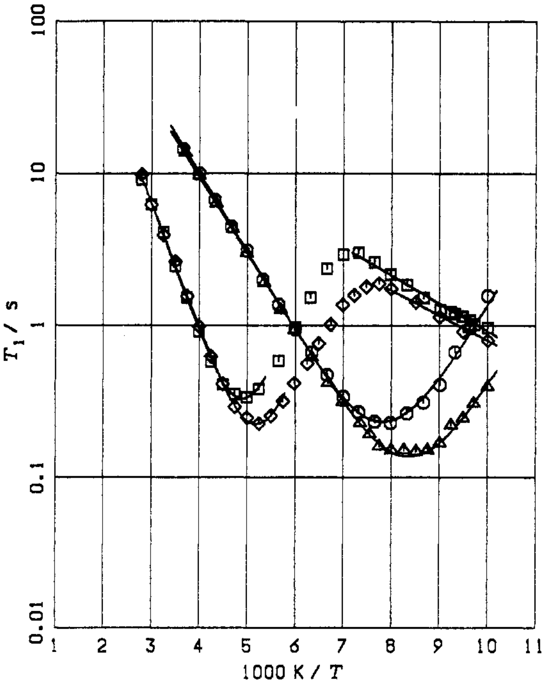

Figure 4. Temperature dependence of the ^1H spin–lattice relaxation times (T_1) for 1-methylanthracene (**1**; ○ at 90.0 MHz, △ at 59.5 MHz) and 1,9-dimethylanthracene (**3**; □ at 90.0 MHz, ◇ at 59.5 MHz).

methyl protons and total protons, respectively, in the molecule. τ is given by the Arrhenius expression

$$\tau = \tau_0 \exp(E_a/RT) \tag{4}$$

where E_a is the activation energy for methyl rotation and τ_0 is the correlation time at infinite temperature.

Each symmetric T_1 curve with a single minimum for **1** (Figures 2 and 4), **2** (Figure 2), **4** (Figures 2 and 5), and **7** (Figure 5) is satisfactorily fitted to eq 1–4 with C, E_a, and τ_0 as adjustable parameters. The T_1 curve for **5** (Figure 3) having two minima of similar intensities can be described by a sum of two BPP equations, and that for **6**

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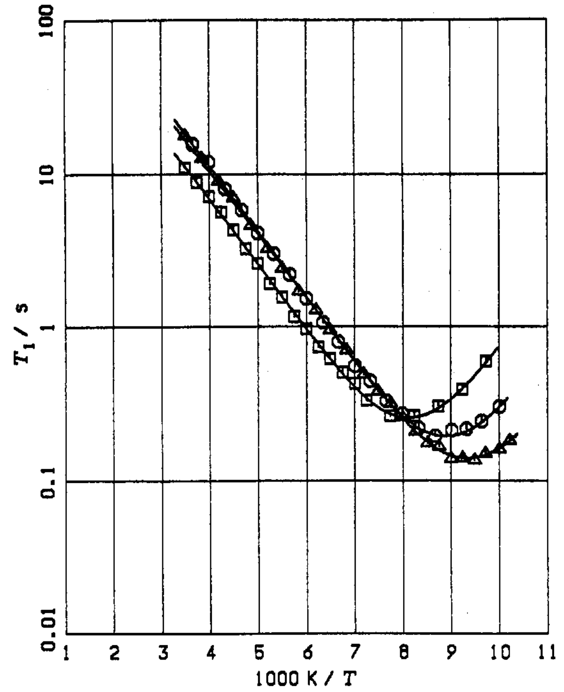

Figure 5. Temperature dependence of the ^{1}H spin–lattice relaxation times (T_1) for 4-methylacridine (4; ○ at 90.0 MHz, △ at 59.5 MHz) and 4-methylacridine hydrogen chloride (7; □ at 90.0 MHz).

(Figure 3) showing slightly different slopes with a sole minimum is well fitted by a sum of two BPP equations with the same C values. The T_1 curve for **3** (Figures 2 and 4) consists of two independent relaxation processes by the 1- and 9-methyl groups. Because of a much lower barrier to rotation of the 9-methyl group in **3**, its T_1 minimum is not observed in the present temperature range. Therefore, the T_1 curves obtained at 90.0 and 59.5 MHz for **3** are fitted to eq 1–4 between 200 and 357 K and between 182 and 357 K, respectively. The activation energy for the 9-methyl group in **3** is determined from the slope between 100 and 130 K (90.0 MHz) or 100 and 125 K (59.5 MHz). The best fit values for the parameters thus obtained are given in Table I, where the C values estimated by eq 3 assuming $r = 1.79$ Å and the observed T_1 minima for **1**–**4** and **7** are also listed. The best fit lines are drawn as solid curves in Figures 2–5.

The C values experimentally obtained for **1**, **2**, and **4**–**7** agree well with the corresponding calculated ones. Agreement is somewhat poor for **3**, probably because exact description is difficult for the spin–lattice relaxation by the 9-methyl group at present. The high-temperature branches of the T_1 curves at 90.0 and 59.5 MHz for **1** (Figure 4), **3** (Figure 4), and **4** (Figure 5) are independent of the field strengths. The ratios of the T_1 minimum at 90.0 MHz to that at 59.5 MHz are 1.58, 1.48, and 1.43 for **1**, **3**, and **4**, respectively, in good agreement with the ratio 1.51 predicted by eq 1 and 2. From these observations we conclude that the spin–lattice relaxation for **1**–**7** is governed by rotation of the methyl group. The activation energy thus obtained can be regarded as the barrier to rotation of the methyl group. Since the best fit parameters determined at the two different field strengths are very close, we employ mainly the activation energy obtained at 90.0 MHz as the methyl barrier.

Side-on Steric Effect on Methyl Rotation. The barrier to rotation of the 4-methyl group in **4** (1.97 kcal mol^{-1}) is slightly but distinctly smaller than those of the 1-methyl groups in **1** (2.36 kcal mol^{-1}) and **10** (2.30 kcal mol^{-1})[6] but is much larger than those of the methyl groups in xylenes (0.4–1.0 kcal mol^{-1}),[12] exhibiting the existence of the steric bulk of the lone-pair electrons of the sp^2 nitrogen atom in **4**.

Table I. Best Fit Parameters to the T_1 Data for 1-7 and Observed T_1 Minima for 1-4 and 7[a]

	ω/MHz[b]	C/(10^9 s^{-2})	E_a/(kcal mol^{-1})	τ_0/(10^{-13} s)	$(T_1)_{\min}$/s[c]
1	90.0	1.72 ± 0.07	2.36 ± 0.05	1.00 ± 0.16	0.234
	59.5	1.93 ± 0.06	2.28 ± 0.03	1.12 ± 0.14	0.148
		1.95[d]			
2	90.0	1.90 ± 0.06	3.07 ± 0.05	0.89 ± 0.14	0.214
		2.34[d]			
3	90.0	1.21 ± 0.06	3.90 ± 0.13	0.72 ± 0.17	0.332
	90.0[e]		0.85 ± 0.08		
	59.5	1.18 ± 0.04	3.76 ± 0.08	0.90 ± 0.15	0.224
	59.5[e]		0.76 ± 0.08		
		1.67[d]			
4	90.0	2.06 ± 0.03	1.97 ± 0.02	1.62 ± 0.13	0.193
	59.5	1.90 ± 0.05	1.90 ± 0.03	2.18 ± 0.22	0.135
		2.13[d]			
5	90.0	1.66 ± 0.19	2.29 ± 0.08	2.41 ± 0.54	
		1.39 ± 0.07	2.17 ± 0.56	0.33 ± 0.88	
		1.67[d]			
6	90.0	1.70 ± 0.05[f]	3.22 ± 0.14	0.98 ± 0.34	
		1.70 ± 0.05[f]	3.14 ± 0.10	0.43 ± 0.17	
		1.95[d]			
7	90.0	1.56 ± 0.04	1.96 ± 0.03	3.60 ± 0.42	0.262
		1.95[d]			

[a] Error is 2.5σ. [b] The Larmor frequencies. [c] Observed T_1 minimum. [d] Calculated value for C by eq 3 with $r = 1.79$ Å. [e] Value for the 9-methyl group. [f] Assumed to be the same value.

The origin of the methyl barrier in the present system should be mainly ascribed to the increase of the van der Waals energy between the methyl group and the adjacent substituent during rotation of the methyl group. According to the description of the MM2 molecular mechanics method,[13] the van der Waals energy (E_{vdw}) between atom i and k is expressed by

$$E_{\text{vdw}} = \epsilon^*[A \exp(-\alpha/p) - Bp^6] \qquad (5)$$

where ϵ^* is a geometrical average of the "hardness" of atom i and k (ϵ_i and ϵ_k), $p = (r_i + r_k)/r$, $r_i(r_k)$ being the van der Waals radius of atom $i(k)$, r is the effective internuclear distance between atoms i and k, and A, B, and α are positive constants. In the repulsive region, the first term is dominant, so the increase of E_{vdw} (ΔE_{vdw}) owing to the decrease of the distance ($-\Delta r$) during methyl rotation can be written by

$$\Delta E_{\text{vdw}} = \alpha\epsilon^* A \exp\left(-\frac{\alpha r}{r_i + r_k}\right)\frac{\Delta r}{r_i + r_k} \qquad (6)$$

where r and Δr are nearly invariant for the atoms concerned. Its derivative with respect to r_i or r_k is positive for $\alpha r/(r_i + r_k) > 1$ in the present system. Thus, ΔE_{vdw} becomes large with the increase of the van der Waals radius of the adjacent substituent.

In the following, we employ usual values of the van der Waals radii for the substituents adjacent to the methyl groups in **1**–**3** and **8**. Since the 1,9-dimethyl groups in **3** take a clashed-gear conformation in the ground state, Charton's minimum value of the methyl group (1.72 Å)[14] is adopted[6,15] as the van der Waals radius of the 9-methyl group in **3**. On the other hand, it is appropriate to use

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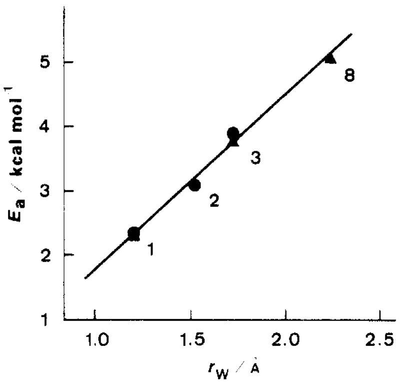

Figure 6. Plot of the experimental barriers (E_a) for the methyl groups against the van der Waals radii (r_W) of the adjacent substituents in 1-methylanthracene (**1**), 1-methylanthraquinone (**2**), 1,9-dimethylanthracene (**3**), and 4-methylphenanthrene (**8**). Filled circles and triangles indicate the barriers determined at 90.0 and 59.5 MHz, respectively. The solid line through the data points denotes the least-squares fit to all the data points for **1**–**3** and **8**.

Charton's maximum value (2.23 Å)[14] for that of the protruding 5-CH group in **8** since the molecular structure of **8** is planar in the crystalline state.[16] As shown in Figure 6, a linear relationship is found between the methyl barriers and the van der Waals radii of the adjacent groups for **1**–**3** and **8**. Plotting the methyl barrier for **4** in Figure 6, we obtain a value of 1.1 Å for the van der Waals radius of the lone-pair electrons of the sp^2 nitrogen atom in **4**. This side-on steric bulk of the lone-pair electrons is much smaller than the head-on one (1.7 Å) estimated from the methyl barrier of 1-methyl-1,10-phenanthrolinium iodide.[17]

From the ^{13}C NMR chemical shifts in **1**–**3** and **8** cited in Figure 1, it is obvious that the ^{13}C chemical shift of the methyl carbon atom moves downfield with increase of the van der Waals radius of the substituent adjacent to the methyl group, though the variation is not linear. The chemical shift of the methyl carbon atom in **4** is equal to that in **1**, consistent with the small difference between the side-on steric bulk of the lone-pair electrons in **4** and that of the 9-hydrogen atom in **1**. Although the two inequivalent methyl groups are detected by the temperature dependence of the ^{1}H spin–lattice relaxation times for both **5** and **6**, no splitting of individual ^{13}C resonance lines is observed for the 1- and 4-methyl carbon atoms in either **5** or **6**.

Buttressing Effects on Methyl Rotation. Two kinds of buttressing effects should be considered for rotation of the 1-methyl group in the anthracene skeleton; the direct steric interaction of the 9-substituent buttressed by the 8-hydrogen atom (the direct buttressing effect) and the remote buttressing effect caused by the steric repulsion between the 4- and 10-substituents. The buttressing effect usually decreases the distance (r) between the methyl group and the adjacent substituent, resulting in an increase of ΔE_{vdw} according to eq 6.

The direct buttressing effect is investigated by comparing the methyl barriers for **1** and **3** with the corresponding barriers for **10** (2.30 kcal mol^{-1})[6] and **11** (3.22 kcal mol^{-1}).[6] The methyl barrier for **1** is nearly equal to that for **10**, whereas the barrier for the 1-methyl group in **3** is 0.68 kcal mol^{-1} larger than that in **11**. Thus, the direct effect in the 1-methylanthracene skeleton is not apparent if the 9-substituent is hydrogen, but increases the barrier of the 1-methyl group if the 9-substituent is a methyl group. It is interesting that similar increment of the methyl barrier for 1-methyltriptycene or 1,4-dimethyltriptycene (0.64 and 0.59 kcal mol^{-1}, respectively) has been observed with introduction of the bridgehead-methyl group(s).[18]

The remote buttressing effect is examined by rotation of the methyl groups in **5** and **6**. The methyl barriers obtained for **5** and **6** agree with the corresponding barriers for **1** and **2**, respectively, within the experimental errors, indicating that the steric repulsion between the 4-methyl group and the 10-hydrogen atom in **5** or the 10-oxygen atom in **6** is not sufficient to manifest the remote buttressing effect. Similarly, no pronounced change has been found in the rotational barriers of the 1-methyl groups in the methyltriptycene system with introduction of the 4-substituents,[18] whereas the rotational barriers of the 9-methyl groups definitely increase by the remote buttressing effect of the 10-substituents.[18,19]

The buttressing effects are also manifest in the ^{13}C chemical shifts of the methyl carbon atoms. The ^{13}C chemical shifts of the methyl carbon atoms in **1** (20.0 ppm) and **10** (20.1 ppm)[6] are very close, while the ^{13}C resonance line of the 1-methyl carbon atom in **3** (26.9 ppm) moves 1.0 ppm downfield from that in **11** (25.9 ppm).[6] The ^{13}C shifts of the 1,4-dimethyl carbon atoms in **5** and **6** are also close to the corresponding shifts of the 1-methyl carbon atoms in **1** and **2**.

Methyl Barrier in the 4-Methylacridine HCl Salt. As indicated in Figure 1, the ^{13}C chemical shifts of the methyl and C9 carbon atoms in **7** appear 2.6 ppm upfield and 1.3 ppm downfield from the corresponding shifts in **4**, respectively. These changes are too small, considering that the positive charge dispersed in the acridine ring should cause notable downfield shifts at least for the ring carbon atoms; for example, a downfield shift as large as 14.87 ppm has been reported for the ^{13}C chemical shift of the C4 carbon atom in 2,4,6-trimethylpyridine upon protonation at nitrogen.[20] Accordingly, the hydrogen atom of HCl is considered to coordinate only loosely to the nitrogen atom in solid-state **7**. Then it is comprehensible that the barrier to rotation of the 4-methyl group in **7** (1.96 kcal mol^{-1}) is nearly equal to that in the parent compound.

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