to equilibrium had elapsed aliquots of each solution were periodically removed and diluted with solvent in exactly the same manner as in the measurement of A_0 for the same solution, and the absorbance (A) at 430 nm was immediately ascertained. When successive aliquots from a given solution showed no further increase in absorbance, the absorbance of the solution was considered to have reached its equilibrium value, A_{eq}; $\Delta A_{eq} = A_{eq} - A_0$. To determine $\Delta A_{100\%}$, the absorbance change that would correspond to complete conversion of **1b** to the selenenic anhydride, the optical density ($A_{100\% \text{ anhyd}}$) of a 4 × 10^{-5} M solution of **2b** in dioxane–0.56 M H_2O was measured at 430 nm, and $\Delta A_{100\%}$ was taken as equal to $A_{100\% \text{ anhd}} - A_0$.

The procedure for studying the equilibration of **1a** with **2a** was generally the same. The initial concentrations of **1a** in the different solutions used ranged from 0.01 to 0.04 M. The concentration of water was 0.14 M. Because **1a** seemed to be somewhat unstable in the presence of 0.01 M H_2SO_4 in this very low water content medium, only a trace of strong acid and rather long reaction times (overnight) were employed.

Kinetics of the Hydrolysis of Selenenic Anhydrides. In connection with the study of the equilibria between selenenic anhydrides and selenenic acids some rates of hydrolysis of both **2a** and **2b** under various conditions were also determined. The general procedure used in carrying out these kinetic runs was that described previously[2b] for studying the kinetics of the hydrolyses of **2a** and **2b** in 60% dioxane.

The experimental first-order rate constants for the hydrolysis of **2b** (5 × 10^{-5} M) in dioxane–0.56 M H_2O in the presence of 0.01 M CF_3CO_2H at various temperatures were as follows (temperature, $k_1 \times 10^3$, s^{-1}): 15.0 °C, 1.22 ± 0.07; 20.0 °C, 1.77 ± 0.08; 25.0 °C, 2.59 ± 0.20; 33.9 °C, 5.18 ± 0.50. For the hydrolysis of **2a** in the same reaction medium with 0.01 M sulfuric acid as catalyst the rate constants were as follows (temperature, $k_1 \times 10^3$, s^{-1}): 15.0 °C, 0.20 ± 0.001; 20.0 °C, 0.31 ± 0.004; 25.0 °C, 0.39 ± 0.009; 30.0 °C, 0.48 ± 0.01; 33.9 °C, 0.62 ± 0.01. The rate of hydrolysis of **2a** in the presence of 0.01 M CF_3CO_2H was much slower than in the presence of the same concentration of sulfuric acid, k_1 being only 2.5 × 10^{-6} s^{-1} at 25 °C. As already noted, this very slow rate was the reason that H_2SO_4, rather than CF_3CO_2H, was used as acid catalyst for establishment of the equilibrium between **2a** and **1a**.

Rates of hydrolysis of **2a** in the presence of 0.01 M perchloric acid were also measured at 25 °C in dioxane containing from 5% to 40% water. The first-order rate constants were as follows (% water, $k_1 \times 10^3$, s^{-1}): 40, 4.2; 20, 2.4; 10, 1.6; 5, 1.2.

Registry No. **1a**, 56790-60-4; **1b**, 84250-81-7; **2a**, 84250-76-0; **2b**, 84250-80-6.

Barriers to Rotation of Peri Methyl Groups in 1,8-Dimethylquinolinium Iodide and Related Compounds

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To investigate peri steric interactions in heterocyclic compounds, rotational barriers of methyl groups in 1,8-dimethylquinolinium iodide (**3**) and related compounds are determined from the temperature dependence of the ^1H spin–lattice relaxation times in the solid state. The barrier to rotation of the 8-methyl (C_{sp^2}–CH_3) group (3.41 ± 0.26 kcal mol^{-1}) in **3** is in good agreement with that in 1,8-dimethylnaphthalene, whereas the barrier to rotation of the 1-methyl (N_{sp^2}–CH_3) group (2.42 ± 0.07 kcal mol^{-1}) in **3** is appreciably smaller. Similarly, the barriers obtained for methyl groups bonded to N_{sp^2} atoms are smaller than the respective barriers for methyl groups bonded to C_{sp^2} atoms in the corresponding carbon systems, suggesting facile bending of the N_{sp^2}–CH_3 groups in the rotational transition state. Also, the steric effect of the lone-pair electrons of the sp^2 nitrogen atom in 1-methyl-1,10-phenanthrolinium iodide (**5**) on the rotation of the 1-methyl group is estimated to be 1.7 Å in terms of the van der Waals radius. This value is notably larger than that (1.1 Å) for the side-on steric effects of the lone-pair electrons of the sp^2 nitrogen atom.

There is continuing interest in steric strain in overcrowded molecules.[1] The magnitude of steric strain between substituents at the peri positions in naphthalene derivatives has been investigated extensively.[2] Quinoline derivatives are also of interest since they have similar geometry. Packer et al.[3] have estimated the steric strain in methylnaphthalenes from the rates of the Menschutkin reaction of methyl iodide with quinoline derivatives in nitrobenzene, assuming the "strained homomorph" concept of Brown.[4] To our knowledge, however, the "strained homomorph" assumption has not been investigated quantitatively. In this regard, a comparison of the barrier to rotation of the 8-methyl group in 1,8-dimethylquinolinium iodide (**3**) with that of the methyl groups in 1,8-dimethylnaphthalene (**9**) reported previously should reveal differences in steric interactions in the two ring systems.[5-8]

Furthermore, it is of interest to determine whether there is any difference in the barriers to rotation of the 1-methyl and 8-methyl groups in **3**. For rotation about N_{sp^2}–C_{sp^3} bonds, Balaban et al.[9] studied hindered rotation of the

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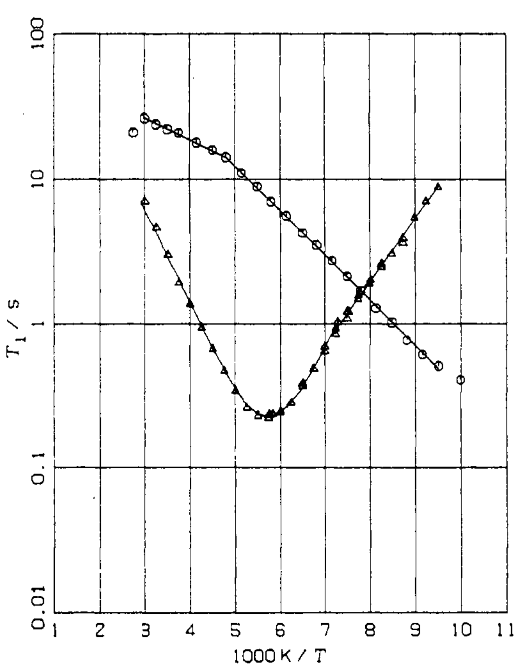

Figure 1. Temperature dependence of T_1 for 1-methyl-1,8-naphthyridinium iodide (1) (○) and 1-methylquinolinium iodide (2) (△).

N-alkyl groups in 1-alkyl-2,4,6-trimethylpyridinium cations using ^{13}C DNMR in solutions. The observed barriers were significantly higher than those reported for $C_{sp^2}-C_{sp^3}$ bonds in related compounds, and they concluded that this result was probably due to the shorter $N_{sp^2}-C_{sp^3}$ bond length. In force-field calculations, however, the standard $N_{sp^2}-C_{sp^3}$ bond length in azoalkanes (1.480 Å)[10,11] is only slightly shorter than the $C_{sp^2}-C_{sp^3}$ bond length (1.496 Å).[12] In the solid state, the $N_{sp^2}-CH_3$ bond lengths in 10-methylacridinium iodide (1.50 Å)[13] and 1,1′-dimethyl-4,4′-bipyridinium tetracyanonickelate(II) (1.51 Å)[14] or tetrachlorocuprate (1.474 Å)[15] are close to or only slightly shorter than the corresponding $C_{sp^2}-CH_3$ bond lengths in 9-methylanthracene (1.501 Å)[16] and 4,4′-dimethylbiphenyl (1.503–1.537 Å).[17] Therefore, factors other than bond length affecting the barrier heights should be taken into consideration.

We have determined the rotation barriers of the methyl groups in 1-methylnaphthyridinium iodide (**1**), 1-methylquinolinium iodide (**2**), 1,8-dimethylquinolinium iodide (**3**), 1-(methyl-d_3)-8-methylquinolinium iodide (**4**), 1-methyl-1,10-phenanthrolinium iodide (**5**), and 1-methylbenzo[*h*]quinolinium iodide (**6**) by measuring the temperature dependence of the proton nuclear spin–lattice relaxation times (T_1) in solids. Comparison of these rotational barriers with those of the corresponding hydrocarbons[5–7] shows how steric congestion of peri methyl rotation in heterocyclic molecules is relieved. Steric effects of lone-pair electrons on barriers to rotation of methyl groups are also discussed. In the following sections, a methyl group bonded to an sp² N or C atom is abbreviated as $N_{sp^2}-CH_3$ or $C_{sp^2}-CH_3$.

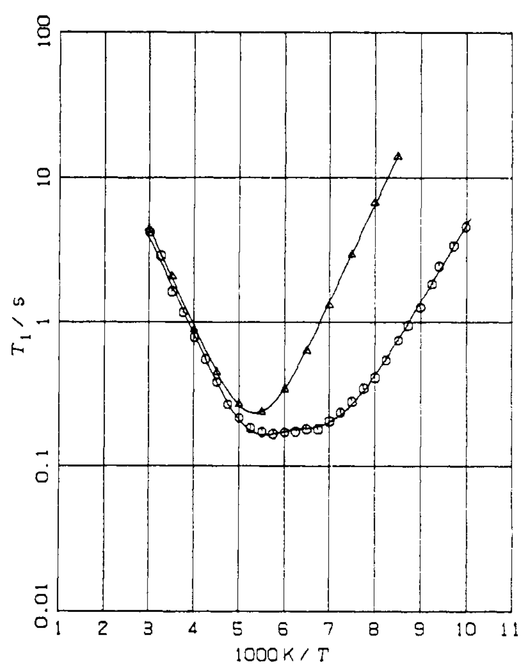

Figure 2. Temperature dependence of T_1 for 1,8-dimethylquinolinium iodide (3) (○) and 1-(methyl-d_3)-8-methylquinolinium iodide (4) (△).

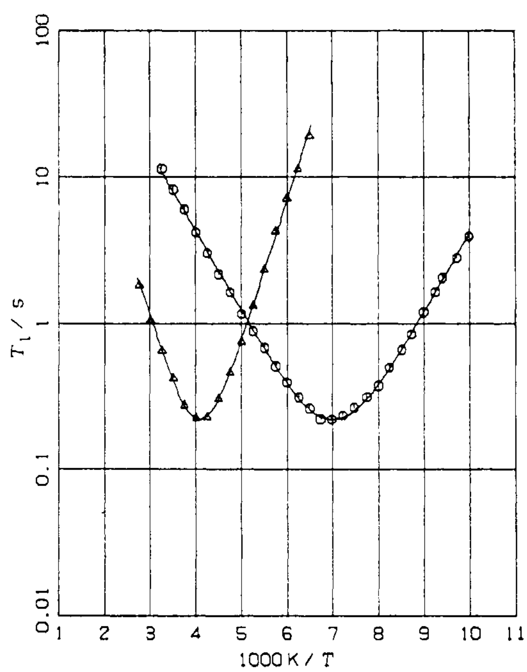

Figure 3. Temperature dependence of T_1 for 1-methyl-1,10-phenanthrolinium iodide (5) (○) and 1-methylbenzo[*h*]quinolinium iodide (6) (△).

Experimental Section

Compounds **1**–**6** were prepared by reaction of the parent heterocyclic compounds with methyl iodide and purified by repeated recrystallizations.[18] The solid samples were degassed by several freeze–pump–thaw cycles in glass tubes. Measurements of T_1 were performed with a home-built pulsed spectrometer

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Table I. Best-Fit Values for the Geometrical Factors (C), the Activation Energies (E_a), and the Correlation Times at Infinite Temperature (τ_0) to the T_1 Data for 1–10[a]

compd	$10^{-9}C$, s^{-2}	E_a, kcal mol^{-1}	$10^{13}\tau_0$, s
1		0.65 ± 0.03[b]	
		1.44 ± 0.03[c]	
2	1.76 ± 0.06[d]	2.96 ± 0.06[d]	2.2 ± 0.4[d]
		1.98 ± 0.08[e]	
3	1.82 ± 0.20[f]	2.42 ± 0.07[f]	2.7 ± 1.0[f]
	1.70 ± 0.22[g]	3.41 ± 0.26[g]	1.2 ± 0.7[g]
4	1.72 ± 0.06	3.14 ± 0.05	2.3 ± 0.3
5	1.83 ± 0.04	2.49 ± 0.03	1.7 ± 0.2
6	1.83 ± 0.08	4.44 ± 0.08	1.2 ± 0.2
7[h]	1.90 ± 0.05	1.90 ± 0.03	2.2 ± 0.2
8[i]	3.76 ± 0.17	2.30 ± 0.05	1.7 ± 0.3
9[i]	3.76 ± 0.17	3.22 ± 0.05	1.0 ± 0.2
10[j]	1.97 ± 0.08	5.05 ± 0.13	1.3 ± 0.4

[a] Error is 2.5σ (variance). [b] Value determined from the branch above 190 K. [c] Value determined from the branch below 190 K. [d] Values determined above 138 K. [e] Value determined below 138 K. [f] Values for the N_{sp^2}–CH_3 group. [g] Values for the C_{sp^2}–CH_3 group. [h] Reference 7. [i] Reference 5. [j] Reference 6.

operated at 90 MHz by methods described previously.[19]

Results and Discussion

Determination of Rotational Barriers of Methyl Groups. Experimental T_1 values are plotted against reciprocal temperature in Figures 1–3. The temperature dependence of T_1 can be described by the Bloembergen–Purcell–Pound (BPP) and Arrhenius expressions[20] (eq 1–4).

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

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

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

where ω is the Larmor frequency, r is the intramethyl proton–proton distance, and N_{all} and N_{Me} are the numbers of total protons and methyl protons in the molecule, respectively. The parameter τ is given by the expression

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

where E_a is the activation energy for methyl rotation.[6]

Since the full T_1 curve was not observed for **1** in the temperature range studied, the activation energy was determined by a least-squares fit of two regions of the high-temperature branch to a straight line. Slight gradient changes at 190 K in the curve for **1** and 138 K for **2** are ascribed to phase transitions. The curve for **2** between 138 and 333 K and the curves for **4**–**6** were fitted to eq 1–4, taking C, E_a, and τ_0 as adjustable parameters. The activation energy for **2** below 138 K was determined by a least-squares fit to a straight line. The curve for **3** was fitted to a combination of two BPP functions. The best-fit values for the parameters are given in Table I, and the best-fit values are shown as solid lines in Figures 1–3.

Experimentally determined barriers for the methyl groups in **1**–**3**, **5**, and **6** are shown in Figure 4 together with those obtained previously for related compounds **7**–**10**. Assignment of the higher barrier in **3** to the C_{sp^2}–CH_3 group was made by reference to the result for **4** (Table I). In Figure 5 the rotation barriers of the N_{sp^2}–CH_3 groups in **1**–**3** and **5** are plotted against those of the corresponding C_{sp^2}–CH_3 groups in **7**–**10**.

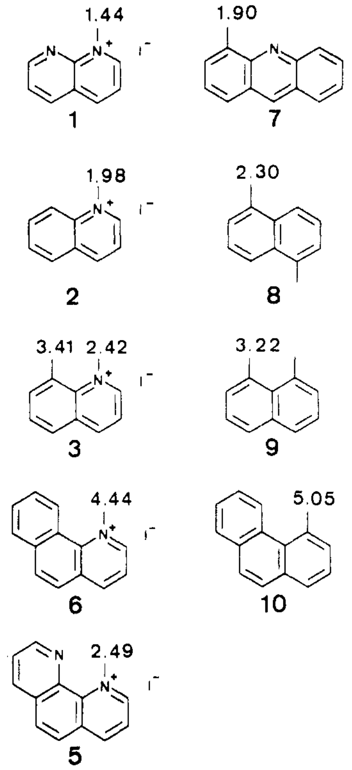

Figure 4. Experimental barriers to rotation of the methyl groups (kcal mol^{-1}).

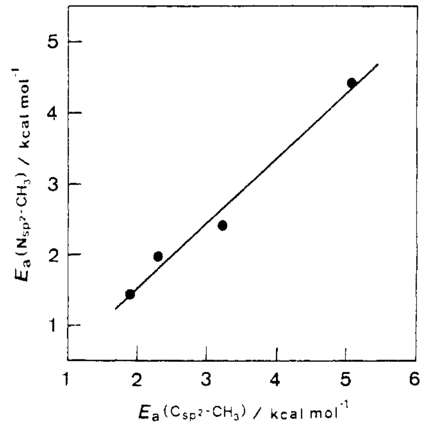

Figure 5. Plot of the rotation barriers of the N_{sp^2}–CH_3 groups in **1**–**3** and **5** against those of the corresponding C_{sp^2}–CH_3 groups in **7**–**10**.

Barriers to Rotation of C_{sp^2}–CH_3 Groups in 3 and 9. From Table I, both the barrier and τ_0 for rotation of the C_{sp^2}–CH_3 group in **3** are in fair agreement with those in **9**, indicating that the rates of rotation are nearly equal. Moreover, the geometrical factors C, with allowance for the number of protons in **3** and **9**, are also similar. These results indicate that the conformations of the adjacent methyl groups in both molecules are similar in both the ground states (clashed-gear conformation) and the rotational transition states (meshed-gear conformation).[21-23]

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It is somewhat surprising that the observed barriers to rotation of the C_{sp^2}–CH_3 groups in **3** and **9** do not reflect the difference in bonding of the adjacent methyl groups. Owing to steric compression of the C_{sp^2}–CH_3 group and the adjacent 2-hydrogen atom, the N_{sp^2}–CH_3 group in **3** and the C_{sp^2}–CH_3 group in **9** cannot have a large variety of ground-state conformations. In the rotational transition state of the C_{sp^2}–CH_3 group the in-plane bending of the adjacent N_{sp^2}–CH_3 group in **3** may not differ appreciably from that of the C_{sp^2}–CH_3 group in **9**, and the barriers to rotation of the C_{sp^2}–CH_3 groups become similar.

Barriers to Rotation of N_{sp^2}–CH_3 Groups. The barriers to rotation of the N_{sp^2}–CH_3 groups in **1**, **2** (below 138 K), **3**, and **6** are lower by about 0.5–0.8 kcal mol^{-1} than those of the C_{sp^2}–CH_3 groups in **7**, **8**, **9**, and **10**, respectively (Figures 4 and 5, Table I). The only exception to this trend is the N_{sp^2}–CH_3 group in **2** in the region 138–333 K compared with the C_{sp^2}–CH_3 group in **8**, which is discussed later.

In considering the reason for these smaller barriers to rotation of the N_{sp^2}–CH_3 groups, the different barriers for the N_{sp^2}–CH_3 and C_{sp^2}–CH_3 groups in **3** are worthy of note. The ground-state conformations in **3** and **9** are considered to be similar, yet it is not likely that the ground state of the N_{sp^2}–CH_3 group in **3** is destabilized compared with that of the C_{sp^2}–CH_3 group in **3** and/or **9**. It is also not likely that intermolecular effects could cause dissimilar barriers to rotation for the adjacent methyl groups in **3**, because the barriers to rotation of the C_{sp^2}–CH_3 groups in **3** and **9** differ only slightly. Therefore, there must be some mechanism for avoiding the steric compression in the rotational transition state of the N_{sp^2}–CH_3 group. The steric repulsion between the rotating methyl group and the adjacent 2-hydrogen atom in the rotational transition state of either the C_{sp^2}–CH_3 or the N_{sp^2}–CH_3 group decreases from that in the ground state. Therefore, if the N_{sp^2}–CH_3 bond is more flexible than the C_{sp^2}–CH_3 bond, the N_{sp^2}–CH_3 group in **3** may bend toward the 2-hydrogen atom to reduce the steric repulsion between the methyl groups, and consequently the rotational barrier for the N_{sp^2}–CH_3 group should become smaller than that for the C_{sp^2}–CH_3 group.

The observed smaller barriers of the N_{sp^2}–CH_3 groups compared with those of the corresponding C_{sp^2}–CH_3 groups shown in Figure 4 are therefore ascribed to facile angle bending of the N_{sp^2}–CH_3 bond in the rotational transition state. As shown in Figure 5, there is good correlation between the barriers to rotation of the N_{sp^2}–CH_3 groups and those of the corresponding C_{sp^2}–CH_3 groups, indicating that these heterocyclic compounds are slightly less strained homomorphs of the corresponding carbocyclic compounds.

As to the larger barrier for the N_{sp^2}–CH_3 group in **2** in the region 138–333 K compared with that in **8**, the observed phase transition in **2** at 138 K indicates a change in crystal packing with a concomitant change in barrier height to internal rotation of the methyl group. In the low-temperature phase the N_{sp^2}–CH_3 group in **2** may become coplanar with the quinoline ring as observed for **8**[24] and **9**.[21] In this phase, the barrier to rotation of the methyl group in **2**, being mainly due to peri steric effects, is lower than that in **8**. On the other hand, in the high-temperature phase the N_{sp^2}–CH_3 group is bent out of the ring plane, and the barrier does not come solely from the peri hydrogen. The phase transition in **1** at 190 K is also of interest. Jones and Wagstaff[25] suggested the existence of neighboring-group participation by one nitrogen atom in the reaction of methyl iodide with the other nitrogen atom of 1,8-naphthyridine. If the methyl group in **1** is linked to or swings between the two nitrogen atoms above 190 K in the solid state, the change in molecular geometry may bring about the phase transition and the change in barrier height. Crystallographic studies should be made to confirm this conjecture. For the compounds studied by Balaban et al.,[9] bond distortion cannot accommodate the steric strain caused by the 2- and 6-methyl groups.

Steric Effect of Lone-Pair Electrons on Methyl Rotation. The side-on steric van der Waals radius of the lone-pair electrons of an sp^2 nitrogen atom appears to be 1.1 Å on the basis of the barriers to rotation of the methyl groups in 4-methylacridine (**7**) and related compounds.[7] The lower barrier to rotation of the methyl group in **1** than that in **2** in the low-temperature phase also demonstrates the small side-on steric bulk of the lone-pair electrons.

The similar barriers to rotation of the N_{sp^2}–CH_3 groups in **3** and **5** allow one to estimate the steric van der Waals radius of the lone-pair electrons in **5** to be ~1.7 Å because the peri steric radius of the methyl groups in **3** is 1.72 Å[5,7] on the basis of their clashed-gear conformation. This estimated value, which is much smaller than the 2.23 Å for the protruding hydrogen atom in **6**,[7] is consistent with the smaller barrier to rotation of the methyl group in **5** than that in **6**. Also, the head-on steric bulk of the lone-pair electrons of an sp^2 nitrogen atom has been reported to be much smaller than that of a hydrogen atom by comparing barriers to ring inversions in some pyridinophanes with those in the corresponding carbocyclophanes.[26] This result may reflect more facile deformation of the lone-pair electrons during rotation and the shorter provisional N–lone pair bond than the C–H bond.

Acknowledgment. We thank the Data Processing Center at Kyoto University and the Computer Center at the Institute for Molecular Science for their efficient service.

Registry No. **1**, 37960-59-1; **2**, 3947-76-0; **3**, 32596-80-8; **4**, 96999-63-2; **5**, 23647-26-9; **6**, 64433-70-1.

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