Pergamon

Tetrahedron Letters, Vol. 35, No. 22, pp. 3723-3726, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)E0670-S

Dynamic Stereochemistry of Tri(2-methyl-1-azulenyl)methyl Cation; Steric Effect of 2-Methyl Groups on Rotational Barriers and Mechanism

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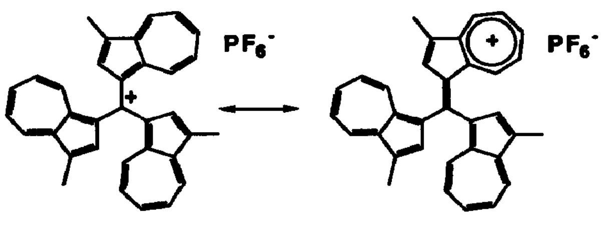
Abstract: The stable carbocation, tri(2-methyl-1-azulenyl)methyl hexafluorophosphate (2) was prepared. Steric effect of three 2-methyl groups was investigated by comparison with the 3,3',3"-trimethyl analogue, tri(3-methyl-1-azulenyl)methyl cation (1). Dynamic stereochemistry of 2 was studied by temperature dependent ^{1}H NMR spectra, which were analyzed by flip mechanism. The threshold rotational mechanism for 2 was a two-ring flip in contrast to a one-ring flip for 1, and the activation energies for 2 (18.6 and 17.5 kcal/mol) were higher than for 1 due to increased crowding in the transition state for the rotation.

The correlated rotation of molecular propellers is commonly analyzed in terms of flip mechanism.[1] For the conformational change of the systems, the lowest energy (threshold) rotational mechanism was uniformly a two-ring flip.[2] Recently, we reported the analysis of the temperature dependent ^{1}H NMR spectra for tri(3-methyl-1-azulenyl)methyl hexafluorophosphate (1) using a flip mechanism, and we concluded that the threshold rotational mechanism for 1 was the first example of a one-ring flip.[3] Since the conjugative effect between cationic carbon (C^+) and three azulene rings for 1 largely contributes to the transition state of the ring flipping as well as to the ground state, the two-ring flip process for 1 become less stable than that of a one-ring flip. The large steric interaction between azulene rings is expected to shift the threshold rotational mechanism from a one-ring flip to a two-ring flip. Here we report the synthesis of the stable carbocation, tri(2-methyl-1-azulenyl)methyl hexafluorophosphate (2), and the steric effect of three 2-methyl groups on the rotational barriers and mechanism.



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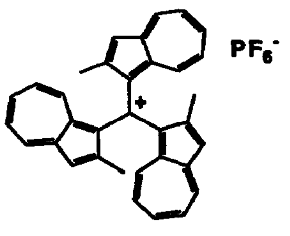
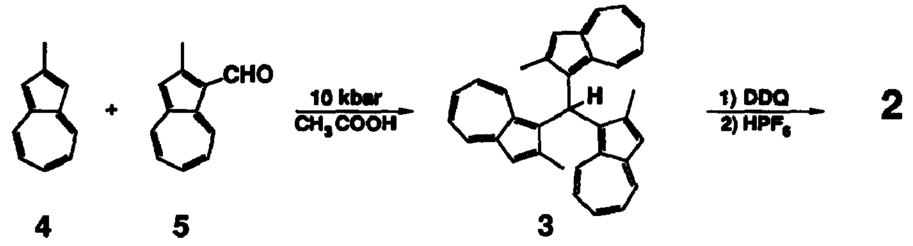


2

The large steric effect was also observed on the synthesis of tri(2-methyl-1-azulenyl)methane (3), the precursor for 2. The reaction of 2-methylazulene (4) with 2-methylazulene-1-carboxaldehyde (5) in acetic acid at room temperature for 21 days, similar condition for the formation of tri(3-methyl-1-azulenyl)methane[4], the precursor for 1, afforded only a trace amount of 3[5], because of the steric effect of 2-methyl groups on azulene rings. However, the high pressure reaction (10 kbar) of 4 with 5 in a 50% acetic acid in dichloromethane solution at 30 °C for 1 d, afforded 3 and 2-methyl-1,3-bis[di(2-methyl-1-azulenyl)methyl]azulene (6)[5] in 49% and 5% yields, respectively. The hydride abstraction of 3 with DDQ in dichloromethane at room temperature was not affected by the three 2-methyl groups, and the oxidation of 3 was proceeded under similar condition for the formation of 1.[4] The addition of 60% aqueous HPF_6 solution to the reaction mixture yielded stable 2[5] in quantitative yield.



The $pK_R{}^+$ value of 2 was determined spectrophotometrically at 24 °C in buffer solutions prepared in 50% aqueous MeCN similar to 1. The higher $pK_R{}^+$ values of 13.4 (2) compared to that of 1 (11.4)[4], was attributed to decrease the stability of the corresponding hydroxyl derivative by the steric effect and to electronic effect of three 2-methyl groups.

^1H NMR (90 MHz, methyl region) spectra of 2 in DMSO-d_6 at various temperature are shown in Figure 2. At 30 °C the NMR spectrum consists of four methyl signals (as indicated a, b, c, and d) in the ratio of ca. 1 : 1 : 1 : 1.5. The NMR spectrum indicated that the rotation of azulene rings was restricted at this temperature. At the same temperature, four methyl signals of 1 already coalesced into one signal due to the free rotation of azulene rings . When the sample was warmed to ca. 80 °C, noticeable line broadening occurred and further warming resulted in coalescence of all four peaks to a singlet, which became nearly sharp at 120 °C.

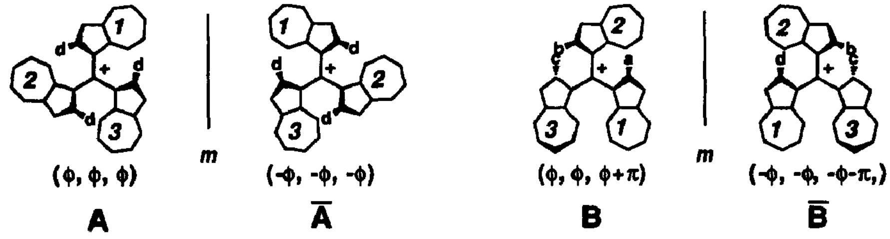


Figure 1. Stereoisomers of 2.

Four isomeric propeller conformations (A, $\bar{A}$, B, and $\bar{B}$) are possible for a molecule of this type including the stereoisomers as indicating in Figure 1, and the possibilities for isomerization for 2 will be analyzed by flip mechanism. Possible interconversions of the stereoisomers for 2 are compatible with those for 1. As the zero- and three-ring flip processes for 2 are unexplainable the temperature dependent ^1H NMR spectra and are also expected to be unfavorable by steric ground, therefore those are excluded from the analysis of dynamic behavior of 2. On the steric effect of three azulene rings, the interconversions of $B\bar{B}$ will be unfavorable compared to those of $A\bar{B}$ (and $\bar{A}B$) in a one-ring flip. In contrast to the process, the interconversions of $B\bar{B}$ will be more favorable than those of $A\bar{B}$ (and $\bar{A}B$) in a two-ring flip. Therefore, the threshold rotational mechanism for 2 are determined by the comparison of energy barriers between the interconversions of $A\bar{B}$ (and $\bar{A}B$) and those of $B\bar{B}$.

The simulation[6] of the temperature dependent ^1H NMR spectra of **2** were achieved similarly to those of **1**, and the results are also shown in Figure 2. In contrast to **1**, the simulation by consideration of only $A\overline{B}$ (and $\overline{A}B$) interconversions was inconsistent with the experimental spectra. The experimental spectra were well consistent with the calculated spectra by consideration of both $A\overline{B}$ (and $\overline{A}B$) and $B\overline{B}$ interconversions.

The energy relationships among the stereoisomers and the magnitudes of the barriers separating these isomers were calculated from the data of the simulation over the range 30 °C to 120 °C. The results are shown schematically in Figure 3. The relative intensities of the signals at 30 °C indicate that $B\overline{B}$ is slightly more stable than $A\overline{A}$ at this temperature. As the sample is warmed, the population of $B\overline{B}$ increases relative to that of $A\overline{A}$. Qualitatively, this indicates a positive entropy difference for the equilibrium of $A\overline{A}\rightarrow B\overline{B}$. $\Delta H°$ (0.97 kcal/mol), $\Delta S°$ (4.7 eu.), and $\Delta G°_{20}$ (-0.40 kcal/mol) for the equilibrium of $A\overline{A}\rightarrow B\overline{B}$ are calculated from the population data for $A\overline{A}$ and $B\overline{B}$. The temperature at which $\Delta G°$ equals to zero (crossover temperature) is therefore ca. -66 °C.

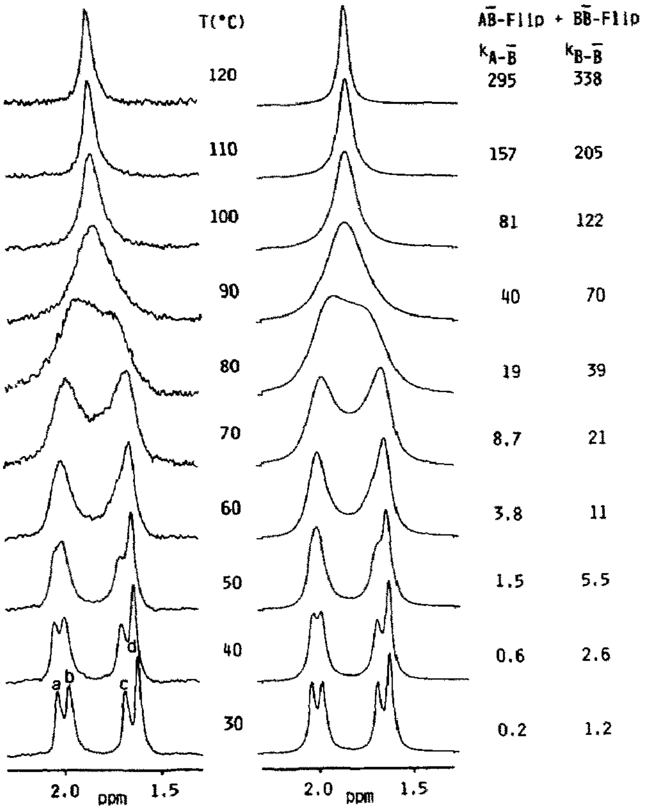


Figure 2. ^1H NMR of **2** (90 MHz, methyl region) at various temperatures. The left-hand panel displays the experimental spectra. The right-hand panel shows the calculated spectra for the combination of the $A\overline{B}$- and $B\overline{B}$-flips.

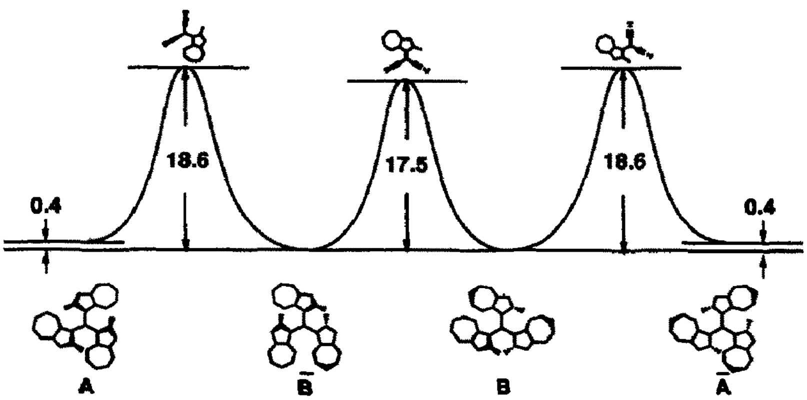


Figure 3. A schematic representation of the energetics (kcal/mol at 20 °C) of stereoisomerization of **2**.

The calculation of the rate data yielded the barrier for the conversion of $B\overline{B}$ to $A\overline{A}$ ($\Delta G^{\neq}_{20}$=18.6 kcal/mol) and that for the enantiomerization of B and $\overline{B}$ ($\Delta G^{\neq}_{20}$=17.5 kcal/mol). Therefore, for the reverse reaction ($A\overline{A} \rightarrow B\overline{B}$), $\Delta G^{\neq}_{20}$= 18.2 kcal/mol. The shift in threshold rotational process from the interconversion of $A\overline{B}$ (and $\overline{A}B$) to those of $B\overline{B}$ indicates that the threshold rotational mechanism for **2** is a two-ring flip in contrast to a one-ring flip for **1**. The activation energies for **2** were higher than that for **1** (for the interconversion of $A\overline{B}$ (and $\overline{A}B$) $\Delta G^{\neq}_{20}$=13.2 kcal/mol and for that of $B\overline{B}$ $\Delta G^{\neq}_{20}$=14.9 kcal/mol) due to increased crowding in the transition state for the rotation.

In conclusion, the dynamic behavior of **2** makes clear the one-ring flip mechanism for **1**. Therefore, the threshold rotational mechanism for molecular propellers is not uniformly a two-ring flip. The mechanism is changeable from a two-ring flip to a one-ring flip by the conjugative effect between central atom and three rings and by the steric effect between three rings.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas No. 02230103 from the Ministry of Education, Science and Culture, Japan.

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5. All new compounds were characterized by their IR, UV, ^{1}H NMR, and ^{13}C NMR spectral data and mass spectroscopy. Selected spectral data for **2** and **3** are given below.

   2: Deep purple powder; mp > 300 °C; UV (MeCN) λ_{max} 231 nm (log ε 4.75), 256 (4.68), 295 (4.61), 332 (4.36), 351 (4.26 sh), 416 (3.93), 430 (3.92 sh), 551 (4.15 sh), 595 (4.54 sh), 624 (4.70), and 649 (4.69); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.72 (d), 8.71 (d), 8.70 (d), 8.69 (d), 7.99 (dd), 7.93 (dd), 7.88 (dd), 7.88 (dd), 7.84 (dd), 7.83 (dd), 7.81 (dd), 7.80 (d), 7.79 (dd), 7.78 (s), 7.69 (s), 7.68 (s), 7.64 (d), 7.62 (s), 7.56 (d), 7.51 (dd), 7.44 (dd), 7.40 (d), 7.34 (dd), 7.27 (dd), 2.05 (s), 1.98 (s), 1.69 (s), and 1.63 (s); ^{13}C NMR (150 MHz, DMSO-d_6) δ 154.93 (s), 154.58 (s, B-C^{+}), 154.55 (s), 154.53 (s), 154.04 (s, A-C^{+}), 154.04 (s), 149.84 (s), 149.24 (s), 148.89 (s), 148.17 (s), 147.00 (s), 146.37 (s), 146.24 (s), 145.60 (s), 141.52 (d), 141.24 (d), 141.02 (d), 140.69 (d), 138.82 (d), 138.57 (d), 138.42 (d), 138.15 (d), 136.62 (d), 136.08 (d), 135.85 (d), 135.26 (d), 133.58 (s), 133.44 (d), 133.35 (s), 133.08 (d), 132.86 (s), 132.85 (d), 132.76 (d), 132.61 (d), 132.49 (s), 132.40 (d), 131.96 (d), 131.91 (d), 127.32 (d), 126.55 (d), 126.28 (d), 125.37 (d), 125.37 (d), 15.82 (q), 15.52 (q), 15.52 (q), and 15.21 (q).

   3: Blue plates; mp 267.5 - 273.0 °C; UV(CH_2Cl_2) λ_{max} 241 nm (log ε 4.65), 273 (4.90 sh), 286 (5.01), 298 (4.93 sh), 309 (4.77 sh), 345 (4.06 sh), 358 (4.10), 375 (3.91), 547 (2.73 sh), 590 (2.87), 634 (2.81 sh), and 705 (2.31 sh); ^{1}H NMR (90 MHz, 50% CD_2Cl_2/CS_2) δ 8.08 (d, 3H, J=9.5, H_8), 7.60 (d, 3H, J=9.9, H_4), 7.42 (s, 1H, CH), 7.31 (dd, 3H, J=9.7 and J=9.5, H_7), 6.66 (dd, 3H, J=9.9 and J=9.5, H_5), and 1.82 (s, 9H, 2-Me); ^{13}C NMR (22.5 MHz, 50% CD_2Cl_2/CS_2) δ 150.65 (s, C_2), 140.22 (s, C_{4a} or C_{8a}), 136.72 (s, C_{4a} or C_{8a}), 135.77 (d, C_6), 134.25 (d, C_8), 132.26 (d, C_4), 129.31 (s, C_1), 123.00 (d, C_7), 122.39 (d, C_5), 119.55 (d, C_3), 37.32 (d, CH), and 16.13 (q, 2-Me).
6. Simulation of the temperature dependent ^{1}H NMR spectra was performed using the program DNMR5 (QCPE **1978**, *10*, 365) by D. S. Stephenson and G. Binsch.

(*Received in Japan* 16 *November* 1993; *accepted* 4 *February* 1994)