Synthesis and Dynamic Stereochemistry of Bis(3-methyl-1-azulenyl)(1-naphthyl)methyl Hexafluorophosphate. Clear Evidence of the One-Ring Flip Mechanism of Molecular Propeller by Controlling the Flipping Ring

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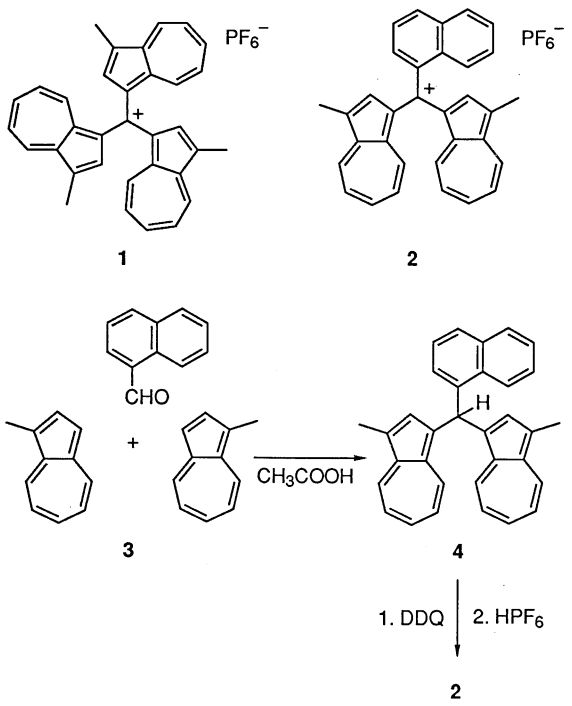
(Received February 22, 1995)

Stable carbocation, bis(3-methyl-1-azulenyl)(1-naphthyl)-methyl hexafluorophosphate was synthesized by the hydride abstraction reaction of the corresponding hydrocarbon. The cation showed extremely high stability with pK_R^+ value (11.0). The low temperature ^1H NMR spectra showed that the flipping ring was controlled by 1-naphthyl group.

The correlated rotation of molecular propellers is commonly analyzed in terms of flip mechanism postulated by Kurkland et al.[1-3] The threshold rotation mechanism for the conformational change of the system was uniformly a sterically most favorable two-ring flip.[4,5] Recently, we have reported that the mechanism of tris(3-methyl-1-azulenyl)methyl hexafluorophosphate (**1**) was the first example of a one-ring flip by the comparison of two different activation energies ($\Delta G^{\neq}$) between four stereoisomers.[6,7] If the flipping ring is possible to control, the one-ring flip will appear more clearly in the temperature dependent NMR spectra. The one-ring flip of **1** arises from the large conjugative interaction between the central cation and the three azulene rings. In case one of the three azulene rings of **1** is replaced by the ring with less conjugative, the ring will flip predominantly. Unsymmetrical 1-naphthyl substituent makes possible to observe the rotation of the naphthyl ring by substituents on the azulene rings in the temperature dependent NMR spectra. Therefore, we synthesized the 1-naphthyl derivative of **1**, i.e., bis(3-methyl-1-azulenyl)(1-naphthyl)methyl hexafluorophosphate (**2**).



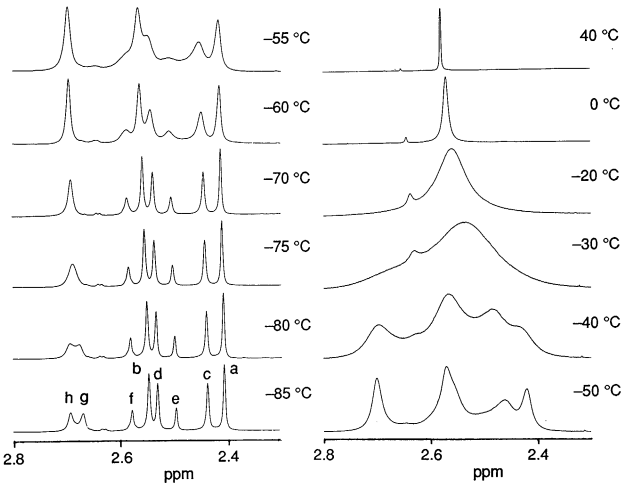


Figure 1. ^1H NMR spectra of **2** (600 MHz, methyl region) in 50% CD_2Cl_2/CS_2 at various temperatures.

The reaction of two molar equivalents of 1-methylazulene (**3**) with 1-naphthylaldehyde in acetic acid at room temperature for 24 h, afforded **4** in 76% yield. Hydride abstraction reaction of **4** with DDQ in dichloromethane followed by the addition of 60% aqueous HPF_6 yielded **2** in 90% yield.[8]

The pK_R^+ value of **2** was determined spectrophotometrically at 24 °C in the buffer solution prepared in 50% aqueous MeCN. The pK_R^+ value of **2** (11.0) is extremely high for a methyl cation substituted with only hydrocarbon groups. The naphthyl substituent slightly increases the pK_R^+ value, compared with bis(3-methyl-1-azulenyl)phenylmethyl hexafluorophophate (**5**) ($pK_R^+ = 10.8$).[7,9]

^1H NMR (600 MHz, methyl region) spectra of **2** in 50% CD_2Cl_2/CS_2 at various temperatures are shown in Figure 1. At -85 °C the NMR consists, in the methyl region, of four sets of two signals with equal intensity (as indicated ab, cd, ef, and gh) in the ratio of intensities of ca. 2.6 : 2.0 : 1 : 1.9. Eight isomeric propeller conformations including the stereoisomers ($A\overline{A}$, $B\overline{B}$, $C\overline{C}$, and $D\overline{D}$) are possible for a molecule of this type. Therefore, the eight resonance signals in the methyl region are attributable to a mixture of these diastereomers, and the signals with equal intensity arise from the methyl groups at the identical stereoisomer. When the sample was warmed to ca. -70 °C, the two signals at the lower field (g and h) coalesced to a singlet, although the other signals at the higher field (ab, cd, and ef) almost remained in the original shapes. Further warming the signals caused noticeable broadening and resulted in coalescence of all eight signals to a singlet. The temperature-dependence of the ^1H NMR spectra was completely reversible.

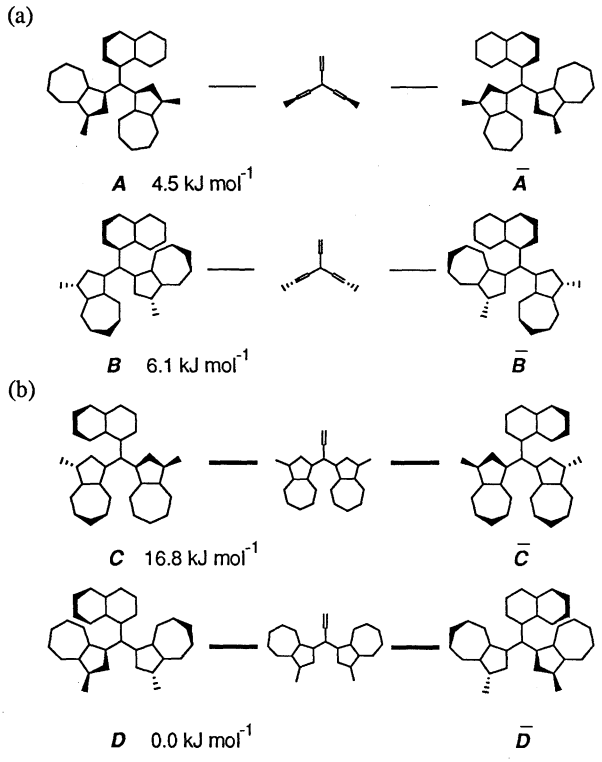


Figure 2. Selected flip mechanism and calculated (PM3) relative heat of formation for the stereoisomers of **2**. (a) three-ring flip. (b) one-ring flip.

The possibilities of stereoisomerism and isomerization of **2** were analyzed by the flip mechanism. There is a total of 20 distinct pathways in the four flip mechanisms (four in zero-ring flip, seven in one-ring flip, six in two-ring flip, and three in three-ring flip). The mechanism, which can explain the temperature dependence of the NMR spectra at the lower temperatures, is limited to the $A \rightarrow \bar{A}$ and $B \rightarrow \bar{B}$ of three-ring flip and the $C \rightarrow \bar{C}$ and $D \rightarrow \bar{D}$ of one-ring flip. The four flip mechanisms and idealized chemical transition states are illustrated in Figure 2. The three-ring flips are easily excluded by the steric factors of the three rings.[10,11] The idealized transition state of $C \rightarrow \bar{C}$ entails the placement of 8-position of the two azulene rings in essentially the same location. This situation is obviously unreasonable for the observed coalescence of the signals (g and h). PM3 calculations[12] of the stereoisomers ($A\bar{A}$, $B\bar{B}$, $C\bar{C}$, and $D\bar{D}$) demonstrate that the $C\bar{C}$ is the most unstable stereoisomer, so that the methyl signals of e and f are assigned to those of $C\bar{C}$. Therefore, observed coalescence of the two signals (g and h) at the lower temperatures arises from the $D \rightarrow \bar{D}$ interconversion of the one-ring flip mechanism.

The rate data determined by the line shape analysis of the signals (g and h) using the DNMR3K program[13] were used to calculate the free energy of the activation for the enantiomerization of $D\bar{D}$ at 20 °C: for the enantiomerization, $\Delta G^{\neq}_{20\,°C} = 33.9 \pm 2.0$ kJ mol^{-1}, which is lower than the $\Delta G^{\neq}_{20\,°C}$ values for the flip of one-azulene ring of **5** (45.2 and 53.8 kJ mol^{-1}).[7,15]

Threshold rotation mechanism for **2** was the one-ring flip of 1-naphthyl ring. The mechanism, which can explain the observed coalescence at the higher temperature is a combination of the one-ring flip with other pathways, such as one-azulene ring flip mechanism for **5**.[7,15] The 1-naphthyl ring flip mechanism for **2** is attributed to the large conjugative effect of azulene rings with the cationic carbon.

References and Notes

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