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Dynamic Stereochemistry of Di(3-methyl-1-azulenyl)phenylmethyl Cation. Flip of One Azulene Ring as the Threshold Rotation Mechanism

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Dynamic stereochemistry of di(3-methyl-1-azulenyl)phenylmethyl hexafluorophosphate (**5**) was studied by temperature dependent ^{1}H NMR spectra. The low temperature NMR indicated that the compound (**5**) exists in three propeller conformations (C_1 and two C_2 symmetry), and at higher temperature the spectra reflect rapid isomerization, which were interpreted by the flip mechanism of one azulene ring. The processes have activation energies of 53.8 and 45.2 kJ mol^{-1}.

Recently, we reported that azulene analogous of triphenylmethyl cations; i.e. tri(1-azulenyl)methyl (**1**), di(1-azulenyl)phenylmethyl (**2**), and (1-azulenyl)diphenylmethyl (**3**) hexafluorophosphate, and their derivatives, were synthesized by hydride abstraction reaction of the corresponding hydrocarbons, and that these cations showed extreme stabilities with high pK_R^+ values.1) ^{1}H NMR spectra of **1** depended on temperature due to the rotation of their three rings. Through the analysis of tri-3-methyl derivative (**4**)1) of **1** by flip mechanism,2,3) the lowest energy (threshold) rotation mechanism of **4** was concluded to be a one-ring flip.4) This was the first example of one-ring flip mechanism in molecular propellers. However, we found that ^{1}H NMR spectra of **2** also depended on temperature due to the rotation of their three rings, and di-3-methyl derivative (**5**)1) of **2** was similarly analyzed by the flip mechanism. Consequently, dynamic stereochemistry of **5** was established by a flip mechanism of one azulene ring as the threshold rotation mechanism, which will be reported in this paper.

^{1}H NMR (600 MHz, methyl region) of **5** in 50%CD_2Cl_2/CS_2 at various temperatures are shown in Fig. 1. At −100 °C the NMR consists, in the methyl region, of four signals (as indicated a, b, c, and d) in the ratio of intensities of ca. 1.2 : 1.2 : 3 : 1. Six isomeric propeller conformations are possible for a molecule of this type including the stereoisomers, and the possibilities for the stereoisomerization of these isomers may be analyzed by flip mechanism. These isomers are consisted of three diastereomeric sets of enantiomers illustrated in Fig. 2. One set of enantiomers (A and $\overline{A}$) is C_1 symmetry and each enantiomer has two nonequivalent methyl groups. The other two sets of enantiomers (B, $\overline{B}$, C, and $\overline{C}$) have C_2 symmetry and each set of enantiomers has two equivalent methyl groups. Therefore, ^{1}H NMR spectrum at −100 °C exhibits four resonance signals in methyl region attributable to a mixture of diastereomers. On the basis of the analysis given above, two resonances (a and b) in the higher field must be corresponding to those of A (and $\overline{A}$). While the other more intense peak (c) and the remaining less intense peak (d) are assigned to those of B (and $\overline{B}$) and C (and $\overline{C}$), respectively, by considering their stabilities based on the analysis of molecular models. Thus, the spectrum of **5** at −100 °C is consistent with the postulated propeller geometry for the ground state conformation, and with a ratio of $A\bar{A}$: $B\bar{B}$: $C\bar{C}$ of ca. 2.4 : 3 : 1. When the sample was warmed to ca. –50 °C, noticeable line broadening occurred and further warming resulted in coalescence of all four peaks to a singlet, which became sharp at 40 °C. Possible interconversion of the stereisomers of **5** may be describing by the flip mechanism. The four flip mechanisms of **5** are illustrated in Fig. 3.

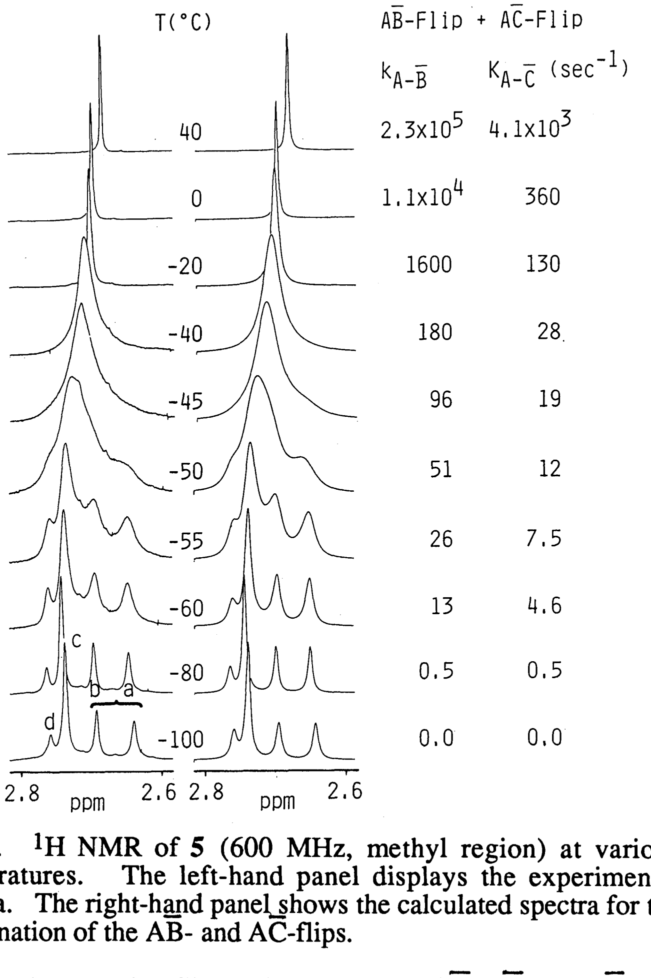


Fig. 1. ^{1}H NMR of **5** (600 MHz, methyl region) at various temperatures. The left-hand panel displays the experimental spectra. The right-hand panel shows the calculated spectra for the combination of the $A\bar{B}$- and $A\bar{C}$-flips.

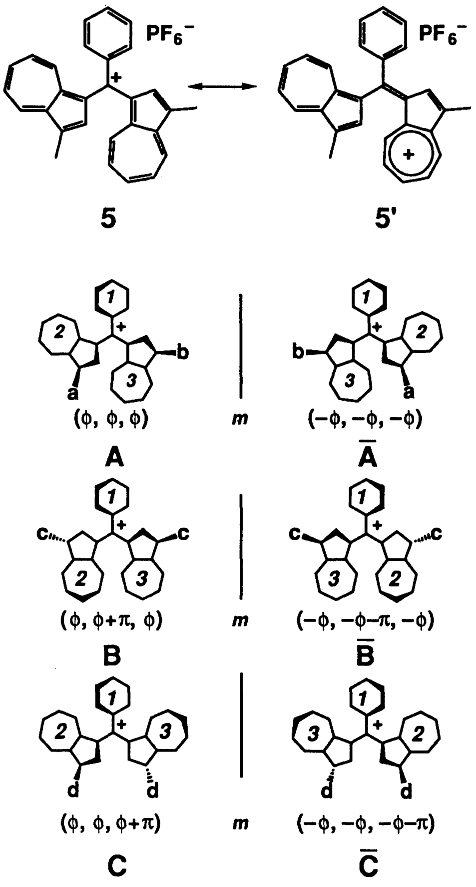
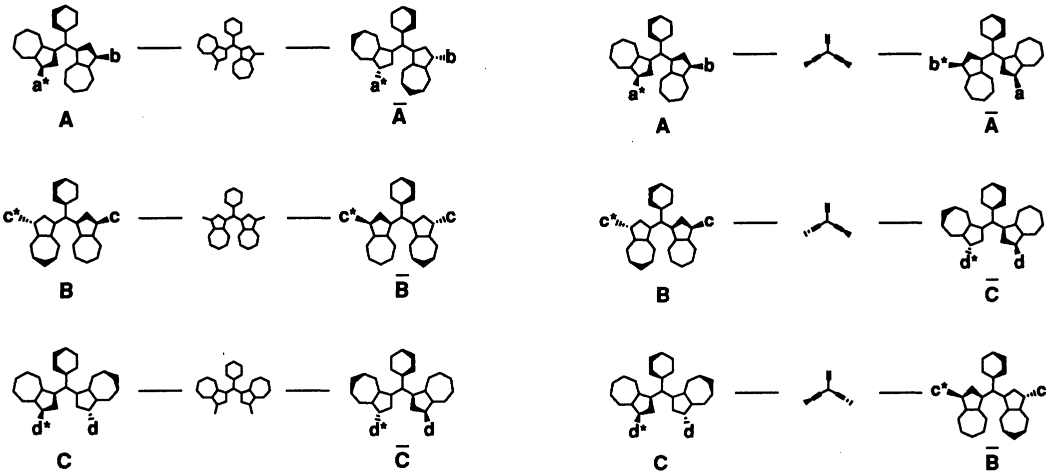


Fig. 2. Stereoisomers of **5**.

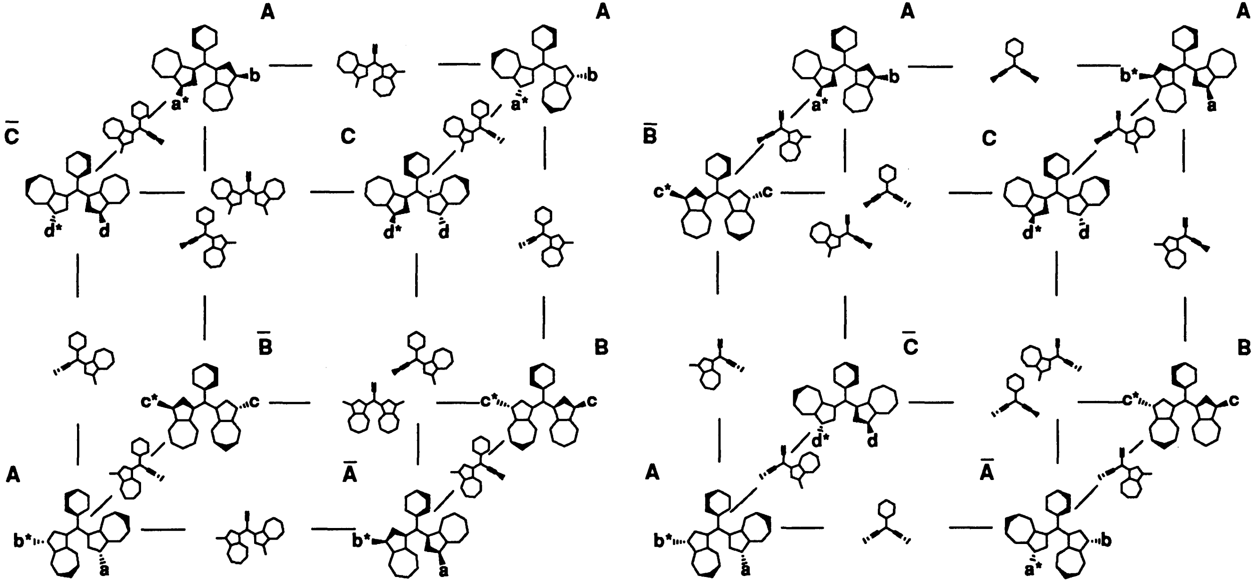
In the zero-ring flip, each conformers ($A\bar{A}$, $B\bar{B}$, and $C\bar{C}$) interconverts to their enantiomers, however, no methyl groups interconverts in this mechanism (Fig. 3a). In one- and two-ring flips, each conformers interconverts to the other three isomers having opposite helicities, therefore, the mechanisms consist of the cubic type interconversions as shown in Fig. 3b and 3c, respectively. In one-ring flip, two sets of exchanges of methyl groups (a→c, b→c and a→d, b→d) are considered by $A\bar{B}$ (and $\bar{A}B$) and $A\bar{C}$ (and $\bar{A}C$) interconversions (Fig. 3b). Whereas, in two-ring flip, two energetically different exchanges (a→b and c→d) are considered by $A\bar{A}$ and $B\bar{C}$ (and $\bar{B}C$) interconversions in addition to the two sets of exchanges (a→c, b→c and a→d, b→d), which are identical with a one-ring flip mechanism (Fig. 3c). Enantiomerization of A and $\bar{A}$, and interconversions of $B\bar{C}$ (and $\bar{B}C$) will occur in three-ring flip (Fig. 3d), however this process has only two exchanges (a→b, c→d) of the methyl groups. The analysis indicates that the flip of phenyl ring does not affect the temperature dependence of the methyl groups.

The simulation$^{5)}$ of the variable temperature ^{1}H NMR spectra of **5** by consideration of only two sets of energetically equal exchanges (a→c, b→c and a→d, b→d) of methyl groups by $A\bar{B}$ (and $\bar{A}B$) and $A\bar{C}$ (and

$\bar{\mathrm{A}}$C) interconversions matches with the experimental spectra. The results of simulation are also shown in Fig. 1. The analysis indicates that the mechanism which can explain the temperature dependence of methyl groups is a one-ring flip of azulene or a two-ring flip of azulene and phenyl rings, or a combination of these with other pathways. Therefore, the flip of one azulene regardless of the flip of phenyl ring is a threshold rotation mechanism of **5**, and the two azulene rings do not flip simultaneously.



(a) Zero-ring flip mechanism of **5**. (d) Three-ring flip mechanism of **5**.



(b) One-ring flip mechanism of **5**. (c) Two-ring flip mechanism of **5**.

Fig. 3. The four flip mechanisms of **5**.

The spectral data permitted the calculation of the energy relationships among the stereoisomers of **5** and the magnitudes of the barriers separated these isomers. The relative intensities of the NMR signals at –100 °C show that the $\mathrm{B\bar{B}}$ is slightly more stable than $\mathrm{A\bar{A}}$ or $\mathrm{C\bar{C}}$ at this temperature. As the sample is warmed, the population of $\mathrm{A\bar{A}}$ increases relative to that of $\mathrm{B\bar{B}}$ or $\mathrm{C\bar{C}}$. Qualitatively, this indicates a positive entropy for the diastereomer ($\mathrm{A\bar{A}}$). The analysis of the temperature dependent NMR over the range –100 °C to –60 °C yields, for the equilibrium $A\bar{A}\rightarrow B\bar{B}$, $\Delta H^\circ=-2.0\pm0.3$ kJ mol^{-1} and $\Delta S^\circ=-9.4\pm1.4$ J K^{-1} mol^{-1}, and for $A\bar{A}\rightarrow C\bar{C}$, $\Delta H^\circ=-3.5\pm0.7$ kJ mol^{-1} and $\Delta S^\circ=-27\pm3.5$ J K^{-1} mol^{-1}. The temperature at which ΔG° equals zero (crossover temperature) are therefore, for $A\bar{A}\rightarrow B\bar{B}$, ca. –61 °C and, for $A\bar{A}\rightarrow C\bar{C}$, ca. –145 °C. The major part of the entropy difference is accounted for the difference in symmetry (C_2 vs. C_1) of the two diastereomers.

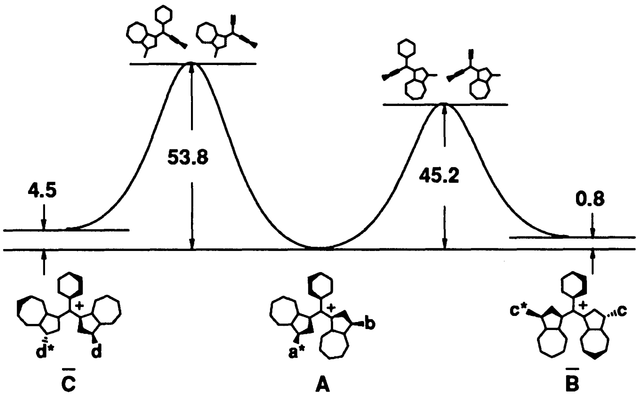


Fig. 4. A schematic representation of the energetics (kJ mol^{-1} at 20 °C) of stereoisomerization of **5**.

The rate data determined by the line-shape analysis were used to calculate free energies of activation for the various exchange processes at 20 °C. The results are shown schematically in Fig. 4. For the equilibrium $A\bar{A}\rightarrow B\bar{B}$, ΔG°_{20} is 0.8 ± 0.5 kJ mol^{-1} and, for $A\bar{A}\rightarrow C\bar{C}$, ΔG°_{20} is 4.5 ± 1.2 kJ mol^{-1}. For the conversion of $A\bar{A}$ to $B\bar{B}$, the calculations yielded $\Delta G^{\neq}_{20}=45.2\pm4.3$ kJ mol^{-1}, and for the reverse reaction ($B\bar{B}\rightarrow A\bar{A}$) $\Delta G^{\neq}_{20}=44.4\pm4.3$ kJ mol^{-1}. The barrier for the conversion of $A\bar{A}$ to $C\bar{C}$ is $\Delta G^{\neq}_{20}=53.8\pm4.3$ kJ mol^{-1}, and for the reverse reaction ($C\bar{C}\rightarrow A\bar{A}$) $\Delta G^{\neq}_{20}=49.3\pm4.5$ kJ mol^{-1}.

The flip of one azulene is a threshold rotation mechanism of **5**. The reason is that the resonance form **5'** largely contribute to the transition state of ring flipping as well as to the ground state. Therefore, in the present case, the transition state for the flip of two azulene ring is less stable than that of one azulene ring.

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