Supplementary Information

Atropisomerism of a monosubstituted perfluoro[2.2]paracyclophane.

A combined synthetic, kinetic, spectroscopic
and computational study

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Kinetics

Measurement of barrier for rotation by nOe difference experiments

The temperature was corrected with the ethylene glycol standard. The temperature measured by the difference of the chemical shifts of the proton signals in ethylene glycol, corrected temp, and the temperature read by the thermocouple, temp, were in the linear relationship

Corrected temp = 0.9835 x temp – 0.1019

<table>
<thead>
<tr>
<th>temp (°C)</th>
<th>temp corrected</th>
<th>T1 (s)</th>
<th>MB(∞)</th>
<th>k=(1-MB(∞))/MB(∞)/T1</th>
<th>1/T</th>
<th>ln(k/T)</th>
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<tbody>
<tr>
<td>95</td>
<td>93.33</td>
<td>1.64</td>
<td>0.9675</td>
<td>0.0205</td>
<td>0.002729</td>
<td>-9.792</td>
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<tr>
<td>115</td>
<td>113.00</td>
<td>1.97</td>
<td>0.8633</td>
<td>0.0804</td>
<td>0.002590</td>
<td>-8.477</td>
</tr>
<tr>
<td>125</td>
<td>122.84</td>
<td>2.01</td>
<td>0.7511</td>
<td>0.1649</td>
<td>0.002525</td>
<td>-7.784</td>
</tr>
</tbody>
</table>

\[
\ln(k/T) \text{ vs. } 1/T
\]

\[
y = -9810.7x + 16.965 \\
R^2 = 0.999
\]

<table>
<thead>
<tr>
<th>$\Delta H$ (kcal/mol)</th>
<th>$\Delta S$ (cal/mol/K)</th>
<th>$\Delta G$ (25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.49</td>
<td>-13.50</td>
<td>23.51</td>
</tr>
</tbody>
</table>

Standard error of $\Delta G_{298}$ = 1.1 kcal/mol.
Measurement of the rate constant of the reaction 5a → 5b at 25 °C

The reaction 5a → 5b was monitored in benzene-d6 at 25 °C (reading of the thermocouple, uncorrected) by 1H NMR, for 18 hrs. Spectra were acquired in 64 transients, with a relaxation delay of 10 s and an acquisition time of 10 s, for a total of 51 spectra. Only 40 of them were taken into calculating the rate constant, because in the last ones the mixture was very close to equilibrium and the errors in ln([5a]-[5a]eq) were large. The signals of H1’’ were used for integration, after baseline correction: 4.30 – 4.19 ppm [5b], 4.03 – 3.84 ppm [5a] + [5b], and 3.75 – 3.63 [5a].

The slope of the plot ln([5a]-[5a]eq) , which is the logarithm of the difference between the concentration of 5a at time t and the concentration at equilibrium, vs. time is the sum of the rate constants for the forward and backward reactions, kf + kb. The equilibrium constant, K = kf/kb is 1, and kf = kb = 3.67 x 10^-5 s^-1. (standard error 0.07 x 10^-5 s^-1). This corresponds to a half-life time of 5.25 hrs.
Figure 1S. $^1$H spectrum of compound 5 in benzene-d6 at 25 °C.
Figure 25. $^{19}$F spectrum of compound 5 in benzene-$d_6$ at 25 °C. (bottom) and TOCSY1D spectra of conformers 5a (top) and 5b.
Figure 3Sa. $^1$H-$^{13}$C gHMBC spectrum of compound 5 in benzene-d$_6$ at 25 °C.
Figure 3Sb. $^1$H-$^{13}$C gHMBC spectrum of compound 5 in benzene-$d_6$ at 25 °C. (expansion).
Figure S3. $^1$H-$^{13}$C gHMBC spectrum of compound 5 in benzene-d$_6$ at 25 °C. (expansion.)
Figure 3Sd. $^1$H-$^{13}$C gHMBC spectrum of compound 5 in benzene-$d_6$ at 25 °C. (expansion).
Figure 4Sa. $^{19}$F-$^{19}$F DQCOSY spectrum of compound 5 in benzene-d$_6$ at 25 °C. (expansion.)
Figure 4Sb. $^{19}$F-$^{19}$F DQ COSY spectrum of compound 5 in benzene-d$_6$ at 25 °C (expansion).
**Figure 4Sc.** $^{19}$F–$^{19}$F DQCOSY spectrum of compound 5 in benzene-$d_6$ at 25 °C. (expansion).
Figure 5S. $^1$H spectrum of compound 6 in benzene-d$_6$ at 25 °C.
Figure 5Sa. $^1$H spectrum of compound 6 in benzene-d$_6$ at 25°C (expansion).
Figure 6. $^1\text{H}-^{13}\text{C}$ gHMBC spectrum of compound 6 in benzene-d$_6$ at 25°C.
Figure 7S. $^{19}$F spectrum of compound 6 in benzene-d$_6$ at 25 °C.
Figure 7Sa. $^{19}$F spectrum of compound 6 in benzene-$d_6$ at 25 °C (expansion).
Figure 7Sb. $^19F$ spectrum of compound 6 in benzene-$d_6$ at 25 °C (expansion).
Figure 7Sa. $^{19}$F-$^{19}$F DQCOSY spectrum of compound 6 in benzene-$d_6$ at 25 °C (expansion).
Figure 7Sb. $^{19}$F–$^{19}$F DQCOSY spectrum of compound 6 in benzene-d$_6$ at 25 °C (expansion).
**Figure 7Sc.** $^{19}$F-$^{19}$F DQCOSY spectrum of compound 6 in benzene-$d_6$ at 25 °C (expansion).
Figure 8S. $^{19}$F-$^{19}$F nOe difference spectrum of compound 6 in benzene-$d_6$ at 25 °C (top). And the $^{19}$F spectrum (bottom).
**Figure 9S.** $^{19}$F-$^{19}$F nOe difference spectrum of compound 5 in benzene-$d_6$ at 25 °C (top) and the 19F spectrum (bottom)