SUPPORTING INFORMATION

Title: Solid-State Structural Study of the Charge-Transfer Complex of 5,7,9-Trimethyl- and 2,11,20-Trithia[3,1]1,3,5)cyclophanes

Author(s): Mikio Yasutake, Koji Araki, Ming Zhou, Rika Nogita, Teruo Shinmyozu*

Ref. No.: O02260
(1) The Variable Temperature $^1$H-NMR Study of 5,7,9-Trimethyl[3$^3$](1,3,5)cyclophane-2-one

The 5,7,9-trimethyl[3$^3$](1,3,5)cyclophane-2-one 10 shows dynamic process in the VT $^1$H-NMR in CD$_2$Cl$_2$ (300 MHz); two kinds of the benzylic protons signals of the CH$_2$COCH$_2$ bridge appear as singlets at 20 °C [3.62 (s, 2H; CH$_2$COCH$_2$), 3.80 (s, 2H; CH$_2$COCH$_2$)]. The signal at 3.62 ppm stays intact to -90 °C and the intactness of this signal may be due to the accidental chemical shift equivalence of the respective methylene proton, while the signal at 3.80 ppm due to the benzylic protons bearing methyl-substituted benzene ring broadens as the temperature is lowered, and finally splits into a pair of doublets ($\delta$ 3.66 (d, $J = 14.6$ Hz) and 3.93 (d, $J = 14.7$ Hz)] at –90 °C. At this temperature, the trimethylene bridge flipping process is also frozen. The energy barrier for this CH$_2$COCH$_2$-bridge flipping process is estimated to be 10.4±0.2 kcal/mol ($\Delta\nu = \nu_A - \nu_B = 81$ Hz, $J_{AB} = 14.7$ Hz, $T_c = -55$ °C). In principle, four conformers (10a-d) are conceivable. At -90 °C, major and minor conformers are observed but the structures cannot be identified by the present data.
Fig. S1. VT$^1$H-NMR spectra of 5,7,9-trimethyl[3,3](1,3,5)cyclophane-2-one 10 in CD$_2$Cl$_2$ (300 MHz).
Fig. S2. VT $^1$H-NMR spectra of 5,7,9-trimethyl[3,3](1,3,5)cyclophane 1 in CD$_2$Cl$_2$ (300 MHz)
Fig. S3. Expanded 1H-NMR spectra of the benzylic proton signals of 2,2,11,11,20,20-hexadeuterio-5,7,9-trimethyl[33](1,3,5)cyclophane 1-[D]6 in CD$_2$Cl$_2$ at -90 °C (500 MHz).