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CONFORMATIONAL CHANGE OF [2·2]METAPARACYCLOPHANE

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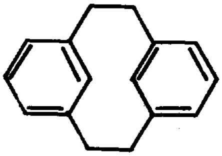
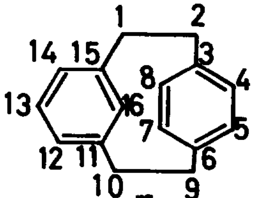
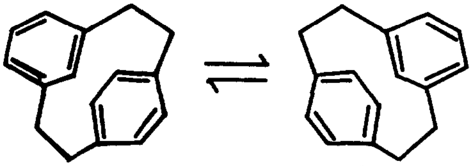
The high temperature NMR spectra of [2·2]metacyclophane (I) were recently interpreted as indicating the rigid nature of its 10-membered ring system.1),2) Activation energy required for interconversion between its two chair forms was estimated to be more than 27 Kcal/mol;3) this was confirmed by the optical resolution study of its certain derivatives.1),2),4) In this paper we have examined the high temperature NMR spectra of [2·2]metaparacyclophane (II)5) from the view-point of its conformational change.


I



II

The 100 MHz NMR spectrum6) of II in hexachlorobutadiene shows resonances at δ 6.35~6.92 (A_2B pattern, $C_{12,13,14}$ aryl protons), at δ 7.25 and 5.75 (A_2B_2 pattern, $C_{4,5}$ and $C_{7,8}$ aryl protons), at δ 5.32 (triplet, C_{16} aryl proton), and at δ 1.95~3.75 (ABCD pattern, methylene protons). The C_{16} and $C_{7,8}$ aryl protons exhibited unusual high field shifts due to the ring current effects of the opposite benzene ring extended over them. These spectral features are indicative of a chair form of the [2·2]metaparacyclophane structure (IIa or IIb). As the temperature of the solution is raised the individual signals of the A_2B_2 pattern due to the $C_{4,5}$ and $C_{7,8}$ aryl protons collapse and coalesce to a broad singlet at about 187°C. Above this temperature the broad line becomes sharp. The observed temperature dependence of the A_2B_2 pattern is in accord with exchange between the A and B proton environments resulting from the rapid interconversion between conformations IIa and IIb. Furthermore, signals of the methylene protons displayed a transision from the ABCD pattern at room temperature to two broad peaks (multiplet, centered at δ2.40 and 2.81) at higher temperatures.



IIa IIb

The rate of exchange k^1 at the temperature of coalescence Tc was calculated by the method of Gutowsky and Holm$^{7)}$ from equation (1), where $\Delta\nu$ is the frequency separation of resolved signals at room temperature. The values of $\Delta G^{\ddagger}$ were derived from the Eyring equation$^{8)}$ (2), a unit transmision coefficient (κ) being assumed. Equation (2) was transformed to (3) for the purpose of caluculation.

$$k^1 = \pi \Delta\nu / \sqrt{2} \quad (1) \qquad\qquad k^1 = \kappa \frac{kT}{h} \exp\left(\frac{-\Delta G^{\ddagger}}{RT}\right) \quad (2)$$

$$G = 2.303RTc(10.319 - \log_{10}k^1 + \log_{10}Tc) \quad (3)$$

When Tc=460°K, k^1(sec^{-1})=409, and $\Delta\nu$ (cps)=184, the energy barrier for [2.2] metaparacyclophane was calculated to be about 21.8 ± 0.3 Kcal/mol.

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