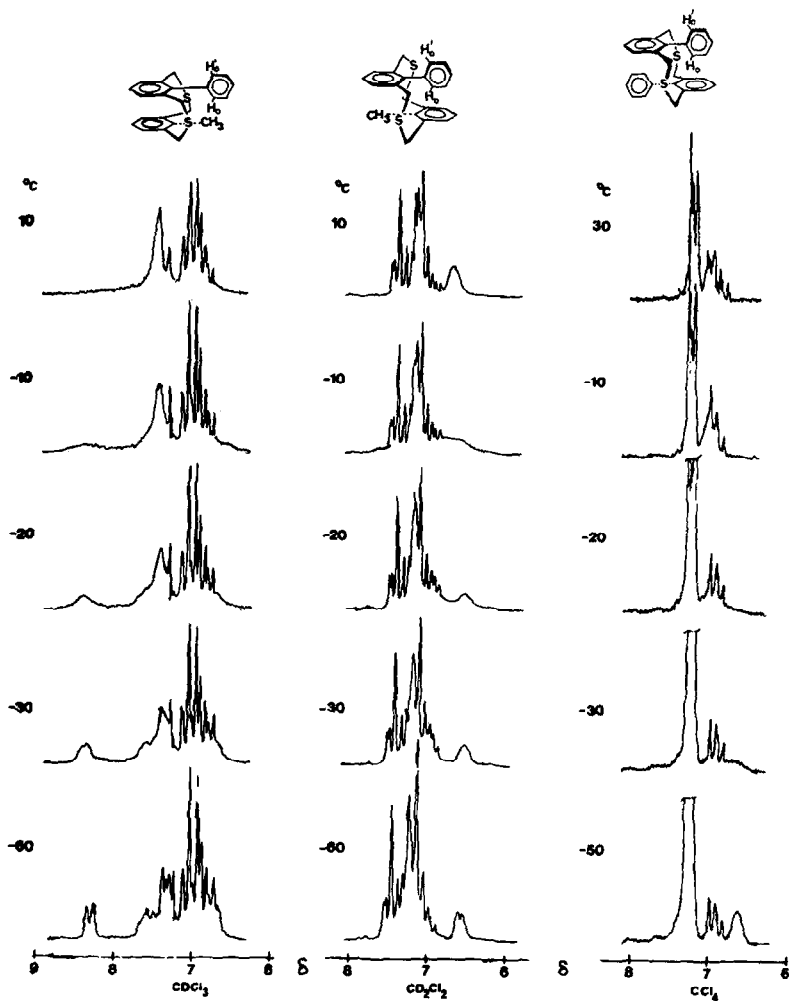
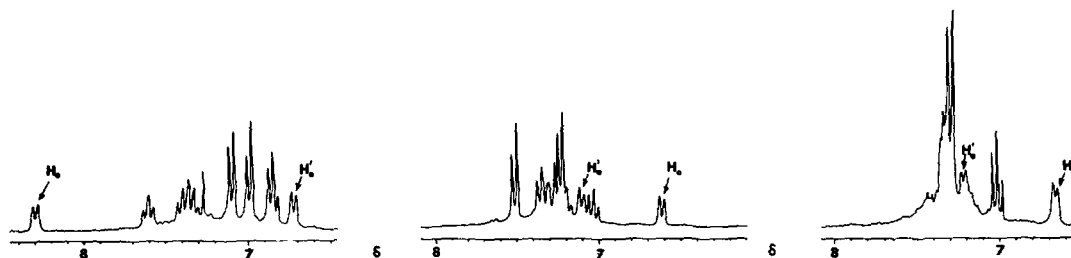




Figure 1: 90 MHz  $^1\text{Hmr}$  Variable Temperature Spectra for aryl proton region of250 MHz  $^1\text{Hmr}$  spectra at  $-60^\circ\text{C}$  for aryl proton region

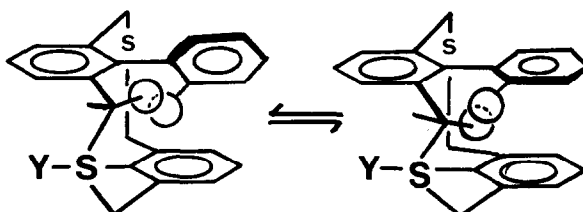
and in **3B** it could be shielded by the opposite substituent ring. The magnitude of these two effects might, however, be different since it is possible for the substituent ring to twist somewhat out of the plane of the cyclophane rings. Nevertheless, we first decided to synthesise the compounds with one internal methyl group, the presence of which has normally made assignment of stereochemistry much easier.<sup>6</sup>

Thus, cyclization<sup>7</sup> of **5**<sup>8</sup> and 2,6-bis(bromomethyl)toluene<sup>6a</sup>, **6**, at 60°C gave a 40% yield<sup>9</sup> of the *syn*, *anti*- mixture **2C**, **3C** in about a 4:1 ratio. Chromatography over silica gel followed by crystallization yielded pure<sup>10</sup> *anti*-**2C**, mp 164.5–165° and pure *syn*-**3C**, mp 170°C. Assignment of stereochemistry was readily made on the basis of the low temperature (–60°C) <sup>1</sup>Hmr spectra, when both compounds were in frozen conformations. The *anti*- compound **2C** shows its internal methyl protons at  $\delta$ 1.46, strongly shielded by the opposite cyclophane ring, consistent with other *anti*- cyclophanes.<sup>6</sup> Whereas *syn*-**3C** shows its methyl protons at  $\delta$ 2.37, almost normal for a toluene, and only marginally shielded from other *syn*- cyclophanes<sup>6</sup> by the opposite phenyl substituent, which indicates that this ring must be more or less edge on (see also below). Further support for this assignment is derived from the chemical shift of the *ortho*-protons of the phenyl substituent, H<sub>o</sub>, H'<sub>o</sub>: in the *anti*- compound **2C**, H<sub>o</sub> ( $\delta$ 6.55) is shielded somewhat from H'<sub>o</sub> ( $\delta$ 7.10) by the opposite cyclophane ring, whereas in *syn*-**3C**, H<sub>o</sub> is strongly deshielded to  $\delta$ 8.31 by steric compression with the opposite methyl group.<sup>11</sup>

Reaction of bromide **4** with thiol **5** yielded about 1% yield of **2B**, **3B** in a 10:1 ratio, from which pure<sup>10</sup> *anti*-**2B**, mp 248–249°C (lit<sup>3</sup>mp 220–226°C), could be separated by chromatography. On the basis of its (–60°C) <sup>1</sup>Hmr spectrum, it was assigned the *anti*- stereochemistry since H<sub>o</sub> and H'<sub>o</sub> appeared at very similar chemical shift ( $\delta$ 6.63 and 7.30) to those of *anti*-**2C**. This was subsequently confirmed by X-ray crystallography.<sup>12</sup>

The 90 MHz <sup>1</sup>Hmr variable temperature spectra for the aryl proton region of **2B**, **2C**, and **3C** are shown in Figure 1, together with the –60°C, 250 MHz spectra (which allow definitive placement of H<sub>o</sub> and H'<sub>o</sub>). The data used to obtain  $\Delta G_c^\ddagger$  values are given in Table 1. It is of extreme interest that these three values are very similar. From molecular models, and X-ray data of **2B**, it seems to us very unlikely that free rotation of the internal phenyl substituent can occur, more likely a flipping (twisting) process, such as shown in Figure 2 is

FIGURE 2: CONFORMATIONAL FLIPPING (TWISTING) PROCESS OF **2(3)**



occurring in which  $H_O$  ( $H'_O$ ) flips from one side of the methylene bridge protons to another. This would be consistent with the similarity of the three barriers, and closeness to that of **1A** ( $\Delta G_c^\ddagger = 54 \text{ kJ. mol}^{-1}$ ).<sup>3</sup> In due course, we hope to be able to make more detailed comments on this process from complete lineshape analyses, and further nmr and X-ray measurements which are now underway.

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Table 1: 90MHz Data Used to Calculate<sup>13</sup>  $\Delta G_c^\ddagger$

Compound			
$\Delta\nu$ (Hz)	141.6	44.3	50.1
$T_c$ (K)	265	262	243
$\Delta G_c^\ddagger$ (kJ. mol <sup>-1</sup> )	52.0	53.9	49.6

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