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SHORT COMMUNICATIONS

DYNAMIC BEHAVIOUR OF [2]METACYCLO[2](3,4)THIOPHENOPHANE

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The conformational analysis of dimethyl[2]metacyclo[2](3,4)thiophenophane (1), which is the thiophene analogue of [2.2]orthometacyclophane, is described. The comparison between the dynamic NMR spectra of 1 and the computer-simulated spectra led to the energy barrier between *syn* and *anti* conformers of 1. This is the first conformational analysis of a [2,2]orthometa-type cyclophane.

We recently reported[1] the synthesis and conformation of four possible isomers of [2]metacyclo[2](*m*,*n*)thiophenophanes [(*m*,*n*)MTPs]. Here we report a study on the dynamics of (3,4)MTP(1), which is thiophene analogue of [2.2]orthometacylophane.[2]

The dynamic ^{1}H NMR spectra* (100 MHz, in nitrobenzene-d^5) of 11- and 13-methyl protons of 1 (6H) and the computer-simulated spectra (DNMR2[3] was used)† are shown in Figure 1. At 27°C, compound 1 was composed of a 2 : 1 mixture of *syn* and *anti* conformers on the 100 MHz NMR time scale. As the temperature increased these signals became broadened and finally coalesced at 115 °C. The rate constant at each temperature was obtained by simulation. The Eyring plot of $1/T$ vis $\ln(k/T)$ afforded $\Delta S^{\ddagger}$ ($3 \cdot 8 \pm 0 \cdot 3$ and $2 \cdot 4 \pm 0 \cdot 3$ cal mol^{-1} K^{-1}) and $\Delta H^{\ddagger}$ ($21 \cdot 1 \pm 0 \cdot 1$ kcal mol^{-1}) (1 cal = 4·184 J). Therefore, the energy barrier ($\Delta G^{\ddagger}$) of the conformational change from *anti* to *syn* at 300 K is $20 \cdot 0 \pm 0 \cdot 2$ kcal mol^{-1} and that from *syn* and *anti* at 300 K is $20 \cdot 4 \pm 0 \cdot 1$ kcal mol^{-1}.

The results are summarized in Figure 2. Hopf and co-workers[2] predicted that the energy barrier of [2.2]orthometacylophane (2) would be between 20 and 24 kcal mol^{-1}. The $\Delta G^{\ddagger}$ value obtained in this work

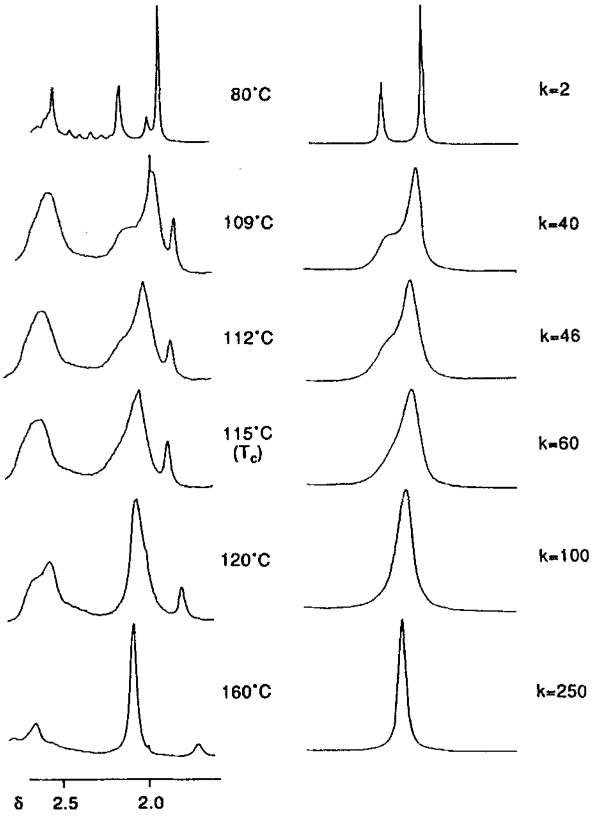

Figure 1. Dynamic NMR spectra of 1 (in nitrobenzene-d_5, 100 MHz) and the simulated spectra

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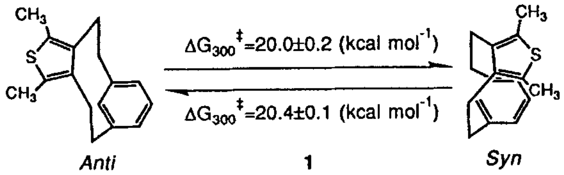
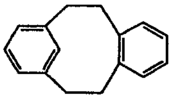


Figure 2. Conformational change of **1**

lies within this range. The reported energy barrier for the flipping of [6]metacyclophane-3-ene (**3**)[4] at 343 K is 16·5 kcal mol^{-1}, which is 3–4 cal mol^{-1} smaller than those of **1**. This energy barrier could probably be caused by the loss of the flexibility of the bridge motion when the C=C double bond is substituted by a thiophene moiety. This is the first dynamic analysis of the strained [2.2]orthometacyclophane system.



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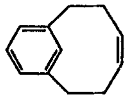

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REFERENCES

1. M. Takeshita and M. Tashiro, *J. Org. Chem.* **56**, 2837 (1991); **57**, 746 (1992).
2. G. J. Bodwell, L. Ernst, M. W. Haenel and H. Hopf, *Agnew. Chem., Int. Ed. Engl.* **28**, 455 (1989); G. J. Bodwell, L. Ernst, H. Hopf, P. G. Jones, J. P. McNally and D. Schomburg, *Chem. Ber.* **123**, 2381 (1990).
3. G. Binsch and D. A. Kleier, *DNMR2*, QCPE No. 140 (1969).
4. J. L. Goodman and J. A. Berson, *J. Am. Chem. Soc.* **107**, 5424 (1985).