A NOVEL THIA[3.2]METACYCLOPHAN-ENE WITH AN UNEXPECTED PREFERENCE FOR THE SYN CONFORMATION

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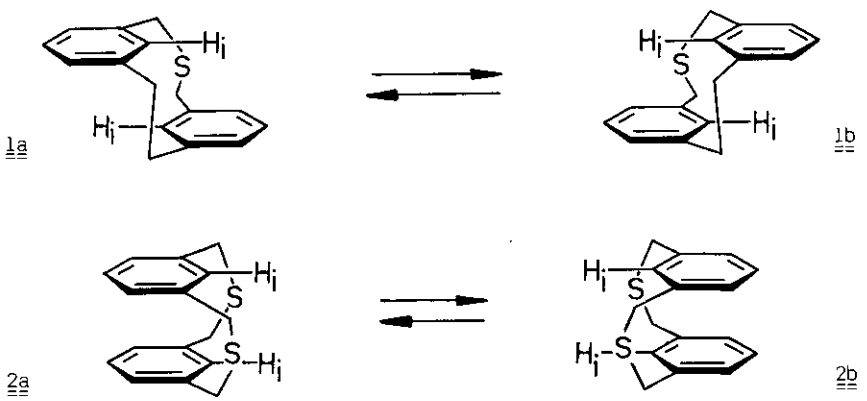
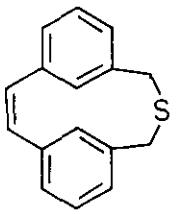
Abstract — Phenanthro(10,11-*l*)-2-thia[3.2]metacyclophan-10-ene 6 has been found by ^{1}H NMR studies to exist in the unexpected *syn* conformation. Comparison with conformational barriers in related systems suggest the absence of ring flipping in 6.

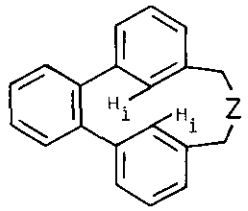
One of the more interesting aspects of thia- and dithiametacyclophane chemistry is their novel conformational behaviour.[1] The *anti-anti* flipping process, e.g. 1a ⇄ 1b (H_i at δ5.43),[2] is the most commonly observed conformational interconversion in [m.n]metacyclophanes (m=n or m≠n) while the *syn* geometry is believed to be less preferred due to steric repulsion between the two stacking parallel aromatic rings. The only known examples of the latter are the [3.3]metacyclophane systems,[3,4] e.g. 2a ⇄ 2b (H_i at δ6.82),[3] in which torsional strains in bridges in the *anti* conformation seems the major cause for the preferred *syn* stereochemistry. Examples of metacyclophan-ene are less well known; the parent thia[3.2]metacyclophan-ene 3 is not known but the synthesis of its derivative 4 was reported by Vogtle.[5] ^{1}H NMR studies[5] showed that 4 exists in an *anti* structure (H_i at δ6.08) and undergoes the conformational process similar to 1a ⇄ 1b involving both ring flipping and bridge rotation.

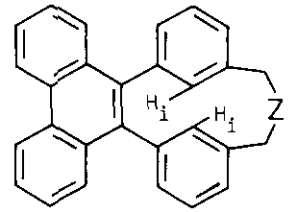


1a 1b

2a 2b







3

4 Z = S

5 Z = SO_2

6 Z = S

7 Z = SO

Our approach to the synthesis of a novel phenanthrodihydropyrene[6] involves, as a precursor, the thiametacyclophan-ene 6 which was initially expected to behave similarly to 4 in its conformational behaviour. Assignments of the aromatic protons are possible in the ^{1}H NMR spectrum of 6 (Figure 1) which is clearly of special interests. No distinct highly shielded aromatic protons characteristic of the *anti* conformation are observed; instead, the 'internal' H9 and H29 (H_i) appear as a broad singlet at δ7.36. This is clearly consistent with the *syn* conformation 6a (compare H_i of *anti* 4). Further evidence is provided by the presence of six protons shifted relatively upfield at δ6.6-7.1 (which appear as an ABX system) — a common consequence of superimposing two parallel benzene rings.[7] The reason for the preferred *syn* conformation can be rationalized by the presence of adverse steric interactions in the *anti* conformation 6b. Molecular model clearly shows that the ene-bridging half of the molecule 6b tends to achieve near planarity thus forcing the protons at C7 and C12, C21 and C25 to be in very close proximity. To our knowledge, 6 is the first novel example of the [m.n]metacyclophane derivatives besides the [3.3]-systems to exist in a *syn* conformation. The *syn* conformation of 6 also serves as a model

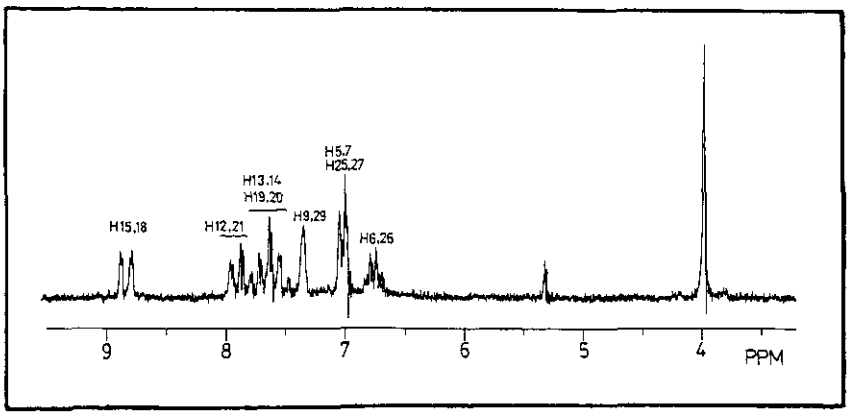
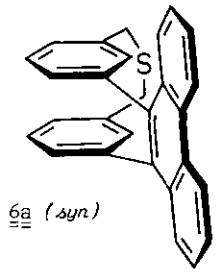
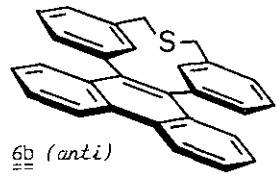


FIGURE 1 ^{1}H NMR spectrum of 6 determined in CD_2Cl_2 at 35°C on a Perkin Elmer R32 (90 MHz) spectrometer.



6a (*syn*)



6b (*anti*)

6a' 6a''

to illustrate the anisotropy of the bridging double bond, an effect still being disputed in a series of *anti* metacyclophane, *anti* metacyclophan-ene and *anti* metacyclophanediene.[8] While the chemical shifts[3] of H_i (δ6.82) and the other aromatic protons (δ6.92) of 2 are very similar,[9] the H_i protons (δ7.36) of 6 are clearly significantly deshielded compared to the *para*-positioned H6 and H26 at δ6.76. *We believe that this is due to the anisotropic effect of the bridging phenanthrene moiety.* Molecular models clearly suggest that the H_i protons are lying in vacinity of the deshielding zone of the 9,10-bond, which is well known to have a high π-bond order, of phenanthrene.

The $-CH_2S-$ protons of 6 appear as a singlet at δ3.98 (Figure 1) comparable to that reported for 4 (δ3.59).[5] Low temperature ^{1}H NMR studies, however, indicated only slight gradual broadening of the signal without actual coalescence of the peak even at -70°C. Although 6 is believed to prefer the *syn* conformation different from the *anti* 4, ring flipping in 6 similar to 2a ⇄ 2b is expected to involve a conformational barrier comparable to (or larger than; see below) that reported for 4 (T_c = -7°C; $\Delta G_c^{\ddagger}$ = 55 kJ mol^{-1}).[5] In fact ring flipping in 6 would require pseudorotation of the aryl rings which will have to overcome the steric hindrance of the protons at C12 and C21 of the bridging phenanthrene. This process is expected to involve a high conformational barrier similar to rotation of aryl rings in 9,10-diarylphenanthrenes.[10] The signal (δ3.98) for the $-CH_2S-$ protons of 6 (Figure 1) is in fact not very sharp suggesting a possibility that 6 does not undergo ring flipping but the AB protons of the bridge have almost identical chemical shifts.[11] This is further supported by the conformational studies of the sulfoxide 7 obtained by oxidation of 6 with bromine in bicarbonate solution.[12] The bridging protons of 7 appear as a clear AB system (δ_A4.55, δ_B4.35; J = 13.5 Hz; Δν = 18.0 Hz). High temperature ^{1}H NMR studies, however, showed no coalescence of the AB quartet up to 150°C. Although the sulfone 5 also showed a higher

conformational barrier ($\Delta G_c^{\ddagger}$ = 68 kJ mol $^{-1}$)[5] than 4, the high conformational rigidity of sulfoxide 7 (T_c > 150°C; $\Delta G_c^{\ddagger}$ > 89 kJ mol $^{-1}$) clearly supports the absence of the ring flipping process in both 6 and 7 at room temperature. Our results presented, however, do not rule out the possibility that the signal at δ3.98 in Figure 1 is an averaged signal resulting from fast wobbling of bridges 6a'⇄6a" similar to that in cycloalkanes and thus is expected to involve a much lower conformational barrier than ring flipping. This has also been observed in related processes in some metacyclophanes.[3,13]

Although the synthesis of *syn* [2.2]metacyclophane has recently been reported,[14] it rapidly isomerizes to the *anti* [2.2]metacyclophane above 0°C. The lack of preference for the *anti* 6b clearly suggests that the *syn* 6a could be a potential precursor, through ring contraction reactions,[15] to stable derivatives of *syn* [2.2]metacyclophane, *syn* [2.2]metacyclophan-ene and *syn* [2.2]metacyclophane-diene (the later two are still unknown). These conversions are currently being investigated.

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