Conformation and Ring Topomerization in *cis-syn-cis*-2,2,6,6-Tetramethoxyperhydroanthracene[1]

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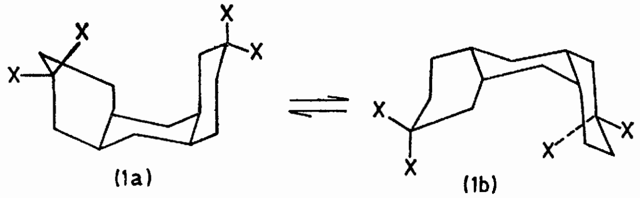
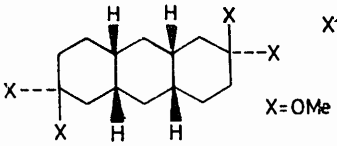
Summary The free activation energy for ring topomerization in *cis-syn-cis*-2,2,6,6-tetramethoxyperhydroanthracene at 212 K equals 47 kJ mol^{-1}.

Ring inversion in cyclohexane derivatives has been extensively studied. Results for *cis*-decalin systems are scarce, and to our knowledge there are no reports on invertomers of perhydroanthracenes, possibly because they are difficult to prepare, although they are interesting because three rings are involved in the topomerization[2] process.

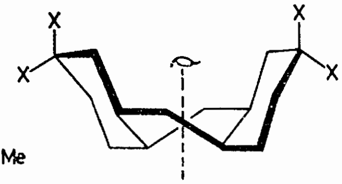
We have studied the temperature dependence of the ^1H n.m.r. spectrum of *cis-syn-cis*-2,2,6,6-tetramethoxyperhydroanthracene (**1**) (Varian HA-100, 10% in CS_2), prepared from the known[3] *cis-syn-cis*-perhydroanthracene-2,6-dione (m.p. 130 °C). At room temperature the methoxy-signals consist of two sharp, equally intense peaks. At lower temperatures ($T_{coal.} = 212$ K) there are four equally intense, but partially overlapping methoxy-signals. The splitting $\delta_{max.} = 5{\cdot}6$ Hz for one of the singlets to a doublet on lowering the temperature could easily be followed and leads to $\Delta G^{\ddagger}_{212} = 47$ kJ mol^{-1}. Methoxy-signals have very favourable relaxation times and, despite the relatively small low-temperature shift difference, the condition $\Delta\nu >> 1/T_2$ is met.



(1a) (1b)



(1)



(2)h

We favour the view that an all-chair/all-chair interconvertion occurs, *e.g.* (**1a**) ⇌ (**1b**). In this conformation, compound (**1**) has no symmetry element, so the four methoxy-groups are diastereotopic[4] and are found to be anisochronous under slow exchange conditions. Under fast exchange conditions (hypothetically planar rings) the effective point group of (**1**) is C_2 (axis perpendicular to the plane of the paper). There is a diastereotopic pair of equivalent methoxy-groups, and two signals are indeed found.

On the other hand the all-chair form of *cis-syn-cis*-perhydroanthracene has been calculated[5] to be only 8·6 kJ mol^{-1} more stable than a conformation in which the central ring assumes a classical boat form (**2**). Compound (**1**), in its all-chair form, moreover is strained by a 1,3-diaxial MeO · · · CH_2 interaction, and this strain has been estimated[6] as high as 8 kJ mol^{-1}. This interaction can be lowered by having the central ring in a boat form (non-classical boats are less likely here, because the torsion angles of a classical boat only fit an annellation with chair forms). A good case can be made for accepting that the central ring in (**1**) exists in the boat form, but in such a conformation (**2**) has a C_2 axis, and cannot give rise to the four different methoxy-signals in the n.m.r. spectrum.

Finally, the barrier to inversion in *cis*-2,2,7,7-tetramethoxydecalin is higher ($\Delta G^{\ddagger}_{236} = 52$ kJ mol^{-1})[7] than in (**1**), despite the fact that in the latter compound three rings are involved in the topomerization, and only two in the former. This can be ascribed to the severe 1,3-diaxial strain in the all-chair form of (**1**) which raises the energy of its ground state.

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