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THE INVERSION OF *CIS-TRANSOID-CIS-* AND *CIS-CISOID-CIS-*PERHYDROANTHRACENE[1]

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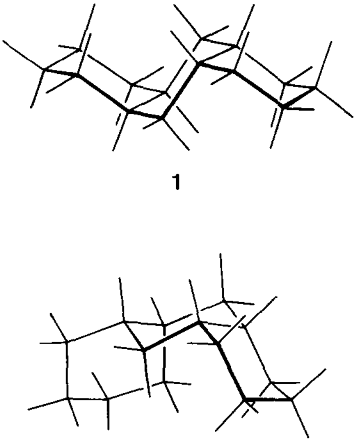
Abstract. The factors responsible for the difference between the inversion barriers of *cis-transoid-cis-* and *cis-cisoid-cis-*perhydroanthracene were explored by molecular mechanics.

The free enthalpies of activation for the inversion of the all-chair conformation of *cis-transoid-cis-*perhydroanthracene[3] (**1**) and of *cis-cisoid-cis-*perhydroanthracene[3,4] (**2**) (Scheme 1) are strikingly different (58.6 vs 47.3 kJ mol^{-1}). The *transoid* isomer has a fairly high barrier, well above that of the bicyclic *cis*-decalin (51.9 kJ mol^{-1}),[5] but for the *cisoid* isomer the barrier hardly exceeds $\Delta H^{\neq}$ of cyclohexane[6] (45.2 kJ mol^{-1}). To understand these experimental results we investigated the all-chair inversion of **1** and of **2** by molecular mechanics.[7]

The results of the molecular mechanics calculations show that two factors are responsible for the difference between the inversion barriers of **1** and **2** (Scheme 2): (i) the ground state (gs) of **2** is predicted to be strained relative to the ground state of **1** by 8.4 kJ mol^{-1}; (ii) the rate determining transition state (ts) of **1** is predicted to lie 7.5 kJ mol^{-1} above that of **2**.

The energy difference between the ground states of **1** and **2** does not need much comment as a difference of this magnitude is readily understood on the basis of the 1,3-synaxial interaction present in the ground state of **2** (Scheme 1). The energy difference between the rate determining

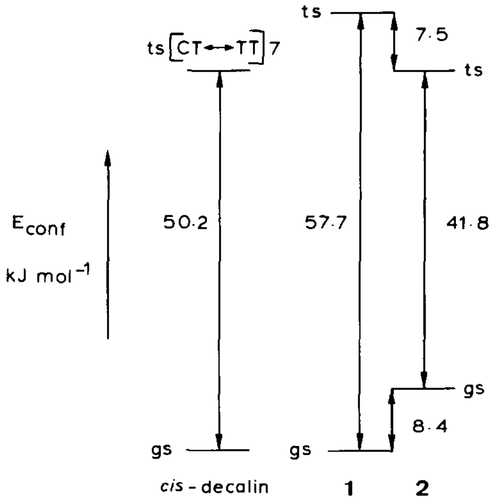
Scheme 1



1

2

Scheme 2



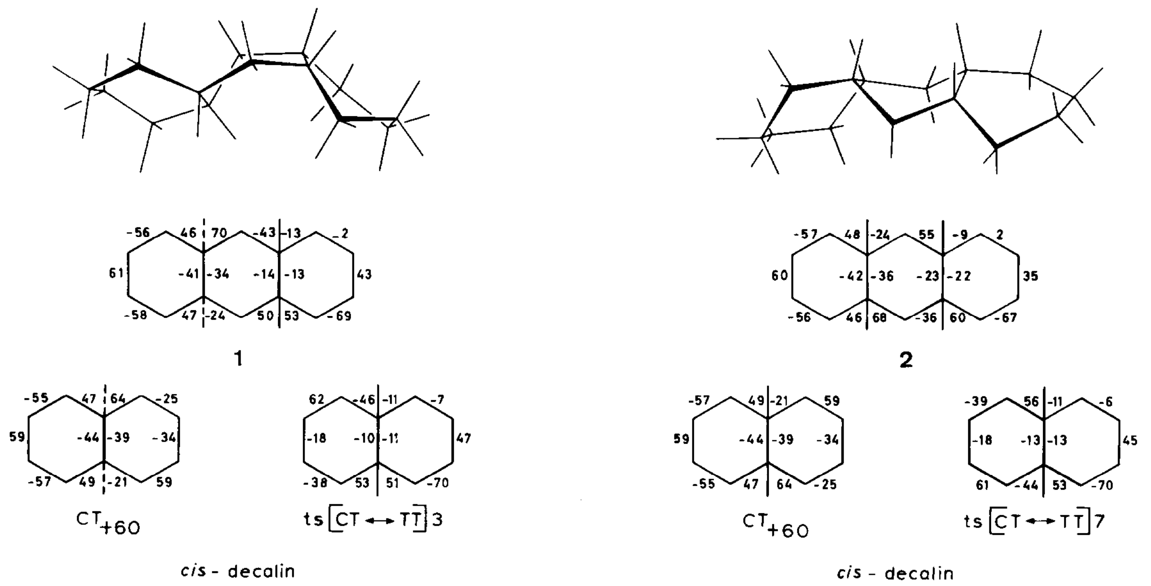


Figure 1. Analysis of the transition states of 1 and 2, both located on the chair-twist-twist to chair-twist-inverted chair step of the inversion, in *cis*-decalin geometries (endocyclic torsion angles are given in degrees).

transition states can be understood when we compare their geometries with geometries previously calculated for *cis*-decalin[8] (Figure 1). The transition state of 2 has lost the excess strain present in the ground state and combines the most favourable chair-twist conformation of *cis*-decalin (CT_{+60}) with the lowest chair-twist to twist-twist transition state of *cis*-decalin (ts[CT↔TT]7). This combination of *cis*-decalin geometries is geometrically not possible for 1. For this compound the rate determining transition state combines the CT_{+60} geometry with a higher energy *cis*-decalin transition state (ts[CT↔TT]3).

We note that the results of our calculations support the proposal of De Pessemier *et al.* about the inversion route of **1**.[9] Full details about these and alternative inversion routes will be given in a forthcoming paper.

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