with $Br_2BH{\cdot}SMe_2$ (5 mmol) for 8 h in the presence of *n*-decane (internal standard, 0.50 mL). The reaction mixture was quenched with NaOH (3 N, 12 mL) and oxidized with H_2O_2 (2 mL, 30%) in the presence of ethanol and THF (5 mL each) as cosolvents. The aqueous layer was saturated with K_2CO_3, and the organic layer was analyzed by GLC. There were formed 0.40 g (3.96 mmol) of 4-methyl-2-pentanol and 0.086 g (0.85 mmol) of 2-methyl-3-pentanol. Hence the regioselectivity is 82% in the 2-position and 18% in the 3-position of *trans*-4-methyl-2-pentene. Similarly, *cis*-4-methyl-2-pentene, 1-methylcyclohexene, *trans*-β-methylstyrene, and 3,3-dimethyl-1-butene were also studied. The data are given in Table I.

2-Methyl-5-hexen-1-ol. To 2-methyl-1,5-hexadiene (30 mmol) in CH_2Cl_2 (10 mL) was added $Br_2BH{\cdot}SMe_2$ in CH_2Cl_2 (30 mmol) dropwise, and the resulting solution was stirred for 1 h at room temperature. The reaction mixture was carefully quenched by addition to ice-cold NaOH (3 N, 30 mL). THF and ethanol (10 mL each) were added as cosolvents, and the boron intermediate was oxidized by H_2O_2 (15 mL, 30%). The organic materials were extracted with ether. The ether layer was washed with water and dried over anhydrous $MgSO_4$. The solvent was stripped off and the crude 2-methyl-5-hexen-1-ol was purified by distillation under reduced pressure. There was obtained 2.2 g of the unsaturated alcohol (2.1 mmol, 70%) whose ^1H and ^{13}C NMR spectra were in agreement with the expected structure: bp 88 °C (25 mmHg); n^{20}_D 1.4415 [lit.[19] bp 68 °C (12 mmHg); n^{20}_D 1.4380].

(4*Z*)-1,4-Octadiene. $Br_2BH{\cdot}SMe_2$ (30 mmol) was added dropwise to a cooled (water bath) solution of 1-octen-4-yne (Farchan, 30 mmol) in CH_2Cl_2. The resulting solution was stirred at room temperature for 1 h and then added carefully into an ice-cold solution of sodium methoxide in methanol (60 mmol). The volatiles were pumped off with the help of aspirator vacuum. The residue was refluxed with HOAc (30 mL) for 3 h. After a conventional workup and distillation, 2.40 g of (4*Z*)-1,4-octadiene (73% yield: bp 116 °C; n^{20}_D 1.4288) was obtained. Its structure and purity were checked by ^{13}C and ^1H NMR analyses.

Acknowledgment. We gratefully acknowledge the National Science Foundation for financial support (Grant CHE 79-18881).

Registry No. 3-Hexyne, 928-49-4; 4-octyne, 1942-45-6; 2-methyl-1-pentene, 763-29-1; cyclooctene, 931-88-4; 1-hexyne, 693-02-7; 2-methyl-2-butene, 513-35-9; 1-methylcyclopentene, 693-89-0; 1-hexene, 592-41-6; 1-octene, 111-66-0; cycloheptene, 628-92-2; 1-phenyl-1-propyne, 673-32-5; *cis*-3-hexene, 7642-09-3; *cis*-4-methyl-2-pentene, 691-38-3; *cis*-4-octene, 7642-15-1; *trans*-3-hexene, 13269-52-8; 3,3-dimethyl-1-butene, 558-37-2; cyclopentene, 142-29-0; *trans*-4-methyl-2-pentene, 674-76-0; phenylacetylene, 536-74-3; *trans*-2,5-dimethyl-3-hexene, 692-70-6; 2,3-dimethyl-2-butene, 563-79-1; *cis*-2,5-dimethyl-3-hexene, 10557-44-5; 1-methylcyclohexene, 591-49-1; styrene, 100-42-5; cyclohexene, 110-83-8; *trans*-β-methylstyrene, 873-66-5; *cis*-β-methylstyrene, 766-90-5; 1-octen-4-yne, 24612-83-7; 2-methyl-1,5-hexadiene, 4049-81-4; 2-methyl-5-hexen-1-ol, 55671-55-1; (*Z*)-1,4-octadiene, 25913-88-6; $Br_2BH{\cdot}SMe_2$, 53793-30-9.

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[19] Colonge, J.; Lasfargues, P. *Bull. Soc. Chim. Fr.* **1962**, 177–182.

[20] Campbell, J. B., Jr. Ph.D. Thesis, Purdue University, 1978.

Empirical Force Field Calculations. 20. Routes in the Inversion of *cis-transoid-cis-* and of *cis-cisoid-cis*-Perhydroanthracene[1,2]

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The inversion of the all-chair (CCC) conformation of *cis-transoid-cis-* (1) and of *cis-cisoid-cis*-perhydroanthracene (2) has been explored by molecular mechanics. The inversion proceeds by the stepwise conversion of chair (C) to twist (T) and twist to inverted chair ($\bar{C}$) forms of the constituent rings. The three basic step sequences leading from CCC to the "half inverted" intermediates TTT and $CT\bar{C}$ have been studied: (1) CCC ⇄ CCT ⇄ CTT ⇄ $CT\bar{C}$; (2) CCC ⇄ CCT ⇄ CTT ⇄ TTT; (3) CCC ⇄ CCT ⇄ TCT ⇄ TTT. In both 1 and 2 sequence 1 provides the calculated path of inversion with the lowest barrier. The CTT to $CT\bar{C}$ conversion is rate determining in both compounds. The calculated enthalpies of activation for 1 and 2 amount to 13.8 and 10.0 kcal mol^{-1}, respectively. The experimental barriers are $\Delta G^{\ddagger}_{319} = 14.1$ kcal mol^{-1} for 1 and $\Delta G^{\ddagger}_{241} = 11.3$ kcal mol^{-1} for 2. The geometries of the ground states and the transition states are discussed in relation to the earlier computational work on the *cis*-decalin inversion. Of the two isomers 1 has the more stable ground state, but it also features the more strained transition state. The calculated energy differences between the ground states (2.0 kcal mol^{-1}) and between the transition states (−1.8 kcal mol^{-1}) explain the relatively high barrier of 1 and the relatively low barrier of 2. The pseudorotating manifolds of 1 and 2 and the interconversions between the various conformations are discussed.

The perhydroanthracenes have played an important role in the development of conformational analysis. The relative stabilities of the five isomers have been predicted successfully quite early.[4] The heat of combustion of the trans-transoid-trans isomer has provided one of the first estimates of the chair–twist energy difference in cyclohexane.[5] More recently, Allinger and Wuesthoff[6] have studied the equilibrium of the five isomers both experimentally and by force field methods. We[7] have now obtained the Gibbs energy of activation for the inversion of the all-chair conformation of *cis-transoid-cis*-perhydroanthracene (1) and of *cis-cisoid-cis*-perhydroanthracene (2, Figure 1). The present $\Delta G^{\ddagger}$ values, 14.1 and 11.3 kcal mol^{-1} for 1 and 2, respectively, are recalculated by using a value of $^1/_2$ for the transmission coefficient κ in the

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[1] Part 19: Peters, J. A.; van Ballegoyen-Eekhout, G. W. M.; van de Graaf, B.; Bovée, W. M. M. J.; Baas, J. M. A.; van Bekkum, H. *Tetrahedron*, in press. Part 18: Vanhee, P.; van de Graaf, B.; Baas, J. M. A.; Tavernier, D. *Tetrahedron Lett.* **1982**, *23*, 3837–8.

[2] Baas, J. M. A.; van de Graaf, B.; Tavernier, D.; Vanhee, P., presented in part at the International Conference on Conformational Analysis, Durham NH, June 1981.

[3] (a) Gent University. (b) Delft University.

[4] Johnson, W. S. *J. Am. Chem. Soc.* **1953**, *75*, 1498–500.

[5] Margrave, J. L.; Frisch, M. A.; Bautista, R. G.; Clarke, R. L.; Johnson, W. S. *J. Am. Chem. Soc.* **1963**, *85*, 546–8.

[6] Allinger, N. L.; Wuesthoff, M. T. *J. Org. Chem.* **1971**, *36*, 2051–3.

[7] Vanhee, P.; De Pessemier, F.; Anteunis, M.; Tavernier, D. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 294–7.

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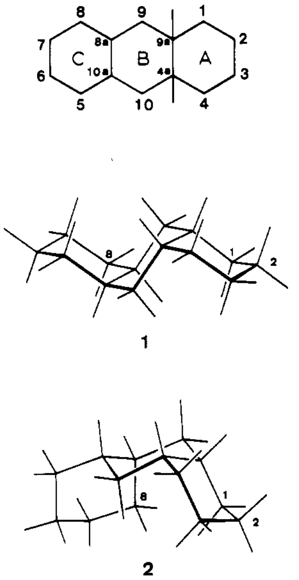


Figure 1. Numbering and calculated ground-state geometries of *cis-transoid-cis*-perhydroanthracene (1) and *cis-cisoid-cis*-perhydroanthracene (2).

Eyring equation. In the case of **2**, $\kappa = {}^1/_2$ is the upper limit (see below). Recently, Fawcett and Heatley[8] have published $\Delta H^\ddagger = 11.3$ kcal mol^{-1} and $\Delta S^\ddagger = -0.3$ cal mol^{-1} K^{-1} for the inversion of the cisoid isomer **2**; their and our value for the Gibbs energy of activation agree within experimental error.

The inversion barriers of **1** and **2** are strikingly different. The transoid isomer has a fairly high barrier,[9] well above that of the bicyclic *cis*-decalin[10] (14.1 vs. 12.4 kcal mol^{-1}), but for the cisoid isomer the barrier hardly exceeds $\Delta H^\ddagger$ of simple cyclohexane[11] (11.3 vs. 10.8 kcal mol^{-1}). The ground state of **2** is severely strained by a 1,3-synaxial interaction (see Figure 1) and here must lie one factor responsible for the low barrier of this hydrocarbon. A full explanation of the different values of the barriers in **1** and **2** must take into account the nature of the inversion paths and, in particular, the geometries of the rate-determining transition states. For this reason we have investigated the all-chair inversion of **1** and of **2** by molecular mechanics.

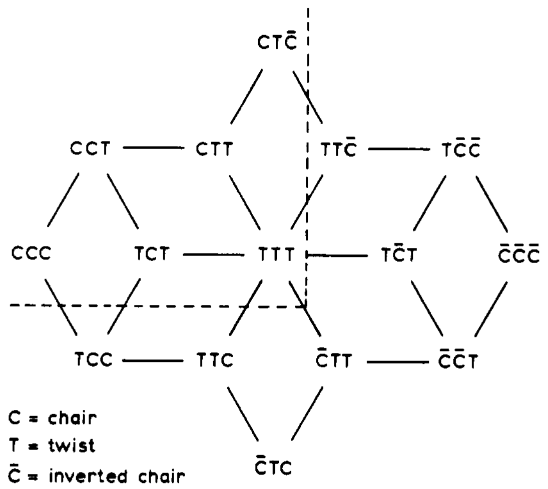
Scheme I is a graph of the various reaction paths by which the all-chair form CCC of **1** and of **2** can proceed to the inverted all-chair form C̄C̄C̄. Each point (vertex) of the graph represents a single conformation (CCC) or a set of conformations interconverting by the pseudorotation of one or more rings in the twist form; the lines (edges) symbolize transitions from chair to twist or vice versa of one and only one ring of the tricyclic system. Each line may represent several reaction paths for the chair to twist transition in question. Because of the symmetry of **1** and **2** only part of the conformational space has to be explored, e.g., the one isolated by the dashed line in Scheme I. In this part there are three basic step sequences leading from CCC to the "half-inverted" conformations TTT and CTC̄:

$$\mathrm{CCC} \rightarrow \mathrm{CCT} \rightarrow \mathrm{CTT} \rightarrow \mathrm{CT\bar{C}}$$

$$\mathrm{CCC} \rightarrow \mathrm{CCT} \rightarrow \mathrm{CTT} \rightarrow \mathrm{TTT}$$

$$\mathrm{CCC} \rightarrow \mathrm{CCT} \rightarrow \mathrm{TCT} \rightarrow \mathrm{TTT}$$

Scheme I



The completely inverted C̄C̄C̄ conformation is formed from these half-inverted intermediates by palindromically symmetric transition sequences.

There are two earlier comments on the all-chair inversion of perhydroanthracenes in the literature. Dale[12] has discussed an inversion mechanism of a tetramethoxylated **2**.[13] He considered the TTT intermediate in some detail but left other possibilities open. De Pessemier et al.[14] have presented a semiquantitative study on the inversion of **1** by way of a CTC̄ intermediate.

Experimental Section

Calculations. The Engler force field[15] and the Delft computer program for molecular mechanics[16] have been used. We have recently published an extensive empirical force field study of the conformational space of *cis*-decalin;[17] 27 stationary states were found. A tetramethylene bridge was added to each of these stationary states to construct the third ring of the perhydroanthracenes. This has been done at each of the two six-membered rings of *cis*-decalin. The geometries so obtained served as starting points for the calculations. Most of the stationary states of **1** and **2** were found in this way. Forced rotation around one or more bonds[18] was used only in a few cases to locate transition states.

It will be clear from this description that an exhaustive study of the conformational space of **1** and **2** was not our aim. Our prime interest lies in the routes of low potential energy for the inversion of **1** and **2**; many of the TTT conformations will be at very high energy anyway.

NMR Measurements. The inversion rate of **1** was determined from the coalescence of the signals from the bridgehead carbon atoms as well as from the coalescence of the C(2,6) and C(3,7) lines in the ^{13}C NMR spectrum. The frequency difference of the signals at slow exchange (373.54 and 324.71 Hz, respectively) was almost invariable with temperature. Therefore, it was assumed that the same values hold at the coalescence temperatures (320 and 318 K, respectively). Using the Eyring equation and assuming a transmission coefficient of ${}^1/_2$, we calculated from the two

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[8] Fawcett, A. H.; Heatley, F. *J. Chem. Res., Synop.* **1981**, 294–5.

[9] It is assumed that the $\Delta S^\ddagger$ value of the inversion barrier of **1** is also small as has been determined for the inversion barrier of **2** (see above) and of *cis*-decalin[10] (0.1 cal mol^{-1} K^{-1}). Symmetry numbers and chirality contribute $R \ln 2$ to $\Delta S^\ddagger$ of **1**, **2**, and *cis*-decalin.

[10] Mann, B. E. *J. Magn. Reson.* **1976**, *21*, 17–23.

[11] Anet, F. A. L.; Bourn, A. J. R. *J. Am. Chem. Soc.* **1967**, *89*, 760–8.

[12] Dale, J. *Top. Stereochem.* **1976**, *9*, 259.

[13] De Pessemier, F.; Tavernier, D.; Anteunis, M. *J. Chem. Soc., Chem. Commun.* **1973**, 594–5.

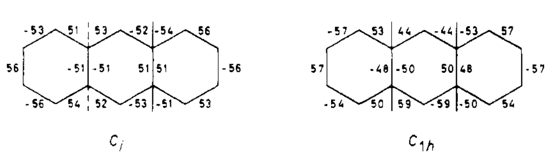
[14] De Pessemier, F.; Anteunis, M.; Tavernier, D. *Bull. Soc. Chim. Belg.* **1978**, *87*, 179–87.

[15] Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005–25.

[16] Van de Graaf, B.; Baas, J. M. A.; van Veen, A. *Recl. Trav. Chim. Pays-Bas* **1980**, *99*, 175–8.

[17] Baas, J. M. A.; van de Graaf, B.; Tavernier, D.; Vanhee, P. *J. Am. Chem. Soc.* **1981**, *103*, 5014–21. The relation between the part of the conformational space described for *cis*-decalin and that of the CB and BA moieties of **1** and **2** in the present study is dependent on the compound, the moiety, and the step in question (Scheme I). The *cis*-decalin geometries depicted in the Figures 6–8 are actually (equienergetic) mirror images of the forms described for *cis*-decalin.

[18] Van de Graaf, B.; Baas, J. M. A. *Recl. Trav. Chim. Pays-Bas* **1980**, *99*, 327–8.



1 2

Figure 2. Endocyclic torsion angles (degrees) of the all-chair ground states of 1 and 2.

coalescences a Gibbs energy of activation $\Delta G^{\ddagger}_{318,320}$ = 14.06 kcal mol^{-1}. The ^{13}C NMR spectrometer was a Brucker WP200 apparatus operating at 50.28 MHz. The tricyclic compound was dissolved in $CDCl_3$ (about 20 mg mL^{-1}) and sealed in a 10-mm NMR sample tube. The solvent was used as a lock and Me_4Si as the internal reference. The ^{1}H noise decoupled ^{13}C NMR spectra were recorded in the pulse FT mode with a flip angle of 36°, the duration of the 90° pulse being 15 μs.

The Gibbs energy of activation of 2 was obtained in an analogous manner by using the signals of the C(1,8) and C(4,5) carbon atoms as coalescence pairs: $\Delta G^{\ddagger}_{241}$ = 11.29 kcal mol^{-1} ($\Delta\nu$ = 67.6 Hz). The ^{13}C NMR spectrometer was a Varian XL-100 apparatus operating at 25.2 MHz. The concentration of the carbon disulfide solution was about 40 mg mL^{-1} (internal lock acetone-d_6, internal reference Me_4Si). The ^{1}H noise decoupled spectra were recorded in the pulse FT mode (acquisition time 0.4 s, pulse width 12 μs).

All settings of the variable temperature unit were checked against the "methanol NMR thermometer". The sensitivity was enhanced by applying an exponential function in the processing of the FID signal.

Results and Discussion

In Tables I and II (supplementary material) we present the conformational energy and the torsion angles of 55 stationary states (minima and transition states) of 1 and of 39 stationary states of 2. Only the ground states and the rate-determining transition states of 1 and of 2 are discussed here; comments on the pseudorotating manifolds and all other interconversions between the various conformations are included in the supplementary material.

All-Chair Ground States. The calculated enthalpy difference between the all-chair ground states of 2 and 1 amounts to 2.0 kcal mol^{-1}. This compares well with the earlier calculations.[6] A comparison of the geometries (Figure 2) also shows the steric strain in 2. While in 1 the torsion angles of ring B are almost identical with those around the central and inner bonds of *cis*-decalin,[17] we have found in ring B of 2 a considerable flattening around the bonds between the axial methylene groups and a puckering on the opposite side. This is a manifestation of the so-called "reflex effect".[19] Despite the flattening the nonbonded distance between two of the hydrogen atoms on the axial methylene groups 1 and 8 is as short as 2.04 Å (see Figure 1).

CCC to C̄C̄C̄ Routes and Barriers. The conformational energy vs. the inversion coordinate for the three possible CCC to C̄C̄C̄ inversion routes of 1 and 2 are shown in the Figures 3 and 4, respectively. The inversion coordinate is composed of the various reaction coordinates of the transitions between each pair of stable conformations. In these figures the most stable conformation of each intermediate and the lowest transition state between them are represented. It can be seen that for both 1 and 2 the inversion route over the CTC̄ intermediate is the easiest one, as De Pessemier et al.[14] have anticipated. The calculated enthalpy of activation for 1 ($\Delta H^{\ddagger}$ = 13.8 kcal mol^{-1}) compares well with the experimental barrier ($\Delta G^{\ddagger}_{319}$ = 14.1 kcal mol^{-1}). The two rate-determining transition states of equal height to be passed for the all-chair inversion corroborate the use of a transmission coefficient $\kappa = {}^1/_2$ in the Eyring equation. In the cisoid isomer 2 calculation and experiment give more divergent numbers ($\Delta H^{\ddagger}_{\text{calcd}}$ = 10.0 vs. $\Delta G^{\ddagger}_{241}$ = 11.3 kcal mol^{-1}). The difference between $\Delta H^{\ddagger}_{\text{calcd}}$ and the experimental barrier of 2 can be imputed on the one hand to a general underestimation of strain in the transition states of six-membered rings by the Engler force field. This underestimation is also found in the calculations on cyclohexane[16] (10.1 vs. 10.8 kcal mol^{-1}) and *cis*-decalin[17] (12.0 vs. 12.4 kcal mol^{-1}). On the other hand, one can argue about the proper value of κ. Judging from the energy profile for 2 (Figure 4), $\kappa = {}^1/_2$ appears to be the upper limit. A value as low as ${}^1/_6$ for the six transition states of almost equal height to be passed between CCC and C̄C̄C̄ gives $\Delta G^{\ddagger}_{\text{exptl}}$ = 10.8 kcal mol^{-1}, a value which agrees better with the calculated enthalpy of activation. As far as the results of Fawcett and Heatley[8] are concerned, $\kappa = {}^1/_6$ does not change the value of $\Delta H^{\ddagger}_{\text{exptl}}$ but results in a much more positive $\Delta S^{\ddagger}$ value (1.9 cal mol^{-1} K^{-1}) from the same experimental data than calculated for $\kappa = {}^1/_2$ (−0.3 cal mol^{-1} K^{-1}). A sizable positive $\Delta S^{\ddagger}$ in 2 seems less probable in view of the decrease of $\Delta S^{\ddagger}$ from 2.8 cal mol^{-1} K^{-1} in cyclohexane[11,20] to 0.1 cal mol^{-1} K^{-1} in *cis*-decalin[10]

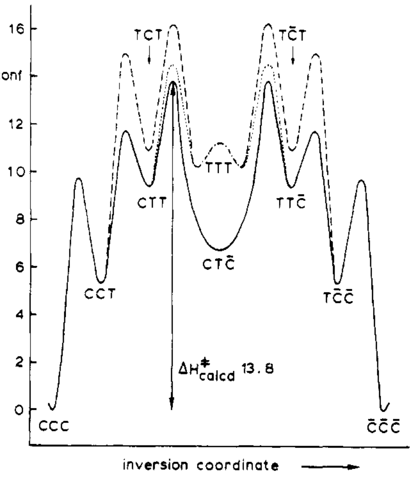


Figure 3. Routes and barriers (kcal mol^{-1}) of the all-chair inversion of 1.

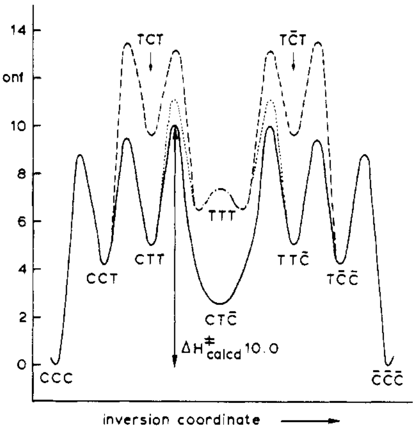


Figure 4. Routes and barriers (kcal mol^{-1}) of the all-chair inversion of 2.

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(19) Sandris, C.; Ourisson, G. *Bull. Soc. Chim. Fr.* **1958**, 1524–6.

(20) At variance with the opinion of Wiberg and Boyd (see footnote 14 in ref 21) the experimental value of 2.8 cal mol^{-1} K^{-1} determined for cyclohexane-d_{11} needs no symmetry number correction. We calculate for the combined contribution from symmetry numbers, chirality, and three equienergetic transition states (in the case of cyclohexane-d_{11}) to $\Delta S^{\ddagger}$ for cyclohexane and cyclohexane-d_{11} a value of *R* ln 6.

(21) Wiberg, K. B.; Boyd, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 8426–30.

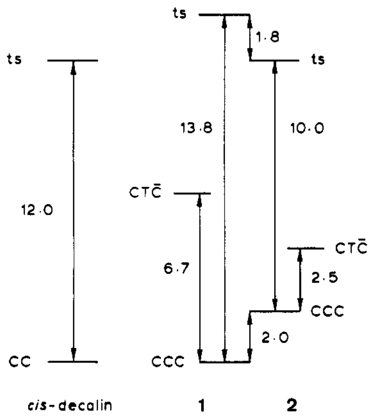

Figure 5. Comparison of the energy (kcal mol^{-1}) of the ground states, of the rate-determining transition states and of the CTC̄ conformers of **1** and **2**.

when the full pseudorotational freedom of the cyclohexane transition state is restricted by an adjacent six-membered ring. However, the determination of $\Delta H^{\ddagger}_{\text{exptl}}$ and $\Delta S^{\ddagger}_{\text{exptl}}$ from line-shape analysis of NMR signals is generally much less accurate than indicated by the reliability resulting from the least-squares fit of $\ln k/T$ vs. T^{-1}.[22] That is why we cannot reject definitely a value of $\kappa = {}^1/_6$ of **2** at this moment.

A formal explanation of the difference between the inversion barriers of **1** and **2** is shown in Figure 5. On the one hand there is the destabilization of the ground state of **2** compared to that of **1** (2.0 kcal mol^{-1}), and on the other hand there is the destabilization of the transition state of **1** compared to that of **2** (1.8 kcal mol^{-1}). Moreover, the CTC̄ conformation of **2** is more stable than that of **1**: the enthalpy difference between CTC̄ and CCC is as large as 6.7 kcal mol^{-1} in the case of **1** and only 2.5 kcal mol^{-1} for **2**. The rate-determining transition state of the CCC to C̄C̄C̄ inversion of **1** and of **2** resembles much more the CTC̄ intermediate than the CCC ground state, and so the smaller inversion barrier of **2** and its smaller CTC̄ minus CCC enthalpy difference are related phenomena.

Further insight into the different barriers of **1** and **2** comes from a comparison of the geometries of the rate-determining transition states with the conformations of *cis*-decalin.[17] Figure 6 shows that the transition state of **2** arises quite naturally from the lowest transition state of *cis*-decalin by the relatively unhindered attachment of a tetramethylene chain to ring B in the cis-cisoid fashion. The geometry of the rings C and B corresponds to the most favorable chair–twist form of *cis*-decalin. There are, of course, minor differences between the transition state of *cis*-decalin and the BA moiety in the transition state of **2**. But, as a first approximation, the conformational energy of the latter should be equal to 10.0 kcal mol^{-1}, i.e., $\Delta H^{\ddagger}_{\text{calcd}}$ for the *cis*-decalin transition state (12.0 kcal mol^{-1}) minus the excess strain due to the 1,3-synaxial interaction present in the ground state of **2** and not in its transition state (2.0 kcal mol^{-1}). The essential thing is not the numerical correspondence for this rough approximation but the qualitative insight that **2** must be expected to have a substantially lower barrier for inversion than *cis*-decalin, as indeed it does ($\Delta G^{\ddagger}_{\text{exptl}}$ = 11.3 vs. 12.4 kcal mol^{-1} with $\kappa = {}^1/_2$).

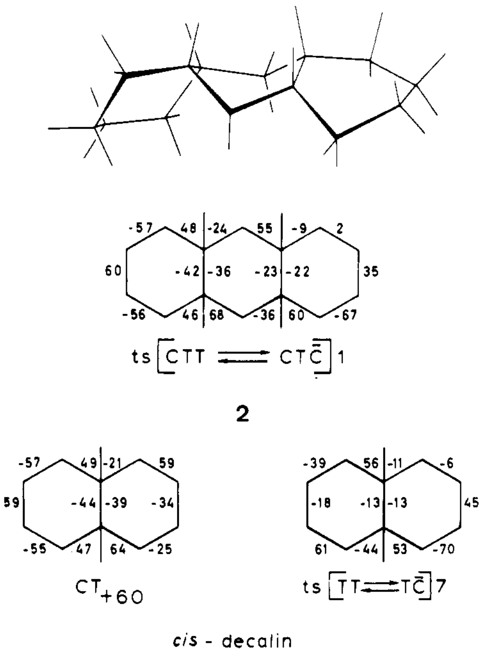

Figure 6. Calculated geometry and endocyclic torsion angles of the transition state of **2**; comparison with *cis*-decalin conformations.

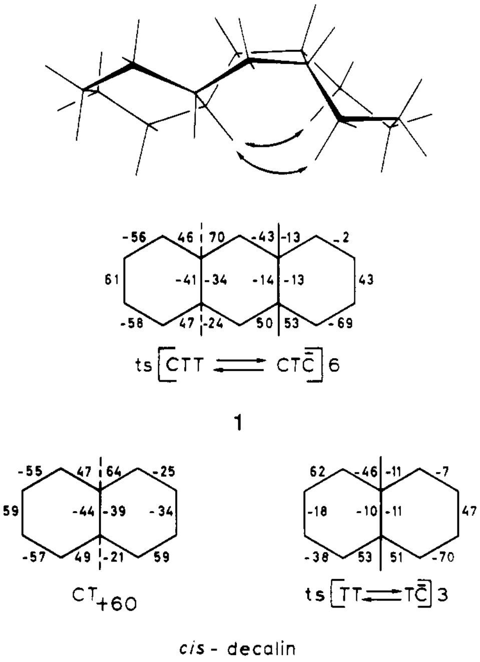

Figure 7. Calculated geometry and endocyclic torsion angles of the transition state of **1**; comparison with *cis*-decalin conformations.

For the transition state of **1** it is not possible to combine the most stable transition state of *cis*-decalin and the most stable chair–twist form in a transoid fashion. In its lowest rate-determining transition state (Figure 7) the converting ring A has about the same geometry as in that of **2** discussed above, but the twisting of ring B is quite different. The geometry of the BA moiety is very similar to a higher lying *cis*-decalin transition state. The geometry of the rings C and B corresponds again to the most favorable chair–twist form of *cis*-decalin. The transition state of **1** is destabilized by some short distances between hydrogen atoms on positions 1 and 4 of the converting ring A and one of the angular hydrogen atoms on the C/B fusion (see the arrows in Figure 7). For instance, the calculated distance between the nearest hydrogen atoms on carbon atoms 4 and 8a is 2.38 Å, quite close to the shortest hydrogen-hydrogen distance in axial methylcyclohexane. Direct steric interactions between the additional methylene

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[22] (a) Shoup, R. R.; Becker, E. D.; McNeel, M. L. *J. Phys. Chem.* **1972**, *76*, 71–8. (b) Binsch, G. *Top. Stereochem.* **1968**, *3*, 125.

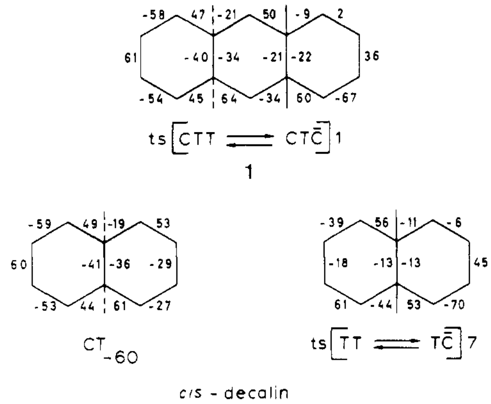

Figure 8. Endocyclic torsion angles of a higher lying transition state of 1; comparison with *cis*-decalin conformations.

groups forming ring C and the rings B and A are absent so that one may expect that this transition state of 1 has the same strain as its component *cis*-decalin transition state: 13.5 kcal mol^{-1}, a value satisfactorily close to the 13.8 kcal mol^{-1} obtained in the full computation. We actually also found a transition state of 1 that combines the lowest *cis*-decalin transition state with a relatively unstable chair–twist form (Figure 8), but its energy lies 0.9 kcal mol^{-1} higher.

In summary one can say that the rate-determining transition states of 1 and 2 are composed of the same most stable chair–twist moiety of *cis*-decalin for rings C and B combined with different chair–twist to twist–twist transition-state geometries for rings B and A; the BA moiety of the transoid isomer assumes a conformation of higher energy.

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Supplementary Material Available: Tables I and II contain the conformational energy, the endocyclic torsion angles of the three six-membered rings, and one exocyclic torsion angle at both ring-fusion sites for each stationary state of 1 and 2. A great number of non-rate-determining chair to twist transition states on the various reaction paths between the different forms depicted in Scheme I are analyzed in Tables III–VIII and are discussed in terms of *cis*-decalin forms. The pseudorotation within the various manifolds of 1 and 2 is elucidated in Figures 9–13 and in Table IX and is discussed in the same manner (25 pages). Ordering information is given on any current masthead page.

Chemistry of Bridged Aromatics. A Study of the Substituent Effect on the Course of Bond Cleavage of 9,10-Dihydro-9,10-ethanoanthracenes and an Oxyanion-Assisted Retro-Diels–Alder Reaction†

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The retro-Diels–Alder reactions of 9,10-dihydro- and 1,4,9,10-tetrahydro-9,10-ethanoanthracenes are dramatically accelerated by an oxyanion substitution on the 2π component, i.e., the ethano bridge. Studies of related systems bearing anionic, cationic, and radical substituents indicate that the cycloreversion is concerted and occurs only if both 4π and 2π fragments are highly resonance stabilized.

The retro-Diels–Alder reaction continues to receive much synthetic[1] as well as mechanistic[2] attention. However, high temperatures, frequently above 250 °C, required to effect the reaction compromise synthetic utility. Recently Grimme et al.[3] have reported that cycloreversion of some Diels-Alder adducts is dramatically accelerated by anionic substituents. For example, cycloreversion of some Diels–Alder adducts of 5-cyanocyclopentadiene is strongly accelerated by deprotonation,[3a] and an alkoxide substituent on the 4π component (at C_1) of the bicyclo[2.2.2]octadiene system accelerates the rate of cycloreversion at least by 10^{16}.[3b] The observed dramatic rate enhancement has been attributed to the formation of resonance-stabilized and weakly basic anions from more strongly basic anionic adducts. Similar oxyanion accelerations have been reported in other types of thermal pericyclic reactions.[4-6] To account for such substituent effects on the rates of pericyclic reactions, Carpenter[7] has recently proposed a comprehensive theoretical model and predicted that [4 + 2] cycloreversion would also be accelerated by anionic, cationic, and possibly radical substituents on the 2π component. In connection with other objectives we have decided to examine if the temperatures required for cycloreversion of 9,10-dihydro-9,10-ethanoanthracenes, which are typically 200 °C or above, could be substantially lowered by introduction of such substit-

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(1) Ripoll, J. L.; Rouessac, A.; Rouessac, F. *Tetrahedron* **1978**, *34*, 19 and references therein.

(2) Sauer, J.; Sustmann, R. *Angew Chem., Int. Ed. Engl.* **1980**, *19*, 779 and references therein.

(3) (a) Grimme, W.; Neukam, W. *Tetrahedron Lett.* **1978**, 2201. (b) Papies, O.; Grimme, W. *Ibid.* **1980**, 2799.

(4) For oxyanion acceleration of [3,3] sigmatropic shifts see: (a) Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765. (b) Evans, D. A.; Nelson, J. V. *Ibid.* **1980**, *102*, 774. (c) Evans, D. A.; Baillargeon, D. J. *Tetrahedron Lett.* **1978**, 3319.

(5) For oxyanion acceleration of [1,3] sigmatropic shifts see: (a) Thies, R. W.; Seitz, E. P. *J. Chem. Soc., Chem. Commun.* **1976**, 846. (b) Thies, R. W.; Seitz, E. P. *J. Org. Chem.* **1978**, *43*, 1050. (c) Wilson, S. R.; Mao, T. M.; Jernberg, K. M.; Ezmirly, S. T. *Tetrahedron Lett.* **1977**, 2559. (d) Franzus, B.; Scheinbaum, M. L.; Waters, D. L.; Bowlin, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 1241.

(6) For oxyanion acceleration of vinylcyclopropane rearrangement see: Danheiser, R. L.; Martinez-Davila, C.; Morin, J. M., Jr. *J. Org. Chem.* **1980**, *45*, 1340.

(7) Carpenter, B. K. *Tetrahedron* **1978**, *34*, 1877.

0022-3263/83/1948-0652$01.50/0