product showed the following yields: **3** (41%) and **1** (4%) with ODCB; **3** (30%) and **1** (5%) with decalin. A 1-mL aliquot was titrated for a 50% and 62% {Cl^+}, respectively.

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Registry No. 2, 24375-05-1; **4**, 34913-44-5; **5**, 69083-99-4; 1-$AdCH_2NH_2$, 17768-41-1; 1-AdNHCl, 24375-06-2; 1-AdNHBr, 5511-20-6; 1-$AdNH_2$, 768-94-5; 1-$AdCH_2NBr_2$, 75558-64-4; 1-$AdNClCOCH_3$, 64741-22-6; 1-AdNClEt, 34913-37-6; 1,1′-azoadamantane, 21245-62-5; 1-AdCl, 935-56-8; 1,3-dichloroadamantane, 16104-50-0; 1-AdBr, 768-90-1; 1-$AdNH_2$, 768-94-5; 1-$AdNHCOCH_3$, 880-52-4; 1-AdNHEt, 3717-44-0; $(CH_3)_3CCH_2Cl$, 753-89-9; 1-AdCN, 23074-42-2.

Conformational Properties of *cis,cis,cis*-1,5,9-Cyclododecatriene. Dynamic Nuclear Magnetic Resonance Spectroscopy and Empirical Force Field Calculations

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Dynamic NMR effects are observed in both the ^1H and ^{13}C NMR spectra of *cis,cis,cis*-1,5,9-cyclododecatriene in the vicinity of −140 to −150 °C. Empirical force field calculations show that the NMR data can be interpreted in terms of a "helix" conformation of C_2 symmetry. This conformation pseudorotates with a calculated strain energy barrier of 6.3 kcal/mol, in agreement with an experimental free-energy barrier of 5.9 kcal/mol. The pseudorotation of the helix takes place via a pair of enantiomeric "saddle" conformations which are calculated to be 0.6 kcal/mol above the helix. Other conformations are calculated to have relatively high strain energies: crown-I (2.0 kcal/mol), crown-II (3.0 kcal/mol), and propeller (7.8 kcal/mol).

cis,cis,cis-1,5,9-Cyclododecatriene (**1**) is a compound of importance as a synthetic intermediate[1] and as a potential homoaromatic system.[2] Unlike the other three stereoisomers of 1,5,9-cyclododecatriene, the all-cis isomer has not been observed as a product of the cyclotrimerization of 1,3-butadiene on Ziegler-type catalysts.[3] However, **1** can be made by a chemical trans-to-cis inversion of the three double bonds in *trans,trans,trans*-1,5,9-cyclododecatriene.[2]

The ^1H NMR spectrum of **1** in the temperature range −115 to 150 °C has been reported to show no change beyond a loss of fine structure below −80 °C.[2] On the basis of molecular models, UV spectroscopy, and the low melting point of **1**, Untch and Martin concluded that this hydrocarbon did not adopt a crown conformation with C_{3v} symmetry.[2] They suggested that **1** was likely to have an all s-trans conformation of C_2 symmetry.

Dale has briefly discussed possible site-exchange paths in **1** in a "helix" conformation with C_2 symmetry and a "propeller" conformation with D_3 symmetry.[4] Ollis and co-workers have reported the dynamic ^1H NMR spectra of a variety of tribenzo-1,5,9-cyclododecatrienes and heterocyclic analogues.[5–7] In solution these compounds were found to exist as "helix" and/or "propeller" conformations. Since the presence of fused benzene rings and of heteroatoms can lead to substantial effects on conformational equilibria and barriers, the data of Ollis et al. cannot be easily extrapolated to the parent system. We now report an investigation of the conformational properties of *cis,cis,cis*-1,5,9-cyclododecatriene by both dynamic NMR spectroscopy and empirical force field calculations.

Experimental Section

cis,cis,cis-1,5,9-Cyclododecatriene was synthesized by the method of Untch and Martin.[2] Its ^{13}C NMR spectrum in $CDCl_3$ at room temperature exhibits chemical shifts at δ 27.9 (CH_2) and 130.7 (CH).

All low-temperature NMR spectra were measured on a superconducting solenoid spectrometer operating at 59 kG.[8] The proton noise decoupled ^{13}C NMR spectra are Fourier transforms of accumulated free-induction decays and were obtained with standard 10-mm tubes under the following conditions: 45° pulse angle, 8K data points, 11-KHz spectrum width, an exponential broadening function corresponding to a broadening of 4 Hz. For variable-temperature studies a mixture of $CHCl_2F$ and $CHClF_2$ (3:1) was used as a solvent and a ^{19}F peak of the solvent was employed for lock purposes. The ^1H NMR spectra were obtained with 5-mm tubes in a frequency-sweep mode, with the magnetic

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[1] Barkovich, A. J.; Vollhardt, K. P. *J. Am. Chem. Soc.* **1976**, *98*, 2667–2668.

[2] Untch, K. G.; Martin, D. J. *J. Am. Chem. Soc.* **1965**, *87*, 3518–3520.

[3] Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 105–115. Breil, H.; Heimbach, P.; Kröner, M.; Müller, H.; Wilke, G. *Makromol. Chem.* **1963**, *69*, 18–40.

[4] Dale, J. *Top. Stereochem.* **1976**, *9*, 199–270.

[5] Brickwood, D. J.; Ollis, W. D.; Stoddart, F. *J. Chem. Soc., Chem. Commun.* **1973**, 638–640.

[6] Ollis, W. D.; Stoddart, F.; Nógrádi, M. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 168–169.

[7] Ollis, W. D.; Price, J.; Stephanatou, J.; Stoddart, F. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 169. Downing, A. P.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc. B* **1970**, 24–34. Downing, A. P.; Ollis, W. D.; Sutherland, I. O.; Mason, J. *Chem. Commun.* **1968**, 329–330. Ollis, W. D.; Stephanatou, J.; Stoddart, J. F.; Ferrige, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 223–224.

[8] Anet, F. A. L.; Basus, V. J.; Bradley, C. H.; Cheng, A. K., paper presented at the 12th Experimental Nuclear Magnetic Resonance Conference, Gainesville, FL, Feb 1971. Bradley, C. H. Ph.D. Thesis, University of California, Los Angeles, CA, 1971.

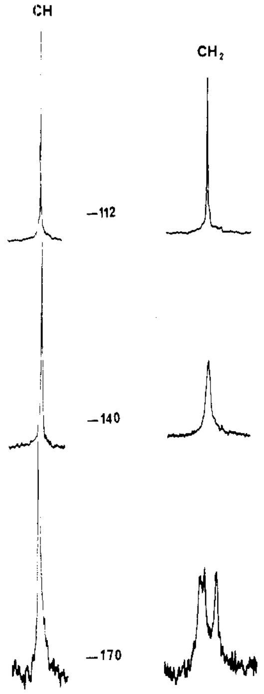

Figure 1. 63.1-MHz ^{13}C NMR spectra of *cis,cis,cis*-1,5,9-cyclododecatriene in $CHCl_2F/CHClF_2$ (3:1) at various temperatures.

field locked on a ^{1}H line of the solvent. Tetramethylsilane was used as an internal reference for both ^{1}H and ^{13}C NMR spectra. Temperatures were measured with a copper–constantan thermocouple situated in the probe and a few centimeters below the sample. As a result of the high power (ca. 10 W) used for decoupling protons, the temperature measurements associated with the ^{13}C spectra are estimated to be of lower accuracy (±3 °C) than are those associated with the ^{1}H spectra (±1 °C).

Theoretical spectra were calculated by means of a Fortran program on the Data General Corp. Nova computer of the NMR spectrometer.[9] Force field calculations were carried out on an IBM-360/91 computer at the Campus Computer Network of UCLA.

Results and Discussion

NMR Data. ^{1}H NMR spectra of *cis,cis,cis*-1,5,9-cyclododecatriene (1) were obtained from −10 to −170 °C. The spectra at temperatures above −120 °C consist of fairly narrow bands at δ 2.2 (methylene protons) and 5.7 (olefinic protons). The methylene resonance broadens below −120 °C and gives rise to two barely resolved bands (δ 2.15 and 2.33) at −160 °C. The two bands do not sharpen at lower temperatures, presumably because they represent several chemical shifts, as will be discussed below. Also, line broadening caused by dipole–dipole relaxation becomes important in molecules as large as 1 at very low temperatures, especially for methylene protons, which are quite close together. Because of these effects, it is difficult to obtain accurate rate constants for the dynamic NMR effect that is occurring in the vicinity of −150 °C. Nevertheless, the conformational process which is taking place can be estimated to have a free-energy barrier of about 6 kcal/mol.

^{13}C NMR spectra of 1 at various temperatures are given in Figure 1. The methylene carbon absorption changes from a single line (δ 29.0) above about −120 °C to three lines (δ 27.2, 30.0 and 30.7) with approximately equal intensities at −170 °C; the coalescence temperature is −141 °C. The olefinic carbon absorption (δ 132.6) remains a relatively sharp singlet to −175 °C, which was the lowest temperature investigated.

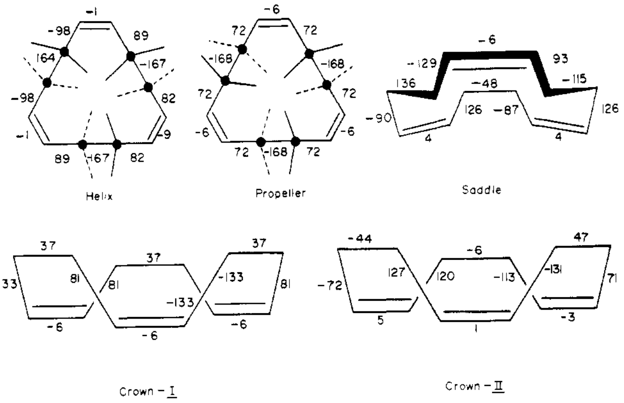

Figure 2. Calculated torsional angles in various conformations of *cis,cis,cis*-1,5,9-cyclododecatriene.

The low-temperature ^{13}C NMR spectrum of 1 can be most simply interpreted in terms of a single conformation which has a plane or a C_2 axis of symmetry. Because the exchange process in 1 involves the averaging of three chemical shifts, the line shape depends on the mechanism of exchange. Force field calculations (see below) show that each of the three sites has an equal probability to go to one of the other two sites. Using this mechanism, we can fit the line shape at −141 °C with a rate constant of 500 s^{-1}. Application of the absolute rate theory[10] with a transmission coefficient of 1 gives a free energy of activation ($\Delta G^{\ddagger}$) of 5.9 ± 0.3 kcal/mol at −141 °C, where all known sources of errors are estimated and included. Although no attempts were made to calculate other activation parameters such as the enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation, the value of $\Delta S^{\ddagger}$ can be estimated to be close to zero,[11] and therefore $\Delta H^{\ddagger}$ should be close to $\Delta G^{\ddagger}$.

Force Field Calculations. Force field calculations of *cis,cis,cis*-1,5,9-cyclododecatriene (1) were performed with Boyd's iterative computer program MOLBUILD,[12] which was modified to allow conformational changes to occur as described by Boyd and Wiberg.[13] The parameters used for torsional and out-of-plane bending of a double bond were those suggested by Ermer and Lifson;[14] all the other parameters were those of Boyd.[12] Approximate coordinates for trial geometries were calculated by means of the program COORD,[15] with torsional angles estimated from Dreiding–Fieser molecular models. The strain energies reported below correspond to molecules in a hypothetical motionless state at 0 K. However, the zero-point energies and vibrational frequencies of the various conformations of 1 are expected to be similar.

The present calculations are based on the Newton–Raphson procedure and will converge to either an energy

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[9] Cheng, A. K.; Anet, F. A. L.; Mioduski, J.; Meinwald, J. *J. Am. Chem. Soc.* 1974, *96*, 2887–2891.

[10] Glasstone, S.; Laidler, K. J.; Eyring, E. "The Theory of Rate Processes"; McGraw-Hill: New York, 1941.

[11] Anet, F. A. L.; Anet, R. In "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975.

[12] Boyd, R. H. *J. Am. Chem. Soc.* **1975**, *97*, 5353–5357. Boyd, R. H.; Breitling, S. M.; Mansfield, M. *AIChE J.* **1973**, *19*, 1016–1026. Boyd, R. H.; Sanwal, S. N.; Shary-Tehrany, S.; McNally, D. *J. Phys. Chem.* **1971**, *75*, 1264–1271. Chang, S. J.; McNally, D.; Shary-Tehrany, S.; Hickey, M. J.; Boyd, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3109–3118. Shieh, C. F.; McNally, D.; Boyd, R. H. *Tetrahedron* **1969**, *25*, 3653–3665. Boyd, R. H. *J. Chem. Phys.* **1968**, *49*, 2574–2583.

[13] Wiberg, K. B.; Boyd, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 8426–8430.

[14] Ermer, O.; Lifson, S. *J. Am. Chem. Soc.* **1973**, *95*, 4121–4132. Anet, F. A. L.; Yavari, I. *Tetrahedron* **1978**, *34*, 2879–2886.

[15] Dewar, M. J. S. *Top. Curr. Chem.* **1971**, *23*, 1–30.

Table I. Calculated Strain Energies[a] (in kcal/mol) of Various Energy-Minimum Conformations of *cis,cis,cis*-1,5,9-Cyclododecatriene

conformation	E_r	E_θ	E_ϕ	E_δ	E_{nb}	E_T	E_Δ
helix	0.330	2.261	7.110	0.054	1.472	11.2	0
saddle	0.264	2.006	7.775	0.043	1.692	11.8	0.6
crown-I	0.375	2.764	7.485	0.066	2.467	13.2	2.0
crown-II	0.428	3.494	6.743	0.024	3.501	14.2	3.0
propeller	0.484	4.033	11.622	0.066	2.773	19.0	7.8

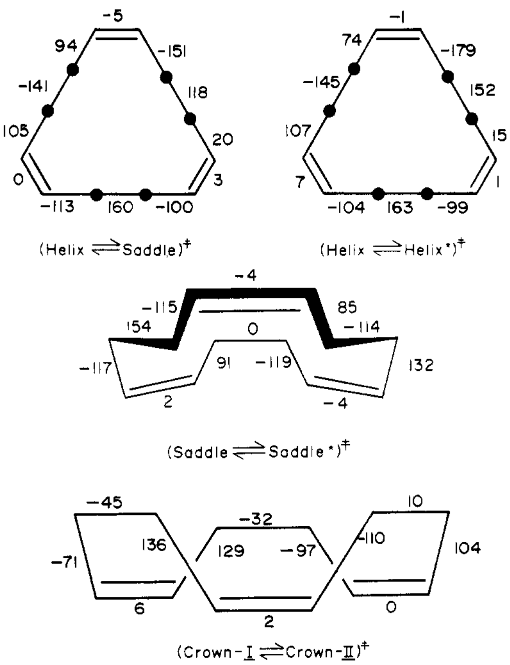
[a] The following symbols are used: E_r, bond length strain; E_θ, angle strain; E_ϕ, torsional strain; E_δ, out-of-plane strain; E_{nb}, nonbonded interaction strain; total strain energy, $E_T = E_r + E_\theta + E_\phi + E_\delta + E_{nb}$; E_Δ, strain energy relative to that of the lowest energy (helix) conformation.

maximum or an energy minimum with respect to distortions corresponding to a normal mode of vibration.[12] Hence, the vibrational frequencies of all the conformations of 1 reported in this work were calculated, and in each case $3N - 6$ real vibrational frequencies were obtained, which indicates that each of these conformations corresponds to a true (local) energy minimum with respect to any small geometric distortion. For the conformational transition states of 1, $3N - 7$ real vibrational frequencies were obtained.

(A) Conformations. Ideally, it would be desirable to have a systematic way of writing down and naming all the low-energy conformations of 1, as was done for the isomeric *trans,trans,trans*-1,5,9-cyclododecatriene.[16] However, 1 presents a more difficult problem than does its all-trans isomer because in 1 both gauche (±60°) and anti (180°) torsional angles have to be considered for the CH_2CH_2 units, whereas only gauche rotamers are possible in the all-trans isomer.[16] Furthermore, there are some low-energy conformations of 1 which have more or less eclipsed (0 or ±120°) torsional angles in the CH_2CH_2 units, and this makes any logical classification scheme for this compound very cumbersome.

Models of 1 were constructed with all possible combinations of roughly gauche and anti arrangements about the CH_2CH_2 units in 1. Energy minimization gave rise to five conformations which are shown in Figure 2 and Table I. Similar conformations have previously been considered for 1 and analogous systems by other authors,[2,4-7] who have not always used the same names to designate the same type of conformation.[17] We have adopted the names listed in Table I. In order to differentiate a pair of mirror-image conformations, an asterisk will be added to the name of one of the two conformations.

The lowest energy conformation of 1 is calculated to be the helix, followed in order of increasing energy by the saddle, crown-I, crown-II, and propeller conformations (Table I). The relative strain energies of these conformations show that 1 should exist almost entirely in the helix conformation at low temperatures. The saddle conformation may become appreciably populated at or above room temperature whereas the two crown conformations of 1 are expected to be present only at very high temperatures. The propeller conformation not only has a very high relative strain energy but its entropy also should be low because of its high symmetry, and thus it should not be populated at any temperature.


(Helix $\rightleftharpoons$ Saddle)‡

(Helix $\rightleftharpoons$ Helix*)‡

(Saddle $\rightleftharpoons$ Saddle*)‡

(Crown-I $\rightleftharpoons$ Crown-II)‡

Figure 3. Calculated torsional angles in various conformational transition states of *cis,cis,cis*-1,5,9-cyclododecatriene.

The force field calculations indicate the presence of a significant amount of strain (11.2 kcal/mol) in the lowest energy conformation of 1 (Table I). The strain in the helix conformation is mainly due to considerable deviations of torsional angles of the six $CH_2CH=$ units from their energy-minimum values (±120°).[18]

The saddle conformation was not considered by Dale[4] or Ollis[5-7] and was only mentioned as a possible conformation in 1 by Untch and Martin,[2] who apparently judged this conformation to be unimportant on the basis of molecular model considerations. In our iterative calculations, the saddle conformation has a relative strain energy of 0.6 kcal/mol (Table I), and, as will be discussed below, this conformation plays an important role in the pseudorotation of the helix conformation of 1. The saddle seems to lie on a flat energy surface since distortion of some of its torsional angles by as much as 20° results in a mere 0.2-kcal/mol increase in the strain energy.[19]

The crowns I and II are the only conformations which have suitable geometries for homoconjugation in 1 (Figure 2). However, these two conformations are calculated to be 2.0 and 3.0 kcal/mol, respectively, less stable than the helix conformation (Table I). It is unlikely that homoconjugation energy can compensate for this energy difference since even in the more favorable *cis,cis,cis*-1,4,7-cyclononatriene and related systems the homoconjugation energy is reported to be negligible.[20] The crown-II conformation has C_1 (nearly C_s) symmetry, and its strain energy is virtually the same as that for a crown-II geometry with C_s symmetry.[21]

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(16) Anet, F. A. L.; Rawdah, T. N. *J. Am. Chem. Soc.* **1978**, *100*, 5003-5007.

(17) The conformations of the all-cis triene 1 with C_2 and D_3 symmetries have been referred to as "propeller" and "helix", respectively, by Dale,[4] whereas Untch and Martin[2] designated these two conformations as "unsymmetrical s-trans" and "symmetrical s-trans", respectively. Actually, Dale adopted the names helix and propeller from Ollis,[6] who used these names to describe the conformations of trisalicydes with C_1 and C_3 symmetries, respectively. The conformations of tribenzo analogues of 1 which have C_2 and D_3 symmetries were left nameless by Ollis[5] and were characterized only by their symmetry point groups.

(18) Torsional strains in the conformations of 1 are at a minimum if the CH_2CH_2 units are staggered (torsional angles of ±60° or 180°) and if the $CH_2CH=$ units are eclipsed (torsional angles of ±120° or 0°).

(19) A saddle geometry (torsional angles: 110°, -150°, 124°, 4°, -96°, 112°, -110°, 5°, 149°, -45°, -64°, and 2°) has a strain energy of 0.8 kcal/mol relative to that of the best helix conformation (Figure 2).

(20) Christoph, G. G.; Muthard, J. L.; Paquette, L. A.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1978**, *100*, 7782-7784 and references therein.

Table II. Calculated Strain Energies[a] (in kcal/mol) of Various Conformational Transition States of *cis,cis,cis*-1,5,9-Cyclododecatriene

transition state[b]	E_r	E_θ	E_ϕ	E_δ	E_{nb}	E_T	E_Δ
[saddle $\rightleftarrows$ saddle*]‡	0.348	2.682	7.923	0.027	2.715	13.7	2.5
[crown-I $\rightleftarrows$ crown-II]‡	0.430	3.607	6.995	0.030	3.799	14.9	3.7
[helix $\rightleftarrows$ saddle]‡	0.455	5.092	8.078	0.027	3.888	17.5	6.3
[helix $\rightleftarrows$ helix*]‡ [c]	0.662	5.037	8.022	0.027	5.050	18.8	7.6

[a] See Table I for the meaning of the symbols. [b] All transition states have C_1 symmetry. [c] See footnote 22.

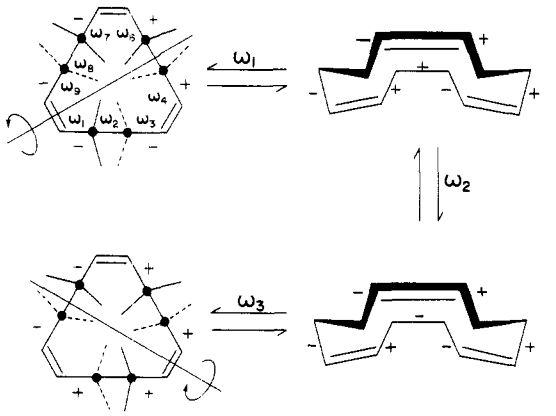

Figure 4. Pseudorotation itinerary for the helix conformation via a pair of enantiomeric saddle conformations in *cis,cis,cis*-1,5,9-cyclododecatriene.

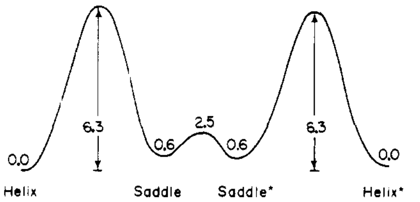

Figure 5. Calculated energy profile for the pseudorotation of the helix conformation via a pair of enantiomeric saddle conformations in *cis,cis,cis*-1,5,9-cyclododecatriene. The energies are in units of kilocalories per mole.

(B) Conformational Interconversions. The pseudorotation paths for the low-energy conformations of 1 were explored by driving[13] the appropriate torsional angles by increments of 10–15°. Four pseudorotation schemes, which are associated with the transition states shown in Figure 3, were investigated. Contributions to the total strain energy of each transition state are listed in Table II.

The helix conformation of 1 pseudorotates via a pair of enantiomeric saddle conformations as intermediates and pseudorotation partners. This process is achieved by driving sequentially the three torsional angles ω_1, ω_2, and ω_3 in the manner displayed in Figure 4; an alternate, but equivalent, pseudorotation path involves driving ω_9, ω_8, and ω_7, respectively. This pseudorotation scheme causes a migration of the C_2 axis of symmetry in the helix conformation (Figure 4). Fast repetition of this process leads to a time-averaged D_{3h} symmetry in 1.

The energy profile for the pseudorotation of the helix conformation discussed above is shown in Figure 5. The first conformational step involves the interconversion of the helix and saddle conformations via a transition state with a barrier of 6.3 kcal/mol. The second step is associated with the degenerate interconversion of the saddle and its mirror image, and this process has a barrier of 2.5 kcal/mol. The last conformational step is the mirror image of the first step, but is carried out in reverse order. Thus, the calculated barrier for converting the helix to its mirror-image conformation is 6.3 kcal/mol.

Dale,[4] who did not consider a saddle conformation for 1, has suggested that the helix conformation can pseudorotate without involving any intermediates by the rotation of a CH_2CH_2 group as a more or less rigid unit by about 180°: one CH_2 group passes through the ring while the other CH_2 undergoes a synchronous rotation outside of the ring and in the opposite direction. In our calculations this pseudorotation has a transition state[22] whose calculated relative strain energy is 7.6 kcal/mol (Table II) and is thus more difficult by 1.3 kcal/mol than the pseudorotation involving the saddle intermediates.

The helix conformation can also pseudorotate by interconverting with the propeller conformation. However, owing to the relatively high strain energy of the latter conformation (7.8 kcal/mol), this process must have a barrier of at least 8 kcal/mol and can thus be excluded from consideration.

The enantiomerization of the crown-I conformation is achieved by the interconversion of this conformation with the crown-II via a transition state which has a barrier of only 1.7 kcal/mol. (Table II and Figure 3).

The two crown conformations of 1 are isolated from the helix and saddle conformations by barriers whose calculated strain energies are substantially higher than 8.0 kcal/mol, and therefore the interconversions of the crown conformations with the saddle and helix are not important.

Conclusions and Comparison with Other Investigations. The spectral behavior of 1 can be interpreted in terms of the results of the force field calculations presented above. The ^{13}C NMR spectrum of 1 at -170 °C is consistent with a single helix conformation which pseudorotates via a pair of enantiomeric saddle conformations. This process has a calculated (strain energy) barrier of 6.3 kcal/mol, in excellent agreement with the (free energy) barrier (5.9 kcal/mol) which is obtained from ^1H and ^{13}C NMR data. However, the present experimental data do not rule out the presence of a small proportion of the saddle conformation provided that the resonances of this conformation happen to be obscured by those of the helix. Unfortunately, neither the ^1H nor the ^{13}C spectra of 1 at low temperatures consist of well separated sharp lines. Since the saddle is calculated to be 0.6 kcal/mol less stable than the helix, it appears very improbable that the major conformation of 1 is the saddle, although it is true that the NMR data on 1 can be interpreted in terms of saddle conformations.[23] The presence of a small amount of the saddle conformation in 1 at low temperatures is not in

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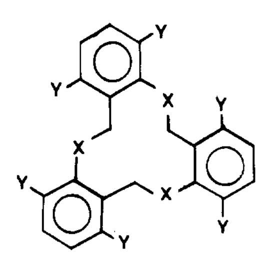
(21) A crown-II geometry with C_s symmetry has one CH_2CH_2 unit which is totally eclipsed (torsional angles: 0°, 116°, 3°, -72°, -46°, 129°, 0°, -129°, 46°, 72°, -3°, -116°), and it is calculated to be only 0.001 kcal/mol less stable than the best crown-II conformation (Figure 2).

(22) The transition state for the direct interconversion (not involving the saddle intermediates) of the helix into its mirror-image conformation is designed as [helix $\rightleftarrows$ helix*]‡.

(23) The saddle should interconvert extremely rapidly with its mirror image, even at -170 °C, and thus the time-averaged symmetry should be C_s, which is consistent with the NMR data. Pseudorotation of the saddle with the helix as a higher energy pseudorotation partner would then give D_{3h} time-averaged symmetry.

disagreement with the force field calculations. At room temperature significant amounts of the saddle may well be present.[24]

The all-s-trans geometry which has been suggested as the likely conformation for 1 by Untch and Martin[2] is the same as our helix conformation. Similar conformations have also been reported for the trithia (**2a**)[6] and 3,6-dimethyl (**2b**)[5] derivatives of tribenzo-1,5,9-cyclododecatriene (**2c**). However, the barriers for the pseudorotation of the helix conformations of **2a** and **2b** are 9.3 and 17.1 kcal/mol, respectively, which are considerably higher than that observed in 1 (5.9 kcal/mol). On the other hand, the difference between the strain energies of the propeller and helix conformations of **2b** has been calculated to be 0.9 kcal/mol,[5] as compared to 7.8 kcal/mol for the corresponding conformations of 1.



2a, X = S; Y = H
2b, X = CH_2; Y = CH_3
2c, X = CH_2; Y = H

Although the propeller conformation is unfavorable in the systems discussed above, such is not the case in compounds where the CH_2CH_2 units in the tribenzo-1,5,9-cyclododecatriene **2c** are replaced by three ester or amide groups.[7]

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Registry No. 1, 4736-48-5.

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[24] The helix has C_2 symmetry and is chiral whereas the saddle has no real axes of symmetry and is chiral. Furthermore, the saddle is more flexible than the helix. Thus the saddle should be favored over the helix by at least $R \ln 2$ (1.4 eu), and at room temperature the helix and saddle are calculated to have closely comparable free energies.

Radical Pathways of Coal Dissolution in Hydrogen Donor Media. 2.[1a] β Scission and 1,2 Aryl Migration Reactions of Radicals Derived from Methylindans and Tetralin at 327-627 °C[1b]

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The 1,2 aryl migration and fragmentation reactions of 1-indanylmethyl (1), 2-tetralyl (2), 2-indanylmethyl (3), 1-tetralyl (4), 2-methyl-1-indanyl (5), and 1-methyl-2-indanyl (6) radicals were studied by flash vacuum pyrolysis of the *tert*-butyl perester precursors at 327-627 °C and 10^{-2} torr. Radicals 1 and 2 are interconverted via a 1,2 aryl migration which is readily reversible at all temperatures. This equilibrium is depleted by β scission of 1 and recyclization to 4 and by β scission of 2 followed by recyclization to 2 or to 3 in modest yields. The reverse neophyl-like rearrangement of 2 to 1 occurs with a lower activation barrier than β scission of 1 to form a 2-(*o*-vinylphenyl)ethyl radical. Enthalpies, entropies, and free energies of reaction were calculated for the above reactions from group additivity parameters, and activation energies were estimated from values reported for simple alkyl radicals. It is shown that the β scission of 4 and recyclization to 1 is important only at very high temperatures (>500 °C) as a mechanism for the isomerization of tetralin and related hydroaromatic structures to alkylindans and that the reverse neophyl-like rearrangement of 2 to 1 is the favored pathway for isomerizations observed during dissolution of coal in hydroaromatic media at elevated temperatures.

The conversion of coal to soluble products is accomplished by heating coal in a hydroaromatic solvent, occasionally under hydrogen pressure, at 400-475 °C for periods of from seconds[2] to a few minutes.[3] Model compound studies have sought to identify coallike organic structures which undergo decomposition on the time scale of coal dissolution.[4] Thermal production of radicals during the dissolution process provides coal-derived radicals which can undergo β scission, addition to available aromatic systems, disproportionation, combination, and hydrogen abstraction either from a hydroaromatic or aliphatic structure in the coal or from the hydroaromatic solvent. The hydroaromatic solvent undergoes isomerization and fragmentation along with oxidation to the corresponding aromatic structure. When tetralin is used as a solvent, *n*-butylbenzene, indan, 1-methylindan, *cis*- and *trans*-decalin, 1,2- and 1,4-dihydronaphthalene, and methylnaphthalenes are minor products, naphthalene and tetralin comprising the major solvent-derived products.[2] Analogous results have been observed with octahydrophenanthrene.[5]

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[1] (a) Paper 1 in this series: James A. Franz and Donald M. Camaioni, *Fuel*, **59**, 803 (1980). Preliminary accounts of this work were presented at the 178th National Meeting of the American Chemical Society, Washington, DC, Sept 1979, Abstract ORGN 205, and the 1979 Materials Research Society Annual Meeting, Symposium H. (b) This work was supported by the U.S. Department of Energy, Processes and Techniques Branch, Division of Chemical Sciences, Office of Basic Energy Sciences, under contract DE-AC06-76RLO-1830, with Battelle Memorial Institute.

[2] Doohee Kang, Larry L. Anderson, and Wendell H. Wiser, "Elucidation of Coal Structural Components by Short-Residence Time Extractive Liquefaction", Technical Report under contract E(49-18)-2006 with the Department of Energy, Aug 1979, University of Utah, Department of Minning and Fuels Engineering, Salt Lake City, UT.

[3] R. C. Neavel, *Fuel*, **55**, 237 (1976).

[4] Ben M. Benjamin, Vernon F. Raaen, P. H. Maupin, L. L. Brown, and C. J. Collins, *Fuel*, **57**, 269 (1978).

[5] (a) D. C. Cronauer, D. M. Jewell, Y. T. Shah, and R. J. Modi, "Investigation of Mechanism of Hydrogen Transfer in Coal Hydrogenation, Phase I Final Report", under DOE Contract No. E(49-18)-2305, Feb 1978; (b) Yatish Y. Shah, and Donald C. Cronauer, *Catal. Rev.—Sci. Eng.*, **20**, 209 (1979).

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