

## Conformational Analysis. LXXIII. The Perhydroanthracenes. An Equilibration Study<sup>1,2</sup>

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The heats of formation of the isomeric perhydroanthracenes (gas phase, 25°) have been calculated by a force-field method described previously to be -57.68, trans-syn-trans; -55.06, cis-trans; -51.82, trans-anti-trans; -52.04, cis-anti-cis; -49.74 kcal/mol, cis-syn-cis. These relative values are consistent with equilibration experiments.

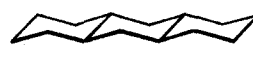
There are five stereoisomers possible for perhydroanthracene, all of which have previously been described in the literature.<sup>3</sup> Because this basic ring system is simple and of wide occurrence in nature, the relative stabilities of the possible stereoisomers are of interest. The conformational analysis of these compounds was carried out at an early date,<sup>4</sup> and the pertinent conformations are shown. The heats of formation (*via* heats of combustion) (gas phase) have been reported for two of the isomers.<sup>5</sup> We now have available a force field which has been developed<sup>6</sup> for studying similar molecules, and it seemed advantageous to reexamine the conformational calculations with the aid of molecular mechanics. In addition, it was deemed desirable to actually bring the isomers to equilibrium and determine the percentage composition of the mixture. Further, by determining the composition as a function of temperature, it is possible to obtain the enthalpies and entropies for the isomerization for each of the equilibria under consideration. The methods and procedures follow generally along the lines discussed previously for the perhydrophenanthrenes<sup>7</sup> and related compounds.<sup>8</sup>

Previous equilibration studies of the perhydroanthracenes have been carried out.<sup>3c,d</sup> They employed aluminum bromide as catalyst, which usually leads to skeletal rearrangements as well as epimerizations. The results showed that the free energy difference between the two most stable isomers was similar to that predicted by Johnson. The other isomers were not detected at the low temperatures (0-25°) used.

### Experimental Section

Perhydroanthracene (a mixture containing 69.7% csc, 26.5% ct, 2.9% cac, and 0.9% tst) was obtained by hydrogenation of anthracene in ethanol with the aid of reduced platinum oxide catalyst and a trace of hydrochloric acid. The reaction was carried out at 2-3-atm pressure at 85°, two replacements of the catalyst being necessary to bring the reaction to completion.

Equilibrations were then carried out on the neat material at 200-350° in sealed glass tubes in the presence of 10% Pd/C catalyst. The equilibrated solid was dissolved in hexane and analyzed by vpc. The individual isomers were identified by comparison with known samples, three of which were provided by Dr. R. L. Clarke (tat, tst, and cac). The remaining two samples (csc and ct) were isolated from the hydrogenation mixture by preparative vpc. They were identified by comparing their physical properties with those described in the literature.



trans-syn-trans (tst)  
meso,  $\sigma = 2$



cis-trans (ct)  
dl,  $\sigma = 1$



trans-anti-trans (tat)  
dl,  $\sigma = 2$



cis-anti-cis (cac)  
dl,  $\sigma = 1$



cis-syn-cis (csc) (chair)  
meso,  $\sigma = 1$



csc (boat)  
dl,  $\sigma = 2$

Synthetic mixtures of isomers were prepared and used to calibrate the vpc analyses. The product ratios were determined in each case in duplicate by planimetry of the vpc traces. Small amounts of side products, probably from dehydrogenation, were noted, but none of these interfered significantly with the analyses. These side products did not appear to change in amount with time after the main products had reached equilibrium, and thus they were at equilibrium too. The possibility that we are looking at steady states rather than equilibria can therefore be discounted.

To be certain that equilibrium had been reached at a given temperature, samples equilibrated for increasing lengths of time were analyzed, and the isomer ratios eventually became constant. At least three vpc traces were obtained for all samples near equilibrium.

### Results

The percentage of each isomer in the equilibrium mixture at each temperature was recorded as an average of several determinations, and these numbers are summarized in Table I. The relative percentages of the two major isomers can be easily determined, but the other three isomers are present in rather small amounts, and the error in their determination is considerable.

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TABLE I  
PERHYDROANTHRACENE ISOMER DISTRIBUTIONS  
AT EQUILIBRIUM

Isomer	Registry no.	Percentage compositions			
		Temp, °C (times, hr)			
		198.5 (1634)	244.4 <sup>a</sup> (195)	293.1 (93)	348.7 (66 <sup>b</sup> )
tst	1755-19-7	85.7	83.1	79.4	73.5
tat	30008-95-8	0.5	0.7	0.8	1.3
ct	29863-90-9	13.4	15.7	19.0	23.7
csc	19128-78-0	0.1	0.1	0.2	0.5
cac	29863-91-0	0.3	0.4	0.7	1.0

<sup>a</sup> Equilibrium may not have been reached. <sup>b</sup> Equilibrium was reached in less than 20 hr.

The experimental enthalpies and entropies were determined from a least-squares plot of  $1/T$  vs.  $\ln K$ , where  $K$  is the equilibrium constant between a given isomer and the most stable (tst) isomer. The results are summarized in Table II.

TABLE II  
EXPERIMENTAL AND THEORETICAL THERMODYNAMIC  
PARAMETERS FOR THE PERHYDROANTHRACENES

Isomer	$\Delta H^\circ_{\text{exptl.}, a, b}$ kcal/mol	$\Delta H^\circ_{\text{calcd.}, b, c}$ kcal/mol	$\Delta S^\circ_{\text{exptl.}}$ eu	$\Delta S^\circ_{\text{theor.}, d}$ eu
tst	0	0	0	0
ct	$2.76 \pm 0.28$	2.62	$+2.1 \pm 0.6$	+2.8
tat	$4.15 \pm 0.81$	5.86	$-1.6 \pm 1.5$	0
cac	$5.58 \pm 0.28$	5.56	$+0.3 \pm 0.4$	+1.4
csc	$8.74 \pm 0.61$	8.13 <sup>e</sup>	$+4.0 \pm 1.2$	+2.2 <sup>f</sup>

<sup>a</sup> The errors given are standard deviations. <sup>b</sup> The estimates made by Johnson from elementary ideas of conformational analysis are in very good agreement with these values. He estimated  $\Delta H^\circ$  as follows: tst, 0; ct, 2.4; cac, 4.8; tat, 5.6; csc, 6.4. The last value is based on a guess (a good one) by Pitzer regarding 1,3-dimethylcyclohexane: C. W. Beckett, K. S. Pitzer, and R. Spitzer, *J. Amer. Chem. Soc.*, **69**, 2488 (1947). <sup>c</sup> Calculated as described in text. <sup>d</sup> Entropy calculated from symmetry and mixing only (see Table III). <sup>e</sup> Contains 0.27 kcal/mol additional owing to the boat form. <sup>f</sup> Contains an additional 0.8-eu entropy of mixing from the boat form.

**Conformational Calculations.**—Using our force field and previously described methodology, the relative enthalpy (at 25°) of each isomeric perhydroanthracene was calculated, and the relative entropies were calculated by considering the symmetry numbers and the

TABLE III  
THEORETICAL ENTROPIES OF SYMMETRY AND MIXING  
FOR THE PERHYDROANTHRACENES

Isomer	Symmetry no.	$\Delta S_{\text{symm.}}$ eu	$\Delta S_{\text{mixing.}}$ eu	$\Delta S_{\text{total.}}$ eu	$\Delta S_{\text{rel.}}$ eu
tst	2 (meso)	-1.4	0	-1.4	0
ct	1 ( <i>dl</i> )	0	+1.4	+1.4	+2.8
tat	4 ( <i>dl</i> )	-2.8	+1.4	-1.4	0
cac	1 (meso)	0	0	0	+1.4
csc	1 (meso)	0	0	0	+1.4

meso or *dl* nature of the product. These quantities are summarized in Tables II and III. The heats of

formation were calculated and are compared with the available experimental values in Table IV.

TABLE IV  
CALCULATED (FORCE FIELD) HEATS OF FORMATION  
FOR THE PERHYDROANTHRACENES (GAS PHASE, 25°)

Isomer	Calcd	Experimental
tst	-57.68	$-58.13 \pm 1.39$
ct	-55.06	
tat	-51.82	$-52.74 \pm 1.47$
cac	-52.04	
csc	-49.74 <sup>a</sup>	

<sup>a</sup> Corrected for the presence of the boat conformation.

The entropies and enthalpies calculated and those measured experimentally are in reasonable agreement with one another. The errors listed in the tables are the standard deviations and measure only the scatter of the points, not the true probable errors which are probably twice as large.

Features of interest are as follows. The trans-syn-trans isomer is the most stable; the calculated and experimental heats of formation<sup>5</sup> (gas phase) are respectively -57.68 and  $-58.13 \pm 1.39$  kcal/mol; so the agreement is excellent. The cis-trans is the next most stable isomer, and one which exists in fairly large amount in the equilibrium mixture. The relative thermodynamic quantities can therefore be measured fairly accurately for this isomer, and the agreement between the calculations and experiment is fair (note the calculations are for the gas phase, while the equilibrium is measured in the liquid). The tat isomer necessarily has the center ring in a boat (twist) form, and the calculated and (gas phase) heats of formation are again in good agreement. In analogy to other boat forms,<sup>9</sup> it might be thought the entropy would be larger than indicated by symmetry considerations, but this does not prove to be the case. The fusion of the boat between two chairs restricts its mobility somewhat, which may be the reason.

The cis-anti-cis isomer has a calculated enthalpy which is in good agreement with experiment. The agreement between the entropies is marginal.

The cis-syn-cis isomer is perhaps the most interesting, because the experimental enthalpy has not been previously known; Johnson's value is only an estimate. The calculated and experimental values are in good agreement. The experimental entropy is larger than expected from the single stable chair conformation, which has a bad syn diaxial interaction that can be relieved if the center ring assumes a boat form. The calculated energy of this form is 2.07 kcal/mol above that of the chair. It is therefore in equilibrium with the chair to the extent of 13% at 271°. The presence of the boat form raises the enthalpy of the compound somewhat (0.27 kcal/mol), and raises the entropy appreciably (0.8 eu). It may be that smaller amounts of other conformations of higher energy increase both the enthalpy and the entropy of the compound at these elevated temperatures, but we have not investigated this possibility.

We believe the calculated heats of formation and the

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TABLE V

THE THERMODYNAMIC QUANTITIES FOR THE PERHYDROANTHRACENES								
Isomer	$\Delta H^{\circ}_{\text{exp}}$	$\Delta S^{\circ}_{\text{exp}}$	$T\Delta S^{\circ}_{\text{exp}}$	$\Delta G^{\circ}_{\text{exp}}^a$	$\Delta H^{\circ}_{\text{calcd}}$	$\Delta S^{\circ}_{\text{calcd}}$	$T\Delta S^{\circ}$	$\Delta G^{\circ}_{\text{calcd}}^a$
tst	0	0	0	0	0	0	0	0
ct	+2.76	+2.1	+1.14	+1.62	2.62	+2.8	+1.52	+1.10
tat	+4.15	-1.6	-0.87	+5.02	5.86	0	0	+5.86
cac	+5.58	+0.3	+0.16	+5.42	5.56	+1.4	+0.76	+4.80
csc	+8.74	+4.0	+2.18	+6.56	8.13	+2.2	+1.20	+6.93

<sup>a</sup> 544 °K.

differences between them are accurate to better than 1 kcal/mol, and the experimental results are in accord with this. Finally, the free energies are given in Table V.

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## A New Approach to the Synthesis of Dibenz[*a,l*]pyrenes<sup>1,2</sup>

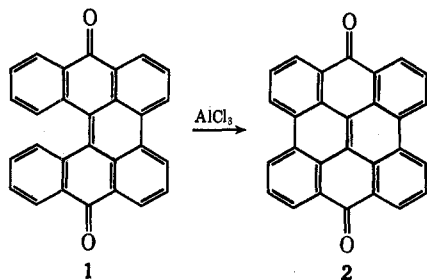
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A new method for the synthesis of dibenz[*a,l*]pyrene and various derivatives has been achieved through an application of the Scholl reaction. The key to the new approach is to use 1-arylbenz[*a*]anthracenes as the precursors to the desired polycyclic aromatic compounds. The parent hydrocarbon and derivatives containing alkyl, halogen, and alkoxy substituents have been prepared as well as the corresponding TNF adducts.

The Scholl reaction,<sup>5</sup> which is the elimination of two aryl-bound hydrogen atoms accompanied by the formation of a new aryl-aryl bond under the influence of a Friedel-Crafts catalyst, has been known for some time. This type of reaction was first observed by Friedel and Crafts who reported the formation of biphenyl from benzene in the presence of aluminum chloride; Homer<sup>6</sup> also reported the formation of dinaphthyl from naphthalene in the presence of aluminum chloride. It was Scholl who, after publishing the synthesis of *meso*-naphthodianthrone (2)<sup>7</sup> from helianthrone (1) using aluminum chloride as the dehydrogenating catalyst, and the



formation of perylene by three different methods,<sup>8</sup> recognized the potentiality and generality of this reaction. Subsequent to extensions of the reaction by

Scholl himself,<sup>9</sup> no important contributions to the Scholl reaction were published until 1950 when Baddely<sup>10</sup> showed that many reactions effected by aluminum chloride and other Friedel-Crafts reagents do not occur in the absence of hydrogen chloride or traces of water. The next and perhaps most significant contribution to the understanding of the Scholl reaction is in the paper of Nenitzescu and Balaban<sup>5</sup> in which they propose that the reaction takes place in three steps: first, a protonation; second, an electrophilic substitution; and finally, a dehydrogenation to yield the final aromatic product.

The suggestion of Nenitzescu and Balaban<sup>5</sup> that the first step in the Scholl reaction is a protolytic reaction yielding a  $\sigma$  complex is well supported.<sup>11</sup> The fact that Scholl reactions occur readily and in high yield when electron-rich positions are involved but fail when the reaction has to take place at electron-poor positions supports the idea that the second step in Nenitzescu and Balaban's mechanism is one of electrophilic substitution. The cyclodehydrogenation of 8-(1-naphthyl)benz[*a*]anthracene to naphtho[2,1-*a*]perylene<sup>12</sup> proceeds readily and in good yield, presumably because an electron-rich position undergoes electrophilic attack. However, benzophenone does not yield fluorenone<sup>9a</sup> under Scholl reaction conditions nor does 1,5-dibenzoylnaphthalene<sup>9e</sup> undergo a Scholl reaction. Both reactions fail presumably because an electrophilic attack would have to occur into a position deactivated by

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