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CONFIGURATIONAL EQUILIBRIA AND ^{13}C NMR SPECTRA OF TETRACYCLIC SATURATED HYDROCARBONS

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Abstract—The stereoisomeric equilibrium composition over Pd/C at high temperature of a series of tetracyclic saturated hydrocarbons having general formula $C_{18}H_{30}$ was determined by gas chromatography and compared with that calculated on the basis of conformational analysis. Several stereoisomers were isolated. Their ^{13}C NMR spectra agree very well with those calculated according to standard procedures. This method of structural determination was applied to perhydronaphthacene, perhydrobenzo(a)anthracene, 2- and 5-methylperhydrobenzo(d,e)anthracene and 2,7-dimethylperhydropyrene.

Following our studies concerning the stereochemistry of perhydrotriphenylene,[1-5] our interest was focused on the examination of other tetracyclic saturated hydrocarbons having general formula $C_{18}H_{30}$. Two of these were obtained in considerable amounts by acid isomerization of perhydrotriphenylene carried out under different experimental conditions.[6,7] Their structures correspond to those of the stablest stereoisomer of perhydronaphthacene and of 2,7-dimethylperhydropyrene (their constitution is reported in 1 and 2, while their stereochemistry is indicated in 1a and 2a). In this paper we discuss the structures of other stereoisomers having constitution 1 and 2 and that of perhydrobenzo(d,e)anthracene (3), of 2- and 5-methylperhydrobenzo(d,e)anthracene (4 and 5 respectively).

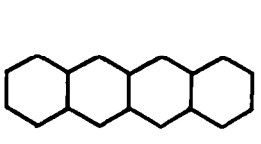
This research was carried out with the purpose of contributing to the knowledge of these polycyclic compounds, as yet unreported in the literature, and with the ultimate aim of contributing to the knowledge of the mechanism of the acid isomerization of perhydrotriphenylene, of which many of these compounds represent significant intermediate stages.

Structural determination

Stereoisomer structures were determined by the joint use of thermodynamic and conformational analyses and ^{13}C NMR spectroscopy. The former technique has in many cases given an unequivocal response by simply examining the composition of the reaction mixture. In any case it constitutes an effective method of selection among the possible structures. In its turn, ^{13}C NMR spectroscopy has allowed the structural determination when dubious cases arise and has supplied results that always agree with those obtained by thermodynamic methods.

In practice we have subjected our compounds to catalytic equilibration over Pd/C at high temperature and under hydrogen pressure.

The equilibrium composition was determined by gas chromatographic analysis and compared with that cal-



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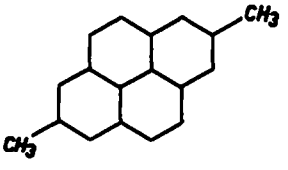

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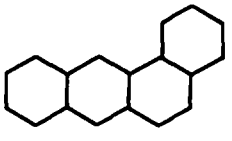

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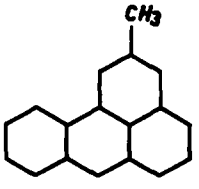

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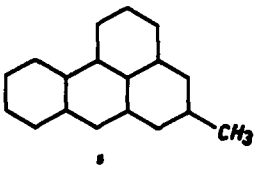

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culated on the basis of conformational analysis. The conformational energy of various stereoisomers was evaluated by Johnson's method,[8] already adopted for the prediction of the isomerization products of cyclic hydrocarbons.[3,9,10] The comparison between the data obtained by this method and by molecular-mechanics calculation has shown that in analogous polycyclic systems (perhydroanthracene and perhydrophenanthrene) the agreement is quite satisfactory, at least for lower-energy stereoisomers, where boat conformations or 1,3-*syn*-diaxial interactions are absent.

We used the simplified equation:

$$x_i = w_i \exp(-1000\, g_i/RT) / \sum w_i \exp(-1000\, g_i/RT)$$

where x_i is the molar fraction calculated at equilibrium, w_i the statistical weight and g_i the number of *gauche* extra-annular interactions present in the i-th stereoisomer. w_i equals $2/\sigma$ for racemic mixtures of chiral molecules or $1/\sigma$ for nonchiral molecules, where σ is the symmetry number of the molecule (1 for point groups C_1, C_s and C_i; 2 for C_2, C_{2h}, C_{2v}, S_4, etc.). The value 1000 cal/mol for *gauche* interaction energy is used in accordance with Weitkamp.[10] At the level of approximation sufficient for our aim, a refinement of this parameter is not required.

The method just described, though simpler from the calculation standpoint, is equivalent to the traditional one,[13] based on the calculation of the equilibrium constants among various isomers. The standard conformational free energy of different stereoisomers is calculated by the equation:

$$\Delta G_i^0 = 1000\, g_i - RT(\ln 2 - \ln\sigma)$$

where the term ln 2 is used only when the compound is chiral and forms a racemic mixture. The difference between ΔG^0 of the i-th stereoisomer and that of the most stable stereoisomer is used to calculate the value of k_{eq} and hence the equilibrium composition.

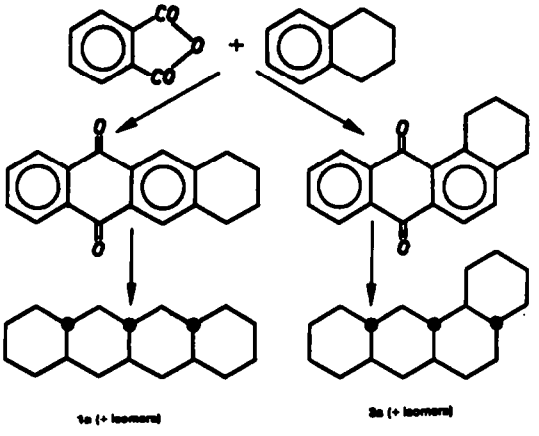
The analysis of ^{13}C NMR spectra was first carried out on the basis of molecular symmetry[14] and subsequently by comparison with the spectra calculated according to the Grant method (method A). For skeletal atoms we adopted the values of the parameters proposed by Dalling and Grant for perhydroanthracenes and perhydrophenanthrenes.[15] For methyl groups we adopted the values reported by the same authors in their study on methylcyclohexanes.[16] A better agreement between estimated and experimental data was obtained by using for the former, whenever possible, the values observed by Dalling and Grant in compounds that are the closest models of ours (in particular TST and TC perhydroanthracene, TAT, TSC and TAC perhydrophenanthrene and 2-methyldecalin[17]) (method B).

Solvent effects of the order of 0.2–0.4 ppm were found and do not substantially affect the validity of this method.

RESULTS

On the basis of combinatory calculations and of symmetry considerations, 14 stereoisomers may be foreseen for structure 1 (enantiomeric pairs are considered as single stereoisomers), 48 for 2, 32 for 3, 64 for 4 and 5. Most stereoisomers exhibit a fairly high relative energy and therefore cannot be obtained in appreciable amounts under thermodynamic control. In the course of the present investigation, 8 saturated tetracyclic hydrocarbons have been identified and characterized. Their melting points and gas chromatographic retention indexes are reported in Table 1, whereas their ^{13}C NMR spectra are reported in Table 2. Out of these compounds, only two, i.e. 1a and 2a, were previously known,[6,7] but only their crystalline properties have been reported.

Perhydronaphthacene. Three stereoisomers have been observed by GC in the equilibrium mixtures obtained both by 1a epimerization and by hydrogenation of an aromatic precursor (Scheme 1). Their molar fractions



Scheme 1.

Table 1. Physical properties of some $C_{18}H_{30}$ tetracyclic hydrocarbons

Compound	Retention indices I				Purity	Melting point
	OV-101		Carbowax 20M			
	180°C	δ I/10°	180°C	δ I/10°	%	°C
1a	1912.2	13.3	2174.8	21.9	> 99	204
1b	1944.2	13.4	2219.8	22.7	> 95	137
1c	1925.3	12.6	2192.7	21.8	≈ 85	n.d.
2a	1784.7	12.2	2014.9	19.8	> 99	191
2b	1802.8	12.1	2030.8	19.7	≈ 80	n.d.
3a	1915.6	13.1	2180.6	22.4	> 96	68
4a	1848.8	12.3	2095.5	20.6	> 98	87[+]
5a	1855.2	12.5	2104.4	21.1	> 99	109

[+] The DTA curve shows the presence of polymorphism.

Table 2. ^{13}C NMR spectra of some $C_{18}H_{30}$ tetracyclic hydrocarbons

Carbon assigned [a]	Chemical shift (ppm from TMS) Exptl.	Predicted Method A	Method B	ref. [b]
Perhydronaphthacene 1a				
5a = 11a	43.68	43.23	43.82	7
4a = 6a = 10a = 12a	43.68	43.23	43.82	7
5 = 6 = 11 = 12	41.81	43.27	42.14	8
1 = 4 = 7 = 10	34.30	35.25	34.38	9
2 = 3 = 8 = 9	27.09	27.23	27.10	10
Perhydronaphthacene 1b				
5a	44.15	43.23	44.18	11
6a	43.67	43.23	43.82	7
10a	43.67	43.23	43.82	7
6	41.98	43.27	42.14	8
11	41.98	43.27	42.14	8
12	40.58	40.68	40.78	12
4a	37.41	38.05	37.50	13
12a	37.12	38.05	37.09	14
11a	36.71	37.70	36.60	15
7	34.36	35.25	34.38	9
10	34.36	35.25	34.38	9
5	33.66	34.73	33.88	18
4	32.72	32.66	32.62	19
2	27.50	27.23	27.57	20
8	27.15	27.23	27.10	10
9	27.15	27.23	27.10	10
1	27.15	26.71	27.07	23
3	21.46	21.70	21.37	24
Perhydronaphthacene 1c				
6a = 12a	44.53	43.23	44.18	11
5 = 11	40.68	40.68	40.78	12
5a = 11a	37.88	38.05	37.50	13
4a = 10a	37.35	37.70	37.09	14
1 = 7	35.21	35.25	34.43	16
4 = 10	34.70	35.25	34.35	17
6 = 12	34.55	34.73	33.88	18
2 = 8	27.19	27.23	27.16	21
3 = 9	27.19	27.23	27.16	22
2-eq,7-eq-Dimethylperhydropyrene 2a				
10b = 10c	51.04	52.51	n.av.	-
3a = 5a = 8a = 10a	43.13	43.23	43.39	47^+
1 = 3 = 6 = 8	41.54	43.27	42.14 [c]	8 [c]
4 = 5 = 9 = 10	33.58	35.25	34.59 [d]	39 [d]
2 = 7	32.02	33.95	33.06	54^+
2 CH_3 = 7 CH_3	22.74	23.12	22.85	57^+
2-ax,7-eq-Dimethylperhydropyrene 2b				
10b	52.36	52.51	n.av.	-
10c	51.01	52.51	n.av.	-
5a = 8a	43.51	43.23	43.39	47^+
6 = 8	41.87	43.27	42.14	8 [c]
1 = 3	40.34	40.68	40.78	12
3a = 10a	35.77	37.70	n.av.	-
4 = 10	34.13	35.25 or	35.02 or	39
5 = 9	33.89	35.25	34.59	40^+
7	32.43	33.95	33.06	54^+
2	28.32	28.77	n.av.	-
7 CH_3 eq	23.04	23.12	22.85	57^+
2 CH_3 ax	19.41	18.82	n.av.	-
Perhydrobenzo(a)anthracene 3a				
12a	47.79	47.87	48.21	37
12b	47.79	47.87	48.21	37
7a	43.40	43.23	43.82	7
11a	43.21	43.23	43.82	7
6a	43.21	43.23	43.61	38
4a	43.21	43.23	43.61	38
7	42.10	43.27	42.14	8
12	37.47	37.74	n.av.	-
5	34.65	35.25	35.02	39
6	34.19	35.25	35.02	39
4	34.19	35.25	34.59	40
8	33.95	35.25	34.38	9
11	33.95	35.25	34.38	9
1	30.08	29.71	30.13	41
3	26.90	27.23	27.14	42
2	26.80	27.23	26.84	43
9	26.80	27.23	27.10	10
10	26.65	27.23	27.10	10
2-eq-Methylperhydrobenzo(d,e)anthracene 4a				
11c	52.83	52.51	n.av.	-
11a	48.08	47.87	48.21	37
11b	45.85	47.87	48.21	37
6a	42.98	43.23	43.82	7
7a	42.39	43.23	43.82	7
3a	41.98	43.23	43.49	47^+
3	41.46	43.27	43.31	49^+
7	41.10	43.27	42.14	8
1	38.93	37.74	n.av.	-
6	34.54	35.25	34.38	9
8	34.54	35.25	34.38	9
4	34.54	35.25	34.15	53^+
2	31.96	33.96	33.06	54^+
11	30.02	29.71	30.13	41
5	26.86	27.23	27.10	10
9	26.50	27.23	27.10	10
10	25.98	27.23	27.10	10
2 CH_3 eq	22.99	23.12	22.85	57^+
5-eq-Methylperhydrobenzo(d,e)anthracene 5a				
11c	52.89	52.51	n.av.	-
11a	48.19	47.87	48.21	37
11b	46.03	47.87	48.21	37
6a	43.51	43.23	43.82	7
7a	43.39	43.23	43.82	7
3a	42.39	43.23	43.49	47^+
4	41.93	43.27	43.31	49^+
6	41.57	43.27	43.31	49^+
7	41.05	43.27	42.14	8
3	34.54	35.25	34.15	53^+
8	34.19	35.25	34.38	9
5	31.96	33.95	33.06	54^+
1	30.14	29.71	30.13	41
11	30.14	29.71	30.13	41
2	26.91	27.23	27.10	10
9	26.50	27.23	27.10	10
10	26.09	27.23	27.10	10
5 CH_3 eq	22.75	23.12	22.85	57^+

a) The single carbons are identified depending on the representation and numbering indicated in formulas 1a - 5a.
b) The number refers to the items in Table IV of ref. 15. When marked with an asterisk, it refers to the items in Table I of ref. 17. Some slight uncertainties may arise either when more than one model molecule is available, or when close resonances have not been individually attributed in the model compound.
c) or 43.31 (49^+).
d) or 34.15 (53^+).

Table 3. Stereochemical analysis of perhydronaphthacene isomerization

Isomer	Point group	σ	w_i	g_i	x_i at 520°K (calculated)
1a	C_{2h}	2	1/2	0	75.25%
1b	C_1	1	2	3	16.50
1c	C_2	2	1	3	8.25

Minor components have been neglected.

(74.4, 16.8 and 8.8% in the former case, and 76.4, 16.2 and 7.4% in the latter) agree very well with those calculated for stereoisomers 1a, 1b and 1c respectively (Table 3). Such attributions have been fully confirmed by spectroscopic investigations on samples isolated by fractional crystallization.

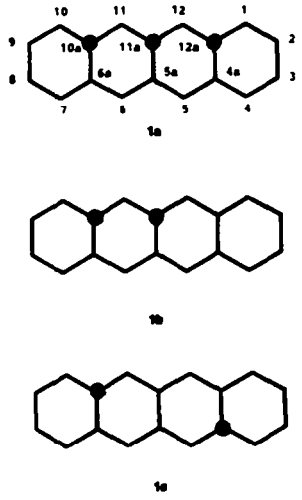


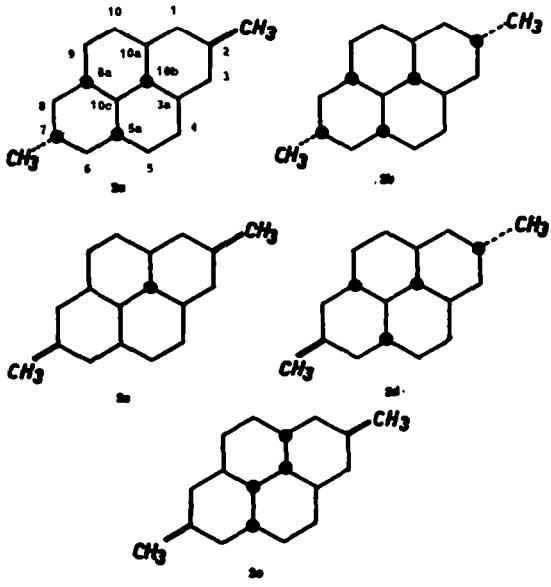
Table 2 compares the experimental ^{13}C NMR spectra with those calculated according to methods A and B. 1a (which possesses five non equivalent carbons) shows five lines practically coincident with those calculated by method B. In the spectrum of 1b (which does not possess symmetry elements and has 18 non-equivalent atoms) particularly significant are the arrangement of resonance lines between 40 and 45 ppm (six carbons, three of which are methylenic and three methinic), the high-field shift (at about 37 ppm) of three methinic carbons affected by the *cis* junction (4a, 11a, 12a) and the isolated signal at 21.46 ppm originated by carbon 3, which is β to a stiff *cis* junction. Isomer 1c exhibits a V-shaped conformation, with two-fold symmetry and 9 non equivalent carbons. In its spectrum four methinic carbons give signals around 37 ppm: two of them are situated in the hollow part of the molecule (4a and 10a) and two on the central *cis* junction (5a and 11a).

The ^1H NMR spectra of 1a, 1b and 1c consist of an unresolved system of multiplets ranging between 0.5 and 2 ppm. Apart from intensity factors, the spectrum of 1a strongly resembles that of TST perhydroanthracene.

Table 4. Stereochemical analysis of 2,7-dimethylperhydropyrene isomerization

Isomer	Point group	σ	w_1	g_1	x_1 at 520°K (calculated)
2a	C_{2h}	2	1/2	0	73.2%
2b	C_s	1	1	2	21.1
2c	C_s	1	1	4	3.0
2d	C_{2h}	2	1/2	4	1.5
2e	C_2	2	1	5	1.2

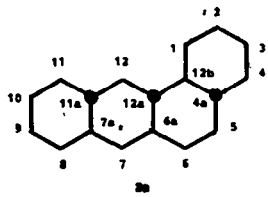
2,7-Dimethylperhydropyrene. Isomer 2a, obtained by acid isomerization from perhydrotriphenylene[6] was equilibrated over Pd/C at 250°. A new isomer formed in high amounts (22.6%) along with small amounts of other compounds. The equilibrium composition calculated at that temperature is reported in Table 4. By comparison, structure 2b may be reasonably assigned to the new stereoisomer. By repeated crystallizations 2b was enriched up to 80% purity.



Structures of 2a and 2b were confirmed by NMR (Table 2). The spectrum of 2a exhibits six lines, in agreement with its symmetry. The two methyls are equivalent and equatorial, as proved by their chemical shift (22.74 ppm). Highly substituted carbons like 10b and 10c give a resonance line at 51.04 ppm. In its turn, the spectrum of 2b exhibits 12 signals (point group C_s). Methyls are no more equivalent and give two lines at 23.04 (equatorial) and 19.41 ppm (axial).

The ^1H NMR spectrum of 2a shows the presence of a broad signal of area 2/30 centered at 0.30 ppm, corresponding to the axial methine protons 10b and 10c. This chemical shift is anomalous in the sense discussed by Segre and Musher[10] and corresponds to one of the highest-field methine protons ever found in non-cyclopropanic hydrocarbons.

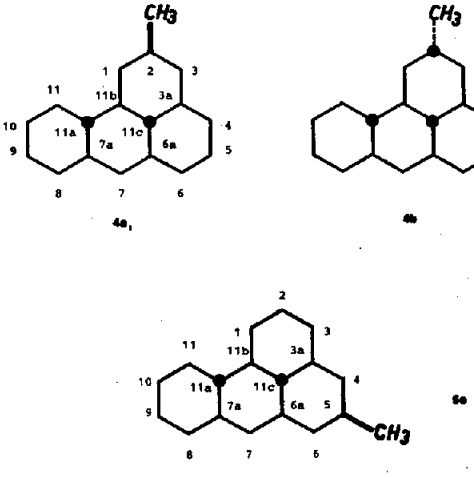
Perhydrobenzo(a)anthracene. In the stablest stereoisomer 3a, all junctions between adjacent rings are *trans* and the molecule possesses a fully equatorial conformation. We obtained this compound in high yield by hydrogenation of an anthraquinone precursor (Scheme 1). Such an attribution is fully confirmed by ^{13}C NMR (Table 2).



Conformational analysis shows the existence of six further isomers with a relatively low energy, each having

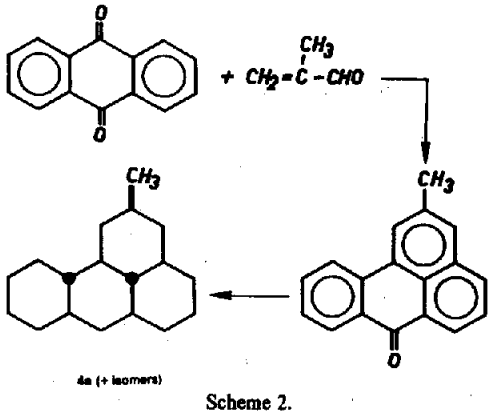
a *cis* junction. Their structure may be formally derived from **3a**, by inverting the configuration of the six asymmetric carbons one at a time. Each isomer has three additional *gauche* interactions over **3a** and their molar fraction at equilibrium should be substantially the same. Hence, on the mere basis of thermodynamic analysis, it is not possible to make a structural attribution for minor compounds present at equilibrium.

2 - Methyl and 5 - methylperhydrobenzo(d,e)anthracene. In the acid isomerization of perhydrotriphenylene a series of compounds with *m/e* 246 and containing a methyl group was observed by GC–MS. One of them was isolated by preparative GC and fractional crystallization. On the basis of possible isomerization processes its most probable structure might be that of the equatorial isomer of 2-methyl or of 5-methylperhydrobenzo(d,e)anthracene (**4a** and **5a** respectively). In order to discriminate between the two hypotheses an authentic sample of **4a** was synthesized by a known route (Scheme 2). It differs from the previous compound, but it is also present in the isomerization products of perhydrotriphenylene.



Structures **4a** and **5a** were respectively attributed to the compounds obtained by synthesis and by isomerization on the basis of their ^{13}C NMR spectra (Table 2).

We notice that all resonance lines except two are common to the two compounds. However, the resonance line of atom 1 should be shifted from 37.7 ppm in **4a** to 29.7 in **5a** (calculated values) and that of atom 6 from 35.2 in **4a** to 43.3 in **5a**. If, for the sake of clarity, we divide the spectrum into five sections (from 22 to 28 ppm, around 30, from 31 to 39, from 40 to 45, from 46 to 53 ppm) the number of signals is distributed as follows: 4, 1, 5, 5, 3 in **4a**; 4, 2, 3, 6, 3 in **5a**. Experimental spectra fully agree with expectations.



Scheme 2.

4a and **5a** exhibit very similar ^1H NMR spectra. In particular both show a multiplet at 0.2–0.5 ppm (area 1/30) analogous to that already observed in **2a** and attributable to tertiary hydrogen **11c**. However **4a** and **5a** differ significantly in melting point and GC retention times (Table 1).

Compound **4a** was subjected to equilibration over Pd/C at 250°. According to the conformational analysis the next isomer should have the same skeleton as **4a**, but with the methyl group in an axial position **4b**. The value of the equilibrium constant between **4b** and **4a** calculated at 520°K is = 1/7. Actually a mixture of stereoisomers is obtained from **4a**, one of which is present in the ratio of 1/8 with respect to **4a**. Such a compound may be thus identified as **4b**.

CONCLUSIONS

This work demonstrates how the combination of catalytic equilibration and of ^{13}C NMR spectroscopy represents an effective method for the study of polycyclic saturated hydrocarbons, which hardly undergo chemical transformations suitable for the determination of their structures. Of the two techniques, the former, i.e. conformational and thermodynamic analyses, was proposed for this purpose about fifteen years ago[19] and successfully adopted in a number of cases, among others by Schneider, Warren and Janoski,[9] Weitkamp[10] and by ourselves.[3] The latter, i.e. the calculation of ^{13}C NMR spectrum, was considered by Grant[15] to be the simplest method for identifying compounds such as saturated hydrocarbons. The combined method proposed here is even more reliable and has already been used successfully in the study of the hydrogenation products of triptycene.[20] The analysis is further facilitated when, as in the present case, all compounds are rigid and consist of a single conformer.

In this type of investigation, molecular symmetry plays an essential role. A typical example is given by the two stereoisomers of perhydronaphthacene **1b** and **1c**. They both have a *cis* junction and the same number of *gauche* interactions; hence they have approximately the same energy. However **1b** belongs to point group C_1, whereas **1c** belongs to C_2. The different entropic contribution due to the different symmetry (or equivalently, the different statistical weight w_i) makes the two compounds sharply distinguishable from the thermodynamic standpoint. As already seen, the amount of **1b** present at equilibrium is twice that of **1c**.

For the same reasons, the ^{13}C NMR spectrum should exhibit 18 lines in **1b** and 9 in **1c** at most. Actually, due to accidental coincidences, 13 lines are observed in **1b** and 8 in **1c**.

Obviously the symmetry factors involved in each of the two techniques are different. In entropy calculation they consist of chirality (in the case of racemic mixtures) and symmetry number (both external and internal[21]), whereas in the determination of the number of non equivalent atoms, it is necessary to take into account, along with the order of the symmetry group of the molecule, the presence of atoms in special positions. Such a discussion has already been reported by us else-

where[14] and may be summarized by the formula (valid for rigid molecules): $p = \Sigma n_i m_i/h$, where p represents the number of non equivalent atoms, n_i is the number of atoms having multiplicity h/m_i, h is the order of symmetry group of the molecule, m_i the number of symmetry operations (including identity) that may be carried out on the molecule leaving unchanged the position of atom i.

In spite of considerable differences in the molecular framework, the compounds discussed in this paper are connected by mechanicistic and thermodynamic relationships. The order of stability is as follows: 1c < 1b < 3a < 1a < 4b < 4a ≃ 5a < 2b < 2a, as may be drawn from both conformational analysis and the increasing number of methyl groups.[9] With the only exception of 1b, which precedes 1c, the same order has been found in the GC retention indices reported in Table 1, in agreement with the results reported by Weitkamp on substituted decalins.[10]

Moreover these compounds are produced by acid isomerization of perhydrotriphenylene in the order indicated, as the activity of the catalyst increases. Further details of this reaction and on the transformations undergone by these products in the presence of acid catalysts will be reported in another paper.

EXPERIMENTAL

M.ps were determined by DTA (Mettler TA 2000). IR spectra were recorded on Perkin–Elmer Mod. 457 and 125 spectrophotometers (K Br pellets). ^{1}H NMR spectra were recorded on a Varian HA 100 spectrometer; ^{13}C NMR spectra on a Bruker HFX/10 spectrometer. In both cases the solvent was deuteriobenzene or $CDCl_3$; TMS was used as an internal standard. GC analyses were carried out on Hewlett-Packard Mod. 5700 or 5750 instruments, using a stainless-steel column (l = 3.5 m, O.D. = 1/8 in.) packed with 2% SE-52 on Chromosorb W-AW-DMCS, 80–100 mesh or a stainless-steel column (l = 2 m, O.D. = 1/8 in.) packed with 10% DEGS on Chromosorb W-AW-DMCS, 80–100 mesh. Retention indices were calculated from chromatograms obtained on a stainless-steel capillary column (l = 50 m, I.D. = 0.01 in.) coated with OV-101 at 180, 190, 200°, or on a stainless capillary column (l = 50 m, I.D. = 0.01 in.) coated with Carbowax 20 M at 160, 170, 180°. GC/MS analyses were carried out on a stainless-steel capillary column (l = 50 m, I.D. = 0.01 in.) coated with DEGS, at 120°, connected with a Varian MAT CH 7 mass spectrometer.

Materials. Compounds 1a, 2a and 5a were obtained by acid isomerization ($AlCl_3$) of perhydrotriphenylene. The preparation of 1a and 2a has already been described.[4,7] 5a was separated on a preparative scale on a F and M Mod. 700 gas chromatograph equipped with a stainless-steel column (l = 2 m, O.D. = 19 mm) packed with 20% Apiezon L on Chromosorb W-AW, 45–60 mesh. The temperature in the column oven was 230° and the carrier gas flow rate 350 cm^3 min^{-1}.

Stereoisomeric mixtures of constitution 1 and 3 were obtained by catalytic hydrogenation (Pd/C, 60 atm H_2, 250°, *n*-heptane) of the quinonic precursor obtained from phthalic anhydride and tetralin according to Schroeter[22] (Scheme 1). Separation between the linear and angular compounds was obtained by fractional crystallization. Thiourea, which forms crystalline adducts with 1a and 1b, was used in order to facilitate the separation.

Compound 4a was obtained by hydrogenation of 2-methylbenzanthrone obtained according to Hey, Nicholls and Pritchett[23] (Scheme 2).

Equilibration of saturated hydrocarbons. A heptane solution of the saturated hydrocarbons was kept at 245–250° in the presence of Pd/C (30–100% by weight in respect to the substrate) under 60 atm H_2. Small samples were drawn from time to time through a needle valve and examined by GC. The reaction was continued until a constant composition was reached. After filtration from the catalyst, single stereoisomers were isolated by the above described procedure.

Table 1 reports the melting points and GC retention indices of the compounds described in this paper.

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