Conformational Behaviour of Medium-sized Rings. Part 7.[1] 5,6,7,12-Tetrahydrodibenzo[a,d]cyclo-octene

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The temperature dependences of the ^1H n.m.r. and broad-band decoupled ^{13}C n.m.r. spectra of 5,6,7,12-tetrahydro-dibenzo[a,d]cyclo-octene (4) have been interpreted in terms of the interconversion of chair- and boat-like conformations. Strain energy calculations on selected conformations of this hydrocarbon (4) have led to useful correlations between calculated and experimental thermodynamic parameters.

THE conformational behaviour of 5,6,11,12-tetrahydro-dibenzo[a,e]cyclo-octene (1) [2-5] and its 1,4,7,10- (2) and 2,3,8,9- (3) tetramethyl derivatives [1,3] has been investigated recently in considerable detail by dynamic ^1H n.m.r. spectroscopy. These compounds showed temperature dependence of their spectra which could be associated with the presence in solution of chair- and
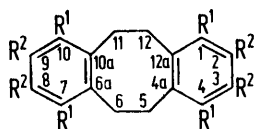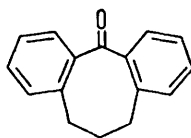

(1) R¹ = R² = H
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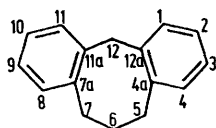
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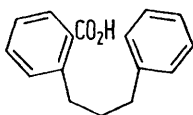
(5)   (6)

boat-like conformations undergoing relatively slow interconversion and inversion processes on the ^1H n.m.r. time-scale. A number of publications have also appeared describing the conformational properties in

solution of some heterocyclic analogues [2,3,6,7] of (1), the related cis,cis-cyclo-octa-1,5-diene,[8] and the syn-3,7-dibromo-derivative.[9] Although the possibility of the existence of more than one conformation of cis,cis-cyclo-octa-1,4-diene has been discussed [10-12] from a theoretical standpoint and the conformational behaviour of some heterocyclic analogues of 5,6,7,12-tetrahydrodibenzo-[a,d]cyclo-octene (4) has been examined by variable temperature ^1H n.m.r. spectroscopy [3,13-15] and strain energy calculations,[15] no experimental data are available for either of these hydrocarbons. In this paper, we discuss the conformational behaviour of the tetrahydro-dibenzocyclo-octene (4) in solution.[16]

The ketone (6) was prepared by a known route [17] involving (i) treatment of o-phthalaldehydic acid with phenylethylmagnesium bromide to give 3-(2-phenyl-ethyl)phthalide, which was (ii) reduced with hydroiodic acid and red phosphorus to afford 2-(3-phenylpropyl)-benzoic acid (5), followed by (iii) cyclodehydration of (5) with polyphosphoric acid. Reduction of the ketone (6) with lithium aluminium hydride in the presence of aluminium chloride gave the hydrocarbon (4).

EXPERIMENTAL

The general methods have been discussed in Parts 3 [18] and 6.[1]

6,7-Dihydrodibenzo[a,d][1,4]cyclo-octen-12(5H)-one (6).[17]—2-(3-Phenylpropyl)benzoic acid (5) [19] (m.p. 92—93°; lit.,[19] 90—92°) (1 g) and polyphosphoric acid (10 g) were heated together at 170 °C for 2.5 h. The mixture was allowed to cool before being poured on to ice (25 g). The aqueous suspension was extracted with ether and the ether layer was

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washed with 5% sodium carbonate solution followed by water, dried (MgSO$_4$), and evaporated to give a crude product which crystallised from benzene–hexane as the pure

FIGURE 1 The broad-band decoupled ^{13}C n.m.r. spectra of 5,6,7,12-tetrahydrodibenzo[a,d]cyclo-octene (4) at (a) +40 °C, (b) +27 °C, (c) −18 °C, and (d) −40 °C in CDCl$_3$. See Table 1 for chemical shift data

dibenzocyclo-octenone (6) (270 mg, 30%), m.p. 145—148° (lit.,[17] 147—149°), τ(CDCl$_3$) 1.84—2.04 (2 H, m, aromatic H-1 and H-11), 2.40—2.96 (6 H, m, other aromatic), 7.36 (4 H, t, J 6 Hz, C-5 and C-7 methylene), and 8.04—8.36

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(2 H, m, C-6 methylene), δ$_C$ (CD$_2$Cl$_2$–CS$_2$) 194.2 (CO), 140.6 and 140.1 (quaternary aromatic), 132.8, 130.7, 129.8, 126.4 (other aromatic), 33.1 (C-6), and 30.5 (C-5 and C-7). No line broadening was observed in this broad-band decoupled ^{13}C n.m.r. spectrum as the sample was cooled down to −80 °C.

5,6,7,12-*Tetrahydrodibenzo*[a,d]*cyclo-octene* (4).—A solution of lithium aluminium hydride (9 mg) and aluminium chloride (30 mg) in dry ether (20 ml) was added dropwise to the ketone (6) (50 mg) dissolved in ether (20 ml) and the mixture was stirred at room temperature. The reaction was followed by t.l.c. on silica gel with chloroform–light petroleum (b.p. 40—60 °C) (1 : 1) as eluant and was complete within 1 h. Dilute hydrochloric acid was added and the ether layer was separated, washed with water, dried (MgSO$_4$), and evaporated to give the crude *product* (4) which was recrystallised from ethanol; yield 37 mg (77%), m.p. 79—80° [Found: C, 91.6; H, 8.0%; M (mass spec.), 208. C$_{16}$H$_{16}$ requires C, 92.3; H, 7.7%; M, 208]; see Table 1 for ^{1}H n.m.r. data and Figure 1 and Table 1 for broad-band
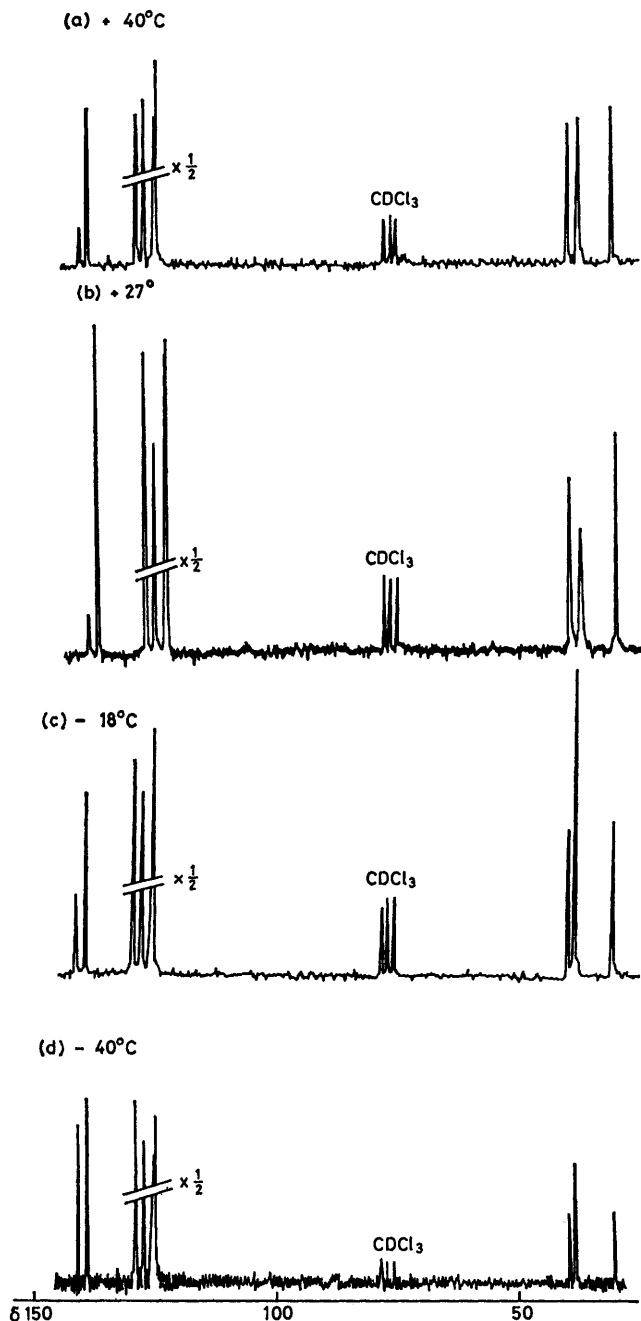
TABLE 1

Temperature-dependent ^{13}C n.m.r. (25.14 MHz) and ^{1}H n.m.r. (100 MHz) spectral parameters for 5,6,7,12-tetrahydrodibenzo[a,d]cyclo-octene (4)

Solvent	Temp. (°C)	Group	δ_C or τ [a]
CDCl$_3$	−40	C_6H_4	δ 142.2 (A), [141.1 (B)],[b] 140.3, 130.2, 128.4, 126.6, 126.1
		C-12	δ 39.0
		C-5,7	δ 37.8 (A), [36.8 (B)] [b]
		C-6	δ 29.7
	+40	C_6H_4	δ 142.0 (AB), 140.5, 130.3, 128.7, 126.6, 126.3
		C-12	δ 39.6
		C-5,7	δ 37.4 (AB)
		C-6	δ 30.4
CDCl$_3$	−40	C_6H_4	τ 2.48—3.20 (m)
		CH_2-12	τ [5.65 (AB2)],[b] 5.72 (A1),[c] 6.32 (B1) [c]
		CH_2-5,7	τ 6.60—7.26 (m)
		CH_2-6	τ 7.40—8.80 (m)
	+40	C_6H_4	τ 2.52—2.32 (m)
		CH_2-12	τ 6.01 (br,s) (AB12)
		CH_2-5,7	τ 7.01 (br,s)
		CH_2-6	τ 8.08 (br,s)

[a] The designations A, B, *etc.*, correspond to the site exchanges cited in Table 2. Sites are designated A and B for uncoupled two-site systems. Sites that represent two time-averaged signals are designated AB. Sites are designated A1, B1, and AB2 for the three-site system where there is coupling in the form of one AB system (A1B1) in addition to a single site (AB2). The site that represents three time-averaged signals is designated AB12. [b] The square brackets indicate that this signal for the minor conformation was inferred from line-shape calculations but was not visible in the spectrum above the noise level. [c] The coupling constant for the A1B1 system is 13.4 Hz.

decoupled ^{13}C n.m.r. data. Wolff–Kishner reduction of the ketone (6), obtained as an impure solid from the cyclodehydration of (5), has been reported [20] to afford an oil, b.p. 141—145° at 0.5 mmHg, which solidified to give a compound with m.p. 135—136°. This compound, which was claimed [20] to be the hydrocarbon (4), was converted into a diacetyl derivative (oil) from which a crystalline 2,4-dinitrophenylhydrazone (m.p. 234—236°) was prepared and characterised on the basis of elemental analysis.

Determination of Rates of Conformational Changes by Dynamic ^{1}H and ^{13}C N.m.r. Spectroscopy.—The methods

used have been described in Parts 1,[2] 2,[15] 3,[18] 4,[21] and 6.[1] The computer programs (coded in FORTRAN IV) used to generate the theoretical line-shapes are now described for the general methods I and II.

Method I.—A program I * for exchange of nuclei between two equally or unequally populated sites A and B, with no mutual coupling. One of the homotopic pairs of quaternary aromatic carbon atoms (*i.e.* either C-4a and C-7a or C-11a and C-12a) in the hydrocarbon (4) gave a broad singlet in the broad-band decoupled [13]C n.m.r. spectrum at room temperature which broadened further before sharpening up as the temperature was lowered (see Figure 1). Also, the singlet for the C-5 and C-7 methylene carbon atoms became sharp as the temperature was lowered (see Figure 1). In both cases, spectral line-shapes were simulated at 0 °C using this program and assuming that a small amount (<5%) of a second conformation in a diastereoisomeric mixture was populating a second site not observable directly in the broad-band decoupled [13]C n.m.r. spectrum. Observed and calculated spectra are shown in Figure 2 for the hydrocarbon (4).
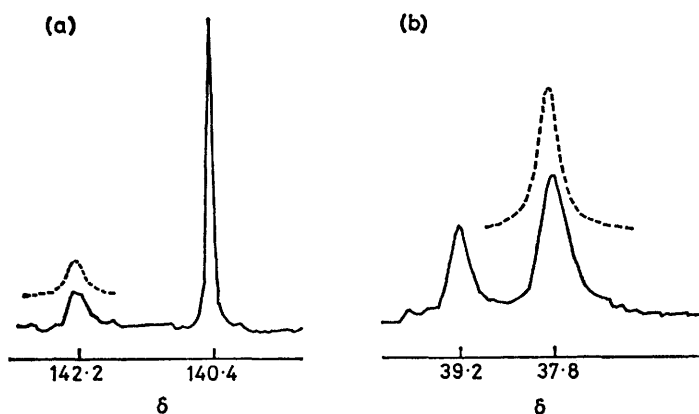

FIGURE 2 Observed (full line) and computed (broken line) spectra of (a) the quaternary aromatic carbons and (b) the C-5 and C-7 methylene carbons of 5,6,7,12-tetrahydrodibenzo-[a,d]cyclo-octene (4) at 0 °C: (a) and (b) k_{AB} 11 s^{-1}, p_A 0.96, p_B 0.04.

Method II.—A program III * for exchange of nuclei between the pairs of sites A1 and B1, A2 and B2, A1 and A2, and B1 and B2 in two AB systems. This program was used to simulate the [1]H n.m.r. spectral line-shapes associated with the C-12 methylene protons of the hydrocarbon (4) between −5 and +42 °C. The exchange rate, k_2, between the sites A2 and B2 † was assumed to be fast compared with the exchange rates, k_{12} and k_{21}, between sites A1 and A2, and B1 and B2, and the exchange rate, k_1, between the sites A1 and B1. Thus, protons in sites A2 and B2 † give rise to a single line (AB2) at the average site chemical shift, whereas the protons in sites A1 and B1 give rise to a typical four-line

* The program numbers (*viz.* I and III) established in Part 3 [16] will be adhered to in this paper; these programs will form the basis of a collection for reference in future Parts of this series.

† It transpires (see Results and Discussion section) that the C-12 methylene protons in the minor conformation are homotopic and so the sites A2 and B2 are indistinguishable. Accordingly, in using program III, identical chemical shifts for the C-12 methylene protons corresponding to sites A2 and B2 were employed. Under these circumstances the value chosen for k_2 is immaterial; in the event, k_2 was fixed at 100 000 s^{-1}.

AB system. In fact, with the hydrocarbon (4), the population, p_2, of the sites A2 and B2 † was so low (<5%) that the singlet expected from these sites at temperatures where $k_2 \longrightarrow \infty$ but $k_{12} \longrightarrow 0$ was not observable directly in the experimental spectra. This problem was overcome by assuming that the signal corresponding to the average chemical shift for the sites A2 and B2 † was obscured by the A1 portion of the A1B1 system. As k_{12} is increased, the B1 portion of the A1B1 system was broadened additionally as compared with the A1 portion in agreement with observation. Good matches between observed and calculated spectral line-shapes were obtained (i) when $p_2 = 0.02$ and (ii) $k_1 = 0.5k_{12}$. Observed and calculated spectra are shown in Figure 3.

Strain Energy Calculations.—These were carried out on selected conformations of the hydrocarbon (4) using a program ‡ (coded in FORTRAN) based upon the procedure reported by Allinger *et al.*[22] Details of the force field employed have been given in a recent review.[3]

RESULTS AND DISCUSSION

The temperature-dependent [1]H n.m.r. spectra of the hydrocarbon (4) in deuteriochloroform demonstrate that two diastereoisomeric conformations are populated in solution. At −5 °C, the spectrum showed an AB system for the C-12 methylene protons which exhibited selective broadening of the B portion. As the temperature was raised the unsymmetrical AB system coalesced to give a broad singlet above room temperature. Decreasing the temperature resulted in the AB system becoming well-resolved and assuming a symmetrical character. Two exchange processes can be identified by line-shape analysis (Figure 3) and may be associated with interconversion of the two diastereoisomeric conformations and slow inversion of one of these two diastereoisomers with its enantiomer. The other conformation constitutes <5% of the diastereoisomeric mixture and is not observable directly by [1]H n.m.r. spectroscopy. Indisputable evidence for the presence of interconverting diastereoisomeric conformations of (4) in deuteriochloroform was obtained from the temperature-dependent broad-band decoupled [13]C n.m.r. spectra (Figures 1 and 2). In particular, the broad resonances observed at +27 °C for (i) one of the constitutionally heterotopic pairs of quaternary aromatic carbons (δ_C 142.0 p.p.m.) and for (ii) C-5 and C-7 (δ_C 37.6 p.p.m.) became sharp singlets when the temperature was raised to +40 °C and also when it was decreased to −40 °C. Although no signal was observable directly in the broad-band decoupled [13]C n.m.r. spectrum at low temperatures for the minor conformation its presence has to be invoked to explain the temperature-dependent behaviour described in (i) and (ii) above. Thus, the exchange process which can be analysed by line-shape methods (Figure 2) must be associated with the interconversion of two diastereoisomeric conformations. Table 1 gives chemical

‡ We thank Professor I. O. Sutherland for a copy of his program.

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[22] N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Amer. Chem. Soc.*, 1971, **93**, 1637.

shift data from both ^{1}H n.m.r. spectra and broad-band decoupled ^{13}C n.m.r. spectra recorded at high and low
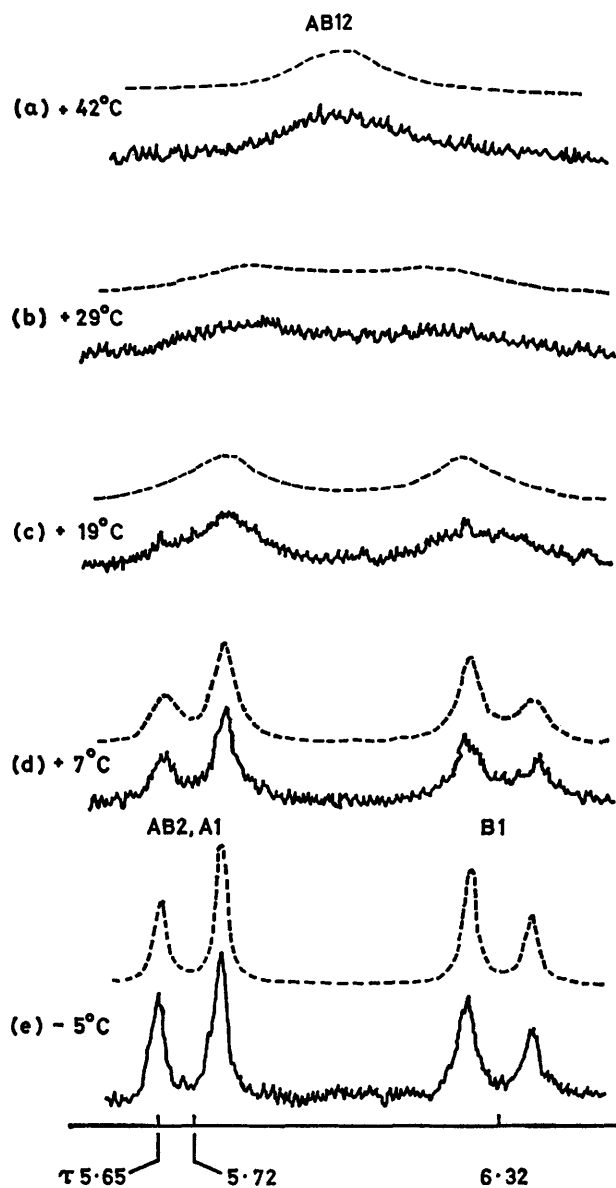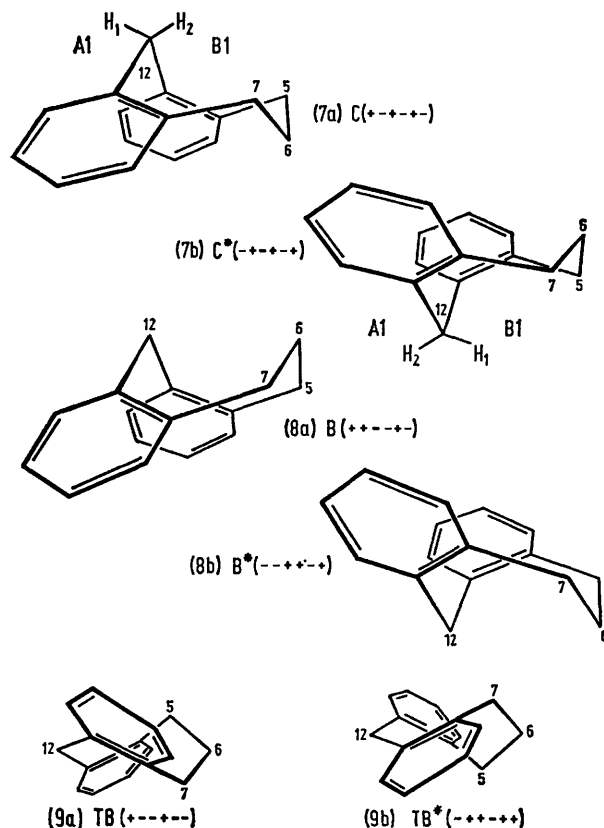

FIGURE 3 Observed (full line) and computed (broken line) spectra of the C-12 methylene protons of 5,6,7,12-tetrahydro-dibenzo[a,d]cyclo-octene (4): (a) at $+42$ °C, k_1 163 s^{-1}, k_2 100 000 s^{-1}, k_{12} 326 s^{-1}, p_1 0.98, p_2 0.02; (b) at $+29$ °C, k_1 51 s^{-1}, k_2 100 000 s^{-1}, k_{12} 102 s^{-1}, p_1 0.98, p_2 0.02; (c) at $+19$ °C, k_1 23.0 s^{-1}, k_2 100 000 s^{-1}, k_{12} 46.0 s^{-1}, p_1 0.98, p_2 0.02; (d) at $+7$ °C, k_1 7.0 s^{-1}, k_2 100 000 s^{-1}, k_{12} 14.0 s^{-1}, p_1 0.98, p_2 0.02; (e) at -5 °C, k_1 2.0 s^{-1}, k_2 100 000 s^{-1}, k_{12} 4.0 s^{-1}, p_1 0.98, p_2 0.02

temperatures. Table 2 gives details of the site exchanges affecting the spectral line-shapes and the thermodynamic parameters associated with conformational changes.

* Conformations are conveniently described [1-3,15,18] by using the usual $+$ and $-$ notation for torsion angles and referring in turn to the single bonds 4a,5, 5,6, 6,7, 7,7a, 11a,12, and 12,12a numbering as in diagram (4)] of the eight-membered ring. Accordingly, the signs of these angles are listed below all conformational diagrams in this paper.

These were derived by comparison (see Figures 2 and 3) of the observed and calculated spectra over a range of temperatures by methods I and II (see Experimental section). Good agreement was attained for the free energy of activation associated with the interconversion process between the two diastereoisomeric conformations using methods I and II on signals arising from the previously identified ^{13}C and ^{1}H n.m.r. probes.

Examination of molecular models of the hydrocarbon (4) focuses attention on the following conformations * which appear to be relatively free from angle strain and torsional strain: (i) a pair of degenerate Chair † conformations C and C* (7a and b) with C_s symmetry, (ii) a pair of degenerate boat conformations B and B* (8a and b) with C_s symmetry, and (iii) a pair of enantiomeric twist-boat conformations TB and TB* (9a and b) with C_2 symmetry. The B (8a and b) and TB (9a and b) conformations belong to a family of flexible Boat † conformations. Strain energy calculations (Table 3) demonstrate that the C (7a and b) and TB (9a and b) conformations correspond to ground-state conformations and that the B conformations (8a and b) pro-

vide relatively low energy (ΔE_T 5.29 kcal mol^{-1}) transition states towards TB $\rightleftharpoons$ TB* inversion. The C-12 methylene protons in the TB conformations (9a and

† The description ' Chair ' is non-specific and refers to both degenerate conformations (C and C*) of the rigid chair type. Similarly, the description ' Boat ' refers to any conformation of the flexible boat family.

b) are homotopic and so cannot give rise to an AB system in the low temperature ^{1}H n.m.r. spectrum of the hydrocarbon (4) even when TB $\rightleftharpoons$ TB* inversion is slow on the ^{1}H n.m.r. time-scale. Thus, the minor conformation was assigned to the TB conformations (9a and b) and the major conformation was identified as the C conformations (7a and b). Protons designated H_1

TB (9) and the transition-state conformations TS1 (10) are summarised in the conformational itinerary depicted in Figure 4. Calculations (Table 3) indicate that the principal sources of strain in the TS1A conformation (10a) arise from angle deformation (E_θ) and torsional strain (E_ϕ) associated with eclipsing of the 5,6-bond. The second type of transition states TS2 (11a) and TS2*

TABLE 2

Site exchanges and thermodynamic parameters associated with conformational change in 5,6,7,12-tetrahydrodibenzo-[a,d]cyclo-octene (4)

N.m.r. probe [a]	Program	Site exchanges	p_A/p_1	p_B/p_2	$\Delta G/$ kcal mol^{-1}	$\Delta G^\ddagger/$ kcal mol^{-1}	Process	Comments
C-4a,7a or C-11a,12a	I	A $\longrightarrow$ B	0.96	0.04	1.73	14.7 [b]	C $\longrightarrow$ Boat	
C-5,7	I	A $\longrightarrow$ B	0.96	0.04	(0 °C)	14.7 [b]	C $\longrightarrow$ Boat	
CH_2-12	III	A1 $\longrightarrow$ A2	0.98	0.02	2.11	14.9 [c]	C $\longrightarrow$ Boat	Assumed
		B1 $\longrightarrow$ B2			(0 °C)			k (A2 $\rightleftharpoons$ B2)
		A1 $\rightleftharpoons$ B1				15.3 [c]	C $\rightleftharpoons$ C*	$\longrightarrow \infty$

[a] Details of ^{13}C and ^{1}H n.m.r. chemical shifts are given in Table 1. [b] Values obtained from ^{13}C n.m.r. line-shape analysis (see Figure 2). [c] Values obtained from ^{1}H n.m.r. line-shape analysis (see Figure 3).

and H_2 [see (7)] undergo exchange between sites A1 and B1 during the degenerate C $\rightleftharpoons$ C* inversion and give rise to the AB system in the ^{1}H n.m.r. spectrum at low temperatures. Hence, a relatively high energy transition state is associated with the Chair $\rightleftharpoons$ Boat interconversions necessary for C $\rightleftharpoons$ C* inversion. Molecular models show that the diastereoisomeric Chair and

(11b) have C_s symmetry and lie (see Figure 4) on the pathways B $\rightleftharpoons$ C* and B* $\rightleftharpoons$ C, respectively. The third type of transition states TS3 (12a) and TS3* (12b) also have C_s symmetry but this time lie (see Figure 4) on the pathways B $\rightleftharpoons$ C and B* $\rightleftharpoons$ C*, respectively. Calculations (Table 3) show that both these types of transition state involve considerable angle deformation

TABLE 3

Calculated strain energies $(E_T/\text{kcal mol}^{-1})$ [a] of various conformations of 5,6,7,12-tetrahydrodibenzo[a,d]cyclo-octene (4)

Conformation	$\phi_{5,6}$	$\phi_{6,7}$	E_r	E_θ	E_ϕ	E_δ	E_{nb}	E_T
C(7a)	$-91.8°$	$+91.9°$	0.04	1.11	3.34	0.08	-0.57	4.00 [e]
B (8a)	$+75.0°$	$-75.0°$	0.15	7.80	0.83	0.08	0.44	9.30
TB (9a)	$-58.3°$	$-59.6°$	0.08	2.75	0.54	0.39	0.25	4.01 [f]
TS1A (10a) [b]	0.0°	$-60.8°$	0.36	14.99	3.03	0.06	1.13	19.57 [e]
TS2 (11a) [c]	$+108.0°$	$-110.0°$	0.58	20.83	5.55	0.06	-0.08	26.94
TS3 (12a) [d]	0.0°	0.0°	0.31	15.44	7.01	1.12	-0.29	23.59

[a] The following energy terms (J. F. Stoddart, 'Organic Chemistry, Series One, Structure Determination in Organic Chemistry,' ed. W. D. Ollis, Butterworths, London, 1973, p. 1) have been used: E_r (bond length strain), E_θ (angle strain), E_ϕ (torsional strain), E_δ (out-of-plane strain in aromatic rings), E_{nb} (non-bonded interactional strain); total strain energy $E_T = E_r + E_\theta + E_\phi + E_\delta + E_{nb}$; for force constants and other empirical parameters, see Part 6.[1] [b] Defined by holding atoms 12, 12a, 4a, 5, 6, and 7 coplanar. [c] Defined by holding atoms 7a, 11a, 12, 12a, and 4a coplanar. [d] Defined by holding atoms 4a, 5, 6, 7, and 7a coplanar. [e] If the difference $(\Delta E_T^\ddagger\ 15.57\ \text{kcal mol}^{-1})$ in strain energies between the C conformation (7a) and the TS1A conformation (10a) is equated with $\Delta H^\ddagger$ then an approximate estimate for $\Delta G_{calc.}$ of 15.2 kcal mol^{-1} follows from recognising that the transition state is favoured on entropy of mixing grounds by $R\ln 2$ cal deg^{-1} mol^{-1} (i.e. there are two equivalent pathways for C $\longrightarrow$ TB interconversion involving chiral transition states). [f] The calculation on the TB conformation (9a) allowed loss of C_2 symmetry during the energy minimisation procedure. The values for $\phi_{5,6}$ and $\phi_{6,7}$ indicate that the minimum energy boat conformation corresponds to a very slightly distorted TB conformation (9a).

Boat conformations are interconvertible by three geo-metrically definable pathways involving the three diastereoisomeric transition states TS1 (10), TS2 (11), and TS3 (12). The transition states of the type TS1 (10) lie on the Chair $\rightleftharpoons$ twist boat pathway and, depending on whether these transition states involve C* $\rightleftharpoons$ TB, C $\rightleftharpoons$ TB*, C $\rightleftharpoons$ TB, or C* $\rightleftharpoons$ TB* interconversions, they are designated as TS1A (10a), TS1A* (10b), TS1B (10c), or TS1B* (10d). The pairs of conformations (i) TS1A (10a) and TS1A* (10b) and (ii) TS1B (10c) and TS1B* (10d) are enantiomers. The pairs of conformations (i) TS1A (10a) and TS1B (10c) and (ii) TS1A* (10b) and TS1B* (10d) are degenerate. The relationships between the ground-state conformations C (7) and

(E_θ) and torsional strain (E_ϕ) and both are appreciably higher in total strain energy (E_T) compared with transition states of the type TS1 (10). Thus, Chair $\rightleftharpoons$ Boat interconversions of the hydrocarbon (4), in common with its heterocyclic analogues,[15] appear to involve TS1 conformations (10) as transition states.

Thermodynamic Parameters for Conformational Changes.—The free energies of activation for C $\longrightarrow$ Boat interconversion and C $\rightleftharpoons$ C* inversion in the hydrocarbon (4) are given in Table 2. The fact that $k_{C \rightleftharpoons C^*} = 0.5\ k_{C \longrightarrow Boat}$ (see Figure 3) at all temperatures examined is consistent with the presence of intermediate Boat conformations in the C $\rightleftharpoons$ C* inversion process. The value $(\Delta G^\ddagger_{exp.} = 14.7—14.9\ \text{kcal mol}^{-1})$

for C ⟶ Boat interconversion is in excellent agreement with the calculated value ($\Delta G_{calc.}$ = 15.2 kcal mol⁻¹ from Table 3) between the C (7a) and TS1A (10a) conformations. Thus, the involvement of TS1 conformations (10) in Chair ⇌ Boat interconversions of the hydrocarbon (4) is established.

Variable temperature ¹H and ¹³C n.m.r. spectroscopy has indicated that the C conformation (7a and b) is the major ground-state conformation and that the contribution in solution from the minimum energy Boat conformation amounts to less than 4% at equilibrium. Strain energy calculations show (Table 3) that the minimum energy Boat conformation corresponds to a very slightly distorted TB conformation (9a). The C conformation (7a) is destabilised largely by torsional strain (E_ϕ) and to some extent by angle strain (E_θ). The TB conformation (9a) is destabilised principally by angle strain (E_θ). Although this conformation (9a) is calculated as having the same total strain energy (E_T) as

FIGURE 4 Conformational changes in 5,6,7,12-tetrahydrodibenzo[a,d]cyclo-octene (4)

the C conformation (7a), variable temperature n.m.r. spectroscopy shows (Table 2) that the C conformation (7a) is at least 1.73 kcal mol⁻¹ more stable than the TB conformation (9a). Problems [1,3] inherent in the calculation of angle strain (E_θ) might be responsible for this small discrepancy between observed and calculated parameters. Error margins of at least ±1 kcal mol⁻¹ should be associated with total strain energies (E_T) particularly when their largest component is comprised of angle strain (E_θ). Strain energy calculations [12] on cis,cis-cyclo-octa-1,4-diene indicate that the minimum energy Boat conformation is a C_s conformation corresponding to the B conformation (8a) of the tetrahydrodibenzocyclo-octene (4). However, it only constitutes about 1% of the equilibrium mixture at room temperature, the major ground-state conformation being the other C_s conformation corresponding to the C conformation (7a) of the tetrahydrodibenzocyclo-octene (4). In this hydrocarbon (4), the B conformation (8a) corresponds to a transition state in which angle strain (E_θ) is large mainly on account of the alleviation of nonbonded

interactional strain (E_{nb}) between hydrogen atoms on C-6 and C-12. Thus, although calculations on cis,cis-cyclo-octa-1,4-diene and its dibenzo-analogue (4) predict the same conformational type for the more stable ground

(10a) TS1A (o o -+-+)

(10b) TS1A* (o o +-+-)

(10c) TS1B (+-o.o+-)

(10d) TS1B* (-+o o-+)

(11a) TS2 (-+-+o o)

(11b) TS2* (+-+-o o)

(12a) TS3 (+ o o -+ -)

(12b) TS3* (-o o +-+)

state of both eight-membered ring compounds, they lead to quite different conclusions regarding the conformational nature of the less stable ground state. This is not surprising in view of our findings [15] for 7,12-dihydro-5H-dibenzo[c,f]thiocin (13) and 5,6,7,12-tetra-hydro-6-methyldibenz[c,f]azocine (14) where strain

(13) X = S
(14) X = NMe
(15) X = NBu^t

energy calculations indicate (i) a minimum energy Boat for the thiocin derivative (13) which lies fairly close to a TB conformation, and (ii) little energy difference between the various Boat conformations that lie on the pathway TB ⇌ B ⇌ TB* ⇌ B* for the azocine derivative (14). In addition, a crystal structure analysis

has shown[23] that 5,6,7,12-tetrahydro-6-t-butyldibenz-[c,f]azocine (15) adopts a Boat conformation midway between B and TB type conformations. Clearly, the situation is a finely balanced one in relation to the myriad of flexible Boat conformations available to the eight-membered rings of cis,cis-cyclo-octa-1,4-diene, the

tetrahydrodibenzocyclo-octene (4), and its heterocyclic analogues [e.g. (13)—(15)].

[23] A. D. Hardy and F. R. Ahmed, *Acta Cryst.*, 1974, **B30**, 1674.