256. π-Bond Configurations, Conformations, and Dynamic Behaviour of Benzo[*c*]octalene and Dibenzo[*c,j*]octalene

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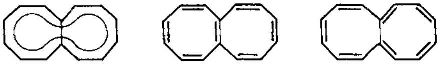
Summary

The π-bond configurations, the conformations, and the dynamic behaviour of dibenzo[*c,j*]octalene (**2**) and of benzo[*c*]octalene (**3**) have been investigated by ^{13}C-NMR. spectroscopy at different temperatures. Dibenzooctalene was found to present π-bond fixation in the octalene unit as in **2b**; with this π-bond fixation the molecule is not planar and takes two different conformations which are rapidly interconverted by inversion of one cyclooctatetraene ring. Monobenzooctalene (**3**) also presents π-bond fixation in the octalene unit but exists as two valence isomers, **3b** and **3c**. Isomer **3c** dominates the dynamic equilibrium. With this π-bond configuration, the molecule is chiral but undergoes several isodynamic processes, namely inversion of the cyclooctatriene and/or of the cyclooctatetraene ring. The valence isomer **3b** can have two different conformations which are rapidly interconverted by inversion of one cyclooctatetraene ring. The interconversion **3c**$\rightleftarrows$**3b** implies the occurrence of a π-bond shift process; this process affects the ^{13}C-NMR. lineshape above 50°.

Introduction. - Detailed analysis of the temperature dependent ^{13}C-NMR. spectrum of octalene (**1**) [1] allowed us to establish that this bicyclic 14π-system presents π-bond fixation as in **1c** [2]. The molecule is chiral and undergoes several isodynamic processes, namely ring inversions and a π-bond shift. In these processes eight isometric[2]) structures (4*R* and 4*S*) are implied. The structure **1b** with a central double bond is not observed; thermochemical arguments indicate that its enthalpy

Scheme 1. *Formal π-bond configurations of octalene* (**1**)



1a **1b** **1c**

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[2]) Isometric structures have identical sets of internuclear distances. Enantiomers are isometric.

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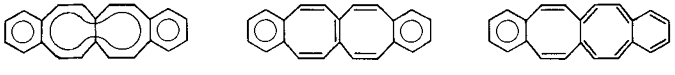
Scheme 2. *Formal π-bond configurations of dibenzooctalene* **2**



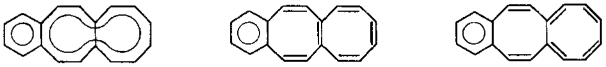
2a **2b** **2c**

of formation should not be very much greater (at most 5-6 kcal/mol) than that of **1c**. The structure **1a** with π-bonds delocalized, if regarded as identical to the transition state for the π-bond shift in **1c**, would be *ca.* 20 kcal/mol higher in energy than **1c** [2].

Fusion of both the C(3),C(4)- and C(9),C(10)-bonds into benzene rings would evidently impose configuration **1b** to the octalene unit. The dibenzo[*c,j*]octalene [3] is therefore expected to exist as **2b**, or possibly as **2a** (*i.e.* with all π-bonds delocalized). Configuration **2c** can be excluded since the molecule would suffer from loss of the resonance stabilization in one benzene unit. With configuration **2b**, the molecule is expected to be non-planar and to exhibit a stereodynamic behaviour related to that of benzocyclooctatetraene.

Fusion of only one of the C(3),C(4)- or C(9),C(10)-bonds of octalene into a benzene ring has a completely different implication. Since the energetic relations between configurations **a**, **b** and **c** of the octalene unit in the resulting benzo[*c*]-octalene (**3**) [5] remain similar to those in octalene (**1**) itself, configuration **3c** is expected to constitute the most stable form. In this bond fixation, the molecule is expected to be chiral and to undergo stereodynamic processes analogous to those observed in octalene **1c**.

Scheme 3. *Formal π-bond configurations of benzooctalene* **3**



3a **3b** **3c**

Structure and dynamic behaviour od dibenzooctalene 2. - The ^{1}H-noise decoupled ^{13}C-NMR. spectrum of **2** recorded above 35° (see *Fig. 1;* spectrum at 100 °C) consists of 6 signals, two of which correspond to quaternary C-atoms as indicated by selective decoupling experiments.

In principle, this spectrum is compatible with structures **2a** or **2b**. On cooling, each signal observed at 35 °C gives rise to two signals of different intensity (see *Fig. 1;* spectrum at −87 °C); this finding indicates that two species undergoing fast interconversion are present in different concentration (in THF-d_8 their relative concentrations are as 1.2:1, in acetone-d_6 as 4:1). On cooling to much lower temperatures (down to −140 °C; in CF_2Br_2/CD_2Cl_2), no further change in the spectrum is observed. The two species responsible for the observations could be i) **2a** and **2b** (**2b** existing as a single conformation), ii) the **2b-anti** and **2b-syn** conformations of **2b** (see *Fig. 2*).

From our investigation of octalene itself (see introduction), we reject the first possibility; the strain energy of the planar structure **2a** is certainly not compensated by the stabilization energy associated with the π-bond delocalization.

The interconversion of the two conformers **2b-anti** and **2b-syn** implies the inversion of one tub-shaped cyclooctatetraene unit. A crude analysis of the line-shape of the ^{13}C-NMR. spectra in the coalescence region provides a value $\Delta G^{\ddagger} = 15.2$ kcal/mol for the activation free energy of this process. The slight increase of $\Delta G^{\ddagger}$ over that observed for the analogous process in cyclooctatetraene ($\Delta G^{\ddagger} = 12.6$ kcal/mol) [6] and in benzocyclooctatetraene ($\Delta G^{\ddagger} = 13.4$ kcal/mol) [7] can easily be explained: the strain accumulated in **2b** on flattening *one* cyclooctatetraene ring

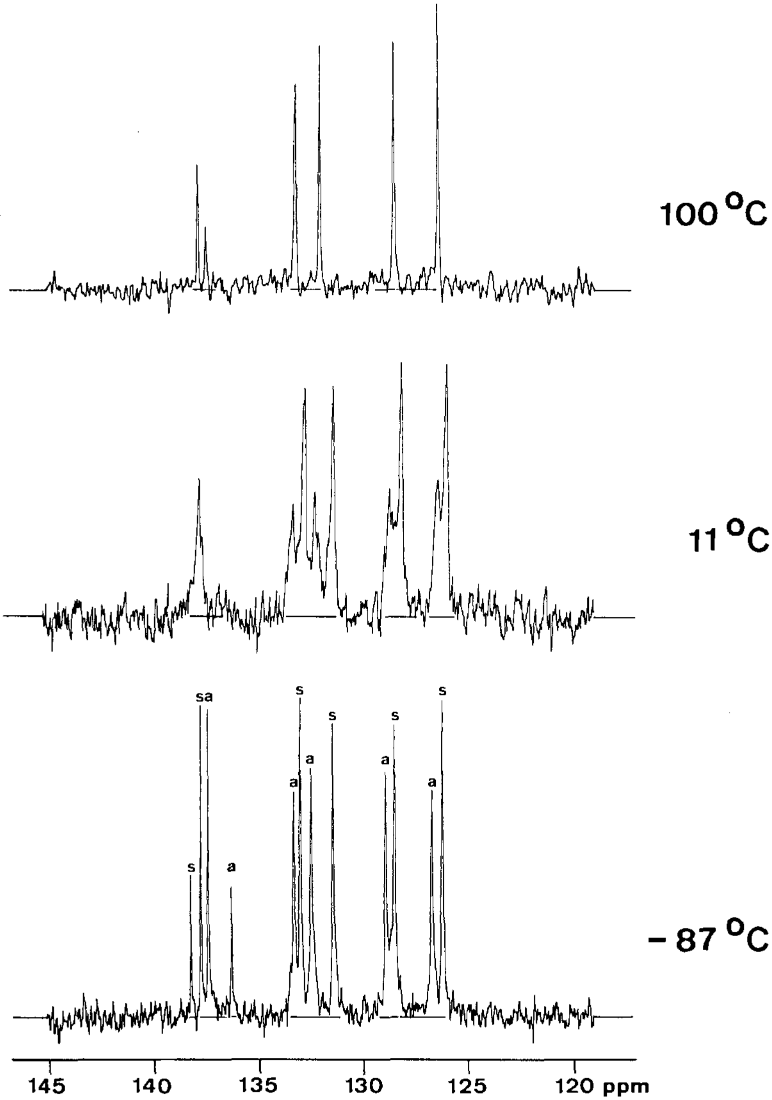
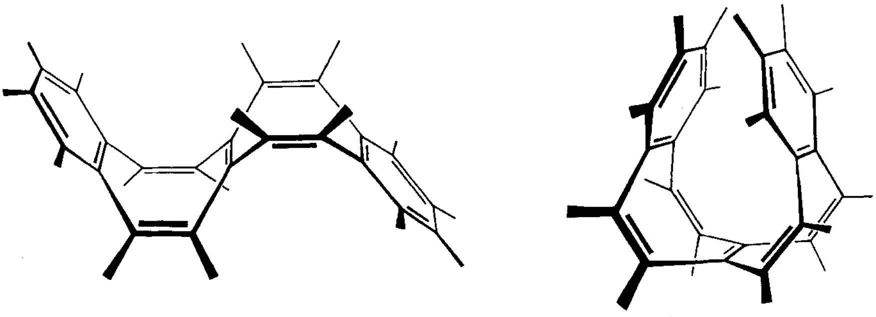


Fig. 1. *^{1}H-noise decoupled ^{13}C-NMR. spectra of dibenzooctalene* **2** *recorded at different temperatures and at 20.1 MHz.* Signals due to the **2b-syn** and **2b-anti** conformers are indicated as **s** and **a**, respectively.



2b-anti **2b-syn**

Fig. 2. *The two conformations of dibenzooctalene with configuration* **2b**

is enhanced by the fact that two double bonds are fused in two other rings, one in a benzene ring and the other in the second eight-membered ring.

Note that two isometric structures **2b-anti** and two isometric structures **2b-syn** are implied in the dynamic behaviour; they are interconverted as indicated on *Figure 3*.

It is not possible to deduce from the spectra which of the two conformers **2b-anti** or **2b-syn** is the more stable. X-ray analysis of a single crystal of **2** reveals that in the solid state only structure **2b-syn** is present [3]. Dissolving this sample at low temperature allows one to record the ^{1}H-(FT)NMR. spectrum of the pure 'cage-isomer' **2b-syn**. On rewarming this solution to room temperature the equilibrium composition **2b-anti**/**2b-syn** is reestablished. One therefore concludes that the major isomer observed in the ^{13}C-NMR. spectra *(Fig. 1)* is **2b-syn**.

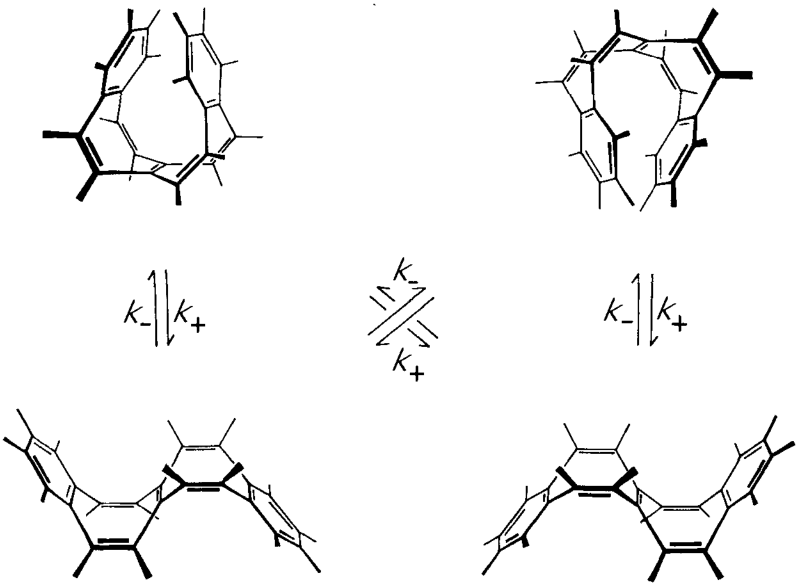


Fig. 3. *Processes leading to the interconversion of the conformers of dibenzooctalene with configuration* **2b**

Structure and dynamic behaviour of benzooctalene 3. - The ^{1}H-decoupled ^{13}C-NMR. spectrum of **3** recorded at 37 °C (100.6 MHz) (see *Fig. 4*) indicates the presence of two species with different energy. The subspectrum of the more abundant species consists of 9 sharp signals, two of which are attributed to

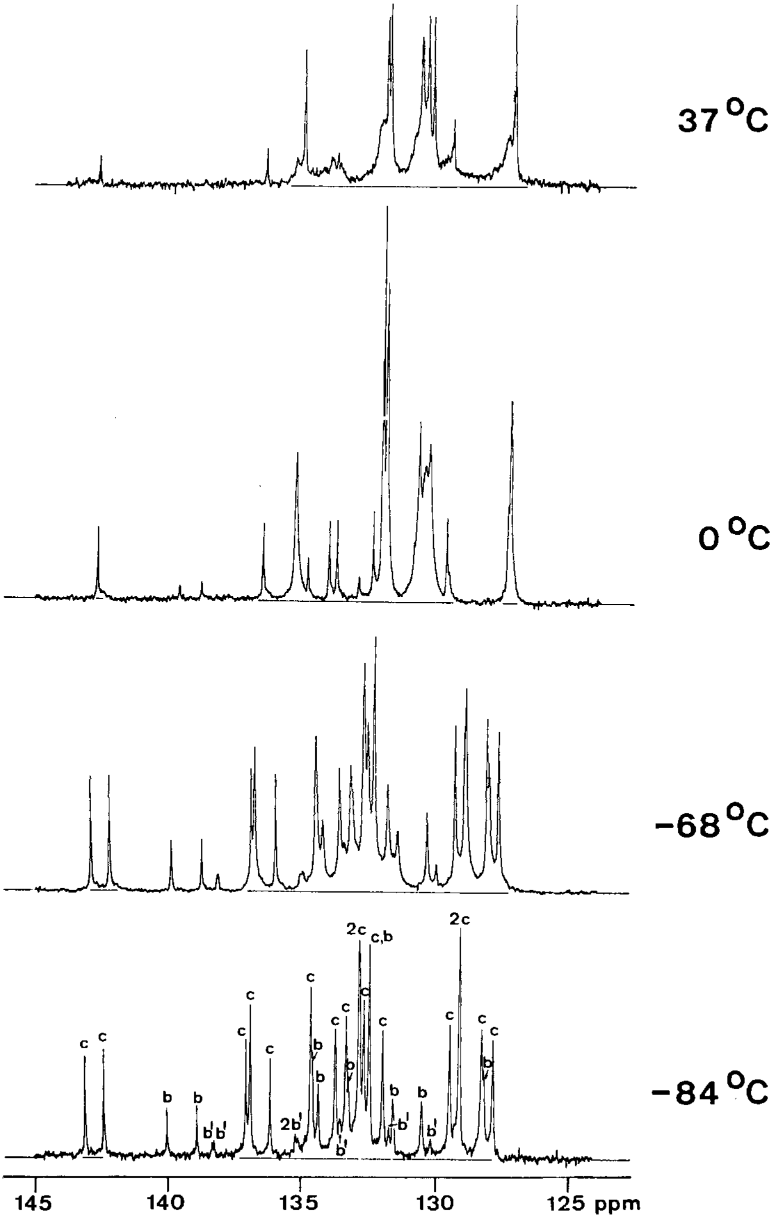


Fig. 4. *^{1}H-noise decoupled ^{13}C-NMR. spectra of benzooctalene* 3 *recorded at various temperatures* (RF: 100.6 MHz)

quaternary C-atoms; the subspectrum of the less abundant one consists of broadened signals which sharpen up into 9 (8 actually resolved) signals on cooling the sample to 0 °C (see *Fig. 4*). Between -30° and -65 °C each signal of the subspectrum of the major isomer progressively splits into two equally intense signals. In addition to the 27 major signals (24 actually resolved), the spectrum recorded at -84 °C exhibits new, distinct, but very weak signals indicating the presence of yet another species (see *Fig. 4*). On cooling to -160 °C no further modification of the spectrum is observed.

The major species responsible for the subspectrum of 18 signals at -84 °C is clearly the chiral isomer **3c**; inversions of the cyclooctatriene ring (k_1) and of the cyclooctatetraene ring (k_2) within that configuration induce the pairwise exchange of signals observed above -68 °C and explain the 9 main signals of the room temperature spectrum. The stereochemical implications of the two ring inversion processes k_1 and k_2 are essentially the same as for octalene itself: inversion of the cyclooctatriene unit (k_1) leaves the absolute configuration unchanged while inversion of the cyclooctatetraene ring (k_2) converts one antipode into the other (see *Fig. 5*). As in octalene, inversion of either ring causes the same pairwise exchange of related magnetic sites, so that a line-shape analysis of the ^{13}C-NMR. signals would allow the determination of k_1+k_2 but not of the individual rate constants.

Preliminary line-shape analysis of the signals of the major isomer **3c** recorded between -65° and -30 °C indicates that the exchange rate (k_1+k_2) is substantially slower than in octalene itself: $\Delta G^{\neq}$ $(k_1+k_2)=10.2$ kcal/mol, the corresponding value in octalene being 8 kcal/mol. Assuming that inversion of the cyclooctatriene

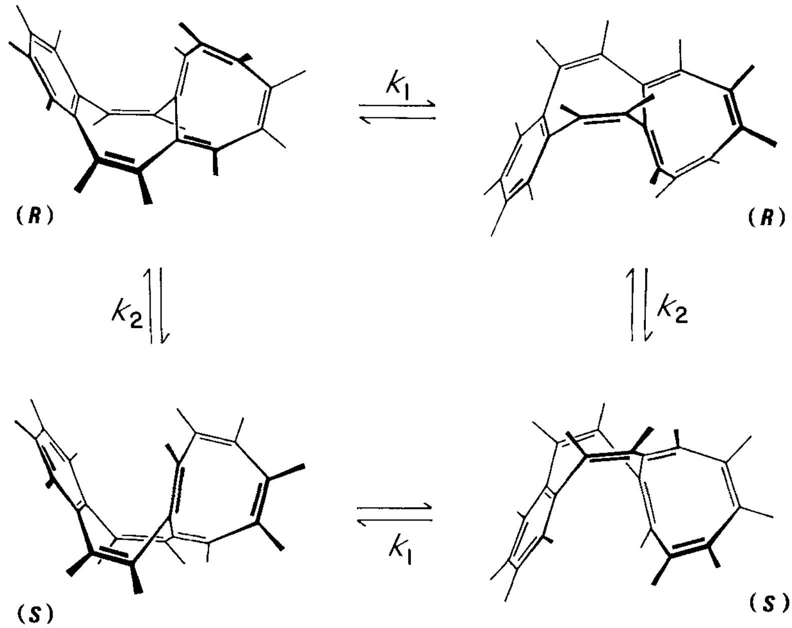
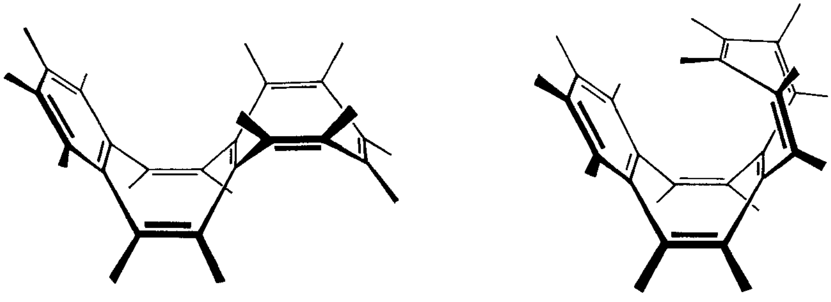


Fig. 5. *Ring inversion processes in benzooctalene with configuration* **3c**



3b-anti **3b-syn**

Fig. 6. *The two conformers of benzooctalene with configuration* **3b**

ring is faster than that of the cyclooctatetraene ring (*i.e.* $k_1 \gg k_2$), it is obvious that the exchange should be faster in **1c** than in **3c**, where the fusion in a benzene ring of one double bond of the cyclooctatriene ring evidently leads to an increase in the *Baeyer* strain when the ring is flattened. This effect was also observed when comparing the ring inversion in cyclooctatriene and in benzocyclooctatriene [7].

The signals of the two other species observed at −84 °C must be attributed to the two conformers **3b-anti** and **3b-syn** of benzooctalene with configuration **3b** (see *Fig. 6*). Both have a symmetry plane passing through the midpoints of the C(3),C(4)- and C(9),C(10)-bonds, so that at low temperatures each gives nine signals (labelled b and b′ on the −84 °C spectrum reproduced on *Fig. 4;* seven signals only are visible from the minor species). These two conformers are inter-

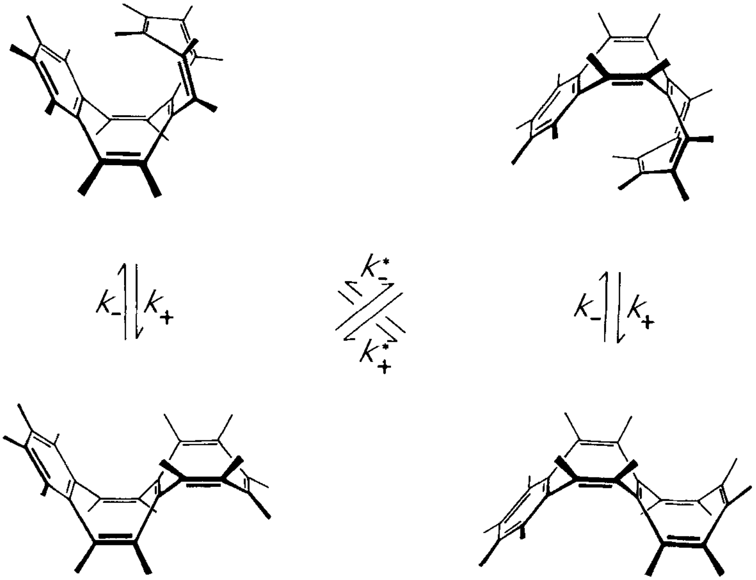


Fig. 7. *Processes leading to interconversion of the conformers of benzooctalene with double bond configuration* **3b**

converted by inverting either of the two cyclooctatetraene rings (see *Fig. 7*). This process is responsible for the disappearance of the ^{13}C-signals of the less abundant species (signals labelled b′) and for the broadening of the signals of the other one (signals labelled b) observed when the temperature is raised to 0 °C.

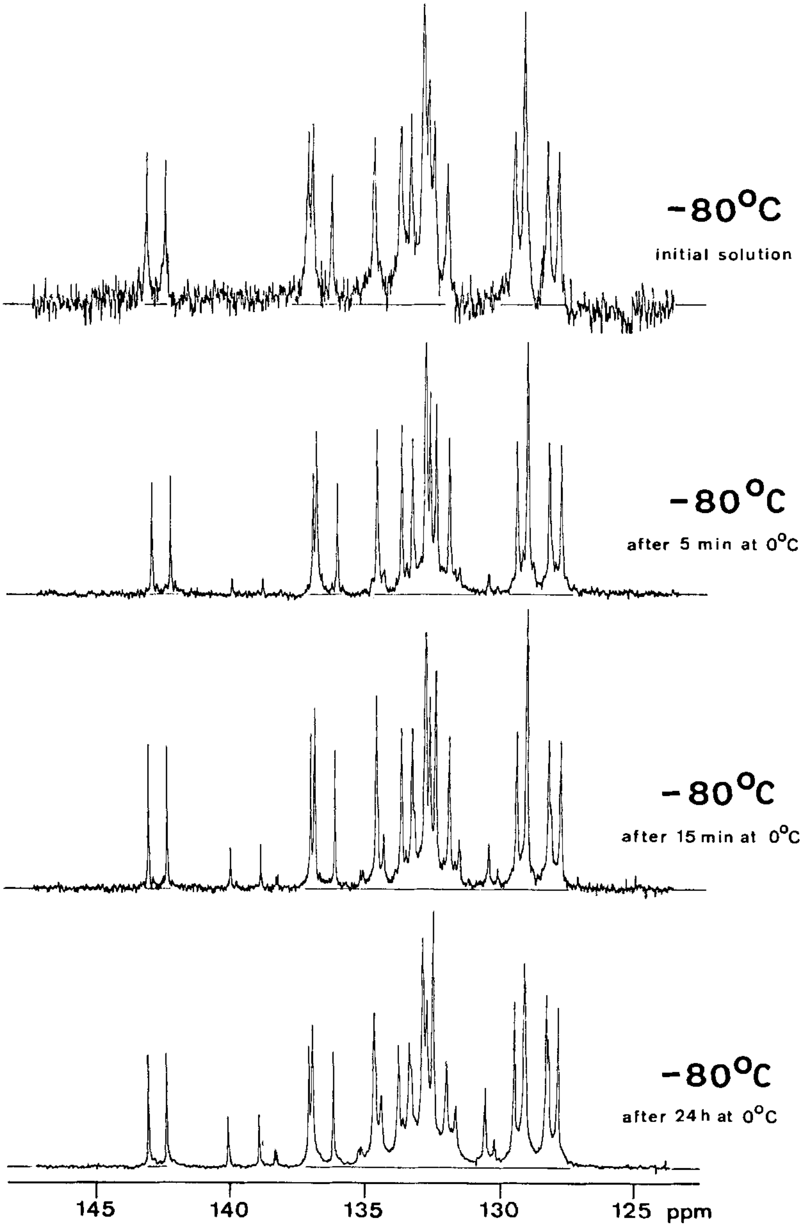


Fig. 8. *^{13}C-NMR. spectrum of pure isomer* **3c** *recorded at −80 °C and its evolution upon heating the solution at 0 °C for several periods of time*

In benzooctalene, both configurations **3c** and **3b** are therefore in equilibrium in solution, whereas for octalene itself the configuration **1c** is the sole species detected.

The above mentioned results characterise the structural and dynamic behaviour of benzooctalene in solution and not in the solid state. According to an X-ray analysis [5] crystals of benzooctalene (obtained from ethanol solution at room temperature) are built exclusively from molecules of structure **3c**. The following experiments provide some information about the interconversion of configuration **3b** (2 conformations) and **3c**:

i) If one dissolves crystalline benzooctalene (pure **3c**) at −80 °C and records the ^{13}C-NMR. spectrum of the solution without rewarming, one observes only the signals of the isomer **3c** (see *Fig. 8*). Interconversion of **3c** into **3b** (**3b-anti** ⇄ **3b-syn**) could be brought about, and its kinetics followed, by allowing the original solution of the pure isomer **3c** to be warmed at 0 °C during controlled periods of time, the spectra being measured at −80 °C. *Figure 8* reproduces some of the ^{13}C-NMR. spectra recorded; isomer **3b** (as conformers equilibrium **3b-anti** ⇄ **3b-syn**) develops progressively, the equilibrium composition $[\mathbf{3c}]/[\mathbf{3b}] = K_{eq} = 2.4$ being obtained after *ca.* 30 min at 0 °C. From the estimated rate of interconversion **3c** → **3b** at 0 °C the activation free energy $\Delta G^{\neq}$ (**3c** → **3b**) is about 19 kcal/mol. One should point out here that the above experiment fully supports the structural assignments (namely identification of **3c** and, indirectly, of **3b**) which have been deduced from the temperature-dependent ^{13}C-NMR. spectra of benzooctalene.

ii) A solution enriched in isomer **3b** could be obtained by crystallizing isomer **3c** out of an equilibrium solution at −80 °C; the crystallization was initiated by adding

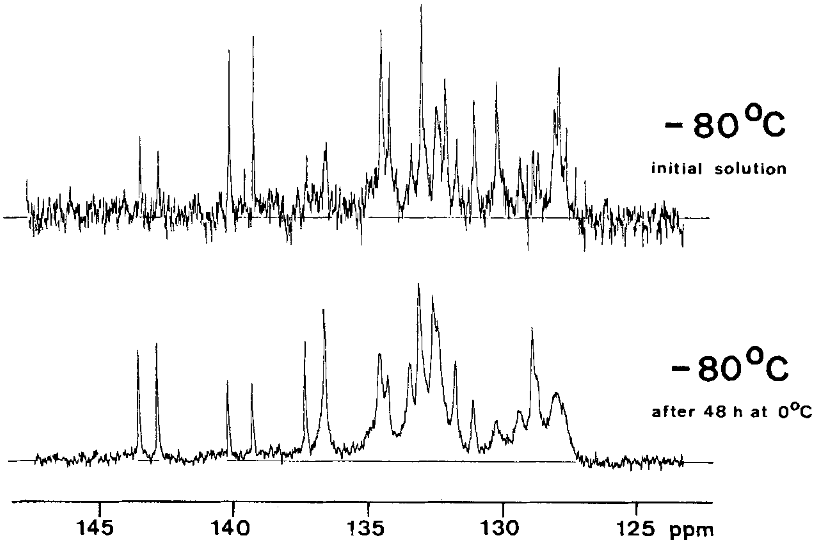


Fig. 9. *^{13}C-NMR. spectrum of isomer* **3b** *enriched up to 75%.* Solvent: ethanol-d_6; temperature: −80 °C; RF.: 100.6 MHz

a tiny crystal of pure isomer **3c** to the cold supersaturated solution (solvent: ethanol-d_6; −80 °C). The ^{13}C-NMR. spectrum of the solution recorded immediately after decantation indicates that **3b** was enriched up to 75% (see *Fig. 9*).

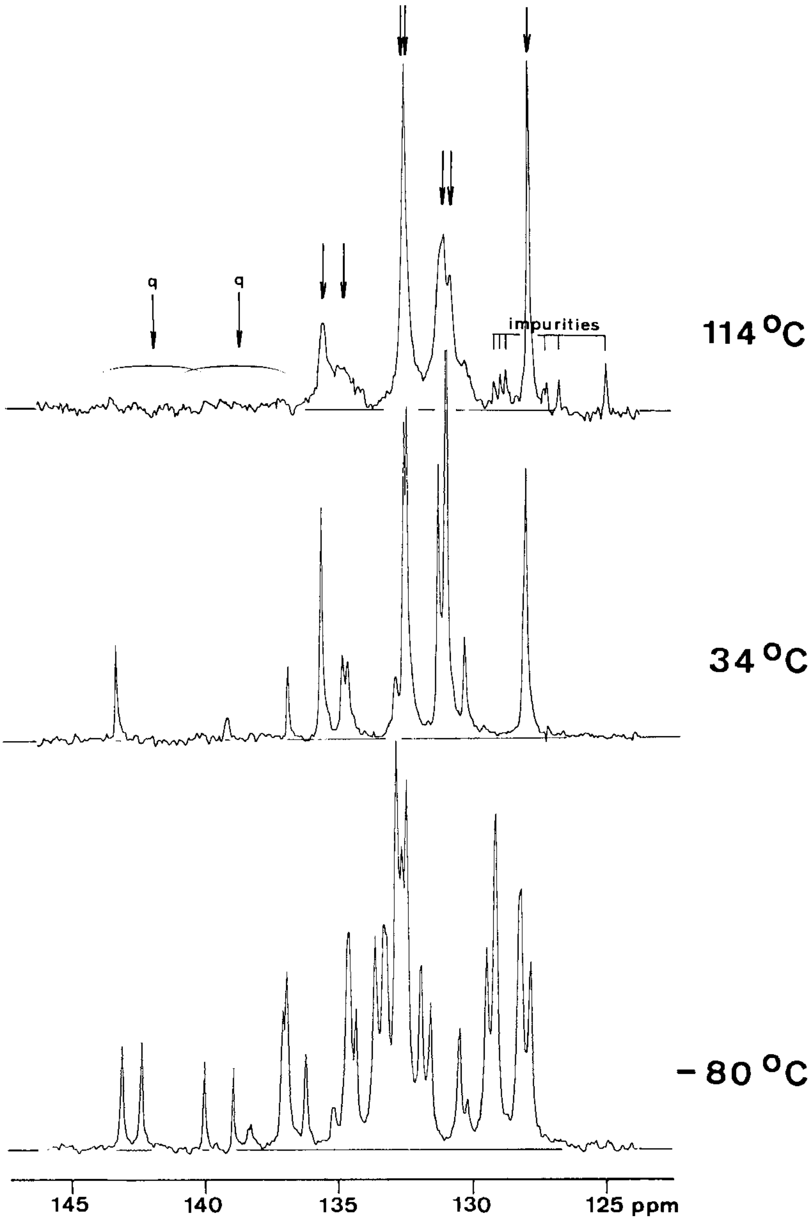


Fig. 10. *^{13}C-NMR. spectra* (^{1}H-decoupled) *of* **3** *recorded at different temperatures.* RF.: 25 MHz; solvents: THF-d_8 (−80 °C, 34 °C), cyclohexane-d_{12} (114 °C); the indicated impurities are formed by thermal decomposition during measurements at elevated temperatures.

After warming the solution at 0 °C for 12 h, the spectrum recorded at −80 °C indicates that **3c** has been formed at the expense of **3b** to reestablish the equilibrium composition [**3c**]/[**3b**] = 2.4 (see *Fig. 9*).

iii) The mechanism for the observed configurational interconversion **3c**$\rightleftarrows$**3b** can be identified as a π-bond shift[3]. Such a π-bond shift could be fast enough at higher temperatures to affect the line-shape of the ^{13}C-NMR. signals, and indeed the ^{13}C-NMR. spectrum recorded at +37 °C (see *Fig. 4*) indicates that some dynamic process is taking place at this temperature: the ^{13}C-signals of the isomer **3b** are broader than those of isomer **3c**, although, at this temperature, the fast exchange limit for the conformational interconversion **3b-anti**$\rightleftarrows$**3b-syn** is already attained.

Since benzooctalene **3** is thermally unstable, we decided to investigate the ^{13}C-NMR. spectra at 25 MHz in order to reduce the temperature at which possible line-shape modifications due to the expected π-bond shift could be clearly identified. *Figure 10* shows that on warming from 34° to 114 °C, the 18-signal spectrum (nine for **3c**; nine for **3b**) is modified towards the nine-line spectrum expected if the π-bond shift interconverting the two configurations **3c**$\rightleftarrows$**3b** is very fast. The arrows on the 114 °C spectrum *(Fig. 10)* indicate the expected positions of the signals in the fast exchange limit: these positions were estimated from the chemical shifts of the signals of **3c** and **3b** at low temperatures and from the identification of exchanging pairs of signals as deduced from the line-shape evolutions observed on spectra not reproduced on *Figures 4* or *10*.

The two signals expected for the quaternary C-atoms in exchange are too broad to be detected at 114 °C; the frequencies characteristic of the magnetic sites between which the exchange occurs are more different for such C-atoms than for the others.

Discussion and conclusion. - The present ^{13}C-NMR. investigation of dibenzo- **2** and of benzooctalene **3** allows us to draw the following conclusions:

a) The π-bonds in the octalene residue are localized in the two compounds **2** and **3** as in octalene **1** itself, although the octalene unit constitutes a 14π-electron system [8].

b) In dibenzooctalene **2**, the fusion of the C(3),C(4)- and C(9),C(10)-bonds with benzene rings imposes the π-bond configuration **2b**, *i.e.* the configuration with a central double bond, to the octalene unit.

c) With this configuration the molecule is not planar but exists as two conformations, **2b-anti** (C_{2h}-symmetry) and **2b-syn** (C_{2v}-symmetry) which are represented on *Figure 2*.

d) The two conformations **2b-anti** and **2b-syn** are interconverted by inversion of one cyclooctatetraene ring, with $\Delta G^{\neq} \simeq 15.2$ kcal/mol, a value slightly greater than that observed for the same process in benzocyclooctatetraene.

e) This dynamical behaviour of dibenzooctalene deserves a more precise description. If the nuclei are labelled one recognizes that each conformation is represented by two isomeric structures and the transition state (in which one

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[3] The occurrence of a π-bond shift in the terminal cyclooctatetraene ring might be considered since the activation free energy of 19 kcal/mol is close to that measured for the π-bond shift in cyclooctatetraene ($\Delta G^{\neq} = 13.3$ kcal/mol) and in several monosubstituted cyclooctatetraene derivatives ($\Delta G^{\neq} = 14.9$ to 16.2 kcal/mol) [6].

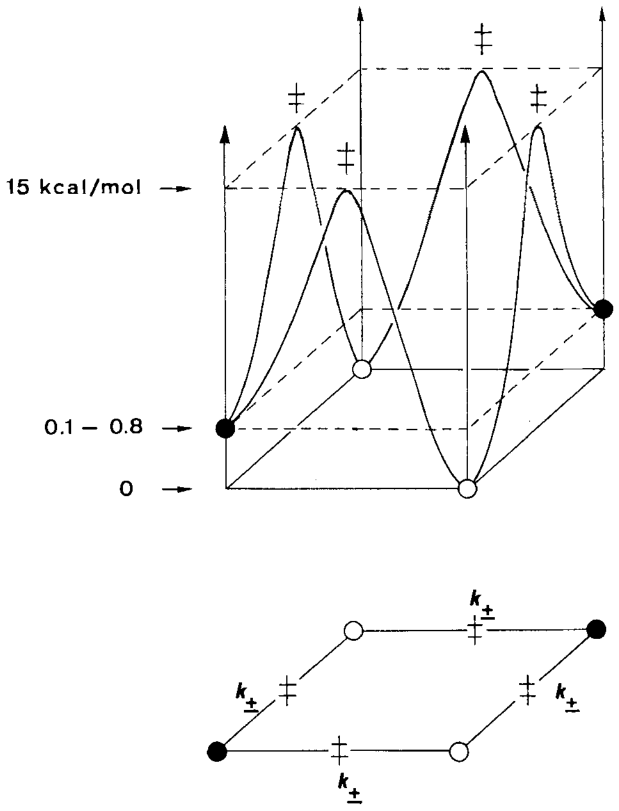

Fig. 11. *Graph representation and energy diagram for the dynamic behaviour of dibenzooctalene* **2b** (compare *Fig. 3*)
○ **2b-syn**, ● **2b-anti**, ‡ transition state

COT-ring is flattened; C_s-symmetry) by four. The dynamic behaviour of dibenzooctalene (with bond fixation as in **2b**) can thus be summarized by the graph and the energy diagram shown in *Figure 11*. Inversion of one COT-ring converts a given conformation into the other; two consecutive inversions (or a less probable synchronous double inversion) are required in order to interconvert a given pair of isometric structures.

f) Benzooctalene exists in solution as a dynamic equilibrium between the structures **3c** and **3b**, with **3c** dominating. The isomer **3c** is chiral and undergoes several isodynamic processes similar to those observed in octalene itself, *i.e.*: i) inversion of the cyclooctatriene ring (k_1), ii) inversion of the cyclooctatetraene ring (k_2), iii) a π-bond shift.

g) If the nuclei are labelled, one recognizes that four isometric structures (2 R and 2 S) with configuration **3c** are implied in the dynamic: inversion of the cyclooctatriene ring (k_1) converts a given structure into its homochiral mate whereas inversion of the cyclooctatetraene (k_2) converts a structure of a given chirality into one of its antipodes. The processes k_1 and k_2 lead to the same pairwise exchange of the nuclei among the 18 different magnetic sites and are responsible for the progressive transformation of the eighteen-signal spectrum observed at -84 °C into the nine-signal spectrum observed at 0 °C (see *Fig. 4*). The activation free energy ΔG^{+} $(k_1+k_2)=10.2$ kcal/mol is in good agreement with those found for the same process in octalene itself (ΔG^{+} $(k_1+k_2)=8$ kcal/mol) and for the cyclooctatriene inversion in benzocyclooctatriene (ΔG^{+} $(k_i)=9.2$ kcal/mol) [7].

h) With configuration **3b** two achiral conformations, **3b-anti** and **3b-syn** (both with C_s-symmetry; see *Fig. 6*) are possible. The ^{13}C-NMR. signals of both conformations are clearly observed at -84°.

i) If the nuclei are labelled, one recognizes that each of these conformations is represented by two isometric structures. The transformation of one conformation into the other can occur *via* two distinct reaction paths, namely by inversion of the external COT-ring or by inversion of the central one; each of the two transition states is also represented by two isometric structures, and there are therefore four rate constants, as indicated on *Figure 7*.

j) If the interconversion **3c**$\rightleftarrows$**3b** proceeds *via* a π-bond shift in the external COT-ring, the transition state could be described as a tube-shaped COT with one double bond fused to a benzene ring and the opposite double bond fused to a planar π-bond delocalized COT-ring (**3d**, 2 isometric structures). If this is the correct mechanism then all the relevant dynamic processes taking place in **3** are summarized on the graph shown in *Figure 12*.

k) One could also postulate that the π-bond shift involves all the π-bonds of the octalene unit; in this case the transition state would be the planar structure **3a**

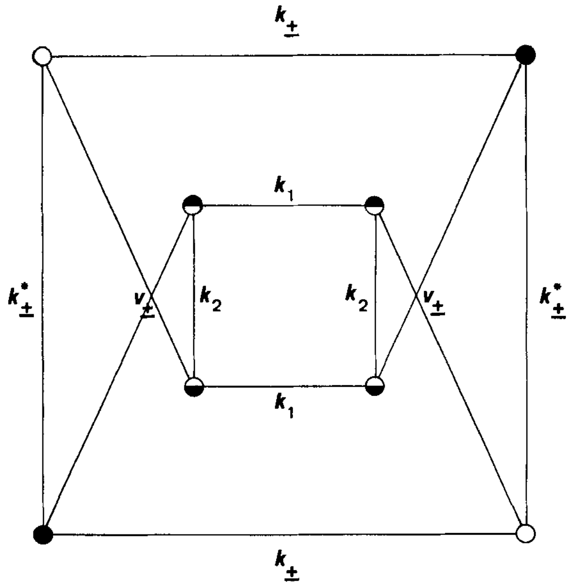

Fig. 12. *Graph representation of all dynamic processes taking place in benzooctalene* 3 *assuming that the interconversion* 3c$\rightleftarrows$3b *occurs* via *π-bond shift in the outer COT-ring* (compare *Fig. 5, 6* and *7*). ○ **3b-syn**, ● **3b-anti**, ◓ **3c** (*R*), ◒ **3c** (*S*). Rates: $k_1, k_2, k_+, k_-, k_+^*, k_-^*, v_+, v_-$

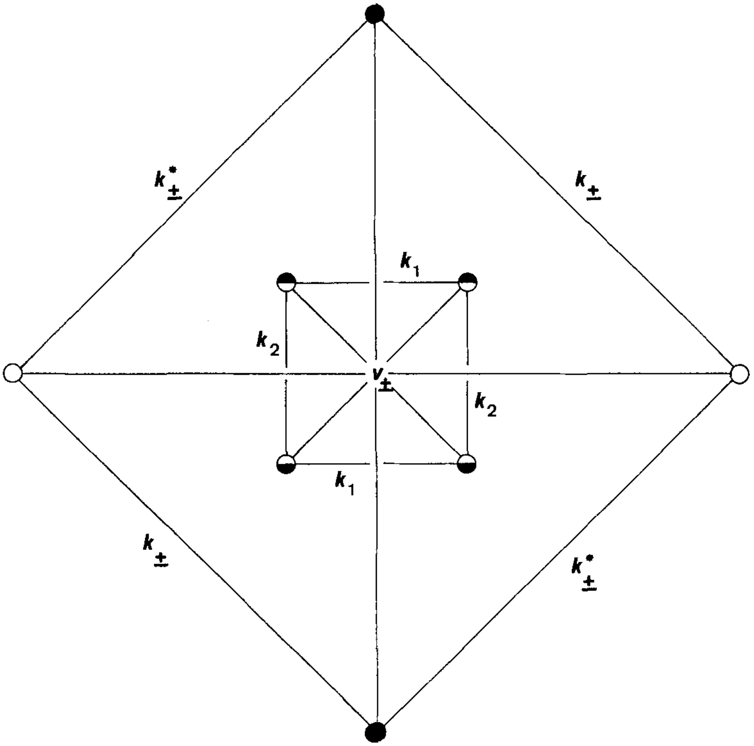

Fig. 13. *Graph representation of all dynamic processes taking place in benzooctalene* **3** *assuming that the interconversion* **3c**$\rightleftarrows$**3b** *occurs* via *a π-bond shift in the octalene perimeter* (i.e. via **3a**) (compare *Fig. 12*). ○ **3b-syn**, ● **3b-anti**, ◓ **3c** (*R*), ◒ **3c** (*S*). Rates: $k_1, k_2, k_+, k_-, k_+^*, k_-^*, v_+, v_-$

and the corresponding graph representing the dynamic behaviour of **3** would be the one shown in *Figure 13*. The essential difference between the two bond shift processes (*via* **3a** or *via* **3d**) is that from transition state **3a** the molecule can fall into any of the eight ground state structures [**3c** (2*R*+2*S*); **3b-anti** (2); **3b-syn** (2)] while from either of the two transition states of type **3d** there are only four ground state structures [**3c** (1*R*+1*S*); **3b-anti** (1); **3b-syn** (1)] into which the molecule can fall.

l) It is not possible, from the preliminary investigation reported here, to decide which mechanism for the π-bond shift (**3c**$\overset{v}{\rightleftarrows}$**3b**) is the correct one. This should, however, be possible from the results of a careful line-shape analysis of octalene and benzooctalene recorded at different temperatures in achiral and chiral solvents, or better, of adequately substituted benzooctalene (substituted *e.g.* with an isopropyl group); such studies are in progress. The π-bond shift responsible for the **3c**$\rightleftarrows$**3b** interconversion is, indeed, fast enough abouve 50 °C to affect the ^{13}C-NMR. line-shape of all signals.

m) The two configurations **3c** and **3b** of benzooctalene are very close in energy, while in octalene only **1c** is present, **1b** being undetectable. Thermochemical arguments based on the enthalpies of formation of groups such as –CH=CH–, –CH=C<, >C=C<, *etc.* suggest that the configurations **1c** and **3c** should be more stable than **1b** and **3b**, respectively, by approximately the same amount, 5-6 kcal/mol. It is, therefore, clear that the explanation of the observed energy differences requires elaborate MO-computations with methods capable of evaluating the subtile balance of all energy terms (π-, σ-, and strain energies).

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