

# CONFORMATIONAL MOBILITY AND FAST BOND SHIFT IN THE ANNULENES

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## ABSTRACT

After a general description of the configuration, of the conformation and of the fast and reversible dynamic processes characteristic of the annulenes, results of an experimental study of [8], [12], [14], [16] and [18]annulenes by N.M.R. spectroscopy are presented. Theoretical analysis of the N.M.R. line shape has allowed a determination of the structures of these compounds and of the thermodynamic and kinetic parameters of their dynamic processes. Study of bond shift in cyclooctatetraene (COT) and of bond shift and ring inversion in alkoxy-COT's point to a small negative resonance energy in the planar conformation of COT. Two configurations of [16]annulene in 3:1 ratio, coded 85 and 91, have been found in solution. Both of them undergo isodynamical conformational mobility and bond shift and a fast exchange between both is also occurring. The newly synthesized [12]annulene of configuration 21 undergoes extremely fast conformational mobility but no bond shift. Conformational mobility is rather slow in [18]annulene and in the major isomer of [14]annulene, of configuration 43. It is very fast in [14]-21 annulene. Exchange between [14]-43- and [14]-21-annulenes is very slow.

The present results agree generally with the calculations of Dewar and Gleicher.<sup>4</sup>

## 1. INTRODUCTION

We use the term annulenes here for the monocyclic conjugated polyenes having the general formula  $C_{2m}H_{2m}$  ( $m=2,3,4\dots$ ) in which all the carbon atoms are trigonally bonded (i.e.  $sp^2$  hybridized)<sup>1</sup>. The size of the ring is indicated by the number  $2m$  (in brackets) of carbon atoms: thus in this nomenclature benzene is the [6] annulene.

The annulenes have great theoretical interest. Each annulene can be represented formally by two Kekulé formulae in which single and double bonds alternate. The possibility of resonance between these two forms and the dependence of the resonance energy on a number of factors, such as the *parity* of  $m$ , the *magnitude* of  $m$  and, for a given ring size (i.e. a given value of  $m$ ), the *real geometry of the molecule* is one of the most important problems in theoretical organic chemistry<sup>2</sup>.

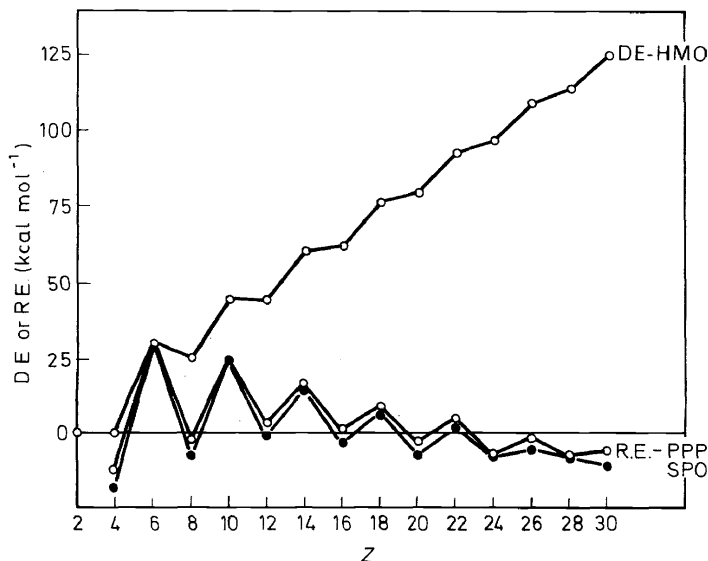
According to the simple Hückel picture, the annulenes, if planar, should all have their total  $\pi$ -energy smaller than  $m$  times that of the ethylene molecule, independent of the actual perimeter geometry. Furthermore, the resulting stability gain, the so-called delocalization energy  $DE^3$ , defined by

$$DE = -(E_{\pi \text{ total}} - m E_{\pi \text{ ethylene}})$$

where  $E_{\pi \text{ total}}$  is the total  $\pi$ -energy and  $E_{\pi \text{ ethylene}}$  is the  $\pi$ -energy in the ethylene molecule, should, according to this simple picture, increase with increasing ring size; however, when expressed per C-atom ( $DE/2m$ ) or per C—C bond ( $DE/m$ ), this stabilization energy should be greater for the annulenes with  $2m=4n+2$   $\pi$ -electrons ( $m$  odd) than for the annulenes with  $m=4n$   $\pi$ -electrons ( $m$  even). This is known as the Hückel rule and is illustrated in *Figure 1*.

Also in accordance with the simple Hückel picture, the annulenes with  $4n+2$   $\pi$ -electrons ( $m$  odd) have a non-degenerate electronic ground state in contrast to the annulenes with  $4n$   $\pi$ -electrons ( $m$  even) which have a degenerate ground state. This degeneracy is actually removed for several reasons: either the ring is not planar, or, if planar, its symmetry is reduced with respect to that of the idealized Hückel perimeter ( $D_{2m, h}$  symmetry) because of angle-strain relaxation or simply of bond alternation; i.e. this degeneracy should not occur in a better approximation than the simple Hückel one.

Although the Hückel rule is found to be surprisingly well verified, it must be pointed out that the predicted stabilization energies of the  $4n$  ( $m$  even) annulenes ( $DE > 0$ ) are in contradiction to the observed instability of these compounds. More elaborate  $\pi$ -energy calculations have been made by Dewar and Gleicher<sup>4</sup> for annulenes with specified, but arbitrarily chosen geometries: these calculations indicate that the resonance energy ( $RE$ )<sup>3</sup> is positive for the  $4n+2$  ( $m$  odd) annulenes and negative for the  $4n$  ( $m$  even) annulenes. The calculations of these authors also predict that this qualitative difference between the two classes of annulenes must disappear for large rings: annulenes with  $2m \geq 24$  should have no resonance energy ( $RE=0$ ) and thus should behave like normal open polyenes; they should present bond alternation independently of the parity of  $m$ . This was also suggested by Longuet-Higgins and Salem<sup>5</sup>. The results obtained by Dewar and Gleicher ( $RE$  values) are also given in *Figure 1* for comparison with the  $DE$  values as found by simple HMO calculations.

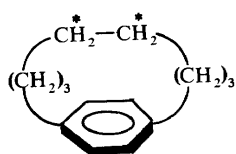


*Figure 1.* Delocalization (HMO) and resonance (PPP, SPO) energy of the annulenes.

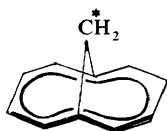
## FAST BOND SHIFT IN THE ANNULENES

We should mention here that few quantitative experimental data concerning the resonance energy in the annulenes are available—in fact only the resonance energy of benzene is known ( $RE_{[6] \text{ annulene}} = 36 \text{ kcal mol}^{-1}$ )—so that a confrontation of the theory with experiment is as yet impossible<sup>6</sup>. We shall see that important information concerning these resonance energies in the annulenes can be gained from the quantitative study (by N.M.R. spectroscopy) of the dynamical processes taking place in these molecules, namely from the study of isodynamical conformational mobilities and isodynamical bond shifts.

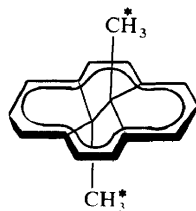
But first of all it should be remembered that N.M.R. spectroscopy also reveals a further important difference between conjugated cyclic systems with  $4n$  (localized) and  $4n + 2$  (delocalized)  $\pi$ -electrons. The application of the magnetic field to such molecules induces a ring current in their  $\pi$ -electron systems; this ring current is diamagnetic in the case of the  $4n + 2$   $\pi$ -system and paramagnetic in the case of the  $4n$   $\pi$ -system<sup>7</sup>. Protons pointing toward the inside of a ring with  $4n + 2$   $\pi$ -electrons experience an extra shielding associated with this induced diamagnetic ring current and their N.M.R. signals are thus shifted toward a higher field; on the contrary, signals from protons pointing outside the ring are shifted toward a lower field. This effect is particularly marked in the following bridged—and thus rigid— $4n + 2$  annulenes:



$$\tau_{\text{CH}_2^*} = 9.4[8]$$



$$\tau_{\text{CH}_2^*} = 10.51[9]$$



$$\tau_{\text{CH}_3^*} = 14.25[10]$$

In the case of the annulenes with  $4n$   $\pi$ -electrons the situation is predicted to be just the opposite: protons pointing towards the inside of a ring with  $4n$   $\pi$ -electrons will experience a deshielding associated with the induced paramagnetic ring current and will have their resonance signal appearing at a much lower field than normal. The first clear evidence for a paramagnetic ring current induced in a  $4n$   $\pi$ -electron system was observed with [16] annulene (see later)<sup>11</sup>.

Ring current effects will show up in a spectacular way in the annulenes of size  $2m \geq 12$ . For such ring sizes, the most stable structures (conformation and configuration) are such that some protons point into the ring while others point outside the ring; the ring current is revealed in these annulenes by the opposite shifts experienced by these two types of protons.

The magnitude of the ring current (deduced from  $\tau$  values of protons pointing toward the inside of the ring f.i.) will give us information on the degree of planarity or non-planarity of the ring and on the degree of bond alternation (which we can express as the ratio of two  $\beta$  values, e.g.  $\beta_1/\beta_2 = \lambda$ ,  $\lambda \leq 1$ ,  $\beta_1$  characterizing the  $\pi$  bonding in the long bonds (C—C) and  $\beta_2$  characterizing the  $\pi$  bonding in the short ones (C=C)). Buckling of the ring in both types of annulenes will reduce the magnitude of the ring current because of the less effective overlap of the  $2p$   $\pi$  atomic orbitals. Bond alternation will diminish the

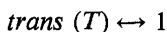
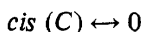
induced paramagnetic ring current in the  $4n$  annulenes. This paramagnetic ring current is in fact predicted to be infinite if the rings are planar and show no bond alternation<sup>7</sup>; this situation, which implies the degeneracy of the highest occupied and lowest unoccupied MOs (the two non-bonding MOs in the HMO approximation), is not likely to occur: the degeneracy will be removed by bond alternation and (subsequent) ring buckling so that the paramagnetic ring current will be reduced to a finite value.

## 2. CONFIGURATIONS AND CONFORMATIONS OF THE ANNULENES

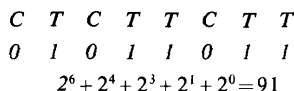
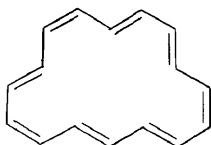
### 2.1. Configurations

The first problem arising in the study of an annulene is to establish its configuration, i.e. the nature (*cis* or *trans*) and the sequence of the double bonds in the Kekulé representation.

In order to designate in a condensed but unambiguous way the configuration of a given annulene, we shall use the following coded notation: we describe the sequence of the *cis* and *trans* double bonds in the Kekulé representation by a binary number, 0 being associated with *cis* (C) and 1 being associated with *trans* (T) double bonds:

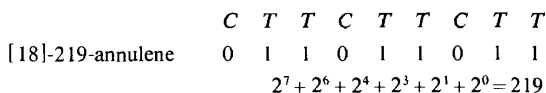
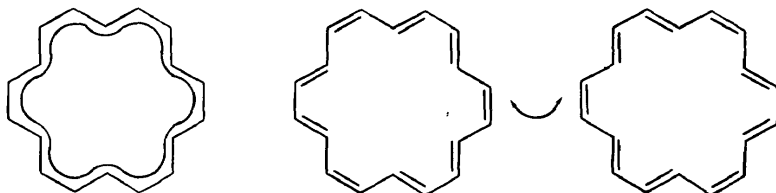


we then write the configuration as the smallest binary number compatible with the configuration; this binary number is then converted to its equivalent denary number. For instance, the following [16] annulene



will be designated as the [16]-91-annulene

We do not imply by this notation that the  $\pi$ -electrons are localized; when applied to the aromatic  $4n + 2$  annulenes—here we codify one of the two hypothetical Kekulé structures—this notation allows us to describe the delocalized configuration corresponding to the coded Kekulé structure (both Kekulé structures have necessarily the same configuration code number). For instance:



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It is clear that the total number of possible configurations, accessible for an annulene of a given ring size  $2m$  is greater the greater the value of  $2m$ . In *Table 1* we have considered the possible configurations of the annulenes up to the size  $2m = 20$ . The second column gives the total number of different configurations that could formally exist for each ring size, including the impossible one in which

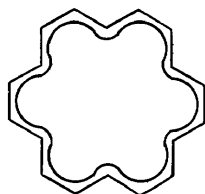
*Table 1.* Configurations of the annulenes

Ring size $2m$	Total number of formal configurations	Forbidden sequences	Number of feasible configurations	Feasible configurations
4	3	<i>T</i>	1	0
6	4	<i>T</i>	1	0
8	6	<i>T</i>	1	0
10	8	<i>TT</i>	3	0, 1, 5
12	13	<i>TT</i>	5	0, 1, 5, 9,  21
14	18	<i>TTT</i>	10	{ 0, 1, 3, 5, 9, 11 19,  21 , 27,  43
16	30	<i>TTT</i>	16	{ 0, 1, 3, 5, 9, 11, 17, 19 21, 27, 37, 43, 45, 51,  85 ,  91
18	44	<i>TTTT</i>	30	.....  219
20	78	<i>TTTT</i>	54	.....
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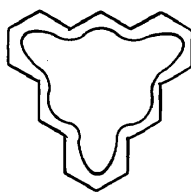
all the double bonds are *trans*. From these formally possible configurations some are excluded for strain reasons. The third column shows those sequences which introduce too much strain in the ring so that they cannot be found in any reasonable configuration (e.g. it is impossible to construct with models an [8] annulene containing 1 *trans* double bond (*T*) or a [12] annulene in which two successive *trans* double bonds (*TT*) would be present). The fourth column gives the number of the feasible configurations, i.e. all those in which the forbidden sequences are not present. These feasible configurations are listed in the fifth column by their code number; we have framed those configurations of the annulenes which are known.

### 2.2 Conformations

The next problem which arises consists in finding what is or are the preferred conformations of an annulene of known configuration. Again, for a large annulene, especially for a  $4n$  annulene which does not tend to be planar, the number of possible conformations for one given configuration can be high. But even a  $4n + 2$  annulene of large size ( $2m \geq 14$ ) with a given configuration can take different planar or quasi-planar geometries. For instance the [18]-219-annulene could take one of the two following planar geometries:

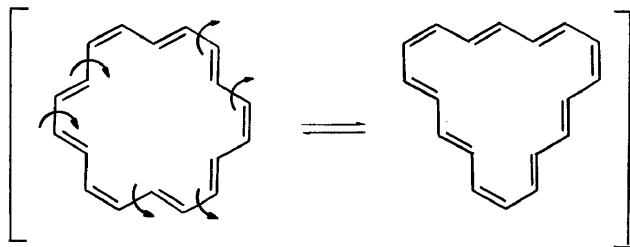


[18]-219  
Conformation 1



[18]-219  
Conformation 2

in which 6 equivalent protons are pointing towards the inside of the ring and 12 towards the outside. These two geometries can be regarded—very arbitrarily, as we realize—as two conformations of the same configuration. We have several reasons for adopting this point of view in discussing the dynamical properties of the  $4n + 2$  annulenes. We will only remark that since these two structures present the same sequence of *cis* and *trans* double bonds in their Kekulé formula, they are consequently related one to the other by synchronous rotation around such bonds which would be single bonds in the hypothetical Kekulé structures (in fact pairs of single bonds adjacent to *trans* double bonds):



We shall see later that in the dynamical processes observed in the [18]-219-annulene, both planar or quasi-planar conformations are implied; their corresponding Kekulé structures are also invoked as possible transition states.

In order to describe succinctly the complex conformation and configuration changes that one large annulene could undergo, we had to develop a code to identify the conformations more or less precisely. For this purpose the sequence of the single bonds in the  $4n$  annulenes or in the hypothetical Kekulé structures of the  $4n + 2$  annulenes are written using the following symbols for denoting the local conformation around each single bond<sup>12</sup>:

*s* for synperiplanar (torsion angle  $\psi = 0^\circ \pm 30^\circ$ )

*g* (*gauche*) for + synclinal ( $\psi = 60^\circ \pm 30^\circ$ )

*g\** for - synclinal ( $\psi = -60^\circ \pm 30^\circ$ )

*a* for antiperiplanar ( $\psi = 180^\circ \pm 30^\circ$ ) as well as for the less probable  $\pm$  anti-clinal conformations ( $\psi = 120^\circ + 30^\circ$  and  $\psi = -120^\circ \pm 30^\circ$ )

(cf. Figure 2)

The conformation sequence is written using these symbols and is properly intercalated in the configuration sequence as shown in the example which

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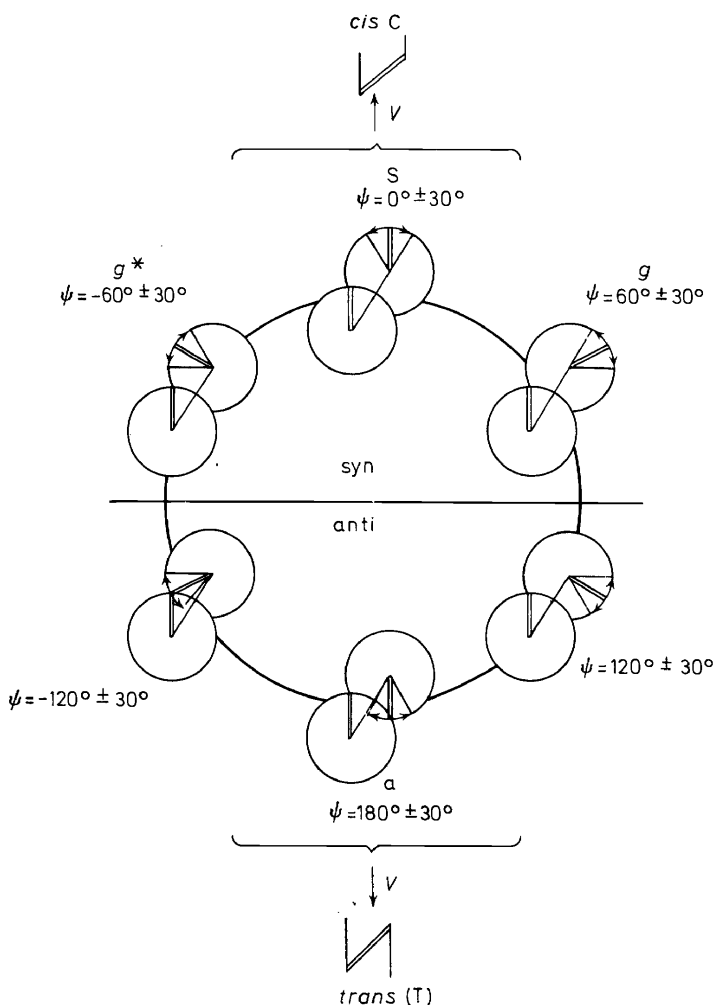
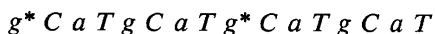


Figure 2. Definition of the conformations around single bonds.

follows. The most stable conformation of the [16]-85-annulene (Figure 3) which can be described as being formed out of four planar butadiene residues (*CaT* or simply  $\overline{CT}^{13}$ ) linked by single bonds in gauche conformation is noted in the following manner<sup>13</sup>:



We can now codify the conformation as we have done with the configuration, i.e. via a binary number, using the following conventions:

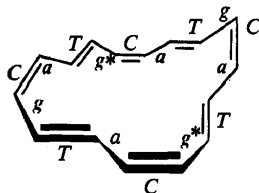
Single bonds around which the local conformation is *syn* (synperiplanar, *s*) or  $\pm$ synclinal ( $g$  and  $g^*$ ) are coded as 0.

Single bonds around which the local conformation is *anti* (*a*) are coded as 1.

(The reason for this simplification is that, upon bond shift, single bonds around which the local conformation is syn (*s*, *g* and *g\**) will become *cis* double bonds while single bonds around which the conformation is anti will become *trans*.)

The binary number describing the conformation is transformed in denary base and is surmounted by a line if the conformation is planar (*s* ( $\psi=0^\circ$ ) and *a* ( $\psi=180^\circ$ ) only).

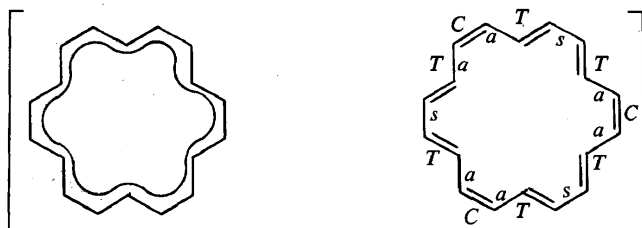
With this convention, the minimum energy conformation of the [16]-85-annulene is coded as 85; the structure is thus called [16]-85-85-annulene.



Configuration	0	1	0	1	0	1	0	1	→ 85
	<i>g</i>	<i>C</i>	<i>a</i>	<i>T</i>	<i>g</i>	<i>C</i>	<i>a</i>	<i>T</i>	<i>g</i>
Conformation	0	1	0	1	0	1	0	1	→ 85
	16 -85-85-annulene								

Figure 3. Codification of the configuration and the conformation of a  $4n$ -annulene.

The two planar conformations of the [18]-219-annulene already discussed are designated as [18]-219-438-annulene (conformation 1) and [14]-219-219-annulene (conformation 2) respectively, e.g.:



Configuration	0	1	1	0	1	1	0	1	1	→ 219
	<i>a</i>	<i>C</i>	<i>a</i>	<i>T</i>	<i>s</i>	<i>T</i>	<i>a</i>	<i>C</i>	<i>a</i>	<i>T</i>
Conformation	1	1	0	1	1	0	1	1	0	→ 438
	18 -219-438-annulene									

Figure 4. Codification of the configuration and the conformation of a  $4n + 2$  annulene.

We shall see later the interest presented by this condensed notation.



### 3. FAST AND REVERSIBLE DYNAMICAL PROCESSES OCCURRING IN THE ANNULENES

#### 3.1. Isodynamical and non-isodynamical processes

The annulenes undergo very fast and reversible dynamical processes which can be detected and quantitatively studied by N.M.R. spectroscopy. We classify these processes as:

##### *Isodynamical*<sup>14</sup>

These are the reversible processes which relate one structure (defined by its configuration *and* its conformation) to another one which is superposable (or enantiomorphous) to the initial one. The initial and the final structures, which are *isodynamic*, could only be differentiated one from the other if the nuclei were labelled.

##### *Non-isodynamical*

These are reversible processes relating two structures which are not superposable or enantiomorphous. The related structures are *not isodynamic*; they can differ by their conformation or by their configuration (or even by their C-atoms connectivity<sup>15</sup>).

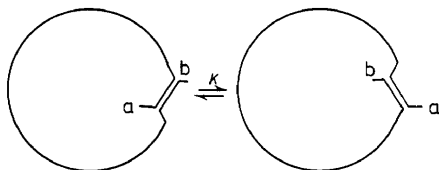
#### 3.2. Fast and reversible dynamical processes taking place in the $4n$ -annulenes ( $m$ even).

Two types of dynamical processes were recognized to take place in the  $4n$ -annulenes:

##### *Conformational mobility*

This includes all those processes by which rotation around single bonds (together with bond angle deformations if required) is taking place. The ring inversion of cyclooctatetraene ([8]-0-0-annulene) (cf. *Figure 5*) is a typical example of an *isodynamical conformational process*: it implies a synchronous rotation around all four single bonds of the molecule accompanied by appreciable bond angle deformations (activation energy  $E_a \cong 12$  kcal mol<sup>-1</sup>).

We should remark here that when a conformational process requires rotation around single bonds with only minute bond angle deformations—this is the



case for the rotation around the nearly parallel single bonds adjacent to a *trans* double bond in the large  $4n$  annulenes—then the process is extremely fast and

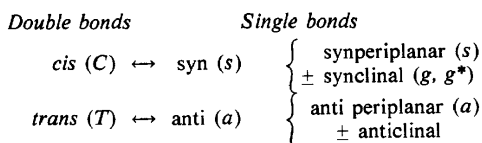
can only be detected by N.M.R. experiments carried out at extremely low temperatures (cf. the conformational mobility of [12]-21-21-annulene).

#### *Bond shifts or reversible valence bond isomerizations*

In these processes the  $\pi$ -electrons migrate from double bonds to single bonds. Such a process was first detected and recognized by Anet and his colleagues<sup>16</sup> in cyclooctatetraene ([8]-0-0-annulene); later it was found in other  $4n$  annulenes.

A bond shift process can leave the configuration and the conformation of the molecule unmodified (isodynamical bond shift) or, on the contrary, it can transform one configuration into another one (non-isodynamical bond shift). The bond shift in the  $4n$  annulenes can be categorized as a symmetry-allowed pericyclic reaction according to the generalization of the Woodward-Hoffmann rules<sup>17</sup>. One will admit—and we now have convincing arguments for this—that in the course of such a process the molecule passes via a planar or quasi-planar transition state.

Obviously, the following correlations will exist between the character of the bonds in the initial and the final structures (cf. *Figure 2*):



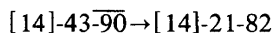
### **3.3. Fast and reversible processes observed in the $4n + 2$ annulenes of large size ( $2m \geq 14$ , $m$ odd).**

#### *Isodynamical conformational mobility*

The  $4n + 2$  annulenes of large size ( $2m \geq 14$ ) present temperature dependent N.M.R. spectra. The dynamical process responsible for this was recognized to be an isodynamical conformational mobility by which the molecule passes via a certain number of isoenergetic structures. These structures can be formally related one to another assuming rotation around bonds which are just single bonds in the hypothetical Kekulé structures. This has been already pointed out in our justification for extending our configuration and conformation codes to the aromatic annulenes (see above).

#### *Configuration changes*

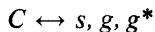
Another type of dynamical process was observed in [14]-annulene; this is the passage from one configuration to another one, namely:



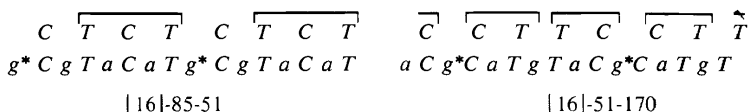
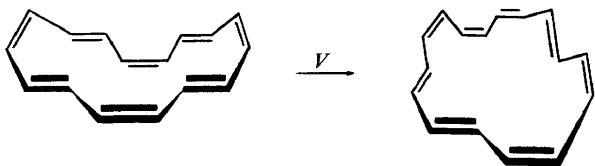
This process formally implies the transformation of a given *trans* double bond of one Kekulé structure corresponding to the 43 configuration into a *cis* double bond; this process is in fact much slower ( $10^{10}$  times slower!) than the isodynamical conformational mobility observed in each structure.

#### 4. ADVANTAGE OF THE CODIFICATION USED FOR DENOTING THE CONFIGURATIONS AND THE CONFORMATIONS OF THE ANNULENES

In the case of the  $4n$  annulenes, the correlations between the stereo character of the single ( $s, g, a$ ) and double ( $C, T$ ) bonds



in structures related one to the other by a bond shift process automatically implies that, upon such a process, the conformation code number of the initial structure becomes the configuration code of the final one. For instance, bond shift in the possible 51 conformation of the [16]-85-annulene will give the [16]-51-annulene:



Furthermore, it is clear that a structure for which the conformation code number is the same<sup>18</sup> as the configuration code number will, upon bond shift, maintain its configuration. For instance, bond shift in the [16]-85-85-annulene leaves the configuration (and the conformation) of the molecule unchanged (see later).

We see that our codes enable us to express easily how annulenes transform upon bond shift and also to discover those privileged structures which can be expected to be stable (i.e. to maintain their configuration and conformation) with respect to bond shift and conformational mobility. We call these privileged structures isodynamical structures.

In the case of the  $4n+2$  annulenes, the privileged structures which can undergo an isodynamical conformational mobility can also be easily discovered (example: [18]-219-219 and [18]-219-438 (note  $438 = 2 \times 219$ )).

For a configuration change, however, the correspondence between the conformation code number of the initial structure and the configuration code number of the final one does not necessarily hold.

#### 5. [8] ANNULENE

Cyclooctatetraene (COT), which is formed out of four *cis* double bonds, is the [8]-0-annulene. It is the only [8] annulene expected to be stable; even the introduction of only one *trans* double bond in the ring ([8]-1-annulene) would at once introduce an extremely high angle strain (cf. Table 1).

The configuration and the conformation of the cyclooctatetraene molecule was unambiguously established by electron diffraction in the gas phase<sup>19</sup>. The conformation adopted by the molecule is that of a rigid tub ( $D_{2d}$  symmetry); the four *cis* double bonds are linked by single bonds around which the local conformation is alternately + synclinal (*g*) and - synclinal (*g\**):



Configuration    0   0   0   0 → 0  
                   *g\** C *g* C *g\** C *g* C  
 Conformation    0   0   0   0 → 0  
                   |8|0-0-annulene

We must point out here that the C—C and C=C bond lengths and the C=C—C bond angle have normal values; the torsion angles are all equal (in absolute value) and are very close to 60° (cf. *Table 2*). Thus the COT molecule is essentially strain-free.

*Table 2.* Geometric parameters of cyclooctatetraene<sup>19</sup>

C=C	C—C	$\theta(\text{C}=\text{C}-\text{C})$	$\psi$
1.340 Å	1.476 Å	126.1°	57.9°

### 5.1 Isodynamical processes in COT and in some of its monosubstituted derivatives

Two isodynamical processes were detected in cyclooctatetraene and some of its derivatives. They were identified by Anet<sup>20</sup> as being:

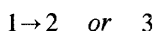
a fast inversion of the ring (*K*) (this process is an isodynamical conformational mobility).

a fast isodynamical  $\pi$ -bond shift (*V*).

By these processes, four isodynamic structures are passed by the molecule (COT or monosubstituted COT) as shown in *Figure 5*.

In the case of COT itself, these four structures are all superposable; in the case of a monosubstituted COT, structures 1 and 2 and also 3 and 4 are pairwise superposable, 1 (2) and 3 (4) are enantiomers. It is important to mention these stereochemical relations between the four structures of a monosubstituted COT at this point. The temperature dependent N.M.R. spectra that one can expect to observe with monosubstituted COT will in fact reflect specifically the following rates:

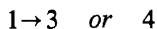
The rate of bond shift corresponding to the process:



(this rate is equal to  $V = v_1 + v_2$ )

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The rate of racemization corresponding to the process



(this rate is equal to  $K + v_2 = K + V/2$ , assuming  $v_1 = v_2 = V/2$ ).

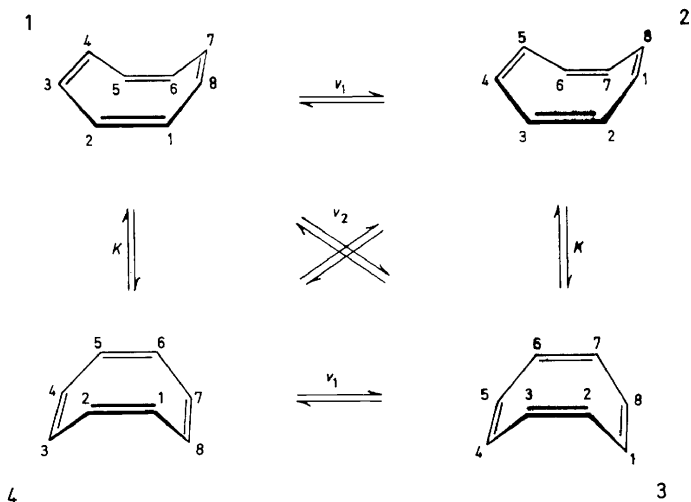


Figure 5. Isodynamical conformational mobility ( $K$ ) and bond shift ( $v_1, v_2$ ) in COT

### 5.2 Transition states for the ring inversion ( $K$ ) and for the bond shift ( $V$ ) processes in COT— $\pi$ resonance energy in the planar $C_8$ perimeter of $D_{8h}$ symmetry

The ring inversion of the [8]-annulene (COT) can take place as a progressive flattening of the molecule and passage via a planar transition state of  $D_{4h}$  symmetry. Energetic considerations (namely calculation of energy changes associated with the bond angle deformations necessarily required for the process) indicate that this symmetrical deformation is the preferred pathway for ring inversion (the  $C=C-C$  bond angle changes from  $\theta = 126^\circ$  to  $135^\circ$  (plane) and to  $126^\circ$ ).

The bond shift process  $V$  can also take place as a progressive flattening of the molecule but now accompanied by symmetrical bond length modifications, i.e. shortening of the  $C-C$  bonds and lengthening of the  $C=C$  bonds; in the transition state, the molecule would be planar and have  $D_{8h}$  symmetry, all bonds lengths being equal.

If the hypothetical transition states considered for the ring inversion  $K$  and the bond shift  $V$  are the real ones, then the difference between the activation enthalpies

$$\Delta H_K^\ddagger - \Delta H_V^\ddagger$$

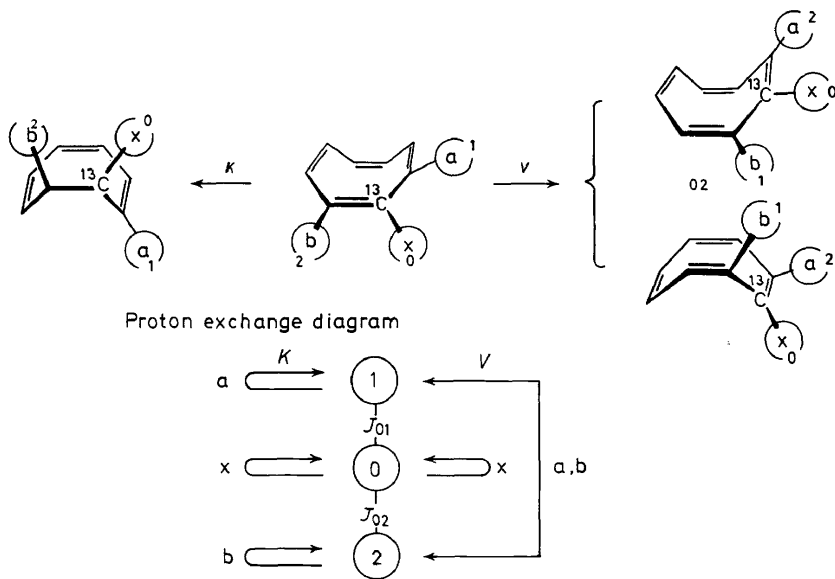
will be a measure of the resonance energy in the delocalized structure of  $D_{8h}$

symmetry. It thus seemed to us very important to carry out a careful quantitative study of the  $K$  and  $V$  processes in appropriately chosen monosubstituted cyclooctatetraenes.

We have therefore studied monosubstituted COT derivatives in which two diastereotopic protons or groups of protons are present. Such groups are indeed required for the determination, by N.M.R. spectroscopy, of the rate of ring inversion  $K$  (in fact  $K + V/2$ ). The rate of bond shift  $V$  will evidently be deduced from the temperature dependent N.M.R. signal of the olefinic ring protons.

### 5.3. Quantitative study of the isodynamical bond shift in COT

All the protons of the COT molecule are magnetically equivalent and thus give one single N.M.R. line. Consequently, no information concerning the isodynamical processes that could take place in the COT molecule can be expected to be gained from this signal which, indeed, is temperature independent. However, if one C atom of the molecule is replaced by the  $^{13}\text{C}$  isotope, then the proton  $x$  directly linked to the  $^{13}\text{C}$  atom (cf. *Figure 6*) has its



*Figure 6.* Ring inversion and bond shift in COT marked with one  $^{13}\text{C}$  nucleus. Related exchange diagram

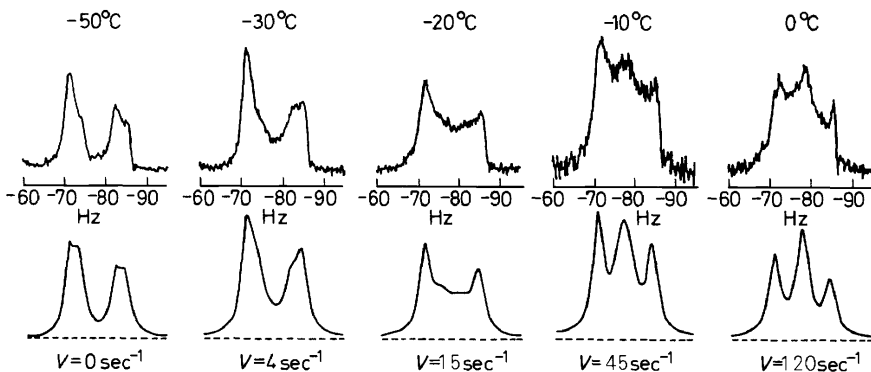
characteristic frequency divided and gives two satellites located at  $\pm \frac{1}{2} J_{\text{Cx}} = \pm 78.2$  Hz from the main line. Each satellite has a fine structure reflecting the spin-spin coupling situation between the proton  $x$  and the other protons of the molecule (note that all these other protons are no more magnetically equivalent but are simply nearly isochronous).

The fine structure of the  $^{13}\text{C}$  satellites was observed by Anet<sup>20</sup> to be temperature dependent. At  $-50^\circ\text{C}$  it is essentially a doublet (cf. *Figure 7*); with temperature increase this doublet is progressively transformed into a more complex signal which has the overall pattern of a triplet (above  $-10^\circ\text{C}$ ). This

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line shape modification with temperature of the  $^{13}\text{C}$  satellites reflects exclusively the bond shift process  $V$ , as can be seen from *Figure 6*, where the protons are labelled by letters and the magnetic sites by figures.

At very low temperature the proton x is strongly coupled with the proton on site 2 ( $J_{02} = 11.4$  Hz) and weakly coupled with the proton on site 1 ( $J_{01} \cong 2.5$  Hz) for a sufficiently long time interval for a doublet to be observed for each



*Figure 7.* Up-field  $^{13}\text{C}$ -satellite of the  $^1\text{H}$ -N.M.R. signal of cyclooctatetraene at different temperatures

satellite. At high temperatures, due to the rapid bond shift, protons a and b will exchange their magnetic sites 1 and 2 so rapidly that the proton x will be coupled with a and b with an average coupling constant  $\frac{1}{2}(J_{01} + J_{02}) \cong 7$  Hz; each satellite will then have a triplet structure. Of course the other nuclei are also coupled with proton x and also with each other, thus complicating the spectrum.

We have reproduced, by computation, the line shape of the up-field  $^{13}\text{C}$ -satellite as recorded at different temperatures. For these calculations we adopted Alexander's formalism<sup>21</sup> and considered only the exchange which is indicated on *Figure 6* (proton exchange diagram). An arbitrary natural line width of 2.5 Hz was used to simulate the effect, on the line shape, of the neglected spin-spin couplings between the protons considered (x, a, b) and the other protons of the molecule. The  $^{13}\text{C}$ -satellite was calculated as the x part of the spectrum, the following magnetic parameters being used:

$$\begin{aligned} v_1 &= v_2 = 0 \text{ Hz} & v_0 &= -78 \text{ Hz} \\ J_{01} &= 2.3 \text{ Hz} & J_{02} &= 11.4 \text{ Hz} \\ \Delta v^\circ &= 2.5 \text{ Hz} \end{aligned}$$

As can be seen in *Figure 7*, the line shape of the high field  $^{13}\text{C}$ -satellite at temperatures up to  $-20^\circ\text{C}$  could be reproduced quite well; the matching of the line shape recorded at higher temperatures was less satisfactory.

From this preliminary analysis, the kinetic parameters for the fast isodynamical bond shift in cyclooctatetraene could be estimated; they are given in *Table 3*.

#### 5.4. Quantitative study of the isodynamical bond shift ( $V$ ) and of the ring inversion ( $K$ ) in COT-*O*-ethyl and COT-*O*-isopropyl

The temperature dependent N.M.R. spectra of the ethoxy- and isopropoxy-cyclooctatetraene<sup>22</sup> are very informative. The evolution with the temperature of the line shape of the signals of the olefinic protons reflects the isodynamical bond shift process  $V$  while the modification with temperature of the signals of the two diastereotopic protons of the  $\text{CH}_2$  group in COT-*O*-ethyl and of the two diastereotopic methyl groups in COT-*O*-isopropyl reflects the racemization rate  $K + V/2$ . *Figure 8* illustrates how the different protons of ethoxy-COT exchange their magnetic sites in the course of the different processes.

##### *Isodynamical bond shift ( $V$ )*

The N.M.R. spectra of ethoxy COT recorded at different temperatures are reproduced in *Figure 9*. At  $-60^\circ\text{C}$ , the signals of the ring olefinic protons consist of a doublet located at  $\tau = 5.38$  (1H) and a multiplet centred at  $\tau = 4.37$  (6H). The signal at  $\tau = 5.38$  is attributed to the proton on the same double bond as the substituent (i.e. magnetic site 2).

Upon temperature increase, this signal coalesces with the signal of the proton on magnetic site 1 which is hidden in the multiplet at  $\tau = 4.37$ . Note also that the signal of the five other protons simplifies with temperature increase. These protons become pairwise equivalent as can be seen from the proton exchange diagram; only the proton on site 7 retains its magnetic site unaffected.

At higher temperatures ( $+130^\circ\text{C}$ ) the protons on magnetic sites 1 and 2 are equivalent and give a doublet at  $\tau = 4.84$  (2H); the olefinic protons give a sharp signal at  $\tau = 4.33$  (5H).

In order to deduce the rate of bond shift  $V$  by a line shape matching of the signals of the olefinic protons, we had to find the precise attribution of the signals in the spectrum at  $-50^\circ\text{C}$ , i.e. in the absence of exchange. This attribution is indicated in *Figure 10*, together with the computed spectrum (265 Hz to 365 Hz from TMS).

The line shape in the presence of exchange was computed as the superposition of the spectrum of a four-spin system (protons on sites 1, 2, 3 and 4) and of that of a three-spin system (protons on sites 5, 6 and 7). An analytical solution of Alexander's equation was established for both cases<sup>23</sup>.

The four-spin system (a, b, c, d) consists of two  $AB$  systems exchanging one against the other: one  $AB$  system (a, c) is characterized by the parameters  $\nu_1$ ,  $\nu_3$  and  $J_{13}$ , the other  $AB$  system (b, d) by the parameters  $\nu_2$ ,  $\nu_4$  and  $J_{24}$ . The exchange taking place is characterized by the rate  $V$  and is represented in the upper part of the exchange diagram.

The three-spin system consists of two nuclei (e, f) exchanging their magnetic sites (5 and 6) but being coupled with a third nucleus (g) on a stable magnetic site (7) with the coupling constants  $J_{56}$  and  $J_{67}$ .

Typical examples showing how the line shape of the signal of the olefinic protons could be reproduced under exchange conditions are given in *Figure 11* (spectrum at  $+30^\circ\text{C}$ ) and in *Figure 12* (coalescence spectrum:  $+55^\circ\text{C}$ ).

From this matching procedure of the line shape of the spectra recorded between  $-10^\circ\text{C}$  and  $+150^\circ\text{C}$ , we could deduce the kinetic parameters for the bond shift which are given in *Table 3*. In this table we also give the kinetic



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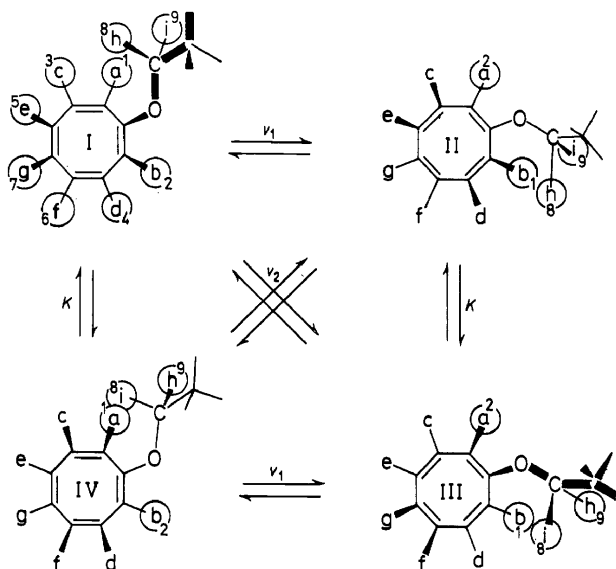


Figure 8 (a). Isodynamical conformational mobility and bond shift in COT-O-CH<sub>2</sub>CH<sub>3</sub>,

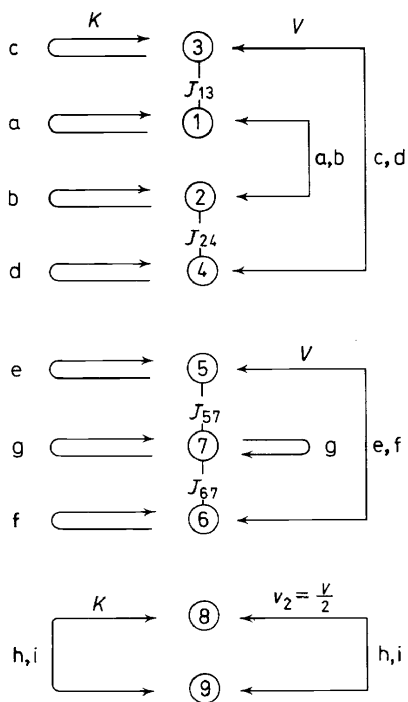


Figure 8 (b). Proton exchange diagram in COT-O-CH<sub>2</sub>CH<sub>3</sub>,

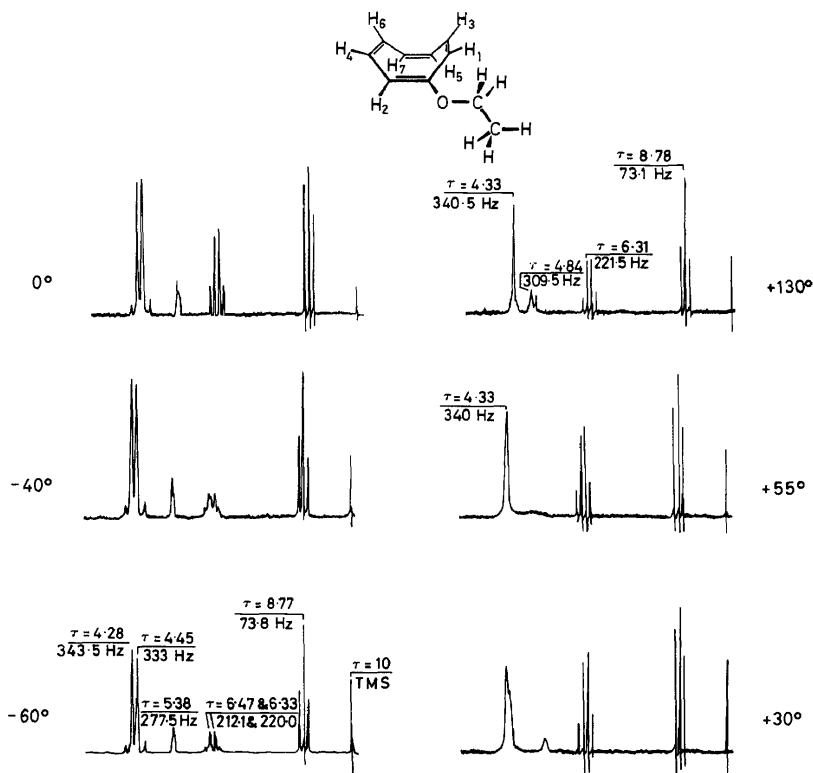


Figure 9. N.M.R. spectra of COT-*O*-CH<sub>2</sub>CH<sub>3</sub>, recorded at different temperatures (radio frequency: 60 MHz)

parameters for the bond shift process *V* in COT-*O*-CH<sub>3</sub>, COT-*O*-isopropyl, and COT-*O*-*tert*-butyl. These data will be discussed later.

#### Isodynamical ring inversion

At -60°C. the N.M.R. signal of the two diastereotopic protons of the CH<sub>2</sub> group in ethoxy-COT is the *AB* part of an *ABX*<sub>3</sub> system. In the first order approximation, it consists of four *AB* quartets with relative intensity 1/3/3/1 (the statistical weights of the four spin states of the pseudo particle X<sub>3</sub>). With increase in temperature, one observes the progressive coalescence of each *AB* subspectrum into one single line; the spectrum under conditions of fast exchange (+30°C) is thus finally a quartet.

## FAST BOND SHIFT IN THE ANNULENES

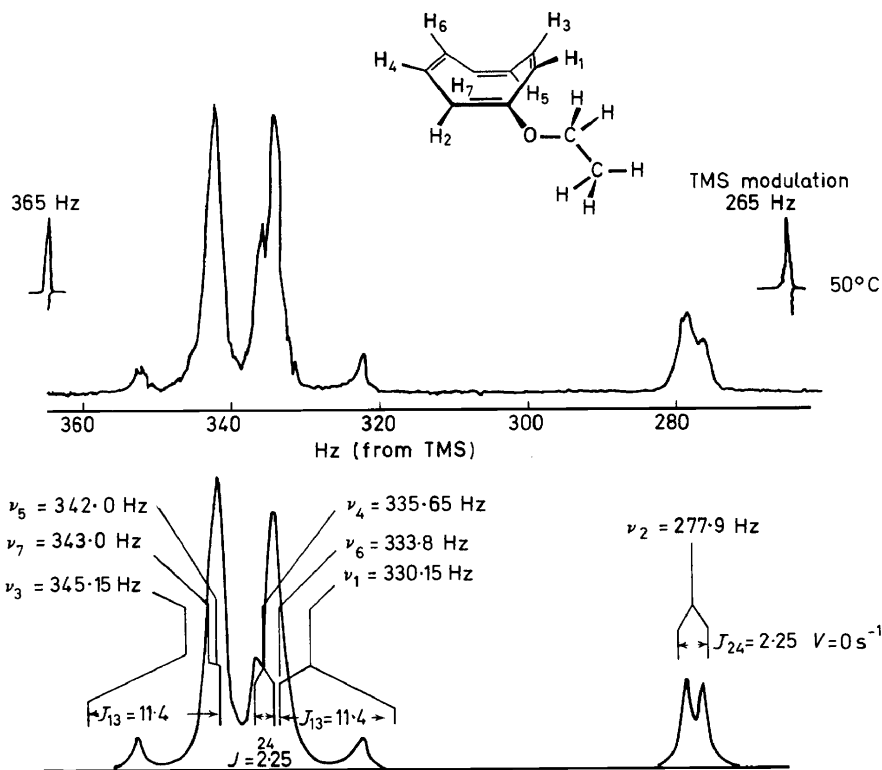


Figure 10. Assignment of the N.M.R. signals of the olefinic protons in COT- $O\text{-CH}_2\text{CH}_3$ ,

The exchange of the two magnetic sites of the two diastereotopic protons of the  $\text{CH}_2$  group is the result of the ring inversion process  $K$  and the specific bond shift  $\nu_2$  ( $=V/2$ ); the rate of exchange is thus  $K + V/2$ , as mentioned before.

This rate of exchange could be deduced at several temperatures between  $-70^\circ$  and  $+30^\circ$  by a matching of the calculated line shape to the observed one. The calculated line shape was simply the superposition—with appropriate weight factors—of four subspectra of  $AB$  systems undergoing exchange. The subspectra were calculated using the analytical formula established by Alexander for the case of two mutually coupled nuclei exchanging their magnetic sites<sup>21</sup>. Figure 13 reproduces three typical experimental spectra of the  $\text{CH}_2$  group and the corresponding calculated ones.

In Table 3 we give the kinetic parameters for the ring inversion  $K$  in ethoxy-COT as deduced from this analysis: we also give the corresponding parameters for the ring inversion  $K$  in isopropoxy-COT deduced from line shape analysis of the signal of the two diastereotopic  $\text{-CH}_3$  groups. The table shows that the rate of ring inversion  $K$  is two orders of magnitude greater than the rate of bond shift  $V$  (for this reason we did not correct the  $K + v/2$  values for the contribution of the bond shift ( $V/2$ )).

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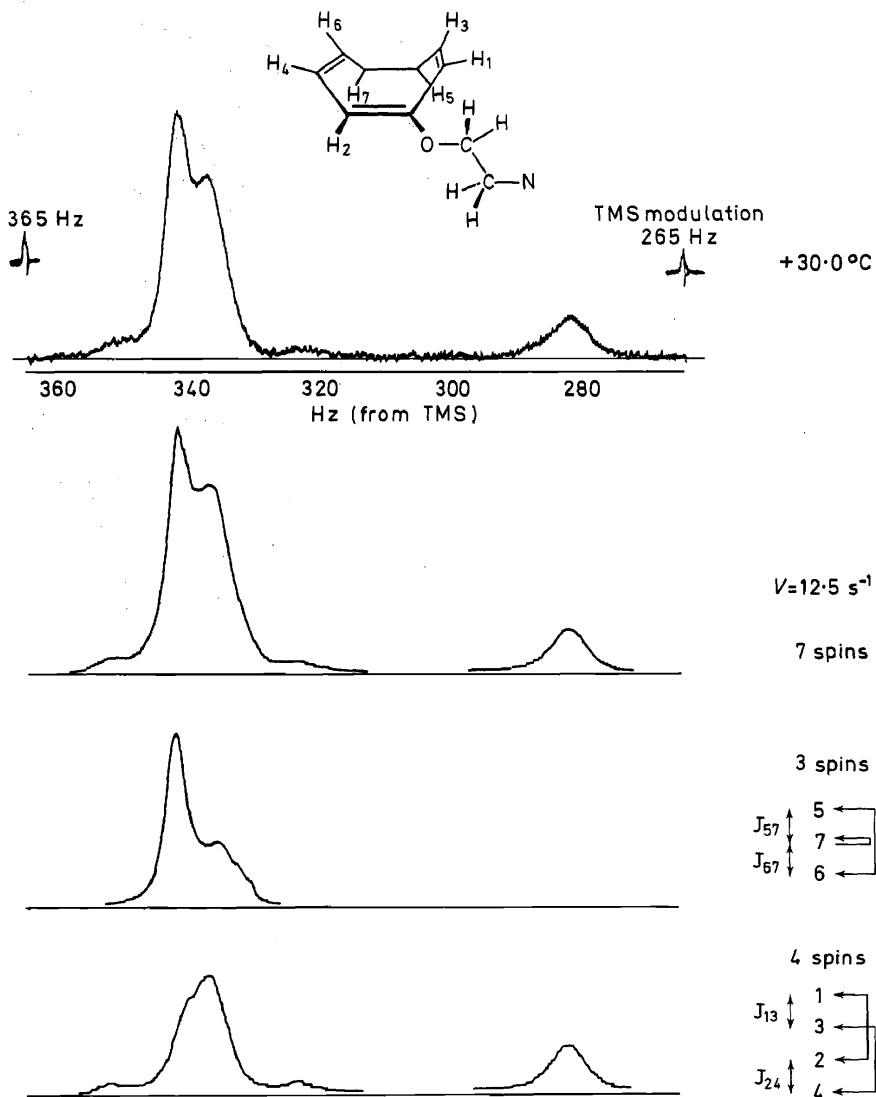


Figure 11. Comparison between the experimental and the detailed calculated N.M.R. spectrum of the olefinic protons in COT-*O*-CH<sub>2</sub>CH<sub>3</sub> at 30.0°C

### 5.5. Experimental value of the resonance energy in the planar C<sub>8</sub> perimeter of D<sub>8h</sub> symmetry

Table 3 indicates that the entropies of activation  $\Delta S_K^\ddagger$  and  $\Delta S_V^\ddagger$  of the two isodynamic processes *K* and *V* are about equal while the enthalpy of activation for the bond shift  $\Delta H_V^\ddagger$  is *ca.* 3.8 kcal mol<sup>-1</sup> higher than the enthalpy of activation for the ring inversion  $\Delta H_K^\ddagger$ . If our view of the transition states is

Table 3. Bond shift ( $V$ ) and ring inversion ( $K$ ) in COT and in monosubstituted COT

	$V(0^\circ)$ $s^{-1}$	$\log A_v$	$E_v^\ddagger$ kcal mol $^{-1}$	$\Delta G_v^\ddagger$ kcal mol $^{-1}$	$\Delta H_v^\ddagger$	$\Delta S_v^\ddagger$ e.u.	$K(0^\circ)$ $s^{-1}$	$\log A_k$	$E_k^\ddagger$ kcal mol $^{-1}$	$\Delta G_k^\ddagger$ kcal mol $^{-1}$	$\Delta H_k^\ddagger$	$\Delta S_k^\ddagger$ e.u.
COT	120 $\pm 20$	13.65 $\pm 0.8$	14.5 $\pm 0.7$	13.3 $\pm 0.1$	13.9 $\pm 0.7$	2.1 $\pm 3$	—	—	—	—	—	—
COT-O-CH <sub>3</sub>	0.61 $\pm 0.04$	12.82 $\pm 0.14$	16.30 $\pm 0.21$	16.21 $\pm 0.04$	15.76 $\pm 0.21$	1.69 $\pm 0.65$	—	—	—	—	—	—
COT-O-C <sub>2</sub> H <sub>5</sub>	0.88 $\pm 0.05$	12.33 $\pm 0.10$	15.48 $\pm 0.15$	16.01 $\pm 0.03$	14.94 $\pm 0.15$	3.93 $\pm 0.48$	604 $\pm 38$	11.97 $\pm 0.18$	11.49 $\pm 0.19$	12.47 $\pm 0.03$	10.96 $\pm 0.19$	-5.58 $\pm 0.82$
COT-O-CH(CH <sub>3</sub> ) <sub>2</sub>	1.86 $\pm 0.09$	13.34 $\pm 0.15$	16.34 $\pm 0.20$	15.61 $\pm 0.03$	15.80 $\pm 0.20$	0.70 $\pm 0.67$	361 $\pm 22$	12.65 $\pm 0.19$	12.61 $\pm 0.21$	12.74 $\pm 0.03$	12.08 $\pm 0.21$	-2.47 $\pm 0.87$
COT-O-C(CH <sub>3</sub> ) <sub>3</sub>	7.29 $\pm 0.64$	10.75 $\pm 0.37$	12.36 $\pm 0.48$	14.86 $\pm 0.05$	11.82 $\pm 0.48$	-11.16 $\pm 1.68$	—	—	—	—	—	—

correct, this means that *ca.*  $3.8 \text{ kcal mol}^{-1}$  are required to delocalize the  $8 \pi$  electrons in the planar  $\text{C}_8\text{H}_8$ ; in other words, the resonance energy in the planar  $\text{C}_8$  perimeter of  $D_{8h}$  symmetry is negative:

$$E_R = \Delta H_K^\ddagger - \Delta H_V^\ddagger = -3.85 \text{ kcal mol}^{-1}$$

It is interesting to note that a negative resonance energy of the same order of

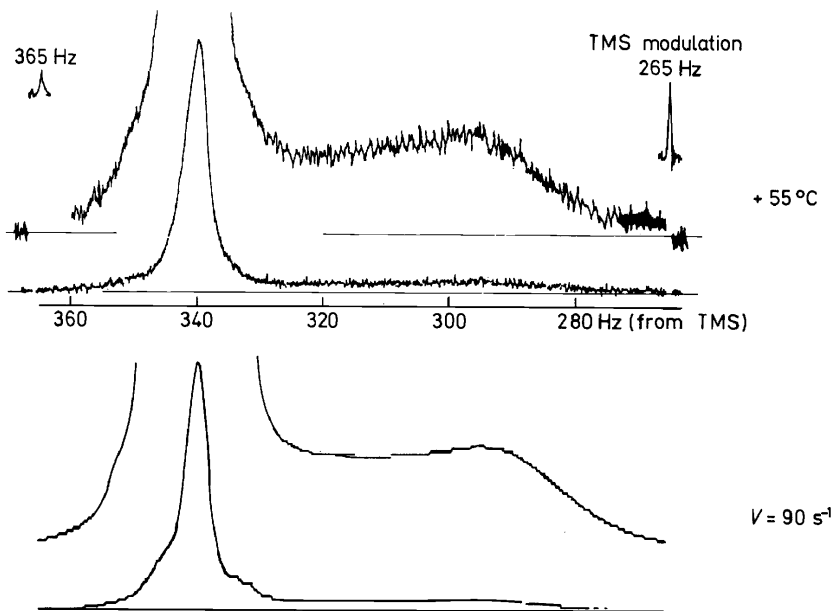


Figure 12. Comparison between the experimental and the calculated N.M.R. spectrum of the olefinic protons in COT- $O\text{-CH}_2\text{CH}_3$  at coalescence ( $55^\circ\text{C}$ )

magnitude was also found by Dewar and Gleicher<sup>4</sup> for an  $8 \pi$ -electron system on a  $D_{8h}$  perimeter on the basis of Pople-Pariser-Parr (PPP) and split- $\pi$ -orbital (SPO) MO calculations (see table in Figure 14).

In Figure 14 and the related table we summarize what is our understanding of the mechanism of the isodynamical ring inversion  $K$  and of the isodynamical bond shift  $V$  in COT and what is the significance of the activation enthalpy parameters.

## 6. [16]ANNULENE

### 6.1. Synthesis of [16]annulene

[16]Annulene was synthesized for the first time by Sondheimer and Gaoni<sup>24</sup>. Their synthesis route is the following. Oxidative coupling (under the Glaser conditions) of *trans*-4-octene-1-diyne gives the cyclic ( $\text{C}_{16}\text{H}_{12}$ ) as well as the linear ( $\text{C}_{16}\text{H}_{14}$ ) dimer. The cyclic dimer is rearranged in the presence of a base

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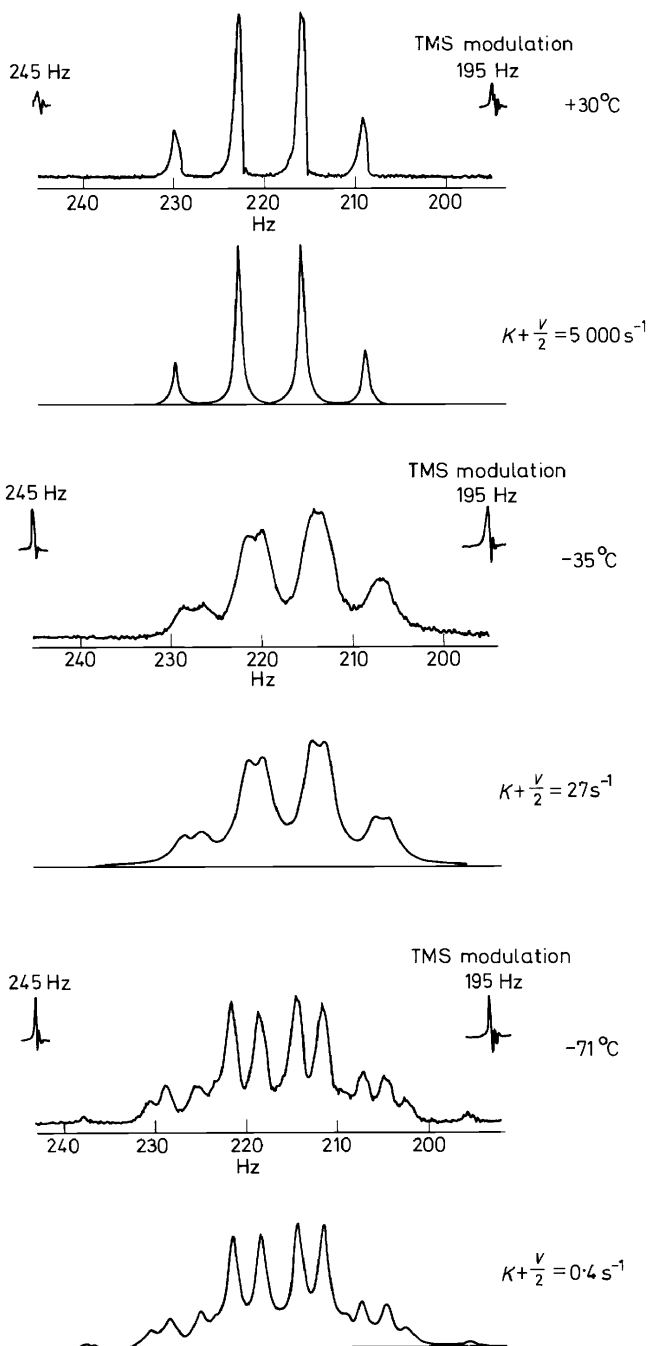


Figure 13. N.M.R. signal of the  $\text{CH}_2$  group of  $\text{COT-O-CH}_2\text{CH}_3$  recorded at different temperatures and their corresponding calculated spectra

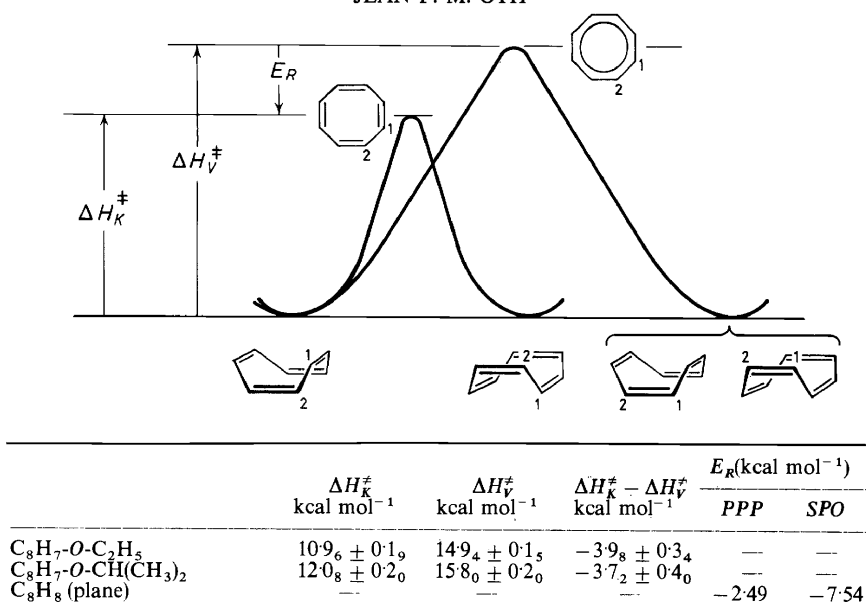
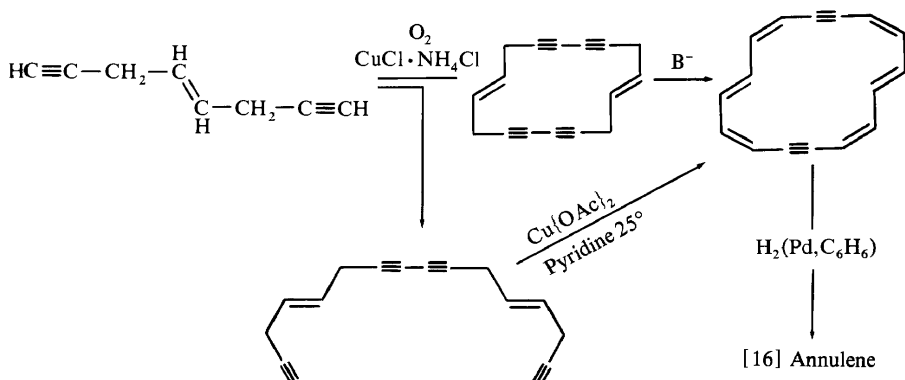


Figure 14. Resonance energy in the planar  $D_{8h}$  conformation of COT

into the 1,9-bisdihydro-[16]annulene. Partial hydrogenation of this compound gives [16]annulene;



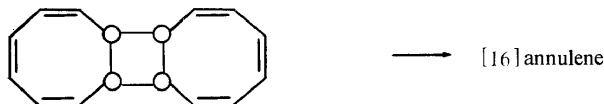
The 85 configuration (i.e. the one in which the double bonds are alternatively *cis* and *trans*) was tentatively assigned by Sondheimer *et al.* to their [16]annulene. No real proof for this configuration was advanced, however. Particularly puzzling was the fact that the N.M.R. spectrum at room temperature, as observed by these authors, consisted of a sharp singlet at  $\tau = 3.27$ .

A much more practical synthesis of [16]annulene was found by Schröder *et al.*<sup>11</sup>. Upon u.v. irradiation, the dimer of COT (melting point 53°) gives in good



## FAST BOND SHIFT IN THE ANNULENES

yield a [16]annulene which was found to be identical with that prepared by Sondheimer *et al.* (same u.v., i.r., and room temperature, N.M.R. spectrum):



Having at our disposal enough material, we hoped to elucidate the following points:

What is the correct configuration of the [16]annulene obtained by the two reported syntheses?

Why are all the protons of the molecules magnetically equivalent at room temperature?

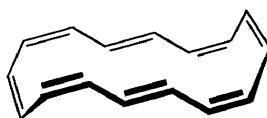
Why is it that two drastically different syntheses yield the same [16]annulene? This is particularly surprising if we realize that 16 different configurations are possible for the [16]annulene (see *Table 1*).

### 6.2. Configurations of [16]annulene deduced from the temperature dependent N.M.R. spectra

Among the 16 possible configurations that a [16]annulene could take, the 0, the 17, the 91 and the 85 configurations have occupied our attention. The 0 and the 17 configurations can be expected to be formed upon irradiation of the dimer of COT: in both of them the two CCC double bond sequences present in the starting tricyclic compound are preserved. From our N.M.R. study we had to conclude that none of these configurations is correct.

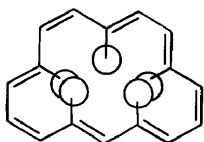


C C C C C C C C  
[16]-0-annulene



C C C T C C C T  
[16]-17-annulene

The 91 configuration was selected by Dewar and Gleicher<sup>4</sup> for their MO calculations. It is the only configuration which can take a planar geometry with all C—C=C bond angles equal to 120° (perimeter drawn on a hexagonal two-dimensional lattice); note, however, that the steric interaction of the internal protons will in fact prevent the planarity of the carbon skeleton, unless some bond angles are greatly increased.



C T C T T C T T  
[16]-91-annulene

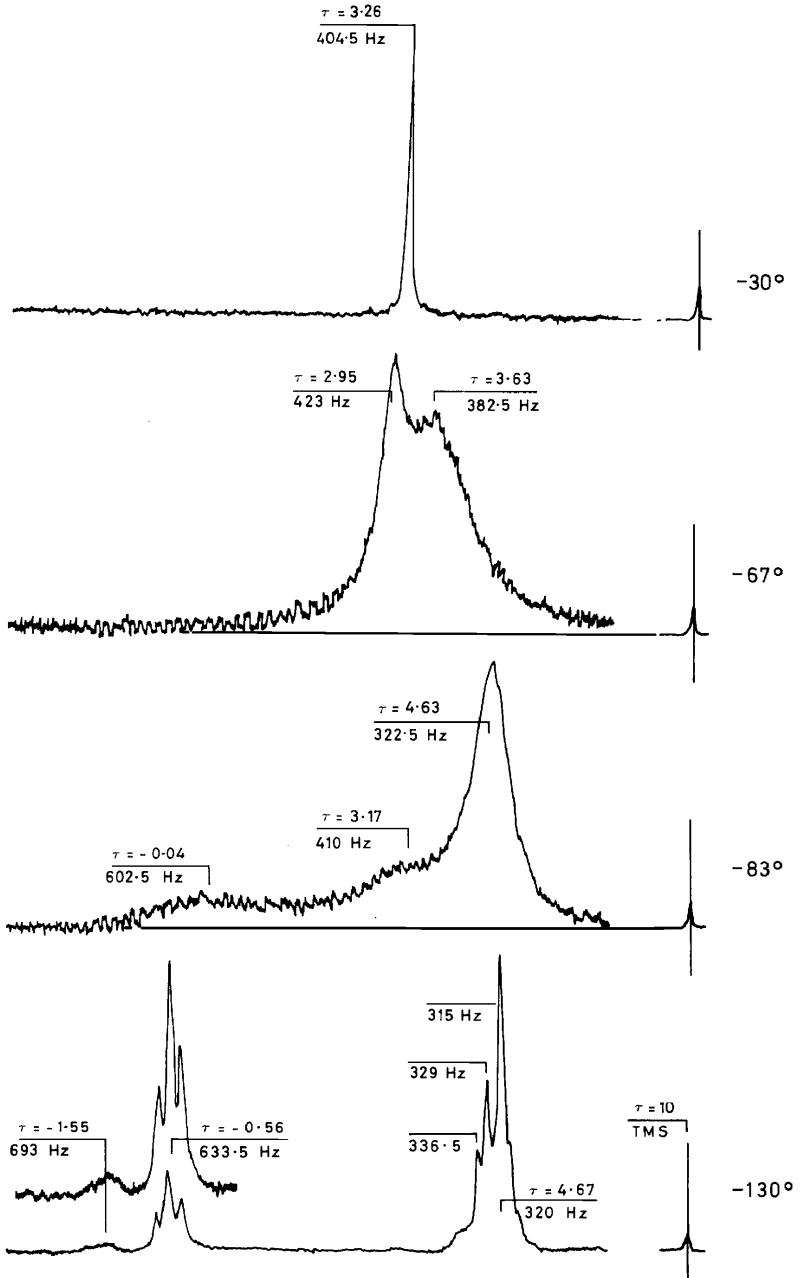


Figure 15. N.M.R. spectra (60MHz) of [16]annulene recorded at different temperatures

The 85 configuration proposed by Sondheimer *et al.*, when constructed with models, appears as a tridimensional, very flexible structure, free from angle strain; this configuration thus appears as a favourable one.

Our N.M.R. investigation at different temperatures<sup>11</sup> led us to conclude that [16]annulene exists as a dynamic equilibrium between these last two configurations, the 85 configuration being preponderant; furthermore we had to conclude that both configurations undergo an isodynamical conformational mobility and an isodynamical bond shift.

### 6.3. Quantitative interpretation of the temperature dependent N.M.R. spectra of [16]annulene

Figure 15 reproduces four characteristic N.M.R. spectra of [16]annulene recorded at different temperatures.

As already indicated, at temperatures above  $-50^{\circ}\text{C}$  all protons of [16]annulene become equivalent and give one single line located at  $\tau=3.26$  ( $-30^{\circ}\text{C}$ ). At very low temperatures (below  $-90^{\circ}\text{C}$ ), the spectrum consists essentially of a triplet located at an extremely low field,  $\tau=-0.56$ , and a multiplet centred at  $\tau=4.67$ ; these two signals are approximately in the intensity ratio of 4 : 12. The very low field signal ( $\tau=-0.56$ ) has to be attributed to protons pointing inside the ring and thus experiencing the paramagnetic ring current induced in the  $4n$   $\pi$ -electron system, the high field signal ( $\tau=4.67$ ) being attributed to outer protons.

This very low temperature spectrum, as well as its modification with temperature, namely the equivalence of all the protons observed above  $-50^{\circ}\text{C}$ , is best understood if we consider that the dominant species is the isodynamical [16]-85-85 structure, i.e. the [16]-85-annulene in a conformation in which four planar butadiene residues are linked one to the other by four *gauche* single bonds ( $S_4$  symmetry, see Figure 3). The four inner protons in this isodynamical structure are magnetically equivalent and are responsible for the low field signal at  $\tau=-0.56$  ( $-130^{\circ}$ ). The other 12 protons pointing outside the ring form 3 sets of four equivalent protons and are responsible for the signal at  $\tau=4.67$ .

The two following processes have to be invoked in order to explain the equivalence of all the protons in that structure above  $-50^{\circ}\text{C}$ :

A simultaneous rotation around all the single bonds in the molecule which brings either the C-atoms 1, 2, 3, 4 or the C-atoms 3, 4, 5, 6 in a plane (see Figure 16); the rate of this isodynamical conformational mobility is noted as  $K_{85}$ .

A bond shift (rate  $V_{85}$ ) (see Figure 16).

By these two isodynamical processes, the molecule passes via 8 superposable structures as shown in Figure 17 (diagram for [16]-85-annulene); each proton can then successively occupy each one of the four magnetic sites, as can be seen from the proton exchange diagram (Figure 18).

There also appears in the spectrum recorded at  $-130^{\circ}\text{C}$  a broad signal located at  $\tau=1.55$  which cannot be accounted for by considering only the [16]-85-85 structure. Careful signal integration showed us that the two signals at low field should correspond to 4.3 protons while the high field signal should correspond to 11.7 protons. This indicates that a second configuration of

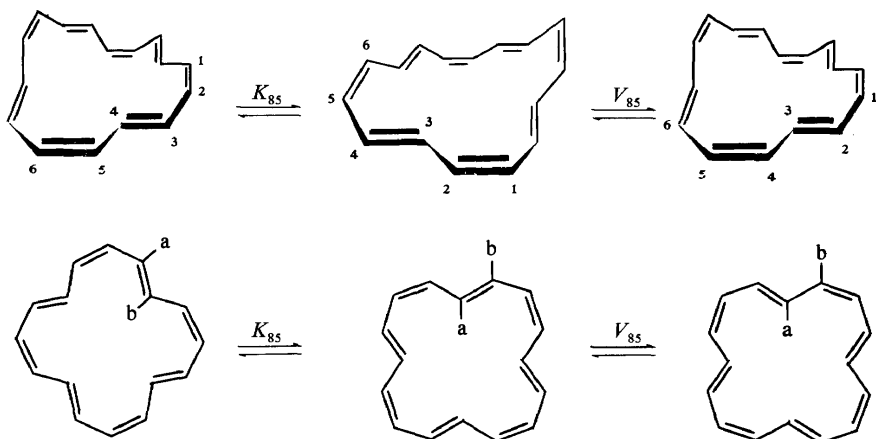
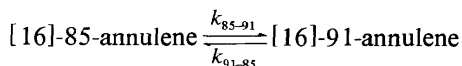


Figure 16. Conformational mobility ( $K_{85}$ ) and bond shift ( $V_{85}$ ) in [16]-85-annulene

[16]annulene, in which more than 4 protons are pointing toward the inside of the ring must also be present. Furthermore, this second configuration should undergo an isodynamical bond shift and an isodynamical conformational mobility, since all the protons in that structure also become equivalent at higher temperatures (cf. the sharp peak located at  $\tau = 2.95$  in the spectrum at  $-67^\circ$  (Figure 15)). Furthermore, these isodynamical processes in this minor isomer should be faster than in the [16]-85-annulene because the signal at  $-1.55$ , due to its internal protons, is already broadened by exchange at  $-130^\circ\text{C}$  (at this temperature the signal of the inner protons of the 85 configuration appears as a well-resolved triplet (cf. Figure 15)).

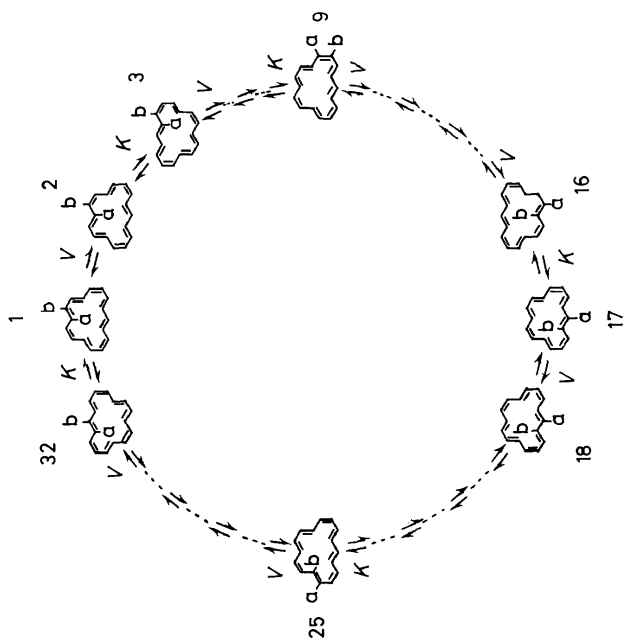
The only configuration which could be found to be in agreement with the N.M.R. spectra (as indicated by quantitative line shape matching, is the 91 configuration already mentioned. The [16]-91-annulene, in which 5 protons are pointing inside the ring, can undergo faster bond shift than the [16]-85-annulene since it can assume a quasi-planar geometry without angle strain. Upon bond shift ( $V_{91}$ ) and conformational mobility ( $K_{91}$ ), the [16]-91-annulene passes via 32 isoenergetic structures (see Figure 17) and each proton can occupy any one of the 16 magnetic sites characteristic of this structure; this explains the narrow line located at  $\tau = 2.95$  in the spectrum at  $-67^\circ\text{C}$ . Thus at  $-67^\circ\text{C}$ , all the protons in each configuration are equivalent. Upon further heating the two signals due to the two configurations become narrower but also merge into one single line, thus indicating that the rates  $k_{85 \rightarrow 91}$  and  $k_{91 \rightarrow 85}$  governing the following dynamical equilibrium



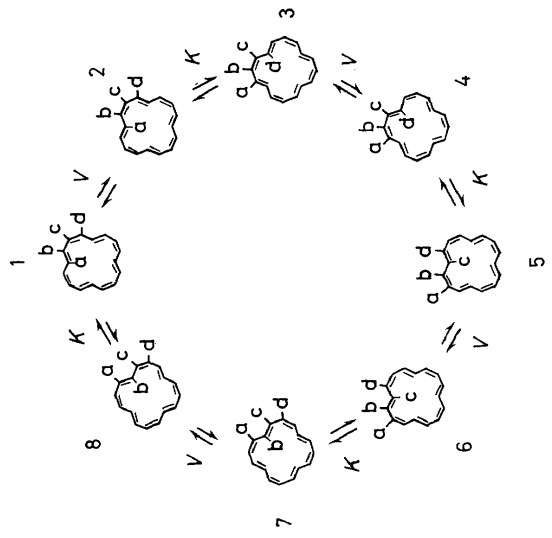
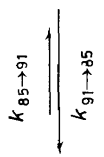
are already very high.

Using the Anderson-Kubo-Sack method<sup>25</sup>, we could reproduce the line shape of the N.M.R. spectra recorded in the temperature range  $-130^\circ\text{C}$  to

FAST BOND SHIFT IN THE ANNULENES



[16]-91-Annulene



[16]-85-Annulene

Figure 17. Exchange between isodynamic structures of [16]-85- and of [16]-91-annulenes

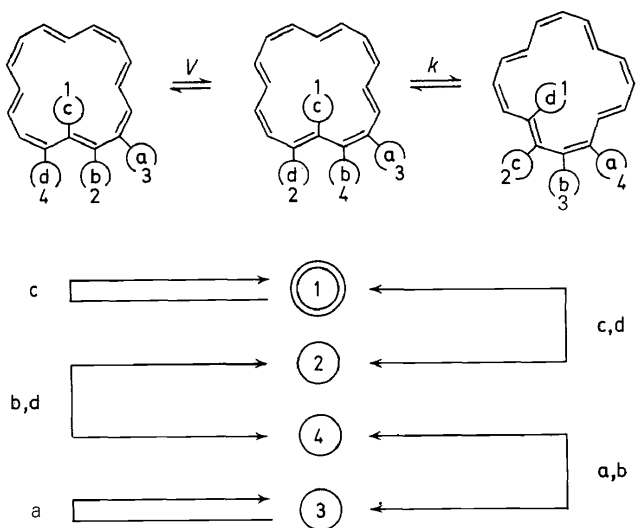


Figure 18. Proton exchange diagram in [16]-85-85-annulene

$-20^{\circ}\text{C}^{23}$ . The following rates had to be introduced in the stochastic exchange matrix and had to be adjusted for the line shape matching:

$V_{85}$	bond shift in [16]-85
$K_{85}$	conformational mobility in [16]-85
$V_{91}$	bond shift in [16]-91
$K_{91}$	conformational mobility in [16]-91
$k_{85 \rightarrow 91}$	rate of isomerization [16]-85 $\rightarrow$ [16]-91
$k_{91 \rightarrow 85}$	rate of isomerization [16]-91 $\rightarrow$ [16]-85

Figure 19 shows, as an example, how well the line shape of the spectrum at  $-79.5^{\circ}\text{C}$  could be reproduced.

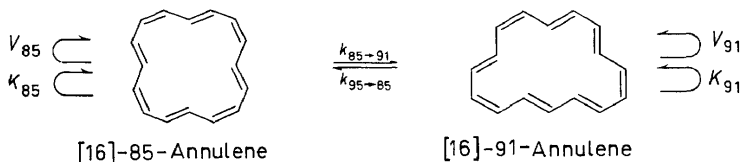
The kinetic parameters characterizing all the dynamic processes taking place in [16]annulene could be obtained by this quantitative analysis of the N.M.R. spectra. They are reported in Table 4.

#### 6.4. The activation enthalpies of the bond shift process and conformational mobility in [16]annulene

It is interesting to note that for each configuration the activation enthalpies for the bond shift and for the conformational mobility are very close or are identical. Although the geometry of the transition state for the two processes cannot be simply related and the case is not the same as for COT (the transition state for the conformational mobility is certainly not planar here), the fact that the activation enthalpy for the bond shift is not greater than that for the conformational mobility implies that the delocalization energy ( $DE$ ) in the planar  $C_{16}$  perimeters (the two transition states for bond shift in [16]-85 and [16]-91-annulene) differs little from 0.

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Table 4.



	$p(0^\circ)$ $s^{-1}$	$p(-100^\circ)$ $s^{-1}$	$\log A$	$E_a$	$\Delta G^\ddagger$ $\text{kcal mol}^{-1}$	$\Delta H^\ddagger$	$\Delta S^\ddagger$ $\text{e.u.}$
$K_{85}$	$690 \times 10^3$	40	13.16	9.15	8.65	8.6	-0.15
$V_{85}$	$625 \times 10^3$	55	12.81	8.75	8.70	8.2	-1.7
$K_{91} = V_{91}$	$17 \times 10^6$	2800	13.79	8.20	6.90	7.7	2.8
$k_{85 \rightarrow 91}$	3500	0.06	11.76	10.25	11.52	9.7	-6.5
$k_{91 \rightarrow 85}$	8250	0.22	11.81	9.90	11.07	9.3	-6.6

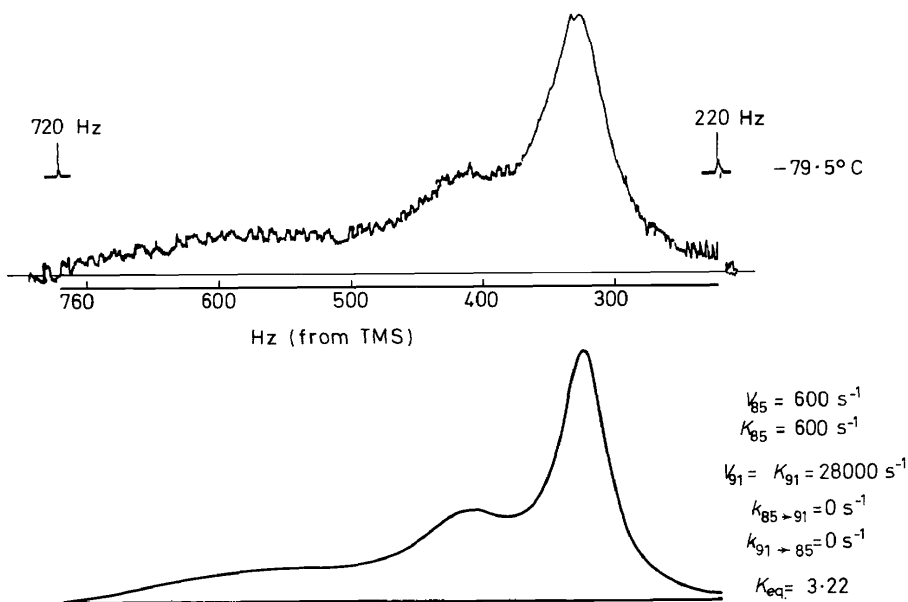


Figure 19

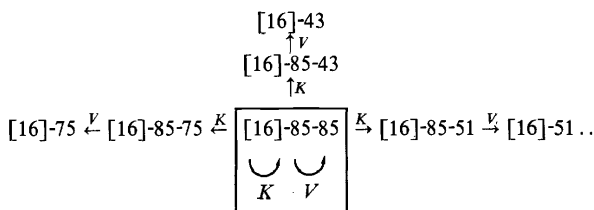
Dewar and Gleicher<sup>4</sup> have reported a resonance energy of +0.99 kcal mol<sup>-1</sup> (PPP) and -3.11 kcal mol<sup>-1</sup> (SPO) in the planar [16]-91 perimeter with equal bond lengths.

**6.5. Mechanism of the fast configuration change [16]-85  $\rightleftharpoons$  [16]-91**

The rapid dynamical equilibrium between the two configurations of [16]annulene can be understood as taking place according to a mechanism of

the following type. Bond shift in [16]-85-annulene in a distorted conformation can lead to another configuration; further bond shift in the intermediate structure can produce another configuration again and so on, so that the passage from the [16]-85 to the [16]-91 configuration would be a sequence of non-isodynamical conformational changes and non-isodynamical bond shifts.

In the following scheme we have envisaged some of the initial steps which could be implied for such a transformation:



A direct transformation [16]-85→[16]-91 implying only one bond shift is difficult to envisage, unless the bond shift is taking place in a highly distorted and strained conformation.

It is interesting to note here that this picture also allows us to understand why two very different syntheses of [16]annulene lead to the same product. Any configuration other than the 85 and 91 resulting from the synthesis would be automatically transformed via bond shifts and conformation changes into the dynamical equilibrium [16]-85⇌[16]-91.

### 6.6. Further proof for the configurations

X-ray analysis<sup>26</sup> indicates that in the crystalline form, [16]annulene exists exclusively in the 85 configuration. Furthermore, the conformation adopted by the molecule is the one proposed, i.e. [16]-85-85. However, the torsion angles around the *gauche* single bonds are only 39° and the internal C—C=C bond angles are 127° to 129°; the molecule is flatter than is indicated by models (in which the bond angles are all 120°).

Monosubstituted [16]annulenes were also prepared and studied by N.M.R. spectroscopy<sup>27</sup>. The two configurations (85 and 91) were found to be present in the compounds studied (COT—COOCH<sub>3</sub> and COT—φ) but their mobility was found to be restricted by the fact that the structures with the substituent inside the ring are excluded.

## 7. [12]ANNULENE

### 7.1. Synthesis of [12]annulene

[12]Annulene can be obtained in solution with a purity of *ca.* 75 per cent by u.v. irradiation at -100°C of syn-tricyclo[8.2.0.0<sup>2,9</sup>]-dodeca-3.5.7.11-tetraene<sup>28</sup>. [12]Annulene was found to be a very unstable compound which rearranges readily at -60°C into *cis*-bicyclo[8.4.0]-dodeca-2.4.6.9.11-pentaene<sup>28</sup>. Special care was thus required in order to undertake its study by N.M.R. spectroscopy.



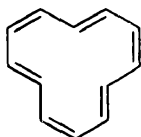
## 7.2. N.M.R. study of the isodynamical conformational mobility in [12]annulene

The most suitable sample of [12]annulene for low temperature N.M.R. studies was obtained by irradiating (at  $-120^{\circ}\text{C}$  for five days in a sealed quartz N.M.R. tube), a solution of syn-tricyclo [8.2.0.0<sup>2,9</sup>]dodeca-3.5.7.11-tetraene in a mixture of THF- $d_6$  and  $\text{CD}_3\text{-O-CD}_3$  (1:1 by volume).

The N.M.R. spectrum of [12]annulene was found to be temperature dependent between  $-170^{\circ}\text{C}$  and  $-80^{\circ}\text{C}$ . Some typical spectra are shown in *Figure 20*.

The spectrum at the lowest temperature ( $-170^{\circ}\text{C}$ ) consists of two broad bands centred at  $\delta = -0.56$  p.p.m. and  $\delta = 1.39$  p.p.m. (internal reference  $\text{C}_6\text{H}_6$ ) with intensities approximately in the ratio of 3:9. With increasing temperature the low-field band coalesces with a component of the high-field signal ( $T_{\text{coalesce}} = -165.7^{\circ}\text{C}$ ). A new broad band then develops at  $\delta = +0.4$  p.p.m. This band sharpens progressively with increasing temperature, while the remaining high-field signal sharpens much faster without any appreciable frequency shift. The resolved spectrum corresponding to the condition of fast exchange can already be seen at  $-110^{\circ}\text{C}$ ; it consists of two signals of the same intensity: one, a quartet, is centred at  $\delta = 0.43$  p.p.m. (i.e. the mean of the  $\delta$  values observed at  $-170^{\circ}\text{C}$ ), the second signal is also a quartet, but with greater separation of the central lines and appears at  $\delta = 1.34$  p.p.m.

The low field-signal in the  $-170^{\circ}\text{C}$  spectrum must be assigned to the internal protons of a cyclic molecule which sustains a paramagnetic ring current, i.e. to a [12]annulene with three internal and nine external protons. Since it is not possible to close a dodecahexaene chain containing two adjacent *trans* double bonds (cf. *Table 1*) and since three internal protons require the presence of three *trans* double bonds, the only possible configuration is that in which *cis* (C) and *trans* (T) double bonds alternate, i.e. the 21 configuration:

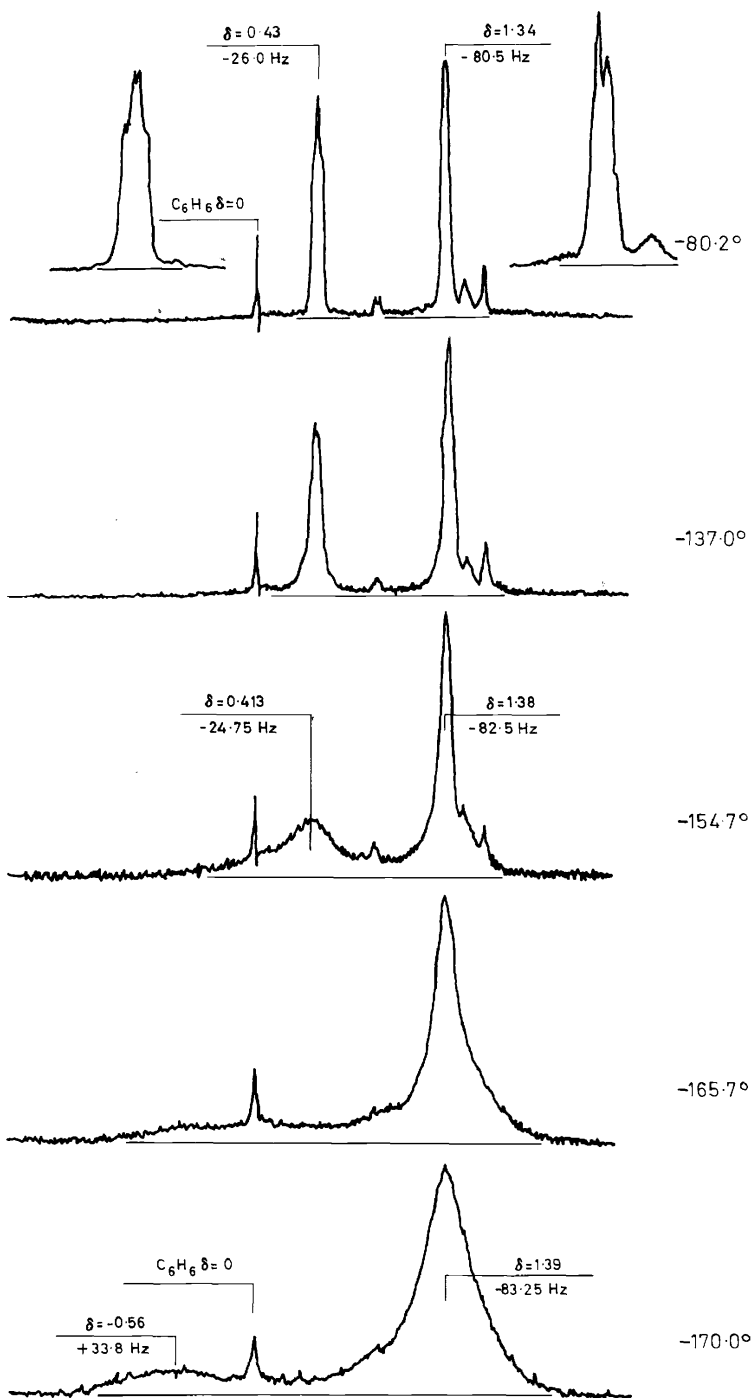


C T C T C T  
 0 1 0 1 0 1 → 21  
 [12]-21-Annulene

This configuration is also supported by the analysis of the temperature dependence of the N.M.R. spectrum. [12]-21-Annulene may undergo an isodynamical conformational mobility; this reversible process *K* occurs by simultaneous rotation around all single bonds and exchanges the protons on magnetic sites 1 and 2 as well as the protons on sites 3 and 4, as can be seen in the exchange diagram shown in *Figure 21*.

Consequently, under the conditions of fast exchange, all the protons on *trans* double bonds become isochronous as do all the protons on *cis* double bonds so that only two chemical shifts (with 6 protons on each) are observed. The high temperature spectrum can thus be immediately understood on the basis of this exchange mechanism.

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20. N.M.R. spectra (at 60  $MHz$ ) of [12]-21-annulene at different temperatures.

## FAST BOND SHIFT IN THE ANNULENES

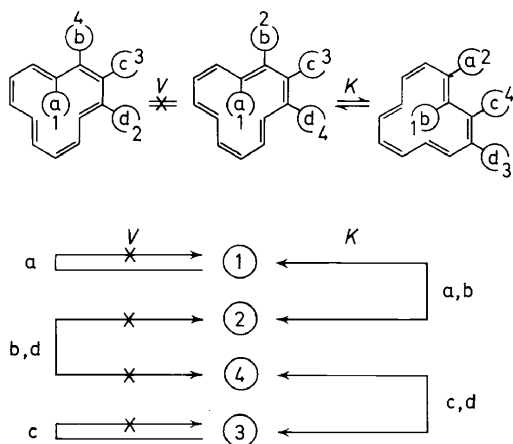


Figure 21. Exchange diagram for the [12]-21-annulene; the letters identify the protons, the numbers the magnetic sites.  $K$  is the rate for a conformational change,  $V$  the rate for a bond shift (valence bond isomerism)

We were unable to observe the spectrum of [12]-21-annulene in the complete absence of exchange, but we could estimate that it should consist of a signal at low field centred at  $\delta=0.75$  p.p.m. (3 protons on site 1) and a signal extending between  $\delta=1.1$  and  $\delta=1.6$  (9 protons on sites 2, 3 and 4).

Using the Anderson-Kubo-Sack method<sup>25</sup> we computed the N.M.R. line shape and fitted the calculated to the experimental spectra recorded between  $-170^\circ\text{C}$  and  $-137^\circ\text{C}$ <sup>29</sup>. These calculations were based on a simplified spectrum under a condition of no exchange as described above. Figure 22 shows an example of such a line shape matching. From our quantitative analysis of the spectra, the kinetic parameters for the conformational mobility could be deduced; they are given in Table 5.

Table 5

$\log A$	$E_a$ kcal mol <sup>-1</sup>	$K(-100^\circ)$ s <sup>-1</sup>	$\Delta G^\ddagger(-100^\circ)$ kcal mol <sup>-1</sup>	$\Delta H^\ddagger(-100^\circ)$ kcal mol <sup>-1</sup>	$\Delta S^\ddagger(-100^\circ)$ e.u.
10.7( $\pm 0.4$ )	4.1( $\pm 0.2$ )	4( $\pm 1$ ) $\times 10^5$	5.5( $\pm 0.1$ )	3.7( $\pm 0.2$ )	-10( $\pm 2$ )

### 7.3. The conformation of [12]-21-annulene

The molecule in the most stable conformation cannot be planar; in fact model considerations indicate that, in order to accommodate the three inner protons with minimum non-bonding interactions and minimum angle strain,

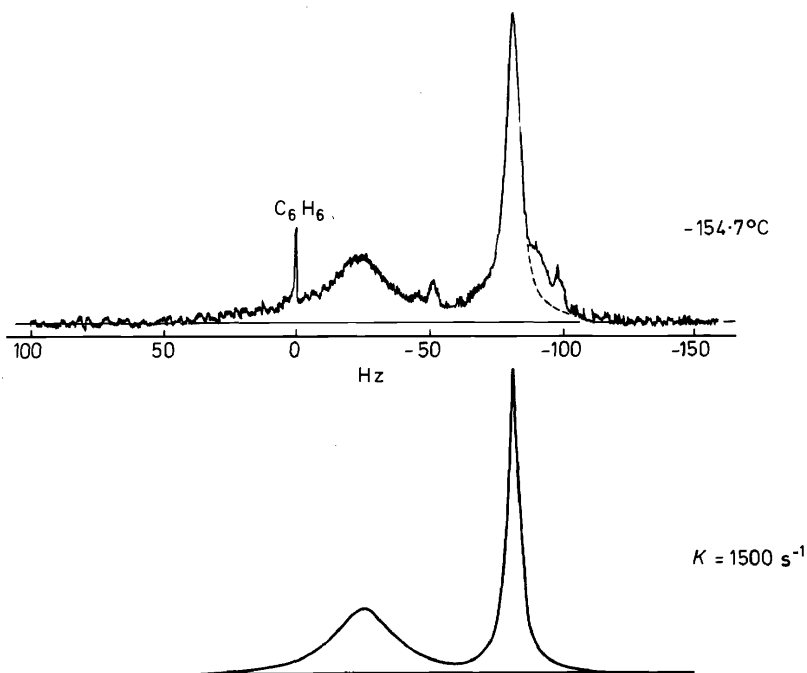
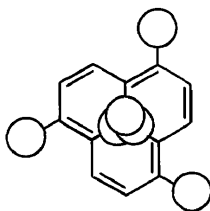
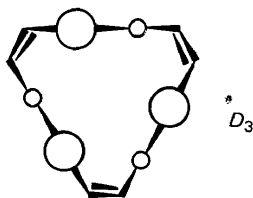


Figure 22. N.M.R. spectrum observed at  $-154.7^{\circ}\text{C}$  and the corresponding calculated spectrum ( $K = 1\,500\text{ s}^{-1}$ )

the mean absolute torsion angle around the single bonds  $\langle |\psi| \rangle$  would have to be as high as  $50^{\circ}$  to  $60^{\circ}$  so that the energy necessary to reach the transition state (of the conformational process) is reduced, thus justifying the very low activation enthalpy observed. Note also that the rotation around all the single bonds of the molecule requires only minute change of the bond angles, as can be seen from the models.



The observed isodynamical conformation change implies that the *trans* double bonds are *not* perpendicular to the mean plane of the ring ( $D_3$  symmetry—absolute torsion angles *close* to  $90^{\circ}$ ) as was suggested by Staab *et al.*<sup>30</sup> in the case of tribenzo[12]annulene:



In fact this geometry is that of one of the possible transition states.

The strong deviation from planarity is also indicated by the relatively small paramagnetic shift of the signal of the inner protons ( $\delta_1 = -0.75$ , i.e.  $\tau_1 = 1.93$ ); in [16]-85-annulene, in which four single bonds are already twisted by  $40^\circ$  (the mean absolute torsion angle  $\langle |\psi| \rangle$  around the eight single bonds is thus  $20^\circ$ ), the inner protons appear at  $\tau = -0.56$ .

#### 7.4. The absence of bond shift in [12]-21-annulene

In principle [12]-21-annulene may undergo an isodynamical valence bond isomerization  $V$ . If this process was present simultaneously with the conformation change, one would observe a complete magnetic equivalence of all the protons at high temperature as is the case in [16]annulene (cf. the exchange diagram in *Figure 21*). In fact, we have not detected any broadening of the high temperature signals up to  $-40^\circ$ .

This would mean that the overcrowding of the inner hydrogens which prevents the formation of a planar transition state also impedes the valence bond isomerization. This observation may be considered, to a certain extent as an indirect proof that the transition states for the bond shift process in the [8]-0, [16]-85 and [16]-91-annulenes must have a planar geometry.

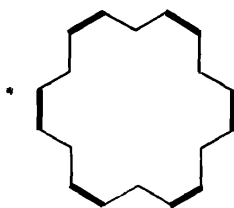
## 8. [18]ANNULENE

### 8.1. Synthesis, N.M.R. and x-ray studies of [18]annulene

[18]Annulene was synthesized by Sondheimer, Wolovsky and Amiel in 1962<sup>31</sup>. Their starting compound was the 1,5-hexadiyne which, upon oxidation with cupric acetate in pyridine gave, *inter alia*, the cyclic trimer. This compound could be rearranged in the presence of a base into the 1,7,13-tridehydro-[18]-annulene, which on partial hydrogenation over palladium yielded [18]annulene.

Gaoni, Melera, Sondheimer and Wolovsky<sup>32</sup> have observed that the N.M.R. spectrum of [18]annulene is temperature dependent; the structure proposed for this annulene was the quasiplanar [18]-219-438-structure already discussed in which 6 protons are pointing toward the inside of the ring (see page 610).

This structure was definitively proved to be correct by x-ray crystallography<sup>33</sup>; furthermore it was shown that the [18]annulene molecule is quasiplanar and has nearly  $D_{6h}$  symmetry. The molecule does not present bond alternation, but the 'external' C—C bonds (heavy lines) were found to be longer (1.419 Å) than the inner C—C bonds (faint lines) (1.382 Å).



[18]-219-438-annulene

## 8.2. Quantitative study of the temperature dependent N.M.R. spectrum of [18]annulene

We have re-investigated the temperature dependent N.M.R. spectrum of [18]annulene in order to elucidate the mechanism by which the protons exchange their magnetic sites. We must first note that the spectrum (*Figure 23*) at  $-60^{\circ}\text{C}$  consists of two signals, one ( $12H$ ) located at  $\tau=0.75$ , the other ( $6H$ ) located at  $\tau=12.88$ .

This very high field signal must evidently be attributed to the inner protons and reflects the diamagnetic current induced in the ring. The fine structure of both signals was found to be unchanged on further cooling.

From the analysis of the fine structure of these two signals it can be concluded that the symmetry of the molecule is indeed  $D_{6h}$ , i.e. there are only two magnetic sites in the molecule ( $\tau_1=12.88$ ,  $\tau_2=0.75$ ,  $J_{12}=13.5$  Hz and  $J_{22}=8.0$  Hz). Upon heating, these two signals become broader, then coalesce into one single bond ( $T_{\text{coales.}}=41^{\circ}\text{C}$ ) and finally give, at high temperature, a sharp single line located at  $\tau=4.55$  ( $121^{\circ}\text{C}$ ).

The exchange observed implies that the molecule undergoes a 'conformational mobility' by which 3 isoenergetic structures are passed as indicated in *Figure 24*. The proton exchange diagram and the exchange probabilities are given in *Figure 25*. (Note:  $p$  denotes probability of the molecule passing from one structure to a specific one of the other two; the probability that the molecule undergoes a transformation is thus  $2p$ .) On the basis of these diagrams, we could establish the exchange matrix<sup>25</sup> required for the line shape computations. Our quantitative analysis of the spectra allowed us to deduce the kinetic parameters given in *Table 6*.

Table 6

$p$ ( $0^{\circ}\text{C}$ )	$\log A$	$E_a$	$\Delta G^{\ddagger}$ kcal mol $^{-1}$	$\Delta H^{\ddagger}$ kcal mol $^{-1}$	$\Delta S^{\ddagger}$ e.u.
9.1 $\pm 0.4$	14.30 $\pm 0.1$	16.7 $\pm 0.2$	14.74 $\pm 0.02$	16.1 $\pm 0.2$	5.1 $\pm 0.6$

## 8.3. Considerations on the isodynamical conformational mobility in [18]-219-annulene

Formally, one can envisage that if the resonance energy in [18]annulene is small it could be overcome with thermal energy. The Kekulé structures (with

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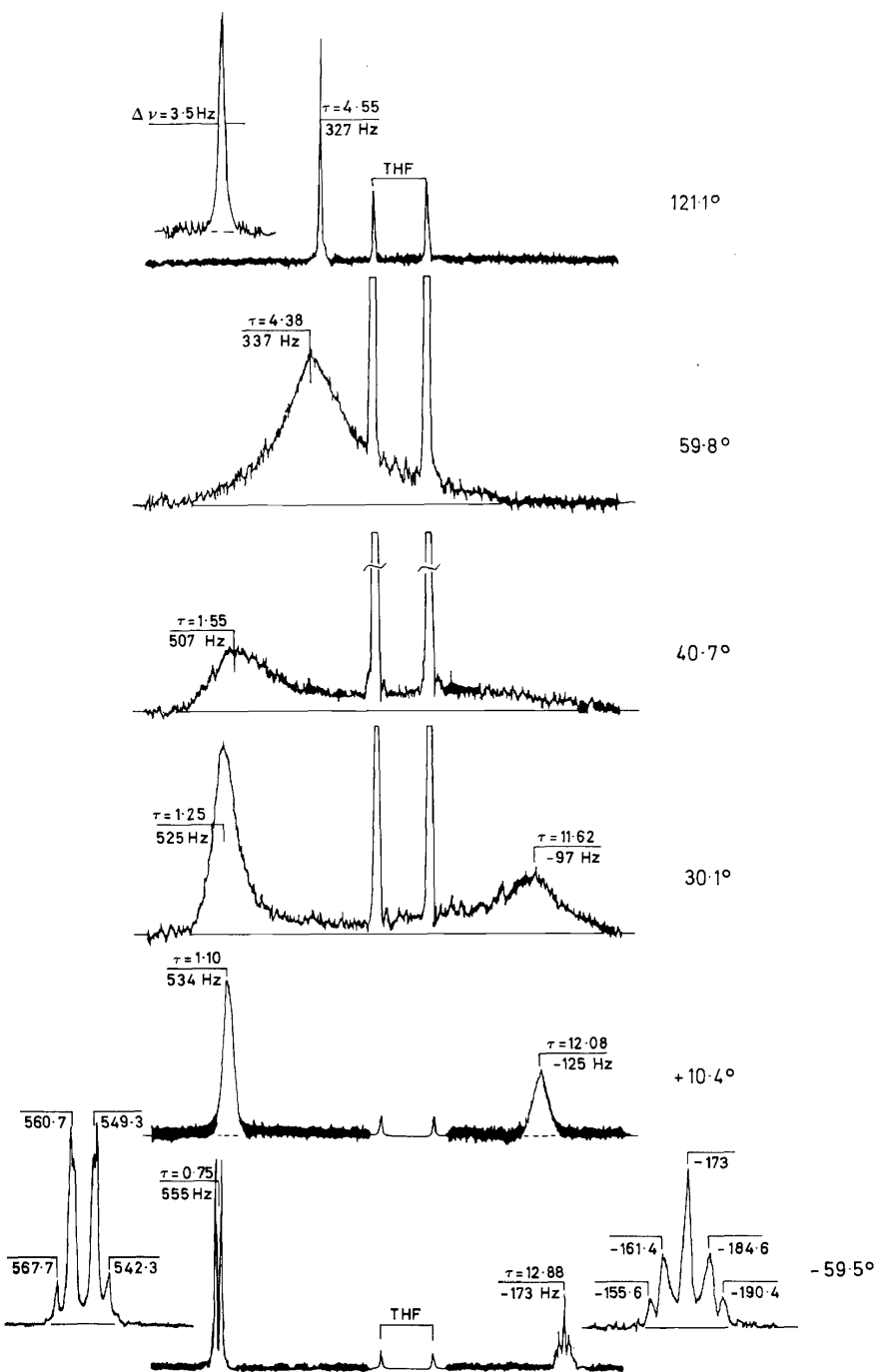


Figure 23. N.M.R. spectra (60 MHz) of [18]annulene at different temperatures

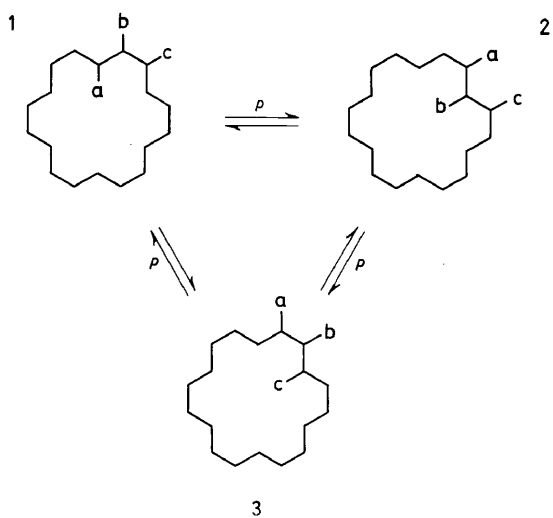
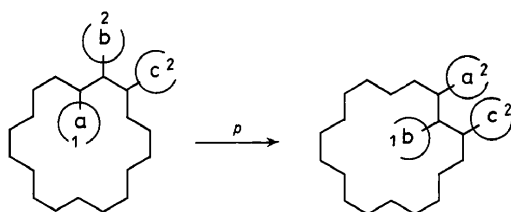
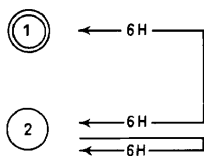


Figure 24. Conformational mobility in [18]-219-438-annulene



Proton exchange diagram



Exchange probabilities

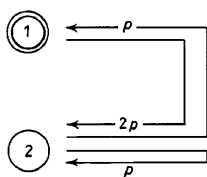
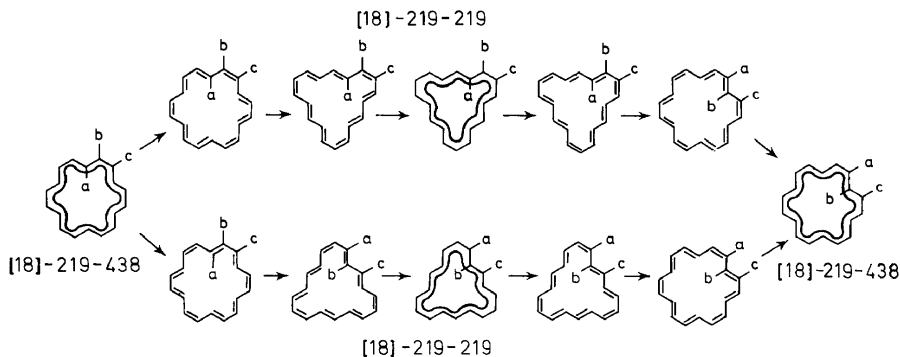


Figure 25



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localized double bonds) can thus formally be regarded as thermally excited molecules; rotation around the single bonds in that excited species could then take place, thus initiating the conformational process observed. One can, for instance, envisage the passage of one structure to another isodynamic one as the sequence of the formal steps indicated in *Figure 26*.



*Figure 26.* Formal reaction path for the conformational mobility in [18]-219-annulene

As we see it, the other 'conformation' ([18]-219-219) of [18]annulene as well as its corresponding Kekulé structures are also invoked in these formal steps. The observed enthalpy of activation  $\Delta H^\ddagger$  for the 'conformational' mobility observed in [18]-219-annulene [ $\Delta H^\ddagger = 16.1 \text{ kcal mol}^{-1}$ ] would then represent the maximum value of the stabilization energy (*RE* or *DE*?) on this molecule.

The reported resonance energy deduced from the heat of combustion of [18]annulene<sup>6</sup>:

$$RE \cong 100 \text{ kcal mol}^{-1}$$

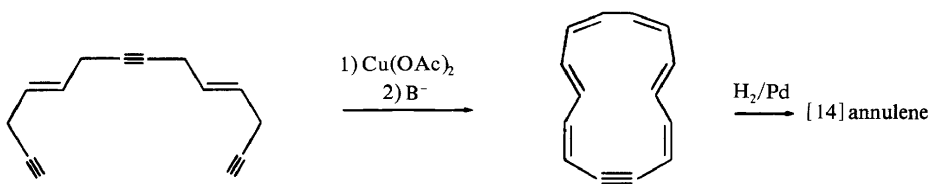
is by no means contradictory to the observed conformational mobility shown by the molecule. The resonance energy calculated by Dewar and Gleicher<sup>4</sup> (PPP:  $8.81 \text{ kcal mol}^{-1}$ ; S  $\pi$ O:  $6.39 \text{ kcal mol}^{-1}$ ) is in agreement with our conclusion concerning the maximum value that this quantity could have, i.e.:

$$RE < \Delta H^\ddagger, \text{ i.e. } 16 \text{ kcal mol}^{-1}.$$

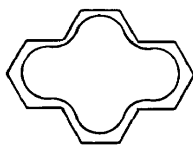
## 9. [14]ANNULENE

### 9.1. Synthesis, N.M.R. and x-ray studies of [14]annulene

The synthesis of [14]annulene was achieved in 1960 by Sondheimer and Gaoni<sup>34</sup> according to the following scheme:



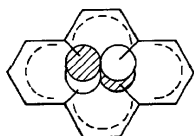
The N.M.R. spectrum of the [14]annulene obtained was found to be temperature dependent<sup>35</sup>. Two species were detected in the N.M.R. spectrum and were shown to be in equilibrium. The major species undergoes a fast isodynamical transformation by which all the protons are magnetically equivalent above  $-25^{\circ}\text{C}$ ; upon cooling at  $-60^{\circ}\text{C}$  the spectrum in the condition of slow exchange was observed and the authors<sup>35</sup> could conclude that this major species has the 43 configuration (4 inner protons).



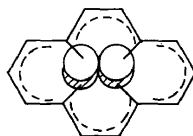
[14]-43-annulene

The other, minor, species also undergoes an extremely fast isodynamical transformation by which all the protons are observed to be equivalent in all the temperature ranges in which the N.M.R. spectrum was investigated ( $-60^{\circ}\text{C}$  to  $+20^{\circ}\text{C}$ ).

The authors<sup>35</sup> have proposed that the two species observed are two conformations of the 43 configuration, these two conformations differing only in the arrangement of the 4 inner protons: the slow (major) conformer would have, according to the authors, its four protons 'interlocked' while in the other conformer they would not be:



'slow(abundant) isomer



'fast' isomer

Preliminary x-ray studies<sup>36</sup> showed that, in the crystalline form, [14]annulene has the 43 configuration; this result thus in part supported the conclusions drawn from N.M.R. studies.

However, it was not clear to us why two very closely related structures like the two proposed conformers of [14]-43-annulene could, at room temperature, have their characteristic signals separated by nearly 0.5 p.p.m. Furthermore, how could each proposed conformer undergo a fast isodynamical mobility which would not automatically interconvert one conformer to the other at a rate comparable to this mobility?

We decided to re-investigate the temperature dependent N.M.R. spectrum in collaboration with Professor Sondheimer<sup>37</sup> in order to obtain unambiguous data for elucidating the structures of these two species.

## 9.2. New study of the temperature dependent N.M.R. spectrum of [14]annulene<sup>37</sup>

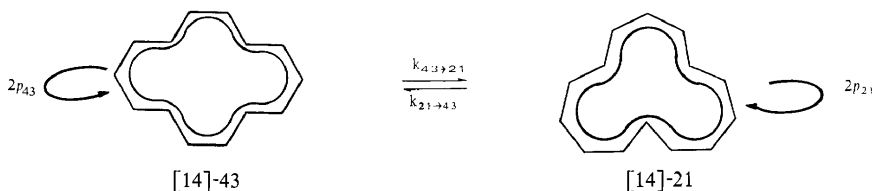
The N.M.R. spectra of [14]annulene (in THF- $d_8$ |CD<sub>3</sub>-O-CD<sub>3</sub> mixture) recorded at different temperatures are shown in *Figure 27*. The two signals of the two species in equilibrium are clearly separated in the spectrum at +25°C ( $\tau = 4.43$ —92 per cent of the main isomer:  $\tau = 3.91$ —ca. 8 per cent of the minor isomer).

### Configuration of the main (slow) isomer

As can be seen, the signal of the main species becomes broader on cooling and is progressively transformed into two signals located at  $\tau = 10.61$  (4H) and  $\tau = 2.12$  (10H) (cf. the spectrum at -126°C). The high field signal (a triplet, 10.61) is attributed to the four isochronous inner protons in the 43 configuration, while the multiplet at low field ( $\tau = 2.12$ ) is attributed to the 10 external protons (on 3 different magnetic sites). The position of these signals clearly reveals the diamagnetic ring current induced in the  $\pi$ -system.

The process responsible for the proton exchange is, of course, an isodynamical conformational mobility. By this process the [14]-43-90-annulene (both conformers discussed above are involved) passes via 7 isodynamic structures and each of the 14 protons can occupy any of the four magnetic sites characteristic of any structure. This can be seen from *Figure 28* or, more clearly, from the exchange diagram represented in *Figure 29*. The quantitative evaluation of the spectra could be carried out using the Anderson-Kubo-Sack method<sup>25</sup> and the kinetic parameters for the dynamical process ( $p_{43}$ ) could be deduced. They are given in *Table 7*.

Table 7.



	$p(0^\circ)$	$p(-100^\circ)$	$\log A$	$E_a$	$\Delta G^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$ e.u.
	$s^{-1}$	$s^{-1}$		kcal mol <sup>-1</sup>			
$p_{43}$	$4.4 \times 10^4$ $\pm 0.2$	0.49 $\pm 0.03$	13.22 $\pm 0.04$	10.72 $\pm 0.08$	10.14 $\pm 0.02$	10.18 $\pm 0.08$	0.2 $\pm 0.4$
$p_{21}$	$9.6 \times 10^6$ $\pm 3$	$9.2 \times 10^3$ $\pm 6$	12.21 $\pm 0.31$	6.5 $\pm 0.2$	7.2 $\pm 0.15$	6.0 $\pm 0.2$	-4.5 $\pm 1.4$
$k_{43 \rightarrow 21}$	$9.5 \times 10^{-5}$ at $-10^\circ$			21			

### Configuration of the less abundant isomer.

The less abundant isomer also shows a temperature dependent N.M.R. spectrum, but in the temperature range between -80°C and -155°C. The

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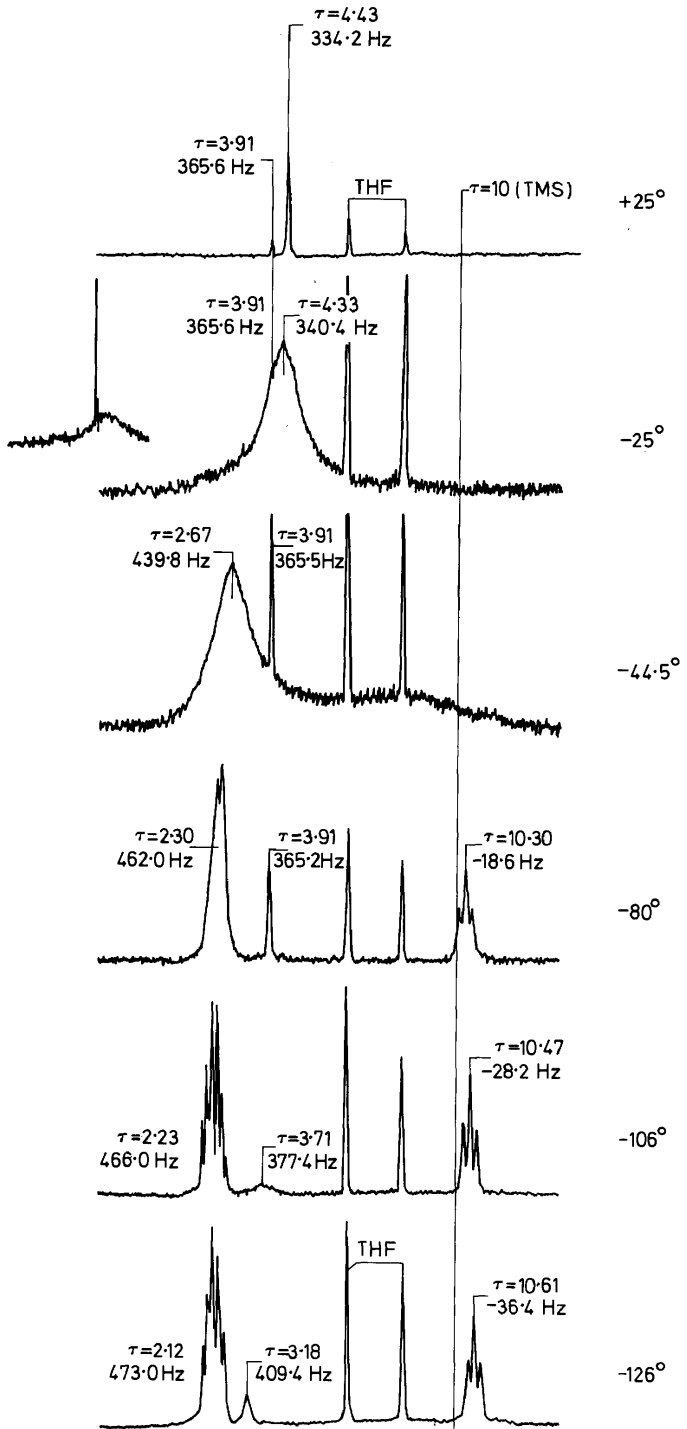
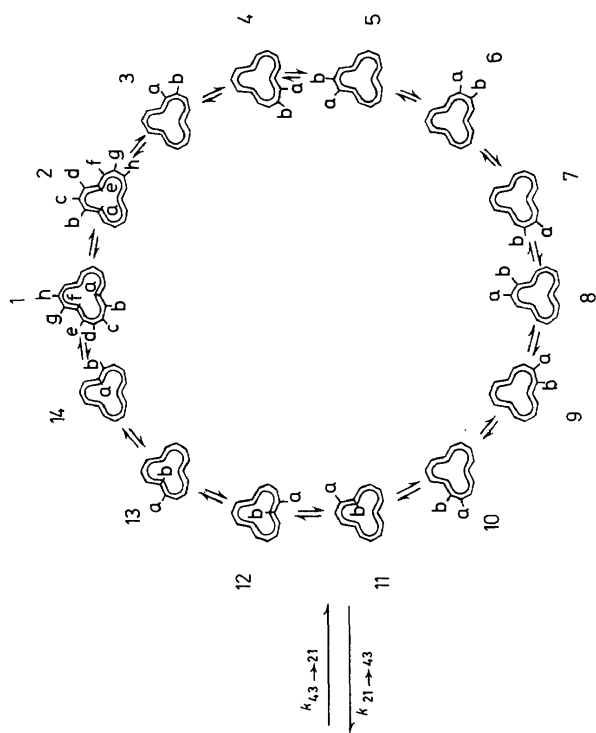
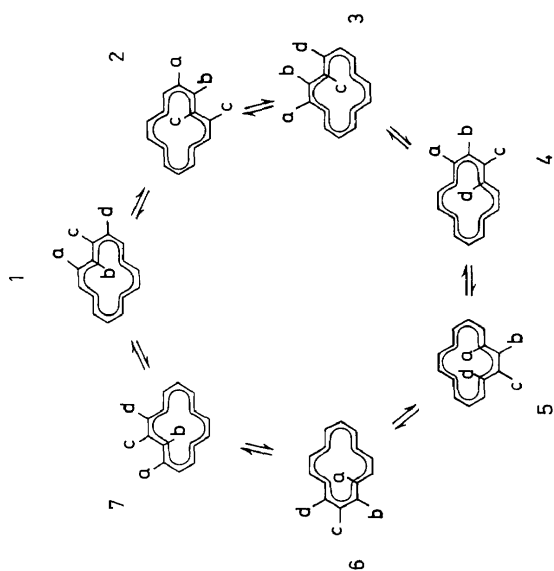


Figure 27. N.M.R. spectra (60 MHz) of [14]annulene at different temperatures

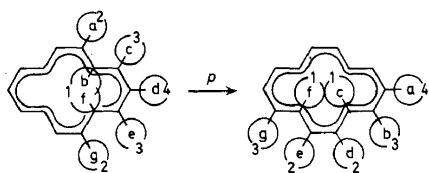


[14]-21-annulene

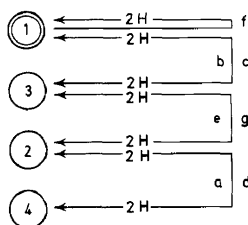


[14]-43-annulene

Figure 28. Exchange between isodynamic structures of [14]-43- and of [14]-21-annulenes



Proton exchange diagram



Exchange probabilities

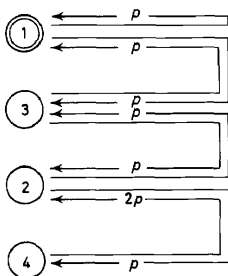
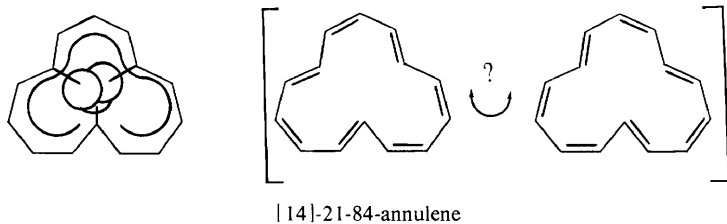


Figure 29

single line observed for this isomer at high temperature ( $\tau = 3.91$ ) gets broader on cooling to below  $-80^\circ\text{C}$ ; it was necessary to cool the sample as low as *ca.*  $-155^\circ\text{C}$  (at this temperature the spectrum had to be measured very quickly since the [14]annulene crystallized out of the solution quite rapidly) in order to obtain a spectrum under conditions of slow exchange. The spectrum obtained at *ca.*  $-155^\circ\text{C}$  indicates the presence of two bands located at  $\tau = 3.18$  and  $\tau \cong 6.45$  (this last band being quite broad). From the position of these two bands and from the position of the signal in the condition of fast exchange ( $\tau = 3.91$  above  $-80^\circ\text{C}$ ) we could conclude that the less abundant isomer has a configuration characterized by the presence of 3 inner and 11 outer protons (note:  $\frac{1}{14} 6.45 + \frac{11}{14} 3.18 = 3.88$  ( $-80^\circ: \tau = 3.91$ )) and by a distorted geometry, since the signal of the inner protons appears only at  $\tau \cong 6.45$ , i.e. at a much lower field than the inner protons of the [14]-43-90 structure. Only the 21 configuration was found to be compatible with these N.M.R. observations. The 21 configuration is indeed characterized by an important distortion of the ring due to the severe steric interaction between the 3 inner protons. In fact this situation is the same

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as in the [12]-21-annulene which has a *cis* (double) bond less. The process responsible for the N.M.R. equivalence of all the protons in the [14]-21-84-annulene implies the passage via 14 isoenergetic structures as indicated in *Figure 28*; by these processes each proton can occupy each of the 8 different magnetic sites characteristic of this structure.

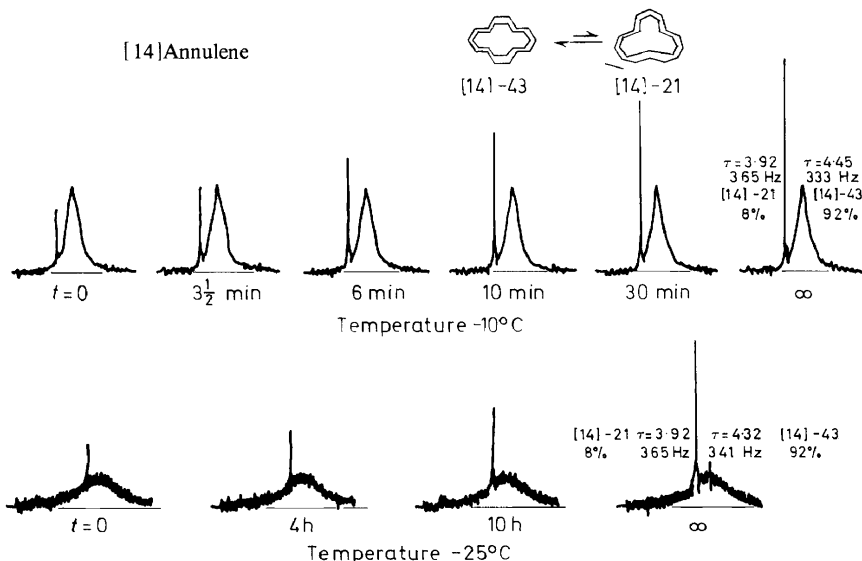


We could deduce the kinetic parameters of this process ( $p_{21}$ ); they are given in *Table 7*.

*Passage from the 43 to the 21 configuration*

The passage from the 43 to the 21 configuration could be followed and measured in the following way: freshly crystallized [14]annulene was introduced in a N.M.R. tube and THF- $d_8$  was condensed in it under vacuum, trapping the THF with liquid nitrogen.

The tube was sealed off and quickly transferred from liquid nitrogen into the N.M.R. probe regulated at e.g.  $-25^\circ\text{C}$ . The spectrum was continuously scanned using a 'saw-tooth' field sweep and a strip chart recorder. The signal of the less abundant isomer was missing or extremely small at the first stage of the experiment but developed with time. *Figure 30* shows two typical kinetic

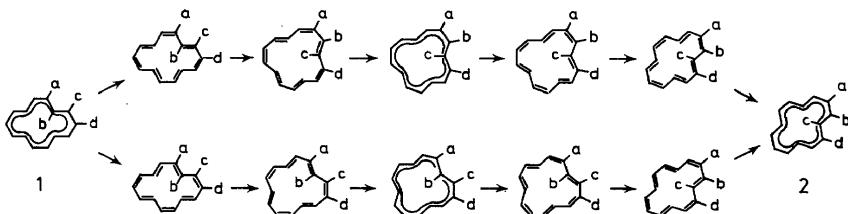


*Figure 30.* Kinetic study of the isomerization [14]-43  $\rightarrow$  [14]-21-annulene by N.M.R. spectroscopy

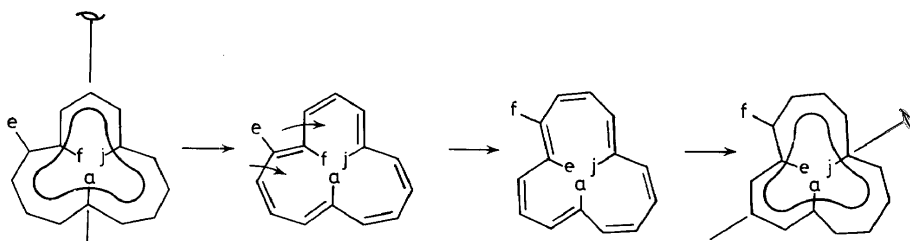
measurements carried out at  $-10^{\circ}\text{C}$  and  $-25^{\circ}\text{C}$ . From these measurements the rate of interconversion  $k_{43 \rightarrow 21}$  could be deduced; it is given in *Table 7*.

### 9.3. Considerations on the isodynamical conformational mobility in the [14]-43 and [14]-21-annulene and on the configuration change

If we envisage the isodynamical conformational processes in the two configurations of [14]annulene as the sequence of formal steps in which the Kekulé structures are implied as indicated in *Figures 31* and *32*, then again, the



*Figure 31.* Formal reaction path for the conformational mobility of [14]-43-annulene



*Figure 32.* Formal reaction path for the conformational mobility of [14]-21-annulene

enthalpies of activation observed will represent the upper limit value for the resonance energies:

$$RE([14]-43) < 10.2 \text{ kcal mol}^{-1}$$

$$RE([14]-21) < 6.0 \text{ kcal mol}^{-1}$$

Dewar and Gleicher<sup>4</sup> have computed the resonance energy in the *planar* 43 configuration; they report values of  $15.86 \text{ kcal mol}^{-1}$  (PPP) and  $14.37 \text{ kcal mol}^{-1}$  (SPO), i.e. greater than the upper limit indicated. One must remember, however, that the [14]-43-annulene must be appreciably distorted from the planar geometry due to the steric interactions between the four inner protons.

The comparable behaviour of the [14]-21 and [12]-21-annulenes is very informative. Both molecules must be particularly distorted; they both exhibit an extremely fast conformational mobility characterized by a very small activation enthalpy (cf. *Tables 5* and *7*); the ring current is also appreciably



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reduced in both structures as compared to other annulenes, but the ring current observed is still of paramagnetic nature in the [12]-21-annulene and diamagnetic in the [14]-21-annulene.

The mechanism for the configuration change can be also rationalized if we consider that the Kekulé structures are implied as transition species: non-isodynamical conformational mobility in the Kekulé structures followed by return in delocalized ground states leads to configuration change. Several intermediate configurations would then be passed in this process.

### 10. CONCLUSIONS

It is clear that all the results we have reported will require a much deeper analysis if we wish to extract all the information they contain. It will be particularly important to make a correct evaluation of the part of the enthalpies of activation which has to be attributed to  $\pi$ -energy changes and of the part which is due to strain energy changes. It will also be important to analyse closely the values reported for the entropies of activations of the different processes, especially in terms of the multiplicity of the reaction pathways.

However, it is already clear that the resonance energy in the  $\pi$ -systems of the *planar* annulenes follows the predictions of Dewar and Gleicher quite closely; the resonance energy does not increase with ring size as predicted by simple HMO considerations, but rather tends rapidly towards a negligible value as the rings become larger (cf. *Figure 1*).

We must always keep in mind, however, that the predictions of Dewar and Gleicher are concerned only with planar molecules having equal bond lengths. They thus predict the resonance energies of the large  $4n + 2$  annulenes but not that of the  $4n$  annulenes which have been shown to be not planar and to present bond alternation; they do predict, however, the resonance energy in the planar delocalized transition states implied for the bond shift process in the  $4n$  annulenes.

### ACKNOWLEDGEMENTS

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