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260. The Dianion of Heptalene

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Summary. Heptalene – a very unstable compound – can be reduced by lithium at – 80° into its dianion. ^{1}H- and ^{13}C-NMR. studies indicate that this dianion, contrary to the neutral molecule, has its π-bonds delocalized. The magnetic field induces in this species a large diamagnetic ring current. The dianion of heptalene is thermally very stable, much more so than the neutral compound. All these observations point to an appreciable stabilization energy associated with the 14π-electron system; this stabilization energy is probably large enough to impose a planar geometry to this dianion.

1. Introduction. – Recently we succeeded in establishing by ^{13}C-NMR. spectroscopy measurements carried out between $-167°$ and $-100°$ that the heptalene molecule shows, in its ground state, π-bond fixation but also undergoes an extremely fast π-bond shift process [1] [2]. The established π-bond fixation and the requirements

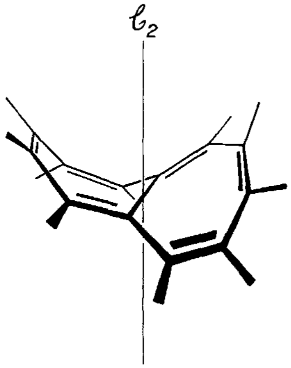

Fig. 1. *The most probable conformation of heptalene*

for a minimized (ring) strain energy imply that the heptalene molecule is most likely non-planar. In its most probable geometry, the heptalene molecule is best described as being formed of two cycloheptatriene boats having in common one single C–C-bond. In this geometry the molecule has a C_2 symmetry and is chiral (see Fig. 1).

If this geometry is the correct one, the heptalene molecule is expected to undergo also an isodynamical double ring inversion, the two cycloheptatriene rings inverting synchronously. Four isodynamic structures (two *R* and two *S*) are than implied by the two dynamic processes as indicated in Fig. 2.

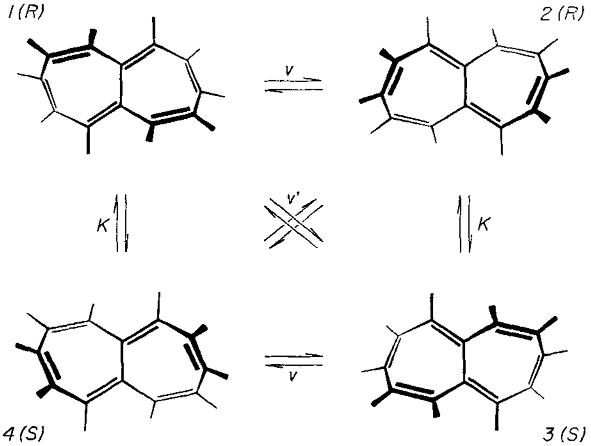

Fig. 2. *The two dynamic processes taking place in heptalene and connecting the four isodynamic structures implied* (v, v': bond shift; *K*: conformational mobility)

The π-bond shift process contributes to a pairwise exchange of nuclei between some of the six different magnetic sites. At −167° six different ^{13}C-signals (each corresponding to two ^{13}C nuclei) are observed, thus indicating π-bond fixation and the presence of only a C_2 symmetry axis; at −100°, due to the fast bond shift process, only four signals with relative intensities 2:4:4:2 are observed thus indicating a mean D_{2h} (or at least C_{2v}) symmetry. The ring inversion process does not contribute to any exchange of nuclei among the six different magnetic sites and cannot be observed with unsubstituted heptalene. The observation of this process requires the substitution of the heptalene molecule by a group containing two diastereotopic nuclei¹).

We were interested to investigate the possibility of reducing heptalene into its dianion. This dianion, possessing 14 π-electrons, is potentially an aromatic species and could have its π-bonds delocalized. If the stabilization energy associated with this π-bond delocalization is large, one could expect the dianion of heptalene to be planar and to possess the D_{2h} symmetry. In order to establish the actual geometry of this new species, ^1H- and ^{13}C-NMR. spectroscopies (at low temperature) are appropriate techniques.

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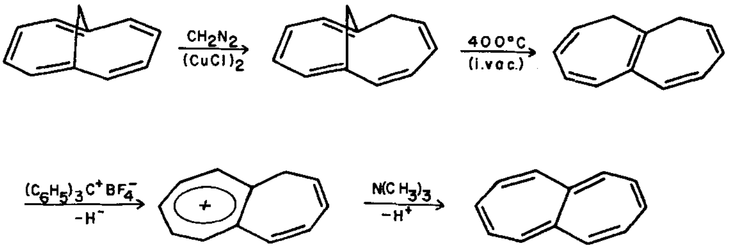
¹) *E.g.* an isopropyl group. If substituted in a position such that the four structures implied are isodynamic, the rate at which the two diastereotopic nuclei would exchange their magnetic environment would be $K + v'$ (or $K + V/2$ if we assume $v = v' = V/2$). This rate is the rate of racemization.

2. Preparation of heptalene. – Heptalene is a very unstable compound; it is extremely sensitive to oxygen and, when oxygen-free, polymerizes readily at room temperature. It has thus to be manipulated preferably in dilute solution and under argon. Heptalene was therefore prepared before each experiment reported here. It was prepared by deprotonation, at –10° in methylenchloride, of the stable cation **1** [3] using trimethylamine as reagent; it was then purified by liquid chromatography (0°, support: Al_2O_3 neutral, eluant: pentane) and obtained in pentane solution. The stable cation **1** was synthetized according to the following scheme [1]:



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3. Polarography. – Before trying to prepare the dianion we have investigated the electrochemical reduction of heptalene by classical polarography and by cyclic voltammetry.

These measurements have been performed at 20° in dry dimethylformamide (DMF) with tetra-*n*-butyl-ammonium perchlorate (TBAP) (1 M) as electrolyte. The reduction was carried out at the dropping mercury electrode, the potential being con trolled and measured with respect to a standard calomel electrode (SCE, 1 N KCl). Two compartments containing DMF/water/1 N KCl and DMF/1 M TBAP separated by G5 fritted glass plugs were used between the reference electrode and the investigated solution. With such a junction diffusion of water into the investigated solution could be avoided during the time required for the measurements.

An adequate volume of the pentane solution containing heptalene was added to the DMF/TBAP solution in the polarographic cell; the pentane was then eliminated by bubbling dry argon through the solution.

Two reduction waves, each corresponding to a one-electron transfer, are observed in the classical polarogram. They correspond to the reduction of heptalene (R) into its radical anion ($R^{\dot{-}}$) and of the radical anion into the dianion (R^{2-}). The characteristic half-wave potentials are reported in Table 1.

Table 1. *Reduction potentials of heptalene* (DMF/1 M, TBAP)

	$E_{1/2}$ [Volt] [a]) +20°C	reversibility	ne^-	process
1st wave	–1.45	rev.	$1e^-$	$R + e^- \rightleftharpoons R^{\dot{-}}$
2nd wave	–2.15	rev.	$1e^-$	$R^{\dot{-}} + e^- \rightleftharpoons R^{2-}$

a) with respect to the SCE (1 N KCl).

Both reduction processes are observed to be reversible by cyclic voltametry. Fig. 3a shows the current potential curve observed on the oscilloscope when scanning the potential of the working electrode – here a hanging mercury drop – linearly with time from -1.0 V to -2.6 V and back at a rate of 32 V s^{-1}. The figure also shows the derivative curve (*i.e.* di/dV *vs.* V) which is simultaneously displayed. The first current peak observed when the potential is scanned from -1 V toward -2.6 V (peak *a*) has its counterpart in the reoxidation halfcycle (peak *d*). The points of inflexion of these peaks, *i.e.* the extrema in the derivative curve, are at the same potential (-1.45 V) thus indicating the reversibility of the fast electron transfer between the electrode and the heptalene molecule.

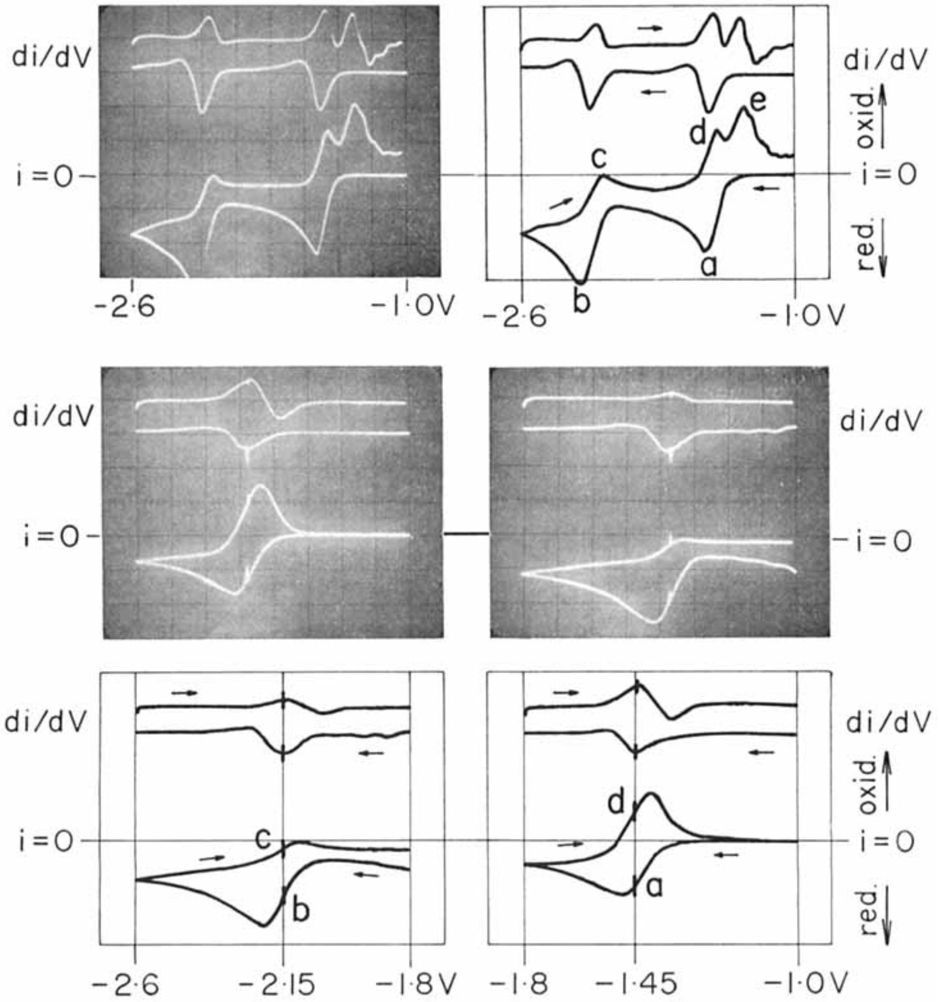

Fig. 3. *Investigation of the reduction of heptalene by cyclic voltametry*; a) the two reduction waves and the reoxidation peaks (above), b) the 1st reduction wave and its reoxidation (below, right), c) the 2nd reduction wave and its reoxidation (below, left).

The second peak which appears during the reduction halfcycle (peak *b*) has also its counterpart in the reoxidation half-cycle (peak *c*). These peaks are again at the same potential (–2.15 V) indicating the reversibility of the second electron transfer. However, as can be seen from Fig. 3a, the reoxidation peak current *c* is smaller than the corresponding reduction peak *b*; this implies that the dianion produced at the electrode is used up, most likely by protonation. Indeed, the peaks *e* observed in the reoxidation half-cycle at –1.3 V indicate the presence of new species²). Their formation can be nearly totally suppressed if great care is taken to avoid moisture when transferring the cold heptalene solution into the polarographic cell and if the heptalene solution is kept over anhydrous magnesium sulfate. Fig. 3b and 3c show the current-potential curves and their derivatives which are observed when the potential is scanned in a narrow potential range (0.5 V at a rate of 16 V s^{-1}) in order to study each reduction process separately. The perfect reversibility of both processes is clearly seen on these figures. The intensified points correspond to electrode potentials of –1.45 V (Fig. 3b) and –2.15 V (Fig. 3c)³).

It is interesting to compare the reduction potentials of heptalene with those of [12]annulene, 1,7-methano-[12]annulene and 1,6-methanol-[12]annulene. The relevant values are listed in Table 2.

Table 2. *Reduction potentials of molecules having a [12] annulene perimeter*; the potentials are given with respect to the standard calomel electrode SCE (1N KCl)

	1st wave	2nd wave	reference
[12]-21-annulene	*ca.* – 1.35ᵃ)	*ca.* – 2.00ᵃ)	[4]
1,6-methano-[12]annulene	– 1.51	– 1.72	[5]
1,7-methano-[12]annulene	– 1.47	– 1.79	[5]
heptalene	– 1.45	– 2.15	this work

ᵃ) The potentials were determined at – 80° on solid mercury without reference electrode; a correction of *ca.* 0.15 V has to be applied to reduce these values to the same potential scale used for the other compounds.

The first reduction potential of heptalene is practically identical with that of 1,7-methano-[12]annulene. This can be understood using PMO considerations [6]: both molecules have the same [12]annulene perimeter (*cis,cis,trans,cis,cis,trans* or [12]-9-annulene in our coded notation [7]). In both species the bridge (a CH_2-bridge or a direct σ-bond) connects two atoms of same parity in the [12]-9-annulene. Consequently, no first-order change in π-binding energy is expected between the hypothetical [12]-9-annulene, heptalene and 1,7-methano-[12]annulene [6]; the same first reduction potential is thus expected for heptalene and 1,7-methano-[12]annulene.

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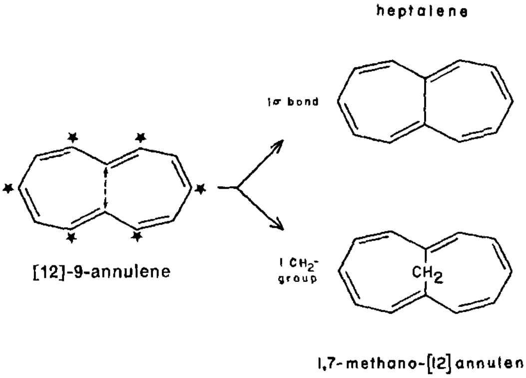
²) These reoxidation peaks are only observed when the potential is scanned to a value at which the dianion is formed; they could correspond to the reoxidation of species such as RH_2^{2-} or RH_2^{-} into the corresponding neutral species RH_2.

³) These intensified spots are obtained using a potential comparator circuitry together with a z-modulation of the trace of the oscilloscope.



The stereochemistry of the known [12]annulene (*cis,trans,cis,trans,cis,trans*; [12]-21-annulene) and of the perimeter of the 1,6-methano-bridged [12]annulene (*cis,cis, cis,trans,cis,trans*; [12]-5-annulene perimeter) are different from that one of heptalene and of the 1,7-methano-bridged [12]annulene; furthermore their [12]annulene perimeter is much more distorted from planarity and their first reduction potentials are thus different. The second reduction potential ($R^{\dot{-}} + e^- \rightleftharpoons R^{2-}$) is more negative for heptalene than for 1,7-methano-[12]annulene. This could be due to the fact that the two radical anions considered have now a very different geometry: the radical anion of heptalene could be planar while that of 1,7-methano-[12]annulene cannot. A more detailed discussion of the potentials reported in Table 2 will be given elsewhere [8].

The reduction potentials observed for heptalene indicate that its dianion R^{2-} can be prepared by reduction with alkali metals.

4. Preparation and NMR. study of the dianion of heptalene. – The dianion of heptalene has been prepared by reducing, with lithium, the neutral molecule in solution in deuterated tetrahydrofurane (THF-d_8). This reduction was carried out in the following way.

A solution of heptalene in pentane, freshly obtained by chromatography, is concentrated by evaporating the pentane in a stream of argon (solution at 0°) and is immediately diluted with deoxygenated THF-d_8. Repeated concentration of the solution under reduced pressure followed by dilution with oxygen-free and dry THF-d_8 leaves a solution containing practically no pentane. This solution is introduced (under an atmosphere of argon) into a 5 mm thin-wall NMR. tube constricted at about 10 cm from bottom end and prolongated by pyrex tubing. This tube is connected to a vacuum line equipped with a lithium press (working under vacuum). The solution is first degassed by freeze and thaw cycles and finally frozen. A lithium wire is pressed under high vacuum into the upper part of the NMR. tube, which is then sealed off (the lithium wire is maintained in the upper part of the NMR. tube by the constriction). The frozen solution is carefully melted and the ^{1}H-NMR. spectrum is recorded at $-80°$ as reference. The tube is then transferred into a dry ice/methanol bath ($-76°$) and the solution is brought into contact with the lithium for controlled periods of inversion of the tube. The ^{1}H-NMR. and the ESR. spectra

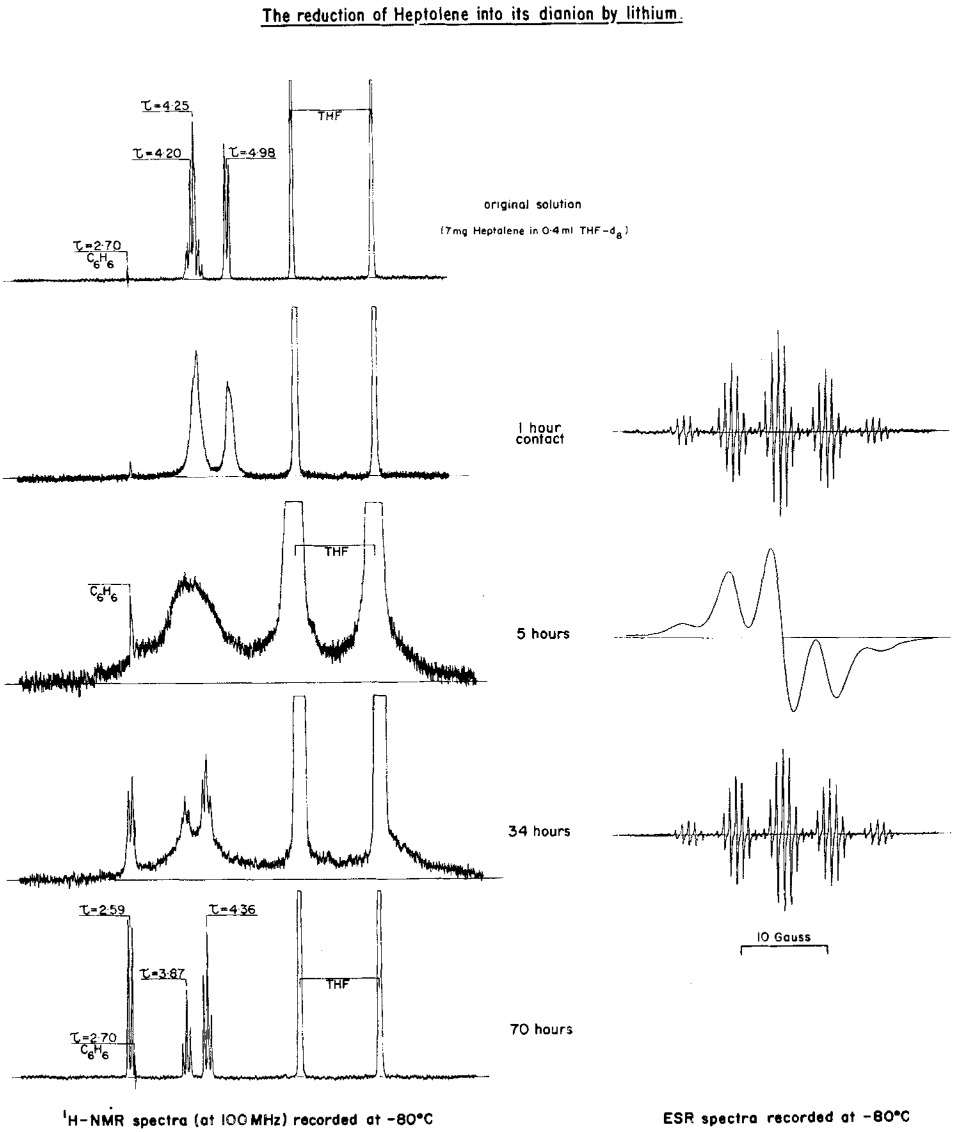


Fig. 4. *^{1}H-NMR. (100 MHz) and ESR. spectra of a solution of heptalene for different contact times with lithium*

are recorded at – 80° after various contact times. Some typical spectra are reproduced on Fig. 4.

After 15 minutes contact a highly resolved ESR. spectrum (with a line width of 40 mG) is observed while the NMR. spectrum remains unchanged. The ESR. spectrum is clearly due to the radical anion of heptalene; the ESR. parameters are the following [9]:

$$a_H\ (4\ H) = -5.35\ G$$

$$a_H\ (2\ H) = 0.79\ G$$

$$a_H\ (4\ H) = 0.69\ G.$$

After 1 hour contact (see Fig. 4) between the solution and the lithium the intensity of the ESR. spectrum increases and the resolution is partly lost both in the ^{1}H-NMR. (due to the paramagnetism of the solution) and in the ESR. spectrum (line width 80 mG). After 5 hours contact one observes the most intense ESR. signal which is poorly resolved but has the same total width as the highly resolved spectrum. At this reduction stage (*ca.* 1 e$^-$ per mol of heptalene) a very broad NMR. signal is detected. On longer contact between the solution and the lithium wire, the ESR. signal decreases in total intensity and the resolution reappears. *E.g.*, after 34 hours contact a resolved ESR. spectrum analogous to that recorded after 5 hours contact is obtained. At the same time three new resolved ^{1}H-NMR. signals located at $\tau = 2.59$, $\tau = 3.87$ and $\tau = 4.36$ ppm are observed. These signals develop in intensity and in resolution as the contact between the solution and lithium is increased; they are the only signals observable after 60 hours when no paramagnetism is detected by ESR., *i.e.* when the reduction is complete. These signals are to be attributed to the dianion of heptalene.

It is interesting to note the parallel evolution of the resolution in both the NMR. and ESR. spectra as functions of the degree of reduction. The observed spectra point to the fact that when both R$^-$ and R (less than 1 e$^-$ per mol) or both R$^-$ and R^{2-} (more than 1 e$^-$ per mol) are present, there is no fast electron exchange between these species (no exchange narrowing is observed in the ESR.). This indicates that the radical anion does not disproportionate and that the radical anion and the dianion are species of great stability.

4a. *The ^{1}H-NMR. spectrum of the dianion of heptalene.* On Fig. 5 are represented the ^{1}H-NMR. spectra of heptalene and of its dianion. The assignments of the different signals are also indicated.

The chemical shifts are very informative. Going from the neutral molecule to the dianion, one expects the center of gravity of the spectrum to change under the influence of two factors:

i) an upfiled shift due to the two extra negative charges introduced; this shift is proportional to the change of the mean π-charge density per C atom and is evaluated as:

$$\Delta\tau = \frac{10.7}{12}\,(14 - 12) = 1.78\ \text{ppm}. \qquad [13]$$

ii) a downfield shift due to the fact that the induced ring current changes in nature; it is paramagnetic in the neutral species and expected to be diamagnetic in the dianion.

In Table 3 we have listed the first moments $\langle\tau\rangle$ of the signals of the ring protons of [12]annulene (only the outer protons are considered), of 1,6-methano-[12]annulene, of 1,7-methano-[12]annulene and of heptalene as well as of their dianions.

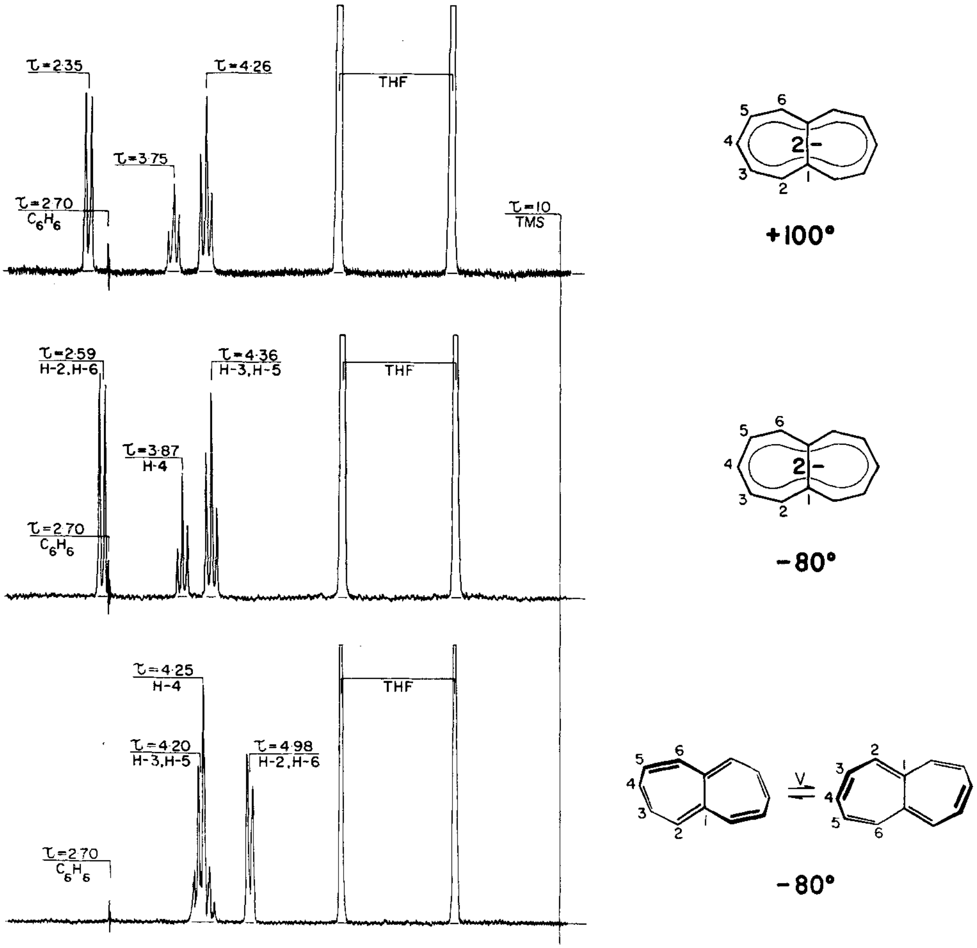


Fig. 5. *The ^{1}H-NMR. spectra* (100 MHz) *of the dianion of heptalene* (as lithium salt) *compared with the ^{1}H-NMR. spectrum of the neutral molecule*

Table 3. *^{1}H-NMR. data for molecules having a [12] annulene perimeter and for their dianions* (in THF-d8 at −80°)

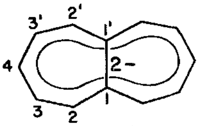
	⟨τ⟩ [ppm] R	⟨τ⟩ [ppm] R^{2-}	Δ ⟨τ⟩ [ppm]	remarks
[12]-21-annulene	4.09 [10]	3.27 [4]	− 0.82	[a]
1,6-methano-[12]annulene	4.29 [11]	3.25 [5]	− 1.04	[b]
1,7-methano-[12]annulene	4.68 [12]	3.34 [5]	− 1.34	[b]
heptalene	4.52	3.55	− 0.97	

[a] Protons pointing inside the ring are not counted.

[b] CH_2-protons are not considered.

Table 3 shows that $\Delta\langle\tau\rangle$, the change in chemical shift observed when going from the neutral to the dianionic species, is of the same magnitude (~1 ppm) for all molecules except 1,7-methano-[12]annulene, for which the change is substantially larger. These shifts clearly indicate that in all dianions the magnetic field induces a large diamagnetic ring current; this points for dianions having their π-bonds delocalized.

The spectrum of the dianion, which is nearly a first order spectrum, points towards a species with D_{2h} (or at least C_{2v}) symmetry. The following parameters are deduced:



$\tau_2 = 2.59$

$\tau_3 = 4.36$

$\tau_4 = 3.87$

$\langle\tau\rangle = 3.54$

$J_{23} = 9.25$ Hz

$J_{34} = 8.70$ Hz

$J_{24}, J_{33'} < 0.2$ Hz

The high field position of H(3) is consistent with the fact that, in the highest occupied MO, the greatest charge density, is found on C(3) and C(1) (see below). The spectrum of the heptalene dianion maintains its habitus in the temperature range from −110 to +100°; only a slight temperature dependence is observed for the chemical shifts of the three signals.

4b. *The ^{13}C-NMR. spectrum of the dianion of heptalene.* On Fig. 6 are reproduced the ^{13}C-spectra of heptalene and of its dianion. The assignment of the different signals, obtained by selective proton decoupling experiments, is also given.

Here again the centre of gravity of the ring carbon signals $\langle\delta\rangle$ is shifted towards higher fields when going from the neutral molecule to the dianion. This shift, which is essentially due to the change in π-electron charges per carbon atom, is expected to be

$$\Delta\langle\delta\rangle = -\frac{160}{12}(14-12) = -26.7\ \text{ppm.} \qquad [15]$$

We find $\Delta\langle\delta\rangle = -32.4$ ppm, *i.e.* a value in relatively good agreement with the predicted one. In Table 4 the displacement of the center of gravity of the ring carbon signals when going from the neutral species to the dianions is also given for the two bridged [12]annulenes. As can be seen, the shifts observed are also of the same magnitude (28 ppm), thus indicating that in the bridged annulene dianions the two extra

Table 4. *^{13}C-NMR. data for molecules having a [12] annulene perimeter and for their dianions* (in THF-d8 at −80°).

	$\langle\delta\rangle$ [ppm] R	$\langle\delta\rangle$ [ppm] R^{2-}	$\Delta\langle\delta\rangle$ [ppm]
[12]-21-annulene	–	–	–
1,6-methano-[12]annulene	130.9 [11] [a]	102.8 [14]	−28.1
1,7-methano-[12]annulene	134.5 [12]	106.4 [14]	−28.1
heptalene	136.1	103.7	−32.4

[a] Spectrum recorded at −20°.

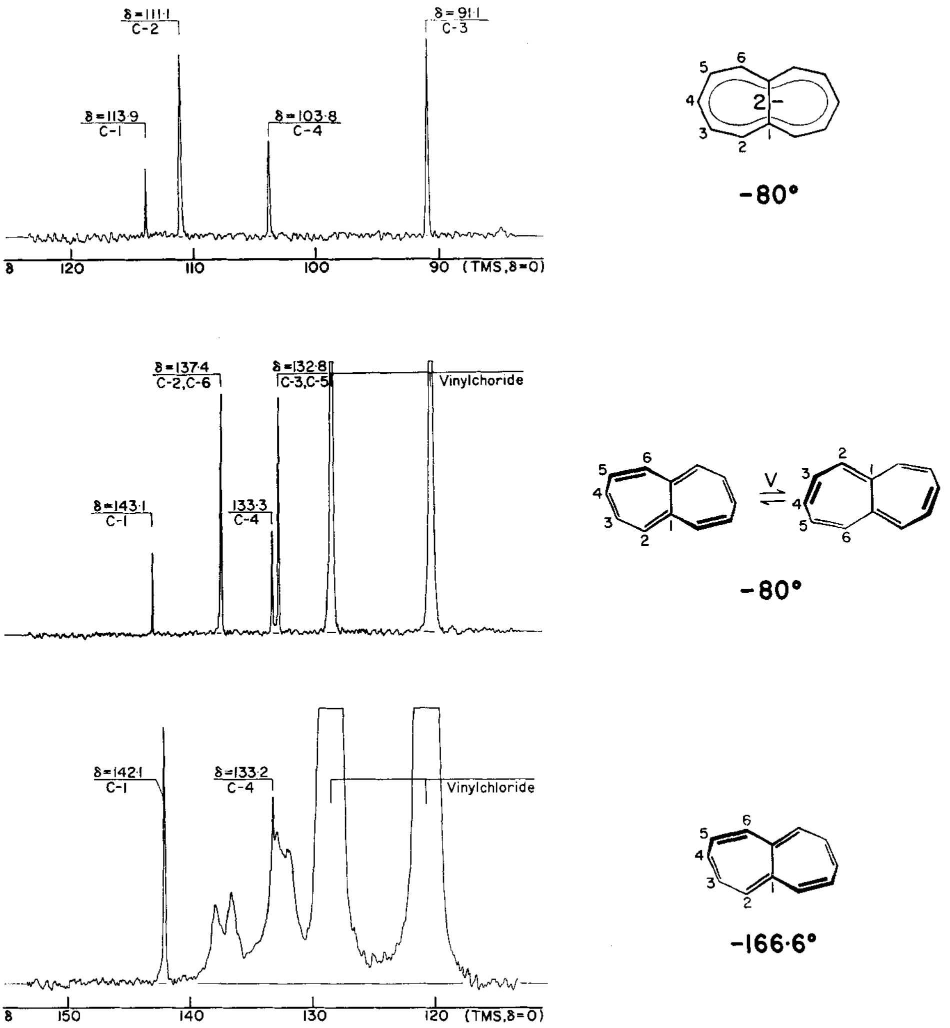


Fig. 6. *The ^{13}C-NMR. spectrum of the dianion of heptalene (as lithium salt) compared with the ^{13}C-NMR. spectra of the neutral molecule*

charges are essentially distributed in the π-system. It is interesting to note here that the sequence of the chemical shifts of C(2), C(3) and C(4) is exactly the same as those of H(2), H(3) and H(4). The high-field position of the signal of C(3) reflects also the large charge density found by MO-calculations (HMO, MINDO/2) on this carbon in the highest occupied MO. The chemical shift of C(1) is not in agreement with the high charge density calculated; however, it should be noted that this carbon atom is quaternary and that its chemical shift cannot simply be compared with those of the other carbon atoms. It should also be pointed out that the sequence of the chemical shifts of the ring carbon atoms is the same in the heptalene dianion and in the 1,7-, methano-[12]annulene dianion but not in the neutral molecules.

5. The thermal stability of the dianion of heptalene. – The ^{1}H-NMR. spectrum of the heptalene dianion was found to be unchanged after heating the NMR. tube at +100° for several hours (see Fig. 5). This indicates a high thermal stability of this charged species, much greater than that of the neutral molecule. This stability was also observed for the bridged [12]annulene dianions and for the dianions of the [12]-21-annulene [4].

6. Conclusions. – The NMR. spectroscopy investigations of the dianion of heptalene and the comparison of the ^{1}H- and ^{13}C-data with those obtained on dianions of other molecules having a [12]annulene perimeter indicate that this species has its π-bonds delocalized (14π-electrons delocalized over $12p_z$ orbitals). The dianion of heptalene is most likely planar, the resonance energy associated with the delocalized 14π-electrons being probably large enough to maintain the perimeter planar, *i.e.* large enough to counterbalance the strain energy accumulated in the planar geometry. This strain energy is estimated to be between 6 and 12 kcal/mol, *i.e.* between 1 and 2 times the energy required to flatten a cycloheptatriene ring.

We acknowledge, with gratitude, the financial support of the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* and the *Swiss Chemical Industries* (Ciba-Geigy AG, Hoffmann-La Roche & Co, Lonza AG and Sandoz AG).

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