POLYCYCLIC AROMATIC IONS

Mordecai Rabinovitz[*] and Abraham Minsky

Department of Organic Chemistry, The Hebrew University of Jerusalem,
Jerusalem 91904, Israel

Abstract – The study of charged polycyclic systems enables a better under-
standing of the nature of the π-delocalization in these series. Pyrene (1)
being aromatic and having 16π-electrons demonstrates the two approaches to
its aromaticity i.e. the contribution of the components and the peripheral
conjugation of 14π-electrons. The preparation and study of anionic species
homoelectronic and isoelectronic to pyrene is reported. The formation of
pyrene dianion and the surprising formation of the diatropic pyrene tetra-
anion demonstrate the importance of the peripheral model. It is shown that
some tetra-anions are asymmetric probably due to the influence of the
counter ion. This phenomenon is related to the charge densities and their
residence on the molecule.

INTRODUCTION

Monocyclic ionic non-benzenoid species exist since the earliest stages of the development
of the term "aromaticity" and extend the aromatic series far beyond the limited boundaries
restricted by the neutral species (1). In the polycyclic series the chemist is confronted
by new characteristics wOich are important in rationalizing aromaticity and are non-existing
in the monocyclic series (2). The problem of the operation of cyclic conjugation in the
polycycles is of major importance. Pyrene (1) demonstrates a problem inherent in many
members of the series namely, the system is aromatic despite having a total number of
16π-electrons. Two approaches were suggested to accound for the aromaticity of pyrene (1).
One considers the partial contributions of the components (3), the other considers the
peripheral π-conjugation of 14π-electrons - known as the peripheral model (4). The latter
model rationalizes the aromaticity of pyrene due to a Huckeloid 14π-peripheral delocaliza-
tion perturbed by an "ethylenic bridge" 1a. However, the aromaticity of pyrene can be
satisfactorily rationalized by either of these theories. The ionic species which will be
described may shed light on the mode of aromaticity of pyrene and related systems.

In recent years we studied ionic polycyclic species aiming at a better understanding of the
aromaticity of the charged as well as the neutral systems.

According to the peripheral presentation pyrene (1), dibenzo[cd,gh]pentalenide dianion (2)
(5), and methylenphenanthrene anion (3), are isoelectronic systems containing 14π + 2π-
electrons and are therefore diatropic. Pyrene dianion (4) and cycloocta[def]fluorenyl
anion (5) can be regarded as 16π + 12π systems and are therefore paratropic. We wish to
discuss briefly our synthesis of derivatives of 2 via a novel base catalysed rearrangement
and the paratropicity of 5. Pyrene tetra-anions will be discussed in detail.

1   **1a**

2   **3**   **4**   **5**
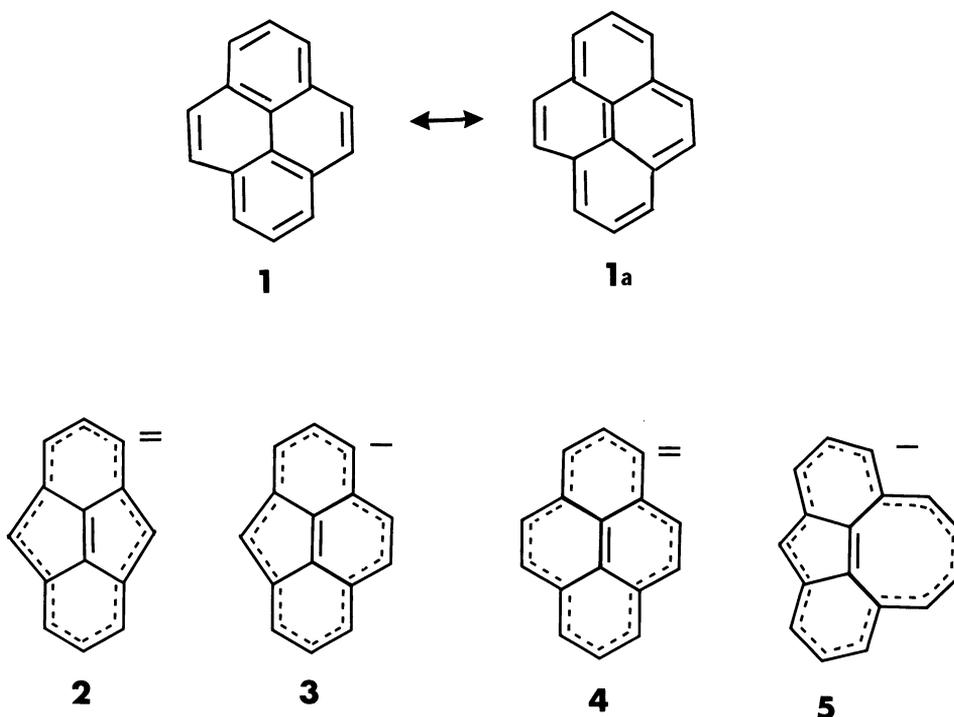
A BASE CATALYSED REARRANGEMENT LEADING TO A SUBSTITUTED DIBENZO[cd,gh]PENTALENE DIANION

We have previously observed (6) that 2,2:6,6-tetradroxymethylbiphenyl reacts in benzene in conc. sulfuric acid to form tetrabenzo[a,de,h,kl]bicyclo[6.6.0]tetradecane (6). Treatment of 6 with n-BuLi in HMPA (150°C) afforded in an unexpected rearrangement product 7 which revealed the following ^{1}HNMR spectrum (100 MHz):

δ ppm 6.41 (d, J=7.3 Hz, H_1, H_3, H_5, H_7)

6.68 (t, J=7.3 Hz, H_2, H_6)

6.80 - 7.47 (m, tolyl ring protons)

2.42 (SR, tolyl methyl group)

Quenching with wet ether afforded a solid m.p. 195°C m/e 358 (M, 100%), (M-C_7H_7, 90%). This compound is ascribed to 4,8-dihyro-4,8bis(2-tolyl)dibenzo[cd,gh]pentalene (8). The synthetic route appears in Scheme 1.


R= P-Tolyl   **6**   **7**   **8**
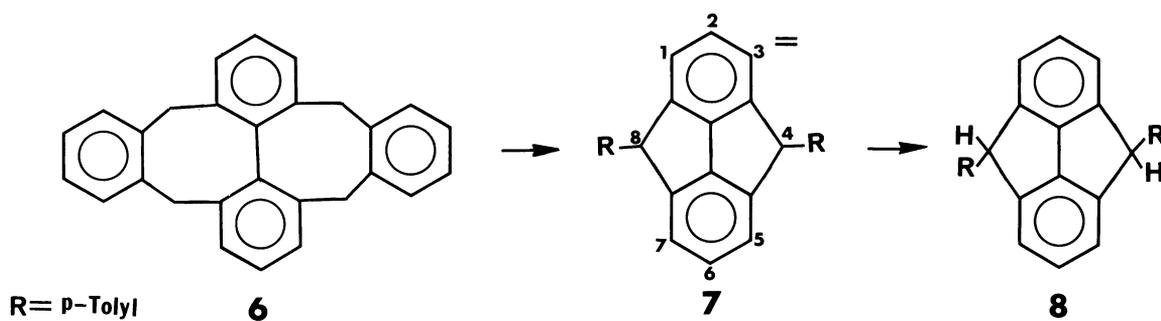
SCHEME 1

Dianion 7 may be visualized as a perturbed [12]annulene with 14π -electrons delocalized in its periphery (a 14π + 12π system). The ease of formation of 7 and its stability should be commented upon. The synthetic challenge of systems like 2 or 7 lies in their high strain energy; i.e., it is necessary to overcome a distance of 3.3 Å by a bridge of a single carbon atom. The ease with which 7 is obtained reflects the energy gained by the formation of the aromatic dianion. The reaction seems to occur via a double benzylic carbanion which then undergoes the rearrangement.

CYCLOOCTA[def]FLUORENYL ANION (5)

We aimed at the preparation of a substrate which should include a planar cyclooctatetraene moiety (7). In this case the paratropic nature of the eight-membered ring as well as that of the entire planar system could be derived. The concept of antiaromaticity and its chemical implications were originated by Breslow (8). While aromaticity ascribes enhanced stabilization of cyclic delocalized molecules relative to their acyclic systems, anti-aromaticity infers the unique destabilization of a delocalized system relative to its acyclic counterpart. The synthetic route of the formation of cycloocta[def]fluorene is depicted in Scheme 2.
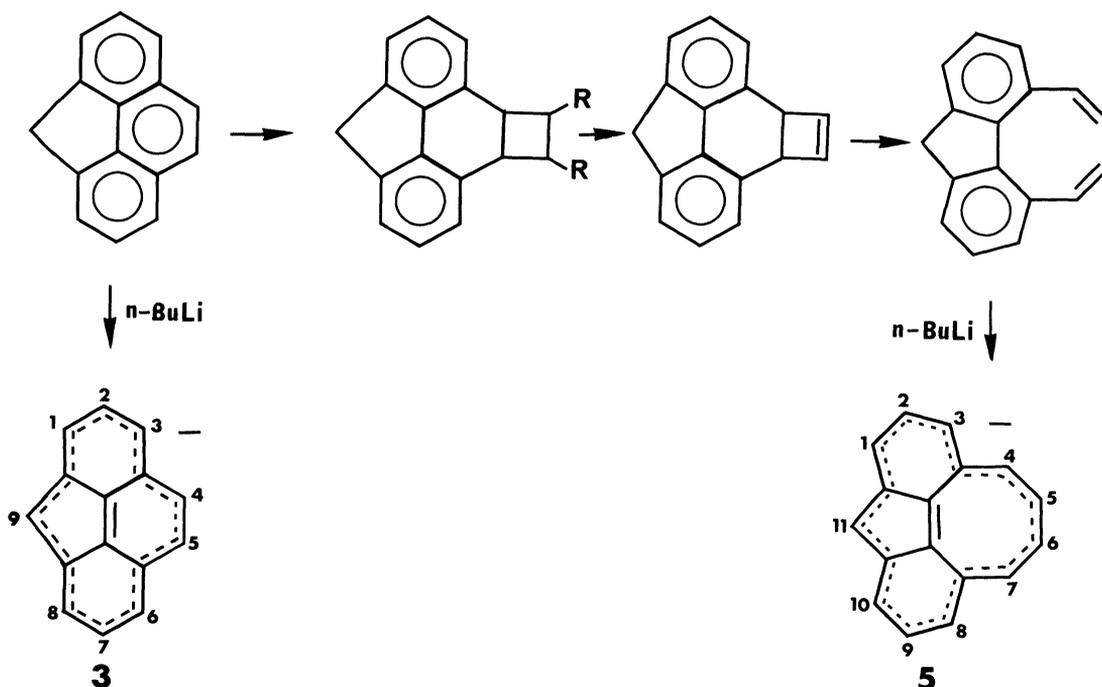
SCHEME 2

We studied the events encountered in the deprotonation of cycloocta[def]fluorene to form anion 5. Cycloocta[def]fluorene includes a fluorene moiety and may, after its deprotona-tion form an anion composed of an aromatic fluorenyl anion and an antiaromatic planar cyclo-octatetraene moiety. On the other hand, if the negative charge is delocalized over the entire framework, it will result in a peripheral 16π-electron system perturbed by an ethylene bridge i.e. 5, which is a 16π + 2π system.

Anion 5 shows the following ^{1}HNMR spectrum (100 MHz):

Anion	Cycloocta[def]fluorene
δ ppm 7.08 (d, J=8 Hz, H_1, H_3, H_8, H_{10})	7.40 (m)
6.38 (t, J=8 Hz, H_2, H_9)	7.40 (m)
5.83 (s, H_{11})	
5.42 (dd, J_1=10 Hz, J_2=4 Hz, H_4, H_7)	5.90 (d)
4.96 (dd, J_1=10 Hz, J_2=4 Hz, H_5, H_6)	5.68 (dd)

It can be seen that relative to the hydrocarbon the anion protons are shifted to highfield
(Δ total = 5.6 ppm). The highest paratropic shift is experienced on the eight-membered
ring protons. These protons are remote from the five-membered ring of the fluorene moiety.
Furthermore, a resonance shielding effect of thenegative charge would cause amplification
of the negative charge at positions 1 and 3 (and 8 and 10). The NMR spectrum of 5 reveals
a different phenomenon; i.e., protons H_2 and H_9 show the most extensive paratropic shift.
We therefore conclude that shielding effects are not the sole explanation for the observed
upfield shifts.

The antiaromaticity of 5 is also demonstrated by the low acidity of the parent hydrocarbon
(7).

The deprotonation of 9-methylenephenanthrene affords anion 3. As previously pointed out
this anion is isoelectronic to pyrene and it should be diatropic. Despite its negative
charge anion 3 shows a total diatropic shift (2.0 ppm) thus demonstrating that the para-
tropicity of 5 does not originate from charge shielding.

Anion 3 (Scheme 2) shows the following ^{1}HNMR spectrum (100 MHz):

| Anion |
|---|
| δ ppm 7.73 (s, H_4, H_5) |
| 7.41 (center of multiplet, H_2,H_3,H_6,H_7) |
| 7.05 (dd, J_1=8, J_2=2 Hz, H_1, H_8) |
| 6.06 (s, H_9). |

It should be noted that protons H_4 and H_5 are shifted diamagnetically to the highest
extent. The observed diamagnetic shift despite the shielding of the negative charge is
attributed to the formation of an aromatic diatropic polycyclic anion a perturbed peri-
pheral[13]annulenyl anion a 14π + 2π system.

POLYCYCLIC BENZENOID TETRA-ANIONS

So far we discussed the formation and properties of systems isoelectronic or homoelectronic
to pyrene namely 14π + 2π or 16π + 2π systems. It seems that pyrene itself represents the
crux of the problem. We therefore undertook a comprehensive study of the reduction
processes of pyrene (1) and its derivatives. We expected that a careful study of the
pyrene system will give rise to different or even contrary types of cyclic conjugation
without altering the carbon framework. Pyrene dianion (4) belongs to the paratropic
species as was shown by Müllen (9). It seemed unexplicable in view of recent findings of
multicharged ions that pyrene would form a paratropic dianion and not a diatropic tetra-
anion i.e. 9.

9
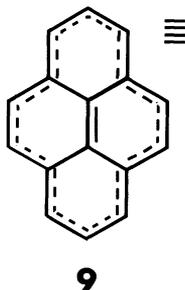
Recently the class of anionic systems was extended to include polycyclic triply and even quadruply charged species e.g. triindene trianion by Katz, dicyclooctatetraenobenzene tetra-anion by Paquette, octalene tetra-anion by Vogel and, acepleiadylene tetra-anion by Müllen (10). We could demonstrate that pyrene can be reduced to form a tetra-anion 9 and thus gain diatropicity and that it undergoes the twofold nmr observable process as follows:

1   **4**   **9**
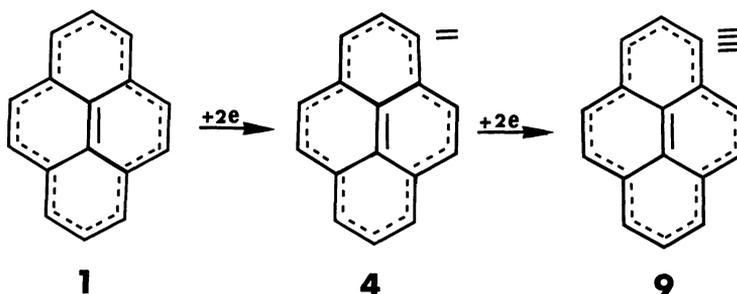
Reaction of pyrene (1) and sodium wire in THF was carried out at room temperature and the process was monitored by ^{1}HNMR spectroscopy. After several hours of exposure of 1 to the metal the spectrum of 1 disappeared. After four days of exposure the solution exhibited a very complex ^{1}HNMR spectrum in the range 4.17-5.99 ppm (Figure 1). These are entirely different parameters as compared with those obtained for 4 (9). The spectrum remains unchanged at room temperature for weeks.

Bubbling of dry oxygen into the solution yields the starting material as a sole product. A similar experiment was also conducted in dimethoxyethane and afforded an identical spectrum. These results indicate that the ^{1}HNMR bands could not originate from a reaction product of the anion with itself or with the neutral pyrene, neither could it originate from a reaction product between the carbanion and the solvent. Quenching experiments with D_2O afforded tetradeuterotetrahydropyrene (m/e=210, P+1=211) as shown by electron capture and chemical ionization mass spectrometry. The quenching product is unstable and oxidizes in the air to yield a mixture of partially deuterated pyrene derivatives (m/e=202-209). We followed the progress of the reduction process by repeated sampling experiments. Samples were taken from the reaction mixture, quenched with water and titrated potentio-metrically to follow the formation of the base. The amount of sodium was monitored by atomic absorption. The concentration of base and sodium increased with time and after four days 3.3-4.0 equivalents of base and 3.2-4.0 sodium atoms per molecule of 1 were
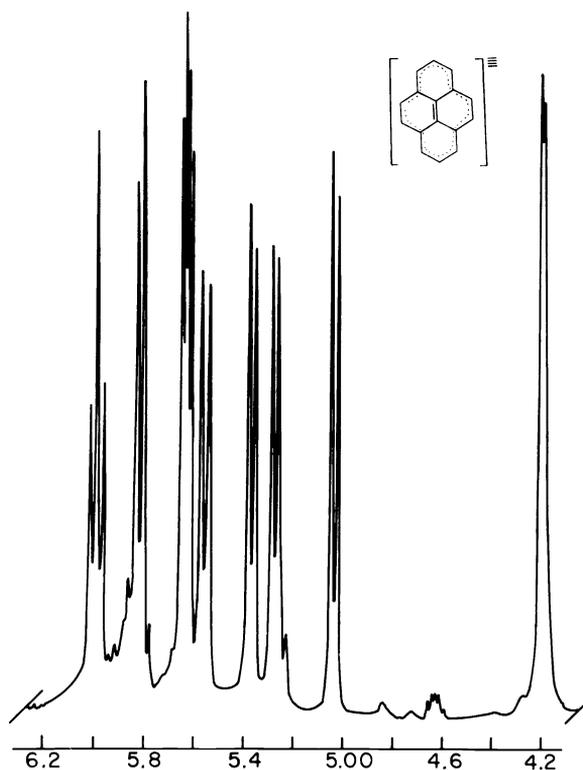
FIGURE 1

detected. These results prove that the species responsible for the above mentioned spectrum should be a quadruply charged one.

An important reason for choosing pyrene as a substrate was that it is a molecule endowed with a high degree of symmetry-D_{2h}-symmetry which is expected to exhibit a simple NMR spectrum. Surprisingly an ABK spectrum is obtained. Moreover, in the ^{13}C spectrum sixteen lines were observed instead of the expected five line spectrum.

Two other derivatives of pyrene were studied i.e. 2,7-ditert.-butyl pyrene (10) and 1,3,6,8-tetraphenyl pyrene (11).

2,7-DITERT-BUTYL PYRENE TETRA-ANION (12)

The reduction process with sodium afforded a paratropic species showing a highfield unresolved spectrum which undergoes a change and finally affords the diatropic spectrum along with the paratropic one. The substituent slows down the process and improves the solubility of the anionic species. With potassium the reduction to the tetra-anion is complete, and only the highly resolved spectrum of the diatropic species is observed.

The ^{1}HNMR spectrum is shown in Figure 2 and in Table 1.

10   **11**   **12**   **13**
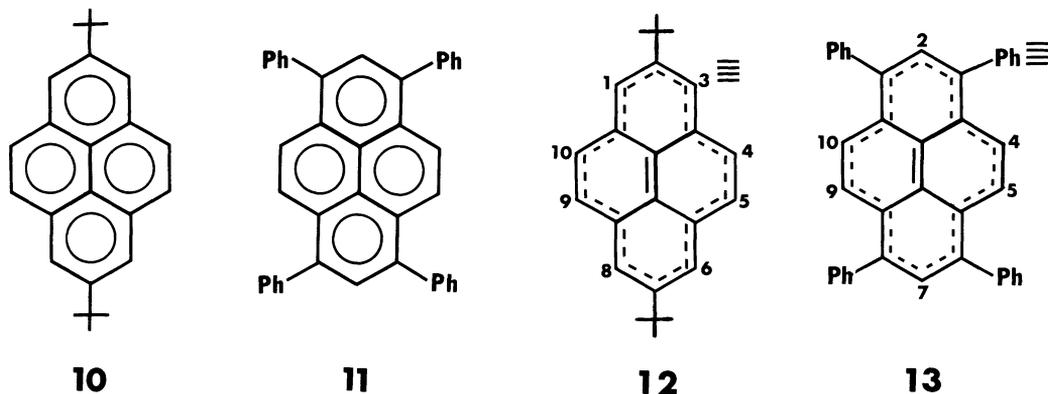
ωβ Calculations of <u>12</u> show that the highest charge density resides on carbon atoms 1, 2, 3, 6, 7, 8. Therefore four counter ions - the positive sodium ions should reside on six
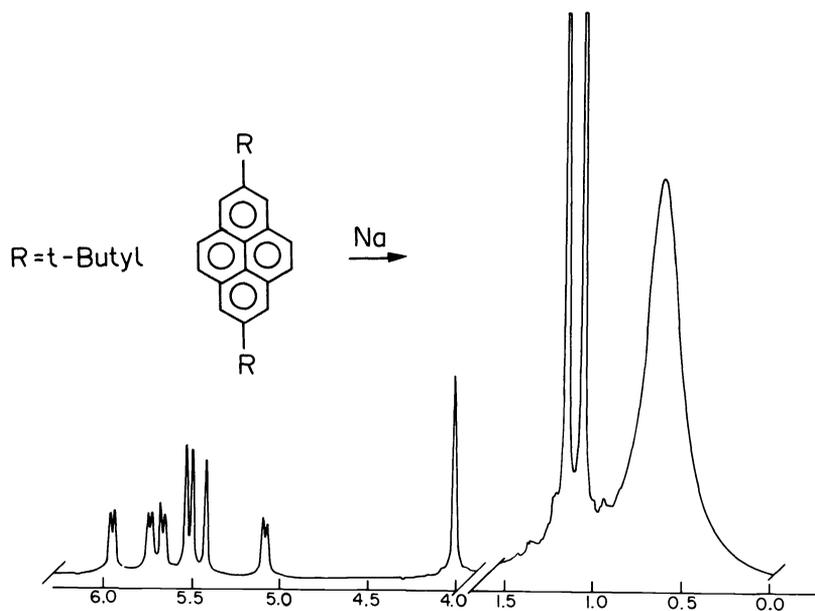

FIGURE 2

position. If a tight ion-pair is formed then a new class of isomerism leading to asymmetry would occur. The four counter ions can uptake either a syn (S) or an anti (A) arrangement:

The ^{1}HNMR parameters of <u>12</u> (Figure 2) are summarized in Table 1. The existence of two isomeric 'syn' (S) and 'anti' (A) forms would result in a ^{1}H spectrum which consists of four doublets assigned to protons 1, 3 (and 6, 8) - two doublets in each form. An AB pattern would result from protons 4, 5 and 9, 10 of the 'anti' form and two singlets for those protons in the 'syn' form (Table 1). Indeed, this is the observed NMR pattern especially in the spectrum of the product of the reaction between <u>10</u> and potassium. Double resonance experiments indicate that the doublet at 6.08 ppm is coupled with the doublet at 5.78 ppm, the doublet at 5.86 ppm is coupled with the one at 5.19 ppm (δ = 5.0 and 4.8 Hz respectively). An AB pattern assigned to protons 4,5; 9,10 of the 'anti' is observed at

R = t-Butyl

Anti (A)   Syn (S)
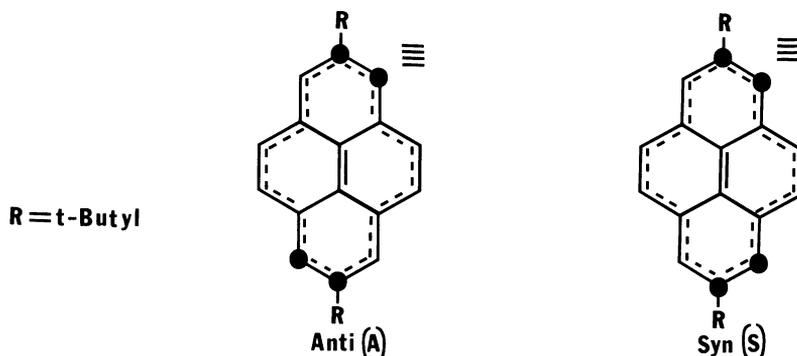
5.57 ppm (center) δ = 8.8 Hz (further coupled to protons 1, 3, 6, 8, J=0.9 Hz). Two doublets located at 5.63 and 4.06 ppm are assigned to protons 4, 5 and 9, 10 respectively - in the 'syn' form.

TABLE 1.   ^{1}HNMR Chemical Shifts (ppm)[a] of 9 and 11

System	δ	Assignment
10	8.16 (s)	1, 3, 6, 8
	8.37 (s)	4, 5, 9, 10
	1.70 (s)	t-butyl protons
12S	5.10 (d, J=4.7 Hz)	1; 8
	5.77 (d, J=4.7 Hz)	3; 6
	5.44 (s)	4, 5
	4.01 (s)	9, 10
	1.02	t-butyl
12A	5.69 (d, J=5.0 Hz)	1, 6
	5.99 (d, J=5.0 Hz)	3, 8
	5.55 (d[b])	4, 5, 9, 10
	1.02 (s)	t-butyl

[a] Referred to $SiMe_4$; for numbering - see Scheme 2.   [b] As it is emphasized in the text, the pattern revealed by protons 4, 5 and 9, 10 is an AB which is clearly shown only in the NMR spectrum of the reaction product of 10 and potassium.

When the tetra-anion was formed with potassium, the formation of the tetra-anion is completed.

1,3,6,8-TETRAPHENYL PYRENE TETRA-ANION (12)

ωβ Calculations of 13 show that most of the negative charge resides on four carbon atoms and proton (carbon atoms 1, 3, 6, 8) and therefore a simple proton spectrum should be expected for the tetra-anions. The spectrum is shown in Figure 3.

This spectrum is indeed simple and so is the carbon spectrum of this species.
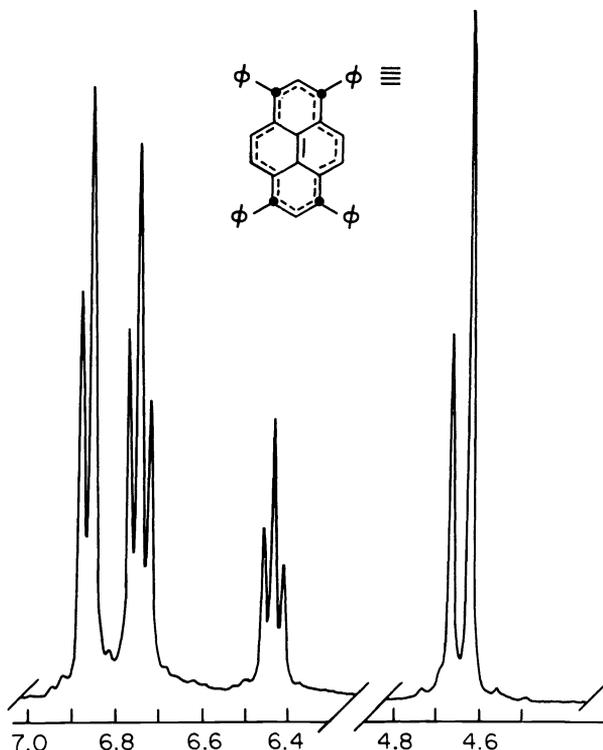
FIGURE 3

<u>CONCLUSIONS</u>

1. Pyrene and its derivatives form easily super charged (quadruply charged) species.
   These tetra-anions are diatropic.

2. The paratropic species can be observed easily in 2,7-alkyl substituted pyrene
   derivatives.

3. We suggest an asymmetry of the tetra-anions made possible due to the formation of
   very tight ion pairing. This asymmetry is unknown to our knowledge.

4. The gradual reduction process allows to follow the alternation of magnetic properties
   of the anions.

5. Our observations support the peripheral model of pyrene and in previous observations
   we could also show that isoelectronic and homoelectronic derivatives of pyrene also
   support this model.

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