

## CONFORMATIONAL STUDIES ON HELICENES—IX<sup>1</sup>

### A HEXAHELICENE CONTAINING AN AROMATIC, CARBOCYCLIC, FIVE-MEMBERED RING

J. H. BORKENT, J. W. DIESVELD and W. H. LAARHOVEN\*

Department of Organic Chemistry, Catholic University, Toernooiveld, 6525 ED Nijmegen, The Netherlands

(Received in the U.K. 12 October 1981)

**Abstract**—The reaction of phenanthro[3.4-c]fluorene (1) with lithium in tetrahydrofuran (THF) or hexamethylphosphoric triamide (HMPT) leads to the fully aromatic phenanthro[3.4-c]fluorenyl anion (2). The influence of the ring current of the five-membered ring and the negative charge on the proton chemical shifts has been analyzed. The low-field position of the A-proton (H(16)) is ascribed to the nearby position of the Li-cation. Even in HMPT the Li<sup>+</sup>2<sup>-</sup> salt appears to be present as a contact ion pair.

It is known that cyclopentadiene and its benzologues indene and fluorene, are weak acids which can be converted into their conjugate bases by the addition of a strong base. Such carbanions are isoelectronic with benzenoid hydrocarbons and are stabilized by delocalization of the negative charge into the  $\pi$ -system. The spectral data of this kind of aromatic anions<sup>2</sup> do not only depend on their molecular structure (ring current effects, negative charge) but also on the position of the counter-ion. In strongly polar solvents they occur predominantly as free ions; at lower polarity of the medium they can combine with the cation to solvent-separated or loose ion pairs, in which the ions may still have their own solvation shell, and eventually to contact or tight ion pairs, which may have an external solvation shell, common to both ions (see Scheme).

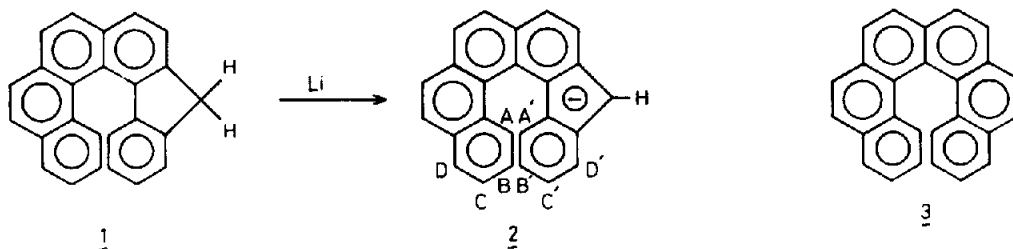


In the preceding paper<sup>1</sup> we reported the synthesis and a conformational study of phenanthro[3.4-c]fluorene (1). In this paper its conversion into the fully aromatic phenanthro[3.4-c]fluorenyl anion (2) and an analysis of its NMR spectrum is described.

intense color indicated the formation of the anion, but the stability of the solution was very poor; the color turned brown within a few minutes.

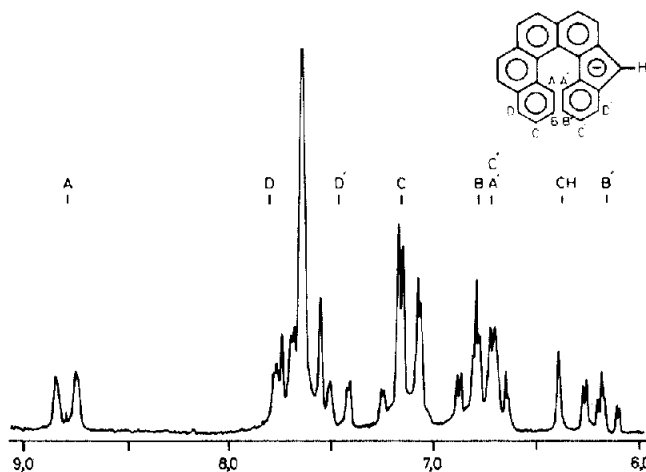
According to van der Kooy<sup>5</sup> the fraction of solvent-separated ion-pairs in a solution of fluorenyl lithium in tetrahydrofuran (THF) is 0.8 at 25°. Therefore, we used this solvent in a second experiment. Addition of n butyl lithium, dissolved in hexane, to a solution of 1 in THF-d<sub>8</sub> under nitrogen led instantaneously to a deep purple color, and now the solution remained stable for several days. In Fig. 1 the <sup>1</sup>H-NMR spectrum of the solution of 2 is reproduced. The spectrum contains a one-proton singlet at 6.39 ppm, which must belong to H<sub>E</sub> in the aromatic 5-membered ring. Another singlet (two protons) is at lower field ( $\delta$  7.64 ppm), and there are two AB patterns ( $\delta$ <sub>A</sub> 7.13,  $\delta$ <sub>B</sub> 7.70, and  $\delta$ <sub>A</sub> 7.14,  $\delta$ <sub>B</sub> 7.57 ppm, respectively). These three signals must be ascribed to the pairs of protons E + F, G + H, and G' + H'. Finally, there are two ABCD patterns belonging to the terminal rings. By decoupling and tickling, and by comparison with the spectra of 1 and of hexahelicene (3) the individual positions of the protons ABCD and A'B'C'D' could be determined (see Table 1).

The most remarkable figure is the  $\delta$ -value of A in 2. It was expected that van der Waals interactions between the opposite parts of the helix in 1 and 2 should be quite



A recommended method to get such compounds as a solvent-separated ion-pair is to use a polar aprotic solvent and a small alkali metal.<sup>3</sup> Therefore, we chose dimethylsulfoxide (DMSO) as the solvent and n-butyl lithium as the source of the alkali metal.<sup>4</sup> When a dry and oxygen-free solution was used, the appearance of an

similar; the 5-membered ring in 1 is nearly planar,<sup>1</sup> and it is known that fluorenyl anions are also planar, in solution as well as in crystals,<sup>6</sup> so that the conformations of 1 and 2 must be very corresponding. Differences in the positions of the protons A, B, C and D in 1 and 2 should then mainly be due to the presence of a ring current in the

Fig. 1. NMR spectrum of 2 in THF- $d_8$  at 90 MHz.

5-membered ring in 2; the protons should be at higher field, just as in the NMR spectrum of 3. Delocalization of the charge in 2 into the other half of the molecule should lead to a shift in the same direction. For the protons B, C and D in 2 these upfield shifts are observed, and as expected decreasingly in this order. However, proton A is shifted downfield over 0.7 ppm relative to 1. The only likely explanation is that 2 is present as a contact ion-pair in which the cation is very near to proton A; with lithium centred above the 5-membered ring at the same side as the helical arm this requirement is rather well fulfilled.

The other data fit rather well into this picture. The aromatization of the five-membered ring in the conversion of 1 into 2 does not lead to  $\delta$ -values for A', B', C' and D', similar to those of 3, because of the additional effect of the negative charge.  $\Delta\delta$ -Values for these protons in 1 and 2 correspond rather well, however, with those of fluorene (4) and fluorenyl anion, (5), especially when for the latter compound  $\delta$ -values of a contact ion-pair are used, and the same is true for proton E' at the 5-membered ring ( $\Delta\delta$  ca. 2.2 ppm for 1 and 2, and for 4 and 5). Small deviations between  $\Delta\delta$ -values in these

Table 1.  $\alpha$ -Values (in ppm) of protons in 1 and 2, measured in THF- $d_8^a$ , and 3, measured in  $CDCl_3$ , compared with data of some related compounds

| Proton | 1                        | 2 <sup>a</sup>                |   | 3                         |
|--------|--------------------------|-------------------------------|---|---------------------------|
| A      | 8.09                     | 8.80                          |   | 7.58                      |
| B      | 7.18                     | 6.80                          |   | 6.65                      |
| C      | 7.52                     | 7.17                          |   | 7.18                      |
| D      | 7.85                     | 7.73                          |   | 7.78                      |
| A'     | 6.39                     | 6.73                          |   | 7.58                      |
| B'     | 6.75                     | 6.19                          |   | 6.65                      |
| C'     | 7.13                     | 6.73                          |   | 7.18                      |
| D'     | 7.61                     | 7.47                          |   | 7.78                      |
| E'     | 4.43 and 4.09            | 6.39                          |   | 7.87                      |
|        | fluorene, 4 <sup>d</sup> | fluorenyl anion, 5            |   | phenanthrene <sup>d</sup> |
|        |                          | contact ion-pair <sup>b</sup> | solvent-separated ion-pair <sup>b,c</sup> |                           |
| A'     | 7.79                     | 8.00                          | 7.82                                      | 8.65                      |
| B'     | 7.37                     | 6.55                          | 6.35                                      | 7.61                      |
| C'     | 7.29                     | 6.90                          | 6.73                                      | 7.57                      |
| D'     | 7.53                     | 7.38                          | 7.21                                      | 7.86                      |
| E'     | 3.91                     | 6.04                          | 5.82                                      |                           |

a.  $\delta$ -Values of 1 in THF- $d_8$  and  $CDCl_3$  are nearly equal.

b. Ref. 9; the contact ion-pair is fluorenylsodium in THF;  $\delta$ -values vary slightly with the alkalic metal in the order of Na>K>Rb.

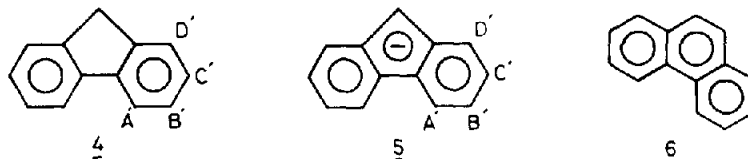
c. Ref.10; data of fluorenyl lithium in THF, which consists of solvent-separated ion-pairs for 80%.

d. Measured in  $CDCl_3$ .

two pairs of compound may be due to delocalization of the charge over a larger number of rings in **2** than in **5**, as appears from the  $\delta$ -values of the protons E, F, G and H in **2** (all  $\delta$ -values lower than 7.8 ppm), in comparison with **3** ( $\delta_{E,F}$ 7.87;  $\delta_{G,H}$ 7.92 ppm).

Because the lithium salt of **2**, otherwise than that of **5**, does not seem to form solvent-separated ion pairs in THF, we studied the salt in some more powerfully cation-solvating solvents. A solution of **2** was diluted

ion-pair. The reason why **2** remains existing in a tight ion-pair, even in very polar solvents is not quite clear. A possible explanation may be given by the following reasoning. Tight ion-pairs of planar anions (like **5**) form sandwichlike associates. The possibility of sandwich-like structure remains on going from tight-to loose ion-pairs. Sandwich-like structures are not possible in salts with helical anions. Therefore the tendency to have the two ions together (as in contact ion-pairs) predominates.



with dimethoxyethane, what leads to a change of the ion-pair character according to UV spectroscopy.<sup>7</sup> The NMR spectrum of the solution did not change, however.

Preparation of **2** in the very polar, aprotic solvent<sup>8</sup> hexamethylphosphoric triamide (HMPT-d<sub>18</sub>), which is extremely powerful in generating solvent separation in ion-pairs, gave again an intensely purple-colored solution. Even when prepared with metallic lithium in high *vacuo* and keeping the tube sealed and in the dark, the color changed into dark green within 24 h, whereas a deposit appeared in the solution. The NMR-spectrum of a freshly prepared solution was, however, exactly the same as that of a THF solution; it changed only gradually by the appearance of new signals at  $\delta$ 8.0–8.2 ppm, until the original spectrum has disappeared completely after a week and had been replaced by another complex spectrum between 6.5 and 8.5 ppm. Apparently, the lithium salt of **2** arises even in HMPT as a contact

#### REFERENCES

- <sup>1</sup>Part VIII is the previous article in this issue.
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