# REDUCTIVE RING CLOSURE OF HELICENES

Ari Ayalon and Mordecai Rabinovitz*
Department of Organic Chemistry, The Hebrew
University of Jerusalem, Jerusalem 91904, Israel

**Summary**: Reduction of [5]-helicene (1) by alkali metal in THF yields a closed condensed polycylic dianion i.e. benzo[ghi]perylene dianion ($3^=$) The ring closure reaction takes place via a closed dihydro intermediate ($2^=$).

Ring closure reactions of anions are an important method for the preparation of complex polycyclic systems. Such reactions have been employed for the preparation of new oligomers which are of great interest in material science both as neutral and as charged species.[1] Binaphthyl and ortho-terphenyl undergo metal induced ring closure reactions to perylene and triphenylene, respectively.[1,2] Benzil dianion and related heterocyclic derivatives also undergo an unexpected ring closure to form polycarbocyclic or heterocylic systems.[3] In the neutral series ring closure reactions occur via light induced concerted mechanism.[4] The thermally induced ring closure reactions of a charged compound, can take place in one of the following routes: (a) Concerted electrocyclic reactions of the dianion - (b) Recombination of a biradical form of the dianion (bis radical-anion)[2], and (c) Intramolecular addition of the radical-ion to a double bond on the opposite end of the molecule, i.e. - the ring closure occurs before the second reduction takes place, and no [5]-helicene dianion is involved.

We wish to report a spectroscopic follow-up of the ring closure reaction of the doubly charged [5]-helicene (dibenzo[c,g]phenanthrene) (1) - a $24\pi$-electron system. The reduction of the [5]-helicenes 1 as well as 4 is carried out in the nmr tube by an alkali metal in $THF_{d8}$.[5] At the beginning of the reduction of 1 the spectrum of the neutral compound disappears and the solution becomes pale red. As the colour turns dark purple, a new spectrum, assigned to the dihydro intermediate, is observed, i.e. 1a,12a-dihydrobenzo[ghi]perylene dianion ($2^=$) (Table 1).

The spectrum of $2^=$ consists of four doublets, two singlets and one double doublet. This pattern is different from that of the neutral 1 which consists of four doublets, one singlet and two double doublets (Table 1). The band at 5.49ppm of $2^=/2Na^+$ appears as a singlet and no coupling to a vicinal proton could be observed due to their mutual stereochemistry. However, the $^{13}C$ satellites ($^1J_{C-H}$ = 123Hz) of this singlet appear as doublets ($^3J_{H-H}$=11Hz). It therefore follows that C-7a and C-7b of $2^=$ are $sp^3$ hydridized

carbons. The scalar coupling between protons H-7a and H-7b proves the formation of a new covalent bond existing between carbons C-7a and C-7b[6]. The value of the coupling constant and the fact that we failed to observe a through-space interaction between H-5a and H-5b in a NOESY experiment of $5^=$, where these protons are no longer equivalent, suggest that these protons in $2^=$ and $5^=$ appear in an _anti_ configuration.

After a few days of exposure of $2^=$ to the alkali metal a new spectrum is observed, while the spectrum of $2^=$ has disappeared. This process is accelerated by raising the temperature to 25-30$^o$C. The new spectrum is assigned to benzo[_ghi_]perylene dianion ($3^=$), and shows an identical spectrum to the one obtained from the reduction of an authentic sample of **3** by an alkali metal. Reaction of $3^=$ with oxygen afforded **3**. From the chemical shifts of $3^=$ (table 1) it can be seen that dehydrogenation of $2^=$ yields a paratropic $4n\pi$ species[7]. In contrast to $3^=$, anion $2^=$ contains $(4n+2)\pi$-electrons and is hence diatropic[8]. Anion $5^=$ behaves similarly to yield $6^=$.
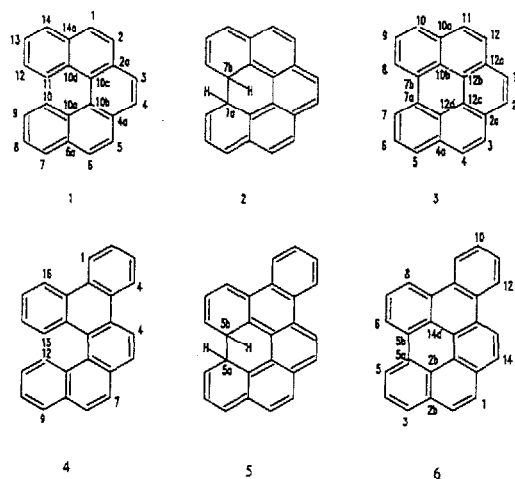


MNDO[9] calculations that have been carried out on the lithium salt $1^=/2Li^+$ show that the most stable structure for the dilithium salt is the one in which the two lithium atoms are located above and below the two terminal rings in such a way that each lithium atom is close to the opposite ring (Figure 1a). This structure gives the lowest energy with two open shells i.e. a biradical form. The calculated radical monolithium $1^{\cdot-}/Li^+$ is found to be most stable when the lithium atom is located above a terminal ring inside the helix. The charges on C-10 and C-11 are -0.35 and -0.07 respectively. The lithium atom is located above the ring containing C-10. The difference in charge between the two carbons suggests an attraction between them in the radical anion stage. The structure of $2^=/2Li^+$ is found to be most stable in an _anti_ configuration (Figure 1b) where the lithium atoms are located

in the same sense as in $1^=/2Li^+$. Calculations show that the syn form of $2^=/2Li^+$ in which the two lithium atoms are located at the the same side of the terminal rings (Figure 1c) is about 8 kcal/mole higher in energy than the anti form.

From the calculations it appears that most of the charge on the anionic moiety is located on the terminal rings, both in $1^=$ and in $2^=$. In $1^=/2Li^+$ most of the charge is concentrated on carbons C-10 and C-11 (-0.43 units of charge on each carbon) and on C-7, C-14 (-0.26 on each). All other carbons bear very small negative charges, thus suggesting a localized dianion.

In $2^=/2Li^+$, however, most of the negative charge is located on carbons C-7a and C-5 (and C-7b, C-9), but in contrast to $1^=$ the other carbons are also considerably charged in an alternant fashion, in accordance with the spectroscopic observation as these carbons and the protons attached to them appear at the highest field (Table 1).

Table 1: Proton and Carbon NMR Chemical Shifts

| Protons[a]: | H-10(H-11) | H-9(H-12) | H-8(H-19) | H-7(H-14) | H-6(H-1) | H-5(H-2) | H-4(H-3) |
|---|---|---|---|---|---|---|---|
| 1 | 8.55(d) | 7.33(dd) | 7.58(dd) | 8.05(d) | 7.99(d) | 8.03(d) | 8.00(s) |
| | H-7a(H-7b) | H-7(H-8) | H-6(H-9) | H-5(H-10) | H-4(H-11) | H-3(H-12) | H-2(H-1) |
| $2^=/2Na^+$ | 4.96(s) | 3.67(d) | 5.97(dd) | 3.95(d) | 6.17(d) | 6.48(d) | 6.22(s) |
| $2^=/2Li^+$ | 4.37(s) | 3.53(d) | 5.89(dd) | 3.95(d) | 6.19(d) | 6.50(d) | 6.25(s) |
| $3^=/2Na^{+b}$ | | 1.2(d) | 4.17(dd) | 2.35(d) | (2.76)(d) | (3.02)(d) | 2.95(s) |
| $3^=/2Li^{+b}$ | | 1.32(d) | 4.00(dd) | 3.22(d) | (2.58)(d) | (2.78)(d) | 2.73(s) |
| $3^b$ | | 9.21(d) | 8.32(dd) | 8.12(d) | (8.21)(d) | (8.26)(d) | 8.47(s) |

| Carbons[a]: | C-4 | C-4a | C-5 | C-6 | C-6a | C-7 | C-8 | C-9 | C-10 | C10a | C-10b |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 128.4 | 128.0 | 128.6 | 127.4 | 134.1 | 129.0 | 127.3 | 125.4 | 130.0 | 132.0 | 133.7 |
| | C-2 | C-2a | C-3 | C-4 | C-4a | C-5 | C-6 | C-7 | C-7a | C-12d | C-12c |
| $2^=/2Na^{+b}$ | 118.1 | (110.4) | 125.0 | 120.6 | (125.5) | 77.2 | 129.9 | 85.2 | 49.8 | (133.3) | (140.0) |
| $3^=/2Na^{+b}$ | 128.5 | (122.8) | 116.5 | 103.7 | (134.3) | 98.6 | 136.0 | 92.3 | (137.3) | (148.1) | (144.9) |
| $3^=/2Li^{+b}$ | 128.1 | (125.3) | 115.8 | 102.0 | (134.3) | 99.1 | 135.0 | 95.5 | (137.7) | (151.2) | (146.3) |

[a] In ppm relative to $Me_4Si$ (THF-$d_8$), 240K.
[b] Data in brackets are assigned tentatively.

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Calculated structure of $1^=/2Li^+$     anti configuration     syn configuration.[9]

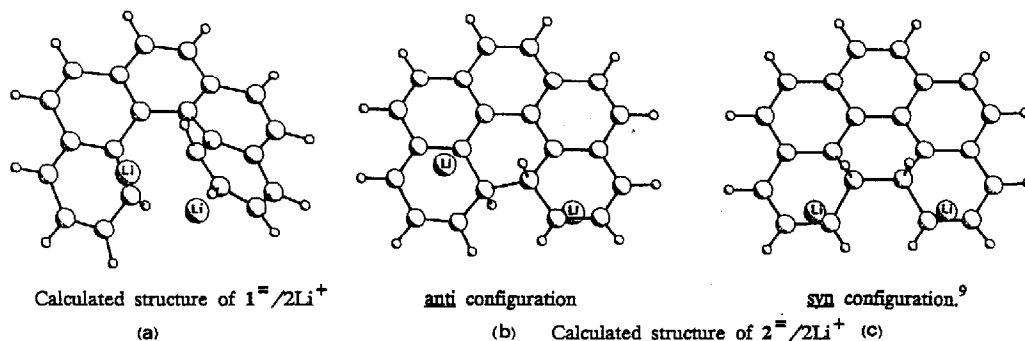(a)      (b)    Calculated structure of $2^=/2Li^+$ (c)

Figure 1

## References

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