# **Development of Expanded Porphyrins**

Literature discussion utilizing two articles by Jonathan L. Sessler et al, *J. Org. Chem* **1987**, *52*, 4394-4397, <https://doi.org/10.1021/jo00228a048> and *J. Am. Chem. Soc* **1988** *110***,** 5586-5588*,* <https://doi.org/10.1021/ja00224a062>

This VIPEr Learning Object is dedicated to Prof. Sessler, the recipient of the Ronald Breslow Award for Achievement in Biomimetic Chemistry at the ACS National Meeting Spring 2021.

**Guiding Questions for** *J. Org. Chem* **1987**, *52*, 4394-4397

1. Macrocycle **1** is described as “synthetic analogues for biologically important porphyrinogens.” Draw the structure of porphin, the simplest porphyrin, and list 3 differences between its structure and the structure of macrocycle **1**.

 

2. After this article was published, macrocycle **1** and related compounds have come to be called “texaphyrins.” Postulate the origin of this name. (Hint: consider the institution where Prof. Sessler is a faculty member.)

3. In the synthesis of macrocycle **1**, what is a likely reason that the authors incorporated 4 ethyl groups and 2 methyl groups onto the periphery of the compound rather than placing hydrogens in those positions?

**Guiding Questions for** *J. Am. Chem. Soc* **1988** *110***,** 5586-5588

4. Write a chemical equation that describes the synthesis of compound **3** based upon the description in the article.

5. What is the covalent bond classification (CBC) of the complex cation contained in compound **3**? What is its corresponding equivalent neutral class? (Hint: look carefully at the 5 nitrogens and the placement of the  bonds in compound **3**.)

6. (a) On page 5587, the authors mention that compound **3** can be considered either an 18 -electron or a 22 -electron system. Draw the structure of **3** and indicate the 18 and 22 electrons in the -system.

(b) With either 18 or 22 electrons, compound **3** would be aromatic. Use Huckel’s rule to show how this is true.

(c) What evidence do the authors provide to support their assertion that compound **3** is aromatic?

7. What is the unusual molecular geometry of compound **4**?

8. Sketch the d-orbital splitting diagram for complex **4** and populate it with the correct number of d electrons. Is compound **4** paramagnetic or diamagnetic?

9. Why did the authors cite the articles in reference 25(a)-(e)?

10. In the past 30 years since the publication of this article, the application of metal complexes similar to **3** has been developed. Briefly summarize the application of such a complex that the Sessler research group reported in 2020 (see [https://doi.org/10.1021/jacs.0c04387)](https://doi.org/10.1021/jacs.0c04387).