

# A JOURNEY FROM 1,3-(DIAMINO)OXYALLYL CATIONS TO NON-KEKULÉ KETOCYANINES

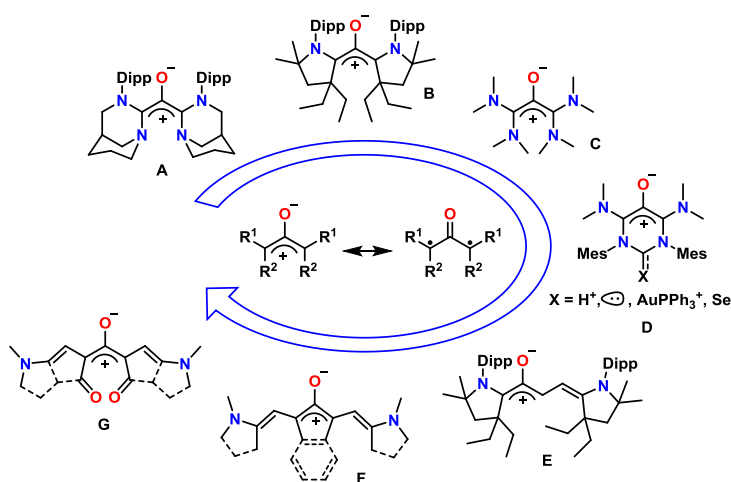


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**Summary:** Oxyallyl cations are non-Kekulé molecules that can only be assigned to zwitterionic or of capto-dative patterns allows them to be not only bench stable but also air-stable. Thus, while strong donating amino groups allow for the design of persistent versions (**A**, **B** and **C**),<sup>[1]</sup> the combination of amino groups and electron-poor amidinium moiety within the same ring leads to an unprecedented air-stable oxyallyl cation **D**, which upon deprotonation it leads to a stable carbene and its related complexes.<sup>[2]</sup> The formal homologation of these species, by extending the conjugated skeleton, leads to a family we named non-Kekulé ketocyanines. These dyes are expected to have a narrower orbital frontier gap resulting in remarkable properties, including a red shift absorption, original redox activity, diradical character, etc.<sup>[3]</sup> These unusual structures have long been regarded as non-viable synthetic targets and fine tuning and design are required, all of which will be discussed in this contribution. More precisely, two families of dyes will be presented, including sterically crowded cyanines (**E**) and electronically stabilized models (**F** and **G**) by introducing electron-withdrawing groups in order to enhance the capto-dative effect.



**Fig. 1** Development of (diamino)oxyallyl cations (**A-D**) towards non-Kekulé ketocyanines (**E-G**).

## References:

1. For a review on the quest for observation and isolation of oxyallyl derivatives, see: Regnier, V.; Martin, D. *Org. Chem. Front.* **2015**, *2*, 1536-1545.
2. Tomás-Mendivil, E.; Devillard, M.; Regnier, V.; Pecaut, J.; Martin, D. *Angew. Chem. Int. Ed.* **2020**, *59*, 11516-11520.
3. Yesudas, K.; Jemmis, E. D.; Bhanuprakash, K. *Phys. Chem. Chem. Phys.* **2015**, *17*, 12988-12999.