



Mendeleev 2024

XIII International Conference on Chemistry
for Young Scientists

BOOK OF ABSTRACTS



St Petersburg
University

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**XIII International Conference on Chemistry
for Young Scientists “MENDELEEV 2024”**

St Petersburg, Russia
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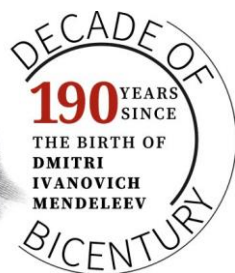
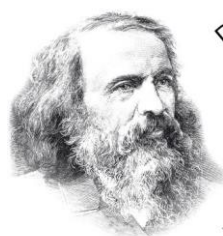
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THEORETICAL STUDY OF «FLIPPING» METALATION OF 4-DIMETHYLAMINOPYRIDINE

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In the 4-dimethylaminopyridine (DMAP) molecule, conjugation of the NMe₂ group leads to suppression of the DOM-effect, as a result of which lithiation occurs only at position 2(6) [1]. In this work, we showed that the introduction of a bulky substituent makes it possible to sterically block positions 2(6), which opens the way to selective lithiation of positions 3(5).

Altogether, quaternization of the pyridine nitrogen atom in general leads to the strengthening of the conjugation of the dimethylamino group with the heteroring and disables its ability to coordinate the organometallic reagent, which leaves no room for the manifestation of the DOM-effect. Thus, chemical interactions of DMAP and its 1-substituted derivatives (F₃B-DMAP, Me₃Si-DMAP, *i*-Pr₃Si-DMAP, etc.) molecules with organolithium reagents are controlled only by acidity and steric accessibility of corresponding CH-bond.

We have developed a new method for assessing the steric accessibility of various positions of the pyridine ring. This method consists of calculating the isosurface region of electron density 0.001 a.u., limited by the electron density basin of the atom under study. The boundaries of the basin are set by the conditions of zero flux of the electron density gradient (Fig. 1). Thus, in DMAP and F₃B-DMAP molecules protons at positions 2(6) are more accessible for organometallic reagent. When moving to Me₃Si-DMAP and *i*-Pr₃Si-DMAP, position 3(5) becomes more sterically accessible. In general, the larger the substituent at position 1 becomes, the more preferable position 3(5) becomes. Moreover, the organolithium reagent (*t*-BuLi·THF₂) is able to coordinate to the aza group of DMAP, thereby sterically blocking the 2(6) positions for the metalation reaction.

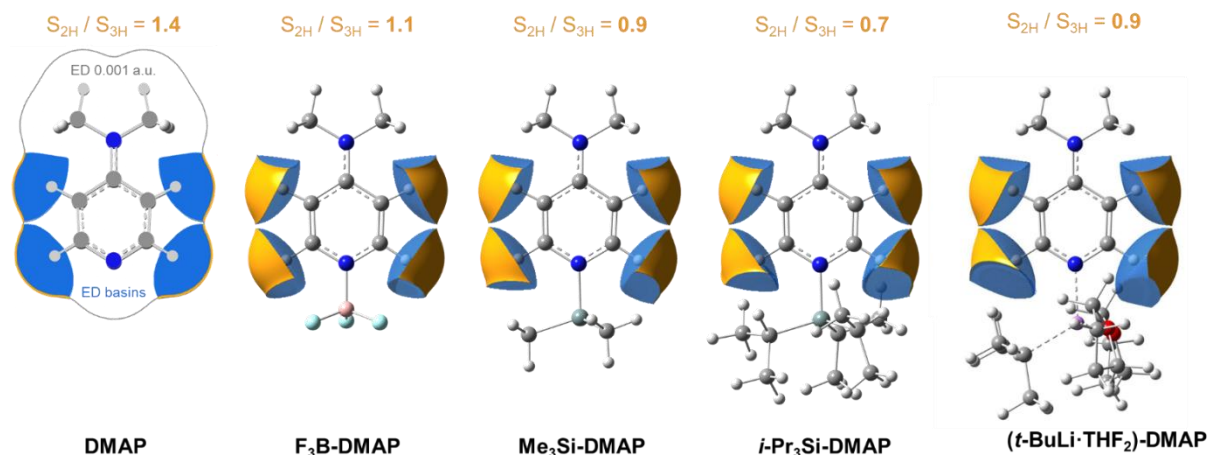


Figure 1. The accessible surface area of pyridine protons in DMAP and its 1-derivatives. The relative ratio of accessible surface areas of C2-H and C3-H is given.

Finally, in addition to steric accessibility, the strength and polarity of CH bonds plays a key role in metalation reactions. CH-polarity has been estimated by the distance between the minima of electron density and electrostatic potential, along the bond path. It has been shown that quaternization of the pyridine nitrogen atom increases the polarity of all CH bonds, especially the C2-H bond.

References

[1] *Chem. Rev.* **1997**, *97*, 721

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