THE ROUTE TO TRANSITION METAL COMPLEXES WITH AZAHELICENES

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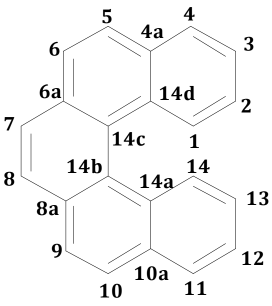
ABSTRACT

Azahelicenes possess an extended conjugated π system which can endow their complexes with useful optical properties, including intense absorption bands in the visible region of the spectrum and photoluminescence. As such, azahelicene complexes may be regarded as promising functional components of light-harvesting and energy transfer systems. For this reason, mono- and diaza[5]helicenes were approached on one hand through gas-phase quanto-mechanic calculations aimed to determine the availability of the nitrogen(s) lone pair and on the other side through X-ray diffraction of their crystals, with the purpose to shed light on the intermolecular forces driving the formation of well-ordered structures in the solid state. Furthermore, N-alkylation of some of these molecules was realized, in order to relate the ease of formation of quaternary salts with the results obtained by density functional calculations. These results provide a rationale for designing new azahelicene-transition metal complexes.

Keywords: Azahelicenes, Transition metal complexes, DFT calculations

The question of electron availability of the different atoms in the structures under investigation (Fig.1) was addressed from different standpoints, with the ultimate purpose of providing a rationale for the design of new azahelicene-transition metal complexes.[1]



1-7	1- to 7-aza[5]helicene
8	5,9-diaza[5]helicene
9	4,10-diaza[5]helicene
10	5,10-diaza[5]helicene
11	2,13-diaza[5]helicene
12	7,8-diaza[5]helicene

Figure 1. A generic [5]helicene with numbering of the skeletal positions.

Proton Affinities (PA) are distributed in the range 995-1010 kJ/mol; in the literature, compounds with PA around 1000 kJ/mol are referred to as *superbases* [19,20]. In comparison, PA of quinoline is considerably lower.

Several symmetric and asymmetric diaza[5]helicenes were also studied, namely the asymmetric 5,9-diazahelicene (**8**) and 4,10-diazahelicene (**9**) and the symmetric 5,10-diazahelicene (**10**) and 2,13-diazahelicene (**11**), as well as 7,8-diaza[5]helicene (**12**) in which case both mono- (**12a**) and di-N-oxide (**12b**) were also taken into account. PA was calculated for both nitrogen atoms, bearing to different values when the two atoms are non-equivalent. In the case of compounds **12a** and **12b**, PA was calculated for protonation of both the non-oxygenated nitrogen atom and the oxygen atom(s).

These calculations give an idea of the availability of lone pairs for a dative bond in a metal-helicene coordination complexes, but the formation and the thermodynamic stability of these latter are also influenced by other factors, such as steric hindrance, ionic radius of the metallic ion and the chelating effect, that can severely affect the stability of one metal complex compared to another.[2]

N-methylation of diazahelicenes give results that are in line with predictions from the theoretical calculations since, as expected, quaternarization of one nitrogen influences the other nitrogen's electron availability strongly or weakly, depending on the relative position of the two atoms. A consequence of this is that, by exploiting this effect, it would be possible to N-alkylate one of the nitrogens, thus making the helicene much more water-soluble, keeping the other nitrogen available for complexation, which could prove useful, e.g., for biological studies.[3,4]

The molecular and crystal structure of 2,13 diaza-[5]helicene (**11**) has been characterized by X-ray crystallography since the relative position of the two nitrogen atoms suggests the possibility of effective complexation. Compounds **12**, **12a** and **12b** were also examined due to their remarkable ease of crystallization, which suggests particularly strong interactions in the solid state. The molecular arrangements in the crystals can be compared with those observed in the previously published crystal structures of other diaza[5]helicenes.[5]

Work is in progress towards the realization of complexes with other transition metals as well as with other helicenes, possibly with a more extended conjugated system (aza[6]helicenes) .

References

[1] T.Caronna, F.Castiglione, A.Famulari, F.Fontana, L.Malpezzi, A.Mele, D.Mendola, I.Natali Sora, *Molecules*, 17, 463-79, (2012).

[2] S.Abbate, T.Caronna, A.Longo, A.Ruggirello, V.Turco Liveri, *J.Phys.Chem.B*, 111, 4089-97, (2007).

[3] R. Passeri, G. G. Aloisi, L. Latterini, F. Elisei, T.Caronna, F.Fontana, I.Natali Sora, *Photochem. Photobiol. Sci.*, *8,* 1574-1582, (2009).

[4] L. Latterini, E. Galletti, R. Passeri, A. Barbafina, L. Urbanelli, C. Emiliani, F. Elisei, F. Fontana, A. Mele, T. Caronna, *J. Photochem. Photobiol. A: Chemistry 222*, 307-313, (2011).

[5] C.Bazzini, T.Caronna, F.Fontana, P.Macchi, A.Mele, I.Natali Sora, W.Panzeri, A.Sironi, *New J.Chem*, 32, 1710-17, (2008).