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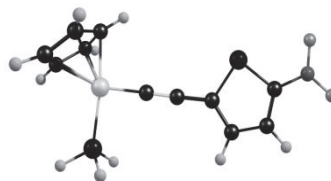
## FIRST HYPERPOLARIZABILITY OF SOME NICKEL- ACETYLIDE COMPLEXES: A DFT STUDY

**Ana Barrocas\***, Paulo J. Mendes, A. J. P. Carvalho

*Centro de Química de Évora, Universidade de Évora, Rua Romão Ramalho, 59, 7000-671 Évora, Portugal*

\*ana.filipa.barrocas@gmail.com

The search for new organometallic materials with second-order nonlinear optical (SONLO) properties is currently the subject of considerable interest due to their potential technologic applications in photonic devices for telecommunications and optical computing. Experimental systematic studies were made on half-sandwich complexes presenting nitrile and acetylide benzene and thiophene-based chromophores [1-3]. The results revealed that the combination of acetylide thiophene ligands with appropriate organometallic fragments would maximize the SONLO response. Also, recent TD-DFT studies on  $\eta^5$ -monocyclopentadienyliron(II) complexes with substituted thienyl-acetylide ligands revealed the fundamental role played by the organometallic fragment on the corresponding SONLO properties [4].



**Figure 1.** Optimized structure for  $\text{NiCp}(\text{PH}_3)\text{CC}\{\text{SC}_4\text{H}_2\}\text{NO}_2$

In our continuous effort to get a better understanding on the electronic factors that may dictate the SONLO properties of  $\eta^5$ -monocyclopentadienylmetal complexes with substituted thienyl-acetylide chromophores, we report herein the preliminary density functional theory (DFT) and time-dependent DFT (TD-DFT) results on the complexes  $[\text{NiCp}(\text{PR}_3)(\text{CC}\{\text{SC}_4\text{H}_2\}_n\text{Y})]$  ( $\text{R}=\text{H}, \text{Ph}$ ;  $\text{Y}=\text{CHO}, \text{CN}, \text{NO}_2$ ;  $n=1,2$ ) using the Gaussian03W program package. For instance, Figure 1 shows the optimized structure for  $\text{NiCp}(\text{PH}_3)(\text{CC}\{\text{SC}_4\text{H}_2\}\text{NO}_2)$ . The effect of the phosphine, the Y-substituent and the conjugated length of the chromophore on the first hyperpolarizability will be evaluated. Some experimental spectroscopic data will be also explained on the basis of the TD-DFT calculations.

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