Among the rare classes of molecules that exhibit both reversible thermo and photochromism in the crystalline state, N-salicylidene aniline aminopyridine can be highlighted.\(^1\) In this work, we have studied the influence of the increase of flexibility and electronic conjugation loss among N-salicylidene aminopyridine derivatives on the optical properties after the introduction of a methylene spacer. Five N-(5-chlorosalicylidene)aminomethylpyridine derivatives were successfully synthesized and their structural and solid state optical properties analyzed. Yellow crystalline powders of CH\(_2\)L\(^3\) and CH\(_2\)L\(^4\)-Cl\(^-\) present both thermo- and photochromism whereas CH\(_2\)L\(^2\) and CH\(_2\)L\(^4\) do not show any switching properties, as probed by diffuse reflectance spectroscopy. Contrary to structural-optical expectations, non-photochromic CH\(_2\)L\(^3\) molecule (P2\(_1\)/n) shows an open crystal structure, and photochromic molecules CH\(_2\)L\(^3\)-Cl\(^2\) (P2\(_1\)/c) present a closed crystal packing, revealed by single crystal X-ray diffraction, which is typical of exclusively thermochromic molecules. After UV irradiation, trans-keto* emission observation in CH\(_2\)L\(^2\) and CH\(_2\)L\(^4\) indicates the unexpected formation of trans-keto form, in these non photochromic anil molecules. Radiative relaxation of the trans-keto* form is in addition detected, for the first time, by fluorimetry for all trans-photochromic anil molecules. Radiative relaxation of the trans-keto* emission in non photochromic N-salicylidene aminomethylpyridines: a structural study. Pierre-Loïc Jacquemin, François Robert, Bernard Tinant, Yann Garcia. Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain, Belgium. E-mail: pierre-loic.jacquemin@uclouvain.be

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N-methylbenzoimidazole-2-selone-dichlorine (1) and benzothiazole-2-selone-dichlorine (2) have been synthesized by the treatment of the corresponding selones with sulfuryl dichloride in dichloromethane. The X-ray crystal structure determinations of 1 and 2 show their 10E3 T-shaped hypervalent chalcogen adduct natures. The both structures are essentially zwitter-ionic, a negative charge resides on the SeCl\(_2\) moiety and a positive charge is supported by the nitrogen atoms. The CSe distances of 1.896(2) Å in 1 and 1.898(2) Å in 2 are representative of the single bonds. Interestingly, the almost linear Cl-Se-Cl systems in 1 \([174.60(2)]\) and 2 \([179.41(2)]\) are differently orientated in relative to the organic fragment plane. In 1, the SeCl\(_2\) moiety is roughly perpendicular to the benzoimidazole plane \([68.73(3)]\), whereas, in 2, this moiety is approximately coplanar to the benzothiazole plane \([30.1(1)]\) (see the figures below). Apparently, the observed planar conformation of 2 is explained by the absence of the steric hindrances, i.e., bulky substituent in the 1-position of the five-membered ring, for the formation of the strong intramolecular N3H3...Cl2 hydrogen bond. In the case of 1, the Cl2 chlorine atom forms the strong intermolecular N3H3...Cl2 hydrogen bond. Due to the hydrogen bonding interactions, the SeCl\(_2\) moiety in 1 and 2 has the asymmetric geometry with the longer SeCl2 bond \([2.5374(5)]\ Å in 1 and 2.4622(6) Å in 2\) as compared to the SeCl1 bond \([2.3352(5)]\ Å in 1 and 2.3377(6) Å in 2\). Thus, the structures of 1 and 2 clearly demonstrate the free rotation of the SeCl\(_2\) moiety around the CSe bond that, in turn, confirms the absence of its significant double character.

Keywords: selenides; hypervalent compounds; X-ray crystallography