

s7.m6.p3 **Structural characterization of a photoactivable caged hydroxide.** A. Bacchi^a, D. Rogolino^a, P. Pelagatti^a, C. Viappiani^b, S. Abbruzzetti^b. *Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Parco Area delle Scienze 17A, I-43100 Parma-Italy. Dipartimento di Fisica, Università di Parma, Parco Area delle Scienze 17A, I-43100 Parma-Italy.*

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There is a general interest in compounds that are able to release an active species under controlled conditions, the so-called "caged compounds". We are interested in investigating fast events in protein folding triggered by proton transfer reactions and to this purpose we have used photoactivatable caged compounds. Proton transfer reactions are among the fastest known reactions and their kinetic characterization has become feasible only after the introduction of photoactivatable caged compounds that release protons or hydroxide ions. The compound 4,4'-bis(dimethylamino)triphenyl methane leuco hydroxide (**1**) was synthesized by hydrolysis of the product of the reaction between 4,4'-bis(dimethylamino)benzophenone and phenyl lithium in ether. The solid-state structure of **1** has been studied by X-ray diffraction techniques at room temperature on a freshly prepared crystal and, after one month, at 123 K, on the same crystal, which presented a marked blue color. The molecular arrangement in the solid state is based on pyramidal hydrogen-bonded tetramers similar to those observed in the crystal structure of triphenylmethanol. The tetramers are made by two kinds of crystallographically different molecules. Three equivalent molecules are oriented so that their OH groups are hydrogen-bonded together in a triangle which is the base of the pyramid. The fourth molecule lies on a three-fold axis and caps the basal triangle by acting as hydrogen bond donor towards the three equivalent basal oxygens. The crystallographic distinction between basal and apical molecules reflects a functional differentiation within the tetramer, shown by the bonding geometry and by the analysis of the thermal motion at different temperatures. This suggests that basal and apical molecules are 'bond length isomers', and that in the apical molecule the C-O bond is weaker, favouring the incipient transfer of the O-H group into the C-O-H cluster and leaving a certain carbocationic character on the carbon atom. The partial conversion of the pale yellow form to the blue one which has occurred in the crystal over a one month period can be explained in terms of heterolytic scissions of the apical C-O bonds, producing stable carbocations and hydroxyl anions trapped in the hydrogen bonds cages in the middle of the tetramers. The presence of a certain amount of dissociated molecules in the blue crystal is detectable by comparison of the thermal parameters in the two data sets.