

## 2-(Hydroxyimino)aldehydes

2-(Hydroxyimino)aldehydes  $RC(=NOH)CHO$  are a class of organic compounds that has been sporadically investigated in the scientific literature, mainly in the context of organic synthesis.

Convenient methods for the synthesis of 2-(hydroxyimino)carbonyl compounds are being continuously proposed: Sugamoto resorted to reduction nitrosation with *t*-butyl nitrite and triethylsilane in the presence of cobalt(II) porphyrin as a catalyst; 3-chloro-2-hydroxyiminopropanal was prepared by Gilchrist and Roberts by addition of nitrosyl chloride to acrylaldehyde at low temperature; Baidya and Yamamoto obtained several HIAs through oxidation of the corresponding aldehydes with aluminum nitrite. Finally, a convenient -oximation reaction of aldehydes has been developed in our laboratory, which affords good to excellent yields of HIAs via organo-SOMO catalysis. This reaction affords HIAs bearing substituents of different bulk and nature, so that a systematic investigation of their physico-chemical properties is now accessible. Oximes in general are highly versatile molecules and HIAs may exhibit yet more interesting properties, thanks to the presence of an oxime and aldehyde group in adjacent position.

In the context of our research on stimuli-responsive polymers bearing the 2-(hydroxyimino)aldehyde (HIA) group, we explore the photochemical behavior and physico-chemical properties of a number of HIAs. Interpretation of experimental data is supported by quantum mechanical calculations.

### 1) Photochemistry and physico-chemical properties

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Recently, we have presented a comprehensive investigation of the photochemistry and physico-chemical properties of this new class of organic compounds. The interpretation of experimental NMR, acidity and redox properties is corroborated by DFT calculations. UV irradiation ( $\lambda = 350$  nm) results in two main phenomena, i.e. *E/Z* photoisomerization, occurring within two hours, and the slower, irreversible formation of cyclobutanol oxime (CBO) derivatives by a Norrish-Yang cyclization. To our knowledge, this is the first time that CBOs are described in the literature. The predominant initial configuration, the extent of light-induced isomerization and the rate of subsequent thermal annealing to the initial *E/Z* population are strongly dependent on HIA substituent. HIAs bearing primary and secondary substituents yield limited configurational inversion, whereas the presence of a tertiary group results in *E/Z* switch. Thermal relaxation in the dark to the initial configuration proceeds over weeks when HIA substituents are secondary or tertiary and is complete within days with a linear alkyl group. However, our results with a primary substituent bearing a remote methacrylate show that branching next to the HIA is not the only factor affecting the rate of thermal relaxation. Cyclization to CBO begins at the same time as *E/Z* isomerization and becomes predominant over long irradiation times. However, it is possible to obtain *E/Z* inversion with little CBO formation over short irradiation times of an HIA bearing a tertiary substituent.

### 2) Synthesis of new sensitive multi-stimulus methacrylate copolymers

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4-[(hydroxyimino)aldehyde]butyl methacrylate and its RAFT copolymerization with oligo(ethylene glycol) monomethylether methacrylate. For comparison, 6-(hydroxyimino)hexyl methacrylate, containing a free oxime group, and 6-oxohexyl methacrylate, with an aldehyde group, are also synthesized and subjected to RAFT copolymerization with OEGMA. DP(GPC) values of all polymers are in the 18-33 range with  $PDI < 1.2$ . Interestingly, the thermal behavior of aqueous solutions of the 2-(hydroxyimino)aldehyde-containing copolymers exhibit a lower cloud point than their analogs, which comprise only a  $C=N(OH)$  or CHO functionality. This effect can be ascribed to the simultaneous presence of a hydrogen donor and acceptor in the 2-(hydroxyimino)aldehyde group. Moreover, we present evidence for the thermally reversible *E/Z* photoisomerism of the 2-(hydroxyimino)aldehyde group (HIA) both in HIABMA and in its copolymers.