

ABSTRACT

A convenient and efficient method to introduce a halogen atom regioselectively into a methylene group of a 1,3-diketone moiety or to an activated phenyl ring of 1-phenyl-3-(3,5-dimethoxyphenyl)propane-1,3-dione using N-X reagents as the most promising reagents for electrophilic halogenation was shown. Deactivation of the diketo fragment of the molecule via complexation with BF_2 , leads to regioselective halogenation at positions 2 or at 2,6 in electron-rich phenyl rings depending on the mole ratio of substrate to reagent. Introduction of a halogen atom at the α -position in the 1,3-dione moiety of 1-phenyl-3-(3,5-dimethoxyphenyl)propane-1,3-dione dramatically changes the conformation, being 1,3-diketone in comparison with the parent compound in which the favored form is keto-enolic. The structures of parent compounds and halo derivatives were determined by X-ray analysis in the solid and by spectroscopic methods in solution. DFT calculations were also performed.

A novel fluorescent dye, the BF_2 -derivative of 1-phenyl-3-(3,5-dimethoxyphenyl)propane-1,3-dione showed polymorphism affording two types of fluorescent single crystals: greenish-yellow emitting prism-like crystals and yellow-emitting plate-like crystals depending on the way of recrystallization. The molecular structure was an anti-conformer in relation to the methoxy group bonded to the phenyl ring or was a syn-anti-conformer, respectively. Solid A (anti-conformer) possesses numerous chromic effects, including mechano-, thermo- and chrono-chromism, the last, however, to a lesser extent, as well as the rearrangement of the amorphous phase into a more stable crystalline phase A, associated with crystallization-induced emission enhancement (CIEE). The solid-state emission can be repeatedly switched regarding its color and efficiency with excellent reversibility by external stimuli. On the other hand, crystalline solid B (syn-anti) undergoes thermal interconversion of syn-anti- to the anti-conformer. The dye shows a solvatochromic effect (SE), is aggregation-induced emission (AIE) active and displays via the sublimation process self-assembling crystalline platelike-microstructures or microfibers which reveal an obvious optical waveguide effect.

All six isomers of dimethoxy curcuminoids were prepared. Conformations in the solid state, which were determined by X-ray single crystallography, ^1H MAS and ^{13}C CPMAS solid-state NMR measurements, depend on the position of methoxy groups in curcuminoid molecules. In solution, dimethoxy curcuminoids are present in the forms that can be described in terms of co-existence of two equivalent tautomers in fast equilibrium. The position of methoxy groups has a minor influence on the enolic hydrogen bond. Theoretical calculations show that the energy gap between HOMO and LUMO depends on the position of methoxy groups. Chlorination and bromination at the α -position of the 1,3-diketone moiety do not change the preferential form being cis keto-enol as in parent compounds.

Photostability of curcuminoids is strongly influenced by the position of the methoxy groups (half-lives in exponential decays varied from 10.0 min to 199 min in the case of 3,5-dimethoxy derivative and 2,5-dimethoxy curcuminoid, respectively). All compounds, especially BF_2 derivatives of curcuminoids that have been synthesized exhibit very interesting photochromic properties and some of them show also AIE, solvatochromic and mechanochromic effects.