

A Series of Polymorphs with Different Colours in Diaminodicyanopyrazine Dyes

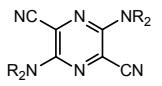
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2,5-Diamino-3,6-dicyanopyrazine dyes have been studied as a novel fluorescent dye because of their intense fluorescence in solution as well as in the solid state [1]. These dyes have also been found to have crystal polymorphs with different colours depending on the amino substituents. The colour difference, in the range from yellow through orange to red, of the polymorphs of dyes **1-4** were investigated in terms of intermolecular interactions.

The colour of these polymorphs were found to reflect different molecular conformation in the crystals. The amino nitrogen in the red and orange phases have a trigonal planar geometry; whereas a tetrahedral conformation of the amino groups was found in the yellow phase. Semi-empirical molecular orbital calculations revealed that this structural feature is well related to the calculated absorption band of a molecule in the crystals. Exciton interaction was also estimated and it was found to be about one order of magnitude smaller than the effect of conformational change. The colour difference is thus considered to be mainly attributed to the change in molecular conformation among the polymorphs.

[1] Matsuoka M., *Colorants for Non-textile Applications*, Freeman H.S. and Peters A.T. ed., Elsevier Science, 2000, 339.

Keywords: dyes, polymorphism, structure-colour relationship



1: R= $-\text{CH}_2-\text{C}_6\text{H}_4\text{Cl}$

2: R= $-\text{CH}_2-\text{C}_6\text{H}_4\text{Cl}$

3: R= $-\text{CH}_2-\text{C}_6\text{H}_4\text{Br}$

4: R= $-\text{CH}_2-\text{C}_6\text{H}_4\text{Br}$