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Two polymorphs with different fluorescent properties of 2,5-bis(dimethylamino)-3,6-dicyanopyrazine dye

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Diaminodicyanopyrazine chromophoric system was developed in 1990's [1]. The derivatives with bulky substituents on the amino groups were found to exhibit a series of polymorphs with different colours [2]. On the other hand, two polymorphs with different fluorescent properties were obtained in the dye having methyl substituents on the amino groups **1**, which is shown in the inset of Figure 1. These two polymorphs are coloured red, but their hues are different, one is dark (**1D**) and the other is bright (**1B**). DSC measurement indicated that **1B** is the stable form and the irreversible phase transition from **1D** to **1B** undergoes. The solid state fluorescence spectra of **1D** and **1B** are shown in Figure 1. These spectra were determined by a conventional fluorophotometer using an accessory for powder samples. The emission maximum of **1B** appears around 637 nm, while that of **1D** shifts to the longer wavelength region with a considerable decrease in the intensity. In order to explain this spectral difference, X-ray structure analysis was performed. Although there was the difference in the planarity of the chromophoric system, molecular orbital calculations showed that there is no remarkable difference in their electronic states corresponding to those in the visible region. The difference was also recognized in their molecular arrangement. In **1D**, molecules adopt a herringbone structure in which the molecules are stacked along the *b*-axis with an interplanar distance of 3.35 Å. In **1B**, molecules are also stacked to form a molecular column. However the large interplanar distance of about 7.08 Å was observed between the stacking molecules, because molecules in the neighbouring columns are slightly inserted between the stacking molecular pair. An interplanar distance and a degree of overlap between stacking chromophoric systems are known to be correlated with fluorescent properties in the solid state [3]. The present difference in fluorescent properties between two polymorphs can be thus attributed to the different molecular arrangement in crystals.

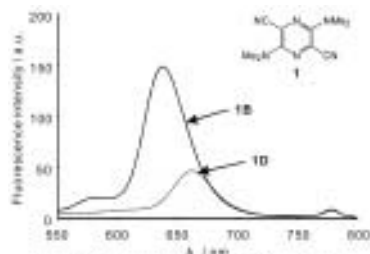


Figure 1 Fluorescent spectra for two polymorphs **1B** and **1D**.

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1-isopropyl-3,5-bis(*o*-fluorophenyl)-1,3,5-triazacyclohexane

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Heterocyclic compounds offer a variety of possibilities for the study of the conformational effects of non bonding electrons [1-2]. The title compound C₁₈H₂₁F₂N₃ adopts a chair conformation with two aryl and one alkyl N-substituents in diaxial-equatorial orientation; two *o*-fluorophenyl in axial and one isopropyl group in equatorial arrangements. It is the product of a mixte condensation reaction between the *o*-fluoroaniline and the isopropylamine with formaline. It's empirical and structural formulas were determined by X-ray analysis [3]. The molecules are located on mirror planes in space group Pnma. The repulsion between axial aryl groups deviates the N-C(aryl) bonds outward from ideal N-tetrahedral angles by 8.11 degrees and lives the N-lone pairs in the thermodynamically stable equatorial position.

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