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Structural and energetic comparison among the stable forms in a polymorphic system of 2,5-diamino-3,6-dicyanopyrazine dyes: the approach toward clarification of polymorph occurrence

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Crystalline materials of organic molecules have attracted attention because they often provide more excellent physicochemical properties than the molecular state [1]. Recently, the example can be easily found in organic optoelectronic materials, such as photoconductors, electroluminescent materials and high-performance pigments. The goal of material design on crystalline molecular solids is to gain a molecule which surely crystallize into the form with a desired property. For this purpose, we should understand the correlation among molecular structure, crystal structure and crystallization. Diaminodicyanopyrazine dyes (Fig. 1), characterized by vivid colour and intense fluorescence, have been developed since 1990's [2]. In a series of the derivatives, some dyes with benzyl substituents on the amino groups were found to exhibit colour polymorphism from yellow to red [3]. Their molecular structures are anticipated exhibiting isostructurality as well as similarity in polymorphic phenomenon, because it is unlikely that such a subtle difference of the substituents gives rise to the serious change of the intermolecular interactions in crystals as well as the degrees of the conformational freedom. However, their occurrences of polymorphism were found to be related with the position and the kind of substituents. The variety of polymorphs was reduced in the following order: in the *para*-derivatives, $1 > 5 > 3$, and in the *ortho*-derivatives, $4 > 2 > 6$, respectively. In this study, this variability was interpreted on the basis of the depth of potential wells of the stable forms. From their thermodynamic relationship, the stable forms of the *para*-derivatives were found to be yellow forms and that of the *ortho*-derivatives were red ones. The calculated lattice energies of the stable forms, corresponding to the depth of the potential well, showed that the yellow form of **3** (**3Y**) has the largest energy among the other stable forms. Only **3Y** did not exhibit the isostructurality in the *para*-derivatives. This indicates that the occurrence of polymorphs in **3** results from the change in the depth of potential well with different packing structures: the deep potential well may reduce the variety of polymorphs.

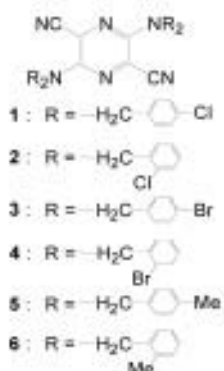


Fig. 1 Chemical structures

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(trans)-4-Chloro-4'-nitrostilbene - a detailed structure analysis of a polar material

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(*trans*)-4-Chloro-4'-nitrostilbene (CNS) has been reported to crystallize in space group $P2_1/c$ [1] but was shown to exhibit Second Harmonic Generation (SHG) if crystallized from the melt [2] or from solution. The SHG response of the material depends on the nature of the solvent used for crystallization.[3] The $P2_1/c$ structure is disordered with the molecules assuming two orientations across a center of symmetry. A careful reinvestigation has revealed the lower symmetry, polar space group $P2_1$. The refinement model allowed for deviations of the site occupancy factor (S.O.F.) from 0.5 and for two domains related by inversion twinning. The S.O.F. was found to depend on the solvent used for crystallization.

solvent	S.O.F.	Flack parameter
acetone	(45.6 ± 0.3) %	(24.5 ± 17.5) %
acetonitrile	(51.1 ± 0.7) %	(12.9 ± 37.4) %
benzene	(42.4 ± 0.3) %	(4.90 ± 21.4) %
DMF	(48.0 ± 0.3) %	(3.5 ± 23.7) %
ethyl acetate	(37.0 ± 0.3) %	(47.2 ± 14.2) %
methanol	(38.5 ± 0.3) %	(51.5 ± 15.0) %
toluene	(40.0 ± 2.9) %	(19.4 ± 15.6) %

Further scrutiny of the data showed weak *superstructure* reflections whose intensities also depend on the solvent. This observation was interpreted in terms of four non-centrosymmetric domains related by twofold rotational symmetry and inversion twinning. Modeling the crystal growth of CNS with a combination of a Markow-chain, an Ising model and Monte Carlo simulations indicated a significant deviation from a S.O.F. of 0.5. The model also predicted two sectors of opposite polarity (parallel to **b**) and apolar sectors.[4] The observed effects on the S.O.F. are not explained by this model, because the solvent is not taken into account. The *surface* polarity of several crystal faces was analyzed by Scanning Pyroelectric Microscopy (SPEM). At least two domains of similar area and of different polarity were recognized.

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