4B2/2004G054

Ab Initio Structure Determination of the colorless form of Thymolphthalein dye by Powder X-ray Diffraction Data

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Introduction

Lactone dyes are widely used as pressure-sensitive papers and pH indicators for its property of the color change by pressure or protonation. While it is suggested that the color changes are caused by opening-closing motion of the lactone ring, there are only a few reports of its crystal structure, because of the difficulty in making good single crystal of lactone dyes. Thus, crystal structure analysis from powder diffraction data is powerful technique to determine the structure of the dye molecule. In this study, the structure of thymolphthalein dye, which is one of the lactone dyes, was determined from high resolution powder diffraction data.

Results and Discussions

The colorless crystals were ground and contained in a spinning 0.5 mmϕ Borosilicate-glass capillary during data collection. X-ray diffraction data were collected on high resolution multiple detector goniometer at the PF 4B2 beamline at rootm temperature, using a wavelength of 1.306Å.

The data were indexed using the first 20 peaks by the program DICVOL04, showing that the cell is monoclinic, lattice parameters a = 11.6166, b = 19.2955, c = 11.6778 (Å), β = 102.004 (°), with figures of merit M(20) = 34.4, F(20) = 120.1. An examination of systematic absences indicates the space group is $P2_1/c$. A Pawley fitting resulted in χ^2(Pawley) = 2.625. Following crystal structure determination was carried out by direct space method with integrated intensities extracted by Pawley refinement.

There are two possible molecular models for Thymolphthalein, one is the lactone form and the other is quinoid form. Therefore, both molecular models were examined in structure determination stage using direct space method. The models were prepared by MMFF calculation using the SPARTAN'04 program. The direct space calculation performed using simulated annealing method by program DASH. The reliability factor of the best solution are *intensity* χ^2 147.1 *profile* χ^2 29.3 for lactone form, *intensity* χ^2 390.0 *profile* χ^2 93.3 for quinoid form. Obviously the result of lactone form was better than quinoide form. The best structure solution was taken as starting structure for Rietveld refinement, which was carried out using the GSAS program. The final Rietveld refinement converged to R_{wp} = 4.09, R_p = 3.00, R_F = 9.01 % (Fig. 2). This result revealed the molecular structure of the colorless powder crystal is lactone form.

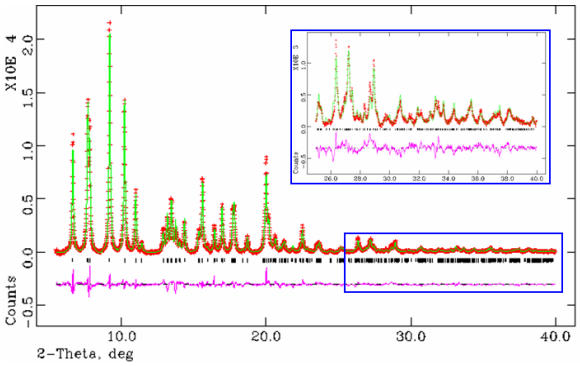
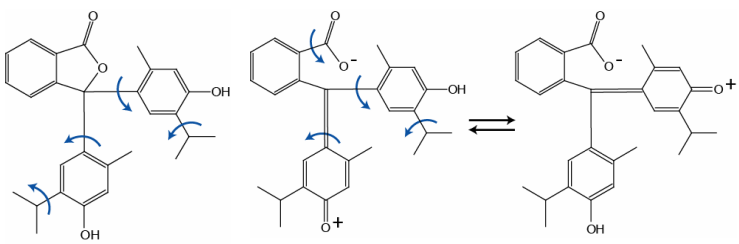


Figure 2 : Final Rietveld plot, red cross : experimental, green solid: calculated, perple lower line : difference

In crystal, O-H···O hydrogen bond (O···O 2.87Å) make thymolphthalein dimer and the hydrogen bond chains are formed by another O-H···O hydrogen bond (O···O 2.82Å) along a axis (Fig.3).



Lactone form Quinoid form

Figure 1 :Molecular structure of Thymolohthalein

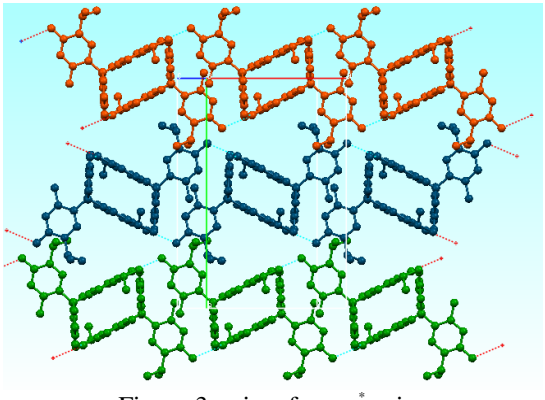


Figure 3 : view from c^* axis

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