

# Development of A New Pyrrolo-Triazole Cyan Coupler

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## Abstract

We developed a new pyrrolo-triazole cyan coupler which could form a cyan dye having excellent hue. 1*H*-pyrrolo[1,2-*b*][1,2,4]triazole coupler not only has excellent color properties but also has good photographic properties. It took 10 years for commercialization, that is, five years for development and the rest for practical application. This new cyan coupler has been introduced in current color paper and color reversal film.

## Introduction

It is well known that in photographic system, phenol or naphthol couplers are generally employed as a cyan coupler. However, dyes formed with these couplers have an unwanted absorption. To solve this problem, recent research explorations have lead to a specific substitution type of the 2,5-dicarbonamido phenols that affect hues with less unwanted absorptions and higher extinctions. From other viewpoints, the field of bridgehead-condensed heterocycles has been focused as a cyan coupler in the past decade. We explored these 5,5-heterocycles systems as a skelton of cyan coupler. As a result, we invented new pyrrolo[1,2-*b*][1,2,4]triazole coupler which could form a cyan dye having excellent hue.<sup>1</sup>

## Results and Discussion

### 1. Molecular design

The structure of new cyan coupler is shown in Table 1. The coupler is ballasted by a highly substituted cyclohexyl ester group of 15 carbon atoms, and bears a strong electron-withdrawing cyano group. The coupling site is -position in the pyrrole ring.

In two-equivalent type, the leaving group is carbamoyloxy group.

Firstly, we investigated pyrrolo-pyrazole coupler. This azomethine dye had few unwanted absorption and showed sharp absorption. However, this type of coupler was unstable itself and it was difficult to make synthesis

because of its lower pKa value. In order to solve this problem, we started to study pyrrolo-triazole coupler.

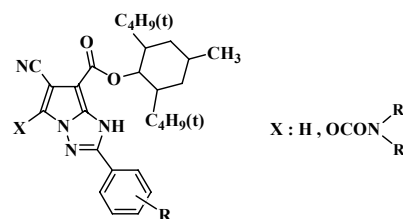
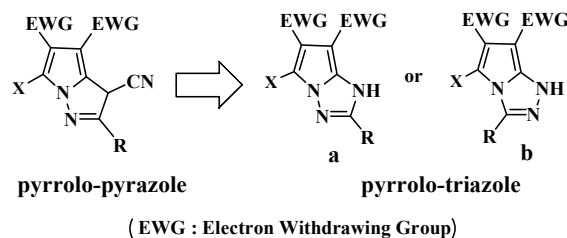


Table 1. Structure of coupler



There are two derivatives in the pyrrolo-triazole (a,b) same as a pyrazolo-triazole magenta coupler. Both couplers exhibit a good performance photographically. The reason we chose pyrrolo[1,2-*b*][1,2,4]triazole (a) is easier to synthesize than synthesis of pyrrolo[2,1-*c*][1,2,4]triazole (b).

We faced many problems to develop this coupler, for instance, dye stability, controlling hue, adjusting pKa value and so on, therefore, we had a long time to improve this type of coupler.

The azomethine dyes formed from this coupler have excellent color properties because of the high planarity (5,5-bicyclic system) in that structure. Especially, cyano and ester group in the pyrrole ring are effective substituents for attaining excellent hue as a cyan dye. Furthermore, 2,6-di-tert-butyl-4-methylcyclohexyl in ester group is the most preferable substituent for attaining stability of the dye.

## 2. Absorption spectra (in solution)

Table 2 shows the structure of the dye and Fig.1 shows absorption spectra in Ethyl Acetate.

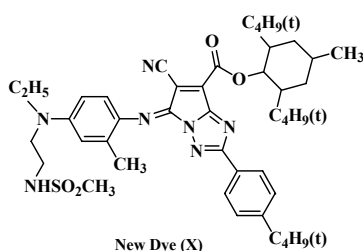


Table 2. Structure of Dye

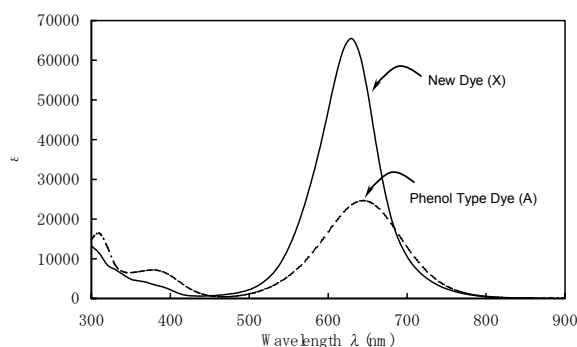


Fig.1 Absorption spectra of cyan dye

New dye's bandwidth exhibits in solution  $BW_{1/2}$  values of approximately 85nm, whereas phenolic cyan dye is of the order of 120nm, and extinction coefficient is about 2.5 times higher than phenolic cyan dye.

## 3. Reflection spectra (in paper)

Fig.2 shows reflection spectra in paper. The new dye indicates ideal hue. The shortwavelength side absorption is sharper than phenolic cyan dye, indicating strong stacking of dyes in paper. The X-ray analysis showed stacking of two molecular dyes.

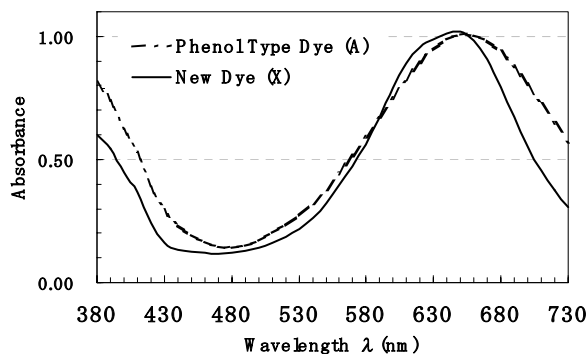


Fig.2 Reflection spectra of cyan dyes

## 4. Dye stability

There was a demand which improves thermal stability more in conventional cyan dyes. Fig.3 shows a data of thermal stability of the new dye. It is approximately 3 times stronger than phenolic cyan dyes. Generally, the dye formed from 5-5 heterocycles couplers resist against thermal fade because the molecular structure is strongly rigid.

Light stability is set to a good level by use of anti fading agent.

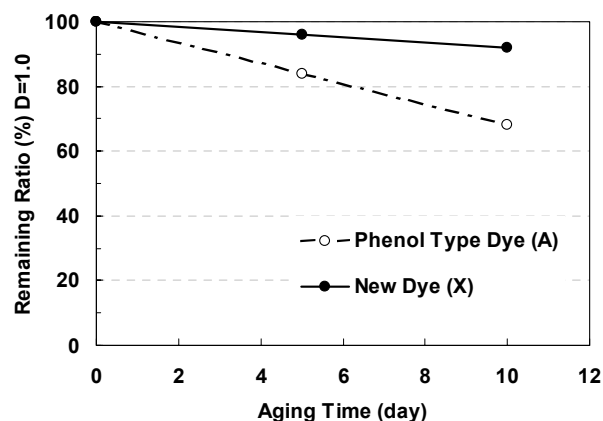


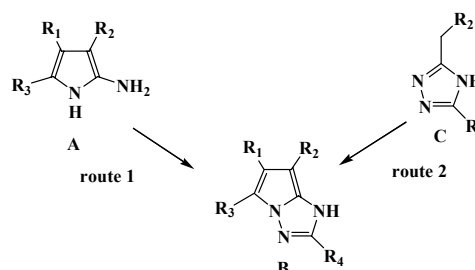
Fig.3 Thermal stability of cyan dyes

## 5. Coupling speed

In spite of having a strong electron-withdrawing group in this coupler, the coupling speed with oxidized developing agent maintain. This reason results from having a high reaction site in the pyrrole ring. Generally, pyrrole ring has a high reactivity with electrophilic reagents.

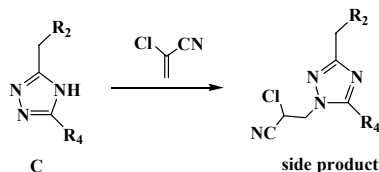
## 6. Synthesis

The synthesis of pyrrolo[1,2-*b*][1,2,4]triazole was already known,<sup>2</sup> but the synthesis of EWG-disubstituted pyrrolo[1,2-*b*][1,2,4]triazoles was not known. Therefore, we needed a new synthetic method of these compounds. Our interest on the synthesis of these compounds let us to study two approaches mainly. One was synthesis from pyrrole ring (route 1), another was synthesis from triazole ring (route 2). Consequently, we found out that route 2 was more effective than route 1. (Scheme 1)

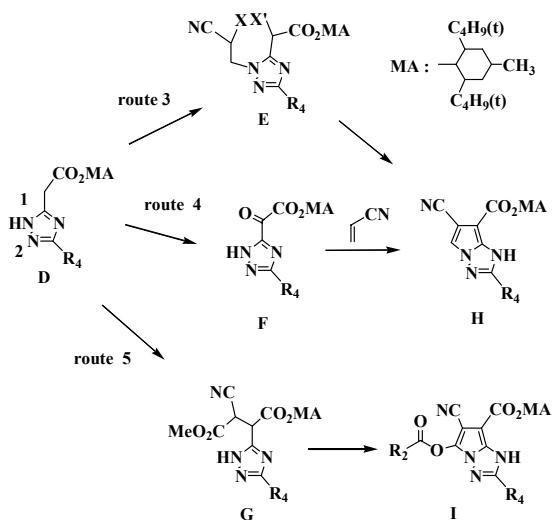


Scheme 1. Two approaches to the pyrrolo[1,2-*b*]triazoles

We developed quite unique synthetic methods, starting from triazoles **D** (Scheme 3). Triazole **D** was known how to make synthesis<sup>3</sup>. There are three methods about four-equivalent (route 3, route 4) and two-equivalent coupler synthesis. (route 5) In route 3, the first step had a problem of regioselectivity of *N*-alkylation. (Scheme 2) This regioselectivity is dependent on the substituent  $R_4$ . The stronger the electron withdrawing group of the substituent  $R_5$ , the higher the regioselectivity of *N*1-alkylation, compared with it, route 5 didn't have such a regioselective problem.

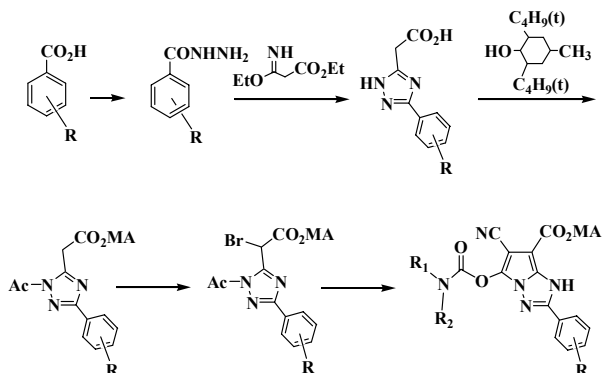


Scheme 2. Unwanted reaction

Scheme 3. Approaches from triazole **D**

Route 4 is a manufacturing synthesis of four-equivalent coupler introduced into the current reversal film.

Route 5 is a very effective route in two-equivalent coupler synthesis. Firstly, there were 10 steps from starting material to coupler, we made effort to optimize synthesis, consequently, it succeeded in synthesis at 5 steps. (Scheme 4)



Scheme 4. Improved synthesis

## Conclusion

We developed a new original cyan coupler, that is, pyrrolo[1,2-*b*][1,2,4]triazole coupler which has excellent hue and good thermal stability. Especially, the reflection spectra indicated ideal hue by stacking of two molecular dyes. Furthermore, we developed the smart process of two-equivalent coupler synthesis.

## References

1. US patent 5,256,526. US patent 5,384,236
2. H.G.O.Becker et al., *Synthesis* **1973**, 414-415.
3. Carroll Temple, Jr. *The Chemistry of Heterocyclic Compounds* **1981**, 37, 30-61.

## Biography

I was born in 1959, and received my B.S. in 1982 and M.S. in 1984 from Kyushu University. I have worked for Fuji Photo Film Co., Ltd. since 1984 and carried out research on the synthesis of organic compounds for photographic materials.