



# Synthesis of tricyanopyrrolidone derivatives as synergists for improving contrast ratio of liquid crystal displays



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## ABSTRACT

The contrast ratio is an important color property of liquid crystal displays. Color properties are classified as colors' purity, contrast ratio, and brightness; these mainly depend on pigment properties. The contrast ratio in particular can be improved by minimizing the light scattering of pigment particles, which is directly related to their degree of dispersion. Therefore, synergists are usually employed to increase the contrast ratio by augmenting the dispersion efficiency. In this study, tricyanopyrrolidone derivatives as blue color synergists were synthesized and examined for their performance to improve the contrast ratio of liquid crystal displays. The results of this study prove that tricyanopyrrolidone derivatives as synergists for blue pigment effectively improve the contrast ratio.

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## 1. Introduction

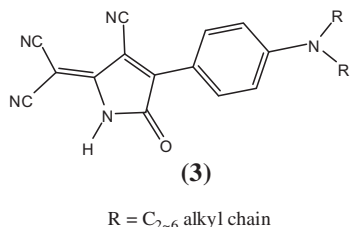
The importance of liquid crystal displays (LCDs) has increased due to the popularity of high-definition televisions and monitors, as well as portable devices such as smart-phones, tablet PCs, and displays, as these devices have continued to necessitate better and better resolutions and picture quality [1–4]. LCDs have color filters that process color images, which consist of red, green, and blue color pixels prepared from a polymeric binder and pigments [5]. During an LCD's image processing, the color filter determines the color properties, which are classified as color purity, contrast ratio, and brightness. We formerly studied that the syntheses of synergists gave rise to higher contrast ratio by modification of red anthraquinone [6]. According to the former study, the synergists improved dispersion of pigments, which gave less scattering of light and good contrast ratio. Even though the properties of dispersants and pigments are known to be important for good dispersion, the former study has proved that synergists as additives are also important to get a better contrast ratio for LCDs. Among the three color properties, this paper will focus on the contrast ratio

synthesizing tricyanopyrrolidone derivatives as synergists in blue. The contrast ratio is important for obtaining a high picture quality, and a poor contrast ratio can neither show deep black nor the precise gradation of black images. Therefore, the contrast ratio is considered an indicator of an LCD's grade in the market.

The contrast ratio is a numerical value that divides the maximum brightness by the minimum brightness. For a good contrast ratio, light should not pass through when polarizers are closed for a dark image. However, a small amount of light does pass through, known as light leakage increased by light scattering of the pigments. From this point of view, to improve the contrast ratio, light scattering should be minimized by particles that have good physical properties such as uniformity of size and shape and small mean size [7,8]. These properties can be obtained by having good pigment dispersion [9,10]. Undoubtedly, as mentioned above, dispersants are important to ensure a good dispersion process, but they are limited regarding ultra-fine particles for color filters. Therefore, a powerful synergist is essential for good dispersion. This is the reason that pigment paste manufacturers are developing more efficient synergists [11].

Synergists as additives usually improve the efficiency of dispersion by preventing the agglomeration of particles. This process improves the particles' physical properties. In this study, three synergists, as shown in Fig. 1, were prepared from malononitrile, diethyl oxalate, and corresponding N,N-dialkyl anilines [12]. The

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**Fig. 1.** The structure of the synergists synthesized from malononitrile and diethyl oxalate.

purity and chemical structures of each synergist were assessed using NMR and Mass spectra.

This paper will discuss the performance of synergists in improving the contrast ratio and compare them with a case without a synergist. For this research, pigment pastes were prepared from these synergists, and the particle sizes of the pastes were analyzed for their dispersion performances. Consecutively, color filter photo resists (CFPRs) were prepared from the pigment pastes to measure and evaluate the contrast ratio.

## 2. Experiment

### 2.1. Equipment

The molecular masses of the synergists were measured using a JMS600 W (JEOL, Japan). The chemical structures and purity of the synergists were analyzed using a 500 MHz NMR (Avance II 500, Bruker, Germany). The  $\lambda_{\max}$  of the synergists was measured using an UV–visible spectrophotometer (UV-1601, Shimadzu, Japan).

The color property and transmittance spectra data were measured using an MCPD 3700 (Otsuka Electronics, Japan). The values of the contrast ratios were recorded using a contrast tester (CT-1, Tsubosaka Electric Co., Japan). A spin coater (Sungwon Electronics, Korea) was used to coat the CFPRs onto glass substrates. The pigments' particle sizes were recorded using a particle size analyzer (Par III, Otsuka Electronics, Japan). The thicknesses of the coated materials on glass were measured using a profiler (alpha-step IQ, KLA-tencor, U.S.). A photomask aligner (MDE-400, Midas System Co., Ltd., Korea) was used for the UV-curing of the CFPRs.

### 2.2. Materials

Malononitrile, diethyl oxalate, N,N-diethyl aniline, and n-hexyl bromide were pure chemicals supplied from Aldrich chemicals (U.S.); n-butyl bromide, aniline, and methanesulfonyl chloride were supplied from Junsei chemicals (Japan). The type of pigment used in this study was CI Pigment Blue 15:6 (Fastogen EP-193, DIC Corp., Japan). The glass (370 mm × 470 mm × 0.63 T, 5 K Super) used as a coating substrate in this study was manufactured by Samsung Corning Precision Glass Ltd. (Korea). The glass was cut into suitable fragments (5 cm × 5 cm) for coating tests. The dispersant used for grinding pigments, Disperbyk 2001, was manufactured by BYK-Chemie (Germany). Several chemicals were used to prepare a color filter photo resist, including dipentaerythritol penta-/hexaacrylate as a multi-functional monomer, supplied by Aldrich Chemicals (U.S.). Irgacure-369 as a photo initiator was supplied by Ciba Specialty Chemicals, and FC-4432 as a surfactant was supplied by 3M Company (U.S.). A binder for the preparation of the color filter photo resist was synthesized using benzyl methacrylate and methacrylic acid supplied by Aldrich Chemicals (U.S.).

### 2.3. Synthesis of malononitrile dimer

#### 2.3.1. Sodium 2-aminoprop-1-ene-1,1,3-tricarbonitrile (1)

A total of 66 g of the malononitrile (1.0 mol) was dissolved in 100 ml of absolute ethanol, and 162 g of 21% sodium ethoxide solution (0.5 mol) was added for one hour to the mixture with cooling. When the addition was finished, the temperature was raised to 60 °C and the mixture was stirred for four hours at that temperature. The resulting mixture was cooled to 4 °C in an ice-water bath. The precipitated pale yellow solid was filtered using the Whatman filter paper No. 5. The collected pale yellow solid was dried in air and was used for next step without further purification. The yield was 87% (67 g).

### 2.4. Synthesis of tricyanopyrrole derivative

#### 2.4.1. Disodium 3-cyano-2-(dicyanomethylene)-2H-pyrrole-4,5-bis(olate)(2)

The malononitrile dimer product (61.6 g, 0.4 mol) and diethyl oxalate (58.4 g, 0.4 mol) were dispersed in 100 ml of absolute ethanol. 130 g of 21% sodium ethoxide solution was added for one hour to the mixture with cooling. When the addition was finished, the temperature was raised to 60 °C and the mixture was stirred for four hours at that temperature. The resulting mixture was cooled to 4 °C in an ice-water bath. The precipitated deep yellow solid was filtered using the Whatman filter paper No. 5. The collected deep yellow solid was dried in air and was used for next step without further purification. The yield was 92%.

### 2.5. Synthesis of aniline derivatives

#### 2.5.1. N,N-dibutylaniline

Aniline (9.3 g, 0.1 mol), 1-bromobutane (28.8 g, 0.21 mol), potassium carbonate (5.6 g, 0.04 mol), copper(I) chloride (0.04 g), and triethylamine (15.1 g, 0.15 mol) were mixed and raised to 140 °C with reflux condenser. The resulting mixture was stirred for 10 h at that temperature. The reaction was checked by TLC (n-hexane/ethyl acetate, 9:1), and 100 ml of water was added to mixture. The resulting mixture was stirred to dissolve triethylamine hydrobromide, potassium bromide, and unreacted potassium carbonate. The mixture was allowed to stand overnight, and the product was separated from the water layer. The volatile material in the product was evaporated using a rotary evaporator and dried with anhydrous magnesium sulfate. Brown liquid was obtained and used for next step without further purification. The yield was 64%.

#### 2.5.2. N,N-dihexylaniline

Preparations were carried out using the same method for N,N-dibutylaniline with 34.6 g (0.02 mol) of 1-bromohexane instead of 1-bromobutane. Brown liquid was obtained and used for next step without further purification. The yield was 66%.

### 2.6. Synthesis of tricyanopyrrolidone derivatives as synergists

#### 2.6.1. 2-(3-Cyano-4-(4-(diethylamino)phenyl)-5-oxo-1H-pyrrol-2(5H)-ylidene)malononitrile (3-1)

A total of 4.6 g of tricyanopyrrole derivative (2) and 3.0 g of N,N-diethylaniline were dissolved in 25 ml of DMF; 4.5 g of methanesulfonyl chloride was added carefully for one hour with cooling. When the addition was finished, the resulting mixture was stirred for four hours at room temperature, and then was stirring for two hours at 70 °C. Methanol (30 ml) was added to the mixture to precipitate the product and then filtered using the Whatman filter paper No. 5. The collected green solid was washed with plenty of water and dried in air. The yield was 43%. The product was refluxed

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