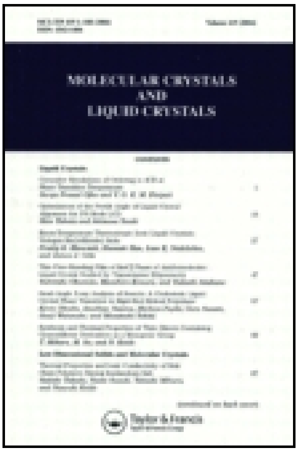

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# 2,3-Dicyanopyrazines Substituted Styryl Electron-Donor Group and Its Application for OLED Emitting Materials

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# 2,3-Dicyanopyrazines Substituted Styryl Electron-Donor Group and Its Application for OLED Emitting Materials

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*2,3-Dicyanopyrazine were designed and synthesized via the Knoevenagel condensation of reaction 2,3-dicyano-5-methylpyrazines with 4-(diphenylamino)benzaldehyde. Their structure was characterized by $^1$H-NMR and FT-IR and elemental analysis. The electroluminescent (EL) performance of multi-layered organic light-emitting devices (OLEDs) fabricated with compound* ***3a*** *as the emitting layer achieved a current efficiency of 1.57 cd/A with green region CIE coordinates of (0.37, 0.51) and* ***3b*** *achieved a current efficiency of 0.238 cd/A with red region CIE coordinates of (0.54, 0.42).*

**Keywords** 2,3-dicyanopyrazine; emitting layer; Knoevanagel reaction; OLED; triphenylamine

## Introduction

Since the initial development of high efficient OLEDs [1,2], much research effort has focused on the development of full-color displays with high efficiency and stability. The light-emitting materials for host emitters are generally required to have both a high emission quantum yield in solid film and the ability to form a thin uniform film. Also required is a suitable electronic level of lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) for electron-hole recombination confinement in this region to produce excitons. Besides the well known host-emitter tri-(8-hydroxyquinolinato) aluminum ($Alq_3$), other emitting materials have also been used as the non-doping emitting layer to achieve emission wavelengths in additional colors including blue, yellow, and orange, for requirements in different applications [3–5]. Among the rest, compounds with intramolecular charge transfer properties are of interest because incorporation of the donor and acceptor in the same molecule can lead to confinement in the recombination zone [6, 7], and hence, good emission [8–10].

2,3-Dicyanopyrazine derivatives have become a potential subject of investigation because of their wide variety of applications for coloring matters, nonlinear optical and electroluminescence (EL) materials [11,12]. We researched many types of dyes derived from 2,3-dicyanopyrazine and determined that styryl-substituted dicyanopyrazine has a rather small molecular size but a strong donor-acceptor chromophoric system [13–15]. In

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*Address correspondence to J. Y. Jaung, Prof. Jae Yun Jaung, Department of Organic and Nano Engineering, Hanyang University, Haengdang-dong, Seongdong-gu, Seoul 133-791, Korea (ROK). Tel.: (+82)2-2220-0492; Fax: (+82)2-2220-4092. E-mail: jjy1004@hanyang.ac.kr this paper, we report the synthesis of dicyanopyrazine oriented styryl fluorescent dyes and evaluate their optical properties for EL materials.

## Experimental

### *Synthesis*

*Synthetic procedure for **2a**.* A solution of 1-(4-(diphenylamino)phenyl)propane-1,2-dione **1a** (5.0 g, 0.016 mol), diaminomaleonitrile (DAMN; 1.73 g, 0.016 mol) and a small amount of *p*-toluenesulfonic acid as the catalyst in methanol (200 ml) was refluxed for 2 h. Methanol was poured into the mixture and stirred for 1 h at room temperature. The precipitate was filtered out and washed with methanol. The crude product was purified by column chromatography over silica gel with 1:5 ethyl acetate:*n*-hexane as the eluant, resulting in compound **2a** (yellow solid, 45%), m.p.: 103°C; $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$ 7.60 (d, Ar-H, 2H, $J = 8.7$ Hz), 7.46 (d, Ar-H, 2H, $J = 8.7$ Hz), 7.15–7.26 (m, Ar-H, 10H), 2.86 (s, -$CH_3$, 3H); Anal. Calcd. For $C_{25}H_{17}N_5$; C, 77.50; H, 4.42; N, 18.08. Found: C: 77.27; H: 4.32; N: 18.36

*Synthetic procedure for **2b**.* Compound **2b** was synthesized by the same procedure with **2a** except that the amount of reagents were 1-(4-*tert*-butylphenyl)propane-1,2-dione **1b** (40 g, 0.14 mol) and DAMN (15.2 g, 0.14 mol) **2b** (white solid, 50%), m.p.: 111°C; $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$ 7.62 (d, Ar-H, 2H, $J = 8.7$ Hz), 7.54 (d, Ar-H, 2H, $J = 8.7$ Hz) 2.85 (s, -$CH_3$, 3H), 1.39 (s, -*t*-Bu, 9H); Anal. Calcd. For $C_{17}H_{16}N_4$; C, 73.89; H, 5.84; N, 20.27. Found: C: 73.44; H: 6.02; N: 19.94

*Synthetic procedure for **3a**.* A solution of **2a** (3.0 g, 7.74 mmol), 4-(diphenylamino)benzaldehyde (2.12 g, 7.74 mmol) and a small amount of piperidine as the catalyst in benzene (20 ml) was refluxed for 21 h under $N_2$ atmosphere. After the reaction was complete, the mixture was cooled to room temperature. Methanol was poured into the mixture and stirred for 1 h at room temperature. The precipitate was filtered out and washed with methanol. The crude product was purified by column chromatography over silica gel with 1:3 ethyl acetate:*n*-hexane as the eluant, resulting in compound **3a** (red solid, 45%); m.p.: 150°C, FT-IR (KBr pellet), $\nu$(cm$^{-1}$) 2232 (C≡N), 1602 (C=C), 1489, 1296; $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$ 7.82 (m, Ar-H, 4H), 7.78 (d, 1H, $J = 15.6$ Hz), 7.42 (m, Ar-H, 8H), 7.32 (m, Ar-H, 8H), 7.18 (d, 1H, $J = 15.6$ Hz), 7.15 (d, Ar-H, 4H, $J = 8.7$ Hz), 6.97 (m, Ar-H, 4H); Anal. Calcd. For $C_{44}H_{30}N_6$: C, 82.22; H, 4.70, N, 13.08. Found: C,82.03; H, 4.82; N. 13.15.

*Synthetic procedure for **3b**.* Compound **3b** was synthesized by the same procedure with **3a** except that the amount of reagents were **2b** (5.0 g, 0.018 mol) and 4-(diphenylamino)benzaldehyde (4.95 g, 0.018 mol). **3b** (red solid, 45%); m.p.:143°C; FT-IR (KBr pellet), $\nu$(cm$^{-1}$) 2229 (C≡N), 1585 (C=C), 1484, 1276; $^1$H-NMR ($CDCl_3$), $\delta$ 8.12 (d, 1H, $J = 15.6$ Hz), 7.65 (d, Ar-H, 2H, $J = 8.7$ Hz), 7.58 (d, Ar-H, 2H, $J = 8.7$ Hz), 7.4 (d, Ar-H, 2H, $J = 8.7$ Hz), 7.32 (m, Ar-H, 4H), 7.18 (d, 1H, $J = 15.6$ Hz), 7.15 (m, Ar-H, 4H), 7.12 (d, Ar-H, 2H, $J = 8.7$ Hz), 7.0 (d, Ar-H, 2H, $J = 8.7$ Hz), 1.39 (s, *t*-Bu, 9H); Anal. Calcd. For $C_{36}H_{29}N_5$: C, 81.33; H, 5.50, N, 13.17. Found: C,80.93; H, 5.75; N. 13.39.

### *Fabrication of OLED*

4,4′,4′′-Tris(*N*-3-methylphenyl-*N*-phenyl-amino)-triphenylamine (2-MTDATA) with a similar HOMO level to indium tin oxide (ITO) was used as the hole-injection layer. *N*,*N*-Bis-(1-naphthyl)-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) was used as the hole-transport layer. Synthesized materials **3a** and **3b** were used as the emitting layer and tris-(8-hydroxyquinoline)aluminium ($Alq_3$) was used as the electron-transport layer. LiF/Al was used as the cathode.

OLEDs were fabricated by a thermal evaporation onto a cleaned glass substrate pre-coated with ITO without breaking the vacuum. Prior to organic layer deposition, the ITO substrates were exposed to UV-ozone flux for 10 min following degreasing with acetone and isopropyl alcohol. All organic layers were grown by thermal evaporation at a base pressure of $< 1 \times 10^{-7}$ Torr. The OLED current density-voltage-luminescence (J-V-L) characteristics were measured simultaneously using a Keithley 2400 programmable source meter and SpectraScan PR650 (Photo Research).

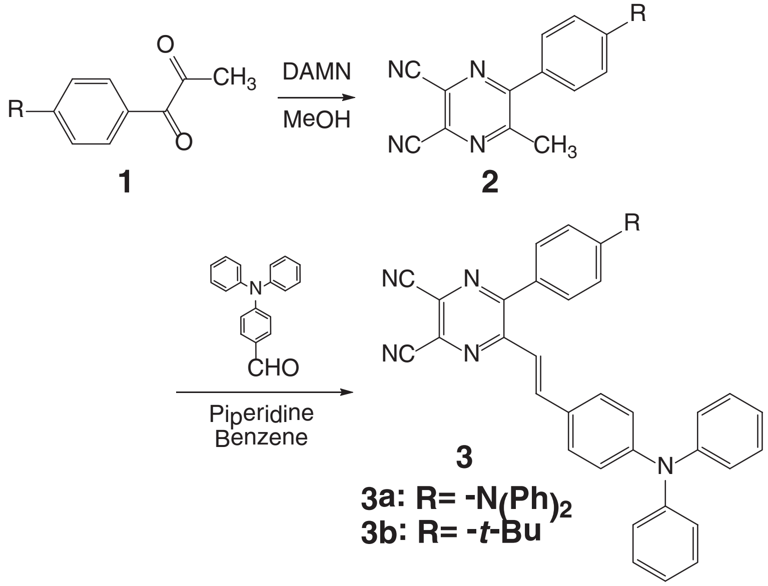
### *Measurements*

Melting points were obtained with a capillary melting point apparatus and were uncorrected. Elemental analysis was checked using a Flash EA-1112 analyzer. $^1$H-NMR spectra were recorded on a VARIAN UnityInova 300MHz FT-NMR spectrometer. UV-visible and fluorescence spectra were measured using a SCINCO S-4100 and SHIMADZU RF-5301PC spectrophotometer. Cyclic voltammetry (CV) experiments were performed with a BAS-100 electrochemical analyzer with a three-electrode configuration consisting of a Pt disk working electrode, an Ag/AgCl reference electrode and Pt wire counter electrode. All measurements were in acetonitrile with 0.1 M tetra-*n*-butylammonium tetrafluroroborate ($TBABF_4$) as the supporting electrolyte.

## Results and Discussion

1-(4-(Diphenylamino)phenyl)propane-1,2-dione (**1a**) and 1-(4-*tert*-butylphenyl)propane-1,2-dione (**1b**) were synthesized from the modification of the described literature [16]. 2,3-Dicyanopyrazines **2** were synthesized from the condensation of $\alpha$-diketones **1** with diaminomaleonitrile in the presence of a catalytic amount of *p*-toluenesulfonic acid in methanol. Due to the strong electron withdrawing effect of the cyano groups on the pyrazine ring, 5-methyl groups show $^1$H-NMR peak at 2.85-2.86 ppm, which are downfield shifts compared to those in toluene observed at 2.09ppm. The deshielded protons were acidic and they were able to undergo Knoevenagel condensation reaction with aryl aldehydes. Compounds **2** were reacted with 4-(diphenylamino)benzaldehyde and resulted **3** in the presence of piperidine as a catalyst [17]. $^1$H-NMR spectra of **3** showed a doublet peak at 8.1-8.2 ppm indicating the presence of a typical *trans* ($J = 15.6$Hz) configuration for the proton in the olefinic moiety. The synthetic route of this study is summarized in Scheme 1.

The optical and electrochemical data of compounds **3** are presented in Table 1. Compound **3a** was expected a bathochromic shift compared to **3b** because triphenylamine substituent have greater electro-donating ability than *t*-butyl phenyl group on **3b** and it would induce increasing the electronic density of HOMO level. However, $\lambda_{\max}$ and $F_{\max}$ of **3a** only show slightly increasing wavelength as shown in figure 1, which announces that the substituent rarely affect the electronic level of the chromophore.



**Scheme 1.** Synthetic route for the 2,3-dicyanopyrazine derivative

The HOMO level was calculated from the CV measurement by assessing the oxidation potential at the first scan under the ferrocene reference electrode. The LUMO level was estimated from the band-gap which was confirmed from the onset point of the UV-absorption band and from the CV-measured HOMO values (Table 1). The HOMO levels of both compounds were higher than that of NPB (−5.5 eV), a known hole-transporting material. In addition, LUMO levels were higher than that of the known electron-transporting material $Alq_3$ (−3.1 eV), which demonstrated that the electronic level was appropriate as an emitting layer.

A multi-layered OLED device was fabricated to identify the EL properties of the synthesized materials. EL devices were fabricated using 2-MTDATA as the hole-injection layer, NPB as the hole-transporting layer, $Alq_3$ as the electron-transporting layer, and the synthesized materials as the emitting layer. ITO and LiF/Al were used as the anode and cathode, respectively, with the following structure ITO/2-MTDATA (80 nm)/NPB (15 nm)/**3a** or **3b** (30 nm)/$Alq_3$ (25 nm)/LiF (1.0 nm)/Al (200 nm). Figure 2 shows I-V

**Table 1.** Optical and electrochemical properties of compounds **3a** and **3b**

| | $^a\lambda_{max}$ (nm) | $F_{max}$ (nm) CHCl$_3$ | Film | $^b\Phi_{F(MEK)}$ | LUMO (eV) | HOMO (eV) | Eg (eV) |
|---|---|---|---|---|---|---|---|
| **3a** | 512 | 603 | 690 | 0.53 | −2.98 | −5.16 | 2.18 |
| **3b** | 510 | 599 | 685 | 0.13 | −3.02 | −5.18 | 2.16 |

[a] In chloroform.

[b] Measured by comparative method in methyl ethyl ketone with Rhodamine B($\Phi_F = 0.67$) in ethanol.

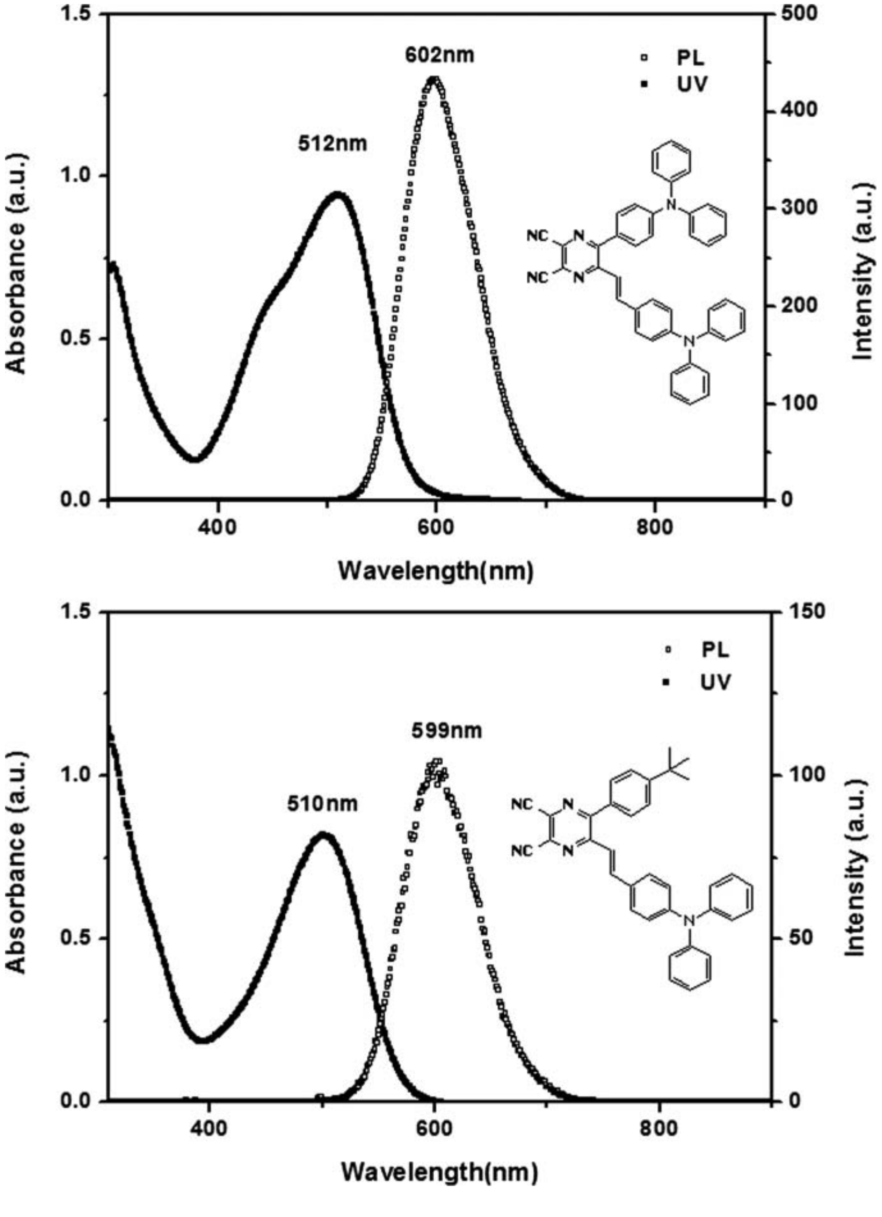


**Figure 1.** Absorption and fluorescence spectra of **3a** and **3b** in chloroform.

curves of the devices. The **3a** device exhibited an I-V characteristic with a slightly increased turn-on voltage.

Figure 3 shows the electroluminescence (EL) spectrum of the fabricated devices. The device containing **3b** as the emitting layer emitted 649 nm in the red area, whereas the **3a** device showed two peaks at 525 and 668 nm. The $EL_{max}$ value at 525 nm corresponds to $Alq_3$. The EL spectrum of **3a** with two peaks may have been caused by the recombination zone shift to the EML/$Alq_3$ interface.

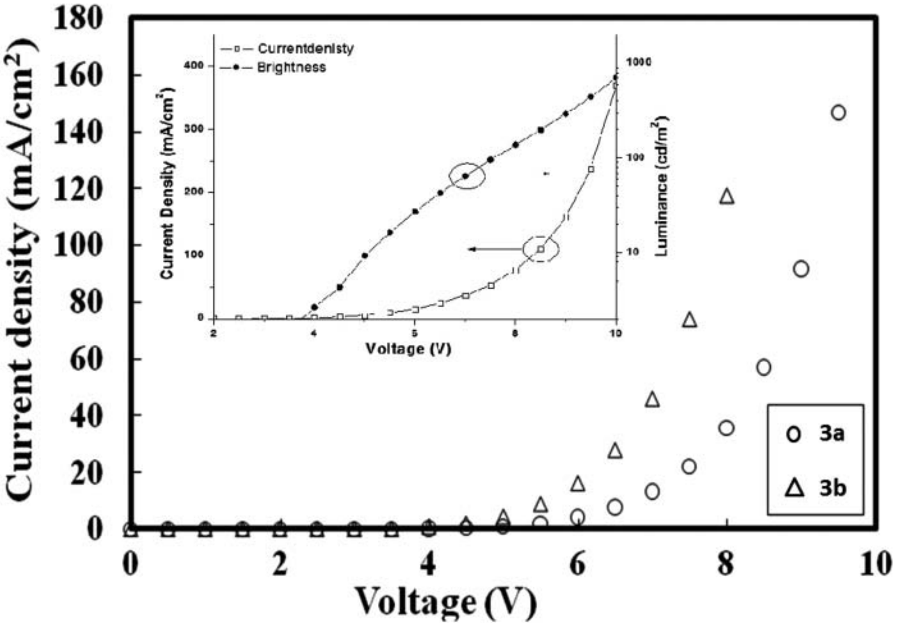


**Figure 2.** Current density-voltage characteristics (outer) of ITO/2-MTDATA (80 nm)/NPB (15 nm)/**3a** (○) or **3b** (Δ) (30 nm)/Alq3 (25 nm)/LiF (1.0 nm)/Al (200 nm) devices and Voltage-luminance curve (inner) of **3b**.

The HOMO levels of **3a** and **3b** were similar, as shown in Table 1, and were indicative of a low barrier similar to the HOMO level of $Alq_3$ (−5.7eV), which is well-known as a green fluorescent material for OLED [18]. Hence, **3a** and **3b** can act as a hole-transporting layer in such fabricated devices due to the generation of the leakage of carriers at the interface between $Alq_3$ layer and emitting layers [19]. However, the emission of the $Alq_3$ layer was only shown in **3a**, which indicates that the greater electron-donating substituent

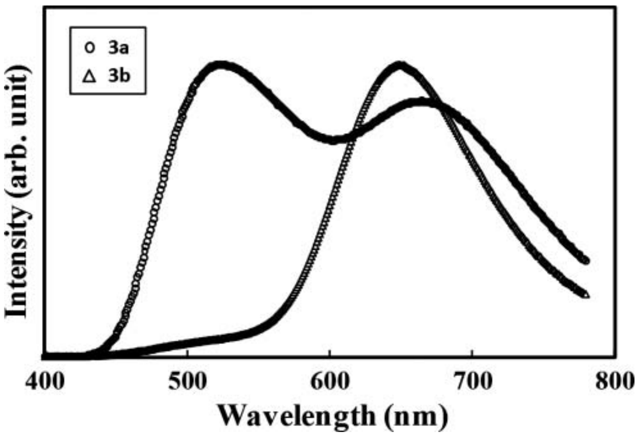


**Figure 3.** EL spectrum of ITO/2-MTDATA (80 nm)/NPB (15 nm)/**3a** (○) or **3b** (Δ) (30 nm)/Alq3 (25 nm)/LiF (1.0 nm)/Al (200 nm) devices at 10 mA/cm$^2$.

**Table 2.** EL performance of multi-layered devices with ITO/2-MTDATA (80 nm)/NPB (15 nm)/**3a** or **3b** (30 nm)/Alq3 (25 nm)/LiF (1.0 nm)/Al (200 nm) structure

| | | $EL_{max}$ (nm) | Voltage (V) | Efficiency (cd/A) | Power efficiency (lm/W) | CIE (x,y) |
|---|---|---|---|---|---|---|
| **3a** | 10 mA/cm$^2$ | 525, 668 | 6.07 | 1.57 | 0.083 | (0.37, 0.51) |
| | 100 mA/cm$^2$ | | 8.82 | 1.71 | 0.124 | (0.37, 0.53) |
| **3b** | 10 mA/cm$^2$ | 649 | 5.5 | 0.238 | 0.074 | (0.54, 0.42) |
| | 100 mA/cm$^2$ | | 8.3 | 0.263 | 0.105 | (0.56, 0.32) |

**3a** was simultaneously acting as a hole-transporting layer and an emitting layer. Introduced substituents were occasionally able to affect not only for the control of electronic levels but hole or electron transferring performances on the OLED device. Thus, it needs a careful consideration when the design of emitting materials [20]. Table 2 lists the efficiency of the fabricated device at a current density of 1.0 mA/cm$^2$. Compound **3a** showed a green CIE value of (0.37, 0.51) and current efficiency of 1.57 cd/A while **3b** showed a red CIE value of (0.54, 0.42) and current efficiency 0.238 cd/A.

## Conclusions

In this study, the synthesized 2,3-dicyanopyrazine derivatives showed emitting properties suitable for application in OLED devices. Their appropriate electronic levels for emmiting layer were existed between those of generally used hole- and electron-transporting layers. Transferring to electron-transport layer from $Alq_3$ to other materials which have a much lower HOMO level and increase block barrier with the HOMO level of the synthesized products may be a method to enhance of the device's efficiency. The research progress for designing the material structure and enhancing the EL devices will be reported elsewhere.

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