

Short Note

## Trimethyl 4,6-Dicyano-5-hydroxybenzene-1,2,3-tricarboxylate

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**Abstract:** A novel synthesis of a fully substituted fluorescent phenol by a one-pot reaction of dimethyl acetylenedicarboxylate and malononitrile in the presence of catalysts has been developed. The structure of the synthesized compound was assigned on the basis of its elemental analysis, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, IR, mass spectral and X-ray data. The photophysical data of the new compound are reported.

**Keywords:** fully substituted phenol; fluorescence; one-pot reaction; malononitrile; dimethyl acetylenedicarboxylate; keto-enol tautomerization

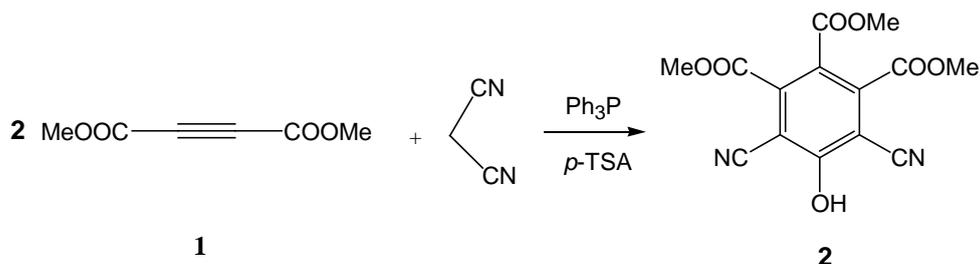
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Optoelectronic devices such as optical fibers, switches, tunable lasers and amplifiers, modulators with various applications need compounds emitting in the blue spectral region [1]. Multi-component reactions (MCRs) are of increasing significance in organic and medicinal chemistry. MCRs allow organic compounds to be synthesized in a few steps or in a one-pot operation [2].

Substituted phenols are of great importance in biosynthesis and also as building blocks in organic synthesis [3,4]. There are a few reports on the synthesis of highly substituted phenols [5]. So the development of a multi-component one-pot procedure for the synthesis of fluorescent poly-functionalized phenol can be seen as urgently interesting for technology upgrading. In continuation of our quest for developing one-pot procedures, here we wish to report a novel one-pot condensation reaction of dimethyl acetylenedicarboxylate **1** and malononitrile in the presence of Ph<sub>3</sub>P (triphenylphosphine) and *p*-toluenesulfonic acid (*p*-TSA) for the synthesis of fully substituted phenol **2** with bright fluorescence property (Scheme 1).

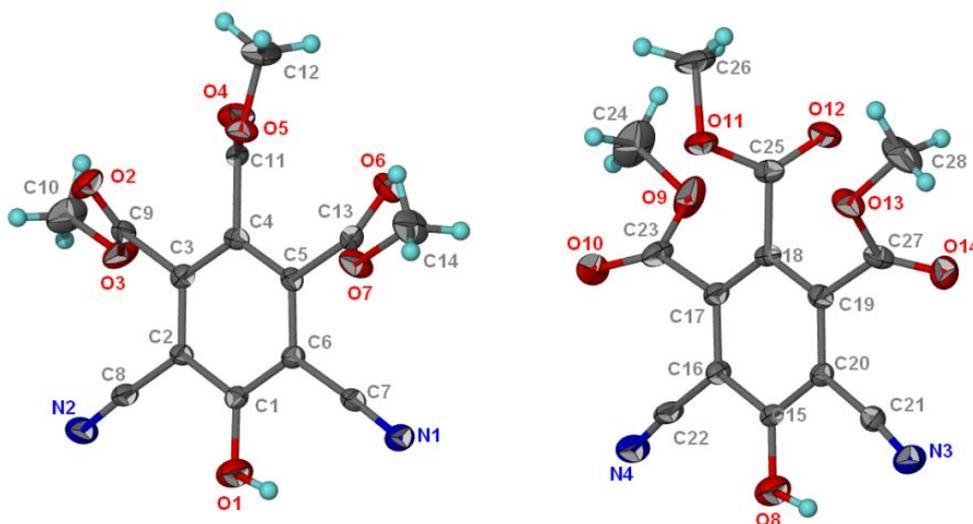
Easy, rapid and mild reaction conditions and also high atom economy of this one-pot procedure make the present method useful for the synthesis of highly functionalized phenols.

**Scheme 1.** Synthesis of trimethyl 4,6-dicyano-5-hydroxybenzene-1,2,3-tricarboxylate.

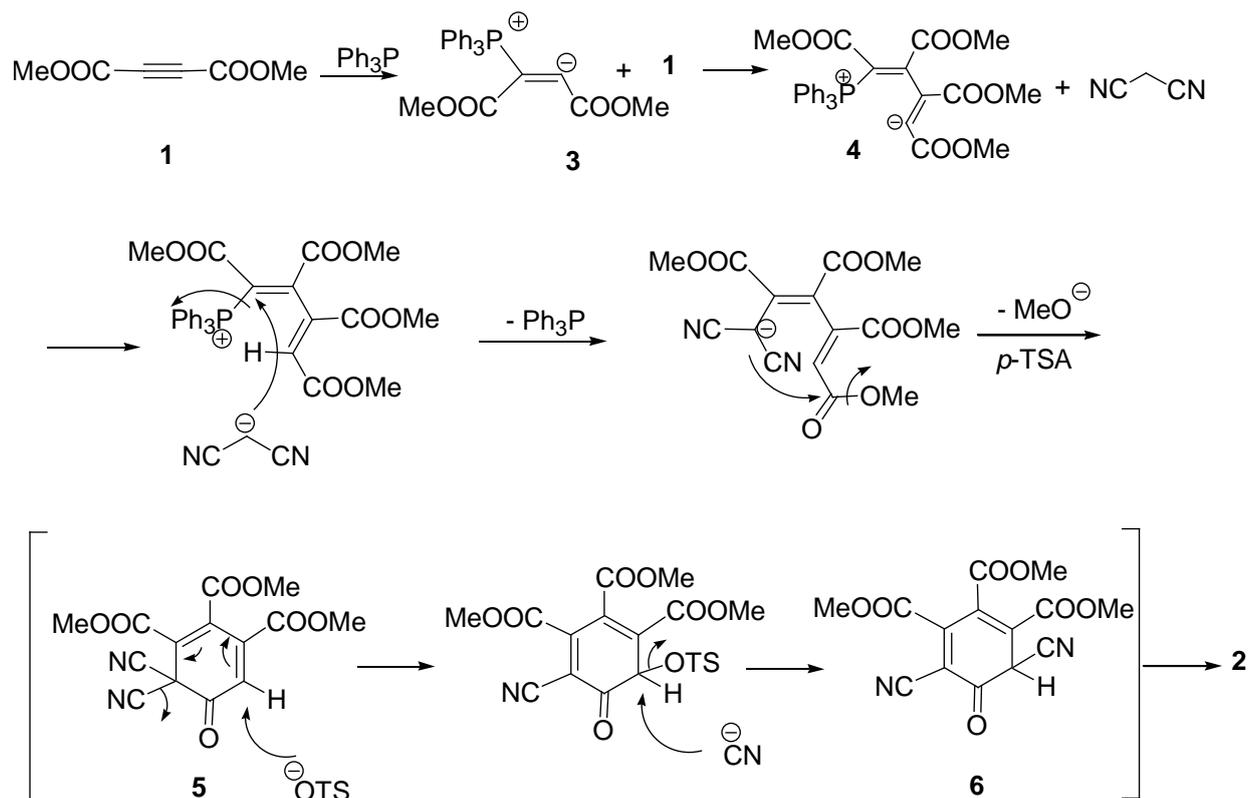


Structure **2** was assigned on the basis of its elemental analysis,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , IR and mass spectral data. The light green crystals of **2** were obtained by slow crystallization from ethyl acetate and its X-ray structure was determined to confirm unambiguously its structure [6] (Figure 1).

**Figure 1.** X-Ray crystal structure of **2**.



A possible mechanism for the synthesis of **2** is shown in Scheme 2. It is suggested that the zwitterion **3** is produced at first by addition of  $\text{Ph}_3\text{P}$  to the acetylenic ester. Then the zwitterion **3** condenses with another ester molecule to produce zwitterion **4**. Attack of the malononitrile anion at **4**, followed by loss of  $\text{Ph}_3\text{P}$  and intramolecular cyclization affords **5**. Elimination of  $\text{CN}^-$  from  $\text{C}_2$  and addition of  $\text{CN}^-$  to  $\text{C}_6$  in the presence of  $\text{OTS}^-$  can produce the intermediate **6**. Finally, **6** can be aromatized to **2** by keto-enol tautomerization. Intermediate **6** was detected in the early stage of the reaction by  $^1\text{H-NMR}$  and IR spectra. The proton adjacent to the CN group appears at  $\delta = 4.53$  for **6** in the  $^1\text{H-NMR}$  spectrum and the carbonyl group of **6** has been detected at  $\nu_{\text{max}} = 1,801 \text{ cm}^{-1}$  in the IR spectrum of the reaction mixture. At the end of this transformation (after 24 h), there was no carbonyl absorption detectable in the IR spectrum. Probably, the stability gained from aromatic ring generation drives this keto-enol tautomerization.

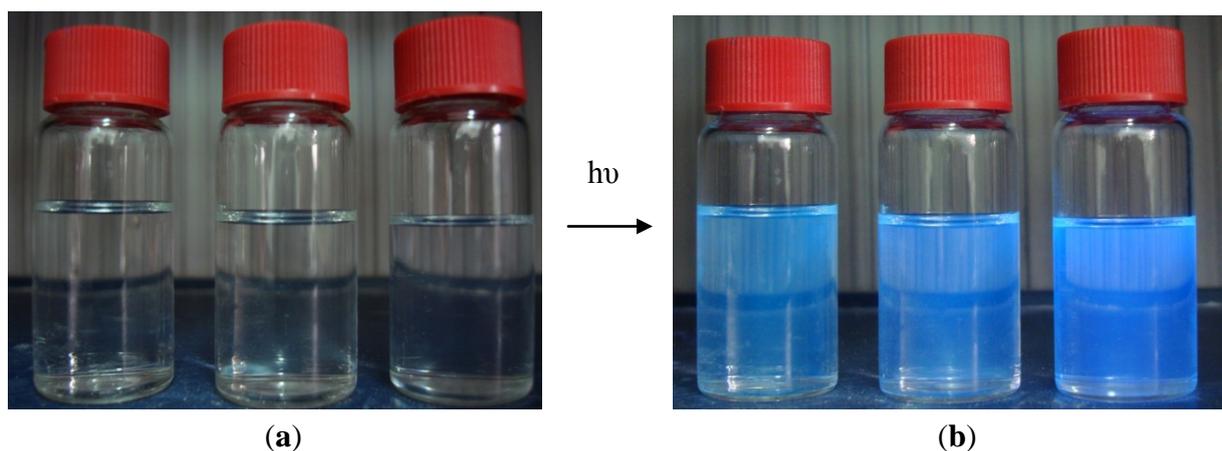
**Scheme 2.** A possible mechanism for the formation of **2**.

Compound **2** is fluorescent and its photophysical data including  $\lambda_{\text{Abs.}}$  (nm),  $\lambda_{\text{Flu.}}$  (nm) have been measured for 0.002 M solutions in  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{CN}$  and  $\text{CHCl}_3$  (Table 1).

**Table 1.** Photophysical data: electronic absorption (*Abs.*) and fluorescence (*Flu.*) of **2**.

Comp.	$\text{CH}_3\text{OH}$		$\text{CH}_3\text{CN}$		$\text{CHCl}_3$	
	$\lambda_{\text{Abs.}}$	$\lambda_{\text{Flu.}}$	$\lambda_{\text{Abs.}}$	$\lambda_{\text{Flu.}}$	$\lambda_{\text{Abs.}}$	$\lambda_{\text{Flu.}}$
<b>2</b>	237	469	226	459	335	455

Figure 2 shows photographs of compound **2** solutions in  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{Cl}$  (a): under visible light and (b): under a UV lamp with  $\lambda = 366$  nm (Philips TL8W/08F8T5/BLC).

**Figure 2.** Photographs of solutions of **2**, from left to right in  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{Cl}$ , respectively.

## Experimental

Elemental analysis for C, H and N was performed using a Thermo Finnigan Flash EA1112 instrument.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were determined on a Bruker 500 spectrometer. IR spectra were measured on a Bruker EQUINOX 55 spectrophotometer with the ATR method. Mass spectra were recorded on a Finnigan-MAT 8430 spectrometer. Photophysical data measurements were made with a Cary Eclipse Fluorescence spectrophotometer.

*Trimethyl 4,6-dicyano-5-hydroxybenzene-1,2,3-tricarboxylate (2)*. To a magnetically stirred solution of dimethyl acetylenedicarboxylate (0.28 g, 2 mmol) in 3 mL of  $\text{CH}_2\text{Cl}_2$ ,  $\text{Ph}_3\text{P}$  (0.26 g, 1 mmol) and malononitrile (0.1 g, 1.5 mmol) in 3 mL of  $\text{CH}_2\text{Cl}_2$  were added dropwise by two dropping funnels at  $-10\text{ }^\circ\text{C}$  over 40 min and stirring was continued at this temperature for 2 h. Then, 0.069 g (40 mol%) *p*-TSA were added. The reaction mixture was warmed up to room temperature and stirred for 24 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel, using *n*-hexane/ethyl acetate (3/1) as the mobile phase. The product was obtained as light green crystals, 0.26 g, 83%. Melting point: 129–130  $^\circ\text{C}$ .

## Structural Characterization

IR,  $\nu_{\text{max}}$ : 3419, 3348, 3252, 2961, 2232, 1728, 1651, 1573, 1430, 1370, 1303, 1240, 1173, 1015  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ): 3.78 (3H, s,  $\text{CH}_3$ ), 3.91 (6H, s,  $2\text{CH}_3$ ), 8.03 (1H, br s, OH) ppm;  $\delta_{\text{C}}$  (125 MHz,  $\text{CDCl}_3$ ): 54.2, 54.6 ( $\text{CH}_3$ ), 96.5 (CN), 113.9, 114.2, 114.4, 155.0 (Ar), 163.7, 165.8 (CO) ppm; MS:  $m/z = 318$  ( $\text{M}^+$ ), 317, 214, 156, 141, 59, 45; Anal. Calcd for  $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_7$ : C, 52.84; H, 3.17; N, 8.80; Found: C, 52.79; H, 3.15; N, 8.62.

## Acknowledgements

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## References and Notes

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6. Crystallographic data for compound **2** reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC No. 842814. These data can be obtained free of charge via [www.ccdc.com.ac.uk/data\\_request/cif](http://www.ccdc.com.ac.uk/data_request/cif).

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