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Reaction between phthalonitrile and phenylacetonitrile

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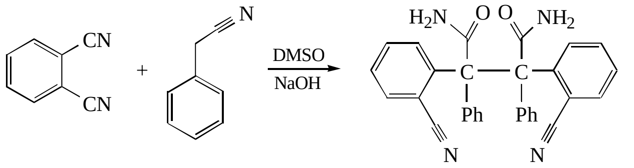
The title reaction performed in the DMSO–NaOH system resulted in the formation of 2,3-diphenyl-2,3-(2′-cyanophenyl)butanedioic acid diamide, which was selectively hydrolysed to 2,3-diphenyl-2,3-(2′-cyanophenyl)butanedioic acid.

Aromatic nitriles are widely used as synthetic intermediates and monomers for preparing polymer materials, organic dyes, *etc.* Nucleophilic substitution is an effective method for the functionalization of arenes containing electron-withdrawing substituents.[1] The CN-activated aromatic nucleophilic substitution for halogens or a nitro group[2-4] and nucleophilic substitution for hydrogen in highly activated arenes[5,6] are well known. However, little is known about this type of functionalization in cyanoarenes. Vicarious nucleophilic substitution for hydrogen in dicyanonaphthalene was reported.[7] Previously,[8] we performed the oxidative nucleophilic substitution of the phenylacetonitrile carbanion for hydrogen in benzonitrile in the DMSO–NaOH system to form , -bis(2-cyanophenyl)phenylacetamide. Roze *et al.*[9] examined nucleophilic substitution in 4-nitrophthalonitrile by dimedone and reported the uncommon replacement of the CN group.

The interaction of phthalonitrile with phenylacetonitrile in DMSO–NaOH resulted in the formation of a compound that decomposed at about 200 °C. The IR spectrum of this compound exhibited absorption bands due to nitrile and amido groups ($\nu_{C\equiv N}$ 2202 cm^{-1}, ν_{N-H} 3350 cm^{-1} and $\nu_{C=O}$ 1620 cm^{-1}). In the region 2000–1700 cm^{-1}, the absorption pattern corresponds to overlapping bands of mono- and disubstituted benzene rings. Figure 1 demonstrates the ^{1}H NMR spectrum of the isolated compound. The ^{13}C NMR spectrum exhibits signals due to a quaternary carbon atom (50 ppm) and carbon atoms of nitrile (121.36 ppm) and amido (170 ppm) groups and an aromatic ring (122.2–140.56 ppm). The mass spectrum of the compound exhibits peaks with *m*/*z* of 246, 219, 190 and 122. An analysis of the spectroscopic data allowed us to propose the following reaction scheme:[†]



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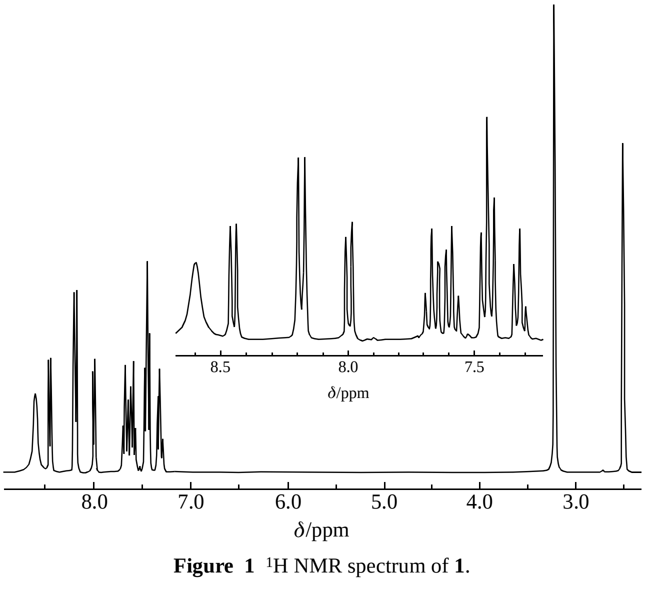


Figure 1 ^{1}H NMR spectrum of **1**.

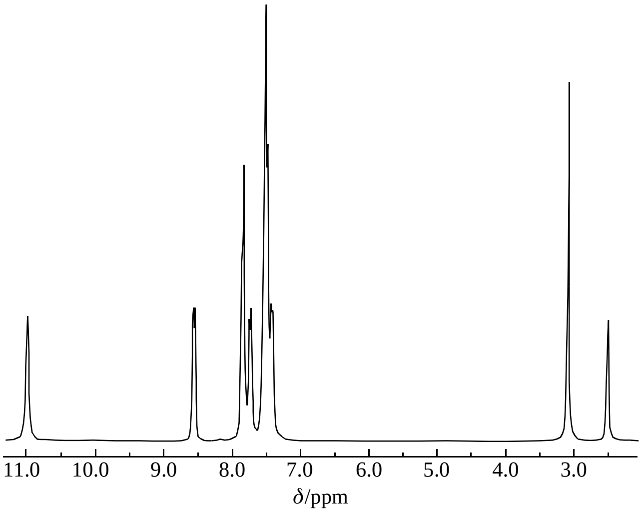
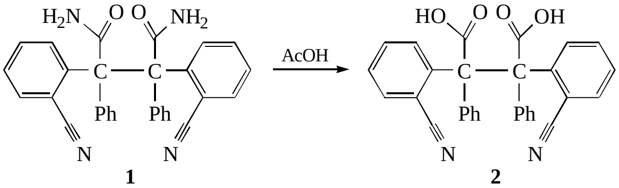


Figure 2 ^{1}H NMR spectrum of **2**.

The reaction can be explained as nucleophilic substitution for a CN group in phthalonitrile, dimerization of the intermediate and formation of 2,3-diphenyl-2,3-bis(2′-cyanophenyl)butanedioic acid diamide **1**.

The above diamide was selectively hydrolysed to 2,3-diphenyl-2,3-bis(2′-cyanophenyl)butanedioic acid **2** (Figure 2) by boiling in acetic acid according to the following reaction:[‡]



1 **2**

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[†] ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer at 300 MHz in [^{2}H$_6$]DMSO, ^{13}C NMR spectra were recorded on a BS567 spectrometer at 25 MHz in [^{2}H$_6$]DMSO, IR spectra were measured on a Specord M-80 instrument in Vaseline oil.

Synthesis of **1**: sodium hydroxide, phenylacetonitrile and phthalonitrile (in the ratio 10:2:1.5) were added to DMSO, and the mixture was intensely stirred at 80–85 °C for 6 h. On completion of the reaction, the reaction mixture was transferred into cold water, and the precipitate was filtered off and washed with water, ethanol and diethyl ether. Yield 80% after recrystallization from toluene–ethanol (1:1), mp 200 °C (decomp.). IR (ν/cm^{-1}): 2202 (C≡N) and 3345 (N–H). MS, *m*/*z* (%): 246 (100), 219 (40), 190 (45), 122 (55). Found (%): C, 76.36; H, 4.84; N, 12.23. Calc. for $C_{30}H_{22}N_4O_2$ (%): C, 76.58; H, 4.71; N, 11.91.

[‡] *Synthesis of* **2**: a solution of **1** was boiled in acetic acid for 6 h. The precipitate formed after cooling the reaction mixture was filtered off, washed with ethanol and dried. Yield 50%, mp 230–232 °C. IR (ν/cm^{-1}): 3220 (O–H), 1724 (C=O), 2208 (C≡N). Found (%): C, 76.39; H, 4.43; N, 6.11. Calc. for $C_{30}H_{20}N_2O_4$ (%): C, 76.26; H, 4.27; N, 5.93.

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