

Short Note

# 9-Vinyl-9*H*-carbazole-3,6-dicarbonitrile

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**Abstract:** Carbazole polymers attract significant attention as promising luminophores, organic electronic and photovoltaic materials, photo/electrocatalysts, energy storage materials, redox mediators and catalysts. However, the oxidation potential of the commercially available poly(vinylcarbazole) is insufficient for some applications such as high-voltage Li-Ion batteries. We have proposed a monomer for the novel polycarbazole with an increased oxidation potential, which will be compatible with high-voltage cathode materials for Li-Ion. In addition, the proposed polymer is an interesting substrate for the further carbonization to obtain N-doped carbons with a high electrocatalytic activity level.

**Keywords:** carbazole; vinylation; one pot; cyanation

## 1. Introduction

Carbazoles are of great interest as a class of compact functional molecules, which meet their applications as dyes and luminophores [1], organic electronic [2] and photovoltaic materials [3,4], photo/electrocatalysts [5], energy storage materials [6,7], redox mediators and catalysts [8]. Due to their highly reversible redox process and easily tunable  $\pi$ -system, the carbazole core is an attractive scaffold for the design of the functional materials for various electrochemical and energy storage applications.

Due to the unique properties of the carbazole core, plenty of carbazole-based polymeric materials are used in various fields of science and technology. The most recognized large-scale commercial poly(N-vinylcarbazole) (PVK) was discovered by Walter Reppe in the 1930s [9] and was established as the first photoconductive polymer [10]. In addition, the PVK is industrially used as a thermoconductive material [11], an emission layer for OLEDs [12] and a photoresist [13]. Carbazole itself can also act as a monomeric unit for the synthesis of conductive polymer, polycarbazole, which is also used in light emission devices, photovoltaics, photochromic devices, sensors and supercapacitors [14].

3,6-dicyanocarbazole was proposed as a redox shuttle with a very high switch-on potential, which can protect Li-Ion batteries from the overpotential fault by providing an internal discharge route [15]. To fit the working potential window of a cathode material to the anodic region, two -CN groups were introduced to the carbazole core. Recently, we proposed a novel protecting principle which serves to prevent Li-Ion batteries from faults caused by overpotential [16]. The protective element comprises the layer between the cathode material and current collector, rapidly increasing its resistance above a certain potential, and thus interrupting the circuit of the battery. Redox polymers containing pendants which attain a positive charge are promising materials for various electrochemical applications, such as energy storage [17] or electrocatalysis [18], and may be employed as well in the role of such protective layer materials. The PVK polymer conceptually may serve as the protective layer as well, although its oxidation potential is too low to match the working window of the common cathode materials.

Herein, we report the monomer 9-vinyl-9*H*-carbazole-3,6-dicarbonitrile, which may be used to synthesize an analog of PVK, with the oxidation potential sufficiently shifted to the cathodic region for the efficient protection of Li-Ion batteries. In addition, this cyanated



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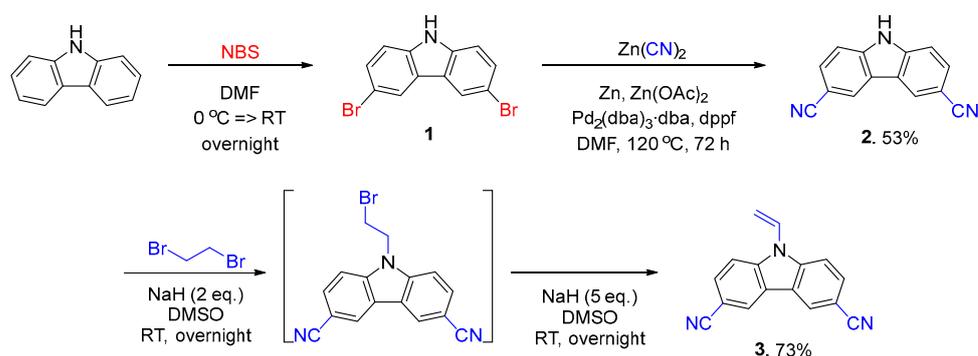


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PVK analog may be further subjected to a thermal or solvothermal carbonization, affording the nitrogen-rich carbon for catalytic and energy storage applications [19]. The reported synthetic method comprises an atom-economic route to acquiring the desired product. The structure of the obtained 9-vinyl-9*H*-carbazole-3,6-dicarbonitrile is confirmed by means of  $^1\text{H}$  and  $^{13}\text{C}$  NMR, as well as FTIR and HRMS.

## 2. Results

9-vinyl-9*H*-carbazole-3,6-dicarbonitrile was prepared from 9*H*-carbazole in three steps, as depicted in Scheme 1. Carbazole was brominated with NBS as described in the literature [20] to afford 3,6-dibromo-9*H*-carbazole **1** in a quantitative yield. The substitution of the bromine atoms in the carbazole **1** was performed using a modified method described earlier [20]. As a result, 9*H*-carbazole-3,6-dicarbonitrile **2** was obtained in 53% yield.



**Scheme 1.** Scheme for the synthesis of the compound **3**.

The attempted vinylation of 9*H*-carbazole-3,6-dicarbonitrile with vinyl acetate catalyzed by  $[\text{Ir}(\text{COD})\text{Cl}]_2$  failed, presumably due to the insufficient nucleophilicity of the nitrogen atom owing to the presence of EWG groups in the molecule. However, we have found that the alkylation of carbazole **2** with 1,2-dibromoethane results in the formation of the title compound 9-vinyl-9*H*-carbazole-3,6-dicarbonitrile **3** in one step, thus comprising a one-pot alkylation–elimination sequence.

In the  $^1\text{H}$  NMR spectrum of the title compound **3** (Figure S3), two doublets at 8.81 and 7.98 ppm accompanied with the doublet of doublets at 7.93 ppm were observed, which is typical for 3,6-disubstituted carbazole. The absence of the NH proton signal in combination with three additional dd signals confirmed the presence of the vinyl group in the molecule. It is noteworthy that the signal of the internal CH proton of the vinyl group is situated in the very low-value field, at 7.56 ppm, which may be explained by the effect of the  $-\text{CN}$  substituents. Two complementary signals of the terminal hydrogen atoms of the vinyl group were found in the typical alkene region at 5.78 and 5.46 ppm. In the  $^{13}\text{C}$  NMR spectrum of the 9-vinyl-9*H*-carbazole-3,6-dicarbonitrile **3** (Figure S4), two new signals at 128.8 and 107.5 ppm were observed. This fact is explained by the presence of a vinyl group in the target compound **3**. The FTIR spectrum of the product revealed the presence of the strong  $\text{C}\equiv\text{N}$  vibration band at  $2224\text{ cm}^{-1}$  and the well-resolved band of  $\text{C}=\text{C}$  vibration of the non-symmetric conjugated vinyl fragment at  $1599\text{ cm}^{-1}$ .

As a result, we have obtained a valuable monomer for the further preparation of the high-potential redox polymer, 9-vinyl-9*H*-carbazole-3,6-dicarbonitrile. The proposed synthetic method is a one-pot vinylation procedure, which affords the desired compound in a high yield.

## 3. Materials and Methods

### 3.1. General Considerations

Reagents of “reagent grade” purity were purchased from Sigma–Aldrich (Europe). DMF and DMSO were distilled from  $\text{CaH}_2$  and stored under  $3\text{ \AA}$  molecular sieves prior

to use. Hexane was dried by standing with activated SiO<sub>2</sub>. <sup>1</sup>H and <sup>13</sup>C-NMR spectra were acquired using a Bruker Avance 400 spectrometer (Bruker Analytische Messtechnik GmbH, Rheinstetten, Germany) at 400 and 101 MHz, respectively, in DMSO-*d*<sub>6</sub>. The Fourier-transform infrared spectra were recorded using the Shimadzu IRAffinity-1 FTIR spectrophotometer (Shimadzu Europa GmbH, Kyoto, Japan) in KBr pellets. The HRMS spectrum was recorded using electrospray ionization using Bruker microTOF apparatus (Bruker Analytische Messtechnik GmbH, Rheinstetten, Germany) in positive mode.

### 3.2. Synthesis of 3,6-Dibromo-9H-carbazole 1

Carbazole (5.00 g, 30 mmol) was dissolved in DMF (50 mL), and the solution was cooled to 0 °C; then, NBS (11.20 g, 63 mmol, 2.1 eq.) in DMF (30 mL) was added. The reaction was allowed to warm to room temperature and stirred overnight. Afterwards, 200 mL of water was added to the reaction mixture to precipitate the product, which was then filtered and dried in air. The obtained substance **1** was isolated by flash chromatography (silica gel, eluent DCM/hexane 1:1). Quantitative yield, 9.75 g.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ, ppm: 11.58 (s, 1H), 8.43 (d, *J* = 2.0 Hz, 2H), 7.53 (dd, *J* = 8.7, 2.0 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H) (Figure S1).

### 3.3. Synthesis of 9H-Carbazole-3,6-dicarbonitrile 2

3,6-Dibromocarbazole (5.00 g, 15.4 mmol), dppf (56 mg, 0.10 mmol), Zn(CN)<sub>2</sub> (2.20 g, 19 mmol), zinc powder (40 mg, 0.62 mmol), Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (180 mg, 0.82 mmol) and Pd<sub>2</sub>(dba)<sub>3</sub>·dba (80 mg, 0.07 mmol) were added to a 100 mL Schlenk flask and dissolved in 50 mL DMF and 0.5 mL water previously degassed by ultrasonication in vacuo. This mixture was heated to 110 °C for 3 days. The resulting suspension was cooled, and then poured into a 100 mL mixture of H<sub>2</sub>O/NH<sub>4</sub>Cl(sat.)/NH<sub>3</sub>(sat.) (50/40/10 *v/v*) and filtered through a suction filter. The filter cake was dissolved in DMF and filtered through a silica gel layer. The solution concentrated in vacuo to ca. 50 mL and cooled up to −10 °C. The obtained crystalline solid was filtered, washed with cold diethyl ether (2 × 20 mL) and dried in air to afford the target product **2** (1.76 mg, 53%) as a colorless crystalline solid.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ, ppm: 12.36 (s, 1H), 8.78 (d, *J* = 1.7 Hz, 2H), 7.84 (dd, *J* = 8.5, 1.7 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H) (Figure S2).

### 3.4. 9-Vinyl-9H-carbazole-3,6-dicarbonitrile 3

Sodium hydride (60% suspension in mineral oil) (184 mg, 4.6 mmol, 2 eq.) was washed with dry hexane (2 × 5 mL) under an argon atmosphere and dried in vacuo. Then, dry DMSO (20 mL) and 9H-carbazole-3,6-dicarbonitrile **2** (500 mg, 2.3 mmol) were added. The resulting mixture was stirred vigorously for 2 h, and 1,2-dibromoethane (1.3 g, 600 μL, 3 eq.) was added to one portion. The resulting solution was stirred overnight and an additional portion of sodium hydride (460 mg, 5 eq.) in dry DMSO (10 mL) was added. This solution was further stirred overnight and poured into 100 mL of water. The precipitate was filtered, washed with diethyl ether (2 × 10 mL) and dried in vacuo, affording the title compound **3** (408 mg, 73%) as a colorless crystalline solid.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ, ppm: 8.81 (d, *J* = 1.6 Hz, 2H), 7.98 (d, *J* = 8.6 Hz, 2H), 7.93 (dd, *J* = 8.6, 1.6 Hz, 2H), 7.56 (dd, *J* = 15.9, 9.2 Hz, 1H), 5.78 (dd, *J* = 15.9, 1.6 Hz, 1H), 5.46 (dd, *J* = 9.2, 1.6 Hz, 1H) (Figure S3). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ, ppm: 141.1, 130.7, 128.8, 126.2, 122.4, 119.5, 112.4, 107.5, 103.6 (Figure S4). FTIR (KBr)  $\tilde{\nu}$ , cm<sup>−1</sup>: 3068 (br, C-H), 2224 (C≡N), 1599 (C=C) (Figure S7). HRMS (ESI) *m/z* [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>10</sub>N<sub>3</sub><sup>+</sup> 244.0869, found 244.0869 (Figures S5 and S6).

**Supplementary Materials:** The following are available online, Figures S1–S7: <sup>1</sup>H and <sup>13</sup>C NMR, FTIR spectra and HRMS data for compound **3**.

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