

## Synthesis of novel bis-( $\beta$ -cyanohydrin) connected by a polyoxyethylene chain and their corresponding (*ZZ*) and (*EE*) bis-acrylonitriles

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**Résumé :** Les bis-( $\beta$ -cyanhydrines) de polyoxyéthylène glycols, obtenus par ouverture des éthers diglycidiques en présence de cyanure de potassium; ont été converties en dinitriles  $\alpha,\beta$ -insaturés correspondant moyennant deux méthodes. La première est réalisée en présence de chlorure de tosyloxy en milieu basique alors que la seconde est menée par action du chlorure de thionyle dans un mélange de toluène-pyridine à 80° C. Chaque méthode de synthèse fournit un mélange de deux isomères *ZZ* et *EE* alors que l'isomère *ZE* n'est pas observé. Le mécanisme de la réaction suit un processus d'élimination du type  $E_2$ .

**Mots Clés:**  $\beta$ -cyanhydrine, nitrile  $\alpha,\beta$ -insaturé, Oligoéthylène glycols diglycidyl éthers; cyanure de potassium.

**Abstract:** Bis-( $\beta$ -cyanohydrins) polyoxyethylene glycols, obtained by opening reaction of diglycidyl ethers in the presence of potassium cyanide, was converted to dinitrile  $\alpha,\beta$ -unsaturated via two methods. The first was carried out in the presence of tosyl chloride in a basic medium while the second was conducted by the action of thionyl chloride in a mixture of toluene-pyridine at 80 °C. Each synthetic method gives a mixture of two isomers *ZZ* and *EE* whereas the *ZE*-isomers are not observed. The mechanism of reaction follows a bimolecular elimination  $E_2$ .

**Key Words:**  $\beta$ -cyanhydrin,  $\alpha,\beta$ -unsaturated nitrile, Oligoethylene glycols diglycidyl ethers, potassium cyanide.

### INTRODUCTION

Over the past years, chiral cyanohydrins have become a versatile source for a variety of chiral building blocks. Several classes of valuable intermediates have been already synthesized, including  $\alpha,\beta$ -unsaturated nitriles [1-4]. These later well-known as synthetic intermediates leading to a variety of products [5]. They are easily transformed into carbocycles [6] and heterocyclic compounds [7]. The conjugate addition to these Michael receptors gives the substituted saturated nitriles [8,9] which used in the synthesis of natural products [10,11]. Similarly, the selective hydrogenation of  $\alpha,\beta$ -unsaturated nitriles conducted to the corresponding amines [12]. It was used as intermediates in the pharmaceutical, agrochemical and fine chemicals [13-16]. The

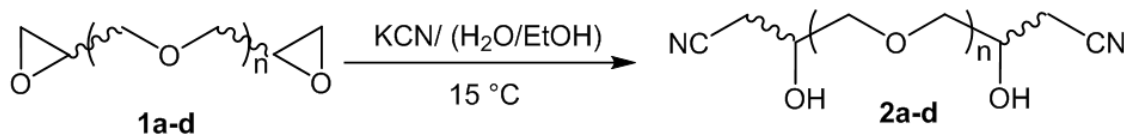
importance of  $\alpha,\beta$ -unsaturated nitriles is the origin of many synthetic methods for their preparation [10].

Due to the possibly different biological activities of stereoisomers, methods for the preparation of pure (*E*)- and (*Z*)-isomers are of particular interest, especially for the synthesis of pharmaceutical [17].

The stereochemistry of carbon-carbon double bonds is important in exhibiting biological activity and other functionality [18]. Also, molecules with C=C and CN groups in conjugation or in close proximity are much more difficult to reduce selectively [19-22].

On the other hand, cyanohydrins as an interface between biology and chemistry are very important synthons in synthetic organic chemistry being

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**Scheme 1:** Synthesis of bis-( $\beta$ -hydroxynitriles) **2a-d**.

widely employed in the synthesis of a large variety of natural and biologically active products [23,24]. For instance, they are good precursors of numerous compounds with different pharmaceutical applications as cardiovascular [26], antibiotics [27-29] and anti-tumor [30]. They are also used as chiral auxiliaries in asymmetric synthesis [31]. The opening reaction of epoxides with cyanide ion is the method of choice used for the preparation of  $\beta$ -hydroxynitriles. Several hydrocyanation reagents employed was described in the literature [32-37]. Kamal *et al.* have carried out the opening of 2-(phenoxyethyl)oxiranes using sodium cyanide in a mixture of water-ethanol at room temperature [38]. Herein, we report the synthesis of a series of new class of bis-( $\alpha,\beta$ -unsaturated nitriles) bridged by a polyoxyethylene chain starting from the corresponding bis-( $\beta$ -cyanohydrins).

## RESULTS AND DISCUSSION

Our strategy started with the hydrocyanation of oligoethylene glycol diglycidyl ethers **1a-d** [39] with potassium cyanide in a hydro-ethanol media at 15°C to give the corresponding bis-(hydroxynitrile)polyoxyethylenes **2a-d** in 25-67 %

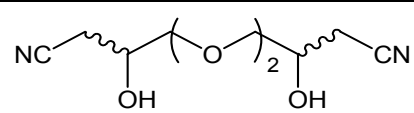
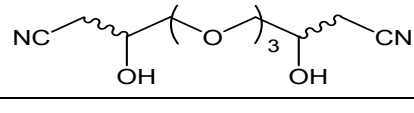
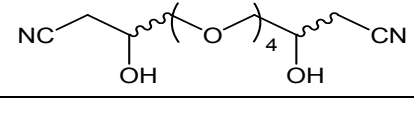
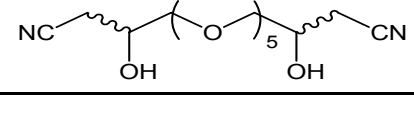
yield after purification with flash column chromatography as shown in Scheme 1.

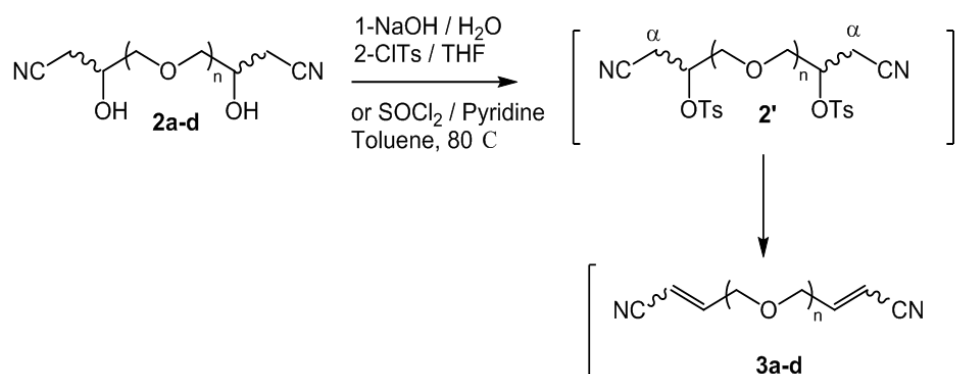
The reaction was carried out under mild conditions using common reagents (KCN) in water and ethanol as solvents. The different hydroxynitriles obtained was collected in table I.

The mechanism of reaction started with the attack of the cyanide ion on the terminal carbon of the epoxide and only the secondary cyanohydrins was observed. The opening reaction in this case follows a bimolecular  $S_N2$  process. It is worth to noting that as the epichlorohydrin used is a racemic mixture, the bis-epoxides **1a-d** and the hydroxynitrile **2a-d** exist as mixtures of diastereoisomers. However, in each case, the two stereogenic centers within the molecule are distant from each other such that diastereoisomers could not be discerned by NMR spectroscopy [40].

When tosyl chloride react with hydroxynitriles **2a-d**,  $\alpha,\beta$ -unsaturated nitriles **3a-d** was obtained as a mixture of *EE* and *ZZ*-isomers as showed in scheme 2. The reaction was carried in two steps and proceeded in one pot in which the tosylation displays presumably the activation step. The first step started by tosylation of hydroxyl groups

**Table I:** Preparation of bis-( $\beta$ -hydroxynitrile) polyoxyethylenes **2a-d**.

	Hydroxynitrile <b>2</b>	Yield (%)
<b>2a</b>		25
<b>2b</b>		37
<b>2c</b>		52
<b>2d</b>		67



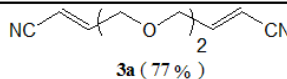
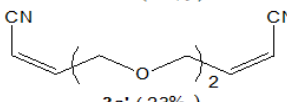
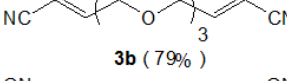
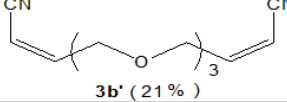
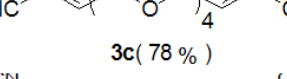
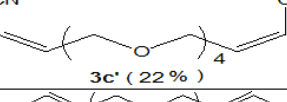
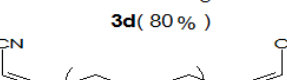
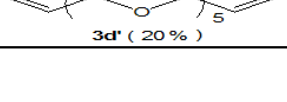
**Scheme 2:** Synthesis of unsaturated nitriles **3a-d** with tosyl chloride.

although the expected tosylate **2'** was not isolated. In the second step, since the reaction was carried in a basic medium, **2'** underwent a smooth elimination of two HOTs (*p*-toluene sulfonic acid) and give the unsaturated nitriles **3a-d**. Attempts to separate the two *EE* and *ZZ*-isomers by columns chromatography were failed. The new unsaturated nitriles **3a-d** was summarised in Table II.

The analysis of the  $^1\text{H}$  NMR spectra showed that the percentage of *ZZ*-isomer in the mixture is about 77 to 80%, while the integration of the *EE*-

isomer is about 20-23%. These results have been determinate from the  $^1\text{H}$  NMR data of signals intensity of the of proton ethylene groups. In fact, the coupling constant in *EE*-isomer  $^3J_{\text{H-H}}$  is 16.0 Hz while that of the *ZZ*-isomers 11.0 Hz. It is worth to note that the *EZ*-isomer is not formed in this case, nor the  $\beta,\gamma$ -unsaturated nitriles involving loss of a  $\gamma$ -hydrogen. The absence of the former of *EZ*-isomer is due to reaction centres are very distant and therefore it react in the same way in accordance with the previous results [41], whereas

**Table II:** Unsaturated nitriles **3a-d** prepared with tosyl chloride

unsaturated dinitriles <b>3</b>	n	Composition of mixture	Overall yield (%)
<b>3a+3a'</b>	2	 <b>3a (77%)</b>	72
		 <b>3a' (23%)</b>	
<b>3b+3b'</b>	3	 <b>3b (79%)</b>	79
		 <b>3b' (21%)</b>	
<b>3c+3c'</b>	4	 <b>3c (78%)</b>	81
		 <b>3c' (22%)</b>	
<b>3d+3d'</b>	5	 <b>3d (80%)</b>	84
		 <b>3d' (20%)</b>	

**Table III:** Synthesis of bis-( $\alpha,\beta$ -unsaturated nitriles) **3a-d** with thionyl chloride

unsaturated dinitriles <b>3</b>	n	Ratio of two isomer in the mixture <sup>a</sup>	Overall yield (%) <sup>b</sup>
<b>3a+3a'</b>	2		37
<b>3b+3b'</b>	3		54
<b>3c+3c'</b>	4		65
<b>3d+3d'</b>	5		80

<sup>a</sup>Ratio of two isomer in the mixture was determined by <sup>1</sup>H NMR,

<sup>b</sup>overall yield after purification with columns chromatography.

the non-formation of  $\beta,\gamma$ -unsaturated nitriles can be assumed be due to the enhanced acidity of hydrogen's in  $\alpha$  position to nitrile group.

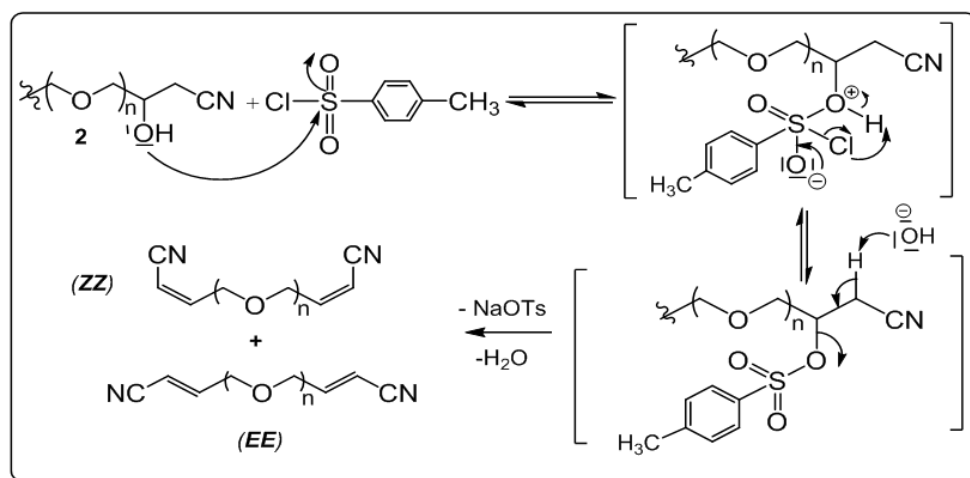
To improve the results for the synthesis of unsaturated nitriles **3a-d**, the reaction was carried using thionyl chloride instead of tosyl chloride (Scheme 2) in two steps and proceeded in one pot in which the thionylation displays presumably the activation step. In this case, the reaction gives also a mixture of two isomers, but the NMR indicates that the percentage of the *EE*-isomer is about 83-86 % whereas the percentage of *ZZ*-isomer is only about 14-17%. The obtained result was grouped in table III.

The mechanism of the tosyl chloride involve in the first step a nucleophilic addition of the hydroxyl group on the tosyl chloride group S=O followed by elimination of hydrogen chloride. The presence of NaOH allows the elimination of the mobile hydrogen in  $\alpha$  of the nitrile group. Removing H<sub>2</sub>O, sodium paratoluene sulfonate (NaOTs) to give the  $\alpha,\beta$ -unsaturated dinitriles of polyoxyethylene via a bimolecular elimination *E*<sub>2</sub> as shown in Scheme 3.

The mechanism of the thionyl chloride is analogous to precedent. Indeed, the first step involve the nucleophilic addition of the hydroxyl group on the S=O group followed by elimination of hydrogen chloride. The presence of pyridine allows the elimination of the mobile hydrogen in  $\alpha$  position of the nitrile group. Removing a pyridine hydrochloride and SO<sub>2</sub> to give the  $\alpha,\beta$ -unsaturated nitriles via bimolecular elimination *E*<sub>2</sub>.

## CONCLUSION

In this work, we have prepared a new series of bis-( $\beta$ -hydroxynitriles) connected with a variable polyoxyethylene chain via the reaction of diglycidyl ethers with potassium cyanide. The obtained bis-( $\beta$ -cyanohydrins) was transformed into the corresponding  $\alpha,\beta$ -unsaturated nitriles with tosyl chloride or thionyl chloride. We have shown that in both cases, the reaction gives a mixture of two *ZZ* and *EE* isomers whereas the *ZE*-isomers are not observed. The mechanism of the reaction follows a bimolecular elimination *E*<sub>2</sub> process in each synthetic method.



**Scheme 3:** Proposed mechanism reaction of cyanohydrins **2** with tosyl chloride.

## EXPERIMENTAL

All commercially available reagents were used without further purification. Liquid chromatography was performed using a forced flow (flash chromatography) of the indicated solvent system on silica gel (230-400 mesh). Analytical thin layer chromatography (TLC) was performed using Silica Gel 60 F254 plates (Fluka 40-60 mm). The developed chromatogram was analyzed by UV lamp (254 nm). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AC-300 at 300 and 75 MHz, respectively.

Deuteriochloroform ( $\text{CDCl}_3$ ), unless otherwise noted, on a 300 MHz instrument. Chemical shifts of  $^1\text{H}$  NMR spectra are reported in parts per million (ppm) on the  $\delta$  scale from an internal standard of residual chloroform (7.27 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, and m = multiplet) and coupling constant in hertz (Hz). Chemical shifts of  $^{13}\text{C}$  NMR spectra are reported in ppm from the central peak of  $\text{CDCl}_3$  (77.23 ppm) on the  $\delta$  scale. Data are reported as follows: chemical shift, multiplicity (s = singlet and m = multiplet). High-Resolution mass spectra (HMRS) were obtained from FINIGAN MAT 95 SBE.

### 1. Preparation of polyoxyethylene hydroxynitriles (**2**)

A solution of 25 mmol of diglycidyl ether **1** was added 3.9 g (60 mmol) of KCN, 150 mL of water and 50 mL of ethanol. The mixture was stirred at 15 °C in a water bath for 48 h. The progress of the reaction is followed by thin layer chromatography with diethyl ether /acetone 30/70. At the end of the

reaction, the organic layer was extracted with dichloromethane (3x25 mL), washed with water (2x25 mL), dried over sodium sulphate and then filtered. The solvent was removed under reduce presser and the crude product is purified with column chromatography with diethyl ether/acetone (30/70) as eluent to give a pure hydroxynitriles **2** as yellow viscous oils.

**3,10-Dihydroxy-5,8-dioxadodecane-1,12-dinitrile (2a):** IR ( $\text{CHCl}_3$ ):  $\nu = 3480$  (OH),  $2220$  ( $\text{C}\equiv\text{N}$ )  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta = 4.08$  (m, 2H,  $2\text{CH}_2\text{OH}$ ), 3.62 (m, 4H,  $2\text{CH}_2\text{O}$ ), 3.53 (m, 4H,  $2\text{CH}_2\text{OCHOH}$ ), 2.65 (m, 4H,  $2\text{CH}_2\text{CN}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75MHz):  $\delta = 118.09$  (s, 2C,  $2\text{C}\equiv\text{N}$ ), 73.59 (s, 2C,  $2\text{CHOH}$ ), 70.50-70.15 (m, 6C,  $6\text{CH}_2\text{O}$ ), 66.18 (s, 2C,  $2\text{CH}_2\text{OCHOH}$ ), 22.28 (s, 2C,  $2\text{CH}_2\text{C}\equiv\text{N}$ ).

**3,13-Dihydroxy-5,8,11-trioxapentadecane-1,15-dinitrile (2b):** IR ( $\text{CHCl}_3$ ):  $\nu = 3507$  (OH),  $2226$  ( $\text{C}\equiv\text{N}$ )  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta = 4.12$  (m, 2H,  $2\text{CH}_2\text{OH}$ ), 3.66 (m, 20H,  $10\text{CH}_2\text{O}$ ), 3.53 (m, 4H,  $2\text{CH}_2\text{OCHOH}$ ), 2.64 (m, 4H,  $2\text{CH}_2\text{CN}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75MHz):  $\delta = 118.05$  (s, 2C,  $2\text{C}\equiv\text{N}$ ), 73.60 (s, 2C,  $2\text{CHOH}$ ), 70.51-70.18 (m, 6C,  $6\text{CH}_2\text{O}$ ), 66.18 (s, 2C,  $2\text{CH}_2\text{OCHOH}$ ), 22.24 (s, 2C,  $2\text{CH}_2\text{C}\equiv\text{N}$ ).

**3,16-Dihydroxy-5,8,11,14-tetraoxaoctadecane-1,18-dinitrile (2c):** IR ( $\text{CHCl}_3$ ):  $\nu = 3492$  (OH),  $2223$  ( $\text{C}\equiv\text{N}$ )  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta = 4.09$  (m, 2H,  $2\text{CH}_2\text{OH}$ ), 3.68 (m, 12H,  $6\text{CH}_2\text{O}$ ), 3.55 (m, 4H,  $2\text{CH}_2\text{OCHOH}$ ), 2.65 (m, 4H,  $2\text{CH}_2\text{CN}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75MHz):  $\delta = 118.04$  (s, 2C,  $2\text{C}\equiv\text{N}$ ), 73.67 (s, 2C,  $2\text{CHOH}$ ), 70.49-70.16



(m, 8C, 8CH<sub>2</sub>O), 66.21 (s, 2C, 2 CH<sub>2</sub>OCHOH), 22.26 (s, 2C, 2CH<sub>2</sub>C≡N).

**3,19-Dihydroxy-5,8,11,14,17-pentaoxauncosane-1,21-dinitrile (2d):** IR (CHCl<sub>3</sub>):  $\nu = 3501$  (OH), 2227 (C≡N) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta = 4.11$  (m, 2H, 2CHOH), 3.65 (m, 16H, 8CH<sub>2</sub>O), 3.56 (m, 4H, 2CH<sub>2</sub>OCHOH), 2.63 (m, 4H, 2 CH<sub>2</sub>CN). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta = 118.07$  (s, 2C, 2C≡N), 73.58 (s, 2C, 2CHOH), 70.48-70.19 (m, 6C, 6CH<sub>2</sub>O), 66.10 (s, 2C, 2 CH<sub>2</sub>OCHOH), 22.30 (s, 2C, 2CH<sub>2</sub>C≡N).

## 2. Preparation of bis-( $\alpha,\beta$ -unsaturated nitrile) polyoxyethylenes (3)

### a) Method A: In the presence of tosyl chloride

2.1g (53 mmol) of sodium hydroxide was dissolved in 10 mL of water and cooled to 0°C. 15 mmol of bis-(cyanohydrins) **2** in 10 mL of THF was added dropwise. After 2h of contact at 0°C, 6.29 g (33 mmol) of *p*-toluenesulfonyl chloride in 15 mL of THF was added dropwise. At the end of the addition, stirring was continued for 5 h at 0°C. The mixture is then poured into a cold solution of HCl (10%) and extracted with methylene chloride (4x40 mL). The organic layer is washed with water (2x30 mL) and then with saturated solution of NaHCO<sub>3</sub> (4x40 mL) and again with water (2x30 mL) until neutral pH. After drying over MgSO<sub>4</sub> and evaporation of the solvent under reduced pressure, the resulting oil was purified by column chromatography with a mixture of petroleum ether and methylene chloride (20/80) to give bis-( $\alpha,\beta$ -unsaturated dinitrile) polyoxy-ethylenes **3** as yellow viscous oil.

### b) Method B: In the presence of thionyl chloride

To a solution of bis-(hydroxynitrile)polyoxyethylene **2** (15 mmol) in 10 mL of dry toluene was added 20 mL of pyridine. The reaction was heating at 80°C and 45 mmol of thionyl chloride was added dropwise. After the addition, the mixture was heated at reflux for 24 hours. The mixture was cooled to room temperature, acidified with hydrochloric acid 10% and extracted with methylene chloride (4x40mL). After separation, the organic layer was washed with water (3x40mL), dried over sodium sulfate and the solvent was removed. The bis-( $\alpha,\beta$ -unsaturated nitriles) of polyoxyethylene **3** was obtained as yellow viscous oil in a pure state relatively and purified by flash column chromatography with methylene chloride as solvent.

### 5,8-Dioxadodecane-2,10-diene-1,12-dinitrile

**(3a+3a')**: IR (CHCl<sub>3</sub>)  $\nu = 1627$  (C=C), 2220(C≡N) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300MHz):  $\delta = 3.25$ -3.28 (m, 4H, 2CH<sub>2</sub>O), *EE-isomer*: 3.81-3.79 (m, 4H, 2CH<sub>2</sub>OCH=CH), 5.41-5.36 (dm, 2H, 2CH<sub>2</sub>OCH=CH, <sup>3</sup>J<sub>HH</sub> = 16.4 Hz), 6.41-6.35 (m, 2H, 2CH<sub>2</sub>OCH=CH); *ZZ-isomer*: 3.95-3.92 (m, 4H, 2CH<sub>2</sub>OCH=CH), 5.16-5.12 (dm, 2H, 2CH<sub>2</sub>OCH=CH, <sup>3</sup>J<sub>HH</sub> = 11.3 Hz), 6.21-6.35 (m, 2H, 2CH<sub>2</sub>OCH=CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta = 68.4$ -71.2 (m, 4C, 4CH<sub>2</sub>O), *ZZ-isomer*: 99.3 (s, 2C, 2 CH=CHCN), 115.3 (s, 2C, 2C≡N), 150.7 (s, 2C, 2 CH=CHCN), *EE-isomer*: 100.5 (s, 2C, 2CH=CHCN), 117.57 (s, 2C, 2C≡N), 151.25 (s, 2C, 2CH=CHCN).

### 5,8,11-Trioxapentadecane-2,13-dien-1,15-dinitrile

**(3b+3b')**: IR (CHCl<sub>3</sub>)  $\nu = 1612$  (C=C), 2226 (C≡N) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300MHz):  $\delta = 3.23$ -3.27 (m, 8H, 4CH<sub>2</sub>O), *EE-isomer*: 3.78-3.82 (m, 4H, 2CH<sub>2</sub>OCH=CH), 5.32-5.37 (dm, 2H, 2CH<sub>2</sub>OCH=CH, <sup>3</sup>J<sub>HH</sub> = 16.5 Hz), 6.34-6.40 (m, 2H, 2CH<sub>2</sub>OCH=CH); *ZZ-isomer*: 3.93-3.97 (m, 4H, 2CH<sub>2</sub>OCH=CH), 5.13-5.17 (dm, 2H, 2CH<sub>2</sub>OCH=CH, <sup>3</sup>J<sub>HH</sub> = 11.5 Hz), 6.23-6.37 (m, 2H, 2CH<sub>2</sub>OCH=CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta = 68,44$ -71,26 (m, 6C, 6CH<sub>2</sub>O), *ZZ-isomer*: 99.3 (s, 2C, 2 CH=CHCN), 115.4 (s, 2C, 2C≡N), 150.74 (s, 2C, 2 CH=CHCN), *EE-isomer*: 100.5 (s, 2C, 2CH=CHCN), 117.5 (s, 2C, 2C≡N), 151.2 (s, 2C, 2CH=CHCN).

**5,8,11,14-Tetraoxaoctadecane-2,16-dien-1,18-dinitrile(3c+3c')**: IR (CHCl<sub>3</sub>)  $\nu = 1618$  (C=C), 2223 (C≡N) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta = 3.22$ -3.26 (m, 12H, 6CH<sub>2</sub>O), *EE-isomer*: 3.81-3.83 (m, 4H, 2CH<sub>2</sub>OCH=CH), 5.35-5.41 (dm, 2H, 2CH<sub>2</sub>OCH=CH, <sup>3</sup>J<sub>HH</sub> = 16.3 Hz), 6.35-6.41 (m, 2H, 2CH<sub>2</sub>OCH=CH); *ZZ-isomer*: 3.92-3.96 (m, 4H, 2CH<sub>2</sub>OCH=CH), 5.12-5.16 (dm, 2H, 2CH<sub>2</sub>OCH=CH, <sup>3</sup>J<sub>HH</sub> = 11.4 Hz), 6.22-6.38 (m, 2H, 2CH<sub>2</sub>OCH=CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta = 68.4$ -71.2 (m, 8C, 8CH<sub>2</sub>O), *ZZ-isomer*: 99.3 (s, 2C, 2CH=CHCN), 115,4 (s, 2C, 2C≡N), 150.7 (s, 2C, 2CH=CHCN), *EE-isomer*: 100.3 (s, 2C, 2CH=CHCN), 117.5 (s, 2C, 2C≡N), 151.2 (s, 2C, 2CH=CHCN).

**5,8,11,14,17-Pentaoxauncosane-2,19-dien-1,21-dinitrile (3d+3d')**: IR (CHCl<sub>3</sub>)  $\nu = 1625$  (C=C), 2227 (C≡N) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta = 3.24$ -3.27 (m, 16H, 8CH<sub>2</sub>O), *EE-isomer*: 3.80-3.82 (m, 4H, 2CH<sub>2</sub>OCH=CH), 5.34-5.40 (dm, 2H, 2CH<sub>2</sub>OCH=CH, <sup>3</sup>J<sub>HH</sub> = 16.2 Hz),

6.36-6.42 (m, 2H, 2CH<sub>2</sub>OCH=CH); *ZZ*-isomer: 3.95-3.97 (m, 4H, 2CH<sub>2</sub>OCH=CH), 5.14-5.18 (dm, 2H, 2CH<sub>2</sub>OCH=CH, <sup>3</sup>J<sub>HH</sub> = 11.2 Hz), 6.24-6.30 (m, 2H, 2CH<sub>2</sub>OCH=CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ = 68.4-71.26 (m, 10C, 10 CH<sub>2</sub>O), *ZZ*-isomer: 99.3 (s, 2C, 2 CH=CNCN), 115.3 (s, 2C, 2C≡N), 150.7 (s, 2C, 2 CH=CNCN), *EE*-isomer: 100.5 (s, 2C, 2 CH=CNCN), 117.6 (s, 2C, 2C≡N), 151.2 (s, 2C, 2 CH=CNCN).

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