

## Cross-conjugated $\omega,\omega'$ -bis(dimethylamino) ketones and dinitriles containing a cycloalkane or piperidine fragment: synthesis and study of spectroscopic properties\*

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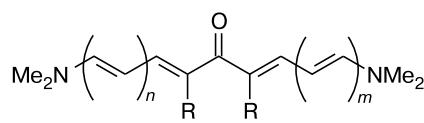
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N-Substituted 4-piperidones react with  $\beta$ -dimethylaminoacrolein aminals to give keto-cyanines containing a piperidine ring. A reaction of 3-dimethylamino-1,1,3-trimethoxypropane with 1-ethoxycarbonylpiperidin-4-ylidenemalononitrile produces a cross-conjugated  $\omega,\omega'$ -bis(dimethylamino) dinitrile. Its yield is doubled when ionic liquids are used. The spectroscopic properties of the compounds obtained are highly sensitive to the structure: replacement of the C=O group in ketocyanines by the C=C(CN)<sub>2</sub> group results in a considerable bathochromic shift of the absorption spectra, while replacement of the central bridging fragment (CH<sub>2</sub>)<sub>3</sub> by (CH<sub>2</sub>)<sub>4</sub> results in a hypsochromic shift. All the compounds obtained exhibit positive solvatochromism.

**Key words:** malononitriles, ketocyanines,  $\beta$ -dimethylaminoacrolein aminal, 3-dimethylamino-1,1,3-trimethoxypropane, ionic liquids, electronic absorption spectra, chromophores, dyes.

Earlier, we have developed methods for the synthesis of ketocyanines,  $\omega,\omega'$ -bis(dimethylamino polyenyl) ketones (BDAK), which are bichromophoric cross-conjugated systems with two polyene chains coupled through a carbonyl group.<sup>1–3</sup> The terminal substituents are electron-donating dimethylamino groups and the central substituent is an electron-withdrawing carbonyl group.

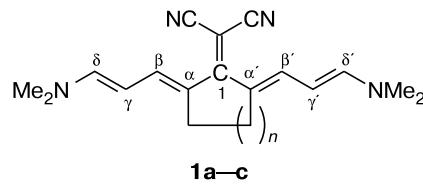


BDAK ( $n = 1, 2$ ;  $m = 1–3$ )

Owing to their electronic structure, BDAK exhibit pronounced solvatochromism,<sup>4,5</sup> strong thermochromism,<sup>6</sup> intense fluorescence, and generation of laser radiation.<sup>7</sup> Being structurally simple, these compounds are convenient models for the study of various photophysical and

photochemical processes (e.g., interactions of the chromophores in the singlet- and triplet-excited states<sup>1,8,9</sup>).

Recently,<sup>10</sup> we have obtained new analogs of BDAK, viz., cross-conjugated  $\alpha,\alpha'$ -bis(3-dimethylaminoprop-2-enylidene)cycloalkylidenemalononitriles **1a–c** containing the dicyanomethylidene fragment instead of the carbonyl group.



$n = 1$  (**a**),  $2$  (**b**),  $3$  (**c**)

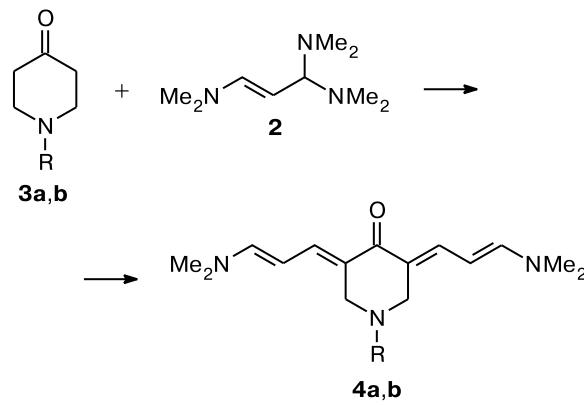
According to recent data,<sup>11,12</sup> cyano-containing polyenes can be employed as materials for nonlinear optics. In addition, interesting fluorescent features have been discovered in merocyanine dyes with electron-withdrawing dicyano substituents.<sup>13,14</sup> Therefore, one can assume that combination of a dimethylamino polyene chain and a cyano group in compounds **1a–c** will impart valuable properties to these compounds.

\* On the occasion of the 75th anniversary of the foundation of the N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences.

The goal of the present work was to obtain new ketocyanines containing the 4-piperidone ring and their dicyanomethylidene analogs and compare their spectroscopic properties.

Condensation of  $\beta$ -dimethylaminoacrolein aminal **2** (see Ref. 15) with N-substituted 4-piperidones **3a,b** ( $75\text{--}80^\circ\text{C}$ , 60–90 min) gave ketocyanines **4a,b** in 90% yields (Scheme 1).

Scheme 1



R = Me (**a**),  $\text{CO}_2\text{Et}$  (**b**)

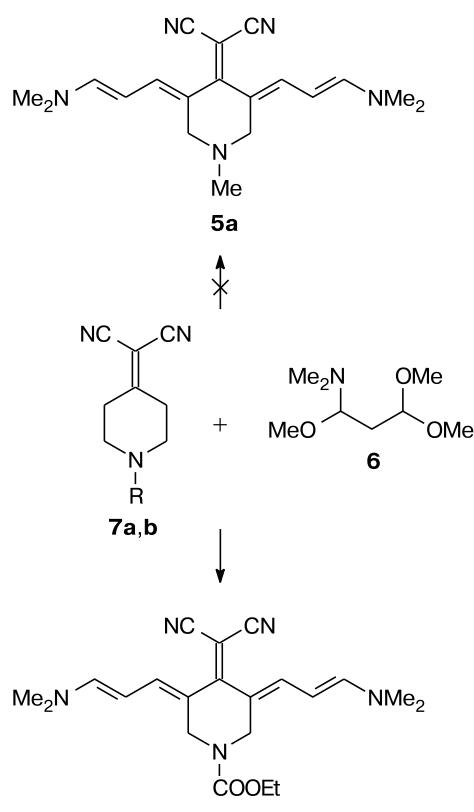
To obtain conjugated dinitriles **5a,b**, which are dicyanomethylidene analogs of ketocyanines **4a,b**, we studied condensations of aminal **2** and 3-dimethylamino-1,1,3-trimethoxypropane (**6**)<sup>16</sup> with 1-methylpiperidin-4-ylidenemalononitrile (**7a**)<sup>17</sup> and 1-ethoxycarbonylpiperidin-4-ylidenemalononitrile (**7b**) (Scheme 2).

Attempted synthesis of polyene dinitriles **5a,b** via condensation of dinitriles **7a,b** with aminal **2** was unsuccessful.

However, a condensation of reagent **6** with dinitrile **7b** (unlike dinitrile **7a**) gave cross-conjugated dinitrile **5b**. The yield of product **5b** depends on the reaction conditions: 23% for neat reagents and 43% in the presence of ionic liquids (1-butyl-3-methylimidazolium tetrafluoroborate [ $\text{bmim}\text{BF}_4^-$ ] or 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide). The structures of cross-conjugated polyenes **4a,b** and **5b** obtained as bright red (**4a,b**) and brown crystals (**5b**) were determined from  $^1\text{H}$  and  $^{13}\text{C}$  NMR, UV-Vis, and mass spectra and elemental analysis data. For signal assignments in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, 2D COSY, HSQC, and HMBC experiments were carried out. The vicinal constants  $^3J_{\beta-\gamma}$  and  $^3J_{\gamma-\delta}$  (12.0 and 12.4 Hz, respectively) suggest a *E*-configuration of the double bonds and an *S-trans*-conformation of the diene fragment in these compounds.

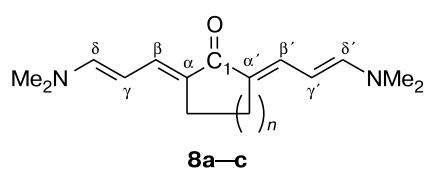
The influence of the structure of cross-conjugated  $\omega,\omega'$ -bisamino polyenes and the solvating effect of the solvent on their spectroscopic properties were studied in

Scheme 2



R = Me (**a**),  $\text{CO}_2\text{Et}$  (**b**)

solvents with different polarities for ketocyanines **4a,b**, dinitrile **5b**, cross-conjugated dinitriles **1a–c** (see Ref. 10), and ketocyanines **8a–c** (see Refs 2, 3).



$n = 1$  (**a**), 2 (**b**), 3 (**c**)

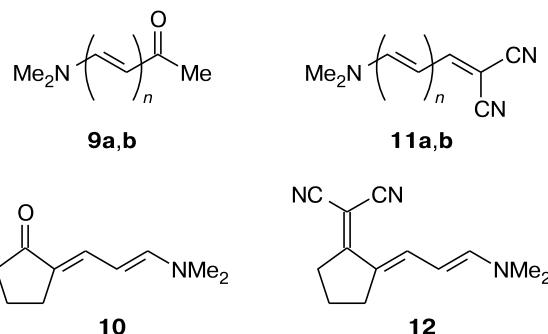
The absorption peaks in the spectra of the above ketocyanines and dinitriles are given in Table 1. It should be noted that the emission intensities of the dinitriles are substantially lower than those of ketocyanines (see data from emission measurements<sup>18</sup>). Since the absorption band of the dinitriles and the ketocyanines shift to the longer wavelengths when polar solvents are used instead of nonpolar ones (positive solvatochromism), this band is obviously due to an intramolecular charge transfer. The amino groups in both the ketocyanines and dinitriles are electron donors, while the cyano fragments in the dinitriles are electron acceptors (like the carbonyl group in the

**Table 1.** Absorption peaks of the dyes in solvents with different polarities

Compound	$\lambda_{\max}/\text{nm}$			
	Heptane	$\text{CHCl}_3$	$\text{EtOH}$	$\text{H}_2\text{O}$
<b>1a</b>	511	568	583	604
<b>1b</b>	534	546	575	592
<b>1c</b>	438	494	512	539
<b>4a</b>	415	460	490	518
<b>4b</b>	418	460	480	519
<b>5b</b>	—	540	575	—
<b>8a</b>	429	475	502	529
<b>8b</b>	416	460	490	521
<b>8c</b>	372	419	446	477

ketocyanine). The absorption bands of the dinitriles are strongly (by 70–100 nm) shifted to the longer wavelengths compared to the corresponding ketocyanines (see Table 1). This can be associated with the lengthening of the chromophore in the dinitriles by the fragment  $\text{C}=\text{C}(\text{CN})_2$ , which is cross-conjugated with the side polyene chains (the chromophores are chains from the amino group (an electron donor) to the  $\text{C}\equiv\text{N}$  groups (electron acceptors)). It should be noted that when both polyene chromophores in ketocyanines are lengthened by one unit, the absorption band of the dye is shifted by ~95 nm,<sup>8</sup> while a lengthening of only one chromophore results in a shift only by ~25 nm (see Refs 4, 8).

In conjugated mono(dimethylamino) ketones, replacement of the carbonyl group by a dicyanomethylidene fragment brings about a considerable bathochromic shift  $\lambda_{\max}$  (by 100–120 nm), which is evident from the absorption peaks of compounds **9**–**12** (Table 2).



$n = 2$  (**a**), 3 (**b**)

In addition, it can be seen in Table 1 that the dyes differing only in the size of the central ring absorb at very different wavelengths: the spectra of ketocyanines and dinitriles with a seven-membered central ring experience a hypsochromic shift compared to their six-membered analogs. Apparently, this is due to the weaker conjugation in the molecules containing the cycloheptane bridge

**Table 2.** Absorption peaks of mono(dimethylamino) ketones and dinitriles in ethanol and the shifts  $\Delta\nu$  and  $\Delta\lambda$  of the peaks for the corresponding ketone–dinitrile pairs

Compound	Mono(dimethylamino) ketones	Mono(dimethylamino) dinitriles	$\Delta\nu/\text{cm}^{-1}$ ( $\Delta\lambda/\text{nm}$ )	
	Compound	$\nu_{\max}/\text{cm}^{-1}$ ( $\lambda_{\max}/\text{nm}$ )	Compound	$\nu_{\max}/\text{cm}^{-1}$ ( $\lambda_{\max}/\text{nm}$ )
<b>9a</b> <sup>2</sup>	26310 (380)	<b>11a</b> <sup>15</sup>	20750 (482)	5560 (102)
<b>9b</b> <sup>15</sup>	22830 (438)	<b>11b</b> <sup>15</sup>	17240 (580)	5590 (142)
<b>10</b> <sup>2</sup>	25000 (400)	<b>12</b> <sup>10</sup>	19230 (520)	5770 (120)

because of its more complex spatial (not planar) conformation characterized by a larger deviation of the central part ( $\text{C}_{\alpha}=\text{C}(1)=\text{C}_{\alpha}$ ) from the conjugation plane.

The solvatochromic shifts for the ketocyanines are much larger than those for the dinitriles (Table 3). This is because ketocyanines contain the carbonyl group tending to form hydrogen bonds in electrophilic solvation. Ketocyanines can be easily protonated and alkylated to give polymethylene salts with equalized C–C bonds, which is confirmed by their <sup>13</sup>C NMR spectra (see Refs 6, 19, 20). Unlike ketocyanines, dinitriles contain no carbonyl group; so they are not protonated and exhibit weaker solvatochromism.

The <sup>13</sup>C NMR spectra of dyes **8b** and **1b** in  $\text{CDCl}_3$  are given in Table 4. The chemical shifts and their differences between adjacent polymethylene C atoms suggest a stronger charge alternation for the  $\text{C}_{\beta}$ ,  $\text{C}_{\gamma}$ , and  $\text{C}_{\delta}$  atoms in dinitrile **1b** compared to ketocyanine **8b**. Therefore, the polymethylene chain of the dinitrile has more equalized bonds than the chain of ketocyanine **8b** (see Refs 19, 20).

**Table 3.** Shifts of the peaks in the S–S spectra of ketocyanines **8a**–**c** and dinitriles **1a**–**c** in polar and nonpolar solvents

Compound	Solvent	$\lambda_{\max}/\text{nm} (\nu/\text{cm}^{-1})$	$\Delta\nu/\text{cm}^{-1}$
Ketocyanines			
<b>8a</b>	Toluene	452 (22124)	2204
	EtOH	502 (19920)	—
<b>8b</b>	Toluene	441 (22675)	2267
	Pr <sup>i</sup> OH	490 (20408)	—
<b>8c</b>	Heptane	372 (26882)	4758
	MeOH	452 (22124)	—
Dinitriles			
<b>1a</b>	Toluene	550 (18182)	1029
	EtOH	583 (17153)	—
<b>1b</b>	Toluene	543 (18416)	779
	Pr <sup>i</sup> OH	567 (17637)	—
<b>1c</b>	Heptane	372 (26882)	—
	MeOH	452 (22124)	—

**Table 4.**  $^{13}\text{C}$  NMR spectra and the chemical shift differences  $\Delta\delta$  of the adjacent polymethine C atoms for dyes **8b** and **1b** in  $\text{CDCl}_3$

Atoms	<b>8b</b>	<b>1b</b>
$\delta$		
$\delta\text{-C}$	149.94	152.38
$\gamma\text{-C}$	95.43	96.62
$\beta\text{-C}$	137.69	142.84
$\alpha\text{-C}$	124.61	122.15
$\Delta\delta$		
$(\delta\text{-C})-(\gamma\text{-C})$	54.51	55.76
$(\beta\text{-C})-(\gamma\text{-C})$	42.26	46.22
$(\beta\text{-C})-(\alpha\text{-C})$	13.08	20.69

Apparently, this is due to the presence of two strong electron-withdrawing  $\text{C}\equiv\text{N}$  substituents in the dinitrile structure and, consequently, stronger intramolecular donor–acceptor interactions in dinitrile **1b**.

## Experimental

The NMR spectra of compounds **4a,b** and **5b** were recorded on a Bruker DRX-500 spectrometer (500.13 ( $^1\text{H}$ ) and 125.76 MHz ( $^{13}\text{C}$ )) in  $\text{DMSO-d}_6$  (**4a,b**, **5b**) and  $\text{CDCl}_3$  (**4a,b**) at 30 °C. Chemical shifts are referenced to the signals for the carbon atoms ( $^{13}\text{C}$ ) and those for residual protons in  $\text{CDCl}_3$  ( $\delta$  77.0 and 7.27) and  $\text{DMSO-d}_6$  ( $\delta$  39.5 and 2.50) ( $^1\text{H}$ ). 2D NMR spectra were recorded as recommended by Bruker standard procedures. The  $^1\text{H}$  NMR spectra of compound **7b** were recorded on a Bruker AM-300 instrument (300 MHz) in  $\text{CDCl}_3$ . Mass spectra (EI) were measured on a Kratos MS-30 instrument (70 eV). Electronic absorption spectra were recorded on a Specord UV-VIS instrument. The course of the reactions was monitored by UV spectroscopy.

The electronic absorption spectra of the dyes were recorded on a Shimadzu UV-101PC spectrophotometer ( $l = 1$  cm). Emission and excitation spectra were recorded on a Shimadzu RF-5301PC spectrofluorimeter. Neither emission nor excitation spectra were corrected for the spectroscopic sensitivity of the instrument (the optical densities of solutions during the emission measurements did not exceed 0.1).

**3,5-Bis(3-dimethylaminoprop-2-enylidene)-1-methylpiperidin-4-one (4a).** Aminal **2** (0.85 g, 4.9 mmol) was added dropwise to 1-methyl-4-piperidone **3a** (0.226 g, 2 mmol). The mixture was heated at 75–80 °C for 50 min. The crystallized mixture was concentrated *in vacuo*. Anhydrous ether was added to the residue and the resulting precipitate was separated and washed with anhydrous ether. The yield of diamino ketone (**4a**) was 0.5 g (90%), red crystals, m.p. 186–188 °C. Found (%): C, 69.70; H, 9.13; N, 15.28.  $\text{C}_{16}\text{H}_{25}\text{N}_3\text{O}$ . Calculated (%): C, 69.81; H, 9.09; N, 15.27. UV,  $\lambda_{\max}/\text{nm} (\epsilon)$ : 490 (97 600) (EtOH), 470 (72 600) ( $\text{CHCl}_3$ ).  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ ),  $\delta$ : 2.32 (s, 3 H, NMe); 2.85 (s, 12 H, NMe<sub>2</sub>); 3.20 (s, 4 H,  $\text{CH}_2$ ); 4.92 (t, 2 H,  $\gamma\text{-H}$ ,  $J = 12.5$  Hz); 6.93 (d, 2 H,  $\delta\text{-H}$ ,  $J = 12.5$  Hz); 7.10 (d, 2 H,  $\beta\text{-H}$ ,  $J = 12.5$  Hz).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 2.48 (s, 3 H, NMe); 2.88 (s, 12 H, NMe<sub>2</sub>); 3.40 (s, 4 H,  $\text{CH}_2$ ); 4.95 (t, 2 H,  $\gamma\text{-H}$ ,  $J = 12.5$  Hz); 6.70 (d, 2 H,

$\delta\text{-H}$ ,  $J = 12.5$  Hz); 7.40 (d, 2 H,  $\beta\text{-H}$ ,  $J = 12.5$  Hz).  $^{13}\text{C}$  NMR ( $\text{DMSO-d}_6$ ),  $\delta$ : 39.50 (NMe<sub>2</sub>), 45.93 (NMe); 55.71 ( $\text{CH}_3$ ); 93.38 ( $\gamma\text{-C}$ ); 120.09 ( $\alpha\text{-C}$ ); 136.06 ( $\beta\text{-C}$ ), 151.34 ( $\delta\text{-C}$ ), 181.68 (CO). MS,  $m/z$  275 [M]<sup>+</sup>.

**3,5-Bis(3-dimethylaminoprop-2-enylidene)-1-ethoxycarbonylpiperidin-4-one (4b).** Aminal **2** (0.53 g, 3.1 mmol) was added dropwise to ethyl 4-oxopiperidine-1-carboxylate **3b** (0.26 g, 1.5 mmol). The reaction mixture was heated at 80–85 °C for 1.5 h. The resulting diamino ketone **4b** was isolated as described above. The yield of ketone **4b** was 0.45 g (90%), red crystals, m.p. 182–185 °C. Found (%): C, 64.91; H, 8.18; N, 12.58.  $\text{C}_{18}\text{H}_{27}\text{N}_3\text{O}_3$ . Calculated (%): C, 64.86; H, 8.11; N, 12.61. UV,  $\lambda_{\max}/\text{nm} (\epsilon)$ : 480 (80 505) (EtOH), 460 (84 165) ( $\text{CHCl}_3$ ).  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ ),  $\delta$ : 1.17 (m, 3 H,  $\text{CH}_3\text{CH}_2\text{O}$ ); 2.90 (s, 12 H, NMe<sub>2</sub>); 4.03 (q, 2 H,  $\text{CH}_3\text{CH}_2\text{O}$ ,  $J = 7$  Hz); 4.25 (s, 4 H,  $\text{CH}_2$ ); 4.95 (t, 2 H,  $\gamma\text{-H}$ ,  $J = 12.4$  Hz); 7.0 (d, 2 H,  $\delta\text{-H}$ ,  $J = 12.4$  Hz); 7.18 (d, 2 H,  $\beta\text{-H}$ ,  $J = 12.4$  Hz).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 1.25 (m, 3 H,  $\text{CH}_3\text{CH}_2\text{O}$ ); 2.90 (s, 12 H, NMe<sub>2</sub>); 4.15 (q, 2 H,  $\text{CH}_3\text{CH}_2\text{O}$ ,  $J = 7$  Hz); 4.38 (s, 4 H,  $\text{CH}_2$ ); 5.05 (t, 2 H,  $\gamma\text{-H}$ ,  $J = 12.4$  Hz); 6.72 (d, 2 H,  $\delta\text{-H}$ ,  $J = 12.4$  Hz); 7.40 (d, 2 H,  $\beta\text{-H}$ ,  $J = 12.4$  Hz).  $^{13}\text{C}$  NMR ( $\text{DMSO-d}_6$ ),  $\delta$ : 14.54 ( $\text{OCH}_2\text{CH}_3$ ); 39.49 (NMe<sub>2</sub>); 43.51 ( $\text{CH}_2$ ); 60.0 ( $\text{OCH}_2\text{CH}_3$ ); 92.87 ( $\gamma\text{-C}$ ); 117.90 ( $\alpha\text{-C}$ ); 137.34 ( $\beta\text{-C}$ ); 152.34 ( $\delta\text{-C}$ ); 154.55 ( $\text{COOEt}$ ); 181.17 (CO). MS,  $m/z$  333 [M]<sup>+</sup>.

**(1-Ethoxycarbonylpiperidin-4-ylidene)malononitrile (7b).** A mixture of ethyl 4-oxopiperidine-1-carboxylate **3b** (5 g, 0.03 mol), malononitrile (2.97 g, 0.045 mol), ammonium acetate (0.89 g), and AcOH (2.04 g) was refluxed in benzene (15 mL) using a Dean–Stark trap for 1.5 h. The reaction mixture was concentrated *in vacuo*. Ether (50 mL) was added and an inorganic precipitate was filtered off. The ethereal solution was washed with a solution of  $\text{NHCO}_3$  and water (three times), dried with calcined  $\text{MgSO}_4$ , and concentrated *in vacuo*. The yield of dinitrile **7b** was 3.2 g (49%), m.p. 79–84 °C. UV (EtOH),  $\lambda_{\max}/\text{nm} (\epsilon)$ : 228 (9000), 270 (5760).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 1.30 (t, 3 H,  $\text{CH}_3\text{CH}_2\text{O}$ ); 2.75 (m, 4 H,  $\text{CH}_2$ ); 3.65 (m, 4 H,  $\text{CH}_2$ ); 4.30 (q, 2 H,  $\text{CH}_3\text{CH}_2\text{O}$ ). MS,  $m/z$  219 [M]<sup>+</sup>.

**[3,5-Bis(3-dimethylaminoprop-2-enylidene)-1-ethoxycarbonylpiperidin-4-ylidene]malononitrile (5b).** *A.* 3-Dimethylamino-1,1,3-trimethoxypropane (**6**) (0.49 g, 2.8 mmol) was added dropwise to dinitrile **7b** (0.2 g, 0.93 mmol). The reaction mixture was stirred at 75–80 °C for 3 h, kept at 20–25 °C for a day, and concentrated *in vacuo*. Water (10 mL) was added and a precipitate was filtered off and washed with water and ether. The precipitate was dissolved in  $\text{CHCl}_3$  (70 mL) and kept over  $\text{SiO}_2$  (L 40/100, 0.4 g) for a day. The silica was separated, the solution was concentrated, and ether was added to the residue. The precipitate was filtered off and washed with ether. The yield of dinitrile **5b** was 0.08 g (23%), brown crystals, m.p. >260 °C. Since compound **5b** is a high-melting solid, its elemental analysis failed. UV,  $\lambda_{\max}/\text{nm} (\epsilon)$ : 575 (62 120) (EtOH), 540 (61 290) ( $\text{CHCl}_3$ ).  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ ),  $\delta$ : 1.15 (t, 3 H,  $\text{CH}_3\text{CH}_2\text{O}$ ); 3.02 (s, 12 H, NMe<sub>2</sub>); 4.00 (s, 4 H,  $\text{CH}_2$ ); 4.08 (q, 2 H,  $\text{CH}_3\text{CH}_2\text{O}$ ); 5.40 (t, 2 H,  $\gamma\text{-H}$ ,  $J = 12$  Hz); 7.35 (d, 4 H,  $\beta\text{-H}$  and  $\delta\text{-H}$ ).  $^{13}\text{C}$  NMR ( $\text{DMSO-d}_6$ ),  $\delta$ : 13.9 ( $\text{OCH}_2\text{CH}_3$ ); 41.9 ( $\text{CH}_2$ ); 60.9 ( $\text{OCH}_2\text{CH}_3$ ); 97.2 ( $\gamma\text{-C}$ ); 145.6 ( $\beta\text{-C}$ ); 155.7 ( $\delta\text{-C}$ ). A number of signals were not accumulated because of the poor solubility of the sample. MS,  $m/z$  381 [M]<sup>+</sup>.

*B.* Reagent **6** (0.49 g, 2.8 mmol) was added dropwise to a stirred solution of dinitrile **7b** (0.2 g, 0.93 mmol) in [bmim]BF<sub>4</sub> (0.625 g, 2.7 mmol). The reaction mixture was stirred at

70–75 °C for 4 h, kept for a day, and concentrated *in vacuo*. Water (5 mL) was added to the residue and the precipitate was filtered off, washed with water and ether, and dissolved in CHCl<sub>3</sub> (50 mL). The solution was kept over SiO<sub>2</sub> (L 40/100, 0.4 g) for a day. The silica was separated and washed with CHCl<sub>3</sub>. Concentration gave dinitrile **5b** (0.15 g, 43%), which was identical with that described above.

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