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J. Bartulin [a] , C. Zuniga [a] , H. Muller [b] , T. R. Taylor [b] & W. Haase [c]

[a] Departamento de Quimica, Facultad de Ciencias, Universidad de Concepcion, Casilla, 3-C, Concepcion, Chile

[b] Departamento de Fisica, Universidade Federal de Santa Catarina, Florianopolis, SC, Brazil

[c] Institut fur Fhysikalische Chemie, Technische Hochschule Darmstadt, West Germany

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Synthesis and Mesomorphic Properties of N-n-Alkyl-N-[4-(2-Cyanoethenylphenyl)]-Piperazines

J. BARTULIN and C. ZUÑIGA

Departamento de Quimica, Facultad de Ciencias, Universidad de Concepcion, Casilla 3-C, Concepcion, Chile

and

H. MULLER and T. R. TAYLOR

Departamento de Fisica, Universidade Federal de Santa Catarina, Florianopolis, SC, Brazil

and

W. HAASE

Institut fur Fhysikalische Chemie, Technische Hochschule Darmstadt, West Germany

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We have synthesized the N-n-alkyl-N′-[4-(2-cyanoethenylphenyl)]-piperazines and studied their physical properties using calorimetric, optical and X-ray methods. Depending on alkyl chain length there are one or two liquid crystal phases. For the lower homologs there is a nematic and a smectic phase with the smectic being identified as probably smectic A and in the higher homologs only the smectic is present. The smectic phase has an interdigitated bilayer and the transition heat of the nematic-smectic transition becomes very small with decreasing alkyl chain length.

INTRODUCTION

In a previous paper we reported the synthesis of mesogenic compounds based on the N-n-alkyl-N′-(4-acylphenyl)-piperazines.[1] Here

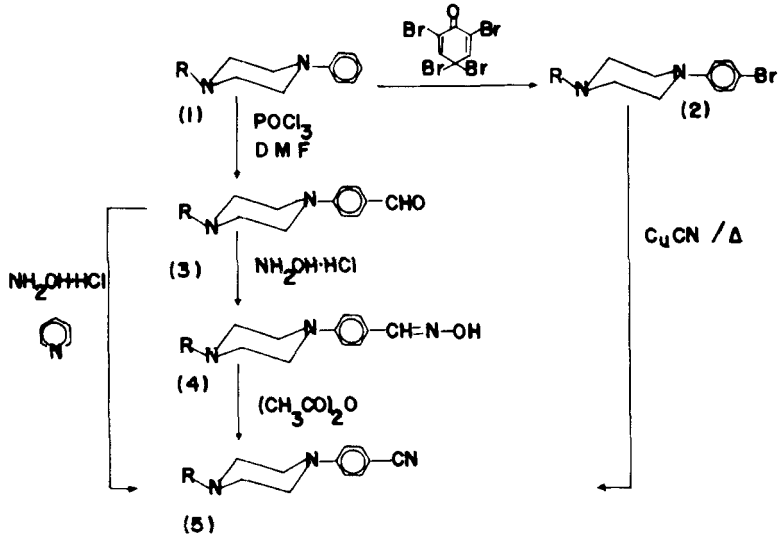
we wish to report our continued work on mesomorphic compounds which are based on the piperazine ring.

Terminal bonded groups along the long molecular axis, such as cyano, are necessary to obtain nematics with positive dielectric anisotropy for use in electro-optical displays.[2] In consideration of these requirements we have synthesized N-n-alkyl-N′-(2-cyanophenyl)-piperazines and N-n-alkyl-N′-[4-(2-cyanoethenylphenyl)]-piperazines.

SYNTHESIS

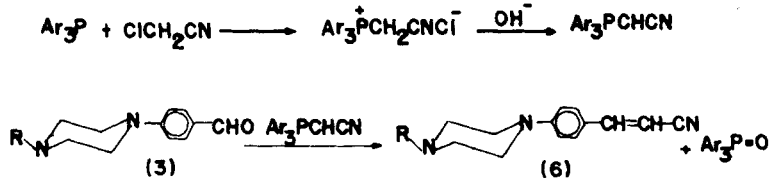
The cyano compounds were synthesized starting with the N-alkyl-N′-phenyl-piperazines (1) obtained by two methods as shown in Scheme 1. The oxime was dehydrated with Ac_2O or the cyano group was obtained directly from the aldehyde by treatment with hydroxylamine hydrochloride and pyridine. An alternative route was starting from the N-alquil-N′-(4-bromophenyl)-piperazines and CuCN in N-methylpyrrolidone. The yields of this reaction were very low. The bromo derivatives were prepared by bromation with N-bromosuccinimide or 2,4,4,6-tetrabromocyclohexa-2,5-dienone which gives exclusive *p*-substitution. None of the N-n-alkyl-N′-(4-cyano-phenyl)-piperazines were mesogenic and this was assumed to be due the fact that the

SCHEME 1



length of the conjugated system (conjugation between the cyano group and the ring nitrogen) was not of sufficient length to produce mesomorphic phases. To increase the length of the conjugated system we decided to synthesize the acrylonitrile derivatives using the Wittig reaction between thet aldehydes and the ylide, ϕ_3PCHCN, as shown in Scheme 2.

SCHEME 2



RESULTS AND DISCUSSION

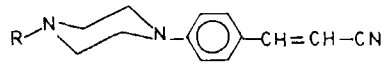
As expected the N-n-alkyl-N'-[4-(2-cyanoethenyl-phenyl)]-piperazines (Scheme 2,6), as shown in Table I, are mesogenic. The first members of the series (n = 4, 5, 6) exhibit a nematic and smectic phase while the higher homologues have only a smectic phase. In Figure 1, the phase transition temperatures are plotted against the number n of carbon atoms in the terminal alkyl chain of the piperazine ring. The behavior is normal; the clearing points rising gradually with alkyl chain length and the nematic phase disappearing with increased alkyl chain length. The phase transition temperatures in Table I and Figure 1 are those determined with a Perkin-Elmer DSC-2 calibrated with Indium. Transition temperatures determined with a Leitz Ortholux-Pol microscope and a Mettler FP-52 hot stage agree to within ± 1°C of those determined with the DSC.

Optical textures and convergent light observations were made with the polarizing microscope. The nematic phase shows the threaded, schlieren or homeotropic texture depending on sample thickness. The texture at the clearing point was that characteristic of the nematic–isotropic transition. The smectic phase displays the focal–conic fan texture and under shearing of the cover slip or in thin samples adopts the homeotropic texture. Homeotropically oriented smectic textures were observed with convergent light and are uniaxial positive.

X-ray diffraction patterns were recorded on a flat plate camera using 1mm Lindemann capillaries in a temperature controlled oven

TABLE I

Transition temperatures and enthalpies for the N-n-alkyl-N'-[4-(2-cyanoethenylphenyl)]-piperazines (6)



Compounds R	K	temp. in °C S	N	I	phase transition K	enthalpies Kcal/mol S	N	I
6*a* n-C_4H_9	· 61.1 ·	(57.7) ·	113.8 ·	·	·	4.46 · 1×10^{-3} ·	0.07 ·	
6*b* n-C_5H_{11}	· 61.8 ·	93.3 ·	122.2 ·	·	·	5.69 · 1×10^{-2} ·	0.14 ·	
6*c* n-C_6H_{13}	· 79.7 ·	113.0 ·	120.6 ·	·	·	6.16 · 0.12 ·	0.22 ·	
6*d* n-C_7H_{15}	· 70.2 ·	125.0 ·	—	·	·	6.06 · 0.68	— ·	
6*e* n-C_8H_{17}	· 59.3 ·	127.4 ·	—	·	·	6.04 · 0.98	— ·	
6*f* n-C_9H_{19}	· 55.0 ·	131.0 ·	—	·	·	7.11 · 1.12	— ·	

K = crystalline, S = smectic, N = nematic, I = isotropic ( ), monotropic transition.

for compounds 6a (C4) at 50°C and 6e (C8) at 75°C. The X-ray patterns are typical of a smectic A phase; that is, one sharp inner ring or reflection corresponding to the layer spacing distance and a diffuse outer ring corresponding to the lateral distance between molecules in the layer. The use of Bragg's law for the inner ring gives *d* values of 25.4 ± 2.0 A° (6*a*) and 31.8 ± 2.0 A° (6*e*) and the calculated lengths 1 are 18.5 A° and 23.0 A° respectively. The ratio *d*/1 is approximately 1.4 as is common for many compounds with a cyano terminal group.[3]

Considering the optical results (uniaxial positive) and the X-ray diffraction results, it appears to be clear that the smectic phase of these compounds is smectic A or since it has a interdigitated bilayer perhaps the notation should be smectic A_d.[3]

The results for the transition heats of the smectic–nematic transition should be noted carefully. With decrease of the alkyl chain length the transition heats fall rapidly and in the case of compound 6*a* is approaching zero. The transition heats are so small for 6*a* and 6*b* that the numbers given easily be in error by 100%. It would appear that these compounds would be good candidates for studying the possible second order nature of the nematic–smectic A transition.

EXPERIMENTAL PART

The structures of the compounds were confirmed, by analysis of their IR (Perkin-Elmer 237 B and 577), ^{1}H-NMR (Varian T-60A) and ^{13}C

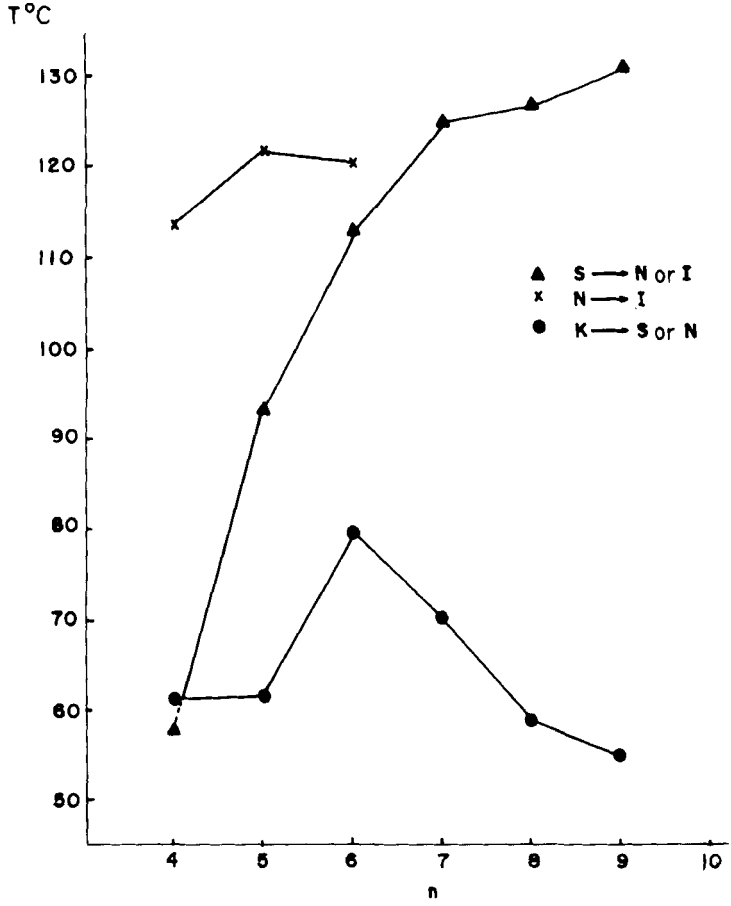


FIGURE 1 Plot of transition temperatures against the number of carbon atoms (n) in the alkyl chain (R) of the N-n-alkyl-N-[4-(2-cyanoethenylphenyl)]-piperazines (6).

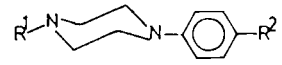
NMR (Varian CFT-20) spectra. Combustion analysis was also carried out (Table II).

Preparation of N-*n*-alkyl-N'-(4-bromophenyl)-piperazine (2) Method I

To a solution of 0.1 mole of N-n-alkyl-N'-phenylpiperazine[1,4] (1) in benzene was added 0.1 mole of N-bromosuccinimide in benzene, the mixture was maintained at 20–30° during the addition, and the stirring continued for a short time. The mixture was filtered, the benzene

TABLE II

Elemental analysis of piperazine derivatives



N°	R^1	R^2	Empirical Formula (mol. weight)	C Calc.	C Found	H Calc.	H Found	N Calc.	N Found
2a	*n*-C_5H_{11}	Br	$C_{15}H_{23}N_2Br$	57.89	57.81	7.40	7.67	9.01	8.90
2b	*n*-C_8H_{17}	Br	$C_{18}H_{29}N_2Br$	61.21	60.98	8.22	8.43	7.93	7.86
5a	*n*-C_5H_{11}	CN	$C_{16}H_{23}N_3$	74.21	74.32	8.95	9.10		
5b	*n*-C_8H_{17}	CN	$C_{19}H_{29}N_3$	76.25	76.05	9.70	10.11		
5c	*n*-C_9H_{19}	CN	$C_{20}H_{31}N_3$	76.67	76.49	9.9	10.10		
6a	*n*-C_4H_9	CH=CH—CN	$C_{17}H_{23}N_3$	75.84	75.35	8.55	8.33		
6b	*n*-C_5H_{11}	CH=CH—CN	$C_{18}H_{25}N_3$	76.32	76.83	8.83	8.39		
6c	*n*-C_6H_{13}	CH=CH—CN	$C_{19}H_{27}N_3$	76.76	76.48	9.09	8.96		
6d	*n*-C_7H_{15}	CH=CH—CN	$C_{20}H_{29}N_3$	77.13	77.15	9.35	9.12		
6e	*n*-C_8H_{17}	CH=CH—CN	$C_{21}H_{31}N_3$	77.54	76.93	9.54	9.67		
6f	*n*-C_9H_{19}	CH=CH—CN	$C_{22}H_{33}N_3$	77.88	77.52	9.73	9.98		

evaporated and the residue recrystallized from ethanol. Yield 60–65%.

Method II

0.02 moles of N-n-alkyl-N′-phenylpiperazine in 20 ml of CH_2Cl_2 was stirred and cooled and 0.02 moles of 2,4,4,6-tetrabromocyclohexa-2,5-dienona[5] in 40 ml of CH_2Cl_2 was added during half hour, maintaining the temperature between −10 and 0°C. The mixture was extracted twice with 20 ml of 2M NaOH to eliminate the tribromophenol. The residue was recrystallized from ethanol. Yield 70%.

N-n-Pentyl-N′-(4-bromophenyl)-piperazine (2a) m.p. 95°C (from EtOH). IR(KBr): 2941 (C—H), 2857 (C—H) and 1592 cm^{-1} (C=C). ^{1}H-NMR($CDCl_3$): 0.92 (*t*, 3, CH_3); 1.1–1.73 (*m*, 6, CH_2); 2.28 (*t*, 2, CH_2N); 2.58 and 3.20 (2*m*, 8, CH_2N); 6.81 and 7.41 (2*d*, 4, J = 9Hz, arom.). ^{13}C-NMR(C_6D_6): 150.78, 132.03, 117.68, 111.61 (C_1, C_3, C_2, C_4 arom.); 53.55 and 48.83 (N—CH_2—CH_2—N′); 58.69 (1, C_1), 29.97 (1, C_3); 26.96 (1, C_2); 22.95 (1, C_4); 14.26 (1, C_5).

Preparation of N-n-Octyl-N′-(4-bromophenyl)-piperazine (2b) m.p. 76°C (from EtOH). IR(KBr): 2915 (C—H), 2849 (C—H) and 1592 cm^{-1} (C=C). ^{1}H-NMR($CDCl_3$): 0.87 (*t*, 3, CH_3); 1.08 – 1.82 (*m*, 12, CH_2); 2.22 (*t*, 2, CH_2N); 2.50 and 3.10 (2*m*, 8, CH_2N); 6.67 and 7.27 (2*d*, 4, J = 9Hz, arom.). ^{13}C-NMR(C_6D_6): 150.87, 132.22, 117.25, 111.69 (C_1, C_3, C_2, C_4, arom.); 53.33 and 49.12 (N—CH_2—CH_2—N′);

58.78 (1, C_1); 32.21 (1, C_6); 29.87 (1, C_5); 29.67 (1, C_4); 27.82 (1, C_3); 27.34 (1, C_2); 22.94 (1, C_7); 14.15 (1, C_8).

Preparation of N-n-Alkyl-N′-(4-cyanophenyl)-piperazine (5)

0.1 mole of N-n-alkyl-N′-(4-formylphenyl)-piperazine[1] was added in one portion to a solution of 0.1 mole of hydroxylammonium chloride in 0.2 mole of pyridine. After stirring for a short time, 100 ml of toluene was added and the mixture heated to reflux with a water separator. Heating was continued until no more water collected. After cooling, the mixture was filtered from the pyridinium chloride, the filtrate was washed twice with water, dried with sodium sulphate, evaporated and the residue recrystallized from aqueous ethanol.

N-n-Pentyl-N′-(4-cyanophenyl)-piperazine (5a) m.p. 40°C; b.p.$_{0.09}$ 155°C.IR(KBr): 2212 (C≡N) and 1600 cm^{-1} (C=C). ^{1}H-NMR: 0.88 (*t*, 3, CH_3); 1.05–1.83 (*m*, 6, CH_2); 2.32 (*t*, 2, N—CH_2); 2.48 and 3.28 (2*m*, 8, CH_2N); 6.82 and 7.46 (2*d*, 4, J = 9H_z, arom.) ^{13}C-NMR: 154.91, 134.50, 115.26, 100.51 (C_1, C_3, C_2, C_4, arom.); 120.00 (1, CN); 53.83 and 48.17 (N—CH_2—CH_2—N′); 59.30 (1, C_1); 30.69 (1, C_3); 27.39 (1, C_2); 23.45 (1, C_4); 14.69 (1, C_5).

N-n-Octyl-N′-(4-cyanophenyl)-piperazine (5b) IR(KBr): 2217 (C≡N) and 1605 cm^{-1} (C=C). ^{1}H-NMR($CDCl_3$): 0.88 (*t*, 3, CH_3); 1.07–1.70 (*m*, 12, CH_2); 2.38 (*t*, 2, CH_2N); 2.57 and 3.33 (2*m*, 8, CH_2N); 6.87 and 7.51 (2*d*, 4, J = 9Hz arom.)

N-n-Nonyl-N′-(4-cyanophenyl)-piperazine (5c) m.p. 50–51°C. IR(KBr): 2217 (C≡N) and 1602 cm^{-1} (C=C). ^{1}H-NMR(CD_3CN): 0.88 (*t*, 3, CH_3); 1.07–1.70 (*m*, 14, CH_2); 2.18 (*t*, 2, CH_2N); 2.45 and 3.27 (2*m*, 8, CH_2N); 6.88 and 7.48 (2*d*, 4, J = 8Hz, arom.) ^{13}C-NMR(CD_3CN): 154.49, 134.17, 114.83, 100.09 (C_1, C_3, C_2, C_4, arom.); 120.69 (1, CN); 53.30 and 47.74 (N—CH_2—CH_2—N′), 59.07 (1, C_1); 32.51 (1, C_7); 30.25 (1, C_5); 29.97 (2, C_4 and C_6); 28.12 (1, C_3); 27.43 (1, C_2); 23.31 (1, C_8); 14.34 (1, C_9).

Preparation of N-n-Alkyl-N′-[4-(2-cyanoethenylphenyl)]-piperazine (6)

A mixture of 0.04 moles of aldehyde and 0.04 moles of cyanomethyl-entriphenylphosphorane[6] dissolved in 150 ml of benzene was heated to reflux for 12 hours.[7] Then 400 ml of petroleum ether was added and the solution left at r.t. until the phenylphosphine oxide precipitate. The solution was filtered, the filtrate evaporated and the residue dissolved in hot petroleum ether, filtered hot and cooled to crystallize

the product. This procedure was repeated again, until all the triphenyl phosphine oxide was eliminated. Yield 50–60%.

N-n-Butyl-N'-[4-(2-cyanoethenylphenyl)]-piperazine (6a) IR (KBr): 2210 (C≡N) and 1595 cm^{-1} (C=C). ^{1}H-NMR($CDCl_3$): 0.92 (*t*, 3, CH_3); 1.10–1.88 (*m*, 4, CH_2); 2.53 and 3.30 (2*m*, 8, CH_2N); 2.37 (*t*, 2, CH_2N); 5.58 and 7.23 (2*d*, —CH=CH—CN, $J_{H\text{-}H\ trans}$ 16 Hz); 6.83 and 7.14 (2*d*, 4, J = 9 Hz, arom.)

N-n-Pentyl-N'-[4-(2-cyanoethenylphenyl)]-piperazine (6b) IR (KBr): 2208 (C≡N) and 1600 cm^{-1} (C=C). ^{1}H-NMR($CDCl_3$): 0.90 (*t*, 3, CH_3); 1.08–1.92 (*m*, 6, CH_2); 2.55 and 3.27 (2*m*, 8, CH_2N); 2.38 (*t*, 2, CH_2N); 5.59 and 7.27 (2*d*, —CH=CH—CN, $J_{H\text{-}H\ trans}$ 16 Hz); 6.85 and 7.34 (2*d*, 4, J = 9 Hz, arom.)

N-n-Hexyl-N'-[4-(2-cyanoethenylphenyl)]-piperazine (6c) IR(KBr): 2212 (C≡N) and 1602 cm^{-1} (C=C). ^{1}H-NMR ($CDCl_3$): 0.90 (*t*, 3, CH_3); 1.06–1,90 (*m*, 8, CH_2); 2.57 and 3.23 (2*m*, 10, CH_2N); 5.60 and 7.27 (2*d*, —CH=CH—CN, $J_{H\text{-}H\ trans}$ = 16 Hz); 6.83 and 7.33 (2*d*, 4, J = 9 Hz, arom.) ^{13}C-NMR($CDCl_3$): 152.96, 128.75, 123.67, 114.39 (C_1, C_3, C_4, C_2, arom.); 149.96 and 91.14 (—CH=CH—CN); 119.00 (1, CN); 58.54 (1, C_1); 52.77 and 47.51 (N—CH_2—CH_2—N'); 31.60 (1, C_4); 27.08 (1, C_3); 26.70 (1, C_2); 22.41 (1, C_5); 13.88 (1, C_6).

N-n-Heptyl-N'-[4-(2-cyanoethenylphenyl)]-piperazine (6d) IR(KBr): 2217 (C≡N) and 1608 cm^{-1} (C=C). ^{1}H-NMR($CDCl_3$): 0.90 (*t*, 3, CH_3); 1.12–1.92 (*m*, 10, CH_2); 2.32 (*t*, 2, CH_2N); 2.57 and 3.33 (2*m*, 8, CH_2N); 5.64 and 7.28 (2*d*, CH=CH—CN, $J_{H\text{-}H\ trans}$ = 16 Hz); 6.87 and 7.37 (2*d*, 4, J = 9 Hz, arom.) ^{13}C-NMR($CDCl_3$): 152.86; 128.74; 123.66; 114.38 (C_1, C_3, C_4, C_2, arom.); 149.94 and 91.05 (CH=CH—CN); 119.07 (1, CN); 52.77 and 47.49 (N—CH_2—CH_2—N'); 58.53 (1, C_1); 31.66 (1, C_5); 29.04 (1, C_4); 27.37 (1, C_3); 26.70 (1, C_2); 22.41 (1, C_6); 13.90 (1, C_7).

N-n-Octyl-N'-[4-(2-cyanoethenylphenyl)]-piperazine (6e) IR(KBr): 2217 (C≡N) and 1605 cm^{-1} (C=C). ^{1}H-NMR($CDCl_3$): 0.88 (*t*, 3, CH_3); 1.06–1.73 (*m*, 12, CH_2); 2.40 (*t*, 2, CH_2N); 2.57 and 3.27 (2*m*, 8, CH_2N); 5.60 and 7.12 (2*d*, —CH=CH—CN, $J_{H\text{-}H\ trans}$ 16 Hz); 6.83 and 7.22 (2*d*, 4, J = 9 Hz, arom.) ^{13}C-NMR ($CDCl_3$): 152.91, 128.77, 123.71, 114.43 (C_1, C_3, C_4, C_2, arom.); 150.07 and 91.10 (—CH=CH—CN); 119.10 (1, CN); 52.81 and 47.52 (N—CH_2—CH_2—N'); 59.59 (1, C_1); 31.71 (1, C_6); 29.37 (1, C_5); 29.09 (1, C_4); 27.43 (1, C_3); 26.72 (1, C_2); 22.53 (1, C_7); 13.94 (1, C_8).

N-n-Nonyl-N'-[4-(2-cyanoethenylphenyl)]-piperazine (6f) IR(KBr): 2212 (C≡N) and 1602 cm^{-1} (C=C). ^{1}H-NMR (C_6D_6): 0.93 (*t*, 3, CH_3); 1.08–1.68 (*m*, 14, CH_2); 2.33 and 3.07 (2*m*, 10, CH_2N); 5.23 and 6.93 (2*d*, —CH=CH—CN, $J_{H\text{-}H\ trans}$ 16 Hz); 6.58 and 6.82 (2d, 4, J = 9 Hz, arom.). ^{13}C-NMR($CDCl_3$): 153.31, 129.00, 124.31, 114.74, (C_1, C_3, C_4, C_2, arom.); 149.60 and 92.08 (—CH=CH—CN); 118.94 (1, CN); 53.20 and 48.04 (N—CH_2—CH_2—N'); 58.70 (1, C_1); 32.22 (1, C_7); 29.96 (1, C_5); 29.59 (2, C_4 and C_6); 27.82 (1, C_3); 27.34 (1, C_2); 22.94 (1, C_8); 14.15 (1, C_9).

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