SYNTHESIS AND MESOGENIC PROPERTIES OF SCHIFF BASES DERIVED FROM AMINOPYRAZOLES

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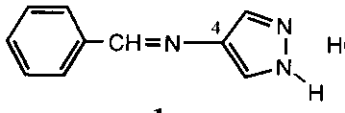
Abstract- Fifteen azomethineimines derived from *C*-aminopyrazoles and aromatic aldehydes have been prepared and fully characterized (IR, MS, ^{1}H and ^{13}C NMR *in solution* and ^{13}C CPMAS NMR). The benzaldehyde bearing at position 4 *n*-decyloxy or a *n*-butyloxycarbonylethyloxy substituents and at position 2 a hydrogen or a hydroxy substituent have been tested for mesogenic properties. Only **5** [1*H*-4-(4-*n*-decyloxy-2-hydroxybenzylideneaminopyrazole)] presents a mesogenic behaviour (smectic A) on cooling.

The search for new compounds, possible candidates for liquid-crystal properties,[1-3] lead us to explore the Schiff bases derived from *C*-aminopyrazoles. Amongst the bridges used to connect the two aromatic halves of liquid crystals, the -CH=N- bridge is found in many cases, usually connecting two aromatic moieties, that is, the Schiff bases resulted from aromatic aldehydes and amines.[4-6] Knowing that aminopyrazoles condense with aromatic aldehydes to yield aldimines,[7,8] in the present work we describe the synthesis of fifteen pyrazolylaldimines (**1**-**15**) from benzaldehyde (**16**), from 4-substituted benzaldehydes (**17**, **18**), from 2-hydroxy-4-substituted benzaldehydes (**19**, **20**) and from 5-nitro-2-furaldehyde (**21**). Compounds (**1**-**3**) were synthesized to find the best experimental conditions for preparing these Schiff bases. The remaining compounds bear promesogenic alkyloxyphenyl groups. Regarding the pyrazole moieties, there are five classes of them: i) compounds (**1**-**6**) derived from 4-aminopyrazole (**22**), ii) compounds (**7**-**9**) derived from 3(5)-aminopyrazole (**23**), iii) compounds (**10**) and (**11**) derived from 3(5)-amino-5(3)-methylpyrazole (**24**), iv) compounds (**12**) and (**13**) derived from 1,3,5-trimethyl-4-aminopyrazole (**25**), and v) compounds (**14**) and (**15**) derived from 1,3-dimethyl-5-aminopyrazole (**26**).



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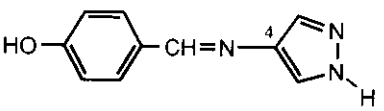

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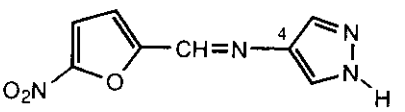

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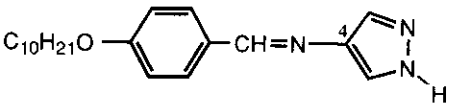

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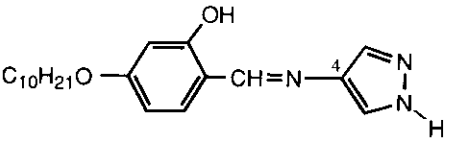

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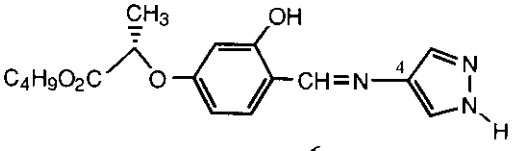

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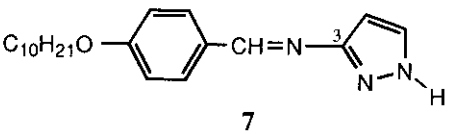

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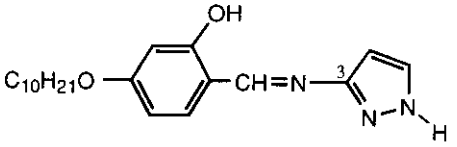

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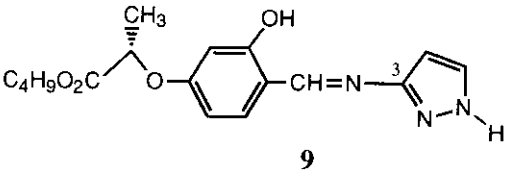

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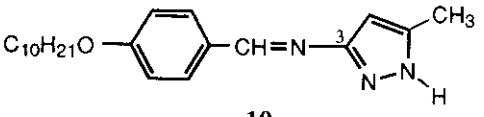

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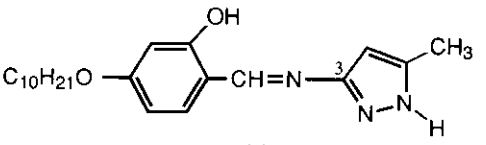

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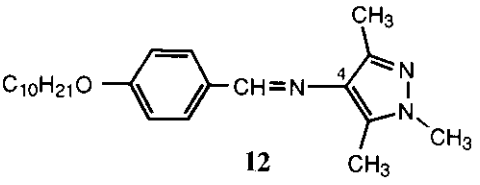

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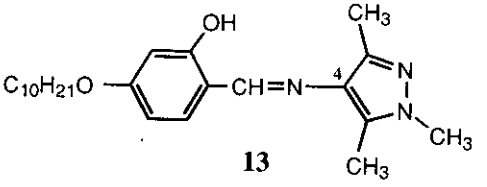

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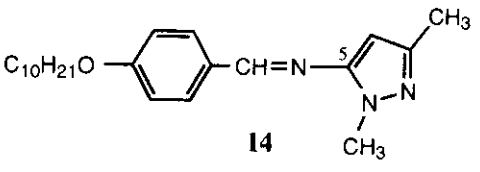

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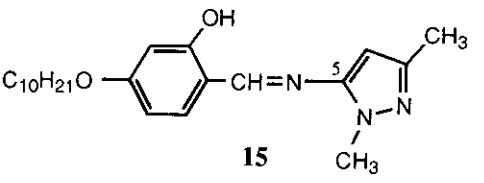

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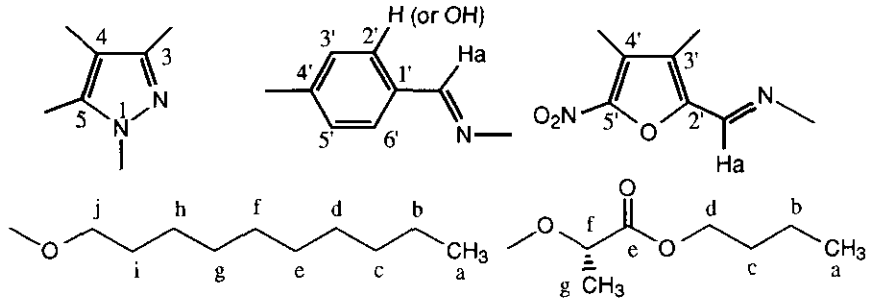
RESULTS AND DISCUSSION

Synthesis of Schiff bases 1-15. All these compounds have been prepared from equimolar amounts of the corresponding aldehydes and aminopyrazoles taking care to use dry ethanol as a solvent, and were purified by column chromatography followed by crystallization.

Structural characterization of compounds (1-15). The compounds have been characterized by NMR (Tables 1 and 2) and IR spectroscopies (Table 4). The numbering used in Tables 1 and 2 is represented below:



^{1}H NMR chemical shifts and ^{1}H-^{1}H coupling constants are reported in Table 1. Concerning annular tautomerism of NH-pyrazoles,[9] it is worth noticing that 4-substituted pyrazole (**5**) shows, in DMSO-d_6 at room temperature, two separate (although broad) signals for H3 and H5 which is a very unusual observation since annular tautomerism is generally fast on NMR time scale. These signals coalesce in CD_3OD (the same phenomenon is observed in ^{13}C NMR, Table 2). The 3(5)-aminopyrazole derivatives (**7-9**) are mixtures of 3 and 5-substituted tautomers because the $^3J(^1H\text{-}^1H)$ coupling constant amounts to 2.2-2.4 Hz.[10]

Table 2 contains the ^{13}C chemical shifts and the $^1J(^1H\text{-}^{13}C)$ coupling constants. Concerning the annular tautomerism of pyrazoles, compound **5** in which the proton exchange between N1 and N2 is very slow, permits to measure ^1J for C3 (186.8 Hz) and for C5 (190.6). In the case of compounds (**7-9**), carbon atoms at position 4 and 3(5) present $^2J(^{13}C\text{-}^1H)$ coupling constants of 8.5 and 6.2 Hz which are intermediate between those of 3- and 5-substituted isomers,[11] proving that they are mixtures of annular tautomers.[9] Compounds (**10**) and (**11**), are 3-aldimino-5-methyl derivatives because the methyl group appears at 11.5 ppm with a ^1J = 170 Hz [compare with (**12-13**)], the difference being due to the tendency of the methyl group to occupy the 5 position.[9,12]

Some spectra of 4-substituted derivatives, compounds (**1**, **3**, **4**, **5**), were recorded in the solid state using the CPMAS technique, but the information they provided (great similarity with solution spectra) was not interesting enough to extend this technique to the remaining compounds. In any case, the most interesting compound (**5**) (see below) has in the solid state the same structure as in solution.

Concerning the *E*/*Z* isomerism about the C=N bond, two observations are pertinent: the ^1J(Ca-Ha) coupling constant (~160 Hz) is typical of an *E* conformation,[13,14] and the ^3J(Ca-H2',6') has values of 4.3 Hz (average between 6.1 and 2.5 Hz) for compounds without an *ortho*-OH group (triplets) and 6.1 Hz for compounds with an *ortho*-OH group (doublets). These two observations together demonstrate that the Schiff bases have the structures depicted below.

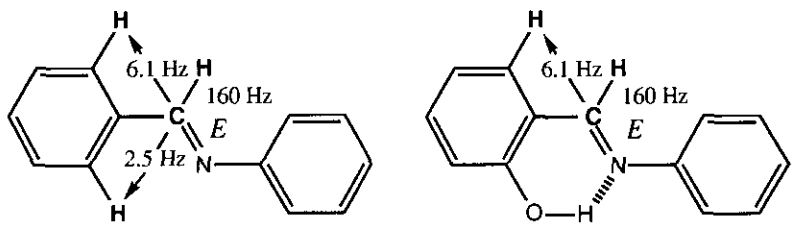


Table 1. ^{1}H NMR data (δ and *J*) for compounds (**1-15**)

Comp	Solvent	1	3	4	5	Ha	2'	3'	4'	5'	6'	4-OH
1	DMSO-d_6	12.9	7.83	----	7.83	8.74	7.83	7.45	7.45	7.45	7.83	----
2	DMSO-d_6	12.7	7.78	----	7.78	8.56	7.65 *J*=8.2	6.83 *J*=8.2	----	6.83 *J*=8.2	7.65 *J*=8.2	9.96
3	DMSO-d_6	13.1	7.98	----	7.98	8.61	----	7.19 *J*=3.3	7.71 *J*=3.3	----	----	----
4	DMSO-d_6 + CF_3CO_2H	12.7	7.77	----	7.77	8.61	7.75 *J*=8.5	6.98 *J*=8.5	----	6.98 *J*=8.5	7.75 *J*=8.5	*a*
5	DMSO-d_6	12.9	7.78 (br)	----	7.98 (br)	8.81	13.44	6.42 *J*=2.2	----	6.50 *J*=8.6 *J*=2.2	7.36 *J*=8.6	*b*
5	CD_3OD	----	7.80	----	7.80	8.71	----	6.41 *J*=2.4	----	6.48 *J*=8.6 *J*=2.4	7.31 *J*=8.6	*c*
6	$CDCl_3$	----	7.70	----	7.70	8.54	13.38	6.42 *J*=2.1	----	6.46 *J*=8.6	7.20 *J*=8.6	*d*
6	DMSO-d_6	12.9	7.85 (br)	----	7.85 (br)	8.83	13.45	6.36 *J*=2.1	----	6.48 *J*=8.4	7.39 *J*=8.4	*e*
7	$CDCl_3$	----	----	6.32 *J*=2.2	7.54 *J*=2.2	8.71	7.85 *J*=8.4	6.95 *J*=8.4	----	6.95 *J*=8.4	7.85 *J*=8.4	*f*
8	$CDCl_3$	----	----	6.32 *J*=2.2	7.56 *J*=2.2	8.81	13.34	6.47	----	6.48 *J*=9.1	7.25 *J*=9.1	*g*
9	$CDCl_3$	----	----	6.34 *J*=2.4	7.56 *J*=2.4	8.83	13.33	6.42		6.42	7.27	*h*

10	$CDCl_3$	----	2.35	6.07	----	8.66	7.81 *J*=8.1	6.91 *J*=8.1	----	6.91 *J*=8.1	7.81 *J*=8.1	*i*
11	$CDCl_3$	----	2.33	6.06	----	8.75	13.41	6.45	----	6.45	7.21 *J*=8.9	*j*
12	$CDCl_3$	3.71	2.35	----	2.31	8.41	7.76 *J*=8.4	6.93 *J*=8.4	----	6.93 *J*=8.4	7.76 *J*=8.4	*k*
13	$CDCl_3$	3.71	2.34	----	2.28	8.44	13.86	6.46	----	6.44 *J*=9.1	7.16 *J*=9.1	*l*
14	$CDCl_3$	3.85	2.24	5.91	----	8.39	7.77 *J*=8.5	6.91 *J*=8.5	----	6.91 *J*=8.5	7.77 *J*=8.5	*m*
15	$CDCl_3$	3.79	2.24	5.96	----	8.44	12.73	6.45	----	6.47 *J*=8.4	7.20 *J*=8.4	*n*

[a] $OC_{10}H_{21}$: 4.01 (2H, t, Hj, ^3J = 6.2), 1.71 (2H, m, Hi, ^3J = 6.5), 1.2-1.3 (14H, m, Hb to Hh), 0.84 (3H, m, Ha). [b] $OC_{10}H_{21}$: 3.97 (2H, t, Hj, ^3J = 6.3), 1.68 (2H, m, Hi), 1.2-1.3 (14H, m, Hb to Hh), 0.83 (3H, t, Ha, ^3J = 6.4). [c] $OC_{10}H_{21}$: 3.99 (2H, t, Hj, ^3J = 6.3), 1.77 (2H, m, Hi), 1.3 (14H, m, Hb to Hh), 0.89 (3H, t, Ha, ^3J = 6.3). [d] $OCH(CH_3)CO_2C_4H_9$: 4.80 (1H, q, Hf, ^3J = 6.7), 4.18 (2H, t, Hd, ^3J = 6.5), 1.55 (2H, s, Hc), 1.63 (3H, d, CH_3g, ^3J = 6.7), 1.33 (2H, m, Hb), 0.89 (3H, t, CH_3a, ^3J = 7.2). [e] $OCH(CH_3)CO_2C_4H_9$: 5.05 (1H, q, Hf, ^3J = 6.7), 4.10 (2H, t, Hd, ^3J = 6.3), 2.07 (2H, s, Hc), 1.50 (3H, d, CH_3g, ^3J = 6.7), 1.25 (2H, m, Hb), 0.82 (3H, t, CH_3a, ^3J = 7.2). [f] $OC_{10}H_{21}$: 4.01 (2H, t, Hj, ^3J = 6.5), 1.81 (2H, m, Hi), 1.3 (14H, m, Hb to Hh), 0.88 (3H, t, Ha, ^3J = 6.6). [g] $OC_{10}H_{21}$: 3.99 (2H, t, Hj, ^3J = 6.6), 1.79 (2H, m, Hi), 1.3 (14H, m, Hb to Hh), 0.88 (3H, t, Ha, ^3J = 6.6). [h] $OCH(CH_3)CO_2C_4H_9$: 4.81 (1H, q, Hf, ^3J = 6.8), 4.18 (2H, t, Hd, ^3J = 6.6), 1.6 (2H, s, Hc), 1.64 (3H, d, CH_3g, ^3J = 6.8), 1.3 (2H, m, Hb), 0.90 (3H, t, CH_3a, ^3J = 7.2). [i] $OC_{10}H_{21}$: 3.95 (2H, t, Hj, ^3J = 6.1), 1.79 (2H, m, Hi), 1.3 (14H, m, Hb to Hh), 0.89 (3H, t, Ha, ^3J = 6.3) [j] $OC_{10}H_{21}$: 3.98 (2H, t, Hj, ^3J = 6.2), 1.78 (2H, m, Hi), 1.3 (14H, m, Hb to Hh), 0.88 (3H, m, Ha, ^3J = 6.5). [k] $OC_{10}H_{21}$: 3.99 (2H, t, Hj, ^3J = 6.4), 1.79 (2H, m, Hi), 1.3 (14H, m, Hb to Hh), 0.88 (3H, m, Ha). [l] $OC_{10}H_{21}$: 3.96 (2H, t, Hj, ^3J = 6.5), 1.78 (2H, m, Hi), 1.25 (14H, m, Hb to Hh), 0.87 (3H, m, Ha, ^3J = 6.3). [m] $OC_{10}H_{21}$: 3.95 (2H, t, Hj, ^3J = 6.4), 1.77 (2H, m, Hi), 1.25 (14H, m, Hb to Hh), 0.87 (3H, m, Ha, ^3J = 6.5). [n] $OC_{10}H_{21}$: 3.96 (2H, t, Hj, ^3J = 6.3), 1.77 (2H, m, Hi), 1.25 (14H, m, Hb to Hh), 0.87 (3H, m, Ha, ^3J = 6.4).

Table 2. ^{13}C NMR data (δ and ^{1}J - under the corresponding chemical shift-) for compounds (**1-15**)

Comp	Solvent	Me-1	C3	C4	C5	Me-3	Me-5	Ca	C1'	C2'	C3'	C4'	C5'	C6'	Chain
1	DMSO-d_6	----	127.0 186.8	134.7	127.0 186.8	----	----	156.9 160.8	136.5	128.8 163.3	127.8 161.9	130.6 168.0	127.8 161.9	128.8 163.3	----
1	CPMAS	----	128.9	133.1	128.9	----	----	155.6	136.7	128.9	128.1	128.9	128.1	128.9	----
2	DMSO-d_6 +CF_3CO_2H	----	126.4 188.0	127.8	126.4 188.0	----	----	156.9 158.8	135.1	129.8 162.3	115.6 160.1	160.0	115.6 160.1	129.8 162.3	----
3	DMSO-d_6	----	128.0 187.6	134.2	128.0 187.6	----	----	143.5 158.9	----	153.7	114.4 188.4	115.3 183.6	156.9	----	----
3	CPMAS	----	128.1	132.7	125.7	----	----	140.8	----	152.5	114.0	119.0	152.5	----	----
4	DMSO-d_6 +CF_3CO_2H	----	126.4 185.7	131.7	126.4 185.7	----	----	156.5 159.3	135.1	129.5 161.0	114.7 160.9	160.9	114.7 160.9	129.5 161.0	*a*
4	CPMAS	----	127.1	134.5	125.7	----	----	155.5	138.8	130.2	116.2	158.5	109.5	130.2	*b*
5	DMSO-d6	----	131.1 186.8	132.3	121.9 190.6	----	----	159.9 164.4	113.0	162.0	101.2 163.4	162.2	106.8 163.4	132.9 158.8	*c*
5	CPMAS	----	127.3	133.0	125.4	----	----	159.7	113.4	160.9	102.0	162.1	107.3	133.0	*d*
6	$CDCl_3$	----	126.2 187.9	132.9	126.2 187.9	----	----	159.8 159.7	113.7	161.1	102.2 162.7	162.5	107.2 163.3	132.9 159.1	*e*
7	$CDCl_3$	----	156.9	94.7 176.2	132.7 189.7	----	----	160.0 158.4	128.3	130.4 160.0	114.4 160.6	161.8	114.4 160.6	130.4 160.0	*f*
8	$CDCl_3$	----	155.7	95.3 177.5	131.0 186.6	----	----	161.8 161.0	112.4	163.4	101.3 160.5	163.4	107.4 163.3	133.4 158.2	*h*
9	$CDCl_3$	----	155.9	95.3 177.4	131.0 187.3	----	----	161.8 161.7	113.4	161.7	102.1 160.3	163.3	107.5 163.4	133.7 158.5	*i*

10	$CDCl_3$	----	142.5	93.8 170.4	157.9	----	11.7 170.7	159.4 158.0	128.6	130.2 159.9	114.3 160.3	161.6	114.3 160.3	130.2 159.9	*j*
11	$CDCl_3$	----	137.5	94.8 174.8	141.6	----	11.3 169.6	161.5 161.3	112.4	156.1	101.2 160.2	163.4	107.3 163.0	133.3 158.7	*k*
12	$CDCl_3$	35.8 139.0	138.6	133.0	129.5	13.0 169.8	9.0 171.5	155.6 157.7	129.8	129.0 159.3	114.3 160.0	160.8	114.3 160.0	129.0 159.3	*l*
13	$CDCl_3$	35.9 139.4	138.7	132.5	126.7	12.8 171.1	9.1 171.4	158.6 160.5	113.1	162.3	101.3 159.6	162.5	106.7 162.6	132.1 156.9	*m*
14	$CDCl_3$	34.1 139.8	150.2	90.2 173.5	147.1	13.8 169.3	----	158.2 158.2	128.3	130.2 160.0	114.4 160.6	161.9	114.4 160.6	130.2 160.0	*n*
15	$CDCl_3$	34.5 139.5	148.0	90.9 173.9	147.3	13.7 169.9	----	160.9 161.2	112.3	162.8	101.2 160.1	163.7	107.7 163.4	133.6 158.0	*o*

[a] $OC_{10}H_{21}$: 67.8 (Cj, ^1J = 144.0), 31.2 (Ci, ^1J = 128.4), 29.0 (Cg), 28.6 (Cf to Cc), 25.4 (Ch, ^1J = 128.6), 22.0 (Cb, ^1J = 124.7), 13.8 (Ca, ^1J = 122.7). [b] $OC_{10}H_{21}$: 66.1 (Cj), 34.2 (Ci), 32.5 (Cg to Cc), 25.4 (Ch), 24.5 (Cb), 14.5 (Ca). [c] $OC_{10}H_{21}$: 67.6 (Cj, ^1J = 143.9), 31.3 (Ci, ^1J = 127.6), 29.0 (Cg), 28.9 (Ce and Cf), 28.7 (Cc and Cd), 25.4 (Ch, ^1J = 128.4), 22.1 (Cb, ^1J = 124.0), 13.9 (Ca, ^1J = 122.6). [d] $OC_{10}H_{21}$: 66.0 (Cj), 33.5 (Ci and Cg), 31.5 (Ce and Cf), 26.3 (Cc and Cd), 25.1 (Ch and Cb), 14.9 (Ca). [e] $OCH(CH_3)CO_2C_4H_9$: 171.8 (Ce), 72.3 (Cf, ^1J = 148.8, ^2J = 4.1), 65.3 (Cd, ^1J = 147.4, ^2J = 4.2), 30.4 (Cc), 18.9 (Cb), 18.4 (CH_3g, ^1J = 130.0, ^2J = 3.8), 13.6 (CH_3a, ^1J = 124.8). [f] $OC_{10}H_{21}$: 67.9 (Cj, ^1J = 142.9), 31.6 (Ci, ^1J = 124.6), 29.3, 29.3, 29.1, 29.0, 28.9 (Cg to Cc), 25.7 (Ch, ^1J = 128.6), 22.4 (Cb, ^1J = 124.7), 13.8 (Ca, ^1J = 122.7). [h] $OC_{10}H_{21}$: 68.0 (Cj, ^1J = 143.2), 31.6 (Ci, ^1J = 127.6), 29.3, 29.3, 29.0, 29.0, 28.9 (Cg to Cc), 25.7 (Ch, ^1J = 128.4), 22.4 (Cb, ^1J = 122.7), 13.8 (Ca, ^1J = 122.6). [i] $OCH(CH_3)CO_2C_4H_9$: 171.7 (Ce), 72.3 (Cf, ^1J = 148.6, ^2J = 4.2), 65.3 (Cd, ^1J = 147.2, ^2J = 4.4), 30.4 (Cc), 18.9 (Cb), 18.4 (CH_3g, ^1J = 129.8, ^2J = 3.9), 13.5 (CH_3a, ^1J = 124.7). [j] $OC_{10}H_{21}$: 67.9 (Cj, ^1J = 140.9), 31.6 (Ci, ^1J = 126.6), 29.3, 29.3, 29.1, 29.1, 28.9 (Cg to Cc), 25.7 (Ch, ^1J = 126.8), 22.4 (Cb, ^1J = 123.5), 13.8 (Ca, ^1J = 123.4). [k] $OC_{10}H_{21}$: 67.9 (Cj, ^1J = 142.9), 31.6 (Ci, ^1J = 128.4), 29.3, 29.3, 29.1, 29.1, 28.9 (Cg to Cc), 25.7 (Ch, ^1J = 128.6), 22.4 (Cb, ^1J = 124.7), 13.8 (Ca, ^1J = 122.7). [l] $OC_{10}H_{21}$: 67.8 (Cj, ^1J = 142.9), 31.6 (Ci, ^1J = 126.6), 29.3, 29.3, 29.2, 29.0, 28.9 (Cg to Cc), 25.7 (Ch, ^1J = 123.1), 22.4 (Cb, ^1J = 123.5), 13.8 (Ca, ^1J = 123.7). [m] $OC_{10}H_{21}$: 67.9 (Cj, ^1J = 143.2), 31.6 (Ci, ^1J = 127.6), 29.3, 29.3, 29.1, 29.0, 28.8 (Cg to Cc), 25.7 (Ch, ^1J = 128.4), 22.4 (Cb, ^1J = 122.7), 13.8 (Ca, ^1J = 122.6). [n] $OC_{10}H_{21}$: 67.9 (Cj, ^1J = 142.8), 31.6 (Ci, ^1J = 128.4), 29.3, 29.3, 29.1, 29.0, 28.9 (Cg to Cc), 25.7 (Ch, ^1J = 128.6), 22.4 (Cb, ^1J = 124.7), 13.8 (Ca, ^1J = 122.7). [o] $OC_{10}H_{21}$: 68.0 (Cj, ^1J = 143.2), 31.6 (Ci, ^1J = 128.4), 29.3, 29.3, 29.1, 29.0, 28.8 (Cg to Cc), 25.7 (Ch, ^1J = 128.6), 22.4 (Cb, ^1J = 124.7), 13.8 (Ca, ^1J = 122.7).

The IMHB between the *ortho*-hydroxy group and the imino nitrogen results in IR (KBr disks, see EXPERIMENTAL, Table 4) in a modification of the C=N stretching. Excluding compounds (**1**) (not oxygen atom at the *para* position) and **3** (nitrofuryl derivative), that are different from the remaining thirteen, the $\nu_{C=N}$ appears as a narrow band between 1593 and 1601 cm^{-1} for compounds without the *ortho*-OH group (**2**, **4**, **7**, **10**, **12**, **14**) and as a broad band between 1607 and 1625 cm^{-1} for Schiff bases with an *ortho*-OH group (**5**, **6**, **8**, **9**, **11**, **13**, **15**). The ν_{O-H} in these last compounds is a broad band, difficult to observe, near 2600-2750 cm^{-1}, characteristic of a O-H···N= IMHB.[15]

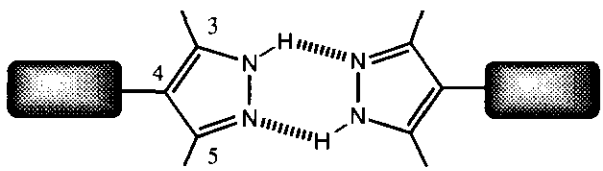
Mesogenic properties

Table 3. Mesogenic properties of compounds (**4-15**) (optical microscopy and DSC). Temperatures in °C and enthalpies in J/g. **C**: crystal, **C'**, **C"**: crystal (phase transition), **I**: liquid (isotropic), $\mathbf{S_A}$: smectic A mesophase, $\mathbf{S_C}$: smectic C mesophase

Compound		Properties
4	Heating:	**C** (120, 66.9 J/g) → **C'** (151, 95.2 J/g) → **I**
	Cooling:	**I** (146.6, 95.6 J/g) → **C'** (101, 67.0 J/g) → **C**
5[a]	Heating:	**C** (69, 18.6 J/g) → **C'** (122, 22.3 J/g) → **C"** (162, 84.2) → **I**
	Cooling:	**I** (157, 76.6 J/g) → $\mathbf{S_A}$ (154) → **C**
6	Heating:	**C** (99, 53.1 J/g) → **I**
	Cooling:	**I** (75, 48.2 J/g) → **C**
7	Heating:	**C** (90, 88.3 J/g) → **I**
	Cooling:	**I** (55) → **C**[b]
8	Heating:	**C** (106, 1.8 J/g) → **C'** (118, 31.6 J/g) → **I**
	Cooling:	**I** (83, 15.8 J/g) → **C**
9	Heating:	**C** (70, 60.3 J/g) → **I**
	Cooling:	**I**: vitrification (no phase transition was observed)[c]
10	Heating:	**C** (76, 2.8 J/g) → **C'** (96, 73.2 J/g) → **I**
	Cooling:	**I**: vitrification (no phase transition was observed)[c]
11	Heating:	**C** (81, 82.1 J/g) → **I**
	Cooling:	**I**: vitrification (no phase transition was observed)[c]
12	Heating:	**C** (66, 125 J/g) → **I**
	Cooling:	**I** (46, 111.2 J/g) → **C**
13	Heating:	**C** (83, 131.0 J/g) → **I**
	Cooling:	**I** (10, 40.0 J/g) → **C**[d]
14	Heating:	**C** (55, 95.4 J/g) → **I**
	Cooling:	**I** (13, 18.6 J/g) → **C**[e]
15	Heating:	**C** (62, 71.7 J/g) → **I**
	Cooling:	**I** (21, 55.8 J/g) → **C**

[a] In the cooling process, a transitory S_C mesophase was observed for a very short temperature interval below the S_A mesophase, the value 76.6 J/g corresponds to the sum of the isotropic liquid-mesophase and mesophase-crystal transition enthalpies. [b] In the microscope, the compound starts to crystallize at 70 °C; the broadness of the corresponding DSC peak precludes the determination of the crystallization enthalpy. [c] No phase transition was observed in DSC nor with the microscope. [d] In the microscope, the compound starts to crystallize at 46 °C. [e] In the microscope, the compound starts to crystallize at 29 °C.

The results of Table 4 are disappointing since only compound (**5**) presents a smectic A phase on cooling. Our expectations for mesogenic behavior were centered on *N*-unsubstituted pyrazole derivatives and specially those (**5**, **6**, **8**, **9** and **11**) with an *ortho* hydroxy group, since we have previously shown that the intramolecular hydrogen bond (IMHB) between the OH and the imine nitrogen stabilizes the structure, favors the planarity of the system and confers mesogenic properties.[16] Our working hypothesis was that these compounds would not behave as liquid crystals in their monomeric structure but they would associate by intermolecular HBs, typical of NH-pyrazoles, to form dimers or trimers,[17-19] and that these dimers or trimers would present liquid crystalline properties. Hydrogen bonds have been successfully used to obtain liquid crystals by Kato and Fréchet[20-29] and by Kreese.[30-32]

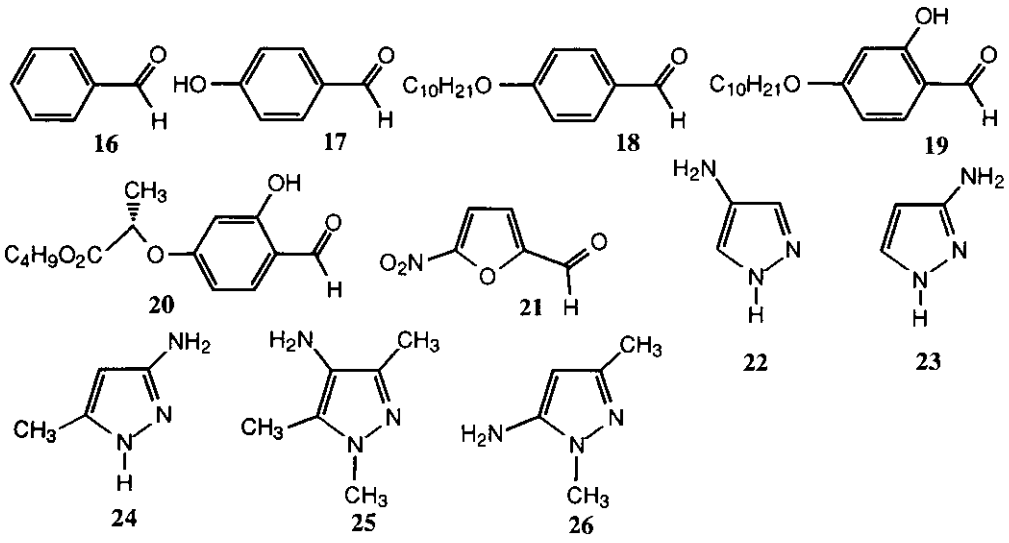


Simple geometrical considerations allow to select, as best candidates, 4-substituted pyrazoles (**5**, **6**) because 3-or 5-substituted pyrazole (**8**, **9**, **11**) dimers will have a global bent conformation. The lack of success points out to the existence of HBs between the pyrazole NH and the imine nitrogen, and so, in future research it would be better to use as spacers -C≡C- or -CH=CH- instead of a -CH=N- group. Another possibility would be to use equimolar mixtures of *p*-substituted benzoic acids and 4-substituted pyrazoles expecting the formation of heterodimers such as found for simple pyrazoles and benzoic acids.[33]

EXPERIMENTAL

Melting points were determined in a capillary tube and are uncorrected. Column chromatography was performed on silica gel Merck 60 (70-230 mesh) using dichloromethane as eluent. The *Rf* values were measured on TLC aluminium sheets of silica gel 60 F_{254} (layer thickness 0.2 mm) with CH_2Cl_2/EtOH (9:1) as eluents. IR spectra (KBr) were recorded on a Philips PU 9714. Polarimetry measurements were carried out with a Perkin-Elmer 241-C polarimeter. MS spectra were obtained with a Shimadzu QP-5000 (electrom impact, 60 eV). ^{1}H NMR (200.13 MHz) and ^{13}C NMR (50.32 MHz) spectra were obtained using a Bruker AC-200 instrument. Chemical shifts (δ) in ppm and coupling constants (*J*) in Hz were measured using Me_4Si as internal standard. The chemical shifts are accurate to 0.01 and 0.1 ppm for ^{1}H and ^{13}C NMR, respectively. Coupling constants are accurate to 0.2 Hz for ^{1}H nmr and 0.5 Hz for ^{13}C NMR. Solid state ^{13}C CPMAS NMR spectra were recorded using the same instrument (50.32 MHz) and the experimental conditions described elsewhere.[34]

The liquid crystal properties were studied with a Perkin-Elmer DSC-7 operated at 10 °C/min under nitrogen and with a Meiji polarizing microscope equipped with a Mettler FP82 hot stage and a FP80 central processor.



Starting Materials. Benzaldehyde (**16**), 4-hydroxybenzaldehyde (**17**), 5-nitro-2-furaldehyde (**21**) are commercial products (Aldrich) as it is 4-*n*-decyloxybenzaldehyde (**18**) (Frinton Laboratories) and butyl (*S*)-(-)-lactate (Aldrich, $[\alpha]_D^{20}$ = -12°, neat). Also commercial are aminopyrazoles (**23**), (**24**) (Aldrich), (**25**) and (**26**) (Lancaster). 4-Aminopyrazole (**22**) was prepared from 4-nitropyrazole as previously described.[11]

4-*n*-Decyloxy-2-hydroxybenzaldehyde (**19**). This compound was prepared using the Williamson etherification[35] of 2,4-dihydroxybenzaldehyde (Aldrich) with 1-bromodecane (Aldrich) in the presence of potassium bicarbonate to avoid the etherification of the 2-hydroxy group. A mixture of 6.9 g (50 mmol) of 2,4-dihydroxybenzaldehyde, 11.1 g (50 mmol) of 1-bromodecane and 5.0 g (50 mmol) of potassium bicarbonate were stirred and refluxed during 48 h in acetone (100 mL). After filtering the inorganic salts, evaporating the solvent under reduced pressure, the residue is purified by flash chromatography (hexane:toluene 3:1), Yield: 6.4 g (46%). ^{1}H NMR ($CDCl_3$): 11.46 (s, 1 H), 9.68 (s, 1 H), 7.39 (d, 1 H, J = 8.8), 6.50 (dd, 1 H, *J* = 2.4, *J* = 8.2), 6.39 (d, 1 H, *J* = 2.4), 3.97 (t, 2 H, *J* = 6.6), 1.98-1.86 (m, 16 H), 0.86 (t, 3 H, *J* = 5.9).

4-*n*-Butyloxycarbonylethyloxy-2-hydroxybenzaldehyde (**20**). This compound was prepared using the Mitsunobu method.[36] 2 g (14.5 mmol) of 2,4-dihydroxybenzaldehyde were disolved in 170 mL of dichloromethane using a 500 mL flask, then 4.56 g (17.4 mmol) of triphenylphosphine were added under argon atmosphere. After 30 min of stirring, 2.12 g (14.5 mmol) of butyl (*S*)-(-)-lactate in 20 mL of dichloromethane were added through a syringue and then 3.03 g (17.4 mmol) of diethyl azodicarboxylate (DEAD) in 20 mL of dichloromethane were slowly added in the same way. The reaction which was carried out at rt was stirred for another 2 h period. After evaporation to dryness, the rose residue was column chromatographed (eluent: hexane/ethyl acetate 20:1) to yield 2.78 g of **20** (Yield: 72%) of a colorless liquid. ^{1}H NMR ($CDCl_3$): 11.40 (s, 1 H), 9.70 (s, 1 H), 7.41 (d, 1 H, J = 8.6), 6.52 (dd, 1 H, *J* = 2.1, *J* = 8.6), 6.32 (d, 1 H, *J* = 2.1), 4.79 (q, 1 H, *J* = 6.8), 4.15 (m, 2 H), 1.62 (d, 2 H, *J* = 6.8), 1.58 (m, 2 H), 1.31 (m, 2 H), 0.87 (t, 3H, *J* = 7.3). $[\alpha]_D^{20}$ = +54° (c = 3.3, $CHCl_3$).

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Table 4. Characterization of the Schiff bases (**1-15**)

Compd	mp (°C)	Yield (%)	Rf	Mol. Form.	$M^{+\cdot}$ (%)		C	H	N	$\nu_{C=N}$ (cm^{-1})
1	173-175[a]	30	0.59	$C_{10}H_9N_3$	171 (18)	Anal. Calcd	70.15	5.30	24.54	1607
						Found:	70.30	5.39	25.77	
2	198-202[a]	47	0.34	$C_{10}H_9N_3O$	187 (46)	Anal. Calcd	64.16	4.84	22.44	1599
						Found:	64.21	4.90	22.48	
3	198-200[a]	70	0.38	$C_8H_6N_4O_3$	206 (16)	Anal. Calcd	46.61	2.93	27.17	1558
						Found:	45.68	3.01	27.15	
4	155-158[a]	53	0.57	$C_{20}H_{29}N_3O$	327 (35)	Anal. Calcd	73.35	8.92	12.83	1601
						Found:	73.26	8.74	12.88	
5	160-163[a]	80	0.64	$C_{20}H_{29}N_3O_2$	343 (22)	Anal. Calcd	69.94	8.51	12.23	1612
						Found:	69.90	8.44	12.21	
6	103-105[b,c]	58	0.61	$C_{17}H_{21}N_3O_4$	331 (100)	Anal. Calcd	61.62	6.39	12.68	1610[f]
						Found:	61.59	6.31	12.63	
7	94-97[a]	37	0.54	$C_{20}H_{29}N_3O$	327 (45)	Anal. Calcd	73.36	8.93	12.83	1594
						Found:	73.58	8.86	12.69	
8	148-151[a]	47	0.56	$C_{20}H_{29}N_3O_2$	343 (29)	Anal. Calcd	69.94	8.51	12.23	1608
						Found:	70.14	8.39	12.35	
9	66-68[b,d]	70	0.70	$C_{17}H_{21}N_3O_4$	331 (100)	Anal. Calcd	61.62	6.39	12.68	1609[f]
						Found:	61.98	6.39	12.22	
10	85-87[a]	18	0.49	$C_{21}H_{31}N_3O$	341 (44)	Anal. Calcd	73.86	9.15	12.30	1593
						Found:	73.80	8.86	12.31	
11	105-108[a]	30	0.59	$C_{21}H_{31}N_3O_2$	357 (36)	Anal. Calcd	70.56	8.74	11.75	1607
						Found:	70.48	8.65	11.92	
12	61-63[e]	11	0.41	$C_{23}H_{35}N_3O$	369 (67)	Anal. Calcd	74.75	9.54	11.37	1599
						Found:	74.53	9.43	11.05	
13	84-88[a]	96	0.59	$C_{23}H_{35}N_3O_2$	385 (100)	Anal. Calcd	71.65	9.15	10.90	1610
						Found:	71.57	9.08	10.56	
14	53-54[e]	18	0.60	$C_{22}H_{33}N_3O$	355 (89)	Anal. Calcd	74.32	9.35	11.82	1598
						Found:	74.65	9.25	11.63	
15	61-63[e]	41	0.57	$C_{22}H_{33}N_3O_2$	371 (100)	Anal. Calcd	71.12	8.95	11.31	1625
						Found:	71.46	9.11	10.97	

[a] Crystallized in ethanol; [b] Crystallized in dichloromethane-hexane (1:1); [c] $[\alpha]_D^{20}$ = +54° (1.53, $CHCl_3$); [d] $[\alpha]_D^{20}$ = +42° (1.76, $CHCl_3$); [e] Crystallized in hexane; [f] Ester band near 1740 cm^{-1}.

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