

SYNTHESIS AND MESOGENIC PROPERTIES OF SCHIFF BASES DERIVED FROM AMINOPYRAZOLES

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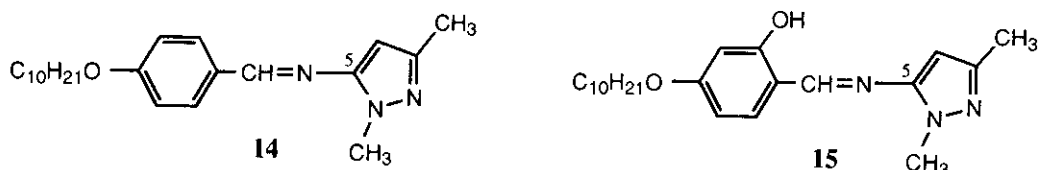
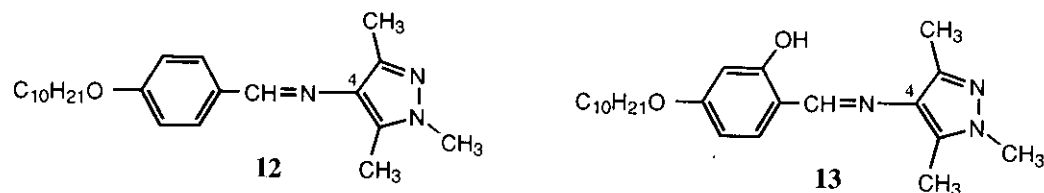
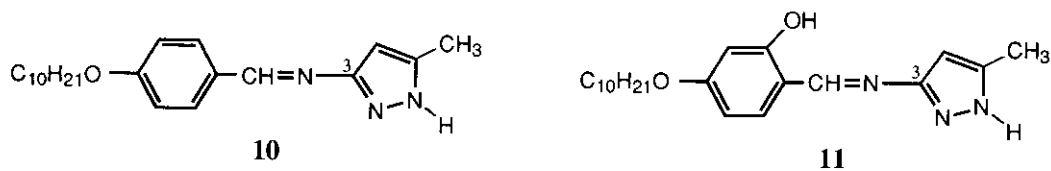
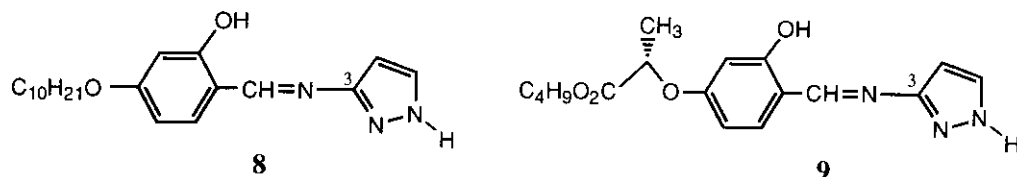
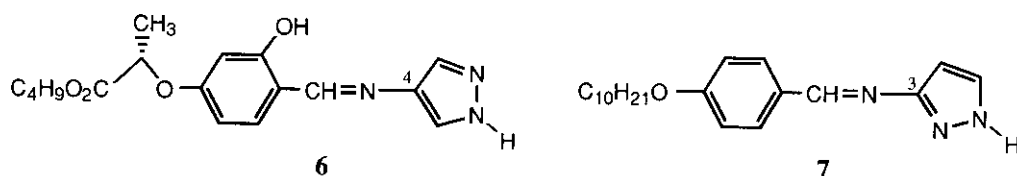
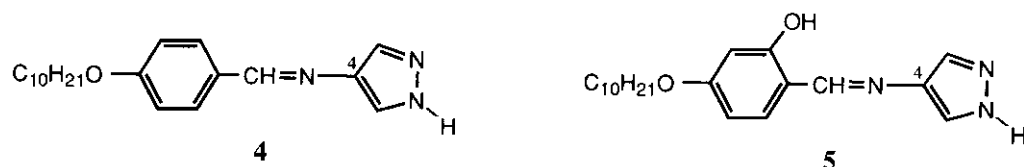
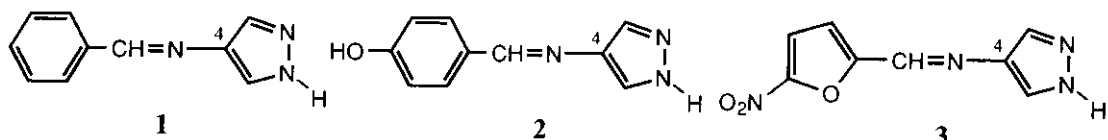
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Abstract- Fifteen azomethineimines derived from *C*-aminopyrazoles and aromatic aldehydes have been prepared and fully characterized (IR, MS, ¹H and ¹³C NMR in solution and ¹³C CPMAS NMR). The benzaldehyde bearing at position 4 *n*-decyloxy or a *n*-butyloxycarbonylethoxy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

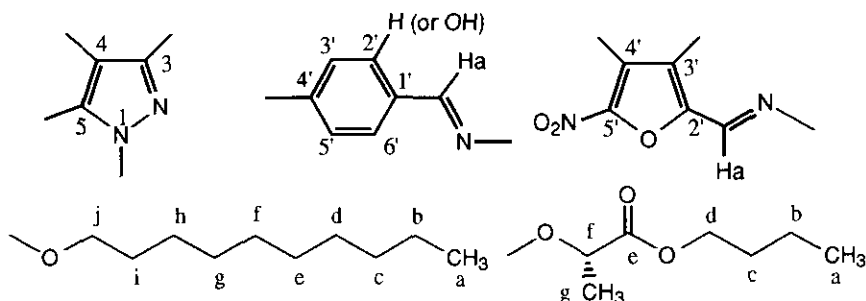
The search for new compounds, possible candidates for liquid-crystal properties,¹⁻³ lead us to explore the Schiff bases derived from *C*-aminopyrazoles. Amongst the bridges used to connect the two aromatic halves of liquid crystals, the -CH=N- bridge is found in many cases, usually connecting two aromatic 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**).



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:



¹H NMR chemical shifts and ¹H-¹H 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-d₆ 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 CD₃OD (the same phenomenon is observed in ¹³C NMR, Table 2). The 3(5)-aminopyrazole derivatives (**7-9**) are mixtures of 3 and 5-substituted tautomers because the ³J(¹H-¹H) coupling constant amounts to 2.2-2.4 Hz.¹⁰

Table 2 contains the ¹³C chemical shifts and the ¹J(¹H-¹³C) 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(¹³C-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.

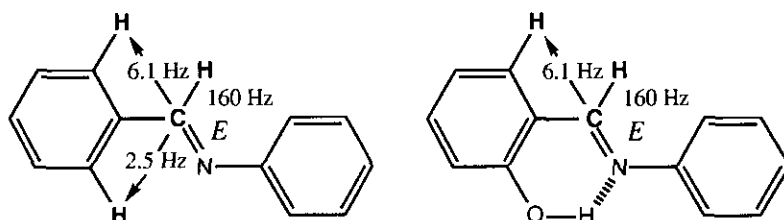


Table 1. ¹H NMR data (δ and J) for compounds (1-15)

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 <i>J</i> =8.2	6.83 <i>J</i> =8.2	----	6.83 <i>J</i> =8.2	7.65 <i>J</i> =8.2	9.96
3	DMSO-d ₆	13.1	7.98	----	7.98	8.61	----	7.19 <i>J</i> =3.3	7.71 <i>J</i> =3.3	----	----	----
4	DMSO-d ₆ + CF ₃ CO ₂ H	12.7	7.77	----	7.77	8.61	7.75 <i>J</i> =8.5	6.98 <i>J</i> =8.5	----	6.98 <i>J</i> =8.5	7.75 <i>J</i> =8.5	<i>a</i>
5	DMSO-d ₆	12.9	7.78 (br)	----	7.98 (br)	8.81	13.44	6.42 <i>J</i> =2.2	----	6.50 <i>J</i> =8.6 <i>J</i> =2.2	7.36 <i>J</i> =8.6	<i>b</i>
5	CD ₃ OD	----	7.80	----	7.80	8.71	----	6.41 <i>J</i> =2.4	----	6.48 <i>J</i> =8.6 <i>J</i> =2.4	7.31 <i>J</i> =8.6	<i>c</i>
6	CDCl ₃	----	7.70	----	7.70	8.54	13.38	6.42 <i>J</i> =2.1	----	6.46 <i>J</i> =8.6	7.20 <i>J</i> =8.6	<i>d</i>
6	DMSO-d ₆	12.9	7.85 (br)	----	7.85 (br)	8.83	13.45	6.36 <i>J</i> =2.1	----	6.48 <i>J</i> =8.4	7.39 <i>J</i> =8.4	<i>e</i>
7	CDCl ₃	----	----	6.32 <i>J</i> =2.2	7.54 <i>J</i> =2.2	8.71	7.85 <i>J</i> =8.4	6.95 <i>J</i> =8.4	----	6.95 <i>J</i> =8.4	7.85 <i>J</i> =8.4	<i>f</i>
8	CDCl ₃	----	----	6.32 <i>J</i> =2.2	7.56 <i>J</i> =2.2	8.81	13.34	6.47	----	6.48 <i>J</i> =9.1	7.25 <i>J</i> =9.1	<i>g</i>
9	CDCl ₃	----	----	6.34 <i>J</i> =2.4	7.56 <i>J</i> =2.4	8.83	13.33	6.42	----	6.42	7.27	<i>h</i>

10	CDCl ₃	----	2.35	6.07	----	8.66	7.81 <i>J</i> =8.1	6.91 <i>J</i> =8.1	----	6.91 <i>J</i> =8.1	7.81 <i>J</i> =8.1	<i>i</i>
11	CDCl ₃	----	2.33	6.06	----	8.75	13.41	6.45	----	6.45	7.21 <i>J</i> =8.9	<i>j</i>
12	CDCl ₃	3.71	2.35	----	2.31	8.41	7.76 <i>J</i> =8.4	6.93 <i>J</i> =8.4	----	6.93 <i>J</i> =8.4	7.76 <i>J</i> =8.4	<i>k</i>
13	CDCl ₃	3.71	2.34	----	2.28	8.44	13.86	6.46	----	6.44 <i>J</i> =9.1	7.16 <i>J</i> =9.1	<i>l</i>
14	CDCl ₃	3.85	2.24	5.91	----	8.39	7.77 <i>J</i> =8.5	6.91 <i>J</i> =8.5	----	6.91 <i>J</i> =8.5	7.77 <i>J</i> =8.5	<i>m</i>
15	CDCl ₃	3.79	2.24	5.96	----	8.44	12.73	6.45	----	6.47 <i>J</i> =8.4	7.20 <i>J</i> =8.4	<i>n</i>

a OC₁₀H₂₁: 4.01 (2H, t, H_j, ³*J* = 6.2), 1.71 (2H, m, H_i, ³*J* = 6.5), 1.2-1.3 (14H, m, H_b to H_h), 0.84 (3H, m, H_a). *b* OC₁₀H₂₁: 3.97 (2H, t, H_j, ³*J* = 6.3), 1.68 (2H, m, H_i), 1.2-1.3 (14H, m, H_b to H_h), 0.83 (3H, t, H_a, ³*J* = 6.4). *c* OC₁₀H₂₁: 3.99 (2H, t, H_j, ³*J* = 6.3), 1.77 (2H, m, H_i), 1.3 (14H, m, H_b to H_h), 0.89 (3H, t, H_a, ³*J* = 6.3). *d* OCH(CH₃)CO₂C₄H₉: 4.80 (1H, q, H_f, ³*J* = 6.7), 4.18 (2H, t, H_d, ³*J* = 6.5), 1.55 (2H, s, H_c), 1.63 (3H, d, CH₃g, ³*J* = 6.7), 1.33 (2H, m, H_b), 0.89 (3H, t, CH₃a, ³*J* = 7.2). *e* OCH(CH₃)CO₂C₄H₉: 5.05 (1H, q, H_f, ³*J* = 6.7), 4.10 (2H, t, H_d, ³*J* = 6.3), 2.07 (2H, s, H_c), 1.50 (3H, d, CH₃g, ³*J* = 6.7), 1.25 (2H, m, H_b), 0.82 (3H, t, CH₃a, ³*J* = 7.2). *f* OC₁₀H₂₁: 4.01 (2H, t, H_j, ³*J* = 6.5), 1.81 (2H, m, H_i), 1.3 (14H, m, H_b to H_h), 0.88 (3H, t, H_a, ³*J* = 6.6). *g* OC₁₀H₂₁: 3.99 (2H, t, H_j, ³*J* = 6.6), 1.79 (2H, m, H_i), 1.3 (14H, m, H_b to H_h), 0.88 (3H, t, H_a, ³*J* = 6.6). *h* OCH(CH₃)CO₂C₄H₉: 4.81 (1H, q, H_f, ³*J* = 6.8), 4.18 (2H, t, H_d, ³*J* = 6.6), 1.6 (2H, s, H_c), 1.64 (3H, d, CH₃g, ³*J* = 6.8), 1.3 (2H, m, H_b), 0.90 (3H, t, CH₃a, ³*J* = 7.2). *i* OC₁₀H₂₁: 3.95 (2H, t, H_j, ³*J* = 6.1), 1.79 (2H, m, H_i), 1.3 (14H, m, H_b to H_h), 0.89 (3H, t, H_a, ³*J* = 6.3). *j* OC₁₀H₂₁: 3.98 (2H, t, H_j, ³*J* = 6.2), 1.78 (2H, m, H_i), 1.3 (14H, m, H_b to H_h), 0.88 (3H, m, H_a, ³*J* = 6.5). *k* OC₁₀H₂₁: 3.99 (2H, t, H_j, ³*J* = 6.4), 1.79 (2H, m, H_i), 1.3 (14H, m, H_b to H_h), 0.88 (3H, m, H_a). *l* OC₁₀H₂₁: 3.96 (2H, t, H_j, ³*J* = 6.5), 1.78 (2H, m, H_i), 1.25 (14H, m, H_b to H_h), 0.87 (3H, m, H_a, ³*J* = 6.3). *m* OC₁₀H₂₁: 3.95 (2H, t, H_j, ³*J* = 6.4), 1.77 (2H, m, H_i), 1.25 (14H, m, H_b to H_h), 0.87 (3H, m, H_a, ³*J* = 6.5). *n* OC₁₀H₂₁: 3.96 (2H, t, H_j, ³*J* = 6.3), 1.77 (2H, m, H_i), 1.25 (14H, m, H_b to H_h), 0.87 (3H, m, H_a, ³*J* = 6.4).

Table 2. ^{13}C NMR data (δ and 1J - 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 ₃ CO ₂ H	----	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 ₃ CO ₂ H	----	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	<i>a</i>
4	CPMAS	----	127.1	134.5	125.7	----	----	155.5	138.8	130.2	116.2	158.5	109.5	130.2	<i>b</i>
5	DMSO-d ₆	----	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	<i>c</i>
5	CPMAS	----	127.3	133.0	125.4	----	----	159.7	113.4	160.9	102.0	162.1	107.3	133.0	<i>d</i>
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	<i>e</i>
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	<i>f</i>
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	<i>h</i>
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>i</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	<i>j</i>
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	<i>k</i>
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	<i>l</i>
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	<i>m</i>
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	<i>n</i>
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	<i>o</i>

^a OC₁₀H₂₁: 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 OC₁₀H₂₁: 66.1 (Cj), 34.2 (Ci), 32.5 (Cg to Cc), 25.4 (Ch), 24.5 (Cb), 14.5 (Ca). ^c OC₁₀H₂₁: 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 OC₁₀H₂₁: 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(CH₃)CO₂C₄H₉: 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 (CH₃g, ¹J = 130.0, ²J = 3.8), 13.6 (CH₃a, ¹J = 124.8). ^f OC₁₀H₂₁: 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 OC₁₀H₂₁: 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(CH₃)CO₂C₄H₉: 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 (CH₃g, ¹J = 129.8, ²J = 3.9), 13.5 (CH₃a, ¹J = 124.7). ^j OC₁₀H₂₁: 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 OC₁₀H₂₁: 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 OC₁₀H₂₁: 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 OC₁₀H₂₁: 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 OC₁₀H₂₁: 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 OC₁₀H₂₁: 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 $\nu_{\text{C=N}}$ 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 $\nu_{\text{O-H}}$ in these last compounds is a broad band, difficult to observe, near 2600-2750 cm^{-1} , characteristic of a O-H...N= IMHB.¹⁵

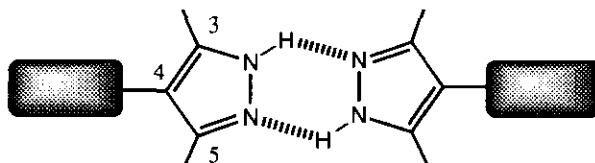
Mesogenic properties

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), S_A: smectic A mesophase, 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) → 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 Fréchet²⁰⁻²⁹ and by Kreese.³⁰⁻³²

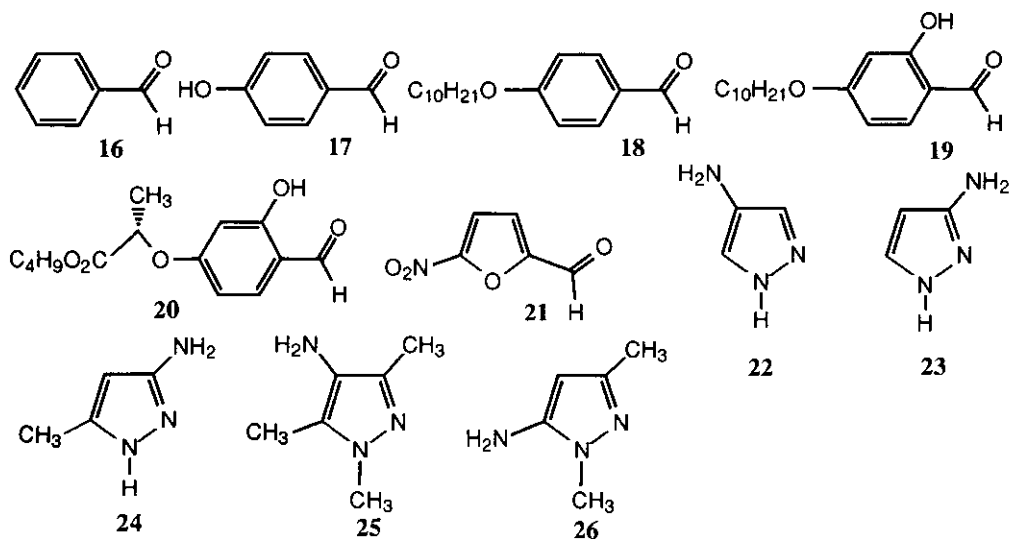


Simple geometrical considerations allow to select, as best candidates, 4-substituted pyrazoles (5, 6) because 3- or 5-substituted pyrazole (8, 9, 11) dimers will have a global bent conformation. The lack of success points out to the existence of HBs between the pyrazole NH and the imine nitrogen, and so, in future research it would be better to use as spacers $-C\equiv C-$ 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 R_f values were measured on TLC aluminium sheets of silica gel 60 F₂₅₄ (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 (electron impact, 60 eV). ¹H NMR (200.13 MHz) and ¹³C 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 ¹H and ¹³C NMR, respectively. Coupling constants are accurate to 0.2 Hz for ¹H nmr and 0.5 Hz for ¹³C NMR. Solid state ¹³C CP/MAS 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, $[\alpha]_D^{20} = -12^\circ$, 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 etherification³⁵ 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%). ¹H NMR (CDCl₃): 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*-Butyloxycarbonyloxy-2-hydroxybenzaldehyde (**20**). This compound was prepared using the Mitsunobu method.³⁶ 2 g (14.5 mmol) of 2,4-dihydroxybenzaldehyde were dissolved 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 syringe 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. ¹H NMR (CDCl₃): 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). $[\alpha]_D^{20} = +54^\circ$ (*c* = 3.3, CHCl₃).

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

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

^a Crystallized in ethanol; ^b Crystallized in dichloromethane-hexane (1:1); ^c $[\alpha]_D^{20} = +54^\circ$ (1.53, CHCl₃); ^d $[\alpha]_D^{20} = +42^\circ$ (1.76, CHCl₃); ^e Crystallized in hexane; ^f Ester band near 1740 cm⁻¹.

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