Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Liquid crystal properties of N-alkyl(ethylpyridinium) bromides ω-substituted with a mesogenic group

E. Bravo-grimaldo[a]; D. Navarro-Rodríguez[b]; A. Skoulios[c]; D. Guillon[c]
[a] Facultad de Ciencias Químicas, Saltillo, Coahuila, Mexico [b] Centro de Investigación en Química Aplicada, Saltillo, Coahuila, Mexico [c] Institut de Physique et Chimie des Matériaux de Strasbourg, Strasbourg Cedex, France

To cite this Article Bravo-grimaldo, E. , Navarro-Rodríguez, D. , Skoulios, A. and Guillon, D.(1996) 'Liquid crystal properties of N-alkyl(ethylpyridinium) bromides ω-substituted with a mesogenic group', Liquid Crystals, 20: 4, 393 — 398
To link to this Article: DOI: 10.1080/02678299608032052
URL: http://dx.doi.org/10.1080/02678299608032052

LIQUID CRYSTALS, 1996, VOL. 20, NO. 4, 393–398

Liquid crystal properties of *N*-alkyl(ethylpyridinium) bromides ω-substituted with a mesogenic group

by E. BRAVO-GRIMALDO, D. NAVARRO-RODRÍGUEZ†
Facultad de Ciencias Químicas, U A de C, Blvd. V. Carranza y José Cárdenas V.,
C.P. 25000, Saltillo, Coahuila, Mexico
†Centro de Investigación en Química Aplicada, Blvd. Enrique Reyna H. No. 140,
C.P. 25100, Saltillo, Coahuila, Mexico

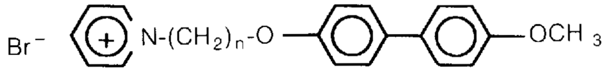
A. SKOULIOS and D. GUILLON*
Institut de Physique et Chimie des Matériaux de Strasbourg, Groupe des Matériaux
Organiques, UMR 046, 23 Rue de Loess, 67037 Strasbourg Cedex, France

(*Received 10 October 1995; 30 November 1995*)

A new series of ethylpyridinium salts *N*-substituted with a 4′-methoxybiphenyl-4-yloxyalkyl group has been synthesized and the mesomorphic properties examined. The effect of positioning the ethyl group at each of the three available positions (2; 3- or 4-) on the pyridinium ring was examined and compounds with alkyl chains containing odd numbers of carbon atoms from C5 to C11 were investigated. It was found that the longer chain (C9–C11) 2- and 4-ethylpyridinium compounds form smectic phases, whereas the corresponding 3-substituted compounds do not. X-ray diffraction studies indicated that the smectic phases were of types A, B and in one case E, with the molecules lying in a head to tail fashion in single layers with interdigitated alkyl chains. We explain the difference in mesogenic properties of the three different ring-substituted compounds in terms of packing considerations in the ionic regions of the structures. It is suggested that the 3-derivatives pack more efficiently than the 2- and 4-substituted compounds.

1. Introduction

Among the ionic thermotropic liquid crystals, alkali metal soaps were the first well-known compounds to exhibit lamellar structures [1]. More recently, several studies relating to pyridinium salts have shown the ability of these materials too to produce thermotropic smectic phases [2–4]. The particular case of the *N*-alkylpyridinium halides (X = Cl, Br or I) ω-substituted with a mesogenic group, (**1**), has permitted us to describe the smectic structure more precisely [5].



1

This structure corresponds to the stacking of single layers of upright molecules laterally arranged head to tail, with the anions sandwiched between the pyridinium rings; the ionic end groups are set in double layers with the oppositely charged species facing each other (see figure 1). It is of interest to note that, despite the van der Waals repulsions operating between the polarizable aromatic groups and the non-polar paraffin chains, these species are intimately interdigitated within the non-ionic sublayers of the smectic phases; this is presumably due to the strength of the coulombic interactions between the pyridinium and halide ions. Let us add that poly-(4-vinylpyridine) fully and partially quaternized with the same mesogenic group also exhibits thermotropic smectic phases with a very similar structure [6].

In order to test the strength of the electrical interactions in the smectic phases exhibited by molecules of the type represented in structure **1**, we thought it of interest to modify the molecular architecture of the pyridinium part, particularly its overall bulkiness. For this purpose, we used a pyridinium ring substituted with an ethyl group successively in one of the three available ring-positions (2-, 3- or 4-). In this paper, we report the synthesis and the liquid crystalline behaviour of a new series of such pyridinium halides obtained by quaternization of ethylpyridine with halogenoalkanes (corresponding to the odd homologues with 5 to 11 carbon atoms) ω-substituted with the same mesogenic group as that in

---

*Author for correspondence

0267-8292/96 $12·00

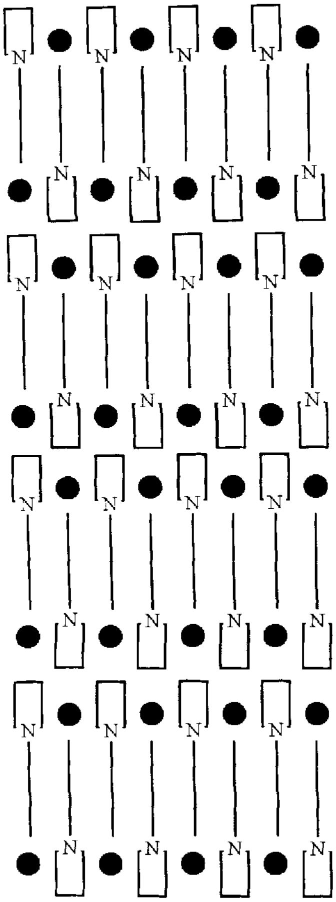


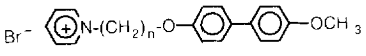
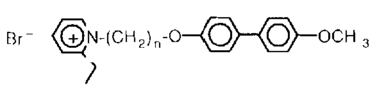
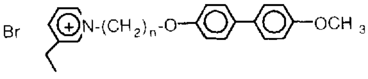
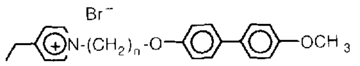
Figure 1. Schematic representation of the molecules in the smectic layers (circles for the anions, straight lines for the non-ionic moities), as postulated in reference [5].

(**1**). The results obtained are discussed in comparison with the previous results corresponding to the compounds with unsubstituted pyridinium rings.

2. Chemical synthesis

Products from table 1 were synthesized by a similar method to that reported in a previous paper [5]. Their chemical architecture is characterized by a polymethylene chain ($n=5$, 7, 9 or 11) substituted at one of its ends by a pyridinium or a 2-, 3- or 4-ethylpyridinium bromide and at the other by a non-ionic 4′-methoxybiphenyl-4-yloxy mesogenic group. The alkyl-mesogenic moiety is attached to the pyridine ring through a quaternization reaction. Due to the high dielectric constants of pyridine and ethylpyridines, no solvent for quaternization was needed. Even though the quaternization kinetics were not studied, it was clear that the 2-ethylpyridinium salts were produced more slowly than the 3- and 4-ethylpyridinium salts. This difference in reactivity is probably due to steric hindrance, most pronounced in the case of the pyridine substituted in the 2-position. All synthesized products were characterized by ^{1}H NMR. Experimental details are given in §6.

Table 1. Chemical structures of the pyridinium salts.

Compound	Molecular structure	n
P-C5		5
P-C7		7
P-C9		9
P-C11		11
2E-C5		5
2E-C7		7
2E-C9		9
2E-C11		11
3E-C5		5
3E-C7		7
3E-C9		9
3E-C11		11
4E-C5		5
4E-C7		7
4E-C9		9
4E-C11		11

3. Liquid crystal properties

The mesomorphic behaviour of the salts synthesized have been studied using differential scanning calorimetry (DuPont Thermal Analyzer 910S, heating and cooling rates of $2\cdot5^{\circ}$C min^{-1}), polarized optical microscopy (Leitz Orthoplan, Mettler FP82 hot stage) and X-ray diffraction. The X-ray patterns were recorded with a Guinier focusing camera (bent quartz monochromator, K_{α_1} copper radiation from a Philips PW1009 X-ray generator, and home-made electrical oven).

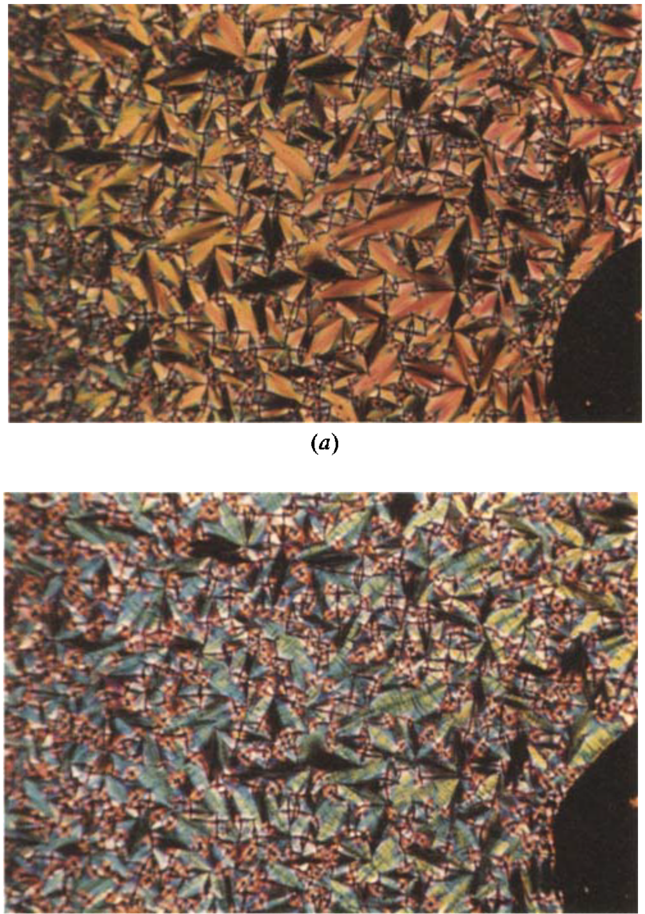
The phase transition temperatures (table 2) of the synthesized products were measured by DSC. The mesophases observed were identified by optical microscopy and X-ray diffraction. It is important to note that the compounds carrying short alkyl chains ($n=5$ and 7) do not show mesomorphic behaviour; they pass from the crystalline state directly to the isotropic liquid (Cr–I). On the other hand, the compounds carrying long alkyl chains ($n=9$ and 11) do show liquid crystalline behaviour in the case of the pyridinium and the 2-ethylpyridinium salts. The 4-ethylpyridinium salts show liquid crystalline properties only for a chain length of 11 carbon atoms. It should be noted that the 3-ethylpyridinium salts show no liquid crystalline properties even for the longest molecules. The reverse transitions from the liquid crystalline to the crystalline state on cooling always show a marked hysteresis.

In figure 2 two typical smectic textures [9] obtained by cooling PC11 from the isotropic melt are represented.

Table 2. Thermal transitions determined by DSC at a cooling rate of 2·5°C min^{-1}.

Compound	Transition temperatures °C							
P-C5	Cr	120	I					
P-C7	Cr	145	I					
P-C9	Cr	144	S_A	160	I			
P-C11	Cr	?	S_B	113.6	S_A	152	I	
2E-C5	Cr	80	I					
2E-C7	Cr	102·6	I					
2E-C9	Cr	80	S_E	88·2	S_A	114·5	I	
2E-C11	Cr	70–85	S_A	112	I			
3E-C5	Cr	178	I					
3E-C7	Cr	117	I					
3E-C9	Cr	92·4	I					
3E-C11	Cr	104·4	I					
4E-C5	Cr	120	I					
4E-C7	Cr	120·3	I					
4E-C9	Cr	115	I					
4E-C11	Cr	92·6	S_A	121	I			

Figure 2(*a*) presents the fan shaped optical texture characteristic of a smectic A phase. Upon further cooling, the texture is preserved without great changes, corresponding to the occurrence of a smectic B phase, but at 95°C lines did develop across the fans, figure 2(*b*).


(*a*)

(*b*)

Figure 2. Focal-conic optical textures of PC11 obtained by cooling from the isotropic melt (*a*) in the smectic A phase at 130°C, and (*b*) in the smectic B phase upon cooling to 95°C, well below the S_A-S_B transition at 113·6°C (cross polarizers, mgnification 180x).

4. Molecular stacking

Data in table 3 have been obtained from X-ray diffraction measurements. The smectic nature of the liquid crystalline phases at high temperatures was established by the presence of two sharp equidistant reflections at low angles, related to the stacking period of the smectic layers. The smectic A type was characterized by a single diffuse band in the wide angle region of the X-ray patterns, located at about 4·5 Å, indicative of the well-known liquid-like ordering of the molecules within the smectic layers. By contrast, the smectic B phase was characterized by the presence in the wide angle region of the X-ray patterns of a single, rather sharp reflection at ≅4·4 Å, indicative of a two dimensional ordering of the molecules within the layers and indexed as the d_{100} reflection from a hexagonal lattice. The E phase was characterized by the presence of two rather sharp Bragg reflections at 4·54 and 4·04 Å, indicative of a two-dimensional ordering of the molecules within the layers and indexed as the d_{11} and d_{20} reflections from a centred rectangular lattice.

In table 3, the smectic periods are compared with the lengths (*L*) of the molecules in their most extended configurations, calculated by molecular modelling (Sybyl software from Tripos) with the counterion (ionic diameter of $Br^- = 3{\cdot}9$ Å [8] included in the lengths of the rod-like molecules. It is clear that the experimental and calculated layer spacings are very close, indicating that the smectic structures are single layered, the molecules

Table 3. Layer spacing (d_A, d_B and d_E) of the smectic layers measured at temperature *T*, compared with the molecular length *L* of the fully extended molecules.

Compound	L/Å	T/°C	d_B/Å	d_E/Å	d_A/Å
P-C9	32·8	150			32·9
P-C11	35·3	90	36·6		
		150			35·6
2E-C9	32·8	70		34·9	
		96			33·6
2E-C11	35·3	105			36·4
4E-C11	37·1	105			37·3

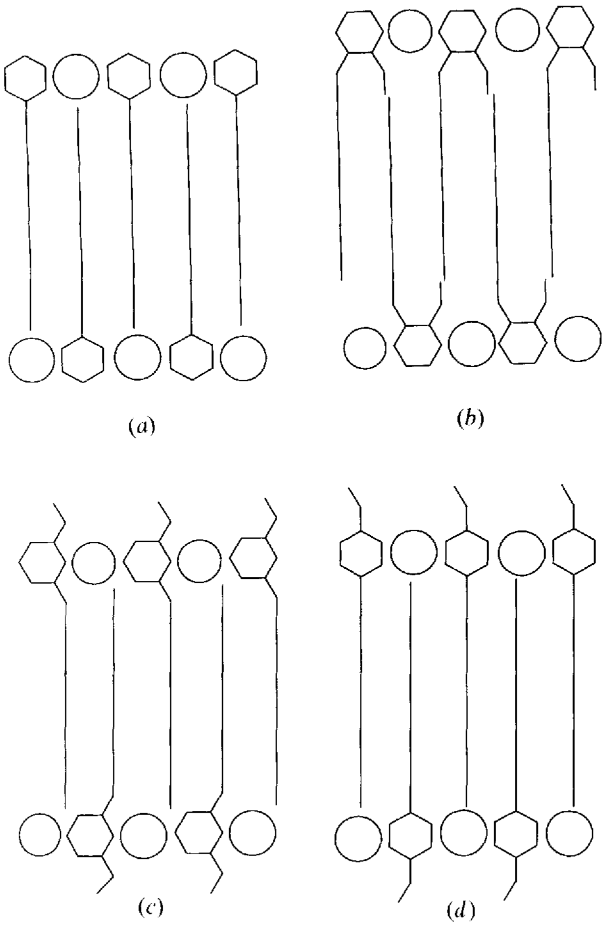


Figure 3. Schematic representation of the head to tail arrangement of the (*a*) pyridinium; (*b*) 2-ethylpyridinium: (*c*) 3-ethylpyridinium and (*d*) 4-ethylpyridinium salts (circles stand for the anions, hexagons for the pyridinium end groups, and lines for the non-ionic parts of the molecules).

being oriented on average perpendicularly to the smectic planes. In such an arrangement, the molecules are laterally positioned head to tail as illustrated in figure 3 (*a*). The anions are sandwiched between the positively charged pyridinium rings in an up and down distribution, as already observed for non-symmetrical molecules forming liquid crystals [2]. The molecules are held together mainly by strong electrical forces, rather than by van der Waals interactions. The molecules interact between adjacent smectic layers through the oppositely charged ions facing each other in the ionic double layers (figure 1).

Close inspection of the experimental data (see table 2) shows that the main effect of the ethyl-substitution of the pyridinium ring is to lower the thermal stability of the mesophases observed, and to leave the thermal stability of the crystal phases (except for the 3E-C5 compound) unaffected. The results show, on the other hand, that the ethylpyridinium salts behave differently depending on the precise position of the ethyl group on the pyridinium ring. No doubt, the presence of an ethyl group affects the packing of the molecules, because it is located just within the region of the ionic moieties which control the molecular stacking. With the ethyl group in the 2-position, the liquid crystalline structure is maintained, the layer spacing (salts 2E-C9 and 2E-C11) being just slightly larger than that of the unsubstituted homologous salts (P-C9 and P-C11). This may be explained by a space filling such as that proposed in figure 3 (*b*), where the ethyl groups point parallel to the flexible alkyl chains, filling the gap between the anion and the methoxy end group of the biphenylyl group of the neighbouring molecule. Such an arrangement is plausible, because it does not affect significantly either the lateral ionic interaction or the formation of the double ionic layers. By contrast, with the ethyl group in the 3-position, no mesophase is developed. In this case, the bulky ethyl group does actually affect the ionic interactions both laterally and across the ionic double layers, figure 3 (*c*). With the ethyl group in the 4-position, mesomorphic behaviour is observed only when the alkyl chains are long enough (salt 4E-C11). In this case the ethyl groups lead to a splitting of the ionic double layer, but leave the lateral ionic interactions unperturbed, figure 3 (*d*). Based upon this consideration, the layer spacing (d) must be higher than for the other salts (substituted and unsubstituted) due to the contribution of the ethyl end group. Table 3 indicates that effectively the d_A value of the 4-ethylpyridinium salt (4E-C11, 37·3 Å) is higher than the d_A values of the 2-ethylpyridinium salts (for example, 2E-C11, 36·4 Å) and this in turn is higher than the d_A values of the unsubstituted pyridinium salts (for example, P-C11, 35·6 Å).

5. Conclusion

The smectic structures (A, B and E) observed with ethylpyridinium bromides *N*-substituted with an ω-(4′-methoxybiphenyl-4-yloxy)alkyl group, correspond to the stacking of single layers of upright molecules laterally arranged head to tail, with the anions sandwiched between the pyridinium rings. In the present work, it has been found that ethyl substitution of the pyridinium ring affects the packing of the molecules because the ethyl group is located just within the ionic moiety which controls the molecular stacking. When the ethyl group is in the 2- or 4- position, the liquid crystalline properties are maintained for long chains. In this case, the molecular arrangement does not affect significantly either the lateral ionic interaction or the formation of the double layer of opposite charges between layers. By contrast, with the ethyl group in the 3- position, no mesophase was developed, probably because of steric hindrance mainly with respect to the double ionic layer formation.

6. Experimental

^{1}H NMR measurements were performed with a Varian spectrometer (Gemini 200 MHz). Thermal stability was studied from 30 to 200°C, at a scanning rate of 2·5°C min^{-1}, under nitrogen, with a 951 thermogravimetric analyser from DuPont Instruments.

The synthesis of *N*-[ω-(4′-methoxybiphenyl-4-yloxy) alkyl]ethylpyridinium bromides was carried out as follows. 4-Hydroxy-4′-methoxybiphenyl (**I**) was synthesized by a classical method [7] using a 4,4′-dihydroxybiphenyl (Aldrich) and dimethyl sulphate. The ω-(4′-methoxybiphenyl-4-yloxy)alkyl bromides (**II**) were obtained by reacting **I** with α,ω-dibromoalkanes (Aldrich), and these in turn were reacted with 2-, 3- or 4-ethylpyridine to obtain the ethyl substituted pyridinium salts under similar conditions to those described in a recent paper [5]. Finally, the pyridinium salts were purified by column chromatography, first by eluting with methylene chloride, then with methylene chloride/methanol 1/1. Products (table 1) were vacuum dried at 40°C for 24 h. Purities of salts were confirmed by silica gel TLC (eluent $\mathrm{CH_2Cl_2}$) and ^{1}H NMR.

It is interesting to point out that the ^{1}H NMR signals from the pyridinium salts are clearly identified because almost no superposed signals appear, particularly for the shorter alkyl chain products (5 carbon atoms). The following ^{1}H NMR spectral data are good examples for such products, see also figure 4.

Chemical shifts (δ, ppm) from figure 4 (pyridinium salt 4-ethyl substituted) correspond to the following: 9·37 (d, $J=6{\cdot}7$ Hz, 2H, 2CH–N$^+$); 7·83 (d, $J=6{\cdot}6$ Hz, 2H, CH–CH–N+); 7·42–7·48, 6·87–6·97 (2m, 8H, Ar); 5·01 (t, $J=10{\cdot}8$ Hz, 2H, $\mathrm{CH_2}$-N$^+$); 3·97 (t, $J=12$ Hz, 2H, $\mathrm{CH_2}$–O-Ar); 3·84 (s, 3H, $\mathrm{CH_3}$-O); 2·93 (q, $J=19$ Hz, 2H, $\mathrm{CH_3}$-$\mathrm{CH_2}$-Py$^+$); 2·09–2·17 (m, 2H,

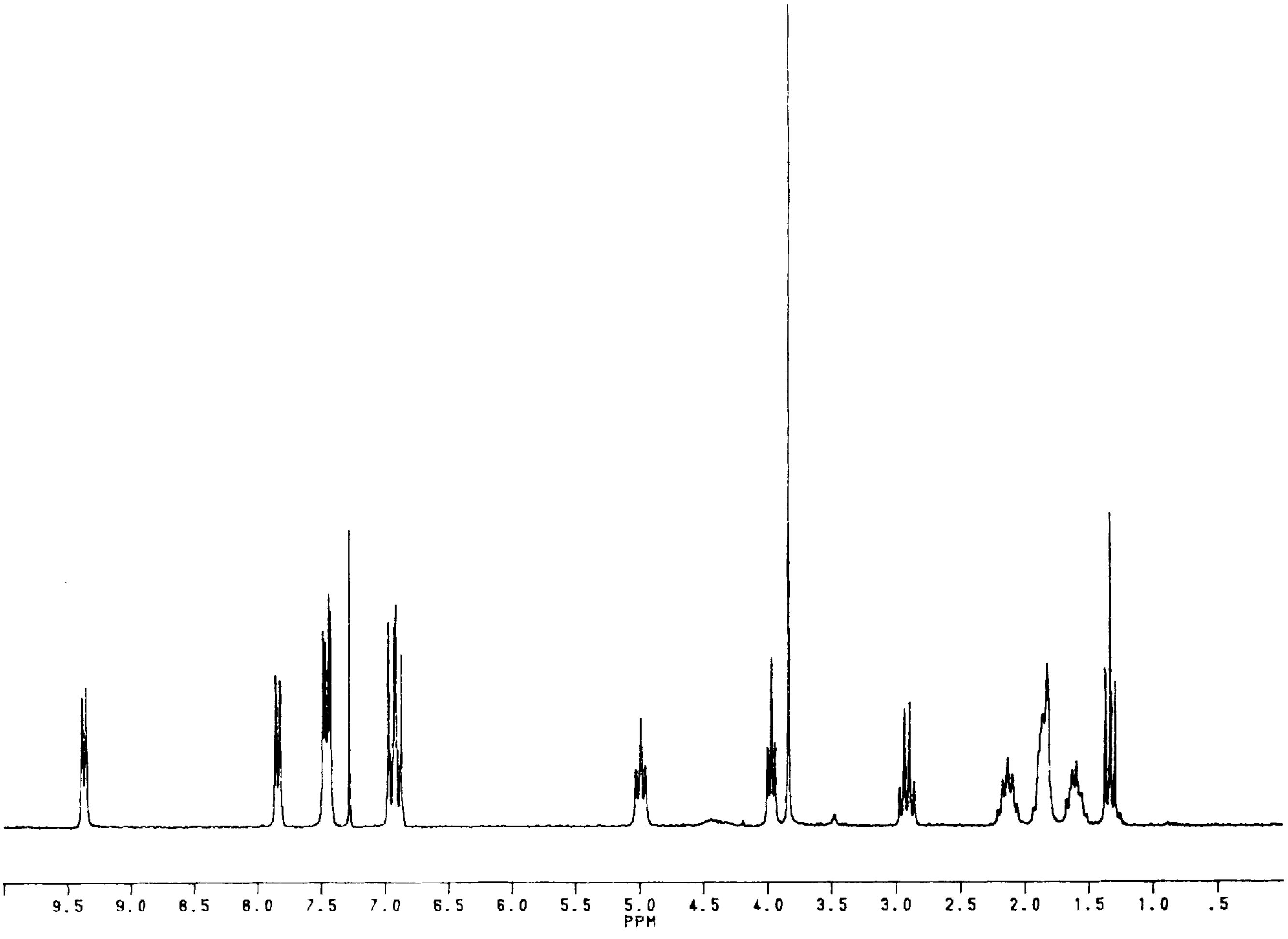


Figure 4. ^{1}H NMR spectrum for *N*-[ω-(4′-methoxy-4-biphenyl-4-yloxy)pentyl]-4-ethylpyridinium bromide ($\mathrm{C_{25}H_{30}O_2NBr}$). Solvent $\mathrm{CDCl_3}$.

CH_2-CH_2-N^+); 1·80–1·90 (m, 2H, CH_2-CH_2-O); 1·55–1·83 (m. 2H, CH_2-CH_2-CH_2-N^+) and 1·34 (t, $J = 15{\cdot}1$ Hz, 3H, CH_3-CH_2-Py^+). For the 2-ethyl substituted pyridinium salts the protons from the pyridinium ring appear at: 9·91 (d, $J = 5{\cdot}2$ Hz, 1H, CH-N^+); 8·38 (t, $J = 11{\cdot}8$ Hz, 1H, CH-CH-CH-N^+); 7·99 (t, $J = 12{\cdot}4$ Hz, H, CH-CH-CH-N^+) and 7·84 (d, $J = 8{\cdot}2$ Hz, 1H, CH-C-N^+). For the 3-ethyl substituted pyridinium salts, the protons from the pyridinium ring appear at: 9·38 (s, 1H, C-CH-N^+); 9·30 (d, $J = 10$ Hz, H, CH-CH-N^+); 8·22 (d, $J = 9$, 1H, CH-C-CH-N^+) and 7·92–8·03 (t, $J = 22$, 1H, CH-CH-N^+). For the longer alkyl chains (7, 9 and 11 carbon atoms), the signal intensity at 1·55–1·83 (m, 2nH, $(CH_2)_nCH_2CH_2N^+$) increases as a function of the chain length.

The products were studied from the point of view of their thermotropic mesomorphism, so it was necessary to establish their thermal stability. It has been observed that they are in general stable up to 200°C, which is higher than the clearing temperatures for any of the materials.

E. B. G. is grateful to the Consejo Nacional de Ciencia y Tecnologia (CONACYT) of Mexico for its financial support during this work. The authors thank the CONACYT-CNRS (Mexico-France) Collaboration Program for its financial support.

References

[1] Skoulios, A., and Luzzati, V., 1961, *Acta Crystallogr.*, **14,** 278.

[2] Bazuin, C. G., Guillon, D., Skoulios, A., and Nicoud, J. F., 1980, *Liq. Cryst.*, **1,** 181.

[3] Südhölter, E. J. R., Engberts, J. B. F. N., and De Jeu, W. H., 1982, *J. phys. Chem.*, **86,** 1908.

[4] Tabrizian, M., Soldera, A., Couturier, M., and Bazuin, G., 1995, *Liq. Cryst.*, **18,** 475.

[5] Navarro-Rodríguez, D., Frère, Y., Gramain, P., Guillon, D., and Skoulios, A., 1991, *Liq. Cryst.*, **9,** 321.

[6] Navarro-Rodríguez, D., Guillon, D., Skoulios, A., Frère, Y., and Gramain, P., 1992, *Makromol. Chem.*, **193,** 3117.

[7] Apfel, M. A., Finkelmann, H., Janini, G. G., Laub, R. J., Lubman, B. H., Price, A., Roberts, W. L., Shaw, T. J., and Smith, T. A., 1985, *Analytical Chem.*, **57,** 851.

[8] Weast, R. C. (editor), 1975, *Handbook of Chemistry and Physics*, 56th edition (Boca Ratou, Florida: CRC Press).

[9] Sackmann, H., and Demus, D., 1973, *Mol. Cryst. liq. Cryst.*, **21,** 239.