Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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Version of record first published: 22 Sep 2006.

To cite this article: J. Barberá , M. Marcos & J. L. Serrano (1989): A Structural Study of Mesogenic p-Alkoxy-Benzoic and -Pyridinic Acids Using Spectroscopic Techniques and MNDO Calculations, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 166:1, 61-74

To link to this article: http://dx.doi.org/10.1080/00268948908037138

Mol. Cryst. Liq. Cryst., 1989, Vol. 166, pp. 61–74
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Printed in the United States of America

A Structural Study of Mesogenic *p*-Alkoxy-Benzoic and -Pyridinic Acids Using Spectroscopic Techniques and MNDO Calculations

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(*Received January 6, 1988; in final form February 26, 1988*)

In order to investigate the relation between molecular structure and liquid crystal properties, structural studies are carried out on three series of compounds: 6-alkoxynicotinic acids, 5-alkoxypicolinic acids, and 4-alkoxybenzoic acids, using IR and ^{1}H NMR spectroscopy and MNDO semi-empirical calculations. Spectroscopic results prove that, whereas inter-molecular O—H bonds favor mesomorphism, inter- and intra-molecular N—H bonds obstruct it. MNDO results show that the type of mesophase is determined by the direction of the molecular dipole moment.

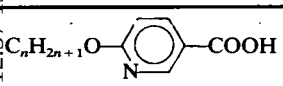
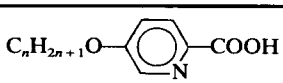
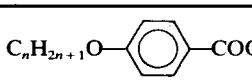
INTRODUCTION

We have recently published several reports dealing with the mesomorphic behavior of three series of compounds (mono- and di-imines, and azines) derived from alkoxy-substituted benzaldehydes and pyridinealdehydes.[1,2,3,4] We have proved that the carbocyclic and 2-pyridinic (picolinic) compounds behave in a similar way, the majority of them displaying nematic mesomorphism over wide ranges of temperature, whereas the 3-pyridinic (nicotinic) compounds have a marked tendency to show smectic A mesomorphism. Spectroscopic studies and quantum-mechanical calculations (MNDO) reveal the important role played by the direction of the molecular dipole moment and by the extension of the electronic conjugation on the mesomorphic properties.

We are now interested in the mesomorphic properties of the alkoxy-substituted pyridinecarboxylic acids, some of which were prepared as intermediates in the synthesis of the above-mentioned mesogens. The mesomorphic behavior of a number of these acids, as well as of the benzene analogues, has been described in the literature.[5,6,7] Data from the literature, together with those determined by us, have enabled us to make a comparative study, the results of which appear to differ, at first sight, from our previous observations in the other series. Thus (see Table I), the picolinic acids (II) are not mesogenic, whereas the nicotinic (I) and benzoic

TABLE I

Mesomorphic data for 6-alkoxynicotinic (I), 5-alkoxypicolinic (II) and 4-alkoxybenzoic (III) acids.[a]

 (I)		 (II)		 (III)
Transition	T°C	Transition	T°C	Transition
C—I	174.6			C—I I—N[b]
C—I	186.4			C—I I—N[b]
C—I I—N[b]	99.8 89.8	C—I	99.0	C—N N—I
C—I	96.8	C—I	94.5	C—N N—I
C—I I—N[b]	92.8 90.6	C—I	80.3	C—N N—I
C—N N—I	88.5 89.5	C—I	95.0	C—N N—I
C—N N—I N—S_C[b]	88.0 94.2 87.3			C—S_C S_C—N N—I
C—S_C S_C—I	87.2 95.1			C—S_C S_C—N N—I

[a] S_C = smectic C mesophase; N = nematic mesophase; I = isotropic liquid.
[b] Monotropic transition.

acids (III) are predominantly nematogenic, the nicotinic acids having smaller thermal ranges than the benzoic acids.

In order to understand the mesomorphic behavior of these compounds and to increase our knowledge of structure-mesomorphism relationships, we have made spectroscopic studies (IR and ^{1}H NMR) and semiempirical quantum-mechanical calculations (MNDO) with the three above-mentioned types of compound: 6-alkoxynicotinic, 5-alkoxypicolinic and 4-alkoxybenzoic acids; we have also tried to account for the mesomorphic properties of these compounds in the light of the information obtained.

RESULTS AND DISCUSSION

Some of the mesomorphic data determined by us for the 6-alkoxynicotinic acids differ to a certain extent from those reported in the literature by Pavluchenko *et al.*[5] Thus, for the octyloxy compound, we have identified a monotropic smectic C mesophase which these authors did not note.

One structural characteristic of the carboxylic acids which distinguishes them from Schiff's bases and azines is the formation of hydrogen bonds. The appearance of mesomorphic phases in carboxylic acids is due to the existence of a dimeric structure originated by intermolecular associations, the dimers having a rod-like shape typical of most mesogenic molecules. On this basis, Pavluchenko *et al.* attribute the absence of mesomorphism in the 5-alkoxypicolinic acids to their strong intramolecular N—H bond. Furthermore, these authors attribute the lower thermal stability of the 6-alkoxynicotinic acids, in comparison with the benzene analogues, to the existence of N—H intermolecular linkages, which partially disrupt the dimeric arrangement.

The different possible molecular structures of the acids which are the subject of this paper are shown in Figure 1.

The formation of the dimer (B) is responsible for the mesomorphic behavior of this kind of compound. This possibility is common to the three types of acid.

The existence of the intramolecular linkage in the 5-alkoxypicolinic acids (structure C) prevents the formation of the dimer. In this case, the zwitterionic tautomeric structure can take part (structure D).[8]

For the 6-alkoxynicotinic acids, and perhaps also for the 5-alkoxypicolinic acids, there may be intermolecular bonds between the hydroxy group and the pyridinic heteronitrogen (structure E); a protonated ionic species is also possible (F). It can be taken for granted that neither (E) nor (F) favour mesomorphism.

IR study using CCl_4 solutions

The presence of the different suggested structures has been checked by several spectroscopic techniques, of which the infrared study proved to be of special interest. The diverse IR bands found for the three types of acid using carbon tetrachloride solutions can be accounted for in terms of the structures (A) to (F).

The butoxy derivatives were selected from each series for the spectroscopic study. The IR results are gathered in Table II (see Figure 2).

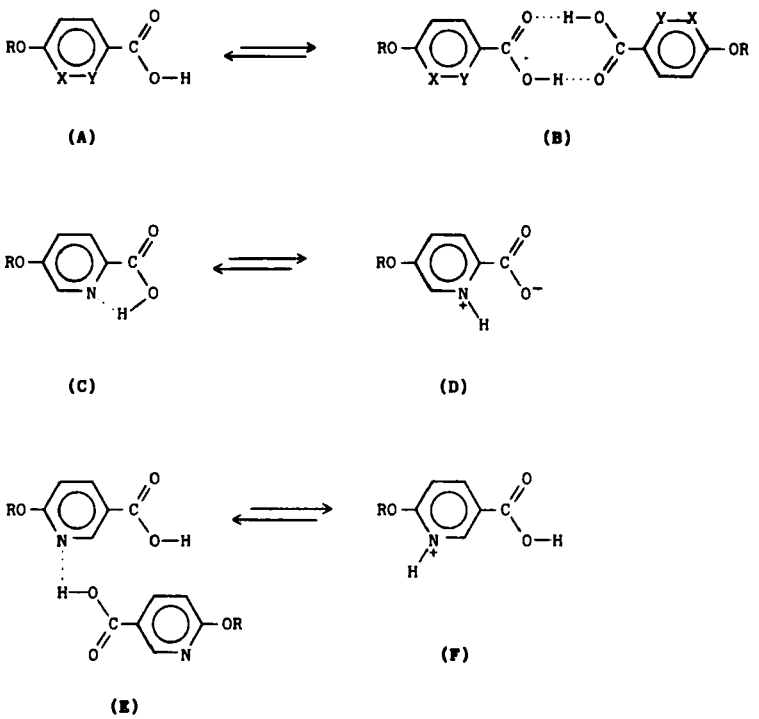


FIGURE 1 Possible structures of *p*-alkoxy-benzoic and -pyridinic acids.

O—H absorptions

The band corresponding to the monomer (A) is well defined for the benzoic (3543 cm^{-1}, band 9) and nicotinic (3538 cm^{-1}, band 1) derivatives. In both cases the band is quite weak, indicating the low percentage of this structure in solution.

In these compounds a very broad band, approximately between 3500 and 2450 cm^{-1} corresponds to the dimer (B). Although its absorption maximum is not well defined, owing to the presence of the stretching absorption of the aromatic and aliphatic C—H bonds, a satellite band is observed at 2669 cm^{-1} (benzoic, band 10) and 2670 cm^{-1} (nicotinic, band 2) indicating the existence of a strongly hydrogen-bonded OH group.[9]

None of the above-mentioned absorptions is observed for the 5-alkoxypicolinic acid and only one band is found at 3339 cm^{-1} (band 6), corresponding to the monomeric structure with an intramolecular bond (C).

N—H absorptions

The important contribution of the zwitterionic tautomeric structure (D) in the picolinic compound is confirmed by the absorption at 2400 cm^{-1} (band 7) typical of the $\overset{+}{N}$—H bond.[10] This absorption also appears for the nicotinic analogue (band

TABLE II

IR data for 6-butoxynicotinic acid (BONA), 5-butoxypicolinic acid (BOPA), and 4-butoxybenzoic acid (BOBA) in CCl_4 solution (c

$\bar{\nu}_{O-H}$					$\bar{\nu}_{C-H}$					$\bar{\nu}^{+}_{N-H}$	$\bar{\nu}_C$
3538		3500–2450	2670	2546	3018		2962	2934	2874	2400	1737
	3339				3018		2966	2935	2876	2400	1769
3543		3500–2450	2669	2554	3016	2997	2961	2934	2875		1734

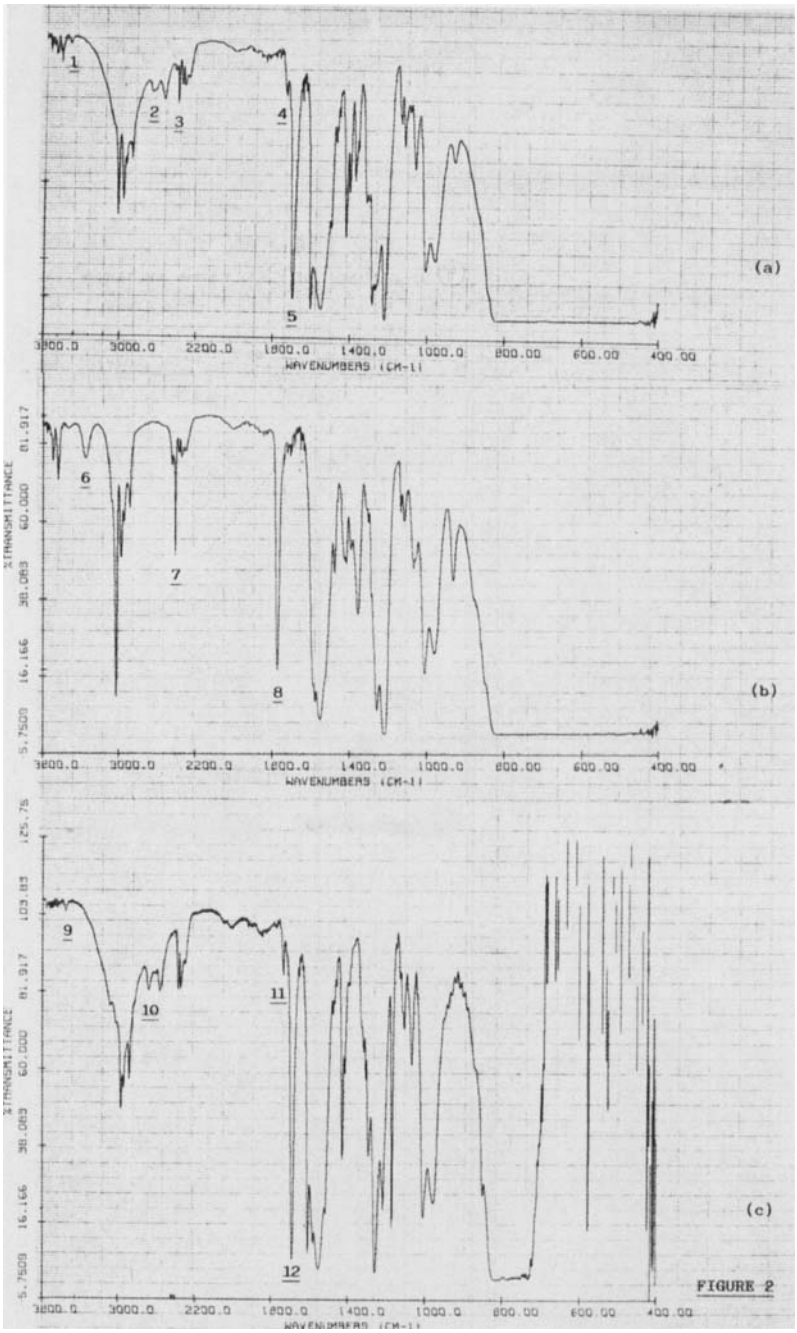


FIGURE 2 IR spectra of 6-butoxynicotinic acid (a), 5-butoxypicolinic acid (b) and 4-butoxybenzoic acid (c) in CCl_4 solution.

3), although with a lower intensity, which indicates the partial contribution of structures (E) and (F) for this isomer.

No absorption near 2400 cm^{-1} occurs with the 4-alkoxybenzoic acid.

C=O absorptions

An examination of the spectral region corresponding to the carbonyl group reinforces these arguments. Thus, a weak band corresponding to the monomer (A) is observed at 1734 cm^{-1} (band 11) for the 4-alkoxybenzoic acid and at 1737 cm^{-1} (band 4) for the 6-alkoxynicotinic acid. The dimeric form in these compounds causes a much stronger absorption at lower frequencies: 1688 cm^{-1} (band 12) for the 4-alkoxybenzoic acid and 1694 cm^{-1} (band 5) for the 6-alkoxynicotinic acid. The differences between the absorption frequencies for the monomeric and the dimeric forms are similar in both cases (46 and 43 cm^{-1} for the benzoic and nicotinic compounds respectively) and the values practically coincide with those found by other authors for associated carboxylic acids.[9]

The spectrum of the 5-alkoxypicolinic acid shows only one carbonyl absorption at 1769 cm^{-1} (band 8), supporting the argument that the structure with an intramolecular bond (C) is the main contributor in this kind of compound. Similar frequency values have been found for carbocyclic acids that form 1:1 complexes with pyridine,[9] a further indication of the formation of the intramolecular linkage between the hydroxy group and the pyridine nitrogen.

IR study using nujol suspensions

We also have made an IR study of these compounds for the solid state (suspension in nujol), and the data obtained are gathered in Table III.

The OH absorption corresponding to the monomeric form does not appear either in the case of the 4-alkoxybenzoic or the 6-alkoxynicotinic acid. On the other hand, the absorption corresponding to the dimers is observed. For the 5-alkoxypicolinic acid, the examination of the OH spectral region indicates the contribution of both the monomeric and the dimeric forms, the contribution of the latter being favoured by the intermolecular proximity

The C=O absorption frequency is similar for the three compounds studied (benzoic 1685 cm^{-1}, nicotinic 1695 cm^{-1}, picolinic 1700 cm^{-1}) and indicates a high degree of dimerisation in the solid state.

TABLE III

OH and CO IR absorptions for 6-butoxynicotinic acid (BONA), 5-butoxy-picolinic acid (BOPA), and 4-butoxybenzoic acid (BOBA) in nujol suspension (cm^{-1})

Compound	$\bar{\nu}_{O-H}$ (monomer)	$\bar{\nu}_{O-H}$ (dimer)			$\bar{\nu}_{C=O}$
BONA		3500–2450	2660	2535	1695
BOPA	3480	3500–2450		2540	1700
BOBA		3500–2450	2670	2560	1685

^{1}H NMR study

The ^{1}H NMR data are set out in Table IV (see Figure 3).

The breadth of the NMR signal corresponding to the hydroxy-proton affords some information concerning the degree of intermolecular association.

The spectrum of the 5-alkoxypicolinic acid shows a sharp peak at δ = 11.62 ppm, indicating the low rate of interchange of the OH proton involved in the strong intramolecular hydrogen bond. The greater breadth of this signal for the nicotinic (δ = 12.2–12.4 ppm) and above all for the benzene analogue (δ = 11.4–12.1 ppm) reflects the faster intermolecular proton interchange in the predominantly dimeric structure.

MNDO study

For the sake of simplicity and in order to reduce the calculation time, the first member of each series, the methoxy derivative, was chosen as a model for the MNDO study. The model molecules used are shown with their simplified nomenclature in Figure 4. All the molecules were allowed to move freely until total optimization. The most interesting MNDO results for a study of the mesogenic properties are set out in Table V.

The geometrical data obtained for the models of the 5-alkoxypicolinic acid are surprising, the dihedral angle δ between the carboxyl group plane and the pyridine ring plane being close to 90° in all cases; this would be impossible for a structure with an intramolecular hydrogen bond and also contradicts the X-ray data for aromatic acids with a dimeric structure.[11] This apparent contradiction is caused by the limitations of the MNDO method, because

a) this method does not take into account the existence of hydrogen linkages;

b) it overestimates the steric or, in this case, electrostatic repulsion between the lone electron pair of the ring nitrogen atom and the lone electron pairs of the carboxyl oxygen atoms (see Figure V(*a*) and (*b*)).

In most of the benzoic and nicotinic model molecules, the previously-mentioned twist angle is close to 0°. It is noticeable that, according to the MNDO calculations, the nicotinic structures with the methyl group in the *anti*-position to the ring nitrogen (Nic-2 and Nic-4) are more unstable (ΔH = −99.94 and −98.63 kcal/mole) than the structures with the methyl group in the *syn*-position (Nic-1 and Nic-3, ΔH = −103.37 and −103.36 kcal/mole). This may be caused by the overestimation of the electrostatic repulsion between the electron pairs of the ring nitrogen and of the methoxy oxygen and/or by the steric repulsion between the hydrogen atoms in the methyl group and in the *ortho*-position of the ring (see Figure 5(c)).

This has caused us to omit the geometrical data calculated by the MNDO method from the discussion and, instead, to concentrate on aspects related to the dipole moments of the molecules.

In one of the previously mentioned papers,[4] we proved that molecules with a dipole moment with only a small component parallel to the molecular axis, and consequently having a direction approximately perpendicular to that axis, showed a marked tendency to exhibit smectic A mesomorphism, whereas a greater parallel

TABLE IV

emical shifts for 6-butoxynicotinic acid (BONA), 5-butoxypicolinic acid (BOPA), and 4-butoxybenzoic acid (BOBA) in $CDCl_3$ solu

	Chemical shifts (ppm)					
(s wide,1H)	8.92(d,1H,J = 2.1)	8.16(dd,1H,J_1 = 8.4,J_2 = 2.1)	6.76(d,1H,J = 8.4)	4.38(t,2H,J = 6.3)	1.25–2.0(m,4H)	0.9
(1H)	8.47(d,1H,J = 2.2)	8.16(d,1H,J = 8.5)	7.34(dd,1H,J_1 = 8.5,J_2 = 2.2)	4.09(t,2H,J = 5.8)	1.25–2.0(m,4H)	0.9
(s wide,1H)	8.04(d,2H,J = 8.2)	6.92(d,2H,J = 8.2)		4.02(t,2H,J = 6.1)	1.25–2.0(m,4H)	0.9

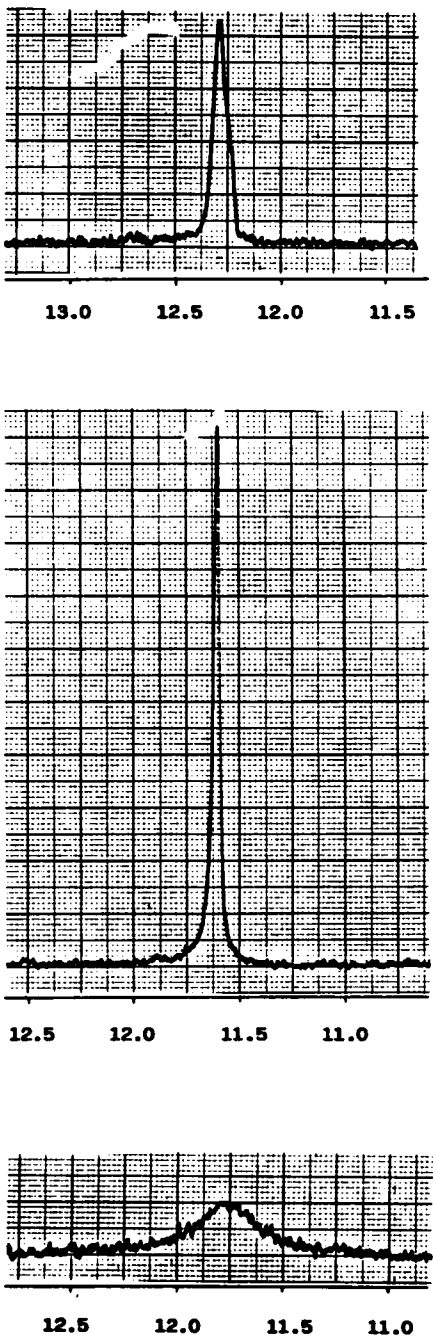


FIGURE 3 ^1H NMR peaks for the OH proton of 6-butoxynicotinic acid (a), 5-butoxypicolinic acid (b) and 4-butoxybenzoic acid (c) in $CDCl_3$ solution.

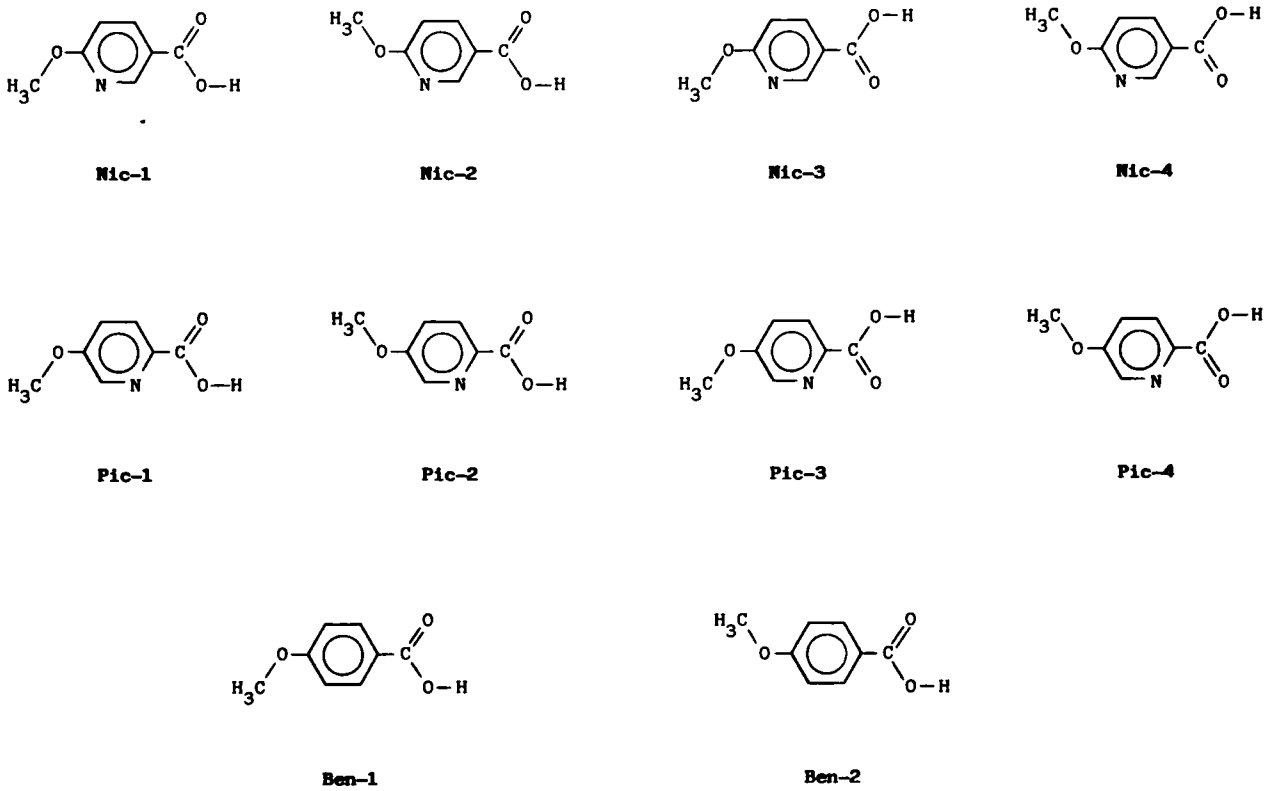


FIGURE 4 Model molecules and their simplified nomenclature used for the MNDO study.

TABLE V

MNDO calculation data for the model molecules studied

Molecule	δ(°)[a]	μ(D)[b]	$\mu_{\parallel}$(D)[b]	$\mu_{\perp}$(D)[b]	α_{μ}(°)[c]	ΔH(kcal/mole)[d]	%[e]
Nic-1	4.5	1.90	1.61	1.00	32.1	−103.37	50.34
Nic-2	70.4	3.03	1.38	2.70	62.9	−99.94	0.15
Nic-3	4.1	2.19	1.64	1.45	41.5	−103.36	49.49
Nic-4	4.8	4.46	1.92	4.02	64.5	−98.63	0.02
Pic-1	84.0	3.18	2.93	1.25	23.0	−98.84	20.83
Pic-2	64.8	4.04	3.28	2.35	35.7	−98.96	25.51
Pic-3	80.7	3.21	2.95	1.26	23.2	−98.75	17.89
Pic-4	87.0	4.31	3.25	2.83	41.0	−99.16	35.77
Ben-1	3.7	3.45	2.54	2.33	42.6	−104.67	48.73
Ben-2	3.7	2.47	2.47	0.07	1.6	−104.70	51.27

[a]Twist angle between the carboxyl group plane and the aromatic ring plane.
[b]Total dipole moment (μ); dipole moment component parallel to the long axis of the molecule ($\mu_{\parallel}$); dipole moment component perpendicular to the long axis ($\mu_{\perp}$).
[c]Angle between the dipole moment and the long axis of the molecule.
[d]Formation heat.
[e]Relative population of each conformer of a molecule.

component and consequently a dipole moment in a direction oblique to the molecular axis favored nematic and smectic C mesomorphism.

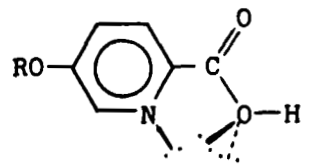
In the present work, if we consider the model molecules with a greater contribution to the two types of mesogenic structure (Nic-1, Nic-3, Ben-1 and Ben-2), the dipole moment has an important parallel component and its direction is therefore oblique to the molecular axis. These compounds display nematic and, for long terminal chains, smectic C mesophases, in accordance with our findings in the above-mentioned study.

CONCLUSIONS

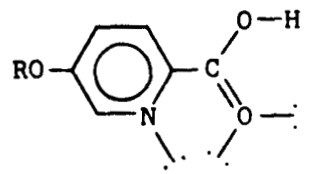
The tendency of a compound to show one type of mesophase or another is determined by the direction of its dipole moment (perpendicular or oblique to the molecular axis). However, in the alkoxy-substituted aromatic acids, another factor must be taken into consideration, *i.e.*, their ability to form inter- and/or intramolecular hydrogen bonds.

From the IR study it can be deduced that, whereas the 4-alkoxybenzoic acids exist predominantly in the O—H bonded dimeric form, the 6-alkoxynicotinic and the 5-alkoxypicolinic acids give rise to O—H or N—H bonded dimers and N—H bonded monomers respectively. This results in a lower mesomorphic stability for the nicotinic acids compared with the benzoic acids, and in the absence of mesomorphism for the picolinic acids.

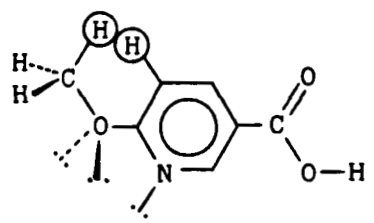
The MNDO results are in accordance with our previous studies, inasmuch as molecules having a dipole moment with an important component parallel to the molecular axis exhibit nematic and smectic C mesomorphism.



(a)



(b)



(c)

FIGURE 5 Scheme of the steric and electronic repulsion in the model molecules studied.

EXPERIMENTAL

Synthesis

The synthesis of the 6-alkoxynicotinic acids has been described previously.[2] Mesmorphic data for the heptyloxy derivative were taken from the literature[5] and the rest were determined by us.

As the butoxy derivatives were selected for the spectroscopic study, only these homologues were prepared in the picolinic and benzoic series and their meso-

morphic data determined. Data corresponding to the other compounds in these series were taken from the literature.[5,6,7]

5-butoxypicolinic acid was synthesized by the *O*-alkylation of 5-hydroxy-2-picoline using 1-bromobutane, potassium hydroxide as base, and 96% ethanol as solvent,[12] followed by oxidation of the methyl group to carboxyl using potassium permanganate.[12] The 4-butoxybenzoic acid was synthesized by *O*-alkylation of 4-hydroxybenzoic acid under the above-mentioned conditions.

Techniques

The compounds were studied by optical microscopy and differential scanning calorimetry. The transition temperatures were determined using a Perkin-Elmer DSC-2 instrument. The scanning rate was 5 K/min and the apparatus was calibrated by measuring the known melting points of benzoic acid (122.4°C), indium (156.6°C), and tin (231.9°C). Optical observations were made using a Meiji polarizing microscope equipped with a Mettler FP-82 heating stage and an FP-80 central processor.

IR spectra were registered with a Perkin-Elmer 283 instrument using nujol suspensions and with a Nicolet MX-10 FT IR instrument using CCl_4 solutions with a concentration of 2.05×10^{-2} M (nicotinic), 1.97×10^{-2} M (picolinic), and 2.04×10^{-2} M (benzoic). ^{1}H NMR spectra were obtained with a Brücker WP-80-CW instrument using $CDCl_3$ solutions and TMS as an internal reference. MNDO calculations were made using a Digital VAX 11/780 computer.

All products were recrystallized several times from an appropriate solvent and their purity checked by the above-mentioned techniques and by thin-layer chromatography.

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