AN INVESTIGATION ON THE USE OF FURAN DERIVATIVES TO OBTAIN THERMOTROPIC COMPOUNDS

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Abstract - A systematic investigation of the mesogenic potential of furan derivatives in terms of geometrical and polar structural characteristics has been carried out. Symmetrical compounds obtained from furancarboxylic acids and hydroquinone or 4,4'-dihydroxybiphenyl, and from 2,5-furandicarboxylic acid and several para-alkoxyphenols were prepared, in order to obtain esters bearing furan rings either in the terminal or in the central position. When the furan ring is the core of the molecule geometric features play a predominant role on the thermal behavior and the mesophase formation is inhibited. When the furan heterocycles are appended to an aromatic core the detrimental role is less manifest, but still present, as shown by comparing the thermal properties of furan derivatives with those of the corresponding fully aromatic compounds.

INTRODUCTION

The role of the presence of furan moieties in affecting the liquid crystal properties of various compounds has been investigated, mostly with structures bearing only one such heterocycle present as end group.[1-7] However, no systematic approach as to the role of geometric and polar structural characteristics has never been attempted in order to rationalize the various experimental observations. More recently, furanic-aromatic polyamides possessing liquid crystal features have been synthesized[8] and their lyotropic properties attributed to the macromolecular aspect of these materials rather than to intrinsic monomer-unit structures.

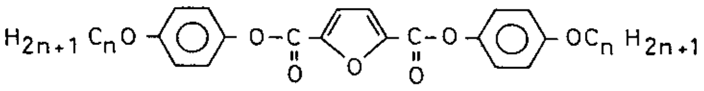
The purpose of the present work is to reach a more general understanding by a systematic structural approach, of how the furan ring(s) can influence the molecular architecture of model compounds containing basic aromatic substructure(s) and consequently their mesogenic potential. In fact, it is already known that the angle formed by 2,5-disubstituted furans is not conducive to favorable molecular alignment in this context,[2] but much less evidence is available concerning the possible positive features related to polar factors which might counterbalance the above geometrical drawback.

The work was carried out using furancarboxylic acids (and diacids) and their corresponding chlorides, which can be easily obtained from the biomass (through 2-furancarbaldehyde or 5-hydroxymethyl-2-furancarbaldehyde), i.e. agricultural wastes and wood or pulping by-products.

RESULTS AND DISCUSSION

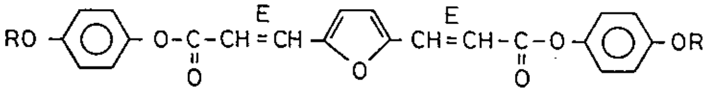
Furan ring in the central position

Series I



1 $n=2$
2 $n=3$
3 $n=4$
4 $n=6$
5 $n=7$

Series II



6 $R=C_2H_5$
7 $R=n\text{-}C_4H_9$
8 $R=n\text{-}C_6H_{13}$

Figure 1. Chemical Structures of Compounds (1-8)

A first series of symmetrical model compounds (series I in Figure 1), obtained from 2,5-furandicarbonyl chloride and different para-substituted phenols, was studied in order to investigate the influence of a furan ring in the central position on their thermal behavior. Different lengths of the flexible tails were introduced because of the major role they can play on the mesophase formation. The thermal stability of all the samples is fairly good and degradation temperatures higher than 300 °C are generally observed, as given in Table 1. The thermal behavior, studied both by differential scanning calorimetry (DSC) and optical microscopy (OM), does not show any liquid-crystalline phase, neither on heating nor on cooling. All the esters melt to an isotropic liquid: the melting temperatures, together with the associated enthalpies, are given in Table 1.

Table 1. Thermodynamic Properties and Decomposition Temperatures for Compounds (1-8)

Compound	Tm/°C	ΔHm/kJmol^{-1}	T_d^a /°C
Series I			
1	165.9	45.4	330
2	168.7	38.8	n.d.
3	165.0	43.5	330
4	137.2	40.3	n.d.
5	136.3	51.7	360
Series II			
6	133.9	35.8	356
7	107.2	35.0	n.d.
8	98.7	34.4	366

a) weight-loss 10%

The corresponding para-substituted phenyl esters of terephthalic acid show a nematic phase or both nematic and smectic phases depending on the length of the terminal alkyl chains.[9,10] The overall results reported above indicate that the presence of a bending due to the 2,5-disubstituted furan moiety with respect to the para bonds in benzene rings, has an inhibiting effect on the formation of a mesophase. This suggests that, as already pointed out before,[2] geometric factors play, with furans, a predominant role in determining the mesophase instability and they are not counterbalanced by polarizability and polarity effects.

The transition temperatures of the fully aromatic compounds, together with those of the corresponding furan derivatives, as a function of chain length of the alkoxy groups, are reported in Figure 2. The introduction of bends associated with the presence of a 2,5-disubstituted furan ring hinders the appearance of the mesophase which cannot be evidenced despite the lowering of the melting temperatures. The higher Tm values for the aromatic compounds arise from the rigidity and linearity of para-phenylene groups which favor the lateral packing of the molecules and enhance the stability of the crystalline structure.

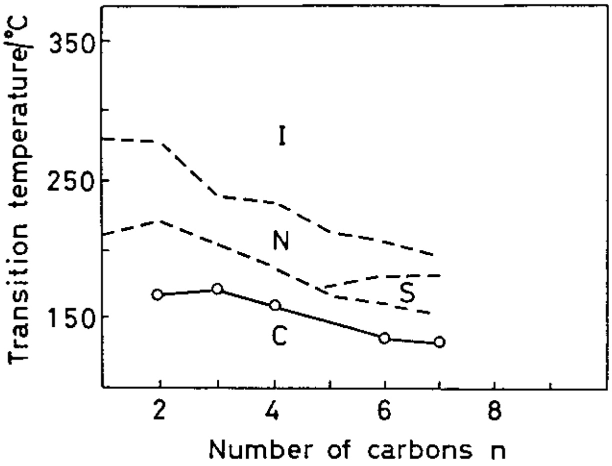


Figure 2. Melting Temperatures of Compounds (1-5) and Phase Behaviour of the Corresponding Fully Aromatic Esters (from ref. 13) as a Function of the Tall Length

Within the general context of a comprehensive investigation on low molecular weight compounds bearing furan rings, a few esters (Series II in Figure 1) of the recently prepared (EE)-2,5-furandiacrylic acid,[11] with some of the para-substituted phenols previously used, were also synthesized.

It was thought that the presence of two double bonds external to the rings might play a favorable role on the geometry of the molecule and impart the structural prerequisites to obtain liquid crystalline phases. However, none of these compounds showed liquid crystalline behavior. Their melting temperatures and enthalpies together with their decomposition threshold are given in Table 1.

Furan rings in the external positions

Quite a few examples of asymmetric liquid crystals, containing one excentric furan ring, are described in the literature.[1,3-7] The inspection of the data shows that, generally, the presence of one furan moiety affects negatively the mesophase stability. However, to our knowledge, no examination of symmetric molecules bearing an aromatic core and two external furan rings has been reported so far. For this reason we have prepared four esters containing one or two aromatic rings (from hydroquinone or 4,4'-dihydroxybiphenyl, respectively) and two furoic or furylacrylic residues in order to assess if a variation in the geometry of the whole molecule can give rise to a stable mesophase. Their structures are given in Figure 3.

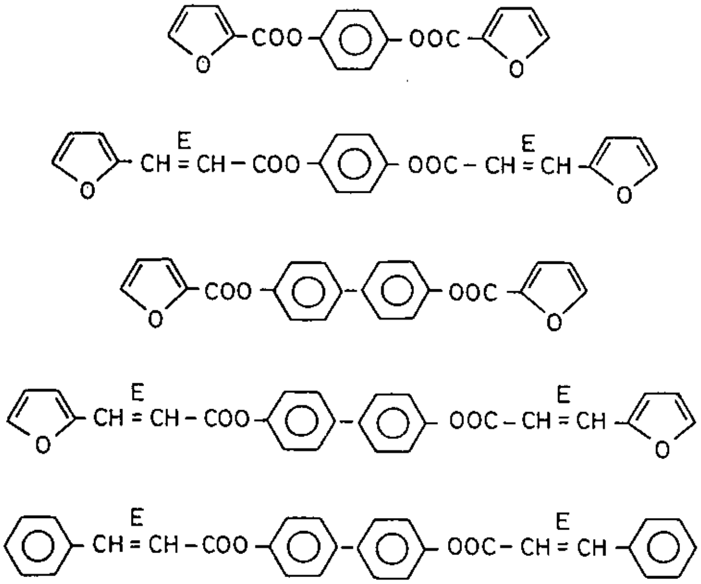


Figure 3. Chemical Structures of Compounds (9–13)

Table 2. Thermodynamic Properties of Compounds (9-13)

Compound	Tm/°C	Ti/°C	ΔHm/kJmol^{-1}	ΔHi/kJmol^{-1}
9	201.7	-	40.4	-
10	174.0	-	38.5	-
11	234.7	-	42.4	-
12[a]	247.7	295.4	41.8	2.4
13[a]	239.9	323.6	36.2	2.4

a) scan rate 40 K/min

The fully aromatic compounds corresponding to compounds (9 and 11) are reported in the literature.[12,13] No indications have been found on cinnamoyl-derivatives related to compounds (10 and 12): model (13) has been, therefore, synthesized to compare its thermal behavior with that shown by its furan-terminated analogue.

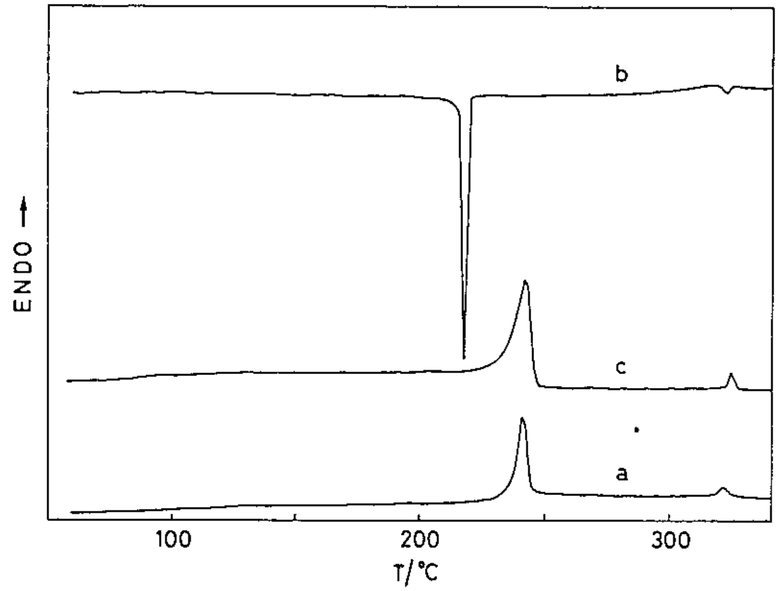


Figure 4. DSC Profiles at 40 K/min of Esters (12) (a: first heating, b: cooling trace, c: second heating)

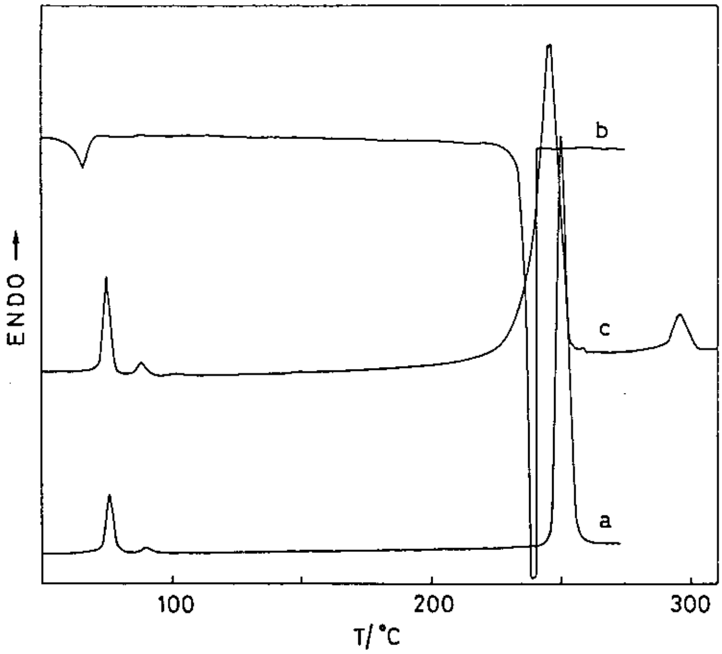


Figure 5. DSC Profiles at 40 K/min of Compound (13) (a: first heating, b: cooling trace, c: second heating)

The thermal stability of these compounds is fairly high (higher than 300°C). From DSC traces and optical observations, it was found that compounds (9-11) melt to an isotropic liquid, whereas compound (12) gives a nematic phase. This is the only ester with two external furan rings showing liquid-crystalline properties in the present context. The transition temperatures of esters (9-13) are summarized in Table 2. Acrylates (12 and 13), whose DSC traces are given in Figures 4 and 5, respectively, have been scanned at 40K/min to reduce the degradation at high temperature; in fact, their clearing points are quite close to the thermal stability threshold. The peak at about 75°C in the DSC profile of 12 is likely to be due to a crystalline polymorphism, although we were unable to detect a crystal I → crystal II transition by optical microscopy. Solid → solid transitions are also shown by other furan derivatives investigated here, such as compounds (9, 8, 6, and 4). By comparing 12 with the corresponding fully aromatic ester (13), it appears that the presence of the furan rings has little influence on the melting temperature, whereas the stability of the nematic phase is greater in 13 than in 12, the nematic-isotropic transition temperature being higher by nearly 27°C. A comparison of the results for 11 and 12 shows that the replacement of a furanacrylic moiety by a furoic one reduces only modestly the melting temperature but strongly depresses the nematic isotropic transition, which indeed vanishes. Thus, although the central 4,4'-dihydroxybiphenyl core of the molecule is a potential mesogenic structure, the bending introduced by the presence of the furan end groups leads to an unfavorable overall geometry, unable to give a mesophase. The further introduction of two double bonds, i.e. with the furanacrylate end groups in compound (12), lengthens the rigid-rod portion of the molecule and makes it compatible with the appearance of liquid crystallinity. On the other hand, the shorter aromatic core of ester (10) does not allow a mesomorphic behavior.

EXPERIMENTAL

Materials

All analytical grade solvents were dried by appropriate drying agents; triethylamine (Et_3N) and pyridine (Py) were refluxed over CaH_2 and distilled under nitrogen. Hydroquinone (Hy) and 4,4'-dihydroxybiphenyl (BP) were crystallized from toluene and ethanol/water (65/35 v/v), respectively. Commercial 2-furoyl chloride, trans-cinnamoyl chloride and p-alkoxyphenols were used as received. 2,5-Furandicarboxylic acid (FDA) and its dichloride (FDC) [14] as well as 3-(2-furyl)acryloyl chloride (FAC) [15] and trans 2,5-furandiacrylic acid (FDAA) [11] were prepared as already described. 2,5-Furandiacryloyl chloride (FDAC) was prepared by refluxing a suspension of FDA (1 g, 6.41 mmol) in toluene (50 ml) with $SOCl_2$ (1 ml, 13.91 mmol) until the mixture became homogeneous. The hot solution was filtered under nitrogen, cooled and kept overnight at -20°C; the resulting yellow crystals were separated and dried under vacuum (yield 95%), mp 156.5 °C. Its spectroscopic features confirmed the expected structure.

General method for preparation of compounds (1-5)

In a typical example FDC (3.87 mmol) dissolved in 8 ml of dry ether was added, dropwise, to a stirred solution of p-alkoxyphenol (9.68 mmol) and Py (1.2 ml, 14.89 mmol) in ether (10 ml). The mixture was allowed to stand at room temperature, under nitrogen atmosphere, for 24 h and then poured into ice water. A proper amount of Na_2CO_3 solution was added to neutralize the resulting mixture and favor the precipitation of the reaction product, which was isolated, washed several times with water, ethanol, ether and recrystallized from a suitable solvent. Their elemental analyses are given in Table 3.

The ^1H-nmr spectra of products (1-5) (solvent CD_2Cl_2; standard Me_4Si) displayed the characteristic singlet resonance for the H3 and H4 protons in the furan rings at 7.4 ppm, the typical two symmetric doublets due to p-substituted benzene protons at 6.9 and 7.1 ppm and the classical features of the aliphatic protons in the end groups. All integrations were as expected. The ^{13}C-nmr spectra of these compounds (CD_2Cl_2; Me_4Si) showed the following peaks: 157 ppm for the C=O; 156 ppm for the C2 and C5 of the furan ring; 147 ppm for the quaternary carbon of the benzene ring attached to the ester function; 144 ppm for the other aromatic quaternary carbon; 122 ppm for the tertiary aromatic carbon atoms on the side of the ester function; 119 ppm for the counterparts on the ether side and 115 ppm for C3 and C4 of the furan ring. The resonances belonging to the aliphatic carbons appeared in the expected range between 15 and 70 ppm, as a function of their distance from the oxygen atom.

The infrared spectra of KBr pellets containing these compounds were characterized by an intense carbonyl band at 1750 cm^{-1}, the typical features of the aliphatic chains just below 3000 cm^{-1}, weaker absorptions at 3115 and 3150 cm^{-1} due to the =CH vibrations from both rings, as well as the typical patterns below 1000 cm^{-1}, arising from p-substituted benzene rings and 2,5-substituted furan rings. The furan ring breathing mode was also clearly present in all spectra, close to 1000 cm^{-1}.

Table 3. Analytical Data for the Phenyl esters (1-8)
(for mp see Table 1)

compound (formula)	yield (%)	solvent	found(%) (required) C	H
1 ($C_{20}H_{15}O_7$)	76	n-hex/AcOEt	66.3 (66.7)	5.0 (5.05)
2 ($C_{21}H_{17}O_7$)	80	n-hex/AcOEt	67.9 (67.9)	5.6 (5.7)
3 ($C_{22}H_{19}O_7$)	70	EtOH/Et_2O	69.0 (69.0)	6.2 (6.2)
4 ($C_{24}H_{23}O_7$)	59	EtOH	70.9 (70.9)	7.2 (7.1)
5 ($C_{25}H_{25}O_7$)	85	EtOH	71.05 (71.6)	7.5 (7.5)
6 ($C_{24}H_{19}O_7$)	61*	n-hex/EtOH	69.4 (69.6)	5.4 (5.4)
7 ($C_{26}H_{23}O_7$)	85*	n-hex	71.1 (71.4)	6.35 (6.35)
8 ($C_{28}H_{27}O_7$)	46*	n-hex	72.8 (72.9)	7.2 (7.1)

*) after recrystallization

General methods for preparation of compounds (6-8)

A solution of FDAC (3.54 mmol) in dry CH_2Cl_2 (15 ml) was added dropwise and under stirring to the *p*-alkoxyphenol (8.89 mmol) dissolved in dry

CH_2Cl_2 (5ml) in the presence of Et_3N (1.48 ml, 10.61 mmol). Reactions were carried out under nitrogen for 24 h at room temperature and the mixture was then poured into a large excess of ether in which the $Et_3NH^+Cl^-$ precipitated. After separation of the salt, the solution was evaporated and the residue crystallized from a suitable solvent. The elemental analyses are reported in Table 3.

The ^1H-nmr spectra (CD_2Cl_2; Me_4Si) evidenced the two pair of symmetric doublets due to acrylic protons, EE *configuration, and to aromatic* protons at 7.6 and 6.6 and at 7.1 and 6.8 ppm, respectively, and the singlet resonance for the protons of the furan rings at 6.7 ppm; aliphatic protons in the tails appeared below 4.0 ppm with the expected patterns. All integrations were as expected. The ^{13}C-nmr spectra displayed the following peaks: 166 ppm for the C=O; 157 and 153 ppm for the quaternary aromatic carbons linked to the ester function and the alkoxy group, respectively; 145 ppm for the quaternary furanic carbons; 132 and 123 ppm for the aromatic tertiary carbons on the side of the ester and ether functions, respectively; 117 ppm for both carbons belonging to the acrylic groups; 115 ppm for C3 and C4 of the furan ring; from 67 ppm downwords for the aliphatic carbons of the end groups.

The ir spectra confirmed the expected structures.

General methods for preparation of compounds (9-13)

The syntheses of these esters were performed following the same procedure as for compounds (1-5), by properly varying the molar ratio between the acid chloride and diphenols (2.5:1). When 4,4'-dihydroxybiphenyl was used, the reaction mixture was never homogeneous, despite the presence of the organic base (Py). The elemental analyses are given in Table 4.

The ^1H-nmr spectra (in CD_2Cl_2; Me_4Si) of models (9) and (11) gave: 7.7 ppm H5 furan ring, 7.4 ppm H3 furan ring, 7.3 ppm aromatic protons on the side of the ester function, 6.6 ppm H4 furan ring, 2.1 ppm other aromatic protons *of model 11. Models 10 and 12: from 7.8 to 7.5 ppm H5 furan* ring and acrylic protons, 7.2 ppm aromatic protons on the side of the ester function, between 6.7 and 6.4 ppm H3 and H4 furan ring and acrylic protons, 2.1 ppm aromatic protons of model (12). All integrations corresponded to the expected structures. The ^{13}C-nmr spectra in CD_2Cl_2 or DMSO-d_6 of esters (9) and (11) showed the following peaks: 157 ppm C=O, from 150 to 147 ppm quaternary carbons of the furan rings and of the benzene rings linked to the ester groups, 144 ppm C5 of furan rings, 139 ppm benzene ring quaternary carbons (model 11), 129 ppm and 123 ppm benzene ring tertiary carbons on the side of the ester function for models (11) and (9), respectively, 122 ppm benzene rings remaining carbon of ester (11), 120 and 113 ppm C3 and C4 of furan rings. Models (10) and (12): 165 ppm C=O, from 151 to 147 ppm quaternary carbons of the furan rings and of the benzene rings linked to the ester groups, 146 ppm C5 furan rings, 138

ppm benzene ring quaternary carbons of model (12), 133 ppm C3 of furan rings, 128 and 123 ppm benzene ring tertiary carbons on the side of the ester function for models (12) and (10), respectively, 122 ppm benzene rings remaining carbon of model (12), 116 ppm C4 of furan rings, 115 and 113 ppm carbon atoms of the acrylic groups.
Ir spectra were in tune with the expected structures.

Table 4. Analytical Data for the Esters (9-13)
(for mp see Table 2)

compound (formula)	yield (%)	solvent	found(%) (required) C	H
9 ($C_{16}H_{10}O_6$)	86	EtOH	64.5 (64.4)	3.35 (3.4)
10 ($C_{20}H_{14}O_6$)	81	EtOH	68.6 (68.6)	4.0 (4.0)
11 ($C_{22}H_{14}O_6$)	92	EtOH/$CHCl_3$	70.6 (70.6)	3.7 (3.7)
12 ($C_{26}H_{18}O_6$)	79	EtOH/AcOEt	73.1 (73.2)	4.2 (4.2)
13 ($C_{30}H_{22}O_4$)	95	n-hex/AcOEt	- -	- -

Techniques

Thin-layer chromatography was used to confirm the purity of each reaction product. Structural investigations were performed by FTir, on a Bruker IFS 48 and by nmr, on a Bruker AM 300. Optical observations were carried out with a Polyvar Pol Reichert optical microscope (OM), equipped with a Mettler FP 82 hot stage (control unit FP 80) or a Linkam THMS 600/TMS 91 system.
Transition temperatures and enthalpies were derived by DSC thermograms recorded with a Mettler TA 3000 system (measuring cell DSC 30) with sample weights from 5 to 10 mg. Heating and cooling rates of 10 or 20 K/min were generally used. Thermal profiles were recorded on an Epson mod. PC A X 2 disk memory device and the standard data analysis programs were used

to evaluate enthalpies and transition temperatures. The thermal stability and decomposition of all the samples were tested by using a Perkin-Elmer TGS 2 analyzer with a heating rate of 20K/min.

CONCLUDING REMARKS

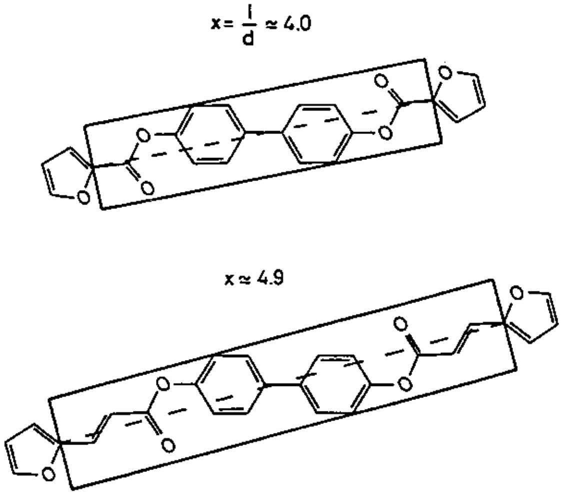


Figure 6. Molecular Structures and Axial Ratios of Compounds (11 and 12)

Three basic structures must be considered:

(i) The 2,5-furandicarboxylic moiety is the core of the molecule which is attached to differently para-substituted benzene rings. The core angle is here about 133°, as calculated on the basis of bond lengths and angles.[16] This geometric feature turns out to be utterly detrimental to the mesogenic potential, no matter what is appended at the outer ends of the molecules.[17] Thus, polarity and polarization play here too modest a role to counterbalance that nagative influence.

(ii) The (EE)-2,5-furandiacrylic moiety is now the core and again various para-substituted aromatic structures are attached at both its ends. Of course, the core angle is here practically the same as in (i) and the major difference comes from the additional external unsaturations. However, the resulting extension of the degree of conjugation does not bring about a sufficient increase in the polar character of these structures so as to induce the appearance of a thermotropic behavior.

(i) + (ii) It seems clear that such a low value of the core angle is the overwhelming factor in inhibiting mesophase formation, as indeed suggested recently in the context of similar structures, but with the thiophene ring.[10]

(iii) The overall structure is now reversed and the core is made up of a para-substituted aromatic system, whereas 2-substituted furan rings appear as end groups. Here, the cores already possess a mesogenic potential which can be revealed by attaching, eg, aromatic moieties to them.[13] When the furan heterocycles are instead appended, a liquid crystal phase is only exhibited by structure (12), ie that displaying the longest linear core and the furanacrylic end groups. In all other instances tested one witnesses once again the detrimental role of the furan ring in that no mesogenic properties are observed. Structures (11 and 12) are shown in Figure 6, together with their respective approximate axial ratios. The comparison of these values tends to explain the difference in the thermal behavior of the respective compounds.

The various novel structures synthesized in this investigation constitute a potential family of monomers for the synthesis of liquid crystalline and/or photocrosslinkable polyesters.

REFERENCES

1. J. A. Nash and G. W. Gray, Mol. Cryst. Liq. Cryst., 1974, 25, 299.
2. M. J. S. Dewar and R. M. Riddle, J. Am. Chem. Soc., 1975, 97, 6658.
3. R. A. Vora and R. Gupta, Mol. Cryst. Liq. Cryst., 1983, 91, 45.
4. S. Miyake, S. Kusabayashi, and S. Takenaka, Bull. Chem. Soc. Jpn., 1984, 57, 2404.
5. R. A. Vora, R. Gupta, and N. C. Patel, Indian J. Chem., Sect. B, 1985, 24, 325.
6. H. Satonaka and T. Sawada, Jpn. Kokai Tokkyo Koho JP 63 60,981 [88 66,981] (Chem. Abstr., 1988, 109, 139802a).
7. A. Fuchs and J. J. H. Douwstra, "Biomass for Energy and Industry", ed. by G. Grassi, G. Gosse, and G. dos Santos, Elsevier Applied Science, London, 1990, Vol.1, p. 494.
8. A. Mitiakoudis and A. Gandini, Macromolecules, 1991, 24, 830.
9. M. J. S. Dewar and R. S. Goldberg, J. Org. Chem., 1970, 35, 2711.
10. R. Cai and E. T. Samulski, Liquid Crystals, 1991, 9, 617.
11. A. Viallet and A. Gandini, J. of Photochemistry and Photobiology, A: Chemistry, 1990, 54, 129.
12. J. P. Schroeder and D. W. Bristol, J. Org. Chem., 1973, 38, 3160.
13. L. A. Karamysheva, E. I. Kovshev, and V. V. Titov, Zh. Org. Khim., 1976, 12, 1508.
14. A. Mitiakoudis, A. Gandini, and H. Cheradame, Polym. Commun., 1985, 26, 246.
15. J. Feder and J. Schuck, Biochemistry, 1970, 9, 2785.
16. L. E. Sutton (editor), "Tables of Interatomic Distances and Configuration in Molecules and Ions" (The Chemical Society) 1958 and 1965, Supplement.
17. D. Macciò, Ph. D. Thesis, University of Genova, Italy, 1988.

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