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MESOMORPHIC BEHAVIOUR OF FORTY BENZYLIDENE-ANILINE-*p,p'*-DIALKOXY DERIVATIVES

DOMENICO GRASSO, CONCETTA GANDOLFO and SALVATORE FASONE

Istituto Dipartimentale di Chimica e Chimica Industriale, Università di Catania, 95125-Catania (Italy)

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ABSTRACT

The transition temperatures of forty mesomorphic homologous benzylidene-aniline-*p,p'*-dialkoxy derivatives are reported.

The transition diagrams show different paths for heating and cooling for most of the compounds. Moreover, some compounds with higher length–breadth ratios, show very complicated thermal cycles with some monotropic phases. In any case, the clearing temperatures (T_c) alternate within every series.

The experimental data are discussed briefly and some general considerations on the structure and mesomorphic behaviour are suggested.

INTRODUCTION

A large number of papers have been published concerning the thermal parameters of mesomorphic dialkyl or alkoxy-alkyl-benzylidene-aniline derivatives [1–4], but no systematic work has been reported concerning dialkoxy-benzylidene derivatives. Therefore, we have begun a systematic study regarding the thermal behaviour of these compounds [5].

The present paper reports data on five series of compounds having the general formula $R{-}O{-}C_6H_4{-}CH{=}N{-}C_6H_4{-}O{-}R'$. The transition temperatures were obtained by means of thermal microscopy and, where indicated, by DSC measurements.

EXPERIMENTAL

All products were synthesized by standard methods from equivalent quantities of amine and aldehyde.

The crude products were purified by several crystallizations from anhydrous ethanol.

Thermal microscopy (TM)

The transition temperatures were observed using a Galileo polarizing microscope with a 20 × 0.22 objective and a Mettler FP 52 microfurnace for sample temperature control. Samples were mounted on a glass slide and covered with a glass cover slip. Special care was taken to ensure clear observation.

Differential scanning calorimetry (DSC)

A Perkin-Elmer DSC model 1B, previously calibrated in terms of temperature and energy using indium as standard, was used for the measurements. Four DSC scans were carried out on each sample; the measurements were recorded at a scan rate of 2°C min^{-1}.

RESULTS AND DISCUSSION

A map of the forty compounds is reported in Table 1, where $-O-C_nH_{2n+1}$ and $-O-C_{n'}H_{2n'+1}$ denote the alkoxy chains on the side of the benzylidene and aniline fragments, respectively. Figure 1 gives all the clarification temperatures, T_c (upper points), and the solid–nematic or the smectic–nematic temperatures (lower points). The nematic transitions are not shown in Fig. 1. Table 2 shows the transition temperatures for all compounds. On the whole, the experimental data suggest some general condiderations.

(i) The clarification temperatures show the characteristic even–odd effect for all the homologous series, with increasing n or n'. Whenever possible, a comparison between the present data with those referring to the alkoxy-ben-

TABLE 1

$H_{2n+1}C_n-O-C_6H_4-CH{=}N-C_6H_4-O-C_{n'}H_{2n'+1}$

n	n'					Series
	2′	3′	4′	5′	6′	
1	1–2′	1–3′	1–4′	1–5′	1–6′	a′
2	2–2′	2–3′	2–4′	2–5′	2–6′	b′
3	3–2′	3–3′	3–4′	3–5′	3–6′	c′
4	4–2′	4–3′	4–4′	4–5′	4–6′	d′
5	5–2′	5–3′	5–4′	5–5′	5–6′	e′
6	6–2′	6–3′	6–4′	6–5′	6–6′	f′
7	7–2′	7–3′	7–4′	7–5′	7–6′	g′
8	8–2′	8–3′	8–4′	8–5′	8–6′	h′
	a	b	c	d	e	Series

TABLE 2

Mesomorphic transition temperatures

Compound	Transition temperatures (°C)	
	Heating	Cooling [a]
1–2′	K 128.7 I	I 121.0 (N) → K
2–2′	K 148.5 I	I 144.0 (N) → K
3–2′	K 126.0 I	I 124.0 (N) → K
4–2′	K 105.2 N 130.1 I	I 124.0 (N) → K
5–2′	K_1 83.5 $K_2$101.5 N 120.1 I	I 124.0 (N) → K
6–2′	K_1 97.1 N 122.7 I	I 122.5 N 88.9 (K_2) → K_1
7–2′	K 101.6 N 120.2 I	I 122.5 N 88.9 (K_2) → K_1
8–2′	K 98.5 N 119.1 I	I 122.5 N 88.9 (K_2) → K_1
1–3′	K 119.0 I	I 96.0 (N) → K
2–3′	$K_1$126.0 $K_2$127.4 I	I 125.2 (N) 114.0 K_2 → K_1
3–3′	K_1 82.0 $K_2$135.0 I	I 125.2 (N) 114.0 K_2 → K_1
4–3′	K_1 79.0 $K_2$120.5 I	I 114.5 (N) 108.0 K_2 → K_1
5–3′	K 104.4 N 106.2 I	I 114.5 (N) 108.0 K_2 → K_1
6–3′	K 99.0 N 110.5 I	I 114.5 (N) 108.0 K_2 → K_1
7–3′	K 102.0 N 107.2 I	I 114.5 (N) 108.0 K_2 → K_1
8–3′	K 99.6 N 109.0 1	I 114.5 (N) 108.0 K_2 → K_1
1–4′	K 114.5 I	I 108.2 (N) → K
2–4′	K 111.8 N 132.8 I	I 108.2 (N) → K
3–4′	K 120.6 I	I 114.9 (N) → K
4–4′	K 125.5 I	I 122.5 (N) → K
5–4′	K 115.6 I	I 114.5 (N) → K
6–4′	K 101.2 N 117.7 I	I 114.5 (N) → K
7–4′	K 99.8 $S_1$101.6 N 113.9 I	I 113.9 N 95.8 (S_3) 94.4 (S_2) → K
8–4′	K 108.6 N 114.8 I	I 114.8 N 99.4 (S) → K
1–5′	K 68.8 I	I 59.4 (N) → K
2–5′	K 94.3 N 121.0 I	I 59.4 (N) → K
3–5′	K 105.8 N 107.2.I	I 59.4 (N) → K
4–5′	K 115.7 I	I 114.7 (N) → K
5–5′	K 113.2 I	I 108.2 (N) → K
6–5′	K 103.6 N 112.5 I	I 108.2 (N) → K
7–5′	K_1 90.8 K_2 93.8 S 98.5 N 109.6 I	I 108.2 (N) → K
8–5′	K 89.2 $S_1$101.8 N 110.8 I	I 110.8 N 101.8 $S_1$88.0 (S_2) 82.0 (S_3) → K
1–6′	K 105.0 I	I 103.1 (N) → K
2–6′	K_1 → $K_2$102.2 N 123.4 I	I 103.1 (N) → K
3–6′	K_1 → $K_2$101.7 N 109.7 I	I 103.1 (N) → K
4–6′	K 103.5 N 117.7 I	I 103.1 (N) → K
5–6′	K 104.7 N 111.7 I	I 103.1 (N) → K
6–6′	K 107.0 N 116.0 I	I 103.1 (N) → K
7–6′	K 101.0 S 102.8 N 113.3 I	I 103.1 (N) → K
8–6′	K 93.7 $S_1$107.3 N 114.8 I	I 114.8 N 107.3 S_1 91.0 (S_2) → K

[a] Symbols in parentheses denote monotropic phases: → represents an undefined temperature transition.

zylidene-alkyl-anilines [6] of corresponding length ($-CH_2-$ equivalent to the $-O-$) shows that the clarification temperatures of the alkoxy derivatives are considerably higher (40–50°C) than in the corresponding alkyl series of compounds.

Similar behaviour has been reported for the homologous alkyl and alkoxy series of the *p*-substituted benzoic acids and for 4′-substituted 4-cyano-biphenyl [4]. Replacement of a terminal alkyl group by an alkoxy group of the same length enhances the thermal stability of the mesophase, as the non-

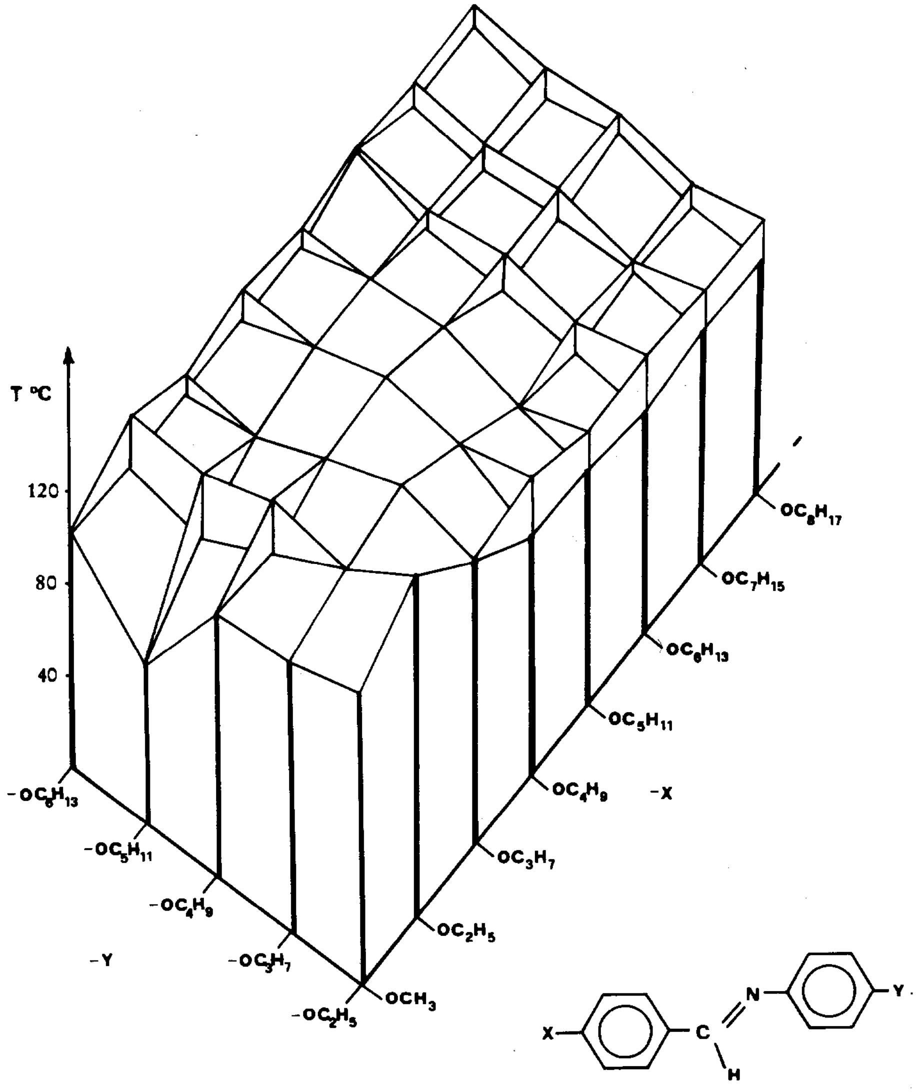

Fig. 1. Clearing temperatures (upper points) and solid–nematic or smectic–nematic transition temperatures (lower points).

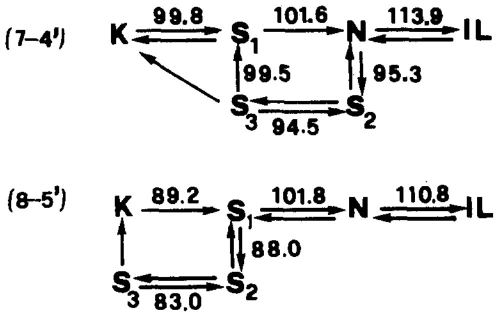

Fig. 2. Transition diagrams for compounds 7–4′ and 8–5′.

bonded electrons of the oxygen are easily coupled to the π electrons of the benzene ring [7–9]. Consequently, the anisotropy of the polarizability increases and leads to higher phase transition temperatures and increased mesophase stability.

(ii) If we consider the data referring to the series of compounds 2–2′, 3–3′, 4–4′, 5–5′, 6–6′ (underlined in Table 1), we can estimate the effect of molecular length in compounds with symmetrical substituents. It is seen that the melting point temperatures decrease progressively on lengthening the molecule, and that (except for compound 6–6′) they do not show a stable nematic phase, unlike compounds of the same length but asymmetrical substituted, as in 7–5′ and 8–4′. Then the symmetry of the substituents is a factor that has a negative effect on the appearance and stability of the nematic phase. This result can be extended to the shorter molecules. In fact, considering the data relative to the series of compounds 6–2′, 5–3′, 4–4′, 3–5′ and 2–6′, it can be seen that while the symmetric compound 4–4′ does not show nematic stable phases, the homologous and asymmetric compounds 5–3′ and 3–5′ show a nematic phase with a small range of stability (1.5°C), and that the homologous compounds 6–2′ and 2–6′, with much more asymmetry, give nematic phases with a range of stability of about 20°C.

(iii) On considering the data concerning the series b′ and a (see Table 1), we can evaluate the effect of lengthening the molecule when it occurs on the aniline or benzylidene side, respectively. It is evident that the data relative to both series are very close. This result, which can be extended to the other series of compounds (i.e. c′–b, d′–c, etc.), suggests a "symmetrical" behaviour of the molecules considered owing to *para* substitution.

(iv) Several of the compounds considered give monotropic phases (see Table 1, data in parentheses). Asymmetrical and longer molecules present transition diagrams which are rather complicated (Fig. 2). In particular, on heating the solid (7–4′), a smectic and a nematic stable phase appear before the clarification point. On cooling the nematic phase, at least two smectic monotropic phases are detectable by thermal microscopy, the second of which, (the smectic phase at lowest temperature), gives alternatively a solid or a stable smectic phase, the latter at 99.5°C.

On heating the solid 8–5′, an analogous behaviour to 7–4′ is obtained. On cooling, two monotropic smectic phases appear after the nematic and smectic stable phases.

(v) The compounds considered show considerable thermal hysteresis between the first thermal cycle and those following.

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