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Gaschromatography on 2,6-naphtalene-bis-(p-alkoxy-benzoate) as liquid crystal phase

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Chimica. — *Gaschromatography on 2,6–naphtalene–bis–(p–alkoxybenzoate) as liquid crystal phase.* Nota di GIUSEPPE CHIAVARI, presentata [(*)] dal Socio G. SEMERANO.

RIASSUNTO. — Questo lavoro descrive l'uso del 2,6–naftalene–bis–(*p*–esilossibenzoato) nell'intervallo di esistenza della sua fase nematica come fase stazionaria in gas–cromatografia. Si ottengono buone separazioni di benzeni di–sostituiti; come previsto, i benzeni para sostituiti risultano ritardati rispetto agli isomeri orto e meta.

INTRODUCTION

Liquid crystals are formed by certain compounds with elongated molecules, which, in determined temperature range, behave mechanically as liquids, while preserving some of the order of crystalline solids.

They represent an intermediate state of matter in which the molecules have lost the typical crystalline form of solid state though they are arranged in parallel alignment or in layers.

The typical orientation of liquid crystal mesophases is favored by a rod-shaped geometry (great ratio length/width) of molecules; this leads to strong intermolecular van der Waals forces that should orient the molecules with their long axes parallel.

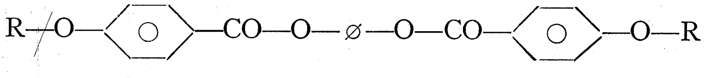
As a consequence of their particular form and distribution, the liquid crystals offer interesting solvent properties with selective solubility for linear molecules, since these are able to fit better into the particular " lattice " of liquid crystal.

The termodynamics of solutions in liquid crystals were investigated by Martire *et al.* [1].

The unusual solvent properties of liquid crystal state have lead to the study of the possibility of their use as stationary phases in gas-liquid chromatography. Significant works have been carried out principally by Dewar [2, 3] and by Kelker [4, 5, 6, 7].

Several compounds forming liquid crystals have in their linear structures 1,4–phenylene units; as stationary phase Dewar [3] used with satisfactory results, a diester whose structure is:

(1)



ø = phenyl– or diphenyl-group
R = *n*–alkyl-group.

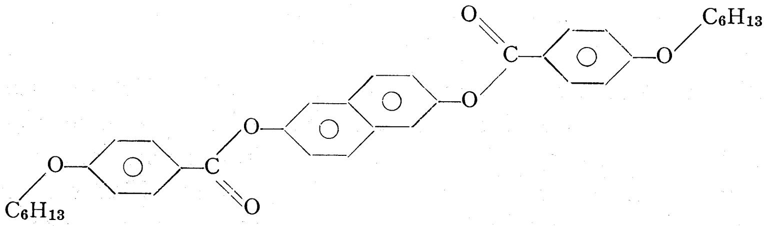
A recent study of Arora *et al.* [8] has examined this class of compounds to define the effects of structural variations on phase transitions.

(*) Nella seduta dell'11 dicembre 1971.

In this paper we report the preparation of a compound with structure similar to (I) but with replacement of central phenylene or diphenylene-group by naphtalene-group to study the effects of a central condensed aromatic group on the transition temperatures and on solvent properties in gas-chromatography.

In a serie of compounds with naphtalene as central group, the 2,6–naphtalene–bis–(para–*n*–hexyloxybenzoate) has been chosen in consideration of the length of its nematic phase.

The figure shows the trans-configuration of the naphtalene derivate, the most probable for the liquid crystal state.



Experimental Section

Apparatus.

Transition temperatures were determined with a Ernst Leitz Wetzlar hot stage melting point apparatus with polarizing microscope. IR spectrum was obtained with an " Infrascan " H 900 spectrometer in nujol.

The chromatograms were obtained with a Fractovap C. Erba gas-chromatograph mod. GT with FID detector, using nitrogen as carrier gas.

Method of synthesis.

The diester were prepared by esterification of the para–(*n*)–alkoxybenzoylchloride with the 2,6–di–hydroxy–naphtalene.

p–(n)–Hexyloxybenzoic acid was prepared from *p*–hydroxybenzoic acid ethylester (Fluka) and (*n*)–hexanbromid (Fluka) according to the method of Gray and Jones [9] and by hydrolysis of the ester with KOH in alcohol.

p–(n)–Hexyloxybenzoic acid chloride was obtained by the usual method of refluxing the acid (1 mol) with thionyl chloride (1,25 mol) in presence of anhydrous pyridine; the thionyl chloride in excess was removed under reduced pressure.

2,6–Di–hydroxy–naphtalene. The commercial product (Koch Light) was recrystallized before use.

2,6–Naphtalene–bis–(para–n–hexyloxy–benzoate) was obtained by the dropwise addition under stirring at room temperature of the 2,6–dihydroxynaphtalene (0,005 mol) dissolved in dry pyridine (25 ml) to the solution of the acid chloride (0,015 mol) in dry pyridine (25 ml). The reaction mixture was allowed to stand overnight at room temperature. The yellowish-white precipitate was filtered, washed with pyridine, water and ethanol and dried at 120° C.

The product was recrystallized twice from C_2H_5OAc. Yield: 20%. Anal. Calcd for $C_{36}H_{40}O_6$: C, 76.03; H, 7.09. Found: C, 76.52; H, 6.83.

The transition temperatures of this ester are:

$$\text{Solid crystal} \xrightarrow{139^\circ} \text{liquid crystal} \xrightarrow{257^\circ} \text{isotropic liquid.}$$

At a cooling rate of 8° C/min. the isotropic-nematic transition supercools max. 1–2° C, whereas the lower temperature more viscous conversion nematic-solid supercools in excess of 30° C.

The infrared spectrum shows the typical absorption bands of aromatic esters with the C=O stretching at 1730 cm^{-1} and the benzene vibrations at 1615, 1585 and 1520 cm^{-1}.

TABLE I.

Retention times (minutes) of Benzene position isomers.

Compound (Boiling point °C)	Liquid Crystal Column at 130° C	Liquid Crystal Column at 180° C	Silicon DC 550 Column at 150° C
m–Chlorotoluene (161°)	4,8	2,5	2,4
p–Chlorotoluene (163°)	5,3	2,7	2,4
m–Cresol–methylether (177°)	6,8	3,1	3,3
p–Cresol–methylether (177°)	7,9	3,4	3,3
o–Dichlorobenzene (179°)	8,5	3,9	3,9
m–Dichlorobenzene (172°)	6,7	3,3	3,4
p–Dichlorobenzene (174°)	7,5	3,5	3,5
o–Dimethoxybenzene (178°)	15,4	5,1	6,3
m–Dimethoxybenzene (215°)	17,7	6,4	7,5
p–Dimethoxybenzene (213°)	23,1	6,9	6,9
m–Methyltoluate (215°)	22,0	6,5	8,4
p–Methyltoluate (217°)	29,4	8,5	8,7
m–Methylacetophenone (221°) (*a*) . . .	23,2	7,6	8,2
p–Methylacetophenone (224°) (*a*) . . .	32,2	9,7	8,9

(*a*) = calculated at 745 mm Hg.

Gas–chromatographic Column.

The packing was prepared with Chromosorb W 80–100 mesh using solutions of the diester in dichloromethane; the packing was 15 % liquid phase by weight. The column was made with 2 *m* × 2 *mm* i.d. annealed stainless tubing.

Gas–chromatographic Procedure.

We used small samples (0,1–0,2 μl of a 5 % solution in carbon disulfide) since solutes lower the nematic-liquid transition temperature. The injection was made 80° above the temperature of the column.

RESULTS AND DISCUSSION

It is interesting to compare the influence of the central aromatic group of naphtalene on transition temperatures with the results obtained from Dewar [3,10] with 1,4–phenylene and 4,4′–diphenylene as central group.

TABLE II.

Central Group	Transition temp, °C
I) 1–4–Phenylene . .	solid $\xrightarrow{121}$ nematic $\xrightarrow{211}$ isotropic $\Delta T = 90^{\circ}$
II) 4,4′–Diphenylene .	solid $\xrightarrow{153}$ smectic $\xrightarrow{181}$ nematic $\xrightarrow{330}$ isotropic $\Delta T = 177^{\circ}$
III) 2,6–Naphtalene . .	solid $\xrightarrow{140}$ nematic $\xrightarrow{257}$ isotropic $\Delta T = 117^{\circ}$

The Table shows that the range of liquid crystal phase of (III) is between (I) and (II).

An investigation is being made in this Laboratory on a series of naphtalene derivates to study the effects of the nature of terminal —R.

The results obtained by using compound (III) as stationary phase are reported in fig. 1 and tabulated in Table II.

We chose disubstituted benzenes whose *m*– and *p*–isomers were known to be difficult to separate. The separations reported are interesting in view of the fact that a 2 *m*. column was used.

The comparison of the results with a " normal " isotropic solvent as silicon oil, reported in Table II, shows the selective adsorption by the mesophase of the linear para isomers eluted after the corresponding ortho and meta-isomers. This effect is evident with all the compounds studied and in same cases, for instance with meta and ortho-dimethoxybenzene, the elution order is reversed in comparison with silicon column.

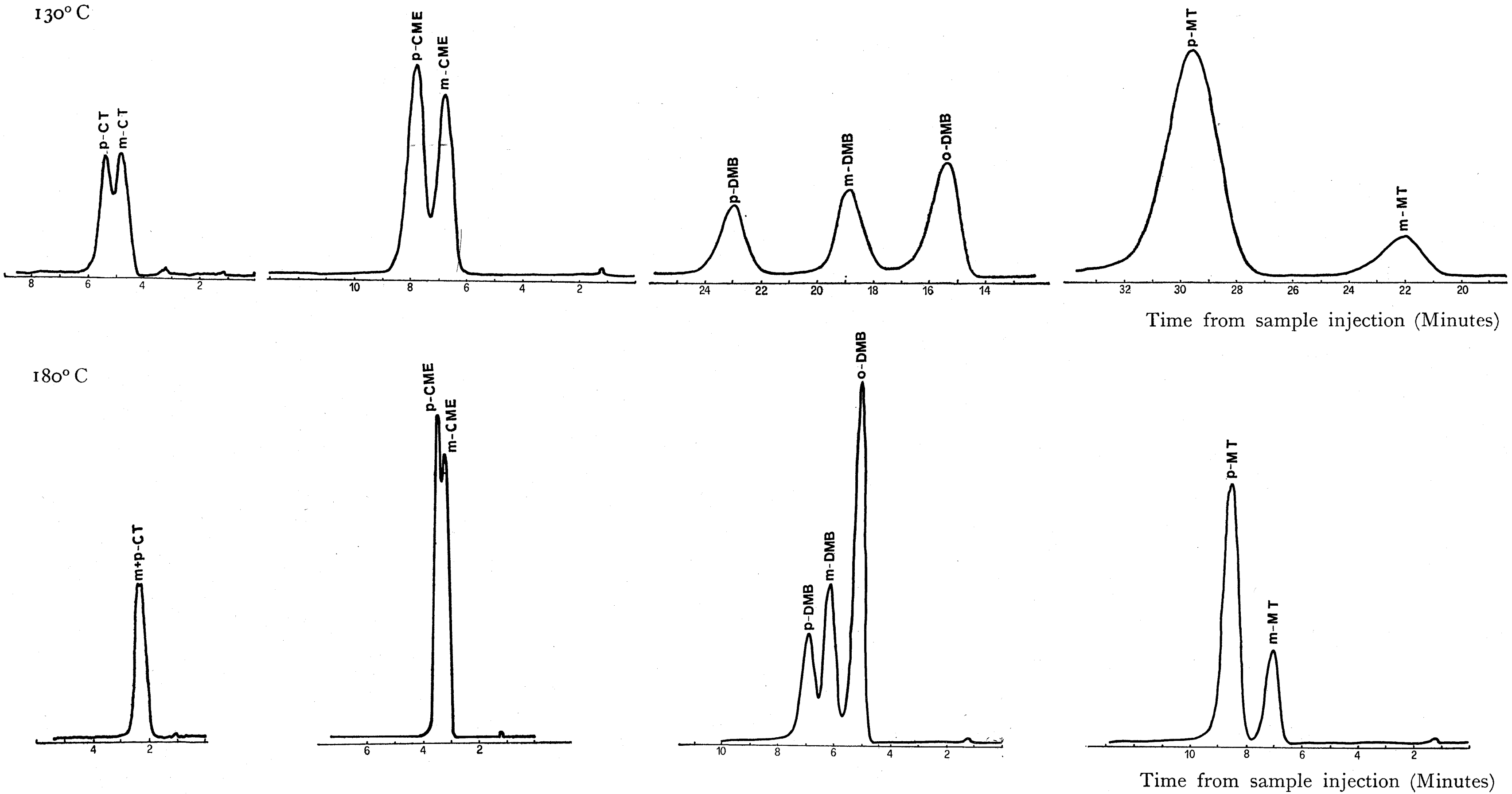


Fig. 1. – Chromatograms on liquid crystal column at 130° and at 180° of mixtures of: *m*– and *p*–Chlorotoluene (CT); *m*– and *p*–Cresolmethylether (CME); *p*– and *m*–Methyltoluate (MT); *o*–, *m*– and *p*–Dimethoxybenzene (DMB). Carrier gas (N_2) flow rate: 12 ml/min.

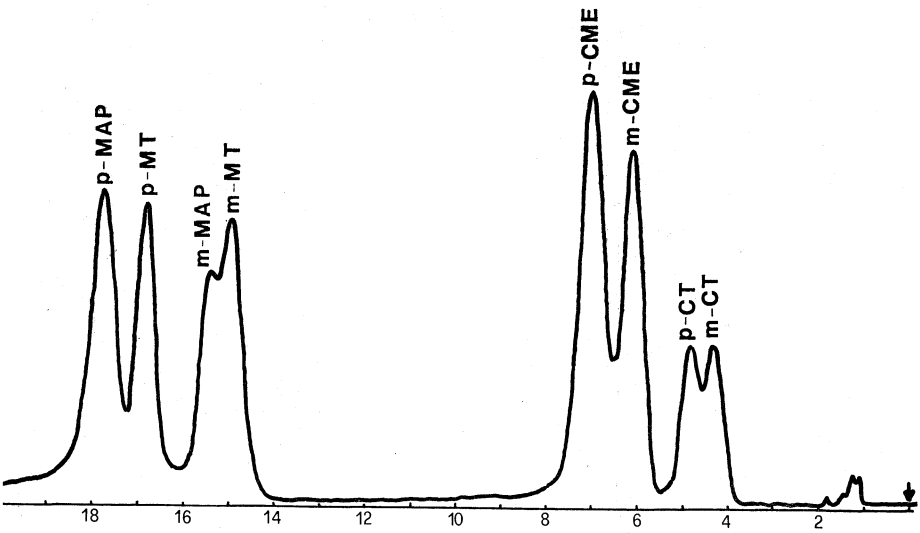


Fig. 2. – Gaschromatogram on liquid crystal column with programmed temperature of mixture: *m*– and *p*–Chlorotoluene (CT), *m*– and *p*–cresolmethylether (CME), *m*– and *p*–methyltoluate, *m*– and *p*–methylacetophenone. Temperature: from 130° to 180° at 5°/min.; Carrier gas (N_2) flow rate: 12 ml/min.

One can observe that at 130°, in supercooled liquid-crystal, the efficiency of substrate is noteworthy and this broadens the temperature range of applicability of the compound.

The gas-chromatogram in fig. 2, obtained with programmed temperature, shows the possibility of application of this analytical procedure.

Elemental analysis was carried out at the Chemical and Physical Laboratory of Montedison (Venice) directed by professor Zilio Grandi; the reported measures constitute Dott. Anna Maria Di Pietra's degree thesis.

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