

**MESOMORPHIC PROPERTIES OF SOME
BIPHENYL BENZOATES**

SEVERAL biphenyl esters exhibit mesomorphic properties^{1,2}. As a part of our programme of study of the structure and properties of liquid crystals, we have synthesized a homologous series of ten biphenyl-4-*p-n*-alkoxybenzoates starting from *p-n*-

alkoxybenzoic acids through their acid chlorides. The transition temperatures and elemental analyses are given in Tables I and II respectively.

TABLE I
Transition temperatures of biphenyl 4-*p-n*-alkoxy benzoates

Compound number	R ^a	Transition temperatures °C		Δ T °C nematic range
1	CH ₃	157	-157.5 (145)	..
2	C ₂ H ₅	161	-162 (157.5)	..
3	C ₃ H ₇	146	-147 (136)	..
4	C ₄ H ₉	158	-159 (142.5)	..
5	C ₅ H ₁₁	144	-145 (113.5)	..
6	C ₆ H ₁₃	132.5	-135.5	3
7	C ₇ H ₁₅	128	-130	2
8	C ₈ H ₁₇	120	-131	11
			S	
9	C ₁₀ H ₂₁	111	-126.5 (106)	15.5
			S	
10	C ₁₂ H ₂₅	110.2	-113.2-124.5	11.3

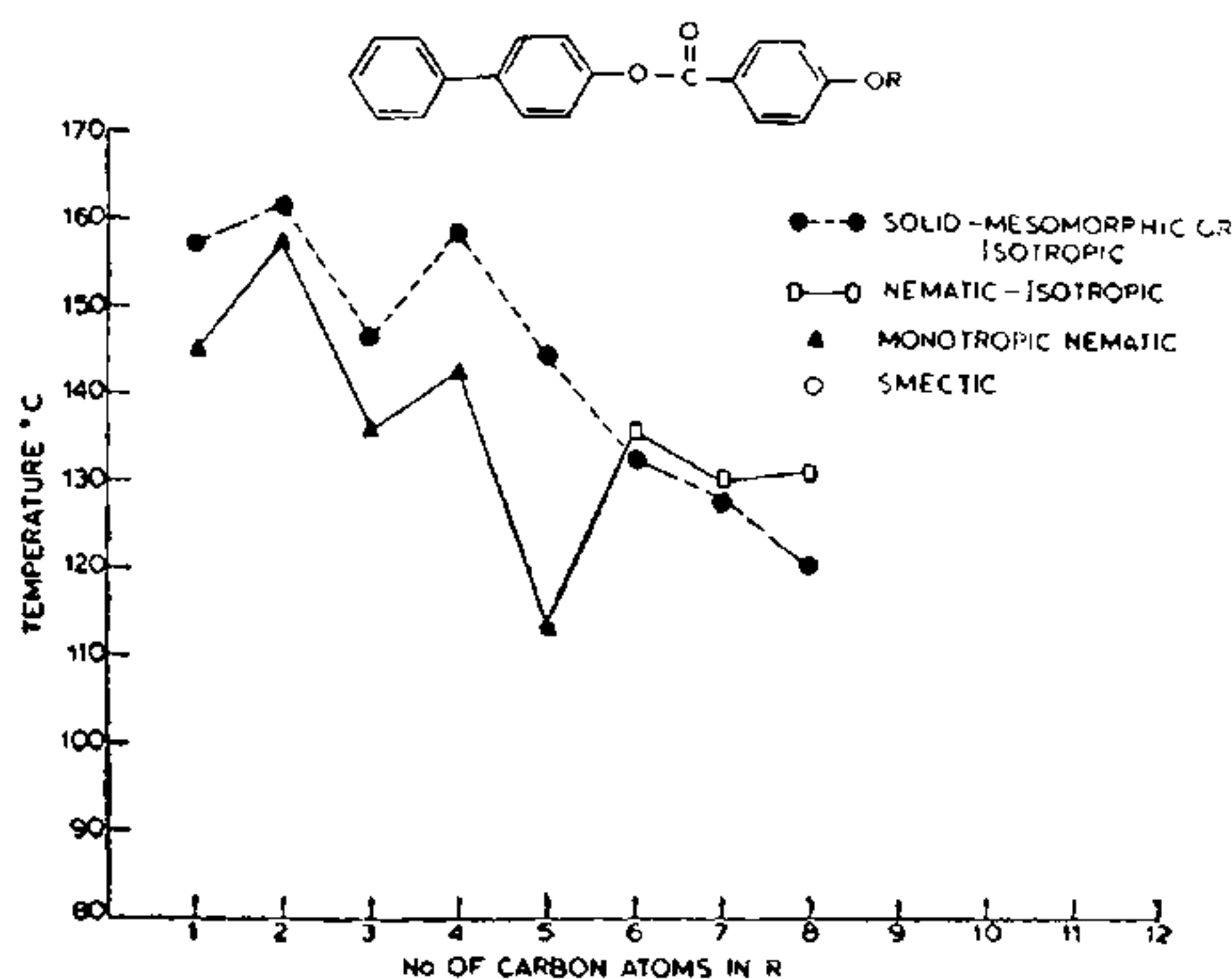
^a All alkyl (R) groups are normal. Temperatures in parentheses indicate monotropic transitions. S indicates the occurrence of a smectic phase.

TABLE II

Compound number	Molecular formula	Calculated %		Found %	
		C	H	C	H
1	C ₂₀ H ₁₆ O ₃	78.94	5.262	78.78	5.50
2	C ₂₁ H ₁₈ O ₃	79.25	5.661	79.52	5.763
3	C ₂₂ H ₂₀ O ₃	79.52	6.024	79.50	6.280
4	C ₂₂ H ₂₃ O ₃	79.77	6.357	79.64	6.45
5	C ₂₄ H ₂₄ O ₃	80.00	6.766	80.00	6.94
6	C ₂₅ H ₂₆ O ₃	80.21	6.952	80.19	7.18
7	C ₂₆ H ₂₈ O ₃	80.42	7.218	80.55	7.57
8	C ₂₇ H ₃₀ O ₃	80.60	7.463	80.22	7.63
9	C ₂₉ H ₃₄ O ₃	81.08	8.108	81.14	7.98
10	C ₃₁ H ₃₈ O ₃	81.21	8.296	81.32	8.28

The first five members of the series exhibit a monotropic nematic mesophase. The hexyl, heptyl, and octyl derivatives are enantiotropic nematic. The smectic mesophase appears at the decyl derivative as a monotropic phase. The plot of the transition temperatures *versus* the number of carbon atoms in the alkyl chain is given in Fig. 1, and shows the usual odd-even effect. The thermal stability of the nematic phase decreases with increasing carbon chain length. It is interesting to note that there is alternation in the crystal to isotropic transition temperatures of the first five members of the series. This alternation is attributed to a similarity in crystal structure, as evidenced from the X-ray study³ of the higher homologues of *p-n*-alkoxybenzoic acids. These esters are thermally

less stable than the corresponding Schiff's bases reported by Gray *et al.*⁴



The transition temperatures were determined in open capillary tubes using a polarizing microscope (Franz Kustner Nacht KG, Dresden, Model HMK 70/3171) in conjunction with a heated stage. Infrared spectra were recorded (nujol mull) on a Perkin-Elmer spectrophotometer, Model 700 and NMR spectra were recorded on a Varian T-60 spectrometer, in CDCl₃ using tetramethylsilane as internal standard. The *p-n*-alkoxybenzoic acids were prepared according to the method of Lauer *et al.*⁵. A typical procedure for the preparation of the ester is given below.

Biphenyl-4-*p-n*-butoxy benzoate.—*p-n*-Butoxybenzoic acid (3.88 g) was refluxed for 3 hours with thionyl chloride (12 ml) using a drop of pyridine. Excess of thionyl chloride was removed under reduced pressure. 4-Hydroxy biphenyl (3.4 g) in dry pyridine (60 ml) was added in one lot to the crude acid chloride, the mixture stirred for 3 hours at room temperature and left overnight. The reaction mixture was poured onto a stirred mixture of concentrated hydrochloric acid and crushed ice, when the ester precipitated out. It was filtered, washed with 10% sodium hydroxide solution, water and dried. Yield, 6.55 g.

The crude ester was chromatographed on neutral alumina (NCl, Poona, Brockmann activity 1) and was eluted with benzene. Removal of the solvent from the eluate afforded a white material, which was crystallized from benzene-light petroleum, m.p. 158–159° C.

ν_{\max} 1720, 1605, 1580, 1510, 1170, 980 and 760 cm⁻¹. δ , 1.0 (s, 3 H, -CH₃); 1.2 2.0 (m, 4 H); 4.18 (t, 2 H, -OCH₂); 7.0 (d, J=8 Hz, 2 H); 7.2, 7.6 (m, 9 H); 8.2 (d, J=8 Hz, 2 H).

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1. Gray, G. W., Jones, B. and Marson, F., *J. Chem. Soc.*, 1957, p. 393.
2. Dewar, M. J. S. and Schroeder, J. P., *J. Org. Chem.*, 1965, 30, 2296.
3. Bryan, R. F., *J. Chem. Soc.*, 1960, p. 2517.
4. Gray, G. W., Hartley, J. B., Ibbotson, A. and Jones, B., *Ibid.*, 1955, p. 4359.
5. Lauer, W. M., Sanders, P. A., Leekley, R. M. and Ungnade, H. E., *J. Am. Chem. Soc.*, 1939, 61, 3050.