New Mesogens with Six, Four, or Three Paraffinic Chains

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The six-, four-, and three-chain derivatives (**1**), (**3**), and (**2**) of biphenyl have been prepared; (**1**) and (**2**) display a columnar mesophase and (**3**) a nematic phase.

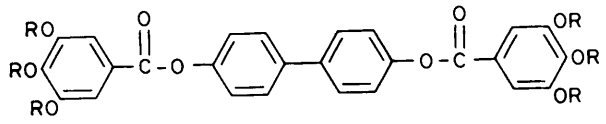
Besides the classical nematic and smectic phases consisting of rod-like molecules, flat,[1] cone-shaped,[2] and macrocyclic[3] molecules have been shown to form thermotropic mesophases (nematic N_D, columnar, or tubular phases). Recently new mesogenic compounds, termed *phasmids*, containing a rigid core ending in two half disk-shaped moieties have been described.[4] Up to now two phasmidic phases have been observed, for example terephthal-bis[4-(3′,4′,5′-tri-n-dodecyloxybenzoyloxy)aniline] which displays a high-temperature columnar mesophase and a low-temperature ribbon phase.†

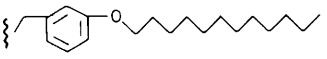
We now report a new phasmidic molecule (**1**) with a shorter rigid core and bulkier ends, having six paraffinic chains as for the other phasmids. Two other derivatives of biphenyl were prepared for comparison, with three [(**2**)] and four [(**3**)] alkane chains. The fact that such molecular structures were still found to be mesogenic is contrary to what is generally accepted concerning the relationships between molecular structure and the properties of thermotropic liquid crystals.

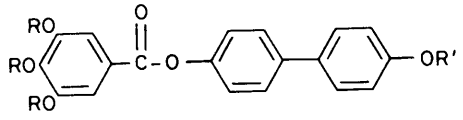
The mesomorphic properties of (**1**), (**2**), and (**3**) were studied by differential scanning calorimetry and polarized light microscopy (Table 1). Preliminary *X*-ray diffraction measurements performed on the mesophases of compounds (**1**) and (**2**) indicate, in both cases, a columnar mesomorphic structure in which the columns are located at the nodes of a hexagonal bidimensional lattice.

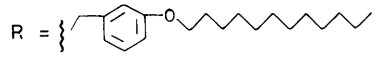
Hexasubstituted dibenzoate (**1**) was obtained by treating (25 °C, 16 h) 4,4′-dihydroxybiphenyl with 2 equiv. of 3,4,5-tri-(*p*-n-dodecyloxybenzyloxy)benzoic acid (**6**) in CH_2Cl_2 in the presence of dicyclohexylcarbodiimide (DCC) and *p*-dimethylaminopyridine (DMAP). It was purified by t.l.c. (silica gel; eluant cyclohexane + 15% EtOAc) and recrystallized from ethanol–diethyl ether (32% yield). Compound (**2**) was prepared by treating (0 °C, 1 h; then 25 °C, 15 h) 4,4′-dihydroxybiphenyl with 0.5 equiv. of the acid chloride of (**6**) in dry pyridine [34% yield from (**6**)]. It was purified by t.l.c. using the same eluant as for (**1**) and recrystallized from methanol–diethyl ether. Compound (**3**) was obtained by

† Some mesogens have been reported with the same five benzene ring architecture but fitted with only two chains in each end (2 + 2 chain rod-like mesogenic compounds termed *biforked* mesogens[5]). They exhibit an interesting polymorphism in which appear nematic, smectic C, ribbon, columnar, and cubic phases.

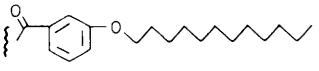


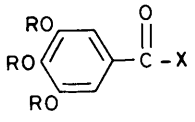
(1) R = 



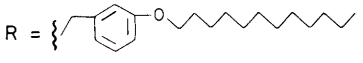


(2) R' = H

(3) R' = 



(4) R = H, X = OMe



(5) X = OMe

(6) X = OH

reaction (25 °C, 12 h) of 4-(*p*-n-dodecyloxybenzoyloxy)-4′-hydroxybiphenyl with 1 equiv. of (**6**) in CH_2Cl_2 in the presence of DCC and DMAP. The diester was purified by t.l.c. using the same eluant as for (**1**) (58% yield) and was recrystallized from diethyl ether. Tribenzylation of methyl gallate (**4**) was performed (80 °C, 8 h) in dry dimethylformamide (DMF) with *p*-n-dodecyloxybenzyl chloride in the presence of 10 equiv. of K_2CO_3;‡ saponification (KOH in 95% ethanol, 1 h reflux) of the crude methyl ester (**5**) afforded acid (**6**)§ in 93% yield from (**4**).¶

Diester (**1**) exhibited a hexagonal columnar phase. This behaviour confirms, as Kok *et al.* have noted,[7] that a benzyloxy group acting as a large and rigid 'anchoring point' can efficiently fill the space surrounding the rigid core and that the presence of the two half 'super-disks' favours columnar mesomorphism.

It is rather surprising that compound (**2**) is mesomorphic with only three paraffinic chains grafted on the *same* end of the molecule. Moreover, the existence of the hexagonal phase despite the presence of a polar group such as a phenolic OH allows us to contemplate the possibility of building up other polar mesogens of this type with an important permanent dielectric dipole moment.‖

The four-chain diester (**3**), consisting of a classical nematogenic rod-like part and a half disk-like part, was prepared with the intention of obtaining thermotropic biaxial nematic properties.[9] This compound actually displays a metastable fluid nematic phase, the optical properties of which are under study.[10]

In conclusion, the results presented here with those of ref. 5 suggest that other mesogenic rod-like molecules such as 3 + 2 chain compounds should exist with the possibility of introducing various polar groups.

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Table 1. Transition temperatures, enthalpies, and lattice constants.

Compound	Transition[a]	Temp./°C	ΔH (kJ mol^{-1})[b]	Lattice constant of the Hex phase (Å)
(**1**)	K → Hex	87[c]		45.7
	Hex → I	90	4.73	
(**2**)	K → Hex	64[c]		53.4
	Hex → I	84	1.42	
(**3**)	K → I	86	95.39	
	N → I	(86)[d]	5.61	

[a] K: crystal, Hex: hexagonal columnar mesophase, I: isotropic liquid, N: nematic phase. [b] Measured on Perkin-Elmer DSC 2. [c] Crystalline polymorphism. [d] Monotropic transition.

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‡ DMF, easier to remove, was substituted for acetophenone used in ref. 6 as the solvent. Ester (**5**) can also be prepared *via* the caesium salt of (**4**) in the same conditions with similar yields (91%). The crude ester was slightly cleaner than that obtained with K_2CO_3 but Cs_2CO_3 is an expensive reagent.

§ This acid, purified by t.l.c. (silica gel; eluant: chloroform + 10% methanol) exhibits mesomorphic properties between 66 °C (m.p.) and 137 °C (appearance of the isotropic liquid with some decomposition).

¶ Mesogenic compounds (**1**), (**2**), (**3**), and (**6**) were characterized by ^{1}H n.m.r., i.r., and elemental analyses.

‖ An example of a columnar phase consisting of polar molecular disks has been recently reported.[8] The advantages offered by such mesophases are possible orientation effects in an electric field.