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Effect of molecular structure on mesomorphism XX. Unsymmetrical dimeric mesogens

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PRELIMINARY COMMUNICATIONS

Effect of molecular structure on mesomorphism

XX†. Unsymmetrical dimeric mesogens

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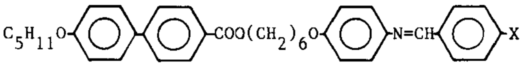
A series of unsymmetrical dimeric mesogens was prepared, members of which were composed of a 4′-pentyloxybiphenyl-4-carboxyl core and a 4′-substituted-benzylidene-4-oxyaniline core joined via an alklyene spacer. The structural variants were cyano, nitro and trifluoromethyl. Comparison of mesophase behaviour of the unsymmetrical dimers with that of corresponding monomeric ‘halves’ and also with that of corresponding symmetrical dimers indicated a tendency for the unsymmetrical dimers to form smectic phases although not as highly ordered as those of some of the monomers corresponding to a relevant core group.

It seemed a natural extension of dimer chemistry (two rigid mesogenic cores connected via a flexible spacer) to prepare unsymmetrical dimers. In addition to their simply being interesting new structures, a number of intriguing issues can only be addressed by examining unsymmetrical dimers. Among these are: dominance of mesophase type by one mesogenic moiety; analogy to 1 : 1 molar binary mixtures of symmetrical twin dimers or ‘monomeric’ halves; and formation of induced or enhanced smectic phases. Relevant to each of these items is the entropic restriction imposed on these unsymmetrical dimers. Covalent attachment of mesogenic cores through a spacer simultaneously biases next neighbour core–core associations both qualitatively and quantitatively. It is also known [1] that in mesogenic dimers, the central methylene spacer is conformationally extended much more than for *n*-alkoxy terminal groups in classic ‘monomeric’ mesogenic species. We have chosen to examine a series of unsymmetrical dimers having the structures:



$X = CN, NO_2, CF_3$

The 4′-pentyloxybiphenyl ester is the constant mesogenic unit with the structural variant *X* being the terminal group at the other end of the molecule.

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† For Part 19 in this series see: SELLENS, R. J., RUNCIMAN, P. J. I., GRIFFIN, A. C., BRYANT, E. S., and HUGHES, W. E., *Molec. Crystals liq. Crystals* (submitted).

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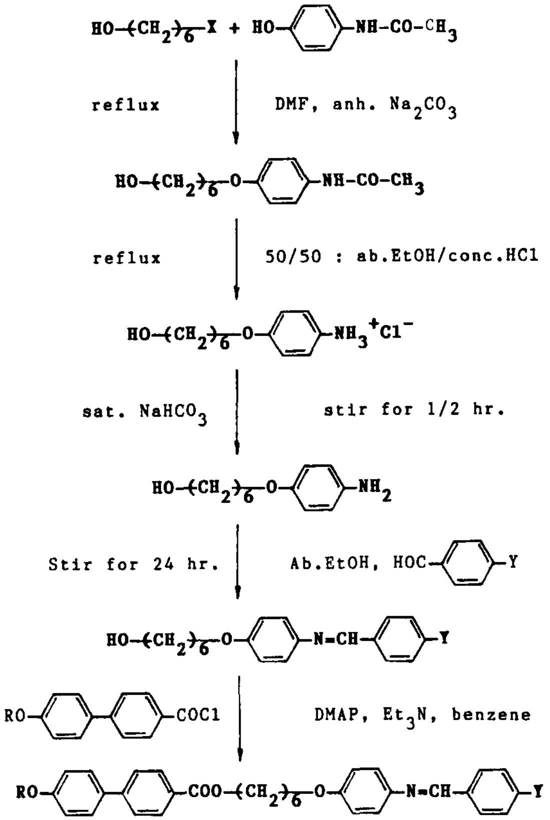
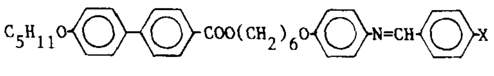


Synthetic scheme for unsymmetrical dimers.

Unsymmetrical dimers were synthesized through the route shown in the figure [2]. These reactions are for the most part straightforward. In each case, however, the most difficult reaction was the final esterification to form the target dimers. Coupling of 4′-alkoxybiphenyl-4-carboxylic acid chloride with the alcohols was ultimately accomplished using benzene as solvent, triethylamine as base and dimethylaminopyridine (DMAP) as supernucleophilic catalyst. Purification of dimers was accomplished by chromatography (either column or thin layer) using silica gel as stationary phase and chloroform as eluant. Structures were determined by F.T. infrared and proton N.M.R. spectroscopy. Elemental analyses also gave results consistent with proposed structures. Differential scanning calorimetry (DuPont 9900) and optical microscopy (Reichert/Mettler FP5/52) were used to examine mesophase properties.

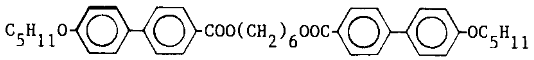
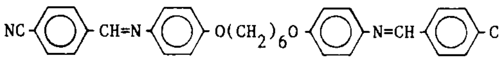
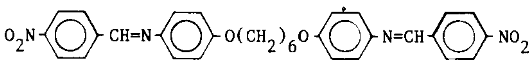
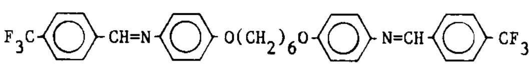
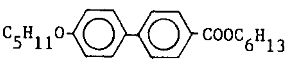
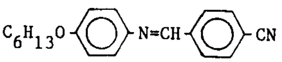
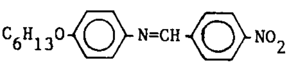
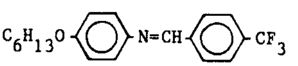
Table 1. Unsymmetrical dimers.



X = CN	K123S_A(118)N(122)I
NO_2	K116S_A132I
CF_3	K130S_X135S_A147I

Table 1 shows transition temperatures and phase types for the three unsymmetrical dimers, each is mesogenic. Although similar in chemical structure except for the small, polar terminal group at one end of the dimer, their mesophase behaviour is quite different. For comparison, transition temperatures for analogous symmetrical dimers and monomers are given in table 2. It can be seen that the unsymmetrical dimers are in general intermediate in solid-mesophase and mesophase-isotropic temperatures between those of the corresponding symmetrical dimers and also those of the corresponding monomers.

Table 2. Symmetrical dimers and monomers.

		$K129S_E139S_A163I$
	[3]	K169.6N246.3I
	[4]	K187.0N217.0I
		K199.4I
	[5]	$K63S_B69S_A88I$
	[6]	K79N107I
	[7]	K94I
	[8]	$K102S_B103I$

Although the constant core (alkoxybiphenyl ester) produces, both in its symmetrical dimer and monomeric counterparts, S_A and S_E phases, the unsymmetrical dimers exhibit N and S_A (CN), S_A (NO_2), and S_A and S_X (CF_3) phases. The identity of the S_X phase is currently undetermined. The effect of covalent attachment of the variable cores (each having a corresponding symmetrical dimer with nematic phases only (CN, NO_2) or no mesophase (CF_3) with the biphenyl ester core having inherent S_A and S_E tendencies, produces an unsymmetrical dimer species with intermediate ordering in the resulting mesophases.

Separately we have examined contact preparations of each analogous monomer binary mixture. Strongly enhanced S_A phases were observed. Further quantitative work with mixed systems is planned to elucidate detailed analogy between unsymmetrical dimers and their 1 : 1 monomeric mixtures. It should be noted in this connection that smectic phases are found for each unsymmetrical dimer.

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