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Low Viscous Compounds of Highly Nematic Character

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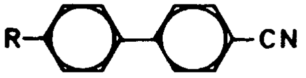
Mixtures of broad nematic temperature ranges that permit acceptably short switching times of electro-optical displays at −40°C can be composed of compounds of relatively low polarity and high transition temperatures from the nematic to the isotropic state (T_{NI}). Structures combining 1,4-phenylene and trans-1,4-cyclohexylene rings are particularly suited for this purpose.

INTRODUCTION

The switching time of electro-optical displays on the basis of liquid crystals — today almost exclusively twisted nematic cells (TNC)[1]–depends directly on the rotational viscosity γ_1, a quantity that was shown to be controlled by free volume.[2] Quite recently, the dependence of γ_1 and shear viscosity η_s on the chemical structure of nematic compounds has been investigated.[3] In accordance with the results obtained with polymers,[4] the glass transition temperature was found to be a reliable corresponding-state parameter for viscosity, giving rise to hopes that γ_1 could be predicted from the chemical structure.[5] Unfortunately, the occurrence of smectic phases totally breaks this relationship with the consequence that distinctly above the transition temperature to a smectic phase γ_1 is enhanced. This paper is intended to show that some classes of compounds of low bulk viscosity and highly nematic character open a way to broad range mixtures that are satisfactorily switchable between −40° and 85°.

Basis compounds

The character of ready-to-use mixtures with respect to their physical parameters is grossly determined by their basis compounds. The temperature-dependent values of γ_1 and η_s of substituted biphenyls (1),[6] phenylpyrimidines (2),[7] phenylcyclohexanes (3),[8] phenyldioxanes (4),[9] and cyclohexane carboxylic esters (5)[10] have been measured.[3] The compounds of type (3) turned out



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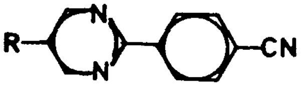

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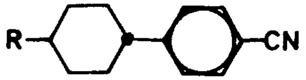

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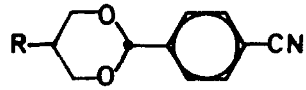

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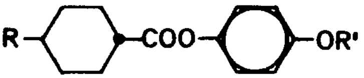


(5)

to be very suitable materials, which is in accordance with measurements of bulk viscosity.[11] Moreover, it is a well-known fact that mixtures on the basis of (3) with a number of mesogenic compounds tend to form smectic phases to a lesser extent than mixtures with different basis compounds.[11]

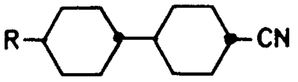
It seemed to be appropriate to lower the bulk viscosity by replacing the cyano group in (3) by less polar groups. On the grounds of an electrodynamic model,[12] it is to be expected that such compounds show a nematic behavior if certain molecular building principles are respected. Table I gives some examples of substituted 4-trans-(4-propylcyclohexyl)benzenes. (7), (8), and (9), and their homologues turned out to be very useful compounds to decrease the viscosity of phenylcylohexane-based phases not causing smectic phases in these mixtures at −40°.[13] The dependence of rotational viscosity on chemical structure has been interpreted with good

TABLE I

1-substituted 4-trans-(4-propylcyclohexyl) benzenes, *mp* = melting point (°C), ν = bulk viscosity extrapolated from Nematic Phase 1132 (E. Merck) at 20° (mm²/s),* = extrapolated values.

	Substituent	mp	T_{NI}	ν
(6)	CN	43	45	20
(7)	OC_2H_5	41	37	7
(8)	F	31	−54*	5
(9)	C_2H_5	−1	−70*	4

results *via* the glass transition temperatures by the use of increments of cohesive energy[15] in the case of compounds of types (1), (2), (3), (5), (7), and (9). According to this, the trans, trans-4′-alkyl-bicyclohexyl-4-carbonitriles (10)[14] should have lower values than the phenylcylohexanes (3). As a matter of fact, the bulk viscosity of a ternary mixture of homologues of (10) turned out to be about 3 times that of a respective mixture of (3)-homologues.[15]



(10)

R = n − alkyl

Even though the γ_1 values of (10) have not been measured so far, it remains doubtful whether the handling of increments of cohesive energies will permit adequately accurate predictions on the viscosity of nematics of quite different chemical structures.

Three-ring compounds

The elongation of the rigid part of the phenylcyclohexane system by another 1,4-phenylen group leads to a number of valuable compounds, exemplified by the derivatives of 4-trans-(4-pentylcyclohexyl)biphenyl (11)[16,17,18] (Table II).

(11)

(13) and its alkyl homologues are very suitable components to raise the T_{NI} of nematic basis mixtures without unacceptably increasing viscosity.[19] It should be noted that in contrast to this, 1,4-bis-(4-alkylphenyl)-trans-cyclohexanes[20] do not exhibit any nematic phases. Surprising is the fact that

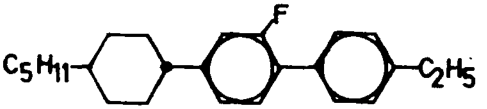
TABLE II

Transition temperatures (°C) and extrapolated bulk viscosities at 20° (mm²/s) of some 4′-substituted 4-trans-(4-pentylcyclohexyl) biphenyls (11), C = crystalline, S = smectic, N = nematic, I = isotropic.

	X	C	S	N	I	ν
(12)	CN	96		222		90
(13)	C_2H_5	34	146	164		20
(14)	OCH_3	80		165		70
(15)	F	100		153		24

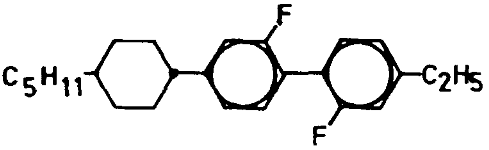
(13) is very soluble in compounds of type (3) and in (7) and (9) and their homologues[19] whereas solubility in cyanobiphenyls (1) is relatively poor.

Interestingly, the aromatic substitution of (13) and its homologues by fluorine results in lower T_{NI} values and in extended temperature intervals of the existence of the nematic phase.[18] This is in accordance with findings obtained by G. W. Gray[21] with fluorinated aromatic esters.



(16)

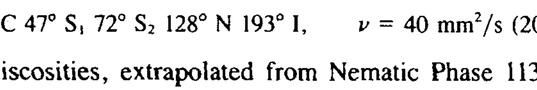
C 26° N 107° I, ν = 27 mm²/s (20°)



(17)

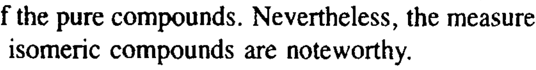
C_1 − 2° C_2 29° N 80° I, ν = 42 mm²/s (20°)

The general formula (5) includes a number of esters of 4-trans-cyclohexane carboxylic acids that found good acceptance, *e.g.* in multiplexable mixtures.[22] A number of phenyl esters of 4-alkylbenzoic acids are also known to be useful as mixing components.[23] The elongation of these two types of molecules by 1,4-trans-cyclohexylene groups resulted in compounds with high T_{NI} values,[24] as it is demonstrated by examples (18) and (19).



(18)

C 67° S (55°) N 154° I, ν = 119 mm²/s (20°)



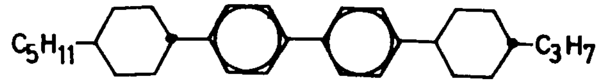
(19)

C 47° S_1 72° S_2 128° N 193° I, ν = 40 mm²/s (20°)

The bulk viscosities, extrapolated from Nematic Phase 1132, which are used throughout this paper have, of course, to be looked at critically because the viscosity of a mixture generally is not a simple function of the viscosities of the pure compounds. Nevertheless, the measured differences between the isomeric compounds are noteworthy.

Four-ring compounds

Among the classes of compounds that arise in combining up to four directly linked 1,4-phenylene or 1,4-trans-cyclohexylene groups[25] the technologically important 4,4′-bis(trans-4-alkylcyclohexyl)-biphenyls[26] should be mentioned, exemplified by (20).



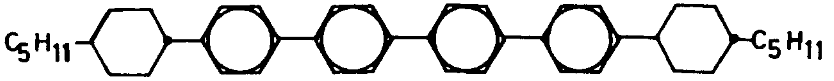
(20)

C 61° S$_1$ 232° S$_2$ 251° N 311° I, ν = 42 mm^2/s (20°)

The high T_{NI} values, and the still relatively low viscosities make these compounds very valuable additives; also, the solubility of (20) and its alkyl homologues in phenylcyclohexane-based mixtures is very good as a consequence of the rule of thumb *similia similibus solvuntur.*

LIMITATIONS TO MOLECULAR DIMENSIONS

As shown by the example of 4,4‴-bis(4-trans-pentylcyclohexyl)-*p*-quarterphenyl (21)[25] which is only slightly soluble in basis mixtures from classes (1) to (5), i.e. max. 0.5 per cent at room temperature, the accumulation of too many aromatic rings puts an end to the applicability of the molecular building principle outlined in compounds (9), (13) and (20).



On the side of compounds with low molecular weight there are obvious limitations set by the high volatility of such components. In this context it should be mentioned that the tendency of *n*-alkyl compounds to adopt a nematic order depends on the matrix it is dissolved in. This quasi-nematic feature is particularly distinct in compounds of type (10) as the virtual clearing points for lauronitrile extrapolated from 5 and 10% solutions in different matrices indicate (Table III).

SOME VIEWPOINTS OF BROAD-RANGE MIXTURES

It is the aim of the synthetic work touched in this paper to supply compounds for nematic phases which permit reliable functioning of non-temperature conditioned displays at all temperatures likely to occur under practical conditions. It is no problem today to obtain mixtures of sufficiently high T_{NI} values. Unfortunately, the components required to increase the T_{NI} also raise the viscosity. To achieve acceptable values at low temperatures, it is also necessary to select components with relatively small values for the activation energy in the exponential function describing the temperature-dependence of nematic phases.[3] Some commercially available

TABLE III

Virtual clearing points (°C) of $CH_3(CH_2)_{10}CN$ in different Matrices

Matrix	clp
N 5[27]	−250
E 7[28]	−170
(10), R = $n-C_3H_7$	−140
(10), R = $n-C_{12}H_{25}$	−60

phases follow this concept.[13] The structures of the basis compounds (3), (4), (5), (8), and (10) have only small values for the optical anisotropy in the range of 0.09 to 0.12, which is particularly useful in TNCs of little angle-dependence of contrast.[29] In transmissive TNCs for complete guidance of the polarized light, the product of Δn and cell thickness must be above the Mauguin limit. Low viscous phases that are still nematic below −40° and have optical anisotropies above 0.16 are being developed,[30] which have integrated higher amounts of compounds with conjugated ring systems.

CONCLUSION

Compounds derived from the phenylcyclohexane system are well suited for nematic broad-range mixtures because of their low viscosity and highly nematic character, permitting broad-range mixtures that avoid smectic phases down to very low temperatures which cannot be achieved with other systems so far.

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