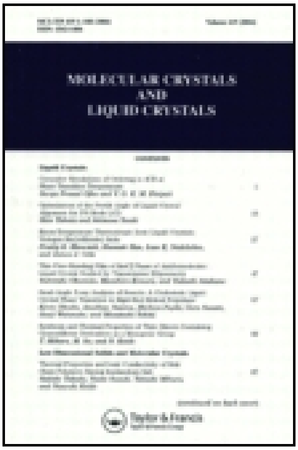


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Flow Aligned Viscosities of Cyanobiphenyls

J. Constant [a] & E. P. Raynese [a]
[a] Royal Signals and Radar Establishment, Malvern, Worcestershire, WR14 3PS, UK
Version of record first published: 21 Mar 2007.

To cite this article: J. Constant & E. P. Raynese (1980): Flow Aligned Viscosities of Cyanobiphenyls, Molecular Crystals and Liquid Crystals, 62:1-2, 115-123

To link to this article: http://dx.doi.org/10.1080/15421408008084014

Mol. Cryst. Liq. Cryst., 1980, Vol. 62, pp. 115–124
0026-8941/80/6202-0115$06.50/0

Flow Aligned Viscosities of Cyanobiphenyls

J. CONSTANT and E. P. RAYNES
Royal Signals and Radar Establishment, Malvern, Worcestershire WR14 3PS, UK.

(Received April 25, 1980)

The flow aligned viscosities of a series of 4-*n*-alkyl- and 4-*n*-alkoxy-4′-cyanobiphenyl liquid crystals have been measured over a range of temperatures. Mixtures of these cyanobiphenyls, some also including a 4-*n*-alkyl-4″-cyano-*p*-terphenyl, have been measured and design rules formulated for producing low viscosity mixtures for use in display devices.

INTRODUCTION

The optical response times (T_{on} and T_{off}) of twisted nematic display devices to a pulsed voltage are an important aspect of performance and indeed often restrict the lower operating temperature. Jakeman and Raynes[1] derived the following expressions for the response times

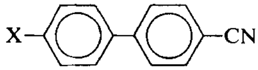
$$T_{on} = \frac{\gamma_1}{\{\varepsilon_0 \Delta\varepsilon E^2 - \bar{k}\pi^2/d^2\}} \tag{1}$$

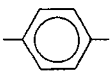
$$T_{off} = \frac{\gamma_1}{\{\bar{k}\pi^2/d^2\}} \tag{2}$$

where γ_1 is the twist viscosity coefficient, $\Delta\varepsilon$ the dielectric anisotropy, $\bar{k}$ an average of the elastic constants, d the cell thickness, and E the applied electric field. Tarry[2] showed that the temperature dependence of the response times is determined by that of the twist viscosity, except close to the nematic-isotropic transition temperature (T_{N-I}) where the temperature dependences of $\Delta\varepsilon$ and $\bar{k}$ become important. Schadt and Muller[3] indicated that γ_1 can be effectively replaced in Eq. (1) and Eq. (2) by the flow aligned viscosity $\bar{\eta}$, a quantity which can be readily and quickly measured for a large range of nematic materials. $\bar{\eta}$ can therefore be used as a guide to the response times

TABLE I

The transition temperatures for the compounds:



X	Name	C → N, S_A or I Temp. (°C)	S_A → N Temp. (°C)	N → I Temp. (°C)
C_2H_5	2 CB	75	—	(22)
n-C_3H_7	3 CB	66	—	(25.5)
n-C_4H_9	4 CB	48	—	(16.5)
n-C_5H_{11}	5 CB	24	—	35.3
n-C_6H_{13}	6 CB	14.5	—	29
n-C_7H_{15}	7 CB	30	—	42.8
n-C_8H_{17}	8 CB	21.5	33.5	40.5
n-C_3H_7O	3O CB	74.5	—	(64)
n-C_4H_9O	4O CB	78	—	(75.5)
n-$C_5H_{11}O$	5O CB	48	—	68
n-$C_6H_{13}O$	6O CB	57	—	75.5
n-$C_7H_{15}O$	7O CB	54	—	74
n-$C_8H_{17}O$	8O CB	54.5	67	80
n-$C_9H_{19}O$	9O CB	64	77.5	80
n-C_5H_{11} 	5 CT	131	—	240

( ) Monotropic transition temperature.

of the materials in display devices. In this paper we report measurements of $\bar{\eta}$ over a range of temperatures for the homologous series of 4-*n*-alkyl- and 4-*n*-alkoxy-4′-cyanobiphenyls[4] and their mixtures, some also including a 4-*n*-alkyl-4″-cyano-*p*-terphnyl.[5] The transition temperatures for these compounds are shown in Table I. Finally conclusions are drawn about the choice of components for wide temperature range mixtures with low viscosities.

EXPERIMENTAL

The flow aligned viscosities were measured in units of centiStokes (cSt) using Cannon-Manning semi-micro viscometers† immersed in a purpose-built double walled glass vessel through which an antifreeze solution was circulated. The temperature was controllable over the range −15°C to +80°C, and was measured to within 1°C by a thermometer placed near the viscometer bulb. It was found to be necessary to clean the viscometers carefully between experiments using different compounds by pumping

† Viscometers supplied by Poulten, Selfe and Lee Ltd., Wickford, Essex, UK.

several batches of fresh isopropyl alcohol through the capillary; this was followed by drying in a hot oven.

CONFIRMATION OF PROPORTIONALITY BETWEEN $\bar{\eta}$ AND T_{off}

The ratio $\bar{\eta}/T_{off}$ was measured at 20°C for a number of mixtures of cyanobiphenyls and a cyanoterphenyl with values of T_{N-I} in the range 57°C to 70°C. A 3 V rms 1 kHz gated sinewave signal was used to measure T_{off} (defined from 100% to 33% transmission) in 12 μm twisted nematic devices. Table II shows that $\bar{\eta}/T_{off}$ is effectively constant for these materials, confirming the results of Schadt and Muller[3] and justifying the assumptions outlined in the introduction.

TABLE II

The relationship between flow aligned viscosity ($\bar{\eta}$) and decay time (T_{off}) for a number of cyanobiphenyl mixtures

Mixture	$\bar{\eta}$ (cSt)	T_{off} (mS)	$\bar{\eta}/T_{off}$	Clearing point (°C)
5 CB + 5 CT	33	70	0.47	65
E1† + 5 CT	34	80	0.43	57
E7†	41	100	0.41	59
E8†	55	120	0.46	70
E4†	80	200	0.40	60
5O CB/7O CB	103	230	0.45	70

† E mixtures were obtained from BDH Chemicals Ltd., Poole, Dorset, UK. These are commercial mixtures of various of the cyanobiphenyls listed in Table I and frequently they contain 5 CT as a component.

MEASUREMENTS ON INDIVIDUAL COMPOUNDS

The flow aligned viscosities were measured over a range of temperatures for both the 4-*n*-alkyl-4′-cyanobiphenyls (Figure 1) and the 4-*n*-alkoxy-4′-cyanobiphenyls (Figure 2). At T_{N-I} all the materials showed the characteristic increase in $\bar{\eta}$ previously seen in other systems.[6] Schadt and Muller[3] have shown that for several nematic compounds

$$\bar{\eta} = \bar{\eta}_0 \exp\left(\frac{A}{kT}\right) \tag{3}$$

where A is an activation energy which is constant over most of the nematic range. Figures 3 and 4 show Eq. (3) to be valid for the isotropic phases of the alkyl- and alkoxy-cyanobiphenyls with $A \simeq 0.3$ eV for the alkyl series,

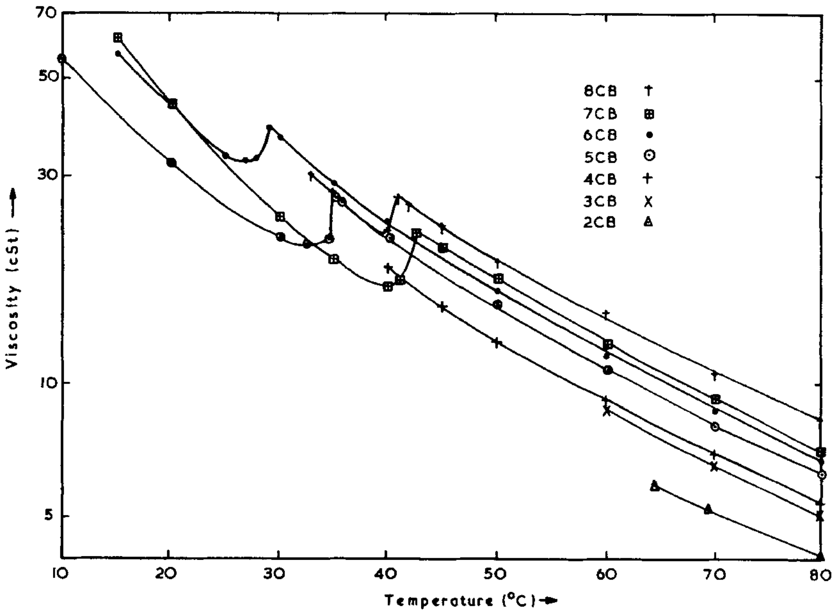


FIGURE 1 Flow aligned viscosities of the 4-n-alkyl-4′-cyanobiphenyls.

slightly lower than values in the range 0.35 eV to 0.49 eV measured for the nematic phases of other systems.[2,3]

Figures 3 and 4 also allow a comparison to be made of the isotropic viscosities extrapolated to 20°C. For the alkyl series this extrapolated viscosity varies from 20 cSt for 2 CB to 55 cSt for 8 CB, with a systematic increase with increasing length of alkyl chain. The isotropic value for 5 CB extrapolated to 20°C is 46 cSt (Figure 3), whereas it is only 32 cSt for the nematic phase (Figure 1). This discrepancy arises from the increase in $\bar{\eta}$ at T_{N-I}, and indicates that $\bar{\eta}$ of 2 CB would in fact be significantly less than 20 cSt if it could be measured for the nematic phase. The alkoxycyanobiphenyls do not show a clear correlation with chain length (Figure 4); this is probably a consequence of the narrowness of the isotropic phase accessible in the experiment. However it is clear that the alkoxycyanobiphenyls are about three times as viscous as the alkyl analogues, with extrapolated values around 100 cSt at 20°C.

MEASUREMENTS ON MIXTURES

The suggestion in the previous section that the alkoxy series appeared significantly more viscous than the alkyl series was confirmed by measurements on an equal weight binary mixture of 5O CB and 7O CB. The value of

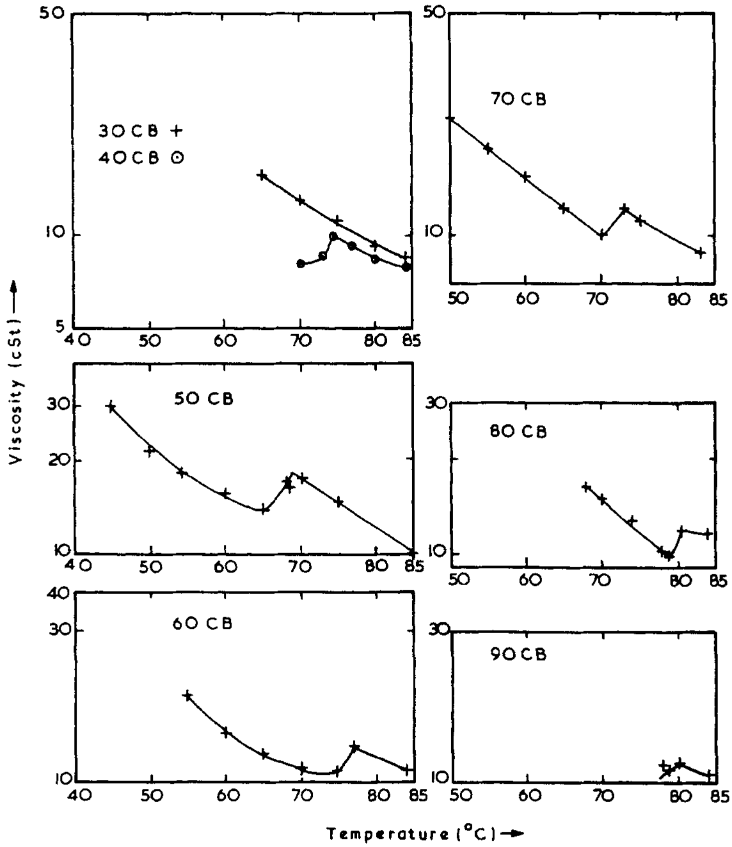


FIGURE 2 Flow aligned viscosities of the 4-*n*-alkoxy-4′-cyanobiphenyls.

$\bar{\eta}$ at 20°C is 100 cSt compared with 32 cSt for 5 CB at 20°C. Measurements were also made on combinations of the 5O CB plus 7O CB mixture with 5 CB (Figure 5). These reveal an approximately logarithmic relationship previously observed for isotropic liquids[7]

$$\log \eta = c_1 \log \eta_1 + c_2 \log \eta_2 \tag{4}$$

where η is the viscosity of the mixture, c_1 and c_2 are the concentrations, and η_1 and η_2 the viscosities of the components. Equation (4) has important implications for making wider temperature range, low viscosity mixtures.

It is obvious from Table I that the nematic ranges of individual alkyl compounds are too narrow for the materials to be used directly in a twisted nematic device, and therefore mixtures have to be made to increase the nematic range to a reasonable value, at least -10°C to $+60$°C. One way of

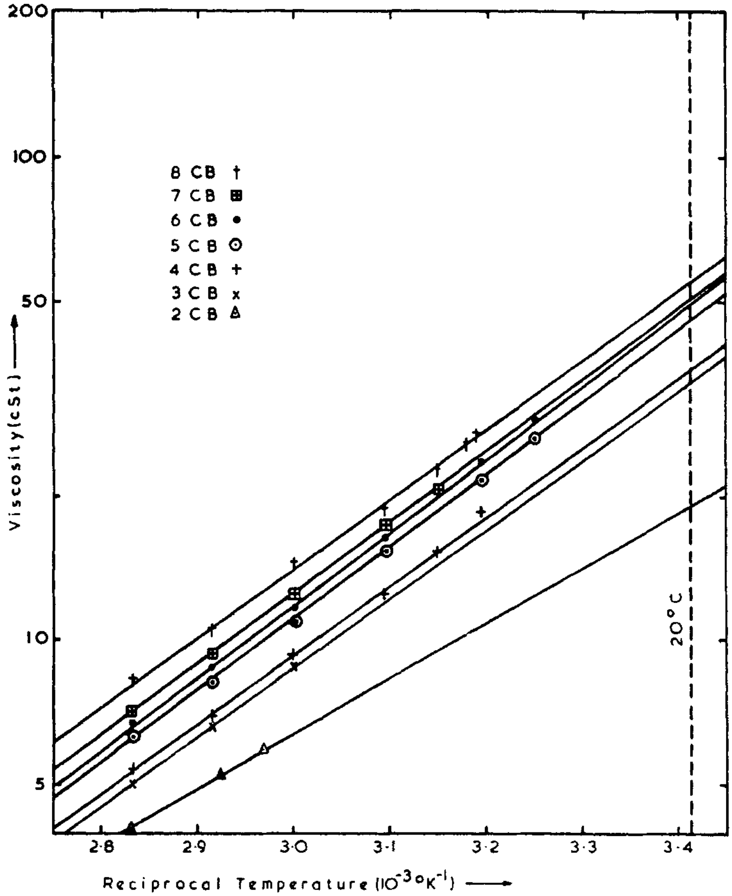


FIGURE 3 Isotropic viscosities of the 4-*n*-alkyl-4′-cyanobiphenyls plotted against the reciprocal of absolute temperature.

TABLE III

Comparison of the flow aligned viscosities of two mixtures with the same clearing point

Composition (wt %)	Clearing point (°C)	Viscosity at 20°C (*cSt*)
5 CB/5O CB/7O CB 30:35:35	60	61
5 CB/5 CT 87:13	60	33

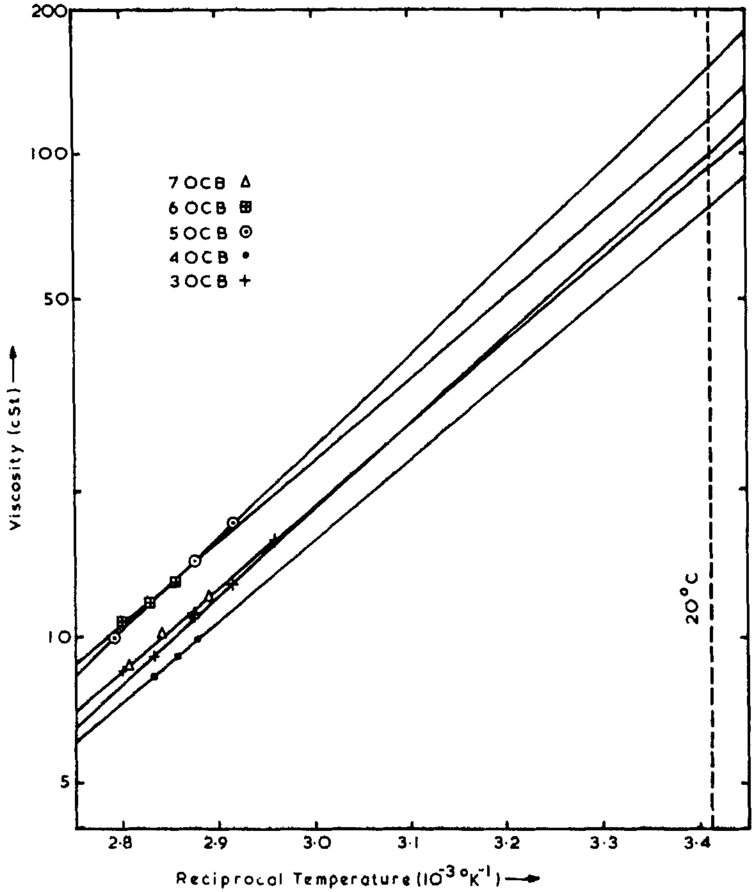


FIGURE 4 Isotropic viscosities of the 4-*n*-alkoxy-4′-cyanobiphenyls plotted against the reciprocal of absolute temperature.

achieving this is to use a large proportion ($\simeq 70\%$) of alkoxycyanobiphenyls, but the viscosities of mixtures of these are high (Figure 5). An alternative method involves the addition of a smaller amount ($\simeq 10\%$) of a material with a high T_{N-I}, such as 5 CT. The two methods are illustrated by the mixtures in Table III, both with T_{N-I} of 60°C. While the 5 CT mixture has a viscosity scarcely above that of pure 5 CB, that of the mixture containing 5O CB and 7O CB is significantly greater.

The low viscosity of the 5 CT mixture arises from the small amount of 5 CT added and the logarithmic dependence in Eq. (4), although 5 CT itself probably has a high viscosity (its melting point is too high for measurement of $\bar{\eta}$ in the present experiment). These trends are confirmed by the data in

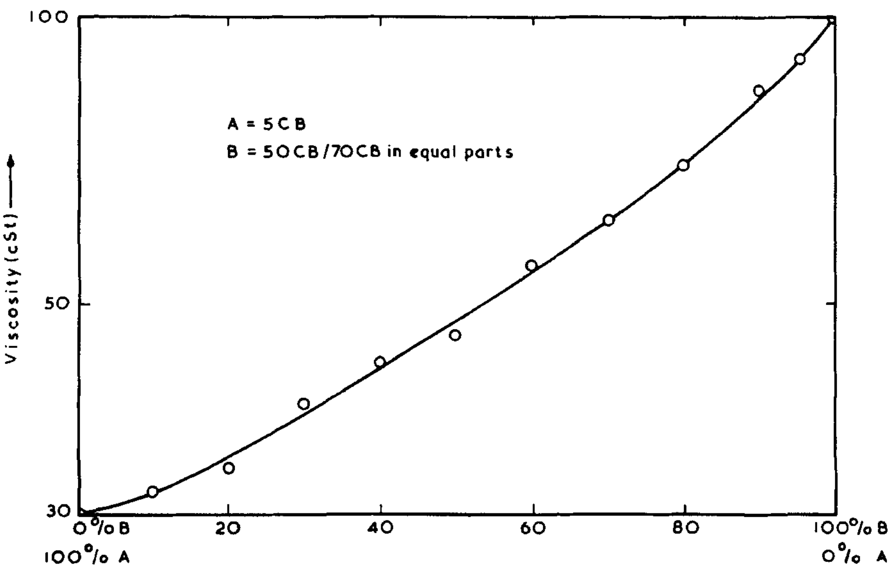


FIGURE 5 Log of flow aligned viscosity as a function of the composition of the mixture 5CB/50CB/70CB.

Table II where the first two mixtures contain no alkoxy cyanobiphenyls, and the rest an increasing amount (E7–16%, E8–47%, E4–57%), with the last mixture containing only alkoxy materials.

We can therefore suggest various design rules for producing mixtures with low viscosities.

i) Use 5 CT to increase T_{N-I} (Table III);
ii) reduce the alkoxycyanobiphenyl content to a minimum (Figure 5);
iii) use short alkyl chains (Figure 1).

These design rules have proved useful for producing wide temperature range, low viscosity mixtures of the cyanobiphenyls.[8]

Acknowledgements

We wish to thank BDH Chemicals Ltd., for supplying all the cyanobiphenyls used.

References

1. E. Jakeman and E. P. Raynes, *Phys. Lett.*, **A39**, 69 (1972).
2. H. A. Tarry, *Electron. Lett.*, **11**, 339 (1975).
3. M. Schadt and F. Muller, *IEEE Trans. Electron Devices ED*, **25**, 1125 (1978).
4. G. W. Gray, K. J. Harrison, and J. A. Nash, *Electron. Lett.*, **9**, 130 (1973).
5. G. W. Gray, K. J. Harrison, and J. A. Nash, *J.C.S. Chem. Comm.*, 431, (1974).
6. M. Miesowicz, *Bull. Acad. Pol.*, **A228** (1936).
7. S. Arrhenius, *Z. Phys. Chem.*, **1**, 285 (1887).
8. Liquid Crystal Catalogue, BDH Chemicals Ltd., Poole, Dorset, BH12 4NN, UK.