New Liquid Crystalline Compounds Based on 1,4-Diarylbuta-1,3-dienes

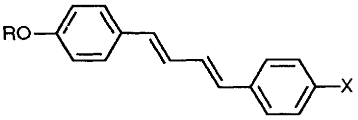
Roger Brettle, David A. Dunmur, Nigel J. Hindley and Charles M. Marson

Department of Chemistry, The University of Sheffield, Sheffield S3 7HF, UK

The first group of fully characterised mesogenic (*E,E*)-1,4-diarylbuta-1,3-dienes, substituted in the *para*-position of one aryl ring by an alkoxy-group and in the *para*-position of the other aryl group by a cyano- or halogeno-group has been prepared by a Wadsworth–Emmons procedure; their physical properties of high birefringence and low viscosity in combination make them particularly suitable for use in liquid crystal display devices when mixed with known liquid crystalline materials.

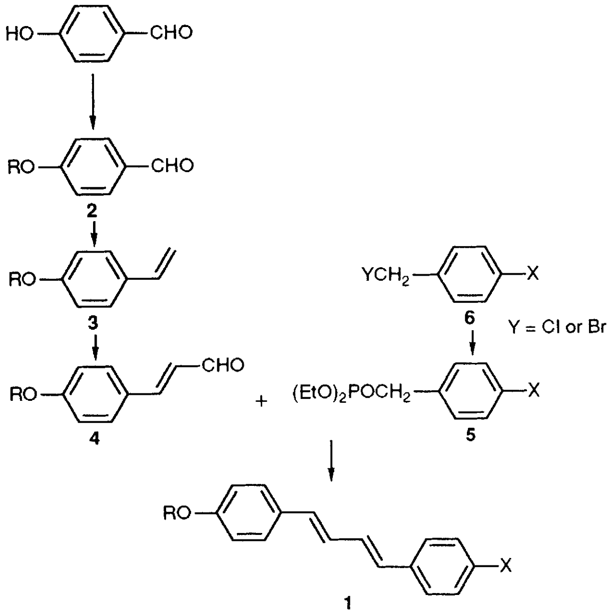
We report the synthesis of the first group of fully characterised (*E,E*)-1,4-diarylbuta-1,3-dienes **1** for use in liquid crystal display devices. Although the conjugated diene group has been previously suggested[1–3] as a useful linking group for mesogens, we believe that the compounds reported represent the first group of 1,4-disubstituted buta-1,3-diene liquid crystals. These compounds exhibit nematic phases at temperatures between 100 and 200 °C, and for longer chain homologues orthogonal smectic phases (A and B) are also observed. As is commonly observed[4] the persistence of the nematic phase was greatest when X = CN.

The dienes were prepared† by the convergent route shown in Scheme 1. 4-Alkoxybenzaldehydes[5] were prepared from 4-hydroxybenzaldehyde and the appropriate 1-bromoalkane; for the lower homologues the condensation was performed in cyclohexanone containing potassium carbonate, but for the higher homologues it was found to be preferable to use ethanolic potassium hydroxide. The (*E*)-4-alkoxycinnamaldehydes **4** were prepared by a two-step procedure; the alkoxybenzaldehydes **2** were first converted into the corresponding styrenes **3** by Wittig methylenation[6] and the styrenes were then formylated by phosphorus trichloride oxide–*N,N*-dimethylformamide.[7] The phosphonates **5** required for the Wadsworth–Emmons condensation[8] were obtained by the Arbuzov reaction of the corresponding 4-substituted benzyl halides with triethyl phosphite.[9] 4-Cyanobenzyl bromide was prepared by the bromination of 4-tolunitrile with *N*-bromosuccinimide[10] and 4-hexyloxybenzyl chloride in two steps from 4-hexyloxybenzaldehyde **2**, (R = C_6H_{13}) by reduction with sodium borohydride followed by reaction with hydrogen chloride in light petroleum.[11] Finally condensation of the (*E*)-4-alkoxycinnamaldehydes **4** with the 4-substituted diethyl benzylphosphonates **5** in the presence of potassium *tert*-butoxide in tetrahydrofuran (THF) led to the desired dienes **1**. In this final Wadsworth–Emmons procedure, as expected,[8] essentially only a single diastereoisomer of the diene was formed in each case. For the case of the diene **1** (R = C_6H_{13}; X = CN) the ^1H NMR spectrum recorded at 400 MHz in $CDCl_3$ showed alkenic signals at δ 6.58 and 6.71 (d, *J* 16 Hz) and at 6.83 and 7.03 (dd, *J* 10 and 16 Hz) clearly establishing the expected (*E,E*)-configuration. Both the *s-cis* and *s-trans*



1

R = $Me(CH_2)_nCH_2$– ; *n* = 2,4,6,7 or 8
X = CN, F, Cl, Br or $OCH_2(CH_2)_4Me$



Scheme 1

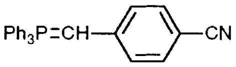
---

† All products were characterised by microanalysis and mass spectroscopy.

Table 1 Liquid crystal phases[a] and transition temperatures for dienes **1**

R	X	Transitions (T/°C)
C_6H_{13}	CN	$K \xrightarrow{107} N \xrightarrow{190} I$
C_6H_{13}	F	$K \xrightarrow{127} S_B \xrightarrow{160} S_A \xrightarrow{166} N \xrightarrow{174} I$
C_6H_{13}	Br	$K \xrightarrow{153} S_B \xrightarrow{189} S_A \xrightarrow{194} N \xrightarrow{198} I$
C_6H_{13}	Cl	$K \xrightarrow{147} S_B \xrightarrow{185} S_A \xrightarrow{189} I$
C_6H_{13}	$C_6H_{13}O$	$K \xrightarrow{187} N \xrightarrow{194} I$
C_4H_9	CN	$K \xrightarrow{137} N \xrightarrow{186} I$
C_7H_{15}	CN	$K \xrightarrow{110} S_A \xrightarrow{119} N \xrightarrow{186} I$
C_8H_{17}	CN	$K \xrightarrow{106} S_A \xrightarrow{147} N \xrightarrow{180} I$
C_9H_{19}	CN	$K \xrightarrow{94} S_A \xrightarrow{167} N \xrightarrow{180} I$
$C_{10}H_{21}$	CN	$K \xrightarrow{95} S_A \xrightarrow{175} N \xrightarrow{180} I$

[a] K = crystalline; S_A = smectic A; S_B = smectic B; N = nematic; I = isotropic liquid.



7

conformations for the (*E*,*E*)-dienes are possible. The two essentially coplanar aryl groups are colinear in the *s-cis*-conformation, but are laterally displaced in a parallel fashion in the *s-trans*-conformation, thus slightly altering the orientation of the principle inertial axis. Condensation of the 4-alkoxycinnamaldehyde **4** (R = C_6H_{13}) with the corresponding Wittig reagent **7**, prepared from **6** (Y = Br; X = CN) and triphenylphosphine followed by treatment with butyllithium gave, as again expected,[12] a mixture of the (*E*,*E*)- and the (*E*,*Z*)-dienes, the newly formed double bond being created in both possible configurations. The (*E*,*Z*) diene rapidly isomerises to the (*E*,*E*) species at ambient temperature. Optical studies of mixtures of these isomers indicate that the (*E*,*Z*) form is not mesogenic.

The liquid crystal transition temperatures of the dienes observed by optical microscopy are listed in the Table 1. Phase types were identified by the optical textures, and phase transitions and temperatures were confirmed by differential scanning calorimetry (DSC).

It appears from this work that the diene linkage between two ring systems, aromatic in this case, is excellent for promoting liquid crystalline behaviour, and at least for shorter chain homologues results in wide nematic ranges. The diene group is another example of four centre linking groups which have been the subject of recent investigation.[13] These new compounds were used as components in nematic mixtures for applications, and the resultant materials exhibited the unusual combination of low viscosity, high birefringence and high dielectric anisotropy. These features resulted in improved operating characteristics (low threshold voltage, fast switching speed) when the materials were tested in TN (twisted nematic) display cells.[14]

Financial support from Hitachi Limited (Electron Tube Division) is gratefully acknowledged, and we also thank Hitachi Research Laboratories for carrying out physical measurements on the materials. Valuable discussions with Dr K. Toriyama are also gratefully acknowledged.

Received, 22nd November 1991; Com. 1/05925D

References

1 H. Kelker and R. Hatz, *Handbook of Liquid Crystals*, Verlag Chemie, Weinheim, 1980.

2 G. W. Gray, in *Liquid Crystals and Plastic Crystals*, ed. G. W. Gray and P. A. Winsor, Ellis Horwood, Chichester, 1974, vol. 1.

3 G. H. Brown and W. G. Shaw, *Chem. Rev.*, 1957, **57**, 1049.

4 K. J. Toyne, *Thermotropic Liquid Crystals, CRAC*, ed. G. W. Gray, Wiley, Chichester, 1987, vol. 22, p. 28.

5 C. Weygand and R. Gabler, *J. Prakt. Chem.*, 1940, **155**, 332; G. W. Gray and B. Jones, *J. Chem. Soc.*, 1954, 467; T. Nogradi, L. Vargha, G. Ivanovics and I. Koczka, *Acta Chim. Acad. Sci. Hung.*, 1954, **4**, 303; H. Edgerson, R. L. Hull and J. R. Fisher, *J. Am. Pharm. Assoc. Sci. Ed.*, 1959, **48**, 320.

6 J. I. G. Cadogan, *Organophosphorus Reagents in Organic Synthesis*, Academic Press, New York, 1979.

7 *Cf.* C. J. Schmidle and P. G. Barnett, *J. Am. Chem. Soc.*, 1956, **78**, 3209.

8 W. S. Wadsworth, Jr., *Organic Reactions*, 1977, **25**, 73.

9 *Cf.* A. Franke, G. Mattern and W. Traber, *Helv. Chim. Acta*, 1975, **58**, 268.

10 M. Julia and F. Chastrette, *Bull. Soc. Chim. Fr.*, 1962, 2247.

11 *Cf.* H. Stephen and C. Weizmann, *J. Chem. Soc.*, 1914, **105**, 1152.

12 J. Gillois, G. Guillern, M. Savignac, E. Stephan and L. Vo-Quang, *J. Chem. Educ.*, 1980, **57**, 161.

13 S. M. Kelly, J. Funfschilling and F. Leenhouts, *Liq. Cryst.*, 1991, **10**, 243; S. Kelly, *Liq. Cryst.*, 1991, **10**, 261; S. Kelly, *Liq. Cryst.*, 1991, **10**, 273.

14 R. Brettle, D. A. Dunmur, N. J. Hindley and C. M. Marson, Jpn. Pat. Filing No. 3-139999, 1991.