

Liquid crystal poly-phenylene/cyclohexylene-
acetonitriles

The present invention is concerned with certain novel acetonitriles, with processes for their preparation, with their use and the use of analogues thereof in liquid crystalline dielectrics, and with the use of the latter
5 in electro-optical display elements.

We have found that acetonitriles of formula IA:



in which R is alkyl, alkoxy or alkanoyloxy, each having up to 8 carbon atoms, and Q represents 2,3 or 4
10 phenylene and/or cyclohexylene radicals which are bonded to one another in the 1, 4-position, are effective liquid crystalline components, particularly for displays based on the principle of dynamic scattering. Their properties are generally similar to those of the compounds
15 described in German OLS 2,636,684.

The determining factor of the shape of the contrast-voltage characteristic of dynamic scattering displays is the anisotropy of the conductivity, which is created by the dissolution of a conducting salt in the dielectric. The solubility of the conducting salts used for this purpose is
20 frequently a source of difficulty with respect to the stability of the displays on storage at low temperatures.

We have found that the acetonitriles of formula IA are particularly suitable as components of liquid
25 crystalline dielectrics as they give rise to liquid crystalline phases which have a relatively high optical anisotropy and a very good dissolving capacity for ionic doping materials, for example conducting salts. The addition of these acetonitriles to liquid crystalline
30 dielectrics which contain conducting salts, increases the dissociation of the latter and thus the conductivity of the dielectric.

In addition, the compounds of formula IA have a very wide range of use: depending on the substituents they contain, these compounds can serve as base materials of which liquid crystalline dielectrics are chiefly composed, but compounds of formula IA can also be added in smaller proportions of, for example, 2 to 25% by weight to liquid crystalline base materials of other classes of compounds, in order to modify the mean dielectric constant of such a dielectric.

According to one aspect of the present invention, therefore, there is provided a liquid crystalline dielectric for electro-optical display elements, which comprises at least two liquid crystalline components, at least one of which is an acetonitrile of formula IA.

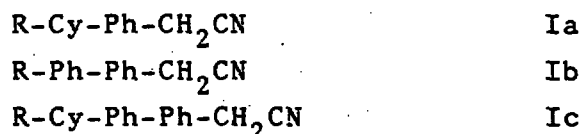
The majority, but not all, of the compounds of formula IA are novel; according to another aspect of the invention, there are provided acetonitriles of formula I:



in which R is alkyl, alkoxy or alkanoyloxy, each having up to 8 carbon atoms, and Q represents 2,3 or 4 phenylene and/or cyclohexylene radicals which are bonded to one another in the 1,4-position, provided that when Q represents two phenylene radicals and R is alkoxy, the alkoxy group contains at least 4 carbon atoms.

The compounds of formula I are colourless in the pure state and form liquid crystalline mesophases in a temperature range which is favourable for electro-optical use.

Preferred compounds according to the invention include 4-cyclohexylphenylacetonitriles of formula Ia, bi phenyl-4-ylacetonitriles of formula Ib, and 4'-cyclohexylbiphenyl-4-ylacetonitriles of formula Ic:



wherein Cy is a 1,4-cyclohexylene radical and Ph is a 1,4-phenylene radical.

Further preferred compounds according to the

invention include phenylacetonitrile derivatives of the following formulae Id to In:

	R-Ph-Ph-Ph-CH ₂ CN	Id
	R-Ph-Cy-Ph-CH ₂ CN	Ie
5	R-Cy-Cy-Ph-CH ₂ CN	If
	R-Ph-Ph-Ph-Ph-CH ₂ CN	Ig
	R-Ph-Ph-Cy-Ph-CH ₂ CN	Ih
	R-Ph-Cy-Ph-Ph-CH ₂ CN	Ii
	R-Ph-Cy-Cy-Ph-CH ₂ CN	Ij
10	R-Cy-Ph-Ph-Ph-CH ₂ CN	Ik
	R-Cy-Ph-Cy-Ph-CH ₂ CN	Il
	R-Cy-Cy-Ph-Ph-CH ₂ CN	Im
	R-Cy-Cy-Cy-Ph-CH ₂ CN	In

15 and cyclohexylacetonitriles of the following formulae Iaa to Inn:

	R-Cy-Cy-CH ₂ CN	Iaa
	R-Ph-Cy-CH ₂ CN	Ibb
	R-Cy-Ph-Cy-CH ₂ CN	Icc
20	R-Ph-Ph-Cy-CH ₂ CN	Idd
	R-Ph-Cy-Cy-CH ₂ CN	Iee
	R-Cy-Cy-Cy-CH ₂ CN	Iff
	R-Ph-Ph-Ph-Cy-CH ₂ CN	Igg
	R-Ph-Ph-Cy-Cy-CH ₂ CN	Ihh
25	R-Ph-Cy-Ph-Cy-CH ₂ CN	Iii
	R-Ph-Cy-Cy-Cy-CH ₂ CN	Ijj
	R-Cy-Ph-Ph-Cy-CH ₂ CN	Ikk
	R-Cy-Ph-Cy-Cy-CH ₂ CN	Ill
	R-Cy-Cy-Ph-Cy-CH ₂ CN	Imm
30	R-Cy-Cy-Cy-Cy-CH ₂ CN	Inn

in which R, Cy and Ph have the above-stated meanings.

In the compounds of formula I, Ia to In and Iaa to Inn which contain cyclohexylene radicals, those
35 stereoisomers are preferred in which the two 1,4

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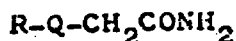
substituents are in the trans-position relative to one another.

In the compounds of formula I, the R radical is preferably straight chain and is thus preferably methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, methoxy, ethoxy, n-propyloxy, n-butyloxy, n-pentyloxy, n-heptyloxy, n-octyloxy, formyloxy, acetoxy, propionyloxy, butyryloxy, pentanoyloxy, hexanoyloxy, heptanoyloxy or octanoyloxy.

Compounds of formula I having a branched chain R group are sometimes of importance because they have better solubility in conventional liquid crystalline base materials, but they are particularly important as chiral doping materials when they have optical activity due to the chain branching. Branched R groups preferably do not contain more than one chain branching. Preferred branched R radicals are isopropyl, 2-methylpropyl, 2-methylbutyl, 3-methylbutyl, 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl, 1-methylhexyl, 1-methylheptyl, isopropyloxy, 2-methylpropyloxy, 2-methylbutyloxy, 3-methylbutyloxy, 2-methylpentyloxy, 3-methylpentyloxy, 2-ethylhexyloxy, 1-methylhexyloxy, 1-methylheptyloxy, isobutyryloxy, 2-methylbutyryloxy, 3-methylbutyryloxy, 3-ethylbutyryloxy, 2-ethylbutyryloxy, 2-, 3- or 4-methylpentanoyloxy, 2- or 3-ethylpentanoyloxy. All R groups contain 1 to 8, preferably 3 to 5, C atoms. Alkyl groups are preferred to alkoxy and alkanoyloxy groups.

According to a further aspect of the present invention, there is provided a process for the preparation of an acetonitrile of formula I, which comprises

(1) treating an acetamide of formula II:



II

in which Q and R have the above-stated meanings, with a dehydrating agent, or

(2) reacting a halogenomethyl compound of formula
III:



III

in which Hal is Cl, Br or I, and Q and R have the above-
stated meanings, with a metal cyanide.

Both these processes can, in principle, be
carried out under conventional conditions as described
in the literature (for example in the standard works,
such as Houben-weyl, Methoden der Organischen Chemie
(Methods of Organic Chemistry), Georg-Thieme-Verlag,
Stuttgart). Known variants of standard procedures which
are not mentioned in this specification can, in
principle, also be used.

The starting materials used in these processes
may be formed in situ, if desired, in such a manner
that they are not isolated from the reaction mixture
but are immediately reacted further to give the desired
compound of formula I.

The compounds of formula I are preferably
prepared by the first process mentioned, that is the
dehydration of the corresponding acetamides of formula
II. Suitable dehydrating agents for use in this process
are, for example, inorganic acid chlorides, such as
 $SOCl_2$, PCl_3 , PCl_5 , SO_2Cl_2 , $COCl_2$, and also P_2O_5 , P_2S_5 ,
 $AlCl_3$ as a double compound with $NaCl$, aromatic sulphonic
acids and sulphonyl halides. The reaction may be
carried out in the presence or absence of an inert
solvent, for example an aromatic hydrocarbon, such as
benzene, toluene or xylene, and is preferably effected
at a temperature of from 50° to $150^\circ C$.

The acetonitriles of formula I can also be
obtained by reaction of chlorine, bromine or iodine
compounds of formula III with a metal cyanide,
preferably $NaCN$, KCN or $Cu_2(CN)_2$, preferably in the
presence of an inert solvent, such as dimethylformamide

or dimethyl sulphoxide, and at a temperature of from 20° to 150°C.

The starting compounds of formulae II and III are largely new. However, they can be prepared by conventional methods from known compounds. Thus, the acetamides of formula II can be obtained by reaction of the corresponding methyl ketones of the formula $R-Q-COCH_3$ with morpholine/sulphur by the Willgerodt method to give the corresponding thiomorpholides, hydrolysis to the acetic acids of the formula $R-Q-CH_2-COOH$, conversion into the chlorides of the formula $R-Q-CH_2-COCl$, and reaction with ammonia. The halogen compounds of formula III can be prepared, for example, by reduction of suitable esters of the formula $R-Q-COOalkyl$ to give the alcohols of the formula $R-Q-CH_2OH$ and subsequent reaction with $SOCl_2$, HBr or HI .

According to a further aspect of the present invention, there is provided a liquid crystalline dielectric for electro-optical display elements, which comprises at least two liquid crystalline components, at least one of which is an acetonitrile of formula I.

The present invention further comprises an electro-optical display element comprising a liquid crystal cell, the latter containing a liquid crystalline dielectric according to the invention.

The dielectrics according to the invention generally consist of 2 to 15, preferably 3 to 12, components, including at least one acetonitrile of formula I. The other constituents are selected from the nematic or nematogenic compounds from the classes of azoxybenzenes, benzylideneanilines, biphenyls, terphenyls, phenyl or cyclohexyl benzoates, phenyl or cyclohexyl cyclohexanecarboxylates, phenylcyclohexanes, cyclohexylbiphenyls, cyclohexylcyclohexanes,

cyclohexylnaphthalenes, 1,4-biscyclohexylbenzenes, 4,4'-biscyclohexylbiphenyls, phenylpyrimidines or cyclohexylpyrimidines, phenyldioxanes or cyclohexyldioxanes, stilbenes which may be halogenated, benzyl phenyl ethers, tolanes and substituted cinnamic acids.

The most important compounds which can be used as constituents of liquid crystalline dielectrics of this type can be characterised by formula IV:



in which C and D are each a carbocyclic or heterocyclic ring system selected from 1,4-disubstituted benzene and cyclohexane rings, 4,4'-disubstituted biphenyl, phenylcyclohexane and cyclohexylcyclohexane systems, 2,5-disubstituted pyrimidine and 1,3-dioxane rings, 2,6-disubstituted naphthalene, dihydro- and tetrahydro-naphthalene, quinazoline and tetrahydroquinazoline,

B is

-CH=CH-	-N(O)=N-
-CH=CY-	-CH=N(O)-
-C≡C-	-CH ₂ -CH ₂ -
-CO-O-	-CH ₂ -O-
-CO-S-	-CH ₂ -S- , or
-CH=N-	-COO-Ph-COO-

or a C-C single bond, Y is halogen, preferably chlorine, or -CN, and R¹ and R² are alkyl, alkoxy, alkanoyloxy

or alkoxycarbonyloxy having up to 18, preferably up to 8 carbon atoms, or one of these radicals is -CN, -NC, -NO₂, -CF₃, F, Cl or Br. In most of these compounds, R¹ and R² are different from one another, one of these radicals generally being an alkyl or alkoxy group.

Other variants of the substituents mentioned are, however, also common. Many such substances or mixtures thereof are commercially available.

The dielectrics according to the invention contain, in general, from 0.1 to 60%, preferably, at least 5%, and more preferably 10-25%, of one or more

compounds of formula I. However, the invention also comprises liquid crystalline dielectrics to which less than 5%, for example 0.1 to 3%, of one or more compounds of formula I have been added, for example for doping purposes. On the other hand, the compounds of formula I can account for up to 60% of the dielectrics according to the invention.

The preparation of the dielectrics according to the invention may be carried out in conventional manner. In general, the desired amount of the components which are used in a smaller quantity is dissolved in the component representing the major constituent, preferably at an elevated temperature. If a temperature above the clear point of the main constituent is chosen for this, the completeness of dissolution can be observed with particular ease.

The liquid crystalline dielectrics according to the invention can be modified by suitable additives in such a way that they can be used in all known types of liquid crystal display elements.

Suitable additives for this purpose, are known to those skilled in the art and are extensively described in the relevant literature. Suitable additives include, for example, conducting salts as previously mentioned, such as, ethyldimethyldodecylammonium 4-hexyloxybenzoate, tetrabutylammonium tetraphenylborate or complex salts of crown ethers (see, for example, I. Haller et al., Mol. Cryst. Liq. Cryst., Volume 24, pages 249-258 (1973)) in order to improve the conductivity, and dichroic dyes or substances for modifying the dielectric anisotropy, the viscosity and/or the orientation of the nematic phases. Compounds of these types are described, for example, in German OLS 2,209,127, 2,240,864, 2,321,632, 2,338,281, 2,450,088, 2,637,430, 2,853,728 and 2,902,177.

In order that the invention may be more fully understood, the following examples are given by way of illustration only. In these examples, m.p. denotes the melting point and c.p. denotes the clear point of a liquid crystalline compound. All parts and percentages are by weight and all temperatures are in degrees Celsius.

Example 1

180 g of SOCl_2 were added to a suspension of 281 g of 4'-pentylbiphenyl-4-yl-acetamide [m.p. 185° ; obtained by reaction of 4-acetyl-4'-pentyl-biphenyl with morpholine/sulfur and subsequent hydrolysis to give 4'-pentylbiphenyl-4-yl-acetic acid (m.p. 160°), reaction with SOCl_2 to give the chloride and reaction with NH_3] in 1 l of toluene at 80° . After stirring at 80° for 6 hours, cooling and pouring into water, 4'-pentylbiphenyl-4-yl-acetonitrile was obtained, m.p. 80° , c.p. -10° .

Examples 2 to 43

Using the procedure of Example 1, the following compounds are obtained by dehydration of the corresponding acetamides:

2. 4'-Methylbiphenyl-4-yl-acetonitrile
3. 4'-Ethylbiphenyl-4-yl-acetonitrile
- 25 4. 4'-Propylbiphenyl-4-yl-acetonitrile
5. 4'-Butylbiphenyl-4-yl-acetonitrile
6. 4'-(2-Methylbutyl)biphenyl-4-yl-acetonitrile
7. 4'-Hexylbiphenyl-4-yl-acetonitrile
8. 4'-Heptylbiphenyl-4-yl-acetonitrile
- 30 9. 4'-Octylbiphenyl-4-yl-acetonitrile
10. 4'-(2-Methylheptyl)biphenyl-4-yl-acetonitrile
11. 4'-Butoxybiphenyl-4-yl-acetonitrile
12. 4'-Pentyloxybiphenyl-4-yl-acetonitrile
13. 4'-Hexyloxybiphenyl-4-yl-acetonitrile
- 35 14. 4'-Heptyloxybiphenyl-4-yl-acetonitrile

23

15. 4'-Octyloxybiphenyl-4-yl-acetonitrile
16. 4'-Formyloxybiphenyl-4-yl-acetonitrile
17. 4'-Acetoxybiphenyl-4-yl-acetonitrile
18. 4'-Propionyloxybiphenyl-4-yl-acetonitrile
- 5 19. 4'-Butyryloxybiphenyl-4-yl-acetonitrile
20. 4'-Pentanoyloxybiphenyl-4-yl-acetonitrile
21. 4'-Hexanoyloxybiphenyl-4-yl-acetonitrile
22. 4'-Heptanoyloxybiphenyl-4-yl-acetonitrile
23. 4'-Octanoyloxybiphenyl-4-yl-acetonitrile
- 10 24. 4-(trans-4-Methylcyclohexyl)phenyl-acetonitrile
25. 4-(trans-4-Ethylcyclohexyl)phenyl-acetonitrile
26. 4-(trans-4-Propylcyclohexyl)phenyl-acetonitrile
27. 4-(trans-4-Butylcyclohexyl)phenyl-acetonitrile
28. 4-(trans-4-Pentylcyclohexyl)phenyl-acetonitrile
- 15 m.p. 53°, c.p. -19°
29. 4-(trans-4-(2-Methylbutyl)cyclohexyl)phenyl-aceto-nitrile
30. 4-(trans-4-Hexylcyclohexyl)phenyl-acetonitrile
31. 4-(trans-4-Heptylcyclohexyl)phenyl-acetonitrile
- 20 32. 4-(trans-4-Octylcyclohexyl)phenyl-acetonitrile
33. 4-(trans-4-(1-Methylheptyl)cyclohexyl)phenyl-aceto-nitrile
34. 4'-(trans-4-Methylcyclohexyl)biphenyl-4-yl-aceto-nitrile
- 25 35. 4'-(trans-4-Ethylcyclohexyl)biphenyl-4-yl-aceto-nitrile
36. 4'-(trans-4-Propylcyclohexyl)biphenyl-4-yl-aceto-nitrile
37. 4'-(trans-4-Butylcyclohexyl)biphenyl-4-yl-aceto
- 30 nitrile
38. 4'-(trans-4-Pentylcyclohexyl)biphenyl-4-yl-aceto-nitrile, m.p. 139°, c.p. 172°

39. 4'-(trans-4-(2-Methylbutyl)cyclohexyl)biphenyl-4-yl-acetonitrile
40. 4'-(trans-4-Hexylcyclohexyl)biphenyl-4-yl-acetonitrile
5 41. 4'-(trans-4-Heptylcyclohexyl)biphenyl-4-yl-acetonitrile
42. 4'-(trans-4-Octylcyclohexyl)biphenyl-4-yl-acetonitrile
43. 4'-(trans-4-(1-Methylheptyl)cyclohexyl)biphenyl-4-yl-acetonitrile
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Example 44

27.9 g of 4-(trans-4-pentylcyclohexyl)benzyl chloride (obtained by chloromethylation of trans-4-pentyl-1-phenylcyclohexane or by esterification of 4-(trans-4-pentylcyclohexyl)benzoic acid, reduction of the methyl or ethyl ester obtained to give 4-(trans-4-pentylcyclohexyl)benzyl alcohol and reaction with PCl_3) were added over a period of 15 minutes at 60° , with stirring, to a mixture of 5.5 g of NaCN and 40 ml of dimethyl sulphoxide. The mixture was heated at 70° for 6 hours, cooled, poured into water and 4-(trans-4-pentylcyclohexyl)phenyl-acetonitrile was obtained, m.p. 53° , c.p. -19° .

25 The acetonitriles specified in Examples 1 to 27 and 29 to 43 can be obtained analogously from the corresponding chlorides.

The following examples of dielectrics according to the invention containing at least one compound of formula I, are given by way of illustration only:-

Example A

- a) A mixture of
15% of 4-ethyl-4'-(trans-4-pentylcyclohexyl)biphenyl,
35 30% of 4-ethyl-2'-fluoro-4'-(trans-4-pentylcyclohexyl)-

- biphenyl,
23% of 4-pentylphenyl 4-methoxybenzoate,
21% of 4-butyl-2-cyanophenyl 4-(trans-4-propylcyclo-
hexyl)-benzoate, and
5 11% of 1-(4-(trans-4-pentylcyclohexyl)phenyl)pentan-
1,3-dione

has the following properties: m.p. -15° ; c.p. $+96^{\circ}$;
viscosity 56 cSt; dielectric anisotropy $\Delta\epsilon=0.5$.

- After adding 0.1% of ethyldimethyldodecyl-
10 ammonium 4-hexyloxybenzoate, a specific resistance of
 $1.2 \times 10^9 \Omega \text{cm}$ is obtained. The lower limit of the
operative temperature range is 0° at a frequency of
32 Hz.

- b) The addition of 5% of 4'-pentylbiphenyl-4-yl-
15 acetonitrile and 5% of 4-(trans-4-pentylcyclohexyl)
biphenyl-4-yl-acetonitrile provides a mixture with the
following properties: m.p. -17° , c.p. $+97^{\circ}$, viscosity
55 cSt, dielectric anisotropy $\Delta\epsilon=0.5$; specific
resistance $4 \times 10^8 \Omega \text{cm}$; lower limit of the operative
20 temperature range -10° .

Example B

- a) A mixture of
15% of trans-1-(4-ethoxyphenyl)-4-propylcyclohexane,
10% of trans-1-(4-butoxyphenyl)-4-propylcyclohexane,
25 20% of 4-ethyl-4'-(trans-4-pentylcyclohexyl)biphenyl,
5% of 4-(trans-4-pentylcyclohexyl)-4'-(trans-4-
propylcyclohexyl)biphenyl,
18% of 4-pentylphenyl 4-methoxybenzoate,
22% of 4-butyl-2-cyanophenyl 4-(trans-4-propylcyclo-
hexyl)benzoate, and
30 10% of 1-(4-(trans-4-pentylcyclohexyl)phenyl)pentan-
1,3-dione

has the following properties: m.p. -10° ; c.p. $+94^{\circ}$;
viscosity 42 cSt; dielectric anisotropy $\Delta\epsilon=0.6$.

- 35 After adding 0.05% of ethyldimethyldodecyl-

ammonium 4-hexyloxybenzoate, a specific resistance of $1.1 \times 10^9 \Omega \text{cm}$ is obtained. The lower limit of the operative temperature range is 0° at a frequency of 32Hz.

- 5 b) Addition of 10% of 4-(trans-4-pentylcyclohexyl) phenyl-acetonitrile provides a mixture with the following properties: m.p. -12° ; c.p. 87° ; viscosity 43 cSt; dielectric anisotropy $\Delta\epsilon - 0.5$; specific resistance $5 \times 10^8 \Omega \text{cm}$; lower limit of the operative temperature range - 10° .



Claims:

1. Acetonitriles of formula I:



in which R is alkyl, alkoxy or alkanoyloxy, each having up to 8 carbon atoms, and Q represents 2,3 or 4 phenylene and/or cyclohexylene radicals which are bonded to one another in the 1,4-position, provided that when Q represents two phenylene radicals and R is alkoxy, the alkoxy group contains at least 4 carbon atoms.

2. 4'-Pentylbiphenyl-4-yl-acetonitrile.

3. 4-(trans-4-Pentylcyclohexyl)-phenyl-acetonitrile.

4. 4'-(trans-4-Pentylcyclohexyl)-biphenyl-4-yl-acetonitrile.

5. A process for the preparation of an acetonitrile of formula I specified in claim 1, which comprises treating an acetamide of formula II:



in which Q and R have the meanings specified in claim 1 with a dehydrating agent.

6. A process for the preparation of an acetonitrile of formula I specified in claim 1, which comprises reacting a halogenomethyl compound of formula III:



in which Hal is Cl, Br or I, and Q and R have the meanings specified in claim 1, with a metal cyanide.

7. A process for the preparation of an acetonitrile of formula I specified in claim 1, substantially as herein described in any of Examples 1 to 44.



- 15 -

8. A liquid crystalline dielectric for electro-optical display elements which comprises at least two liquid crystalline components, at least one of which is an acetonitrile of formula IA:



in which R is alkyl, alkoxy or alkanoyloxy, each having up to 8 carbon atoms, and Q represents 2,3 and 4 phenylene and/or cyclohexylene radicals which are bonded to one another in the 1,4-position.

9. A liquid crystalline dielectric according to claim 8, substantially as herein described in Example A and B.

10. An electro-optical display element comprising a liquid crystal cell, the latter containing a dielectric according to claim 8 or 9.
