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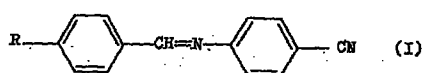


(54) LIQUID CRYSTALLINE SCHIFFS' BASES

(71) We, F. HOFFMANN-LA ROCHE & CO., AKTIENGESELLSCHAFT, a Swiss Company of 124—184 Grenzachstrasse, Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to liquid crystalline Schiffs' bases. More particularly, the invention is concerned with Schiffs' bases, a process for the manufacture thereof, nematic mixtures for electro-optical purposes containing same and a process for the production of nematic mixtures. The invention is also concerned with dielectrics useful for electro-optical purposes and with a process for the production thereof.

The Schiffs' bases provided by the present invention are compounds of the general formula



wherein R represents the ethyl, n - propyl, n - butyl, n - pentyl, iso - hexyl, n - hexyl, n - heptyl or n - octyl group.

The compounds of formula I possess, in the liquid crystalline form, a positive anisotropy of the dielectric constants ($\epsilon_{11} > \epsilon_{\perp}$, ϵ_{11} signifying the dielectric constant along the longitudinal axis of the molecule and $\epsilon_{\perp}$ signifying the dielectric constant perpendicular thereto).

In an electric field, the nematic liquid crystals orient themselves (because $\epsilon_{11} > \epsilon_{\perp}$) with the direction of their largest dielectric constant (i.e. with their longitudinal axes) parallel to the field direction. This effect is used, inter alia, in the interaction between embedded molecules and liquid crystal molecules (guest-host interaction) described by J. H. Heilmeyer and L. A. Zanoni [Applied Physics Letters 13, 91 (1968)]. A further interesting applica-

tion of the dielectric field orientation exists in the rotation cell discovered by M. Schadt and W. Helfrich [Applied Physics Letters 18, 127 (1971)].

The electro-optical rotation cell is essentially a condenser having transparent electrodes whose dielectric is formed essentially from a nematic substance with $\epsilon_{11} > \epsilon_{\perp}$. The longitudinal axes of the liquid crystals are arranged in twisted form between the condenser plates in the fieldless state, the twisting structure being defined by the given wall orientation of the molecules. After the application of an electrical potential to the condenser plates, the molecules adjust themselves with their longitudinal axes in the field direction (i.e. perpendicular to the surface of the plates), whereby linear polarised light is no longer rotated in the dielectric (the liquid crystal is uniaxially perpendicular to the surface of the plates). This effect is reversible and can be used for electrically controlling the optical transmissivity of the condenser.

In such "light rotation cells" it is desirable to use compounds which possess a low melting point and a slight viscosity. The compounds hitherto used for this purpose have the disadvantage that they first show nematic properties at relatively high temperatures so that electro-optical apparatuses provided with such liquid crystals have to be heated and possibly thermostatted. Further, the known compounds possess a high viscosity which, for example, leads to the considerable disadvantage in electro-optical apparatuses that their operation requires relatively large voltages and long response times.

It has now been surprisingly found in accordance with the present invention that the compounds of formula I exhibit not only the necessary large positive anisotropy of the dielectric constants but also, individually or in the form of mixtures with one another or with other nematic or non-nematic substances, they are liquid crystalline and exhibit a slight viscosity at relatively low tem-

peratures. Their use is therefore possible with lower voltage and the response time is shorter. A further advantage of the compounds of formula I is that they can form supercooled nematic phases, which leads to a high stability in the nematic region. This is very important from the practical point of view.

The compounds of formula I are preferably used in the form of mixtures with one another or with other nematic or non-nematic substances.

Especially preferred are mixtures whose composition corresponds to a eutectic.

More especially preferred are mixtures of

15 p - [(p - n - hexylbenzyliden)amino]benzonitrile with

p - [(p - n - butylbenzyliden)amino]benzonitrile in a molar ratio of 2:1 to 1:2,

20 p - [(p - n - propylbenzyliden)amino]benzonitrile with

p - [(p - n - hexylbenzyliden)amino]benzonitrile in a molar ratio of 1:2,

p - [(p - n - heptylbenzyliden)amino]benzonitrile with

25 p - [(p - n - butylbenzyliden)amino]benzonitrile in a molar ratio of 2:1,

p - [(p - n - octylbenzyliden)amino]benzonitrile with

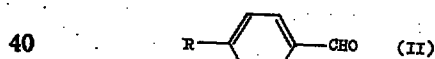
30 p - [(p - n - pentylbenzyliden)amino]benzonitrile in a molar ratio of 2:1 and

p - [(p - n - butoxybenzyliden)amino]benzonitrile with

p - [(p - n - hexylbenzyliden)amino]benzonitrile in a molar ratio of 1:2.

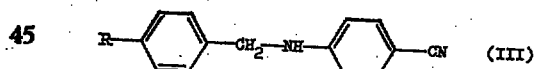
35 The compounds of formula I can be manufactured in accordance with the process provided by the present invention by

a) reacting a compound of the general formula



wherein R has the significance given earlier, with p - aminobenzonitrile, or

b) dehydrogenating a compound of the general formula



wherein R has the significance given earlier.

In embodiment a) of the process provided by the present invention, a p - alkylbenzaldehyde of formula II is reacted with p - aminobenzonitrile. This reaction is expediently carried out in an inert organic solvent; for example, an alcohol such as methanol, ethanol, or isopropanol, a hydrocarbon such as benzene, toluene or xylene or a chlorinated hydrocarbon such as chloroform, methylene chloride or ethylene chloride. The reaction temperature lies between 0°C and 160°C, preferably at between 20°C and 130°C. The reaction is advantageously carried out at normal pressure. By carrying out the reaction in a water-immiscible solvent, the water formed is advantageously separated by means of a water separator. The reaction is accelerated by the addition of a catalytic amount (up to 5% of the aldehyde weight) of a strong inorganic acid such as sulphuric acid or hydrochloric acid or a strong organic acid such as methanesulphonic acid, p - toluenesulphonic acid, benzenesulphonic acid etc.

In embodiment b) of the process provided by the present invention, compounds of formula I are manufactured by dehydrogenating a corresponding compound of formula III. For the dehydrogenation there can be used any dehydrogenating known per se for analogous dehydrogenations; for example, potassium permanganate, selenium dioxide, hypochlorite, ferric chloride, chromic acid and silver oxide. Especially preferred is manganese dioxide in a chlorinated hydrocarbon such as chloroform, methylene chloride or ethylene chloride or in a hydrocarbon such as benzene, toluene or xylene. In accordance with a preferred aspect, manganese dioxide (8 moles per mol of compound of formula III) is first heated under reflux in benzene for 5 hours (the water obtained being separated by means of a water separator), the compound of formula III is then added and the mixture heated a further 10 hours under reflux (the water formed being again separated). The reaction is advantageously carried out at normal pressure.

The physical properties of the compounds of formula I are given in the following Table:

TABLE

R	Melting point (m.p.) °C	Clearing point (cl.p) °C
A ethyl	76.2—77.0	63.0—59.7*
B n-propyl	64.8—65.5	77.6
C n-butyl	38.1—38.7	62.6
D n-pentyl	45.6—46.4	75.0
E n-hexyl	32.2—33.0	64.5
F i-hexyl	37.7—38.5	45.3
G n-heptyl	32.7—33.0	72.3
H n-octyl	32.5—32.8	68.8**

* monotrope

** smectic up to 54.4°

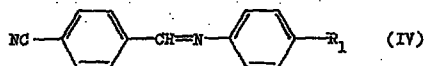
The compounds of formula I are preferably used in the form of mixtures with one another, mixtures which correspond to a eutectic being especially preferred. Examples of some mixtures are given in the following Table:

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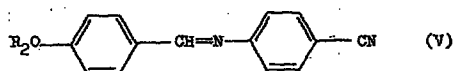
TABLE

Mixture (in mol %)	Melting point (m.p.) °C	Clearing point (cl.p) °C
33% A + 67%E	<10	54.4
33% B + 67%E	<10	62.7
33% C + 67%E	<10	56.8
33% D + 67%E	7	61.7
33% G + 67%E	10	63.7
33% H + 67%E	2	62.9
33% B + 67%G	16	70.8
33% C + 67%G	<10	67.5
33% D + 67%G	12	71.6
33% B + 67%H	<10	65.1
33% C + 67%H	<10	64.5
33% D + 67%H	<10	68.4
33% E + 67%C	<10	59.6

The compounds of formula I can also be used in the form of mixtures with other known nematic or non-nematic substances; for example with compounds of the general formula

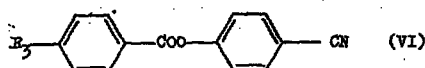


wherein R₁ represents a straight-chain alkyl group containing 4 to 7 carbon atoms, or with compounds of the general formula



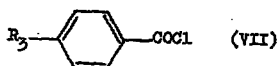
wherein R₂ represents a straight-chain alkyl group containing 4 to 7 carbon atoms or a straight-chain alkanoyl group containing 2 to 8 carbon atoms,

or with compounds of the general formula



wherein R₃ represents a straight-chain alkyl group containing 4 to 8 carbon atoms or a straight-chain alkoxy group containing 5 to 8 carbon atoms.

The compounds of formula VI are described and claimed in our copending Application No. 9052/73 (Serial No. 1,373,610) and can be prepared, for example, by esterifying a compound of the general formula



wherein R₃ has the significance given earlier, with p - hydroxybenzonitrile in a conventional manner.

The following Examples illustrate the process provided by the present invention:

Example 1.

A mixture of 5.9 g (0.05 mol) of p-aminobenzonitrile and 6.7 g (0.05 mol) of p-ethylbenzaldehyde in 100 ml of benzene is treated with 150 mg of p - toluenesulphonic acid, gassed with nitrogen and heated under reflux for 1 hour (bath temperature 120°C). The water formed is separated by means of a water separator. During a further 1 hour, the benzene condensed in the reflux condenser is then led back to the reaction vessel through a layer of 50 g of aluminium oxide (activity I). After cooling, 2 g of solid potassium carbonate are added, the mixture is filtered and

the filtrate freed from the solvent in a vacuum at 50°C (bath temperature). There remain behind 11.5 g of a yellow oil which crystallise with cooling. Purification is carried out by several recrystallisations from isopropanol to a constant melting point and until byproducts are no longer observed in the gas chromatogram. The pure p - [(p - ethylbenzyliden)amino]benzonitrile melts at 76.2°—77.0°C and is liquid crystalline with cooling from 63.0°—59.7°C. UV (ethanol): $\epsilon_{271} = 25800$ (shoulder at 316 nm). The nuclear magnetic resonance, mass spectrum, infrared and microanalysis data confirm the structure.

Example 2.

A mixture of 5.9 g (0.05 mol) of p-aminobenzonitrile and 7.4 g (0.05 mol) of p - n-propylbenzaldehyde in 100 ml of benzene is treated with 150 mg of p - toluenesulphonic acid and reacted as described in Example 1. After evaporation, there remain behind 12.5 g of a yellowish oil which crystallise with cooling. Purification is carried out by several recrystallisations from isopropanol as described in Example 1. The pure p - [(p - n-propylbenzyliden)amino]benzonitrile has a melting point of 64.8°—65.5°C and a clearing point of 77.6°C. UV (ethanol): $\epsilon_{280} = 24300$ (shoulder at 310 nm). The nuclear magnetic resonance, mass spectrum, infrared and microanalysis data confirm the structure.

Example 3.

A mixture of 11.8 g (0.1 mol) of p-aminobenzonitrile and 16.2 g (0.1 mol) of p - n-butylbenzaldehyde in 200 ml of benzene is treated with 300 mg of p - toluenesulphonic acid and reacted as described in Example 1. After the addition of 3 g of solid potassium carbonate, the mixture is filtered and evaporated. There are obtained 27.0 g of a yellow oil which crystallise with cooling. Purification is carried out by several recrystallisations from isopropanol as described in Example 1. The pure p - [(p - n-butylbenzyliden)amino]benzonitrile has a melting point of 38.1°—38.7°C and a clearing point of 62.6°C. UV (ethanol): $\epsilon_{280} = 24900$ (shoulder at 314 nm). The nuclear magnetic resonance, mass spectrum, infrared and microanalysis data confirm the structure.

Example 4.

A mixture of 5.9 g (0.05 mol) of p-aminobenzonitrile and 8.8 g (0.05 mol) of p - n-pentylbenzaldehyde in 100 ml of benzene is treated with 150 mg of p - toluenesulphonic acid and reacted as described in Example 1. After evaporation, there remain behind 13.9 g of a yellow oil which crystallise with cooling. Purification is carried out by several recrystallisations from isopropanol as described in Example 1. The pure p - [(p - n-pentyl-

benzyliden)amino]benzonitrile has a melting point of 45.6°—46.4°C and a clearing point of 75.0°C. UV (ethanol): $\epsilon_{279} = 24400$ (shoulder at 314 nm). The nuclear magnetic resonance, mass spectrum, infrared and microanalysis data confirm the structure.

Example 5.

A mixture of 5.9 g (0.05 mol) of p-amino-benzonitrile and 9.5 g (0.05 mol) of p - n-hexylbenzaldehyde in 100 ml of benzene is treated with 150 mg of p - toluenesulphonic acid and reacted as described in Example 1. After evaporation, there remain behind 14.4 g of a brownish oil which crystallise with cooling. Purification is carried out by several recrystallisations from isopropanol as described in Example 1. The pure p - [(p - n - hexylbenzyliden)amino]benzonitrile has a melting point of 32.2°C—33.0°C and a clearing point of 64.5° C. UV (ethanol): $\epsilon_{291} = 23500$ (shoulder at 310 nm). The nuclear magnetic resonance, mass spectrum, infrared and microanalysis data confirm the structure.

The starting material is prepared as follows:

p - n - Hexylbenzaldehyde is prepared according to the method of A. Rieche et al., Chem. Ber. 93, 88 (1960):

To a cooled mixture of 42.5 g (0.274 mol) of n - hexylbenzene, 146 ml of methylene chloride and 48 ml (0.437 mol) of titanium tetrachloride there are added dropwise 25.1 g (0.218 mol) of dichloromethyl ether with nitrogen gassing and stirring over a period of 20 minutes at 0°—5°C. The mixture is stirred for 15 minutes at 0°—5°C and then for 15 minutes at 20°C. The dark brown solution is poured on to 600 g of ice, extracted with ether, the organic layer washed with water, sodium carbonate solution and again with water, dried over sodium sulphate and the solvent removed under a vacuum. There are thus obtained 48.7 g of a brownish oil which, according to gas chromatography, consist of up to 41% of n - hexylbenzene, up to 12% of o - hexylbenzaldehyde and up to 47% of p - n - hexylbenzaldehyde. The mixture is separated by distillation in an efficient column. The pure p - n - hexylbenzaldehyde boils at 113°—115°C/2.7 mm.

Example 6.

A mixture of 5.9 g (0.05 mol) of p-amino-benzonitrile and 9.5 g (0.05 mol) of p - isohexylbenzaldehyde in 100 ml of benzene is treated with 150 mg of p - toluenesulphonic acid and reacted as described in Example 1. After evaporation, there remain behind 14.2 g of a yellow oil which crystallises with cooling. Purification is carried out by several recrystallisations from isopropanol as described in Example 1. The pure p - [(p - isohexylbenzyliden)amino]benzonitrile has a melting point of 37.7—38.5°C and a clearing point of 45.3°

C. UV (ethanol): $\epsilon_{280} = 23900$ (shoulder at 308 nm). The nuclear magnetic resonance, mass spectrum, infrared and microanalysis data confirm the structure.

The starting material can be prepared as follows:

To a cooled mixture of 110.3 g (0.68 mol) of isohexylbenzene, 380 ml of methylene chloride and 124.5 ml (1.13 mol) of titanium tetrachloride there are added dropwise 65.0 g (0.565 mol) of dichloromethyl ether with nitrogen gassing over a period of 20 minutes at 0°—5°C. The mixture is stirred for 15 minutes at 0°—5°C and then for 15 minutes at 20°C. The dark brown solution is poured on to 1555 g of ice and extracted with ether. After drying and evaporation of the solvent, there remain behind 121.3 g of a brownish oil which are pre-purified by normal distillation under a vacuum. The fraction distilling at up to 143°C/13 mm (25.7 g) consists of isohexylbenzene, the fraction distilling at 143°—146°C/13 mm (65.0 g) consists, according to gas chromatography, of up to 20% of o - isohexylbenzaldehyde and up to 78% of p - isohexylbenzaldehyde. This mixture is separated by distillation in an efficient column. The pure p - isohexylbenzaldehyde boils at 141°—145°C/14 mm.

Example 7.

A mixture of 5.9 (0.05 mol) of p - amino-benzonitrile and 10.2 g (0.05 mol) of p - n-heptylbenzaldehyde in 100 ml of benzene is treated with 150 mg of p - toluenesulphonic acid and reacted as described in Example 1. After cooling, there remain behind 15.4 g of a yellow oil which crystallise with cooling. Purification is carried out by several recrystallisations from isopropanol as described in Example 1. The pure p - [(p - n - heptylbenzyliden)amino]benzonitrile has a melting point of 32.7°—33.0°C and a clearing point of 72.3°C. UV (ethanol): $\epsilon_{281} = 24100$ (shoulder at 310 nm). The nuclear magnetic resonance, mass spectrum, infrared and microanalysis data confirm the structure.

The starting material can be prepared as follows:

To a cooled mixture of 97.3 g (0.548 mol) of n - heptylbenzene, 310 ml of methylene chloride and 102 ml (0.924 mol) of titanium tetrachloride there are added dropwise 53.3 g (0.463 mol) of dichloromethyl ether with nitrogen gassing over a period of 20 minutes at 0°—5°C. The mixture is stirred for 15 minutes at 0°—5°C and then for 15 minutes at 20°C. The dark brown solution is poured on to 1270 g of ice and extracted with ether. After drying and evaporation of the solvent, there remain behind 106.1 g of a brown oil which is pre-purified by normal distillation under a vacuum. The fraction distilling at up to 165°C/17 mm (23.2 g) consists of n-heptylbenzene, the fraction distilling at 166°—

168°C/17 mm (55.7 g) consists, according to gas chromatography, of up to 20% of o-heptylbenzaldehyde and up to 77% of p-n-heptylbenzaldehyde. This mixture is separated by distillation in an efficient column. The pure p-n-heptylbenzaldehyde boils at 166°–168°C/12 mm.

Example 8.

A mixture of 5.9 g (0.05 mol) of p-amino-benzonitrile and 10.9 g (0.05 mol) of p-n-octylbenzaldehyde in 100 ml of benzene is treated with 150 mg of p-toluenesulphonic acid and reacted as described in Example 1. After evaporation there remain behind 16.5 g of a yellow oil which crystallise with cooling. Purification is carried out by several recrystallisations from isopropanol as described in Example 1. The pure p-[(p-n-octylbenzyliden)amino]benzonitrile has a melting point of 32.5°–32.8°C and a clearing point of 68.8°C. Up to 54.4°C the compound is smectic. UV (ethanol): ϵ_{280} = 24200 (shoulder at 312 nm). The nuclear magnetic resonance, mass spectrum, infrared and microanalysis data confirm the structure.

The starting material can be prepared as follows:

To a cooled mixture of 86.8 g (0.456 mol) of n-octylbenzene, 255 ml of methylene chloride and 82.6 ml (0.748 mol) of titanium tetrachloride there are added dropwise 43.2 g (0.375 mol) of dichloromethyl ether with nitrogen gassing over a period of 20 minutes at 0°–5°C. The mixture is stirred for 15 minutes at 0–5°C and then for 15 minutes at 20°C. The dark brown solution is poured on to 1030 g of ice and extracted with ether. After drying and evaporation of the solvent, there remain behind 96.8 g of a brown oil which is pre-purified by normal distillation under a vacuum. The fraction distilling at up to 160°C/14 mm (22.9 g) consists of n-octylbenzene, the fraction distilling at 161°–180°C/14 mm (52.8 g) consists, according to gas chromatography, of up to 18% of o-n-octylbenzaldehyde and up to 76% of p-n-octylbenzaldehyde. This mixture is then separated by distillation with an efficient column. The pure p-n-octylbenzaldehyde boils at 170°–173°C/13 mm.

Example 9.

34.7 g (0.40 mol) of manganese dioxide [prepared according to J. Org. Chem. 29, 1540 (1964)] are boiled under reflux in a nitrogen stream together with 500 ml of benzene for 5 hours and the water formed is separated with a water separator. Then there are added 11.80 g (0.05 mol) of p-[(p-ethylbenzyl)amino]benzonitrile [prepared, for example, by reacting 4-fluorobenzonitrile with p-ethylbenzylamine according to J. Org. Chem. 31, 2319 (1966)], the mixture is boiled under reflux a further 10 hours and

the water separated as described earlier. After cooling, the mixture is filtered through Celite (trade mark), re-washed with benzene and freed from solvent under a vacuum (bath temperature 50°C). There are obtained 10.5 g of a yellow oil which crystallise with cooling. Purification is carried out by several recrystallisations from isopropanol as described in Example 1. There is thus obtained pure p-[(p-ethylbenzyliden)amino]benzonitrile which is identical in all respects with the product obtained according to Example 1.

The following Example illustrates the preparation of a compound of formula VI hereinbefore:

Example A.

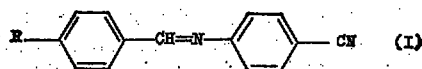
3.1 g (26 mmol) of p-hydroxybenzonitrile are dissolved in 40 ml of absolute pyridine. 6 g (28.5 mmol) of p-n-pentylbenzoic acid chloride in 20 ml of benzene are then introduced dropwise at room temperature and the mixture is subsequently stirred overnight. After heating for a short time, the mixture is worked up as described in Example 1 to give 7.5 g of crude ester. This is chromatographed on silicagel using toluene/acetone (19:1). From the uniform fraction there are obtained, after recrystallisation from hexane, 2.6 g of p-n-pentylbenzoic acid p-cyanophenyl ester having a melting point of 60.5° and a monotropic clearing point of 56.5°C.

The acid halide starting material can be prepared as follows:

15 g of p-n-pentylbenzoic acid are dissolved in 100 ml of thionyl chloride and boiled under reflux for 1 hour. The excess thionyl chloride is then removed by distillation and the acid chloride is distilled in a high vacuum. It has a boiling point of 104°C/2 mm.

WHAT WE CLAIM IS:—

1. Compounds of the general formula



wherein R represents the ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, isohexyl, n-heptyl or n-octyl group.

2. p-[(p-ethylbenzyliden)amino]benzonitrile.
3. p-[(p-n-propylbenzyliden)amino]benzonitrile.
4. p-[(p-n-butylbenzyliden)amino]benzonitrile.
5. p-[(p-n-pentylbenzyliden)amino]benzonitrile.
6. p-[(p-n-hexylbenzyliden)amino]benzonitrile.
7. p-[(p-isohexylbenzyliden)amino]benzonitrile.
8. p-[(p-n-heptylbenzyliden)amino]benzonitrile.

168°C/17 mm (55.7 g) consists, according to gas chromatography, of up to 20% of o-heptylbenzaldehyde and up to 77% of p-n-heptylbenzaldehyde. This mixture is separated by distillation in an efficient column. The pure p-n-heptylbenzaldehyde boils at 166°—168°C/12 mm.

Example 8.

A mixture of 5.9 g (0.05 mol) of p-amino-benzonitrile and 10.9 g (0.05 mol) of p-n-octylbenzaldehyde in 100 ml of benzene is treated with 150 mg of p-toluenesulphonic acid and reacted as described in Example 1. After evaporation there remain behind 16.5 g of a yellow oil which crystallise with cooling. Purification is carried out by several recrystallisations from isopropanol as described in Example 1. The pure p-[(p-n-octylbenzyliden)amino]benzonitrile has a melting point of 32.5°—32.8°C and a clearing point of 68.8°C. Up to 54.4°C the compound is smectic. UV (ethanol): $\epsilon_{280} = 24200$ (shoulder at 312 nm). The nuclear magnetic resonance, mass spectrum, infrared and microanalysis data confirm the structure.

The starting material can be prepared as follows:

To a cooled mixture of 86.8 g (0.456 mol) of n-octylbenzene, 255 ml of methylene chloride and 82.6 ml (0.748 mol) of titanium tetrachloride there are added dropwise 43.2 g (0.375 mol) of dichloromethyl ether with nitrogen gassing over a period of 20 minutes at 0°—5°C. The mixture is stirred for 15 minutes at 0—5°C and then for 15 minutes at 20°C. The dark brown solution is poured on to 1030 g of ice and extracted with ether. After drying and evaporation of the solvent, there remain behind 96.8 g of a brown oil which is pre-purified by normal distillation under a vacuum. The fraction distilling at up to 160°C/14 mm (22.9 g) consists of n-octylbenzene, the fraction distilling at 161°—180°C/14 mm (52.8 g) consists, according to gas chromatography, of up to 18% of o-n-octylbenzaldehyde and up to 76% of p-n-octylbenzaldehyde. This mixture is then separated by distillation with an efficient column. The pure p-n-octylbenzaldehyde boils at 170°—173°C/13 mm.

Example 9.

34.7 g (0.40 mol) of manganese dioxide [prepared according to J. Org. Chem. 29, 1540 (1964)] are boiled under reflux in a nitrogen stream together with 500 ml of benzene for 5 hours and the water formed is separated with a water separator. Then there are added 11.80 g (0.05 mol) of p-[(p-ethylbenzyl)amino]benzonitrile [prepared, for example, by reacting 4-fluorobenzonitrile with p-ethylbenzylamine according to J. Org. Chem. 31, 2319 (1966)], the mixture is boiled under reflux a further 10 hours and

the water separated as described earlier. After cooling, the mixture is filtered through Celite (trade mark), re-washed with benzene and freed from solvent under a vacuum (bath temperature 50°C). There are obtained 10.5 g of a yellow oil which crystallise with cooling. Purification is carried out by several recrystallisations from isopropanol as described in Example 1. There is thus obtained pure p-[(p-ethylbenzyliden)amino]benzonitrile which is identical in all respects with the product obtained according to Example 1.

The following Example illustrates the preparation of a compound of formula VI hereinbefore:

Example A.

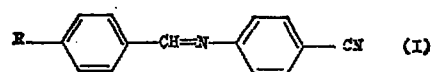
3.1 g (26 mmol) of p-hydroxybenzonitrile are dissolved in 40 ml of absolute pyridine. 6 g (28.5 mmol) of p-n-pentylbenzoic acid chloride in 20 ml of benzene are then introduced dropwise at room temperature and the mixture is subsequently stirred overnight. After heating for a short time, the mixture is worked up as described in Example 1 to give 7.5 g of crude ester. This is chromatographed on silicagel using toluene/acetone (19:1). From the uniform fraction there are obtained, after recrystallisation from hexane, 2.6 g of p-n-pentylbenzoic acid p-cyanophenyl ester having a melting point of 60.5° and a monotropic clearing point of 56.5°C.

The acid halide starting material can be prepared as follows:

15 g of p-n-pentylbenzoic acid are dissolved in 100 ml of thionyl chloride and boiled under reflux for 1 hour. The excess thionyl chloride is then removed by distillation and the acid chloride is distilled in a high vacuum. It has a boiling point of 104°C/2 mm.

WHAT WE CLAIM IS:—

1. Compounds of the general formula



wherein R represents the ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, isohexyl, n-heptyl or n-octyl group.

2. p-[(p-ethylbenzyliden)amino]benzonitrile.

3. p-[(p-n-propylbenzyliden)amino]benzonitrile.

4. p-[(p-n-butylbenzyliden)amino]benzonitrile.

5. p-[(p-n-pentylbenzyliden)amino]benzonitrile.

6. p-[(p-n-hexylbenzyliden)amino]benzonitrile.

7. p-[(p-isohexylbenzyliden)amino]benzonitrile.

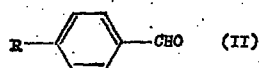
8. p-[(p-n-heptylbenzyliden)amino]benzonitrile.



9. p - [(p - n - octylbenzyliden)amino]benzonitrile.

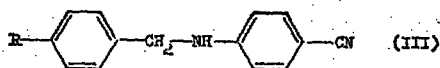
10. A process for the manufacture of the compounds of formula I given in claim 1, which process comprises

a) reacting a compound of the general formula



wherein R has the significance given in claim 1, with p-aminobenzonitrile, or

b) dehydrogenating a compound of the general formula



wherein R has the significance given in claim 1.

11. A process according to claim 10 for the manufacture of p - [(p - ethylbenzyliden)amino]benzonitrile, wherein p - ethylbenzaldehyde is reacted with p - aminobenzonitrile.

12. A process according to claim 10 for the manufacture of p - [(p - n - propylbenzyliden)amino]benzonitrile, wherein p - n - propylbenzaldehyde is reacted with p-aminobenzonitrile.

13. A process according to claim 10 for the manufacture of p - [(p - n - butylbenzyliden)amino]benzonitrile, wherein p-n-butylbenzaldehyde is reacted with p - aminobenzonitrile.

14. A process according to claim 10 for the manufacture of p - [(p - n - hexylbenzyliden)amino]benzonitrile, wherein p - n - hexylbenzaldehyde is reacted with p - aminobenzonitrile.

15. A process according to claim 10 for the manufacture of p - [(p - isoheptylbenzyliden)amino]benzonitrile, wherein p - isoheptylbenzaldehyde is reacted with p - aminobenzonitrile.

16. A process according to claim 10 for the manufacture of p - [(p - n - heptylbenzyliden)amino]benzonitrile, wherein p - n - heptylbenzaldehyde is reacted with p - aminobenzonitrile.

17. A process according to claim 10 for the manufacture of p - [(p - n - octylbenzyliden)amino]benzonitrile, wherein p - n - octylbenzaldehyde is reacted with p - aminobenzonitrile.

18. A process according to claim 10 for the manufacture of p - [(p - ethylbenzyliden)amino]benzonitrile, wherein p - [(p - ethylbenzyl)amino]benzonitrile is dehydrogenated.

19. A process for the manufacture of the

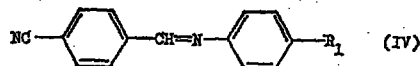
compounds of formula I given in claim 1, substantially as hereinbefore described with reference to Examples 1 to 9.

20. Compounds of formula I given in claim 1, when manufactured by the process claimed in any one of claims 10 to 19 inclusive.

21. A nematic mixture for electro-optical purposes which consists of a mixture of compounds of formula I given in claim 1 with one another and/or with other nematic substances and/or with non-nematic substances.

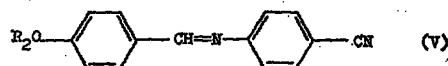
22. A nematic mixture according to claim 21 which consists of compounds of formula I given in claim 1.

23. A nematic mixture according to claim 21 which consists of compounds of formula I given in claim 1 and compounds of the general formula



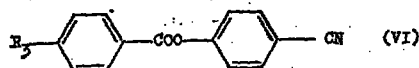
wherein R₁ represents a straight-chain alkyl group containing 4 to 7 carbon atoms.

24. A nematic mixture according to claim 21 which consists of compounds of formula I given in claim 1 and compounds of the general formula



wherein R₂ represents a straight-chain alkyl group containing 4 to 7 carbon atoms or a straight-chain alkanoyl group containing 2 to 8 carbon atoms.

25. A nematic mixture according to claim 21 which consists of compounds of formula I given in claim 1 and compounds of the general formula



wherein R₃ represents a straight-chain alkyl group containing 4 to 8 carbon atoms or a straight-chain alkoxy group containing 5 to 8 carbon atoms.

26. A nematic mixture according to any one of claims 21 to 24 inclusive, wherein p-[(p-n-hexylbenzyliden)amino]benzonitrile is present as the compound of formula I.

27. A nematic mixture according to any one of claims 21 to 24 inclusive, wherein p-[(p-n-heptylbenzyliden)amino]benzonitrile is present as the compound of formula I.

28. A nematic mixture according to any





* C L M S *

one of claims 21 to 24 inclusive, wherein p - [(p - n - octylbenzyliden)amino]benzonitrile is present as the compound of formula I.

5 29. A nematic mixture according to any one of claims 21, 22 and 26 which consists of p - [(p - ethylbenzyliden)amino]benzonitrile and p - [(p - n - hexylbenzyliden)amino]benzonitrile.

10 30. A nematic mixture according to any one of claims 21, 22 and 26 which consists of p - [(p - n - propylbenzyliden)amino]benzonitrile and p - [(p - n - hexylbenzyliden)amino]benzonitrile.

15 31. A nematic mixture according to any one of claims 21, 22 and 26 which consists of p - [(p - n - butylbenzyliden)amino]benzonitrile and p - [(p - n - hexylbenzyliden)amino]benzonitrile.

20 32. A nematic mixture according to any one of claims 21, 22 and 26 which consists of p - [(p - n - pentylbenzyliden)amino]benzonitrile and p - [(p - n - hexylbenzyliden)amino]benzonitrile.

25 33. A nematic mixture according to any one of claims 21, 22, 26 and 27 which consists of p - [(p - n - heptylbenzyliden)amino]benzonitrile and p - [(p - n - hexylbenzyliden)amino]benzonitrile.

30 34. A nematic mixture according to any one of claims 21, 22, 26 and 28 which consists of p - [(p - n - octylbenzyliden)amino]benzonitrile and p - [(p - n - hexylbenzyliden)amino]benzonitrile.

35 35. A nematic mixture according to any one of claims 21, 22 and 27 which consists of p - [(p - n - propylbenzyliden)amino]benzonitrile and p - [(p - n - heptylbenzyliden)amino]benzonitrile.

40 36. A nematic mixture according to any one of claims 21, 22 and 27 which consists of p - [(p - n - butylbenzyliden)amino]benzonitrile and p - [(p - n - heptylbenzyliden)amino]benzonitrile.

45 37. A nematic mixture according to any one of claims 21, 22 and 27 which consists of p - [(p - n - pentylbenzyliden)amino]benzonitrile and p - [(p - n - heptylbenzyliden)amino]benzonitrile.

50 38. A nematic mixture according to any one of claims 21, 22 and 28 which consists of p - [(p - n - propylbenzyliden)amino]benzonitrile and p - [(p - n - octylbenzyliden)amino]benzonitrile.

55 39. A nematic mixture according to any one of claims 21, 22 and 28 which consists of p - [(p - n - butylbenzyliden)amino]benzonitrile and p - [(p - n - octylbenzyliden)amino]benzonitrile.

60 40. A nematic mixture according to any one of claims 21, 22 and 28 which consists of p - [(p - n - pentylbenzyliden)amino]benzonitrile and p - [(p - n - octylbenzyliden)amino]benzonitrile.

65 41. A nematic mixture according to any

one of claims 21, 24 and 26 which consists of p - [(p - n - hexylbenzyliden)amino]benzonitrile and p - [(p - n - butoxybenzyliden)amino]benzonitrile.

42. A process for the production of nematic mixtures for electro-optical purposes, which process comprises mixing compounds of formula I given in claim 1 with one another and/or with other nematic substances and/or with non-nematic substances.

43. A process according to claim 42, wherein compounds of formula I given in claim 1 are mixed with one another.

44. A process according to claim 42, wherein a compound of formula I given in claim 1 is mixed with a compound of formula IV given in claim 23.

45. A process according to claim 42, wherein a compound of formula I given in claim 1 is mixed with a compound of formula V given in claim 24.

46. A process according to claim 42, wherein a compound of formula I given in claim 1 is mixed with a compound of formula VI given in claim 25.

47. A process according to any one of claims 42 to 46 inclusive, wherein p - [(p - n - hexylbenzyliden)amino]benzonitrile is used as the compound of formula I.

48. A process according to any one of claims 42 to 46 inclusive, wherein p - [(p - n - heptylbenzyliden)amino]benzonitrile is used as the compound of formula I.

49. A process according to any one of claims 42 to 46 inclusive, wherein p - [(p - n - octylbenzyliden)amino]benzonitrile is used as the compound of formula I.

50. A process according to any one of claims 42, 43 and 47, wherein p - [(p - ethylbenzyliden)amino]benzonitrile is mixed with p - [(p - n - hexylbenzyliden)amino]benzonitrile.

51. A process according to any one of claims 42, 43 and 47, wherein p - [(p - n - propylbenzyliden)amino]benzonitrile is mixed with p - [(p - n - hexylbenzyliden)amino]benzonitrile.

52. A process according to any one of claims 42, 43 and 47, wherein p - [(p - n - butylbenzyliden)amino]benzonitrile is mixed with p - [(p - n - hexylbenzyliden)amino]benzonitrile.

53. A process according to any one of claims 42, 43 and 47, wherein p - [(p - n - pentylbenzyliden)amino]benzonitrile is mixed with p - [(p - n - hexylbenzyliden)amino]benzonitrile.

54. A process according to any one of claims 42, 43, 47 and 48, wherein p - [(p - n - heptylbenzyliden)amino]benzonitrile is mixed with p - [(p - n - hexylbenzyliden)amino]benzonitrile.

55. A process according to any one of claims 42, 43, 47 and 49, wherein p - [(p - n - octylbenzyliden)amino]benzonitrile is mixed

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with p - [(p - n - hexylbenzyliden)amino]-benzonitrile.

56. A process according to any one of claims 42, 43 and 48, wherein p - [(p - n-propylbenzyliden)amino]benzonitrile is mixed with p - [(p - n - heptylbenzyliden)amino]-benzonitrile.

57. A process according to any one of claims 42, 43 and 48, wherein p - [(p - n-butylbenzyliden)amino]benzonitrile is mixed with p - [(p - n - heptylbenzyliden)amino]-benzonitrile.

58. A process according to any one of claims 42, 43 and 48, wherein p - [(p - n-pentylbenzyliden)amino]benzonitrile is mixed with p - [(p - n - heptylbenzyliden)amino]-benzonitrile.

59. A process according to any one of claims 42, 43 and 49, wherein p - [(p - n-propylbenzyliden)amino]benzonitrile is mixed with p - [(p - n - octylbenzyliden)amino]-benzonitrile.

60. A process according to any one of claims 42, 43 and 49, wherein p - [(p - n-butylbenzyliden)amino]benzonitrile is mixed with p - [(p - n - octylbenzyliden)amino]-benzonitrile.

61. A process according to any one of claims 42, 43 and 49, wherein p - [(p - n-pentylbenzyliden)amino]benzonitrile is mixed with p - [(p - n - octylbenzyliden)amino]-benzonitrile.

62. A process according to any one of claims 42, 45 and 47, wherein p - [(p - n - hexylbenzyliden)amino]benzonitrile is mixed with p - [(p - n - butoxybenzyliden)amino]-benzonitrile.

63. A dielectric for electro-optical purposes containing a compound as claimed in any one of claims 1 to 10 inclusive in liquid crystalline form.

64. A dielectric for electro-optical purposes consisting of a liquid crystalline mixture as claimed in any one of claims 21, 22 and 26 to 41 inclusive.

65. A dielectric for electro-optical purposes consisting of a liquid crystalline mixture as claimed in any one of claims 23 to 25 inclusive.

66. A process for the production of a dielectric for electro-optical purposes, which process comprises using nematic compounds of formula I given in claim 1 or mixtures thereof with one another and/or with other nematic substances and/or with non-nematic substances.

67. A process according to claim 66, wherein a mixture of compounds of formula I is used.

68. A process according to claim 66, wherein a mixture of a compound of formula I with a compound of formula IV given in claim 23 is used.

69. A process according to claim 66, wherein a mixture of a compound of formula I with

a compound of formula V is given in claim 24 is used.

70. A process according to claim 66, wherein a mixture of a compound of formula I with a compound of formula VI given in claim 25 is used.

71. A process according to any one of claims 66 to 70 inclusive, wherein p - [(p - n-hexylbenzene)amino]benzonitrile is used.

72. A process according to any one of claims 66 to 70 inclusive, wherein p - [(p - n-heptylbenzyliden)amino]benzonitrile is used.

73. A process according to any one of claims 66 to 70 inclusive, wherein p - [(p - n-octylbenzyliden)amino]benzonitrile is used.

74. A process according to any one of claims 66, 67 and 71, wherein a mixture of p - [(p - ethylbenzyliden)amino]benzonitrile and p - [(p - n - hexylbenzyliden)amino]-benzonitrile is used.

75. A process according to any one of claims 66, 67 and 71, wherein a mixture of p - [(p - n - propylbenzyliden)amino]benzonitrile and p - [(p - n - hexylbenzyliden)-amino]benzonitrile is used.

76. A process according to any one of claims 66, 67 and 71, wherein a mixture of p - [(p - n - butylbenzyliden)amino]benzonitrile and p - [(p - n - hexylbenzyliden)-amino]benzonitrile is used.

77. A process according to any one of claims 66, 67 and 71, wherein a mixture of p - [(p - n - pentylbenzyliden)amino]benzonitrile and p - [(p - n - hexylbenzyliden)-amino]benzonitrile is used.

78. A process according to any one of claims 66, 67, 71 and 72, wherein a mixture of p - [(p - n - heptylbenzyliden)amino]-benzonitrile and p - [(p - n - hexylbenzyliden)amino]benzonitrile is used.

79. A process according to any one of claims 66, 67, 71 and 73, wherein a mixture of p - [(p - n - octylbenzyliden)amino]-benzonitrile and p - [(p - n - hexylbenzyliden)-amino]benzonitrile is used.

80. A process according to any one of claims 66, 67 and 72, wherein a mixture of p - [(p - n - propylbenzyliden)amino]benzonitrile and p - [(p - n - heptylbenzyliden)-amino]benzonitrile is used.

81. A process according to any one of claims 66, 67 and 72, wherein a mixture of p - [(p - n - butylbenzyliden)amino]-benzonitrile and p - [(p - n - heptylbenzyliden)-amino]benzonitrile is used.

82. A process according to any one of claims 66, 67 and 72, wherein a mixture of p - [(p - n-pentylbenzyliden)amino]benzonitrile and p - [(p - n - heptylbenzyliden)amino]benzonitrile is used.

83. A process according to any one of claims 66, 67 and 73, wherein a mixture of p - [(p - n - propylbenzyliden)amino]benzonitrile and p - [(p - n - octylbenzyliden)-amino]benzonitrile is used.



84. A process according to any one of claims 66, 67 and 73, wherein a mixture of p - [(p - n - butylbenzyliden)amino]benzonitrile and p - [(p - n - octylbenzyliden)amino]benzonitrile is used.

85. A process according to any one of claims 66, 67 and 73, wherein a mixture of p - [(p - n - pentylbenzyliden)amino]benzonitrile and p - [(p - n - octylbenzyliden)amino]benzonitrile is used.

86. A process according to any one of claims 66, 69 and 71, wherein a mixture of p - [(p - n - hexylbenzyliden)amino]benzonitrile and p - [(p - n - butoxybenzyliden)amino]benzonitrile is used.

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