Liquid Crystals for Non-linear Optics: Mesophases Formed by Push–Pull Stilbenes and Diacetylenes

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The push–pull stilbene and diacetylene derivatives (**1f**—**h**) and (**2c**—**k**) display nematic and smectic phases, which may be of special interest for their non-linear optical properties.

The search for new materials exhibiting non-linear optical properties represents an active field of molecular engineering.[1—4] Non-centrosymmetric, highly polarizable organic molecules are likely to yield materials displaying especially large macroscopic optical non-linearity. Conjugated systems bearing a donor group at one end and an acceptor group at the other end should possess such properties. Furthermore, enhanced physical properties may be expected if these molecules are incorporated into organized supramolecular arrangements such as liquid crystals. Numerous organic molecules, in particular stilbene and diacetylene derivatives, have been found to present large optical non-linearity.[1—3]

We report here some results on two types of molecules which have been designed to combine several features of interest both from the molecular and the materials point of view: the mesogenic push–pull stilbenes (**1f**—**h**) and diacetylenes (**2c**—**k**); the latter combine three features each worth investigating for their own sake: the diacetylene unit, push–pull substitution, and liquid crystalline properties.

Reaction of *p*-nitrophenylacetic acid with *p*-acetamidobenzaldehyde (**3a**) (piperidine–pyridine 1 : 10, reflux) gave the amide (**1a**) (58% yield; m.p. 251.5 °C, lit.[5] 255 °C). Deacylation (conc. HCl, ethanol, reflux) of (**1a**) afforded 4-amino-4′-nitro-*trans*-stilbene (**1b**) (80% yield; m.p. 249 °C from pyridine, lit.[5] 245 °C). The alkylated derivatives (**1d**—**h**) have been obtained either by condensation (piperidine–pyridine 1 : 4, reflux) of *p*-nitrophenylacetic acid with the aldehydes

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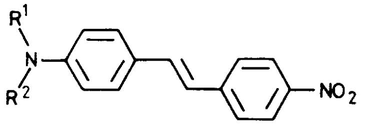
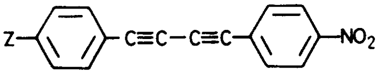
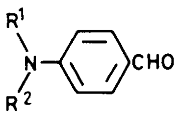
† ER 285 of the CNRS.


(**1**)

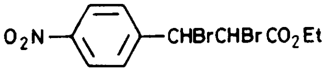
a; R^1 = MeCO, R^2 = H
b; R^1 = R^2 = H
c; R^1 = R^2 = Me
d; R^1 = n-C_7H_{15}, R^2 = Me
e; R^1 = n-$C_{12}H_{25}$, R^2 = Me
f; R^1 = n-$C_{12}H_{25}$, R^2 = H
g; R^1 = n-$C_7H_{15}O$-*p*-$C_6H_4CH_2$, R^2 = H
h; R^1 = n-$C_{12}H_{25}O$-*p*-$C_6H_4CH_2$, R^2 = H
i; R^1 = n-$C_{12}H_{25}O$-*p*-$C_6H_4CH_2$, R^2 = Me

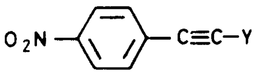

(**2**)

a; Z = NO_2
b; Z = NH_2
c; Z = n-$C_6H_{13}NH$
d; Z = n-$C_7H_{15}NH$
e; Z = n-$C_8H_{17}NH$
f; Z = n-$C_9H_{19}NH$
g; Z = n-$C_{10}H_{21}NH$
h; Z = n-$C_{11}H_{23}NH$
i; Z = n-$C_{12}H_{25}NH$
j; Z = $CH_2{=}CH[CH_2]_3NH$
k; Z = $CH_2{=}CH[CH_2]_6NH$
l; Z = $Me[OCH_2CH_2]_2NH$
m; Z = $Et[OCH_2CH_2]_2NH$
n; Z = $Me[OCH_2CH_2]_3NH$
p; Z = $Et[OCH_2CH_2]_3NH$


(**3**)

a; R^1 = MeCO, R^2 = H
b; R^1 = n-C_7H_{15}, R^2 = Me
c; R^1 = n-$C_{12}H_{25}$, R^2 = Me


(**4**)


(**5**)

a; Y = CO_2H
b; Y = H

(**3b**) and (**3c**) prepared according to ref. 6 without purification [compound (**1d**) recrystallized from a benzene–cyclohexane mixture and (**1e**) recrystallized from cyclohexane; red crystals; *ca.* 10% yield], or by direct alkylation[7] of (**1b**) with n-$C_{12}H_{25}Br$ (1 equiv.) in *N,N'*-dimethylpropylene urea (DMPU)[8] at 70 °C (**1f**), or with *p*-$ROC_6H_4CH_2Cl$ (0.9 equiv.) in *N,N'*-dimethylformamide (DMF) at 80 °C, (**1g**) and (**1h**), both in the presence of an excess of $NaHCO_3$. The secondary amines were purified by t.l.c. (silica gel, $CHCl_3$ eluant) and recrystallized from cyclohexane [(**1f**) 37% yield; red crystals] or from MeCN[(**1g**) and (**1h**) *ca.* 30% yield; red crystals]. Methylation of (**1h**) with methyl iodide gave (**1i**).

Double dehydrobromination of the dibromide (**4**) derived from ethyl *p*-nitrocinnamate gave the acetylenic acid (**5a**),[9] which was decarboxylated to *p*-nitrophenylacetylene (**5b**) (65% overall yield).[10] Coupling of two molecules of (**5b**) [2 equiv. $Cu(AcO)_2{\cdot}1H_2O$, pyridine–methanol 1 : 1][11] gave di-(*p*-nitrophenyl)diacetylene (**2a**) (95% yield).[12] The mono-reduced amino-nitro compound (**2b**) was obtained by treatment of (**2a**) with stannous chloride [3.6 equiv. $SnCl_2{\cdot}2H_2O$ in tetrahydrofuran (THF) in the presence of 10 equiv. conc. HCl, 60 °C, 15 min]. After neutralization with dilute NaOH (0 °C), unreacted (**2a**) (13%) was crystallized from THF, and crude (**2b**) was purified by crystallization from $CHCl_3$ and flash chromatography of the mother liquors (silica gel, CH_2Cl_2 55% yield; bright copper-orange crystals from $CHCl_3$, m.p. 262 °C decomp.); the diamine (25% yield; m.p. 205 then 217 °C, lit.[12] 203 °C) was also obtained. Direct alkylation of (**2b**)[7] with the appropriate bromide or toluene-*p*-sulphonate (5—10 equiv. in DMPU, $NaHCO_3$ 10 equiv., 90 °C) gave the monoalkylated derivatives (**2c—p**) which were purified by flash chromatography or t.l.c. [eluant for (**2c—k**): $CHCl_3$–hexane 4 : 1 to 1 : 1, *ca.* 50% yield; for (**2l—p**): CH_2Cl_2–diethyl ether 9 : 1, 20–30% yield] and crystallized from EtOAc, or from EtOAc–hexane or EtOAc–EtOH mixtures. All new compounds had spectral and microanalytical properties in agreement with their structure.

Twelve compounds (**1f—h**) and (**2c—k**) among the twenty new molecules synthesized, (**1d—i**), and (**2b—p**), present one or several mesophases which have been examined under the polarizing microscope.‡ Their transition temperatures have been measured by differential scanning microcalorimetry (Table 1).

Table 1. Transition temperatures (°C) measured for compounds of types (**1**) and (**2**).[a]

(**1d**)	$K \xrightarrow{141} I$	(**2c**)	$K \xrightarrow{127{\cdot}5} N \xrightarrow{146} I$
(**1e**)	$K \xrightarrow{133} I$	(**2d**)	$K_1 \xrightarrow{100} K_2 \xrightarrow{115{\cdot}5} N \xrightarrow{132} I$
(**1f**)	$K \xrightarrow{109} S_E \xrightarrow{141} I$	(**2e**)	$K \xrightarrow{124} N \xrightarrow{136} I$
(**1g**)	$K (\xrightarrow{94} S_E) \xrightarrow{100} S_A \xrightarrow{174{\cdot}5} I$	(**2f**)	$K_1 \xrightarrow{105} K_2 (\xrightarrow{109} S_A) \xrightarrow{112} N \xrightarrow{127{\cdot}5} I$
(**1h**)	$K_1 \xrightarrow{99} K_2 \xrightarrow{108} S_A \xrightarrow{178} I$	(**2g**)	$K (\xrightarrow{117} S_A) \xrightarrow{122} N \xrightarrow{130} I$
(**1i**)	$K \xrightarrow{133} I$	(**2h**)	$K \xrightarrow{112} S_A \xrightarrow{125} N \xrightarrow{129} I$
		(**2i**)	$K (\xrightarrow{120} S_A) \xrightarrow{124} I$
		(**2j**)	$K_1 \xrightarrow{128} K_2 \xrightarrow{143} N \xrightarrow{149{\cdot}5} I$
		(**2k**)	$K_1 \xrightarrow{111} N \xrightarrow{128} I$
		(**2l**)	$K \xrightarrow{104} I$
		(**2m**)	$K \xrightarrow{88} I$
		(**2n**)	$K \xrightarrow{61} I$
		(**2p**)	$K \xrightarrow{61} I$

[a] K: crystal; N: nematic phase; S_A: smectic A phase; S_E: smectic E phase; I: isotropic liquid; ( ): metastable mesophase; S_E: optical textures are indicative of a smectic E phase (L. Liébert, personal communication).

The stilbene derivatives (**1f—h**) present only smectic mesophases of type A and/or of type E, in which the molecules are organized in parallel layers with their main axis oriented perpendicularly to the surface of the layers without particular organization (S_A) or following a pseudo-hexagonal lattice with a 'herring-bone' packing (S_E).[14] The mesomorphic domain is considerably enlarged by the presence of a *p*-alkoxybenzyl group (compounds **1g**, **h**). On the other hand, comparing (**1e**)

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‡ Some other mesogenic mono-alkylated aniline derivatives have been reported.[13]

with (**1f**) and (**1h**) with (**1i**) shows that N-methylation destroys the mesomorphic order.

The mesogenic diacetylenic compounds of type (**2**) present, in addition to a smectic A phase, a nematic phase in which the only order is the parallelism of the main axes of the molecules, whereas their centres of gravity are randomly distributed. The mesomorphic properties of compounds (**2c—i**) are those of a homologous series: for the short chains, only a nematic phase is observed, compounds (**2c—e**); when the chain length increases, smectic mesomorphism appears first, together with the nematic phase, compounds (**2f—h**), and then exists alone for the C_{12} chain in (**2i**). The polyoxygenated compounds (**2l—p**) exhibit, as expected, lower melting points, but they are not mesogenic.

The compounds of types (**1**) and (**2**) are highly polarizable, push–pull conjugated systems which should present interesting optical properties. Indeed, the N,N-dimethyl parent stilbene derivative (**1c**) (DMANS) has a large ground state dipole moment (*ca.* 7.5 D[§]) which increases strongly (by *ca.* 25 D) in the first singlet excited state;[15] furthermore, it presents very pronounced non-linear optical properties.[1—3] The dipole moment of (**1h**) is 5.04 D for the neat isotropic phase and 5.75 D in solution (1.55% in CCl_4); a value of 6.1 D may be calculated.

Preliminary measurements of the non-linear optical properties showed that compound (**1g**) (powder) has a second harmonic generation effect similar to urea,[16] whereas push–pull diacetylenes (**2b**), (**2d—f**) (powder) show a frequency doubling slightly stronger than observed for quartz.[16]

More detailed studies on the liquid crystalline, electrical, and optical properties of compounds of types (**1**) and (**2**) are in progress. The results already obtained show that they represent a promising series of materials. Further developments could include the incorporation of such molecules into polymers and Langmuir–Blodgett films, as has been reported for hemicyanine and aminonitrostilbene derivatives.[17] Enhancement of the properties may be expected on increasing the length of the conjugated chain and/or modifying the donor and acceptor groups in systems such as trienes,[18] divinyldiacetylenes,[2] and even more so in push–pull carotenoids[19] as suggested earlier.[20]

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[§] 1 D = 3.33×10^{-30} C m.