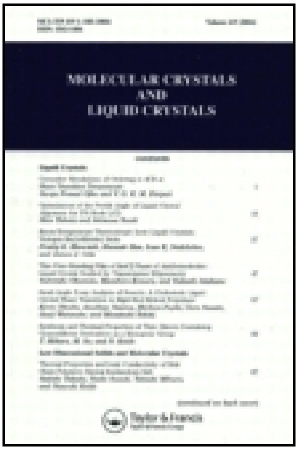

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New Conjugated Bis(AZO) Mesogens with “Push-PULL” Substituents

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NEW CONJUGATED BIS(AZO) MESOGENS WITH "PUSH-PULL" SUBSTITUENTS

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Two series of conjugated bis(azo) compounds with "push" (alkoxy, acyloxy) and "pull" (nitro) substituents at the end positions were synthesized and their thermal behavior investigated. Smectic A and nematic mesophases were observed over long temperature intervals. Surprisingly, photoirradiation of these compounds does not give detectable amounts of the expected photoisomerized isomers.

Keywords: azo compounds; push-pull; photoisomerization

INTRODUCTION

Azo compounds were discovered around 1850 by W. H. Perkin in an attempt to prepare synthetic quinine. The new compounds were soon patented, and the era of azo dyes began: it soon flourished, but then started to decline almost 100 years later [1].

In the present period, there is a revival of interest in azo compounds as potentially useful for several modern applications, for example, in host-guest systems for full-color reflective displays [2]; for photocontrolled alignment exploiting their *E-Z* photoisomerization [3]; and for obtaining photochemical switches for liquid crystalline systems [4], both chiral [5,6]

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and achiral [7], molecular shuttles [8], and photoresponsive gels [9]. Azo compounds have also been recently employed to obtain single-molecule light-powered machines [10]. Several mono(azo) mesogens are described in the literature [11], some [12,13] very recently; also, V-shaped mesogens containing two nonconjugated azo groups have been described recently [14].

In connection with our research on molecular rectifiers [15,16], we were interested in preparing conjugated bis(azo) compounds with "push" (–OR) and "pull" (–NO_2) substituents at the *para* end positions; we noticed that some compounds were mesogenic.

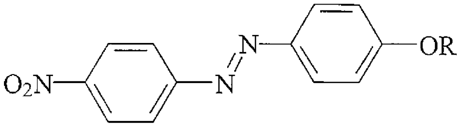
Although the effect of nitro substitution in calamitic liquid crystals has been the subject of a recent review [17], only a few nitro-containing mono (azo) mesogens (see, for example, compounds **1a–c** [11,18] have been reported (Scheme 1).

Considering that these mesogens are new, have interesting colors, and when used as dopants in host–guest systems should not disorganize the liquid crystalline hosts [12,13]; and considering also that similar structures are known to generate second harmonics [19], we thought of carrying out an investigation on this class of compounds. In particular, the ester-type **2a–f** and ether-type **2g–1** derivatives were synthesized. All of the derivatives displayed liquid crystalline properties (Scheme 2).

RESULTS AND DISCUSSION

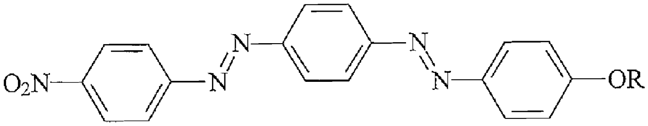
Synthesis

Derivative **3** ("disperse orange 3") was diazotized with $NaNO_2$/HCL and copulated with phenol in aqueous NaOH. The resulting bis(azo) phenol **4** was then either *O*-acylated at room temperature (r.t.) with an acyl chloride



1a, R = C_2H_5; C_8H_{17}
1b, R = 10-bromo-1-decyl
1c, R = n-alcanoyl
1d, R = *p*-bromobenzoyl; *p*-nitrobenzoyl; *p*-methoxybenzoyl; *p*-methylbenzoyl

SCHEME 1



2a, R = COC_4H_9
2b, R = COC_5H_{11}
2c, R = COC_6H_{13}
2d, R = COC_7H_{15}
2e, R = COC_8H_{17}
2f, R = COC_9H_{19}
2g, R = C_5H_{11}
2h, R = C_6H_{13}
2i, R = C_7H_{15}
2j, R = C_8H_{17}
2k, R = C_9H_{19}
2l, R = $C_{10}H_{21}$

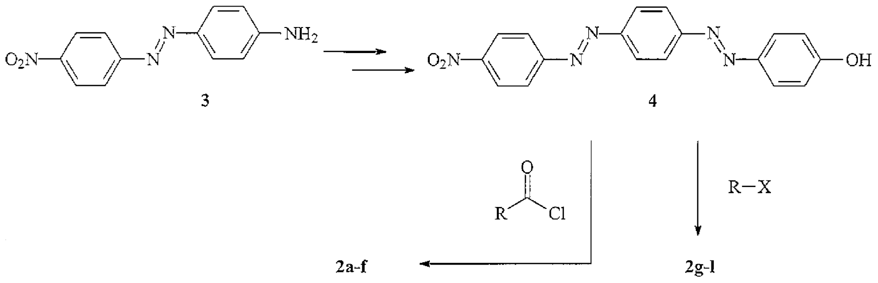
SCHEME 2

in tetrahydrofurane (THF) in the presence of triethylamine to give **2a–f** or *O*-alkylated with an alkyl halide in the presence of $CsCO_3$ in refluxing N,N-dimethylformamide (DMF) to give **2g–l** (Scheme 3).

Thermal Behavior

The thermal behavior of compounds **2a–l** was investigated by differential scanning calorimetry and optical polarizing microscopy; all the compounds show mesogenic behavior. The phase assignment based on the optical textures (Figure 1 shows a representative example of photomicrographs obtained for **2j**) and the phase transition temperatures are reported in Table I.

In the ester-type derivatives (**2a–f**), smectic A and nematic phases are present in a wide range of temperatures. By increasing the length of the R substituent, while the Cr-SmA and N-I transitions are essentially



SCHEME 3

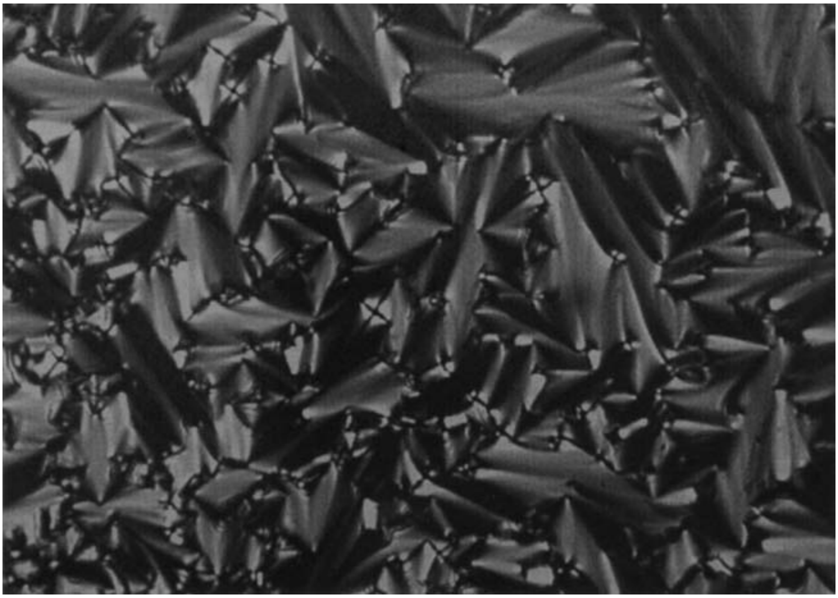


FIGURE 1 SmA optical texture of **2j** at 190°C (crossed polars, magnification × 100).

unaffected as expected, the SmA-N transition temperature increases, and the range of existence of the nematic phase is reduced from 120°C for **2a** to ca. 40°C for **2f**.

TABLE I Transition Temperatures for Derivatives **2a–l** (all N-I transitions occur with partial decomposition)

Compound	Phase	Temp(°C)	Phase	Temp(°C)	Phase	Temp(°C)	Phase
2a	Cr	149	SmA	200	N	320	I
2b	Cr	150	SmA	198	N	300	I
2c	Cr	148	SmA	205	N	260	I
2d	Cr	146	SmA	230	N	260	I
2e	Cr	144	SmA	240	N	280	I
2f	Cr	145.5	SmA	261	N	300	I
2g	Cr	160	SmA	245	N	270	I
2h	Cr	160	SmA	254	N	280	I
2i	Cr	158	SmA	255	N	270	I
2j	Cr	158	SmA	267	N	270	I
2k	Cr	158	SmA	272			I
2l	Cr	158	SmA	263			I

A similar trend is observed for the ether-type compounds (**2g–l**). In the case of **2g**, the derivative with the shortest substituent, the nematic phase exists only in a relatively short interval (ca. 25°C): this interval reduces on increasing the methylene number and finally disappears for **2k** (and **2l**).

Photochemical Behavior

It is well known that azobenzene-type compounds undergo an efficient and fully reversible *E-Z* photoisomerization reaction. Mesogens incorporating the azobenzene moiety or doped with azobenzene derivatives are therefore promising materials for optical switching as a consequence of the reversible shape transformation of the photoactive molecules and the consequent effect on phase transitions [4–7].

Absorption spectra of **2f** and **2j** in the 220–600 nm range are reported in Figure 2. As expected, the main absorption band, corresponding to a $\pi\pi^*$ transition, is red shifted for the either-type derivative **2j**. Chloroform solutions of derivatives **2f** and **2j** (*E,E* form) were irradiated at different wavelengths (marked with arrows in Figure 2), and the photochemical transformations were followed by UV-V is absorption. Surprisingly, in all the experiments we did not observe any phototransformation under the experimental conditions used.

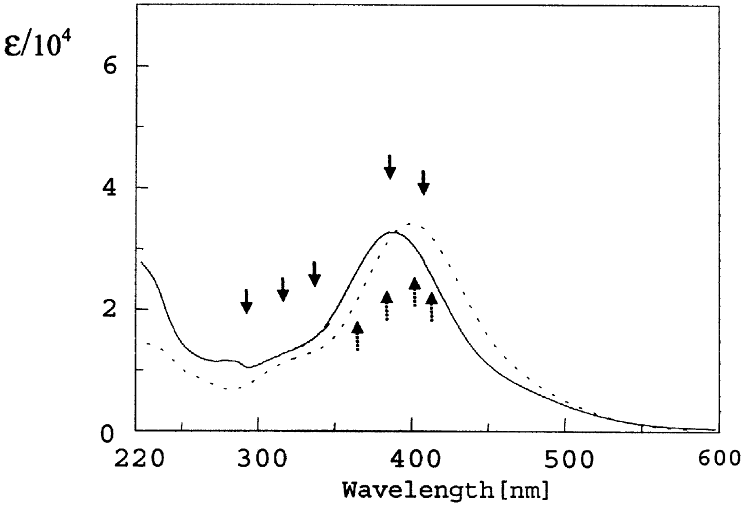


FIGURE 2 Absorption spectra of **2f** (full line) and **2j** (dashed line) in chloroform. Full line and dashed arrows indicate the wavelength used for the photoirradiation of **2f** and **2j**, respectively.

The reason for the absence of a detectable amount of photoisomerized isomers from the *para*-bis(azo) derivatives **2f** and **2j** in the same conditions in which azobenzene (and even "push-pull" substituted (mono)azobenzenes) [20] shows the *E-Z* phototransformation reaction is under investigation. A possible explanation for such a reduced photoreactivity, which emerges from preliminary results on similar compounds [21], is related to the extensive electronic conjugation of the two azo groups in the *para*-bis(azo) compounds: this conjugation renders the two azo groups photochemically nonindependent. On the other hand, analogous *meta*-bis(azo) derivatives, in which the conjugation between the two azo units is substantially lower, show the usual photoisomerization.

EXPERIMENTAL PART

General Information

The optical texture observation was performed with a Zeiss Standard polarizing optical microscope equipped with a Linkam hot stage or a Leitz Ortholux polarizing optical microscope carrying a Mettler FP 82 heating stage equipped with a Mettler FP 80 temperature controller. The thermal transitions were determined with both optical microscopy and differential scanning calorimetry (Perkin-Elmer DSC-7). Light excitation in the photochemical experiments was performed by a mercury arc lamp (interference filters were used to select the spectral range) or by the Xe lamp of a JASCO J710 spectrometer (wavelengths were selected with the instrument monochromator). ^{1}H NMR and ESI-MS spectra were measured on Varian Gemini 200 and ZMD Micromass spectrometers, respectively.

Synthesis

4-[4′-(4″-nitrophenylazo)phenylazo]phenol 4

4-(4′-nitrophenylazo)aniline **3** from Aldrich was purified by column chromatography. **3** (2.06 mmol) and 1.3 ml HCl conc. were stirred in 2 ml H_2O at 0°C. A cooled solution of $NaNO_2$ (2.06 mmol) in 1 ml H_2O was slowly added, keeping the temperature below 4°C. The excess of $NaNO_2$ was eliminated, adding several drops of urea in water solution. The brown diazonium salt solution thus obtained was added to a solution of phenol (2.74 mmol) and NaOH (17.5 mmol) in 3 ml water at 0°C. The resulting solution was acidified with HCl conc. and then filtered and washed with water. After purification by column chromatography (petroleum benzine:Et_2O 50:50), dark red, amorphous dust of 4-[4′-(4″-nitrophenylazo)phenylazo]phenol **4** was separated in a 60% yield. ^{1}H NMR δ (200 MHz, $CDCl_3$: 8.46 (d, 2H); 8.16 (d, 2H); 8.14 (d, 2H); 7.98 (d, 2H). MS-ESI: 346 $(M\text{-}H)^-$.

4-[4′-(4″-nitrophenylazo)phenylazo]phenyl alkanoates **2a–f**

4-[4′-(4″-nitrophenylazo)phenylazo]phenol **4** (1 eq) was stirred overnight with the appropriate acyl halides and Et_3N (5 eq) in anhydrous THF at room temperature under argon. The mixtures were filtered, washed with a little methanol, and dried under vacuum. The compounds were purified with column chromatography in about 50% yields. ^{1}H NMR δ (200 MHz, $CDCl_3$): all the compounds gave similar values of δ, differing only in the number of alkyl chain CH_2 protons; δ 8.34 (d, 2H), 8.00–8.10 (m, 4H), 7.95 (d, 2H), 7.24 (d, 2H), 2.59–2.62 (t, 2H), 1.78–1.80 (q, 2H), 1.20–1.52 (m, alkyl chain CH_2), 0.85–0.93 (t, 3H) MS-ESI: m/z; **2a** 501.3 $(M)^-$, 524 $(M+Na)^+$; **2b** 487.5 $(M)^-$, 510.5 $(M+Na)^+$; **2c** 473.5 $(M)^-$, 497 $(M+Na)^+$; **2d** 459.5 $(M)^-$, 482.5 $(M+Na)^+$; **2e** 445.4 $(M)^-$, 468.5 $(M+Na)^+$; **2f** 431.4 $(M)^-$, 454.5 $(M+Na)^+$.

4-[4′-(4″-nitrophenylazo)phenylazo]alkoxybenzene **2g–l**

4-[4′-(4″-nitrophenylazo)phenylazo]phenol **4** (1 eq) with the appropriate alkyl halides (1.5 eq) and Cs_2CO_3 (1.5 eq) in *N,N*-dimethylformamide were stirred under argon atmosphere and heated at reflux. After 24 h, the solution was concentrated under vacuum, dissolved in ether, and then filtered. The ether solution was extracted with water, and the combined organic layers were dried ($MgSO_4$). The solid was purified by column chromatography (petroleum benzine: CH_2Cl_2) and gave about 55% yield. ^{1}H NMR (200 MHz, $CDCl_3$): all the compounds gave similar spectra, differing only in the number of alkyl chain CH_2 protons; δ 8.40 (d, 2H), 7.99–8.18 (m, 4H), 7.97 (d, 2H), 7.02 (d, 2H), 4.04–4.08 (t, 2H), 1.82–1.85 (q, 2H), 1.20–1.55 (m, alkyl chain CH_2), 0.88–0.90 (t, 3H).

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