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T. Hanemann[a]; E. Soto Bustamante[a]; T. Weyrauch[a]; W. Haase[a]
[a] Institut für Physikalische Chemie, Technische Hochschule, Darmstadt, Germany

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Synthesis and characterization of new liquid-crystalline dyes for non-linear optics

by T. HANEMANN, E. A. SOTO BUSTAMANTE,
T. WEYRAUCH and W. HAASE*

Institut für Physikalische Chemie, Technische Hochschule,
Petersenstr. 20, D-6100 Darmstadt, Germany

We present the synthesis and a description of the physical properties of several organic dyes containing stilbene as well as azomethine groups. The preparations of all compounds started from a common precursor, 4-amino-4′-nitrostilbene, followed by condensation with aromatic aldehydes. The mesomorphic properties and spectroscopic data were established using polarizing microscopy, DSC measurements, X-ray and UV/Vis spectroscopy. Three of the compounds showed enantiotropic smectic phases, two of them highly ordered S_E and S_B phases, and a nematic phase. In addition quantum chemical calculations concerning the electronic properties were carried out.

1. Introduction

One basic condition to achieve a large hyperpolarizability in an organic compound is the presence of an extended unsaturated π electron system, for example, aromatic moieties combined with ethylenic or related sub-units. Additionally polar substituents with opposite electron affinities, like amino- and nitro-groups, have to be suitably attached to the conjugated system. As a result large ground state dipole moments up to 15 D arise [1–3].

The subject of this work is the synthesis of new model dyes which combine on the one hand, potential non-linear optical properties and on the other, liquid-crystalline behaviour, and the subsequent full characterization of their physical properties. The basic idea is the elongation of the aromatic system of the stilbene unit; prominent representatives of the stilbene type are DHANS or DANS which show very high hyperpolarizabilities. A longer π system should move the main absorption band closer to the excitation wavelength in SHG measurements (in our set-up: 1064 nm), by analogy with related bis-azo and bis-stilbene compounds, and should increase the efficiency of the frequency conversion.

2. Experimental

2.1. *General considerations*

The compounds have been characterized by ^{1}H NMR spectroscopy using WM 300 spectrometer (300 MHz, Bruker) and mass spectrometry. The UV/Vis spectra were recorded with a Cary 17 spectrophotometer (Varian). The phase transition temperatures were determined using a differential scanning calorimeter (Dupont 990 Thermal Analyzer) with an accuracy of ±0·1 K. A polarizing microscope (Leitz Orthoplan Pol) in conjunction with a hot stage (Mettler Hotstation FP 82) and a SVHS video system

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* Author for correspondence.

(Sony, Panasonic) allowed observation of the phase transitions and the mesomorphic textures. For X-ray diffraction measurements, the samples were contained in 1·0 mm glass capillaries (Lindemann) and held in a copper block. The temperature was controlled within ±0·5 K and measured with a calibrated thermocouple located close to the sample. X-ray diffraction was performed using a flat camera with Cu–K_α radiation. The photographs of the oriented samples (using a permanent magnet of 0·8 T) were taken for all phases under cooling conditions of the samples, starting from the isotropic liquid down to the crystalline phase.

2.2. *Synthesis*

The basic approach used was to elongate the conjugated system of the common starting material 4-amino-4′-nitrostilbene **1** by condensation with aromatic aldehydes. Molecules which contain both a stilbene unit and an azomethine group are known in the literature, but no liquid-crystalline behaviour has been described [4–7]. The synthesis of **1** was effected according to a modified procedure of Ashley *et al.* [8], starting from 4-nitrophenylacetic acid and 4-acetamidobenzaldehyde, in two steps with a total yield of 64 per cent. By condensation of **1** with aromatic aldehydes, three new azomethines **2a–2c** were synthesized; compounds **2d** and **2e** are known [5, 7] but here for the first time precise analytical data are presented (see figure 1).

2.2.1. *Common syntheses of* **2a, 2b, 2d** *and* **2e**

3·0 g of **1** (12·5 mmol) and an equimolar amount of the aldehyde (2,4-dimethoxybenzaldehyde, 4-(1,1-diethoxymethyl)benzaldehyde, 2-hydroxy-1-naphthylaldehyde and 4-(*N*,*N*-dimethylamino)benzaldehyde were dissolved in 30 ml of pure ethanol and boiled for 24 h. After cooling to room temperature the solvent was evaporated *in vacuo* and the crude product recrystallized from ethoxyacetic acid.

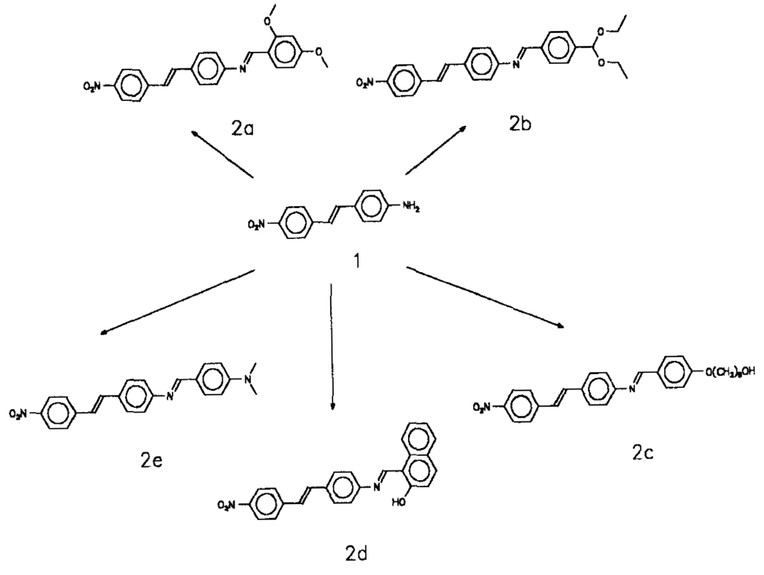

Figure 1. Synthetic scheme for all the azomethines.

2.2.2 *Synthesis of* **2c**

6·0 g (51·0 mmol) of 4-hydroxybenzaldehyde were dissolved in a mixture of 70 ml of pure ethanol, 30 ml of triethylamine and 3·0 g of potassium hydroxide. After stirring for one hour at room temperature, 30·0 g (220·0 mmol) of 6-chlorohexanol and a catalytic amount of potassium iodide were added and the mixture boiled for 48 h. The mixture was then filtered and the solvent evaporated under reduced pressure. The remaining oil was mixed with water and shaken with diethyl ether. The organic extracts were dried (sodium sulphate), the solvent was evaporated and the crude product purified using column chromatography (silica gel, dichloromethane); the yield was 10·0 g (90·0 per cent). 2·0 g (9·0 mmol) of the product 4-(6-hydroxyhexyloxy)benzaldehyde and 2·1 g of **1** (8·7 mmol) were dissolved in 20 ml of ethanol and refluxed for 72 h. Then the solvent was evaporated under reduced pressure and the crude product recrystallized from ethanol. All compounds were obtained in good yields; table 1 shows the data with respect to **1** and the elemental analyses for all the azomethines.

2.2.3. *4-(2,4-dimethoxybenzylideneamino)-4′-nitrostilbene* **2a**

^{1}H NMR ($CDCl_3$)δ: 8·85 (s, 1 H, N=CH), 8·21 (d, 2 H, CH-nitroarom.), 8·12 (d, 1 H, CH-arom.), 7·62 (d, 2H, CH-nitroarom.) 7·56 (d, 2 H, CH-arom.), 7·28 (d, 1 H, CH=CH), 7·24 (d, 2 H, CH-arom.), 7·10 (d, 1 H, CH=CH), 6·60 (dd, 1 H, CH-arom.), 6·48 (d, 1 H, CH-arom.), 3·89 ppm (s, 6 H, CH_3). MS (70 eV) *m*/*z* 388 (M^+, 100 per cent).

2.2.4. *4-(4-(1,1-Dimethoxy)benzylideneamino)-4-nitrostilbene* **2b**

^{1}H NMR ($CDCl_3$)δ, 8·50 (s, 1 H, N=CH), 8·23 (d, 2 H, CH-nitroarom.), 7·92 (d, 2 H, CH-arom.), 7·66 (d, 2 H, CH-nitroarom.), 7·59 (d, 2 H, CH-arom.), 7·58 (d, 2 H, CH-arom.), 7·29 (d, 1 H, CH=CH), 7·26 (d, 2 H, CH-arom.), 7·14 (d, 1 H, CH=CH), 5·57 (s, 1 H, CH-acetal), 3·61 (m, 4 H, CH_2), 1·26 ppm (t, 6 H, CH_3). MS (70 eV) *m*/*z* 430 (M^+, 100 per cent).

2.2.5. *4-(4-(6-hydroxyhexyloxy)benzylideneamino)-4-nitrostilbene* **2c**

^{1}H NMR ($CDCl_3$)δ: 8·42 (s, 1 H, N=CH), 8·22 (d, 2 H, CH-nitroarom.), 7·85 (d, 2 H, CH-arom.), 7·63 (d, 2 H, CH-nitro-arom.), 7·58 (d, 2 H, CH-arom.), 7·26 (m, 3 H, CH-arom., CH=CH), 7·19 (d, 1 H, CH=CH), 6·98 (d, 2 H, CH-arom.), 4·04 (t, 2 H, OCH_2), 3·68 (t, 2 H, CH_2OH), 1·25 ppm (m, 8 H, CH_2). MS (70 eV) *m*/*z* 444 (M^+, 100 per cent).

2.2.6. *4-(2-hydroxy-1-naphthylideneamino)-4-nitrostilbene* **2d**

^{1}H NMR ($CDCl_3$)δ: 15·4 (s, 1 H, OH), 9·38 (s, 1 H, N=CH), 8·24 (d, 2 H, CH-nitroarom.), 8·12 (d, 1 H, CH-arom.), 7·82 (d, 1 H, CH=CH), 7·73 (d, 1 H, CH-arom.),

Table 1. Yields and elemental analytical data for all compounds synthesized.

Compound	Yield/%	Elemental analysis: found (calculated)/%		
		C	H	N
2a	78	71·68 (71·13)	5·02 (5·15)	7·13 (7·22)
2b	70	71·52 (71·56)	6·05 (5·97)	6·44 (6·51)
2c	69	72·03 (72·97)	6·20 (6·31)	6·33 (6·31)
2d	87	75·30 (76·14)	4·53 (4·57)	7·09 (7·11)
2e	70	73·90 (74·39)	5·58 (5·66)	11·24 (11·32)

7·66 (d, 2 H, CH-nitroarom.), 7·65 (d, 2 H, CH-arom.), 7·54 (d, 1 H, CH-arom.), 7·41 (d, 2 H, CH-arom.), 7·35 (m, 2 H, CH-arom.), 7·15 (m, 1 H, CH-arom.), 7·10 ppm (d, 1 H, CH=CH). MS (70 eV) *m/z* 394 (M^+, 100 per cent).

2.2.7. *4-(4-*N,N*-dimethylaminobenzylideneamino)-4-nitrostilbene* **2e**

^{1}H NMR ($CDCL_3$), δ: 8·36 (s, 1 H, N=CH), 8·22 (d, 2 H, CH-nitroarom.), 7·82 (d, 2 H, CH-nitroarom.), 7·63 (d, 2 H, CH-arom.), 7·56 (d, 2 H, CH-arom.), 7·29 (d, 1 H, CH=CH), 7·22 (d, 2 H, CH-arom.), 7·11 (d, 1 H, CH=CH), 6·75 (d, 2 H, CH-arom.), 3·08 ppm (s, 6 H, CH_3). MS (70 eV) *m/z* 371 (M^+, 100 per cent).

2.3. *Computational conditions*

Previously we have shown [9] the possibility of reproducing electronic spectra of aromatic compounds containing different aromatic sub-structures, with satisfactory accuracy, using an adopted model hamiltonian based on the INDO approximation. Structural parameters like bond lengths and angles have been taken from the literature [10, 11]. In the subsequent SCF/CI calculations a 15 * 15 array has been used, i.e. 15 occupied and 15 unoccupied electronic states have been considered; the CI calculations refer to isolated molecules in the gas phase at zero temperature. The deviations between the calculated transition energies and the experimental values are less than 10 per cent.

3. Results and discussion

3.1. *Transition temperatures and textures*

It is known that simple stilbene derivatives with simple terminal alkyl or alkoxy groups [12–15] or more complicated push-pull moieties like amino- and nitro-groups [16] possess liquid-crystalline properties. Molecules with long terminal aliphatic chains or *p*-substituted aromatic rings with long chains often show higher ordered smectic phases [15, 16]. The phase transition temperatures of all the azomethines are summarized in table 2, and figure 2 shows the DSC traces of all the liquid-crystalline compounds. Compounds **2b** and **2c** possess highly ordered smectic phases (S_E and S_B: mosaic textures) and a nematic phase (schlieren texture), but **2a** gives only a nematic phase (schlieren texture). Full characterization of the phases was achieved using flat film X-ray measurements with the equipment described. A comparison of the investigated azomethines with dyes containing analogous linkages (stilbene, azo-) shows that elongation of the aromatic system does not destroy the mesomorphic properties (see figure 3 and table 3). Quite similar molecules to **3** and **6** with, in the one case a dodecyl aliphatic chain and in the other, an oxygen bridge instead of the azo-group and just one alkyl substituent show similar phase sequences. The first has a S_E phase between 109°C and 141°C, and the second a monotropic S_E phase at lower temperatures [16].

Table 2. Transition temperatures for the azomethines.

Compound	Phase behaviour
2a	C 178·3°C N 181·3°C I
2b	C 99·0°C S_E 126·9°C S_B 132·0°C S_A 164·2°C N 179·2°C I
2c	C 159·1°C S_E 166·5°C S_B 176·8°C N 300·0°C (decomp.)
2d	C 300·0°C (decomp.)
2e	C 307·0°C (decomp.)

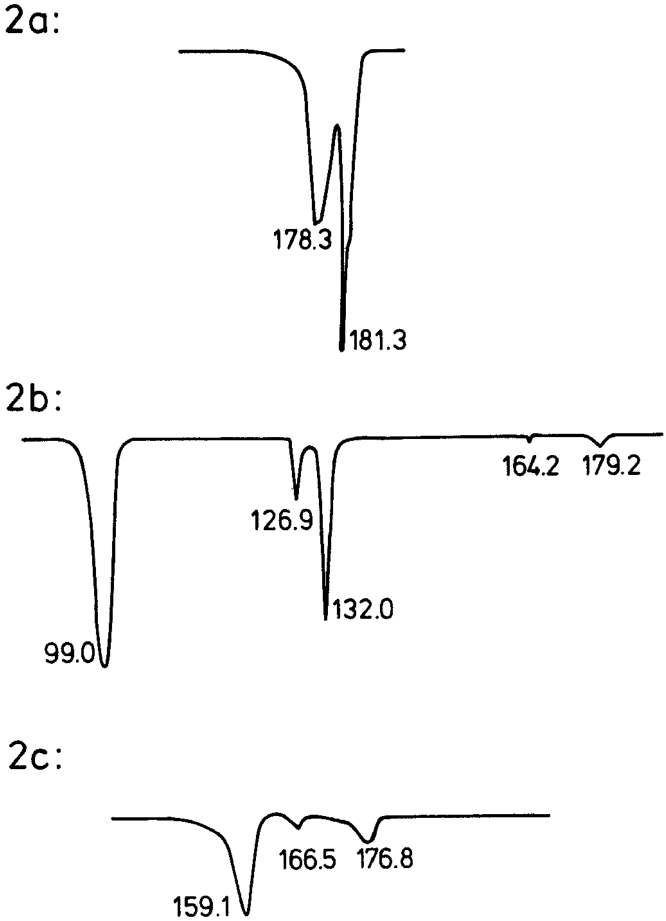

Figure 2. DSC traces for compounds **2a**, **2b** and **2c**.

Table 3. Transition temperatures for related stilbene, azo- and mixed stilbene/azo-compounds.

Compound	Phase behaviour
3	C 112·1°C S_E 132·0°C I
4	C 224·0°C S_X 262·0°C I
5	C 92·5°C S_C 103·5°C I
6	C 171·0°C S_C 180·0°C I
7	C (111·7°C S_E) 139·6°C I

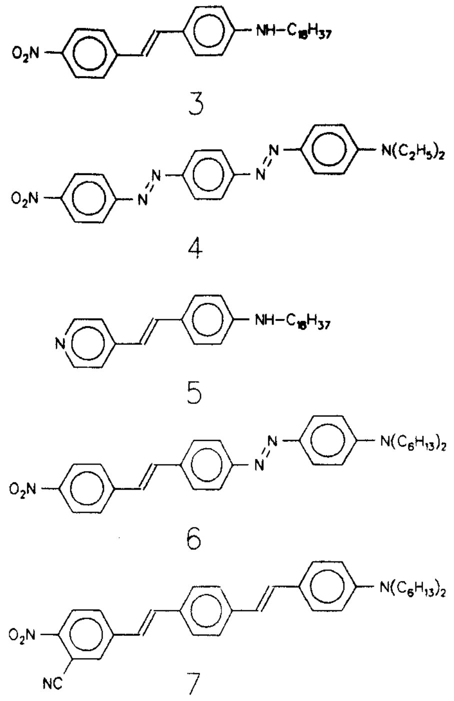

Figure 3. Structures of related stilbene, azo- and mixed stilbene/azo-compounds.

3.2. *UV/Vis spectroscopic and quantum chemical results*

UV/Vis spectra of all the compounds in different polar and non-polar solvents were recorded in order to obtain the main absorbance regions and the related extinctions. Former investigations on dye molecules containing only a stilbene framework show that such molecules possess, in the visible spectral region, only one absorption band, which is polarized in the plane of the aromatic system with the major component in the principal axis of the molecule [9, 17]. In pure *trans*-stilbene (maximum at 297 nm) and azobenzene (maxima at 281 and 314 nm), a C_{2h} symmetry exists. The strongest electronic transition is denoted as ^1A_g–$^1B_{1u}$ and polarized parallel to the molecular axis. In the case of simple benzylideneanilines (maxima at 240 and 312 nm) with a central azomethine bond, a lower symmetry is given. An exact correspondence between the bands of stilbene and azobenzene is unknown, so the main band may also be denoted as ^1A_g–$^1B_{1u}$ transition [18]. Additional bands at lower wavelengths with lower intensity (for example ^1A_g–$^1B_{2u}$ and ^1A_g–$^1B_{3g}$), which are also present in azobenzene, appear. The investigated dyes show the same polarization direction as the more simple ones estimated using UV/Vis dichroism measurements on oriented thin films of a guest–host system with CB5 as the liquid-crystalline matrix. The same information was obtained from our INDO/MO calculations. All compounds examined show a very broad absorption range (FWHM up to 90 nm), with large molar extinction coefficients (see table 4), analogous to similar stilbene compounds, only in the case of compound **2d** additional bands with lower intensity can be observed (see figure 4).

X-ray and quantum mechanical investigations on the molecular structure of simple aromatic azomethines show that the two benzene rings attached to the azomethine

Table 4. Main absorption maxima and extinctions for all the dye molecules in toluene and DMSO.

Compound	$(\lambda/\text{nm})/(\varepsilon/\text{l mol}^{-1}\,\text{cm}^{-1})$	
	Toluene	DMSO
2a	392/73000	399/108000
2b	382/67000	391/71000
2c	386/45100 (CH_2Cl_2)	395/50000
2d	409/55000	433/80000
2e	406/44000	419/38000

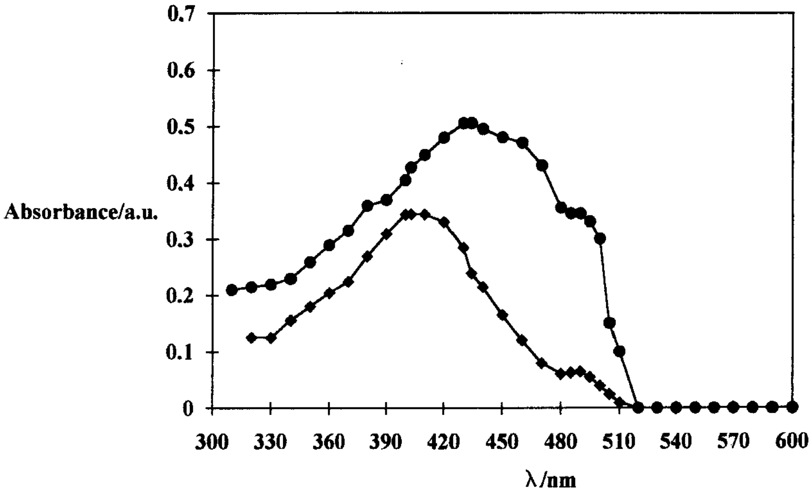

Figure 4. UV/Vis absorption spectra of **2d** in toluene (◆) and DMSO (●).

Table 5. Absorption maxima of *bis*-azo-**4**, mixed stilbene/azo- **6**, and *bis*-stilbene **7** compounds.

Compound	λ/nm	
	Acetone	DMSO
4	510	528
6	472	485
7	478	495

double bond are twisted from coplanarity by about 60°, whereas the stilbene and azo geometry can be treated as all-coplanar [19, 20]. *Bis*-stilbene, *bis*-azo- or mixed stilbene/azo-compounds always absorb at higher wavelengths because of the rigid planar aromatic system (see table 5). In the case of the *bis*-stilbene compound **7**, only the cyano-substituted dye was available. The conjugated system in the azomethine compounds has to be separated into two fragments with a twist angle of about 60°. As a consequence, the effective π system of the stilbene moiety has not changed and the

Table 6. Calculated dipole moments and absorption maxima.

Compound	p/D	λ/nm
2a	9·7	411
2b	10·2	398
2c	8·2	409
2d	6·2	427, 391
2e	8·7	412

absorption range should be similar to that of the starting material, as found by experiment (395 nm, toluene). In the case of compound **2d** only, the formation of a hydrogen bond between the hydroxy group and the imine-nitrogen allows for a more planar structure of the two aromatic systems close to the azomethine bond and leads to absorptions at higher wavelengths (see figure 4). The typical bands related to aromatic azomethines can be observed here also, because they are shifted to higher wavelengths as a result of the better conjugation and the influence of the attached substituents of the stilbene moiety.

As mentioned, our INDO/MO model allows for the calculation of dipole moments, electronic transition energies and the polarization of the related absorption bands. We have shown before that the calculated values, even for the dipole moments, agree quite well with experimental results [9]. Table 6 presents the calculated data for all the azomethine dyes synthesized, and a comparison of our measured spectra with calculated data shows a reasonable agreement (see table 4). The position of the different substituents in the aromatic frame and their influence on the electronic properties as assessed from the experiments agree with the calculated data for the resulting dipole moments and absorption maxima.

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