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Versatile optical materials: fluorescence, non-linear optical and mesogenic properties of selected 2-pyrazoline derivatives

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A study of the structure–property relationships in a series of 3-(4-*n*-decyloxyphenyl)-1-(*p*-X-phenyl)-2-pyrazolines has been performed. By simply changing the substituent in the 1-phenyl ring we were able to tune the physical properties of the compounds. If this ring is non-substituted or substituted with a 4-methoxy, 4-chloro or 4-carboxy group, the pyrazoline compounds are fluorescent. If the ring is 4-nitro- or 2,4-dinitro-substituted, the compounds have interesting second-order non-linear optical properties. The first hyperpolarizability has been measured using the Hyper-Rayleigh Scattering technique in solution. The 4-nitro derivative displays liquid crystalline behaviour, showing a monotropic smectic A phase with a partial bilayer structure due to an antiparallel arrangement of molecules as confirmed by X-ray studies in the mesophase.

Introduction

Materials with optical properties are very interesting for applications in many areas of technology, including fluorescent materials which have been extensively used as optical brighteners, fluorescent dyes and scintillators.[1] Non-linear optical (NLO) materials have also attracted great interest for applications in optical signal processing such as frequency doubling, amplifiers, modulators for laser technology, data storage and telecommunications.[2]

Organic compounds are being extensively studied for non-linear optical properties, as molecular materials, and their properties are highly dependent on their structural characteristics. For second-harmonic generation, organic materials have to show a high first hyperpolarizability (β) and also possess a non-centrosymmetric organization in order to achieve a macroscopic effect. To obtain this particular arrangement several approaches are possible and these include the use of crystals, poled polymers, Langmuir–Blodgett (LB) films and liquid crystals. Moreover, organic compounds have other advantages such as low dielectric constants, low switching times and easy processability.[3]

Typical organic molecules with large hyperpolarizabilities are systems with donor and acceptor groups separated by a conjugated system (π-system) such as benzene, stilbene or stilbazolium.[2,4–6]

The aim of the work described in this paper is to obtain molecular materials that combine NLO, fluorescent and mesogenic properties. The existence of mesogenic properties helps the macroscopic molecular orientations which are very important to both optical and technical applications.[3c] In this context, we have introduced the structural characteristics of organic NLO materials into molecules that exhibit fluorescent properties. For these reasons, we have prepared new organic compounds with the 1,3-diphenyl-2-pyrazoline group as the π-system. These compounds show fluorescent properties[1a,b,7] and, by means of relatively straightforward synthetic procedures, allow the introduction of suitable substituents for the promotion of second-order non-linear optical properties. Molecular calculations (CNDO) have been carried out and show the 1,3-diaryl-2-pyrazolines to be very promising materials for second-order non-linear optics.[8a,b] Moreover, measurements of the electrooptic half-wave voltage have shown the potential of pyrazolines as high efficiency electrooptic materials.[8c]

In order to promote mesomorphism in these structures we have introduced an *n*-decyloxy substituent as a terminal chain in the 4-position of one of the aromatic rings (Scheme 1). Moreover, this group increases the solubility of the pyrazoline derivatives in organic solvents and favours the necessary arrangements to obtain LB films.[9]

In the other aromatic ring we have introduced a variety of groups such as H, OCH_3, COOH and NO_2, in order to study the influence of both acceptor and donor groups on the optical and mesogenic properties of the compounds.

In total, seven new compounds have been synthesised in order to investigate the points outlined above.

Results and Discussion

Synthesis

The synthetic route to the compounds is shown in Scheme 1. Compounds **2**–**6** were prepared by the reaction of 4-*n*-decyloxyphenyl vinyl ketone **1** with the appropriately substituted phenylhydrazine (route c), by adapting literature methods.[10] Ethanol was chosen as the solvent at a temperature of 30–40 °C to ensure the dissolution of the reactants and the precipitation of the cyclised products. The use of acid catalysis (acetic acid) favours cyclisation as opposed to the formation of phenylhydrazone derivatives or Michael addition products.

The reaction follows a general mechanism that was studied by Coispeau and Elguero.[11] 1,2-Addition of the primary nitrogen atom of the phenylhydrazine occurs at the carbonyl group of compound **1**, followed by cyclisation by means of an electrocyclic reaction involving six electrons.

When X = COOH and NO_2 (compounds **5** and **6**), the nucleophilic power of the secondary nitrogen atom of the phenylhydrazine derivative is diminished due to the presence of an electron withdrawing substituent, whereas the primary nitrogen atom is affected to a lesser extent. As a consequence, the carboxy derivative needed a longer reaction time and, in

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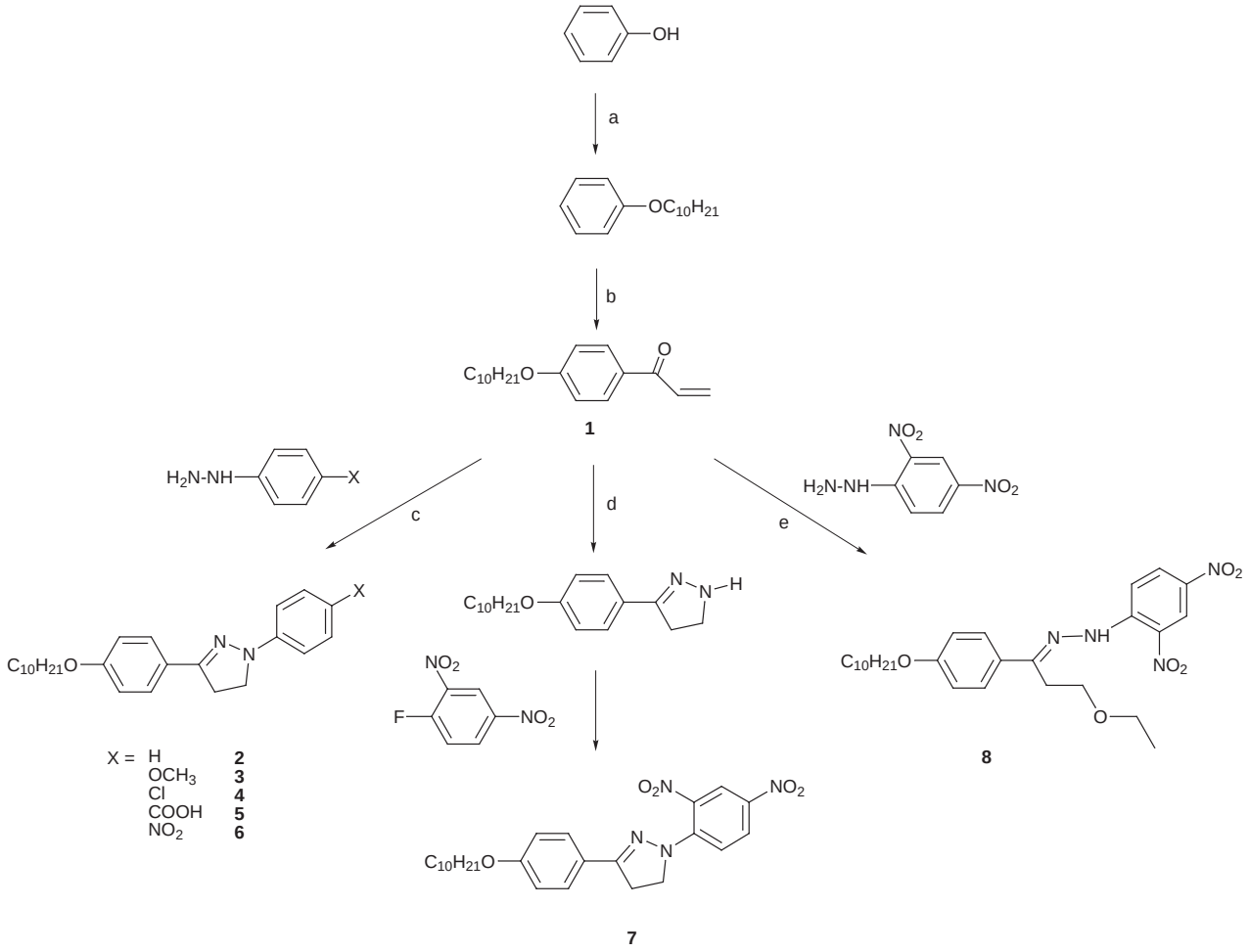


Scheme 1 Synthetic routes to the pyrazoline and phenylhydrazone compounds

the nitro derivative, the yield is lower than in the other compounds.

When the phenylhydrazine bears two electron withdrawing groups, as in the 2,4-dinitrophenylhydrazine, route c proved unsuccessful even after heating under reflux for several hours. Indeed this method led to the formation of a phenylhydrazone derivative resulting from the attack of a molecule of 2,4-dinitrophenylhydrazine on the carbonyl group and of a molecule of ethanol on the double bond (route e, compound **8**). It has been reported that 2,4-dinitrophenylhydrazones can only be cyclised under extreme conditions (boiling acetic acid containing hydrobromic acid).[12]

Therefore, compound **7** was synthesised in two consecutive steps (route d). In the first step 3-(4-decyloxyphenyl)-2-pyrazoline is generated *in situ* to react react with 1-fluoro-2,4-dinitrobenzene by a nucleophilic aromatic substitution using an adaptation of described methods.[13]

Absorbance and fluorescence properties

In order to compare the absorbance and fluorescence properties of these compounds we recorded the absorbance spectra and the emission spectra in solution in THF. The pyrazoline derivatives **2**–**5** exhibit fluorescent emission. The data for these fluorescent compounds are given in Table 1, and an example of these spectra is given in Fig. 1. The concentrations of the solutions were of the order of 10^{-7} M, except for the methoxy derivative (compound **3**), which needed solutions ten or hundred times more concentrated.

On the other hand, no significant emission was found for the nitro derivatives (pyrazolines **6** and **7**, and phenylhydrazone **8**). The lack of fluorescence in these compounds could be explained by the presence of the nitro groups, which cause a non-radiative deactivation of the excited state due to a rapid dissipation of electronic energy.[14] In addition to this, the hydrazone system present in compound **8** is less rigid and has more rotational freedom than pyrazoline systems.

We can observe (Table 1) a relationship between the acceptor character of the substituent X and the emission wavelength (λ_{em}). The stronger the acceptor character of X, the lower λ_{em}. On the other hand, the opposite tendency is observed for the intensities of the emission maxima (I/c in Table 1): the stronger the acceptor character of X, the higher the intensity.

Generally, the groups that produce a higher bathochromic effect and higher molar absorptivity in the absorption spectrum exhibit a stronger emission, except for the compound with X = OCH_3, which has a slighty larger absorption λ_{max} but weaker fluorescent emission than the compound with X = H. These results can be accounted for by structural and electronic effects. When the acceptor strength of X increases, the molecular planarity increases because the contribution of resonance form B, in which the N1 atom has an sp^2 character, becomes greater.

The quantum yields of compounds **2**–**5** are high (see Table 1). The values are relative to quinine sulfate ($Q_F = 0.55$)[15] and have been obtained at an excitation wavelength of 340 nm. Compound **2** (X = H) displays the highest value (0.80). The quantum yield trend is different from the I/c trend. This could be due to the differences between the irradiation wavelength (340 nm) and the absorption maxima (λ_{max}) of each compound.

The Stokes shift (difference between absorption and fluorescence maxima) increases as the donor character of X increases. The fact that electron-donor substituents induce higher Stokes shifts is in agreement with previous studies on related pyrazolines.[1a,b]

Table 1 Absorption and emission UV–visible spectral data of 2-pyrazolines **2**–**5** (in THF)

Compound	λ_{max} /nm	log ε^a (λ_{max})	log ε^b (340 nm)	c/M $\times 10^{-7}$ (em)^c	λ_{em}/ nm	I/c^d	Stokes shift/ cm^{-1} ^{e}	Q_F ^{f}
2	355	4.30	4.24	5.4	426	1700	4695	0.80
3	360	4.26	4.21	15.9	454	740	5750	0.55
4	357	4.33	4.27	4.6	424	1740	4425	0.70
5	369, 387$_{sh}$	4.54	4.31	2.7	413	2700	3885	0.66

^{a}Extinction coefficient at the absorption maximum wavelength. ^{b}Extinction coefficient at the excitation wavelength. ^{c}Concentration of the solution in which the emission spectrum has been performed. ^{d}Intensity maximum normalised to a concentration of 1×10^{-5} M. ^{e}Difference between the absorption and emission maxima in wavenumbers. ^{f}Quantum yield relative to quinine sulfate ($Q_F = 0.55$). sh: shoulder.

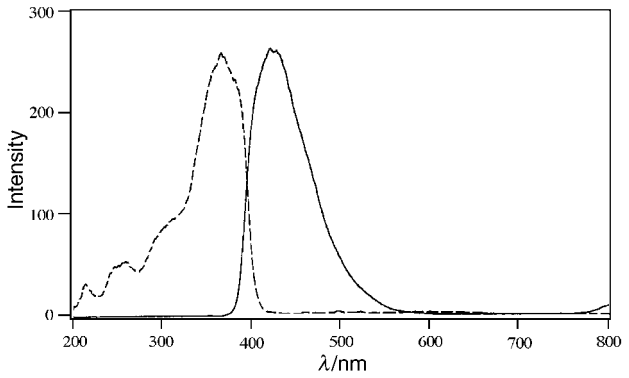
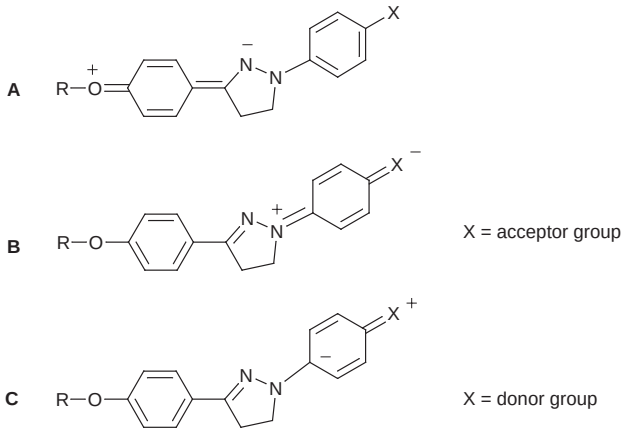


Fig. 1 Excitation spectrum (---) and emission spectrum (—) for compound **5**



Resonance forms of the 1-(*p*-X-phenyl)-3-(*p*-alkoxyphenyl)-2-pyrazoline

Non-linear optical properties

The first hyperpolarizability (β) of each of the nitro derivatives (compounds **6**–**8**) was measured using the Hyper-Rayleigh Scattering (HRS) technique.[16]

This technique relies on the fact that a small part of an intense Nd-YAG laser pulse at optical frequency ω (1064 nm) is scattered at 2ω (532 nm) due to local orientational fluctuations of the molecules. Because the HRS signal is directly proportional to β^2, only absolute values of β can be deduced. A detailed description of the experimental set-up has been described elsewhere.[17]

We were unable to measure the first hyperpolarizability for the other pyrazoline derivatives (**2**–**5**) because of the interference of the HRS signal with another incoherent process: multiphoton fluorescence in the region of 532 nm.

If we consider compounds **6**–**8** as asymmetric conjugated π-electron systems with donor and acceptor groups in the 4-position, β_{zzz} is by far the largest component of β_{HRS}.[18] The β_0 values (extrapolated to infinite wavelengths) have been calculated according to the two-level model.[19] The β_{HRS} values were measured in chloroform solution relative to standard solutions of *p*-nitroaniline (*p*-NA) in the same solvent ($\beta_{p\text{-NA}} = 23 \times 10^{-30}$ esu).

The absorption spectra in chloroform and the quadratic coefficient as a function of molar concentration in the same solvent are shown in Fig. 2 and 3 respectively for compounds **6**–**8**.

The absorption maxima and β values for compounds **6**–**8** are given in Table 2.

We would have expected that compound **7**, bearing two nitro groups in the *ortho*- and *para*-positions, would have a β value higher than that of compound **6**, bearing only one nitro group in the *para*-position. This would be expected because

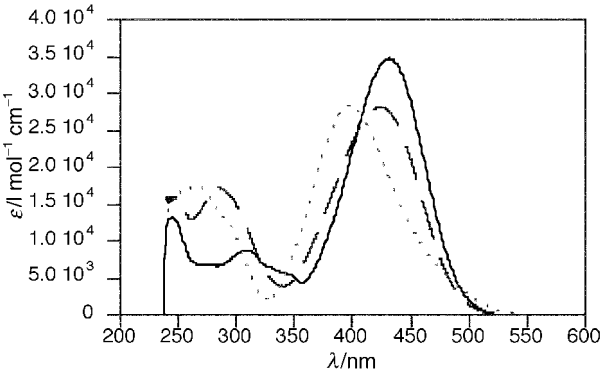


Fig. 2 Normalised UV–visible spectra of the nitro derivatives in chloroform: (—) compound **6**, (---) compound **7** and (·····) compound **8**)

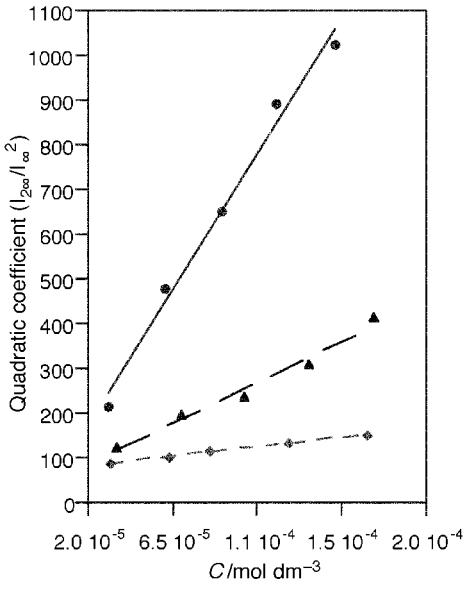


Fig. 3 Quadratic coefficient (I_{2w}/I_w^2) *versus* molar concentration plot of the nitro derivatives at room temperature in chloroform (1064 nm): (●) compound **6**, (▲) compound **7** and (◆) compound **8**

Table 2 Absorption maxima (in $CHCl_3$) and first hyperpolarizabilities (1064 nm, $CHCl_3$) of the nitro derivatives.

Compound	λ_{max}/ nm	log ε	β_{HRS} ($\times 10^{-30}$ esu)	β_{0HRS} ($\times 10^{-30}$ esu)
6	430	4.5	393	114
7	424	4.4	215	66
8	396	4.4	130	51

the intramolecular charge transfer should be higher in the first case, and therefore, the lowest transition energy should be lower (*i.e.* λ_{max} should be higher). However, the absorbance spectra show that compound **7** absorbs at a wavelength lower than compound **6**. This effect has already been seen in other related compounds such as 1-(4-nitrophenyl)-2-pyrazoline and 1-(2,4-dinitrophenyl)-2-pyrazoline.[13b] This phenomenon indicates that there is more efficient charge transfer in compound **6** than in compound **7**, which can be explained by a higher degree of planarity and higher resonance effect in the mononitro derivative. Indeed, the presence of a second nitro group in the *ortho*-position of the phenyl ring (compound **7**) must cause a decrease in the charge transfer due to the deviation from planarity of the phenyl ring at the N1 position due to steric effects. The effect of this is a decrease in β with respect to compound **6**. To verify this, we tried to grow crystals of these pyrazolines but all efforts proved unsuccesful. The crystal structure analysis of similar molecules, such as 1-(2′,4′-dinitrophenyl)pyrazole[20] and 4-bromo-1-(2′,4′-dinitrophenyl)pyrazole,[21] taken from the literature reveal that the nitro group in the *ortho*-position is not conjugated with its phenyl ring (the dihedral angles are 69 and 65° respectively). Moreover, the dihedral angles between the pyrazole ring and the phenyl ring are 27 and 22° respectively, higher than the 19° of a similar compound with only one nitro group in the *para*-position, 4-bromo-3-methyl-1-(4′-nitrophenyl)pyrazole.[22]

The β value of the hydrazone derivative (compound **8**) is lower than those measured in the pyrazoline derivatives. This indicates that, in terms on NLO properties, the pyrazoline derivatives are better systems than the hydrazone derivative, due to the presence of the heterocyclic ring which prevents the conformational freedom of the C=N–N atoms of the hydrazone, thus enhancing the conjugation and, consequently, β.

Mesogenic properties

The thermal behaviour of all the compounds has been studied by polarizing optical microscopy and differential scanning calorimetry (DSC). All the compounds melt to give an isotropic liquid (see Table 3). However, compound **6** shows mesomorphic behaviour on cooling, displaying a monotropic smectic A phase. The texture of this mesophase is typically fan-shaped. The compound melts at 93 °C on heating and shows hysteresis in the cooling scan, with the smectic A phase appearing at 71 °C and remaining metastable until the cooling cycle is complete (−20 °C at 10 °C min^{-1}). In the second heating cycle a cold crystallization takes place and the sample melts again at a similar temperature to the first scan (Fig. 4).

Table 3 Optical, thermal and thermodynamical properties of 2-pyrazolines **2**–**8**

Compound	Transition[a]	T/ °C (ΔH/kJ mol^{-1})
2	C–I	108
3	C–I	161
4	C–I	143
5	C–I	239
6	C–I	93.1 (31.0)
	I–S_A	71.4 (−1.3)
7	C–I	162
8	C–I	106

[a]C–I: crystal–isotropic liquid transition; I–S_A: isotropic liquid–smectic A mesophase transition

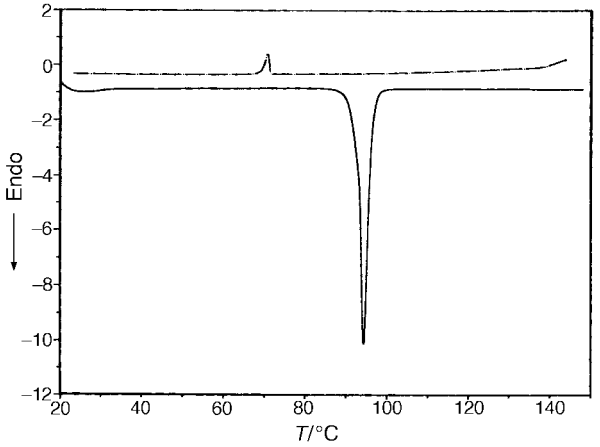


Fig. 4 DSC thermogram for compound **6**; solid line: first heating; dashed line: first cooling

The poor mesogenic behaviour of the compounds in this series could be due to the fact that their molecular structure deviates significantly from linearity. Indeed, in the crystal structure of 1,3-diphenyl-2-pyrazoline the angle between the axis of the phenyl rings is 35°.[23]

The fact that compound **6** is the only derivative with liquid crystalline properties is probably due to the aforementioned effect that the nitro group induces a planar structure with conjugation throughout the whole molecule. Furthermore, the presence of terminal groups possessing a large dipole moment is known to make intermolecular interactions stronger through dimer associations leading to an antiparallel arrangement.[24] This is supported by the X-ray diffraction study of the supercooled mesophase of compound **6** at room temperature, which confirms its smectic structure with a layer thickness $d = 37$ Å. If we compare this value with the molecular length estimated from Dreiding stereomodels, assuming an all-*trans* conformation of the hydrocarbon chain, $L = 29.5$ Å, we can conclude that the mesophase has a partial-bilayer structure (S_{Ad} mesophase).

Although compound **5** also has an acceptor group in the 4-position, it is not mesogenic. The existence of dimers in benzoic acid derivatives due to hydrogen bonding is a well known phenomenon that leads to liquid crystalline behaviour in systems such as 4-alkoxybenzoic acids.[25] This type of association is present in compound **5** in the solid state (an IR band is present at 1676 cm^{-1}, which is typical for a hydrogen bonded COOH). However, this association leads to a much higher melting point in compound **5** than in all the other pyrazoline derivatives (see Table 3). These strong interactions in the solid could be responsible for the lack of liquid crystallinity.

Experimental

General methods

All compounds have been characterised satisfactorily by elemental analysis, ^{1}H NMR and IR spectroscopy and mass spectrometry. Microanalyses were performed with a Perkin-Elmer 240C microanalyser. ^{1}H NMR spectra were recorded on a Varian Unity 300 spectrometer; coupling constants J are given in Hz. IR spectra were obtained on a Perkin-Elmer 1600 (FTIR series) spectrometer. Mass spectra were obtained on a VG Autospec EBE (FAB$^+$, 3-NBA matrix). Absorption spectra were obtained on a Kontron Uvikon 940 Spectrophotometer. Fluorescence spectra were obtained on a Perkin-Elmer

LS-50 Luminometer using quartz cells with a 1 cm optical path-length. The quantum yields were measured using quinine sulfate as the standard ($Q_F = 0.5$) at an excitation wavelength of 340 nm. The melting points and the optical textures of the mesophase were studied with an Olympus polarizing microscope equipped with a Linkam THMS 600 heating-cooling stage and a TMS 91 central processor. The transition temperatures were measured by differential scanning calorimetry with a TA Instruments 2000 calorimeter operated at a scanning rate of 10 °C min^{-1}. The apparatus was calibrated with indium (156.6 °C, 28.4 J g^{-1}) as the standard. X-ray diffraction patterns were obtained using a Pinhole camera (Anton-Paar) operating with a point-focused Ni-filtered Cu-Kα beam. The sample was held in Lindemann glass capillaries (1 mm diameter) and heated with a variable-temperature attachment. The diffraction pattern was collected on flat photographic film.

4-*n*-Decyloxyphenyl vinyl ketone 1

67 mmol (8.94 g) of aluminum chloride and 65 mmol (5.88 g) of acryloyl chloride were suspended in 150 ml of dry carbon tetrachloride and cooled in an ice bath. 65 mmol (15.21 g) of decyl phenyl ether was added dropwise and the mixture was stirred for 2 h. The red mixture was poured into a suspension of calcium chloride in water. The aqueous layer was discarded and the organic layer washed with saturated aqueous sodium hydrogen carbonate, dried over calcium chloride, and the solvent removed under reduced pressure. The residue was purified by column chromatography on silica gel using hexane–ethyl acetate (20:1) as the eluent. Yield: 50%. Mp 36 °C. Anal. calc. for $C_{19}H_{28}O_2$: C, 79.17; H, 9.72. Found: C, 78.94; H, 10.31%. IR (Nujol, NaCl): ν(C=O) 1664, ν(C=C) 1602, ν(C=C arom.) 1509 cm^{-1}. ^{1}H NMR ($CDCl_3$, 293 K): δ 0.86 (t, J 6.8, 3H), 1.25–1.44 (m, 14H), 1.75–1.80 (m, 2H), 4.00 (t, J 6.6, 2H), 5.85 (d, J 10.5, 1H), 6.41 (d, J 17.0, 1H), 6.92 (d, J 8.8, 2H), 7.16 (dd, J 16.8, J 10.1, 1H), 7.94 (d, J 8.6, 2H). MS m/z (%): 289 (43, [M^+]), 261 (100).

3-(4′-*n*-Decyloxyphenyl)-1-phenyl-2-pyrazoline 2

2 mmol (0.58 g) of **1** was dissolved in 20 ml of absolute ethanol and 2 mmol (0.22 g) of phenylhydrazine. A drop of acetic acid was added and the mixture was stirred at room temperature for two hours. The yellow precipitate was filtered off under vacuum and recrystallized from ethanol. Yield: 55%. Mp 108 °C. Anal. calc. for $C_{25}H_{34}ON_2$: C, 79.36; H, 8.99; N, 7.41. Found: C, 79.04; H, 8.58; N, 7.45%. IR (Nujol, NaCl): ν(C=N) 1600, ν(C=C arom.) 1501, ν(C—O) 1258 cm^{-1}. ^{1}H NMR ($CDCl_3$, 293 K): δ 0.89 (t, J 6.8, 3H), 1.28–1.50 (m, 14H), 1.76–1.83 (m, 2H), 3.23 (t, J 10.2, 2H), 3.86 (t, J 10.2, 2H), 3.98 (t, J 6.5, 2H), 6.87 (t, J 7.8, 1H), 6.91 (d, J 8.7, 2H), 7.12 (d, J 7.8, 2H), 7.26 (t, 2H), 7.67 (d, J 8.8, 2H). MS m/z (%): 378 (100, [M^+]), 237 (27).

3-(4′-*n*-Decyloxyphenyl)-1-(4″-methoxyphenyl-2-pyrazoline 3

2 mmol (0.35 g) of 4-methoxyphenylhydrazine chlorhydrate was dissolved in a mixture of ethanol–water (5:1) and a solution of 2 mmol (80 mg) of sodium hydroxide in 5 ml of ethanol was added. The mixture was poured into a solution of 2 mmol (0.58 g) of **1** in 15 ml of ethanol. Several drops of acetic acid were added (until pH = 5) and the reaction mixture was stirred for two hours at 40 °C. The yellow precipitate was filtered off under vacuum and recrystallized from acetonitrile. Yield: 50%. Mp 161 °C. Anal. calc. for $C_{26}H_{36}O_2N_2$: C, 76.47; H, 8.82; N, 6.86. Found: C, 76.04; H, 7.91; N, 6.92%. IR (Nujol, NaCl): ν(C=N) 1604, ν(C=C arom.) 1510, ν(C—O) 1251 cm^{-1}. ^{1}H NMR ($CDCl_3$, 293 K): δ 0.87 (t, J 7.3, 3H), 1.25–1.55 (m, 14H), 1.75–1.77 (m, 2H), 3.18 (t, J 10.0, 2H), 3.77 (t, J 10.0, 2H), 3.77 (s, 3H), 3.96 (t, J 6.6, 2H), 6.86 (d, J 8.5, 2H), 6.88 (d, J 8.3, 2H), 7.07 (d, J 8.3, 2H), 7.63 (d, J 8.5, 2H). MS m/z (%): 408 (100, [M^+]).

1-(4′-Chlorophenyl)-3-(4″-*n*-decyloxyphenyl-2-pyrazoline 4

This compound was synthesized from 4-chlorophenylhydrazine chlorhydrate and **1** and purified using the same procedure as described for compound **3**. Yield: 45%. Mp 143 °C. Anal. calc. for $C_{25}H_{33}ON_2Cl$: C, 72.73; H, 8.00; N, 6.79. Found: C, 72.51; H, 7.94; N, 6.79%. IR (Nujol, NaCl): ν(C=N) 1604, ν(C=C arom.) 1510, ν(C—O) 1261 cm^{-1}. ^{1}H NMR ($CDCl_3$, 293 K): δ 0.88 (t, J 7.3, 3H), 1.27–1.46 (m, 14H), 1.76–1.79 (m, 2H), 3.23 (t, J 10.1, 2H), 3.81 (t, J 10.1, 2H), 3.98 (t, J 6.5, 2H), 6.90 (d, J 8.1, 2H), 7.02 (d, J 8.1, 2H), 7.22 (t, J 8.1, 2H), 7.65 (d, J 8.1, 2H). MS m/z (%): 412 (100, [M^+]).

1-(4′-Carboxyphenyl)-3-(4″-*n*-decyloxyphenyl)-2-pyrazoline 5

A solution of 2 mmol (0.30 g) of 4-hydrazinobenzoic acid in 15 ml of hot absolute ethanol was added to a solution of 2 mmol (0.58 g) of **1** in 10 ml of absolute ethanol. A drop of acetic acid was added and the mixture was stirred at 40 °C for 4 h. The yellow precipitate was filtered off and washed several times with hot ethanol. Yield. 50%. Mp 239 °C. Anal. calc. for $C_{26}H_{34}O_3N_2$: C, 73.93; H, 8.06; N, 6.63. Found: C, 73.63; H, 7.94; N, 6.47%. IR (Nujol, NaCl): ν(C=O) 1676, ν(C=N) 1606, ν(C=C arom.) 1511, ν(C—O) 1258 cm^{-1}. ^{1}H NMR ($CDCl_3$, 293K): δ 0.86 (t, J 7.3, 3H), 1.25–1.50 (m, 14H), 1.75–1.77 (m, 2H), 3.29 (t, J 10.4, 2H), 3.90 (t, J 10.4, 2H), 3.93 (t, J 7.1, 2H), 6.91 (d, J 9.0, 2H), 7.06 (d, J 8.7, 2H), 7.68 (d, J 9.0, 2H), 7.99 (d, J 8.7, 2H). MS m/z (%): 422 (100, [M^+]), 261 (63).

3-(4′-*n*-Decyloxyphenyl)-1-(4″-nitrophenyl)-2-pyrazoline 6

This compound was synthesized from 4-nitrophenylhydrazine and **1** using the same procedure as described for compound **5**. The reaction mixture was stirred for 6 h at 40 °C. The solvent was evaporated and the crude product purified by column chromatography on silica gel using hexane–ethyl acetate (1:1) as the eluent. Yield: 30%. Mp (DSC) 93 °C (I 71 °C SmA on cooling). Anal. calc. for $C_{25}H_{33}O_3N_3$: C, 70.92; H, 7.80; N, 9.93. Found: C, 70.44; H, 7.63; N, 10.06%. IR (Nujol, NaCl): ν(C=N) 1593, ν(C=C arom.) 1507, ν(NO_2) 1299, ν(C—O) 1246 cm^{-1}. ^{1}H NMR ($CDCl_3$, 293 K): δ 0.88 (t, J 7.1, 3H), 1.20–1.34 (m, 14H), 1.78–1.80 (m, 2H), 3.36 (t, J 10.2, 2H), 3.98 (t, J 10.2, 2H), 4.00 (t, J 6.6, 2H), 6.94 (d, J 9.0, 2H), 7.03 (d, J 9.2, 2H), 7.69 (d, J 9.5, 2H), 8.18 (d, J 9.5, 2H). MS m/z (%): 423 (100, [M^+]).

3-(4′-*n*-Decyloxyphenyl)-1-(2″, 4″-dinitrophenyl)-2-pyrazoline 7

1.39 mmol (0.4 g) of **1** was added to a solution of 4.17 mmol (0.26 ml, 80%) of hydrazine hydrate in 10 ml of absolute ethanol. This reaction was carried out under an argon atmosphere. The reaction mixture was heated under reflux for 3 h. Distillation under argon afforded ethanol, water and hydrazine. The white residue of 3-(4′-decyloxyphenyl)-2-pyrazoline was suspended in 10 ml of absolute ethanol and placed into an ice bath. 70 mmol (130 mg) of 2,4-dinitrofluorobenzene was added. The dinitrophenyl derivative precipitated instantaneously. The suspension was stirred for 3 h and the orange precipitate was filtered off and recrystallized from ethanol. Yield: 55%. Mp 162 °C. Anal. calc. for $C_{25}H_{32}O_5N_4$: C, 64.10; H, 6.84; N, 11.96. Found: C, 64.04; H, 6.94; N, 11.88%. IR (Nujol, NaCl): ν(C=N) 1603, ν(C=C arom.) 1510, ν(NO_2) 1306, ν(C—O) 1252 cm^{-1}. ^{1}H NMR ($CDCl_3$, 293 K): δ 0.86 (t, J 6.6, 3H), 1.26–1.44 (m, 14H), 1.75–1.80 (m, 2H), 3.35 (t, J 9.6, 2H), 3.95 (t, J 9.6, 2H), 3.97 (t, J 6.3, 2H), 6.90 (d, J 8.8, 2H), 7.06 (d, J 9.3, 1H), 7.59 (d, J 8.8, 2H), 8.20 (dd, J 9.3, J 2.5, 1H), 8.46 (d, J 2.5, 1H). MS m/z (%): 468 (100, [M^+]).

N^1-[4′-Decyloxy-α-(2″-ethoxyethyl)benzylidene]-N^2-(2,4-dinitrophenyl)hydrazine 8

A mixture of 8 mmol (2.30 g) of **1**, 8 mmol (1.58 g) of 2,4-dinitrophenylhydrazine, 60 ml of absolute ethanol and several drops of acetic acid was heated under reflux for 12 h. The mixture was evaporated to dryness and the orange solid was purified by column chromatography on silica gel using hexane–ethyl acetate (15:1) as the eluent and recrystallized from ethanol. Yield: 30%. Mp 106 °C. Anal. calc. for $C_{27}H_{38}O_6N_4$: C, 63.03; H, 7.39; N, 10.89. Found: C, 62.98; H, 7.42; N, 10.95%. IR (Nujol, NaCl): ν(NH) 3278, ν(C=N) 1615, $\nu(NO_2)$ 1615, ν(C=C arom.) 1508, $\nu(NO_2)$ 1326, 1307, ν(C—O) 1250 cm^{-1}. ^{1}H NMR ($CDCl_3$, 293 K): δ 0.86 (t, J 6.6, 3H), 1.1 (t, J 7.0, 3H), 1.25–1.40 (m, 12H), 1.4–1.5 (m, 12H), 1.77–1.82 (m, 2H), 3.13 (t, J 5.6, 2H), 3.51 (q, J 7.0, 2H), 3.78 (t, J 5.6, 2H), 4.00 (t, J 6.6, 2H), 6.93 (d, J 8.9, 2H), 7.80 (d, J 9.1, 2H), 7.59 (d, J 8.8, 2H), 7.99 (d, J 9.6, 1H), 8.27 (dd, J 9.6, J 2.6, 1H), 9.13 (d, J 2.6, 1H), 11.88 (s, 1H). MS m/z (%): 515 (100, [M^+]), 332 (67).

Conclusions

The pyrazoline structure has shown a special ability to strongly interact with UV and visible radiation in both linear and non-linear optical senses. Thus, the compounds with the terminal groups OCH_3, H, Cl and COOH behave as fluorescent materials with large Stokes shifts and high quantum yields. The nitro derivatives exhibit significant β_o values measured by the HRS technique. Surprisingly, the compound with only one nitro group shows a higher first hyperpolarizability than that with two nitro groups. All of these optical phenomena can be explained on the basis of structural factors. Furthermore, these compounds tend to be oriented in a parallel form behaving as promising promesogenic materials. Elongation of the central unit could provide the desirable liquid crystal properties. The combination in the same structure of all these properties can open new technological applications for these classical materials.

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References

1 (*a*) A. Wagner, C. W. Schellhammer and S. Petersen, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 699; (*b*) C. D'Ambrosio, H. Leutz, M. Taufer and H. Güsten, *Appl. Spectrosc.*, 1991, **45**, 484; (*c*) *Luminescent Materials*, ed. G. Blasse and B. C. Grabmaier, Springer-Verlag, Berlin, 1994.
2 (*a*) *Nonlinear Optical Properties of Organic and Polymeric Materials*, ed. D. J. Williams, *ACS Symposium Series 233*, American Chemical Society, Washington DC, 1983; (*b*) *Materials for Nonlinear Optics: Chemical Perspectives*, ed. S. R. Marder, J. E. Sohn and G. D. Stucky, *ACS Symposium Series 455*, American Chemical Society, Washington DC, 1991; (*c*) *Molecular Nonlinear Optics*, ed. J. Zyss, Academic Press, New York, 1994.
3 (*a*) D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 690; (*b*) *Nonlinear Optical Properties of Organic Molecules and Crystals*; ed. D. S. Chemla, J. Zyss, Academic Press., Orlando, 1987; (*c*) *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; ed. P. N. Prasad and D. J. Williams, John Wiley and Sons, New York, 1991.
4 J. L. Oudar and D. S. Chemla, *J. Chem. Phys.*, 1977, **66**, 2664.
5 J. L. Oudar, *J. Chem. Phys.*, 1977, **67**, 446.
6 (*a*) L.-T. Cheng, W. Tam, S. H. Stevenson, G. R. Meredith, G. Rikken and S. R. Marder, *J. Phys. Chem.*, 1991, **95**, 10 631; (*b*) L.-T. Cheng, W. Tam, S. H. Stevenson, G. R. Meredith, G. Rikken and S. R. Marder, *J. Phys. Chem.*, 1991, **95**, 10 643.
7 (*a*) H. Strähle, W. Seitz and H. Güsten, *Ber. Bunsen-Ges. Phys. Chem.*, 1976, **80**, 288; (*b*) H.Güsten, G. Heinrich and H. Frühbeis, *Ber. Bunsenges. Phys. Chem.*, 1977, **81**, 810; (*c*) H. Güsten, P. Schuster and W. Seitz, *J. Phys. Chem.*, 1978, **82**, 459.
8 (*a*) J. O. Morley and D. Pugh, in *Organic Materials for Nonlinear Optics.*, ed. R. A. Hann and D. Bloor, *Spec. Publ. R. Soc. Chem. 69*, Kent, 1989, p. 28; (*b*) J. O. Morley, V. J. Docherty and D. Pugh, *J. Mol. Electron.*, 1989, *5*, 117; (*c*) S. Allen, in *Organic Materials for Nonlinear Optics.*, ed. R. A. Hann and D. Bloor, *Spec. Publ. R. Soc. Chem. 69*, Kent, 1989, p. 137.
9 Y. R. Peterson, in *Molecular Electronics*, ed. O. J. Ashwell, Research Studies Press LTD, Exeter, 1992, ch. 3.
10 R. S. Theobald, in *Rodd's Chemistry of Carbon Compounds*, 2nd Edition, ed. S. Coffey and M. F. Ansell, *Vol. 4, Heterocyclic Compounds, Part C*, ed. M. F. Ansell, Elsevier, New York, 1986; ch. 1.
11 G. Coispeau and J. Elguero, *Bull. Soc. Chim. Fr.*, 1970, 2717.
12 L. Chambers, M. L. Willard, *J. Am. Chem. Soc.*, 1962, **82**, 3373.
13 (*a*) S. G. Beech, J. H. Turnbull and W. Wilson, *J. Chem. Soc.*, 1952, 4686; (*b*) J. Elguero and R. Jacquier, *Bull. Soc. Chim. Fr.*, 1966, 610.
14 N. Rajalakshimi, in *Ultra-Violet and Visible Spectroscopy. Chemical Applications*, ed. C. N. R. Rao, 2nd edn., Butterworth, London, 1967, ch. 10.
15 G. C. Guilbaut, in *Practical Fluorescence*, 2nd edn., ed. G. C. Guilbaut, Marcel Dekker, New York, 1990, p. 16.
16 (*a*) R. W. Terhune, P. D. Maker and C. M. Savage, *Phys. Rev. Lett.*, 1965, **14**, 681; (*b*) K. Clays and A. Persoons, *Phys. Rev. Lett,* 1991, *66*, 2980.
17 K. Clays and A. Persoons, *Rev. Sci. Instrum.* 1992, **63**, 3285.
18 K. Clays, A. Persoons and L. De Maeyer, *Modern Nonlinear Optics*, ed. M. Evans and S. Kielich, *Adv. Chem. Phys. Ser., Vol. 85, Part 3*, Wiley, New York, 1993.
19 (*a*) J. L. Oudar, and D.S. Chemla, *J. Chem. Phys.*, 1977, **66**, 2664; (*b*) S. J. Lalama and A. F. Garito, *Phys. Rev. A*, 1979, **20**, 1179.
20 F. R. Fronczek, F. J. Parodi and N. H. Fischer, *Acta Crystallogr., Sect. C*, 1989, **45**, 2027.
21 J. L. Galigne and J. Falgueirettes, *Acta Crystallogr., Sect. B*, 1969, **25**, 1637.
22 J. Lapasset and J. Falgueirettes, *Acta Crystallogr., Sect. B*, 1972, **28**, 791.
23 B. Duffin, *Acta Crystallogr., Sect. B*, 1968, **24**, 1256.
24 (*a*) *Smectic Liquid Crystals*, ed. G. W. Gray and J. W. G. Goodby, Leonard Hill, Glasgow, 1984, pp. 6–8; (b) A. J. Leadbetter, *Thermotropic Liquid Crystals* (*Critical Reports on Applied Chemistry, Vol. 22*), ed. G. W. Gray, Wiley, Chichester, **1987**, pp. 12–15.
25 (*a*) C. M. Paleos, D. Tsiourvas, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1696; (*b*) *Molecular Structure and the Properties of Liquid Crystals*, ed. G. W. Gray, Academic Press, New York, 1985, p. 147.

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