Structure-Activity Relationship of New Organic NLO Materials Based on Push-Pull Azodyes. 1
Synthesis and Molecular Properties of the Dyes

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Abstract. Several new push-pull azobenzene dyes were synthesized by diazonium salt coupling of electron-poor anilines with N,N-dialkylanilines. Their dipole moments and first-order hyperpolarizabilities were evaluated respectively from the concentration dependence of the dielectric constant of solutions in apolar solvents and by the electric-field-induced-second-harmonic-generation (EFISH) technique. Investigation of the influence of both nature and steric hindrance of the electron-withdrawing group allowed to highlight a significant deviation from linearity in the relationship between dipole moments and first-order hyperpolarizabilities. This effect was particularly noticeable when multiple electron withdrawing groups pointing in different directions were present on the same phenyl ring.

Among the large number of push-pull conjugated structures used for second-order nonlinear optical measurements, azobenzenes seem to present the best compromise between ease of synthesis, good stability and large values of the first-order hyperpolarizabilities (β). Compounds of this class, such as the ubiquitous 4-nitro-4'-[N-(2-hydroxyethyl)-N-ethyl]aminoazobenzene (Disperse Red 1) have been extensively studied for their nonlinear optical properties either dispersed in [1–9] or linked to [9–14] a macromolecular matrix; however, in spite of the large number of data, to the best of our knowledge systematic investigations of the influence of variations of the chemical structure (that is shape, flexibility, polarity, possibility of hydrogen bonding) both on the solid-state and solution NLO properties of azobenzene-based molecules have not been performed yet.

Recently we have undertaken a rather thorough study on the relationship between chemical structure and NLO properties of azobenzene dyes, in different physical and chemical states; this involved a) the preparation of a series of push-pull azobenzenes, bearing a dialkylamino group on the electron-rich benzene ring and having electron-withdrawing groups differing for shape, that is steric hindrance and length, and electronegativity and the study of their molecular NLO features; b) a X-rays structural analysis, looking for NLO crystal activity; c) the investigation of the dependence of orientability and orientation stability on chemical structure for dispersions of the chromophores in a polymer host, or d) for polymers bearing the same structures in the side chains.

In the present paper we report on the synthesis and molecular characterisation, including dipole moments (μ) and second order hyperpolarizabilities (β) measurements, of several new azobenzene dyes, whereas data relevant to points b–d will constitute the object of forthcoming papers.

Dipole moments were evaluated from the concentration dependence of the dielectric constant of azodyes solutions in an apolar solvent, according to the Debye-Guggenheim equation, neglecting the concentration dependence of the refractive index. Hyperpolarizabilities were obtained in the form of the product $\mu\beta$ by EFISH measurements at 1907 nm, according to an established

literature procedure[14]; β_0 values, the first hyperpolarizabilities extrapolated at zero frequency, are also given, thus allowing for a comparison between compounds having different absorption spectra.

The μ and β values of the new chromophores were compared to those obtained for a well known azo-dye, Disperse Red 1, used as reference. All model compounds have been numbered progressively from **M1** to **M8**; accordingly, for sake of shortness and homogeneity, by following the commercial Disperse Red 1 will be referred to as **M0**.

Experimental

Materials. 2-Cyanoacetic acid, *N*-phenylpiperidine and *N*-phenylpiperazine were distilled under reduced pressure; fractions having boiling point 103 °C/0.05 mm, 97 °C/0.7 mm, and 125 °C/7 mm, respectively, were collected and stored in the dark under dry nitrogen atmosphere. The other commercial reagents from Aldrich and Fluka and were used as received. The purity of the compounds has always been checked *via* both TLC and GC.

(−)-Menthyl 2-cyanoacetate

A solution of 5.0 g (60 mmol) of 2-cyanoacetic acid in 60 mL of benzene was placed in a 100 mL flask equipped with a Dean–Stark apparatus, then 9.4 g (60 mmol) of (−)-menthol and 0.53 g (1.2 mmol) of *p*-toluenesulfonic acid trihydrate were added and the resulting solution was refluxed for 3 h. When no further formation of water was detected, the solution was concentrated to about 15 mL, then 50 mL of ethanol were added, and the volume reduced again to 20 mL. The solution was finally cooled at −15 °C to give long colourless needles (10.4 g, 78 %). − ^{1}H NMR (CDCl$_3$) δ/ppm = 5.0 (1H, dt, C*H*–O-), 3.75 (2H, s, C*H*$_2$–COO), 2.2–0.95 (18H, m, menthyl protons). − FT-IR (KBr pellet): ν/cm^{-1} = 3000–2850 (ν C-H aliphatic), 2223 (ν CN), 1730 (ν C=O), 1450 (δ CH$_2$), 1230 and 1130 (ν C–O–C).

Octyl 2-cyanoacetate

The procedure above reported was repeated by using 1-octanol as starting material instead of (−)-menthol. The crude product was distilled to give 85% yield of a colourless liquid having *b.p.* 142 °C/8 mm and density 0.94 g/l. − ^{1}H NMR (CDCl$_3$) δ/ppm= 4.2–4.3 (2H, t, COO–C*H*$_2$–CH$_2$-), 3.75 (2H, s, NC–C*H*$_2$–COO), 1.7 (2H, m, COO–CH$_2$–C*H*$_2$-), 1.3 (10 H, m, (C*H*$_2$)$_5$–CH$_3$), 0.85 (3H, t, C*H*$_3$). − FT-IR (liquid film): ν/cm^{-1} = 3000–2850 (ν C-H aliphatic), 2223 (ν C≡N), 1730 (ν C=O), 1475 (δ CH$_2$), 1205 and 1070 (ν C–O–C).

Ethyl *p*-amino-α-cyanocinnamate (A6)

A mixture of 0.2 mL (3.2 mmol) of piperidine and 0.6 mL of acetic acid was added to a solution of 6.4 g (53 mmol) of *p*-aminobenzaldehyde and 6.0 (53 mmol) of ethyl 2-cyanoacetate in 150 mL of dioxane. The reaction mixture was refluxed for 10 h, then the solvent was removed under vacuum, and the

residue was dissolved in 50 mL of CH$_2$Cl$_2$; the resulting solution was washed with water to neutrality and dried over Na$_2$SO$_4$. After removal of the solvent under vacuum, the residue was eluted with CH$_2$Cl$_2$ on silica gel, to yield a microcrystalline yellow solid (7.1 g, 62%). − ^{1}H NMR (CDCl$_3$) δ/ppm = 8.1 (1H, s, C*H*=C), 7.8–7.9 (2H, d, C*H* *meta* to NH$_2$), 6.7 (2H, d, C*H ortho* to NH$_2$), 4.5 (2H, s, N*H*$_2$), 4.35 (2H, q, COO–C*H*$_2$-), 1.4 (t, 3H, C*H*$_3$). − FT-IR (KBr pellet): ν/cm^{-1} = 3450 and 3352 (ν N-H), 3090 (ν C-H aromatic), 2950–2850 (ν C-H aliphatic), 2221 (ν C≡N), 1687 (ν C=O), 1637 (δ NH$_2$), 1608 (ν C=C), 1572 and 1515 (aromatic ring), 1325 (ν C–N), 1275 and 1235 (ν C–O–C), 1178 and 830 (δ aromatic protons). − UV-VIS (CHCl$_3$): λ = 385 nm, ε = 33500 L/(mol cm). FLU (dioxane): λ = 362 nm (shoulders at 380 e 398 nm). DSC: 101 °C (crystal–crystal, 1.5 kJ/mole); 163 °C (melting, 30.1 J/g).

p-Amino-α-cyanocinnamonitrile (A5)

The procedure above reported was repeated by using 2-cyanoacetonitrile as starting material instead of ethyl 2-cyanoacetate. The crude product was crystallized from 2:1 ethanol/chloroform mixture to give 59% of a microcrystalline golden solid. − ^{1}H NMR (DMSO-d$_6$) δ/ppm = 8.2 (1H, s, C*H*=C), 7.8–7.9 (2H, d, C*H meta* to NH$_2$), 6.3–6.8 (4H, m, N*H*$_2$ and C*H ortho* to NH$_2$). − FT-IR (KBr pellet): ν/cm^{-1} = 3459 and 3355 (ν N-H), 3090 ν C-H aromatic), 2219 (ν C≡N), 1631 (δ NH$_2$), 1608 (ν C=C), 1567 and 1517 (ν aromatic ring), 1326 (ν C–N), 1177 and 839 (δ C-H aromatic). − UV-VIS (dioxane): λ = 394 nm, ε = 35800 L/(mol cm). FLU (dioxane): λ_{max} = 362 nm (shoulders at 380 e 398 nm). DSC: 213 °C (melting, 27.0 kJ/mole).

Octyl *p*-amino-α-cyanocinnamate (A7)

The procedure above reported was repeated by using octyl 2-cyanoacetate as starting material instead of ethyl 2-cyanoacetate to give 51% of a solid product. − ^{1}H NMR (CDCl$_3$): δ/ppm = 8.1 (1H, s, C*H*=C), 7.8–7.9 (2H, d, C*H meta* to NH$_2$), 6.7 (2H, d, C*H ortho* to NH$_2$), 4.5 (2H, s, N*H*$_2$), 4.25 (2H, q, COO–C*H*$_2$–CH$_2$-), 1.75 (2H, m, COO–CH$_2$–C*H*$_2$-), 1.3 (10 H, m, C*H*$_3$-(C*H*$_2$)$_5$), 0.9 (3H, t, C*H*$_3$). − FT-IR (KBr pellet): ν/cm^{-1} = 3455 and 3352 (ν N-H), 3090 (ν C-H aromatic), 2950–2850 (ν C-H aliphatic), 2213 (ν C≡N), 1687 (ν C=O), 1637 (δ NH$_2$), 1608 (ν C=C), 1571 and 1517 (ν aromatic ring), 1327 (ν C–N), 1279 and 1230 (ν C–O–C), 1173 and 830 (δ C-H aromatic). − UV-VIS (CHCl$_3$): λ_{max} = 385 nm, ε = 35500 L/(mol cm). FLU (dioxane): λ_{max} = 362 nm (shoulders at 380 e 398 nm). DSC: 44 °C, (crystal–crystal, 0.6 kJ/mole); 142 °C (melting, 13.1 kJ/mole).

(−)-Menthyl *p*-amino-α-cyanocinnamate (A 8)

The procedure above reported was repeated by using (−)-menthyl 2-cyanoacetate as starting material instead of ethyl 2-cyanoacetate, to give 59% of solid product. − ^{1}H NMR (CDCl$_3$): δ/ppm = 8.1 (1H, s, C*H*=C), 7.8–7.9 (2H, d, C*H meta* to NH$_2$), 6.7 (2H, d, C*H ortho* to NH$_2$), 4.8–4.9 (1H, dt, COO–C*H*), 4.6 (2H, s, N*H*$_2$), 2.1–0.8 (18H, m, menthyl protons). − FT-IR (KBr pellet): ν/cm^{-1} = 3461 and 3370 (ν N-H), 3090 (ν C-H aromatic), 2950–2850 (ν C-H aliphatic), 2216 (ν C≡N), 1703 (ν C=O), 1644 (δ NH$_2$), 1615 (ν C=C),

1567 and 1518 (v aromatic ring), 1321 (v C–N), 1276 and 1215 (vC–O–C), 1174 and 832 (δ C-H aromatic). – UV-VIS (CHCl₃): λ_{max}= 385 nm, ε = 32800 L/(mol cm). FLU (dioxane): λ_{max} = 362 nm (shoulders at 380 e 398 nm). DSC: 73 °C (crystal–crystal, 1.0 kJ/mole); 139 °C (melting, 14.4 kJ/mole).

4-Nitro-4'-(N-piperidinyl)azobenzene (M1)

A solution of 1.0 g (14 mmol) of NaNO₂ in 3 mL of water was slowly added to a solution of 2.0 g (14 mmol) of 4-nitroaniline in 70 mL of acetic acid, cooled just above the freezing point; the colour turned to light orange. The solution was left to warm up to room temperature and stirred for 20 minutes; then the temperature was lowered to 7–8 °C and 2.3 g (14 mmol) of N-phenylpiperidine dissolved in 10 mL of acetic acid were added; the colour turned to red–violet. The solution was warmed up to room temperature and stirred for 5 hours, then 300 mL of water were added and pH was brought to 6 with addition of NaHCO₃; the precipitate was filtered, dissolved in 100 mL of CH₂Cl₂, washed with 10% NaHCO₃ and with water till neutrality, dried on Na₂SO₄, concentrated at the rotating evaporator and finally eluted with CH₂Cl₂ on silica gel, to give a crystalline red solid (3.4 g, 76%) having $m.p.$ 192 °C. – ¹H NMR (CDCl₃): δ/ppm= 8.3 (2H, dd, CH ortho to NO₂), 7.9 (4H, m, C$\underline{H}$ ortho to N=N), 6.95 (2H, d, CH ortho to NR₂), 3.45 (4H, s, N–C$\underline{H}_2$–CH₂), 1.7 (6H, s, N–CH₂–(C$\underline{H}_2$)₃-CH₂). – FT-IR (KBr pellet): v/cm⁻¹= 3100–3000 (v C-H aromatic), 2940–2840 (v C-H aliphatic), 1600 and 1510 (v aromatic ring + v_a NO₂), 1359 (v =C–N), 1340 (v_s NO₂), 1241 (v C–N stretching), 855 and 820 (δ C-$\underline{H}$ aromatic). – UV-VIS (CHCl₃): λ_1 = 479 nm, ε_1 = 27500 L/(mol cm); λ_2 = 286 nm, ε_2 = 11200 L/(mol cm).

4-Nitro-4'-(N-piperazinyl)azobenzene (M2)

The procedure reported for **M1** was repeated by using N-phenyl-N'-trifluoroacetylpiperazine (prepared from N-phenylpiperazine according to a literature procedure [15]) as starting material instead of N-phenylpiperidine. The crude 4-nitro-4'-[(N'-trifluoroacetyl)-N-piperazinyl)azobenzene was recrystallized from acetone (72% yield). 5.0 g (12 mmol) of 4-nitro-4'-[(N'-trifluoroacetyl)-N-piperazinyl)azobenzene were dissolved in 300 mL dioxane and 6.5 ml of a 55% tetrabutylammonium hydroxide solution in water were added, then the solution was heated to reflux for 3 h, concentrated to about 100 ml and cooled at 0 °C. The precipitate was filtered and recrystallised from dioxane, to give 3.2 g (85%) of a crystalline red solid that did not melt or decompose up to 260 °C. – ¹H NMR (CDCl₃): δ/ppm = 8.3 (2H, d, C$\underline{H}$ ortho to NO₂), 7.9 (4H, m, CH ortho to N=N), 7.0 (2H, d, C$\underline{H}$ ortho to NR₂), 3.4 (4H, s, HN–C$\underline{H}_2$–CH₂), 3.1 (6H, s, CH₂–C$\underline{H}_2$–N–C₆H₄), 1.8 (1H, s, NH). – FT-IR (KBr pellet): v/cm⁻¹= 3500 (v N-H), 3100–3000 (v C-H aromatic), 2950–2840 (v C-H aliphatic), 1590 and 1510 (v aromatic ring + v_a NO₂), 1356 (v =C–N), 1338 (v_s NO₂), 1241 (v C–N), 859 and 824 (δ C-H aromatic). – UV-VIS (CHCl₃): λ_1 = 453 nm, ε_1 = 27500 L/(mol cm); λ_2 = 283 nm, ε_2 = 11700 L/(mol cm).

4-Cyano-4'-(N-piperidinyl)azobenzene (M3)

The procedure reported for **M1** was repeated by using 4-cyanoaniline as starting material instead of 4-nitroaniline to

give 71% of a solid product having $m.p.$ = 205 °C. – ¹H NMR (CDCl₃): δ/ppm= 7.9 (4H, m, C$\underline{H}$ on the cyano substituted ring), 7.75 (4H, d, C$\underline{H}$ meta to NR₂), 6.95 (2H, d, C$\underline{H}$ ortho to NR₂), 3.45 (4H, s, N–C$\underline{H}_2$–CH₂), 1.7 (6H, s, N–CH₂–(C$\underline{H}_2$)₃-CH₂). – FT-IR (KBr pellet): v/cm⁻¹= 3100–3000 (v C-H aromatic), 2940–2840 (vC-H aliphatic), 2223 (vC≡N), 1595 and 1507 (v aromatic ring), 1360 (v =C–N), 1240 (v C–N), 850 and 820 (δCH aromatic). – UV-VIS (CHCl₃): λ_1 = 448 nm, ε_1 = 26300 L/(mol cm); λ_2 = 278 nm, ε_2 = 11900 L/(mol cm).

4-Nitro-2-cyano-4'-(N-piperidinyl)azobenzene (M4)

The procedure reported for **M1** was repeated by using a 1:10 sulfuric acid/acetic acid as solvent and 4-nitro-2-cyanoaniline as starting material instead of 4-nitroaniline to give 58% of a solid product having $m.p.$ = 147 °C. – ¹H NMR (CDCl₃): δ/ppm = 8.6 (1H, d, C$\underline{H}$ ortho to CN and NO₂), 8.4 (1H, dd, C$\underline{H}$ ortho to NO₂), 8.0 (3H, dt, C$\underline{H}$ ortho to N=N), 6.9 (2H, dt, CH ortho to NR₂), 3.55 (4H, s, N–C$\underline{H}_2$–CH₂), 1.8 (6H, s, N–CH₂–(C$\underline{H}_2$)₃-CH₂). – FT-IR (KBr pellet) v/cm⁻¹= 3100–3000 (v C-H aromatic), 2940–2850 (v C-H aliphatic), 2229 (v C≡N), 1600 and 1519 (v aromatic ring + v_a NO₂), 1357 (v =C–N), 1339 (v_s NO₂), 1241 (vC–N), 851 and 820 (δC-H aromatic). – UV-VIS (CHCl₃): λ_1 = 538 nm, ε_1 = 40500 L/(mol cm); λ_2 = 296 nm, ε_2 = 21900 L/(mol cm).

4-(2,2-Dicyanovinyl)-4'-(N-piperidinyl)azobenzene (M5)

The procedure reported for **M1** was repeated by using 4-(2,2-dicyanovinyl)aniline as starting material instead of 4-nitroaniline to give 58% of a solid product having $m.p.$ = 228 °C. – ¹H NMR (CDCl₃): δ/ppm = 8.2 (1H, s, C₆H₄–C$\underline{H}$=C), 8.1 (2H, d, CH ortho to vinyl group), 7.9 (4H, m, C$\underline{H}$ ortho to N=N), 6.9 (2H, d, C$\underline{H}$ ortho to NR₂), 3.45 (4H, s, N–C$\underline{H}_2$-CH₂), 1.8 (6H, s, N–CH₂–(C$\underline{H}_2$)₃-CH₂). – FT-IR (KBr pellet): v/cm⁻¹= 3100–3000 (v C-H aromatic), 2950–2820 (v C-H aliphatic), 2224 (v C≡N), 1596 and 1510 (v aromatic ring), 1362 (v=C–N), 1247 (vC–N), 837 (δC-H aromatic). – UV-VIS (CHCl₃): λ_1 = 518 nm, ε_1 = 31500 L/(mol cm); λ_2 = 333 nm, ε_2 = 13800 L/(mol cm).

4-(2-Cyano-2-carboxyethylvinyl)-4'-(N-piperidinyl) azobenzene (M6)

The procedure reported for **M1** was repeated by using 4-(2-cyano-2-carboxyethylvinyl)aniline as starting material instead of 4-nitroaniline to give 61% of a solid product having $m.p.$ = 115 °C. – ¹H NMR (CDCl₃): δ/ppm= 8.25 (1H, s, C₆H₄-C$\underline{H}$=C), 8.1 (2H, d, C$\underline{H}$ ortho to vinyl group), 7.9 (4H, m, C$\underline{H}$ ortho to N=N), 6.9 (2H, d, C$\underline{H}$ ortho to NR₂), 4.4 (2H, q, COOC$\underline{H}_2$CH₃), 3.45 (4H, s, N–C$\underline{H}_2$–CH₂), 1.8 (6H, s, N–CH₂–(C$\underline{H}_2$)₃-CH₂), 1.4 (3H, t, CH₂C$\underline{H}_3$). – FT-IR (KBr pellet): v/cm⁻¹= 3100–3000 (v C-H aromatic), 2940–2820 (v C-H aliphatic), 2222 (v C≡N), 1726 (v C=O), 1602 and 1508 (v aromatic ring), 1365 (v =C–N), 1281 and 1207 (v C–O–C), 1243 (v C–N), 855 and 820 (δ C-H aromatic). – UV-VIS (CHCl₃): λ_1 = 488 nm, ε_1 = 33500 L/(mol cm); λ_2 = 321 nm, ε_2 = 15100 L/(mol cm).

4-(2-Cyano-2-carboxyoctylvinyl)-4'-(N-piperidinyl) azobenzene (M7)

The procedure reported for **M1** was repeated by using 4-(2-

cyano-2-carboxyoctylvinyl)aniline as starting material instead of 4-nitroaniline to give 68% of a solid product having $m.p.$ = 93 °C. – ^{1}H NMR (CDCl$_3$): δ/ppm = 8.25 (1H, s, C$_6$H$_4$-CH=C), 8.1 (2H, d, CH *ortho* to vinyl group), 7.9 (4H, m, CH *ortho* to N=N), 6.9 (2H, d, CH *ortho* to NR$_2$), 4.25 (1H, dt, COO–CH$_2$–CH$_2$), 3.45 (4H, s, N–CH$_2$–CH$_2$), 1.8 (6H, s, N–CH$_2$–(CH$_2$)$_3$-CH$_2$), 1.75 (2H, m, COO–CH$_2$–CH$_2$-), 1.3 (10 H, m, CH$_2$–(CH$_2$)$_5$–CH$_3$), 0.9 (3H, t, CH$_2$–CH$_2$). – FT-IR (KBr pellet): v/cm^{-1} = 3100–3000 (v C-H aromatic), 2930–2850 (v C-H aliphatic), 2223 (v C≡N), 1720 (v C=O), 1601 and 1509 (v aromatic ring), 1364 (v =C–N), 1268 and 1199 (v C–O–C), 1242 (v =C–N), 849 and 822 (δ C-H aromatic). – UV-VIS (CHCl$_3$): λ_1 = 491 nm, ε_1 = 34600 L/(mol cm); λ_2 = 326 nm, ε_2 = 15500 L/(mol cm).

4-(2-Cyano-2-carboxymenthylvinyl)-4'-(N-piperidinyl)-azobenzene (**M8**)

The procedure reported for **M1** was repeated by using 4-(2-cyano-2-carboxymenthylvinyl)aniline as starting material instead of 4-nitroaniline to give 63% of a solid product having $m.p.$ = 159 °C. – ^{1}H NMR (CDCl$_3$): δ/ppm = 8.25 (1H, s, C$_6$H$_4$-CH=C), 8.1 (2H, d, CH *ortho* to vinyl group), 7.9 (4H, m, CH *ortho* to N=N), 6.9 (2H, d, CH *ortho* to NR$_2$), 4.85 (1H, dt, COOCH), 3.45 (4H, s, N–CH$_2$–CH$_2$), 2.1–0.8 (24H, m, menthyl and piperidine protons). – FT-IR (KBr pellet) v/cm^{-1} = 3100–3000 (v C-H aromatic), 2950–2860 (v C-H aliphatic), 2223 (v C≡N), 1717 (v C=O), 1598 and 1508 (v aromatic ring), 1361 (v =C–N stretching), 1285 and 1201 (v C–O–C), 1241 (v C–N), 849 and 825 (δ C-H aromatic). – UV-VIS (CHCl$_3$): λ_1 = 490 nm, ε_1 = 34600 L/(mol cm); λ_2 = 328 nm, ε_2 = 19300 L/(mol cm).

Physicochemical Measurements

IR spectra were recorded by a NICOLET 5SXC FT-IR spectrometer on KBr pellets. UV spectra were recorded by a PERKIN-ELMER Lambda 9 spectrometer. – ^{1}H NMR spectra were recorded at a Brucker 300 MHz spectrometer on CDCl$_3$ solutions; tetramethylsilane (TMS) was used as an internal standard. Fluorescence spectra were recorded on 1.4 × 10^{-6} M solutions in 1 cm quartz cells by a SPEX Fluorolog fluorimeter (excitation wavelength = 280 nm). Melting points were measured under nitrogen atmosphere at an heating rate of 10 °C/min by a Mettler TA 4000 calorimeter, equipped with a DSC 30 low temperature cell.

Optical Characterisation

All solution measurements were performed in dioxane freshly distilled on Na/K alloy. The values Γ_L = 6.2×10^{-22} m^2/V^2 at 1907 nm and ε = 2.209 were used for pure dioxane [14].

EFISH measurements

The experimental set-up depicted in Figure 1 was used. The 1907 nm fundamental wavelength was obtained from a Nd:YAG laser at 1064 nm and a hydrogen Raman cell at 25 atm, using the Stokes shift at 4155 cm^{-1}. The anti-Stokes lines were absorbed by the RG 1000 and RG 39 filters, while the 1064 nm radiation was deflected by dielectric mirrors. The lenses L1 and L2 focused the beam at the entrance and the

exit of the Raman cell. The second harmonic signal was detected by a photomultiplier (PM), cooled at –9 °C. To minimize the electrochemical degradation of the sample, the high voltage (7 kV, corresponding to an electric field of 14 kV/cm) was pulsed (1 msec pulse duration) and synchronized with laser pulses. The wedged sample cell was moved in the direction perpendicular to the incident beam and the Maker fringes were measured as a function of the change in optical path length. A 2.5% wt. solution of 2-methyl-4-nitroaniline was used as a reference (Γ_L = 1.3·10^{-21} m^2/V^2 at 1907 nm) [14].
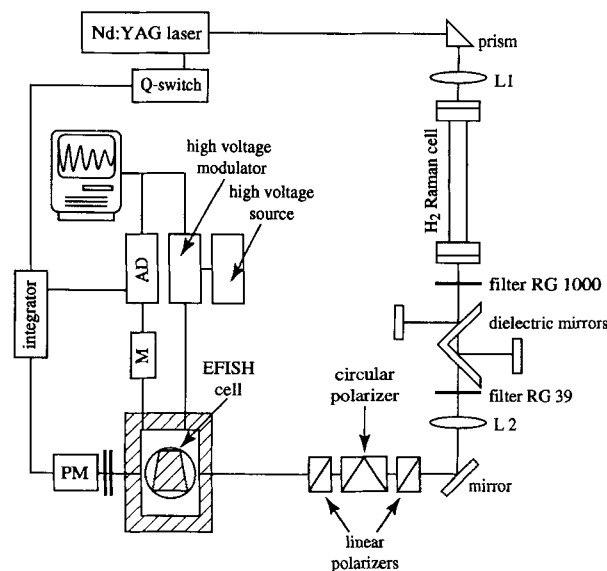

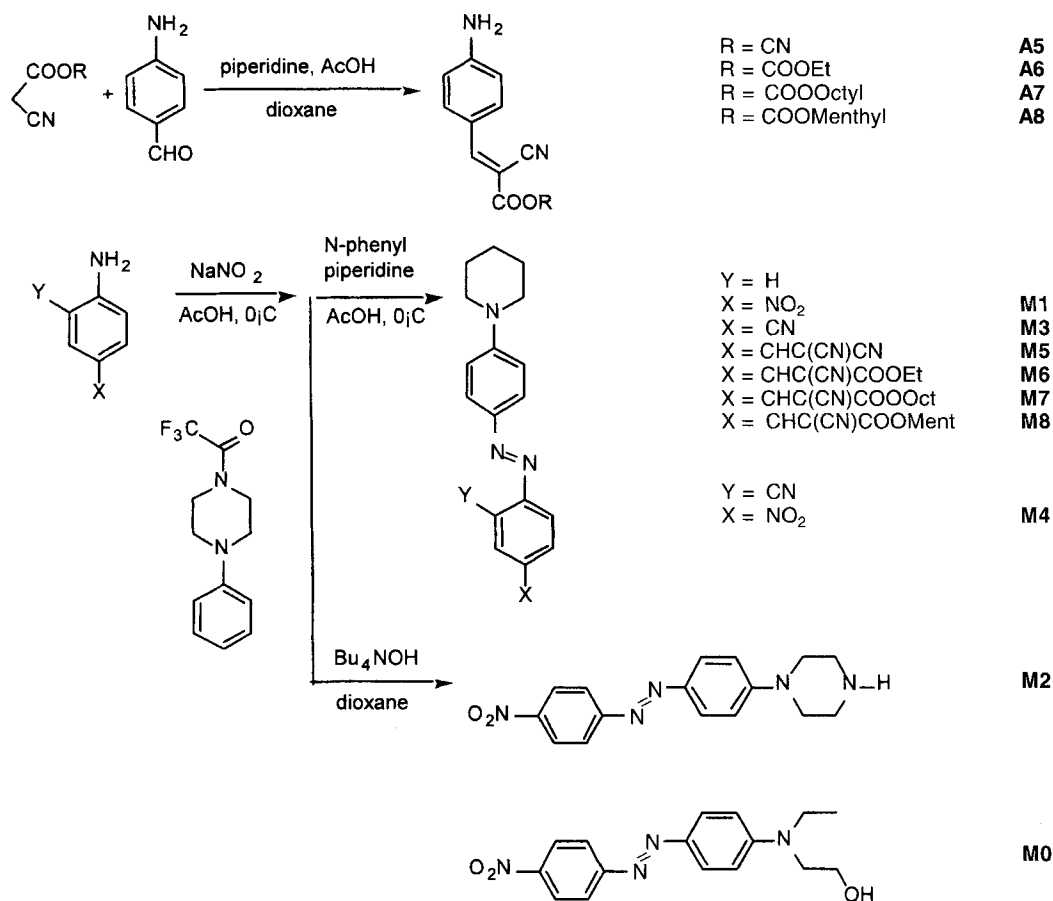**Fig. 1** Schematic of apparatus for EFISH measurements

Dipole Moment Measurements

The capacity of a 2 ml cell was recorded at eleven frequencies in the 180–1800 kHz range. The average value was taken as the static capacity of the condenser.

Results and Discussion

Synthesis. The synthetic pathway used for the preparation of different azobenzene derivatives is sketched in Scheme 1. Esterification of 2-cyanoacetic acid, the Knoevenagel reaction between 4-aminobenzaldehyde and 2-cyanoacetic acid derivatives, and N-phenylpiperidine coupling with the diazonium salts of the prepared electron-poor anilines constitute the key steps of the adopted synthetic scheme. In the case of **M2**, a protection/deprotection sequence of the secondary amine [15] of N-phenylpiperazine became necessary, in order to avoid its reaction with the diazonium salt.

2-Cyanoacetic acid esters were synthesized by the Fisher procedure because of the failure of alternative

R = CN   A5
R = COOEt   A6
R = COOOctyl   A7
R = COOMenthyl   A8

Y = H
X = NO_2 M1
X = CN   M3
X = CHC(CN)CN   M5
X = CHC(CN)COOEt   M6
X = CHC(CN)COOOct   M7
X = CHC(CN)COOMent   M8

Y = CN
X = NO_2 M4

M2

M0

Scheme 1

methods. In fact 2-cyanoacetyl chloride, obtained by reaction with thionyl chloride in THF solution, resulted to have a lower stability than what reported in the literature [16], decomposing not only to the already known pyridine derivatives, but also to highly conjugated oligomeric and polymeric species. Analogously the use of dicyclohexylcarbodiimide (DCCI) as a coupling agent failed almost completely, giving mainly rise to coloured compounds.

Knoevenagel condensations were performed by following the usual literature procedures [17, 18]; as expected only the E-isomers were formed, as evidenced by ^{1}H-NMR analysis [19]. Fluorescence emission and UV-VIS absorption spectra of the different anilines did not show any appreciable dependence on type and bulkiness of the substituents. This result indicates that the electronic distribution on the phenyl ring of the anilines remains basically unchanged. A crystal–crystal transition was observed in the DSC heating curves of A6, A7 and A8 anilines, containing an aliphatic ester group. This transition can be tentatively related to the reorganization of the aliphatic chain, also by taking into account that its temperature decreases on increasing the conformational mobility of the alkoxy group. The diazonium salt coup-

ling was generally performed in acetic acid, that ensured a good solubility of both anilines and diazonium salts; however a 1:9 mixture of sulfuric and acetic acid was used for the synthesis of M4 and M5, due to the insolubility of the starting anilines in acetic acid.

Dipole Moment and First-order Hyperpolarizability Measurements

The dipole moments of the investigated azobenzene derivatives, as obtained from the concentration dependence of the dielectric constant of dioxane solutions, are summarized in Table 1. M0 showed a μ value higher than that of the corresponding compound containing a cyclic electron donor group (M1). The presence of a secondary amine on the six membered ring (M2) did not affect μ, suggesting that intramolecular hydrogen bonding should not occur in solution. Surprisingly, substitution of the nitro group with a nitrile group did not change μ either. The insertion of a second non-collinear electron-withdrawing group, as in M4, clearly led to an appreciable decrease of μ.

An increase of length of the alkyl ester group from two (M6) to eight (M7) carbon atoms had no effect, whereas substitution of the linear alkyl chain with a

Tab. 1 Dipole moment and first-order hyperpolarizabilities of the investigated azobenzene chromophores.

Chromophore	μ (Debye)[a]	λ_{max} (nm)[b]	β^{1907} $(10^{-40}$ m^{2}V^2)	β_0 $(10^{-40}$ m^{2}V^2)
M0	8.7	482	109 ± 13	76 ± 8
M1	8.1	479	105 ± 13	76 ± 8
M2	8.2	453	76 ± 9	55 ± 6
M3	8.0	448	84 ± 8	63 ± 6
M4	5.0	538	248 ± 11	155 ± 8
M5	9.0	518	126 ± 15	80 ± 11
M6	5.7	488	105 ± 15	71 ± 11
M7	5.5	491	134 ± 15	92 ± 11
M8	6.4	490	113 ± 15	76 ± 11

[a] Estimated error ±0.2 D.   [b] At 25 °C in chloroform solution.

cyclic menthyl residue (**M8**) brought roughly a 10% increase of the dipole moment; no simple explanation can be provided on the basis of the molecular geometry.

The large difference between the μ value of **M5** and those of the other derivatives of α-cyanocinnamic acid can be attributed to the much higher electron-withdrawing power of the 2,2-dicyanovinyl group.

Nonlinear susceptibilities of the investigated azobenzene derivatives were measured in solution by EFISH, a well known technique [14, 20] based on a third order nonlinear optical effect due to the mixing of the oscillating laser electromagnetic radiation with a static electric field used to give a preferential dynamic orientation to dipoles in solution. The measured nonlinear susceptibilities Γ_L are expressed as

$$\Gamma_L = N f^0 (f^\omega)^2 f^{2\omega} (\gamma + \mu_g \beta_z / kT)$$

where N is the density of the molecules, f's are local field factors and β_z is the vectorial component of β along the dipole moment axis; for rigid rod molecules β_z approximates well the tensorial component β_{zzz}; the γ contribution is generally neglected.

To minimize solvent-solvent and solute-solvent interactions an infinite dilution extrapolation was used, [14, 21] where $\mu_g \beta_z$ is expressed as a function of the concentration dependence of nonlinear susceptibility, dielectric constant, specific volume and refractive index.

The first-order hyperpolarizabilities (β) of the azobenzene compounds were evaluated from the relevant μ values and the nonlinearities measured via EFISH, and then reported to zero frequency.

We used an ubiquitous compound (Disperse Red 1, called here **M0**) as a reference, due to the variability that often occurs in literature for the results of β measurements by different investigators; for example, comparing our results for **M0** with the ones of Singer et al. [22], we had a perfect agreement for the dipole moment and a conspicuous difference for β.

No significant difference was found between β values of **M0** and **M1**, thus indicating that the presence of either dialkyl or cycloalkyl substituents on the nitrogen atom in 4'position does not have an appreciable influence on the molecular nonlinear optical properties. The markedly lower β_0 value of **M2** as compared to **M1** must be attributed to the presence of the piperazine ring; also if not explaining the invariance of the dipole moment, an intramolecular hydrogen bonding between secondary amine and the aniline nitrogen in a boat structure could lower the electrondonor power of the latter and explain the β_0 behavior.

As expected, substitution of a nitro group with a cyano group lowered β_0, even if the ground state dipole moment did not change; by using the two level model approximation, the change in β_0 can be ascribed to the larger dipole moment of nitro derivatives in the first excited state.

Introduction of a second electron-withdrawing group (**M4**) gave rise to a dramatic increase of β. A large expansion of conjugation was already suggested by the 50 nm spectral shift of the UV absorption maximum of **M4** with respect to **M1**, nonetheless a 120% increase of β in spite of a 40% decrease of the dipole moment was really unexpected. In this case the two level model cannot be used; in fact the β value evaluated by EFISH measurement refers to the β component along the dipole moment axis, that for **M4** is not aligned with the molecular z axis. In the two level model on the contrary only the tensorial component along this latter axis (β_{zzz}) is taken into account.

Variation of the structure of the alkyl ester group (**M6**, **M7** and **M8**) or substitution of the ester functionality with a second nitrile group (**M5**) did not exhibit a significant influence on hyperpolarizability.

Conclusions

The preparation of several new azobenzene dyes with enhanced second order nonlinear optical properties was effected by simple synthetic and purification procedures that generally afforded high yields of very low cost chromophores, that nonetheless presented attractive first-order hyperpolarizability values.

In particular **M4** resulted to be rather interesting and in principle worth of further exploitation. Indeed it can be obtained by a one-step synthesis, it is highly soluble in most solvents and exhibits a β_0 value twice as large as that of the often used Disperse Red 1.

Evaluation of both μ and β values could help to improve the chromophore design. Indeed, second harmonic generation, and more generally second order nonlinear optical properties of electric field oriented materials (crystals of these chromophores have been proved to be NLO-inactive [23]) depend both on β and on the

product $\mu \cdot \beta$, that determines the orientation. In fact high μ values can be exploited to achieve high degrees of chromophore orientation by poling in an electric field. The results concerning the series of investigated compounds highlighted a nonlinear relationship between μ and β; this was particularly conspicuous for **M4** and **M5**, where the lowest and the highest dipole moments corresponded respectively to the highest hyperpolarizability and to a hyperpolarizability comparable to that of Disperse Red 1.

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