Experimental and Theoretical Study of a New Class of Acceptor Group in Chromophores for Nonlinear Optics: 2-Substituted 4-Methylene-4*H*-oxazol-5-ones

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Push−pull organic molecules that combine a polyfunctionalized electron-donating carbazole moiety with a new acceptor group, 4-methylene-4*H*-oxazol-5-ones, were synthesized and characterized as nonlinear optical chromophores with promising $\mu\beta$ values. First-order hyperpolarizability and dipole moments were calculated by MNDO, AM1 and PM3 methods. Theoretical $\mu\beta$ values were compared to experimental data measured in solution by electric-field-induced second-harmonic generation (EFISH). The different factors that could influence the NLO response, especially the gain or loss of aromatization stabilization during the charge-transfer process, were studied. The thermal stability of these new chromophores is also reported.

Introduction

Organic molecules with delocalized π-electron systems may display large nonlinear responses which make them attractive for use in integrated optics. Several factors determine the second-order nonlinear optical (NLO) response of molecules.[1] First, the presence and nature of electron-donating and -accepting units in the molecule is the main factor. Second, the extension of the conjugation path is crucial to the transfer of charge between the substituents in the presence of electric fields. Moreover, several authors point to the hypothesis that the loss of aromatic stabilization in the charge-separated form of the ground state results in a decrease of the nonlinear optical response. A strategy was proposed in which the loss of aromaticity at one end of the charge-separated form would be compensated by a gain of aromaticity at the opposite end. Therefore, compounds with acceptors that can gain the aromaticity state in their charge-separated resonance form could have larger hyperpolarizability values than compounds unable to achieve this stabilization.[2]

As part of our research into new materials[3] we are especially interested in polysiloxane side-chain liquid-crystal polymers (SCLCPs) with polyfunctionalized carbazole units in their side chains. Carbazole-derived compounds have photoconductivity properties[4] and a second-order nonlinear optical response when electron acceptor groups are incorporated into the carbazole unit.[5] The possibility that synthesized carbazole-based polymeric films[6] might show both photoconductivity and an electrooptic effect made them suitable candidates for photorefractive applications. For these reasons, and also to examine the effect of the gain of aromaticity in the acceptor moiety in the charge-transfer form on hyperpolarizability values, novel push−pull chromophores with a new class of acceptor group, 4-methylene-4*H*-oxazol-5-ones were studied (Figure 1).

These new chromophores can be represented by three main resonance forms: A, B, and C (Figure 2), where form A represents the electronic structure of the mol-

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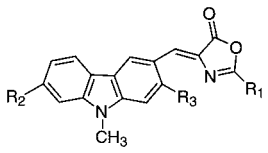

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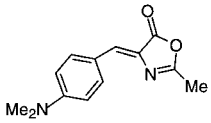

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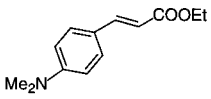

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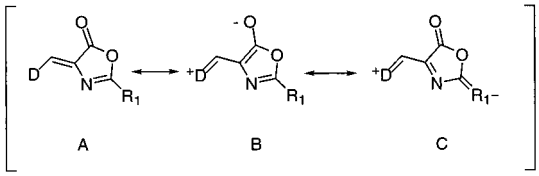
Comp.	R_1	R_2	R_3
1	Ph	H	H
2	Me	H	H
3	OMe	H	H
4	Ph-OMe	H	H
5	Ph-NO_2	H	H
6	Ph	OMe	OMe
7	Ph-OMe	OMe	OMe
8	Ph-NO_2	OMe	OMe
9	Ph-OMe	$O(CH_2)_{10}CH_3$	OMe
10	Ph-NO_2	$O(CH_2)_{10}CH_3$	OMe

Figure 1. New oxazolone-derived chromophores.



D=donor unit, like carbazole in compounds **1**-**10** or

4-*N*,*N*′-dimethylaminophenyl in compound **11**

Figure 2. Main resonance forms of new oxazolone-derived chromophores.

ecule without charge separation, and resonance forms B and C belong to representations with intramolecular charge transfer (ICT). When the ICT process is considered, the donor unit lost its aromatic character and simultaneously the oxazolone ring can (B) or cannot (C) acquire aromaticity. The predominance of one of them will be influenced by the nature of substitution R_1 in the oxazolone ring. The aim of this work is to show experimental evidences over the effect of the aromatization of the acceptor group on the hyperpolarizability values.

Experimental Section

Materials. Commercially available reagents and solvents were used without further purification, unless indicated otherwise. Flash chromatography was carried out on E. Merck Kiesegel 60 (230−400 mesh).

Analytical Techniques. The ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature with a Bruker ARX-300. ^{1}H chemical shifts are quoted relative to TMS and ^{13}C chemical shifts relative to solvent signals. IR spectra were obtained on a Perkin-Elmer 1330 infrared spectrophotometer and UV−vis spectra on a Cary 5E spectrophotometer. Melting points are uncorrected. Mass spectra were measured on a Hewlett-Packard 5988-A spectrometer. Elemental analyses were carried out by the Servei D'Anàlisi Elemental del CSIC of Barcelona, Spain.

Thermal analyses were performed using a Mettler-30 differential scanning calorimeter at heating rate of 20 K/min or in a Mettler Toledo STAR^e to study thermal stability over 300 °C: in both cases under N_2 at 80.0 mL/min.

Synthesis of 4-Methylene-2-aryl-4*H*-oxazol-5-ones (1, 4−10). General Procedure. To a mixture of 1.00 mmol of 9-methyl-9*H*-carbazole-3-carbaldehyde (**22**, **23**, or **26**), 1.00 mmol of the corresponding *N*-acylglycine, and 1.00 mmol of NaAcO (anhydrous) under N_2 atmosphere was added 3.00 mmol of Ac_2O. The mixture was stirred and heated at 80 °C for 1 h. Then it was cooled to 0 °C and diluted with ethanol. The product was filtered and washed with water and cold ethanol. The crude product was purified by flash chromatography on silica gel and finally recrystallized.

Synthesis of 4-Methylene-2-alkyl-4*H*-oxazol-5-ones (2, 3, and 11). General Procedure. To a mixture of 1.00 mmol of 9-methyl-9*H*-carbazole-3-carbaldehyde (**22**) or 4-*N*,*N*-dimethylaminobenzaldehyde, 1.00 mmol of the corresponding *N*-acylglycine and 1.00 mmol of NaAcO (anhydrous) in the presence of 4 Å molecular sieves and under N_2 atmosphere were added 6.00 mmol of Ac_2O. The mixture was stirred and heated at 60 °C for 1 h and then at 120−140 °C for 10 h. It was cooled to room temperature and diluted with chloroform. The crude product was purified by flash chromatography on silica gel and recrystallized.

4-(9-Methyl-9*H*-carbazole-3-ylmethylene)-2-phenyl-4*H*-oxazol-5-one, 1. The product was recrystallized from chloroform−methanol giving yellow-orange needles. Thus 366 mg of **1** were obtained (yield 75%). TLC (SiO_2, CH_2Cl_2, UV): R_f = 0.69. Mp: 221−223 °C. IR (KBr): u_{max} = 1790 (C=O), 1595 (C−C arom), 1476, 1323, 1252 (C−O−C), 1148 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.98 (dd, CH^4, $J_{4,2}$ = 1.8 Hz, $J_{4,1}$ = 0.5 Hz, 1 H), 8.43 (dd, CH^1, $J_{1,2}$ = 9 Hz, $J_{1,4}$ = 0.5 Hz, 1 H), 8.26−8.19 (m, CH$^{5,2'',6''}$, 3 H), 7.60−7.31 (m, CH$^{2,7,8,3',3'',4'',5''}$, 7 H), 3.92 (s, N−CH_3, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 192.42 (C_{oxaz}^{5}), 143.24 (C^{8a}), 134.37 (C^{9a}), 133.32 (C^1), 131.31 (C$^{3'}$), 130.73 (C_{oxaz}^{4}), 129.44 (C$^{4''}$), 128.52 (C$^{2'',6''}$), 127.80 (C$^{3'',5''}$), 127.31 (C^7), 127.01 (C^2), 126.54 (C^5), 126.43 (C^{5a}), 125.44 (C^{4a}), 121.20 (C^3), 120.91 (C^4), 120.75 (C^6), 109.55 (C^8), 109.45 (C^1), 29.83 (N−CH_3) ppm. MS−CI−NH_3: *m*/*z* = 353 (M + 1, 100%), 370 (M + 18, 5%). UV [λ (nm), (ϵ), $CHCl_3$] = 442 (35 800), 338 (12 400), 286 (25 600), 240 (27 700). Anal. Calcd for $C_{23}H_{16}N_2O_2$: C, 78.40; H, 4.58; N, 7.95. Found: C, 78.28; H, 4.47; N, 7.98.

2-Methyl-4-(9-methyl-9*H*-carbazole-3-ylmethylene)-4*H*-oxazol-5-one, 2. The crude product was purified by flash chromatography with $CHCl_3$ on silica gel and recrystallized from CH_3OH. Thus 315 mg of a yellow-orange product was obtained (yield 57%). TLC (CH_2Cl_2, SiO_2, UV): R_f = 0.67. ^{1}H

NMR (200 MHz, $CDCl_3$): $\delta = 8.84$ (d, CH^4, $J_{4,1} = 2$ Hz, 1 H), 8.27 (dd, CH^1, $J_{1,2} = 8.4$ Hz, $J_{1,4} = 2$ Hz, 1 H), 8.18 (m, CH^5, 1 H), 7.53−7.31 (m, $CH^{2,6,7,8,3'}$, 5 H), 3.88 (s, N−CH_3, 3 H), 2.45 (s, $C_{oxaz}{}^2$-CH_3, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 164.29 ($C_{oxaz}{}^5$), 142.61 (C^{8a}), 141.60 (C^{9a}), 133.37 ($C^{3'}$), 130.45 ($C_{oxaz}{}^4$), 129.63 ($C^{5,7}$), 126.52 (C^{5a}), 125.53 (C^{4a}), 124.53 ($C^{2,4}$), 120.76 (C^8), 120.08 (C^6), 108.96 (C^1), 29.31 (N−CH_3), 15.65 (CH_3) ppm. MS−CI−NH_3: m/z = 291 (M + 1, 100%), 308 (M + 18, 9%); UV [λ (nm), (ϵ), $CHCl_3$]: 469 (49 600), 298 (62 700), 262 (56 800), 234 (46 700). UV [λ (nm), (ϵ), $CHCl_3$]: 409 (35 100), 330 (16 700), 293 (19 100). Anal. Calcd for $C_{18}H_{14}N_2O_2$: C, 74.40; H, 4.86; N, 9.65. Found: C, 74.25; H, 4.83; N, 9.58.

2-Methoxy-4-(9-methyl-9*H*-carbazole-3-ylmethylene)-4*H*-oxazol-5-one, 3. The crude product was first purified by flash chromatography with (CH_2Cl_2/hexane 9:1) on silica gel and then by TLC preparative (CH_2Cl_2, silica gel). Thus 77 mg of a mixture of both isomers Z/E (7:3) was obtained (yield 35%). TLC (CH_2Cl_2,UV): $R_f = 0.51$. ^{1}H NMR (200 MHz, $CDCl_3$) major isomer: $\delta = 9.00$ (s, CH^4, 1 H), 8.39−8.16 (m, 2 H), 7.63−7.22 (m, 4 H), 3.89 (s, N−CH_3, 3 H), 2.45 (s, O−CH_3, 3 H) ppm. ^{1}H NMR (200 MHz, $CDCl_3$) minor isomer: $\delta = 8.83$ (s, CH^4, 1 H), 8.39−8.16 (m, 2 H), 7.63−7.22 (m, 4 H), 3.89 (s, N−CH_3, 3 H), 2.45 (s, O−CH_3, 3 H) ppm. UV [λ (nm), (e), $CHCl_3$]: 409 (13 200), 331 (10 900), 293 (14 200). Anal. Calcd for $C_{18}H_{14}N_2O_3$: C, 70.58; H, 4.61; N, 9.15. Found: C, 70.98; H, 4.82; N, 9.30.

2-(4-Methoxyphenyl)-4-(9-methyl-9*H*-carbazole-3-ylmethylene)-4*H*-oxazol-5-one, 4. The crude product was purified by flash chromatography with a mixture of CH_2Cl_2/hexane (9:1) on silica gel. A mixture of both isomers Z/E (8:2) was obtained. A second purification by TLC preparative (CH_2Cl_2, silica gel) gave 90 mg (yield 35%) of the major isomer. TLC (CH_2Cl_2, UV): $R_f = 0.59$. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta =$ 9.04 (m, 1 H), 8.22−8.02 (m, 2 H), 7.73−7.00 (m, 2 H), 3.93 (s, O−CH_3, 3 H), 3.91 (s, N−CH_3, 3 H) ppm. MS−CI−NH_3: 383 (M + 1, 100%). Anal. Calcd for $C_{24}H_{18}N_2O_3$: C, 75.20; H, 4.74; N, 7.33. Found: C, 75.38; H, 4.92; N, 7.21.

4-(9-Methyl-9*H*-carbazole-3-ylmethylene)-2-(4-nitrophenyl)-4*H*-oxazol-5-one, 5. First, 267 mg of crude product was obtained and purified by flash chromatography with a mixture of CH_2Cl_2/hexane (85:15) on silica gel. Then 176 mg of pure product was obtained (yield 62%). TLC (SiO_2, CH_2Cl_2, UV): $R_f = 0.49$. Mp: 280−281 °C. IR (KBr): $\upsilon_{max} = 1763$ (C═O st), 1589 (C−C ar), 1520 (NO_2 st as), 1314 (NO_2 st si), 1252 (C−O−C), 1163 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta =$ 8.95 (s, CH^4, 1 H), 8.40 (m, CH^1, 1 H), 8.47−8.12 (m, $CH^{5,2'',6''}$, 3 H), 7.61−7.35 (m, $CH^{2,6,7,8,3'',5''}$, 6 H), 3.93 (s, N−CH_3, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 136.63$ ($C^{1''}$), 131.73 ($C^{3'}$), 131.14 ($C_{oxaz}{}^4$), 129.58 ($C^{4''}$), 128.78 ($C^{2'',6''}$), 126.85 ($C^{3'',5''}$), 126.52 (C^7), 124.44 (C^2), 124.14 (C^5), 123.81 (C^{5a}), 122.41 (C^{4a}), 120.71 (C^3), 120.50 (C^4), 109.22 (C^6), 29.44 (N−CH_3) ppm. MS−FAB(+)−NBA: 397 (M, 10%). UV [λ (nm), (ϵ), $CHCl_3$]: 472 (35 500), 343 (17 200), 288 (20 100), 242 (27 700). Anal. Calcd for $C_{23}H_{15}N_3O_4$: C, 69.51; H, 3.80; N, 10.58. Found: C, 69.45; H, 3.79; N, 10.54.

4-(2,7-Dimethoxy-9-methyl-9*H*-carbazole-3-ylmethylene)-2-phenyl-4*H*-oxazol-5-one, 6. First, 818 mg of crude was obtained and purified by flash chromatography with a mixture of CH_2Cl_2/hexane (9:1) on silica gel. A mixture of both isomers (Z/E) in a relation of 98:2 was obtained from the ^{1}H NMR spectra. After recrystallization from chloroform−methanol, purification of the product was needed by sublimation in a vacuum to eliminate the chloroform molecules included during the crystallization procedure. Thus, 490 mg of an unique isomer was obtained (yield: 60%). TLC (SiO_2, CH_2Cl_2, UV): $R_f = 0.35$. Mp: 264−266 °C. IR (KBr): $\upsilon_{max} = 1786$ (C═O st), 1607 (C−C arom), 1580 (C−C arom), 1369, 1252 (C−O−C), 1227 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 9.52$ (s, CH^4, 1 H), 8.22−8.17 (m, $CH^{2'',6''}$, 2 H), 8.00 (s, CH^1, 1 H), 7.98 (d, CH^5, $J_{5,6} = 8$ Hz, 1 H), 7.61−7.50 (m, $CH^{3'',4'',5''}$, 3 H), 6.90 (dd, CH^6, $J_{6,5} = 8$ Hz, $J_{6,8} = 2$ Hz, 1 H), 6.81 (d, CH^8, $J_{8,6} = 2$ Hz, 1 H), 6.69 (s, $CH^{3'}$, 1 H), 4.00 (s, C^2−O−CH_3, 3 H), 3.93 (s, C^7−O−CH_3, 3 H), 3.75 (s, N−CH_3, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 158.89$ ($C_{oxaz}{}^5$), 136.18 ($C^{1''}$), 132.50 ($C^{3'}$), 131.66 ($C_{oxaz}{}^2$), 129.18 ($C_{oxaz}{}^4$), 128.87 ($C^{4''}$), 127.92 ($C^{2'',6''}$), 127.36 ($C^{3'',5''}$), 126.08 (C^7), 124.69 (C^2), 120.93 (C^5), 120.77 (C^{5a}), 117.98 (C^{4a}), 117.08 (C^3), 115.38 (C^4), 108.01 (C^6), 93.84 (C^8), 90.34 (C^1), 55.97 (O−CH_3), 55.74 (O−CH_3), 29.28 (N−CH_3) ppm. MS−FAB(+)−NBA: 412 (M, 88%); UV [λ (nm), (ϵ), $CHCl_3$]: 467 (28 700), 297 (23 800), 256 (24 500). Anal. Calcd for $C_{25}H_{20}N_2O_4$: C, 72.80; H, 4.89; N, 6.80. Found: C, 73.02; H, 4.89; N, 6.68.

4-(2,7-Dimethoxy-9-methyl-9*H*-carbazole-3-ylmethylene)-2-(4-methoxyphenyl)-4*H*-oxazol-5-one, 7. The crude was purified by TLC preparative (CH_2Cl_2, silica gel). 271 mg (yield 64%) of a mixture of both isomers Z/E (9:1) was obtained. TLC (CH_2Cl_2, UV): $R_f = 0.46$. ^{1}H NMR (200 MHz, $CDCl_3$), major isomer: $\delta = 9.58$ (s, 1 H), 8.22−7.84 (m, 3 H), 7.09−6.75 (m, 6 H), 4.04−3.78 (m, 12 H) ppm. ^{1}H NMR (200 MHz, $CDCl_3$) minor isomer: $\delta = 9.50$ (s, 1 H), 8.22−7.84 (m, 3 H), 7.09−6.75 (m, 6 H), 4.04−3.78 (m, 12 H) ppm. Anal. Calcd for $C_{26}H_{22}N_2O_5$: C, 70.58; H, 5.01; N, 6.33. Found: C, 70.99; H, 4.95; N, 6.27.

4-(2-Methoxy-9-methyl-7-undecyloxy-9*H*-carbazole-3-ylmethylene)-2-(4-methoxyphenyl)-4*H*-oxazol-5-one, 9. The product was purified by flash chromatography with CH_2Cl_2 on silica gel and recrystallized from $CHCl_3$/CH_3OH. Thus, 55 mg (yield 49%) of the desired product was obtained. TLC (SiO_2, CH_2Cl_2, UV): $R_f = 0.44$. IR (KBr): $u_{max} = 2925$, 2851, 1783 (C═O st), 1634, 1605, 1509, 1262, 1225, 1173 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 9.53$ (s, CH^4, 1 H), 7.97 (d, CH^5, $J_{5,6} = 8.0$ Hz, 1 H), 8.16 (d, $CH^{3'',5''}$, $J_{3'',2''} = J_{5'',6''} = 9.0$ Hz, 2 H), 7.06 (d, $H^{2'',6''}$, $J_{2'',3''} = J_{6'',5''} = 9.0$ Hz, 2 H), 7.96 (s, CH^1, 1 H), 6.89 (d, CH^6, $J_{6,5} = 8.0$ Hz, 1 H), 6.71 (s, $CH^{3'}$, 1 H), 6.83 (s, CH^8, 1 H), 4.07 (t, O−CH_2−, 2 H), 4.01 (s, C^2-O−CH_3, 3 H), 3.92 (s, O−CH_3, 3 H), 3.76 (s, N−CH_3, 3 H), 1.82 (m, O−CH_2−CH_2−, 2 H), 1.28 (m, O−CH_2−CH_2−$(CH_2)_8$−CH_3, 16 H), 0.89 (t, O−$(CH_2)_{10}$−CH_3, 3 H) ppm. MS−FAB(+)−NBA: 582 (M, 30%); UV [λ (nm), (ϵ), $CHCl_3$]: 469 (49 600), 298 (62 700), 262 (56 800), 234 (46 700). Anal. Calcd for $C_{36}H_{42}N_2O_5$: C, 74.20; H, 4.81; N, 7.26. Found: C, 74.36; H, 4.67; N, 7.34.

4-(2-Methoxy-9-methyl-7-undecyloxy-9*H*-carbazole-3-ylmethylene)-2-(4-nitrophenyl)-4*H*-oxazol-5-one, 10. The product was purified by flash chromatography with CH_2Cl_2 on silica gel and recrystallized from $CHCl_3$. Thus 65 mg (yield 48%) was obtained. TLC (SiO_2, CH_2Cl_2, UV): $R_f = 0.51$. IR (KBr): $\upsilon_{max} = 2917$, 2853, 1794 (C═O st), 1609 (NO_2 st as), 1592 (C−C ar), 1545, 1520, 1342 (NO_2 st si), 1268 (C−O−C), 1248, 1227 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 9.45$ (s, CH^4, 1 H), 8.42−8.29 (m, $CH^{2'',3'',5'',6''}$, 4 H), 8.09 (s, CH^1, 1 H), 7.92 (d, CH^5, $J_{5,6} = 8.5$ Hz, 1 H), 6.90 (d, CH^6, $J_{6,5} = 8.5$ Hz, 1 H), 6.81 (s, CH^8, 1 H), 6.72 (s, $CH^{3'}$, 1 H) 4.04 (t, O−CH_2−, 2 H), 4.03 (s, O−CH_3, 3 H), 3.76 (s, N−CH_3, 3 H), 1.82 (m, O−CH_2−CH_2, 2 H), 1.28 (m, O−CH_2−CH_2−$(CH_2)_8$−CH_3, 16 H), 0.89 (t, O−$(CH_2)_{10}$−CH_3, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 142.32$ ($C^{1''}$), 133.54 ($C^{3'}$), 128.97 ($C^{2'',6''}$), 127.66 (C^5), 127.01 (C^4), 122.71 ($C^{3'',5''}$), 104.24 (C^6), 104.16 (C^8), 75.33 (O−CH_2−), 56.81 (O−CH_3), 44.61 (N−CH_3), 33.61 (−CH_2−), 31.03 (−CH_2−), 31.00 (−CH_2−), 30.06 (−CH_2−), 27.10 (−CH_2−), 23.22 (CH_3−CH_2−), 14.11 (CH_3−CH_2−), ppm. MS−FAB(+)−magic bullet [DTT/DTE (3:1)]: 597 (M, 100%). UV [λ (nm), (ϵ), $CHCl_3$]: 502 (29 900), 304 (29 200), 261 (32 500). Anal. Calcd for $C_{35}H_{39}N_3O_6$·$CHCl_3$: C, 60.30; H, 5.62; N, 5.86. Found: C, 62.10; H, 6.00; N, 6.08.

4-(4-Dimethylaminobenzyliden)-2-methyl-4*H*-oxazol-5-one, 11. The crude product was purified by flash chromatography using CH_2Cl_2 as eluent on silica gel and recrystallized from AcOEt. 596 mg were obtained (yield 62%). TLC (SiO_2, CH_2Cl_2, UV): $R_f = 0.34$. IR (KBr): $\upsilon_{max} = 1763$ (C═O st), 1580 (C−C arom), 1530, 1371, 1269 (C−O−C), 1160 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.00$ ($CH^{6,2}$, $J_{2,3} = J_{6,5} = 9.2$ Hz, 2 H), 7.09 (s, $CH^{3'}$, 1 H), 6.70 (d, $CH^{3,5}$, $J_{3,2} = J_{5,6} = 9.2$ Hz, 2 H), 3.08 (s, N−$(CH_3)_2$, 6 H), 2.37 (s, $C_{oxaz}{}^2$−CH_3, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 168.66$ ($C_{oxaz}{}^5$), 162.40 ($C_{oxaz}{}^3$), 152.01 (C^4), 134.32 ($C^{1'}$), 132.77 (C^2), 123.81 ($C_{oxaz}{}^1$), 121.50 (C^1), 111.58 (C^3), 40.03 (N−CH_3), 15.59 (CH_3) ppm. UV [λ (nm), (ϵ), $CHCl_3$]: 432 (19 400), 261(4500). Anal. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.10; N, 12.20. Found: C, 67.82; H, 6.25; N, 12.00.

Ethyl 3-(4-Dimethylaminophenyl)acrylate, 12. A solution of 360 mg (2.40 mmol) of *N*-dimethylaminobenzaldehyde and 630 mg (4.80 mmol) of monoethyl malonate in 24 mL (0.24 mmol) of piperidine and 1 mL of piridine was prepared under N_2 atmosphere. The solution was heated to reflux for 5 h. Then the solvent was evaporated and the formed precipitate was dissolved in hot acetone, precipitated from water and washed with cold acetone. A second recrystallization from acetone−water gave 473 mg (yield 90%) of product **12**. TLC (SiO_2, CH_2Cl_2, UV): $R_f = 0.57$. IR (KBr): $\upsilon_{max} = 2934, 2979, 1703$ (C═O st), 1624, 1603, 1526, 1366, 1186 (C−O−C), 1155, 1036 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.62$ (d, CH^3, $J_{3,2} = 16$ Hz, 1 H), 7.42 (d, $CH^{2',6'}$, $J_{2',3'} = J_{6',5'} = 8.8$ Hz, 2 H), 6.66 (d, $CH^{3',5'}$, $J_{3',2'} = J_{5',6'} = 8.8$ Hz, 2 H), 6.22 (d, CH^2, $J_{2,3} = 16$ Hz, 1 H), 4.24 (q, CH_3-CH_2-, $J = 7$ Hz, 3 H), 3.02 (s, $N-(CH_3)_2$, 6 H), 1.33 (t, $-CH_2-CH_3$, $J = 7$ Hz, 2 H) ppm.;UV [λ (nm), (ϵ), $CHCl_3$]: 361 (19 200), 229 (160 000). Anal Calcd for $C_{13}H_{17}NO_2$: C, 71.20; H, 7.81; N, 6.40. Found: C, 71.04; H, 7.70; N, 6.40.

(4-Methoxybenzoylamino)acetic Acid, 15. To a solution of 470 mg (11.72 mmol) of NaOH and 1.24 g (11.72 mmol) of Na_2CO_3 in 12 mL of water were added 880 mg (11.72 mmol) of glycine at room temperature and then 2.00 g (11.72 mmol) of 4-methoxybenzoyl chloride previously prepared from 4-methoxybenzoic acid and $SOCl_2$. The solution was cooled to 0 °C for 15 min and then heated to room temperature for 2 h. The mixture was acidified with HCl concentrated to pH = 3. The solvent was evaporated and the white precipitate was filtered and washed with diethyl ether. A 1.56 g (yield 65%) of product **15** was obtained. TLC (SiO_2, AcOEt/CH_3OH (1:1), UV): $R_f = 0.54$. ^1H NMR (200 MHz, CD_3OD): $\delta = 7.75$ (d, $CH^{3,5}$, $J_{3,2} = J_{5,6} = 9.2$ Hz, 2 H), 6.91 (d, $CH^{2,6}$, $J_{2,3} = J_{6,5} = 9.2$ Hz, 2 H), 3.99 (s, $-CH_2-$, 2 H), 3.77 (s, $O-CH_3$, 3 H) ppm. ^{13}C NMR (50 MHz, DMSO): $\delta = 176.81$ (COOH), 169.62 (CONH), 165.02 (C^4) 127.31 ($C^{2,6}$), 126.15 (C^1), 116.33 ($C^{3,5}$), 56.02 ($O-CH_3$), 49.27 ($NH-CH_2-COOH$), ppm. Anal. Calcd for $C_{10}H_{11}NO_4$: C, 57.41; H, 5.30; N, 6.70. Found: C, 57.56; H, 5.48; N, 6.83.

(Methoxycarbonylamino)acetic Acid, 17. To a solution of 1.98 g (49.42 mmol) of NaOH and 5.08 g (47.98 mmol) of Na_2CO_3 in 50 mL of water was added 3.58 g (47.71 mmol) of glycine at room temperature. The solution was cooled to 0 °C, and 4.53 g (47.94 mmol) of CH_3COCl was added. After 1 h, it was brought to room temperature for 2 h more. The mixture was acidified with concentrated HCl to pH = 3. The solvent was evaporated and the white precipitate was extracted with diethyl ether (Soxhlet). 5.93 g (yield 95%) of product **17** was obtained. Mp: 93−94 °C. IR (KBr): $\upsilon_{max} = 3374$ (N−H st), 3118 (COO−H st), 1740 (C═O st acid), 1692 (C═O st amide), 1545 (amide II), 1200, 1055 cm^{-1}. ^1H NMR (200 MHz, D_2O): $\delta = 3.73$ (s, $-CH_2-$, 2 H), 3.49 (s, $O-CH_3$, 3 H) ppm. ^{13}C NMR (50 MHz, D_2O): $\delta = 177.15$ (COOH), 162.19 ($-NH-CO-$), 55.54 ($O-CH_3$), 44.89 ($-CH_2-$) ppm. MS−CI−NH_3: $m/z = 134$ (M + 1, 2%), 151 (M + 18, 100%), 168 (M + 35, 49%). Anal. Calcd for $C_4H_7NO_4$: C, 36.10; H, 5.30; N, 10.52. Found: C, 36.27; H 5.47; N, 10.97.

2,7-Dimethoxy-9-methyl-9*H*-carbazole, 21. To a solution of 660 mg (22.00 mmol) of NaH (80%) in 20 mL of dry DMF under nitrogen atmosphere was added a solution of 2.50 g (11.00 mmol) of 2,7-dimethoxycarbazole (**19**) in 10 mL of DMF (anhydrous). After half an hour at room temperature, the solution was heated to 60 °C. Then 1.72 g (12.14 mmol) of CH_3I in 10 mL of DMF (anhydrous) was added to the solution. The reaction was stirred to 60 °C for 2 h, and then cold water was slowly added until formation of a precipitate. The product was extracted with AcOEt and washed with water. The organic layer was dried over $MgSO_4$ and the solvent was evaporated. Thus, 2.65 g (yield 99%) of product **19** was obtained. TLC (SiO_2, CH_2Cl_2, UV): $R_f = 0.54$. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.85$ (d, $CH^{4,5}$, $J_{4,3} = J_{5,6} = 9.2$ Hz, 2 H), 6.84 (d, $CH^{1,8}$, $J_{1,3} = J_{8,6} = 2.2$ Hz, 2 H), 6.83 (dd, $CH^{3,6}$, $J_{3,4} = J_{6,5} = 9.2$ Hz, $J_{3,1} = J_{6,8} = 2.2$ Hz, 2 H), 3.93 (s, $O-CH_3$, 6 H), 3.75 (s, $N-CH_3$, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 158.09$ (C^2), 142.31 (C^{8a}), 119.99 (C^4), 116.78 (C^{4a}), 106.89 (C^3), 93.07 (C^1), 55.69 ($O-CH_3$), 29.09 ($N-CH_3$), 15.59 (CH_3) ppm. Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.80. Found: C, 74.83; H, 6.62; N, 5.93.

Synthesis of 9-Methyl-9*H*-carbazole-3-carbaldehydes (22, 23, 26). General Procedure. To a solution of 10.00 mmol of the corresponding 9-methyl-9*H*-carbazole (**20**, **21** or **25**) in 10 mL of DMF (anhydrous) under nitrogen atmosphere at 0 °C was added 12.00 mmol of $POCl_3$. The solution was heated at 80−90 °C for 2 h. After that, the mixture was diluted with water (250 mL) and treated with K_2CO_3 until pH = 14. The product was extracted with $CHCl_3$ and washed with water. The organic layer was dried over $MgSO_4$ and the solvent was evaporated. The crude was purified by flash chromatography on SiO_2.

9-Methyl-9*H*-carbazole-3-carbaldehyde, 22. The crude was purified by flash chromatography with (CH_2Cl_2/hexane 1:1) on silica gel. Thus, 1.66 g of the desired product was obtained (yield 75%). TLC (SiO_2, CH_2Cl_2, UV): $R_f = 0.36$. Mp: 71.5−72 °C. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 10.09$ (s, CHO, 1 H), 8.60 (m, CH^4, 1 H), 8.15 (m, CH^5, 1 H), 8.02 (dd, CH^1, $J_{1,2} = 8.4$ Hz, $J_{1,4} = 1.4$ Hz, 1 H), 7.56 (m, CH^7, 1 H), 7.48−7.43 (m, $CH^{2,8}$, 2 H), 7.33 (m, CH^6, 1 H), 3.89 (s, $N-CH_3$, 3 H) ppm. UV [λ (nm), (ϵ), $CHCl_3$] = 330 (15 100), 291 (33 600), 275 (35 700), 243 (27 400). Anal. Calcd for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69. Found: C, 80.47; H, 5.48; N, 6.87.

2,7-Dimethoxy-9-methyl-9*H*-carbazole-3-carbaldehyde, 23. The crude product was purified by flash chromatography with (CH_2Cl_2/hexane 1:1) on silica gel. Thus, 1.98 g of the desired product was obtained (yield 78%). TLC (SiO_2, CH_2Cl_2, UV): $R_f = 0.30$. Mp: 155−157 °C. IR (KBr): $\upsilon_{max} = 2929$ (−CH st), 2838 (CHO, comb Fermi), 1665 (C═O), 1630, 1605, 1225, 1115 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 10.48$ (s, CHO, 1 H), 8.45 (s, CH^4, 1 H), 7.88 (d, CH^5, $J_{5,6} = 8.8$ Hz, 1 H), 6.88 (dd, CH^6, $J_{6,5} = 8.8$ Hz, $J_{6,8} = 2$ Hz, 1 H), 6.83 (s, CH^8, $J_{8,6} = 2$ Hz, 1 H), 6.72 (s, CH^1, 1 H), 4.03 (s, C^2-O-CH_3, 3 H), 3.93 (s, C^7-O-CH_3, 3 H), 3.76 (s, $N-CH_3$, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 189.94$ (CHO), 121.28 (C^4), 120.92 (C^5), 112.80 (C^3), 108.62 (C^1), 94.35 (C^6), 90.84 (C^8), 56.37 ($O-CH_3$), 56.23 ($O-CH_3$), 29.86 ($N-CH_3$) ppm. MS−EI: $m/z = 269$ ($M^{+\bullet}$, 100%), 254 (M − CH_3, 45%). UV [λ (nm), (ϵ), $CHCl_3$]: 346 (4100), 301 (17 900), 244 (12 700). Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.77; H, 5.82; N, 5.47.

7-Methoxy-9-methyl-9*H*-carbazole-2-ol, 24. A 0.5 M solution of sodium ethanethiolate was prepared by adding 13.3 mL (180.30 mmol) of EtSH to a suspension of 3.60 g (120.00 mmol) of NaH (80%) in 150 mL of dry DMF at 0 °C under N_2 and then by stirring the mixture for 15 min at room temperature. A solution of 5.80 g (24.00 mmol) of the carbazole **21** in DMF was added to the former solution and heated to 130 °C. After 3 h, the reaction was stopped by carefully adding a few drops of water to the ice cooled solution. A further 100 mL of water was added, followed by acidification with 2 N HCl. The product, **24**, was isolated by extraction with AcOEt. The solvent was evaporated and the residue was purified by flash chromatography with (AcOEt/hexane 4:6) on silica gel. 3.37 g were obtained (yield 62%). TLC (SiO_2, CH_2Cl_2, UV): $R_f = 0.37$. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.84$ (d, CH^4, $J_{4,3} = 8.2$ Hz, 1 H), 7.80 (d, CH^5, $J_{5,6} = 7$ Hz, 1 H), 6.84 (d, CH^1, $J_{1,3} = 2.2$ Hz, 1 H), 6.81 (dd, CH^3, $J_{3,4} = 8.2$ Hz, $J_{3,1} = 2.2$ Hz, 1 H), 6.79 (d, CH^8, $J_{8,6} = 3$ Hz, 1 H), 6.70 (dd, CH^3, $J_{3,4} = 8.2$ Hz, $J_{3,1} = 2.2$ Hz, 1 H), 4.82 (s, OH, 1 H), 3.93 (s, $O-CH_3$, 3 H), 3.72 (s, $N-CH_3$, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 158.72$ (C^7), 153.67 (C^2), 143.95 (C^{9a}), 142.81 (C^{8a}), 120.12 (C^4), 119.99 (C^5), 117.62 (C^{4a}), 117.58 (C^{5a}), 107.62 (C^3), 106.95 (C^1), 94.87 (C^6), 93.12 (C^8), 55.73 ($O-CH_3$), 29.10 ($N-CH_3$) ppm. MS−CI−NH_3: $m/z = 228$ (M + 1, 100%), 245 (M + 18, 1%). Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.98; H, 5.77; N, 6.17. Found: C, 74.15; H, 5.89; N, 6.23.

2-Methoxy-9-methyl-7-undecyloxy-9*H*-carbazole, 25. A solution of 3.00 g (13.22 mmol) of 9-methyl-7-methoxy-9*H*-carbazole-2-ol (**24**) in 120 mL of dry DMF was added to a suspension of 790 mg (26.44 mmol) of NaH (80%) in 30 mL of dry DMF. The solution was stirred for 1 h at 60 °C. Thereafter 3.42 g (14.53 mmol) of 1-bromoundecane in 50 mL of dry DMF was added and after a further 5 h with stirring at 60 °C the reaction was completed. A few drops of water were carefully

added to the ice cooled solution, and then 200 mL of water was added, followed by acidification with 2 N HCl. The product, **25**, was isolated by extraction with chloroform. The organic solution was dried with Na_2SO_4, and the solvent was evaporated. The residue was purified by flash chromatography first with hexane and thereafter with CH_2Cl_2 on silica gel. Thus, 4.28 g of the desired product was obtained (yield 87%). TLC (SiO_2, CH_2Cl_2, UV): $R_f = 0.72$. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.84$ (d, CH^4, $J_{4,3} = 7.2$ Hz, 1 H), 7.83 (d, CH^5, $J_{5,6} = 7.6$ Hz, 1 H), 6.83 (m, CH^{1,3,6}, 3 H), 6.80 (d, CH^8, $J_{8,6} = 2.2$ Hz, 1 H), 4.07 (t, O−CH_2−, 2 H), 3.92 (s, O−CH_3, 3 H), 3.74 (s, N−CH_3, 3 H), 1.81 (m, O−CH_2−*CH_2*−, 2 H), 1.27 (m, O−$(CH_2)_2$−*$(CH_2)_8$*−CH_3, 16 H), 0.88 (t, O−$(CH_2)_{10}$−*CH_3*, 3 H) ppm. Anal. Calcd for $C_{25}H_{35}NO_2$: C, 78.70; H, 9.25; N, 3.67. Found: C, 78.55; H, 9.60; N, 3.71.

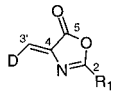
2-Methoxy-9-methyl-7-undecyloxy-9*H*-carbazole-3-carbaldehyde, 26. The general procedure reported for compound **22** was followed. The crude was purified by flash chromatography with (CH_2Cl_2) on silica gel. Thus 0.96 g of product **26** was obtained (yield 35%), and 1.09 g (yield 40%) was obtained of the isomer with the formyl group in *ortho* position to the undecyloxy chain, 2-methoxy-9-methyl-7-undecyloxy-9*H*-carbazole-6-carbaldehyde. TLC (SiO_2, CH_2Cl_2, UV): $R_f = 0.39$. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 10.54$ (s, CHO, 1 H), 8.46 (s, CH^4, 1 H), 7.88 (d, CH^5, $J_{5,6} = 9.2$ Hz, 1 H), 6.87 (dd, CH^6, $J_{6,5} = 9.2$ Hz, $J_{6,8} = 2.1$ Hz, 1 H), 6.85 (s, CH^8, $J_{8,6} = 2.1$ Hz, 1 H), 6.74 (s, CH^1, 1 H), 4.17 (t, O−CH_2−, 2 H), 3.93 (s, O−CH_3, 3 H), 3.77 (s, N−CH_3, 3 H), 1.88 (m, O−CH_2−*CH_2*−, 2 H), 1.28 (m, O−$(CH_2)_2$−*$(CH_2)_8$*−CH_3, 16 H), 0.88 (t, O−$(CH_2)_{10}$−*CH_3*, 3 H) ppm. MS−CI−NH_3: $m/z = 409$ ($M^{+\bullet}$, 100%), 410 (M + 1, 16%). Anal. Calcd for $C_{26}H_{35}NO_3$: C, 76.25; H, 8.61; N, 3.42. Found: C, 76.35; H, 8.70; N, 3.47.

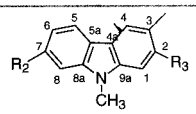
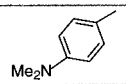
EFISH Measurements. $\mu\beta$ values of the described compounds were obtained from EFISH measurements performed at 1.38 or 1.91 μm. To obtain these two wavelengths, a Q-switched Nd:YAG laser with a pulse width of 8 ns operating at 10 Hz was used in two configurations. In the former, the radiation at 1.06 μm from the laser was frequency doubled and the resulting green emission was used to excite a dye laser with DCM as colorant. The dye laser output was passed through a H_2 Raman shifter cell in order to obtain the IR emission at 1.38 mm as the second Stokes peak of the incident radiation. In the latter, the light from the Nd:YAG was directly passed into the Raman cell, obtaining the 1.9 μm radiation as the first Stokes of the incident one. A computer-controlled NLO spectrometer from SOPRA completes the EFISH experimental setup. In this spectrometer the excitation light is linearly polarized and separated into two beams. The less intense of them is directed to a *N*-(4-nitrophenyl)-L-prolinol (NPP) powder sample whose second harmonic signal is used as reference to monitor the laser intensity fluctuations. Two interference filters in both the reference and sample arms are used to remove the residual excitation light from the beam, before being detected by a photomultiplier (Hamamatsu 2949 and R206 models for the visible and near-infrared regions, respectively). Each compound was measured using chloroform ($CHCl_3$) as solvent. The EFISH liquid cell has the usual wedge shape bounded by two silica windows, so the Maker fringes pattern is obtained by translation of the cell perpendicular to the laser beam. The angle between the windows was about 2 and 3.5° for the 1.38 and 1.9 μm measurements, respectively. Voltage pulses of 10 μs and 5 kV were applied to the electrodes in the cell in order to provide a uniform electric field parallel to the light polarization in the sample region. $\mu\beta(0)$ values were obtained from $\mu\beta$ values by using a simple two-level model.[7]

Several solutions of NPP were measured in order to perform a calibration of our system. The NPP $\mu\beta$ values obtained under the same experimental conditions as in carbazole derivatives measurements were $(125 \pm 10) \times 10^{-48}$ and $(100 \pm 10) \times 10^{-48}$ esu at 1.38 and 1.91 mm, respectively.

Computational Methods. Molecular orbital calculations were carried out on empirical structures for all the compounds using the semiempirical MNDO, AM1, and PM3 Hamiltonians[8] of the MOPAC 93[9] program on a Silicon Indigo 2 computer with full optimization of all bond lengths, angles and torsion angles except where stated otherwise. The SCF convergence was set to 10^{-8} for calculations of both the geometries and the NLO properties (PRECISE option in MOPAC). The eigenvector following (EF) method of convergence was employed because it performs well when searching for global minima.

Table 1. Synthesized Oxazolone-Based Chromophores



Comp.	D	R_1	R_2	R_3	η (%)
					
1		Ph	H	H	75
2		Me	H	H	57
3		OMe	H	H	35
4		Ph-OMe	H	H	35
5		Ph-NO_2	H	H	62
6		Ph	OMe	OMe	60
7		Ph-OMe	OMe	OMe	64
8		Ph-NO_2	OMe	OMe	-[a]
9		Ph-OMe	O$(CH_2)_{10}CH_3$	OMe	35
10		Ph-NO_2	O$(CH_2)_{10}CH_3$	OMe	45
11		Me	--	--	62

[a] The product was neither isolated nor identified because of its high insolubility in common organic solvents.

Results and Discussion

Oxazolones with a different substitution pattern in position 2 of the ring were synthesized (Table 1). The synthesized oxazolone compounds were condensed with different aryl carbaldehydes to obtain new push−pull chromophores. New carbazole−oxazolone and *N*,*N*-dimethylaminophenyloxazolone chromophores were prepared. All these new molecules, apart from compounds **9** and **10**, were synthesized following the synthetic paths shown in Scheme 1.

Oxazolone compounds were prepared via the Erlenmeyer reaction[10] from *N*-acylamino acids. The conversion of *N*-acylamino acids into oxazolones has been described under various conditions: with acid anhydride, either alone or in acetic acid as a solvent; with acetic anhydride and anhydrous sodium acetate; using lead acetate in THF or bismuth (III) acetate[11] as a catalyst in place of sodium acetate. Cyclodehydrating agents other than acetic anhydride, such as carbodiimide[12] or ethyl chloroformate,[13] have been also assayed.

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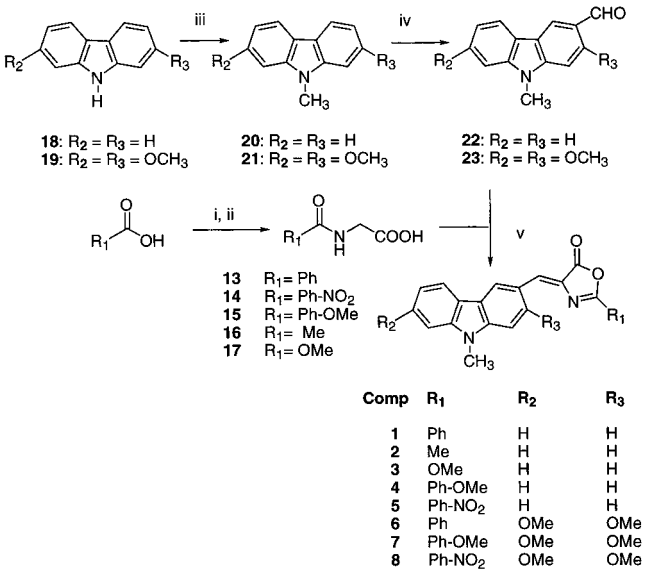
Scheme 1. Synthetic Route to the Carbazole−Oxazolone Systems 1−8



Comp	R_1	R_2	R_3
1	Ph	H	H
2	Me	H	H
3	OMe	H	H
4	Ph-OMe	H	H
5	Ph-NO_2	H	H
6	Ph	OMe	OMe
7	Ph-OMe	OMe	OMe
8	Ph-NO_2	OMe	OMe

Following the experimental conditions previously reported in the literature,no product or very low yields were obtained for systems **2** and **3**, which were only detected by TLC when the temperature was raised to 150 °C. Preparation of oxazolone systems has a limiting step: the cyclation of acylglycine, the first step in the Erlenmeyer reaction. We found that gradual heating first to 60 °C, together with the use of molecular sieves (4 Å) as cyclodehydrating agent, seemed to be decisive for successful cyclization. Subsequent heating to higher temperatures (120−140 °C) was required for the condensation step with the carbaldehyde. Under these conditions not only aromatic-substituted oxazolones but also alkyl-substituted ones, were obtained in moderate to good yields. Compounds with aromatic substitution in position 2 of the oxazolone ring gave better yields with milder conditions, shorter reaction times, and lower temperatures than were needed for systems with nonaromatic substitution.

First, the acylglycines *N*-benzoylglycine (**13**), *N*-4-nitrobenzoylglycine (**14**), *N*-4-methoxybenzoylglycine (**15**), *N*-acetylglycine (**16**), and *N*-methoxycarbonylglycine (**17**) were synthesized under stricter pH control conditions. Syntheses of **13**, **14** and **16** have been already described in the literature.[14−16] **17** was synthesized with a 95% yield, improving the reported yield (66%) for its analogous *N*-ethoxycarbonylglycine[17] using the starting products glycine and methoxycarbonyl chloride with an equimolecular mixture of NaOH/Na_2CO_3. **15** was synthesized in a manner similar to that used for **17**, using a basic blend of NaOH/Na_2CO_3 at 0 °C with glycine and 4-methoxybenzoyl chloride.

9-Methyl-9*H*-carbazole-3-carbaldehyde (**22**) and 2,7-dimethoxy-9-methyl-9*H*-carbazole-3-carbaldehyde (**23**) were first synthesized from 9*H*-carbazole (**18**) and 2,7-dimethoxy-9*H*-carbazole[3] (**19**) in a two-step procedure. Methylation of the nitrogenated position was performed in standard conditions, although 9-methyl-9*H*-carbazole (**20**) could also be directly purchased. Whereas 9-methyl-9*H*-carbazole (**20**) was prepared from commercial carbazole at room temperature, the 2,7-dimethoxy-9-methyl-9*H*-carbazole (**21**) was obtained at 60 °C, a difference explained by the existence of the methoxy groups in system **21** causing lower acidity of the 9*H*-proton. The *N*-methylated carbazoles were formylated through a Vilsmeier−Haack reaction using *N*,*N*-dimethylformamide with phosphorus oxychloride yielding the desired carbaldehydes **22** and **23**.

4-(9-Methyl-9*H*-carbazole-3-ylmethylene)-2-phenyl-4*H*-oxazol-5-one (**1**) and 4-(2,7-dimethoxy-9-methyl-9*H*-carbazole-3-ylmethylene)-2-phenyl-4*H*-oxazol-5-one (**6**) were synthesized in yields of 75% and 60% respectively, by heating at 80 °C for 1 h a mixture of *N*-benzoylglycine/**22** or **23**/NaAcO/Ac_2O with a molar ratio of 1:1:1:3. Compound **6** was seen as a mixture of isomers *Z*/*E* (98:2) in the analysis of the ^{1}H NMR spectra. *Z* was the major isomer obtained in the Erlenmeyer synthesis.[18] Oxazolone **5** was prepared with a yield of 62% starting from **14**.

System **8** was not successfully attained due to its very low solubility in organic solvents. It could not be purified, and an NMR spectrum could not be obtained. For comparative purposes we synthesized a new compound, 4-(2-methoxy-9-methyl-7-undecyloxy-9*H*-carbazole-3-ylmethylene)-2-(4-nitrophenyl)-4*H*-oxazol-5-one (**10**) (Scheme 2), to obtain a soluble system similar to **8** with a little structural modification. In product **10** a long C_{11} alkoxy chain replaced the methoxy substitution of **8**. Product **10** had higher solubility than **8**.

Compounds 2-(4-methoxyphenyl)-4-(9-methyl-9*H*-carbazole-3-ylmethylene)-4*H*-oxazol-5-one (**4**) and 4-(2,7-dimethoxy-9-methyl-9*H*-carbazole-3-ylmethylene)-2-(4-methoxyphenyl)-4*H*-oxazol-5-one (**7**) were synthesized with yields of 35% and 65%, respectively. Despite the low solubility of system **7** in organic solvents, it could be isolated and characterized. System **9** with an undecyloxy chain introduced instead of a methoxy group was synthesized in a similar way to **10**. The longer alkoxy chain undoubtedly accounted for the good solubility of **9** and **10**.

Syntheses of **9** and **10** from **21** were achieved by a linear synthesis through the following synthetic steps: selective monodeprotection of one of the two methoxy groups in the carbazole compound using NaSEt at 130 °C and subsequent alkylation of the phenol **24** formed with the corresponding bromoalcane. Then formylation of the resulting carbazole system **25** by a Vilsmeier−Haack reaction gave 2-methoxy-9-methyl-7-undecyloxy-9*H*-carbazole-3-carbaldehyde (**26**), which yielded the desired products **9** and **10** when reacted with the corresponding *N*-acylglycine derivatives **14** and **15** by the Erlenmeyer reaction (Scheme 2).

The nonaromatic 2-substituted oxazolone **2**, 2-methyl-4-(9-methyl-9*H*-carbazole-3-ylmethylene)-4*H*-oxazol-5-one, could not be prepared following the above conditions applied for 2-aryl-substituted oxazolone systems

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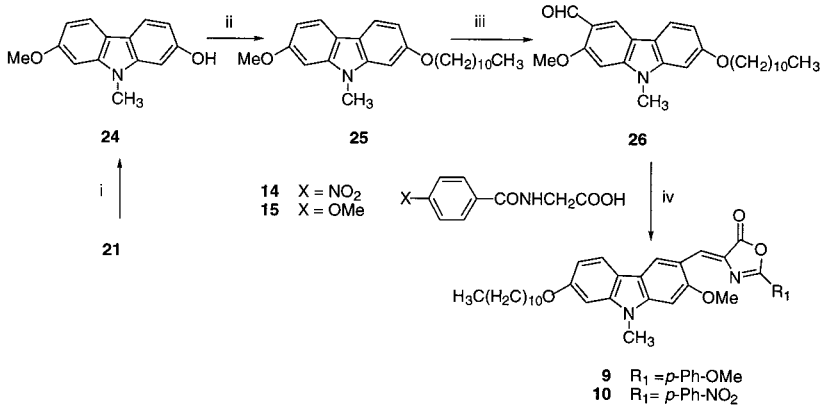
Scheme 2. Route to Products 9 and 10



1 and **4**−**10**. However, it was synthesized with a yield of 57% when the reaction was performed in an excess of Ac_2O and molecular sieves of 4 Å were added to the reaction flask. First, it was gently heated to 60 °C for 1 h, and then temperature was progressively increased to achieve an effective condensation between the aldehyde and the oxazolone ring. Until 100 °C, no formation of product was observed, but as the temperature reached the reflux temperature of Ac_2O, the reaction ran fast.

Following the previously cited variants for the synthesis of **2**, 2-methoxy-4-(9-methyl-9*H*-carbazole-3-ylmethylene)-4*H*-oxazol-5-one, **3** could be also obtained.

Not only were carbazole−oxazolone systems synthesized but also *N*,*N*′-dimethylaniline−oxazolone compound **11** as well (Table 1). Compound **11** was synthesized under the same experimental conditions as carbazole derivatives **2** and **3** from 4-*N*,*N*′-dimethylaminobenzaldehyde and *N*-acetylglycine.

System **12** was obtained by a Döbner reaction in a 90% yield starting from 4-(*N*,*N*′-dimethylamino)benzaldehyde and ethyl malonate using a piperidine-pyridine catalytic medium.

Compounds **1**−**5** incorporate different substitutions in the oxazolone ring, from electron-releasing (Me, OMe) to electron-withdrawing (NO_2, Ph−NO_2) groups, or neutral phenyl substitution. Compounds **6**−**10** were used to study the effect of additional donor groups on carbazole, donor moiety in carbazole−oxazolone chromophores. The high insolubility of systems **7** and **8** in common solvents rendered all attempts to clarify its NLO behavior useless. Compounds **9** and **10**, analogous to **7** and **8,** respectively, but with longer alkoxy chains to increase solubility, permitted the experimental measurement of the NLO properties of these chromophores.

To determine the influence of the gain of aromatic stabilization energy during the ICT process[2,19,20] over $\mu\beta$ values, not only carbazole−oxazolone systems but also 4-*N*,*N*′-dimethylaminophenyloxazolone (**11**) and ester compound **12** were analyzed.

NLO properties were analyzed from the experimental values obtained by the electric-field-induced second-harmonic (EFISH) generation technique. Table 2 shows the experimental $\mu\beta$ values and longest absorption maximum wavelengths in chloroform for the new chromophores.

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Table 2. Optical and EFISH Data of All Studied Chromophores.

compd	λ (nm)[a]	$\mu\beta$ (10^{-48}esu)^2	$\mu\beta(0)$ (10^{-48}esu)
1	442	155 ± 10[c]	82 ± 5
2	406	100 ± 10	78 ± 8
3	408	95 ± 15	75 ± 10
4	444	190 ± 20	141 ± 15
5	472	430 ± 50[c]	200 ± 23
6	467	255 ± 30[c]	125 ± 15
6	467	210 ± 20	150 ± 15
9	469	290 ± 30	207 ± 20
10	502	550 ± 50	370 ± 40
11	432	210 ± 20	158 ± 15
12	362	56 ± 10	46 ± 8

[a] Longest absorption maximum wavelengths in chloroform. [b] EFISH value in chloroform at 1.91 mm. [c] Values were obtained at 1.38 mm.

The system 4-(2-methoxy-9-methyl-7-undecyloxy-9*H*-carbazole-3-ylmethylene)-2-(4-nitrophenyl)-4*H*-oxazol-5-one (**10**) showed the highest $\mu\beta$ value of the series with (550 ± 50) × 10^{-48} esu, followed by the analogous system **5**, but without alkoxy substitution in the carbazole moiety (Table 2). For the two compounds, R_1 is a *p*-NO_2−phenyl group (Figure 1).

The main point of interest is the effect on hyperpolarizability values of oxazolone having aromatization in the charge-transfer form or not.

When $\mu\beta(0)$ values of compounds **1**, **2**, and **3** are examined, similar experimental values are obtained, although compound **1** has a phenyl group in a conjugated framework, observable from the absorption UV−vis spectrum, instead of the methyl and methoxy substitution of compounds **2** and **3**, respectively. These last two groups, which are slightly donor, could favor the charge-transfer resonance form B (Figure 2) that represents the aromatization of the oxazolone ring, instead of resonance form C. The NLO figures of compounds **6** and **9** can be analyzed similarly. The two products have the maximum absorption band at practically the same wavelength, but $\mu\beta(0)$ values are 150 × 10^{-48} and 207 × 10^{-48} esu, respectively. The presence of a methoxy group which is donor in character in the para position of the phenyl substitution of the oxazolone ring should inhibit the resonance form C, favoring the aromatic resonance form B for compound **9**.

From the observation of the NLO behavior of compounds **6**, **9**, and **10**, two different patterns can be recognized as operating in the oxazolone ring, whose modeling can be used to enhance the $\mu\beta(0)$ values of

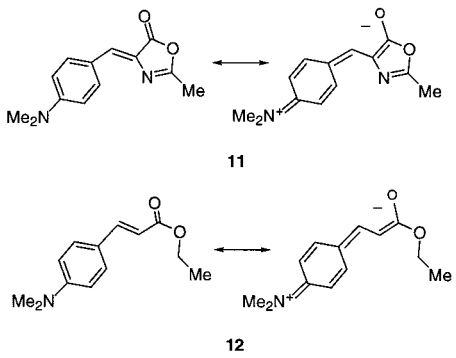

Figure 3. Resonance forms for **11** and **12**.

chromophores with oxazolone as acceptor unit. One pattern is that defined by the carboxylate unit and the other by the imine group. The influence of R_1 over the latter makes resonance form B or C predominant in the ICT process. The introduction of acceptor groups that favor resonance form C give rise to the highest $\mu\beta(0)$ values in this study (compounds **5** and **10**). Therefore, the major factor that determines NLO properties is the charge polarization due to strong acceptor groups. However the increase of the $\mu\beta(0)$ can also be managed with the introduction of donor-releasing groups, such as alkoxy substitution, through an aromatization process, in which the charge should be placed predominantly in the carboxylate unit. This result could be of great importance when liquid crystal materials with NLO properties are searched, and the introduction of strong withdrawing groups could alter or destroy the liquid crystal phase.[3b]

Additional evidence of the positive effect of aromatization in the ICT process on hyperpolarizability values is obtained from products **11** and **12**. Both compounds have a carboxylate group as the acceptor unit. However, in compound **11**, this forms part of the oxazolone ring. Because of the nature of the substitution at R_1, charge-transfer resonance form B and thus aromatization of the acceptor system should predominate (Figure 3). The experimental $\mu\beta(0)$ values are 158×10^{-48} and 46×10^{-48} esu, respectively. Since the main difference between them in terms of donor/acceptor strength is the presence of the imine unit as part of the oxazolone ring, and thus the possibility of aromatization of the oxazolone ring, this factor may affect the final value of hyperpolarizability.

The effect of the presence of the two additional donor alkoxy groups in carbazole moiety on hyperpolarizability values was analyzed by comparing systems **1**−**6**, **4**−**9**, and **5**−**10**. Table 2 shows that methoxy groups in carbazole enhance $\mu\beta$ values. This result apparently contradicts studies carried out by our research team on substituted carbazoles with tricyanovinyl as acceptor group,[5b] in which systems with methoxy groups had lower hyperpolarizability values than analogous systems without methoxy groups. Theoretical semiempirical calculations suggest that geometrical considerations are responsible for this behavior.[5b,21]

Regarding Table 2, it could appear quite surprising the difference between the two $\mu\beta(0)$ values given for compound **6**. They are derived from EFISH $\mu\beta$ data obtained at the two wavelengths used in the experiments after applying the two-level model.[7] The two-level model has been largely used in push−pull systems in which charge transfer occurs along the molecular dipole axis. So, the hyperpolarizability tensor β has only a significant β_{zzz} component parallel to that axis (one-dimensional model). Although the above-mentioned difference for $\mu\beta(0)$ values of compound **6** is not very representative in view of the experimental errors, it could suggest the presence of significant b components along other directions. In this sense some articles have been recently published[22,23] pointing to the non-one-dimensional character of the optical nonlinearity of several carbazole derivatives. However semiempirical calculations (MOPAC93/PM3) carried out for compound **6** have shown a main diagonal component β_{zzz} along the dipole axis, and it is more than two times higher than the largest off-diagonal component.

Different semiempirical approaches have been applied in the literature to study NLO properties, for instance PPP,[24] CNDO,[25] INDO,[26] MNDO,[27] AM1,[28] and PM3,[29] using either numerical finite field (FF),[30] analytical coupled Hartree−Fock (CHF),[31] time-dependent Hartree−Fock (TDHF),[32] or sum-over-states (SOS)[33] techniques. Although correlations between experimental and theoretical data vary slightly for the different methods, they are useful for trend predictions of the molecular design of new compounds for nonlinear optical applications. The influence of different conformers on first-order hyperpolarizability calculated has already been discussed in the literature: the MOPAC-TDHF values are close to the measured ones.[34]

Molecular geometries of the previous synthesized systems were optimized by three semiempirical methods:[8] MNDO, AM1 and PM3, with the time-dependent Hartree−Fock (TDHF) technique incorporated into the semiempirical MOPAC 93 program[9] to determine the most appropriate one for this kind of compound. Table 3 shows dipole moment m, hyperpolarizability $\beta(0)$ and $\mu\beta(0)$ values, as well as the heat of formation for carbazole−oxazolone systems from theoretical calculations. Theoretical $\mu\beta(0)$ values, calculated at 0.0 eV, are compared with the experimental $\mu\beta(0)$ values obtained from the EFISH data.

The graph in Figure 4 points to the strong deviation that MNDO values show. AM1 and PM3 show much more acceptable adjustment in experimental values, with PM3 the best, especially in cases of compounds **2**,

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Table 3. Semiempirical Calculations Carried out with Compounds 1,2,3,5 and 6

	MNDO				AM1				PM3				
comp.	μ 10^{-18} esu)	$\beta(0)$ (10^{-30} esu)	$\mu\beta(0)$ (10^{-48} esu)	$\Delta H°_f$ (kcal/mol)	μ (10^{-18} esu)	$\beta(0)$ (10^{-30} esu)	$\mu\beta(0)$ (10^{-48} esu)	$\Delta H°_f$ (kcal/mol)	μ (10^{-18} esu)	$\beta(0)$ (10^{-30} esu)	$\mu\beta(0)$ (10^{-48} esu)	$\Delta H°_f$ (kcal/mol)	exptl $\mu\beta(0)$[a] (10^{-48} esu)
1	4.3	7.6	33	39.1	5.0	27.0	135	81.8	4.1	15.9	65	44.2	82 ± 5
2	4.1	7.7	32	5.4	4.9	24.3	119	47.4	3.7	18.9	70	8.5	78 ± 8
3	4.9	5.4	26.5	−27.5	6.0	20.7	124	17.6	4.5	16.4	74	−22.4	75 ± 10
5	6.1	11.1	68	55.4	7.5	47.0	352	87.0	6.2	34.1	211	36.1	200 ± 23
6	3.9	4.0	16	−38.8	4.8	14.3	69	10.2	4.0	17.7	71	−31.2	125 ± 15

[a] From EFISH data in chloroform at 1.38 mm for all compounds except for compound **2** and **3**, which were obtained at 1.91 mm.

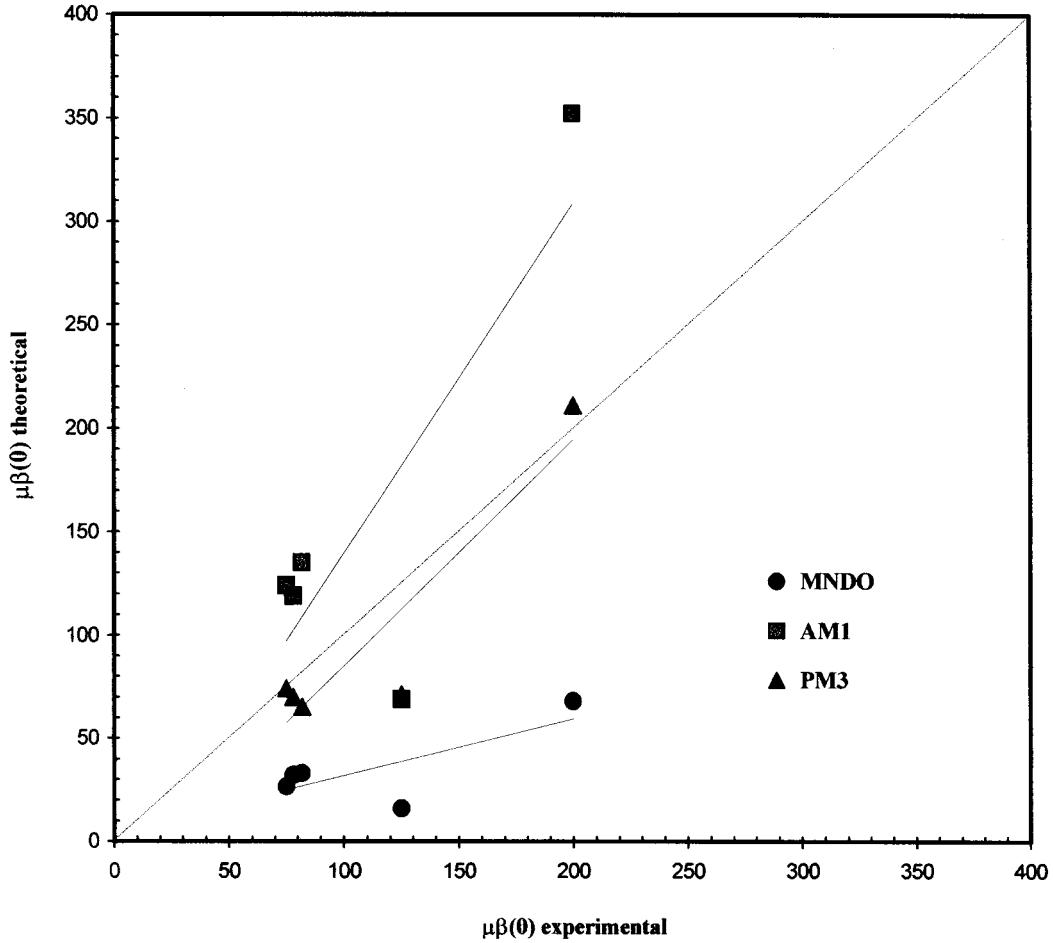


Figure 4. Correlation between experimental and predicted $\mu\beta(0)$ values.

3, and **5**, where computed values fall into the error interval of the experimental measurement. The largest deviation was found for system **6**, derived from 2,7-dimethoxycarbazole: 35% by PM3, 37% by AM1, and 85% by MNDO. The lack of correlation between theoretical and experimental values for carbazole-derived systems with methoxy groups in ortho position to the acceptor group has already been detected and studied elsewhere.[5b]

Linear fit gave rise to the following correlation: $\mu\beta(0)_{calcd} = \mu\beta(0)_{exptl} \times 0.9103$ for PM3; $\mu\beta(0)_{calcd} = \mu\beta(0)_{exptl} \times 1.4675$ for AM1; $\mu\beta(0)_{calcd} = \mu\beta(0)_{exptl} \times 0.3077$ for MNDO. AM1 method overestimates the hyperpolarizability values and MNDO results are below the experimental one. For compounds **1** and **6**, by MNDO, phenyl substitution in the oxazolone shows angles to the oxazolone ring of 66.6 and 65.7° out-of-plane, respectively. It is already known[9] that in aromatic compounds with oxygenated substitution the MNDO method leaves these groups out of the plane defined by the aromatic unit. This effect was observed neither by AM1 (2.4 and 3.9°) nor by PM3 (3.3 and 6.5°). A clear difference between the two last methods concerns the geometry of the *N*-methyl group. In AM1 calculations nitrogen shows hybridization close to sp^2, while by PM3 hybridization is almost wholly sp^3 for all the calculated compounds. This is common to other organic molecules: the PM3 method generates results with sp^3 hybridization for nitrogen, while with AM1, it is possible to obtain either sp^2 or sp^3 hybridization, depending on the case.[9]

The same effects previously commented on for **1** and **6** were observed in system **5**. By MNDO, the nitro group in the phenyl placed in para position to the oxazolone ring adopts an almost perpendicular conformation (88.3°) to the phenyl plane, and the phenyl a dihedral angle of 67.3° to the oxazolone. By AM1 the system nitrophenyloxazolone remained in the same plane (0.1°, nitro-

Table 4. Effect of the Hybridization of Carbazolyl Nitrogen on NLO Properties for Compound 5

entry	method	μ (10^{-18} esu)	$\beta(0)$ (10^{-30} esu)	$\mu\beta(0)$ (10^{-48} esu)
1	AM1	7.5	47.0	352
2	AM1/PM3[a]	7.0	50.4	353
3	PM3	6.2	34.1	211
4	PM3/AM1[a]	6.6	32.3	213

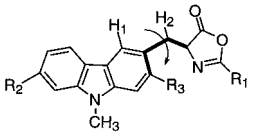
[a] The internal coordinates were fixed with the values obtained from optimized AM1 geometry, and only the coordinates referring to the *N*-methyl were optimized by PM3 (or vice versa in entry 4).

Table 5. Effect of the Hybridization of Carbazolyl Nitrogen on NLO Properties for Compound 6

entry	method	μ (10^{-18} esu)	$\beta(0)$ (10^{-30} esu)	$\mu\beta(0)$ (10^{-48} esu)
1	AM1	4.8	14.3	69
2	AM1/PM3[a]	4.2	15.5	65
3	PM3	4.0	17.7	71
4	PM3/AM1[a]	4.5	16.4	74

[a] The internal coordinates were fixed with the values obtained from optimized AM1 geometry, and only the coordinates referring to the *N*-methyl were optimized by PM3 (or vice versa in entry 4).

Table 6. Torsion Angle between Oxazolone Ring and Carbazole



	ω (deg)		
compd[a]	MNDO	AM1	PM3
1	68.1	23.6	30.2
2	67.7	21.2	28.6
3	74.6	25.7	32.7
5	64.5	21.7	29.3
6	257.2	304.3[b])	217.6[b])

[a] The structure drawn has torsion angle 0°, with H_1 and H_2 adjacent. Positive angles are clockwise from the paper plane defined by the oxazolone ring. [b] This represents angles of 55.7 and 37.6° away from the plane for AM1 and PM3, respectively.

phenyl; 2.5°, phenyloxazolone). The same trends were found with PM3.

To evaluate the carbazolyl nitrogen hybridization factor in the estimated $\mu\beta(0)$ values, molecules **5** and **6** were studied. The internal coordinates were fixed with the values obtained from the optimized AM1 geometry, and then only the coordinates referring to the *N*-methyl group were re-optimized by the PM3 method (and vice versa). Results are recorded in Tables 4 and 5.

When the final $\mu\beta(0)$ values of both calculations, AM1 fully optimized (entry 1 in Tables 4 and 5) vs AM1 optimized plus *N*-methyl-PM3 re-optimization (entry 2 in Tables 4 and 5), were compared, similar values were obtained. This shows the insignificant influence of the hybridization of the nitrogen atom on the predicted NLO properties. The same conclusion was reached when results of entries 3 and 4 (Tables 4 and 5) were compared.

To understand the differences in the predicted $\mu\beta(0)$ values between the two methods, AM1 and PM3, an overview of the degree of planarity in the two methods was needed (Table 6). The more planar the global system is, the higher the hyperpolarizability and the dipole moment values are. This is clearly seen when predicted $\mu\beta(0)$ values in Table 3 are compared with the torsion angle (ω) between the oxazolone system and the carbazole plane collected in Table 6. As the PM3 angle is usually larger than that defined by AM1 for all compounds, PM3 hyperpolarizability values are lower than those estimated by AM1.

Table 7. Heats of Formation Values for Different Conformers of Compound 6 by PM3 Calculations.

angle (deg)	$\Delta H°_f$ (kcal/mol)	angle (deg)	$\Delta H°_f$ (kcal/mol)
0.0	−24.7	180.0	−31.1
30.0	−27.4	210.0	−31.2
45.0	−28.9	240.0	−30.7
75.0	−29.9	255.0	−30.2
90.0	−30.1	270.0	−29.8
105.0	−30.3	285.0	−29.6
120.0	−30.7	315.0	−28.1
135.0	−31.1	330.0	−26.6
165.0	−30.8	345.0	−26.0

The difference between experimental and calculated $\mu\beta(0)$ values for compound **6** should be noted. The low theoretical value would indicate that semiempirical calculations for compound **6** slightly overestimate the steric hindrance promoted by the methoxy group in ortho position to the oxazolone. Figure 5 shows the HOMO and LUMO of the optimized geometry for compound **6**. This deviation from planarity was already observed in carbazole-derived systems with a methoxy group in the ortho position to acceptor groups like tricyanovinyl.[5b] Steric hindrance promoted by the methoxy group results in a theoretical torsion angle of 217.6° between oxazolone and carbazole moiety, i.e., 37.6° away from planarity, a higher figure than for the other systems of Table 6. This explains the lower result obtained with the PM3 method than with the EFISH one.

For the remaining molecules, all angles were nearly 30° by PM3 and 25° by AM1. A conformational study was made for **6**, in which the geometries for different torsion angles were optimized by the PM3 method. The keywords used were: PM3 GRADIENTS PRECISE GEO−OK GNORM=0.01 EF POINT=24 STEP=15. Table 7 shows heats of formation, and Figure 6 collects the relationship between $\beta(0)$, dipole moment, and the product $\mu\beta(0)$ with torsion angle for the different conformations calculated. The experimental $\mu\beta(0)$ was $(125 \pm 15) \times 10^{-48}$ esu and the theoretical value (110×10^{-48} esu) was near the experimental figure when the plane of the carbazole and the plane of the oxazolone ring formed an angle round to 180°. Heats of formation confirmed that planar conformations around 180° are the most favored. They are accessible energetically from the theoretical minimum (217.3°) because the difference of the heats of formation between them is less than 0.2 kcal/mol, so system **6** can be expected to adopt a planar form easily, thus reaching the observed experimental values in solution.

Compounds **12**, **27**, and **28** are models of the different structural patterns incorporated in the oxazolone ring. They were analyzed for their contribution to hyperpolarizability associated with the oxazolone ring as acceptor unit. Figure 7 shows the formulas of these three compounds.

Table 8 shows the theoretical calculations by the PM3 method for the NLO properties of compounds **12**, **27**,

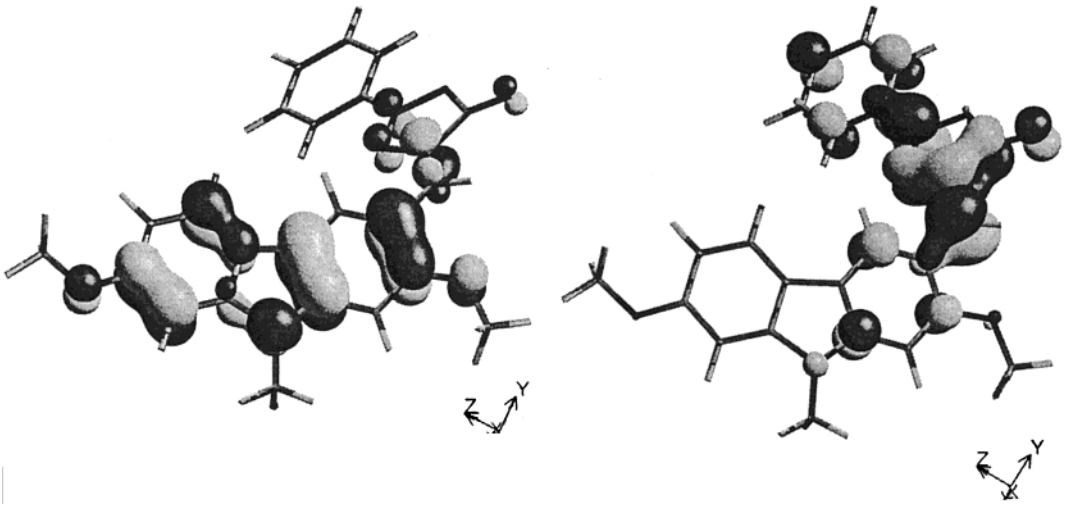


Figure 5. HOMO (left) and LUMO (right) of compound **6**, calculated with PM3.

and **28**. System **12**, with the carboxylate unit, has higher computed hyperpolarizability than system **27**, with the imine one. Compound **28** with both patterns recognized in the oxazolone ring, but without being connected so as to form an oxazolone unit, gave a low hyperpolarizability value, far from the experimental one for oxazolone derivative **11**. It seems that the two patterns operate in a noncooperative way, presumably due to the fact that the two functions are not coplanar for steric hindrance. In system **11**, with a methyl substitution in the oxazolone ring the charge-transfer resonance form C is not favored and resonance aromatic form B should be expected to be the predominant form in the ICT process.

Thermal Stability. One of the most attractive applications of the NLO chromophores is their incorporation into polymers for electrooptic devices. Polymers with second-order nonlinear optical chromophores are aligned by electric-field poling near the glass transition temperature of the polymer host. Thus, NLO chromophores are required to show not only a high nonlinear response but also thermal stability up to 200 °C. As such, the carbazole−oxazolone chromophores newly defined here are stable chromophores.

The decomposition temperature of this kind of compounds, carbazole−oxazolone chromophores, is 300 °C. Thermal stability studies of these NLO compounds were performed by differential scanning calorimetry (DSC) and also monitored by ^{1}H NMR at 200 MHz. First decomposition signs were observed after a period of 20−30 min at 300 °C.

Conclusions

4-Methylene-4*H*-oxazol-5-ones were introduced as new acceptor groups in derived carbazole chromophores. Their NLO properties were measured by the EFISH technique. Promising values were obtained, the best result being for system **10**, a dialkoxycarbazole conjugated with an oxazolone unit substituted with a nitrophenyl group.

Several factors that can affect the hyperpolarizability value were analyzed experimentally and theoretically. Two patterns operated in the oxazolone ring placed as

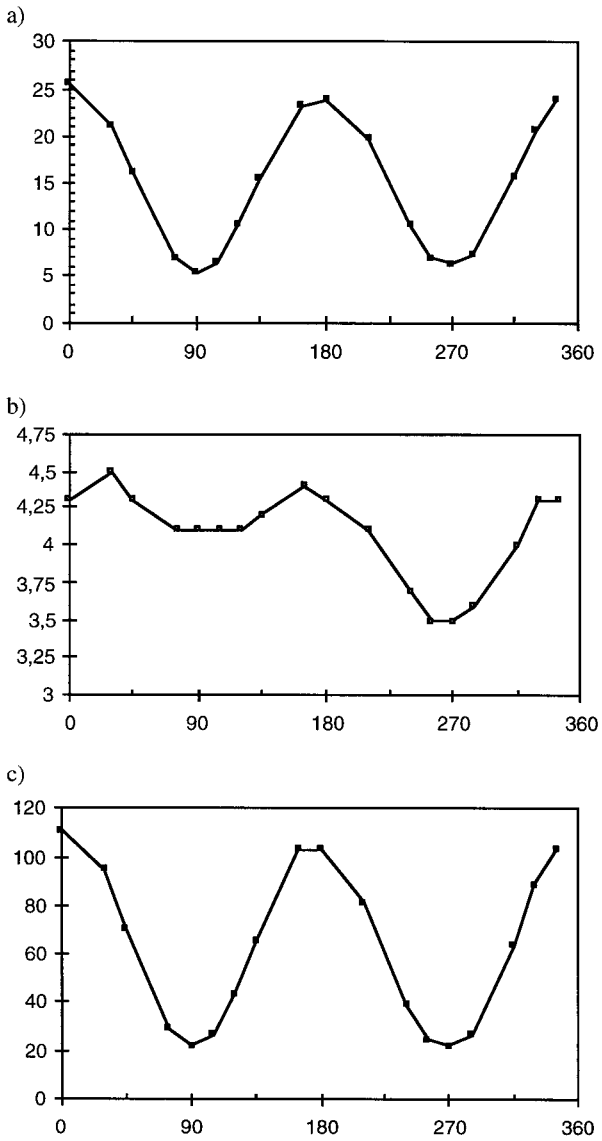
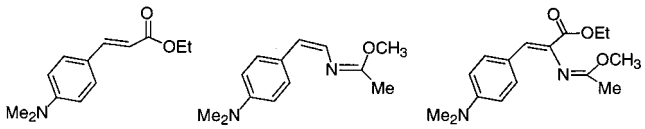


Figure 6. Relationship between calculated $\beta(0)$, dipole moment, and the product $\mu\beta(0)$ with torsion angle by PM3 for compound **6**. (a) Relationship between hyperpolarizability $\beta(0)$ and torsion angle. (b) Relationship between dipole moment (μ) and torsion angle. (c) Relationship between $\mu\beta(0)$ and torsion angle.



12 **27** **28**

Figure 7. Systems **12**, **27**, and **28** theoretically studied.

Table 8. Semiempirical Calculations for Compounds 12, 27, and 28

	PM3			
compd	μ (10^{-18} esu)	$\beta(0)$ (10^{-30} esu)	$\mu\beta(0)$ (10^{-48} esu)	$\Delta H°_f$ (kcal/mol)
12	6.1	15.1	92	−54.2
27	3.6	6.5	23	5.8
28	4.1	8.2	34	−73.2

acceptor unit in donor−acceptor chromophores, whose modeling can be used to enhance the $\mu\beta(0)$ values.

One way is to place strong electron acceptor groups in the R_1 substitution of the oxazolone ring, to increase the ICT throughout extension of the conjugate path and stabilization of the polar zwitterion form C. The second way is the possibility of placing electron donor groups in the R_1 substitution of the oxazolone ring, to increase the ICT favoring the aromatic resonance form B. Although it was found that increasing the $\mu\beta(0)$ values is always higher when using strong acceptor groups, enhancement of $\mu\beta(0)$ values via aromatization of oxazolone could be an alternative strategy to manage a high NLO response.

The PM3 method is the best semiempirical Hamiltonian for the study of these systems. However, when methoxy groups are introduced in ortho position to the oxazolone acceptor, PM3 overestimates the steric hindrance produced and theoretical values are quite different from experimental ones, as we observed for compound **6**. A conformational study undertaken showed that conformers with torsion angles between carbazole and oxazolone around 180° can exist in solution and that these conformers' $\mu\beta$ values are very close to the experimental one.

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