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Synthesis of polyconjugated carbazolyl–oxazolones by a tandem hydrozirconation–Erlenmeyer reaction. Study of their hyperpolarizability values

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Abstract—New push–pull systems with carbazole as donor moiety and oxazolone as electron withdrawing group have been synthesized by an $AgClO_4$-catalyzed hydrozirconation and ulterior Erlenmeyer reaction. Studies carried out with the semiempirical quantum method PM3 (MOPAC93) pointed a low dependence of the hyperpolarizability value on the number of double bonds at the conjugated bridge by $\beta(0) \propto n^{0.8}$. Introduction of rigidity in the polyene chain or additional donor groups in the carbazole moiety pointed to exertion of a large effect on hyperpolarizability values that could avoid unnecessary efforts in costly path elongation synthesis. © 2002 Elsevier Science Ltd. All rights reserved.

Carbazole derived compounds have technological interest due to their photoconducting[1] and second-order non-linear optical[2] properties, being suitable candidates for photorefractive[3,4] and electroluminescence[5,6] applications. In a previous paper,[7] the synthesis and study of non-linear optical properties of push–pull 2,3,7,9-polysubstituted-carbazole chromophores has been reported. Conformational and solvent effects[7] were studied by semiempirical quantum calculations. The incidence of these aspects and others like the aromatization effect has been widely reported.[8] However, one of the main factors that modifies the NLO response is the length of the conjugated linkage between donor and withdrawing moieties.[9–16] So, the elongation of the conjugated path is a well established strategy to enhance NLO properties.

Following our studies on non-linear optical (NLO) and electronic properties of polysubstitued-carbazoles,[7] we have examined carbazole–oxazolone compounds as new NLO-chromophores. We were interested in analyzing the NLO-behaviour of carbazole–oxazolone compounds as well as the influence of the length and the nature of the conjugated bridge in the push–pull system on hyperpolarizability values. We have also investigated the effect of placing additional donor groups into the carbazole unit to enhance the non-linear optical response. Here we present the synthesis of new carbazole–oxazolone (Cz-OXA) chromophores (Fig. 1) and their experimentally and theoretically determined hyperpolarizabilities. These new systems have the carbazole donor moiety and the oxazolone ring linked through a polyethylene bridge of *n* double bonds.

The synthesis of the Cz-[*n*]-OXA compounds was performed starting from 9-methyl-9*H*-3-carbazolecarbaldehyde **1**, prepared from commercially available carbazole, following the scheme of Fig. 2. Among the different options for the homologation of polyethylene systems from conjugated aldehydes,[17–20] the hydrozirconation method of Maeta and Suzuki has been considered.[21] Hydrozirconation is a one-step Grignard-type

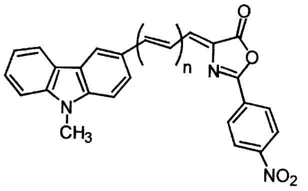

Figure 1. Cz-[*n*]-OXA systems.

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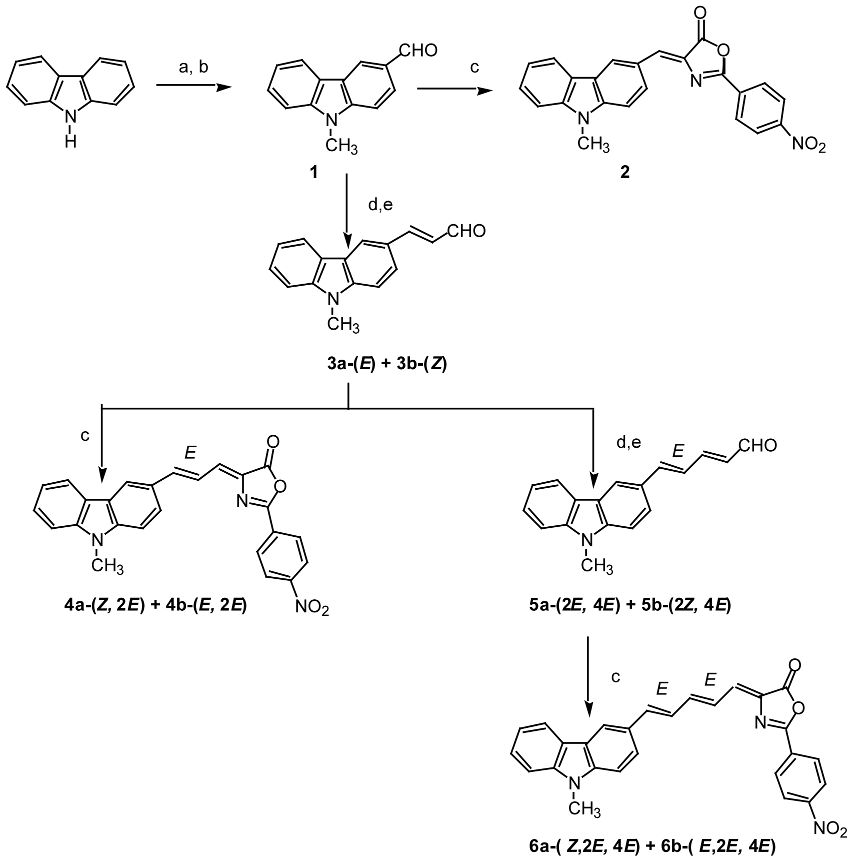

Figure 2. Synthetic scheme for **2**, **4** and **6**. *Reagents and conditions*: CH_3Cl, 60°C, 12 h; (b) DMF, $POCl_3$, 90°C; (c) 2-(4-nitrophenylcarboxamido)acetic acid, Ac_2O, NaOAc, Δ; (d) 1-ethoxyethyne, Cp_2ZrHCl, $AgClO_4$; (e) HCl (3N).

reaction for two- or four-carbon homologation of aldehydes by an $AgClO_4$-catalyzed addition of zirconocene chloride (Schwarz' reactive) to an alkoxyalkyne.[22] After acidic hydrolysis[23,24] the desired product with the elongated alkenyl chain was obtained (**3**, 65%; **5**, 60%). Product **3**, 3-(9-methyl-9*H*-3-carbazolyl)-2-propenal,[25] was yielded as an *E*/*Z* 95:5 mixture. Pure *E* isomer **3a** was obtained by recrystallization in $CHCl_3$ in a 40% yield. After Erlenmeyer reaction[26–28] with 2-(4-nitrophenylcarboxamido)acetic acid, system **4** 4-[3-(9-methyl)-9*H*-3-carbazolyl)-2-propenylidene]-2-(4-nitrophenyl)-4,5-dihydro-1,3-oxazol-5-one,[29] was recovered (85%) as a diastereomeric mixture *Z*,2*E*,/*E*,2*E*=6:4 (^{1}H NMR). Pure *Z*,2*E* isomer (**4a**) was obtained after recrystallization in $CHCl_3$ (35%). Synthesis of 4-[5-(9-methyl)-9*H*-3-carbazolyl)-2,4-pentadienylidene]-2-(4-nitrophenyl)-4,5-dihydro-1,3-oxazol-5-one **6** was carried out by a two-carbon homologation reaction of compound **3a** to achieve first 5-(9-methyl)-9*H*-3-carbazolyl)-2,4-pentadienal[30] **5** in 60% yield with a diastereomeric excess of 78% (2*E*,4*E*/2*Z*,4*E*=89:11) before recrystallization. Pure 2*E*,4*E* system (**5a**) was obtained after recrystallization in $CHCl_3$. Erlenmeyer reaction yields compound **6** (60%).[31] Pure 4-[(*Z*,2*E*,4*E*)]-4,5-dihydro-1,3-oxazol-5-one isomer (**6a**) was isolated with a 44% yield after recrystallization in $CHCl_3$/AcOEt.

Hyperpolarizability values were experimentally obtained for all the synthesized systems. $\mu\beta$ values calculated by PM3-MOPAC93[32,33] and experimental EFISH values for compounds **2** ($n=0$), **4** ($n=1$) and **6** ($n=2$) are registered in Table 1. PM3 method was chosen because of the good accordance with experimental data observed for other polysubstituted-carbazole systems.[7] Optimized geometries for compounds **2**, **4** and **6** resulted in an all *trans* disposition of the polyethylene chain. When *n* increases, a slight deviation from planarity is observed in the polyethylene bridge. The representation of $\mu\beta(0)$ values in front of *n* (number of double bonds) shows that no substantial variation is expected above $n=9$ (Fig. 3), being the estimated dependence of $\mu\beta(0)$ on *n* by $\mu\beta(0)\propto n^{0.8}$. In spite of the good concordance found between the $\mu\beta(0)$ experimental value and that calculated by PM3 for $n=0$, the theoretical $\mu\beta(0)$ values show poor accordance with experimental EFISH values when *n* increases ($n=1$, $n=2$). The experimentally found dependence of $\mu\beta(0)$ values on *n* was $\mu\beta(0)\propto n^{0.5}$, sensible lower than the expected one. The two level model[34] 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 component parallel to that axis (one-dimensional model). Although the above mentioned difference for experimental and theoretical $\mu\beta(0)$ values are significant for those molecules with more

Table 1. Theoretical values for Cz-[*n*]-OXA systems and EFISH experimental values at 1.38 μm in $CHCl_3$ for systems with $n=0$ (**2**), 1 (**4a**), 2 (**6a**)

n	ΔH_f^0 (kcal/mol)	μ (10^{-18} esu)	$\beta(0)$ (10^{-30} esu)	$\mu\beta(0)$ (10^{-48} esu)	λ_{ICT} (nm)	$\mu\beta_{EFISH}$ (10^{-48} esu)	$\mu\beta(0)_{EFISH}$ (10^{-48} esu)
0	36.5	6.2	33.5	208	479	430±50	200±23
1	48.3	7.0	59.0	413	501	400±50	260±30
2	62.5	7.2	81.9	590	526	570±60	365±40
3	76.4	7.4	102.5	758			
4	90.3	7.5	119.9	900			
5	104.3	7.6	134.2	1020			
6	118.2	7.6	145.7	1107			
7	132.2	7.7	154.9	1193			
8	146.1	7.7	162.3	1250			
9	160.0	7.7	168.2	1295			

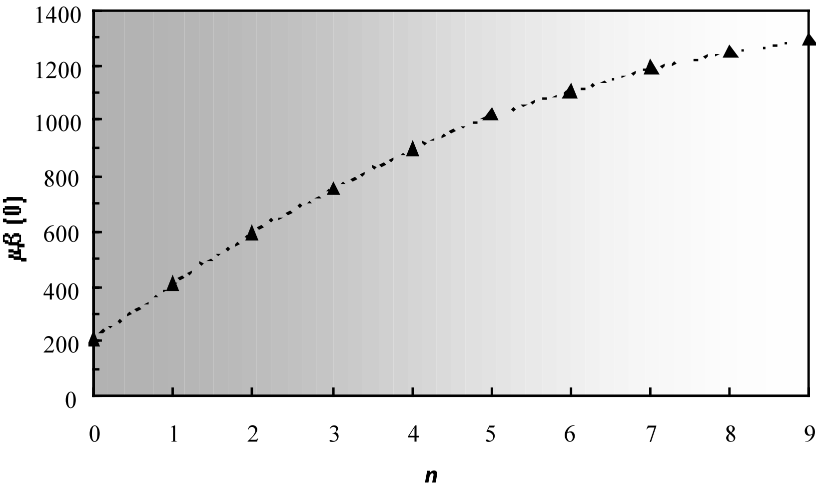

Figure 3. Theoretical dependence of $\mu\beta(0)$ values on n by PM3 method.

than one double bond between the donor and the acceptor group and not for the first example of the series ($n=0$), it could suggest the presence of significant β components along other directions. Regarding the nature of the chromophores, where the carbonyl of the oxazolone moiety and the nitrophenyl groups act as acceptors in different directions, we may consider the oxazolone chromophore to be a two-dimensional (2D) chromophore. Some articles have been recently published[35,36] pointing to the non one-dimensional character of the optical non-linearity of several carbazole derivatives. However, semiempirical calculations (MOPAC93/PM3) carried out for all the polyene compounds of Table 1 have shown a main diagonal component βxxx along the dipole axis, clearly higher than the other off-diagonal components (Table 2). Moreover, the poor accordance between experimental and theoretical values increases as *n* increases, in opposite sense of the relative meaning of the calculated off-diagonal components.

A plausible explanation for the deviation between experimental and theoretical $\mu\beta(0)$ values could be the loss of planarity that long polyconjugated systems

Table 2. Tensor components of the hyperpolarizability ($\beta(0)/10^{-30}$ esu) calculated by PM3 method for the systems represented in Fig. 1

n	βxxx	βxyy	βxzz	βyxx	βyyy	βyzz	βzxx	βzyy	βzzz
1	87	12	0	28	4	0	2	0	0
2	130	10	0	30	2	0	2	0	0
3	169	8	0	29	1	0	2	0	0
4	202	6	0	25	0	0	2	0	0
5	228	5	0	21	0	0	2	0	0
6	249	4	0	17	0	0	2	0	0
7	266	3	0	13	0	0	2	0	0
8	279	3	0	10	1	0	2	0	0

exhibit in solution. When *n* increases, a progressive coiling occurs in the polyconjugated chain and electronic delocalization on *p* orbitals decreases. Intramolecular charge transfer is not as effective as expected for a planar conformation and hyperpolarizability rises only in a soft way. To investigate whether the loss of planarity could be related to the lower correlation found ($\mu\beta(0)\propto n^{0,5}$) a theoretical study with more rigid systems was undertaken. Table 3 shows the theoretical $\mu\beta(0)$ values referred to rigid polyconjugated Cz-OXA systems, where a cyclohexenyl unit has been introduced to restrict conformational freedom (Fig. 4). Both $\mu\beta(0)$ theoretical values of non-rigid Cz-[*n*]-OXA systems (Fig. 1, Table 1) and rigid-Cz-[*n′*]-OXA systems (Fig. 4, Table 3) are very close for short conjugated chains, but when the length of the conjugated bridge increases higher theoretical hyperpolarizability values are predicted for rigid systems.

The effect of two additional donor groups, alkoxy groups, placed in the donor moiety of the push–pull Cz-[*n*]-OXA system has also been considered. System **7**, 4-(2-methoxy-9-methyl-7-undecyloxy-9*H*-carbazol-3-yl-methylene)-2-(4-nitrophenyl)-4,5-dihydro-1,3-oxazol-5-one (Fig. 5), has also been synthesized following the same reaction scheme reported for compound **2** in Fig. 2, from 2,7-dimethoxycarbazole as starting material.[37] Hyperpolarizability values of compound **7** have been determined from EFISH measurements at 1.9 μm in $CHCl_3$ being $\mu\beta=550\pm50\times10^{-48}$ esu and $\mu\beta(0)=330\pm40\times10^{-48}$ esu. Comparing the NLO-properties obtained applying the two structural modifications, it can be pointed that the effect of the addition of two conjugated double bonds to the polyene chain ($n=2$, Fig. 1) is equivalent to the introduction of two alkoxy donor groups into the carbazole unit. That points to be a synthetic alternative to avoid unnecessary, difficult and low yielded synthesis of high polyconjugated systems.

Table 3. Theoretical values for systems represented in Fig. 4 by PM3 method

n′	ΔH_f^0 (kcal/mol)	μ (10^{-18} esu)	$\beta(0)$ (10^{-30} esu)	$\mu\beta(0)$ (10^{-48} esu)
2	37.5	8.0	66.8	534
3	51.3	8.3	94.9	788
4	79.5	8.4	143.9	1209
6	107.4	8.0	168.2	1346

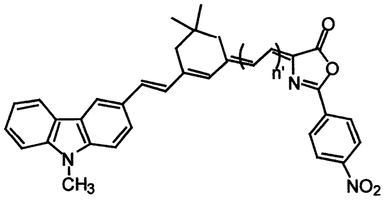

Figure 4. Rigid Cz-[*n′*]-OXA systems analyzed by PM3 method.

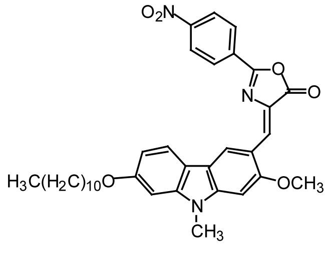

Figure 5.

Although the semiempirical calculations (MOPAC/PM3) carried out for all the compounds have shown a main diagonal component along the dipole axis, there are too some non-negligible components. HRS measurements could be interesting in order to obtain further information about these components. Synthesis of carbazole–oxazolone push–pull systems substituted with different additional donor groups and rigid polyconjugated chain are also currently being undertaken in our group.

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25. System **3**: TLC (SiO_2, CH_2Cl_2, UV): $R_f=0.28$. Mp: 126.3–128.0°C. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=9.72$ (d, CHO, $J=8$ Hz, 1H), 8.30 (dd, CH, $J=1.8$ Hz, $J=1.4$ Hz, 1H), 8.13 (dd, CH, $J=8$ Hz, $J=1.2$ Hz, 1H), 7.73 (dd, CH, $J=8.4$ Hz, $J=1.4$ Hz, 1H), 7.69 (d, CH, $J=15.8$ Hz, 1H), 7.55 (m, CH, $J=1.2$ Hz, $J=8.4$ Hz, $J=7.6$ Hz, 1H), 7.44 (d, CH, $J=8.4$ Hz, $J=1.8$ Hz, 1H), 7.43 (d, CH, $J=8.4$ Hz, $J=1.2$ Hz, 1H), 7.31 (m, CH, $J=7.6$ Hz, $J=8$ Hz, $J=1.2$ Hz, 1H), 6.80 (dd, CH, $J=8$ Hz, $J=15.8$ Hz, 1H), 3.90 (s, N-CH_3, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=193.67$, 154.54, 142.6, 141.41, 126.51, 126.08, 125.79, 125.01, 123.23, 122.46, 121.73, 120.43, 119.91, 108.99, 108.94, 29.34 ppm. Anal. (calcd for $C_{16}H_{13}NO$, found): %C (81.68, 81.70), %H (5.57, 5.71), %N (5.95, 5.96).
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28. General procedure for *Erlenmeyer reaction*: 500 μL of Ac_2O were added under a N_2 atmosphere to a mixture of 0.42 mmol of formilcarbazole, 0.42 mmol of 4-nitrobenzoilglycine and 0.42 mmol of anhydrous NaAcO. The mixture was stirred first at 60°C for 30 min, and then at 110°C for 1 h. H_2O was added dropwise and the mixture extracted with (25 mL×3) CH_2Cl_2. Organic extracts were washed with water, dried, filtered and evaporated. Flash chromatography (CH_2Cl_2) afforded a mixture *cis*/*trans*. The mixture was separated by recrystallization in AcOEt or $CHCl_3$.
29. System **4**: TLC (SiO_2, CH_2Cl_2, UV): $R_f=0.57$. Mp: 258.5–259.5°C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=8.38$ (d, CH, $J=1.5$ Hz, 1H), 8.36 (d, CH, $J=9$ Hz, 2H), 8.31 (d, CH, $J=9$ Hz, 2H), 8.14 (dd, CH, $J=7$ Hz, $J=1$ Hz, 1H), 7.79 (dd, CH, $J=8.5$ Hz, $J=1.5$ Hz, 1H), 7.74 (dd, CH, $J=15.5$ Hz, $J=11.5$ Hz, 1H), 7.52 (m, CH, $J=8.0$ Hz, $J=7.0$ Hz, $J=1$ Hz, 1H), 7.43 (dd, CH, $J=15.5$ Hz, $J=1$ Hz, 1H), 7.42 (d, CH, $J=8$ Hz, $J=1$ Hz, 1H), 7.41 (d, CH, $J=8.5$ Hz, 1H), 7.34 (dd, CH, $J=11.5$ Hz, $J=1$ Hz, 1H), 7.31 (m, CH, $J=7$ Hz, $J=1$ Hz, 1H), 3.89 (s, N-CH_3, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=$ 168.90, 164.84, 149.61, 148.23, 142.33, 141.34, 132.32, 128.37, 128.28, 127.57, 126.49, 124.10, 121.70, 120.66, 120.08, 109.17, 109.13, 29.36 ppm. MS-FAB(+)-NBA: 423 (M, 100%). Anal. (calcd for $C_{25}H_{17}N_3O_4$, found): %C (70.91, 70.20), %H (4.05, 4.14), %N (9.93, 9.85). (Calcd for $C_{25}H_{17}N_3O_4 \cdot CHCl_3$ [recrystallization in $CHCl_3$], found): %C (57.53, 58.80), %H (3.34, 3.50), %N (7.74, 7.82), %Cl (19.59, 18.32).
30. System **5**: TLC (SiO_2, CH_2Cl_2, UV): $R_f=0.23$. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=9.62$ (dd, CHO, $J=8$ Hz, $J=0.8$ Hz, 1H), 8.23 (d, CH, $J=1.8$ Hz, $J=1.4$ Hz, 1H), 8.12 (dd, CH, $J=7.6$ Hz, $J=1$ Hz, 1H), 7.67 (dd, CH, $J=8.4$ Hz, $J=1.4$ Hz, 1H), 7.57–7.00 (m, CH, 7H), 6.27 (dd, CH, $J=14.8$ Hz, $J=8$ Hz, 1H), 3.87 (s, N-CH_3, 3H) ppm. Anal. (calcd for $C_{18}H_{15}NO$, found): %C (82.73, 82.80), %H (5.79, 5.81), %N (5.36, 5.27).
31. System **6**: TLC (SiO_2, CH_2Cl_2, UV): $R_f=0.57$. Mp: 263–266°C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=8.36$ (d, CH, $J=1.5$ Hz, 1H), 8.34 (d, CH, $J=9$ Hz, 2H), 8.19 (d, CH, $J=9$ Hz, 2H), 8.10 (dd, CH, $J=7.5$ Hz, $J=1$ Hz, 1H), 7.65 (dd, CH, $J=8.5$ Hz, $J=1.5$ Hz, 1H), 7.61 (dd, CH, $J=14$ Hz, $J=1$ Hz, 1H), 7.50 (m, CH, $J=8$ Hz, $J=7$ Hz, $J=1$ Hz, 1H), 7.40 (dd, CH, $J=8$ Hz, $J=1$ Hz, 1H), 7.36 (dd, CH, $J=14$ Hz, $J=12$ Hz, 1H), 7.28 (m, CH, $J=7$ Hz, $J=7.5$ Hz, 1H), 7.22–7.09 (m, CH, 4H), 3.86 (s, N-CH_3, 3H) ppm. MS-MALDI-TOF: $m/z=449.2$ (M). UV [λ(nm), (ε), $CHCl_3$]: 526 (33300), 366 (11170). Anal. (calcd for $C_{27}H_{19}N_3O_4 \cdot CHCl_3$, found): %C (59.12, 61.13), %H (3.54, 3.73), %N (7.39, 7.70), %Cl (18.70, 18.43).
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