Structure and Optical Properties of 2,3,7,9-Polysubstituted Carbazole Derivatives. Experimental and Theoretical Studies

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Push−pull organic molecules that combine a polyfunctionalized aromatic electron-donating carbazole moiety with nitro or cyano acceptor groups, linked directly or through a polyenic chain, have been prepared and characterized as nonlinear optical (NLO) chromophores. A methoxycarbonyl group has been introduced to prepare future polysiloxane side-chain liquid-crystal polymers (SCLCPs) with NLO properties. The effect of this linking group as well as the influence of an additional methoxy donor group on the second-order NLO response have been experimentally and theoretically examined. Semiempirical calculations have been performed at the PM3 level using the time-dependent Hartree−Fock technique. Solvent influence on calculated $\mu\beta$ values has been studied via the COSMO algorithm implemented in the MOPAC program.

Introduction

Organic molecules with delocalized π-electron systems and an asymmetric response to applied electric fields may display a large second-order nonlinear optical (NLO) response, which makes them interesting for several applications in the field of optical communications, optical switching, and optical signal processing. Several factors determine the magnitude of this response that can be characterized by the molecular $\mu\beta$ values.[1] On one hand, it is well-known that the strength of the electron-donating and -accepting substituents in the molecule is a determining factor. On the other hand, the extension and topology of the conjugation path plays a fundamental role in the transfer of charge density between the substituents in the presence of electric fields. In the search for efficient NLO chromophores the necessity of understanding the relationships between chemical structure and molecular nonlinearities has been clearly established.[2]

In the past years, a great deal of effort in molecular design for nonlinear optics has been devoted to the search for multifunctional compounds. In this way carbazole-derived compounds are of interest because of their well-known photoconducting properties[3] and their second-order nonlinear optical response when electron-acceptor groups are incorporated into the carbazole unit.[4] For technological applications noncentrosymmetric bulk materials, showing long-term stability and good processability, are required. Among various NLO materials, poled NLO films are currently considered the most promising. A number of carbazole-based polymers[5] have shown both photoconductivity and electrooptic effect. These properties are needed for a material to be photorefractive and in the last years several multifunctional carbazole-based photorefractive polymers have been synthesized.[6]

As part of our research on new materials,[7] we are especially interested in polysiloxane side-chain liquid-crystal polymers (SCLCPs) with polyfunctionalized car-

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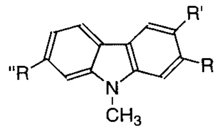


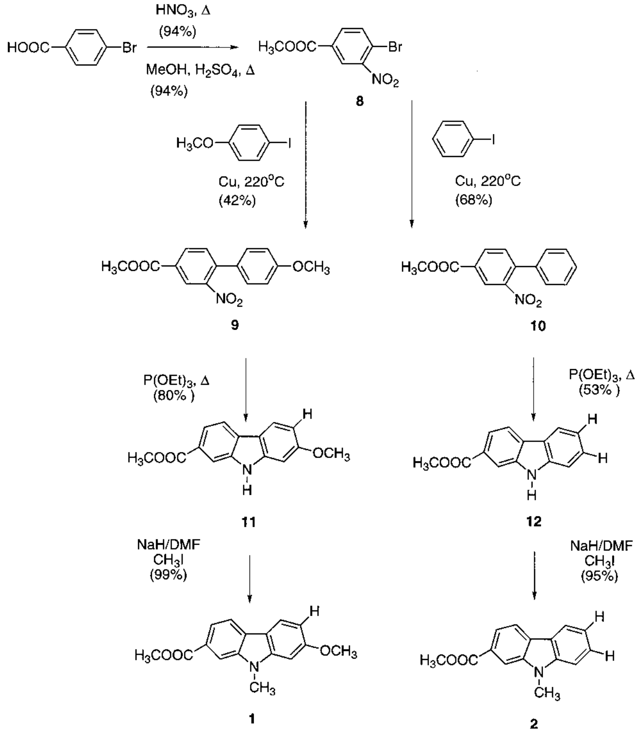
R"	R	R'	Comp.
$COOCH_3$	OCH_3	H	**1**
$COOCH_3$	H	H	**2**
$COOCH_3$	OCH_3	NO_2	**3a**
CH_2OH	OCH_3	NO_2	**3b**
$COOCH_3$	OCH_3	$CH = CH\ NO_2$	**4**
$COOCH_3$	OCH_3	$CH = C\ (CN)_2$	**5**
$COOCH_3$	OCH_3	$C\ (CN) = C\ (CN)_2$	**6**
$COOCH_3$	H	$C\ (CN) = C\ (CN)_2$	**7**

Figure 1. New synthesized carbazole chromophores.

bazole units in the side chains. Several works have been published about the preparation of ordered bulky materials from polysiloxane-substituted polymers achieved from mechanical deformation.[8] To prepare polymers with liquid-crystal behavior from carbazole derivatives, the carbazole unit should fulfill certain structural requirements. The methoxycarbonyl group has been demonstrated to be useful in linking the potential mesogenic NLO-carbazole system to the polysiloxane backbone.[9] Furthermore, the methoxycarbonyl group favors the solubility of the carbazole-derived monomers. However, the presence of this electron-withdrawing group could get into competition for electron delocalization with the other stronger acceptor, diminishing the NLO response.

To examine the electron donor ability of the 2-methoxycarbonyl-9-methylcarbazole derivatives and to achieve high second-order nonlinear responses, we have prepared new carbazole-derived chromophores substituted with strong conventional (nitro, nitrovinyl, dicyanovinyl, and tricyanovinyl) electron-withdrawing groups conjugated to the nitrogen atom (Figure 1). The effect of these substitutions and the influence of an additional methoxy donor group in the carbazole unit on its NLO properties has been analyzed from the experimental $\mu\beta$ values obtained by the electric-field-induced second-harmonic (EFISH) generation technique. Theoretical calculations have been carried out using the PM3 semiempirical approach[10] with the time-dependent Hartree–Fock (TDHF) technique incorporated into the semiempirical MOPAC93 program.[11] The calculations performed on isolated molecules in vacuo have been compared with that carried out with the COSMO algorithm[12] to investigate the infuence of the solvent on the calculated $\mu\beta$ values.

Scheme 1. Synthetic Paths to the Obtention of Polysubstituted Carbazole Parent Compounds



Results and Discussion

Synthesis. We present a new type of 2,3,7,9-polysubstituted carbazole-derived chromophores, different from other reports with usually only an electron-acceptor bonding onto the carbazole ring. Prior to the preparation of the NLO systems **3**–**7**, the parent compounds 7-methoxy-2-methoxycarbonyl-9-methylcarbazole (**1**) and 2-methoxycarbonyl-9-methylcarbazole (**2**) were synthesized (Scheme 1). 7-Methoxy-2-methoxycarbonylcarbazole (**11**) and 2-methoxycarbonylcarbazole (**12**) were obtained by Ullmann's coupling at 210 °C and a Cadogan cyclization reaction at 160 °C of the corresponding biphenyl compounds as reported for 2,7-dimethoxycarbazole[7] (Scheme 2). The corresponding *N*-methylcarbazoles were obtained in quantitative yields under standard conditions. From **1** the mononitrated compound **3a** was prepared using a mixture of $Cu(NO_3)_2/Ac_2O/AcOH$ at 30 °C for 30 min (80%). To compare the influence of the extension of the conjugation path on the NLO response, the nitrovinyl analogue **4** was also synthesized. The NLO-carbazolyl systems **4** and **5** were prepared from the same intermediate **13** previously obtained from **1** by a Vilsmeier–Haack reaction[13] (90%). The condensation of **13** with nitromethane yielded the nitrovinyl compound **4** (70%) and condensation with malononitrile gave the dicyanovinyl product **5** (81%). The 6-(1,2,2-tricyanovinyl)-7-methoxy-2-methoxycarbonyl-9-methylcarbazole (**6**) was synthesized by reaction of **1** with tetracyanoethylene at 55 °C for 48 h (37%). 6-(1,2,2-Tricyanovinyl)-2-methoxycarbonyl-9-methylcarbazole (**7**) was synthesized to quantify the influence of the donor methoxy group on the NLO response. It was prepared from **2** in the same way as its analogous derivative **6** but with a very low yield (12%). Compound **3b** with a hydroxymethyl substitution instead of the carbomethoxy one was prepared from compound **3a** by treatment with sodium borohydride. The synthetic paths are outlined in Scheme 2. All the compounds were

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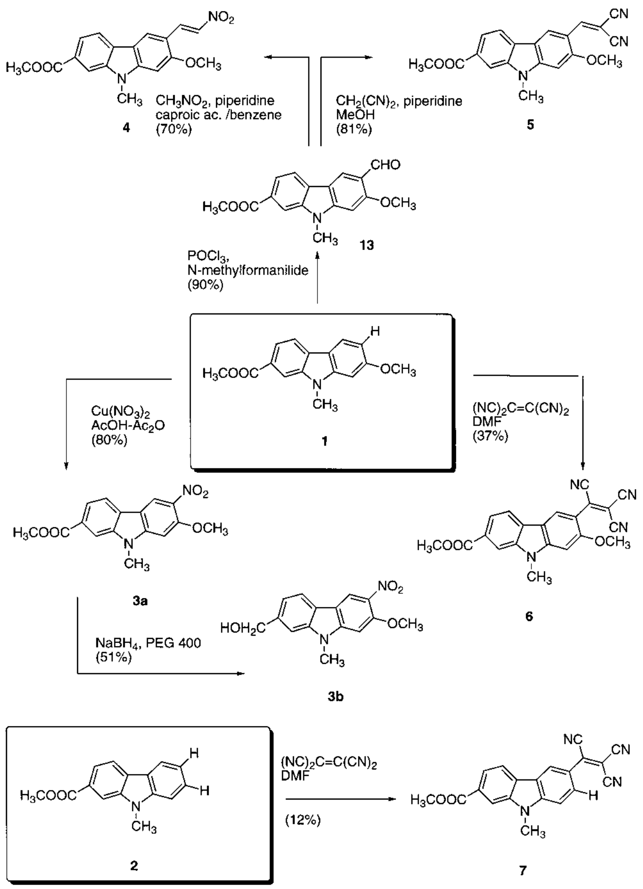
Scheme 2. Synthetic Paths to the Obtention of Carbazole Chromophores



fully characterized by NMR, IR, UV/vis, and elemental analysis.

Thermal Stability. One of the most attractive applications of the NLO chromophores is their incorporation into polymers for electro-optic 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.

The T_d (decomposition temperature) of these NLO compounds is relatively high, near the melting point (290 °C). Thermal stability studies of these compounds were performed by differential scanning calorimetry (DSC) and monitored by NMR ^1H of 200 MHz. The samples were isothermally and consecutively heated from 125 to 275 °C in steps of 25 °C for 30 min at each temperature. The tricyanovinyl derivatives **6** and **7** were also heated to 275 °C for 3 h. No decomposition products were detected.

Optical Properties. UV–vis absorption spectra of these compounds were obtained to compare their intramolecular charge-transfer properties. As expected, the two tricyanovinyl derivatives **6** and **7** were the most red-shifted, indicating the stronger electron-withdrawing nature of the tricyanovinyl group than the dicyanovinyl, nitrovinyl, or nitro groups. Nitro and cyano derivatives showed different optical absorption properties when their spectra were measured in different solvents. On one hand, when increasing solvent polarity attending to its dielectric constants, from 9.08 to 45 for CH_2Cl_2 and DMSO, respectively (Table 1), the longest wavelength absorption maximum shifted to lower energy ($\Delta\lambda = 7-19$ nm) for the nitro derivatives, but remained almost unchanged for cyano derivatives. The null or small shifts detected in this absorption band indicate that the dielectric constant of the solvent does not affect the intramolecular charge transfer, in accordance with theoretical results discussed below. Solvatochromism is usually considered indicative of high nonlinear optical response, as can be deduced from the two level model. Despite the not noticeable solvatochromism measured in cyano derivatives, they show relatively high first hyperpolarizability values. Moreover, the hydrogen-bonding effect in the solvation of these structures also appears to be minimal. When MeOH was used instead of nonprotic solvents (CH_2Cl_2), the absorption bands remained unchanged or moved only slightly to higher energy (see cyano compounds **6** and **7**). It may be concluded that neither the dielectric nor the hydrogen-bonding effects affect the intramolecular charge transfer of these NLO chromophores. Further, the two tricyanovinyl derivatives **6** and **7** showed a charge-transfer band at about the same $\lambda_{MAX} =$ 479 nm for the nonmethoxy derivative **7** and 475 nm for the 7-methoxy derivative **6**. Thus, the addition of an extra donor group in the molecule has little effect on the position of the charge-transfer band, but diminishes the transition probability, as from its molar absorptivity coefficient ($\epsilon = 70\,700$ L mol^{-1} cm^{-1} for **7** and $\epsilon = 20\,570$ L mol^{-1} cm^{-1} for **6**).

Table 1 shows experimental data on the optical properties of the carbazole-derived chromophores: the position of the longest wavelength absorption maximum at different solvents, the molar absorptivity coefficients, the experimental $\mu\beta$ values, and the $\mu\beta(0)$ values deduced from a two-level model.

NLO Response. As shown in Table 1, the increase in the relative strengths of acceptor substituents enhances the NLO response of the new polysubstituted carbazole-derivative chromophores. $\mu\beta$ values of 50, 175, and 360 (units of 10^{-48} esu) have been obtained when passing from nitro to dicyanovinyl and tricyanovinyl groups. The enlargement of the conjugation path also produces the usual increase of $\mu\beta$ values, as can be seen when comparing the nitro and nitrovinyl groups (50×10^{-48} and 225×10^{-48} esu). The experimental $\mu\beta$ values obtained for the two nitro compounds **3a** and **3b** suggest that the carbomethoxy substitution in the carbazole system does not exert a weighty effect on the NLO response of the carbazole-derived chromophores, which mainly depend on the nature of the strongest acceptor group.

We should remark that the decrease in the nonlinear response from compound **7** ($\mu\beta = 440 \times 10^{-48}$ and 360×10^{-48} esu at the two wavelengths used) to compound **6** ($\mu\beta = 360 \times 10^{-48}$ and 280×10^{-48} esu) is opposite to what was expected if the methoxy substituent acts in a cooperative way with the donor nitrogen atom of the carbazole unit. These two molecules are identical except that **6** has a methoxy group linked to the carbazole moiety in the ortho position with respect to the tricyanovinyl acceptor unit. It has been pointed out before[14] that a decrease in the first-order hyperpolarizabilities of *ortho*-methoxy-substituted dicyanovinylbenzenes due

Table 1. Optical Properties of New Carbazole Chromophores

compd	R′	R	λ_{MAX}(nm) CH_2Cl_2, MeOH DMSO	ϵ_{MAX}, CH_2Cl_2, L mol^{-1} cm^{-1}	$\mu\beta(\times 10^{-48})$ esu[a]	$\mu\beta(0)$ $(\times 10^{-48})$ esu
1	H	OCH_3	322, −, −	28 233	−	−
2	H	H	357, −, −	4 405	−	−
3a	NO_2	OCH_3	374, 373, 381	12 170	50(10)[b]	33(7)
3b	NO_2	OCH_3	−, −, 381	18 500[c]	50(10)[d]	40(8)
4	$CH{=}CHNO_2$	OCH_3	402, 404, 421	16 666	225(30)[b]	130(15)
5	$CH{=}C(CN)_2$	OCH_3	424, 421, 422	31 395	175(25)[b]	98(14)
6	$C(CN){=}C(CN)_2$	OCH_3	475, 466, 476	20 570	360(30)[b]	169(10)
7	$C(CN){=}C(CN)_2$	H	479, 465, 474	70 700	440(40)[b]	205(15)
6	$C(CN){=}C(CN)_2$	OCH_3	475, 466, 476	20 570	280(30)[d]	195(20)
7	$C(CN){=}C(CN)_2$	H	479, 465, 474	70 700	360(20)[d]	250(15)

[a] All EFISH measurements were performed in CH_2Cl_2 as the solvent except for compound **3b**, for which DMSO was used. [b] EFISH measurements performed at 1.38 μm. [c] ϵ_{MAX}, in DMSO. [d] EFISH measurements performed at 1.9 μm.

to the loss of molecular planarity occurs. To clarify these results and to determine the extension of the prevention of the coplanarity between the tricyanovinyl group and the carbazole ring, a quantum-chemical approach was also performed.

Theoretical Calculations. *1. Structural Aspects.* To examine the effect of the methoxy and the methoxycarbonyl groups on the UV−vis absorption spectra and NLO response of carbazole-derived chromophores, semiempirical calculations were performed. Different semiempirical approaches have been applied to study NLO properties, for instance, PPP,[15] CNDO,[16] INDO,[17] MNDO,[18] AM1,[19] and PM3,[20] using either numerical finite field (FF),[21] analytical coupled Hartree−Fock (CHF),[22] time-dependent Hartree−Fock (TDHF),[23] or sum-over-states (SOS)[24] techniques. Although correlations between experimental and theoretical data are slightly different for the different methods, they are useful for trend predictions in the molecular design of new compounds for nonlinear optical applications. The influence of different conformers on the calculated first-order hyperpolarizabilities is already discussed in the literature. In this respect, the MOPAC-TDHF values are that close to the measured ones.[25] First-order hyperpolarizabilities are usually estimated in the gas phase, whereas the NLO experimental values are obtained from EFISH measurements performed in solution. The importance of the solvent effects in calculation of molecular hyperpolarizabilities has been investigated. Different methods have been used, between them the SCRF−CI method,[24] the COSMO algorithm first implemented in MOPAC 93[12] and since then in several quantum chemical package programs, for example, Gaussian 94,[26] GAMESS,[27] ADF,[28] and Turbomole.[29]

Table 2 shows selected geometrical parameters of the PM3 (MOPAC-TDHF) optimized structures for all the carbazole-derived chromophores. The PM3 optimized geometries in the gas phase for all the molecules were nonplanar, except for nitro compounds **3a**, **3b**, and **4**. The differences between the heats of formation ($\Delta\Delta H^\circ_f$) calculated for the planar (torsion angles, ω, of 0° or 180°) and the full optimized structures in the gas phase were within the range 11.5−8.2 kcal/mol for **6**, 5.7−0.2 kcal/mol for **5**, and 3.3−2.7 kcal/mol for compound **7** (see Table 3).

The same qualitative results were obtained when the geometrical structures were optimized assuming a dielectric medium by using the COSMO solvent model.[12] When low dielectric constants were considered, like those of dichloromethane or chloroform solvents, similar results were obtained independently of the selected solvent. The presence of the solvent had little effect on the calculated molecular geometries. The PM3/COSMO optimized geometries for the cyano derivatives **5**−**7** were nonplanar (see torsion angles $C_8-C_5-C_6-C_7$ in Table 2).

Table 3 shows the heats of formation (ΔH°_f) calculated for the optimized geometries and the restricted planar geometries (torsion angles 0° and 180°). The heats of formation calculated for PM3/COSMO geometries are lower than those found in the gas phase. The differences between one of the two possible planar structures and the optimized structure are below 2.6 kcal/mol, but for compound **6** the difference is 6.7 kcal/mol. In the gas phase and in solution the planar conformations are predicted to be energetically accessible at room temperature for all carbazole derivatives except for compound **6**.

Bond distances for carbazole derivatives have been analyzed (Table 2). For carbazole and *N*-methylcarbazole the symmetric distribution of the π-electron density is reflected in the bond distances N_1-C_2 and $N_1-C_{2'}$. As was mentioned in the Introduction, the carbazole derivatives investigated for their NLO behavior were all substituted by a methoxycarbonyl group in the 2 position of the carbazole unit. This substitution is needed when the incorporation of the carbazole deriva-

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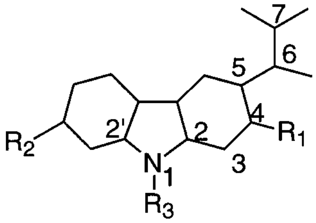
Table 2. Selected Geometrical Parameters of the PM3 Optimized Structures for All the Carbazole-Derived Chromophores



		bond length (Å)			
compd	ω, $C_8-C_5-C_6-C_7$[a,b]	$N_1-C_{2'}$[a,b]	N_1-C_2[a,b]	C_5-C_6[a,b]	C_6-C_7[a,b]
Cbz (NH)	–	1.436(1.414)	1.436 (1.414)	–	–
Cbz (NMe)	–	1.422(1.421)	1.422 (1.421)	–	–
1	–	1.442(1.440)	1.439 (1.444)	–	–
2	–	1.440(1.421)	1.440 (1.419)	–	–
3a	0[c]	1.443(1.432)	1.426(1.404)	1.494(1.470)[e]	1.220(1.226)[e]
3b	0[c]	1.432(1.431)	1.410(1.403)	1.491(1.459)[e]	1.220(1.230)[e]
4	0[d]	1.442(1.441)	1.430(1.427)	1.455(1.451)	1.347(1.352)
	180	1.442(1.429)	1.431(1.410)	1.454(1.449)	1.344(1.350)
5	0	1.443(1.441)	1.430(1.425)	1.451(1.447)	1.353(1.355)
	180	1.443(1.430)	1.432(1.410)	1.452(1.447)	1.351(1.354)
	46.8 (45.6)	1.443(1.426)	1.432 (1.411)	1.457 (1.454)	1.349 (1.352)
6	0	1.443 (1.441, *1.438*)	1.428 (1.423, *1.418*)	1.465 (1.460, *1.456*)	1.368 (1.370, *1.372*)
	180	1.444 (1.443, *1.442*)	1.429 (1.425, *1.422*)	1.466 (1.462, *1.458*)	1.366 (1.368, *1.369*)
	90.6 (87.1, *83.4*)	1.441 (1.427, *1.427*)	1.432 (1.411, *1.411*)	1.472 (1.470, *1.469*)	1.355 (1.355, *1.355*)
7	0	1.427 (1.437)	1.411 (1.423)	1.463 (1.460)	1.364 (1.365)
	180	1.440 (1.438)	1.428 (1.424)	1.464 (1.461)	1.364 (1.365)
	113.9 (124.2)	1.440 (1.424)	1.432 (1.412)	1.471 (1.466)	1.356 (1.357)
TCNE	–	–	–	–	1.358 (1.356)

[a] Values in brackets refer to PM3/COSMO results in chloroform. [b] For compound **6**, values in italics in the brackets refer to PM3/COSMO results in DMSO. [c] Geometries for $\omega = 0$, 180 and those calculated without restrictions are the same.[d] Geometries for $\omega = 0$ and that calculated without restrictions are the same. [e] $C_6{=}N$ and $C_7{=}O$ from group NO_2 in compounds **3a** and **3b**.

tive as a side chain into the polysiloxane is planned to obtain liquid-crystal polymers. Nevertheless, this linking group might have a detrimental effect on the second-order NLO response. So it has been analyzed theoretically the effect on the NLO behavior of the presence of two electron-withdrawing groups, one stronger than the other, when they operate in a contradictory manner. 2-Methoxycarbonyl-9-methylcarbazole **2** was examined, showing no difference between the bond distances $N_1-C_{2'}$ and N_1-C_2 or a slight difference when the COSMO algorithm was considered. Carbazole derivative **3b**, in which the methoxycarbonyl group was replaced for the hydroxymethyl one, has been also studied and compared with **3a**. For the two derivatives **3a** and **3b**, the shorter bond lengths are those corresponding to N_1-C_2 and not to the $N_1-C_{2'}$ bond lengths. These results point out the small effect in the delocalization of the π-electron density due to the presence of the methoxycarbonyl group in the carbazole molecule, as also shown from the experimental $\mu\beta$ values reported above for compounds **3a** and **3b** (Table 1). The substitution by a strong electron-withdrawing group in compounds **3**–**7** is clearly manifested in the analysis of the mentioned bond distances.

2. Molecular Orbitals and Predicted Nonlinear Optical Properties. The $\mu\beta(0)$ values have been calculated for the two possible planar geometries and for the full optimized ones for all compounds. However, although the theoretical results reproduce the general trends of the experimental $\mu\beta(0)$ values, the PM3 calculated $\mu\beta(0)$ values of the cyanocarbazole derivatives by using the optimized geometry are far from the experimental data. In this type of calculation the molecular stabilization attributable to conjugative effects is underestimated as opposed to steric factors. When the solvent effect is simulated by the COSMO model with different values of the dielectric constant, the fit between experimental and calculated data is improved. The $\mu\beta(0)$ values calculated for the planar geometries match much better with experimental EFISH data than those of the optimized conformers, although they are overestimated for all compounds. Access to the planar conformations in solution would explain the high experimental $\mu\beta(0)$ values for the cyanocarbazole derivatives. When considering the nitrocarbazole derivatives **3a**, **3b**, and **4**, where there is no steric hindrance to the planar conformation, as deduced from the $\Delta H°_f$ calculated for nonrestricted optimized geometries, the calculated $\mu\beta(0)$ match the experimental values, although they are slightly overestimated.

It is remarkable that the calculated $\mu\beta(0)$ value for the optimized structure of the *ortho*-methoxy susbstituted compound **6** ($\omega = 87.1°$) was only 34×10^{-48} esu, far from the experimental one ($169 \pm 10 \times 10^{-48}$ esu). Figure 2 shows the HOMO and LUMO (PM3/COSMO calculations) for the optimized geometry ($\omega = 83.4°$) and for the planar geometry ($\omega = 0°$) of compound **6**. While for the planar conformation the HOMO and the LUMO are extended over the carbazole unit and the tricyanovinyl acceptor, for the $\omega = 83.4°$ conformer the HOMO is localized over the carbazol unit and the LUMO over the tricyanovinyl acceptor. No overlap between the HOMO

Table 3. Heats of Formation ($\Delta H°_f$, kcal/mol), Electric Dipole Moments (μ, 10^{-18} esu), First-Order Hyperpolarizabilities ($\beta(0)$, 10^{-30} esu) Calculated by PM3 in Vacuo, in Solvent and Experimentally Determined ($\mu\beta(0)$, 10^{-48} esu) for All the Carbazole-Derived Chromophores

compd	$\omega^{a,b}$	$\Delta H°_f$ (kcal/mol)^b	μ (10^{-18} esu)^b	$\beta(0)$ (10^{-30} esu)^b	$\mu\beta(0)$ (10^{-48} esu)^b	$\mu\beta(0)_{exp}{}^c$ (10^{-48} esu)
3a	0^d	−72.7	5.8	5.1	30	33 ± 7
		(−88.1)	(7.5)	(6.6)	(49)	
3b	0^d	−38.9	8.3	5.1	42	40 ± 7
4	0^e	−60.6	7.0	12.4	87	
		(−78.0)	(8.6)	(19.0)	(163)	
	180	−58.7	6.6	12.0	79	130 ± 15
		(−75.1)	(8.4)	(21.5)	(181)	
5	0	25.1	6.3	15.3	96	
		(13.2)	(8.3)	(20.1)	(167)	
	180	30.6	5.2	15.3	80	
		(19.2)	(7.2)	(24.0)	(173)	
	46.8	24.9	7.9	5.0	39.5	98 ± 14
	(45.6)	(11.7)	(7.5)	(15.2)	(114)	
6	0	72.3	6.3	21.7	136	
		(58.9, *53.5*)	(8.1, *9.3*)	(30.1, *36.4*)	(244, *339*)	
	180	75.6	6.1	22.3	136	
		(62.2, *56.9*)	(8.1, *11.4*)	(32.3, *37.6*)	(262, *429*)	
	90.6	64.1	4.4 [4.6^f]	5.3 [5.2^f]	23 [24^f]	169 ± 10
	(87.1, *83.4*)	(52.2, *46.7*)	(5.4, *6.6*, [6.7^f])	(6.3, *6.6*, [8.3^f])	(34, *44*, [57^f])	
7	0	105.1	5.3	29.6	157	
		(91.4)	(6.3)	(34.3)	(216)	
	180	104.5	4.8	27.7	133	
		(91.5)	(6.2)	(37.3)	(231)	
	113.8	101.8	3.6	8.1	29	205 ± 15
	(125.8)	(88.9)	(5.6)	(19.9)	(114	

[a] Torsion angle has been fixed to 0° or 180° or it has not been fixed and the geometry has been fully optimized. [b] Calculated values by PM3; values in brackets refer to PM3/COSMO results in chloroform with RSOLV = 3.22 and EPS = 4.8, while values in italics for compound **6** are calculated with PM3/COSMO in DMSO with EPS = 45 and RSOLV = 3.43. [c] From the EFISH method in dichloromethane at 1.38 μm, but for compound **3b** in DMSO at 1.9 μm. [d] For compounds **3a** and **3b**, 0, 180, and the optimized geometry represent the same conformer. [e] For compound **4**, the geometries of $\omega = 0$ and the nonrestricted have the same results. [f] Values refer to Boltzmann distribution in chloroform, considering conformers obtained from the rotation of the torsion angle between the accepting group and the donor group (carbazole).

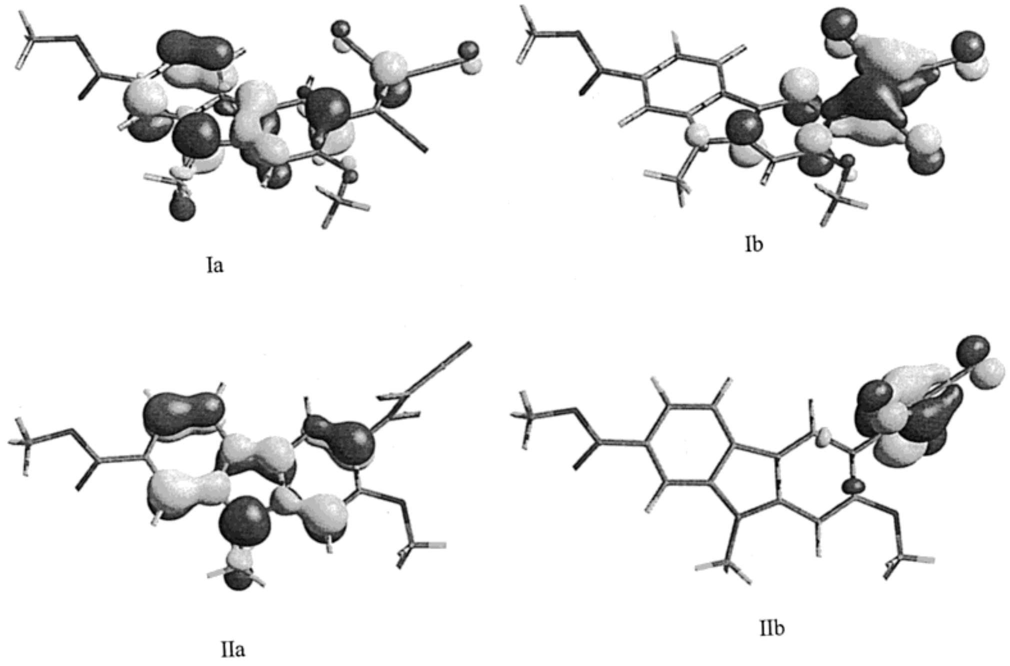


Figure 2. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the planar (ω = 0°) (Ia, Ib) and optimized geometry (ω = 83.4°) (IIa, IIb) of **6**.

and the LUMO, which is a requisite for a pull−push system with a NLO response, is predicted. From the theoretical results the charge-transfer band should be forbidden because of the almost orthogonal arrangement of the HOMO−LUMO orbitals, giving rise to a weak nonlinear response. The access to the planar conformation is not allowed at room temperature according to the predicted heats of formation ($\Delta\Delta H°_f$ = 6.7−10 kcal/mol) because of the steric hindrance promoted by the *ortho*-substituted methoxy group. The measured UV−vis absorption band and the NLO response of compound **6** are less intense than those of the unsubstituted compound **7**. According to theoretical results, this decrease is due to the interruption in the conjugation of the π-system of compound **6**, but calculations clearly overestimate the influence of the steric hindrance.

A whole conformational study for this compound was carried out with the PM3 method (key words: step =

10, point = 36). The analysis was performed for the molecule in the gas phase and also by application of the COSMO method for chloroform $\epsilon = 4.8$. For each conformation $\mu\beta(0)$ was calculated. A statistical distribution (Boltzman's distribution)[30] was used to calculate the NLO properties of the whole conformational mixture. No significant variation of the $\mu\beta(0)$ value was detected when considering the whole conformational equilibrium with respect to the optimized PM3 geometry (Table 3) in either study, in the gas phase or in chloroform solution.

It has been reported[31] that the PM3/COSMO method is primarily a theoretical model for high dielectrics. When the PM3/COSMO method was used with $\epsilon = 45$ to simulate a more polar solvent (DMSO) for compound **6**, no better prediction for its NLO response was found (Table 3).

Conclusions

Various push−pull polysubstituted carbazole derivatives have been synthesized for the development of SHG materials. All these compounds showed good thermal stability, being stable at 275 °C for more than 30 min. Special mention should been done to the tricyanovinyl derivatives, which were stable at 275 °C for 3 h without detecting descomposition products. Their UV−visible absorption spectra and its hyperpolarizabilities have been determined experimentally. Semiempirical calculations using the PM3/COSMO approach with the time-dependent Hartree−Fock technique were performed. The theoretical results reproduce the general trend of the experimental $\mu\beta$ values. The need for a solvent computational model to estimate theoretical hyperpolarizabilities has been shown. Nevertheless, steric factors are overestimated as opposed to conjugative effects by theoretical calculations. Theoretical calculations and experimental data have shown that a methoxycarbonyl substitution in the carbazole unit that favors mesophase behavior does not diminish in a significant way the NLO response of the studied carbazole derivatives.

The high thermal stability, NLO response, and the multifunctional character of these molecules make them suitable for incorporation into polymers, which could be potentially used as both photoconductive and NLO chromophores in photorefractive polymers.

Experimental Section

Materials. Commercially available reagents and solvents were used without further purification, unless indicated otherwise.

Analytical Techniques. All substances were characterized by ^{1}H NMR and ^{13}C NMR with a Bruker ARX-300 (300 MHz),-Varian Gemini-2000 (200 MHz), and Varian-500 (500 MHz) and by IR with a Perkin-Elmer 1330 Infrared Spectrophotometer. ^{1}H chemical shifts are quoted relative to TMS and ^{13}C chemical shifts relative to solvent signals. Elemental analyses were carried out by the Servei d'Anàlisi Elementals del CSIC de Barcelona. Thermal analyses were performed using a Mettler-30 differential scanning calorimeter at a heating rate of 20 K/min. UV−vis spectra were performed in a Cary 5E spectrophotometer.

EFISH Measurements. $\mu\beta$ values of all compounds were obtained from EFISH measurements performed at 1.38 or 1.9 μm. To obtain these two wavelengths, a Q-switched Nd:YAG laser with a pulse width of 8 ns operating at a repetition rate of 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 to obtain the IR emission at 1.38 μm 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 a reference to monitor and correct the laser intensity fluctuations. Two monochromators in both the reference and sample arms are used to separate the second-harmonic beam from the residual excitation beam, before being detected by a photomultiplier (Hamamatsu 928 and R426 models at the visible and near-infrared region, respectively). Each compound was measured using dichloromethane (CH_2Cl_2) as solvent. The EFISH liquid sample 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 direction. The angle between the windows was 2° and 3.5° for the 1.38- and 1.9-μm measurements, respectively. High-voltage pulses of 10 μs and 5 kV were applied to the electrodes in the cell to provide a uniform electric field parallel to the light polarization in the sample region.

Several solutions of NPP were measured to perform a kind of calibration of our system. The NPP $\mu\beta$ values obtained in the same experimental conditions as in carbazole derivatives measurements are 125×10^{-48} and 110×10^{-48} esu at 1.38 and 1.9 μm, respectively.

Computational Methods. Molecular orbital calculations were carried out for all the compounds using the semiempirical MNDO/ PM3[10] Hamiltonian of the MOPAC 93[11] program on a Silicon Indigo 2 workstation with full optimization of all bond lengths, angles, and torsion angles except where stated otherwise. The SCF convergence criterion was set to 10^{-8} for the calculations of both the geometries and the NLO properties (PRECISE option in MOPAC). The eigenvector following (EF) method was employed for the molecular geometry optimizations.

Solvent effects were considered at the PM3 level using the COSMO algorithm[12] incorporated in the MOPAC 93 program. All reported calculations used the values of DISEX = 2.0 and NSPA = 40 [where DISEX is the maximum distance, in angstroms, of intersegmental interactions and NSPA is the number of surface segments per atom]. Solvent radii were calculated by taking half the maximum molecular length, as determined computationally. The maximum molecular length was defined by the maximum interatomic separation plus the van der Waals radii of the two terminal atoms: RSOLV calculated for chloroform was 3.22 and 3.43 for DMSO.

7-Methoxy-2-methoxycarbonyl-9-methylcarbazole, 1. A solution of 2.05 g (8 mmol) of **12** in 30 mL of dry DMF was added to a suspension of 265 mg (8.84 mmol) of NaH (80%) in 20 mL of dry DMF. The solution was stirred for 30 min at 60 °C. Thereafter, 1.325 g (8.84 mmol) of iodomethane in 10 mL of dry DMF was added and after a further 20 min with stirring at 60 °C the reaction was completed. A few drops of water were carefully added to the ice-cooled solution, and then 100 mL water was added, followed by acidification with 2 N HCl. The product **1** was isolated and recrystallized from MeOH. The mother liquors were purified by flash chromatography with dichloromethane on silica gel. The product **1** was obtained quantitatively; mp 133−134 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.11 (d, $J = 8$ Hz, 1H), 8.08 (d, $J = 1.5$ Hz, 1H), 8.06 (d, $J = 8.5$ Hz, 1H), 7.77 (dd, $J = 8.0$, 1.5 Hz, 1H), 7.16 (d, $J = 2.0$ Hz, 1H), 6.84 (dd, $J = 8.5$, 2.0 Hz, 1H), 3.89 (s, 3H), 3.888

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(s, 3H), 3.881 (s, 3H); ^{13}C NMR (50 MHz, DMSO-d_6) δ 167.2 (C=O), 160.1 (C), 143.9 (C), 140.0 (C), 126.4 (C), 125.2 (C), 125.0 (C), 122.2 (CH), 120.0 (CH), 119.3 (CH), 110.3 (C), 109.0 (CH), 93.4 (CH), 55.8 (CH_3), 52.2 (CH_3); 29.4 (CH_3); MS (CI, NH_3) *m*/*z* 304 ($C_{16}H_{15}NO_3\cdot N_2H_7^+$, 34), 287 ($C_{16}H_{15}NO_3\cdot NH_4^+$, 100), 270 ($C_{16}H_{15}NO_3\cdot H^+$, 27), 269 ($C_{16}H_{15}NO_3{}^{+\cdot}$, 2). Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.35; H, 5.61; N, 5.20. Found: C, 71.26; H, 5.68; N, 5.20.

2-Methoxycarbonyl-9-methylcarbazole, 2. A solution of 2 g (8.8 mmol) of 2-methoxycarbonylcarbazole **13** in 20 mL of dry DMF was added to a suspension of 293 mg (9.7 mmol) of NaH (80%) in 20 mL of dry DMF. The solution was stirred for 30 min at room temperature. Thereafter, 611 μL (9.7 mmol) of iodomethane was added and after a further 30 min a mixture of water–ice was carefully added. The product **13** was isolated and recrystallized from MeOH. The mother liquors were purified by flash chromatography with dichloromethane on silica gel. Yield: 2.0 g (95%); mp 105–106 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.26 (dd, J = 8.0, 0.5 Hz, 1H), 8.22 (dt, J = 8.0, 1.0 Hz, 1H), 8.17 (d, J = 1.5 Hz, 1H), 7.81 (dd, J = 8.0, 1.5 Hz, 1H), 7.65 (d, J = 8.5 Hz, 1H), 7.54 (ddd, J = 8.5, 7.0, 1.5 Hz, 1H), 7.25 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 3.93 (s, 3H), 3.90 (s, 3H).

7-Methoxy-2-methoxycarbonyl-9-methyl-6-nitrocarbazole, 3a. $Cu(NO_3)_2\cdot 3H_2O$ (153 mg, 0.61 mmol) was dissolved in 7 mL of Ac_2O and 3.5 mL of AcOH and then 300 mg (1.1 mmol) of **1** was added. The mixture was stirred for 30 min and then poured into ice water. The precipitate was filtered and dried. The product was purified by flash chromatography in dichloromethane on silica gel and recrystallized from $CHCl_3$/Et_2O. Yield: 282 mg (80%); mp 234–235 °C; ^{1}H NMR (300 MHz, $CHCl_3$-d_1) δ 8.75 (s, 1H), 8.12 (s, 1H), 8.02 (dd, J = 8.1, 0.9 Hz, 1H), 8.00 (dd, J = 8.1, 1.2 Hz, 1H), 6.88 (s, 1H), 4.10 (s, 3H), 3.99 (s, 3H), 3.90 (s, 3H); MS (CI, NH_3) *m*/*z* 332 ($C_{16}H_{14}N_2O_5\cdot NH_4^+$, 100), 315 ($C_{16}H_{14}N_2O_5\cdot H^+$, 17), 314 ($C_{16}H_{14}N_2O_5{}^{+\cdot}$, 1); UV ($CH_2Cl_2$): $\lambda(\epsilon)$ = 374 (12170), 297.0 (46511), 241.2 (38294); Anal. Calcd for $C_{16}H_{14}N_2O_5$: C, 61.14; H, 4.49; N, 8.91. Found: C, 60.76; H, 4.35; N, 8.74.

7-Hydroxymethyl-2-methoxy-9-methyl-3-nitrocarbazole, 3b. 3 (60 mg, 0.19 mmol) was dissolved in 1.5 mL of PEG 400 and 22 mg (0.57 mmol) of sodium borohydride was added portionwise. The solution was slowly brought to 65 °C and stirred for 3 h. Diluted HCl (10%) was added to the reaction mixture dropwise. The products were extracted with ethyl acetate, and the organic layer was dried with sodium sulfate and evaporated. The product was purified by flash chromatography in hexane/ethyl acetate (1:1) on silica gel. Yield: 28 mg (51%); mp 234–235 °C; ^{1}H NMR (200 MHz, DMSO-d_6) δ 8.78 (s, 1H), 8.16 (d, J = 8.0 Hz, 1H), 7.68 (s, 1H), 7.36 (s, 1H), 7.21 (d, J = 8.0 Hz, 1H), 5.38 (t, 1H), 4.63 (d, J = 5.8 Hz, 2H), 4.02 (s, 3H), 3.88 (s, 3H); MS (CI, NH_3) *m*/*z* 304 ($C_{15}H_{14}N_2O_4\cdot NH_4^+$, 11), 287 ($C_{15}H_{14}N_2O_4\cdot H^+$, 100).

7-Methoxy-2-methoxycarbonyl-9-methyl-6-(2-nitrovinyl)carbazole, 4. Carbazole **14** (100 mg, 0.33 mmol) was dissolved in a solution of 22 mg (0.36 mmol) of nitromethane and 40 mg (0.34 mmol) of caproic acid in 5 mL of anhydrous benzene in the presence of molecular sieves of 4A. Three drops of piperidine were added and the mixture was heated to reflux for 1.5 h. After the solvent was evaporated, the product was purified by flash chromatography in dichloromethane on silica gel. Yield: 80 mg (70%); mp 295–296 °C; ^{1}H NMR (200 MHz, DMSO-d_6) δ 8.75 (s, 1H), 8.37 (d, J = 13.6 Hz, 1H), 8.16 (d, J = 13.6 Hz, 1H), 8.15 (d, J = 8.0 Hz, 1H), 8.12 (s, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.31 (s, 1H), 4.08 (s, 3H), 3.94 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (50 MHz, $CHCl_3$-d_1) δ 166.6 (C=O), 159.6 (C), 146.1 (C), 140.7 (C), 136.1 (CH), 135.2 (CH), 126.2 (C), 125.4 (CH), 120.9 (CH), 119.6 (CH), 115.5 (C), 111.7 (C), 112.5 (CH), 110.7 (CH), 92.5 (CH), 54.8 (CH_3), 52.1 (CH_3), 29.4 (CH_3); IR (KBr) 1707, 1636, 1601, 1574, 1298, 1240 cm^{-1}; MS (CI, NH_3) *m*/*z* 358 ($C_{18}H_{16}N_2O_5\cdot NH_4^+$, 100), 341 ($C_{18}H_{16}N_2O_5\cdot H^+$, 80); UV ($CH_2Cl_2$): $\lambda(\epsilon)$ = 255 (44761), 311 (36666), 402 (16666); Anal. Calcd for $C_{18}H_{16}N_2O_5$: C, 63.55; H, 4.74; N, 8.23. Found: C, 63.03; H, 4.68; N, 8.14.

6-(2,2-Dicyanovinyl)-7-methoxy-2-methoxycarbonyl-9-methylcarbazole, 5. Malononitrile (73 mg, 1.08 mmol) was dissolved in 5 mL of methanol and three drops of piperidine were added to the solution. Then, 293 mg (0.98 mmol) of carbazole **14** in 5 mL of methanol was added and the mixture was stirred at room temperature for 24 h. The precipitate was filtered and washed with methanol. The product was purified by flash chromatography in CH_2Cl_2/MeOH (9.9/0.1) on silica gel. Yield: 275 mg (81%); mp 274–275 °C; ^{1}H NMR (300 MHz, $CHCl_3$-d_1) δ 8.99 (s, 1H), 8.33 (s, 1H), 8.05 (m, 1H), 8.01 (dd, J = 8.1, 0.9 Hz, 1H), 7.96 (dd, J = 8.1, 1.2 Hz, 1H), 6.73 (s, 1H), 4.03 (s, 3H), 3.98 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (75 MHz, $CHCl_3$-d_1) δ 167.2 (C=O), 159.5 (C), 153.7 (CH), 147.4 (C), 141.2 (C), 127.6 (C), 126.4 (C), 122.4 (CH), 122.3 (CH), 119.8 (CH), 116.6 (C), 115.3 (C), 114.5 (C), 113.8 (C), 110.7 (CH), 90.5 (CH), 56.2 (CH_3), 52.3 (CH_3), 29.6 (CH_3); IR (KBr) 2215, 1717, 1636, 1261 cm^{-1}; MS (CI, NH_3) *m*/*z* 363 ($C_{20}H_{15}N_3O_3\cdot NH_4^+$, 100); UV ($CH_2Cl_2$): $\lambda(\epsilon)$ = 247.0 (28604), 309.5 (31626), 340.5 (26976), 424 (31395); Anal. Calcd for $C_{20}H_{15}N_3O_3$: C, 69.55; H, 4.37; N, 12.16. Found: C, 69.34; H, 4.40; N, 12.10.

6-(1,2,2-Tricyanovinyl)-7-methoxy-2-methoxycarbonyl-9-methylcarbazole, 6. Carbazole **1** (100 mg, 0.37 mmol) was dissolved in 5 mL of anhydrous dimethylformamide under an argon atmosphere. Then, 60 mg (0.46 mmol) of tetracyanoethylene (freshly distilled) was added and the solution was heated to 50 °C for 72 h. The cooled mixture was dropped into a water/ice solution and the product was extracted with $CHCl_3$. The organic solution was dried with Na_2SO_4 and evaporated. The product was purified by flash chromatography in CH_2Cl_2 on silica gel. Yield: 51 mg (37%); mp >280 °C; ^{1}H NMR (300 MHz, $CHCl_3$-d_1) δ 8.38 (s, 1H), 8.18 (s, 1H), 8.10 (dd, J = 8.1, 0.6 Hz, 1H), 8.06 (dd, J = 8.1, 1.2 Hz, 1H), 6.92 (s, 1H), 4.15 (s, 3H), 4.03 (s, 3H), 3.95 (s, 3H); IR (KBr) 2217, 1810, 1630, 1599, 1499, 1449, 1369 cm^{-1}; MS (CI, NH_3) *m*/*z* 388 ($C_{21}H_{14}N_4O_3\cdot NH_4^+$, 100); UV ($CH_2Cl_2$): $\lambda(\epsilon)$ = 254.2 (81500), 320.0 (46750), 475.0 (2325); Anal. Calcd for $C_{20}H_{15}N_3O_3$: C, 69.10; H, 3.81; N, 15.18. Found: C, 67.54; H, 3.79; N, 15.24.

6-(1,2,2-Tricyanovinyl)-2-methoxycarbonyl-9-methylcarbazole, 7. Carbazole **2** (500 mg, 2.09 mmol) was dissolved in 10 mL of anhydrous dimethylformamide under an argon atmosphere. Then, 300 mg (2.3 mmol) of tetracyanoethylene (freshly distilled) was added and the solution was heated to 50 °C for 48 h. The cooled mixture was dropped to a water/ice solution and the product was extracted with CH_2Cl_2. The organic solution was dried with Na_2SO_4 and evaporated. The product was purified by flash chromatography in CH_2Cl_2 on silica gel. Yield: 82 mg (12%); mp 295–296 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.90 (d, J = 1.5 Hz, 1H), 8.48 (d, J = 8.5 Hz, 1H), 8.30 (d, J = 1.5 Hz, 1H), 8.21 (dd, J = 9.0, 1.5 Hz, 1H), 7.99 (d, J = 9.0 Hz, 1H), 7.96 (d, J = 8.5 Hz, 1H), 4.04 (s, 3H), 4.03 (s, 3H), 3.93 (s, 3H); IR (KBr) 2218, 1709, 1632, 1599, 1599, 1454, cm^{-1}; MS (CI, NH_3) *m*/*z* 358 ($C_{19}H_{12}N_4O_2\cdot NH_4^+$, 100); UV ($CH_2Cl_2$): $\lambda(\epsilon)$ = 246.0 (99494), 294.3 (59000), 353.2 (34000), 479.0 (70700); Anal. Calcd for $C_{19}H_{12}N_4O_2$: C, 69.50; H, 3.68; N, 17.06. Found: C, 69.49; H, 3.61; N, 16.99.

4-Bromo-3-nitromethylbenzoate, 8. 4-Bromo-3-nitrobenzoic acid[32] (69.2 g, 0.28 mol) was added to a mixture of 170 mL of methanol and 17 mL of concentrated sulfuric acid previously heated to reflux for 1 h. The formed solid was filtered and recrystallized from methanol to give 68.2 g (94%) of **8**; mp 102–104 °C; ^{1}H NMR (200 MHz, $CHCl_3$-d_1) δ 8.47 (d, J = 2.0 Hz, 1H), 8.07 (dd, J = 8.4, 2.0 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (50 MHz, $CHCl_3$-d_1) δ 164.1 (C=O), 135.4 (CH), 133.4 (CH), 130.2 (C), 126.4 (CH), 119.8 (C), 52.9 (CH_3); IR (KBr) 3098, 1719, 1601,1541, 1358, 1036 cm^{-1}; MS (CI, NH_3) *m*/*z* 294–296 ($C_8H_6NO_4Br\cdot N_2H_7^+$, 96–100), 277–279 ($C_8H_6NO_4Br\cdot NH_4^+$, 12–11).

4′-Methoxy-4-methoxycarbonyl-2-nitrobiphenyl, 9. A mixture of 22.4 g (0.086 mol) of **8** and 40.3 g (0.172 mol) of *p*-iodoanisole was stirred mechanically and heated to 220 °C. Then, 50 g of activated copper bronze was added gradually to the stirred melt. After 4 h of heating, the reaction was completed. The cooled mixture was transferred into a Soxhlet extraction apparatus and extracted with AcOEt. After the

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[32] Hübner, H. *Justus Liebigs Ann. Chem.* **1884**, *222*, 178.

solvent was evaporated, product **9** was recrystallized from MeOH. The mother liquors were purified by flash chromatography with a mixture of hexane/AcOEt (8/2) on silica gel. Yield: 10.4 g (42%); mp 99−100 °C; ^{1}H NMR (200 MHz, acetone-d_6) δ 8.35 (d, J = 1.7 Hz, 1H), 8.23 (dd, J = 8.0, 1.7 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.31 (d, J = 8.7 Hz, 2H), 7.0 (d, J = 8.7 Hz, 2H), 3.92 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (50 MHz, acetone-d_6) δ 164.1 (C═O), 161.6 (C), 150.2 (C), 140.6 (C), 133.7 (CH), 133.6 (CH), 131.1 (C), 130.4 (C), 129.6 (C), 125.9 (CH), 115.5 (CH), 56.0 (CH_3), 53.4 (CH_3); IR (KBr) 3098, 1719, 1601,1541, 1358, cm^{-1}; MS (CI, CH_4) m/z 316 ($C_{15}H_{13}NO_5\cdot C_2H_5^+$, 51), 288 ($C_{15}H_{13}NO_5\cdot H^+$, 100).

4-Methoxycarbonyl-2-nitrobiphenyl, 10. A mixture of 20 g (76.9 mmol) of **8** and 45 g (220 mmol) of iodobenzene was stirred mechanically and heated to 220 °C. Then, 40 g of activated copper bronze was added gradually to the stirred melt. After 1.5 h the mixture was cooled and transferred into a Soxhlet extraction apparatus and extracted with chloroform. The product **10** was purified by distillation at 185−190 °C (1.5 mmHg). Yield: 13.48 g (68%); mp 94−95 °C; ^{1}H NMR (300 MHz,$CHCl_3$-d_1) δ 8.48 (d, J = 1.4 Hz, 1H), 8.27 (dd, J = 7.8, 1.4 Hz, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.5−7.2 (m, 5H), 3.99 (s, 3H); ^{13}C NMR (50 MHz, $CHCl_3$-d_1) δ 165.2 (C═O), 149.8 (C), 140.8 (C), 136.9 (C), 133.2 (CH), 132.8 (CH), 130.9 (C), 129.2 (CH), 128.1 (CH), 125.7 (CH), 53.5 (CH_3); MS (CI, NH_3) m/z 292 ($C_{14}H_{11}NO_4\cdot N_2H_7^+$, 13), 275 ($C_{14}H_{11}NO_4\cdot NH_4^+$, 100), 258 ($C_{14}H_{11}NO_4\cdot H^+$, 1), 257 ($C_{14}H_{11}NO_4{}^{+\cdot}$, 2).

7-Methoxy-2-methoxycarbonylcarbazole, 11. A mixture of 9.5 g (0.033 mol) of **9** in 30 mL of triethylphosphite was heated to reflux under a nitrogen atmosphere for 4 h. After cooling, the product was collected by suction filtration and washed thoroughly in dichloromethane. The mother liquors were purified by flash chromatography with a mixture of hexane/AcOEt (7/3) on silica gel. Yield: 6.7 g (80%) of **12**; mp 229−230 °C; ^{1}H NMR (200 MHz, DMSO-d_6) δ 11.4 (br s, 1H), 8.15−8.0 (m, 3H), 7.75 (d, J = 8.0 Hz, 1H), 7.03 (d, J = 2.0 Hz, 2H), 6.84 (dd, J = 8.0, 2.0 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (50 MHz, DMSO-d_6) δ 167.2 (C═O), 159.8 (C), 142.9 (C), 139.2 (C), 126.8 (C), 125.0 (C), 122.2 (CH), 119.7 (CH), 119.3 (CH), 115.6 (C), 112.1 (CH), 109.1 (CH), 94.6 (CH), 55.5 (CH_3), 52.2 (CH_3); IR (KBr) 3098, 1719, 1601, cm^{-1}; Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.57; H, 5.13; N, 5.48. Found: C, 70.38; H, 5.10; N, 5.45.

2-Methoxycarbonylcarbazole, 12. A mixture of 6.42 g (0.025 mol) of **10** in 18 mL of triethylphosphite was heated to reflux under a nitrogen atmosphere for 4 h. After cooling, the product was collected by suction filtration and washed thoroughly in methanol. The mother liquors were purified by flash chromatography with dichloromethane on silica gel. Yield: 3 g (53%) of **12**; mp 183−184 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.52 (br s,1H), 8.21 (d, J = 8.5 Hz, 1H), 8.18 (d, J = 8.0 Hz, 1H), 8.11 (d, J = 1.0 Hz, 2H), 7.77 (dd, J = 8.0, 1.0 Hz, 1H), 7.55 (d, J = 8.5 Hz, 1H), 7.46 (ddd, J = 8.5, 7.5, 1 Hz, 1H), 7.20 (dt, J = 7.5, 0.5 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (75 MHz, $CHCl_3$-d_1) δ 167.2 (C═O), 141.3 (C), 139.3 (C), 127.3 (CH), 126.5 (C), 126.4 (C), 121.8 (C), 121.3 (CH), 120.4 (CH), 119.5 (CH), 119.4 (CH), 112.5 (CH), 111.6 (CH), 52.5 (CH_3); IR (KBr) 3300, 2980, 1700, 1450, cm^{-1}; MS (CI, CH_4) m/z 254 ($C_{14}H_{11}NO_2\cdot C_2H_5^+$, 14), 226 ($C_{14}H_{11}NO_2\cdot H^+$, 100), 225 ($C_{14}H_{11}NO_2{}^{+\cdot}$, 23).

6-Formyl-7-methoxy-2-methoxycarbonyl-9-methylcarbazole, 13. Carbazole **1** (1 g, 3.7 mmol) was added to a mixture of 0.6 g (4.46 mmol) of N-methylformanilide and 415 μL (4.46 mmol) of $POCl_3$ in 5 mL of $CHCl_3$. The mixture was heated at reflux for 8 h and then a solution of 1.75 g of NaAcO in 8 mL of water was added. The product was extracted with CH_2Cl_2. The extract was washed with water and dried. After evaporation of the solvent, the product was recrystallized from $CHCl_3$. Yield: 1 g (90%); ^{1}H NMR (200 MHz, $CHCl_3$-d_1) δ 10.32 (s, 1H), 8.59 (s, 1H), 8.1−7.9 (m, 3H), 6.77 (s, 1H), 4.06 (s, 3H), 3.98 (s, 3H), 3.87 (s, 3H).

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