

7,7-Diarylnorbornanes: Novel Nonclassical NLO-Active Chromophores

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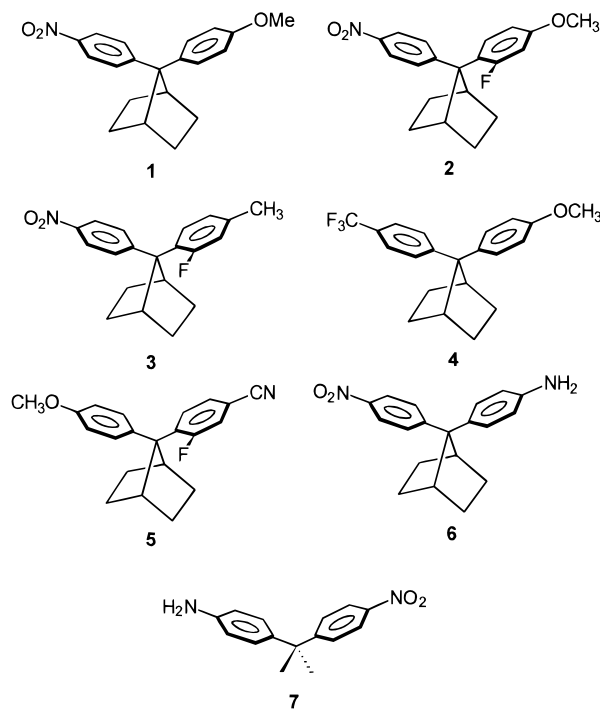
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The second-order nonlinear susceptibility of some novel 7,7-diarylnorbornane compounds in chloroform solution has been measured by EFISH at a fundamental wavelength $\lambda = 1064$ nm. Values of β_z for the cofacial apical molecules (**1–6**) are enhanced in comparison to those reported for the uncoupled aryl rings. Highest value, $\beta_z(1064 \text{ nm}) = 21 \times 10^{-30}$ esu, similar to that reported for the linearly conjugated *p*-nitroaniline molecule, was measured for the amino (donor) and nitro (acceptor) substituted compound **6**. This result emphasizes the role of homoconjugative interactions, promoted by exchange coupling through the ipso (apical) C atoms, on interannular charge-transfer and nonlinear optical response. On the other hand, the propeller compound **7**, where the aryl rings are twisted, does show only a small enhancement in comparison to the predictions of an additive model.

Introduction

Inorganic crystals such as KH_2PO_4 (KDP) or BaB_2O_4 (BBO) are used on an industrial scale for frequency doubling and parametric amplification and oscillation. However, very efficient nonlinear optical (NLO) organic materials are being developed with promising possibilities for optoelectronic technologies.¹ Some key advantages on their inorganic counterparts are chemical flexibility, easy processability, and low cost. So far, one-dimensional molecules consisting of donor and acceptor units connected through a π -conjugated bridge have been most extensively investigated.^{2,3} These molecules may exhibit large ground state and mesomeric dipole moments and consequently a high value for the dominant diagonal component β_{zzz} of the quadratic hyperpolarizability tensor $\beta(2\omega; \omega, \omega)$. However, for the relevant case of frequency doubling from the near-infrared (NIR) into the visible spectral range, a very wide transparency window is needed. This condition is not fulfilled by most chromophores in which the increase in NLO response is accompanied by significant red-shifts in the optical absorption spectra.^{1–3} Consequently, their performance for photonic devices is severely hampered by a strict nonlinearity–transparency tradeoff.

Promising strategies to enhance the β hyperpolarizability^{4–6} and overcome the transparency–nonlinearity tradeoff are being recently pursued. They include molecules with purely octupolar contribution to the β tensor,^{7–8} zwitterionic systems,⁹ and those containing heteroatoms such as Si, S, P,^{10–13} and transition metals. Other approaches rely on donor–acceptor compounds in which the charge-transfer between the two groups takes place via nonclassical interactions instead of through a direct π -conjugated bridge.^{3,14–16} This concept involves orbital coupling via electric multipole,¹⁷ electron exchange¹⁸ or through-bond¹⁹ (superexchange) interactions. One may also quote the reported

Figure 1. Chemical structure of compounds **1–7**.

(per chromophore) enhancement in β as well as in optical transparency in donor– π –acceptor functionalized 4-calixarenes.²⁰

To afford new data about nonclassical interactions as a basis for NLO activity, an alternative molecular design strategy has been followed. We have chosen the 7,7-diarylnorbornane compounds,²¹ in which the aryl groups are arranged in an apical cofacial disposition (apical homoconjugated), forced by the steric effect of the four *exo*-norbornylic C–H bonds. To increase the CT interactions some efficient D/A combinations (compounds **1–6**) have been tested (Figure 1). They provide an interesting

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SCHEME 1

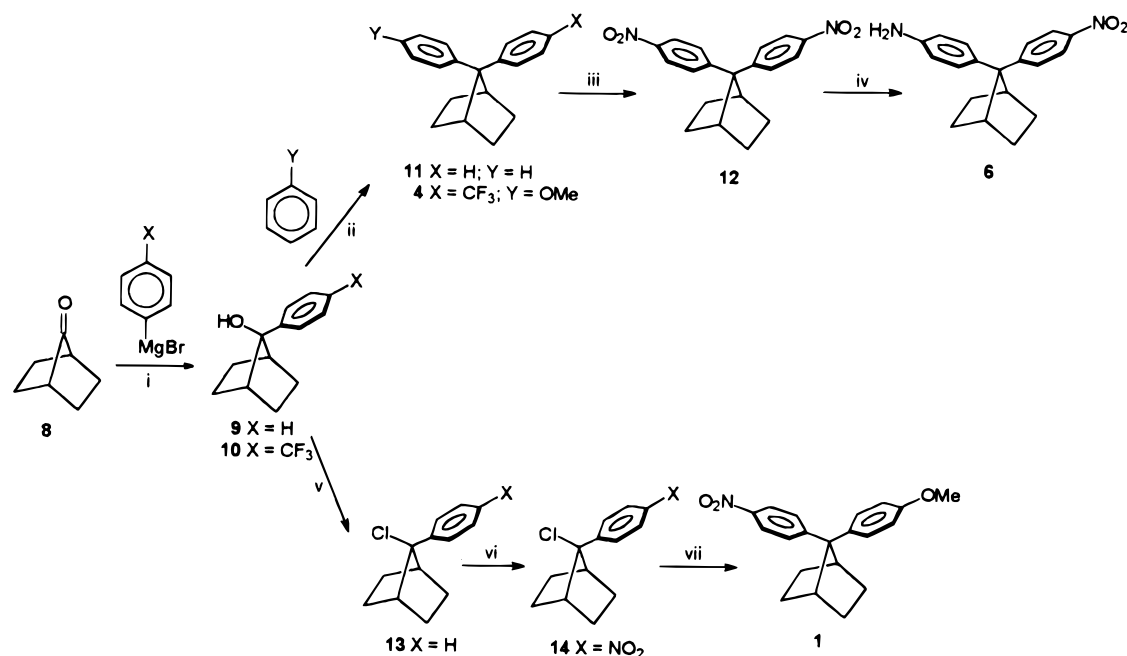


TABLE 1: Electric Dipole Moments Calculated by the Semiempirical PM3 Method and EFISH First Hyperpolarizabilities of Compounds 1–7 and PNA as a Reference

compound	μ (D)	μ_{add} (D)	$\gamma_o^{\parallel} (\gamma_o^{\perp})$ (10^{-34} esu)	$\mu\beta_z$ (10^{-47} esu)	β_z (1064 nm) (10^{-30} esu)	$\beta_z(0)$ (10^{-30} esu)	β_{add} (10^{-30} esu)
1	6.0	4.1	2	5	9	8	1.5
2	6.5		3	6	9	8	
3	6.5		3	6	9	8	
4	3.6		1	1	3		
5	3.9		1	3	7	7	
6	5.2	4.2	5 (2)	11	21	19	1.9
7	5.4	4.2	2	4	7	6	1.9
PNA	7.8 (6.2 ^a)	5.5	8 (2)	17	21 (27 ^b)	19 (24 ^b)	2.5

^a Experimental value of the PNA ground-state dipole moment. ^b Calculated using the experimental value of the PNA ground-state dipole moment.²⁴

example to explore the effects of homoconjugative interactions between aromatic molecules and compare them to those arising from conventional conjugative coupling. In fact, a strong electronic interaction between both aryl rings is revealed by intense homoconjugative (AHK) bands²¹ as well as charge-transfer (CT) bands appearing in the high- and low-energy regions of the UV spectrum, respectively. This coupling is induced by the short $C_{\text{ipso}}-C_{\text{ipso}}$ distance (2.46 Å in the case of 7,7-diphenylnorbornane) measured by X-ray diffraction.²¹ These bands are not observed (or are very weak) in the case of the related conformationally unstable diarylmethane derivatives.^{21,22} Comparative data on the propeller compound **7**, where the aryl rings are nearly orthogonal and destroy the interannular interaction, have also been obtained. It is expected that the new results obtained on these compounds should clarify the role of non- π -conjugative (nonclassical) interactions on the NLO response.

Results

Synthesis. The synthesis of compounds **1–6** was carried out according to the procedure described previously by us²¹ for the synthesis of **2**, **3**, and **5** (Scheme 1).

Dipole Moments. To have information on the asymmetry of the charge distribution in the ground state, the electric dipole moments of our diarylnorbornane derivatives have been calculated by the semiempirical PM3²³ method and are listed in Table 1. These values have been compared with those inferred from

a simple additive rule for the dipole moments of the two independent D/A-substituted aryl rings in some of the compounds²⁴ (see also Table 1) taking into account that the angle between the two subunits is 101°. ²¹ One obtains, thus, definite evidence for a significant amount of electrostatic interactions between both aryl rings in the ground state (even for the propeller compound **7**).

Linear Spectra. Absorption spectra for all compounds are shown in Figure 2. They show strong optical absorption below 400 nm and so leave a large visible window for frequency-doubling from the near-infrared. The spectrum of *p*-nitroaniline (PNA) is also included for comparison. The location of the CT bands are marked on the spectra. The assignment of these bands was carried out by comparison with the spectra of diarylmethanes and 2,2-diarylpropanes as well as monosubstituted 7,7-diarylnorbornanes.

NLO Results. The mean second-order hyperpolarizability $\gamma^{\parallel}(2\omega; \omega, \omega, 0)$ (eq 1) of compounds **1–6** was measured at $\lambda = 1064$ nm in CHCl₃ solution by the electric field induced second harmonic (EFISH) technique²⁵ using a parallel geometry, i.e., the fundamental light polarization vector parallel to the applied electric field. For this configuration, the average hyperpolarizability is,

$$\gamma^{\parallel}(2\omega; \omega, \omega, 0) = \gamma_e^{\parallel} + \gamma_o^{\parallel} = \gamma_e^{\parallel} + \mu\beta_z/5kT \quad (1)$$

where γ_e^{\parallel} and γ_o^{\parallel} , respectively, correspond to the electronic and

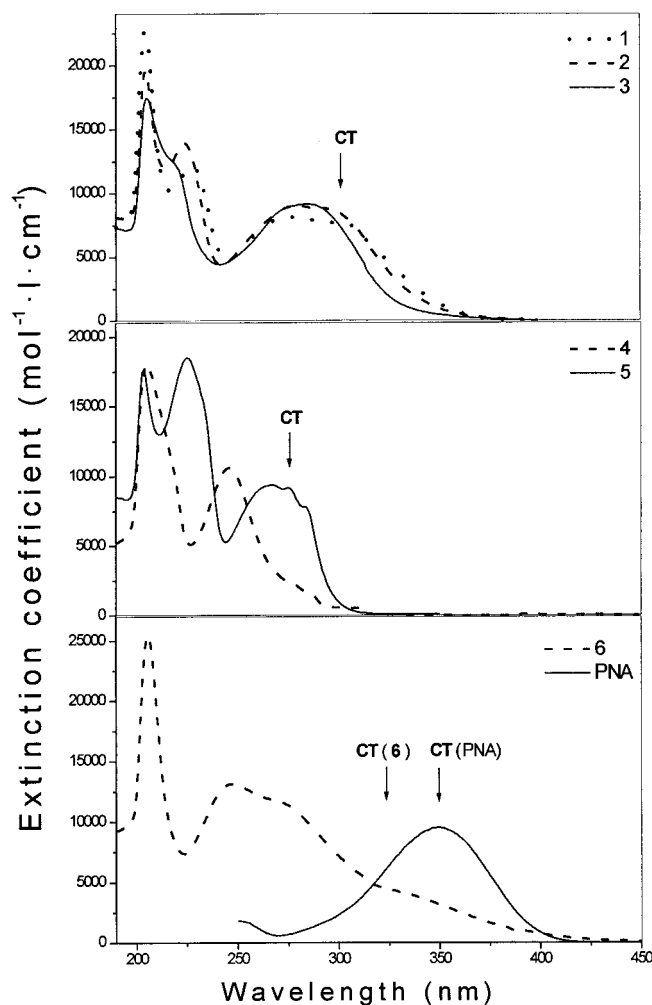


Figure 2. Absorption spectra for compounds 1–6 and PNA as reference. The position of charge-transfer (CT) transitions are marked with arrows.

orientational contributions to the cubic hyperpolarizability γ . μ stands for the permanent electrical dipole moment of the molecular ground-state assumed to lie along the z axis. β_z represents the z -projection of the vector (dipolar) component of the quadratic hyperpolarizability tensor. Then, the scalar product $\mu\beta_z$ has been calculated from eq 1 by neglecting the electronic part γ_e of the cubic hyperpolarizability tensor. This may be a reasonable approximation for experiments where excitation is performed at a light wavelength far from resonance.²⁶ Using the calculated μ values in Table 1, β_z have been obtained. The results are listed in Table 1, which also includes the data measured by us for PNA used as a reference compound. For the cofacial aryl compounds, β_z values increase with the strength of the donor/acceptor substituents and reach a maximum, $\beta_z = 21 \times 10^{-30}$ esu, for the amino/nitro molecule **6**. On the other hand, the propeller compound (**7**), having also amino and nitro substituents but twisted π -orbitals for the apical C atoms, presents a much lower value, $\beta_z = 6.7 \times 10^{-30}$ esu.

For the amino/nitro-substituted molecule having the highest β_z , additional EFISH experiments were carried out with the polarization of the fundamental light perpendicular to the electric field.²⁷ Under this condition one measures the averaged orientational component (γ_o^\perp) of the mean second-order hyperpolarizability γ that is also listed in Table 1. One sees that the ratio between the averaged orientational cubic hyperpolarizabilities is $\gamma^\perp/\gamma^\parallel = 3$. This result is expected for any molecular symmetry if Kleinman conjecture is obeyed (β_{ijk} independent

TABLE 2: Wavelengths of Homoannular (λ_{\max}) and CT (λ_{CT}) Bands, Extinction Coefficients (ϵ), and Transparency Limit (ϵ at λ of 415 nm) of 1–7

compound	$\lambda_{\max}(\text{CHCl}_3)$	ϵ_{\max}	$\lambda_{CT}(\text{CHCl}_3)^a$	ϵ_{CT}	ϵ_{415}
1	276	8100	303	7000	0
2	279	7800	299	7600	0
3	272	8500	292	9100	0
4	248	9800			0
5	278	7800	278	7800	0
6	272	9200	325	4700	150
7	274	9800	315 ^b	2700 ^b	20
PNA			348	9500	40

^a Calculated by the first derivative method. ^b Shoulder.

of ijk permutation), i.e., the frequencies involved are far from resonance and the applied electric field is not too high ($\mu E/kT \ll 1$). Assuming the validity of this conjecture, the expression for β_z appearing in eq 1 is written

$$\beta_z = \beta_{zzz} + \beta_{zxx} + \beta_{zyy} \quad (2)$$

On the other hand, the existence of a dominant low-energy charge-transfer (CT) transition (see Figure 2) justifies the use of a two-level model to describe the SHG response. Then, the wavelength dependence of β_z is given by

$$\beta_z(2\omega; \omega, \omega) = \beta_z(0) \frac{\omega_0^4}{(\omega_0^2 - \omega^2)(\omega_0^2 - 4\omega^2)} \quad (3)$$

where ω_0 stands for the frequency of the relevant charge-transfer band and $\beta_z(0)$ is the static β value ($\omega = 0$). By using this expression and the measured frequencies for the charge-transfer transitions (Table 2) one can compute $\beta_z(0)$ which are also included in Table 1. Relative values of diagonal (β_{zzz}) and off-diagonal ($\beta_{zxx} = \beta_{zxx}$ and $\beta_{zyy} = \beta_{zyy}$) components to β_z cannot be determined from our experiments. Consequently, one cannot ascertain the departures of our molecules from the well-known behavior for a linear molecule ($\beta_{zxx} = \beta_{zxx} = \beta_{zyy} = \beta_{zyy} = 0$).

Discussion

It is, first, remarkable that the β_z values (particularly for compound **6**) are much larger than those (β_{add}) obtained by an additive rule²⁸ for the two aryl moieties (see Table 1). They have been calculated by adding the β values corresponding to the two independent monosubstituted aryl rings.²⁴ The observed differences confirm that interannular charge transfer is, indeed, contributing to the SHG response. This is also in accordance with the evidence obtained from the ground-state dipole moments (Table 1). Because of the molecular geometry of our complexes,²¹ the charge transfer should be mediated by any of the following mechanisms: multipolar (van der Waals) coupling between orbital wave functions, exchange interaction between the overlapped π -orbitals of the apical C atoms, or through-bond (superexchange) mechanisms. The first one, which does not require orbital overlapping, is expected to yield a small contribution to interannular charge transfer in accordance with the distances separating the atoms in the two aryl rings.²¹ Through-bond interactions, operating through the bridging apical C bonds could make a significant contribution as illustrated in some calculations for different types of saturated hydrocarbon (including norbornylic) bridges¹⁹ and from experiments¹⁰ and calculations¹¹ on some organosilicon compounds. However, this interaction is strongly inhibited for *kinked* systems,¹⁹ as is the case for our diarylnorbornanes where the bond angle is around 100° .²¹ Therefore, electron exchange coupling induced by

π -orbital overlapping between the nearest apical C atoms appears to be the dominant interaction. Consequently, it should yield a major contribution to charge transfer and to the NLO response. In fact, this mechanism also accounts for the strong reduction in β measured for the twisted compound **7**. Moreover, it may be also responsible for the homoconjugation (AHK) and CT bands in the absorption spectra. The similar values found for β_z between **6** and PNA shows that these nonclassical homoconjugative interactions could be as strong as conventional π -conjugative interactions.

In contrast with the apical homoconjugation of our compounds, tryptycenes may be considered as lateral homoconjugated.¹⁴ Clear enhancements in the SHG response have been also observed in some of these compounds presenting significant transannular charge transfer. In this case, through-bond interactions may be responsible for the charge transfer and NLO response. On the other hand, either through-bond¹⁹ or exchange mechanism¹⁸ should be operative for parallel cofacial diarylnaphthalenes (DAN) compounds¹⁵ and might be also responsible for the observed enhancement in SHG response.

The relevant NLO activity of compound **6** suggest a significant light-induced D/A interaction. However, it is noteworthy that this interaction has not been observed in the ground state. In fact, the potential barrier to molecular rotation around $C_{\text{ipso}}-C_7$ bonds in 7,7-diarylnorbornanes arises from the electrostatic interactions between both aryl rings but it is independent of the D/A properties of the substituents.²¹ This result stresses that one cannot extrapolate the interactions acting on the ground state when trying to account for NLO behavior.

Anyhow, more definite conclusions on the responsible processes for the enhanced NLO response in our diarylnorbornanes would require additional experiments on molecules with different conformations so that one might modify in a controlled way the amount of π -overlapping and distances between interacting orbitals.

Conclusions

Diarylnorbornanes **1–6** have been shown to present significant SHG hyperpolarizabilities while keeping a wide transparency window including the blue spectral region. In particular, for the amino/nitro derivative, **6**, its β_z is comparable to that measured for the linear conjugated PNA molecule, whereas its relevant absorption peaks occur at lower wavelengths. The NLO response is associated with interannular charge transfer mediated by exchange coupling through the apical C atoms. Therefore, homoconjugation offers a possible route for enhanced optical nonlinearities without significant transparency restrictions.

Experimental Section

General. NMR spectra were recorded on a Varian XL 300 (299.94 MHz for ^1H and 75.43 MHz for ^{13}C) spectrometer and a Bruker-AC 250 (250.13 MHz for ^1H and 62.90 MHz for ^{13}C) spectrometer. Chemical shifts are given in ppm relative to TMS. IR spectra were recorded on a Perkin-Elmer 781 spectrometer. Mass spectra were recorded on a GC-MS HP-5989 (60 eV) mass spectrometer. For gas chromatography, a Perkin-Elmer 300 chromatograph equipped with capillary OV-101 column was used. UV spectra were measured in a Perkin-Elmer Lambda-3 spectrometer using methanol and chloroform as solvents. Flash chromatography was performed over Merck silica gel 60 (230–400 mesh). Melting points were measured in a Gallenkamp apparatus and are uncorrected. All reactions involving organometallic reagents were carried out under argon

atmosphere. Et_2O and benzene were distilled from deep blue sodium/benzophenone solutions. CH_2Cl_2 and CHCl_3 were distilled from phosphorous pentoxide. Starting materials and reagents obtained from commercial sources were used without further purification.

All compounds described in the present work, except **6**,²⁹ were obtained according to procedures described by us previously.²¹ The syntheses of substrates **2**, **3**, **5**, **9**, **11**, **13**, and **14** is also described elsewhere.²¹ **7** was prepared following the same procedure used for **6**.²⁹

7-(4-Methoxyphenyl)-7-(4-nitrophenyl)norbornane (1). Yield 91%. mp 199.2–202.0 °C. IR (KBr): ν 3010, 2980, 2880, 1605, 1590, 1510, 1345, 1260, 1190, 1040, 830 cm^{-1} . ^1H NMR (250 MHz, CDCl_3 , 25 °C): δ 8.10 (d, J = 9.0 Hz, 2 H), 7.55 (d, J = 9.0 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 6.79 (d, J = 8.5 Hz, 2H), 3.72 (s, 3H), 3.10–3.00 (m, 2H), 1.75–1.65 (m, 2H), 1.65–1.50 (m, 2H), 1.45–1.30 (m, 4H). ^{13}C NMR (63 MHz, CDCl_3 , 25 °C): δ 157.8, 154.4, 145.7, 136.4, 128.4, 128.0, 123.9, 114.1, 64.5, 55.2, 42.0, 28.4, 28.3. MS m/z (%): 323 (M^+ , 100), 306 (27), 242 (32), 121 (17). UV–vis (CHCl_3): λ_{max} (ϵ) 276 (8100), 303 (7000) nm.

7-(4-Methoxyphenyl)-7-(4-trifluorophenyl)norbornane (4). Yield 85%. mp 132.0–133.5 °C; IR (CHCl_3): ν 3010, 2970, 2880, 1610, 1510, 1330, 1250, 1220, 1160, 1130, 1070, 830 cm^{-1} . ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ 7.53 (d, J = 9.0 Hz, 2 H), 7.48 (d, J = 9.0 Hz, 2 H), 7.33 (d, J = 8.7 Hz, 2H), 6.79 (d, J = 8.7 Hz, 2H), 3.76 (s, 3H), 3.13–3.08 (m, 2H), 1.73–1.63 (m, 2H), 1.63–1.53 (m, 2H), 1.38–1.28 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ 157.4, 150.4, 137.1, 128.2, 127.4, 127.5 (c, J = 32.2 Hz), 124.8 (c, J = 272.0 Hz), 125.3 (c, J = 3.0 Hz), 113.8, 64.1, 55.1, 41.8, 28.3. MS m/z (%): 346 (M^+ , 100), 277 (41), 265 (62), 201 (27), 183 (42), 159 (39), 121 (54), 115 (20), 91 (24), 77 (20), 41 (32). UV–vis (CHCl_3): λ_{max} (ϵ) 248 (9800) nm.

7-(4-Aminophenyl)-7-(4-nitrophenyl)norbornane (6). To a solution of 0.34 g (1 mmol) of **12** and 0.49 g (6 mmol) of cyclohexene in 20 mL of ethanol was added 40 mg of 10% Pd/C. After refluxing for 1 h, the reaction mixture was filtered and the solvent was evaporated at reduced pressure. The residue was purified by flash chromatography (toluene/ethanol 20/1). Compound **6** was obtained in 50% yield. mp 201.0–203.0 °C. IR (KBr): ν 3483, 3398, 3010, 2957, 1622, 1595, 1521, 1346 cm^{-1} . ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ 8.06 (d, J = 8.4 Hz, 2 H), 7.52 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 6.55 (d, J = 8.4 Hz, 2H), 3.55 (s, 2H), 3.05–2.95 (m, 2H), 1.70–1.60 (m, 2H), 1.60–1.48 (m, 2H), 1.40–1.25 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ 154.5, 145.3, 144.2, 134.1, 128.0, 127.7, 123.6, 115.2, 64.2, 41.7, 28.1, 28.1. MS m/z (%): 308 (M^+ , 100), 227 (34), 106 (22), 77 (10). UV–vis (CHCl_3): λ_{max} (ϵ) 249 (11800), 272 (9200), 325 (4700) nm.

2-(4-Aminophenyl)-2-(4'-nitrophenyl)propane (7). Yield 40%. mp 76.7–79.0 °C. IR (CHCl_3): ν 3460, 3380, 3010, 2970, 1622, 1595, 1510, 1346, 1215, 855, 705 cm^{-1} . ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ 8.10 (d, J = 9.0 Hz, 2 H), 7.38 (d, J = 9.0 Hz, 2H), 6.97 (d, J = 8.7 Hz, 2H), 6.62 (d, J = 8.7 Hz, 2H), 3.62 (bs, 2H), 1.66 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ 159.1, 145.8, 144.5, 139.0, 127.6, 127.5, 123.2, 114.9, 42.7, 30.5. MS m/z (%): 256 (M^+ , 47), 241 (100), 195 (23). UV–vis (CHCl_3): λ_{max} (ϵ) 274 (9800), 315 (2700) nm.

7-(4-Trifluorophenyl)-7-norbornanol (10). Yield 65%. mp 78.0–79.2 °C. IR (CCl_4): ν 3595, 3400, 2950, 2875, 1620, 1415, 1330, 1230, 1175, 850 cm^{-1} . ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ 7.62 (s, 4 H), 2.43–2.37 (m, 2 H), 2.20–2.10 (m, 2 H), 1.75 (s, 1 H), 1.50–1.20 (m, 6 H). ^{13}C NMR (75 MHz,

CDCl₃, 25 °C): δ 146.3, 129.8 (c, J = 32.2 Hz), 127.5, 125.5 (c, J = 4.0 Hz), 124.0 (c, J = 272.0 Hz), 87.5, 42.1, 28.3, 27.2. MS m/z (%): 256 (M⁺, 6), 201 (55), 188 (33), 187 (60), 173 (100), 145 (51), 68 (29), 55 (77), 41 (36).

7,7-Di(4-nitrophenyl)norbornane (12). Yield 94%. mp 263.8–264.5 °C. IR (KBr): ν 3020, 2975, 2860, 1615, 1530, 1350, 850, 710 cm⁻¹. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ 8.12 (d, J = 9.0 Hz, 4H), 7.58 (d, J = 9.0 Hz, 4H), 3.18–3.10 (m, 2H), 1.65–1.55 (m, 4H), 1.50–1.40 (m, 4H). ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ 151.6, 146.0, 128.1, 124.0, 65.3, 41.9, 28.0. MS m/z (%): 338 (M⁺, 14), 308 (37), 279 (36), 278 (100), 277 (41), 197 (37), 189 (24), 186 (30), 185 (28), 149 (28), 144 (24), 130 (33), 106 (69). UV–vis (MeOH): λ_{max} (ε) 205 (18800), 284 (16900) nm.

NLO Measurements. EFISH experiments have been performed in chloroform solutions, as a function of molecular concentration. Light at fundamental wavelength, λ = 1064 nm, was emitted by a Q-switched Nd:YAG laser. A liquid cell with thick windows in the wedge configuration²⁵ was used to obtain a Maker fringes pattern. The incident beam was synchronized with a DC field applied to the solution in order to break its centrosymmetry.

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