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Triphenylcarbinol Derivatives as Molecules for Second-Order Nonlinear Optics

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A series of novel tris D-π-A substituted triphenylcarbinol derivatives have been synthesized and studied for their molecular second-order nonlinear optical properties by electric field induced second harmonic generation (EFISH) and hyper Rayleigh scattering (HRS). Compared to their phenyl analogs with only one D-π-A system, the triphenylcarbinol derivatives **7** and **10–12** exhibit an increased hyperpolarizability ($\langle\beta\rangle_{HRS}$) without the undesired red-shift of the charge-transfer band. The dipole moments and the hyperpolarizabilities are dependent on both the close proximity (3–4 Å) and the orientation of the three NLO-phore units. The nature of the acceptor substituent strongly influences the magnitude of the $\langle\beta\rangle_{HRS}$ values. The tris(nitrophenyl) derivative **7** exhibits a $\langle\beta\rangle_{HRS}$ value of 15×10^{-31} esu, which is almost the same as that of its reference compound *p*-nitroanisole **13**, whereas the tris(nitrostilbene) derivative **12** exhibits a $\langle\beta\rangle_{HRS}$ value of 338×10^{-30} esu which is more than 3 times larger than that of its reference compound 4-methoxy-4′-nitrostilbene **16**.

Introduction

Currently, there is a large interest in organic materials (polymers) that contain a high density of π-conjugated organic molecules with both electron-donating and -accepting groups (D-π-A molecules) for application in nonlinear optical (NLO) processess as frequency doubling of laser light and electrooptical switching.[1–4] To investigate the influence of multiple D-π-A systems on the hyperpolarizability (β) and the nonlinear susceptibility ($\chi^{(2)}$), we recently published a novel class of NLO-phores, viz. calix[4]arenes, which can combine up to four D-π-A moieties in one molecule.[5] The distances between the four π-systems in calix[4]arenes are about 4–8 Å, and the mutual influence on β could clearly be demonstrated.[6] Electronic interactions between neighboring aryl moieties have also been reported by Norvez and Barzoukas,[7] who found a 5-fold increase of the β_z value of the monoacceptor-substituted 2-nitrotriptycene in comparison with nitrobenzene. These authors suggest transannular charge transfer in order to explain this large β_z value. The distance of about 3 Å between the three nonconjugated π-systems in triptycene is smaller than in calix[4]arenes. Recently, Di Bella et al.[8] published a theoretical study on the dependency of $\beta_z(\chi^{(2)})$ on the distance and orientation of a number of D-π-A substituted molecules. It was calculated that at interplanar distances of 3.5 Å and shorter, very strong mixing of the π-systems takes place, resulting in a strong orientationally dependent increase or decrease of the overall $\beta_x(\chi^{(2)})$ value.

To investigate further the effect of close proximity of NLO-phore groups we have synthesized and studied the NLO-properties of a series of triphenylcarbinol derivatives, which combine three (nonconjugated) D-π-A systems in one molecule. The influence of the short distances of about 3–4 Å between the three D-π-A substituted aromatic rings on the NLO properties will be presented (Figure 1).

Triphenylcarbinols with donor/acceptor groups substituted at the 2- and 5-positions of the aromatic rings will have a resulting dipole moment that can be oriented in a strong electric field to allow for EFISH measurements. The microscopic β values have been measured with both

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[†] Organic Chemistry.

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(6) For the tetrakis D-π-A substituted calix[4]arenes in the "aligned" *cone* it was found that the measured β_z value was slightly lower than expected from the vectorial addition of four individual D-π-A moieties. This slightly lower value can be explained by interference of the cofacial π-systems in these tetrakis D-π-A substituted calix[4]arenes. For mono D-π-A substituted calix[4]arenes a hypsochromic shift of 10–20 nm of the charge-transfer band maximum was observed in comparison with reference compounds with the same D-π-A system. Moreover, a larger β value was measured for the mono-D-π-A-substituted calix[4]arenes than for the reference compounds. The three unsubstituted aromatic rings in calix[4]arene do not contribute to the larger β value by a simple vectorial addition of the NLO-phore units since unsubstituted tetrahydroxycalix[4]arene has a $\langle\beta_z\rangle$ value smaller than 1×10^{-30} esu. The red shift of the mono-acceptor-functionalized calix[4]arenes is most probably caused by the interaction of the NLO-phores with the neighboring aromatic rings in calix[4]arenes. This interaction may cause a stabilization of the highly polarized NLO-phoric unit in the excited state, leading to a lower excitation energy, this in turn results in higher β_z values for the mono-D-π-A-substituted calix[4]arenes.

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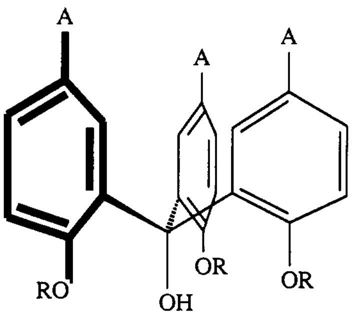


Figure 1. A 2,5-D-π-A-substituted triphenylcarbinol.

the EFISH and HRS technique. The internal distances of the aromatic rings in triphenylcarbinols are fixed, but the mutual orientations of the rings are not strictly defined because the rings are relatively free to rotate around the α-bond to the central carbon atom.[9] The rate of rotation of the rings in **10** has been determined by variable-temperature ^{1}H NMR measurements in solution.

Results and Discussion

Synthesis of the Donor-Substituted Triphenylcarbinol 6. Triphenylcarbinol **6**, containing electron-donating methoxy substituents at the 2-positions of the aromatic rings, was obtained in 65% yield by reaction of 6-bromo-2-methylanisole (**3**) with methyl 2-methoxy-3-methylbenzoate (**5**) under the influence of *tert*-butyllithium in THF (Scheme 1).[10]

Triphenylcarbinol **6** shows a characteristic hydroxyl signal at δ 5.90 in the ^{1}H NMR spectrum and a signal at δ 81.4 for the central carbon atom of Ar_3–COH in the ^{13}C NMR spectrum. Compound **3** was obtained by bromination of *o*-cresol (**1**) according to the literature[11] to give 6-bromo-2-methylphenol (**2**), followed by alkylation of the hydroxyl group with dimethyl sulfate.[12] Benzoate **5** was obtained by reaction of 3-methylsalicylic acid (**4**) with dimethyl sulfate, as was confirmed by the ^{1}H NMR signals at δ 3.91 and 3.83 and the ^{13}C NMR signals at δ 59.1 and 49.8 for the methyl ether and methyl ester moieties, respectively.

Introduction of Electron-Withdrawing Substituents in Triphenylcarbinols. The 5-nitro-substituted triphenylcarbinol **7** could only be synthesized from **6** under neutral conditions in low yield by reaction of **6** with copper(II) nitrate hexahydrate in acetic anhydride (Scheme 2).[13] The introduction of the nitro group was confirmed by the NO_2 vibrations at 1522 and 1343 cm^{-1} in the IR spectrum and two characteristic aromatic doublets (J_m = 2.6 Hz) at δ 8.13 and 7.95 in the ^{1}H NMR spectrum.

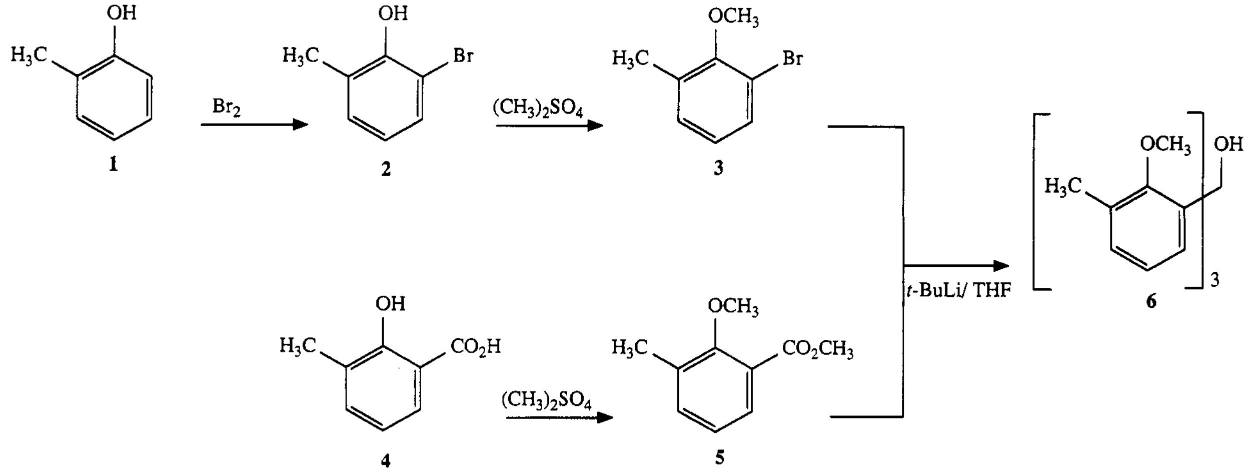
The introduction of a bromine atom in the three aromatic rings by reaction of **6** with *N*-bromosuccinimide (NBS) in DMF in the dark[14] in 75% yield gave exclusively the tris(5-bromophenyl) derivative **8** as was proven by the two singlets at δ 7.28 and 7.11 in the ^{1}H NMR spectrum and the characteristic isotope pattern for three bromo atoms in the mass spectrum. To allow the substitution of the bromo atoms by formyl groups via bromo–lithium exchange with *tert*-butyllithium, the carbinol group was methylated with methyl iodide in THF and NaH as a base, to give **9** in 84% yield. The methoxy signal in **9** is present at δ 2.99 in the ^{1}H NMR spectrum and at δ 53.7 in the ^{13}C NMR spectrum. For complete bromo–lithium exchange in compound **9**, it was necessary to increase the temperature after addition of *tert*-butyllithium in THF, from −70 to −50 °C. After subsequent cooling to −70 °C, DMF was added to the mixture and the aldehyde **10** was obtained in 80% yield. The characteristic signal of the formyl groups is present as one singlet in the ^{1}H NMR spectrum at δ 9.88.

For the synthesis of compounds with longer conjugated π-systems, aldehyde **10** was reacted with *p*-cyanobenzyl phosphonate or *p*-nitrobenzyl phosphonate under Wittig–Horner conditions to give the tris(*p*-cyanostilbene) (**11**) and the tris(*p*-nitrostilbene) derivatives (**12**) in 17% and 11% yield, respectively.[15] The double bond in all stilbene units has the *E* configuration as followed from the coupling constant (J = 16.2 Hz) for the ethenyl protons in the ^{1}H NMR spectra. The IR spectra of **11** and **12** exhibit the characteristic C≡N stretch vibration at 2225 cm^{-1} and the NO_2 vibrations at 1522 and 1343 cm^{-1}, respectively.

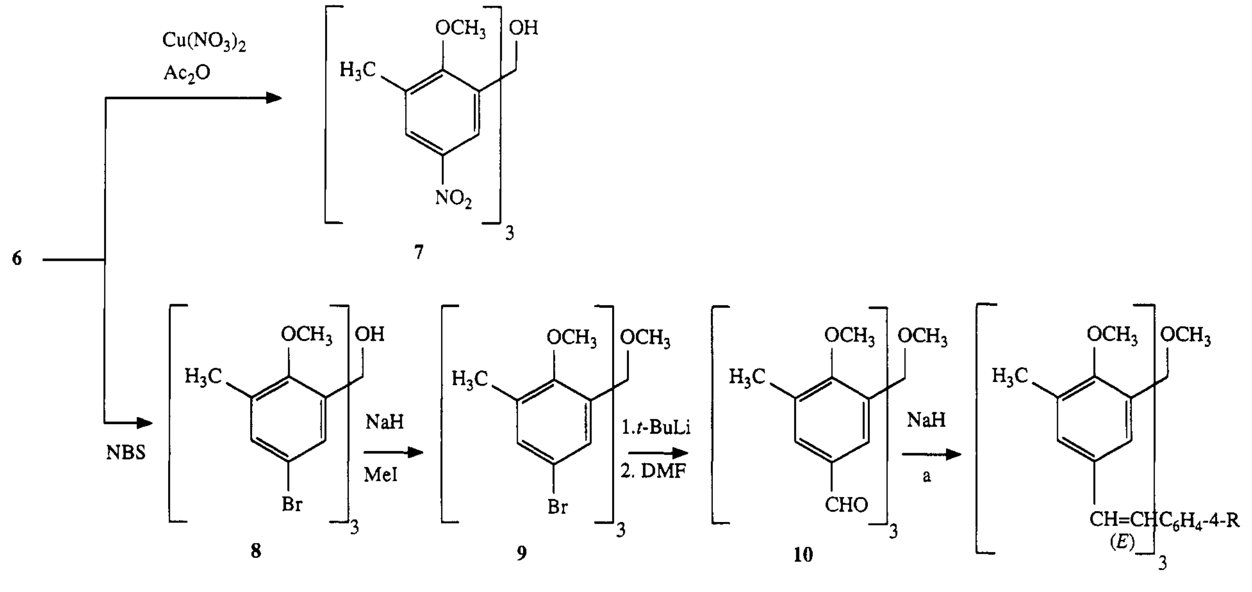
Hyperpolarizabilities of the Triphenylcarbinol Derivatives 7 and 10–12. The averaged hyperpolarizabilities of the triphenylcarbinol derivatives **7** and **10–12** have been determined both with the EFISH ($\langle\beta_z\rangle$)[3,16] and HRS[17] techniques ($\langle\beta\rangle_{HRS}$). The measured averaged dipole moment ($\langle\mu\rangle$), the $\langle\beta\rangle$ values measured at 1064 nm, and the charge-transfer band maximum (λ_{CT}) of the triphenylcarbinol derivatives and of the reference compounds **13–16** are given in Table 1.

The dipole moments of the triphenylcarbinol derivatives show an unexpected behavior when compared with their reference compounds. For the tris(nitrophenyl) **7** and the tris(formylphenyl) derivatives **10** slightly higher dipole

Scheme 1



Scheme 2



a = $(H_5C_2O)_2P(O)CH_2C_6H_4$-4-R

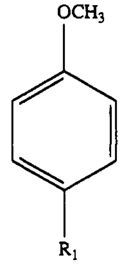
11 R=CN

12 R=NO_2

Table 1. Dipole Moments, Hyperpolarizabilities, and Charge-Transfer Bands of the Triphenylcarbinol Derivatives 7 and 10–12 and Their Reference Compounds 13–16[a]

compd	μ [D]	$\langle\beta_z\rangle$(EFISH)^{b,c}	$\langle\beta\rangle$(HRS)^{b,d}	λ_{CT} [nm]
7	6^e	6^e	15	290
13	4.6	12	12	302
10	4.3	10	14	272
14	3.2	8	9	269
11	3.3	48	80	340
15	5.4	46	47	340
12	4.6	179	338	376
16	4.5	100	105	377

[a] In $CHCl_3$. [b] $\langle\beta\rangle$(1064 nm) values (in 10^{-30} esu). [c] Error of 20%. [d] Error of 25%. [e] Error of 40%, because of low concentrations.



13 R$_1$ = NO_2

14 R$_1$ = CHO

15 R$_1$ = (E)CH=CHC$_6$H$_4$CN

16 R$_1$ = (E)CH=CHC$_6$H$_4$NO$_2$

moments are observed, than for the reference compounds p-nitroanisole 13 and p-anisaldehyde 14, respectively. However, for the tris(nitrostilbene) derivative 12 the dipole moment is identical with that of the reference compound 16, whereas the tris(cyanostilbene) derivative 11 has an even lower dipole moment than the reference compound 15. If the overall dipole moment would be simply the vectorial addition of the averaged dipole moments of the three substituted aromatic rings, almost twice the value of that of the reference compound would have been expected. This 2-fold increase of the dipole moment can be calculated by the vectorial addition of the two extreme conformations in the direction of the central C–O bond (z axis).[18] The average contribution of the three phenyl rings to the total dipole moment in the x and y directions are cancelled. The much lower overall dipole moments which are experimentally observed for the triphenylcarbinol derivatives indicate a strong electronic interaction of the three substituted aromatic rings.[8]

The small distances of 3–4 Å between the aromatic rings in the triphenylcarbinol derivatives can give rise to strong orientationally dependent mixing of the π-systems, which

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(15) The crude yield of the all E isomers 11 and 12 was larger than 80% according to the ^{1}H NMR spectra. Unfortunately, after workup the yield of all E isomers had dropped to 17% and 11%, respectively.

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(18) In Figure 2 only one aromatic ring of a triphenycarbinol is depicted in two extreme orientations with respect to the central C–OH axis. In the most parallel orientation an angle of 11° is calculated between the axis of the D-π-A unit and the central C–OH axis. In the most antiparallel orientation this angle is 109°. Assuming fast rotation of the aromatic rings, the projection of the dipole moment of the D-π-A unit in the direction of the central axis is given by a vectorial addition of the two extreme orientations. Since three D-π-A units are present in the molecule, the averaged dipole moment has to be multiplied by a factor of 3. The calculated average dipole moment in the direction of the C–OH axis is given by 3(cos 11° + cos 109°) = 1.9.

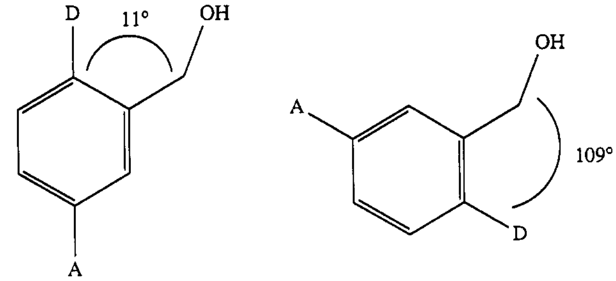

Figure 2. One aromatic ring of a triphenylcarbinol in two extreme orientations.

can increase or decrease the hyperpolarizabilities of the molecule.[8] Since the three aromatic rings are free to rotate, the internal distances and orientations are not known. Therefore, the influence of the orientation dependent mixing of the π-systems on the β values of the triphenylcarbinol derivatives cannot be predicted. The $\langle\beta_z\rangle$ and $\langle\beta\rangle_{\mathrm{HRS}}$ values of the reference compounds **13–16** are almost the same. The $\langle\beta\rangle_{\mathrm{HRS}}$ values of the triphenylcarbinol derivatives **7** and **10–12**, however, are about a factor 1.5–2 times larger than their $\langle\beta\rangle_z$ values. Differences in the $\langle\beta\rangle$ values obtained with the two techniques are not unexpected since the HRS technique measures all components of the β-tensor,[17] whereas the EFISH technique measures only the projection of the vectorial of the β-tensor on the overall dipole moment $(\langle\beta_z\rangle)$.[3,16] The projection value of the components of the β-tensor on the z axis is not significantly influenced by the static E-field applied in the EFISH experiment, since the orientation of the small dipoles induced by an E-field of only 20 kV·cm^{-1} in the EFISH measurement is very small. The influence of this relatively weak E-field on the intramolecular rotations and orientations is therefore negligible.

To interpret the measured $\langle\beta\rangle$ values correctly, it is important to know the averaged orientation of the three NLO-phores in solution. From variable-temperature ^{1}H NMR (400 MHz) experiments with **10** in CD_2Cl_2, it could be concluded that the three aromatic systems in this triphenylcarbinol derivative are magnetically equivalent at room temperature, indicating that the rotations around the α-bond are fast on the NMR (chemical shift) time scale. In the ^{1}H NMR spectrum of **10** the signals become broadened at −60 °C, indicating hindered rotation of the phenyl rings. At −90 °C the ring substituents (CH_3, OCH_3, and CHO) manifest themselves as spin systems each consisting of two singlets with an intensity ratio of 2:1. NOESY[19] experiments revealed that **10** freezes out in a conformation in which one ring is in an alternate position with respect to the other two rings.[20] From full line-shape analysis of the methyl region of the variable ^{1}H NMR spectra an activation energy of 9 ± 1 kcal·mol^{-1} for the rotation of one ring was calculated. From extrapolation of the ln(k) vs $1/T$ plot the rate of rotation at room temperature (298 K) could be determined: $k = (7 \pm 3) \times 10^5$ s^{-1}. This means that during the pulse time of 10 ns in the hyperpolarizability measurements the phenyl rings show no rotation. Therefore, the hyperpolarizabilities obtained are the averaged results of the different β values for the various conformational populations in the EFISH and HRS measurements, i.e., $\langle\beta\rangle$. The dipole moments of these populations are different from the averaged dipole moments $\langle\mu\rangle$ measured with a capacitance bridge over a period of 10 min which is given in Table 1. The $\langle\beta_z\rangle_{\mathrm{EFISH}}$ values in Table 1 were calculated with the averaged dipole moment. Since the dipole moment and the hyperpolarizability are coupled variables, the averaged product $\langle\mu\beta_z\rangle$ is different from $\langle\mu\rangle\langle\beta_z\rangle$ and the $\langle\beta_z\rangle_{\mathrm{EFISH}}$ should be treated with care.

The $\langle\beta\rangle_{\mathrm{HRS}}$ values are not dependent on the dipole moment. These values can be used to investigate the influence of the acceptor substituent on the hyperpolarizability of triphenylcarbinols. The $\langle\beta\rangle_{\mathrm{HRS}}$ values are related to the orientations of the three D-π-A systems and the influence of the mixing of the π-systems in these orientations. It was found that the relative increase of the β_{HRS} values of the triphenylcarbinol derivatives **7** and **10–12** compared with their reference compounds is very different for the different substituents. The $\langle\beta\rangle_{\mathrm{HRS}}$ value observed for triphenylcarbinol **7** is almost equal to that of the reference compound. This low $\langle\beta\rangle_{\mathrm{HRS}}$ value indicates a conformational population distribution in which the orientation and probably also the electronic interactions of the three NLO-phore units on the HRS time scale are unfavorable. The triphenylcarbinol derivatives **10** and **11** exhibit an almost 2-fold increase of their $\langle\beta\rangle_{\mathrm{HRS}}$ values compared with the reference compounds and for the tris(nitrostilbene) derivative **12** the $\langle\beta\rangle_{\mathrm{HRS}}$ value is more than 3 times larger than the value of the reference compound. This indicates a conformational population distribution of **12** in which the orientation of the three NLO-phore units is favorable to obtain a high $\langle\beta\rangle_{\mathrm{HRS}}$ value. To explain the $\langle\beta\rangle_{\mathrm{HRS}}$ value of **12**, which is more than 3 times as large as the $\langle\beta\rangle_{\mathrm{HRS}}$ value of its reference compound, probably favorable electronic interactions that increase the $\langle\beta\rangle$ value of the three NLO-phore units have to be considered.

It should be noted that the triphenylcarbinol derivatives have λ_{CT} values that are almost equal to those of the reference compounds but exhibit higher hyperpolarizabilities measured with the HRS technique. Therefore, we conclude that by combining three D-π-A units in one molecule, it is possible to increase the hyperpolarizability of a molecule without introducing an undesired bathochromic shift of the charge-transfer band.

Experimental Section

6-Bromo-2-methylphenol (**2**),[11] p-nitrobenzyl phosphonate and p-cyanobenzyl phosphonate[21] were synthesized according to the literature. 6-Bromo-1-methoxy-2-methylbenzene (**3**) was obtained by using a modified[12a,b] literature procedure.[12c] All solvents were freshly distilled prior to use and all reactions were carried out under an argon atmosphere. The petroleum ether (PE) used had a boiling point range of 40–60 °C.

Melting points were determined with a Reichert melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded with Bruker AC250, AM500, and Varian 400 spectrometers in $CDCl_3$ with Me_4Si as internal standard. Mass spectra were obtained using a Finnigan MAT 90 spectrometer and IR spectra using a Nicolet 5SXC FT-IR spectrophotometer. The UV/vis spectra were recorded on a Philips PU 8700 series UV/visible spectrophotometer. The presence of CH_2Cl_2, $CHCl_3$ or CH_3OH in the analytical samples was confirmed by ^{1}H NMR spectroscopy.

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(20) One of the aromatic protons of each ring shows, at −90 °C, the same spectral features as the aromatic substituents (two singlets with intensity ratio of 2:1). The other aromatic proton of each ring clearly shows the presence of three singlets. Though two of these resonances are strongly overlapping, this indicates that the frozen conformation does not possess perfect mirror-image symmetry.

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The EFISH[16a,b] and HRS[17] experiments were performed as previously described.

Methyl 2-Methoxy-3-methylbenzoate (5). To a suspension of 3-methylsalicylic acid (4, 50 g, 1.29 mol) in acetonitrile (850 mL) were added NaOH (33 g, 0.83 mol) and dimethyl sulfate (120 mL, 1.29 mol). After 48 h of vigorous stirring, the suspension was made slightly acidic by addition of a 1 M HCl solution. The product was taken up in diethyl ether (1 L), washed with saturated solutions of $NaHCO_3$ (3 × 250 mL), ammonia (2 × 200 mL), and NaCl (2 × 200 mL), dried over $MgSO_4$, and evaporated in vacuo. Column chromatography (SiO_2, PE:EtOAc 10:1) afforded 5 (50 g, 0.27 mol) as an oil. Yield 83%; bp 130–131 °C (17 mmHg); ^{1}H NMR δ 7.6–6.9 (m, 3 H, Ar H), 3.82 (s, 3 H, CO_2CH_3), 3.75 (s, 3 H, $ArOCH_3$), 2.23 (s, 3 H, $ArCH_3$); ^{13}C NMR δ 164.5 (s, ArC–O), 156.1 (s, CO_2), 132.8, 126.8, and 121.2 (d, Ar C), 130.4 and 122.3 (s, Ar C), 59.1 (q, CO_2CH_3), 49.8 (q, OCH_3), 13.7 (q, CH_3); IR (KBr) 1730 (C=O) cm^{-1}; mass spectrum, *m/e* 180.080 (M^+, calcd 180.079). Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.15; H, 6.43.

2-Methoxy-3-methyl-α,α-bis(2-methoxy-3-methylphenyl)-benzenemethanol (6). To a solution of 3 (52 g, 0.26 mol) in THF (500 mL) was added *t*-BuLi (95 mL of 1.5 M in pentane, 2.0 mol) at −78 °C and the mixture was stirred for 10 min. Subsequently 5 (23 g, 0.13 mol) was added slowly, and the reaction mixture was allowed to warm to room temperature overnight. Most of the THF was removed under reduced pressure and the mixture was acidified to neutral pH by addition of a 1 M HCl solution. The product was taken up in diethyl ether (500 mL), washed with saturated solutions of $NaHCO_3$ (3 × 200 mL) and NaCl (2 × 200 mL), dried over $MgSO_4$ and evaporated in vacuo to yield 6 (32 g, 0.083 mol) as a white powder. Yield 65%; mp 135–136 °C; ^{1}H NMR δ 7.1–6.9 (m, 9 H, Ar H), 5.90 (s, 1 H, OH), 3.22 (s, 9 H, $ArOCH_3$), 2.29 (s, 9 H, $ArCH_3$); ^{13}C NMR δ 157.2 (s, ArC–O), 139.4 and 131.4 (s, Ar C), 131.1, 127.8 and 122.9 (d, Ar C), 81.4 (s, COH), 60.0 (q, $ArOCH_3$), 17.0 (q, $ArCH_3$); IR (KBr) 3480 (OH) cm^{-1}; mass spectrum, *m/e* 392.197 (M^+, calcd 392.199). Anal. Calcd. for $C_{25}H_{28}O_4$: C, 76.50; H, 7.19. Found: C, 76.03; H, 7.05.

2-Methoxy-3-methyl-5-nitro-α,α-bis(2-methoxy-3-methyl-5-nitrophenyl)benzenemethanol (7). To copper(II) nitrate hexahydrate (18 g, 75 mmol) was added acetic anhydride (60 mL, 0.53 mol), and the mixture was stirred for 0.5 h at 35 °C to form the nitrating agent diacetyl orthonitric acid.[15] Carbinol 6 (1.00 g, 0.25 mmol) dissolved in acetic anhydride (10 mL) was added slowly to the solution. After this stirred for 10 min, water (100 mL) was added slowly to the mixture, and the precipitated product was filtered off, washed with water (2 × 25 mL), saturated $NaHCO_3$ (3 × 25 mL), and water (2 × 25 mL). The product was taken up in CH_2Cl_2 (25 mL) dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by column chromatography (SiO_2, PE/EtOAc 5:1) and recrystallized from MeOH to give pure 7 (0.12 g, 0.23 mmol). Yield 9%; mp 223–225 °C; ^{1}H NMR δ 8.13 (d, 3 H, *J* = 2.5 Hz, Ar H), 7.95 (d, 3 H, *J* = 2.7 Hz, Ar H), 5.72 (s, 1 H, OH), 3.40 (s, 9 H, $ArOCH_3$), 2.42 (s, 9H, $ArCH_3$); ^{13}C NMR δ 162.0 (s, ArC–O), 143.0 ($ArC–NO_2$), 138.2 and 133.2 (s, Ar C), 127.3 and 123.0 (d, Ar C), 80.1 (s, COH), 60.8 (q, $ArOCH_3$), 17.6 (q, $ArCH_3$); IR (KBr) 1522 and 1343 (NO_2) cm^{-1}; mass spectrum, *m/e* 527.156 (M^+, calcd 527.154); UV ($CHCl_3$) λ_{max} = 290 nm, ϵ = 25 × 10^3 $L{\cdot}mol^{-1}{\cdot}cm^{-1}$. Anal. Calcd for $C_{25}H_{25}N_3O_{10}{\cdot}0.66CH_3OH$: C, 56.17; H, 5.08; N, 7.66. Found: C, 55.78; H, 4.65; N, 7.78.

5-Bromo-2-methoxy-3-methyl-α,α-bis(5-bromo-2-methoxy-3-methylphenyl)benzenemethanol (8). To a solution of 6 (10.0 g, 0.025 mol) in DMF (600 mL) in a dark flask was added *N*-bromosuccinimide (18.6 g, 0.105 mol) in DMF (600 mL). After stirring for 5 days at 50 °C the DMF was removed under reduced pressure, and the product was taken up in diethyl ether (1 L), washed with saturated solutions of $NaHCO_3$ (3 × 500 mL) and NaCl (2 × 400 mL), dried over $MgSO_4$, and evaporated in vacuo. The solid product was washed with cold methanol (100 mL) to yield 8 (11.8 mol) as a white powder. Yield 75%; mp 112–115 °C; ^{1}H NMR δ 7.28 (s, 3 H, Ar H), 7.11 (s, 3 H, Ar H), 5.79 (s, 1 H, OH), 3.24 (s, 9 H, $ArOCH_3$), 2.27 (s, 9 H, $ArCH_3$); ^{13}C NMR δ 156.1 (s, ArC–O), 140.0 and 133.8 (s, Ar C), 134.2 and 130.4 (d, Ar C), 116.0 (s, ArC–Br), 80.2 (s, COH), 60.2 (q, $ArOCH_3$), 17.0 (q, $ArCH_3$); IR (KBr) 3490 (OH) cm^{-1}; mass spectrum, *m/e* 625.929 (M^+, calcd for $C_{25}H_{25}{}^{79}Br_3O_4$: 625.930). Anal. Calcd for $C_{25}H_{25}Br_3O_4$: C, 47.74; H, 3.98. Found: C, 47.76; H, 4.23.

5-Bromo-2-methoxy-3-methyl-α,α-bis(5-bromo-2-methoxy-3-methylphenyl)benzenemethanol Methyl Ether (9). To a suspension of NaH (1.0 g, 33 mmol) in THF (20 mL) was added a solution of 8 (3.0 g, 4.8 mmol) in THF (40 mL). After 30 min excess methyl iodide (6.0 mL) was added and the mixture was stirred for 16 h at 35 °C. The reaction was quenched by the addition of water (100 mL). The product was taken up in diethyl ether (100 mL), washed with water (2 × 150 mL), dried over $MgSO_4$ and evaporated in vacuo to give 9 (2.58 g, 4.0 mmol) as a white powder. Yield 84%; mp 197–202 °C; ^{1}H NMR δ 7.3–7.2 (m, 6 H, Ar H), 3.32 (s, 9 H, $ArOCH_3$), 2.99 (s, 3 H, $COCH_3$), 2.25 (s, 9 H, $ArCH_3$); ^{13}C NMR δ 156.6 (s, ArC–O), 135.7 and 133.6 (s, Ar C), 133.9 and 131.6 (d, Ar C), 115.1 (s, ArC–Br), 86.8 (s, $COCH_3$), 60.1 (q, $ArOCH_3$), 53.7 (q, OCH_3), 17.2 (q, $ArCH_3$); mass spectrum, *m/e* 643.212 (M^+, calcd for $C_{26}H_{27}{}^{79}Br_3O_4$: 643.215). Anal. Calcd for $C_{26}H_{27}Br_3O_4$: C, 48.50; H, 4.20. Found: C, 48.80; H, 4.24.

5-Formyl-2-methoxy-3-methyl-α,α-bis(5-formyl-2-methoxy-3-methylphenyl)benzenemethanol Methyl Ether (10). To a solution of 9 (1.0 g, 1.6 mmol) in THF (60 mL) was added *t*-BuLi (4.0 mL of 1.5 M in pentane, 6.0 mmol) at −78 °C and the mixture was stirred for 30 min at −50 °C. Subsequently the mixture was cooled to −78 °C, and DMF (1.5 mL, 19.4 mmol) was added, whereupon the reaction mixture was allowed to warm to room temperature. Most of the THF was removed under reduced pressure and the mixture was acidified to neutral pH by the addition of a 1 M HCl solution. The product was taken up in diethyl ether (40 mL), washed with saturated solutions of $NaHCO_3$ (3 × 50 mL) and NaCl (2 × 50 mL), dried over $MgSO_4$ and evaporated in vacuo to yield 9 (0.8 g, 0.96 mmol) as a white foam. Yield 60%; mp 184–187 °C (CH_2Cl_2/PE); ^{1}H NMR δ 9.88 (s, 3 H, CHO), 7.69 (s, 6 H, Ar H), 3.40 (s, 9 H, $ArOCH_3$), 3.06 (s, 3 H, $COCH_3$), 2.36 (s, 9 H, $ArCH_3$); ^{13}C NMR δ 191.6 (d, CHO), 162.9 (s, ArC–O), 134.5, 132.5, and 130.7 (s, Ar C), 133.1 and 131.1 (d, Ar C), 87.1 (s, $COCH_3$), 60.3 (q, $ArOCH_3$), 53.7 (q, OCH_3), 17.0 (q, $ArCH_3$); IR (KBr) 1692 (C=O) cm^{-1}; mass spectrum, *m/e* 490.197 (M^+, calcd 490.199); UV ($CHCl_3$) λ_{max} = 272 nm, ϵ = 34 × 10^3 $L{\cdot}mol^{-1}{\cdot}cm^{-1}$. Anal. Calcd for $C_{29}H_{30}O_7{\cdot}CH_2Cl_2$: C, 62.61; H, 5.60. Found: C, 62.90; H, 5.61.

5-[(*E*)-1-(4-Cyanophenyl)ethenyl]-2-methoxy-3-methyl-α,α-bis(5-[(*E*)-1-(4-cyanophenyl)ethenyl]-2-methoxy-3-methylphenyl)benzenemethanol Methyl Ether (11). *p*-Cyanobenzyl phosphonate (0.89 g, 3.50 mmol) was added slowly to a suspension of NaH (0.5 g, 16.7 mmol) in DMF (30 mL) and the reaction mixture was stirred for 7 min in a dark flask. Subsequently, a solution of aldehyde 10 (0.50 g, 1.02 mmol) in DMF (10 mL) was added dropwise in 5 min, and stirring was continued for 19 h. Ethyl acetate (75 mL) was added to the mixture, the organic layer was washed with a saturated aqueous solution of NH_4Cl (5 × 50 mL) and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by repeated recrystallization from CH_3CN/MeOH to give 11 (0.25 g, 0.32 mmol) as a white powder. Yield 32%; mp 145–147 °C; ^{1}H NMR δ 7.60 (d, 6 H, *J* = 8.3 Hz, Ar H), 7.52 (d, 6 H, *J* = 8.3 Hz, Ar H), 7.40 (d, 6 H, *J* = 2.5 Hz, Ar H), 7.15 (d, 3 H, *J* = 16.3 Hz, CH=CH), 6.91 (d, 3 H, *J* = 16.3 Hz, CH=CH), 3.33 (s, 9 H, $ArOCH_3$), 3.13 (s, 3 H, $COCH_3$), 2.32 (s, 9 H, $ArCH_3$); ^{13}C NMR δ 158.4 (s, ArC–O), 87.6 (s, $COCH_3$), 60.1 (q, $ArOCH_3$), 53.9 (q, OCH_3), 17.5 (q, $ArCH_3$); IR (KBr) 2225 (CN) cm^{-1}; mass spectrum, *m/e* 787.342 (M^+, calcd 787.341); UV ($CHCl_3$) λ_{max} = 340 nm, ϵ = 60 × 10^3 $L{\cdot}mol^{-1}{\cdot}cm^{-1}$. Anal. Calcd for $C_{53}H_{45}N_3O_4{\cdot}0.66CH_3OH$: C, 79.65; H, 5.94; N, 5.19. Found: C, 79.32; H, 5.73; N, 5.24.

2-Methoxy-3-methyl-5-[(*E*)-1-(4-nitrophenyl)ethenyl]-α,α-bis(2-methoxy-3-methyl-5-[(*E*)-1-(4-nitrophenyl)ethenyl]-phenylbenzenemethanol Methyl Ether (12). *p*-Nitrobenzyl phosphonate (2.21 g, 0.66 mmol) was added slowly to a suspension of NaH (0.5 g, 16.7 mmol) in DMF (75 mL), and the reaction mixture was stirred for 1 h. A solution of aldehyde 10 (0.66 g, 1.35 mmol) in DMF (10 mL) was added dropwise in 5 min, and subsequently the mixture was stirred for 3 h. Water (25 mL) was added to the mixture, and the precipitated product was filtered off and washed with water (3 × 25 mL). The residue was purified by column chromatography (SiO_2, $CHCl_3$) to yield 12 (0.19 g, 0.23 mmol) as a yellow powder. Yield 17%; mp 170–172 °C; ^{1}H NMR δ 8.18 (dd, 6 H, J = 8.8 and 2.5 Hz, Ar H), 7.58 (d, 6 H, J = 8.9 Hz, Ar H), 7.44 (d, 6 H, J = 2.9 Hz, Ar H), 7.22 (d, 3 H, J = 16.3 Hz, CH=CH), 6.98 (d, 3 H, J = 16.3 Hz, CH=CH), 3.37 (s, 9 H, ArOCH$_3$), 3.16 (s, 3 H, COCH$_3$), 2.38 (s, 9 H, ArCH$_3$); ^{13}C NMR δ 158.0 (s, ArC–O), 146.5 (s, ArC–NO$_2$), 87.6 (s, COCH$_3$), 60.2 (q, ArOCH$_3$), 53.9 (q, OCH$_3$), 17.5 (q, ArCH$_3$); IR (KBr) 1339 and 1513 (NO$_2$) cm^{-1}; FAB mass spectrum (NBA), *m/e* 847.4 (M$^+$, calcd 847.3); UV (CHCl$_3$) λ_{max} = 376 nm, ϵ = 60 × 10^3 L·mol^{-1}·cm^{-1}. Anal. Calcd for $C_{50}H_{45}N_3O_{10}\cdot 0.9CHCl_3$: C, 63.99; H, 4.84; N, 4.40. Found: C, 64.07; H, 4.85; N, 4.54.

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