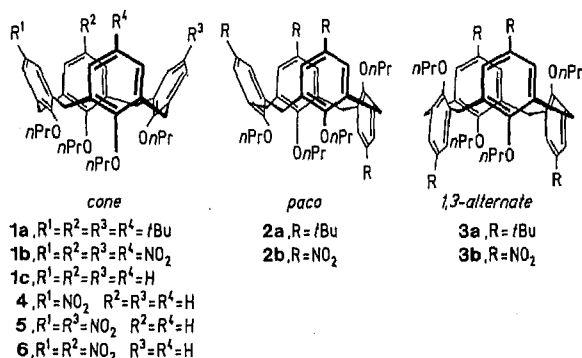


Nitrocalix[4]arenes as Molecules for Second-Order Nonlinear Optics**

By Erik Kelderman, Lode Derhaeg, Gerard J. T. Heesink, Willem Verboom, Johan F. J. Engbersen, Niek F. van Hulst, Andre Persoons, and David N. Reinhoudt*

Organic molecules with π electron systems and unsymmetric charge distributions are promising for use in nonlinear optics (NLO), for example for frequency-doubling of laser light and electro-optic switching.^[1-3] In the molecules investigated so far the "NLO-phore", that is the structural unit responsible for the nonlinear optical properties, consists of one single π electron system with one or more electron donors and/or acceptors (D- π -A molecules). Extension of the conjugated system increases the nonlinear hyperpolarizability β , but unfortunately this is accompanied by a shift of the charge-transfer absorption band (CT band) to longer wavelength, thereby restricting the applicability in frequency-doubling.^[1-5] Here we describe a novel class of compounds which combine more D- π -A systems resulting not only in an increased hyperpolarizability, and dipole moment, but also in a shift of the CT bands to shorter wavelengths.

Calix[4]arenes are cyclophanes that consist of four phenol moieties connected by methylene bridges.^[6] Functionalization of these phenols allows the combination of four D- π -A units within a single calix[4]arene molecule. These calix[4]arenes can be present in four idealized conformations^[6-9] with different relative orientations of the intramolecular NLO-phores (Scheme 1).



Scheme 1.

In the *cone* conformer (e.g. **1**) the four oxygen atoms of the phenol hydroxyl groups are all on the same side of the calix, whereas in the partial cone (*paco*) conformer (e.g. **2**) only

three are. The *1,2-* and *1,3-alternate* conformers (e.g. **3**) have idealized point and radial symmetry, respectively. The different conformers are not interconvertible^[7b] when the hydroxyl groups are alkylated by groups larger than 2-hydroxyethyl.^[10] *n*-Propylation of *para-tert*-butylcalix[4]arene^[6] in *N,N*-dimethylformamide (DMF) at room temperature for 5 days with sodium hydride as a base afforded only **1a** in 93% yield. However, when the reaction was carried out in refluxing benzene with potassium *tert*-butoxide as a base, a 1:1 mixture of **2a** and **3a** in an overall yield of 70% was obtained. The *paco* (**2a**) and *1,3-alternate* conformers (**3a**) could be isolated by crystallization of the crude mixture from chloroform/methanol and chloroform/hexane, respectively. Subsequent *ipso* nitration^[11] of **1a**–**3a** afforded the desired tetranitrocalix[4]arenes **1b**–**3b** in 70% yield. The mononitro- **4**, 5,17-dinitro- **5**, and the 5,11-dinitrocalix[4]arene **6** were obtained by reaction of tetrapropoxycalix[4]arene^[12] **1c** with nitric acid in dichloromethane and subsequent separation of the mixture of nitrocalix[4]arene products by column chromatography.

To determine the influence of the different orientations of the D- π -A dipoles in the tetranitrocalix[4]arenes^[13] on the hyperpolarizability β we have studied the *cone*, *paco*, and the *1,3-alternate* conformers **1b**, **2b**, and **3b**, respectively, by electric field induced second harmonic generation (EFISH).^[14] The data obtained for **1b**–**3b** are summarized in Table 1.

Table 1. Hyperpolarizability in the direction of the field-induced z axis β_z , dipole moment μ , and the wavelength of the longest wavelength absorption for the nitrocalix[4]arenes **1b**–**6** and the reference compounds **7** and **8**.

	$\beta_z \times 10^{30}$ [esu]	μ [D]	λ_{\max} [nm]
1b	30	13.8	291
2b	27	6.7	291
3b	0	0	291
4	16	4.5	308
5	15	7.8	302
6	20	8.7	307
7	12	4.6	302
8	–	–	288

Compound **1b** has a β_z value of 30×10^{-30} esu, about 30% of the value of the reference compound 4-methoxy-4'-nitrostilbene (MONS),^[14a] which has a more extended π system. Moreover **1b** has a large dipole moment of 13.8 D. The *paco* conformer **2b** also has a comparably high β_z value, but its dipole moment is only 6.7 D. As expected, the centrosymmetric *1,3-alternate* conformer **3b** exhibits no frequency-doubling of 1064 nm laser light (Nd:YAG laser).

In order to examine whether the β_z values of the four individual D- π -A units are additive, we synthesized a series of *cone* nitrocalix[4]arenes besides **1b** with NO₂ groups in various numbers and positions (**4**, **5**, and **6**) and compared their β values and UV spectra with the reference compounds 4-nitroanisole (**7**) and 2,6-dimethyl-4-nitro-1-*n*-propoxybenzene (**8**).^[3, 15] The β_z value of the mononitrocalix[4]arene **4** is slightly greater than that of 4-nitroanisole (**7**). Surprisingly, 5,17-dinitrocalix[4]arene **5** has almost the same β_z value. The conformational flexibility of the four aromatic rings in the *cone* conformers and the intramolecular repulsion of the charged D- π -A systems might explain the relatively low β_z value of **5**. In addition, the local field factor $F(\omega)$, which describes the influence of the electrostatic field in the neigh-

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borhood of the NLO-phore on β [Eq. (a)], is expected to be lower for two cofacial D- π -A aromatic rings.^[1,2] In Equation (a), $\Delta\mu$ is the difference between the dipole moment in the ground and first excited state and f is the oscillator strength of the CT band. 5,11-Dinitrocalix[4]arene **6**, on the other hand, has a slightly higher β_z value than **5**. This may be due to a more parallel and noncofacial orientation of the D- π -A moieties in **6**. The larger dipole moment of 8.7 D, possibly due to reduced dipole-dipole repulsion in **6**, lends further support.

$$\beta_{CT} = \frac{3e^2\hbar^2 F(\omega) f \Delta\mu}{2m} \quad (\text{a})$$

From these results it can be concluded that the D- π -A moieties in the calix[4]arenes **1b** and **4–6** do not behave as completely independent NLO-phores. This is also in line with the UV spectra. The λ_{max} values of the nitrocalix[4]arenes **1b** and **4–6** show a remarkable trend when compared to the reference compound 2,6-dimethyl-4-nitro-1-*n*-propoxybenzene (**8**). The longest wavelength band of **4** ($\lambda_{max} = 308$ nm) is shifted bathochromically by 20 nm relative to that of **8** ($\lambda_{max} = 288$ nm). This difference must be due to interactions with the other aromatic rings of the calix[4]arene. Remarkably, with increasing numbers of nitro substituents, the λ_{max} values for the CT band of the nitrocalix[4]arenes in the cone conformation decrease slightly, whereas the μ values and the β_z values increase. A λ_{max} of shorter wavelength indicates a more restricted electron transfer from the ground state to the first excited state ($F(\omega)$). According to Equation (a), a lower $F(\omega)$ will cause the β_z value to decrease, and this effect may contribute to the nonlinear increase of β_z with an increase in the number of strong dipoles in a calix[4]arene molecule.

The large dipole moment of **1b** (13.8 D) in combination with the preorganized framework of the four NLO-phores can be used to orient **1b** in a polymeric methylmethacrylate (PMMA) matrix by corona-poling with a strong DC electrical field.^[16] For a film with 4.5 wt % of **1b** the degree of orientation^[17] $\cos^3\theta$ obtained was 0.28, whereas a similar film with 2 wt % of poled *N,N*-dimethylaminonitrostilbene (DANS) gave the much lower $\cos^3\theta$ value of 0.02 under identical conditions. In Equation (b), N is the density of molecules with nonlinear optical properties in the film, and F is the local field factor.^[18]

$$\langle \cos^3\theta \rangle = \frac{2d_{33}}{NF\beta_z} \quad (\text{b})$$

The NLO efficiencies d_{33} of poled films with 4.5 and 25 wt % of **1b** were initially 0.21 and 1.1 pmV⁻¹, respectively. Measurements over a period of two months showed a decrease of the d_{33} value to 60% of the initial value, that is to 0.13 and 0.65 pmV⁻¹, respectively. These values were attained in about one week and did not change thereafter. For comparison, the d_{33} of a film with 2 wt % of DANS had decreased to 30% of the initial value of 0.21 pmV⁻¹ after one week and was inactive after one month.^[19]

The high stability of the film of **1b** is probably a result of the bulkiness of the calix[4]arene skeleton, the restricted rotation of the individual D- π -A moieties, and the complexation of the methyl groups of the polymer backbone with this molecule.

In conclusion, this new class of NLO compounds possesses a unique combination of four nonconjugated D- π -A dipoles in one molecule. These compounds combine high β_z ,

and μ values with relatively low λ_{max} values. The low λ_{max} values make them suitable for frequency-doubling 820 nm emission from diode lasers to blue laser light at 410 nm.^[4, 5] The high μ value of the tetranitrocalix[4]arene **1b** enables a high degree of orientation upon poling in a polymeric matrix. Further functionalization leading to extended π electron systems with high β_z values and the synthesis of polymerizable calixarenes with high dipole moments are currently under investigation.

Experimental Procedure

All new compounds were fully characterized by ¹H and ¹³CNMR spectroscopy, mass spectroscopy, elemental analysis, UV-VIS and IR spectroscopy.

General procedure for *ipso* nitration of the *tert*-butylcalix[4]arenes **1a**, **2a**, and **3a**: To a solution of calix[4]arene **1a**, **2a**, and **3a** (3.00 mmol) in a mixture of CH₂Cl₂ (30 mL) and glacial acetic acid (30 mL) was added 100% HNO₃ (10 mL, ca. 240 mmol) at 0°C. The reaction mixture was stirred at room temperature until the black-purple color had discharged and subsequently poured into water (200 mL). The aqueous layer was extracted with CH₂Cl₂ (2 × 50 mL). The combined organic layers were washed with water (2 × 50 mL), dried over MgSO₄, and concentrated. Recrystallization of the crude reaction products from methanol gave analytically pure compounds.

¹HNMR spectroscopic data of **2b** and **3b** (conditions: 250 MHz, CDCl₃, 25°C, TMS): **2b**: $\delta = 8.23, 8.15$ (s, 4H; ArH), 7.89, 7.11 (d, 4H, $J = 2.7$ Hz; ArH), 4.1–3.3 (m, 16H; ArCH₂Ar and OCH₂), 2.2–1.8 (m, 8H; CH₂CH₃), 1.2–1.1 (m, 9H; CH₃), 0.62 (t, 3H, $J = 7.5$ Hz; CH₃). **3b**: $\delta = 7.96$ (s, 8H; ArH), 3.80 (t, 8H, $J = 7.3$ Hz; OCH₂), 3.74 (s, 8H; ArCH₂Ar), 2.0–1.9 (m, 8H; CH₂CH₃), 1.05 (t, 12H; CH₃).

Procedure for nitration of calix[4]arene **1c**: To a solution of **1c** (1 g, 1.7 mmol) in a mixture of CH₂Cl₂ (100 mL) and acetic acid (4 mL) was added 65% nitric acid (1 mL, 25 mmol, 15 equiv) whereupon the mixture was stirred for 0.5 h at room temperature. The reaction was stopped by the addition of water (100 mL), and the product mixture was extracted with CH₂Cl₂ (3 × 25 mL). The combined organic layers were washed with water (3 × 25 mL), saturated sodium bicarbonate solution (3 × 25 mL), and water (3 × 25 mL), dried over MgSO₄, and concentrated. The reaction mixture consisted mainly of mononitrocalix[4]arene **4** (30%) and traces of 5,17-dinitrocalix[4]arene **5** and 5,11-dinitrocalix[4]arene **6**. The same reaction with **1c** for 3 h afforded **5** and **6** in 30% and 10% yields, respectively. The products were separated by column chromatography SiO₂/CH₂Cl₂.

4: M.p. 192–193°C; ¹HNMR: $\delta = 7.25$ (s, 2H; ArH-NO₂), 7.0–6.8 (m, 6H; ArH), 6.22 (s, 3H; ArH), 4.47 and 3.20 (ABq, 4H, $J = 13.7$ Hz; ArCH₂Ar), 4.42 and 3.16 (ABq, 4H, $J = 13.5$ Hz; ArCH₂Ar), 4.0–3.7 (m, 8H; OCH₂), 2.0–1.8 (m, 8H; CH₂CH₃), 1.1–0.9 (m, 12H; CH₃); ¹³CNMR: $\delta = 161.2, 157.0, 155.6$ (s, ArC-O), 142.4 (s, ArC-NO₂), 76.8, 76.5, 76.4 (t, OCH₂), 30.9, 30.8 (t, ArCH₂Ar), 23.2, 22.9 (t, CH₂CH₃), 10.4, 10.3, 10.0 (q, CH₃).

5: M.p. 185–186°C; ¹HNMR: $\delta = 7.42$ (s, 4H; ArH), 6.74 (s, 6H; ArH), 4.47 and 3.25 (ABq, 8H, $J = 13.7$ Hz; ArCH₂Ar), 4.0–3.8 (m, 8H; OCH₂), 2.0–1.8 (m, 8H; CH₂CH₃), 1.2–0.9 (m, 12H; CH₃); ¹³CNMR: $\delta = 161.7, 156.1, 142.3, 136.1, 134.0$ (s, ArC), 128.7, 123.2, 122.9 (d, ArC), 77.1, 76.7 (t, OCH₂), 30.8 (t, ArCH₂Ar), 23.1, 22.9 (t, CH₂CH₃), 10.1, 10.0 (q, CH₃).

6: M.p. 151–152°C; ¹HNMR: $\delta = 7.5–7.4$ (m, 4H; ArH-NO₂), 6.6–6.5 (m, 6H; ArH), 4.6–4.4 and 3.3–3.1 (3 ABq, 8H, $J = 13.7$ Hz; ArCH₂Ar), 4.0–3.7 (m, 8H; OCH₂), 1.9–1.8 (m, 8H; CH₂CH₃), 1.0–0.9 (m, 12H; CH₃); ¹³CNMR: $\delta = 162.2, 156.4$ (s, ArC-O), 142.5 (s, ArC-NO₂), 31.1, 30.8 (t, ArCH₂Ar), 23.3, 23.2 (t, CH₂CH₃), 10.3, 10.2 (q, CH₃).

The EFISH measurements are described in ref. [14].

Poled films were prepared in a clean room facility with dust class 1000 and at 20°C and 5% humidity. A solution of **1b** (4.5 wt %)/PMMA ($M = 33000$) in chloroform was spun on pyrex glass yielding thin films with thicknesses in the range of 0.25–1 μ m. The film was orientated by corona-poling with a field of 8 kV at 110°C for 15 min and allowed to cool to room temperature while the high voltage was maintained. The SHG efficiency of the film was measured at 1064 nm against a sample of α -quartz as reference to determine the absolute d_{33} value.

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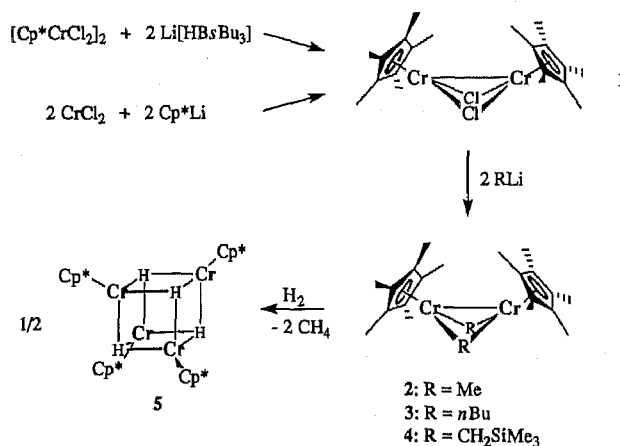
$\{[\text{Cp}^*\text{Cr}(\mu_3\text{-H})]_4\}$ —a Paramagnetic Chromium Hydride with a Cubane Structure**

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During the course of our exploration of paramagnetic organometallic complexes of chromium(III)^[1] many attempts at preparing hydride complexes have come to naught. However, we have now discovered a novel class of electron-deficient alkylchromium(II) compounds, which undergo efficient

hydrogenolysis to yield unusual paramagnetic chromium hydrides.^[2] Herein we report the synthesis, structural characterization, and some unusual magnetic properties of the latter.^[3]

Addition of two equivalents of $\text{Li}[\text{HBtBu}_3]$ to a solution of $[(\text{Cp}^*\text{CrCl}_2)_2]$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) in THF yielded the reduction product $[(\text{Cp}^*\text{Cr}^{\text{II}}(\mu\text{-Cl})_2)]$ (**1**) instead of the desired complex $[(\text{Cp}^*\text{Cr}^{\text{III}}(\text{H})\text{Cl})_2]$. Alerted to the stability of this rather simple starting material for organometallic compounds with divalent chromium,^[4] we found that **1** may also be prepared in reasonable yield (65%) directly from Cp^*Li and CrCl_2 (Scheme 1). The X-ray crystal structure determination revealed that **1** is a dinuclear complex with pseudo C_{2v} symmetry and a Cr–Cr distance of 2.642(2) Å. The effective magnetic moment (μ_{eff}) of this compound is temperature dependent and gradually rises to $2.0 \mu_B$ per dimer at room temperature, consistent with some degree of metal–metal bonding.



Scheme 1.

Complex **1** was easily alkylated and thereby yielded a series of extremely electron-deficient alkylchromium(II) complexes of the type $[(\text{Cp}^*\text{Cr}(\mu\text{-R})_2)]_2$ **2–4** (Scheme 1). The methyl complex **2** was structurally characterized by X-ray diffraction. As expected, the substitution of the 3-center/4-electron chloride bridges with the 3-center/2-electron methyl bridges causes a dramatic decrease in the Cr–Cr distance (2.263(3) Å).^[5] The greater strength of the metal–metal interaction is also evident in the magnetic behavior of **2**; μ_{eff} for the dinuclear complex only reaches $0.92 \mu_B$ at room temperature. Finally, the muted reactivity of the compound supports the presence of a strong metal–metal bond. Complex **2** is thermally stable up to 100°C in solution and does not react with ethylene under mild conditions; although **2** is eventually cleaved by bis(dimethylphosphino)ethane (dmpe) to produce the known $[(\text{Cp}^*\text{Cr}(\text{dmpe})\text{CH}_3)]_2$,^[1b] the reaction is very slow (several hours at room temperature). **2** is one of the few chromium(II) complexes thought to exhibit multiple Cr–Cr bonds despite the absence of binucleating ligands akin to carboxylates.^[6]

In our experience alkylchromium(III) complexes have largely resisted hydrogenolysis; in contrast **2** reacted slowly with H_2 at room temperature to generate methane and a black paramagnetic precipitate. Elemental analysis and IR spectroscopy of the solid indicated the presence of Cp^* ligands. Well-formed crystals of this material were eventually grown from hot toluene; however, only a rough crystal structure could be obtained due to disorder that likely resulted from an unresolvable superlattice.^[7] This problem was finally overcome when the EtMe_4C_5 ligand was used instead

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