Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Calix[4]arenes as molecules for second order nonlinear optics

Erik Kelderman[a]; Lode Derhaeg[b]; Willem Verboom[a]; Johan F. J. Engbersen[a]; Sybolt Harkema[c]; Andre Persoons[b]; David N. Reinhoudt[a]

[a] Laboratory of Organic Chemistry, University of Twente, Enschede, The Netherlands [b] Department of Chemistry, University of Leuven, Belgium [c] Laboratory of Chemical Physics, University of Twente, Enschede, The Netherlands

To cite this Article Kelderman, Erik , Derhaeg, Lode , Verboom, Willem , Engbersen, Johan F. J. , Harkema, Sybolt , Persoons, Andre and Reinhoudt, David N.(1993) 'Calix[4]arenes as molecules for second order nonlinear optics', Supramolecular Chemistry, 2: 2, 183 — 190

To link to this Article: DOI: 10.1080/10610279308038314

URL: http://dx.doi.org/10.1080/10610279308038314

SUPRAMOLECULAR CHEMISTRY, Vol. 2, pp. 183–190
Reprints available directly from the publisher
Photocopying permitted by license only

Calix[4]arenes as molecules for second order nonlinear optics

ERIK KELDERMAN, LODE DERHAEG[‡], WILLEM VERBOOM, JOHAN F. J. ENGBERSEN, SYBOLT HARKEMA[†], ANDRE PERSOONS[‡] and DAVID N. REINHOUDT*

Laboratory of Organic Chemistry, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands, [†]Laboratory of Chemical Physics, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands and [‡]Department of Chemistry, University of Leuven, Belgium

(Received July 30, 1992)

The synthesis of a novel class of molecules for second order nonlinear optics, i.e. calix[4]arenes with extended π-systems, is described. These compounds are obtained via Wittig-Horner reactions of the formylated calix[4]arenes 5 and 6 to give the stilbene derivatives 7–9, or by diazotization of calix[4]arene, 1, followed by alkylation to give the phenylazocalix[4]arenes 11 and 12. The molecular second order nonlinear optical properties (β_z) of these calix[4]arenes have been measured by electric field-induced second harmonic generation. The influence of different acceptors as well as the influence of the different conformations of the calix[4]arenes on β_z values were determined. Surprisingly, the wavelength of the charge-transfer band λ_{max} is lower when β_z increases upon increasing the number of acceptors.

INTRODUCTION

π-Conjugated organic molecules with both electron-donating and electron-accepting substituents are promising for use in nonlinear optics (NLO), e.g. frequency doubling of laser light and electro-optical switching.[1–3] In the molecules investigated so far the NLO-phore consists of one single π-conjugated system with one or more donors and/or acceptors (D-π-A molecules). Extension of the conjugated system increases the nonlinear hyperpolarizability (β), but this also shifts the charge transfer absorption band (CT band) to a longer wavelength, thereby restricting the applicability for frequency doubling.[1–5] Recently,[6] we have described a novel class of NLO-phores, i.e. calix[4]arenes, which combine up to four D-π-A moieties in one molecule. Calix[4]arenes are cyclophanes that consist of four phenol moieties connected by methylene bridges.[7] Most applications of calix[4]arenes so far are based on the complexing ability of neutral molecules and cationic species.[7] However, specific control of the conformation of the four phenolic moieties in the calix[4]arene also offers the possibility of organizing four dipole moments in space. Covalent coupling of NLO-phores to polymeric backbones[8] also offers this possibility but conformational control in the absence of an electrical field is virtually impossible. In functionalized calix[4]arenes the number and positions of the D-π-A units with respect to each other can be varied because calix[4]arenes can be made rigid in four different extreme conformations,[6,7,9] with different relative orientations of the individual NLO-phores. When all four phenolic oxygens are alkylated by groups that are larger than ethyl, the different conformations are no longer interconvertible.[9b]

Recently, we have reported the NLO properties of a series of functionalized nitrocalix[4]arenes (e.g. 3 and 4).[6] The β_z values were found to increase upon increasing the number of nitro groups in calix[4]arenes in the fixed 'cone' conformation. In contrast to the literature, this increase of the β_z values is not accompanied by a shift to higher wavelengths of the CT bands. In the highly ordered 'cone' conformer, four NLO-phores are already orientated in one direction. Upon poling of these compounds in thin films a higher degree of orientation than for single D-π-A systems is achieved.[6]

In this paper we report the synthesis of calix[4]arenes with more extended π-systems to achieve higher β_z values, as determined by electric field-induced second harmonic generation (EFISH).[10]

---

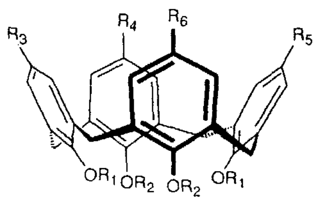
*To whom correspondence should be addressed.

RESULTS

Synthesis

Aldehydes **5** and **6** were synthesized via Gross formylation[11] of tetrapropoxycalix[4]arene **2**,*,† followed by condensation with the appropriate phosphonate via a Wittig-Horner reaction to yield the stilbenes **7**–**9**.

Chart 1.



1 $R_1=R_2=R_3=R_4=R_5=R_6=H$

2 $R_1=R_2=n\text{-Pr}\ R_3=R_4=R_5=R_6=H$

3 $R_1=R_2=n\text{-Pr}\ R_3=NO_2\ R_4=R_5=R_6=H$

4 $R_1=R_2=n\text{-Pr}\ R_3=R_4=R_5=R_6=NO_2$

5 $R_1=R_2=n\text{-Pr}\ R_3=CHO\ R_4=R_5=R_6=H$

6 $R_1=R_2=n\text{-Pr}\ R_3=R_4=R_5=R_6=CHO$

7 $R_1=R_2=n\text{-Pr}\ R_3=(E)C{=}CC_6H_4NO_2\ R_4=R_5=R_6=H$

8 $R_1=R_2=n\text{-Pr}\ R_3=R_4=R_5=R_6=(E)C{=}CC_6H_4NO_2$

9 $R_1=R_2=n\text{-Pr}\ R_3=R_4=R_5=R_6=(E)C{=}CC_6H_4CN$

10 $R_1=R_2=H\ R_3=R_4=R_5=R_6=(E)N{=}NC_6H_4NO_2$

11 $R_1=H\ R_2=n\text{-Pr}\ R_3=R_4=R_5=R_6=(E)N{=}NC_6H_4NO_2$

12 $R_1=R_2=n\text{-Pr}\ R_3=R_4=R_5=R_6=(E)N{=}NC_6H_4NO_2$ (*paco*)

Monoaldehyde **5** was synthesized in 30% yield by reaction of **2** with 5 equiv. of α,α-dichloromethyl methyl ether and 5 equiv. of $SnCl_4$ as the Lewis acid at −10°C for 5 min. The ^1H-NMR spectrum of **5** shows two AB systems for the methylene bridge atoms at δ 4.40, 4.35 and 3.13, 3.06 (J = 13.3 Hz), and one aldehyde signal at δ 9.46. Reaction of **2** with 10 equiv. of α,α-dichloromethyl methyl ether and 10 equiv. of $TiCl_4$ as the Lewis acid at room temperature for 3 h, gave the tetraaldehyde **6** in 71% yield. The ^1H-NMR spectrum of **6** shows only one AB system for the methylene bridge atoms at δ 4.51 and 3.36 (J = 13.8 Hz), and one aldehyde signal at δ 9.58.

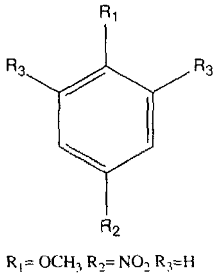
The mono(nitrostilbene) **7** and tetrakis(nitrostilbene) derivative **8** were obtained by reaction of the aldehydes **5** and **6** in DMF with deprotonated *p*-nitrobenzyl phosphonate in yields of 51% and 30%, respectively. The tetrakis(cyanostilbene) derivative **9** was obtained by a Wittig-Horner reaction of **6** with *p*-cyanobenzyl phosphonate in 15% yield. Characteristic for the *E*-isomers in the ^1H-NMR spectrum is the coupling constant of 16.3 Hz for the ethenyl protons at δ 7.0.

Instead of an ethenyl spacer between the two aromatic rings, an azo spacer can also be introduced in the π-conjugated system. Reaction of calix[4]arene **1** with *p*-nitrophenyldiazonium tetrafluoroborate yielded **10**,[12] but its insolubility in chloroform prevented the measurement of $\mu\beta$ values for compound **10** by EFISH. The solubility could be increased by alkylation of **10** with *n*-propyl iodide and NaH as a base in DMF at room temperature to give the syn-25,27-di-*n*-propylated derivative **11** (δ 8.89 OH) in 65% yield. Reaction of **10** at 80°C gave the tetra-*n*-propylated derivative **12** in 25% overall yield but as a mixture of conformers. The 'paco' conformer of **12** could be obtained as pure crystals in 15% yield after recrystallization from diethyl ether. The paco conformation of **12** clearly followed from the characteristic absorption for the methylene bridge carbon atoms[13] in the ^{13}C-NMR spectrum at δ 35.9 and 30.7.

Measurements

In order to examine whether the β_z values of the four individual D-π-A units are additive, we measured a series of cone nitrocalix[4]arenes (**3** and **4**),[6] formylated calix[4]arenes (**5** and **6**), *p*-nitrostilbenecalix[4]arenes (**7** and **8**), and *p*-cyanostilbenecalix[4]arenes (**9**) by EFISH, and compared their β_z values and absorption spectra with those of the reference[3,14] compounds **13**–**18**.

Chart 2.



13 $R_1=OCH_3\ R_2=NO_2\ R_3=H$

14 $R_1=OCH_3\ R_2=NO_2\ R_3=CH_3$

15 $R_1=OCH_3\ R_2=CHO\ R_3=H$

16 $R_1=OCH_3\ R_2=(E)C{=}CC_6H_4NO_2\ R_3=H$

17 $R_1=N(CH_3)_2\ R_2=(E)C{=}CC_6H_4NO_2\ R_3=H$

18 $R_1=OCH_3\ R_2=(E)C{=}CC_6H_4CN\ R_3=H$

19 $R_1=OH\ R_2=(E)N{=}NC_6H_4NO_2\ R_3=CH_3$

20 $R_1=OCH_3\ R_2=(E)N{=}NC_6H_4NO_2\ R_3=CH_3$

---

*The tetrapropoxycalix[4]arene **2** could be obtained exclusively in the cone conformation in 80% yield by reaction of calix[4]arene[7c] with 1-iodopropane in NaH/DMF at room temperature for 20 h. Using somewhat different reaction conditions, Shinkai *et al.*[9c] found a mixture of cone and partial cone conformations of which the latter is the major isomer. For a general study in which the possible factors are discussed that determine the ultimate conformation of tetra-*O*-alkylated calix[4]arenes, see ref 9(d). †From here forward the prefix 'tetrapropoxy' is omitted from the calix[4]arene to improve readability.

Table 1 Maximal absorption wavelengths (λ_{max}), dipole moments (μ) and hyperpolarizabilities (β_z) of the calix[4]arenes **3–12** and reference compounds **13–19**[a,b]

	λ_{max} (nm)	μ (D)	β_z(1064) ($\times 10^{-30}$ esu)	β_z(1910) ($\times 10^{-30}$ esu)
3	308	4.5	16	10
4 (cone)	291	13.8	30	21
4 (paco)	291	6.7	27	19
13	302	5.0 (4.6)[c]	12	8 (5.1)[c]
14[d]	288	–	–	–
5	278	4.2	18	13
6	269	10.7	19	14
15	269	3.2 (3.5)[e]	8	6 (2.2)[c]
7	386	5.2	113	52
8	370	15.3	280	142
16	377	4.5 (4.5)[c]	100	52 (28)[c]
17	424	(6.2)		(83)
9	345	13.1	100	57
18	340	5.4 (5.5)[c]	46	26 (9.3)[c]
11	356	13.0	161	88
12 (paco)	370	10.5	169	85
19	386	5.5	92	43
20	365	4.3	42	22

[a] In $CHCl_3$, μ and β_z values ±20%.
[b] Data in parentheses is from ref 3.
[c] In *p*-dioxane.
[d] Ref 14.
[e] Neat.

The hyperpolarizability β_z, the dipole moment μ, and the absorption maximum of the charge transfer band λ_{max} of **3–12** and the reference compounds **13–20** are summarized in Table 1.

The β_z values of the mono-acceptor functionalized calix[4]arenes **3** and **7** are comparable with those of the corresponding reference compounds **13** and **16**. Increasing the number of acceptors increases the β_z values but not entirely cumulatively. This may be partly due to the conformational flexibility of the four aromatic rings in the cone conformation of the D-π-A systems. In order to determine the relative orientations of the NLO-phores in the cone conformation, we have elucidated the crystal structure of the tetranitrocalix[4]arene derivative **4** (Fig 1).

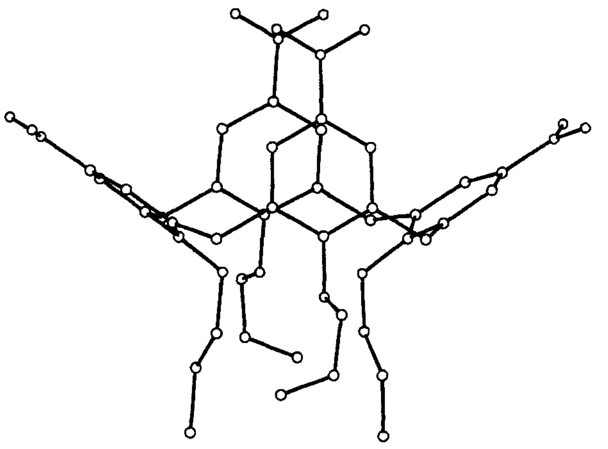


Figure 1 ORTEP drawing of compound **4** in the cone formation.

Based upon the crystal structure, the vectorial contribution of the four D-π-A units to β_z is expected to be about 3-times that of a mono-acceptor substituted calix[4]arene. The β_z value of 21.10^{-30} esu of the tetranitrocalix[4]arene **4** is, however, only twice the β_z value of 10.10^{-30} esu of the mononitrocalix[4]arene **3**. The β_z values of 13.10^{-30} and 14.10^{-30} esu of the monoaldehyde and tetraaldehyde calix[4]arenes **5** and **6** are, surprisingly, almost the same. The β_z value of **5** is, however, twice that of the β_z value of 6.10^{-30} esu of the reference compound **15**. The tetrakis(cyanostilbene)calix[4]arene derivative **9** exhibits a β_z value of 57.10^{-30} esu which is twice that of the β_z value of 26.10^{-30} esu of the reference compound **18**. The β_z value of 142.10^{-30} esu of the tetrakis(nitrostilbene) derivative **8** is, however, about 3-times larger than the β_z value of 52.10^{-30} esu of the mono(nitrostilbene) derivative **7** and the reference compound **16**. The β_z values of 88.10^{-30} and 85.10^{-30} esu of the corresponding cone tetrakis(nitrophenylazo) derivative **11** and the paco tetrakis(nitrophenylazo) derivative **12** are about twice as high as the β_z value of 43.10^{-30} esu of the reference compound **19**, but at least 3-times as high as the β_z value of 22.10^{-30} esu of the methylated reference compound **20**.

The λ_{max} value has shifted from 278 nm for the monoaldehyde **5** to 269 nm for the tetraaldehyde **6**. The tetranitrocalix[4]arene **4** has shifted hypsochromically by as much as 17 nm compared with the mononitrocalix[4]arene **3**. The λ_{max} value for the tetrakis(nitrostilbene) derivative **8** is 16 nm lower than that of the mono(nitrostilbene) derivative **7**.

DISCUSSION

If NLO-phores attached to polymers or in calix[4]-arenes are considered to be totally independent moieties, the vectorial addition of their β_z values should yield the overall β_z value. However, recently Marks *et al.*[15] found that the overall β_z value depends strongly upon the distance and relative orientation of NLO-phores. The increase of the β_z values, upon increasing the number of substituents in calix[4]arenes in the cone conformation, depends on the proximity of the D-π-A systems. The strong NLO-phores tetrakis(nitrostilbene) derivative **8** and the tetrakis(nitrophenylazo) derivatives **11** and **12** exhibit a 3-fold increase in their β_z values; however, the weaker NLO-phores **4** and **9** exhibit only a 2-fold increase, while a weak NLO-phore such as the tetraaldehyde **6** exhibits no cumulative increase in its β_z value. The interaction of the NLO-phores in calix[4]arenes is also reflected in the decrease in λ_{max} upon increasing the number of electron-withdrawing substituents.[15-17] Currently, theoretical calculations on the NLO properties of calix[4]arenes are in progress.

The β_z value of the tetrakis(nitrostilbene) derivative **8** of 142.10^{-30} esu at 1910 nm, is amongst the highest values reported so far and comparable with that of *N*,*N*-dimethylamino-4-nitrostilbene **17** (83.10^{-30} esu, $\lambda_{max} = 424$ nm).[3] The λ_{max} value of 370 nm for **8** compared with that of 424 nm for reference compound **17** renders the calix[4]arene much more transparent for frequency doubling to shorter wavelengths. The tetrakis(cyanostilbene) derivative **9** exhibits an even lower λ_{max} of 345 nm, and more importantly is totally transparent above 405 nm, which renders this compound very promising for generation of blue laser light at 410 nm.[4,5,*]

Comparison of the β_z values of the tetrakis(nitrostilbene) derivative **8** with the corresponding cone tetrakis(nitrophenylazo) derivative **11** clearly indicates that for closely interacting π systems in calix[4]arenes an ethenyl moiety is better than an azo moiety.

The cone nitro conformer of **4** has a slightly higher β_z value than the paco conformer of **4**. However, for the paco tetrakis(phenylazo) conformer of **12**, the β_z value is comparable to that of the cone tetrakis-(phenylazo) conformer **11**.

Since the cone conformers of **4** and **11** have larger dipole moments than the paco conformers of **4** and **12** the former compounds are more easily poled in polymers in a strong electric field, which is important for the material properties.[6]

CONCLUSIONS

The application of calix[4]arenes as NLO compounds is presented. This new class of NLO compounds possesses a unique combination of four non-conjugated D-π-A dipoles in one molecule. In the cone conformation four D-π-A NLO-phores are orientated in the same direction giving rise to a hypsochromic shift of the CT band and an increase of the β_z values. The D-π-A moieties in the calix[4]arenes do not behave totally independently. The functionalized calix[4]arenes are pre-eminently suited for the study of the mutual influence of D-π-A units by selectively varying their number and positions.

EXPERIMENTAL SECTION

Melting points are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ with Me_4Si as an internal standard. Positive ion fast atom bombardment (FAB) mass spectra were obtained with *m*-nitrobenzyl alcohol as the matrix. The calix[4]arenes* **1**,[7c] **2**,[12] **3**,[6] **4**,[18] and **10**[12] and reference compounds **19**[17] and **20**[17] were prepared according to literature procedures. CH_2Cl_2 was distilled from CaH_2 and stored over molecular sieves. Petroleum ether refers to the fraction with a b.p. of 40–60°C. Silica gel (particle size 0.040–0.063 mm, 230–240 mesh) was obtained from Merck (Darmstadt). All commercially available chemicals and reference compounds were obtained from Janssen (Geol). *p*-Nitrobenzyl phosphonate and *p*-cyanobenzyl phosphonate were synthesized according to literature procedures.[19]

---

* We also synthesized the 25,26,27,28-tetra-(*n*-propoxy)-5,11,17,23-tetrakis-[(*E*)-4-(sulphonmethylphenyl)vinyl]-calix[4]arene which exhibits a λ_{max} of 335 nm and is totally transparent above 295 nm, in at least 50% yield. However, very rapid *E–Z* isomerization at slightly elevated temperatures (refluxing diethyl ether) or on column chromatography (SiO_2 or Al_2O_3), inhibited purification of this compound.

* For reasons of simplicity and in order to reduce space taken up the Gutsche convention[25] is followed using 25,26,27,28-tetrahydroxycalix[4]arene instead of the official Chemical Abstracts name pentacyclo[$19.3.1.1^{3,7}.1^{9,13}.1^{15,19}$]octacosa-1(25),3,5,7,(28),-9,11,13(27),15,17,19(26),21,23-dodecaene-25,26,27,28-tetraol.[3,7,9,13,17]

In the workup procedures the organic layers were dried with $MgSO_4$ whereupon the solvent was removed under reduced pressure. The presence of CH_2Cl_2 in the analytical samples was confirmed by ^{1}H-NMR spectroscopy.

5-Formyl-25,26,27,28-tetra-(*n*-propoxy)calix[4]arene (5)

To a mixture of α,α-dichloromethyl methyl ether (1.7 ml, 15 mmol) and freshly distilled $SnCl_4$ (1.7 ml, 15 mmol) in CH_2Cl_2 (50 ml) was added a solution of calix[4]arene **2** (1.78 g, 3 mmol) in CH_2Cl_2 (30 ml) at -10°C and the reaction mixture was stirred for 5 min. The reaction was quenched by the addition of 2 M HCl (100 ml). The organic layer was washed with 2 M HCl (5×100 ml). After column chromatography (SiO_2/CH_2Cl_2), in addition to 25% of starting material **2**, pure **5** was obtained as an oil, which partly solidified upon standing for several weeks. Yield 30%; m.p. 177–178°C (CH_2Cl_2); ^{1}H-NMR δ 9.46 (s, 1 H, CHO), 6.90 (s, 2 H, ArH), 6.7–6.6 (m, 6 H, ArH), 6.4–6.3 (m, 3 H, ArH), 4.40, 4.35 and 3.13, 3.06 (2 AB q, 8 H, J = 13.3 Hz, $ArCH_2Ar$), 3.9–3.7 (m, 8 H, OCH_2), 1.9–1.7 (m, 8 H, OCH_2CH_2), 1.0–0.8 (m, 12 H, CH_3); ^{13}C-NMR δ 191.7 (d, CHO), 162.0, 156.9, 156.2 (s, ArC–O), 31.0 (t, $ArCH_2Ar$), 10.5, 10.2 (q, CH_3); mass spectrum (EI), *m/e* 620.349 (M^+, calcd. for $C_{41}H_{48}O_5$: 620.350). IR (KBr) 1694 (C=O) cm^{-1}. UV-visible ($CHCl_3$) λ_{max} 278 (ε 1.3×10^4), $f = 0.3$. Anal. calcd. for $C_{41}H_{48}O_5$: C, 79.32; H, 7.79. Found: C, 78.82; H, 7.72.

5,11,17,23-Tetraformyl-25,26,27,28-tetra-(*n*-propoxy)calix[4]arene (6)

To a mixture of α,α-dichloromethyl methyl ether (3.4 ml, 30 mmol) and freshly distilled $TiCl_4$ (3.3 ml, 30 mmol) in CH_2Cl_2 (50 ml) was added a solution of calix[4]arene **2** (1.78 g, 3 mmol) in CH_2Cl_2 (30 ml) at room temperature and the reaction mixture was stirred for 3 h. The reaction was quenched by the addition of 2 M HCl (100 ml). The organic layer was washed with 2 M HCl (5×100 ml). After recrystallization from ethanol pure **6** was obtained. Yield 71%; m.p. 275–278°C (ethanol); ^{1}H-NMR δ 9.58 (s, 4 H, CHO), 7.16 (s, 8 H, ArH), 4.51 and 3.36 (AB q, 8 H, J = 13.8 Hz, $ArCH_2Ar$), 3.94 (t, 8 H, J = 7.2 Hz, OCH_2), 1.91 (m, 8 H, OCH_2CH_2), 1.02 (t, 12 H, J = 7.2 Hz, CH_3); ^{13}C-NMR δ 191.3 (d, CHO), 161.9 (s, ArC–O), 135.6 (s, ArC–CH_2), 131.4 (s, ArC–CHO), 130.2 (d, ArC–H), 77.2 (t, OCH_2), 30.9 (t, $ArCH_2Ar$), 23.3 (t, OCH_2CH_2), 10.2 (q, CH_3); mass spectrum (EI), *m/e* 704.338 (M^+, calcd. 704.335). IR (KBr) 1696 (C=O) cm^{-1}. UV-visible ($CHCl_3$) λ_{max} 270 (ε 3.2×10^4), $f = 1.0$. Anal. calcd. for $C_{44}H_{48}O_8$: C, 74.98; H, 6.86. Found: C, 74.92; H, 6.88.

General procedure for condensation of aldehydes 5 and 6 with *p*-nitrobenzyl phosphonate and formation of 7 and 8

A solution of *p*-nitrobenzyl phosphonate (0.33 g, 1.2 mmol or 1.31 g, 4.8 mmol) in DMF (5 ml) was added slowly to a suspension of excess NaH (0.2 g, 8 mmol) in DMF (20 ml) and the reaction mixture was stirred for 30 min. Subsequently a solution of **5** or **6** (1 mmol) in DMF (25 ml) was added to the mixture. After stirring for 18 h a saturated aqueous solution of NH_4Cl (50 ml) was added to the mixture. The mixture was extracted with EtOAc (3×50 ml), followed by washing of the combined organic layers with a saturated solution of NH_4Cl (5×50 ml). Column chromatography (SiO_2/CH_2Cl_2) afforded pure **7** and **8**.

5-[(*E*)-4-(Nitrophenyl)vinyl]-25,26,27,28-tetra-(*n*-propoxy)calix[4]arene (7)

Yield 51%; m.p. 115–116°C (CH_3OH); ^{1}H-NMR δ 8.15, 7.51 (d, 2 H, J = 8.7 Hz, ArH–NO_2), 6.97 (d, 1 H, J = 16.3 Hz, CH=), 6.8–6.4 (m, 12 H, ArH and CH=), 4.47, 4.44 and 3.17, 3.14 (2 AB q, 8 H, J = 13.8 Hz, $ArCH_2Ar$), 3.9–3.8 (m, 8 H, OCH_2), 2.0–1.9 (m, 8 H, OCH_2CH_2), 1.0–0.9 (m, 12 H, CH_3); ^{13}C-NMR δ 157.8, 156.7 and 156.5 (s, ArC–O), 77.2, 76.7 and 76.6 (t, OCH_2), 31.0 (t, $ArCH_2Ar$), 23.3 and 23.2 (t, OCH_2CH_2), 10.3 (q, CH_3); mass spectrum (EI), *m/e* 620.349 (M^+-C_7H_5NO, calcd. 620.350). IR (KBr) 1631 (C=C), 1384 (NO_2) cm^{-1}. UV-visible ($CHCl_3$) λ_{max} 386 (ε 2.2×10^4), $f = 0.7$. Anal. calcd. for $C_{48}H_{53}NO_6 \cdot 0.4CH_2Cl_2$: C, 75.12; H, 7.01; N, 1.81. Found: C, 75.10; H, 7.22; N, 1.69.

5,11,17,23-Tetrakis[(*E*)-4-(nitrophenyl)vinyl]-25,26,27,28-tetra-(*n*-propoxy)calix[4]arene (8)

Yield 30%; m.p. > 310°C decomposed (CH_2Cl_2/petroleum ether); ^{1}H-NMR δ 7.95, 7.36 (d, 8 H, J = 8.7 Hz, ArH–NO_2), 6.96 (d, 4 H, J = 16.3 Hz, CH=), 6.89 (s, 8 H, ArH), 6.75 (d, 4 H, J = 16.3 Hz, CH=), 4.51 and 3.25 (AB q, 8 H, J = 13.6 Hz, $ArCH_2Ar$), 3.92 (t, 8 H, J = 7.4 Hz, OCH_2), 1.95 (m, 8 H, OCH_2CH_2), 1.02 (t, 12 H, J = 7.4 Hz, CH_3); ^{13}C-NMR δ 157.8 (s, ArC–O), 77.2 (t, OCH_2), 31.2 (t, $ArCH_2Ar$), 23.3 (t, OCH_2CH_2), 10.3 (q, CH_3); FAB mass spectrum, *m/e* 1181.4 [$(M + H)^+$, calcd. 1181.4]. IR (KBr) 1631 (C=C), 1384 (NO_2) cm^{-1}. UV-visible ($CHCl_3$) λ_{max} 370 (ε 11.5×10^4), $f = 2.9$. Anal. calcd. for $C_{72}H_{68}N_4O_{12}$: C, 73.20; H, 5.80; N, 4.74. Found: C, 72.80; H, 5.87; N, 4.56.

5,11,17,23-Tetrakis[(*E*)-4-(cyanophenyl)vinyl]-25,26,27,28-tetra-(*n*-propoxy)calix[4]arene (9)

A solution of *p*-cyanobenzyl phosphonate (1.21 g, 4.8 mmol) in DMF (5 ml) was added slowly to a suspension of excess NaH (0.2 g, 8 mmol) in DMF (20 ml) and the reaction mixture was stirred for 3 min. Subsequently solid **6** (0.70 g, 1 mmol) was added to the mixture. After stirring for 18 h a saturated aqueous solution of NH_4Cl (50 ml) was added to the mixture, whereupon the product precipitated out. The product was filtered off, washed with a saturated solution of NH_4Cl (3 × 50 ml), and water (3 × 50 ml). After trituration with methanol, **9** was obtained as a white powder. Yield 15%; m.p. 195–196°C (CH_3OH); ^{1}H-NMR δ 7.40, 7.32 (d, 8 H, $J = 8.5$ Hz, ArH–CN), 6.90 (d, 4 H, $J = 16.2$ Hz, CH═), 6.87 (s, 8 H, ArH), 6.69 (d, 4 H, $J = 16.2$ Hz, CH═), 4.51 and 3.24 (AB q, 8 H, $J = 13.4$ Hz, $ArCH_2Ar$), 3.92 (t, 8 H, $J = 7.4$ Hz, OCH_2), 1.95 (m, 8 H, OCH_2CH_2), 1.03 (t, 12 H, $J = 7.4$ Hz, CH_3); ^{13}C-NMR δ 157.6 (s, ArC–O), 77.0 (t, OCH_2), 31.2 (t, $ArCH_2Ar$), 23.3 (t, OCH_2CH_2), 10.3 (q, CH_3); FAB mass spectrum, *m/e* 1101.9 $[(M + H)^+$, calcd. 1101.5]. IR (KBr) 2225 (CN) cm^{-1}. UV-visible ($CHCl_3$) λ_{max} 345 (ε 6.5 × 10^4), $f = 1.30$. Anal. calcd. for $C_{76}H_{68}N_4O_4$: C, 82.88; H, 6.22; N, 5.09. Found: C, 83.00; H, 6.28; N, 4.89.

5,11,17,23-Tetrakis[(*E*)-4-(nitrophenyl)azo]-25,27-di-(*n*-propoxy)calix[4]arene (11)

A solution of 5,11,17,23-tetrakis[4-(nitrophenyl)azo]-calix[4]arene **10**[12] (0.2 g, 0.2 mmol) in DMF (5 ml) was added slowly to a suspension of excess NaH (0.2 g, 8 mmol) in DMF (20 ml), which turned immediately blue. After stirring for 30 min, *n*-propyl iodide (0.5 ml, 5 mmol) was added to the mixture. After 30 h a saturated aqueous solution of NH_4Cl (50 ml) was added to the mixture. The product was extracted with EtOAc (3 × 50 ml), followed by washing of the combined organic layers with a saturated aqueous solution of NH_4Cl (5 × 50 ml). Column chromatography (SiO_2/CH_2Cl_2) gave pure **11**. Yield 65%; m.p. 212–214°C (diethyl ether); ^{1}H-NMR δ 8.89 (s, 2 H, OH), 8.37, 8.20, 7.98 and 7.78 (d, 2 H, $J = 9.0$ Hz, ArH–NO_2), 7.94, 7.64 (s, 8 H, ArH), 4.47 and 3.73 (AB q, 8 H, $J = 13.3$ Hz, $ArCH_2Ar$), 4.16 (t, 8 H, $J = 6.0$ Hz, OCH_2), 2.18 (m, 8 H, OCH_2CH_2), 1.41 (t, 12 H, $J = 7.4$ Hz, CH_3); ^{13}C-NMR δ 79.0 (t, OCH_2), 31.6 (t, $ArCH_2Ar$), 23.6 (t, OCH_2CH_2), 10.9 (q, CH_3); FAB mass spectrum, *m/e* 1105.4 $[(M + H)^+$, calcd. 1105.3]. IR (KBr) 1343 (NO_2), 3280 (OH) cm^{-1}. UV-visible ($CHCl_3$) λ_{max} 354 (ε 6.1 × 10^4). Anal. calcd. for $C_{58}H_{48}N_{12}O_{12}$: C, 63.04; H, 4.38; N, 15.21. Found: C, 62.81; H, 4.26; N, 14.89.

5,11,17,23-Tetrakis[(*E*)-4-(nitrophenyl)azo]-25,26,27,28-tetra-(*n*-propoxy)calix[4]arene (12) (paco conformer)

A solution of **10**[12] (0.2 g, 0.2 mmol) in DMF (5 ml) was added slowly to a suspension of excess NaH (0.2 g, 8 mmol) in DMF (20 ml), which turned immediately blue. After stirring for 30 min, *n*-propyl iodide (1 ml, 1 mmol) was added whereupon the mixture was heated at 80°C. After 30 h, when the mixture had become dark-red, a saturated aqueous solution of NH_4Cl (50 ml) was added to the mixture. The product was extracted with EtOAc (3 × 50 ml), followed by washing of the combined organic layers with a saturated aqueous solution of NH_4Cl (5 × 50 ml). After column chromatography (SiO_2/CH_2Cl_2) a mixture of conformers of **12** was obtained in the ratio cone:paco: 1,3-alt = 10:77:13 in a total yield of 26%. The paco conformer of **12** could be obtained as pure red crystals by recrystallization from diethyl ether. Yield 15%; m.p. > 170°C decomposed (diethyl ether); ^{1}H-NMR δ 8.44, 7.91, 7.48 (d, 4 H, $J = 8.9$ Hz, ArH–NO_2), 8.10, 8.06 (d, 2 H, $J = 8.9$ Hz, ArH–NO_2), 8.04, 7.93 (s, 2 H, ArH), 7.61, 7.05 (d, 2 H, $J = 2.4$ Hz, ArH), 4.2–3.3 (m, 16 H, $ArCH_2Ar$ and OCH_2), 2.2–2.0 (m, 8 H, OCH_2CH_2), 1.3–1.2 (m, 12 H, CH_3); ^{13}C-NMR δ 36.0, 30.7 (t, $ArCH_2Ar$), 24.1, 23.8, 22.2 (t, OCH_2CH_2), 11.4, 11.0, 9.1 (q, CH_3); FAB mass spectrum, *m/e* 1189.1 $[(M + H)^+$, calcd. 1189.4]. IR (KBr) 1343 (NO_2) cm^{-1}. UV-visible ($CHCl_3$) λ_{max} 370 (ε 9.6 × 10^4). Anal. calcd. for $C_{64}H_{60}N_{12}O_{12}$: C, 64.64; H, 5.09; N, 14.13. Found: C, 64.92; H, 5.03; N, 14.00.

X-ray structure determination of 4

Crystal data. $C_{40}H_{44}N_4O_{12}\cdot CH_2Cl_2$, monoclinic, space group $C2/c$; $a = 14.827(4)$ Å, $b = 16.642(6)$ Å, $c = 17.475(6)$ Å, $\beta = 96.89(4)°$; $V = 4281$ Å^3; $Z = 4$; $d_{calc} = 1.33$ g cm^{-3}, $\mu = 2.13$ cm^{-1}. Reflections were measured in the $\omega/2\vartheta$ scan mode, using graphite monochromated Mo K_α radiation [scan width (ω) $(1.0 + 0.35 \tan \vartheta)°$, $3 < \vartheta < 25°$]. The structure was determined by direct methods[20] and refined with full-matrix least-squares methods. A total of 2263 reflections with $F_0^2 > 3\sigma(F_0^2)$ was used in the refinement. The asymmetric unit contained one half of a calix[4]-arene and dichloromethane molecule, the other halves being generated by a 2-fold rotation axis. The number of parameters refined was 332 (scale factor, extinction parameter, positional parameters of the heavy atoms and the H-atoms; owing to high thermal motion the H atoms of one of the propoxy groups were treated as riding atoms; thermal parameters refined anisotropically for the heavy atoms, isotropically for the

H atoms). The final R factors were $R = 5.8\%$, $R_w = 7.1\%$. All calculations were done with SDP.[21]

EFISH measurements

As a source of fundamental radiation a 1.064 μm, 10 Hz pulsed, Nd:YAG laser with seeder was used. The laser beam passes through a RG830 visible filter and is focussed into the EFISH cell. The harmonic light is filtered out with an IR cut-off filter and a 532 nm interference filter. The second harmonic light is detected with a photo-multiplier and analysed with a boxcar integrator and a computer. The EFISH cell consists of two BK7 windows which form a wedge with an angle of about 1 deg. The distance between the windows is 0.1–0.2 mm and the distance between the high voltage electrodes is 3 mm. This cell is mounted on a translation stage, so that it can be displaced perpendicularly to the laser beam. This enables the path length to be changed continuously. If the second harmonic intensity is measured as a function of the path length, a sinusoidal interference pattern is obtained. A quartz wedge which is used as a reference, is mounted on the same translation stage.

The analysis points were fitted to a sine squared function.[22] This fit provides the SHG amplitude and the coherence length. The third order susceptibility (Γ value) of the solution is calculated with the help of the data recorded for the quartz wedge.[23,24] For each compound five different solutions in the 0.1–1.0 mM concentration range were measured. From the value of Γ as a function of concentration, γ^{EFISH} can be deduced from equation 1.

$$\gamma^{\mathrm{EFISH}} = \gamma_e + \mu\,\beta/5\,k\,T \qquad (1)$$

The γ_e term is the electronic part of the second order hyperpolarizability and is usually negligibly small[1,23,24] compared with the second term and was therefore ignored in our calculations. With the knowledge of the dipole moment μ, the hyperpolarizability β_z of the molecules can be calculated. In the calculations of β_z, both vectors $\mu\,\beta$ and μ are assumed to be parallel.

Dipole moment measurements

The dipole moment of the calix[4]arene derivatives was obtained by measuring the dielectric constant of five different solutions in the 0.1–1.0 mM concentration range. The data were analysed according to the equation of Onsager.[23]

ACKNOWLEDGEMENT

This investigation was supported by the Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO). We wish to thank J. M. Visser, J. L. M. Vrielink, T. W. Stevens and A. M. Montanaro-Christenhusz of the Department of Chemical Analysis for recording the IR, UV-visible and mass spectra and performing the elemental analyses.

SUPPLEMENTARY MATERIAL AVAILABLE

Tables of positional and thermal parameters, bond distances and angles (7 pages) are available from the authors.

REFERENCES

1 Williams, D.J.; *Angew. Chem.* **1984**, *96*, 637.
2 Chemla, D.S.; Zyss, J. (Eds.): *Nonlinear Optical Properties of Organic Molecules and Crystals*, Academic Press, Orlando **1987**; vols 1 and 2.
3 Cheng, L.-T.; Tam, W.; Meredith, G.R.; Rikken, G.L.J.A.; Meijer, E.W.; *Proc. SPIE* **1989**, *1147*, 61.
4 Nijhuis, S.; Rikken, G.L.J.A.; Havinga, E.E.; ten Hoeve, W.; Meijer, E.W.; *J. Chem. Soc., Chem. Commun.* **1990**, 1093.
5 Staring, E.G.J.; Rikken, G.L.J.A.; Seppen, C.J.E.; Nijhuis, S.; Venhuizen, A.H.J.; *Adv. Mater.* **1991**, *3*, 401.
6 Kelderman, E.; Derhaeg, L.; Heesink, G.J.T.; Verboom, W.; Engbersen, J.F.J.; van Hulst, N.F.; Persoons, A.; Reinhoudt, D.N.; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1075.
7 (a) Gutsche, C.D.; in *Calixarenes; Monographs in Supramolecular Chemistry* (Stoddart, J.F., ed.), Royal Society of Chemistry, Cambridge, **1989**. (b) Vicens, J.; Böhmer, V., (Eds.); *Calixarenes. A Versatile Class of Macrocyclic Compounds.* Kluwer Academic, Dordrecht, **1991**. (c) Gutsche, C.D.; Lin, L.-G.; *Tetrahedron* **1986**, *42*, 1633.
8 Staring, E.G.J.; *Recl. Trav. Chim. Pays-Bas* **1991**, *110*, 492 and references therein.
9 (a) van Loon, J.-D.; Arduini, A.; Coppi, L.; Verboom, W.; Pochini, A.; Ungaro, R.; Harkema, S.; Reinhoudt, D.N.; *J. Org. Chem.* **1990**, *55*, 5639 and references therein. (b) Groenen, L.C.; van Loon, J.-D.; Verboom, W.; Harkema, S.; Casnati, A.; Ungaro, R.; Pochini, A.; Ugozzoli, F.; Reinhoudt, D.N.; *J. Am. Chem. Soc.* **1991**, *113*, 2385. (c) Iwamoto, K.; Araki, K.; Shinkai, S.; *J. Org. Chem.* **1991**, *56*, 4955. (d) Groenen, L.C.; Ruël, B.H.M.; Casnati, A.; Timmerman, P.; Verboom, W.; Harkema, S.; Pochini, A.; Ungaro, R.; Reinhoudt, D.N.; *Tetrahedron Lett.* **1991**, *32*, 2675.
10 (a) Derhaeg, L.; Samyn, C.; Persoons, A.; in *Organic Molecules for Nonlinear Optics and Photonics* (Messier, J., Kazjar, F. and Prasad, P., eds.), Kluwer Academic, The Netherlands, **1991**, p. 177. (b) Kelderman, E.; Verboom, W.; Engbersen, J.F.J.; Harkema, S.; Heesink, G.J.T.; Lehmusvaara, E.; van Hulst, N.F.; Reinhoudt, D.N.; Derhaeg, L.; Persoons, A.; *Chem. Mater.* **1992**, *4*, 626.
11 Arduini, A.; Manfredi, G.; Pochini, A.; Sicuri, A.R.; Ungaro, R.; *J. Chem. Soc., Chem. Commun.* **1991**, 936.
12 Shinkai, S.; Araki, K.; Shibata, J.; Tsugawa, D.; Manabe, O.; *J. Chem. Soc. Perkin Trans. 1* **1990**, 3333.
13 Jaime, C.; de Mendoza, J.; Prados, P.; Nieto, P.M.; Sánchez, C.; *J. Org. Chem.* **1991**, *56*, 3372.
14 Sadler Research Laboratories Division of Bio-Rad Laboratories, inc., *Standard Ultraviolet Spectra Collection*, Researchers, Editors & Publishers, Philadelphia P.A., USA, **1980**.

15 Di Bella, S.; Ratner, M.A.; Marks, T.J.; *J. Am. Chem. Soc.* **1992**, *114*, 5842.
16 Kasha, M.; Rawls, H.R.; Ashraf El-Bayoumi, M.; *Pure Appl. Chem.* **1965**, *11*, 371.
17 Tsuge, A.; Moriguchi, T.; Mataka, S.; Tashiro, M.; *Chem. Lett.* **1992**, 579.
18 Verboom, W.; Durie, A.; Egberink, R.J.M.; Asfari, Z.; Reinhoudt, D.N.; *J. Org. Chem.* **1992**, *57*, 1313.
19 Arbuzow, B.A.; *Pure Appl. Chem.* **1964**, *9*, 307.
20 Germain, G.; Main, P.; Woolfson, M.M.; *Acta Crystallogr.* **1971**, *A27*, 368.
21 B.A. Frenz and Associates Inc., Structure Determination Package, College Station, TX, and Enraf-Nonius, Delft, **1983**.
22 Teng, C.C.; Garito, A.F.; *Phys. Rev. B* **1983**, *28*, 6766.
23 Levine, B.F.; Bethea, C.G.; *J. Chem. Phys.* **1975**, *63*, 2666.
24 Huijts, R.A.; Hesselink, G.L.J.; *Chem. Phys. Lett.* **1989**, *156*, 209.
25 Gutsche, C.D.; Dhawan, B.; No, K.H.; Muthukrishnan, R.; *J. Am. Chem. Soc.* **1981**, *103*, 3782.