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Evaluation of Optical Nonlinearities in Calixarenes

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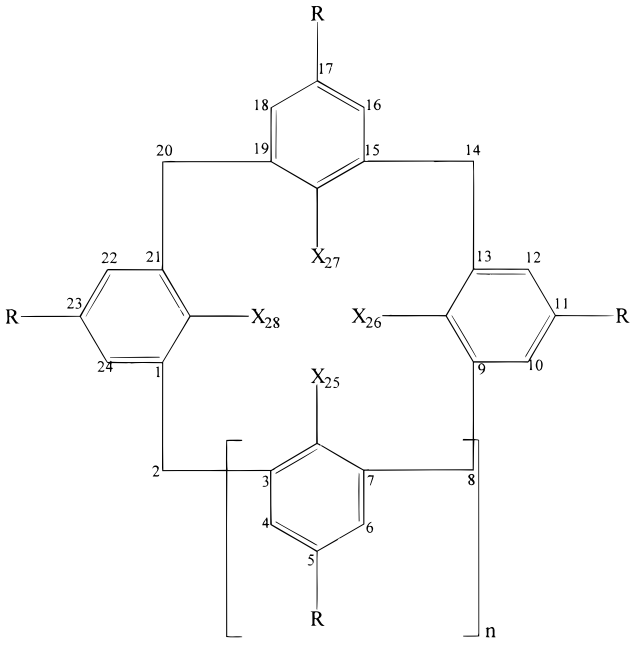
The structure and dipole moments of a series of donor acceptor calixarenes (**1**−**3**) containing from four to six aromatic rings have been calculated in their *cone* conformations using the AM1 method. The nonlinear optical properties of these systems have been evaluated in terms of their first hyperpolarizabilities using a semiempirical sum-over-states approach. All of the calixarenes studied are predicted to have large dipole moments, but their hyperpolarizabilities are critically dependent on the number of excited states included in the evaluation and on the orientation of the donor substituent. An increase in calixarene ring size has only a modest effect on the electronic properties. The limited space at the head of the calix(4)arene ring forces the substituents in both the methoxy (**1c**) and methylamino (**1e**) derivatives into unfavorable conformations, which substantially reduces the conjugation between their lone pair electrons and the π-electron system of the respective aromatic rings to give poor hyperpolarizabilities. When the lone pair electrons of the amino derivative are locked into an orthogonal position with respect to the aromatic ring plane by appropriate bridging alkyl groups, the resulting structure (**1f**) shows considerable potential as a nonlinear optical material for poled polymer films with an extremely large dipole moment of 24.4 D and a calculated hyperpolarizability of 49.9 $\times$ 10^{-30} cm^5 esu^{-1}.

Introduction

The calixarenes have attracted considerable attention because of their ability both to selectively bind a variety of metals cations and to function as clathrates and thus to accommodate and trap many organic guest molecules in an ordered fashion.[1−3] In the simplest cases of the *cone* conformers, the calix(4)arenes (**1**, $n = 1$) are constructed of four phenyl rings linked by methylene bridges with typically four alkyl groups such as the *tert*-butyl group at the 5, 11, 17, and 23-positions positioned at the bottom of the molecule with four hydroxyl groups at the 25, 26, 27, and 28-positions at the top of the macrocyclic ring[4] (see Scheme 1). In more complex systems, the hydroxyl groups have been replaced wholly or partly by an ester,[5,6] ether,[7,8] thiol,[9,10] amino,[11] or phosphate group.[12] Similarly, derivatives have been prepared where the alkyl groups at the 5, 11, 17, and 23-positions have been replaced by the sulfonato,[13,14] cyano,[7] bromo,[15] nitro,[8,16] and ethanethiol groups.[15] The size of the calixarene ring is variable, and examples of calix(5)arenes (**2**, $n = 2$),[17,18] calix(6)arenes (**3**, $n = 3$),[12,19−21] and calix(7)arenes (**4**, $n = 3$)[22,23] are known (Scheme 1).

The *cone* conformers are examples of donor−acceptor aromatics which are locked in a noncentrosymmetric arrangement. As a consequence, these molecules would be expected to have very large dipole moments and should possess, in principle, large molecular hyperpolarizabilities which could be utilized in the field of nonlinear optics for second harmonic generation (SHG) or electrooptic modulation (EOM)[24]. In the former, light from a semiconductor laser is converted from typically 830 to 415 nm for data recording, and it is essential that the molecule is transparent at the SHG wavelength to prevent reabsorption of the converted light.[24] However, in the latter there is no such restriction provided the absorption band is well removed from the transmission wavelength of typically 1350 nm.[24]

SCHEME 1: Generalized Structures for Calixarenes 1−4 with the Numbering System Superimposed for Calix(4)arene (1)[a]



[a] Key: a R = ^{t}Bu, X = OH; b R = NO$_2$, X = O^{n}Pr; c R = NO$_2$, X = OMe; d R = CMe$_2$CH$_2$CMe$_3$, X = OH; e R = NO$_2$, X = NHMe; f R = NO$_2$, X = −CH$_2$NCH$_2$−.

In applications involving poled polymer films, very large dipole moments are required to enable the molecule to be orientated by a strong electric field near the glass transition temperature so that the resulting noncentrosymmetric molecular alignment is retained on cooling. Although many conventional donor−acceptor systems, such as *N*-methyl-4-nitroaniline (**5a**), have a fairly large dipole moment, ranging from 6.66 D in benzene to 7.12 D in dioxan,[25] which would enable the molecule to be orientated in an electric field, more polar molecules with larger values, such as the donor−acceptor calixarenes, would be expected to show substantially enhanced behavior in the

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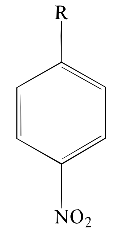
poling process provided they also possessed large molecular hyperpolarizabilities.



(**5**)
a R = NHMe
b R = OMe

One previous study has demonstrated the nonlinear potential of some calix(4)arenes such as the 5,11,17,23-tetranitro-25,26,27,28-tetrakis(*n*-propoxy) derivative (**1b**), which possesses both a substantial dipole moment and molecular hyperpolarizability and is transparent at SHG wavelengths.[26] Other more promising candidates with larger ring size and stronger donor groups have not been explored partly because of synthetic difficulties, and the present work has been carried out to assess the possible potential of these more complex systems as nonlinear materials for poled polymer films.

Methods of Calculation

Although there has been a considerable number of theoretical studies, and methods developed at various levels of theory, to calculate the nonlinear properties of polar organic systems in terms of their hyperpolarizabilities,[27−42] there have been no reported studies on the calixarenes partly because of their size, which would preclude the use of ab initio methods. In the present studies, the structures of a series of speculative donor-acceptor calixarenes were optimized using the standard version of the AM1[43] method of the MOPAC package[44] (keywords “prec ef xyz”). Their molecular hyperpolarizabilities were calculated using the CNDOVSB method,[30,31] which is based on an initial configuration interaction treatment of ground and excited state wave functions followed by a sum-over-states treatment of singly excited states to evaluate all 27 components of the hyperpolarizability tensor for the SHG effect. However, the most relevant quantity for these studies is the vector component of the hyperpolarizability defined as

$$\beta_x = \beta_{xxx} + (1/3)\sum_{i\neq x}(\beta_{xii} + 2\beta_{iix}) \tag{1}$$

where β_x is aligned along the direction of the dipole moment (x). The values obtained are directly related, therefore, to the nonlinear coefficients derived both from electric field induced second harmonic generation in solution and in poled polymer films where molecules are orientated along the direction of their dipole moments by a strong dc field.[24] The calculations were carried out with the same parameterisation adopted previously using between 50 and 300 excited states for the evaluation of the hyperpolarizability, both at zero frequency to give a static field value β_0, and at an applied field of 1.17 eV (1.06 microns) to give a frequency dependent value, $\beta_{1.17}$ as in earlier work.[30,31]

Results and Discussion

1. Structural Aspects. There are a considerable number of experimental structures present in the Cambridge Structural Database[45] that are closely related to the calixarenes discussed here. However, the most relevant template for the donor−acceptor calix(4)arenes described here is the 5,11,17,23-tetranitro-25,26,27,28-tetrakis(*n*-propoxy) derivative (**1b**).[8] In this structure, the nitro groups are essentially coplanar with the respective aromatic ring but the propoxy groups are arranged so that the first carbon on each chain is approximately perpendicular to the respective ring with two of the others twisted toward the center of the cavity. The ether oxygens at the 25 and 27-positions appear to be mainly sp^3 hybridized with a bond length of 1.381 Å to the aromatic ring and an angle to the first propyl carbon of 113°. Those at the 26 and 28-positions appear to be predominantly sp^2 hybridized with a bond length of 1.362 Å to the aromatic ring and an angle of 116° to the first propyl carbon. Because some of the hydrogen positions at the alkyl chains are clearly erroneous in this structure (**1b**),[8] they were removed and readded at the correct angles for subsequent calculations (see below).

TABLE 1: Calculated Transition Energies, Dipole Moments, and Hyperpolarizabilities of the Calixarenes (1−3), 4-Nitro-*N*-methylaniline (5a), and 4-Nitroanisole (5b)[a]

		CNDOVSB				AM1		
structure	N	λ	f	β_0	$\beta_{1.17}$	μ_g	ΔH_f	V
1b	50	312	0.36	26.0	38.8	17.0		623.6
	300	318	0.22	13.5	21.7			
1c[b]	50	306	0.27	27.0	39.9	18.3	−27.1	531.1
1c[c]	50	293	0.88	26.6	39.1	19.4	−26.5	531.2
	100	297	0.54	22.9	33.7			
	150	298	0.53	17.7	26.9			
	200	298	0.52	13.4	21.4			
	300	298	0.52	13.3	21.0			
1e	300	308	0.52	14.6	24.6	20.3	131.6	542.0
1f	300	330	1.02	25.9	49.9	24.4	271.3	560.6
2c	300	306	0.14	15.7	24.7	22.3	−39.1	662.1
3c	300	304	0.21	19.4	30.3	23.6	−47.2	793.6
5a[d]	50	340	0.55	9.82	19.8	7.86	25.1	130.1
5a[e]	50	333	0.53	8.72	17.0	7.54	25.0	
5b[d]	50	309	0.45	5.46	9.46	5.99	−13.6	126.8
5b[f]	50	291	0.37	2.86	4.74	5.17	−10.3	

[a] N is the number of configurations and excited states used in the calculation; λ and f are the transition energy (in nm) and oscillator strength respectively of the lowest energy excited state; β_0 and $\beta_{1.17}$ are the vector components of the hyperpolarizabilities in the direction of the dipole moment at zero field and 1.17 eV respectively defined in eq 1 (in units of 10^{-30} cm^5 esu^{-1}); μ_g and ΔH_f are the dipole moment (in D) and heat of formation (in kcal mol^{-1}); V is the molecular volume (in Å^3). [b] C_{2v} symmetry. [c] C_{4v} symmetry. [d] Planar sp^2 conformation for donor substituent. [e] Pyramidal sp^3 conformation for methylamino nitrogen. [f] Methoxyl carbon perpendicular to the ring plane.

In the related 4-nitroanisole (**5b**),[46] which can be considered a simplified component of the macrocycle, the conformation of the alkyl group is different to that found in the calixarene (**1b**). In this structure (**5b**), the methyl carbon lies almost in the plane of the aromatic ring with a bond length of 1.351 Å between the ether oxygen and the aryl carbon and an angle to the methyl carbon of 119° resulting in substantial overlap between the lone pair of electrons at the sp^2-hybridized ether oxygen and the delocalized π-electron system of the aromatic ring. However, the corresponding overlap between the sp^2 donor oxygens at the 26 and 28-positions and the aromatic ring is severely curtailed in calixarene (**1a**) because of the almost orthogonal position of the first carbon of the propyl groups, which twists the lone pair of electrons into unfavorable positions thus reducing the full donating power of the alkoxy group.

An initial calculation carried out on the modified crystal structure of calix(4)arene (**1b**) gave a molecular hyperpolarizability at 1.17eV of 38.8, which substantially overestimates the experimental value of 30 (given in units of 10^{-30} cm^5 esu^{-1} throughout)[26] (Table 1). However, the calculated transition energy of 312 nm is reasonably close to the experimental value of 291 nm[26] (Table 1), though the dipole moment is overestimated at this level of theory as a consequence of the parameterization required to reproduce the spectroscopic data[30]. An alternative single-point calculation at the AM1 level also overestimates the dipole moment to give a value of 17.0 versus 13.8 D experimentally[26] for reasons that are not entirely clear.

It is apparent that the size of the four *n*-propyl groups present in macrocycle (**1b**) distort the C_4 symmetry of the calix(4)arene ring and reduce the conjugation between the donor and acceptor groups. It is possible also that these groups will adopt different conformations in solution in the absence of crystal packing forces, and this may account for the disparity between the calculated and experimental dipole moments. This problem would be alleviated in the corresponding less sterically crowded methyl derivative (**1c**), which in principle should retain C_4 symmetry and show better conjugation between the two groups resulting in enhanced electronic properties. To explore this possibility , the *cone* conformer of this calix(4)arene was optimized at the AM1 level from the modified crystal structure of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetraoxycalix(4)arene oxomolybdenum[47] by (1) replacing the alkyl groups by nitro groups and (2) deleting the metal oxide and adding methyl groups to the retained oxygens at the 25,26,27,28-positions. The resulting structure retains C_4 symmetry with each methyl carbon perpendicular to the connected phenyl ring with a calculated dipole moment of 19.4 D (Table 1). A corresponding AM1 optimized structure derived from the *n*-propyl calix(4)arene (**1b**) is equally valid, but this shows C_2 symmetry with the molecular energy within 0.5 kcal mol^{-1} of the more symmetrical structure though the dipole moment is slightly smaller (Table 1).

Initial calculations were carried out on the more symmetrical structure (**1c**) for simplicity to give a similar hyperpolarizability at 1.17eV of 39.1 to the *n*-propyl derivative (**1b**), but the dipole moment is larger at 19.4 versus 17.0 respectively (Table 1). The calculated hyperpolarizability and dipole moment of this structure (**1c**) are between three and four times larger than those obtained for the AM1 optimized structure of 4-nitroanisole (**5b**), which is calculated to have values of 9.46 and 5.99 D respectively (Table 1), in line with the presence of four similar active units in the former. However, this comparison is not really valid because the calculated structure (**5b**) shows the methyl carbon to be essentially planar with the aromatic ring so that the lone pair of electrons at the sp^2 methoxyl oxygen atom is fully conjugated with the ring. A related calculation on an alternative AM1 optimized structure for 4-nitroanisole (**5b**) where the methyl carbon is constrained to lie in an orthogonal position relative to the ring plane (now similar to the conformation found in the calixarene) gives significantly different results with the molecule 3.3 kcal mol^{-1} less stable than the sp^2 conformer and the dipole moment significantly smaller at 5.17 D (Table 1). This structural change also reduces the transition energy from a value of 309 nm in the sp^2 conformer to 291 nm, which is now a similar value to that obtained for calixarene (**1c**) at 293 nm (Table 1). The enhanced transparency of the calixarenes compared with the closely related aromatics is clearly a consequence of the reduced conjugation between the donor oxygen and the connected aromatic ring. However, the hyperpolarizability of the twisted 4-nitroanisole (**5b**) is now approximately half the value of the planar conformer at 4.74 , and it follows that the value obtained for calixarene (**1c**) at 39.1 appears to be substantially enhanced relative to four of these simple aromatic units.

2. Effect of the Number of Excited States. The number of π-electrons in calixarene (**1c**) is substantially larger than that found in 4-nitroanisole (**5b**), and the number of excited states contributing to the hyperpolarizability would be expected to be larger, though the overall value would still be expected to be dominated by one major main charge transfer state for each donor acceptor moiety. However, an increase in the number of states used both in the CI treatment and for the evaluation of the hyperpolarizability from 50 to 100 results in a fall in the value from 39.1 to 33.7 at 1.17eV and from 26.6 to 22.9 at zero field. These values drop even further with an increasing number of excited states to give values of 26.9 and 17.7 at the same field strengths respectively using 150 states (Table 1). The reduction continues with an increasing number of excited states, but the value appears to stabilize at around 21 at 1.17eV using from 200 to 300 excited states (Table 1).

The final value of 21.0 obtained for calixarene (**1c**) at 1.17eV is around 10% larger than that anticipated from the twisted structure of 4-nitroanisole (**5b)** at 4.74, presumably because of the additional small contribution from the methylene bridges present. Overall, therefore, the hyperpolarizability of calixarene (**1c**) is predicted to be approximately twice the value obtained with the preferred conformation of 4-nitroanisole (**5b**), though its dipole moment is three times larger. A repeat calculation on the crystal structure of the tetrakis(*n*-propoxy) derivative (**1b**)[8] using 300 excited states shows the same trends as the tetramethoxy calixarene (**1c**) with the hyperpolarizability falling to 21.7 from the originally calculated value of 38.8 at 1.17eV (Table 1). The correlation with the experimental value of 30 is not particularly satisfactory, and one explanation for the discrepancy lies in the value of the dipole moment (μ), which is used to evaluate the experimental hyperpolarizability from the measured product $\mu\beta$.[26] If the calculated dipole moment of 17.0 D is used for this evaluation, instead of the experimental value of 13.8 D, the derived hyperpolarizability at 24.3 is much closer to the wholly theoretical value.

3. Effect of Ring Size. An expansion in the ring size to give the corresponding calix(5)arene (**2c**), which was constructed from the 5,11,17,23,29-pentakis(1,1,3,3-tetramethyl-n-butyl)-31,32,33,34,35-pentahydroxycalix(5)arene (**2d**)[18] by replacing the alkyl groups by nitro groups and converting the hydroxy groups into methoxy groups to give an AM1 optimized structure with a dipole moment of 22.3 D (Table 1). This cone-shaped molecule, with the methyl groups orthogonal to each aromatic ring, is flatter than calix(4)arene (**1c**), but the vector component of the hyperpolarizability of 24.7 at 1.17eV is only 10% or so larger than the latter (Table 1).

The corresponding calix(6)arene (**3c**) was constructed from the 5,11,17,23,29,35-hexa-*t*-butyl-37,38,39,40,41,42-hexahydroxycalix(6)arene (**3a**)[20] again by replacing the alkyl groups by nitro groups and converting the hydroxy groups into methoxy groups. Here there is considerably more conformational flexibility for the *cone* conformer than in previous cases, and the resulting AM1 optimized structure must be considered as one of several possible conformers. This molecule (**3c**) after optimisation has the methyl groups again orthogonal to each aromatic ring though each aromatic ring appears to be twisted relative to its neighbor. The dipole moment of 23.6 D (Table 1) is slightly larger than that of the other calixarenes, but the hyperpolarizability at 30.3 is approximately 50% larger than that of the corresponding calix(4)arene (**1c**).

The full additive power of the individual donor acceptor rings does not appear to be transmitted into the vector component of the hyperpolarizability, and calix(5)arene (**2c**) and calix(6)arene (**3c**) show little advantage over calixarene (**1c**) either in terms of the value at zero field or at 1.17eV or in terms of the dipole moment, which shows only a relatively small increase with an increasing number of aromatic rings, especially when the overall size of the macrocycle is considered. Thus the molecular volume increases from 531 Å^3 for calixarene (**1c**) to 662 Å^3 for calixarene (**2c**) and finally to 794 Å^3 for calixarene (**3c**), and the effective hyperpolarizability per unit volume is therefore greatest for the smallest calixarene (**1c**).

4. Effect of Other Donor Groups. The effect of donor groups other than the methoxyl group was explored for calix(4)arene (**1c**) in an attempt to maximize the π-electron interaction between the substituent and each attached aromatic ring. Although the dimethylamino group is one of the strongest electron donors, attempts to insert it into (**1c**) by replacing the methoxyl groups produced an almost orthogonal arrangement of the methyl groups relative to each aromatic ring with virtually no overlap between the lone pair of electrons at the donor nitrogen and delocalized π-electrons of the ring. However, the methylamino group can be accommodated in place of the methoxyl group, but the resulting AM1 optimized structure (**1e**) shows C_4 symmetry with each amino nitrogen hydrogen bonded by a distance of 2.21 Å to a hydrogen atom on a neighboring amino group. This arrangement results in an sp^3 conformation at the nitrogen atom with the methyl group almost perpendicular to each aromatic ring with the consequence that there is only a small overlap between the nitrogen lone pair of electrons and each aromatic ring. As a result, the dipole moment shows little enhancement over the methoxyl derivative (**1c**) at 20.3 D, and the hyperpolarizability is only marginally larger at 24.6 (Table 1).

Comparative calculations at the AM1 level on 4-nitro-*N*-methylaniline (**5a**), which is a simplified component of calixarene (**1e**), show little difference between the sp^2 and sp^3 conformers with the molecular energies separated by only 0.1 kcal mol^{-1} (Table 1). The hyperpolarizabilities of either of these conformers are comparable to calixarene (**1e**) and range from 17.0 to 19.8, but the dipole moments are substantially smaller and range from 7.54 to 7.86 D (Table 1). Because the loss of nonlinear activity in calixarene (**1e**) is due to the reduced overlap between the donor group and each aromatic ring, an alternative calixarene where the nitrogen lone pairs are now locked into an orthogonal position with respect to the aromatic ring plane by an appropriate bridging group would be expected to show enhanced nonlinear behavior. Accordingly, a derivative of this type was constructed from the tetramethylamino calixarene (**1e**) by removing the amino hydrogens and alkyl groups and then joining each nitrogen to its neighbor by a bridge of two carbon atoms.

The resulting calixarene (**1f**) retains C_4 symmetry after AM1 optimisation, and the calculated dipole moment at 24.4 is significantly larger than that of the simpler derivative (**1e**), which has a value of 20.3 D (Table 1). In this structure (**1f**), the dialkylamino groups are sp^3 hybridized with each of the first carbons inclined at a torsion angle of 21° to the aromatic ring plane. The cone of this calixarene (**1f**) is slightly flatter than the simpler derivative (**1e**) as shown by the relative distances of 4.27 and 4.28 Å between opposite nitrogens of the amino nitrogens at the top of the macrocycle and 9.64 and 9.25 Å respectively between opposite nitrogens of the nitro groups at the bottom. The calculated hyperpolarizability of this calixarene (**1f**) at 49.9 is approximately twice the value of the simpler derivative (**1e**) and three times the value of 4-nitro-*N*-methylaniline (**5a**). It follows therefore that it is possible to greatly enhance the optical nonlinear potential of calixarenes by a careful selection of bridging groups that are able to maximize the overlap between the substituent lone pair and the respective aromatic ring.

Conclusions

The size of the donor acceptor macrocycle appears to have little overall effect on the nonlinear potential along a given series, and the most effective structure is calix(4)arene (**1c**). Both the type and orientation of the donor groups attached to the calixarene have a considerable impact on their nonlinear properties. Structures where the lone pair of electrons at each donor substituent are orientated to maximize interactions with its respective aromatic ring, such as the alkylamino derivative (**1f**), possess large hyperpolarizabilities coupled with very large dipole moments, which makes them exciting nonlinear candidates for application as poled polymer films.

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