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A fluorescent bicyclic calix[4]arene–oxacyclophane with planar chirality: resolution, chiroptical properties, and absolute configuration



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ABSTRACT

A new inherently chiral calix[4]arene ICC 1 has been disclosed. The dissymmetry of 1 is generated from a chirality plane in the quinol moiety of a 1,3-bridged bicyclic calix[4]arene. ICC 1 has been resolved by enantioselective HPLC, and the chiroptical properties of both isolated antipodes (pS)-1 and (pR)-1 confirm their enantiomeric nature. The absolute configuration of the (pS)-1/(pR)-1 enantiomeric pair was established through time-dependent density functional theory (TDDFT) calculations of electronic circular dichroism (CD) spectra.

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1. Introduction

The first inherently chiral calix[4]arene (ICC), with an AABC (order of *p*-substituted phenolic units) substitution pattern at the calixarene upper rim, was synthesized by Gutsche over thirty years ago.¹ However, the term 'inherently chiral' was only coined later by Böhmer² to describe certain calixarenes that due to their nonplanar shape are able to produce chiral entities due to the absence of an inversion center or a symmetry plane. This concept of intrinsic chirality, that is not based on the attachment of homochiral moieties to a pre-existing calixarene scaffold, but generated solely from achiral synthons, was further elaborated upon and extended to other classes of molecules by Mandolini and Schiaffino³ and more recently by Szumna.⁴ Prominent research has steadily continued in this field.^{5,6} Among calix[*n*]arenes, calix[4]arenes are the most often used platforms for the synthesis of ICCs, due to their lower conformational mobility, as compared to the higher calixarene homologs (calix[5-8]arenes), usually presenting wellpreorganized bowl-shaped intramolecular cavities, which are particularly useful for host-guest chemistry. Interest in the synthesis of ICCs is directly related to their potential applications in chiral recognition processes (e.g. as enantioselective sensors, chiral stationary phases for column chromatography, NMR chiral shift reagents), chiral self-assembly, and enantioselective catalysis (as chiral ligands and organocatalysts). The major routes developed so far toward ICCs involve asymmetric substitution either at the upper or lower rims of a calixarene skeleton (resulting in AABC and ABCD arrangements of phenolic units), and single or multiple *meta*-substitution of phenolic arrays. Earlier examples² as well as the latest developments^{5,6} of these ICCs have been reviewed. Another interesting and much underdeveloped route to ICCs is derived from the planar chirality attained by some (conformationally rigid) lower rim symmetrically-bridged calixarenes.^{7,8} Indeed, and to the best of our knowledge, only one example exists that reports on the inherent chirality of a calix[4]arene containing 1,3-bridged macrocyclics (amides) with a C_2 symmetry.⁸

Exploring this approach to ICCs, we have designed a series of fluorescent chiral calix[4]arenes (e.g. **III** and **IV**, Fig. 1) having in common the asymmetric environment associated with the oxacyclophane ring. These new ditopic molecular receptors were primarily envisaged as potential enantioselective sensors due to their rigidified and well-preorganized structures, an essential prerequisite for successful molecular recognition.^{5,9} Their bicyclic nature offers different upper and lower rim-sized cavities and electronic environments, which may prove valuable in hosting structurally complementary guests, while the bis-aryleneethynylene segment provides, among other things, a highly sensitive tool for the luminescent evaluation of host-guest recognition events.

This goal has in part been accomplished with our recently synthesized calix[4]arene **1** (**III**, Ar = Ph; Fig. 1), which turned out to be a highly sensitive and selective chemosensor for isomeric nitroanilines.¹⁰ Calix[4]arene **1** is a deep-blue emitter ($\lambda_{max} \text{ em} = 410 \text{ nm}$),



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Figure 1. Selected molecular structures of potential ICCs having ditopic receptor sites.

that exhibits a high fluorescence quantum yield ($\Phi_{\rm F}$ = 0.64, in CHCl₃; $\lambda_{\rm exc}$ = 350 nm) and great photostability.¹⁰

2. Results and discussion

The inherent chirality of calix[4]arene **1** arises from the existence of a chirality plane in the quinol moiety of the oxacyclophane ring, since rotation about the *O*-phenyl-*O* axis is precluded. The plane of chirality (see Fig. 2, left) is defined by the atoms ABXY in the quinol, and Z at the benzylic carbon as the pilot atom. Application of the sequence-rule-preferred path¹¹ (Y \rightarrow X \rightarrow B from an observer positioned at Z) indicates a counterclockwise rotation resulting in a (*pS*)-configuration for that enantiomer.

ICC **1** may be obtained in three steps from the parent calix[4]arene.¹⁰ Full structural assignments based on NMR spectroscopy ($^{1}H/^{13}C$ NMR, $^{10}NOESY$, COSY, and HSQC) led us to deduce the most stable conformation of calix[4]arene **1** in solution. Calix[4]arene **1** exists in a distorted cone conformation, with the two distal substituted rings (B rings, 6.69 ppm, Fig. 1) pinched together and the unsubstituted phenolic rings (A rings) splayed outwards, as inferred from the stronger NOE cross-peaks between the equatorial bridged methylene protons (pair of doublets at 3.24 and

3.33 ppm, ArCH H_{eq} Ar) and the aryl protons of the A rings (7.05 ppm) (Fig. 3).

Although the desymmetrization of the calixarene framework should occur, in principle, upon the formation of the oxacyclophane macrocycle (diiodo derivative I, Fig. 1), a rigid conformation immobilized in C₂ symmetry is only attained after attachment of the phenyleneethynylene substituents (III, Fig. 1). This was deduced from the NMR signals of compound **1** attributed to ArCH₂Ar, which appear as two sets of pairs of doublets at 3.24 and 3.33 ppm (equatorial H), and 4.33 and 4.34 ppm (axial H), and the signals assigned to the geminal protons of the benzylene units, appearing as four doublets at 4.92, 5.06, 5.26, and 5.48 ppm.¹² In contrast, the corresponding signals in the diiodo derivative I show a doublet for each of the ArCH₂Ar protons and two singlets for the remaining benzylic protons due to the conformational lability of the oxacyclophane moiety, denoting an apparent C_{2v} symmetry on the NMR time-scale at 298 K. A Monte Carlo conformational search performed on (pS)-1 (Fig. 2) fully corroborates the foregoing stereochemical correlations.¹³ The lowest-energy conformer which resulted from calculations is the one that has a twisted arrangement of the phenyleneethynylene units (Fig. 4, left), differing by ca. 0.5 kcal mol^{-1} from the planarized structure (Fig. 4, right). It is known, however, that in solution phenyleneethynylene units are rotationally disordered because of the low barrier of rotation (below 1 kcal mol⁻¹) around the ethynylic bond.¹⁴ An exclusive planar packing has also been observed for oligomeric phenyleneethynylene models in the solid state.¹⁵

The inherent chirality of **1** was firstly evidenced by ¹H NMR in the presence of a chiral shift reagent. We found that upon the addition of (*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol [(*S*)-Pirkle's alcohol]¹⁶ to **1**, the signals of the bridged methylene (ArCH_{eq}H_{ax}Ar), benzylic ArCH_cH_dOAr, and phenylene ArH_e protons (Fig. 5) split into pairs of identical intensities. This is consistent with the formation of diastereomeric pairs, and thus a clear indication that **1** consists of a pair of enantiomers. Additional peak splitting was observed for the benzylene protons, although they partially overlapped with Pirkle reagent (~7.58–7.64 ppm; ArH_f) or CHCl₃ (~7.20–7.25 ppm; ArH_g). The strongest and clearest splittings involve protons of the oxacyclophane macrocycle, thus suggesting that the Pirkle's alcohol mainly interacts with the *exo* cavity of calix[4]arene **1**.

The resolution of racemic **1** was next attempted using a chiralpacked column. We found that both enantiomers of (\pm) -**1** could be separated [Fig. 6a] using a LiChroCart-(*R*,*R*)-Whelk01 (250 × 4 mm; mobile phase: hexane/propan-2-ol; 98:2 v/v).¹⁷ After repeated



Figure 2. Inherently chiral calix[4]arene 1.



Figure 3. Partial NOESY spectrum (CDCl₃, 400 MHz, 298 K) of (±)-calix[4]arene 1.



Figure 4. Best conformer of (*pS*)-**1** obtained from MMFF94 Monte Carlo analysis (twisted, left), and that after forced planarization of phenyleneethynylene units (right).

injections (20 μ L) of racemic **1** (1 mg/mL), two fractions could be recovered in ca. 50% yield. Reruns of the two isolated fractions [Fig. 6b and c] revealed an enantiomeric excess (ee) of 100% for the first eluted fraction (F₁) and 97% ee for the second (F₂). Further purification of the latter fraction under the same conditions furnished an enantiomerically pure sample.

The circular dichroism (CD) and absorption spectra of both fractions are shown in Figure 7.¹⁸ As expected, the CD spectra of F_1 and F_2 are mirror images of each other, thus confirming the enantiomeric nature of the two samples.

The absorption bands of both enantiomers of **1** may be assigned to three characteristic regions: below \sim 310 nm, corresponding to phenolic and benzylic rings of the calixarene moiety, between \sim 280 and 330 nm attributed to the quinol moiety, and that of the conjugated phenyleneethynylene units which develops at longer wavelengths (>325 nm), contributing also in the 260– 320 nm region. These assignments were deduced from the contribution of the 'individual' participating chromophores, as shown in Figure 8.

In the CD spectra, the first Cotton effect ($\lambda_{max} = 354$ nm) should result from the phenyleneethynylene chromophore transitions. F₁ shows a negative monosignate Cotton effect [(-)₃₅₄-1] while the reciprocal effect originates from F₂ [(+)₃₅₄-1].

When the enantiomer $(+)_{354}$ -1 was heated in CH₃CN up to 80 °C while monitoring its CD spectra, no thermal racemization was observed, denoting the conformational stability of ICC 1. The spectra (not shown) showed no change upon temperature variation, thus demonstrating they are substantially allied with (or behave as) a single conformation.

In order to reproduce the CD spectra of **1**, and thus assign the absolute configuration of the $(+)_{354}/(-)_{354}$ -**1** enantiomeric pair, we planned to employ a well established protocol¹⁹ consisting of time-dependent density functional theory (TDDFT) calculations²⁰ on DFT-optimized structures representing the whole conformational ensemble in solution. However, this protocol is complicated by several issues: (1) the molecular size; (2) the presence of several chromophores with many low-lying states; (3) the conformational



Figure 5. Partial ¹H NMR spectra (CDCl₃, 300 MHz, 298 K) of (a) calix[4]arene 1 (5 mM), and (b) calix[4]arene 1 after the addition of 10 equiv of (S)-Pirkle's alcohol.

freedom of the phenyleneethynylene unit. While the first two points merely impose long computational times, the last one renders the common spectroscopic averaging procedure questionable.²¹ Therefore, rather than trying to pursue a rigorous protocol, we decided to limit ourselves to a more pragmatic approach by selecting a few representative structures of 1, differing in the orientation of the terminal phenyl rings of the 1,4-bis-phenylethynylbenzene unit. First, starting from the MMFF geometries discussed above with an arbitrary (*pS*)-configuration, the *t*-butyl groups were replaced by methyl groups, and these simplified structures were optimized with DFT at B3LYP/6-31G(d) level. Apart from the two structures with two planar and two perpendicular phenyl rings (labeled as 0/0 and 90/90, respectively, in Figure 9), we generated a third structure with one planar and one perpendicular phenyl (0/90), and a fourth structure with both rings twisted by 45° (45/45). In this step, two possible different arrangements of the OH groups within the calix[4]arene rim were evidenced; for each arrangement of the phenyl rings, the two conformers had similar energies (and very similar calculated CD spectra).

TDDFT calculations were carried out on all structures (four phenyl-differing structures, Fig. 9, with two OH-related conformers each) at CAM-B3LYP/SV level in vacuo. Generally speaking, the phenyleneethynylene rotamerism affected both the transition frequencies and the spectroscopic profiles; however the four structures gave consistent spectra in the lowest-energy region. Figure 10 shows the CD spectra calculated (as average on the OH-conformers) on the 0/0, 0/90 and 45/45 structures. All of the spectra showed a negative couplet-like feature in the long-wavelength region (250–400 nm in the calculated spectra), followed by a positive band at shorter wavelengths (centered around 220– 230 nm). The major CD features observed for the $(-)_{354}$ -1 enantiomer are then consistently reproduced by the calculations, taking into account a systematic blue-shift. Thus, the two enantiomers of **1** may be assigned the following absolute configuration: (pS)- $(-)_{354}$ -**1** for the first eluted (F₁) and (pR)- $(+)_{354}$ -**1** for the second eluted (F₂), respectively.

The population and orbital analysis on the calculated structures allowed us to understand the origin of the couplet-like feature observed between 275 and 400 nm. At first sight, one would assign the two bands to the exciton coupling²² between the quinol and the phenyleneethynylene moieties. In fact, this latter chromophore has two π - π * transitions in this region (centered around 300 and 360 nm), which are both approximately long-axis polarized but whose transition dipoles are in fact slightly tilted from each other. Hence, they couple both and differently with the π - π * transitions of the quinol around 300 nm, resulting in two CD bands of opposite signs (vertical bars in Fig. 10), which are not a true exciton couplet.

3. Conclusion

An inherently chiral calix[4]arene **1** with planar chirality has been, for the first time, resolved into its enantiomers (pS)-**1** and (pR)-**1**, their chiroptical properties evaluated, and the corresponding absolute configurations determined by TDDFT calculations. The short and simple synthetic procedures toward these newly designed ICCs can be easily extended to other ditopic molecular receptors with different electronic and/or configurational layouts, thus paving the way for the consistent development of this new class of fluorescent chiral calix[4]arenes, which may find real potential as enantioselective sensors and catalysts. The progress of the field will be intimately linked to the successful disclosure of more practical resolution methods of these ICCs.



Figure 6. Chromatograms showing the enantioresolution of ICC **1** (a) and those of the corresponding isolated fractions F_1 (b) and F_2 (c). Separation parameters: column: LiChroCart-(*R*,*R*)-Whelk01 (250 × 4 mm); eluent: hexane/propan-2-ol; 98:2 v/v; flow rate: 1 mL/min; UV detection at 350 nm.

4. Experimental

4.1. General

¹H NMR and H-decoupled ¹³C NMR spectra were collected on Brüker AVANCE II⁺ spectrometers (300 and 400 MHz) and the reported chemical shifts (δ /ppm) are internally referenced to TMS; *J* values are given in Hz. The splitting parameters for ¹H NMR are denoted as follows: s (singlet), d (doublet), t (triplet), and m (multiplet). ¹H–¹H Correlation Spectroscopy (COSY), ¹³C–¹H Heteronuclear Single Quantum Correlation (HSQC), and Nuclear Overhauser Effect Spectroscopy (NOESY) NMR techniques were used for spectroscopic assignments. Circular Dichroism (CD) and UV–vis spectra were recorded on a JASCO J-815 CD spectrometer using



Figure 7. CD (bottom) and absorption (top) spectra of the enantiomers of calix[4]arene 1 (5.4×10^{-6} M in CH₃CN, 298 K). The region above 230 nm has been expanded in the CD spectra to facilitate the comparison with the calculations (see Fig. 10).

1-cm quartz cells. Chiral resolutions were performed on a Jasco Liquid Chromatography System equipped with a Jasco PU-2089 Plus Pump, a Jasco CO-2065 Plus Column Oven, and a Jasco UV-1575 UV-vis Detector, using a LiChroCart-(R,R)-Whelk01 (250 × 4 mm) column, and hexane/propan-2-ol as eluent at 298 K.

4.2. Materials

Calixarene derivatives **1–3** (see Fig. 8) were synthesized according to our reported methods,¹⁰ and are fully characterized by FT-IR, ¹H/¹³C NMR, and microanalysis. Calix[4]arene **4** was obtained following a literature procedure.²³ 2,5-Bis(phenylethynyl)benzene-1,4-diol **5** was prepared in 60% as a yellow solid from 2,5-diiodo-1,4-hydroquinone²⁴ and phenylacetylene (98%, Aldrich) via a Sonogashira cross-coupling reaction in toluene/triethylamine using dichlorobis(triphenylphosphine)palladium (II) (5% molar; 98%, Aldrich), copper(I) iodide (5% molar; 98%, Aldrich), and triphenylphosphine (5% molar; 98%, Merck; recrystallized from hexane), after stirring at 35 °C for 70 h. Triethylamine (99%, Riedel-de-Haën) was previously dried from CaH₂ and distilled under N₂ prior to use, and toluene was previously dried from Na, distilled under N₂, and stored over Na. (*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol (\geq 98%, Aldrich) was used as received.

5. Computational methods and analysis

Conformational analysis was carried out with the Monte Carlo method using a molecular mechanics model (MMFF94 force field), as implemented in Spartan'10.²⁵ The conformational analysis resulted in two families of structures: one with the 1,4-bis-phenylethynylbenzene unit with its long axis roughly perpendicular to the calix[4]arene axis, and one where the 1,4-bis-phenylethy-nylbenzene unit was substantially bent, that is, with one of its terminal phenyls pointing toward the calix[4]arene and in close contact with one of its A rings. This latter family was neglected based on NMR arguments.²⁶ MMFF-optimized structures were



Figure 8. Absorption spectra of compounds 1-5 (5.0×10^{-5} M in CHCl₃, 298 K).



Figure 9. DFT-optimized geometries [B3LYP/6-31G(d) in vacuo] for selected structures of the methyl-truncated analogue of (*pS*)-**1**. The notation '0/0', '0/90' etc. indicates the torsional angles of the 1,4-bis-phenylethynylbenzene unit. For each structure, a second conformation of the OH groups in the calix[4]arene rim was obtained (not shown).

re-optimized with DFT at B3LYP/6-31G(d) level, after substituting the *t*-butyl groups with methyl ones. DFT and TDDFT calculations were run with Gaussian'09.²⁸ The DFT optimizations found as



Figure 10. CD spectra calculated at CAM-B3LYP/SV//B3LYP/6-31G(d) level in vacuo on three representative structures of (*pS*)-1. Each spectrum is the Boltzmann average at 300 K of the very similar spectra calculated for two different rotamers (relative to OH groups). Gaussian band-shape with 0.3 eV exponential half-width. Vertical bars represent calculated rotational strengths for the lowest-energy conformer of the 0/0 structure (which is the global energy minimum).

lowest-energy structures those with planar 1,4-bis-phenylethynylbenzene unit (structure labeled 0/0 in Fig. 9). In order to generate the other representative structures (0/90, 90/90 and 45/45 in Fig. 9), the necessary dihedral angles were constrained to the appropriate values. TDDFT calculations were run on DFT-optimized structures with CAM-B3LYP functional and SV basis set;²⁹ for some selected structures, it was checked that the larger SVP basis set did not substantially affect the calculated spectra. Up to 90 excited states (roots) were included in the CAM-B3LYP/SV calculations. CD spectra were generated from dipole-length rotational strengths by applying a Gaussian band-shape with 0.3 eV exponential half-width, using the Specdis software.³⁰

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overestimation of attractive dispersion forces in vacuo by MMFF, and they were neglected based on NMR results (see Section 5).

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