Synthesis and Chiroptical Properties of Chiral Azoaromatic Dendrimers with a C_3-Symmetrical Core

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ABSTRACT New chiral azoaromatic dendrimeric systems have been synthesized starting from 1,3,5-benzenetricarbonyl trichloride as the core molecule. The simultaneous presence of the (*S*)-3-hydroxy pyrrolidinyl ring as the optically active moiety and the azobenzene donor-acceptor conjugated system as the photochromic group with permanent dipole moment, makes these systems potentially interesting as materials for advanced applications in nanotechnologies. All the compounds obtained have been characterized with particular attention to the effects induced by changing the electron-withdrawing group in the chromophoric moiety and to their optical activity. A strong nonlinear enhancement of chiroptical properties related to the number of chiral units linked to the symmetrical core is observed in these derivatives, which indicates the presence of conformationally chiral substructures. *Chirality 22:99–109, 2010.*

KEY WORDS: chiral dendrimers; chiral nanotechnology; chiroptical properties; photochromic materials; azobenzene; multifunctional materials

INTRODUCTION

Intense attention has currently arisen in investigations dealing with chiral nanotechnology[1,2] and the amplification of chirality of polymeric materials.[3–5]

In this context, chiral dendrimers,[6–10] supramolecular helical polymers,[5,11,12] and optically active low molecular weight compounds with C_3 symmetry have found increasing interest, because they are expected to be useful in chemical operations including asymmetric catalysis, chiral recognition, and resolution.[13,14] This field has been investigated by Moberg[15] and reviewed recently, with particular attention on C_3-symmetrical nanoarchitecture (supramolecular and macromolecular), by Gibson.[16]

It is well known that polymers containing azoaromatic moieties are of remarkable potential interest for several advanced technological applications, such as optical data storage,[17] nonlinear optical (NLO) switches,[18] holographic memories[19,20] and in general as materials exhibiting photoresponsive properties when irradiated with light of suitable frequency and intensity.[21–23]

Furthermore, the presence of a chiral group of one prevailing configuration interposed between the polymeric backbone and the *trans*-azoaromatic chromophore allows the polymers to display both the properties typical of dissymmetric systems (optical activity, exciton splitting of dichroic absorptions), as well as features typical of photochromic materials (photorefractivity, photoresponsiveness, NLO properties).[24,25]

In addition, we have recently observed[26,27] that it is possible to photomodulate the chiroptical properties of thin films of chiral photochromic polymers by irradiation with circularly polarized (CP) light of one single left (L) or right (R) rotation sense. This unexpected new phenomenon seems to open new possibilities for the use of azobenzene-containing materials as chiroptical switches, besides the usual applications in optics.

The need to seek new optical materials and devices has led in recent years to the study of photoresponsive dendritic macromolecular systems.[28–30] This class of compounds is very attractive because of their unique physical properties[31,32] related to their three-dimensional branched structure and globular symmetrical conformation. Furthermore, the incorporation of specific functional groups within their structural interior or their periphery, makes them available as potential advanced materials.[28,33]

Several studies are reported in the literature in this direction[28,34]; for instance, a dendritic polyisophthalate endcapped with 12 naphthyl groups[35] is promising as a device for optical storage of information and holographic recording, because of its compact shape and low molecular weight which provides low viscosity and good compatibility with monomers and corresponding polymers.

However, relatively few studies have been conducted on the preparation of photochromic chiral dendrimers and their structural–chiroptical properties. By selecting appropriate chiral elements of one single configuration and placing them in predefined positions, the influence of the three-dimensional disposition of these chiral elements on

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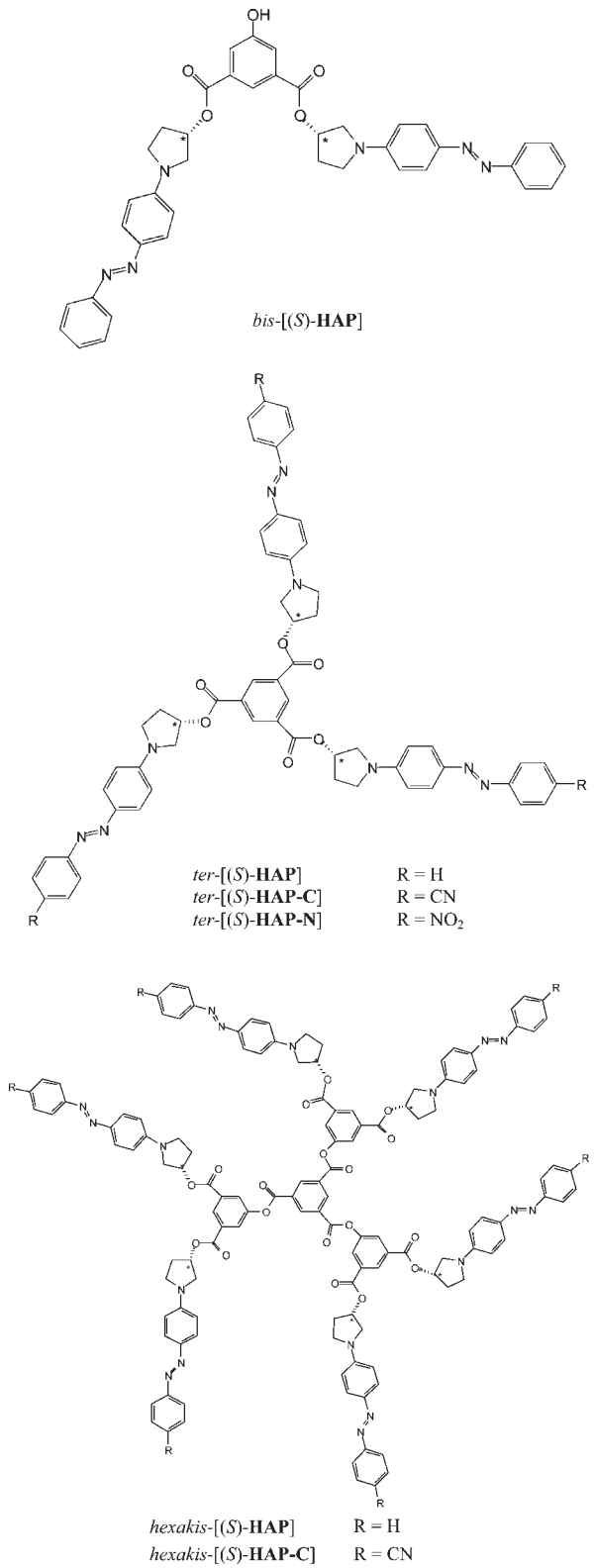


Fig. 1. Chemical structures of *bis*-[(*S*)-**HAP**], *ter*-[(*S*)-**HAP-R**] and *hexakis*-[(*S*)-**HAP-R**].

the chiroptical properties of photochromic optically active materials containing the *trans*-azoaromatic moiety can then be evaluated.

In this context, we have focused our attention on the synthesis of a couple of novel derivatives with a C_3-symmetric core functionalized with three and six optically active azoic alcohols (see Fig. 1). With the aim of investigating the interactions which can be established between chromophores, systems with different electron-withdrawing groups in 4′ position of the azoaromatic residue have also been prepared and studied.

All the derivatives obtained have been fully characterized and their spectroscopic properties compared with those of a model compound, *bis*-[(*S*)-**HAP**] (see Fig. 1), in order to better understand the structure–property relationships of these compounds, with particular attention to optical activity and chiroptical properties.

MATERIALS AND METHODS

General

^{1}H and ^{13}C NMR spectra were obtained at room temperature, on 5–10% $CDCl_3$ solutions, unless otherwise stated, using a Varian NMR Gemini 300 spectrometer. Chemical shifts are given in ppm from tetramethylsilane (TMS) as the internal reference. ^{1}H NMR spectra were run at 300 MHz by using the following experimental conditions: 24,000 data points, 4.5-kHz spectral width, 2.6-sec acquisition time, 128 transients. ^{13}C NMR spectra were recorded at 75.5 MHz, under full proton decoupling, by using the following experimental conditions: 24,000 data points, 20-kHz spectral width, 0.6-sec acquisition time, 64,000 transients. FTIR spectra were recorded with a Perkin-Elmer 1750 spectrophotometer, equipped with an Epson Endeavor II data station, on samples prepared as KBr pellets. Melting points (uncorrected) were determined in glass capillaries on a Büchi 510 apparatus with a heating rate of 1°C/min.

UV–Vis absorption spectra were recorded at 25°C in the 700–250 nm spectral region with a Perkin-Elmer Lambda 19 spectrophotometer on DMA solutions by using cell path lengths of 0.1 cm.

Concentrations in azobenzene chromophore of about $3 \cdot 10^{-4}$ mol L^{-1} were used.

Optical activity measurements were made at 25°C with DMA solutions with a Perkin Elmer 341 digital polarimeter, equipped with a Toshiba sodium bulb, using a cell path length of 1 dm. Specific and molar rotation values at the sodium D line are expressed as deg dm^{-1} g^{-1} cm^3 and deg dm^{-1} mol^{-1} dL, respectively.

Circular dichroism (CD) spectra were recorded at 25°C on DMA solutions on a Jasco 810 A dichrograph, using the same path lengths and solution concentrations as for the UV–Vis measurements. $\Delta\varepsilon$ values, expressed as L mol^{-1} cm^{-1} were calculated from the following expression: $\Delta\varepsilon = [\Theta]/3300$, where the molar ellipticity $[\Theta]$ in deg cm^2 $dmol^{-1}$ refers to one azobenzene chromophore.

Chemicals

The azoic alcohols (*S*)-(−)-3-hydroxy-1-(4-azobenzene) pyrrolidine [(*S*)-**HAP**], (*S*)-(−)-3-hydroxy-1-(4′-cyano-4-azo-

benzene) pyrrolidine [(*S*)-**HAP-C**] and (*S*)-(−)-3-hydroxy-1-(4′-nitro-4-azobenzene) pyrrolidine [(*S*)-**HAP-N**] were synthesized as previously reported.[36,37]

Chloroform, CH_2Cl_2, THF, toluene, and DMF were purified and dried according to the reported procedures[38] and stored under nitrogen. All other reagents and solvents (Aldrich) were used as received.

General Procedure for the Synthesis of Chiral Trimesic Acid Esters

Method A. A solution of 1,3,5-benzenetricarbonyl trichloride (1) (0.00075 mol) in dry CH_2Cl_2 (8 ml) was added dropwise, under nitrogen, to an ice-cooled solution of the opportune azoic alcohol (0.005 mol) in dry CH_2Cl_2 (30 ml), in the presence of triethylamine (TEA) (0.022 mol) and a catalytic amount of 4-dimethylamino pyridine (DMAP). The mixture was kept ice-cooled for 2 h, then left at room temperature for one night, filtered and washed with 0.1 M HCl, 5% Na_2CO_3 and finally with water. The organic layer was dried (Na_2SO_4) and the solvent evaporated under reduced pressure to give crude *ter*-[(*S*)-**HAP-R**].

Method B. A solution of the opportune azoic alcohol (0.0041 mol), 18-crown-6 ether (0.0037 mol) and DMAP (0.008 mol) in dry toluene (160 ml) was kept 2 h at reflux under nitrogen in a Dean-Stark trap. A solution of **1** (0.00124 mol) in dry toluene (8 ml) was then added dropwise and the solution kept at reflux over night. The reaction mixture was filtered and the crude product purified by column chromatography (SiO_2 70–230, CH_2Cl_2/Ethyl Acetate 4:1 v/v as eluent) followed by crystallization from $CHCl_3$.

Ter-{(*S*)-3-[1-(4-Azobenzene)-Pyrrolidine] Trimesate [*ter*-[(*S*)-HAP]]

Ter-[(*S*)-**HAP**] was purified by column chromatography (SiO_2 70–230, CH_2Cl_2/Ethyl Acetate 4:1 v/v as eluent) and subsequent crystallization from THF/Abs. Ethanol (M.p. 201–206°C).

Elemental analysis: found C 71.4%, H 5.4%, N 13.2%; calculated for $C_{57}H_{51}N_9O_6$ (958,1): C 71.46%, H 5.37%, N 13.16%.

Method A: Yield 25%

^{1}H NMR (DMF-d_7): 7.32 (s, 3H, core) 7.22-7.12 (m, 12H, arom *meta* to amino group and arom 2′-H), 6.88-6.70 (m, 9H, arom 3′- and 4′-H), 6.10 (dd, 6H, arom *ortho* to amino group), 5.08 (s, 3H, CH—O), 3.23-2.85 (m, 12H, 2- and 5-CH_2), 1.78 (m, 6H, 4-CH_2) ppm.

^{13}C NMR (DMF-d_7): 166.1 (C=O core), 152.1, 149.8, 144.5 (arom 4-, 1- e 1′-C), 135.9 (CH core), 133.5 (1-C core), 131.6 (arom 4′-C), 131.2 (arom 3′-C), 127.0 (arom 3-C), 124.0 (arom 2′-C), 114.0 (arom 2-C), 77.7 (*C*H—O), 55.6 (N—*C*H_2—CH), 47.9 (N—*C*H_2—CH_2), 32.9 (CH—*C*H_2—CH_2) ppm.

FTIR (KBr): 3065 (ν_{C-H} arom), 2850 and 2983 (ν_{C-H} aliph), 1720 ($\nu_{C=O}$), 1597 and 1515 ($\nu_{C=C}$ arom), 1385 and 1245 (ν_{C-O}), 819 (δ_{CH} 1,4-disubst. arom ring), 768 and 689 (δ_{CH} monosubst. arom ring), 742 (δ_{CH} 1,3,5 trisubst. arom ring) cm^{-1}.

Ter-{(*S*)-3-[1-(4′-cyano-4-azobenzene)-pyrrolidine]} trimesate [*ter*-[(*S*)-HAP-C]]

Ter-[(*S*)-**HAP-C**] was purified by column chromatography (SiO_2 70–230, CH_2Cl_2/Ethyl Acetate 4:1 v/v as eluent) and subsequent crystallization from $CHCl_3$ (M.p. 221–225°C).

Elemental analysis: found C 69.6%, H 4.7%, N 16.3%; calculated for $C_{60}H_{48}N_{12}O_6$ (1033.1): C 69.76%, H 4.68%, N 16.27%.

Method A: Yield 28%.

Method B: Yield 48%.

^{1}H NMR (DMF-d_7): 7.40-7.20 (m, 12H, arom *ortho* and *meta* to CN; 6H, arom *metha* to amino group; 3H, core), 6.05 (dd, 6H, arom *ortho* to amino group), 5.10 (s, 3H, CH—O), 3.20-2.90 (m, 12H, 2- and 5-CH_2), 1.80 (m, 6H, 4-CH_2) ppm.

^{13}C NMR (DMF-d_7): 164.7 (C=O core), 156.0, 151.6, 144.3 (arom 4-, 1- and 1′-C), 134.5 (1-C core), 134.2 (arom 3′-C), 132.2 (arom 4′-C), 126.5 (arom 3-C), 123.2 (arom 2′-C), 119.4 (CN), 112.7 (arom 2-C), 112.3 (CH core), 76.2 (*C*H-O), 54.2 (N—*C*H_2—CH), 46.7 (N—*C*H_2—CH_2), 31.5 (CH—*C*H_2—CH_2) ppm.

FTIR (KBr): 3063 (ν_{C-H} arom), 2854 (ν_{C-H} aliph), 2223 (ν_{CN}), 1720 ($\nu_{C=O}$), 1597 and 1517 ($\nu_{C=C}$ arom), 1381 and 1242 (ν_{C-O}), 846 and 821 (δ_{CH} 1,4-disubst. arom ring), 742 (δ_{CH} 1,3,5 trisubst. arom ring) cm^{-1}.

Ter-{(*S*)-3-[1-(4′-nitro-4-azobenzene)-pyrrolidine]} trimesate [*ter*-[(*S*)-HAP-N]].

Ter-[(*S*)-**HAP-N**] was crystallized from $CHCl_3$ (M.p. 232–236°C).

Elemental analysis: found C 62.5%, H 4.4%, N 17.4%; calculated for $C_{57}H_{48}N_{12}O_{12}$ (1093.1): C 62.63%, H 4.43%, N 15.38%.

Method B: Yield 38%

^{1}H NMR (nitrobenzene-d_6): 8.98 (s, 3H, core), 8.30 (dd, 6H, arom *ortho* to NO_2), 7.97 (dd, 6H, arom *meta* to amino group and arom 2′-H), 6.75 (dd, 4H, arom *ortho* to amino group), 5.90 (s, 3H, CH-O), 4.0-3.70 (m, 12H, 2′- e 5′-CH_2), 2.50 (m, 6H, 4′-CH_2) ppm.

^{13}C NMR (nitrobenzene-d_6): 165.0 (C=O core), 157.8 (arom 4′), 151.7, 148.2, 145.1 (arom 4-, 1- and 1′-C), 132.3 (1-C core), 127.0 (arom 3′-C), 125.2, 123.8 (arom 3-C and 2′-C), 112.7 (arom 2-C), 112.3 (CH core), 76.0 (*C*H—O), 54.1 (N—*C*H_2—CH), 46.8 (N—*C*H_2—CH_2), 31.9 (CH—*C*H_2—CH_2) ppm.

FTIR (KBr): 3093 (ν_{C-H} arom), 2919 and 2856 (ν_{C-H} aliph), 1723 ($\nu_{C=O}$), 1603 and 1515 ($\nu_{C=C}$ arom), 1381 and 1243 (ν_{C-O}), 1338 ($\nu_{N=O,s}$), 858 and 825 (δ_{CH} 1,4-disubst. arom ring), 743 (δ_{CH} 1,3,5 trisubst arom ring) cm^{-1}.

Synthesis of Chiral First Generation Dendrimers: ter-*(di-{(*S*)-3-[1-(4-azobenzene)pyrrolidine]}-isophthalate) Trimesate [*hexakis-*[(*S*)-HAP]] and* ter-*(di-{(*S*)-3-[1-(4′-cyano-4-azobenzene)pyrrolidine]}-isophthalate) Trimesate [*hexakis-*[(*S*)-HAP-C]]*

***Ter*-(dimethyl isophthalate) trimesate (3).** This product was prepared with a synthetic approach similar to that one previously reported by Shi and coworkers,[35] but with a different purification procedure. A solution of 1 (0.001 mol) in dry toluene (20 ml) was added dropwise,

under nitrogen to a mixture of 5-hydroxy dimethyl isophthalate (2) (0.03 mol) and TEA (catalytic amount). The stirred mixture was refluxed and monitored by FTIR until the signal at 1761 cm^{-1} related to the acyl chloride disappeared. The solvent was evaporated under reduced pressure and the crude product **3** purified by column chromatography (SiO_2 70–230, CH_2Cl_2/Ethyl acetate 15:1 as eluent) (Yield 66%).

^1H NMR ($CDCl_3$): 9.25 (s, 3H core), 8.65 (s, 3H arom isophthalate 2′-H), 8.20 (s, 6H arom isophthalate 4′ and 6′-H), 3.99 (s, 18H, CH_3) ppm.

FTIR (KBr): 3089 (ν_{C-H} arom), 2957 and 2846 (ν_{C-H} aliph), 1733 ($\nu_{C=O}$), 1592 ($\nu_{C=C}$ arom), 1461 (δ_{as} CH_3), 1433 (δ_s CH_3), 1329 and 1256 (ν_{C-O}), 758 (δ_{CH} isophthalate arom ring), 743 (δ_{CH} 1,3,5 trisubst. arom ring) cm^{-1}.

***Ter*-(5-hydroxyisophthalic acid) trimesate ester (4).** To a solution of **3** (0.00115 mol) in $CHCl_3$ (10 ml) 10 ml a aqueous solution of 40% KOH and methanol were added until the two layers were totally mixed. The solution was left under stirring for 1 h and the obtained white solid filtered and dissolved in water previously acidified with aq. HCl (pH = 1). The product was finally extracted with ethyl acetate, dried over Na_2SO_4 and the organic phase evaporated under reduced pressure to give a white material (yield 97%).

^1H NMR (DMSO-d_6): 10.20 (s, 6H, —OH), 8.73 (s, 3H, core), 7.99 (s, 3H, arom isophthalate 2′-H), 7.50 (s, 6H, arom isophthalate 4′ and 6′-H) ppm.

FTIR (KBr): 3420 (ν_{O-H}), 3087 (ν_{C-H} arom), 2960 and 2890 (ν_{C-H} aliph), 1702 ($\nu_{C=O}$), 1600 ($\nu_{C=C}$ arom), 1412 and 1278 (ν_{C-O}), 744 (δ_{CH} 1,3,5 trisubst. arom ring) cm^{-1}.

***Hexakis*-[(*S*)-HAP].** A solution of **4** (0.142 mmol) in 15 ml $SOCl_2$ (14.6 mmol) was refluxed for 3 h under nitrogen. Excess $SOCl_2$ was then removed under reduced pressure and the residue, dissolved in 5 ml of dry toluene, was added to a solution of (*S*)-**HAP** (0.0013 mol) in 50 ml of dry toluene in presence of 18-crown-6 ether (0.17 g) and **DMAP** (0.16 g). The reaction mixture was refluxed for 20 h under nitrogen and the solvent then evaporated. The remaining residue was dissolved in CH_2Cl_2, washed with 0.1 M HCl, 5% Na_2CO_3 and finally with water. The organic layer was dried over Na_2SO_4 and the solvent evaporated under reduced pressure to give the crude product. *Hexakis*-[(*S*)-**HAP**] was purified by column chromatography (SiO_2 70–230, CH_2Cl_2/ethyl acetate 4:1 v/v as eluent) and crystallized in abs. ethanol (Yield 29%).

Elemental analysis: found C 70.3%, H 4.9%, N 11.4%; calculated for $C_{129}H_{108}N_{18}O_{18}$ (2198.4): C 70.48%, H 4.95%, N 11.47%.

^1H NMR (DMF-d_7): 8.05 (s, 3H isophthalate 2-H), 7.95 (s, 3H core), 7.90-7.80 (m, 24H, arom *meta* to amino group and arom 2′-H), 7.68 (s, 6H isophthalate 4 and 6-H), 7.58-7.40 (m, 18H, arom 3′- and 4′-H), 6.83-6.65 (dd, 12H, arom *ortho* to amino group), 5.78 (s, 3H, CH—O), 3.85-3.53 (m, 24H, 2′- and 5′-CH_2), 2.50-2.30 (m, 12H, 4′-CH_2) ppm.

^{13}C NMR (DMF-d_7): 165.3 (C=O isophthalate), 162.7 (C=O core), 158.9 (5-C isophthalate), 153.5 (arom 4-C), 150.6 (arom 1′-C), 143.9 (arom 1-C), 133.5 (C core), 132.3 (CH core), 130.0 (arom 4′-C), 129.6 (arom 3′-C), 125.5 (arom 3-C), 122.4 (arom 2′-C), 121.3 (2-C isophthalate), 121.0 (4- and 6-C isophthalate), 112.3 (arom 2-C), 75.5 (*C*H—O), 54.1 (N—*C*H_2—CH), 46.4 (N—*C*H_2—CH_2), 31.5 (CH—*C*H_2—CH_2) ppm.

FTIR (KBr): 3061 (ν_{C-H} arom), 2919 and 2850 (ν_{C-H} aliph), 1718 ($\nu_{C=O}$), 1602 and 1515 ($\nu_{C=C}$ arom), 1385 and 1221 (ν_{C-O}), 821 (δ_{CH} 1,4-disubst. arom ring), 759 and 689 (δ_{CH} monosubst. arom ring), 723 (δ_{CH} 1,3,5 trisubst. arom ring) cm^{-1}.

***Hexakis*-[(*S*)-HAP-C].** Following the procedure described for *hexakis*-[(*S*)-**HAP**], this product was purified by column chromatography (SiO_2 70–230, CH_2Cl_2/ethyl acetate 15:1 v/v as eluent) and crystallized in abs. ethanol (Yield 24%).

Elemental analysis: found C 68.9%, H 4.4%, N 14.2%; calculated for $C_{135}H_{102}N_{24}O_{18}$ (2348.4): C 69.05%, H 4.38%, N 14.31%.

^1H-NMR (DMF-d_7): 8.12-7.84 (m, 24H, arom *ortho* and *meta* to CN; 12H, arom *meta* to amino group; 3H, core; 3H, isophthalate 2-H), 7.65 (s, 6H, isophthalate 4 and 6-H), 6.83 (dd, 6H, arom *ortho* to amino group), 5.75 (s,3H, CH-O), 3.95-2.64 (m, 24H, 2- and 5-CH_2), 2.36-2.60 (m,12H, 4-CH_2) ppm.

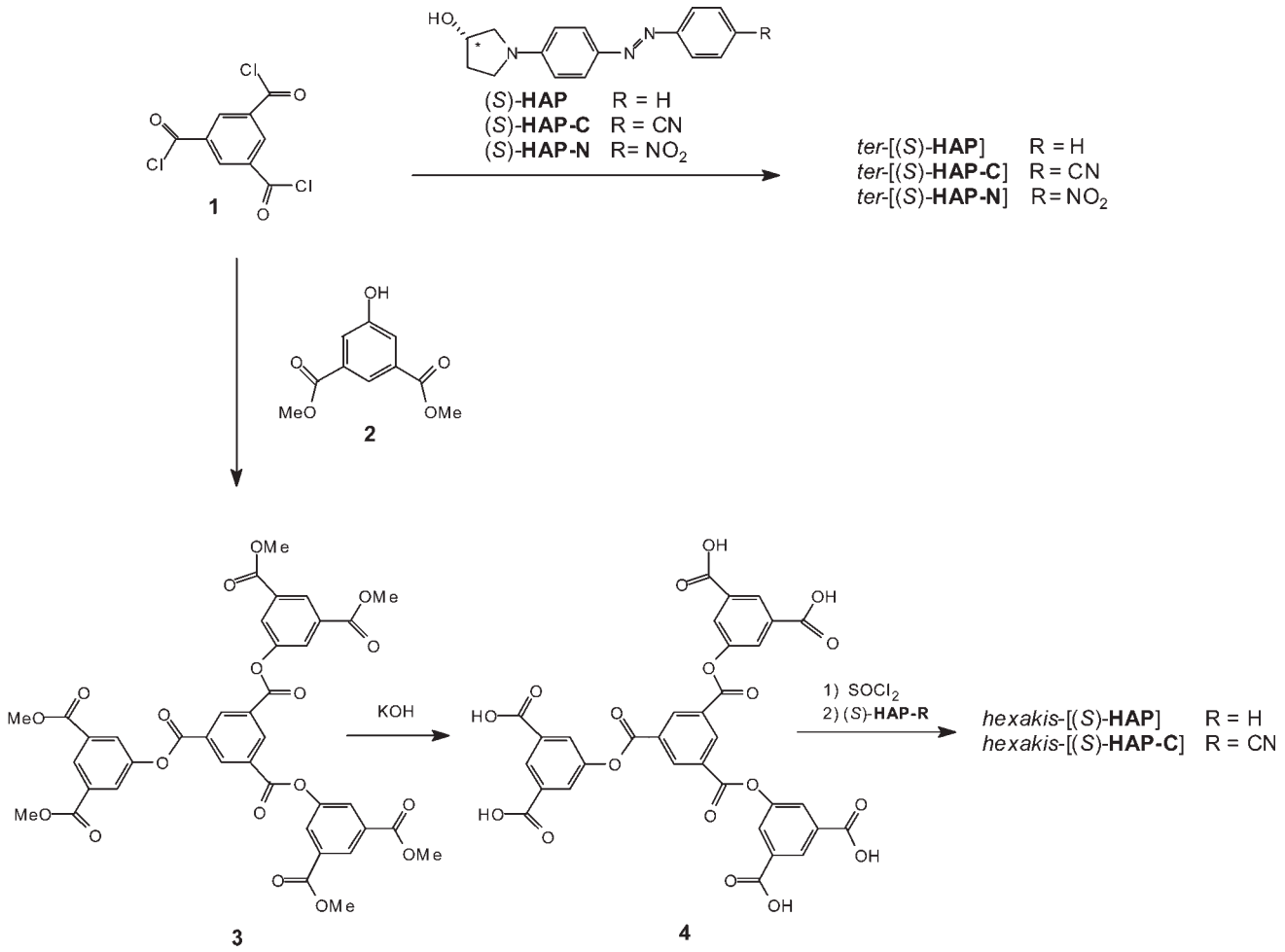
^{13}C NMR (DMF-d_7): 165.3 (C=O isophthalate), 162.7 (C=O core), 158.9 (5-C isophthalate), 155.8 (arom 4-C), 151.4 (arom 1′-C), 143.9 (1-C arom) 133.0 (C core), 132.3 (CH core), 134.0 (arom 3′-C), 126.4 (arom 3-C), 123.0 (arom 2′-C), 121.2 (2-C isophthalate), 121.0 (4- and 6-C isophthalate), 119.3 (CN), 112.6 (arom 2-C), 112.0 (arom 4′-C), 75.4 (*C*H—O), 54.1 (N—*C*H_2—CH), 46.5 (N—*C*H_2—CH_2), 31.4 (CH—*C*H_2—CH_2) ppm.

FTIR (KBr): (ν_{C-H} arom), 2854 (ν_{C-H} aliph), 2223 (ν_{CN}), 1720 ($\nu_{C=O}$), 1596 and 1516 ($\nu_{C=C}$ arom), 1378 and 1224 (ν_{C-O}), 846 and 821 (δ_{CH} 1,4-disubst. arom ring), 742 (δ_{CH} 1,3,5 trisubst. arom ring) cm^{-1}.

*Synthesis of Model Compound bis-{(S)-3-[1-(4-azobenzene)-pyrrolidine]}-5-Hydroxy Isophthalate [*Bis-*[(S)-HAP]]*

***bis*-{(*S*)-3-[1-(4-azobenzene)-pyrrolidine]}-5-(*tert*-butyldimethylsiloxy) isophthalate (7).** A solution of 5-(*tert*-butyldimethylsiloxy) isophthalic acid (5) (0.00266 mol), synthesized in two steps as reported in literature by Miller starting from commercial 5-hydroxyisophthalic acid,[39] was refluxed in 8 ml of $SOCl_2$ overnight under nitrogen. Excess of $SOCl_2$ was evaporated under reduced pressure and the intermediate 5-(*tert*-butyldimethylsiloxy)isophthaloyl dichloride (6),[39] dissolved in 10 ml of dry toluene, was added to a solution of (*S*)-**HAP** (7.98 mmol) in 130 ml of dry toluene in the presence of 18-crown-6 ether (1.40 g) and **DMAP** (1.70 g). The reaction mixture was kept at reflux for 20 h under nitrogen atmosphere, filtered, and the solvent evaporated. The remaining residue was dissolved in CH_2Cl_2 and washed with HCl 0.1 M, 5% Na_2CO_3 and finally with water.

The organic layer was dried (Na_2SO_4) and the solvent evaporated under reduced pressure to give the crude product **7** which was purified by column chromatography (SiO_2 70–230, CH_2Cl_2/ehtyl Acetate 15:1 v/v). Yield 61%.



Scheme 1. Synthesis of chiral derivatives *ter*-[(*S*)-**HAP-R**] and *hexakis*-[(*S*)-**HAP-R**].

^{1}H NMR ($CDCl_3$): 8.18 (s, 1H, arom isophthalate 2-H), 7.96-7.80 (m, 8H, arom *metha* to amino group and 2′-H), 7.65 (s, 2H, arom isophthalate 4- and 6-H), 7.52-7.40 (m, 6H, arom 3′- and 4′-H), 6.65 (dd, 4H, arom *ortho* to amino group), 5.68 (s, 2H, CH—O), 3.85-3.59 (m, 8H, 2- and 5-CH_2), 2.40 (m, 4H, 4-CH_2) ppm.

***Bis*-[(*S*)-HAP].** A solution of **7** (1.64 mmol) in 150 ml of dry THF and 1.6 ml of tetrabutylammonium fluoride (**TFBA**) 1 M in THF was stirred for 1 h. The solvent was evaporated and the obtained solid dissolved in CH_2Cl_2, washed with HCl 0.1 M, 5% Na_2CO_3 and finally with water. The organic layer was dried (Na_2SO_4) and the solvent evaporated under reduced pressure to give the crude product which was purified by chromatography (SiO_2 70–230, CH_2Cl_2/ethyl acetate 15:1 v/v) (Yield 46%, M.p. 75–80°C).

Elemental analysis: found C 70.6%, H 5.3%, N 12.2%; calculated for $C_{40}H_{36}N_6O_5$ (680.8): C 70.57%, H 5.33%, N 12.35%.

^{1}H NMR ($CDCl_3$): 8.18 (s, 1H, arom isophthalate 2-H), 7.94-7.80 (m, 8H, arom *meta* to amino group and 2′-H), 7.65 (s, 2H, arom isophthalate 4- and 6-H), 6.65 (dd, 4H, arom *ortho* to amino group), 5.68 (s, 2H, CH-O), 3.85-3.55 (m, 8H, 2′-, and 5′-CH_2), 2.35 (m, 4H, 4′-CH_2) ppm.

^{13}C NMR ($CDCl_3$): 165.8 (C=O), 157.3 (arom isophthalate 5-C), 153.7 (arom 4-C), 150.1 (arom 1′-C), 144.6 (arom 1-C), 132.3 (arom isophthalate 1- and 3-C), 130.2 (arom 4′-C), 129.6 (arom 3′-C), 125.9 (arom 3-C), 123.3 (arom isophthalate 2-C), 122.9 (arom 2′-C), 121.7 (arom isophthalate 4- and 6-C), 112.3 (arom 2-C), 75.4 (*C*H—O), 54.4 (N—*C*H_2—CH), 46.5 (N—*C*H_2—CH_2), 32.0 (CH—*C*H_2—CH_2) ppm.

FTIR (KBr): 3412 (ν_{O-H}), 3056 (ν_{C-H} arom), 2926 and 2852 (ν_{C-H} aliph), 1722 ($\nu_{C=O}$), 1602 and 1515 ($\nu_{C=C}$ arom), 1382 and 1240 (ν_{C-O}), 821 (δ_{CH} 1,4-disubst. arom ring), 759 and 689 (δ_{CH} monosubst. arom ring), 723 (δ_{CH} 1,3,5 trisubst. arom ring) cm^{-1}.

RESULTS AND DISCUSSION

Synthesis and Characterization

The trimesic acid ester derivatives *ter*-[(*S*)-**HAP**], *ter*-[(*S*)-**HAP-C**] and *ter*-[(*S*)-**HAP-N**] (see Fig. 1), have been obtained by direct esterification of 1,3,5-tricarbonyl benzene trichloride (1) with the opportune azoic alcohol by two different synthetic pathways in order to optimize the reaction yields (Scheme 1).

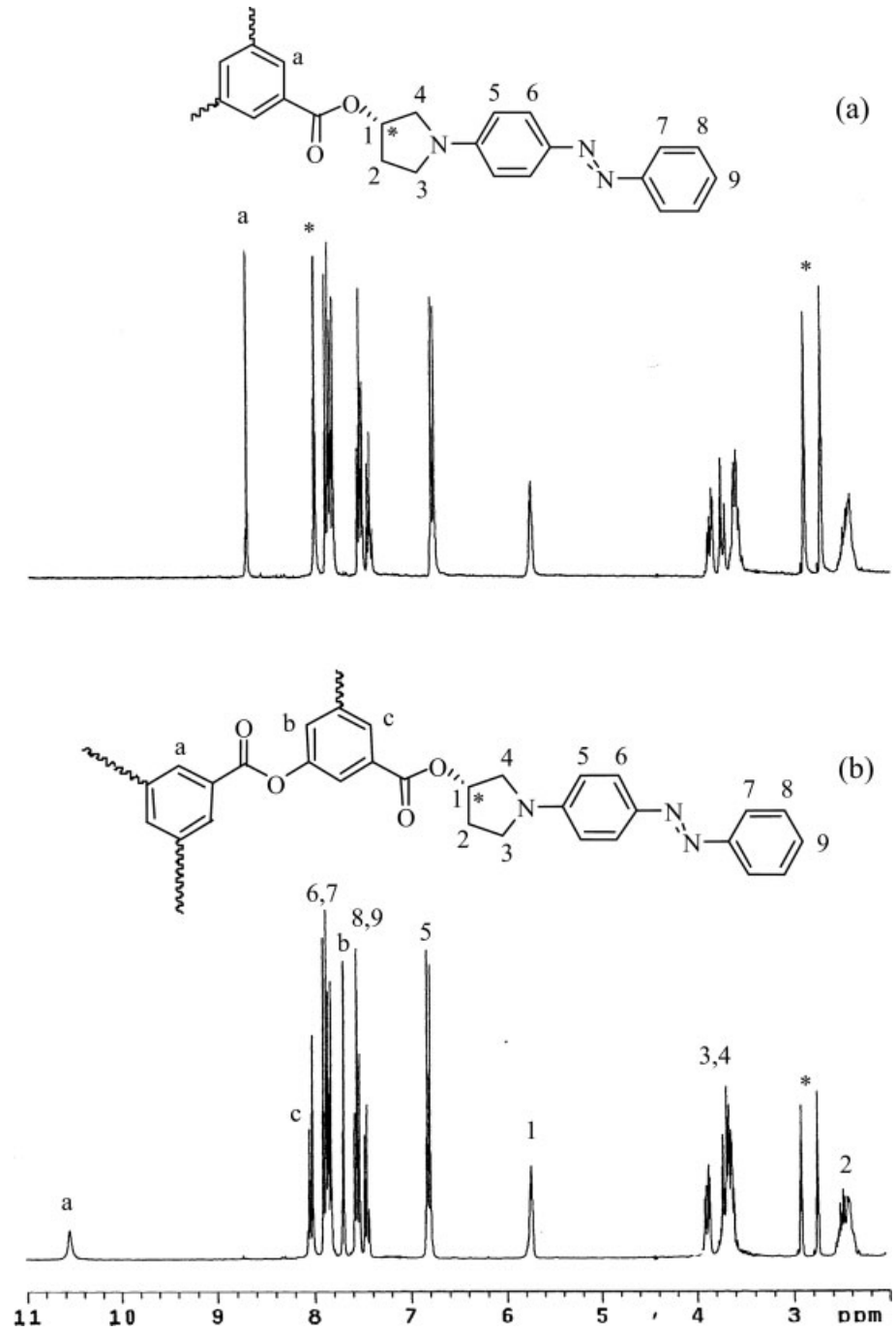
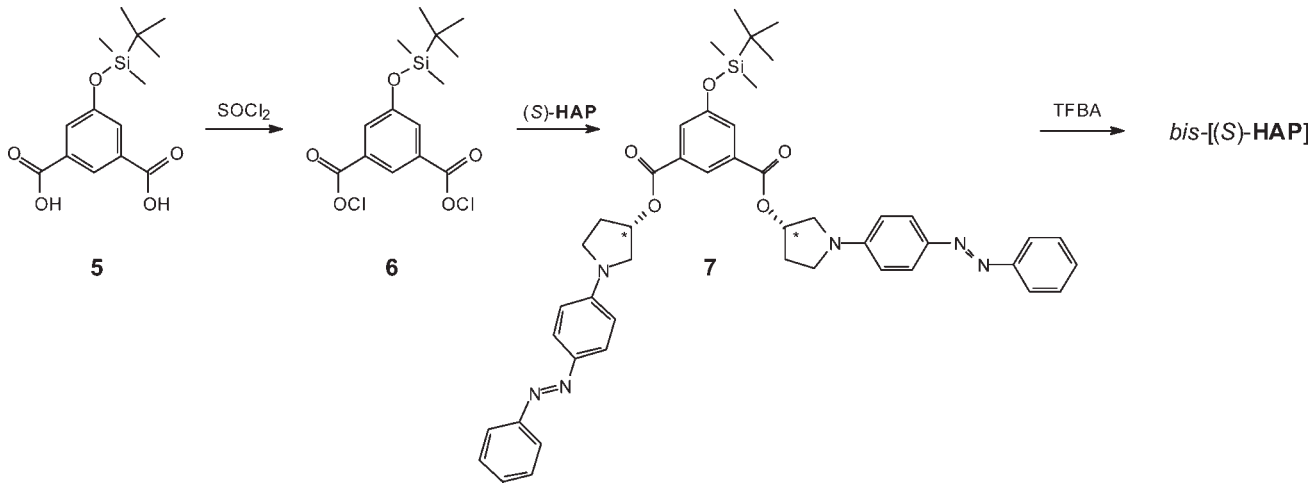


Fig. 2. H^1 NMR spectra in DMF-d_7 solution of **(a)** *ter*-[(*S*)-**HAP**] and **(b)** *hexakis*-[(*S*)-**HAP**]. Starred signals refer to solvent resonances.

Performing the reaction in dry CH_2Cl_2 in the presence of **TEA** and **DMAP**, the desired compounds are obtained with yields around 25–28%; better results (yields around 45–48%) are however achieved by a synthetic pathway similar to that one previously reported by McGrath,[28–30] using 18-crown-6 ether as complexing agent and **DMAP** as catalyst and neutralizing agent of the HCI produced.

The structures of these products have been confirmed by ^{1}H- and ^{13}C NMR, FTIR, and elemental analysis. As an example, the ^{1}H NMR spectrum of *ter*-[(*S*)-**HAP**] in DMF-d_7 showing, among the other resonances, a singlet at 8.60 ppm related to the aromatic protons of the aromatic core, is reported in Figure 2.

The synthesis of *hexakis*-[(*S*)-**HAP-R**] derivatives has been carried out, starting from the functionalization of **1** with 5-hydroxydimethyl isophthalate (2) by a procedure similar to that one reported in the literature.[35] The obtained intermediate **3** has been then hydrolyzed in excess of KOH by monitoring the reaction progress until the disappearance, in the FTIR spectrum, of the signal at



Scheme 2. Synthesis of the model compound *bis*-[(*S*)-**HAP**].

1733 cm^{-1} related to the methyl ester, the structure of the acid product **4** being finally confirmed by ^{1}H and ^{13}C NMR. This dendritic acid was previously obtained by hydrolysis of **3** in the presence of $AlCl_3$ and NaI in water/acetonitrile after 15 h reaction.[35] By using selective alkaline hydrolysis in $CHCl_3$/water/methanol 1:1:1 v/v mixture, instead, we have been able to obtain product **4** in quantitative yield, after about 1 h reaction.

Compound **4** has been treated with $SOCl_2$ and finally functionalized with the azoic alcohols (*S*)-**HAP** or (*S*)-**HAP-C**, in the presence of **DMAP** and 18-crown-6 ether, to give the *hexakis* systems which have been characterized by FTIR, ^{1}H and ^{13}C NMR.

The ^{1}H NMR spectrum of *hexakis*-[(*S*)-**HAP**] in DMF-d_7, reported as an example in Figure 2, displays, besides the signals also shown by the *ter*-derivative, three singlets related to the aromatic protons of the isophthalic rings (3H at 8.05 and 6H at 7.65 ppm, protons b and c, respectively, in Fig. 2b) and the aromatic core (3H at 10.45 ppm, proton a in Fig. 2b).

We have also synthesized *bis*-[(*S*)-**HAP**] (see Fig. 1) as a model compound for the three constituent units of *hexakis*-[(*S*)-**HAP**]. This new product has been obtained in two steps by reaction of 5-(*tert*-butyldimethylsyloxy)isophthaloyl dichloride (6), synthesized as reported in the literature,[39] with the azoic alcohol (*S*)-**HAP** to give intermediate **7**, subsequently desilylated with **TFBA**[40] (Scheme 2).

As reported in Table 1, the yields of dendrimeric derivatives decrease from *ter*-[(*S*)-**HAP-R**] to the first generation product, *hexakis*-[(*S*)-**HAP-R**] because of the reduced reactivity of the acid substrate, essentially because of steric hindrance of the azoic ester produced that prevents further functionalization. Repeated attempts to obtain the second generation product by direct esterification of the hexa-acyl chloride of **4** with *bis*-[(*S*)-**HAP**] in the presence of **DMAP** and 18-crown-6 ether, however, were unsuccessful, affording incomplete functionalization of **4** with formation of complex mixtures of several products constituted by mono- and bis-azo derivatives. Such behavior, which is consistent with the findings from other convergent dendrimer syntheses,[6,41,42] rules out the possibility of obtaining higher generation dendrimers capped with azoaromatic groups by this synthetic pathway.

TABLE 1. Characterization data of dendrimeric derivatives

Samples	Yield (%)	$[\alpha]_D^{25}$ [a]	c (g/dL)	$[\Phi]_D^{25}$ [b]	*M* (g/mol)	*n*[c]	$[\Phi_n]_D^{25}/n$[d]
bis-[(*S*)-**HAP**]	92	+561	0.165	+3819	680.76	2	+1912
ter-[(*S*)-**HAP**]	25[e]	+553	0.235	+5298	958.09	3	+1755
ter-[(*S*)-**HAP-C**]	28[e], 48[f]	n.d.		n.d.	1033.12	3	n.d.
ter-[(*S*)-**HAP-N**]	38[f]	n.d.		n.d.	1093.08	3	n.d.
hexakis-[(*S*)-**HAP**]	29	+854	0.134	+18774	2195.36	6	+3128
hexakis-[(*S*)-**HAP-C**]	24	n.d.		n.d.	2270.21	6	n.d.
(*S*)-**PAP**[g]		+4.0[g]	0.501[g]	+14.0[g]	351.45	1	+14.0[g]

[a]Specific optical rotation in DMA solution, expressed as deg dm^{-1} g^{-1} cm^3.
[b]Molar optical rotation in DMA solution, expressed as deg dm^{-1} mol^{-1} dL and calculated as ($[\alpha]_D^{25} \cdot M/100$), where *M* represents the molecular weight of the product.
[c]*n* represents the number of chiral residues present in each molecule.
[d]Molar optical rotation per one chiral residue in DMA solution, expressed as deg dm^{-1} mol^{-1} dL and calculated as ($[\Phi]_D^{25}/n$).
[e]Synthetic method A.
[f]Synthetic method B.
[g]In $CHCl_3$ solution,. Ref. 36.

TABLE 2. UV-vis spectra of dendrimeric derivatives in DMA solution at 25°C

Samples	1st band		2nd band		3rd band	
	λ_{max}[a]	$\varepsilon_{max}\cdot10^{-3}$[b]	λ_{max}[a]	$\varepsilon_{max}\cdot10^{-3}$[b]	λ_{max}[a]	$\varepsilon_{max}\cdot10^{-3}$[b]
bis-[(*S*)-**HAP**]	417	33.5	318	8.6	270	14.2
ter-[(*S*)-**HAP**]	416	34.5			266	12.8
ter-[(*S*)-**HAP-C**]	457	36.3			275	14.5
ter-[(*S*)-**HAP-N**]	489	33.3			286	11.9
hexakis-[(*S*)-**HAP**]	418	33.0	317	9.0	268	14.6
hexakis-[(*S*)-**HAP-C**]	460	35.1	316	7.1	276	13.7

[a]Wavelength of maximum absorbance, expressed in nm.
[b]Expressed in L mol^{-1} cm^{-1} and calculated for one mole of azoaromatic chromophore.

Optical Activity

The optical activity data of the investigated products are reported in Table 1.

Previous ^{1}H NMR data[36] concerning the optical purity of 4′-unsubstituted pivaloyl derivative bearing one azoaromatic group in the side-chain, (*S*)-(+)-3-pivaloyloxy-1-(4-azobenzene) pyrrolidine [(*S*)-**PAP**], prepared through a similar synthetic pathway, indicated that this compound had an enantiomeric excess higher than 90%, thus excluding the possibility of racemization at the pyrrolidine asymmetric center in the course of the synthesis. Thus, a similar optical purity has reasonably been assumed also for the derivatives reported in the present paper.

The specific $\{[\alpha]_D^{25}$ (optical rotation values of *bis*- and *ter*-[(*S*)-**HAP**] in DMA solution appear similar, while a remarkable increase of activity is observed on passing to the *hexakis* derivative (Table 1). The optical rotation values of 4′-substituted azoaromatic derivatives could not be measured at the sodium D-line due to their high absorbance at that wavelength.

Of course, the related molar optical rotation values $([\Phi]_D^{25}$ (of *bis*-, *ter*- and *hexakis*-[(*S*)-**HAP**] derivatives increase noticeably with the molecular weight, however, each compound bears a different number *n* of chiral groups, the molar optical rotation per chiral unit, calculated as $[\Phi]_D^{25}/n$, allows a better comparison among the samples. Even so, the values in the last column of Table 1 confirm that *hexakis*-[(*S*)-**HAP**] is characterized by a greater optical activity than *bis*- and *ter*-[(*S*)-**HAP**], thus indicating that the chirality of these derivatives depends strongly on the increased branching of the system. Indeed, the related model compound (*S*)-**PAP**, containing only one (*S*)-**HAP** unit, previously investigated,[36] displays negligible optical activity, as reported in Table 1 ($[\Phi_n]_D^{25}$ +14 deg dm^{-1} mol^{-1} dL, in $CHCl_3$), and the molar rotation $[\Phi_n]_D^{25}/n$ of *bis*-[(*S*)-**HAP**], the constituent dendron of *hexakis*-[(*S*)-**HAP**] is remarkably lower (+1912 deg dm^{-1} mol^{-1} dL against +3128 deg dm^{-1} mol^{-1} dL).

These findings appear to be related, as previously reported,[6,43,44] to the presence of a dendritic chiral substructure, induced, in this case, by an optically active group of one prevailing absolute configuration (*S*), favoring the assumption of a preferred chiral arrangement of the dendritic structure of the samples.

UV–Vis Analysis

The UV–Vis spectra of all dendrimeric derivatives in DMA solution (Table 2) exhibit, in the 250–700 nm spectral region, two absorption bands; one, more intense, is centered between 410 and 500 nm and is attributed to electronic transitions such as *n*-π*, π-π* and internal charge transfer of the azobenzene chromophore. The other, centered at around 260–290 nm, is attributed to the π-π* electronic transition of the aromatic ring.[45] In addition, the spectra of *bis*-[(*S*)-**HAP**] and *hexakis*-[(*S*)-**HAP-R**] show a further UV band close to 318 nm, related to the electronic transitions of the 5-hydroxyisophthalate residue (Table 2). When this dendritic fragment is absent, as in *ter*-[(*S*)-**HAP-R**], no absorbance is displayed in that spectral region.

As expected, a remarkable bathochromic shift is noted in both the UV–Vis bands on passing from *ter*-[(*S*)-**HAP**] to *ter*-[(*S*)-**HAP-C**] and to *ter*-[(*S*)-**HAP-N**] (see Fig. 3). This effect is clearly related, as previously reported,[46–49] to the increasing electron-withdrawing capability of the 4′-substituent at the azoaromatic chromophore and hence to

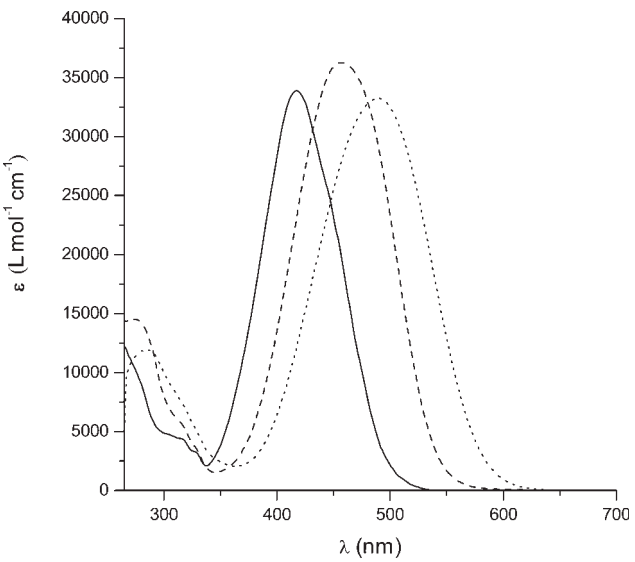


Fig. 3. UV–Vis spectra in DMA solution of *ter*-[(*S*)-**HAP**] (—), *ter*-[(*S*)-**HAP-C**] (- - -), and *ter*-[(*S*)-**HAP-N**] (····).

TABLE 3. CD spectra of dendrimeric derivatives in DMA solution at 25°C

Samples	1st band					2nd band		3rd band	
	λ_1[a]	$\Delta\varepsilon_1$[b]	λ_0[c]	λ_2[a]	$\Delta\varepsilon_2$[b]	λ_3[a]	$\Delta\varepsilon_3$[b]	λ_4[a]	$\Delta\varepsilon_4$[b]
bis-[(*S*)-**HAP**]	430	+3.75				320	−0.82	267	+0.26
ter-[(*S*)-**HAP**]	448	+4.92	395	386	−0.38			n.d.	n.d.
ter-[(*S*)-**HAP-C**]	492	+6.73	446	422	−1.78			273	−0.23
ter-[(*S*)-**HAP-N**]	524	+5.61	471	446	−1.37			289	−0.28
hexakis-[(*S*)-**HAP**]	430	+3.30				320	−0.77	268	+0.28
hexakis-[(*S*)-**HAP-C**]	491	+4.39				321	−0.49	283	+0.25
(*S*)-**PAP**[d]	410	−0.51						258	+0.22

[a]Wavelength (in nm) of maximum dichroic absorption.
[b]$\Delta\varepsilon$ expressed in L mol^{-1} cm^{-1} and calculated for one mole of azoaromatic chromophore.
[c]Wavelength (in nm) of the cross-over point of dichroic bands.
[d]In $CHCl_3$ solution,. Ref. 36.

the extent of conjugation, giving rise to a progressive reduction of the electronic transition energy in the system.

As reported in Table 2, no substantial difference in λ_{max} and extinction coefficient values was found on passing from *bis*- to *ter*- and *hexakis*-[(*S*)-**HAP**]. Such behavior, noted in other dendrimeric systems,[40] suggests that each chromophore unit is actually isolated in solution without any effect originated in the dendrimeric structure, or that dipolar interchromophoric interactions between azoaromatic moieties bonded to the same aromatic ring are of the same extent in all the samples. This has, of course, important consequences in the CD spectra, where the electronic transitions related to the azoaromatic chromophore are used as probes of conformational chirality.

Chiroptical Properties

To investigate further optical activity in dilute solution, the CD spectra of all samples have been recorded and the molar ellipticity values ($\Delta\varepsilon$), normalized to the number *n* of chiral residues present in each structure, measured (Table 3).

As reported in Figure 4, the CD spectra of *ter*-derivatives show two dichroic bands of opposite sign and different intensity in the 350–600 nm region. Being connected to the electronic transitions of the first UV band, the dichroic signals show the expected bathochromism related to the substituent effect mentioned above. In contract with previously reported linear methacrylic polymers[36,37,50] bearing the same optically active pyrrolidine group linked in the side chain through the nitrogen atom to the azoaromatic chromophore, the cross-over points appear slightly shifted with respect to the UV maxima absorptions.

As the first UV band is due to several electronic transitions which can be affected differently by the overall system chirality, the resulting CD spectra could originate in the overlap of a very intense positive band likely connected to the shoulder present in the UV–Vis spectra of all the *ter*-[(*S*)-**HAP-R**] at about 445, 490, and 520 nm, respectively, and a less intense positive excitonic couplet connected to the maximum of the first UV band. The

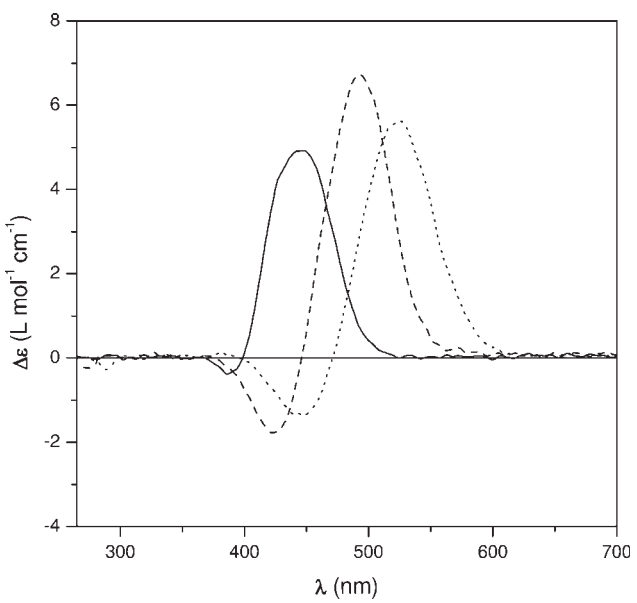


Fig. 4. CD spectra in DMA solution of *ter*-[(*S*)-**HAP**] (—), *ter*-[(*S*)-**HAP-C**] (- - -), and *ter*-[(*S*)-**HAP-N**] (····).

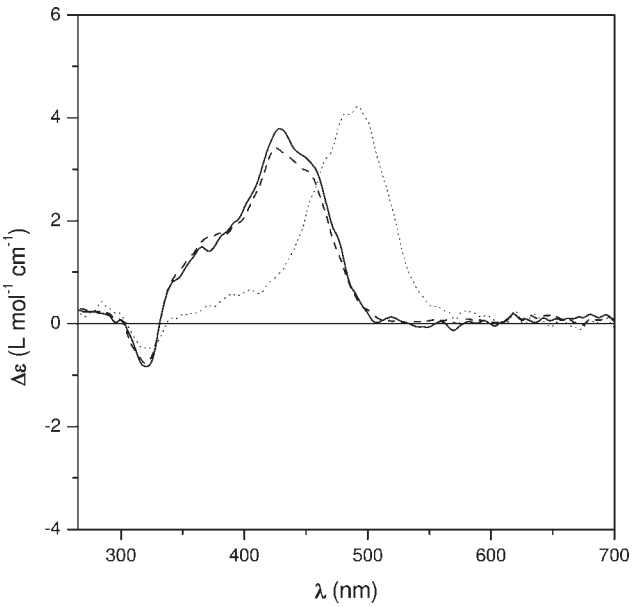


Fig. 5. CD spectra in DMA solution of *bis*-[(*S*)-**HAP**] (—), *hexakis*-[(*S*)-**HAP**] (- - -), and *hexakis*-[(*S*)-**HAP-C**] (····).

presence of this last signal may suggest the existence to a small extent of cooperative interactions between azoaromatic chromophores disposed in a mutual chiral geometry.[51] Indeed, the CD spectrum of model (*S*)-**PAP**[36] displays only two weak bands at 410 and 258 nm (Table 3), related to the UV–Vis absorptions, indicating that the absence of the above interactions is a consequence of the lack of any structural restriction.

By contrast, very different CD spectra are shown by *bis*- and *hexakis*-[(*S*)-**HAP**] with respect to *ter*-[(*S*)-**HAP-R**] (see Fig. 5). These compounds display positive and structured dichroic bands due to the overlap of several electronic transitions related to the first UV band. Instead, around 320 nm a weak negative signal is present, attributable to the isophthalic ring transitions which, therefore, are also affected by the chirality of the system. As expected, *hexakis*-[(*S*)-**HAP-C**] shows a similar behavior, but the dichroic bands are shifted to higher wavelengths because of the substituent effect (see Fig. 5).

The similarity between the CD spectra of *bis*- and *hexakis*-[(*S*)-**HAP**] indicates that the electronic transitions of the azoaromatic chromophore and the isophthalic residue are unaffected by the extension of the dendrimeric structure of the samples. Actually, each pair of azoaromatic moieties bonded to the isophthalic ring appears to behave independently from the others. This behavior could be ascribed to easier rotation around the ester bond with respect to the *ter*-derivatives, which display a more crowded central aromatic ring with a higher local density of chromophores and hence a reduced rotational freedom.

These findings indicate that the CD spectra are in agreement with the results of UV–Vis spectra, but do not confirm the much higher optical rotation values given by the *hexakis* derivative with respect to *bis*-[(*S*)-**HAP**].

Further research aimed to clarify the structural features and the chirality of the above-described systems, particularly in the solid state, are currently in progress, along with the investigation of their photoresponsive properties, carried out by irradiation with linearly polarized (producing birefringence modulation) and circularly polarized light (possibility of chiroptical switching).

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