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TETRAHEDRON: *ASYMMETRY*

Chiroptical and conformational properties of (*R*)-1-phenylethylamine derivatives of persubstituted benzene

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Abstract

Chiral derivatives of 2,4,5,6-tetrachloro-1,3-dicyanobenzene **1** with one, two and three (*R*)-1-phenylethylamino ((*R*)-PEA) units **2**–**4** are prepared and their chiroptical and conformational properties discussed on the bases of the UV/CD, NMR and MM2 data. High polarity of the persubstituted benzene ring leads to peculiar UV and IR spectra of achiral model compounds **5**–**7**, whereas relatively rigid conformations of the chiral analogues **2**–**4** are reflected in the CD spectra. Strong exciton coupling (EC) appears in the CD spectrum of pseudo-C_3-symmetric **4**; this type of interaction seems not to be present in the C_1-symmetric **2** and C_2-symmetric **3**. The absence of a molecular cleft in the chiral structures **2**–**4** could explain their inability to recognise the enantiomers of some racemates in the NMR experiment.

1. Introduction

Separation of enantiomers by liquid chromatographic (LC) methods on chiral stationary phases (CSPs) is possible through reversible diastereomeric association between the chiral environment in the column and the solute enantiomers.[1] CSPs are usually classified with respect to their general structural types. The first group is based on synthetic or natural polymers and is completely and intrinsically homochiral. The second group consists of chiral selectors of low molecular weight which are bound to a hard, incompressible matrix, usually silica (brush-type selectors). The latter group of chiral stationary phases has definite advantages over the former in that chiral selectors can be rationally designed.[2] This means that they can be selected on a rational basis because their enantiorecognition properties can often be evaluated from NMR studies on solutions containing racemic solute and chiral selectors, or can be envisaged by computer modelling, based on the well-defined types of chemical interactions. Prompted by our recent findings that (*R*)-1-phenylethylamine ((*R*)-PEA) and other 1-arylethylamines can be used as

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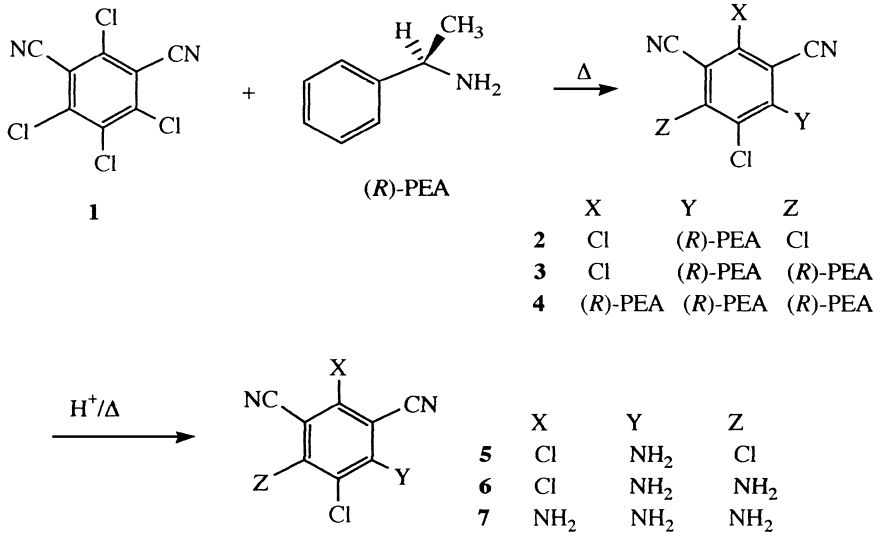
chiral ligands for catalytic complexes,[3,4] or as stoichiometric chiral auxiliaries,[5] and by the observation that three chlorine atoms in the persubstituted ring of 2,4,5,6-tetrachloro-1,3-dicyanobenzene **1** can be regioselectively substituted by thiolate anions,[6] we entered this study of model selectors with one, two, and three (*R*)-PEA units bound to **1**. Herewith we describe structural, conformational and chiroptical properties of these potential chiral selectors.

2. Results and discussion

Preparation of **2**–**4** can be carried out in a completely regioselective manner, due to significant differences in reactivity of the chlorine atoms in 2,4,5,6-tetrachloro-1,3-dicyanobenzene **1** towards sterically crowded (*R*)-PEA as a nucleophile. Mono-, di- and trisubstitution at C(4)-, C(4)- and C(6)-, and C(4)-, C(6)- and C(2)-positions, respectively, can be achieved with over 95% regioselectivity. In order to get an insight into the chromophoric system, achiral polysubstituted amino-chloro-cyanobenzenes **5**–**7** have been prepared by acid hydrolysis of **2**–**4** (Scheme 1).



Scheme 1.

2.1. ^1H NMR spectra and MM2 calculations of the preferred conformations

Characteristic ^1H NMR signals are presented in Table 1. The NMR signals of the two (*R*)-PEA groups in **3** are superimposed, and exhibit small upfield shifts from the corresponding ones in the monosubstituted derivative **2**. This indicates a C_2-symmetric arrangement of two (*R*)-PEA groups on the time scale of the NMR experiment, in a conformation that does not permit any significant mutual shielding of the groups in the two (*R*)-PEA units.

In the compound **4**, having pseudo-C_3 symmetry, the signals of the third (*R*)-PEA group are significantly shifted upfield relative to the first two, consistent with two phenyl rings being on the same side of the polysubstituted aromatic ring. If the shielding effect between two phenyl rings were operative, the upfield shift of the *two* groups should be higher than the third one on the opposite side of the plane of the central ring. Since the chemical shifts of only *one* of the (*R*)-PEA groups, constitutionally also different

Table 1
Characteristic ^{1}H NMR data for **2–4** (in $CDCl_3$)

Compd.	n[a]	δCH	δNH	δCH3	δCH	δNH	δCH3
2	1	5.76	5.91	1.68			
3	2	5.62	5.34	1.60			
4	3	5.44	5.09	1.48	5.18	4.76	1.24

[a] Number of PEA units present in the molecule

from the former two, are found upfield, they are assigned to those between the two electron-shielding π-basic cyano groups.

The lowest energy minimum conformation of **2A** is found by MM2 to contain a N–H···Cl hydrogen bond and is characterised by the large (+73°) dihedral angle (φ′) defined by C(1)N(1′)C(2′)C(1′′) bonds. It places two aromatic rings in a nearly perpendicular position and C(1′)-Me group in the nearly coplanar position (φ′′=−167°) relative to the persubstituted aromatic ring. Conformer **2B** is characterised by nearly the same dihedral angles φ′ and φ′′ but higher energy content (ΔE 2.18 kcal mol^{-1}) due to the absence of an N–H···Cl bond, Table 2.

Table 2
Total energy (E_{tot}), selected dihedral angles and (NH···Cl) distance for selected conformation of **2**, **3** and **4**

Compound	**2**		**3**[a]		**4**[a]	
	A	**B**	**A**	**B**	**A**	**B**
Etot / kcalmol^{-1}	15.84	18.02	14.65	20.04	14.40	16.09
φ'/ °	73	71	71	72	73	71
φ''/ °	-167	-169	-169	-169	-167	-170
d(NH···Cl) / Å	2.22	-	2.22, 2.22	-	2.17, 2.20	2.15

φ' Represents the dihedral angle defined by the C(1)N(1')C(2')C(1'') bonds
φ'' Represents the dihedral angle defined by the C(1)N(1')C(2')-Me bonds
[a] For each PEA unit dihedral angles φ' and φ'' are nearly equal.

The minimum energy conformation of **3A** is characterised by nearly equal dihedral angles (φ'_1–φ'_2=71°) and (φ''_1–φ''_2=−169°) between the phenyl rings and the persubstituted benzene ring and by a bifurcated N–H···Cl···H–N hydrogen bond (Fig. 1). Such a conformation has C_2 symmetry on the time scale of the NMR experiment. Hydrogen bonding stabilisation of the conformer **3A** over **3B** is more pronounced than in **2** and amounts to 2.7 kcal mol^{-1} per hydrogen bond.

The energy minimum conformation of **4A** in Fig. 1 is characterised by the nearly equal dihedral angles and φ′ and φ′′ for all (*R*)-PEA units, and a bifurcated hydrogen bond. Such an arrangement of (*R*)-PEA units lowers the symmetry, and conformer **4B** with higher energy content (ΔE 1.7 kcal mol^{-1}) having only one N–H···Cl bond possesses pseudo-C_3 symmetry (C_3 symmetry is perturbed by the presence of a Cl atom instead of a CN group at C(5)).

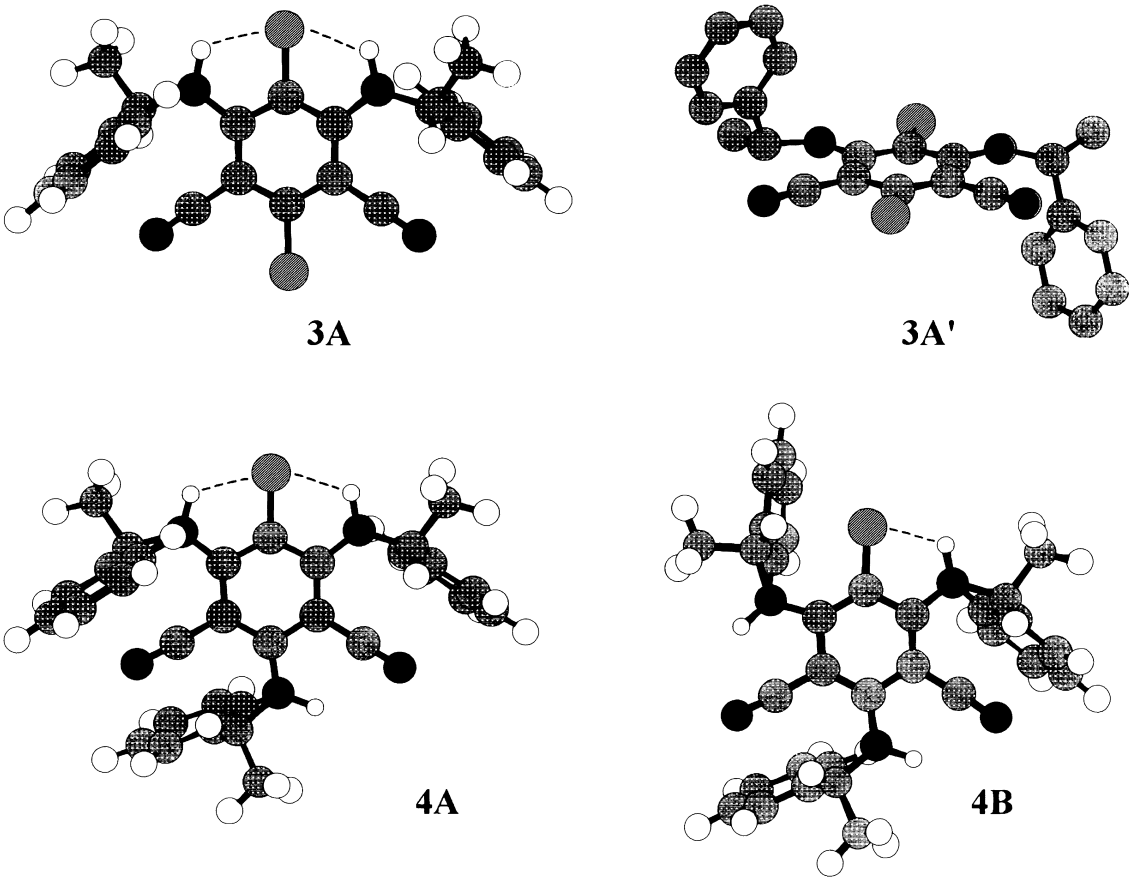


Figure 1. Force field calculated stable conformers of **3** and **4**. **3A** and **3A′** are two projections of the conformer **3A**; **4A** and **4B** are two energy minima conformers of **4**

2.2. UV/IR and CD spectra

UV spectra of polysubstituted achiral derivatives **5–7**, comprising the basic chromophoric system, are presented in Fig. 2 and Table 3.

A characteristic feature of these spectra is the monotonous red shift of the maximum of the first and strongest band, but non-monotonous change of its intensity. This band is red shifted in **5**, which is obtained by substitution of the chlorine atom at C(4) in **1** for an amino group. In the UV of **6** and **7**, with two and three amino groups, respectively, this maximum is found at 252 nm. The intensity of this band changes in the order **1**≤**5**∼**7**≤**6**, however.

This phenomenon is due to differential degrees of polarisation in the molecules **1** and **5–7**, depending on their overall symmetry and the electronic properties of the substitutents on the ring. Starting compound **1** possesses two planes of symmetry and two different electron-attracting substitutents, chlorine and the cyano group. Already the first amino group, present in the position C(4), produces polarisation by favouring the two push–pull resonance forms **5a** and **5b** (Fig. 3) and eliminates the second (vertical) symmetry plane, which results in the appearance of the well-defined band at 286 nm.

Two amino groups in **6** can give two resonance forms **6a** and **6b** (Fig. 3) because of the presence of the second plane of symmetry, which results in the appearance of the well-separated shoulder at 275 nm.

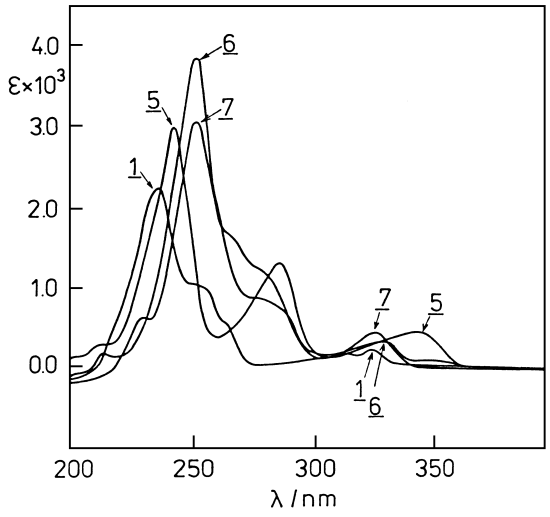


Figure 2. UV spectra of the compounds **1** and **5**–**7**

Table 3
UV Spectra of the compounds **1**–**7** (in MeCN)

Compd	λ_1 (ε x 10^4)	λ_2 (ε x 10^4)	λ_3 (ε x 10^4)	λ_4 (ε x 10^4)	λ_5 (ε x 10^4)	λ_6 (ε x 10^4)
1		236.5 (2.22)	255 (sh, 1.05)		324.9 (0.23)	
2	206.2 (2.21)	239.2 (sh, 2.58)	246.8 (3.08)	297.8 (2.07)	338.6 (sh, 0.52)	351.6 (0.57)
3			269.0 (1.93)	299 (sh, 0.49)	345.5 (0.29)	
4			271.0 (2.46)	295 (sh, 0.70)	335.0 (0.65)	
5		242.5 (2.98)	286.2 (1.30)		344.0 (0.45)	
6		251.7 (3.80)	267 (sh, 1.05)	280 (sh, 1.65)	330.0 (0.33)	
7		252.0 (3.05)	275 (sh, 0.82)		325.4 (4.35)	

Compound **7** retains the second plane of symmetry and three amino groups contribute to the three polar resonance forms, **7a**, **7b** and **7c**, giving the UV a shoulder at 265 nm.

The long-wavelength band for **5** is found at 344 nm; for the compounds with vertical symmetry it appears at shorter wavelength and is less intense; at 324 nm, 330 nm, and 325 nm for **1**, **6** and **7**, respectively.

General features of the IR spectra of **5**–**7** strongly change in the region 1400–1650 cm^{-1}; its complexity increases with the number of amino groups. Two strong bands at 1405 cm^{-1} and 1460 cm^{-1} for **5** become closer for **6**, at 1455 cm^{-1} and 1490 cm^{-1}, and even closer for **7**, at 1460 cm^{-1} and 1480 cm^{-1}. This indicates weakening of the strong N–H···Cl H-bonding in **5**. The other two well-defined bands for **5**, at 1570 cm^{-1} and 1640 cm^{-1}, for **6** appear as a sharp band at 1590 cm^{-1} and multiplet of bands between 1610–1660 cm^{-1}, and for **7** as two multiplets at 1550–1590 cm^{-1}, and 1610–1660 cm^{-1}.

UV and CD spectra of chiral compounds **2**–**4** are presented in Figs. 4–6.

It can be seen that polar *ortho*-iminoquinomethane-like resonance structures of **2**–**4** could explain the 'anomalies' in the UV spectra in the same way as discussed for their achiral congeners **5**–**7**. The polar structures comprise a 'push–pull ethylene' type interaction,[7] i.e. the resonance structures that perturb the aromaticity of the benzene ring while maintaining a high degree of conjugation. Phenyl groups at the stereogenic centres in **2**–**4** thus face the persubstituted benzene rings at different degrees and with

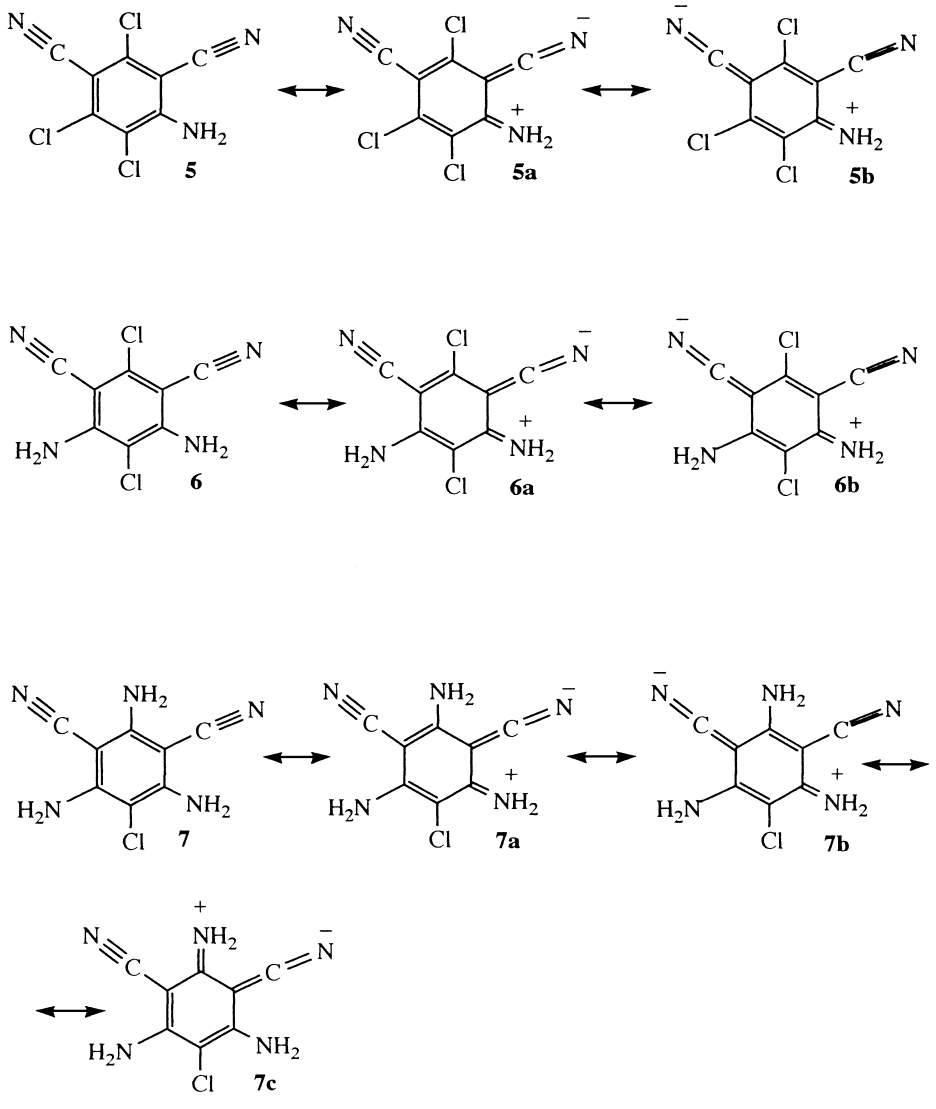


Figure 3. Resonance structures of **5**–**7**

different direction polarities. This gives rise to the peculiar change of their UV spectra with degree of substitution.

Mono-arylamino derivative **2**, which possesses C_1 symmetry, exhibits a UV spectrum that significantly differs from those of **3** and **4**. It exhibits four distinct bands with the maxima at 206 nm, 247 nm, 298 nm, and 352 nm. The CD spectrum of **2** follows this feature. The four extrema appear: at 214 nm, at ca. 255 nm (actually two local positive maxima are observable at 248 nm and 258 nm), then at 298 nm and 352 nm. Their intensity and zero point position indicate the absence of exciton coupling (EC) between the 1′-phenyl ring of (*R*)-PEA and the persubstituted aromatic ring.[8]

Assuming conjugation between the persubstituted benzene ring and the lone pair at the amine nitrogen in **2**, there are two conformers, G1 and G2, which are similar to *s-cis*- and *s-trans*-geometric isomers (Fig. 7). The N–H···Cl bonding leads to the rotamers $G1g^+$ and $G1g^-$, with torsional angles φ=73° and

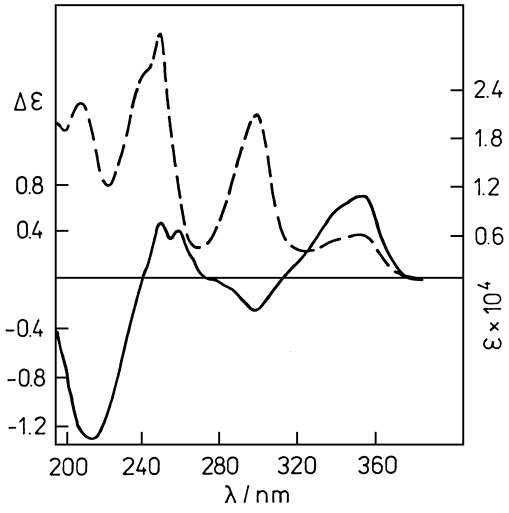


Figure 4. UV and CD spectra of compound **2**

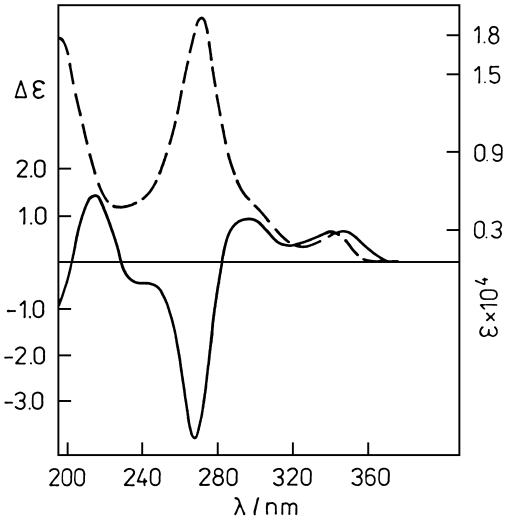


Figure 5. UV and CD spectra of compound **3**

φ=−61°, respectively. G1a$^+$ and G1a$^-$, with *s-trans*-conformation, differ in the sign of the torsion angle ϑ for C(1)N(2)C(3)C(4) bonds; φ=169° or G1a$^+$, φ=−169° for G1a$^-$.

The UV spectrum of **2** is more complex than that of **3**. The high intensity of the bands at 247 nm and 298 nm indicates that the dominant conformers are G1g$^+$ and G1g$^-$. These structures allow charge transfer interaction between the phenyl ring of (*R*)-PEA and the cyano group. The complexity of the spectrum is likely to be caused by the presence of G2 or conformers G1a$^+$, G1a$^-$.

Compound **3** possesses C_2-symmetric arrangement, and its UV spectrum exhibits one strong band at 269 nm (ε 1.93×10^4), ca. 17 nm red shifted from the corresponding band in the UV spectrum of its achiral congener **6**. There is a strong negative CD band at 269.5 nm (Δε 38.6) and a positive one at the longer-wavelength side (298.5 nm, Δε 9.4). These bands cannot be regarded as a couplet derived from exciton coupling, due to the same position of the UV and CD bands.[10] Its increased intensity may be due to the presence of one single dominant conformation fixed by both N–H···Cl bonds and charge transfer interaction between the phenyl and cyano group.

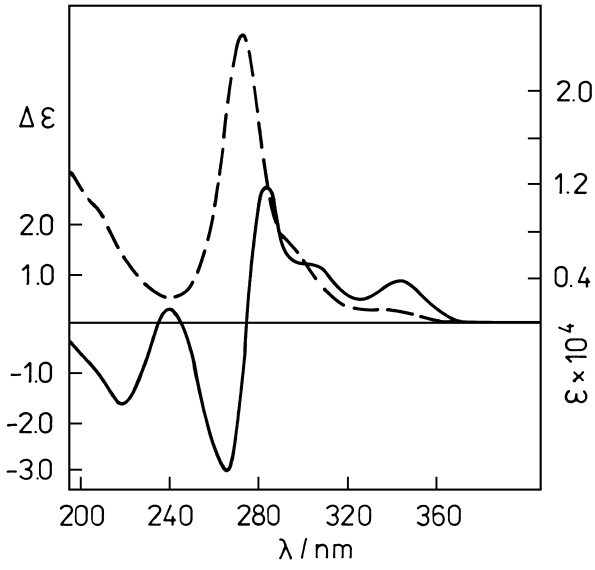


Figure 6. UV and CD spectra of compound **4**

Compound **4** has C_1 symmetry; the general shape of its UV spectrum resembles that of **3**, but the intensity of the 270 nm band is ca. 25% higher. In the CD spectrum of **4** there is, however, a strong positive band at 282 nm ($\Delta\varepsilon$ 27.5) and a more intense negative one at 265.5 nm ($\Delta\varepsilon$ 30.3). This exciton splitting in the CD spectrum suggests interaction between the third (*R*)-PEA group (between two cyano groups) and the charge transfer system of the remaining chromophore of the molecule.

All attempts, using standard NMR techniques,[9] to observe enantiorecognition by **2**–**4** of racemates listed in the Experimental, failed. Close proximity of the chiral (*R*)-PEA unit to the persubstituted benzene ring presumably forms a compact assembly which cannot act as a molecular cleft, indispensable for multiple interactions between the racemic analyte and chiral compounds **2**–**4**.[10]

It can be concluded that in the chiral structures **2**–**4** the core chromophore is a highly polar, persubstituted aromatic ring. Conformational energy minima correspond to pseudo-C_2-symmetric conformer **3A** and pseudo-C_3-symmetric **4A**, both with bifurcated N–H···Cl···H–N bonds. Strong exciton splitting at ca. 275 nm in the CD of **4** reflects positive helicity between the (*R*)-PEA group in the position C(2) and the polar chromophoric core system.

3. Experimental

IR: Perkin–Elmer 297 spectrometer for KBr pellets. ^{1}H and ^{13}C NMR: Varian Gemini XL 300 spectrometer for $CDCl_3$ solutions, δ in ppm relative to TMS as internal reference, and *J* in hertz. Melting point: Electrothermal melting point apparatus. UV: Pay Unicam 8700 Series spectrophotometer. CD: Jobin–Yvon VI dichrograph, calibrated with epiandrosteron.

Materials: 2,4,5,6-tetrachloro-1,3-dicyanobenzene (**1**, ≥99% purity) was obtained from Caffaro S.p.A., *R*-(+)-, *rac*-1-phenylethylamine were purchased from Fluka AG. Silica gel for column chromatography (0.04–0.06 mm), and all solvents were from J. T. Baker Co., p.a. grade.

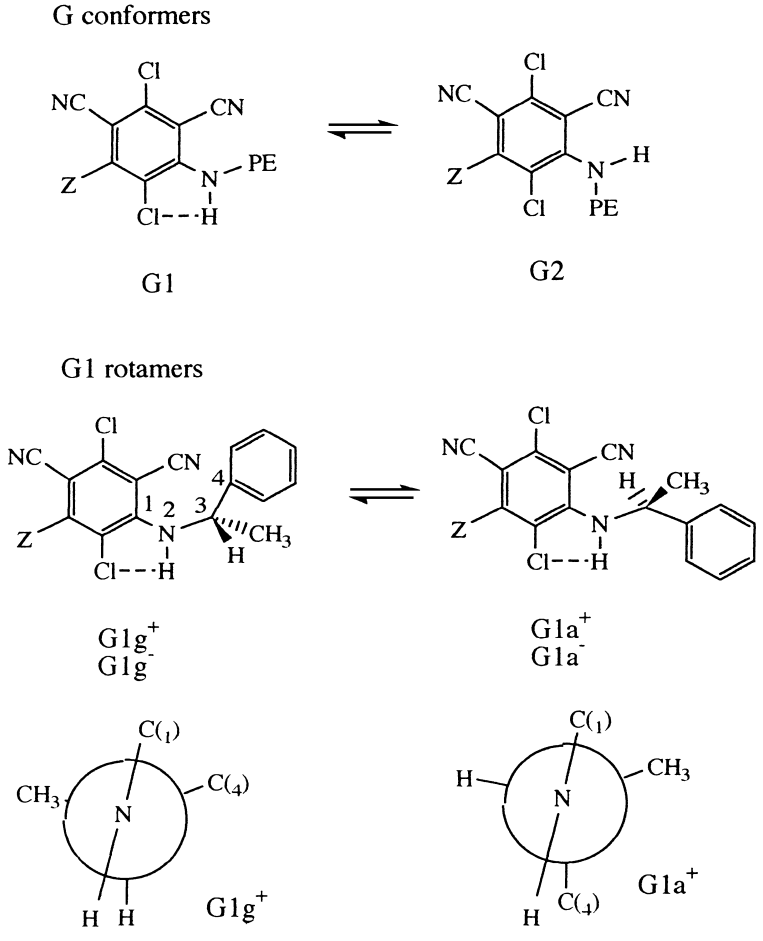


Figure 7. Conformers and rotamers of **2**

*3.1. 4-*N*-((*R*)-1′-Phenylethylamino)-2,5,6-trichloro-1,3-dicyanobenzene **2***

Compound **1** (2.00 g, 7.52 mmol) and (*R*)-PEA (4.56 g, 37.6 mmol) were heated at 100°C until complete dissolution of **1**. The reaction was quenched by rapid cooling, and the reaction mixture applied onto a silica gel column (100 g). Elution by toluene:*n*-hexane (1:1) afforded 2.58 g (97%) of pure **2**, slightly-yellow powder, mp 120–121°C (from MeOH); ^{1}H NMR: 1.68 (d, 3H, J=6.4 Hz), 5.76 (dq, 1H, J_1=8.0 Hz, J_2=6.4 Hz), 5.90 (d, 1H, J=8.0 Hz), 7.25–7.39 (m, 5H); ^{13}C NMR: 24.58, 54.01, 96.06, 104.02, 112.88, 113.96, 119.89, 125.78, 128.16, 129.16, 139.51, 141.76, 142.17, 148.77. Anal. calcd for $C_{16}H_{10}N_3Cl_3$ (350.62): C, 54.80; H, 2.87; N, 11.98%. Found: C, 54.69; H, 2.67; N, 11.86%.

*3.2. 4,6-Di-*N*-((*R*)-1′-phenylethylamino)-2,5-dichloro-1,3-dicyanobenzene **3***

Compound **1** (2.00 g, 7.52 mmol) and (*R*)-PEA (4.56 g, 37.6 mmol) were heated with MeOH (20 ml) at 100°C oil temperature for 24 h. The solvent was evaporated in vacuo and the reaction mixture purified on a silica gel column (100 g). Elution by toluene:*n*-hexane (1:1) afforded 3.15 g (96%) of pure **2**, slightly coloured oil. ^{1}H NMR: 1.60 (d, 6H, J=6.7 Hz), 5.34 (d, 2H, J=8.7 Hz), 5.63 (dq, 2H, J_1=8.7 Hz, J_2=6.7 Hz), 7.24–7.36 (m, 10 H); ^{13}C NMR: 24.50, 53.92, 90.72, 105.48, 115.20, 125.78, 127.75,

128.89, 142.70, 148.17. Anal. calcd for $C_{24}H_{20}N_4Cl_2$ (435.34): C, 66.21; H, 4.63; N, 12.87%. Found: C, 66.20; H, 4.70; N, 12.78%.

*3.3. 2,4,5-Tri-*N-*((*R*)-1′-phenylethylamino)-5-chloro-1,3-dicyanobenzene **4***

Compound **1** (0.50 g, 1.9 mmol) and (*R*)-PEA (2.28 g, 18.8 mmol) were heated at 150°C oil temperature for 20 h. The reaction mixture was diluted with MeOH (1.0 ml) and applied onto a silica gel column (50 g). Elution by toluene afforded 0.90 g (92%) of pure **2**, slightly coloured oil. ^{1}H NMR: 1.24 (d, 3H, J=6.4 Hz), 1.48 (d, 6H, J=6.4 Hz), 4.73 (d, 1H, J=8.5 Hz), 5.09 (d, 2H, J=8.2 Hz), 5.18 (dq, 1H, J_1=8.5 Hz, J_2=6.4 Hz), 5.44 (dq, 2H, J_1=8.2 Hz, J_2=6.4 Hz), 7.23–7.48 (m, 15H); ^{13}C NMR: 22.46, 23.89, 54.12, 54.81, 79.02, 99.07, 117.35, 126.01, 126.30, 127.50, 128.60, 128.69, 142.62, 142.97, 149.59, 155.28. Anal. calcd for $C_{32}H_{30}N_5Cl$ (520.01): C, 73.89; H, 5.81; N, 13.46%. Found: C, 73.64; H, 5.55; N, 13.40%.

*3.4. General procedure for preparation of **5**–**8***

Optically inactive compounds **2**–**4** (1.0 g) were prepared from **1** and racemic (*R*)-PEA following the same procedures as described above for the enantiomerically pure compounds. Crude products were dissolved in MeOH (25.0 ml), and to the ice-cooled solution conc. sulfuric acid (10.0 ml) was added dropwise. After 10 min stirring at ambient temperature, water (300 ml) was added, the resulting precipitate collected on filter and washed, first with dil. sodium bicarbonate solution, then with water.

*3.4.1. 4-Amino-2,5,6-trichloro-1,3-dicyanobenzene **5***

Yield: 435 mg (61.9%), mp 284–285°C. IR: 3420, 3320, 3220, 2220, 1640, 1570, 1540, 1460, 1290, 1220, 1210, 1030, 850, 740 cm^{-1}; ^{1}H NMR (DMSO-d_6): 7.91 (s, 2H); ^{13}C NMR (DMSO-d_6): 95.43, 100.23, 113.93, 116.96, 139.17, 140.03, 151.96. Anal. calcd for $C_8H_2N_3Cl_3$ (246.47): C, 38.98; H, 0.81; N, 17.05%. Found: C, 38.73; H, 1.21; N, 16.58%.

*3.4.2. 4,6-Diamino-2,5-dichloro-1,3-dicyanobenzene **6***

Yield: 469 mg (90.2%), mp 336–338°C. IR: 3460, 3360, 3240, 2220, 1620, 1450, 1350, 1240, 770, 740 cm^{-1}; ^{1}H NMR (DMSO-d_6): 6.92 (s, 4H); ^{13}C NMR (DMSO-d_6): 86.60, 98.26, 114.78, 139.86, 150.36. Anal calcd for $C_8H_4N_4Cl_2$ (227.05): C, 42.31; H, 1.77; N, 24.68%. Found: C, 42.36; H, 2.05; N, 24.24%.

*3.4.3. 2,4,6-Triamino-5-chloro-1,3-dicyanobenzene **7***

Yield: 303 mg (76.0%), mp 327–328°C. IR: 3480, 3350, 3240, 2200, 1630, 1590, 1560, 1480, 1460, 1350, 1250, 790, 750 cm^{-1}; ^{1}H NMR (DMSO-d_6): 6.11 (s, 2H), 6.28 (s, 4H); ^{13}C NMR (DMSO-d_6): 70.86, 89.20, 116.50, 150.53, 153.98. Anal. calcd for $C_8H_6N_5Cl$ (207.62): C, 46.27; H, 2.91; N, 33.73%. Found: C, 46.33; H, 3.07; N, 33.47%.

3.5. ^{1}H NMR experiments of chiral recognition

Solutions of **2**–**4** (0.05 mmol) and racemic compounds, 3,5-dinitrobenzoyl-1′-phenylethylamide, benzoyl-1′-phenylethylamide, *N*-3,5-dinitrobenzoylglycine isopropylester, Tröger's base (0.05 mmol), in $CDCl_3$ (0.5 ml) were prepared in the NMR tube and the spectra run at ambient temperature. Comparison with the NMR spectra in the absence of chiral selector revealed no separation of the enantiotopic protons.

Acknowledgements

MM2 calculations were performed using ChemOffice Ultra 4.5, CambridgeSoft Corp., MA (USA), Serial # 496311. The convergence criteria for the gradient of the potential energy surface (RMS gradient) was set to 0.1.

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10. This assumption is confirmed by preliminary results with some chiral selectors that contain 1-naphthylethylamine (NEA) bound to **1** in 4,6-positions. These structures still exhibit poor recognition, which is significantly enhanced, however, when a proper spacer is incorporated between persubstituted aromatic ring and NEA unit.