Crystal Structures of Chiral Diastereoisomers of a Carbon-Based High-Spin Molecule**

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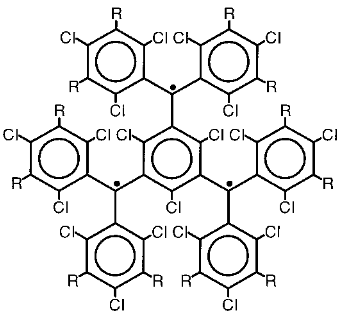
The study of organic magnetic materials constitutes a whole field of basic research which has grown because of the capacity of covalent bonds to enhance magnetic interactions.[1] Owing to the versatility of organic synthesis, organic materials can be prepared that display two or more unusual physicochemical properties simultaneously, for instance, magnetism and electron transfer or electron transport.[2a–c] Nevertheless, there are still no examples of purely organic materials that have magnetic properties and are chiral;[3] novel properties are expected for such compounds.[4] Here we report for the first time the crystal structures of the stereoisomers and the resolution of optically active enantiomers of a purely organic high-spin molecule having carbon radical centers.



1 R = H
2 R = Cl

Table 1. Electrochemical and spectroscopic properties of **1** and **2**.

	1	**2**[a]
$E^{1/2}$[b]	– 0.07	– 0.41
	– 0.35	– 0.71
	– 0.62	– 1.00
$\lambda(\varepsilon)$[c]	377 (7.2×10^4)	388 (9.1×10^4)
	495 (3.1×10^3)	508 (4.6×10^3)
	539 (3.0×10^3)	558 (4.4×10^3)

[a] Data of **2** are from ref. [5c] and are given for comparison. [b] Standard reduction potentials ($E^{1/2}$) measured in V vs. $Ag^+/AgCl$ in 0.1 M ($tBu_4N)PF_6$ solution of CH_2Cl_2 using Pt wires as working and counter electrodes; [c] Wavelengths (λ) in nm and molar extinction coefficients (ε) in $M^{-1}cm^{-1}$.

Open-shell compound **1** was synthesized by an established two-step procedure from its chlorinated hydrocarbon precursor.[5a–c] Both its electrochemical and spectroscopic properties (Table 1) are similar to those of the previously described perchlorinated analogue **2**,[5c] but the absence of chlorine atoms in all *meta* positions leads to an improved solubility in apolar solvents and, apparently, a greater tendency to form high-quality single crystals. For triphenylmethyl-based molecules with three radical centers such as **1** theoretical studies[5,6] led us to assume that only two pairs of enantiomers were expected,[5c] one having C_2 symmetry and one showing D_3 symmetry. Crystallization efforts in *n*-alkanes yielded systematically the same kind of crystalline material. One of these samples afforded a single crystal of **1**/*n*-heptane 1:1 clathrate suitable for X-ray diffraction which, once solved, showed the structure of the C_2 diastereomer (Figure 1, top).[7a] Only once were we lucky enough to get a single crystal of **1**/*n*-pentane 2:1 clathrate[7b] containing the D_3 diastereomer (Figure 1, bottom). Both crystal structures are centrosymmetric and contain racemic mixtures of enantiomers. Molecules such as **1** and **2** may be thought of as constituted of three triphenylmethyl moieties sharing the innermost ring. From the conformational point of view, the overall molecular symmetry is determined by the combined helicities—plus (*P*) or minus (*M*)—of all the propellerlike moieties. In a D_3 conformation all three moieties have the same helicity (in other words, the combined helicity is either *PPP* or *MMM* depending on the enantiomer in question). In contrast, in a C_2 conformation the helicity of one of the moieties is opposite to that of the other two (in other words, the combined helicity of its enantiomers is either *MMP* or *PPM*). In terms of geometry, the helicity in each moiety may be expressed by the sign of the torsion angle defined by the following four atoms: the bridge-C(ar) atom of the innermost ring, the radical-C atom, the bridge-C(ar) atom of an external aromatic ring, and the *ortho*-C(ar) atom of the ring that is *syn* with respect to the first bridge-C(ar) atom. The noncoplanarity is thus accounted for by the absolute value of this torsion angle (Figure 1, insets). As a matter of fact, molecules of **1**/*n*-heptane clathrate show average torsion angles of 48 ± 5°, 48 ± 2°, and $-45 \pm 3°$, while those of **1**/*n*-pentane clathrate have average angles of 50 ± 2°, 49 ± 2°, and 49 ± 1°. Notwithstanding minor distortions due to crystal packing forces, these values indicate that the structures formally correspond to C_2 and D_3 conformations of **1**, respectively. The degree of noncoplanarity in each moiety is very similar to that found in simple triphenylmethyl monoradicals,[5a] indicating that the strongest steric interactions by far are those in the immediate surroundings of the radical center inside each moiety. Moreover, in both conformers all the distances between the geometrical centers of aromatic rings belonging to different moieties are greater than 5 Å, and no van der Waals contacts between atoms of different moieties are evident. Overall, triphenylmethyl moieties of **1** can be considered to be fairly independent of each other, regardless of the specific conformation. The three open-shell centers of both diastereomers show no or small deviations from planarity of at most 0.10 Å, which is in agreement with the values measured for analogous monoradicals.[5a] Bond lengths such as C(radical) – C(ar) average out at 1.46 ± 0.01 Å for the C_2 isomer and 1.49 ± 0.04 Å for the D_3, implying partial delocalization of the unpaired electron towards the aromatic

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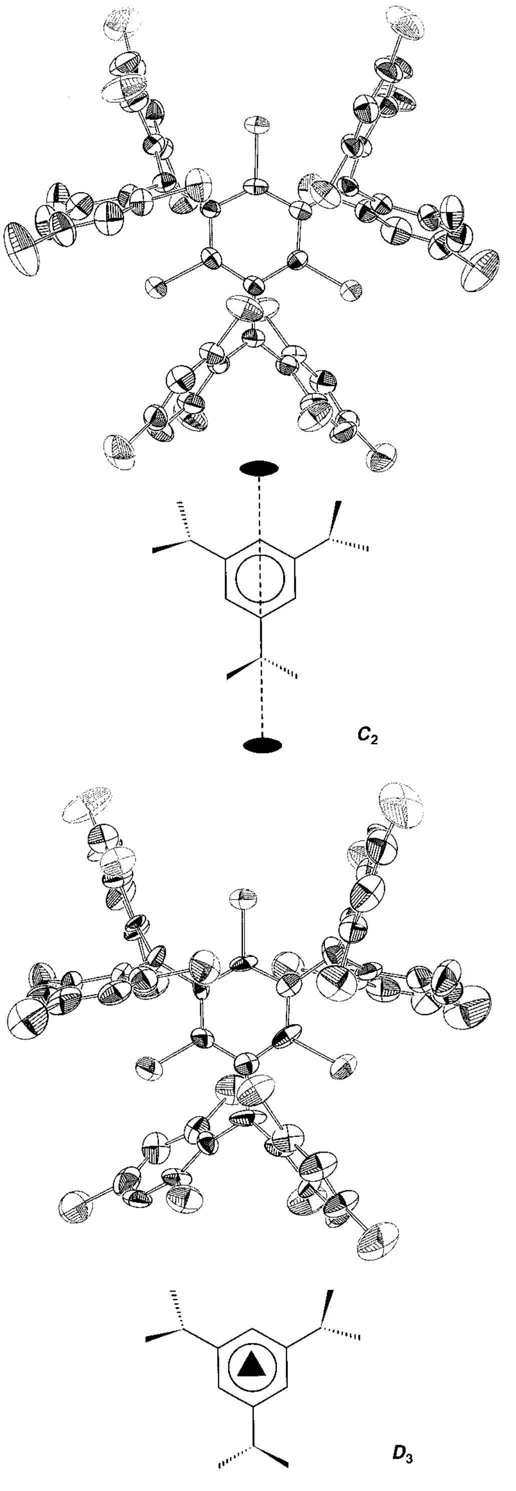

Figure 1. ORTEP views of the crystallized diastereomers of **1** having C_2 (top) and D_3 symmetry (bottom). Insets show schematically the orientation of the principal symmetry axis for each diastereomer.

rings. Other relevant bond lengths such as C(ar) – C(ar) (1.39 ± 0.03 Å for the C_2 isomer, 1.38 ± 0.03 Å for the D_3) and C(ar) – Cl (1.73 ± 0.01 Å and 1.74 ± 0.03 Å, for the C_2 and D_3 isomers, respectively) largely coincide with those observed in highly chlorinated triphenylmethyl radicals.[5a] Intermolecular distances in both crystals are very similar to those observed in analogous monoradical compounds[5a] so that regions with the largest spin densities of neighboring molecules are far away from each other.

Standard reversed-phase HPLC confirmed that **1** crystallizes in a single diastereomeric form (C_2) almost systematically, in the same way as its perchlorinated analogue **2**.[5c] This diastereomer is the most abundant one in solution, even though in such media it converts very slowly into the other diastereomer at room temperature, indicating a high energy barrier for this process. Such a dynamic process can be quenched by lowering the temperature and it can be therefore properly characterized. Thus, we determined an equilibrium constant at 298 K for the interconversion process in acetonitrile/THF (2:1) of $K_{eq} = C_2/D_3 = 0.34 \pm 0.01$. This value remains largely unchanged in other solvent mixtures such as toulene/CH_2Cl_2 (3:1). Kinetic studies of the C_2/D_3 equilibrium yielded an activation free energy of $\Delta G^{\neq}_{298} = 93 \pm 1\ \mathrm{kJ\,mol^{-1}}$. We carried out analytical chiral chromatography on the pure C_2 diastereomer of **1** in hexane/2-propanol (90:10) using an on-line dual detection technique (UV and polarimetry) in order to resolve the C_2 diastereomer into its optically active enantiomers. As expected, the UV signal recorded throughout shows two peaks (Figure 2) which, in spite of a slight overlap, can be mathematically deconvoluted. The area of both peaks is the same, as required for the resolution of any racemic mixture. This data was used further to simulate the polarimetric signal (Figure 2, inset). Despite a poor signal-to-noise ratio due to the concentration of the chiral species, an

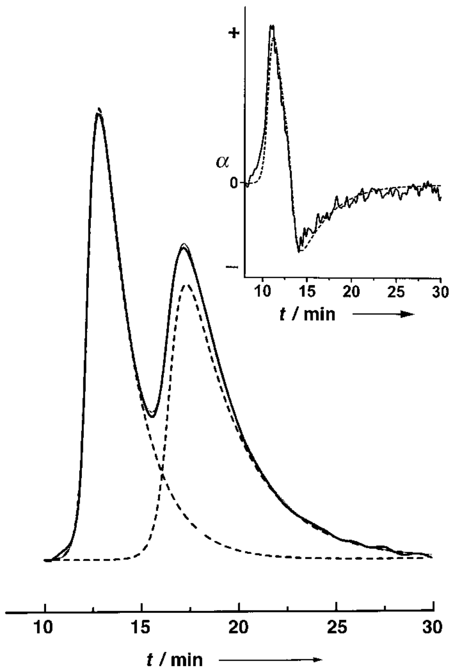

Figure 2. HPLC resolution of the C_2 racemic mixture of **1**. UV signal (240 nm); heavy line: experimental; thin line: simulated; dashed line: deconvoluted peaks. The ratio of peak areas is 1.04 ± 0.02. Inset: polarimetric signal (589 nm); solid line: experimental; dashed line: simulated. The separation was carried out using a Daicel CHIRALPAK OT(+) column (0.46 × 25 cm) with a flow rate of 1.0 mL min^{-1}, *n*-hexane/2-propanol (9:1) at 261 K.

excellent agreement between simulation and experiment was found, fully confirming the resolution of the two truly enantiomeric species.

The ESR spectrum of the C_2 diastereomer of **1** in frozen media shows a pattern characteristic of a single molecule in a quartet spin state. The derived zero-field splitting parameters (Table 2) are in accordance with the assignment of nonaxial C_2 symmetry to this species. The data were then used to simulate the ESR dipolar spectrum of an equilibrated mixture of the two diastereomers of **1** (Figure 3). The overall shape of the spectrum requires the presence of about 25% of another diastereomer with axial symmetry. This finding is in full agreement with the expected D_3 symmetry of **1** as well as with the C_2/D_3 equilibrium ratio estimated by HPLC analysis. At higher concentrations of the radical, and in accordance with the expected $S = 3/2$ spin state for the molecule, both the $\Delta M_s = \pm 2$ ($g \sim 4$) and $\Delta M_s = \pm 3$ ($g \sim 6$) signals at half and one-third of the original field, respectively, are clearly observed in the ESR spectra (Figure 3, insets). Since signals in the $g \approx 6$ spectral range only for states higher than or equal to a quartet, the evidence of the latter signal provides straightforward proof of the spin state of **1**. The dependence of the integrated intensity of this signal with temperature followed the Curie law in the temperature range 4–70 K, confirming that **1** has a $S = 3/2$ high-spin ground state in diluted, frozen solutions. Furthermore, both magnetic susceptibility and magnetization measurements on a polycrystalline sample of **1** showed Curie–Weiss behavior typical of a robust quartet state ($S = 3/2$) with thermally inaccessible (up to 300 K) low-spin excited states, ($C = 1.83$ emu K mol^{-1} and $\theta = -0.3$ K) although the structure is nonplanar.[8] The very low value of the Weiss constant indicates that the intermolecular interactions are very weak and, if anything, antiferromagnetic. Therefore, the overall magnetic behavior is close to that of an ideal paramagnet, in complete agreement with the long intermolecular distances observed in the reported crystal structures.

Table 2. Zero-field splitting parameters and principal g values of **1** and **2** obtained from their ESR spectra.[a]

	1		**2**[b]	
Symmetry	C_2	D_3	C_2	D_3
$\lvert D' \rvert$[c]	36.5	46.0	38.5	53.5
$\lvert E' \rvert$[c]	3.3	0	1.1	0
g_x	2.0013	2.0028	2.0029	2.002
g_y	2.0035	2.0028	2.0029	2.0024
g_z	2.0023	2.0033	2.0012	2.0024

[a] Spectra recorded in glassy toluene/CH_2Cl_2 (3:1) at 165 K. [b] From ref. [5c]. [c] Values of zero-field splitting parameters ($\lvert D' \rvert$, $\lvert E' \rvert$) are given in G.

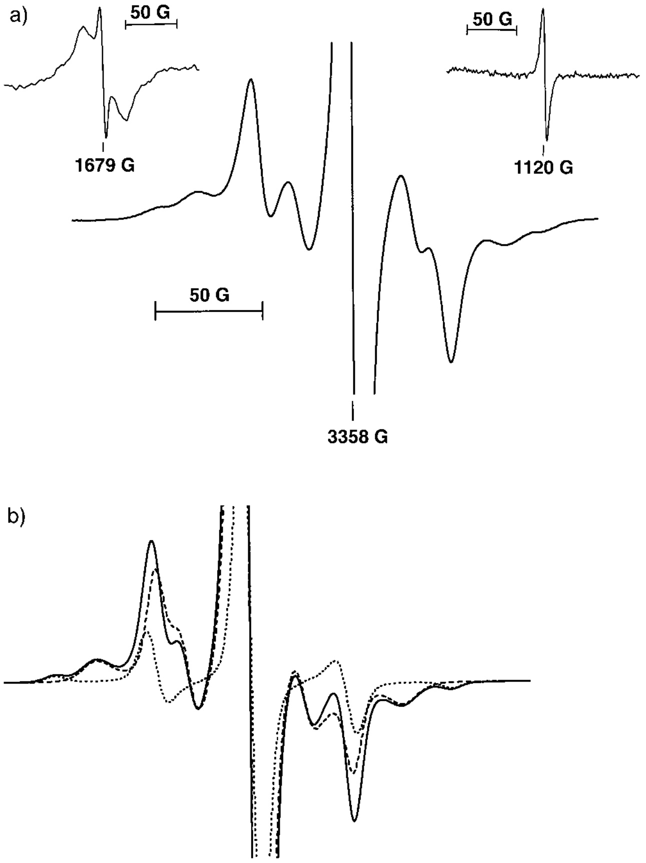

Figure 3. ESR spectrum of an equilibrated mixture of C_2 and D_3 diastereomers in a glassy toluene/CH_2Cl_2 (3:1) matrix at 165 K. a) Experimental; b) simulated; solid line: mixture; heavy dashed line: C_2 isomer; light dashed line: D_3 isomer. Insets show the half-field signal at 115 K (left), and the one-third-field signal at 5 K (right).

We have described the synthesis and most relevant properties of the first purely organic high-spin molecule which was resolved into its enantiomers by chiral HPLC. The isomerism was characterized by a combination of indirect techniques and, for the first time, by single-crystal X-ray diffraction. In this respect, the two solid-state structures, each corresponding to a different diastereomer of the molecule, constitute the first two examples of crystal structures of a carbon-based high-spin radical.

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A Chemically and Electrochemically Switchable [2]Catenane Incorporating a Tetrathiafulvalene Unit[**]

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Highly efficient constructions of mechanically interlocked molecules,[1] such as catenanes and rotaxanes, have followed rapidly in the wake of the development of self-assembly[2] in synthetic supramolecular chemistry.[3] The opportunity now exists to control the relative dispositions of one component with respect to the other(s) in such molecules by either chemical[4] or electrochemical[4a, 5] means. In this context, the tetrathiafulvalene[6] (TTF) unit represents a particularly attractive building block, since it can be oxidized sequentially and reversibly to the monocation ($E_{1/2} = +0.32$ V) and the dication ($E_{1/2} = +0.72$ V). Its redox properties, together with its ability to form[7, 8] a strong green 1:1 complex in both the solution and solid states with cyclobis(paraquat-*p*-phenylene) tetrakis(hexafluorophosphate),[9] have been largely responsible for its incorporation into the thread-like components of pseudorotaxanes,[10] as well as into catenanes[11] and rotaxanes.[8, 12] Here, we describe 1) the self-assembly of a [2]catenane comprising a macrocyclic polyether ring with two π-electron-rich "stations"—namely a 1,5-dioxynaphthalene moiety and a TTF unit—and the π-electron-deficient cyclobis(paraquat-*p*-phenylene),[9] 2) its solid-state structure and superstructure, 3) its spectroscopic characterization in solution, and 4) its ability to be switched both chemically and electrochemically, at the molecular level, between two different "states".

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