

Heterohelicene Derivatives

**A Highly Configurationally Stable
[4]Heterohelicenium Cation****

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Helicenes and heterohelicenes, which present fascinating left- or right-handed chiral helical structures (of *M* and *P* configuration respectively), have been intensively studied for their excellent self-assembling, chiroptical, photochromic, and nonlinear optical properties, as well as in asymmetric molecular recognition and synthesis, sensors, and polymer fields.^[1,2]

The large helicenes, such as [6]helicene, are configurationally stable at room temperature.^[1] The enantiomers can be separated, stored over long periods of time, and used for the above-mentioned applications. The barrier of interconversion between the *M* and *P* enantiomers of smaller [4](hetero)helicene derivatives is however much lower as the racemization takes place rapidly in solution at room

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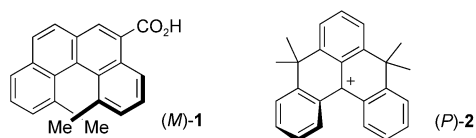
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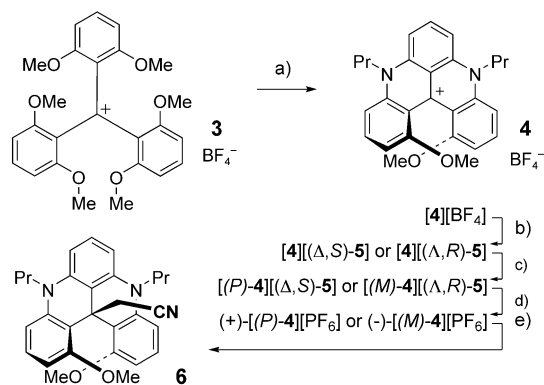


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temperature.^[3] Only the 1,12-dimethylbenzo[*c*]phenanthrene derivatives **1** have been reported in a nonracemic form.^[4] Newman and Wise have shown that **1** racemizes at rather high temperatures (greater than 250 °C); its enantiomeric purity and absolute configuration are however unknown. Hellwinkel and co-workers recognized that the doubly bridged triaryl carbenium ions **2**, which are charged analogs of [4]helicenes, may exhibit chirality.^[5] However, only a few examples of such carbenium ions have been synthesized and investigated in this context, and none of these cationic compounds were resolved. High configurational stability of [4]helicene compounds is, therefore, unknown and debatable.



Recently, the reactions of primary amines with the readily available salts of the known cation **3** have been described (Scheme 1).^[6] Dimethoxyquinacridinium systems (**4**, pre-



Scheme 1. a) $n\text{PrNH}_2$, NMP, 45 min, 110 °C, 85%; b) $[\text{Me}_2\text{NH}_2][(\Delta,S)\text{-}5]$ or $[\text{Me}_2\text{NH}_2][(\Lambda,R)\text{-}5]$ (1.3 equiv), CH_2Cl_2 /acetone, then chromatography (Al_2O_3 , CH_2Cl_2), 96–97%, d.r. 1:1; c) precipitation in C_6H_6 /THF (3:1), 30%, d.r. > 49:1; d) KPF_6 (excess), CH_2Cl_2 /H₂O (1:1), 97%, e.r. > 49:1; e) NaH, CH_3CN , 20 °C, 55%. A *P* configuration for **4** and **6** is shown arbitrarily. NMP = *N*-methylpyrrolidone.

pared from *n*-propylamine; Scheme 1, step a) can be isolated in good yields. These compounds are the result of consecutive *ortho* $\text{S}_{\text{N}}\text{Ar}$ reactions of the primary amines with **3**. The molecular framework of the cation contains four *ortho*-condensed aromatic rings. As such, compounds **4** may be regarded as [4](hetero)helicene derivatives. Herein, we report on the resolution, the absolute configuration assignment by vibrational circular dichroism (VCD) spectroscopy, and the very high configurational stability of **4**; this compound, prepared and resolved in only two steps from **3**, and being more stable ($\Delta G^\ddagger = 172.8 \text{ kJ mol}^{-1}$ at 200 °C) than the famous [6]helicene.

It appeared to us that strong steric repulsions should exist between the methoxy substituents in positions 1 and 13 of compounds **4**, which would prevent the systems from being planar. These derivatives would thus adopt a twisted helical

conformation typical of helicene derivatives. This was confirmed by X-ray diffraction analysis of the $[\mathbf{4}][\text{Ph}_4\text{B}]$ salt, which crystallized as a racemate with both enantiomers included in the structure (Figure 1).^[7]

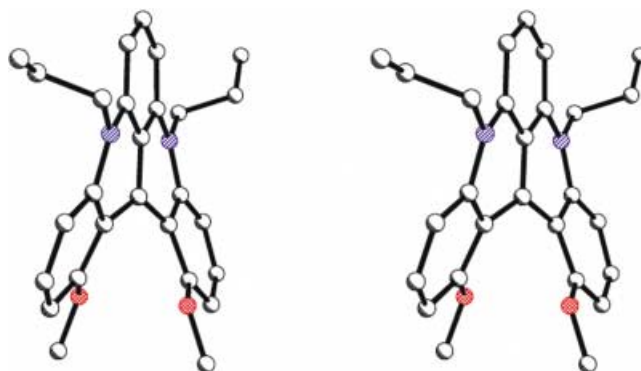
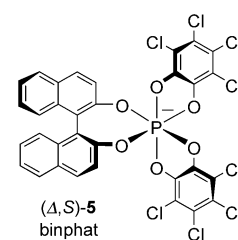


Figure 1. A stereoview showing the molecular geometry of **4** as obtained from the solved X-ray structure of the tetraphenylborate salt. The anion and the hydrogen atoms are omitted for clarity; nitrogen (blue), oxygen (red).

In the molecular structure of **4**, the two oxygen atoms are positioned exactly above one another, and their separation regulates the inner pitch of the helicene system (2.7 Å). In the case of the carbohelicenes, such as [6]helicene, pitches of 3.2–3.3 Å were found.^[1b] In this skeleton the twisting is mainly manifested in the bonds between the central carbon atom and the two methoxy-substituted rings and in the bonds between these rings and the nitrogen bridges.

The chiral nature of dimethoxyquinacridinium ion **4** was ascertained, but the degree of its configurational stability was debatable. As the determination of the racemization barrier of a chiral substance usually requires the physical separation of its enantiomers, a resolution to obtain **4** in an enantiomerically pure form was considered. For the resolution of chiral cations, the most obvious approach is to form diastereomeric salts by pairing the racemic cation with an enantiopure anion, and then attempt to separate the diastereomers through solubility differences.^[8] Recently, the synthesis of the chiral hexacoordinated phosphorus-centered binphat anion (**5**) was reported (as Δ or Λ enantiomers).^[9] This anion can be prepared following a three-step one-pot protocol using enantiopure binol, tetrachlorocatechol, *o*-chloranil, and $\text{P}(\text{NMe}_2)_3$. With (*S*)-binol, only one of the four possible diastereomers ($\Delta\delta$) is usually isolated (85 % yield). This anion is an efficient NMR chiral-shift and asymmetry-inducing agent for cationic substances and, in particular, organic derivatives.^[9,10]

An anion pairing of the racemic cation **4** and an enantiopure binphat anion ($[(\Delta,S)\text{-}5]$ or $[(\Lambda,R)\text{-}5]$) was therefore considered. Previously, it has been observed that anion **5** confers to its salts a poor affinity for polar chromatographic phases as they elute rapidly over basic alumina.^[10b,c] For the preparation of the diastereomeric salts, solutions of racemic $(\pm)\text{-}[\mathbf{4}][\text{BF}_4]$ (1.0 equiv) in CH_2Cl_2 /acetone (1:1) and of



[Me₂NH₂][(Δ ,*S*)-**5**] or [Me₂NH₂][(Δ ,*R*)-**5**] (1.3 equiv) in acetone were prepared and mixed together. Preparative column chromatography experiments (Al₂O₃, CH₂Cl₂) afforded salts [**4**][(Δ ,*S*)-**5**] or [**4**][(Δ ,*R*)-**5**] as the only eluted compounds in good yields (96–97 %).

NMR spectroscopic analysis of the isolated salts revealed an efficient NMR enantiodifferentiation of chiral cation **4** by the enantiopure counterion **5**.^[10] Two sets of signals were observed in both ¹H and ¹³C NMR spectra; one for each the *P* and *M* enantiomers of **4**. Integration of the respective signals indicated a 1:1 ratio (Figure 2, spectrum b). The [**4**][(Δ ,*S*)-

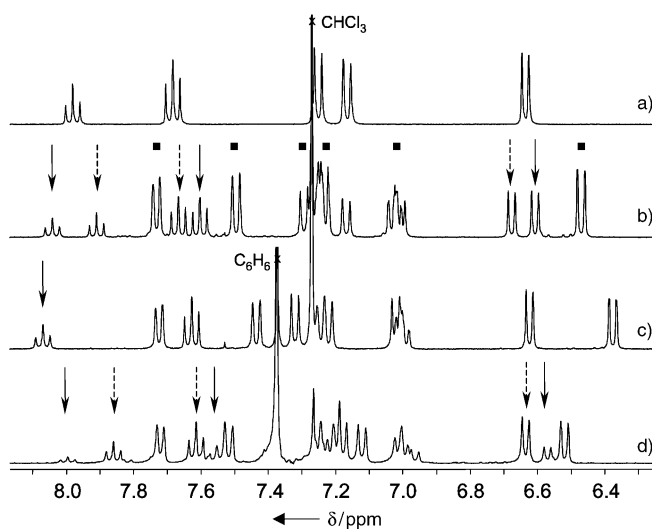


Figure 2. Sections of the ¹H NMR spectra (400 MHz, CDCl₃, δ = 8.16–6.25 ppm) of: a) (±)-[**4**][BF₄]; b) [**4**][(Δ ,*S*)-**5**], d.r. 1:1; c) [*P*-**4**][(Δ ,*S*)-**5**], d.r. > 49:1; d) [**4**][(Δ ,*S*)-**5**], d.r. 2.4:1. Plain and dashed arrows indicate some of the signals of [*P*-**4**][(Δ ,*S*)-**5**] and [*M*-**4**][(Δ ,*S*)-**5**], respectively. ■ represents the signals of anion **5**.

salt was then dissolved in a minimum amount of benzene/THF (3:1) and the resulting solution placed for 24 h at low temperature (–25 °C). After slowly warming up the solution to 20 °C, a green solid was collected by filtration (30 %). This compound was analyzed by ¹H NMR spectroscopy (CDCl₃) which revealed the presence of a single set of signals (Figure 2, spectrum c), diastereomeric ratio d.r. > 49:1.^[11] The mother liquor was concentrated in vacuo and ¹H NMR analysis revealed an excess of the other diastereomeric salt (70 %; Figure 2, spectrum d), d.r. 2.4:1). From the [**4**][(Δ ,*R*)-**5**] salt, similar results were obtained allowing the isolation of a solid and a mother liquor with analogous yields and selectivities. This physical separation of the diastereomeric salts demonstrated that cation **4** is configurationally stable at room temperature. The isolated diastereomerically pure or enriched fractions were converted into the hexafluorophosphate salts in near quantitative yield (97 %) by treatment of the substrates with an excess of KPF₆ in CH₂Cl₂/H₂O. From [**4**][(Δ ,*S*)-**5**], the salts (+)-[**4**][PF₆] (enantiomeric ratio e.r. > 49:1)^[12,13] and enantioenriched (–)-[**4**][PF₆] were obtained from the solid and the mother liquor, respectively. Enantiopure (–)-[**4**][PF₆] (e.r. > 49:1)^[13] was obtained using the solid fraction from [**4**][(Δ ,*R*)-**5**].

Unfortunately, X-ray quality crystals of the diastereomerically pure salts could not be obtained. The absolute configuration of the separated enantiomers of **4** was determined by VCD.^[14,15] A sample of (+)-[**4**][PF₆] (e.r. > 49:1) was analyzed by this method. As expected, positive and negative signals were measured (Figure 3). Using the molecular structure of **4**

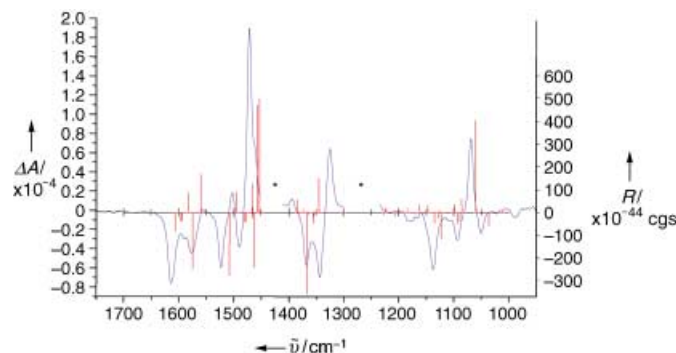


Figure 3. Experimental (blue) vibrational circular dichroism spectrum and theoretical rotational strength (red) of (+)-[(*P*)-**4**][PF₆]. The spectral region marked with asterisks was not accessible because of strong solvent absorption (*R* is the calculated rotational strength and ΔA is the experimental differential absorption).

determined by X-ray diffraction analysis, density functional theory (DFT) closed-shell calculations were performed using the Gaussian98 program.^[16,17] A geometry was optimized for the *P* enantiomer of cation **4**. The rigidity of the molecule allows us to consider that the geometry of the minimum obtained in the gas phase is not strongly influenced by the presence of a solvent. Infrared and VCD spectra were then calculated and assigned. The simulations reproduced the overall shape of the spectrum with regards to its absorbance and sign patterns (Figure 3). The positions of the bands were quite well reproduced (within 15 cm^{–1}) and the relative intensities compared well with the experiment for the majority of the peaks. Overall, a good agreement between the experimental and theoretical spectra was observed allowing the assignment of a *P* configuration for the carbenium ion in the (+)-[**4**][PF₆] salt. For (–)-[**4**][PF₆], the predominant configuration of **4** corresponds therefore to the *M* helicity. Starting from [**4**][(Δ ,*R*)-**5**], the [(*M*)-**4**][(Δ ,*R*)-**5**] and [(*P*)-**4**][(Δ ,*R*)-**5**] salts are thus obtained predominantly in the solid and mother liquor respectively.

The initial question of the determination of the inter-conversion barrier between the enantiomers of **4** could then be examined. In the literature, kinetics of the racemization of helicenes have usually involved chiroptical methods.^[1a] Accurate measurements of the racemization kinetics were realized using the high rotatory power of these derivatives. Unfortunately, the intense absorption of cation **4** in the visible region limited the use of chiroptical methods.^[12] To precisely analyze the racemization kinetics, an accurate chromatographic method to determine the enantiomeric purity of **4** was sought.^[18]

Previously, Siegel et al. and Krebs, Laursen, and co-workers have shown that reactive carbanions can attack the center of some structurally related carbenium ions to

generate rigid neutral molecular cavities.^[19] The reactivity of acetonitrile toward [4][PF₆] salts was studied in the presence of NaH at room temperature, and the desired product **6**, formed by the addition of CH₃CN, was isolated (Scheme 1). Evidently, the helicity of the [4]helicene skeleton remains after the addition of the central acetonitrile moiety and **6** is therefore chiral. Supposing a high configurational stability for **4**, a similarly high barrier of racemization was foreseen for **6**; the addition of the nucleophile occurring most probably with retention of the absolute sense of the helical configuration.

From (±)-[4][PF₆], (–)-(M)-[4][PF₆], and (+)-(P)-[4][PF₆]^[13] compounds (±)-**6**, (–)-**6**, and (+)-**6** were obtained, respectively. Chiral stationary phase (CSP) HPLC (Chiralpak AD-H, Daicel) analysis of the racemic sample (±)-**6** revealed a baseline-to-baseline separation of two peaks (*t*_R = 34.9 and 35.7 min) integrating in a 1:1 ratio. For sample (–)-**6**, an enantiomeric excess of 96.4% (major enantiomer: *t*_R = 34.9) was determined; this precise value being in full agreement with the enantiomeric purity measured by NMR for the (–)-(M)-[4][PF₆] salt.^[13]

By utilizing this method, the racemization of **4** was studied. Solid samples of (–)-(M)-[4][PF₆] were heated in a metal bath, removed at given times, and reacted with CH₃CN/NaH at 20°C to give **6**, which was analyzed by CSP-HPLC. An interconversion between the *M* and *P* enantiomers was only observed at temperatures equal to, or higher than 200°C. Measurements at four different temperatures (200, 210, 220, and 230°C) were performed and first-order kinetics observed. From the enantiomeric excesses determined by CSP-HPLC, the kinetic constants (*k*) and the activation parameters were determined (see the Supporting Information), which are summarized in Table 1. At 200°C, the free energy of

Table 1: Racemization of (–)-(M)-[4][PF₆]. *T* is the experimental temperature, *k* the kinetic constant, *t*_{1/2} is the half-life, Δ*H*[‡], Δ*S*[‡], and Δ*G*[‡] are the enthalpy, the entropy, and the free energy of activation, respectively.

<i>T</i> [°C]	<i>k</i> [s ^{–1}]	<i>t</i> _{1/2} [h]	Δ <i>H</i> [‡] [a]	Δ <i>S</i> [‡] [b]	Δ <i>G</i> [‡] [a]
200	1.05 × 10 ^{–6}	182.7	218.7	97.1	172.8
210	2.89 × 10 ^{–6}	66.6	218.6	96.9	171.8
220	9.5 × 10 ^{–6}	20.3	218.5	96.7	170.8
230	2.99 × 10 ^{–5}	6.4	218.5	96.6	169.9

[a] kJ mol^{–1}. [b] J mol^{–1} K^{–1}.

activation (Δ*G*[‡]) of the racemization is 172.8 kJ mol^{–1} and the half-life (*t*_{1/2}) is 182.7 h. This compares favorably with the [6]helicene at 196°C (Δ*G*[‡] = 154.3 kJ mol^{–1}, *t*_{1/2} = 13.4 min).^[1a,20]

In conclusion, we have shown that the dimethoxyquainacridinium cations **4** are (hetero)helicenium cations that can be simply prepared and resolved. Kinetic measurements have demonstrated a very high configurational stability for this helical species through the use of accurate chromatography analysis. This study also includes the first application of vibrational circular dichroism in the study of chiral helical derivatives and demonstrates the very high potential of this technique.

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