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Concerning restricted rotations in pyridinyl anisoles and pyridinyl phenols bearing saturated handles, and their solid state structures

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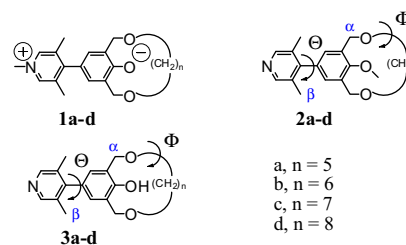
ABSTRACT

The variable-temperature («dynamic») NMR measurements of series of pyridinyl anisoles and pyridinyl phenols each of them bearing *ortho*, *ortho'* handles of various lengths at oxygenated ring lead to the following results: (i) at room temperature, a restricted rotation around the intercylic bond of pyridinyl anisoles and pyridinyl phenol bearing short handles formed by 9–10 atoms is underscored, (ii) all handles at the former derivatives are blocked on one side of the oxygenated ring face, and (iii) handles of 11–12 atoms long at phenol rings are able to move freely. The solid-state packing indicates that all saturated chains are substantially perpendicular to the oxygenated ring.

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Introduction

Twisted pyridinium phenolates are promising molecules for nonlinear optical (NLO) applications due to their huge quadratic hyperpolarisabilities.^{1–9} Unfortunately, until now two difficulties remain. First of all, the formation of aggregates greatly contributes to reduce the solubilities of pyridinium phenolates.¹⁰ Second, hydrogen bonds are readily formed between the negative oxygen atom of phenolate functionality and water or hydroxyl groups of linear alcohols.¹¹ These drawbacks may be avoided by introducing bulky groups at the *ortho* position of the phenolate.^{4–12} In this context, we have recently synthesised pyridinium phenolates bearing saturated handles of various lengths (compounds **1a–d**, Scheme 1).¹³ A moderate twist angle was introduced by anchoring two methyl groups at the *meta* position of the pyridine ring to retain reasonable NLO responses. No aggregate formation has been demonstrated at concentration of between 10^{–2} and 10^{–4} M and that EFISHG experiments have been readily performed on compounds **1b–d**.¹³ However, before considering any application of



Scheme 1. Pyridinium phenolates **1a–d** and their precursors.

these derivatives, it seemed us essential to understand the dynamic behaviour of the introduced handles.

The molecular structure of compounds **1a–d** undergoes two structural movements: a twist θ , around the C–C intercylic bond and an alkyl chain swing ϕ . Variable-temperature ¹H NMR (dynamic NMR or D NMR) is a method of choice to study these processes. Unfortunately, **1a–d** are too poorly soluble in the commonly used NMR solvents. Despite the differences in chemical functions (OCH₃, OH, O[–]) and solubilities, we focused our attention on their synthetic precursors, namely the pyridinyl anisoles **2a–d** and the pyridinyl phenols **3a–d** (Scheme 1).¹³ Thus, studying series

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of variable temperatures ^1H NMR spectra, one should obtain valuable information concerning the conformation of **2a–d** and **3a–d** in solution, according to the handle length and the nature of the oxygenated substituent, hydroxyl or methoxy, anchored on the biaryl structure. The solid state structures of derivatives **2b–c** and **3d**, obtained by X-ray diffraction analysis are also described in the present work.

Discussion

Dynamic NMR results

^1H NMR spectra of compound **2d** recorded between 273 and 393 K in $\text{C}_2\text{D}_2\text{Cl}_4$ are shown in Figure 1.¹⁴ Consider the significant signals each after the other. First, in the studied temperature range and on the NMR time scale, the benzylic protons α appear as an AB system ($\delta = 3.92$ and 4.64 ppm, $\Delta\nu = 300$ Hz, $J = 12.4$ Hz), indicating an almost prohibited swing (Φ rotation). No coalescence is detected until 393 K. The methoxy group is therefore bulky enough to drastically slow the swing of the saturated handle from one side of the molecule to the other. Besides, at room temperature, the two sharp singlets at around 1.70 ppm, that correspond to the two β methyl groups at the pyridine ring are non equivalent on the NMR time scale, a consequence of the restricted intercylic bond twist (Θ rotation). By increasing the temperature of measurement, the two singlets coalesce into a broad signal around 337 K. Above this temperature, the two methyls become isochronous and the rotation of the biaryl system around the intercylic bond becomes fast.

Spectra of compounds **2a–c** were recorded analogously and comparable results are obtained (Table 1).¹⁴ The coalescence temperatures of the methyl substituents β are respectively close to 339 K for **2a** and **2b** and to 328 K for **2c**.

The NMR spectra of pyridinyl phenol **3d** were recorded in CD_2Cl_2 from room temperature to 175 K (Fig. 2).¹⁴ In this case, at room temperature, benzylic protons α appear as a singlet indicating an easy swing of the alkyl handle. With the temperature lowering, the signal at 4.65 ppm gradually broadens and coalescence is attained around 200 K. Below this temperature, the signal splits into two doublets ($\Delta\nu_\alpha = 377$ Hz, $J_\alpha = 13.2$ Hz); swinging is again extremely slow. It should be noted, that the coalescence temperature of protons β singlet (methyl group) is indeterminable because of it is below the studied temperature range.

The NMR spectra of **3c** are quite similar.¹⁴ However, the slightly shorter handle leads to a higher coalescence temperature, namely 298 K (Table 1).

^1H NMR spectra of pyridinyl phenols **3a–b**, that bear short handles of 9–10 atoms ($n = 5$ and 6), are comparable to those already recorded for pyridinyl anisoles **2a–d** (vide supra) (Fig. 3).¹⁴ In the studied temperature range, the two methyl groups β of **3a–b** are non equivalent indicating a restricted rotation around the intercylic bond. The coalescence temperatures have been respectively found equal to 333 K (Table 1). Regarding benzylic protons, they appear again as an AB system and very likely, short saturated chains remain on one face of the phenol ring and swing to the other side extremely slowly.

The thermodynamic parameters associated with the studied structural independent rotations Θ and Φ were then calculated. Therefore, experimental spectra were first compared with simulated ones obtained using WINDNMR program.¹⁵ This allows the determination of rate constants (k) by visual comparison of theoretical and experimental spectra at different temperatures. The dependence of rate constant logarithm as a function of temperature was considered to obtain accurate activation energies values (E_a) for which errors do not exceed 1% (Table 1).¹⁶ From these data, free Gibbs energies of activation (ΔG^\ddagger), corresponding activation enthalpies (ΔH^\ddagger) and activation entropies (ΔS^\ddagger) are calculated applying Eyring equation.^{17–19} The values of all calculated thermodynamic parameters are compiled in Table 1.

First consider pyridinyl anisoles **2a–d** and pyridinyl phenols **3a–b** bearing short handles (i.e., consisting in 9–10 atoms, $n = 5$ and 6). All ΔG^\ddagger corresponding to Θ rotations (Table 1, lines 1–6) are of the same order of magnitude, confirming the nonimpact of the chain length on the rotation energy barrier. This is in qualitative agreement with the rotation barriers, equal to 14.5–14.8 kcal mol⁻¹, calculated by DFT computation at the B3LYP/6-31G(d) level, for biaryls bearing a single bulky group at the *ortho* position of the intercylic bond.^{20,21}

Furthermore, the chemical shift difference ($\Delta\nu$) between β proton signals of compounds **2a–d** and **3a–b** (Table 1, lines 1–6) decrease with the increase of chain length, suggesting either a slight intercylic angle closure or a slight bending of oxygenated aromatic ring.

As it has been mentioned above, long handles (i.e., consisting in 11–12 atoms, $n = 7$ and 8) of compounds **3c–d** swing easily. As expected, the corresponding ΔG^\ddagger values (Table 1, lines 9 and 10) decrease with the length of handles. At room temperature, the estimated rates of swing Φ are reciprocally equal to 830.5 s⁻¹ and 9.8 10⁶ s⁻¹, for **3c** and **3d**.

The obtained low and negative ΔS^\ddagger values indicate a favourable intercylic twist, at temperature above 330–340 K for **2a–b** and

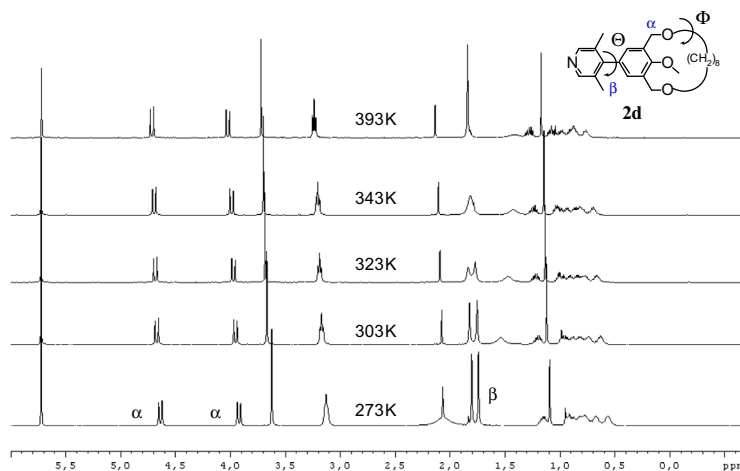


Figure 1. Compound **2d** ^1H NMR spectra in $\text{C}_2\text{D}_2\text{Cl}_4$ from room temperature to 393 K recorded at 400.13 MHz.

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