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C-bis-pivot lariat ethers: Synthesis and spectral investigations on new 15- and 17-membered coronands containing dimethoxyphosphoryl groups

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Abstract

The reactions of dibenzo-diaza crown ethers (coronands) (**1** and **2**) with dimethylphosphite led to the formation of the mixture of meso and racemic C-bis-pivot lariat ethers (**3** and **4**) containing dimethoxyphosphoryl groups. We have failed to make the resolution of the mixture, nevertheless, the detailed characterization and spectral investigations of compounds **3** and **4** have been made by elemental analyses, FTIR, ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, COSY, DEPT, HETCOR and HMBC spectral data. The salient features of the spectral data of these compounds have been presented.

Keywords: Synthesis of C-bis-pivot lariat ethers; Diastereomeric mixtures (meso and racemates); HETCOR; DEPT; HMBC

1. Introduction

Phosphorus is well known to be widely present in natural products. There are numerous possibilities for structural variation of these compounds with potential biological activity [1]. α-Aminophosphonic acids are bioisosteres of natural aminoacids that serve as important surrogates in order to modify biological processes to inhibit enzyme activity [2] and bacterial growth [3]. In addition, α-aminophosphonic acids and their alkyl esters are of interest also in hydrometallurgy in order to extract metals [4] and in diagnostic medicine as screening agents, once complexed with lanthanides and actinides [5,6]. Furthermore, these compounds, as well as their dialkyl and monoalkyl esters, are widely used in agrochemistry as antifungal agents [7], herbicides [8] and as plant regulators. In the last 10 years, the phosphonate compounds were also studied due to the possibility of their applications in different areas of chemistry: such as semiconductor particle formation of quantum size in matrix with metallic phosphonated shells [9]; as catalysers for selective oxidation of sulfides to sulfoxides [10]; cholesterol lowering agents [11]; use of phosphonated complex in forming proteins [12,13]; stereoselectivity in nucleotides [14] principally those which are related to the anti-HIV drugs [15] and synthesis of neoplastics agents.

Generally, aminoalkylphosphonates are known to have fungicidal [16], antibacterial [17], antitumoral [18,19] and antibiotic [20,21] activities.

The phosphorus containing macrocycles and cryptands have been reviewed in the literature [22,23]. Although the open-chain alkylphosphonates are known since 1960 [24,25], the first example of macrocyclic multidentate compounds containing alkyl phosphonates bonded to the carbon atoms (C-bis-pivot lariat ether type) has newly been published [26]. In that paper, the solid-state structure of a C-bis-pivot lariat ether has been reported.

In this study, we report the syntheses of analogous C-bis-pivot lariat ethers (**3** and **4**) (Scheme 1a) and their detailed spectroscopic characterizations. Whole assignments of ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and DEPT spectra for the compounds were made with the help of H–H correlation spectroscopy (H–H COSY), as well as heteronuclear chemical shift correlation (HETCOR) and heteronuclear multiple-bond correlation (HMBC).

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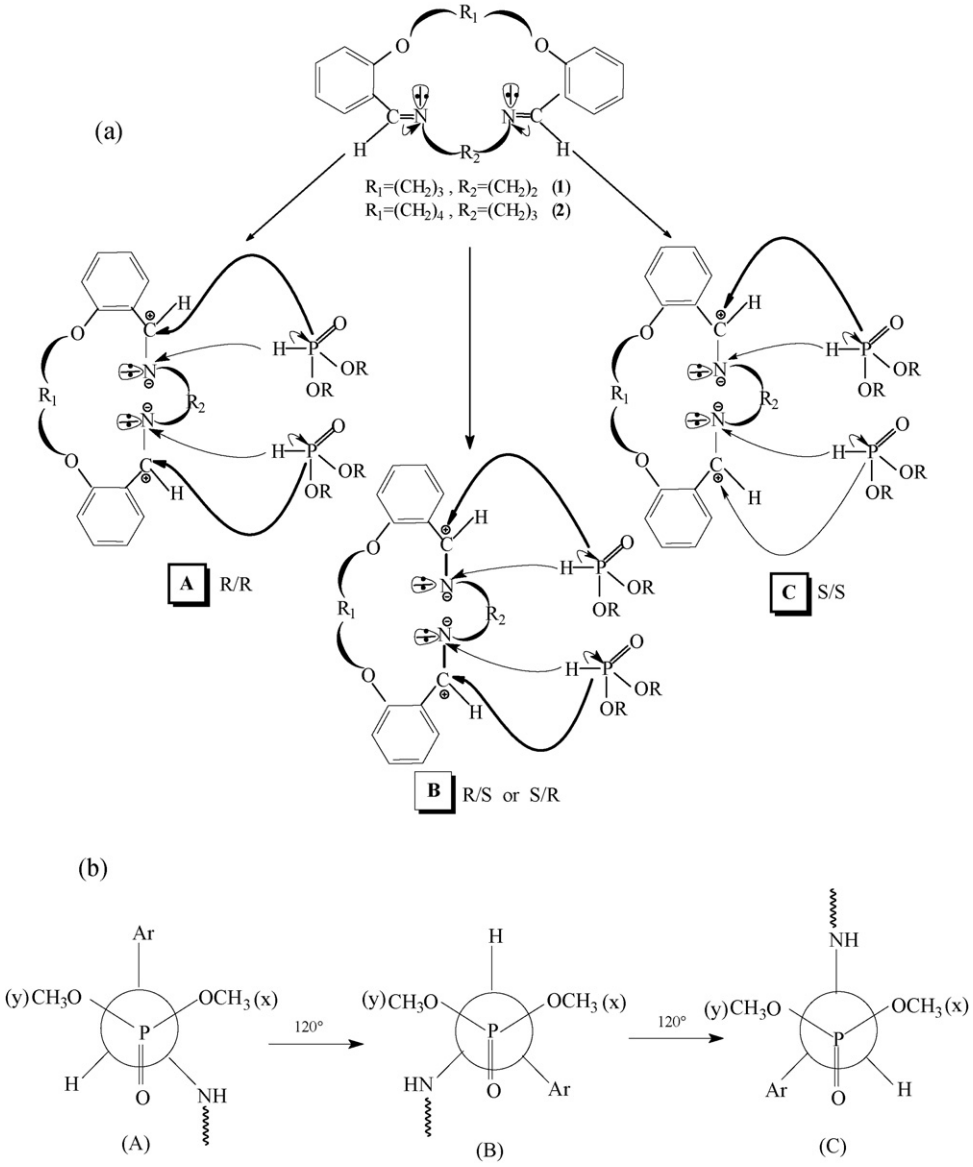

Scheme 1.

2. Experimental

2.1. Reagents and materials

Dimethylphosphite, $P(O)(H)(OMe)_2$, 1,2-diaminoethane and 1,3-diaminopropane were purchased from Fluka and distilled under pressure before use. All experimental manipulations were carried out under argon atmosphere. Solvents ethyl alcohol (99%), 2-propanol (99%), tetrahydrofuran (99.8%) and ethyl acetate (98%) were dried by standard methods prior to use. Melting points were measured on a Gallenkamp apparatus using a capillary tube. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, HETCOR and HMBC spectra were obtained on a Bruker DPX FT-NMR (500 MHz) spectrometer ($SiMe_4$ as internal standard and 85% H_3PO_4 as an external standard). Spectrometer equipped with a 5 mm PABBO BB- inverse gradient probe. The concentration of

Table 1
Experimental and analytical data

Compound	Empiric formula	MW	Yield (%)	m.p. (°C)	Calculated (found) %		
					C	H	N
1	$C_{19}H_{20}N_2O_2$	308.62	95	165	74.02 (74.12)	6.49 (6.42)	9.09 (8.99)
2	$C_{21}H_{24}N_2O_2$	336.15	82	168	75.00 (74.80)	7.14 (7.10)	8.33 (8.30)
3	$C_{23}H_{34}N_2O_8P_2$	528.54	68	174	52.27 (52.25)	6.43 (6.79)	5.30 (5.31)
4	$C_{25}H_{38}N_2O_8P_2$	556.21	41	143	53.95 (53.65)	6.83 (6.89)	5.03 (5.22)