

¹³C-Nuclear Magnetic Resonance Study of 1,2- and 1,4-Naphthoquinones and their Derivatives

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Received: August 22, 1989; November 20, 1989

Foram registrados os espectros de ¹³C-NMR de 21 diferentes derivados de naftoquinonas substituídas possuindo anéis de furano, diidrofurano e pirano ligados à estrutura de 1,2 ou 1,4-naftoquinonas. A análise dos espectros mostra que o deslocamento químico do C-3 (séries 1,4) e C-1 (séries 1,2) dependem do tamanho do anel heterocíclico. Esses sinais podem ser usados para distinguirmos entre *ortho* de paraquinonas e diidrofurano de piranonaftoquinonas.

The ¹³C NMR spectra of 21 differently substituted naphthoquinone derivatives having furan, dihydrofuran and pyran rings attached to a 1,2 or 1,4-naphthoquinone skeleton have been recorded. Analysis of these spectra has shown that the chemical shift of C-3 (1,4 series) and C-1 (1,2 series) depends on the size of the heterocyclic ring. These signals can be used as a probe distinguishing between *ortho* and *para*-quinones and of dihydrofuran from pyranonaphthoquinones.

Key Words: *naphthoquinones, naphthopyrandiones, naphthofurandiones.*

Introduction

During previous work dealing with a program of synthesis of biologically active naphthoquinones¹ and ¹³C NMR spectroscopy of numerous compounds of this class², we undertook a ¹³C NMR study of 1,2- and 1,4-naphthofurandiones and 1,2- and 1,4-naphthopyrandiones (Fig. and Table 1). Although some reports³⁻⁵ on the ¹³C NMR spectra of naphthoquinones have appeared, to our knowledge there is no exclusive report of such studies on naphthofurandiones and naphthopyrandiones. The information derived from the spectral analysis of compounds 1-21 can be used to differentiate between *ortho* and *para*-substituted isomers and establish the size of the heterocyclic ring attached on the naphthoquinone moieties.

Experimental

The preparation of the compounds studied in this work has been reported elsewhere^{1,2}. All spectra were obtained with the use of pulsed Fourier transform techniques. The carbon chemical shifts were measured downfield from TMS, in CDCl₃ solution in 5mm tubes (100 mg/ml). The pulse width was 20μs, corresponding to a field angle of 45 degrees, and the spectra were recorded at 25.5 MHz on a Varian XL-100 spectrometer. The numbering systems utilized are shown in compounds 1, 12 and 14 (Fig. 1).

Results and Conclusions

In order to use ¹³C NMR analysis to determine posi-

tion and size of the attached ring, it is necessary to find a probe which can be easily located in the ¹³C NMR spectra, has an unambiguous assignment and is distant from other functional groups. The carbon C-13 in furan or pyran of the 1,4-series, corresponding to C-1 in the 1,2-series, proved to be the most satisfactory for this purpose. A deshielding effect of ca. 7 ppm in the 1,2-naphthoquinones series (e.g., 13) as compared to the 1,4-series (e.g., 15) was observed. This increase in the δ value may be due to better conjugation with the carbonyl in the 1,2-series. The size of the heterocyclic ring also affects these carbons and a smaller deshielding effect of ca. 5 ppm in 1,4-naphthopyrandiones compared with 1,4-naphthofurandiones (e.g. 9 and 12) was observed. The same effect was present in the 1,2-series. The orientation of the methyl group attached to C-15 is *syn* to the group in C-12 (compounds 10, 12, 15, and 16) due to a γ-effect.

The magnitude of the observed effect for these two carbons is sufficiently large to make it useful for distinguishing between *ortho* and *para*-naphthoquinones with a furan or pyran ring attached to them.

Acknowledgement

This work is part of the MSc Thesis of C.G.T. de Oliveira and of V.F. Ferreira submitted to the NPPN-UFRJ; it was supported by the CNPq, CEPG-UFRJ and FINEP. The authors are grateful to Prof. A.J.R. da Silva, Central Analítica/NPPN-UFRJ, for the ¹³C NMR spectra.

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