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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

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To cite this Article Kleinpeter, E. , Heydenreich, M. , Chatterjee, S. K. and Rudolf, W. -D.(1994) 'Study of the π -Electron Distribution in Push-Pull Alkenes by ^1H and ^{13}C NMR Spectroscopy', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 95: 1, 387 – 388

To link to this Article: DOI: 10.1080/10426509408034246

URL: <http://dx.doi.org/10.1080/10426509408034246>

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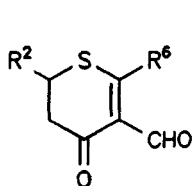
STUDY OF THE π -ELECTRON DISTRIBUTION IN PUSH-PULL ALKENES BY ^1H AND ^{13}C NMR SPECTROSCOPY

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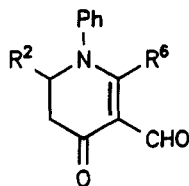
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INTRODUCTION

The restricted rotation about the partial C,C double bond of push-pull olefines, $(\text{Acc})_2\text{C}=\text{C}(\text{Don})_2$, can be studied by dynamic NMR¹ and 2D-EXSY NMR spectroscopy². The barriers to rotation ΔG^\ddagger , thus estimated³, and the ^{13}C chemical shift difference of the two olefinic carbon atoms^{4,6}, $\Delta\delta_{\text{C}=\text{C}}$, proved useful to indicate the degree of double bond character (charge separation) quantitatively and hereby to quantify the push-pull effect of the compounds studied. In this paper, two groups of integrated push-pull olefines (differently substituted 3,4-dihydro-4-oxo-2H-thiins 1 and 2,3-dihydro-4-(1H)-pyridones 2) were studied by means of ^1H and ^{13}C NMR spectroscopy as well as by accompanying force field calculations according to the preferred conformation of the 6-membered rings and the π -polarization along the C,C double bond of the push-pull alkene moiety. Because of ring closure, the $\Delta\delta_{\text{C}=\text{C}}$ parameter was employed for the latter information.



1



2

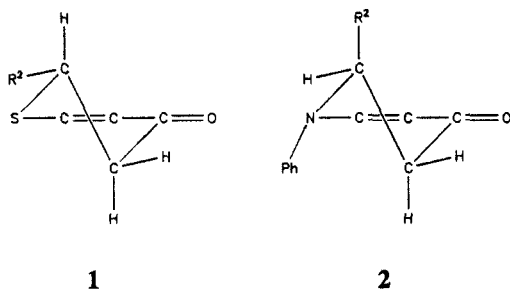
$\text{R}^2 = \text{Ph}$, 2-furyl, 2-thienyl,
 2,6,6-trimethyl-1-cyclohexen-1-yl

$\text{R}^6 = \text{S-Alk}$, NHPH

CONFORMATION OF THE 6-MEMBERED RINGS

Conformationally relevant information comes from the *vicinal* H,H coupling constants in the C^2, C^3 moiety. The ABX ^1H NMR spectra were carefully simulated and thus the *scalar* coupling constants extracted. Characteristically different values in 1 ($^3J_{\text{H}^2, \text{H}^3} = 2.7 - 3.6$ Hz and 11.0 - 15.5 Hz, respectively) and in 2 ($^3J_{\text{H}^2, \text{H}^3} = 2.5 - 3.2$ Hz and 5.8 - 6.8 Hz) were measured. Employing the KARPLUS equation⁷ dihedral angles between the H-2 and

the two H-3 protons of *ca.* 60° and 180°, respectively, were obtained for **1**, but 30° and 70°, respectively, for **2**. The R² substituent in **1** is *equatorially* positioned, R¹ and R² in **2** are *di-axial*. Parallel force-field calculation of the two kinds of compounds corroborate these conformational positions; generally *half-chair* conformations for the 6-membered rings were achieved. The energetically most stable conformation of **1** and **2** is given in the following Figure.



The CHO substituents in **1** and the Salk and NHPH substituents in **2** were found *in-plane* with the nearly flat O=C⁴-C³=C²-S and O=C⁴-C³=C²-N moieties, respectively. The other substituents are twisted due to steric hindrance.

PUSH-PULL CHARACTER

Since the barrier to C,C rotation cannot be employed to quantify the push-pull effect of these integrated push-pull alkenes **1** and **2**, the ¹³C chemical shift difference Δδ_{C-5,C-6} of the carbon atoms of the partial double bond was used to estimate the charge separation. Even smallest variations in the electron-withdrawing effect of the various donor and acceptor substituents along the push-pull moieties (Don)₂C=C(Acc)₂ were reflected in the ¹³C chemical shift difference Δδ_{C-5,C-6}, allowing to quantify the push-pull effect of the present compounds.

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