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n - π INTERACTION STUDIED BY CARBON-13 NMR SPECTROSCOPY

Yasuhisa Senda*, Jun-ichi Ishiyama and Shin Imaizumi

Department of Applied Science, Faculty of Engineering, Tohoku University
Aramaki, Sendai 980, Japan

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There are several studies on n_O-π_{CC} interaction in unsaturated ethers by photoelectron spectroscopy.[1] We attempted to examine such interaction by ^{13}C NMR spectroscopy and the spectra of several cyclic allylic alcohols and ethers were measured.

The chemical shift differences ($\Delta\delta$) between resonances for sp^2 carbons of methylene-1,3-dioxanes (1,2), 2-cyclohexenol (3), 2-cyclopentenol (4), 5,6-dihydro-2H-pyrane (5) and 2,5-dihydrofuran (6) in which the oxygen atoms are at the homoallylic position, and those of corresponding hydrocarbons were obtained. The $\Delta\delta$ values thus obtained are compared with those of set of saturated compounds. These values are tabulated in Table.

The $\Delta\delta$ values for β and γ-carbons of saturated 1,3-dioxanes, and corresponding cyclohexanes are -2.9 ~ -1.9 ppm and -11.2 ~ -10.3 ppm, respectively. On the other hand,.those of methylene-1,3-dioxanes and corresponding methylenecyclohexanes are -10.2 ~ -10.0 ppm and +3.2 ~ +3.5 ppm., respectively. The upfield shifts of the β-carbon resonances of methylene-1,3-dioxanes compared to the resonances of corresponding hydrocarbons are larger than those of the saturated compounds. The γ-carbon resonances for methylene-1,3-dioxanes moved downfield compared to those for the corresponding hydrocarbons in reverse of the saturated compounds. Similar trends were observed in the $\Delta\delta$ values between 3 and 4, and the corresponding saturated compounds.

Eliel and his coworkers found that the upfield shifts of the anti γ-carbon by the oxygen atom in the saturated ring system is larger than those of the gauche γ-carbon. They suggested that this may be due to the hyperconjugative type (through-bond) interaction of free electron pairs centred on the oxygen atom with the C_α-C_β bond accompanied by a subsequent alternation of the electron density at the γ-anti-periplanar carbon.[2]

The appreciable upfield β-shifts and downfield γ-shifts which occur when the oxygen atoms are located at the homoallylic position cannot be explained only by the hyperconjugative type interaction as in the case of the saturated system. The conclusion of Hoffmann and his coworkers on σ-π conjugation[3] gives certain suggestive information on our ^{13}C NMR results. When the oxygen atoms are fixed at an anti-clinal position with respect to the double bond, the through-space interaction between the π-type n-orbital of the oxygen atom and the vacant $p\pi^*$-orbital results in a decrease of the electron density of the oxygen atoms (Fig. 1). The enhanced effective electronegativity of this oxygen atom, therefore, attenuates the hyperconjugative through-bond interaction between the C-O σ-orbital and the pπ-orbital (Fig. 2). We envisage that the electron delocalisation of the π-orbital by such through-space and through-bond interactions results in the upfield shifts of β-carbon resonances and the downfield shifts of the γ-carbon resonances.

Such a trend was hardly found on the carbon chemical shifts of **5** and **6** in which the oxygen atom is placed at a syn-periplanar position with respect to the double bond. This may be due to the following two reasons. First, the through-space interaction of the π-type n-orbital with the $p\pi^*$-orbital is inhibited by the anti-symmetric $p\pi^*$-orbital of another sp^2 carbon (Fig. 3). Second, the hyperconjugative interaction of the pπ-orbital and the C-O σ-orbital occurs little because these two orbitals are placed almost perpendicular with each other (Fig. 4).

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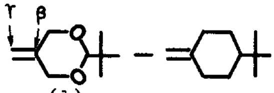
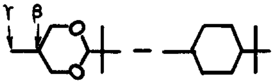
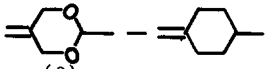
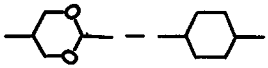
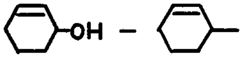
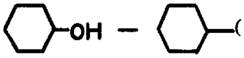
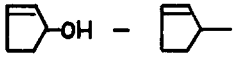
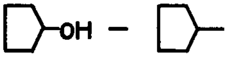
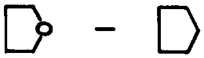
TABLE

Chemical Shisft Difference between Alcohols and Ethers, and Corresponding Hydrocarbons

	Δδ				Δδ	
	β	γ			β	γ
 (1)	-10.0	+3.5		(*trans*)	-2.9	-10.3
 (2)	-10.2	+3.2		(*trans*)	-1.9	-11.2
 (3)	-3.6	+3.3		(axial)	-0.6	-2.1
				(equatorial)	+0.7	-1.4
 (4)	-2.9	+4.2			+0.2	-2.0
 (5)	-0.2	-2.7			-0.5	-3.6
 (6)	-4.2				-0.4	

^{13}C FT-NMR spectra were obtained at 25.15 MHz with a JEOL JNM-MH-100 spectrometer equipped with a JNM-MFT-100 Fourier transform accessory using $CDCl_3$ solution. All chemical shifts are expressed in δ (ppm downfield from internal TMS). Each observed chemical shift is estimated to be accurate to ±0.1 ppm. FT measurement conditions were as follows: spectral width, 6250 Hz; acquisition time, 0.65 sec; pulse flipping angle, 45°; number of data points, 8192.

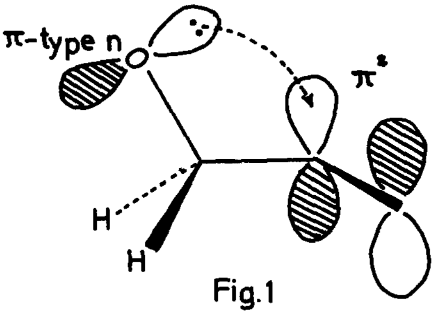


Fig.1

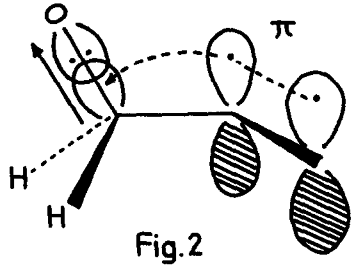


Fig.2

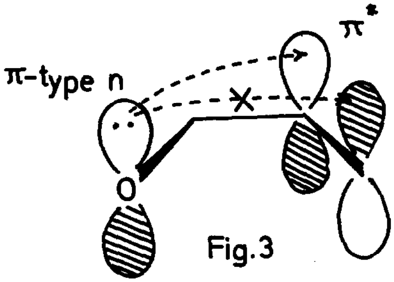


Fig.3

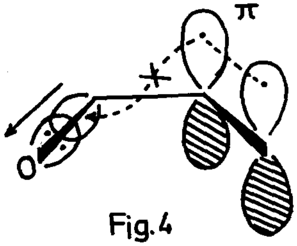


Fig.4