Configuration and ^{13}C NMR Spectra of Alkylcyclopropane Derivatives

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Eight alkylcyclopropane derivatives were prepared in a conventional manner and analysed by ^{13}C NMR spectroscopy. Additivity parameters were calculated from the chemical shifts of the endocyclic carbons, and the configurational structures derived for these compounds are confirmed by the internal coherence found for this set of parameters.

INTRODUCTION

Eight alkylcyclopropane derivatives have been prepared by the method proposed by Simmons and Smith[1] and analysed by infra-red and nuclear magnetic resonance spectroscopy. The multiplicity and frequency of the ^{13}C resonance lines have been used to establish the identity of these compounds.

The chemical shifts of the endocyclic carbons have been empirically calculated as a function of substitution parameters and terms taking into account the steric interaction resulting from the configuration of the substituents.

Confirmation of the identity of the proposed configurational structures of the synthesized compounds was given by the internal coherence found for this set of additive parameters.

EXPERIMENTAL

The alkylcyclopropanes were obtained by stereospecific addition of the appropriate olefin to a methylene iodate–CuZn(I) mixture. The compounds were purified by distillation and separated by chromatography. The IR spectra taken after purification all show characteristic C—H and cyclic C—C vibration bands at 3070–3010 and 1020 cm^{-1}, respectively. The boiling points, densities and refractive indices of the compounds were measured by classical methods and are reported in Table 1.

Table 1. Boiling points (1 atm), densities and refractive indices of alkylcyclopropanes

Substituent	B.p. (°C)	d^{20} (g cm^{-3})	n_D^{20}
1-Pentyl	127.0	0.7437	1.4130
1,1-Diethyl	88.6	0.7598	1.4075
1-Butyl-1-ethyl	140.0	0.8445	1.4192
t-Butyl	80.5	0.7443	1.4005
1-*t*-Butyl-2,2-dimethyl	117.0	0.7578	1.4150
1-Methyl-1-isopropyl	80.0	0.7255	1.4000
1-Methyl-1-neopentyl	126.5	0.7928	1.4175

The ^{13}C spectra were recorded on a Varian CFT 20 spectrometer under the following conditions: spectral width, 2000 Hz; acquisition time, 1.023 or 2.047 s; $\alpha = 25°$; free induction decay stored into 8 K data points. All chemical shifts were measured relative to TMS using CDCl$_3$ as solvent.

The identification of the ^{13}C nuclei in each cyclopropane was performed in three steps: determination of the chemical shift on a spectrum recorded with complete decoupling of the protons, determination of the degree of substitution from the fine structure of the spectra with 'off-resonance' decoupling and the differentiation of the endocyclic carbons on the basis of related ^1J(CH) constants (order of magnitude: 160 Hz).

Signals related to the hydrocarbon substituents were assigned on the basis of ^{13}C chemical shifts of alkanes reported in the literature.[2,3]

DISCUSSION AND RESULTS

The endocyclic carbons of the eight studied cyclopropane derivatives show 17 chemical shifts which can be calculated empirically as a function of twelve substituent increments (χ_i).

The equation used

$$\delta_j = \delta_0 + \sum_i a_{ji}\chi_i \qquad (1)$$

includes six direct substitution contributions (α, β, γ, α', β', γ') as well as six crossed interaction terms

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Table 2. Substituent effect parameters (ppm) for the ^{13}C chemical shifts of cyclopropane

α	8.70	α'	8.95
β	5.46	β'	−1.84
γ	−0.45	γ'	0.09
gem (CH_3)	−1.62	*gem'* (CH_3)	−2.86
gem (R)[a]	−4.82	*gem'* (R)	0.58
cis (CH_3)	−4.26	*cis'* (CH_3)	0.00

[a] R: hydrocarbon chain.

between substituents, depicted in Table 2. δ_j and δ_0 (−2.8 ppm) are the chemical shifts of carbon j in the cyclopropane derivative and in the unsubstituted cyclopropane, respectively; a_{ji} is the number of contributions of type i which has to be taken into account in the empirical calculation of the chemical shift, δ_j.

The substituent parameters are defined in Fig. 1, in the same manner as those assigned by other authors.

The α and β substituent parameters are deshielding, as they are for the alkanes studied by Grant.[2] The α' parameter is also deshielding, as expected, since the substituent is β to the considered carbon atom. The γ and β' parameters are shielding, while the γ' parameter is small in magnitude and of minor importance.

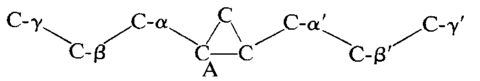

Figure 1. Definition of the substituent effects used in the calculation of the chemical shift of carbon A.

In addition to the α, β, γ, α', β', γ' parameters, it is found that better results are obtained if a *cis* correction factor is included when α and α' are located *cis* to one another. Moreover, a *gem* correction factor is included when carbon A has two α parameters. The *cis* and *gem* parameters highlight the importance of steric factors originating from the so-called 'steric compression shift' in these systems.

In the case of the other carbons of the ring, the steric interaction parameters are defined by the symbols *cis'* and *gem'*. Thus, the substituent effects on the disubstituted carbons of 1,1,2,2-tetramethylcyclopropane are given as $2\alpha + 2\alpha' + 2cis(CH_3) + gem(CH_3) + gem'(CH_3)$, i.e. 22.3 ppm relative to cyclopropane or 19.5 ppm relative to TMS.

The above defined substitution increments (Table 2) were determined by matrix inversion built on a_{ji} coefficients and independent chemical shifts reported in Table 3; some of these are close to previously published values.[4] Chemical shifts recalculated from the substituent parameters are listed in parentheses in Table 3.

The agreement between the calculated and observed chemical shifts justifies an additivity relationship between these chemical shifts and the substitution increments and confirms the structures of the cyclopropane derivatives prepared.

Table 3. ^{13}C chemical shifts of alkylcyclopropane derivatives (ppm relative to TMS)[a]

	Endocyclic carbons			Other carbons				
Substituent	C-1	C-2	C-3	C-α	C-β	C-γ	C-δ	C-ε
1-Pentyl	10.9(10.9)	4.3(4.4)	4.3(4.4)	34.8	29.3	31.8	22.7	14.0
1,1-Diethyl	21.3(20.7)	11.3(12.0)	11.3(12.0)	28.2	10.4			
1-Butyl-1-ethyl	20.2(20.2)	11.6(12.1)	11.6(12.1)	35.4	28.8	23.0	14.0	
				28.6	10.5			
t-Butyl	22.7(22.3)	0.3(0.6)	0.3(0.6)	29.3	28.2			
1-*t*-Butyl-2,2-dimethyl	36.9(37.3)	16.4(16.4)	16.1(15.7)	30.8	30.3			
				30.0				
				20.5				
1-Methyl-1-isopropyl	20.1(20.7)	13.0(12.0)	13.0(12.0)	36.1	19.3			
				17.9				
1-Methyl-1-neopentyl	13.9(13.9)	14.3(14.1)	14.3(14.1)	53.2	32.5	30.9		
				25.1				
1,1,2,2-Tetramethyl	19.5(19.5)	19.5(19.5)	27.3(27.3)	22.3				

[a] Experimental values and calculated values (in parentheses) from parameters of Table 2.

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