Studies on the PMR Spectra of Oxetanes. VI
2-(3-Chlorophenyl)oxetane and 2-(2-Chlorophenyl)oxetane at 60 and 100 MHz

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The 100 MHz spectra of the phenyl protons in 2-(3-chlorophenyl)oxetane and 2-(2-chlorophenyl)oxetane have been analysed. The 60 MHz PMR chemical shifts and proton-proton coupling constants have been studied in the temperature range from −20 °C to +80 °C. The chemical shifts were sensitive to temperature, while the coupling constants were not, except the long range $^5J^m$ coupling constant between the methine proton and the meta positioned phenyl proton in 2-(2-chlorophenyl)oxetane.

1. Experimental

The compounds 2-(2-chlorophenyl)oxetane (I) and 2-(3-chlorophenyl)oxetane (II) were synthesized at the Department of Chemistry, University of Oulu[1]. Solutions of 10 mole % in carbon tetrachloride (CCl_4) were prepared. Tetramethylsilane (TMS) was used as an internal standard.

The 100 MHz PMR spectra were recorded by a Varian HA 100 spectrometer and the 60 MHz spectra by a Varian A 60 spectrometer. The temperature was controlled by a V-6040 controller unit. The accuracy of the temperature in all measurements is ±2 °C. The calibration was carried out by the normal sideband technique (sidebands of TMS) using a Krohn-Hite 4100 push-button oscillator and an Advance TC 9 timer counter. Three spectra in each sweep direction were recorded and average values were used in the analyses. The accuracy of the line positions is approximately ±0.1 Hz or better.

The proton chemical shifts and proton-proton coupling constants were obtained from the spectra by the programme LAOCN3[2]. The error limits given in the tables usually result from the computations. Programmes ABCDE[3] for a five 1/2-spin system and PIIRTO[3] for plotting the stick and lorentzian spectra have been used.

The computations were performed with a UNIVAC 1108 and a Honeywell 1644 computer.

2. Introduction

During the last four years several NMR studies on substituted oxetanes have been published and referred partly in parts IV[4] and V[5] of this series. In addition, Fomichev et al.[6] reconsidered 2-methyloxetane with better resolution in order find out if the ring is puckered or not. The ring puckering vibration in oxetane has been a subject of many studies. Besides infrared techniques[7] also PMR techniques in nematic solvents[8, 9] have been used. Some Russian investigators[10] have analysed the 100 MHz PMR spectrum of 2-phenyloxetane and have been able to reveal the diagonal long range H–H coupling constants in the oxetane ring. They have obtained a value −0.26 Hz for the trans coupling constant and −0.35 Hz for the cis coupling constant. The signs were determined to be negative by tickling experiments.

Recently a 300 MHz PMR study of 2-methyloxetane, 2-phenyloxetane, 2-(4-chlorophenyl)oxetane, and 2-(2-chlorophenyl)oxetane in carbon tetrachloride and d_6-benzene solution has been made[11].

In this work the 100 MHz spectra of the phenyl protons of 2-(2-chlorophenyl)oxetane (I) and 2-(3-chlorophenyl)oxetane (II) have been analysed. Furthermore, the temperature effect on the oxetane and phenyl proton chemical shifts and coupling constants in I, and on the oxetane proton chemical shifts and coupling constants in II have been studied by the 60 MHz spectra.

3. Analyses of the Spectra

Both compounds contain nine hydrogen atoms. The spectra arising from the nine protons are, however, even at the field of 1.4 T, rather clear, except that the resonance region of the phenyl protons in II does not exhibit enough lines for a complete ana-

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lysis. Therefore, in this case the 100 MHz spectrum was first analysed by simulating the spectrum with different values of parameters and then the 60 MHz spectrum was calculated with the best values obtained. Good agreement was established in both spectra. The principles of the subspectral method are described in Part III of this series [12].

3.1. *Spectra of the Phenyl Protons*

The spectrum of the phenyl protons in I was treated as an ABCDX system, where X refers to the methine proton in the oxetane ring. Since the proton X produces a "triplet" with rather broad components, the transition frequencies belonging to X were excluded from the iteration. Consequently, the coupling constants J_{iX} (i = A, B, C, D) were determined by the transitions dominated by the nuclei i. The RMS errors illustrating the fits varied from 0.080 Hz to 0.041 Hz, the number of observations being 54 to 48 in the case of I at different temperatures.

When analysing the spectrum of II it appeared that the phenyl protons form an AA′BCX spin system together with the methine proton X. In addition, the protons A and A′ are strongly coupled to B (J_{AB} and $J_{A'B}$ are both about 8 Hz), the chemical shift difference $\nu_B - \nu_{A,A'}$ being about 4.4 Hz. For these reasons and the fact that also in this case the X transitions could not be used, the coupling constants were not obtained with very good accuracy (see Table 1), though the difference between the observed and calculated transition frequencies is less than 0.1 Hz for all lines. From the 60 MHz spectrum of the phenyl protons of II only a few lines from the AA′B part can be resolved, and thus they do not give enough equations for a complete analysis.

Table 1. Chemical shifts [a] and coupling constants (in Hz) of the phenyl protons in 2-(2-chlorophenyl)oxetane (I) and 2-(3-chlorophenyl)oxetane (II) analysed from the 100 MHz spectra.

	(I) [b]		(II) [c]
ν_3	723.34 ± 0.02	ν_2	733.83 ± 0.05
ν_4	713.42 ± 0.01	ν_4	717.55 ± 0.05
ν_5	725.76 ± 0.01	ν_5	721.93 ± 0.05
ν_6	768.62 ± 0.01	ν_6	717.55 ± 0.05
J_{34}	7.99 ± 0.02	J_{24}	2.05 ± 0.05
J_{35}	1.21 ± 0.01	J_{26}	1.72 ± 0.06
J_{36}	0.35 ± 0.02	J_{25}	0.42 ± 0.06
J_{37}	0.12 ± 0.02	J_{27}	−0.68 ± 0.05
J_{45}	7.41 ± 0.03	J_{45}	7.9 ± 0.2
J_{46}	1.73 ± 0.02		—
J_{47}	−0.63 ± 0.02	J_{47}	−0.36 ± 0.08
J_{56}	7.71 ± 0.01	J_{56}	8.1 ± 0.2
J_{57}	0.49 ± 0.02	J_{57}	0.37 ± 0.04
J_{67}	−0.88 ± 0.01	J_{67}	−0.76 ± 0.10

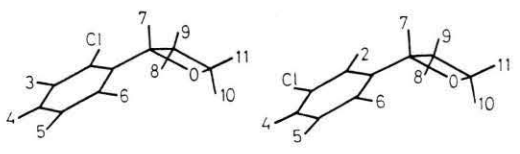
[a] In Hz relative to internal TMS.

[b] Error limits given by LAOCN3.

[c] Error limits have been estimated by studying the sensitivity of the spectrum to each parameter.

3.2. *Spectra of the Oxetane Protons*

In both cases the spectral parts of the five oxetane protons can be analysed as ABCDE systems, but the transitions arising mainly from the methine nucleus E (nucleus X in the phenyl spin system) could not even now be included in the calculations. For the reasons given above the coupling constants between the methine proton and the other protons in the oxetane or the phenyl ring cannot be determined as accurately as the other ones. In addition, the chemical shift of the methine proton (E) could not be obtained from the analysis, but it was measured from the mid point of the central peak of the triplet. Labelling of the protons is as given in Figure 1.



(I) (II)

Fig. 1. Labelling of the protons in 2-(2-chlorophenyl)oxetane I and 2-(3-chlorophenyl)oxetane II.

4. Results

4.1. *100 MHz Spectra*

The magnetic parameters obtained from the analyses of the 100 MHz spectra at room temperature are given in Table 1. The error limits for I are as given by LAOCN3, while the ones for II have been estimated by studying the effect of each parameter on the calculated frequency values. The error limits for II are greater than those for I for the reasons described in the previous chapter.

Despite of the relatively great errors some significant differences or equalities between the corresponding values of I and II can be pointed out. Firstly, the resonance region of I is much wider than that of II. For example, the proton 6 resonates at a field about 51 Hz lower in I than in II. Secondly, there exist some interesting changes in the proton-proton coupling constants. One such change can be found in the meta coupling constants; in I $J_{46} = 1.73$ Hz (the corresponding value in II is not observable) and $J_{35} = 1.21$ Hz while in II $J_{26} = 1.72$ Hz and $J_{24} = 2.05$ Hz. Also the ortho coupling constants are in II somewhat greater than in I. On the other hand, the para coupling constants, J_{36} in I and J_{25} in II, are almost equal.

The long range coupling constants between the methine proton in the oxetane ring and the phenyl protons also seem to depend on the position of the chlorine substituent. A common feature for these coupling constants is that in I they are greater by their absolute values than in II. Most clearly this comes out in J_{47} over six bonds: in I the value is -0.63 Hz, while in II it is only -0.36 Hz. The signs of these coupling constants have been determined with the aid of the spectrum of 2-(2,4-dichlorophenyl)oxetane[5] and by the INDO-FPT calculations[13].

4.2. 60 MHz Spectra

4.2.1. Temperature Dependence of the Proton Chemical Shifts

Chemical shifts for the oxetane protons are collected in Tables 2 and 3, and illustrated graphically in Figure 2. Values at extreme temperatures deviate typically by 1 – 2 Hz in I, while in II the corresponding changes are only of the order of 0.5 – 1 Hz. The temperature coefficients seem in general to be of the same sign, the behaviour of ν_7 of II forming the only exception from this rule.

A noteworthy fact is that the resonances of the oxetane protons 7 and 8 in I which lie closest to the phenyl ring, and accordingly the resonance of the proton 8 in II move to lower applied fields, and the resonances of the other oxetane protons to higher applied fields with increasing temperature. A very similar behaviour is seen in Fig. 3 where the chemical shifts of the phenyl protons in I have been plotted (see also Table 4). In seeking an explanation for these observations one notes that in the equilibrium conformation where the oxygen atom lies fairly close to the plane of the phenyl ring[13], the protons 7 and 8 are also situated closest to the chlorine substituents. Thus it may be imagined as one possibility that the observed changes are related to the rotation (or vibration) about the C – C bond between the rings.

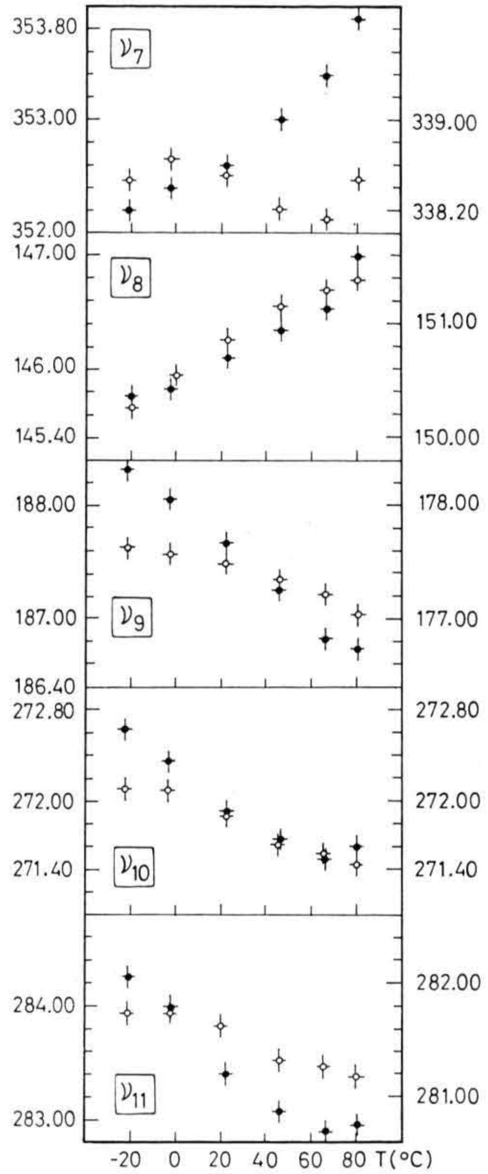


Fig. 2. Chemical shifts (in Hz) of the oxetane protons in 2-(2-chlorophenyl)oxetane I (blacked circles) and in 2-(3-chlorophenyl)oxetane II (open circles) at various temperatures. Ordinate at the left for I and at the right for II.

4.2.2. Temperature Dependence of the Coupling Constants

As it can be found in Tables 2 and 3 the effect of temperature on the coupling constants between the oxetane protons is not very noticeable although some tendency exists. In both cases the sum $J_{78} + J_{79}$ seems to decrease by about 0.15 Hz when the temperature increases from -21 °C to $+80$ °C. Both

Table 2. Proton chemical shifts of the oxetane part (in Hz relative to internal TMS) and proton-proton coupling constants of 2-(2-chlorophenyl)oxetane, (I), analysed from the 60 MHz spectra.

Temperature	+80 °C	+66 °C	+46 °C	+22 °C	−3 °C	−21 °C
ν_7 [a]	353.88	353.42	352.02	352.59	352.40	352.23
ν_8	146.98 ± 0.02	146.54 ± 0.01	146.34 ± 0.01	146.10 ± 0.01	145.82 ± 0.01	145.78 ± 0.01
ν_9	186.76 ± 0.02	186.81 ± 0.01	187.14 ± 0.01	187.67 ± 0.01	188.05 ± 0.01	188.35 ± 0.01
ν_{10}	271.61 ± 0.02	271.50 ± 0.02	271.64 ± 0.02	271.88 ± 0.02	272.34 ± 0.01	272.63 ± 0.01
ν_{11}	282.96 ± 0.02	282.89 ± 0.02	283.08 ± 0.02	283.38 ± 0.02	283.97 ± 0.02	284.27 ± 0.02
J_{79}	6.96 ± 0.03	6.93 ± 0.03	6.94 ± 0.02	6.97 ± 0.02	6.94 ± 0.02	6.98 ± 0.02
$J_{7,10}$	8.08 ± 0.03	8.11 ± 0.03	8.15 ± 0.02	8.17 ± 0.02	8.24 ± 0.02	8.23 ± 0.02
J_{78}	−0.03 ± 0.04	−0.03 ± 0.03	−0.04 ± 0.03	−0.03 ± 0.03	−0.03 ± 0.02	−0.03 ± 0.02
$J_{7,11}$	−0.01 ± 0.04	−0.03 ± 0.04	−0.04 ± 0.03	−0.03 ± 0.03	−0.03 ± 0.03	−0.03 ± 0.03
J_{89}	−10.98 ± 0.02	−10.96 ± 0.02	−10.99 ± 0.02	−10.99 ± 0.02	−11.02 ± 0.01	−11.03 ± 0.01
$J_{8,10}$	9.02 ± 0.03	9.02 ± 0.03	9.04 ± 0.02	9.08 ± 0.02	9.10 ± 0.02	9.14 ± 0.02
$J_{8,11}$	7.63 ± 0.03	7.47 ± 0.02	7.47 ± 0.02	7.47 ± 0.02	7.39 ± 0.02	7.43 ± 0.02
$J_{9,10}$	5.97 ± 0.03	6.00 ± 0.02	6.03 ± 0.02	6.06 ± 0.02	6.07 ± 0.02	6.08 ± 0.02
$J_{9,11}$	8.12 ± 0.03	8.19 ± 0.02	8.21 ± 0.02	8.24 ± 0.02	8.25 ± 0.02	8.25 ± 0.02
$J_{10,11}$	−5.75 ± 0.03	−5.87 ± 0.03	−5.89 ± 0.02	−5.91 ± 0.02	−5.88 ± 0.02	−5.87 ± 0.02

[a] Measured from the center of the triplet. Errors are in each case of the order of ± 0.15 Hz.

Table 3. Proton chemical shifts of the oxetane part (in Hz relative to internal TMS) and proton-proton coupling constants of 2-(3-chlorophenyl)oxetane, II, analysed from the 60 MHz spectra.

Temperature	+80 °C	+66 °C	+46 °C	+22 °C	−3 °C	−21 °C
ν_7 [1]	338.46	338.13	338.22	338.51	338.64	338.46
ν_8	151.40 ± 0.01	151.28 ± 0.01	151.18 ± 0.01	150.89 ± 0.01	150.58 ± 0.01	150.27 ± 0.01
ν_9	177.05 ± 0.01	177.22 ± 0.01	177.38 ± 0.01	177.50 ± 0.01	177.59 ± 0.01	177.63 ± 0.01
ν_{10}	271.45 ± 0.02	271.58 ± 0.01	271.62 ± 0.01	271.86 ± 0.01	272.10 ± 0.01	272.13 ± 0.02
ν_{11}	281.18 ± 0.02	281.27 ± 0.01	281.33 ± 0.01	281.61 ± 0.01	281.76 ± 0.01	281.75 ± 0.02
J_{78}	6.99 ± 0.02	7.01 ± 0.02	7.06 ± 0.02	7.07 ± 0.02	7.05 ± 0.02	7.09 ± 0.02
J_{79}	8.03 ± 0.02	7.99 ± 0.02	8.00 ± 0.02	8.03 ± 0.02	8.07 ± 0.02	8.08 ± 0.02
$J_{7,10}$	−0.02 ± 0.03	−0.02 ± 0.02	−0.03 ± 0.02	−0.03 ± 0.02	−0.03 ± 0.02	−0.02 ± 0.02
$J_{7,11}$	−0.03 ± 0.03	−0.03 ± 0.02	−0.03 ± 0.02	−0.03 ± 0.02	−0.03 ± 0.02	−0.04 ± 0.02
J_{89}	−10.87 ± 0.02	−10.84 ± 0.01	−10.85 ± 0.01	−10.85 ± 0.02	−10.88 ± 0.01	−10.91 ± 0.02
$J_{8,10}$	9.03 ± 0.02	9.09 ± 0.02	9.11 ± 0.02	9.10 ± 0.02	9.12 ± 0.01	9.19 ± 0.02
$J_{8,11}$	7.65 ± 0.02	7.67 ± 0.01	7.72 ± 0.01	7.71 ± 0.02	7.71 ± 0.01	7.76 ± 0.02
$J_{9,10}$	5.73 ± 0.02	5.67 ± 0.02	5.71 ± 0.02	5.73 ± 0.02	5.74 ± 0.02	5.72 ± 0.02
$J_{9,11}$	8.12 ± 0.02	8.10 ± 0.01	8.15 ± 0.01	8.12 ± 0.02	8.16 ± 0.01	8.20 ± 0.02
$J_{10,11}$	−5.74 ± 0.02	−5.76 ± 0.01	−5.81 ± 0.01	−5.75 ± 0.02	−5.76 ± 0.01	−5.81 ± 0.01

[1] As in Table 2.

Table 4. Proton chemical shifts of the phenyl part (in Hz relative to internal TMS) and proton-proton coupling constants of 2-(2-chlorophenyl)oxetane, I, analysed from the 60 MHz spectra.

Temperature	+80 °C	+66 °C	+46 °C	+22 °C	−3 °C
ν_3	434.11 ± 0.05	433.97 ± 0.04	434.05 ± 0.03	434.44 ± 0.04	434.76 ± 0.03
ν_4	427.96 ± 0.06	427.60 ± 0.04	427.89 ± 0.04	428.55 ± 0.04	429.18 ± 0.09
ν_5	435.20 ± 0.05	435.09 ± 0.03	435.31 ± 0.03	435.72 ± 0.03	436.55 ± 0.03
ν	462.08 ± 0.03	461.61 ± 0.02	461.30 ± 0.02	461.06 ± 0.02	460.77 ± 0.02
J_{34}	7.82 ± 0.06	7.96 ± 0.04	7.92 ± 0.04	8.01 ± 0.05	7.94 ± 0.04
J_{35}	1.25 ± 0.04	1.22 ± 0.03	1.25 ± 0.03	1.26 ± 0.02	1.23 ± 0.02
J_{36}	0.38 ± 0.08	0.39 ± 0.05	0.32 ± 0.05	0.44 ± 0.06	0.45 ± 0.06
J_{37}	−0.01 ± 0.10	0.15 ± 0.06	0.06 ± 0.05	−0.03 ± 0.06	0.15 ± 0.05
J_{45}	7.77 ± 0.07	7.36 ± 0.04	7.42 ± 0.04	7.55 ± 0.05	7.45 ± 0.04
J_{46}	1.73 ± 0.07	1.73 ± 0.05	1.74 ± 0.05	1.67 ± 0.06	1.69 ± 0.05
J_{47}	−0.42 ± 0.10	−0.51 ± 0.07	−0.45 ± 0.07	−0.39 ± 0.06	−0.51 ± 0.07
J_{56}	7.68 ± 0.08	7.74 ± 0.05	7.90 ± 0.05	7.86 ± 0.05	7.79 ± 0.05
J_{57}	0.51 ± 0.09	0.49 ± 0.06	0.38 ± 0.04	0.37 ± 0.06	0.26 ± 0.05
J_{67}	−0.83 ± 0.05	−0.92 ± 0.03	−0.92 ± 0.03	−0.92 ± 0.04	−0.91 ± 0.05

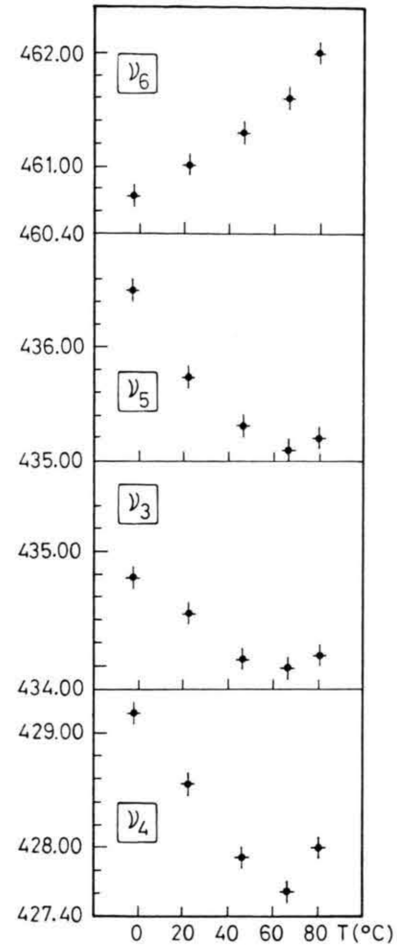


Fig. 3. Chemical shifts (in Hz) of the phenyl protons in 2-(2-chlorophenyl) oxetane at various temperatures.

cis coupling constants, $J_{8,10}$ and $J_{9,11}$, seem to decrease while the trans coupling constant, $J_{8,11}$ seems to increase and the other, $J_{9,10}$, to decrease slightly when the temperature is increased in I. It is rather difficult to interprete these results, but perhaps the changes could be connected at least partly with the changes in the dihedral angles of the H – C – C – H fragments [6].

As it was stated earlier in this paper, the spectral part of the phenyl protons in II consists of only a few resolvable lines at 60 MHz and thus does not give enough information for determining all the parameters. Consequently, only the coupling constants of I could be analysed as a function of temperature. The results in the temperature range from – 3 °C to + 80 °C are listed in Table 4. The error limits are rather large, larger than the errors for the oxetane proton coupling constants, and thus no definite conclusions can be drawn. However, the coupling constant J_{57} from the meta position in the phenyl ring to the oxetane methine proton is monotonically increasing when the temperature rises, while the other long range coupling constants between the rings, J_{37}, J_{47}, and J_{67}, stay almost constant.

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[2] S. Castellano and A. A. Bothner-By, J. Chem. Phys. **41**, 3863 [1964].

[3] Written by the author.

[4] J. Jokisaari, E. Rahkamaa, and H. Malo, Z. Naturforsch. **26 a**, 973 [1971].

[5] J. Jokisaari and E. Rahkamaa, Z. Naturforsch. **28 a**, 30 [1973].

[6] A. A. Fomichev, R. G. Kostyanovskii, I. A. Zon, I. M. Gella, K. S. Zakharov, and V. I. Markov, Dokl. Akad. Nauk. USSR **204**, 644 [1972].

[7] J. Jokisaari and J. Kauppinen, J. Chem. Phys. **59**, 2260 [1973] and references collected.

[8] K. C. Cole and D. F. R. Gilson, J. Chem. Phys. **56**, 4363 [1972].

[9] C. C. Khetrapal, A. Kunwar, and A. Saupe, Mol. Phys. **25**, 1405 [1973].

[10] I. A. Zon, private communication.

[11] K. Pihlaja, J. Jokisaari, M. Anteunis, P. O. I. Virtanen, and H. Ruotsalainen, to be published.

[12] J. Jokisaari, Z. Naturforsch. **26 a**, 136 [1971].

[13] J. Jokisaari, Z. Naturforsch. **29 a**, 1907 [1974].