Zusammenfassung

Die Analyse des reinen Rotationsspektrums von F_2 ergibt für die Rotationskonstanten B_0 und D_0 Werte, die in ausgezeichneter Übereinstimmung mit den Ergebnissen von EDWARDS und Mitarbeitern[4] sind. Die in unserer Arbeit erreichte, etwas geringere Genauigkeit gegenüber der photographischen Registrierung ist durch die photoelektrische Meßmethode und vor allem durch die geringere Brennweite des Doppelmonochromators bedingt. Die Auswertung des Rotationsschwingungsspektrums bezüglich $\Delta G_{1/2}$ führt zu einer geringen Diskrepanz gegenüber den veröffentlichten Werten, die nicht völlig geklärt ist. In unserem Fall wird der Peak des Q-Zweiges der Grundschwingungsbande gemessen. Photographisch registrierte Spektren beziehen sich auf Kantenmessungen. Eine Berücksichtigung der Kante würde aber hier die Abweichung noch vergrößern. Für die Bestimmung der Anharmonizitätskonstante, für die in der vorliegenden Arbeit erstmals ein experimenteller Wert angegeben wird, ist dies jedoch ohne wesentlichen Einfluß, da sie durch Differenzmessung aus der Hot Band und dem Grundton ermittelt wird. Außerdem wurde die Rotationskonstante B_1 des Schwingungsniveaus $v=1$ bestimmt. Damit werden die Moleküldaten des Grundzustandes von F_2 vervollständigt.

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Studies on the PMR Spectra of Oxetanes

V. 2-(3,4-Dichlorophenyl)oxetane and 2-(2,4-Dichlorophenyl)oxetane

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The 60 MHz proton magnetic resonance spectra of 2-(3,4-dichlorophenyl)oxetane and 2-(2,4-dichlorophenyl)oxetane in 10 mole per cent CCl_4 solution have been analyzed using the sub-spectral method. The proton chemical shifts and the proton-proton couplings have been determined. Some aspects concerning the effects of the 3- and 2-chlorines in the phenyl ring on the magnetic parameters have been put foward.

The proton-proton couplings ${}^4J^{o}$ and ${}^5J^{m}$ from the benzyl proton to the ortho and meta protons in the phenyl ring, respectively, were found to be opposite in sign. Comparing the absolute values of these couplings, it was concluded that the rotation around the Ph-C bond between the phenyl and oxetane rings is more hindered in 2-(2,4-dichlorophenyl)oxetane than in 2-(3,4-dichlorophenyl)oxetane.

Introduction

A short summary of the earlier works on the nuclear magnetic resonance of oxetanes has been given in Part IV[1] of this series. Furthermore, PIHLAJA et al.[2] have published PMR data for 2,4- and 2,3,4-methyl substituted oxetanes.

In the studies carried out in this laboratory on the 2-substituted oxetanes, the 60 MHz spectral parts of the oxetane ring protons of 2-phenyloxetane[3], 2-(4-

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[1] J. JOKISAARI, E. RAHKAMAA, and H. MĄLO, Z. Naturforsch. **26a**, 973 [1971].

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methylphenyl)oxetane, 2-(2,4-dimethylphenyl)oxetane, 2-(2,4,6-trimethylphenyl)oxetane[4] and 2-methyloxetane[5], and the spectral parts of the oxetane and phenyl ring protons of 2-(4-halophenyl)oxetanes[1] have been analyzed.

In the present paper, part V of the series, the proton chemical shifts and the proton-proton couplings of 2-(3,4-dichlorophenyl)oxetane and 2-(2,4-dichlorophenyl)oxetane are reported. The present protons form 8-spin systems, which were treated by the sub-spectral method.

Experimental

The preparation and purification of 2-(3,4-dichlorophenyl)oxetane (I) and 2-(2,4-dichlorophenyl)oxetane (II) have been described elsewhere[6]. Solutions of 10 mole per cent were made of each in carbon tetrachloride (CCl_4), and a small amount of tetramethylsilane (TMS) was added to serve as an internal reference standard.

The spectra have been registered at room temperature with the Varian A60 spectrometer four times to each sweep direction using a sweep width of 100 Hz. Calibration has been carried out as described in part IV[1].

In the iterative calculation processes of the spectral parameters, the averages of three spectra registered to both directions were used as the observed transition frequencies. Taking into account the accuracy of the frequency counter and oscillator on the one hand and the accuracy of spectral measurements on the other, the accuracies of the line positions can be estimated to be 0.1 Hz or better.

Theoretical spectra and spectral parameters have been calculated using the programs ABCDEIT[7], LAOCN 3[8] and SIX[9], and the computers IBM 360/30, IBM 360/50 and UNIVAC 1108.

Spectral Analysis

The oxetane protons, the numbering of which is illustrated in Fig. 1, form an ABCDE spin system in 2-substituted oxetanes and the phenyl protons could be treated separately, if the proton-proton couplings from the 2-substituents to the oxetane ring protons can be neglected. In the cases of this work, however, the couplings between the benzyl proton, proton 1 in the oxetane ring, and the phenyl protons differ significantly from zero relative to other couplings between phenyl and oxetane parts. Due to this, the spectra of the present 8-spin systems have been solved through sub-spectral analyses.

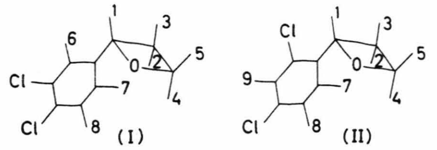

Fig. 1. Numbering of the protons in 2-(3,4-dichlorophenyl)-oxetane and 2-(2,4-dichlorophenyl)oxetane.

The spectral part of the oxetane protons 2,3,4 and 5 has been analyzed as the BCDE part of the ABCDE spin system. The lines of proton 1 have not been used in the iteration, since only a "triplet" of three line groups can be resolved. The fine structure of the components cannot be observed with the resolution of 0.4 Hz of our spectrometer. The "triplet" of the oxetane proton 1 can be calculated as the D part of the ABCDEF spin system, where the ABC part arises from the three phenyl protons and the EF part from the oxetane protons 2 and 3. The influence of the diagonal couplings between the oxetane protons was neglected in the calculation, because they are practically zero.

Table 1. The chemical shifts[a] and couplings of the oxetane protons with the error limits calculated by LAOCN3.

	(I)	(II)	(III)
ν_1	337.15 ± 0.05	348.84 ± 0.05	336.64 ± 0.05
ν_2	150.82 ± 0.01	144.70 ± 0.01	148.67 ± 0.02
ν_3	178.62 ± 0.01	186.98 ± 0.02	174.84 ± 0.01
ν_4	272.31 ± 0.01	271.09 ± 0.01	269.45 ± 0.02
ν_5	282.43 ± 0.01	283.50 ± 0.01	279.85 ± 0.02
J_{12}	7.01 ± 0.02	6.98 ± 0.02	7.11 ± 0.03
J_{13}	7.88 ± 0.02	8.13 ± 0.02	7.88 ± 0.03
J_{14}	—0.01 ± 0.02	0.04 ± 0.03	—0.04 ± 0.03
J_{15}	—0.08 ± 0.02	—0.04 ± 0.03	—0.16 ± 0.03
J_{23}	—10.90 ± 0.01	—11.03 ± 0.01	—10.84 ± 0.02
J_{24}	9.15 ± 0.02	9.06 ± 0.02	9.11 ± 0.02
J_{25}	7.70 ± 0.02	7.47 ± 0.01	7.82 ± 0.02
J_{34}	5.75 ± 0.02	6.08 ± 0.01	5.67 ± 0.02
J_{35}	8.26 ± 0.02	8.12 ± 0.01	8.06 ± 0.02
J_{45}	—5.82 ± 0.02	—5.78 ± 0.01	—5.75 ± 0.02

a) Chemical shifts are in Hz relative to TMS.

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The proton chemical shifts and the proton-proton couplings produced by the spectral analysis for (I) and (II) are presented in Table 1. The agreements of the theoretical and the measured line positions can be described by the RMS errors, which were 0.053 Hz and 0.045 Hz, the number of lines being 63 and 62 for (I) and (II), respectively. From Figs. 2 and 3 it can be seen that the calculated relative intensities also correspond to the observed intensities. When determining the couplings J_{1i} ($i = 2, \ldots, 9$), no frequencies of proton 1 were included in the calculations. Therefore the error limits that are given in Tables 1 and 3 for these couplings are probably too small.

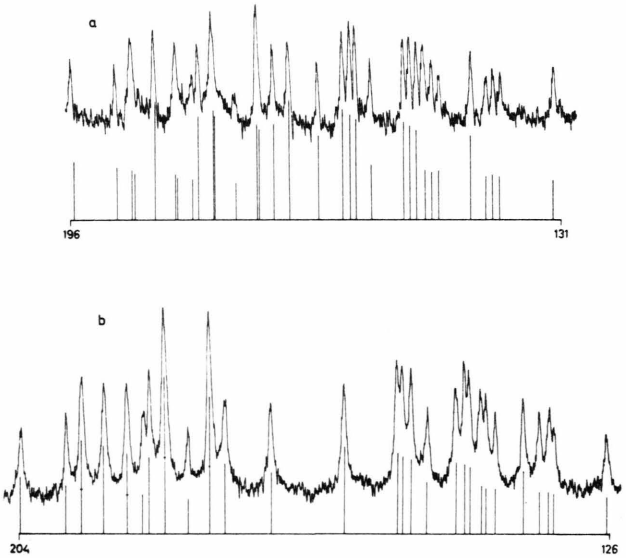

Fig. 2. Spectral part of the oxetane protons 2 and 3
a) in 2-(3,4-dichlorophenyl)oxetane and
b) in 2-(2,4-dichlorophenyl)oxetane.

The phenyl protons have been calculated as the ABC part of the ABCD system. The assignments of the proton resonances are based on the magnitudes of the ortho, meta and para couplings of the substituted benzenes, since it is commonly known that $J^o > J^m > J^p$.

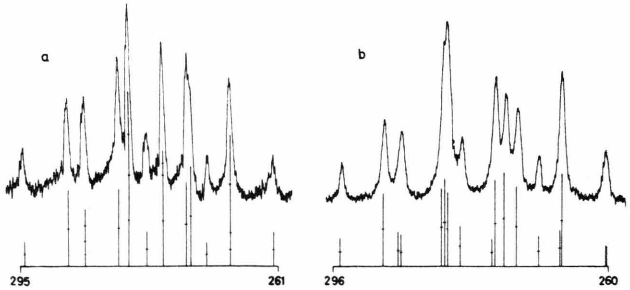

Fig. 3. Spectral part of the oxetane protons 4 and 5
a) in 2-(3,4-dichlorophenyl)oxetane and
b) in 2-(2,4-dichlorophenyl)oxetane.

The couplings of the phenyl protons to the other oxetane protons, except to the benzyl proton, were assumed to be of minor importance. The initial guess values for the nonzero couplings were the absolute values measured roughly from the spectra. In the spectra, 17 lines were assigned for (I) and 21 lines for (II). From the iterations with these numbers of observations resulted the RMS errors of 0.012 Hz and 0.054 Hz, respectively. Tables 2 and 3 contain the parameters giving the best fits between observed and calculated spectra illustrated in Figs. 5 and 6. The good agreements which can be seen in these figures support the assumption made above that only the couplings from the phenyl protons to the benzyl proton affect the observed spectrum.

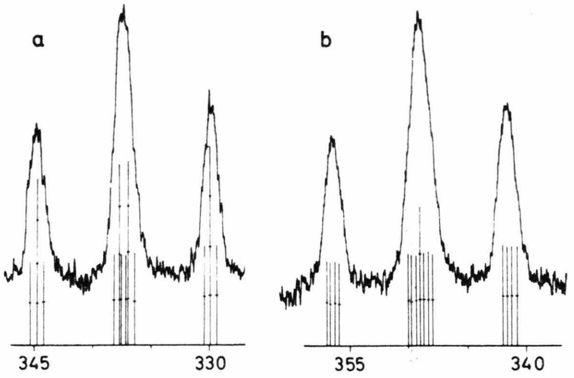

Fig. 4. Spectral part of the benzyl proton, proton 1,
a) in 2-(3,4-dichlorophenyl)oxetane and
b) in 2-(2,4-dichlorophenyl)oxetane.

Table 2. The chemical shifts and couplings of the phenyl protons.

	(I)		(II)
ν_6	445.82 ± 0.02	ν_7	458.05 ± 0.02
ν_7	428.69 ± 0.02	ν_8	436.02 ± 0.03
ν_8	442.09 ± 0.02	ν_9	437.45 ± 0.03
J^o_{78}	8.27 ± 0.02	J^o_{78}	8.22 ± 0.05
J^m_{67}	2.00 ± 0.02	J^m_{89}	1.92 ± 0.03
J^p_{68}	0.43 ± 0.02	J^p_{79}	0.53 ± 0.05

Table 3. The couplings between the benzyl proton and the phenyl protons.

	(I)		(II)
J_{16}	±0.59 ± 0.02	J_{17}	±0.81 ± 0.04
J_{17}	±0.63 ± 0.02	J_{13}	± ±
J_{18}	∓0.08 ± 0.02	J_{18}	∓0.47 ± 0.03
J_{12}	∓ ∓	J_{19}	∓0.08 ± 0.04

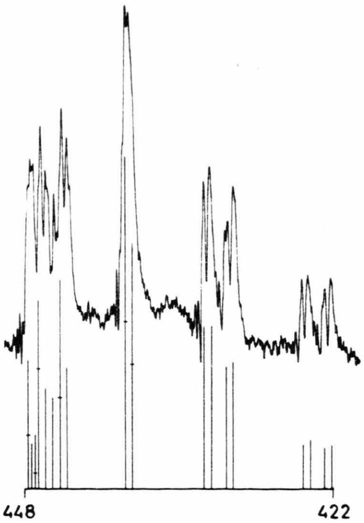

Fig. 5. Spectral part of the phenyl protons in 2-(3,4-dichlorophenyl)oxetane.

Discussion

The oxetane proton chemical shifts and couplings have been listed in Table 1, where, furthermore, the results of the analysis of 2-(4-chlorophenyl)oxetane (III) are given for comparison.

It can be seen that disregarding ν_4 the ortho positioned chlorine causes significantly greater changes in the chemical shifts than the meta positioned chlorine.

The differences in the chemical shifts of (I) and (II) when compared with the corresponding values of trimethylene oxide[10] are probably due mainly to the ring current effect of the substituent, whereas phenomena arising from chlorines are responsible for the different values in the molecules (I) and (II). Differences in ring current and inductive effects, different magnetic anisotropy effects from the ortho and meta chlorines, and deformation of the oxetane ring are probably acting. In addition, the ortho chlorine in (II) probably causes greater hindrance to the rotation around the Ph-C bond between the rings than does the meta chlorine in (I). Quantitative influences of these factors are very difficult to estimate.

Among the couplings between the oxetane protons, the geminal coupling J_{23} and the vicinal trans-couplings J_{25} and J_{34} have undergone greatest changes. The other geminal coupling J_{45} is in all substances practically the same. The diagonal couplings J_{14} and J_{15} are small and they need not necessarily differ from zero having no effects on the spectrum.

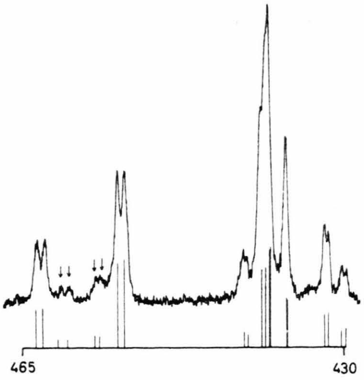

Fig. 6. Spectral part of the phenyl protons in 2-(2,4-dichlorophenyl)oxetane. The combination peaks, which were used in determining the signs of the couplings ${}^4J^{m}$ and ${}^5J^{o}$, have been marked by arrows.

The different values of the couplings can be at least partly related to the deformation of the oxetane ring. For instance SAMITOV et al.[11] have calculated for some methyl substituted oxetanes structures where the rings are 25—30 degrees off the average plane.

The phenyl proton chemical shifts and couplings are presented in Table 2. The couplings between the phenyl and oxetane protons are given in Table 3. The values of the ortho, meta and para couplings in the phenyl ring are close to the corresponding values measured by DISCHLER[12] for 1,2,4-trichlorobenzene. When comparing these values in (I) and (II), one must take into account that the spectrum of (II) appeared to be very insensitive to the changes in the para coupling J^{p}_{79}, where the difference is 0.1 Hz.

As it was pointed out earlier, the determination of the couplings J_{1i} ($i = 2, \ldots, 9$) has been based solely on the analysis of the spectral part of the phenyl protons. Equally good agreements can be reached with two combinations of the couplings J_{1i} ($i = 6, \ldots, 9$) (cf. Table 3). The iterative analysis of the spectrum of molecule (I) produced for ${}^5J^{m}_{18}$ a sign opposite to ${}^4J^{o}_{16}$.

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and $^4J^{\rm o}_{17}$. The opposite signs of $^4J^{\rm o}_{17}$ and $^5J^{\rm m}_{18}$ in (II) can be determined by the low-intensity combination lines in the region 456.7—461.0 Hz from internal TMS (see Figure 6).

In several 4-spin systems it is possible to deduce the relative signs of all the six couplings by comparing the observed and calculated intensities [13]. Such a method cannot be applied in the present case, since a change of the signs of the couplings J_{1i} ($i = 6, \ldots, 9$) does not cause any observable changes in intensities. Furthermore, the lines produced by the benzyl proton cannot be used. The reason for this is that no individual lines can be observed from the components of the "triplet" with the resolution of 0.4 Hz. Nor do the double resonance methods [14] provide any help, for the lines of the ABC sub-spectra which correspond to the spin states $+1/2$ and $-1/2$ are positioned fully symmetrically to the change of the sign.

In substituted benzaldehydes [15–17] and in 2-fluoro-4-chloro-5-nitrotoluene [18] it has been observed, using double resonance, that the couplings from the CHO proton and the CH_3 protons to the ortho proton in the ring are negative and those to the meta proton positive. In Table 3 both combinations are given, because it has not been possible in this case to show which one is correct.

The couplings $^4J^{\rm o}_{16}$ and $^4J^{\rm o}_{17}$ in (I) are equal in the error limits and less by 0.2 Hz than $^4J^{\rm o}_{17}$ in (II). In the latter molecule the couplings $^5J^{\rm m}_{18}$ and $^5J^{\rm m}_{19}$ to the meta positions in the phenyl ring are clearly different from each other. It was earlier reported that the corresponding long rang couplings $^5J^{\rm m}$ are zero in the error limits in 2-(4-halophenyl)oxetanes. The absolute values of the couplings from the phenyl protons 7 and 8 lying at the same side of the Ph-C bond to the benzyl proton are greater in (II) than in (I). These observations suggest the possibility that the rotation around the Ph-C bond is more hindered in (II) than in (I).

Both of the molecules studied in this work have shown that $|^4J^{\rm o}| > |^5J^{\rm m}|$. The same order has been observed in 2-fluoro-4-chloro-5-nitrotoluene [18] in the couplings from the methyl protons to the ring protons, while in many substituted benzaldehydes [16–18] the situation is converse.

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