Studies on the PMR Spectra of Oxetanes

II. 2-(4-Methylphenyl) oxetane, 2-(2,4-Dimethylphenyl) oxetane and 2-(2,4,6-Trimethylphenyl) oxetane

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The oxetane parts of 2-(4-methylphenyl) oxetane, 2-(2,4-dimethylphenyl) oxetane and 2-(2,4,6-trimethylphenyl) oxetane have been analysed as the ABCDE spin systems from the 60 MHz PMR spectra. The chemical shifts and the proton-proton couplings of the protons in the oxetane rings have been solved through iterative calculations. The possible phenomena which may affect the chemical shifts and couplings have been investigated. One of the most dominating factor seems to be the non-planarity of the oxetane ring. The ring current effects of the 2-substituents and the field effects of the methyl groups shift the resonances of the oxetane ring protons.

In 1958 the 25 MHz PMR spectrum of oxetane was published, but only the proton chemical shifts were reported[1]. At the present time also the proton-proton couplings are known[2,3], but there exist rather large deviations and wide error limits in the reported results. This is due to the fact that the analyses of symmetrical six-spin systems A_4B_2 (or four-spin systems A_2B_2) are extremely difficult because of overlapping lines. Often sums of some couplings only can be evaluated.

Difficulties, which arise from the symmetry properties of the molecule do not appear in the 2-substituted oxetanes. The unsymmetrical 2-substitution leads either through space or through bonds to different shieldings and consequently, to different chemical shifts of the protons in the oxetane ring[4,5]. We have found that also the couplings between the protons in the oxetane ring change when one of the 2-protons is substituted.

As a part from a more extensive study the analyses of the oxetane rings in 2-(4-methylphenyl)-oxetane, 2-(2,4-dimethylphenyl)oxetane and 2-(2,4,6-trimethylphenyl) oxetane have been carried out as the ABCDE spin systems from the 60 MHz proton magnetic resonance spectra. The numbering of the protons in question has been illustrated in Fig. 1. The assignment of the protons has been based on studying the shielding effects of different substituents[4,5]. The observed and calculated spectra have been shown in Figs. 2, 3 and 4.

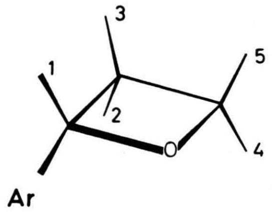

Fig. 1. Numbering of the protons.

Because the double resonance experiments did not indicate any observable couplings between the protons of the phenyl and oxetane rings, it was possible to treat the oxetane rings as the ABCDE spin systems. However, the methyl substituents in the phenyl ring disturbed the spectra, because the signals of the protons 2 and 3 were partly overlapped by the lines of the methyl protons at 60 MHz. Consequently, we were not able to include all the lines belonging to the protons 2 and 3 to the iterative calculations of the spectral parameters.

Experimental

The compounds have been synthetized and purified using the methods described elsewhere[6].

Solutions of 10 mol per cent in CCl_4 were prepared by weighing the compounds directly to NMR tubes. A

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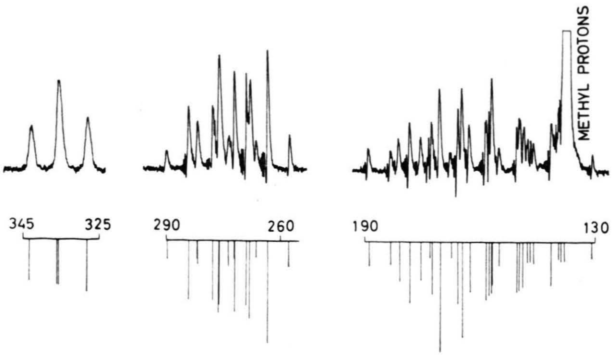

Fig. 2. Observed and calculated spectra of 2-(4-methylphenyl)-oxetane.

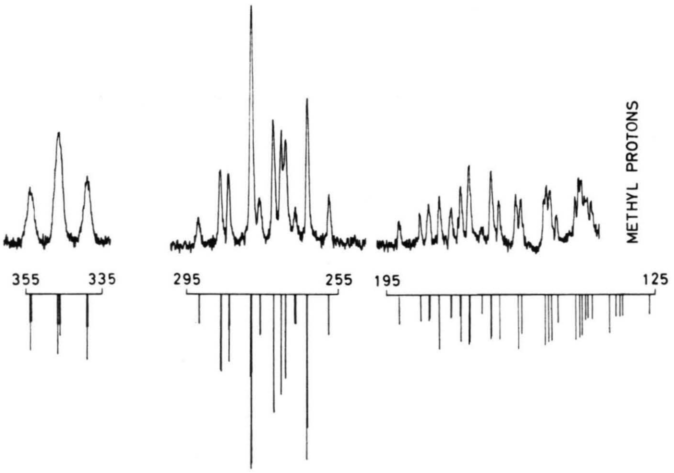

Fig. 3. Observed and calculated spectra of 2-(2,4-dimethylphenyl) oxetane.

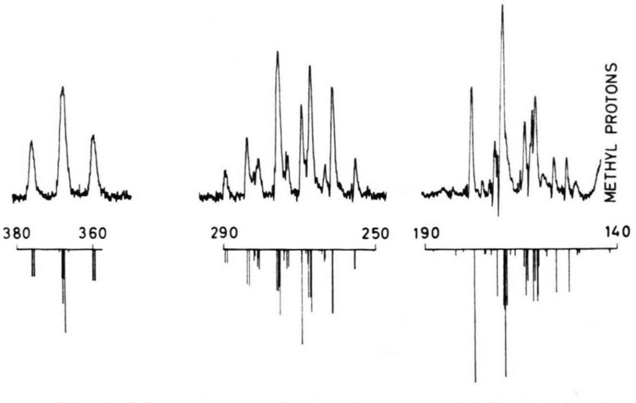

Fig. 4. Observed and calculated spectra of 2-(2,4,6-trimethylphenyl) oxetane.

small amount of TMS was added to serve as an internal standard. The spectra were recorded three times in both sweep directions on a Varian A 60 spectrometer, and calibrated by the normal sideband technique using a Krohn-Hite 4100 pushbutton oscillator, which was constantly monitored by an Advance TC 9 timer counter. The mean values of the six measurements were taken to the iterative processes. The double resonance experiments were performed by a Varian V-6058 spin decoupler.

The proton chemical shifts and proton-proton couplings as well as the transition frequencies and the relative intensities were calculated by the ABCDEIT program[7]. This program has been written especially for the IBM 360/30 computer.

The spectral parameters were estimated to be accurate to ± 0.1 Hz or better.

Results and Discussion

Before the computation of the final parameters was started the approximate chemical shifts were measured and the couplings of 2-phenyloxetane[4] were employed as the first guess values. Using these parameters the calculated spectra were computed. On the basis of these spectra we were able to identify some of the measured lines. Thereafter the parameters could be corrected and the number of identi-

	2-phenyloxetane	2-(4-methylphenyl)-oxetane	2-(2,4-dimethylphenyl)-oxetane	2-(2,4,6-trimethyl-phenyl) oxetane
ν_1	347.61	335.60	346.17	367.50
ν_2	157.97	149.97	144.80	163.17
ν_3	178.73	172.00	175.25	168.97
ν_4	277.40	268.38	268.11	265.76
ν_5	287.36	277.95	279.87	277.45
J_{12}	7.31	7.17	7.07	7.86
J_{13}	7.79	7.98	7.90	8.04
J_{14} [a]	−0.02	−0.03	0.16	−0.20
J_{15} [a]	−0.03	−0.03	0.08	0.52
J_{23}	−10.91	−10.76	−10.42	−10.74
J_{24}	9.15	9.12	9.07	9.32
J_{25}	7.74	7.75	7.61	8.19
J_{34}	5.62	5.62	5.68	4.97
J_{35}	8.19	8.11	8.17	7.86
J_{45}	−5.75	−5.70	−5.71	−5.89

[a] R. LOZACH and B. BRAILLON[2] have obtained for oxetane $J_{14} = (+)0.14$ Hz and $J_{15} = +0.20$ Hz. E. LUSTIG et al.[3] have estimated them to be smaller than 0.3 Hz.

Table 1. Proton chemical shifts in Hz relative to TMS and proton-proton couplings of 2-phenyloxetane[4], 2-(4-methylphenyl) oxetane, 2-(2,4-dimethylphenyl) oxetane, and 2-(2,4,6-trimethylphenyl) oxetane.

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[7] J. JOKISAARI and A. SIIKALUOMA, Suomen Kemistilehti **B 43**, 11 [1970] and J. JOKISAARI, Series of the Department of Physics, University of Oulu, April 1970.

fied lines increased. After some iterations the satisfactory agreements, shown in Figs. 2, 3, and 4, were reached. The analysis of 2-(2,4,6-trimethylphenyl)-oxetane was a little more troublesome, since the spectral part of the protons 2 and 3 contains only a few lines resolvable at 60 MHz.

The calculated chemical shifts and couplings have been shown in Table 1. Also the corresponding values of 2-phenyloxetane have been collected for the sake of comparison in Table 1. In Table 2 the changes of the chemical shifts caused by the methyl groups in the phenyl ring have been given. As the results indicate the para positioned methyl group has shifted the resonances of all the protons to the higher applied magnetic field compared to 2-phenyloxetane. Particularly ν_1 has changed more than ν_4 and ν_5, although the proton 1 on one hand, and the protons 4 and 5 on the other hand, are in the same position to the oxygen atom in the oxetane ring. This kind of shift may be partly explained with hyperconjugation, though it has been recently discussed that hyperconjugation can be treated quantum-mechanically as being a short range effect[8], i. e. it is essentially limited to the neighboring bonds only. The influence of a CH_3-substitution through conjugated chains of bonds on the chemical shift of the proton 1 may be so small that it is mainly masked by influences arising from changes in the anisotropy of susceptibility of the phenyl group on substitution.

i	$\nu_i(A)-\nu_i(B)$	$\nu_i(B)-\nu_i(C)$	$\nu_i(C)-\nu_i(D)$	$\nu_i(A)-\nu_i(D)$
1	12.01	−10.57	−21.33	−19.89
2	8.00	5.17	−18.37	−5.20
3	6.73	−3.25	6.28	9.76
4	9.02	0.27	2.35	11.64
5	9.41	−1.92	2.42	9.91

A = 2-Phenyloxetane
B = 2-(4-Methylphenyl) oxetane
C = 2-(2,4-Dimethylphenyl) oxetane
D = 2-(2,4,6-Trimethylphenyl) oxetane

Table 2. Effects of the CH_3 groups on the chemical shifts of the oxetane protons in consecutive substitutions.

In many theoretical studies it has been suggested that the ring current caused by an external magnetic field has an effect on the chemical shifts of the ring protons in benzene and substituted benzenes[9–12]. This shielding effect can not be neglected when the molecules in question are under investigation. To confirm the existence of the ring current effect the chemical shifts of the methyl protons have been measured relative to TMS. In 2-(4-methylphenyl) oxetane the chemical shift of the para positioned methyl protons has been measured to be $\nu^{\text{para}}_{CH_3} = 138.0$ Hz. In 2-(2,4-dimethylphenyl) oxetane $\nu^{\text{para}}_{CH_3} = 123.7$ Hz and for the ortho positioned methyl protons we have obtained $\nu^{\text{ortho}}_{CH_3} = 135.7$ Hz. The values $\nu^{\text{para}}_{CH_3} = 131.6$ Hz and $\nu^{\text{ortho}}_{CH_3} = 141.7$ Hz have been found in 2-(2,4,6-trimethylphenyl) oxetane. Neither the ortho positioned methyls nor the oxetane ring may have any strong field effects on the chemical shift of p-CH_3 protons because of the long distances. Consequently, it is evident that the variation of $\nu^{\text{para}}_{CH_3}$ arises from the changes in the magnetic field caused by the ring current. The fact that the chemical shift of the p-CH_3 protons is not a linear function of the number of the methyl groups is due to the unsymmetry of the 2,4-dimethylphenyl substituent.

It is evident that the ortho methyl groups have a field effect on the protons in the oxetane ring – especially on the protons 1, 2 and 3 – because of the anisotropy of the methyls. When studying the proton 1 it can be found that the ortho methyl group in 2-(2,4-dimethylphenyl) oxetane has changed the chemical shift ν_1 by 10.57 Hz and the two ortho methyls together in 2-(2,4,6-trimethylphenyl) oxetane by 31.90 Hz to the lower applied field compared to ν_1 in 2-(4-methylphenyl) oxetane. Also it can be found that ν_2 and ν_3 have shifted closer to each other in 2-(2,4,6-trimethylphenyl)-oxetane.

It has been suggested that in 2-(2,4,6-trimethylphenyl) oxetane the greatest factor changing the chemical shifts of the oxetane protons is the hindered rotation of the substituent due to the CH_3-substitution[6]. Evidently this is one of the phenomena, but as the results of this work show the ring current and the field effects must be taken into account.

One more reason to the changes of the chemical shifts and the proton-proton couplings may be the

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distortion of the oxetane ring from its planar structure, which has been found in unsubstituted oxetane [13–17].

In oxetane [2] and 2,2-d_2-oxetane [3] the trans-couplings are equal to each other as well as the cis-couplings and the latter ones are stronger. It can be seen in Table 1 that the corresponding couplings of the aryloxetanes are different in magnitude. The geminal and vicinal couplings are opposite in sign, as can be expected [3]. It has also been found that the geminal couplings in aryloxetanes are 0.2 – 0.7 Hz stronger than in 2,2-d_2-oxetane. The diagonal couplings J_{14} and J_{15} are weak. One interesting result of this work is the stability of the average values of the trans-couplings and those of the cis-couplings, as has been shown in Table 3. We believe that the most important reason to the varying values of the couplings and to the constant averages is the nonplanar structure of the oxetane ring, which is due to the unsymmetrical substitutions.

	Cis-couplings $(J_{24}+J_{35})/2$	Trans-couplings $(J_{25}+J_{34})/2$
Oxetane [2]	8.70	6.60
2,2-d_2-oxetane [3]	8.65 ± 0.39	6.87 ± 0.18
2-Methyloxetane [5]	8.61	6.69
2-Phenyloxetane [4]	8.67	6.68
2-(-Methylphenyl) oxetane	8.62	6.69
2-(2,4-Dimethylphenyl) oxetane	8.62	6.64
2-(2,4,6-Trimethylphenyl)oxetane	8.59	6.58

Table 3. Average values of cis- (J_{24} and J_{35}) and trans- (J_{25} and J_{34}) couplings.

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