Studies on the PMR Spectra of Oxetanes

III. 2-Methyloxetane

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The 60 MHz PMR sub-spectral analysis of 2-methyloxetane (A_3BCDEF spin system) has been carried out approximating some weak couplings to zero. The proton chemical shifts and the proton-proton couplings are reported. Also the proton chemical shifts of symmetrically substituted 2,2-dimethyloxetane and 3,3-dimethyloxetane have been investigated. The anisotropy and inductive effects of the methyl groups, together with the evidently nonplanar structure of the oxetane ring in 2-methyloxetane, affect the spectral parameters of the protons under inspection.

The proton-proton couplings of oxetane [1] have been evaluated from A_4B_2 spectral analysis and from A_2B_2 analysis in 2,2-D_2-oxetane [2]. These studies show that the trans-couplings are weaker than the cis-couplings.

The analysis of the spin systems mentioned above requires a spectrometer with very high resolution. However, there exist difficulties in determining all the couplings with great accuracy. When substituting the other 2-CH_2 proton by some magnetically anisotropic group, like phenyl [3], methyl substituted phenyl [4], or methyl group as is in this work, the resonance frequencies of the oxetane ring protons shift from each other. Consequently, more information for the spectral analysis can be obtained.

The labelling of the protons in 2-methyloxetane is illustrated in Fig. 1. The observed spectrum and the calculated sub-spectra are shown in Fig. 2. The

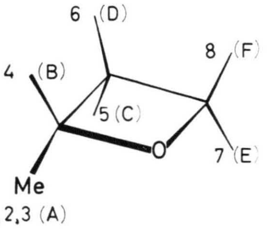

Fig. 1. The labelling of the protons in 2-methyloxetane.

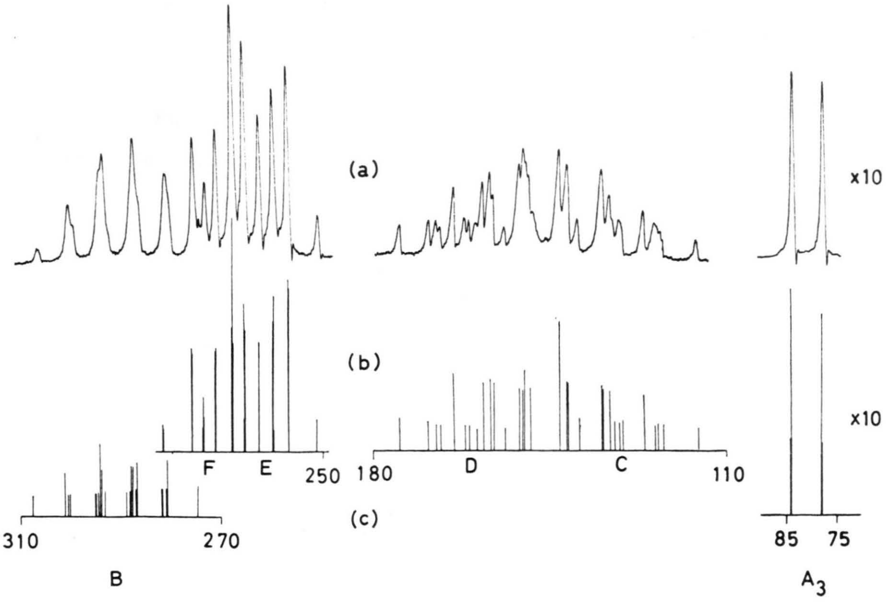

Fig. 2. a) Observed spectrum, b) calculated CDEF part of the BCDEF spin system, c) calculated A_3B part of the A_3BCD spin system.

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[1] R. LOZACH and B. BRAILLON, Bull. Soc. Chim., France **748** [1967].

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assignment of the spectral lines is based on the shielding effects of the oxygen atom and the substituent in the molecule.

Experimental

2-Methyloxetane [5, 6], 2,2-dimethyloxetane [7] and 3,3-dimethyloxetane [8] have been synthetized in the Department of Chemistry, University of Oulu.

Solutions of 10 mole per cent in CCl_4 were prepared. A small amount of TMS was added to serve as an internal reference relative to which all the lines were measured. The spectra were recorded on a Varian A 60 (operating at 60 MHz) spectrometer three times for each sweep direction. Calibration was carried out by the conventional sideband technique using a Krohn-Hite model 4100 oscillator constantly monitored by an Advance TC 9 timer counter.

The proton chemical shifts and proton-proton couplings were computed by the IBM 360/30 using the programs ABCDEIT [9] and SIX, which is a program to compute the theoretical spectrum of a six spin system. Both of the programs have been written in this laboratory.

Sub-spectral Analysis of the A_3BCDEF Spin System in 2-methyloxetane

As the total number of nuclei determining the spectrum increases, the number of transitions increases very rapidly. Consequently, the limited memory capacity of the computer necessitates to apply some additional methods, if possible. In the case of 2-methyloxetane the analysis was carried out by the sub-spectral analysis doing some approximations.

The eight protons of 2-methyloxetane form an A_3BCDEF spin system (Fig. 1). It has been shown that the ${}^4J_{\text{trans}}$-couplings (J_{BE} and J_{BF}) are very weak ones [1, 3, 4]. In this work it has been supposed that

$$\text{(i)} \qquad J_{\text{BE}} = J_{\text{BF}} = 0 \,.$$

From the absorption lines of the methyl group it can be seen that the only significant couplings from the methyl protons are those to the B proton. Consequently, it can be written to a good approximation

$$\text{(ii)} \qquad J_{\text{AC}} = J_{\text{AD}} = J_{\text{AE}} = J_{\text{AF}} = 0 \,.$$

Starting from the common Hamiltonian

$$H = \sum_i \nu_i I_z(i) + \sum_{i<j} \sum J_{ij} \bar{I}(i) \cdot \bar{I}(j) , \qquad (1)$$

and taking into account the equalities (i) and (ii) the Hamiltonian H_8 of the A_3BCDEF system is

$$H_8 = \nu_{\text{A}} F_z(A) + \sum_{i=4}^{8} \nu_i I_z(i) + J_{\text{AA}} \sum_{i=1}^{2} \sum_{j=2}^{3} \bar{I}(i) \cdot \bar{I}(j) + J_{\text{AB}} \bar{F}(A) \cdot \bar{I}(B)$$
$$+ \sum_{j=5}^{6} J_{\text{B}j} \bar{I}(B) \cdot \bar{I}(j) + \sum_{i=5}^{7} \sum_{j=6}^{8} J_{ij} \bar{I}(i) \cdot \bar{I}(j) , \qquad (2)$$

where $F_z(A) = \sum_{i=1}^{3} \bar{I}_z(A_i)$ and $\bar{F}(A) = \sum_{i=1}^{3} \bar{I}(A_i)$, and index i is always less than j, and the couplings from all the A protons to the B proton are equal.

Equation (2) may be presented in the form

$$H_8 = [\nu_{\text{A}} F_z(A) + \sum_{i=4}^{8} \nu_i I_z(i) + J_{\text{AA}} \sum_{i=1}^{2} \sum_{j=2}^{3} I_z(i) I_z(j) + J_{\text{AB}} F_z(A) I_z(B)$$
$$+ \sum_{j=5}^{6} J_{\text{B}j} I_z(B) I_z(j) + \sum_{i=5}^{7} \sum_{j=6}^{8} J_{ij} I_z(i) I_z(j)] + \tfrac{1}{2} \{ J_{\text{AA}} \sum_{i=1}^{2} \sum_{j=2}^{3} [\bar{I}_+(i) \cdot \bar{I}_-(j) + \bar{I}_-(i) \cdot \bar{I}_+(j)]$$
$$+ J_{\text{AB}} [\bar{F}_+(A) \cdot \bar{I}_-(B) + \bar{F}_-(A) \cdot \bar{I}_+(B)] + \sum_{j=5}^{6} J_{\text{B}j} [\bar{I}_+(B) \cdot \bar{I}_-(j) + \bar{I}_-(B) \cdot \bar{I}_+(j)] \qquad (3)$$
$$+ \sum_{i=5}^{7} \sum_{j=6}^{8} J_{ij} [\bar{I}_+(i) \cdot \bar{I}_-(j) + \bar{I}_-(i) \cdot \bar{I}_+(j)] \} ,$$

where the first part [ ] produces the diagonal elements and the second part $\frac{1}{2}\{ \; \}$ the off-diagonal elements of the quantum-mechanical Hamilton matrix.

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Further, on the basis of the expressions (i) and (ii), the Hamiltonians H_6 and H_5 can be written for the A_3BCD and BCDEF spin systems, respectively. The labelling of the protons is still the same as in Fig. 1.

$$\begin{aligned} H_6 = {} & [\nu_A F_z(A) + \sum_{i=4}^{6} \nu_i I_z(i) + J_{AA} \sum_{i=1}^{2} \sum_{j=2}^{3} I_z(i)\, I_z(j) + J_{AB} F_z(A)\, I_z(B) \\ & + \sum_{j=5}^{6} J_{Bj} I_z(B)\, I_z(j) + J_{CD} I_z(C)\, I_z(D)] \qquad (4) \\ & + \tfrac{1}{2}\{J_{AA} \sum_{i=1}^{2} \sum_{j=2}^{3} [\bar{I}_+(i) \cdot \bar{I}_-(j) + \bar{I}_-(i) \cdot \bar{I}_+(j)] + J_{AB}[\bar{F}_+(A) \cdot \bar{I}_-(B) + \bar{F}_-(A) \cdot \bar{I}_+(B)] \\ & + \sum_{j=5}^{6} J_{Bj}[\bar{I}_+(B) \cdot \bar{I}_-(j) + \bar{I}_-(B) \cdot \bar{I}_+(j)] + J_{CD}[\bar{I}_+(C) \cdot \bar{I}_-(D) + \bar{I}_-(C) \cdot \bar{I}_+(\mathrm{D})]\}, \end{aligned}$$

$$\begin{aligned} H_5 = {} & [\sum_{i=4}^{8} \nu_i I_z(i) + \sum_{j=5}^{6} J_{Bj} I_z(B)\, I_z(j) + \sum_{i=5}^{7} \sum_{j=6}^{8} J_{ij} I_z(i)\, I_z(j)] \qquad (5) \\ & + \tfrac{1}{2}\{\sum_{i=5}^{6} J_{Bj}[\bar{I}_+(B) \cdot \bar{I}_-(j) + \bar{I}_-(B) \cdot \bar{I}_+(j)] + \sum_{i=5}^{7} \sum_{j=6}^{8} J_{ij}[\bar{I}_+(i) \cdot \bar{I}_-(j) + \bar{I}_-(i) \cdot \bar{I}_+(j)]\}. \end{aligned}$$

Comparing Eqs. (3) and (4), and on the other hand Eqs. (3) and (5) the following equations for H_8 are obtained:

$$H_8 = H_6 + [\sum_{i=7}^{8} \nu_i I_z(i) + \sum_{i=5}^{7} \sum_{j=7}^{8} J_{ij} I_z(i)\, I_z(j)] + \tfrac{1}{2}\{\sum_{i=5}^{7} \sum_{j=7}^{8} J_{ij}[\bar{I}_+(i) \cdot \bar{I}_-(j) + \bar{I}_-(i) \cdot \bar{I}_+(j)]\}, \qquad (6)$$

and

$$\begin{aligned} H_8 = H_5 + {} & [\nu_A F_z(A) + J_{AA} \sum_{i=1}^{2} \sum_{j=2}^{3} I_z(i)\, I_z(j) + J_{AB} F_z(A)\, I_z(B)] \qquad (7) \\ & + \tfrac{1}{2}\{J_{AA} \sum_{i=1}^{2} \sum_{j=2}^{3} [\bar{I}_+(i) \cdot \bar{I}_-(j) + \bar{I}_-(i) \cdot \bar{I}_+(j)] + J_{AB}[\bar{F}_+(A) \cdot \bar{I}_-(B) + \bar{F}_-(A) \cdot \bar{I}_+(B)]\}. \end{aligned}$$

Because the sum terms in Eq. (6) do not affect the A and B transitions it is clear that these transitions are the same when calculated either from the A_3BCDEF or the A_3BCD spin systems. Naturally the corresponding energy eigenvalues are not equal in these systems, but differ from each other by a constant introduced by the second term in Eq. (6). Similarly, according to Eq. (7) the transitions arising from the C, D, E, and F protons are obtained as well from the BCDEF as from the A_3BCDEF spin systems. In Fig. 2 the A_3B part of the A_3BCD spin system and the CDEF part of the BCDEF spin system are shown.

Results and Discussion

In Table 1 the spectral parameters of 2-methyloxetane have been collected. To gain information on the phenomena which affect the chemical shifts and couplings, the chemical shifts of 2,2-dimethyloxetane and 3,3-dimethyloxetane have been measured and are shown in Table 2. The spectrum of 2,2-dimethyloxetane consists of two triplets arising from the 3- and 4-protons and a sharp methyl peak and the one of 3,3-dimethyloxtane of two sharp peaks, one arising from the 2,4-protons and the other from the methyl protons.

Table 1. Proton chemical shifts and proton-proton couplings of 2-methyloxetane in Hz. Chemical shifts are relative to TMS.

ν_B = 290.79	ν_C = 134.22	ν_D = 158.10	ν_E = 262.08	ν_F = 269.66
J_{BC} = 6.86	J_{BD} = 7.43	(J_{BE} = 0.15)	(J_{BF} = −0.23)	
J_{CD} = −10.77	J_{CE} = 8.93	J_{CF} = 7.77		
J_{DE} = 5.61	J_{DF} = 8.30			
J_{EF} = −5.79				
ν_A = 81.00				
J_{AB} = 6.20				

Table 2. Proton chemical shifts (in Hz relative to TMS) of oxetane, 2,2-D_2-oxetane, and methyl substituted oxetanes.

	$\nu_{2,4\text{-}CH_2}$	$\nu_{3\text{-}CH_2}$	ν_{CH_3}
Oxetane [20] (neat)	277.8	157.8	
2,2-D_2-oxetane [2] (neat)	278.4	157.8	
2-Methyloxetane (in CCl_4)	B 290.79	C 134.22	81.00
	E 262.08	D 158.10	
	F 269.66		
2,2-Dimethyloxetane (in CCl_4)	259.5 ± 0.2	140.6 ± 0.2	81.4 ± 0.2
3,3-Dimethyloxetane (in CCl_4)	253.7 ± 0.2	—	76.5 ± 0.2

When studying symmetrically substituted 2,2-dimethyloxetane and 3,3-dimethyloxetane it can be found that in these compounds the methyl groups have caused shifts in the resonance frequencies of the 3- and 4-protons and the 2,4-protons, respectively, to the higher applied field compared to the corresponding chemical shifts in trimethylene oxide and 2,2-D_2-oxetane. In 2-methyloxetane shifts to the higher as well as to the lover applied field have been observed. There are only a few papers published which concern the PMR spectra of substituted oxetanes. However, it can be noted that YATES and SZABO [10] have reported shifts to the same direction for the protons H_A, H_B, and H_X in 3-substituted-oxetan-3-ols (soluted in dimethylsulphoxide) as in this work for the protons E, F, and B in 2-methyloxetane. In both cases the protons are in the same position to the methyl group.

Using the Eq. (9) of APSIMON et al. [11] for the screening effect of a freely rotating methyl group and the molecular dimensions of CHAN et al. [12] shifts to the higher applied field were computed for all the protons in question in all three molecules. However, the change in the anisotropy of the C – H bond, due to the CH_3-substitution, was neglected and the rings were supposed to be of the same shape as in trimethylene oxide.

It is commonly accepted that the methyl groups are electron donors [13]. This has been found to be true in the case where the methyl group is attached to carbon atoms of sp or sp^2 hybridization. However, there are evidences that for sp^3 hybridized carbon atom the situation is no more the same [14, 15], but the methyl group may not affect at all the degree of hybridization or it may be even an electron withdrawing group [14].

The inductive effect of the methyl group is mainly affecting the proton B in 2-methyloxetane, whereas this effect is small on the 3-carbon and practically zero on the 4-carbon, as will be discussed later in this paper. However, in 2,2-dimethyloxetane the change in the chemical shift (relative to unsubstituted oxetane) of the 4-protons is greater than the one of the 3-protons. Accordingly, in 3,3-dimethyloxetane the resonance of the 2,4-protons has shifted about 6.9 Hz more to the higher applied field than the resonance of the 3-protons in 2,2-dimethyloxetane though the situation is geometrically quite symmetric. Taking into account the facts mentioned above it may be concluded that the changes possibly arise from the structural distortions (enhanced rhomboid) in the ring structure due to the CH_3-substitutions.

The ring-puckering vibration in trimethylene oxide has been investigated in several far-infrared and microwave works [12, 16–19]. CHAN et al. [18] found that in this case the ring-puckering mode vould have a rather large amplitude; of the order of 0.06 Å for the ground vibrational state. This corresponds to the dihedral angle of 14° between the C – C – C and C – O – C planes. However, the oxetane ring is planar so that at any instant the displacements

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of the oxygen atom and all the three carbon atoms from this plane are symmetrical[19]. A double minimum ring-puckering potential function with low energy barrier (about 15 cm^{-1}) has also been deduced for oxetane[17–19].

This planar structure of the oxetane ring means that the oxygen atom is symmetrically located to the geminal protons and, consequently, no differences in the shieldings of the geminal protons may appear. However, in 2-methyloxetane the CH_3-substitution may lead to a nonplanar structure of the ring. Therefore the geminal protons may be differently shielded by oxygen, and the differences between the chemical shifts can further be explained. An additional reason to the changes might be the enhanced rhomboid structure of the ring when one or two protons have been substituted by methyl groups.

The proton-proton couplings have been determined for 2-methyloxetane only (Table 1). As it can be found, the cis-couplings are stronger than the trans-couplings and the geminal couplings have an opposite sign to the vicinal couplings.

The geminal couplings $^2J_{\mathrm{HH}}$ have been found to depend on the s-character of the carbon atom and to increase algebraically with the increase of the s-character of the carbon atom[20]. Using the J_{CH} values of LIPPERT and BRIGGE[21] for trimethylene oxide and the equation[22]

$$J_{\mathrm{CH}} = 500\, a_{\mathrm{H}}^2 \tag{8}$$

the approximate s-character a_{H}^2 for the 2,4-carbons is 0.296 and for the 3-carbon 0.275. The magnitudes of these values are in harmony with the values of $J_{44} = -6.02 \pm 0.23$ Hz and $J_{33} = -11.15 \pm 0.25$ Hz found for the geminal couplings in 2,2-D_2-oxetane[2]. In 2-methyloxetane the corresponding couplings are -5.79 Hz and -10.77 Hz (± 0.1 Hz in each case). These are nearly equal to the values of 2,2-D_2-oxetane. It could be concluded that the methyl group affects only slightly the s-character of the 3-carbon and not at all the s-character of the 4-carbon. In all the substituted oxetanes J_{EF} (in this work, J_{45} in the others) is practically independent on the electronegativity of the substituent, but J_{CD} (J_{23} in the other works) varies in the range from -11.15 to -10.42 Hz[2–4]. This may indicate small changes in the dihedral angles, but as it was discussed in the previous chapters, also the puckered conformation of the ring is one possibility.

A noteworthy observation in this work, and in the others[3, 4], is the constancy of the mean values of the trans-couplings, 6.69 Hz, and cis-couplings, 8.61 Hz. Also the cis to trans ratios have been calculated; $J_{\mathrm{BD}} : J_{\mathrm{BC}} = 1.08$, $J_{\mathrm{CE}} : J_{\mathrm{CF}} = 1,15$, and $J_{\mathrm{DF}} : J_{\mathrm{DE}} = 1.48$. According to the $\cos^2 \Phi$ relationship of KARPLUS[23] these may be interpreted by the changes of the dihedral angles *.

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* *Note added in proof.* Recently the 100 MHz PMR spectrum of 2-methyloxetane was published by YU. YU. SAMITOV, A. V. BOGATSKII, and G. A. FILIP, in: Dokl. Akad. Nauk, SSSR, **192**, 138 [1970]; CA **73**, 44755m [1970]. Some of the couplings were reported with the conclusions about the conformation.