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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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PROTON MAGNETIC RESONANCE OF 2,2-DIMETHYLPROPANE-1,3-DIOL SULFITE AND CARBONATE

Proton magnetic resonance is currently being successfully used to study the conformation of cyclic compounds ([1,2]). We have studied the conformation of the cyclic esters of carbonic and sulfurous acids of 2,2-dimethylpropane-1,3-diol. Figure 1 shows the p.m.r. spectra of these compounds, recorded on a YaMR-KGU-1 spectrometer at $\nu = 24.458$ MHz ([3]).

Fig. 1

The structure of the compounds studied at first glance differs only in the replacement of the carbon atom of the carbonyl group by a sulfur atom, and it would seem that the p.m.r. spectra of these two compounds should be close or identical. However, the spectra of the carbonate and the sulfite differ sharply from one another. The spectrum of the carbonate is simple and consists of two peaks with relative integral intensity 2 : 3, corresponding to protons of methylene groups with chemical shift $\tau = 6.13 \pm 0.04$ ppm* and of two methyl groups with chemical shift $\tau = 9.03 \pm 0.04$ ppm. The spectrum of 2,2-dimethylpropane-1,3-diol sulfite consists of a quartet and a doublet with relative intensity 2 : 3. The quartet ($\tau = 5.37; 5.79; 6.55; 7.02$ ppm), centered at $\tau = 6.17$ ppm, corresponds to two methylene groups; the doublet ($\tau = 8.78; 9.15$ ppm), with center at $\tau = 9.03$ ppm, corresponds to two methyl radicals.

The indicated difference in the spectra of the carbonate and the sulfite is well explained by the conformation of the cyclic esters. As is known ([4]), the CO_3 grouping in derivatives of carbonic acid is planar, whereas the SO_3 grouping in derivatives of sulfurous acid has a pyramidal structure ([4,5]). The conformational formulas of the carbonate and sulfite are shown in Fig. 2. As can be seen, owing to the planar structure of the CO_3 group, the transition of one chair form into the other gives an equivalent structure. The frequency of these transitions is evidently sufficiently high to cause averaging of the values chemical shift of the axial and equatorial protons of the methylene groups, as occurs in cyclohexane (6). In the case of the sulfite, the two conformational forms are not equivalent, and the energy of thermal vibration at room temperatures is apparently insufficient to invert the configuration of SO_3, as a result of which a difference arises in the chemical shifts of the axial and equatorial hydrogens of the methylene groups and splitting of the peak of the methylene groups.

The quartet resonance of the protons of the methylene groups is due to the interaction of the axial protons H_A with the equatorial H_B. Thus, we have a simple AB system. The spin Hamiltonian of such a system has been well studied and has the form (7):

$$\mathscr{H} = -\left\{\omega_A I_{AZ} + \omega_B I_{BZ} + J I_{AZ} I_{BZ} + \frac{1}{2} J \left(I_A^+ I_B^- + I_A^- I_B^+\right)\right\},$$

where $J = J_{AB} = J_{BA}$ is the constant of indirect spin-spin coupling of protons A and B. The results of solving the problem for the case when the difference between the chemical shifts of protons A and B is $\delta_{AB} = \tau_A - \tau_B = 1.10$ ppm, and the coupling constant J is equal to 11 Hz, are summarized in Table 1. In it, for comparison, are also given experimental data obtained from the spectrum.

Table 1

Position and intensity of the lines of the quartet of methylene protons at $\delta_{AB} = 1.10 \cdot 10^{-6}$ and $J_{AB} = 11$ Hz

Line position, $\times 10^6$	Line position, $\times 10^6$	Relative line intensity	Relative line intensity
theoretical	experimental ±0.04	theoretical	experimental
$\tau_1 = \frac{1}{2}(\omega_A + \omega_B - J - R) = 6.98$	7.02	$A_1 = 1 - J/R = 1$	1
$\tau_2 = \frac{1}{2}(\omega_A + \omega_B + J - R) = 6.54$	6.55	$A_2 = 1 + J/R = 2.1$	2

* Chemical shifts were determined relative to the peak of tetramethylstannane, which has the value $\tau = 10.00$, and are indicated in millionths of the applied field (ppm). Measurements showed that the values of τ for tetramethylstannane and tetramethylsilane coincide.

Fig. 2

Figure 2: Fig. 2

Line position, $\times 10^6$	Line position, $\times 10^6$	Relative line intensity	Relative line intensity
$\tau_3 = \frac{1}{2}(\omega_A + \omega_B - J + R) = 5.80$	5.79	$A_3 = 1 + J/R = 2.1$	2
$\tau_4 = \frac{1}{2}(\omega_A + \omega_B + J + R) = 5.36$	5.37	$A_4 = 1 - J/R = 1$	1
		$R = \sqrt{J^2 + \delta_{AB}^2}$	

The observed difference in the chemical shifts of the axial and equatorial protons of the methylene groups and the splitting of the peak of the methylene protons of the sulfite can be explained and used for studying the magnetic anisotropy of chemical bonds. Buckingham (8) showed that polar groups of atoms in one part of a molecule, acting on hydrogen atoms in another part of it, change the magnitudes of the chemical shift of protons according to the formula:

$$\Delta\tau_{\text{el}} = -2 \cdot 10^{-12} \cdot E_z - 10^{-18} \cdot E^2, \tag{1}$$

where E_z is the component of the electric field E of the dipole in the direction of the X–H bond. The quantities E and E_z can be determined using the laws of electrostatics, starting from the assumed geometrical structure of the molecules. In the case of the molecule of 2,2-dimethylpropane-1,3-diol sulfite, the bond $\mathrm{S} = \mathrm{O}$ has the greatest electric polarity. It is a $p^2 - pd$ hybrid double bond with a moment corresponding to an increase in negative-

electric charge on the terminal oxygen by the amount $\delta^- = -\frac{1}{3}e$, where e is the electron charge [9], as shown in Fig. 2. In addition, the polarity of the S–O and O–C bonds must be taken into account. The results of such calculations for axial and equatorial protons are given in Table 2. As is seen from Table 2, the action of the dipole moments of the bonds causes the resonance of the axial protons to shift by $0.144 \cdot 10^{-6}$ toward higher fields in comparison with the equatorial protons.

Fig. 2

In the above calculations it was taken into consideration that, because of the symmetrical arrangement of the protons $\mathrm{H_A}$ and $\mathrm{H_B}$ with respect to the adjacent

C–O bond, these protons receive the same shift $\Delta\tau_{\text{el}}$, and only the action on the protons H'_{A} and H'_{B} of the dipole moment of the C–O bond adjacent to the protons H''_{A} and H''_{B} was taken into account. Since the general theoretical expressions for the quantities $\overline{E_z}$ and E^2, entering into formula (1), are very cumbersome, in order to estimate the values of $\Delta\tau_{\text{el}}$ we used the angles found from a geometrical model of the molecule with an accuracy of $+1 \div 2°$. In the calculations the following values were adopted for the dipole moments of the bonds: $p_{\text{S=O}} = 3.0$ D, $p_{\text{S–O}} = 1.0$ D, $p_{\text{C–O}} = 0.86$ D [4].

Table 2

Calculated values of the shifts of the resonance lines of methylene and methyl protons under the action of the electric dipoles of the bonds

Bond	$\Delta\tau_{\text{el}} \cdot 10^6$, protons H_A	$\Delta\tau_{\text{el}} \cdot 10^6$, protons H_B	$\Delta\tau_{\text{el}} \cdot 10^6$, methyl protons, axial	$\Delta\tau_{\text{el}} \cdot 10^6$, methyl protons, equatorial
S=O	−0.104	−0.173	−0.106	−0.071
(C–O)*	–	–	−0.126	−0.136
(S–O)′	+0.195	+0.124	+0.041	+0.027
(S–O)″	−0.025	−0.028	+0.041	+0.027
Total . .	+0.066	−0.078	−0.191	−0.180

* Calculated taking both bonds into account.

Thus, the action of the dipole moments of the bonds shifts the resonance of the axial protons by 0.144 ppm toward higher fields relative to the equatorial protons, while the peaks of the axial methyl protons relative to the equatorial ones are shifted by 0.024 ppm toward lower fields. The remaining part of the chemical shift, equal for the protons H_A and H_B to $\Delta\tau_{\text{an}} = 1.10 - 0.144 = 0.96$ ppm, is due to the magnetic anisotropy of the chemical bonds. The contribution made by the magnetic anisotropy of the bonds to the chemical shifts of the protons can be estimated from the formula

$$\tau_{\text{an}} = \frac{10^{24}}{3NR^3} \sum (1 - 3\cos^2\gamma_i)\chi_{ii}, \qquad (2)$$

where N is Avogadro' s number, χ_{ii} are the components of the magnetic-susceptibility tensor of the bond, and γ_i are the angles formed by the i axis and the line of length R (in Å),

connecting, for example, protons H_A and H_B with the beginning of the axes of the principal susceptibilities.

The magnitude of the magnetic anisotropy of the $S{=}O$ bond can be found from the PMR spectrum of isobutylene sulfite (^{2}) and then the contribution made by the anisotropy of this bond to the chemical shift of the protons H_A and H_B in 2,2-dimethylpropane-1,3-diol sulfite can be calculated. The remaining part of the chemical shift of the protons H_A and H_B, CH_3^3 and CH_3^3, is evidently due to the anisotropy of the S—O and C—O bonds, which can be determined from formula (2). The effect of bonds 1 and 3 on the shift of the protons H_A and H_B is manifested to the same extent, as is the effect of bonds 2 and 4. Therefore the anisotropy of the C—C bonds need not be taken into account. The results of these calculations will be described in detail in another paper.

The absence of splittings of the carbonate lines apparently indicates, as noted above, rapid transitions from one chair form to another. Hence it is clear that investigation of this sample at different temperatures may reveal the presence of such transitions. On the other hand, these lines are relatively broad, and it is possible that the existing multiplet structure of the lines was not resolved because of the insufficient resolving power of the instrument. It is therefore of some interest to study both compounds at resonance frequencies of 40 and 60 MHz and with higher resolution. It is quite possible that this will also clarify the presence or absence of spin-spin interaction of the protons of the methylene and methyl groups.

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