Anomalous Chemical Shifts and the Conformation of Cyclic Esters of Sulfurous and Selenious Acids

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Abstract

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Anomalous Chemical Shifts and the Conformation of Cyclic Esters of Sulfurous and Selenious Acids

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Earlier [1,2], from an analysis of NMR spectra, we showed that molecules of cyclic esters of sulfurous acid do not invert their configuration and, probably, exist in the unexpected preferred conformation II with an axial sulfite oxygen. This conclusion is in contradiction with the recent publication by Lauterbur et al. [3] on the isomerism of pentane-2,4-diol sulfite and with the work [4] on the conformation of 4-tert-

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a $-R_1 = H_x,\ R_2 = H_y$
b $-R_1 = \mathrm{CH_3},\ R_2 = \mathrm{CH_3}$
c $-R_1 = H_x,\ R_2 = Cl$
d $-R_1 = Cl,\ R_2 = H_y$

butylthiane 1-oxides, but agrees with the conclusions of works on the structure of cis- and trans-4-chlorothiane 1-oxides [5], studied by measurement of dipole moments and by dissolution rate, and on the conformation of trimethylene sulfite, studied by IR and NMR spectra [6].

In the present work a complete substantiation of conformation II is given on the basis of an analysis of anomalous chemical shifts. These shifts are revealed, first, from a comparison of the experimental and theoretically calculated NMR spectrum of propane-1,3-diol sulfite (PDS, IIa). Figure 1 gives its NMR spectrum, recorded at frequency $\nu_0 = 60$ MHz; below it is the theoretical spectrum corresponding to a six-spin system of the type A_2B_2XY, where A and B denote, respectively, axial and equatorial protons at atoms C(1) and C(3). The theoretical spectra both for PDS and for PDSe (propane-1,3-diol selenite) coincide with the experimental ones only in the case when the constants $J_{\mathrm{HH}'}$ are chosen in accordance with the graphs of Karplus and Conroy [7], correlating the constants $J_{\mathrm{HH}'}$ with valence (H—C—H′) and dihedral (H—C—C—H′) angles.

Fig. 1. A –NMR spectrum of propane-1,3-diol sulfite at $\nu_0 = 60$ MHz; RYa-2303 spectrometer.
B –theoretical spectrum corresponding to a six-spin system of the type A_2B_2XY, with
$J_{AA'} = 0,\ J_{AB'} = 0,\ J_{BB'} = 0.$

In this case, as is evident from Fig. 1 and from the data of Table 1, the protons of axial hydrogens are less shielded than their geminal equatorial partners. This fact is reflected in Table 1 by the negative sign before $\delta_{BA} = \delta_B - \delta_A$ and $\delta_{XY} = \delta_X - \delta_Y$. The indicated peculiarity of the shifts of H_A and H_B, secondly, finds direct confirmation in the values of the chemical shifts of the protons of pentane-2,4-diol sulfite. Obviously, the meso-symmetric conformer of this compound with two spatially close axial methyl groups is excluded; therefore both hydrogens at

Table 1

Chemical shifts δ and spin-spin coupling constants $J_{\mathrm{HH'}}$ in sulfites and selenites

δ, ppm ($\pm$0.01) and $J_{\mathrm{HH'}}$, Hz ($\pm$0.1 Hz)	Sulfite with H_x, H_y; b.p. 69–69.5°/15	Dimethyl sulfite; b.p. 80°/26	Selenite with H_x, H_y; b.p. 79.2–80°/3, m.p. 88–89°	Dimethyl selenite; b.p. 63°/6, m.p. 84–85°	Chloro sulfite with H_x; m.p. 62°	Chloro sulfite with H_y; m.p. 42°
δ_B^*	$3,72\ (-1,00)$**	$3,29\ (-1,14)$	$3,76\ (-1,08)$	$3,16\ (-1,34)$	$3,75\ (-1,17)$	$3,90\ (-0,71)$
δ_A	$4,73$	$4,43$	$4,84$	$4,50$	$4,94$	$4,61$
δ_X	$1,49\ (-0,72)$	–	$1,41\ (-0,79)$	–	$3,98$	–
δ_Y	$2,21$	–	$2,20$	–	–	$\sim 4,18$
$\delta_e(\mathrm{CH_3})$	–	$0,78\ (-0,39)$	–	$0,68\ (-0,45)$	–	–
$\delta_a(\mathrm{CH_3})$	–	$1,17$	–	$1,13$	–	–
J_{AB}	12	$10,5$	12	$12,0$	$10,8$	~ 10
J_{AY}	12	–	12	–	–	~ 10
J_{AX}	$3,0$	–	$3,0$	–	$\sim 1,3$	–
J_{BY}	$4,56$	–	$4,6$	–	–	$4,3$
J_{BX}	$3,0$	–	$3,0$	–	$\sim 1,3$	–
J_{XY}	14	–	13	–	–	–

* Chemical shifts are given relative to the internal standard TMS, in ppm; the shift of TMS, in accordance with the recommendation of the IUPAC Commission on Molecular Spectroscopy, is taken as $\delta_{\mathrm{TMS}} = 0$; the samples were 30–40% (wt.) solutions in $\mathrm{CCl_4}$.

** The nonequivalence of the corresponding protons is indicated in parentheses. In sulfites IIb and in selenite IIb the protons H_A (ax.) and H_B (eq.) form a nuclear spin system of the AB type, the resonance lines of which form a quadruplet (two doublets). Therefore the values δ_{BA} were determined from the formula

$$\delta_{BA} = \sqrt{R^2 - J_{AB}^2},$$

Fig. 2. NMR spectra of two isomers of 2-chloropropane-1,3-diol sulfite at $\nu_0 = 60$ MHz and $\nu_0 = 100$ MHz ($JNM = 4H = 100$

Figure 1: Fig. 2. NMR spectra of two isomers of 2-chloropropane-1,3-diol sulfite at $\nu_0 = 60$ MHz and $\nu_0 = 100$ MHz ($JNM = 4H = 100$

where R is the distance between the centers of the AB doublets in the quadruplet.

C(2) and C(4) must be axial. For them, Ref. (^{3}) gives the shift $\delta = 4.98$ ppm, i.e., a value close to $\delta'_A = 4.72$ ppm (PDS), $\delta_A = 4.84$ ppm (PDSe), and $\delta_A = 4.52$ ppm (Ib), which we assigned to axial protons.

Conversely, in cyclohexane, 1,3-dioxanes (^{2}) (methylene protons in positions 4 and 6, but not in position 5), and in certain other analogous compounds, axial protons resonate in stronger magnetic fields than equatorial protons.

Fig. 2. NMR spectra of two isomers of 2-chloropropane-1,3-diol sulfite at $\nu_0 =$ 60 MHz and $\nu_0 = 100$ MHz ($JNM = 4H = 100$)

Let us consider the causes that give rise to the inversion of the chemical shifts of axial and equatorial protons in PDS and PDSe. We believe that inversion of the shifts of the protons at atoms C(1) and C(3) arises only in conformation II, when the semipolar oxygen approaches the axial hydrogens closely, and that the main contribution to the inversion is made by the anisotropy of the diamagnetic susceptibility and the electric fields of the S–O, S=O bonds and of the O and S (or Se) atoms. In the inversion of the shifts of protons Hx and Hy and of the methyl groups at C(2), the main contribution is made by the anisotropy of the lone pair of electrons ($2p_z^2$) of the two ether oxygens.

Allowance for all these effects is possible using the formulas of McConnell and Buckingham–Masher (^{8}). However, it must be taken into account that practical application of these formulas is always accompanied by the assumption of the dipole approximation (^{2}). From this point of view, the use of the nonequivalence of methyl protons is more justified. Quantitative calculations lead to the following equations*:

for 2,2-dimethylpropane-1,3-diol sulfite

$$\delta_{ea}(\mathrm{CH_3}) = K - 0.009 \cdot \Delta\chi_{S=O} - 0.040 \cdot 10^{-6} \quad \text{(conformation I)}, \tag{1}$$

$$\delta_{ea}(\mathrm{CH_3}) = K + 0.008 \cdot \Delta\chi_{S=O} - 0.010 \cdot 10^{-6} \quad \text{(conformation II)};$$

for 2,2-dimethylpropane-1,3-diol selenite

$$\delta_{ea}(\mathrm{CH_3}) = M - 0.012 \cdot \Delta\chi_{Se=O} + 0.044 \cdot 10^{-6} \quad \text{(conformation I)},$$

$$\delta_{ea}(\mathrm{CH_3}) = M + 0.007 \cdot \Delta\chi_{Se=O} + 0.016 \cdot 10^{-6} \quad \text{(conformation II)}, \qquad (2)$$

* The averaging was carried out over six positions of the methyl protons.

where

$$K = 0.102 \cdot \Delta\chi_O + 0.069 \cdot \Delta\chi_{C-H} - 0.017 \cdot \Delta\chi_{S-O} - 0.082 \cdot \Delta\chi_{C-O};$$

$$M = 0.102 \cdot \Delta\chi_O + 0.069 \cdot \Delta\chi_{C-H} - 0.012 \cdot \Delta\chi_{Se-O} - 0.080 \cdot \Delta\chi_{C-O}.$$

To choose a definite conformation from the two possibilities I and II, using the experimental data $\delta_a^S(\mathrm{CH_3}) = 0.39$ ppm and $\delta_{eq}^S(\mathrm{CH_3}) = 0.45$ ppm, from equations (1) and (2) we obtained for conformation II the values:

$$\Delta\chi_{S-O} = 11.4 \cdot 10^{-6}\ \mathrm{cm^3 \cdot mol^{-1}}; \qquad \Delta\chi_{Se-O} = 10.9 \cdot 10^{-6}\ \mathrm{cm^3 \cdot mol^{-1}}.$$

This result is consistent with the assumption that the axial methyl is less shielded than the equatorial one. Under the opposite assumption, and for conformation I, unrealistic quantities are obtained.

The values of the anisotropy of susceptibility $\Delta\chi_{C-O} = 5.2 \cdot 10^{-6}\ \mathrm{cm^3 \cdot mol^{-1}}$ and $\Delta\chi_O(2p_z^2) = 8 \cdot 10^{-6}\ \mathrm{cm^3 \cdot mol^{-1}}$, needed for the estimates, were found by us from an analysis of the NMR spectrum of 5,5-dimethyl-1,3-dioxane (9). The symmetry axis of the lone-pair orbital was chosen perpendicular to the plane in which the C–O–C atoms lie. The value $\Delta\chi_{S=O} = 12.5 \cdot 10^{-6}\ \mathrm{cm^3 \cdot mol^{-1}}$ was estimated by us earlier (1). We estimated the anisotropy of the Se=O bond, $\Delta\chi_{Se=O} = 11.5 \cdot 10^{-6}\ \mathrm{cm^3 \cdot mol^{-1}}$, from the spectrum of tetramethylene selenite, assuming that at room temperature the five-membered ring is on the average planar in time and that, for a $p^2 - pd$ hybrid Se=O bond, $\chi_{xx} \approx \chi_{yy} > \chi_{zz}$. For $\Delta\chi_{C-H}$ the upper limiting value $+1.5 \cdot 10^{-6}\ \mathrm{cm^3 \cdot mol^{-1}}$, theoretically calculated by Tidd (10), was chosen.

The axial position of the S=O group is also retained in cis- and trans-2-chloropropanediol-1,3 sulfites. Fig. 2 gives the NMR spectra of both isomers. From the upper spectrum, corresponding to the isomer with m.p. 62°, it can be seen that the nonequivalence of the protons H_A and H_B is still large, while the proton at C(2) corresponds to a line with $\delta = 3.98$ ppm with a small spin splitting. These data prove that the molecules of the isomer under consideration are in conformation II, and that the hydrogen atom at C(2) is equatorial. A quantitative analysis of the molecule, taking $p_{C-Cl} = 1.9$ D, $R_{C-Cl} = 1.77$ Å and placing the center of group G at the point $R = 1.24$

Å from carbon, shows that the axial C—Cl group does not change the value $\delta_{BA}(H)$ if $\Delta\chi_{C-Cl} = 5.2 \cdot 10^{-6}$ cm$^3 \cdot$ mol^{-1}.

The spectrum of the isomer with m.p. 42° at the frequency $\nu_0 = 60$ MHz proved to be complex; therefore the spectrum was also recorded at $\nu_0 = 100$ MHz (Fig. 2, B). A qualitative analysis only of the z-components of the proton spins of the molecule shows that the band of three sharp lines ($\delta = 4.51$; 5.61 and 4.72 ppm) can be associated only with the resonance of the protons H_A; in this case the terminal hydrogen to Cl must necessarily be axial. In other words, inversion of the shifts of the protons H_A and H_B also takes place in this isomer, but their nonequivalence is substantially smaller than in the first isomer. This fact indicates that the geometry of the molecules of the second isomer is somewhat changed. This change, apparently, is mainly manifested in an increase of the angle $\angle O = S—O$.

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1. B. A. Arbouzov, Yu. Yu. Samitov, *Tetrahedron Letters*, No. 8, 473 (1963).
2. Yu. Yu. Samitov, R. M. Aminova, *Zh. strukturn. khim.*, **5**, 208, 538 (1964).
3. R. C. Lauterbur, J. G. Pritchard, R. L. Vallmer, *J. Chem. Soc.*, 1963, 5307.
4. H. B. Henbest, S. A. Khan, *Proc. Chem. Soc.*, 1964, 56.
5. C. R. Johnson, D. McCants, *J. Amer. Chem. Soc.*, **86**, 2935 (1964); J. C. Martin, J. Uebel, ibid., **86**, 2936 (1964).
6. D. G. Hellier, J. G. Tillett et al., *Chem. and Chem. Ind.*, **50**, 1956 (1963).
7. H. S. Gutowsi, M. Carplus, D. M. Granti, *J. Chem. Phys.*, **31**, 1278 (1959); G. Konroi, in: *Advances in Organic Chemistry*, **2**, 1964, p. 308.
8. H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957); A. D. Buckingham, *Canad. J. Chem.*, **38**, 300 (1960); J. I. Musher, *J. Chem. Phys.*, **37**, 34

(1962).

9. H. Fribolin, S. Kabuss et al., *Tetrahedron Letters*, No. 16, 683 (1962).
10. J. Tillieu, *Ann. Phys.*, **2**, 471, 631 (1957).

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