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CONFORMATION AND ANISOTROPY OF CHEMICAL BONDS IN CYCLIC ETHERS INVESTIGATED BY N.M.R. SPECTROSCOPY

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In the given work conformations of cyclic ethers of carbonic and sulphureous acids of 2.2-dimethylpropandiol-1.3, propandiol-1.3 and ethandiol-1.2 have been studied. Part of n.m.r spectra of protons (PMR) is shown in Fig. 1. The spectra (a,b,d) were obtained using n.m.r. spectrometer operating at 24.46 Mc/s[1] at resolution of 5 parts in 10^8 got by means of Anderson's shims[2], spectrum (c) attained by JNM-3 high-resolution spectrometer.

In PMR spectrum of 2.2-dimethylpropandiol-1.3 carbonate (a) a wide methylene peak showing an unresolved multiple structure with a chemical shift $\tau=6.13\pm0.04$ p.p.m. (4) and the peak of methyl groups with $\tau=9.03\pm0.04$ p.p.m. (6)[+] may be found. The crystals of the compound were dissolved in CCl_4 at concentration of ~35%. The sulphite spectrum (b) consists a methylene quartet the centre of which has $\tau=6.17$ p.p.m. (4) and a methyl duplicate with the centre $\tau=9.09$ p.p.m. (6). Unresolved multiplicity may be found in each peak of the quartet arising from indirect spin-spin interaction with CH_3 group. The sulphite sample was degassed by means of repeatedly freezing, pumping out till 10^{-3} mm Hg and defreezing again.

The fact that we have a striking difference in the spectrum of carbonite and that of sulfite is explained by conformations of cyclic ethers. It is well known that the CO_3 group of carbonic acid derivatives is flat whereas the SO_3group of sulphureous acid derivatives is pyramidal[3]. The conformational formulars carbonite and sulfite see Fig. 1. Thanks to the flat structure of CO_3 group the transition of one form of the chaire into the other gives an equivalent structure. If it is sulphite both conformational forms

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[+] The brackets show relative integral intensivity of the lines.

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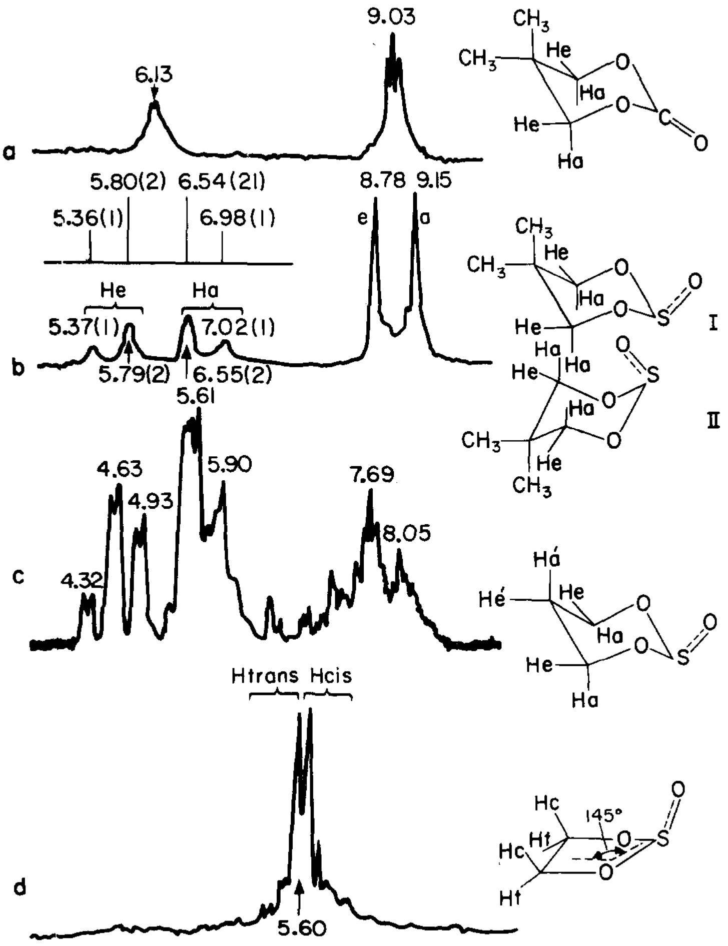
9.03
6.13
a
5.80(2) 6.54(21)
5.36(1)
6.98(1)
8.78 9.15
e
a
He
Ha
5.37(1)
7.02(1)
b
5.79(2)
6.55(2)
5.61
4.63
5.90
4.93
7.69
8.05
c
4.32
Htrans Hcis
d
5.60
CH3
He
Ha
O
C
I
II
S
Há
Hé
Hc
Ht
145°

FIG. 1

are not equivalent and that is why we have an axial and equatorial unequivalence of H in CH_2 and splitting peak of CH_3. The quartet of methylene protons **arises** from axial and equatorial proton interaction, i.e. we have merely AB system. Spin Hamiltonian of the like system is well known[4]. The theoretical spectrum of methylene protons in case of $\delta_{AB} = \tau_a - \tau_e = 1.10$ p.p.m. and $J_{AB} = 11$ C/S is shown in Fig. 1 (b).

Such like differences in shifts of cis-, trans-, axial and equatorial protons of CH_2 and the splitting of CH_3 peak of sulphites may be explained by action of electrical fields of bonds and their magnetic anisotropy.

Buckingham[5] for the change in proton shielding in X-H bond gives the formula

$$\Delta\delta^{el} = -2 \times 10^{-12} E_z - 10^{-18} E^2 - \dots \qquad (1)$$

were E_z-electric field component in the direction of X-H. E and $\mathbf{E}_z$ may be defined by supposed geometrical molecular model. The change of chemical shift due to anisotropy $\Delta\chi^G = \chi_{\parallel} - \chi_{\perp}$ for dipolar approximation and if G-group of electrons has axial symmetry according to McConnel[6] is

$$\Delta\delta^{an} = \frac{\Delta\chi^G}{3 R^3 N} \left\langle 1 - 3 \operatorname{Cos}^2\theta \right\rangle_{av} \qquad (2)$$

Formulas (1) and (2) have been used for the structure analysis of moleculars.

Ethylene sulfite. A symmetrical spectrum (Fig. 1,d) corresponding to A_2B_2 system[7] is indicative of the fact that OSO_2 atoms do not invert their configuration. The values $\Delta\tau_{el} = \Delta\delta^{el}_t - \Delta\delta^{el}_c$ for **an** uneven ring placing dipole on different distances on S=O have been found, and then the value of $\Delta\chi$ has been defined by (2) according to the remainder. Supposing S=O bond has $\chi_{xx} \approx \chi_{yy} > \chi_{zz}$ the value $\Delta\chi_{S=O} = 13.5\ 10^{-6} cm^3 mole^{-1}$ has been found. This value is typical of a structure given in Fig. 1(d) the centre of dipole being at a distance of 0,49 A° from the terminal oxygen. For $\Delta\chi > 0$ H_{trans} protons peak are shifted 0.20 p.p.m. to lower field from the H_{cis} protons. Another conformational structure and $\chi_{xx} > \chi_{yy} \approx \chi_{zz}$, seeming to be more real for p^2-pd hybrid double bond, results in an unreal

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[6] H.M. McConnel J. Chem Phys. 27, 226 (1957).

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value $\Delta\chi_{S=O}$.

2.2-dimethylpropandiol-1.3 sulphite. The value $\Delta\chi_{S=O}=13.5 \times 10^{-6}\mathrm{cm}^3\mathrm{mole}^{-1}$ as well as $\delta_{AB}= \tau_a - \tau_e = 1.10$ p.p.m. known from spectrum (Fig.1,b) have been used for estimating of anisotropy of the other bonds. According to the structure II the values $\Delta\chi_{S-O}=13 \times 10^{-6}\mathrm{cm}^3\mathrm{mole}^{-1}$, $\Delta\chi_{C-O}=9 \times 10^{-6}\mathrm{cm}^3\mathrm{mole}^{-1}$ have been obtained. In case of I we get less satisfactory results. Van-der-Vaal's radii of atoms do not contradict structure II. PMR spectra of this compound have been investigated at different temperature. No changes in spectra have been found.

Propandiol-1.3 sulphite (Fig. 1,c). Calculations using the information concerning the moleculars of the preceding compounds show that anisotropy of all bonds shift the resonance H_e protons 1.44 p.p.m. to the lower field if compared to H_a protons but the influence of the electric fields lessens this value to 1.02 p.p.m. The entire unequivalence of H'_a and H'_e protons is 0.04 p.p.m. Thus in this case we have $A_2B_2X_2$ system.

Ethylene carbonate. Calculations carried out using Narasimhan and Roger's data[8] (i.e. $\Delta\chi'_{C=O}= \chi_{zz} - \chi_{yy} = 2.5 \times 10^{-6}\mathrm{cm}^3\mathrm{mole}^{-1}$, $\Delta\chi''_{C=O}= \chi_{zz} - \chi_{xx}=6.6 \times 10^{-6}\mathrm{cm}^3\cdot\mathrm{mole}^{-1}$) and if it is supposed that the centre of dipole be placed at terminal oxygen of C=O bond, indicate that H_{cis} and H_{trans} protons are not equivalent and as far as 0.19 p.p.m. from each other, *cis*-protons being stronger shielded than those of *trans*-.

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