

CONFORMATION OF NON-AROMATIC RING COMPOUNDS, Part 57 (1)

DIPOLE MOMENTS OF CIS- AND TRANS-2-ALKOXY-4-METHYLTETRAHYDROPYRANS

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(Received in UK 8 September 1969; accepted for publication 18 September 1969)

In a previous paper (2) the conformational features of six 2-alkoxytetrahydropyrans (Fig.1, R = Me, Et, n-Pr, i-Pr, n-Bu, t-Bu) were discussed on the basis of dipole moment and NMR results. The main conclusions concerning the conformational equilibrium and the physical properties (μ and $J = J_{AX} + J_{BX}$ in the $-\text{CH}_2-\text{CHOR}-$ moiety) of the individual conformers are summarized below:

(i) Inspection of the unfavourable interactions in each of the six possible conformers (Fig.1), i.e. rabbit-ear interaction (3), A-value alkoxy group, and gauche-interaction R/O₁ or R/C₃, suggests that only conformers A1, E1 and E2 can occur in the equilibrium to a significant extent, E1 being more stable than E2.

(ii) The J values of the individual conformers can be expected to be independent of the rotational isomerism about the exocyclic C-OR bond, and can, therefore, be obtained from related compounds fixed in the axial or equatorial conformation. For the axial and equatorial forms J_A and J_E were taken equal to 4.5 and 10.5 c/s, respectively.

(iii) With the aid of the values of J_A and J_E and the vicinal couplings of the equilibrating compounds, the axial-equatorial equilibrium was studied. The axial position of the alkoxy group is the more stable one to the extent of 0-1 kcal/mole. A very good quantitative agreement was found with the results from equilibration studies on 4- or 6-methyl substituted 2-alkoxytetrahydropyrans (6,7).

(iv) The dipole moment of each conformer was calculated from the C-O-C partial moments and the directions of the individual oxygen lone pairs (assumed to be localized in sp³ orbitals). In forms with two rabbit-ear interactions (E3) μ was calculated to be ~ 2.9 D; one rabbit-ear interaction gives rise to $\mu \sim 2.1$ D (A2, A3, E1, E2) and if no rabbit-ear interaction is present (A1), $\mu < 1$ D.

(v) For the six compounds in benzene and in carbon tetrachloride a linear correlation between μ^2 and J was found, obeying the relation :

$$\mu^2 = 0.67 J - 2.25 \quad (1)$$

This indicates that only two forms (8,9) with different μ^2 and/or J values are predominant in solution. From J_A and eq.(1) an extrapolated value of μ_A is obtained: 0.87 D, in good agreement with the theoretical value for form A1. J_E yields $\mu_E = 2.18$ D, in good agreement with the value calculated for E1 and E2. So the theoretical conclusions in (1) and (iv) are fully confirmed by this experimental method.

(vi) An independent indication of the reliability of the picture described above was found from the X-ray results of pyranosides in the solid state (10): In each case the conformation of the anomeric alkoxy group corresponds either to form A1 or to form E1.

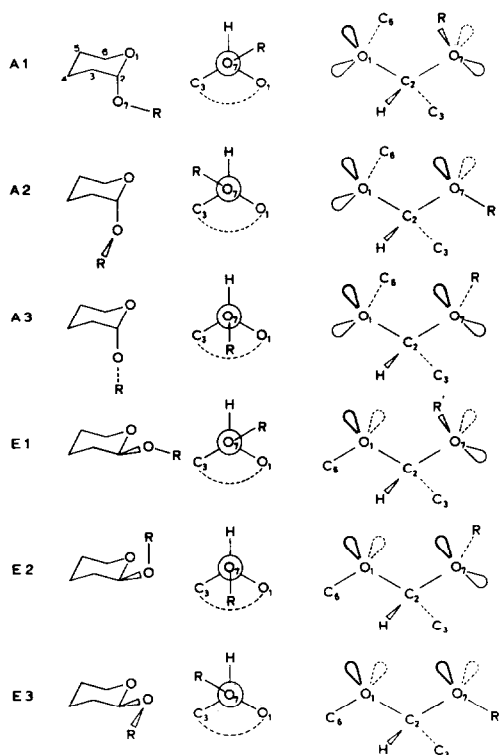


Fig.1. The conformers of 2-alkoxy-tetrahydropyrans with Newman-projections about the exocyclic C-OR bond and the conformations of the O-C-O- moiety.

In order to have a direct test of the validity of the results obtained, we now present the experimental dipole moment results of a number of 4-methyl substituted 2-alkoxy-tetrahydropyrans, in which the alkoxy group is practically completely (~ 100%) in the axial (trans compounds) or equatorial (cis compounds) position (6).

Table 1. Dipole moments (D) of 2-alkoxy-4-methyltetrahydropyrans

Compound	n_D^{25}	Solvent	μ
cis-2-methoxy	1.4242	benzene	2.03
		carbon tetrachloride	2.04
trans-2-methoxy	1.4200	benzene	0.8
		carbon tetrachloride	0.8
cis-2-ethoxy	1.4251	benzene	2.04
		carbon tetrachloride	2.06
trans-2-ethoxy	1.4215	benzene	0.8
		carbon tetrachloride	0.8
cis-2-t-butoxy	1.4272	benzene	2.14
		carbon tetrachloride	2.12
trans-2-t-butoxy	1.4232	benzene	0.9
		carbon tetrachloride	0.9

The compounds listed in Table 1 were prepared and separated by preparative glc as described (2,7). The dipole moments were determined at 25°C according to the method of Halverstadt and Kumler (11) as previously described (12). Full details concerning the syntheses and the dielectric measurements will be published elsewhere (13). From the NMR spectra at 60 Mc/s (Jeol JNM-MH-60 spectrometer) and at 100 Mc/s (Varian HA-100) the values used for J_A and J_E (see above (ii)) appeared to be correct. From Table 1 the following conclusions appear:

- 1) The axial form of the 2-alkoxytetrahydropyrans (trans-4-methyl compounds) has a dipole moment of 0.8-0.9 D, in excellent agreement with the value previously found by means of the μ^2/J method (see above (v)).
- 2) The equatorial form (cis-4-methyl compounds) has a dipole moment of about 2.05 D in the case of the methoxy and ethoxy compounds, the moment of the t-butoxy derivative being a little higher, possibly due to a small difference in geometry of the RO-C-O-C fragment on account of the bulkiness of the t-butyl group. The magnitude is in fair agreement with the results from theoretical calculation and from the μ^2/J method (see iv and v).
- 3) These results confirm our previous conclusions, i.e. that in the case of the equilibrating compounds only A₁, E₁ and E₂ can occur in the equilibrium to a significant extent. So far, the individual occurrence of E₁ and E₂ cannot be estimated.

Acknowledgement

We are indebted to Professor Dr. E.Havinga for his interest during this investigation.

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