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ANOMERIC EFFECT AND INFRA-RED ν_{C-D} STRETCHING FREQUENCY IN TETRAHYDROPYRAN COMPOUNDS

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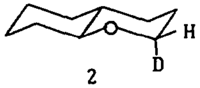
ABSTRACT - *The stretching frequencies of equatorial and axial fused tetrahydropyran C2-D bonds appear around 2190 and 2100 cm^{-1} , with a wide multiplicity. These frequencies are lowered by 20 to 70 cm^{-1} when an OR group is added on C2. An sp^2 hybridization of the exocyclic oxygen may explain this variable effect.*

The stretching frequency of a C-D bond (2130-2180 cm^{-1}) is higher, in cyclohexane, for an equatorial bond than for an axial one [1,2]. If the C-D group is bonded to an oxygen [3,4] (or a nitrogen [5]), its frequency is lowered to 2050-2100 cm^{-1} when the bond is in the plane of one of the oxygen lone pairs [4]. As for the anomeric effect, the explanation is an electronic delocalization n(O) → σ^*(C-D).

In this work, the tetrahydropyran molecules 1, 2, 3 and 4 are investigated and the conformation of the OR group is discussed.

1



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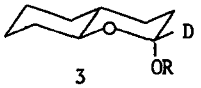

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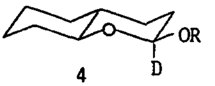
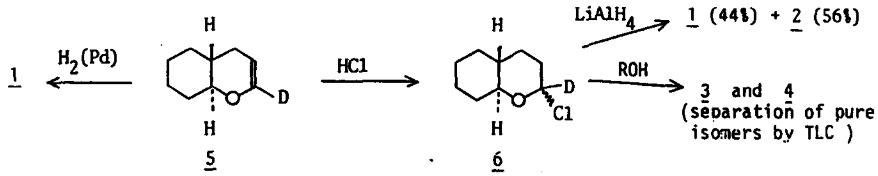


4

a) R = CH_3 ; b) R = $C(CH_3)_3$; c) R = $CH_2-C_6H_5$
d) R = C_6H_5 ; e) R = $pMeOC_6H_4$; f) R = $pClC_6H_4$

The preparation of these products is shown in the following scheme :



The spectra were registered in solution (0.5 cm cell), neat or, for the solids, in KBr. The non-deuteriated products were synthetized for the structure determination and introduced in the reference cell (double beam Spectrometer PYE UNICAM SP3 200) to alleviate small signals not belonging to the C-D band (cases of 3e and 4d).

The C-D stretching bands of isomers 1 and 2 are well separated (fig.1). As expected the frequencies are centered around 2200 cm^{-1} for 1 (2185 cm^{-1}, equatorial deuterium) and around 2100 cm^{-1} for 2 (2103 cm^{-1}, axial deuterium). An interesting multiplicity appears, especially for 2 and in the CCl_4 solutions, with $\Delta\nu$ = 22 ± 2cm^{-1} for 2 (axial deuterium) and 9 ± 2 cm^{-1} for 1 (equatorial). This multiplicity is not well explained and cannot occur, as in other cases, from a rotational isomerism [2,6].

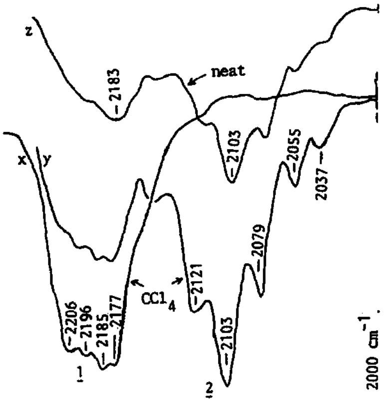
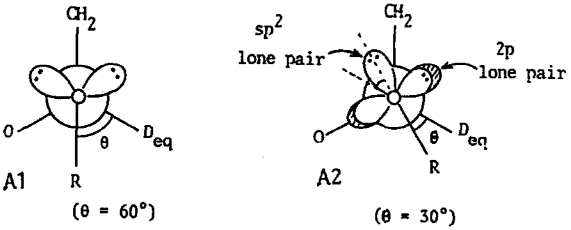


Fig. 1
The C-D stretching bands of compounds 1 and 2
x : CCl_4 solution of compound 1 (25 mmol.l^{-1})
y : CCl_4 solution of compound 1 (44%) + 2 (56%) (50 mmol.l^{-1})
z : neat 1 + 2
In the $CHCl_3$ solution, the component at 2121 cm^{-1} is higher than that at 2103 cm^{-1}

The molecules 3 show, for an equatorial deuterium, a variable lowering of the ν_{C-D} frequency depending of the bulkiness of the R group ($\Delta\nu$ = -15 to -25 cm^{-1} for phenyl or *tert*-But groups, about -50 cm^{-1} for methyl or benzyl groups, fig.2). The conjugation of an exocylic oxygen lone pair with σ^*(C-D) seems better for a small R group. In the conformation A1, the exocyclic oxygen has two sp^3 lone pairs overlapping $\sigma^*(C\text{-}O_{endo})$ (this is the stabilizing *exo*-anomeric effect) et σ^*(C-D). But such a conformation is not expected to be very sensitive to the steric hindrance of R. Recently, it has been proposed that the two oxygen lone pairs are not equivalent (sp^2 hybridization of the endocyclic oxygen) [7]. The 2p(O) orbital being higher than an sp^2 or sp^3 lone pair gives a better overlap with σ^* of the polar group and is more concerned with the stabilizing anomeric effect. In the conformation A2, the exocyclic oxygen is hybridized sp^2 and it is the remaining sp^2 lone pair which reduces the ν_{C-D}frequency. With such an hybridization the steric interactions of R are released (the oxygen bond angle is increased to 120°), but for a more bulky R group, we may have $\theta > 30°$, which reduces the overlaps and the $\Delta\nu$ value.

Molecules 3



The molecules 4 exhibit a similar behaviour, with a variable lowering for the ν_{C-D} frequency of the axial deuterium ($\Delta\nu$ = -20 cm^{-1} for the bulky R groups phenyl or *tert*-But and -30 cm^{-1} for R = methyl or benzyl, fig.3). But in this case there is a supplementary multiplicity, arising around 2030 cm^{-1} ($\Delta\nu$ = -70 cm^{-1}) for 4a (R = CH_3). The first band (ν = 2072 to 2085 cm^{-1}) is well explained by the conformation B1, similar to A2. The new one, observed for 4a, may correspond to another conformation, probably B2, allowed only for

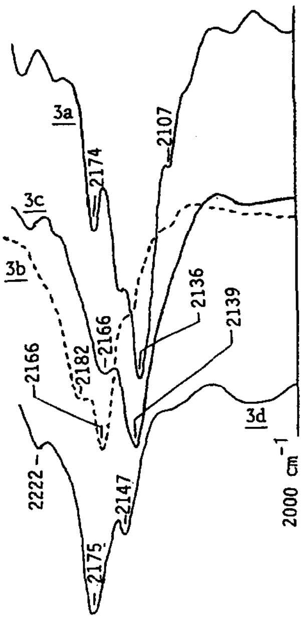


Fig.2:Solution CCl$_4$

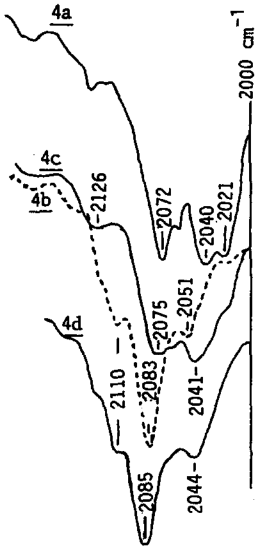


Fig.3:Solution CCl$_4$

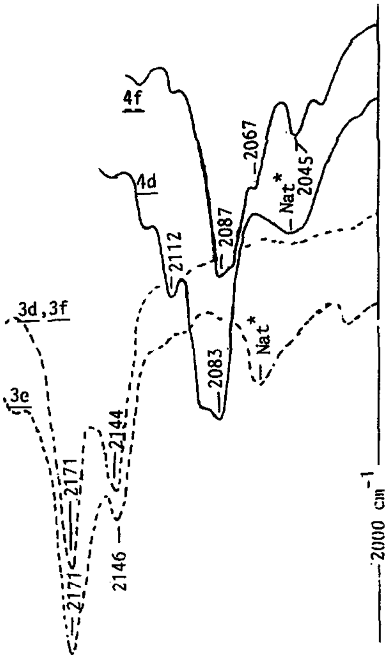


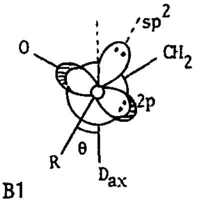
Fig.4: KBr pellets

The C-D stretching bands of molecules 3 and 4 .
Solution 0.025 mole/litre
Solid state 1mg/200mg KBr

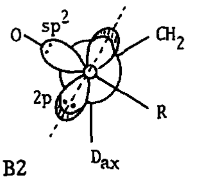
Fig.2 : 3d, 3e, 3f give about the same spectra.
Fig.3 : 4d, ν = 2044, 2085, 2110 cm^{-1}; 4e, ν = 2043, 2083, 2111, 2127 cm^{-1}(pMeO-C$_6$H$_4$)
4f, ν = 2046, 2087, 2110, 2127 cm^{-1}(pCl-C$_6$H$_4$)
Fig.4 : Nat* : band belonging to the natural product (3e, 4d).
The products 4c and 4e give spectra of low intensity (not significative).
(The multiplicity observed in the solid state is not related to a conformational mixture).

small R groups. An important part of the *exo*-anomeric effect is lost (overlap with the lower sp^2 lone pair) but the higher 2p orbital, interacting with σ^*(C-D) gives a greater lowering $|\Delta\nu|$.

Molecules 4.



B1



B2

Concerning the electronic influence of the aromatic R groups, the effect is slight in molecules 4 and no observable in molecules 3 (fig.2 and 3). The phenyl group is probably conjugated to the 2p lone pair in A2, giving an electronic effect on the anomeric stabilization [8]. It may undergo a little rotation in B1, becoming more conjugated to the sp^2 lone pair. As expected, an attractive substituent reduces the $|\Delta\nu|$ value.

The ν_{C-D} stretching frequency is interesting to distinguish equatorial or axial tetrahydropyran C2-D bonds. It appears very sensitive to the presence of an anomeric group and to the orientation of the lone pairs of the oxygen atoms. All the results and the discussion seem in good agreement with the hypothesis of an sp^2 hybridization of the exocyclic oxygen. The publication of other applications of these results is following.

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