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BIFURCATED HYDROGEN BONDS IN Z-2-PHENYL-1,3-DIOXAN-5-OLS

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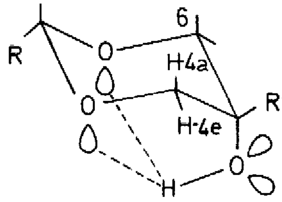
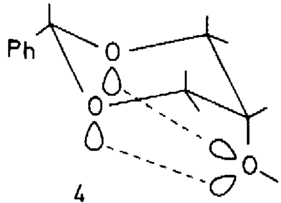
Hydroxyl protons of 1,3-dioxan-5-ols with an axial OH group in 5-position such as 1a - c form inter- and intramolecular hydrogen bonds [1-5]. Below a concentration of 0.005 M in CCl_4 intermolecular hydrogen bonding is negligible. The single OH absorption at 3587 cm^{-1} in the IR spectra of 1b has been attributed to an intramolecular bond, and there is no absorption at 3630 cm^{-1} which could be associated with a free hydroxyl group. The nature of this intramolecular hydrogen bond, however, is not well understood. Baggett [1] writes conformation 1b where the OH proton is equally bound to both ring oxygens in a bifurcated hydrogen bond, but concedes "whether a bifurcated hydrogen bond is present in the actual compound is not known". Bifurcated



1a: R = R' = H

b: R = C_6H_5, R' = H

c: R = C_6H_5, R' = CH_3



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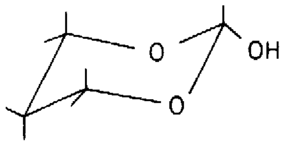

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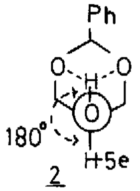

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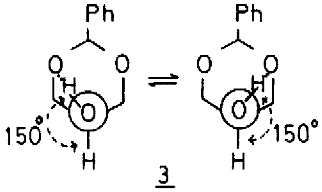

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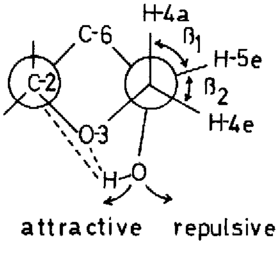

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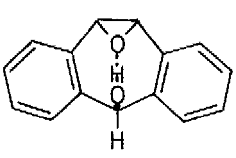

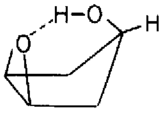

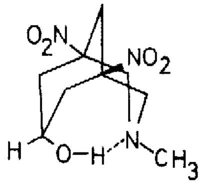

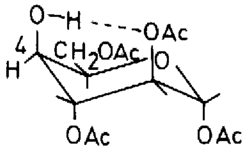

$^3J_{HCOH}$: 12.5 Hz 6

12.3 Hz 7

12 Hz 8

9.8 Hz 9

hydrogen bonds have been found in some cases in crystals $^{6)}$ but apparently in only one case in solution $^{7)}$.

For compound 1b the following alternatives will be considered : 1) The OH proton is fixed in an attractive bifurcated hydrogen bond to both ring oxygens, the OH bond bisecting the ring (conformation 2). 2) Repulsive forces press the OH proton into conformation 2 $^{8)}$, e.g. repulsion between the free electron pairs of the ring oxygens and the free electron pairs of the OH group is minimized in conformation 1 and at a maximum in conformation 4. 3) The OH proton is rapidly flipping between two "normal" hydrogen bonds to only one ring oxygen, as indicated in 3 (potential with two minima).

In conformation 2 the OH proton and H-5e form a dihedral angle of 180°, while in both conformations 3 the dihedral angle is 150°. It has been amply demonstrated, that the $^3J_{HCOH}$ coupling depends on the dihedral angle in a similar manner as the $^3J_{HCCH}$ coupling, for instance $^{9)}$:

$$^3J_{HCOH}(\beta) = 10.4 \cos^2\beta - 1.5 \cos\beta + 0.2 \quad (\mathrm{Hz})$$

For $\beta = 180^\circ$ one calculates $^3J_{HCOH}(180) = 12.1$ Hz and for 150° it follows $^3J_{HCOH}(150) = 9.3$ Hz. Couplings between 12.0 and 12.5 Hz have been found in cases where the OH proton is fixed by an intramolecular hydrogen bond in an antiperiplanar arrangement ($\beta = 180^\circ$) to a vicinal proton, e.g. 6 - 8 $^{10-12)}$. For compound 9 $^3J_{HCOH} = 9.8$ Hz was reported $^{13)}$. Here the OH proton forms a hydrogen bond to O-2, and the dihedral angle between H-4 and OH should be about 150°.

In carefully purified and degassed 0.005 M solutions in CCl_4 the OH proton of compound 1b appears as a doublet at 2.71 ppm with a $^3J_{HCOH}$ coupling of 12.1 Hz (mean of 10 measurements) $^{14)}$. Rapid oscillation between the two conformations 3 can therefore be ruled out, because in both forms 3 the dihedral angle between the OH proton and H-5e is 150°, giving a mean of 150° for which a coupling of 9-10 Hz should be expected. The $^3J_{HCOH}$ coupling of 1b is dependent on concentration and solvent: in 0.1 M solution in CCl_4 one finds $^3J_{H-5e,OH} = 11.8$ Hz. The IR spectra of this solution show some intermolecular hydrogen bonding (3450 cm^{-1}). In 1.5 M solution in $CHCl_3$ $^3J_{H-5e,OH}$ is 10.5 Hz and for all concentrations in DMSO-d_6 one observes $^3J_{H-5e,OH} = 5.1$ Hz indicating about equal populations of conformations with $ß = 60^\circ$ and $ß = 180^\circ$. It can be concluded that the OH proton of 1b in dilute solutions in CCl_4 is positioned midway between the two ring oxygens (2).

Evidence that attractive forces cause this conformation comes from the ^3J couplings of H-4a and H-4e (resp. H-6a and H-6e) to H-5e, which are sensitive to the ring conformation, because they depend on the dihedral angles $ß_1$ and $ß_2$, as defined in 10. In 0.3 M solutions in $CDCl_3 : C_6D_6$ (1 : 1) $^3J_{H-5e,OH}$ of compound 1b is 11.17 Hz indicating 91% of conformation 2. Although the OH proton is thus not completely intramolecularly fixed the observed values of $^3J_{H-4a,H-5e} = 1.47$ Hz and $^3J_{H-4e,H-5e} = 1.87$ Hz reflect mainly the geometry of conformation 2. For 1.3-dioxanes without OH at C-5 reported values for $^3J_{H-4a,H-5e}$ range around 2.6 Hz and for $^3J_{H-4e,H-5e}$ around 1.3 Hz 15,16). The small value for the H-4a,H-5e coupling found for 1b may be interpreted as resulting from the electronegativity of the OH substituent which, being antiperiplanar to H-4a, is in an optimal position to reduce the H-4a,H-5e coupling 17). However, the unusual large value for $^3J_{H-4e,H-5e}$ cannot be explained by the electronegativity of the OH group. Here ring distortion must be the reason. If the ring oxygens attract the OH group the C-5-O bond will be pulled a little into the ring. Consequently the angle $ß_2$ decreases and $ß_1$ increases leading to a smaller $^3J_{H-4a,H-5e}$ and a larger $^3J_{H-4e,H-5e}$ coupling compared to 1.3-dioxanes without an axial OH at C-5. If on the other hand repulsive forces between the free electron pairs of the ring oxygens and those of the OH oxygen were to determine conformation 2, the C-5-O bond should be turned away from the ring resulting in larger coupling between H-4a and H-5e and smaller coupling between H-4e and H-5e compared to dioxanes without such an OH group.

In less than 0.005 M solution in CCl_4 the dioxane 1a shows two absorptions at 3635 and 3594 cm^{-1} 4) which obey Beer's law and can be assigned to the free OH in conformation 5 and an intramolecular bond (1a). In compound 1b the phenyl group as a holding group ($\Delta G^\circ \approx 12$ $kJmol^{-1}$ 8)) fixes conformation 1b and no absorption for a free OH is found in the IR. Assuming that a free OH of 1b would also absorb around 3635 cm^{-1}, as 1a, the intramolecular hydrogen bond in

1b (as well as in 1a) must be attractive, for only attractive forces between OH and the acceptor oxygen shift the OH stretching vibration to smaller wave numbers.

Thus, the experimental findings demonstrate an attractive bifurcated hydrogen bond in 1b. Similar bifurcated hydrogen bonds have been found in 5-substituted dioxanols like 1c, where an abnormally large $^4J_{HCCOH}$ coupling of 1.1 Hz to the methyl protons can be observed.

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