# CONFORMATIONAL STUDY OF BLOCKED PENTOFURANOSES AND THEIR 1,5-ANHYDRO DERIVATIVES BY $^1$H NMR SPECTROSCOPY

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Preferred conformations of the furanose ring and conformer population about the $C_{(5)}$—$C_{(4)}$ bond in a series of benzoylated pentofuranosyl cyanides have been determined from their $^1$H NMR spectra. For the 1,5-anhydropentofuranose derivatives the results of the $^1$H NMR spectral analysis have been compared with the quantum chemical calculations.

The conformation of the furanose ring was studied mainly on nucleosides and their derivatives[1,2]. Analogous studies on C-nucleosides concerned compounds containing D-ribose[1] or 2-deoxy-D-ribose[3] as the sugar component. In order to extend this conformational investigation also to C-nucleosides derived from other pentofuranoses, we set out to investigate the $^1$H NMR spectra of protected pentofuranosyl cyanides which are easily accessible[4-6] and can be regarded as simplest models of C-nucleosides. Our study also includes 1,5-anhydro derivatives of pentofuranoses which can serve as models with highly fixed conformation of the furanose ring.

## EXPERIMENTAL

The preparation of the compounds *I*—*IX* will be described elsewhere[6]. They were measured at 23°C in deuteriochloroform (about 10 mg of compound in 0·4 ml of solvent) on a Varian XL-200 (200 MHz) instrument with tetramethylsilane as internal standard. Assignment of signals to the corresponding protons was done on the basis of the observed multiplicities, chemical shifts and decoupling experiments. The chemical shifts and coupling constants, given in Table I, were estimated by spectra simulation; accuracy ±0·01 ppm and ±0·1 Hz, respectively. A complete analysis of the spectrum of the *arabino* cyanide *II* was not possible because of an overlap of the strongly interacting protons H-4, H-5 and H-5′ and therefore the structurally similar methyl glycoside *V* was also measured.

## RESULTS AND DISCUSSION

### *Chemical Shifts*

The chemical shifts of protons in compounds *I*—*IX*, refined by simulation of the spectra, are given in Table I. The order of the proton signals in the spectra of the

protected pentofuranosyl cyanides *I*–*IV*, goirg from the lowest field, is H-2, H-3, H-1 and H-4, and finally H-5 and H-5′. Configurational changes of substituents at $C_{(1)}$, $C_{(2)}$ and $C_{(3)}$ cause only small noncharacteristic changes in the proton shifts which vary within relatively narrow range (from 0·07 ppm for H-5 and H-5′ to 0·37 ppm for H-3) and are thus not suitable for configurational or conformational studies. In the spectra of 1,5-anhydropentofuranoses *VI*–*IX* the H-1 signal occurs invariably at the lowest field. For the 2,3-dibenzoyl derivatives *VII* and *VIII* the H-1, H-2, H-3 and H-4 proton signals are shifted downfield relative to the di-O-isopropylidene derivatives *VI* and *IX*. The *endo*-H-5 signal reflects sensitively the substitution, being shifted downfield with growing number and proximity of the *endo*-oriented substituents in the order *VI*, *VII*, *VIII* and *IX*. On the other hand, the *exo*-H-5 signal is substantially less affected. However, the chemical shifts in the spectra of *VI*–*IX* are of no use for conformational considerations.

*Coupling Constants*

The proton coupling constants for compounds *I*–*IX*, refined by the simulation procedure, are listed in Table I. As expected, the geminal coupling of the H-5 and H-5′ protons is substantially larger in pentofuranoses *I*–*V* ($J_{5,5'} \approx 12$ Hz) than in the 1,5-anhydro derivatives *VI*–*IX* ($J_{5,5'} \approx 7$ Hz) in which the $CH_2$ group is part of the five-membered ether ring. The long-range interactions across four bonds ($J_{1,3}$, $J_{1,4}$, $J_{2,4}$, $J_{3,5}$ and $J_{3,5'}$) in the pentofuranoses *I*–*V* are very small (0 to 0·5 Hz) and manifest themselves only by a moderate widening of signals of some protons. For conformational interpretation they are of no great importance, since they can be caused by conformational flexibility or geometry of the preferred conformation, unfavourable for long-range coupling ($^4J_{H,H}$). Spectra of the undoubtedly more rigid 1,5-anhydro derivatives *VI*–*IX* exhibit greater coupling ($^4J_{H,H} \sim 1$ Hz) only between the H-3 and H-5-*exo* protons (in *VIII* and *IX*) and between the *cis*-oriented protons H-2 and H-4 (in *VII* and *IX*). Although an advantageous planar zig-zag arrangement is seen on models, the $J_{1,4}$ interactions are very small, the reason being probably the presence of oxygen atom in the interaction path.

Vicinal proton coupling constants were used for conformational study of the furanose rings in compounds *I*–*IX* and rotamer population about the $C_{(5)}$—$C_{(4)}$ bond in compounds *I*–*IV*. A comparison of various Karplus-like relationships[7–9] used for five-membered rings shows that for given values of $^3J_{H,H}$ the calculated dihedral angles $\Phi$ do not differ very much (differences smaller than 8°). In our calculations we employed the relationship (*1*) described in ref.[8]

$$J = 10{\cdot}2 \cos^2 \Phi - 0{\cdot}8 \cos \Phi \,. \qquad (1)$$

The effect of the anhydro oxygen $O_{(5)}$ on the $J_{1,2}$ constant in the 1,5-anhydropento-

furanoses *VI*–*IX* was described by the relationship (*2*) (ref.[10])

$$J_{exp} = J_{calc}(1 - 0{\cdot}1\,\Delta E)\,, \qquad (2)$$

where $\Delta E$ is the electronegativity difference[11] between the nitrile group ($E = 2{\cdot}69$) and oxygen atom ($E = 3{\cdot}31$), $J_{calc}$ the vicinal coupling constant calculated from the equation (*1*) and $J_{exp}$ the experimental value. Using the relationships (*1*) and (*2*)

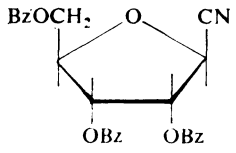
TABLE I

$^1$H NMR Parameters of pentafuranose derivatives *I*–*IX*

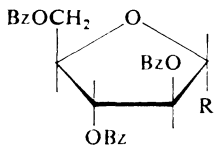
| Compound | Chemical shifts, ppm | | | | | |
|---|---|---|---|---|---|---|
| | H-1 | H-2 | H-3 | H-4 | H-5 | H-5′ |
| *I* | 4·98 | 6·01 | 5·86 | 4·72 | 4·73 | 4·61 |
| *II* | 5·11 | 5·79 | 5·73 | 4·68–4·80 | | |
| *III* | 4·95 | 5·77 | 5·99 | 4·87 | 4·68 | 4·68 |
| *IV* | 5·02 | 5·97 | 6·10 | 4·90 | 4·71 | 4·65 |
| *V* | 5·19 | 5·53 | 5·60 | 4·59 | 4·86 | 4·71 |
| *VI* | 5·45 | 4·29 | 4·34 | 4·71 | 3·43[a] | 3·31[b] |
| *VII* | 5·97 | 5·17 | 5·12 | 4·95 | 3·77[a] | 3·85[b] |
| *VIII* | 5·70 | 5·19 | 5·30 | 5·24 | 3·58[a] | 4·09[b] |
| *IX* | 5·46 | 4·45 | 4·65 | 4·75 | 3·57[a] | 4·33[b] |

| | Coupling constants, Hz | | | | | |
|---|---|---|---|---|---|---|
| | $J_{1,2}$ | $J_{2,3}$ | $J_{3,4}$ | $J_{4,5}$ | $J_{4,5'}$ | $J_{5,5'}$ |
| *I* | 4·3 | 5·2 | 5·4 | 3·6 | 4·0 | −12·6 |
| *II* | 1·0 | 1·0 | 2·0 | [d] | [d] | [d] |
| *III* | 1·0 | 1·2 | 3·7 | 5·7 | 5·7 | [d] |
| *IV* | 5·1 | 5·0 | 4·8 | 7·2 | 4·8 | −11·9 |
| *V* | 0·3 | 1·3 | 4·3 | 5·0 | 3·5 | −12·0 |
| *VI* | 0·0 | 5·5 | 0·0 | 3·7 | 0·0 | − 7·2 |
| *VII* | 2·4 | 1·4 | 0·0 | 4·3 | 0·0 | − 7·6 |
| *VIII* | 0·2 | 1·7 | 5·1 | 3·1 | 0·0 | − 7·4 |
| *IX* | 2·3 | 8·3 | 4·8 | 3·5 | 0·0 | − 6·7 |

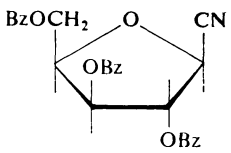
[a] H-5-*exo* proton; [b] H-5-*endo* proton; [c] only the following long-range interactions are greater than 0·5 Hz: in *VII* $J_{2,4} = -1{\cdot}4$, in *VIII* $J_{1,3} = -0{\cdot}9$ and $J_{3,5} = -1{\cdot}5$, in *IX* $J_{2,4} = -1{\cdot}2$ and $J_{3,5} = -1{\cdot}4$ Hz; [d] the parameter values were not determined.




*I*




*II*, R = CN
*V*, R = $OCH_3$

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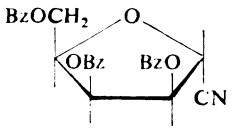


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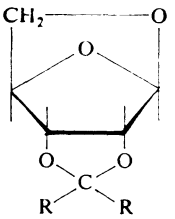
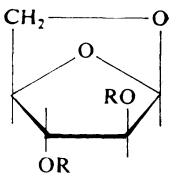
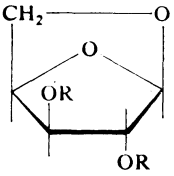


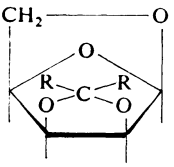

*VI*, R = $CH_3$
*X*, R = H




*VII*, R = Bz
*XI*, R = H




*VIII*, R = Bz
*XII*, R = H




*IX*, R = $CH_3$
*XIII*, R = H

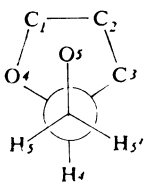
TABLE II

Proton dihedral angles $\Phi_{i,j}$, preferred conformations and populations of rotamers about the $C_{(5)}$—$C_{(4)}$ bond in pentofuranose derivative *I*— *V*

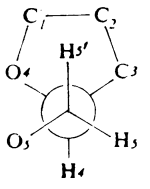
| Compound (configuration) | Torsion angles $\Phi_{i,j}$ | | | Preferred conformation | Rotamer populations | | |
|---|---|---|---|---|---|---|---|
| | $\Phi_{1,2}$ | $\Phi_{2,3}$ | $\Phi_{3,4}$ | $(\Phi_{1,2}, \Phi_{2,3}, \Phi_{3,4})$ | $g_+$ | $t$ | $g_-$ |
| *I* (β-*ribo*) | 128 | 41 | 133 | ${}^3E$ (105, 45, 165) ↔ ${}^2E$ (165, 45, 105) | 0·54 | 0·25 | 0·19 |
| *II* (α-*arabino*) | 69 | 106 | 114 | ${}_1E$ (75, 105, 120) | *a* | *a* | *a* |
| *III* (β-*xylo*) | 106 | 67 | 50 | ${}^3E$ (105, 75, 45) | 0·16 | 0·42 | 0·42 |
| *IV* (α-*lyxo*) | 132 | 42 | 44 | ${}^3E$ (135, 45, 45) | 0·10 | 0·33 | 0·57 |
| *V* (α-*arabino*) | 75 | 109 | 131 | ${}^0_1T$ (75, 105, 135) | 0·47 | 0·33 | 0·20 |

[a] The parameter values were not determined.

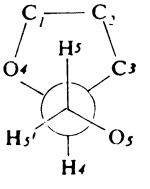
we calculated the values of the proton dihedral angles $\Phi_{1,2}$, $\Phi_{2,3}$ and $\Phi_{3,4}$ (Tables II and III) and compared them with those[12] in the conformations[13] of the pseudorotation cycle[14,15]. This comparison revealed either one markedly prevailing conformation or more conformational types, indistinguishable on the $^1$H NMR time scale.




*g*+




*t*




*g*−

The population of the $g_+$, $t$ and $g_-$ rotamers about the $C_{(5)}$—$C_{(4)}$ bond was determined using the relationships (*3*)–(*5*) (ref.[1]) and is also given in Table II. The H-5 and H-5′ proton signals were assigned according to the published[16] convention:

$$g_+ = (13 - (J_{4,5} + J_{4,5'}))/10 \qquad (3)$$

$$t = (J_{4,5'} - 1{\cdot}5)/10 \qquad (4)$$

$$g_- = (J_{4,5} - 1{\cdot}5)/10\,. \qquad (5)$$

TABLE III

Proton dihedral angles in 1,5-anhydropentofuranoses as determined from models, derived from $^1$H NMR and calculated by MINDO/3 method

| Configuration | From models for $_0E$ | | | Compound | From $^1$H NMR | | | Compound | From MINDO/3 calc. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\Phi_{1,2}$ | $\Phi_{2,3}$ | $\Phi_{3,4}$ | | $\Phi_{1,2}$ | $\Phi_{2,3}$ | $\Phi_{3,4}$ | | $\Phi_{1,2}$ | $\Phi_{2,3}$ | $\Phi_{3,4}$ |
| *VI-ribo* | 90 | 0 | 90 | *VI* | 90 | 39 | 90 | *X* | 82 | 6 | 87 |
| *VII-arabino* | 35 | 125 | 90 | *VII* | 57 | 110 | 90 | *XI* | 38 | 126 | 83 |
| *VIII-xylo* | 90 | 125 | 30 | *VIII* | 79 | 112 | 19 | *XII* | 74 | 119 | 38 |
| *IX-lyxo* | 35 | 0 | 35 | *IX* | 58 | 19 | 44 | *XIII* | 50 | 5 | 42 |

*Conformations of Benzoylated Pentofuranosyl Cyanides*

The found $^3J_{H,H}$ constants for the *ribo*-derivative *I* and the corresponding angles $\Phi_{H,H}$ calculated from them are in accord with an interconversion between the $^3E$ and $^2E$ conformations. For an equal population of both conformations the averaged values are $\Phi_{1,2} = 135°$, $\Phi_{2,3} = 45°$ and $\Phi_{3,4} = 135°$, which agree well with those calculated from the experimental coupling constants $J_{H,H}$ (Table II). The benzoylated substituents at $C_{(2)}$ and $C_{(3)}$ are *cis*-oriented and their mutual interaction can stabilize the $^3E$ and $^2E$ forms in which one of the substituent-bearing carbon atoms is out of the ring plane and the $O_{(2)}$—$C_{(2)}$—$C_{(3)}$—$O_{(3)}$ segment has a *gauche* arrangement. The $^3E$ and $^2E$ conformations also correspond to the energy minima calculated by the PCILO method[13,17]. Conformation $^3E$ was suggested[18] for methyl β-ribofuranoside on the basis of analysis of non-bonding interactions and a very similar conformational type ($^2_3T$) was derived[19] from $^1$H NMR data for the fully esterified ribofuranosides. The preferred rotamer about the $C_{(5)}$—$C_{(4)}$ bond appears to be the $g_+$ form in which the benzoyloxy group points above the furanose ring and the $O_{(4)}$—$C_{(4)}$—$C_{(5)}$—$O_{(5)}$ segment has a gauche arrangement.

The *arabino*-derivatives *II* and *V* exist in very similar conformations of the type $_1E$ and $^0_1T$, respectively, situated in a narrow interval of the pseudorotation pathway ($P = 126°$ and 108°, respectively). The conformation $^0_1T$ of the derivative *V* is the most advantageous from the point of the anomeric effect and was suggested already earlier by Stevens and Fletcher[19]. An analysis of non-bonding interactions[18] in methyl-α-arabinofuranoside led to rather different conformations $^2_3T$ and $^3_2T$. The differences show the importance of the ester groups for the conformation of the furanose ring. In the form $_1E$ the $O_{(4)}$—$C_{(1)}$—$C_{(2)}$—$O_{(2)}$ segment is approximately gauche, the groupings $O_{(1)}$—$C_{(1)}$—$C_{(2)}$—$O_{(2)}$ and $O_{(2)}$—$C_{(2)}$—$C_{(3)}$—$O_{(3)}$ are *trans*-oriented and the dihedral angle $O_{(3)}$—$C_{(3)}$—$C_{(4)}$—$O_{(4)}$ is about 120°. Similarly to the *ribo*-derivative *I*, the rotamer $g_+$ is preferred for the rotation about the $C_{(5)}$—$C_{(4)}$ bond.

For the *xylo*-derivative *III* the $^3E$ form is preferred. It can be characterized by approximate gauche arrangement of the segments $O_{(4)}$—$C_{(1)}$—$C_{(2)}$—$O_{(2)}$ and $O_{(3)}$—$C_{(3)}$—$C_{(4)}$—$O_{(4)}$ and anti conformation of the $O_{(2)}$—$C_{(2)}$—$C_{(3)}$—$O_{(3)}$ segment. For fully esterified β-xylofuranose derivatives this conformational type was already suggested[19] on the basis of $^1$H NMR data as alternative to the very similar type $^2_3T$. A quite different conformation ($^2_3T$ or $_3E$) was deduced by Bishop and Cooper[18] for methyl-β-xylofuranoside from analysis of non-bonding interactions. In the *xylo*-derivative *III* the substituent on $C_{(3)}$ is *endo*-oriented (in contrast with the *exo*-orientation in the *ribo*- and *arabino*-derivatives *I* and *II*) and its interaction with the substituent on $C_{(4)}$ obviously destabilizes the $g_+$ rotamer about the $C_{(5)}$—$C_{(4)}$ bond, preferring thus the $g_-$ and *t* rotamers in which the benzoyl group points outside the furanose ring.

Also for the *lyxo*-derivative *IV* we found the $^3E$ conformation to be the most stable one. The segments $O_{(2)}—C_{(2)}—C_{(3)}—O_{(3)}$ and $O_{(3)}—C_{(3)}—C_{(4)}—O_{(4)}$ have approximately *gauche* arrangement and only the segment $O_{(4)}—C_{(1)}—C_{(2)}—O_{(2)}$ is *anti*-oriented. Since the $g_+$ rotamer about the $C_{(5)}—C_{(4)}$ bond is destabilized by the *endo*-oriented $C_{(3)}$-substituent (similarly to the situation in *III*), the rotamer $g_-$ is preferred. Our conclusions differ substantially from the conformational interpretation of $^1$H NMR data of Stevens and Fletcher[19] for tetra-O-benzoyl-α-lyxofuranose (suggested types $^4_3T$ or $_3E$) as well as from the analysis of non-bonding interactions for methyl-α-furanoside[18] (suggested types $^3_2T$ or $_3E$).

The conformation of the furanose ring in compounds *I* – *V* is influenced by various factors of which the dominant ones are obviously non-bonding steric interactions (caused by the bulky benzoyl substituents) and dipole-dipole or electrostatic interactions (among which we can include also the anomeric and *gauche* effects). Since the studied set represents *trans*-1,2-disubstituted C-glycosides, the anomeric effect should not be so significant as in the case of O-glycosides. The importance of the *gauche* effect[20] can be seen from the preferred conformations of all the above discussed compounds. According to character of the substituents, also attractive interaction between the aromatic rings can operate as *e.g.* in substituted N,N'-diaryl-N,N'-dimethylurea[21] and paracyclophanes[22,23] or attractive interactions between the ester groups as such[24]. The differences between the preferred conformations of the benzoyl cyanides *I*–*IV*, found by us, and the described conformations of aldopentofuranose[19] and methylfuranoside[18] esters show how the character of substituents is important for the furanose ring conformation.

*Conformation of* 1,5-*Anhydro Derivatives* VI–IX

The anhydro bridge in derivatives *VI*–*IX* restricts markedly the flexibility of the furanose ring. In the di-O-isopropylidene derivatives *VI* and *IX* also the ketal five-membered ring contributes to the conformational fixation. As seen on models, the structure of the compounds *VI*–*IX* enforces the $_0E$ conformation of the furanose ring, characterized by the dihedral angles $\Phi_{H,H}$ given in Table III. We can assume that the conformation will not be substantially influenced by character or configuration of substituents on $C_{(2)}$ and $C_{(3)}$. In accord with this, the coupling constants $J_{1,2}$, $J_{2,3}$ and $J_{3,4}$ are markedly larger for the *cis*- than for the *trans*-vicinal protons (the respective values are $J_{1,2} \approx 2{\cdot}5$ and $\sim 0$, $J_{2,3} \sim 5{\cdot}5-8{\cdot}3$ and $\sim 1{\cdot}5$; $J_{3,4} \sim 5$ and $\sim 0$), similarly to those for 1,6-anhydrohexofuranoses[25]. Table III lists the proton dihedral angles for compounds *VI*–*IX* obtained from the values of $J_{H,H}$ using the relationships (*1*) and (*2*). The $\Phi_{i,j}$ values are compared with those calculated by the MINDO/3 method[26] for the structurally similar 1,5-anhydropentofuranoses *X*–*XIII*. To simplify the calculation, the benzoyl groups were taken as hydroxy groups and

the isopropylidene group as a methylene group. In some cases, there are substantial differences between $\Phi_{i,j}$ values, obtained from the $^3J_{H,H}$ values and those calculated by the MINDO/3 method (in five of twelve cases the difference is $\geqq 15°$). We assume that the structural simplification, used in the quantum chemical calculation, cannot be responsible for such large differences. The fact that large differences in $\Phi_{i,j}$ exist for most *cis*-oriented protons whereas for the *trans*-hydrogens the agreement is substantially better indicates that the employed relationship $^3J_{H,H} = f(\Phi)$ is inadequate in the region $\Phi = 0-60°$ (ref.[27]), giving higher values than the quantum chemical calculation. Since marked deviations occur not only for $\Phi_{1,2}$ but also for $\Phi_{2,3}$ and $\Phi_{3,4}$ they cannot be explained by an underestimated effect of the anhydro oxygen atom. However, the MINDO/3 calculations show that the bond lengths and angles in the 1,5-anhydropentofuranoses differ from those in the monocyclic derivatives *I*–*IV*. It is possible that these changes in geometry affect the $^3J_{H,H}$ constants more in compounds with *cis*-oriented hydrogens than in derivatives with *trans*-relations of hydrogens and that the dihedral angles, derived from these constants do not correspond to the actual values. Thus, *e.g.* for the *ribo*-derivative *VI* the dihedral angle $\Phi_{2,3} = 39°$ (determined from $J_{2,3}$ and markedly different from the value $\Phi_{2,3} = 0°$ in the standard ${}_0E$ conformation) should necessarily mean also marked deviations of the $\Phi_{1,2}$ and $\Phi_{3,4}$ values from 90° in the ${}_0E$ form. Similar discrepancies are found also with derivatives *VII*–*IX*. It can be concluded that in these cases the usual Karplus relationship does not afford correct values of the $\Phi_{i,j}$ angles and that the quantum chemical calculation gives a far more realistic picture of conformations of the 1,5-anhydropentofuranose derivatives *VI*–*IX*.

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