Conformation of C-1-Substituted Pyranos-1-yl and Pyranosan-5-yl Radicals Evidence for a Quasi-Homo-Anomeric Stabilization Effect[1)]

Hans-Gert Korth[a], Jean-Pierre Praly[b], László Somsák[c], and Reiner Sustmann*[a]

Institut für Organische Chemie der Universität Essen[a],
Postfach 103764, D-4300 Essen 1, F.R.G.

Laboratoire de Chimie Organique 2, Université Claude-Bernard Lyon 1[b],
43 Boulevard du 11-Novembre-1918, F-69622 Villeurbanne Cedex, France

Lehrstuhl für Organische Chemie der Universität Debrecen[c],
Postfach 20, H-4010 Debrecen, Hungary

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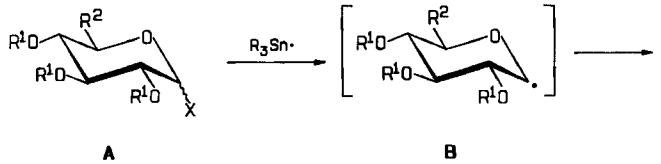
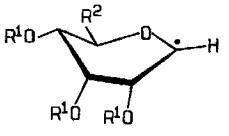
Acetylated 1-cyano- and 1-chloro-pyranos-1-yl radicals and 5-acetoxycarbonyl-, 5-methoxycarbonyl-, and 5-unsubstituted pyranosan-5-yl radicals were generated from the corresponding bromides by bromine abstraction with trimethyltin radicals. The conformation of these radicals, as deduced from the ESR hyperfine splittings, is explained by the combined action of a quasi-anomeric and a homo-anomeric stabilization effect. A captodative substitution pattern of the radical center does not influence the conformations.

Free radical reactions have become a standard methodology in organic synthesis in recent years[2)]. Because these reactions may be carried out under nonpolar conditions, they constitute a valuable supplement to other synthetic methods. Experience has shown that free radical reactions may also be applied successfully in the area of carbohydrate chemistry, sometimes leading to products of high stereoselectivity[3)]. These observations were the incentive to study the conformation of the intermediate carbohydrate radicals by ESR spectroscopy[4-6)]. The synthetically useful generation of carbohydrate radicals by halogen abstraction from organohalogen compounds also proved viable for the observation of their ESR spectra. Whereas free-radical chain reactions are used in synthesis, for spectroscopic studies it is more appropriate to generate the carbohydrate radicals by nonchain processes.

As in our earlier work[1,4-6)], in this study we used the photochemical cleavage of hexamethylditin to generate trimethyltin radicals which act as halogen abstractors in inert solvents, viz. benzene, fluorobenzene, or tetrahydrofuran. Though the carbohydrate radicals often gave ESR spectra of low signal-to-noise ratio, evaluation of the spectral parameters was always possible.



A B

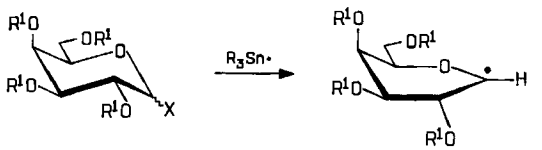


C

R^1 = Me, Ac, Bz X = Br, I, SePh, CO*t*Bu
R^2 = H, CH_2OR^1

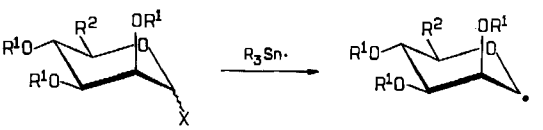
The most interesting finding in our previous studies was that π-type pyranosyl radicals derived from all-equatorially substituted pyranosyl (glucosyl) precursors **A** are transformed into a twisted boat-like ($B_{2,5}$) conformation **C**[7)] instead of retaining the $^4C_1$ conformation of the starting material. The primary radical **B** could only be observed in a low-temperature matrix[9)]. The $B_{2,5} \rightarrow {}^4C_1$ conformational conversion was explained by a "quasi-anomeric" stabilization due to interaction of the radical's SOMO with a σ* orbital of the adjacent β-C–O bond in a coplanar arrangement (see Discussion).

Stronger steric interactions in galactosyl-type pyranosyl radicals **E** prevent a complete conformational change, compromising in half-chair conformations.



D E

In mannopyranosyl radicals **G** the axially oriented β-C–O bond allows the proposed stabilizing interaction without the need to change the conformation, i.e. the $^4C_1$ chair conformation of the precursor is conserved in the radical.



F G

We report here on the conformation of C-1-cyano and -chloro-substituted pyranos-1-yl (**1R–6R**), C-5-methoxycarbonyl-substituted (**7R–8R**), C-5-unsubstituted, and C-5-acetoxymethyl-substituted (**9R–10R**) pyranosan-5-yl

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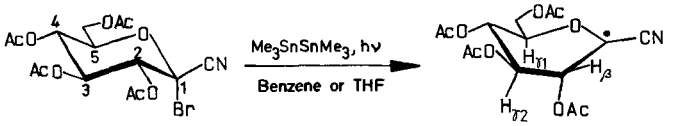
radicals. Radicals **1R**–**4R**, **7R**, and **8R** are characterized by the presence of a donor (OR) and an acceptor (CN or CO_2CH_3) at the radical center, thus classifying them as captodatively substituted systems[10]. It will be interesting to see how they compare with other pyranosyl radicals.

Results

As shown below for 2,3,4,6-tetra-*O*-acetyl-1-bromo-D-glucosyl cyanide (**1**), the pyranosyl radicals were obtained in all cases by bromine abstraction with trimethyltin radicals. The ESR-spectral parameters are listed in Table 1.



1 **1R**

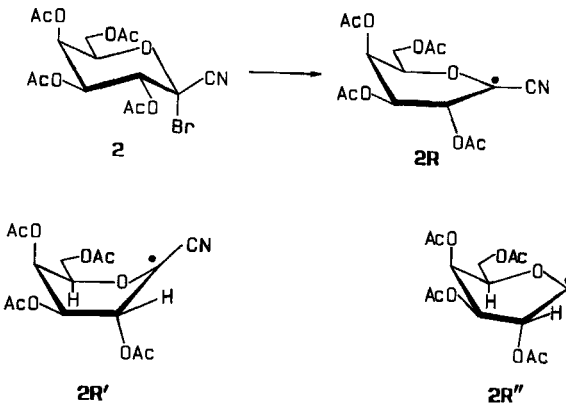
The equilibrium conformation[11] of the radicals was deduced from the angular dependence of the β-hydrogen splitting by means of the commonly used eq. (1)[12] with $A = 0.3 \pm 0.2$ mT and $B = 4.9 \pm 0.5$ mT, where Θ describes the dihedral angle between the direction of the singly occupied p orbital and the β-C–H bond.

$$a(\beta\text{-H}) = A + B\langle\cos^2\Theta\rangle \qquad (1)$$

Radical **1R**, obtained from the 1-bromo-D-glucosyl cyanide **1**, can be compared directly with the corresponding C-1-unsubstituted radical **C** (R^1 = Ac, R^2 = CH_2OAc)[5]. Both are characterized by a small β-hydrogen coupling constant (1.343 mT for **1R** and 1.407 mT for **C**). The γ couplings are also of the same magnitude. Thus, the conformation of **1R** should be very similar to that of **C**. Although a radical-stabilizing cyano group is present at C-1 in **1R**, the $B_{2,5}$ conformation remains unaltered in **1R**.

The 1-cyano-galactosyl radical **2R** (Figure 1) may also be compared directly with the corresponding C-1-unsubstituted galactosyl radical **E** (R^1 = Ac). Again, the presence of a cyano group at C-1 in **2R** has no detectable effect on the magnitude of the β-H coupling constant; it is evident that the cyano group does not influence the conformation.

At temperatures above +7°C an additional four-line signal appeared with increasing intensity in the center of the ESR spectrum (Figure 1). This new signal shows small hyperfine splittings similar to that of **2R** (Table 1), except that the large β-H splitting is now replaced by a very small one of ca. 0.07 mT. The new signal is very likely due to another conformer of **2R**. Possible structures are the $^{1,4}B$ boat **2R′** or the $B_{2,5}$ boat conformer **2R″**, both of which should exhibit a small β-H splitting but still have the γ_1 hydrogen at C-5 in axial position. Though the ESR data do not allow an unequivocal discrimination, the conversion into a different conformation is nevertheless clearly indicated.



2 **2R** **2R′** **2R″**

Table 1. ESR data[a] of C-1-substituted pyranosyl and pyranosan-5-yl radicals

substrate	radical	g[b]	T[°C]	a(β-H)	a(γ_1-H)	a(γ_2-H)	a(other)	a_X	X
1[c]	**1R**	2.00360(5)	17	1.343	0.397	0.103		0.303	N
			24	1.370	0.397	0.103		0.303	N
2[c]	**2R**	2.00331(1)	7	2.646	0.346	0.045	0.025[f]	0.305	N
			37	2.566	0.347	0.046		0.303	N
2[c]	**2R′,2R″**	2.00372(5)	37	0.070	0.347	0.046	0.025	0.303	N
3[c]	**3R**	2.00334(1)	37	1.630	0.240	0.227	<0.020[g]	0.300	N
4[c]	**4R**	2.00338(1)	31	2.266	0.320	0.050	0.025[g]	0.307	N
5[d]	**5R**	2.00465(3)	−16	2.333	0.137			0.533	Cl
			4	2.149	0.139			0.521	Cl
6[e]	**6R**		23	0.275	0.133			0.690	Cl
7[e]	**7R**[i]		30	0.587	0.163	0.408	0.103[h]		
8[e]	**8R**[i]	2.0037(1)	2	0.530	0.350		0.132[h]		
			2	0.530	0.350		0.102[h]		
			24	0.547	0.335		0.128[h]		
			24	0.547	0.335		0.103[h]		
9[e]	**9R**	2.00307(1)	−8	1.441	0.186		1.870[j]		
10[e]	**10R**	2.00302(5)	12	1.328	0.200	0.106	1.085[k]		
							0.831[k]		

[a] Estimated error in the hyperfine splittings ±0.003 mT. – [b] Estimated error in the last digit given in parentheses. – [c] Solvent fluorobenzene. – [d] Solvent THF. – [e] Solvent benzene. – [f] a(δ-H). – [g] a(γ_1-H) or a(δ-H). – [h] a(3 δ-H, CH_3). – [i] Two rotational isomers of the CO_2Me group of similar coupling constants. – [j] a(α-H). – [k] a(β_2-H, C-6).

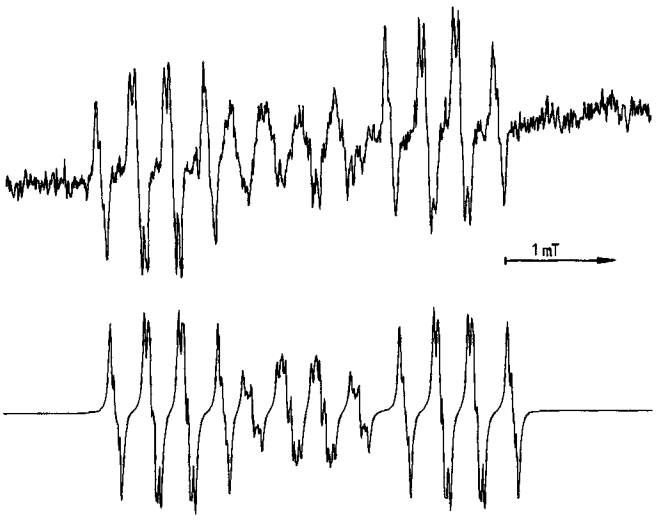
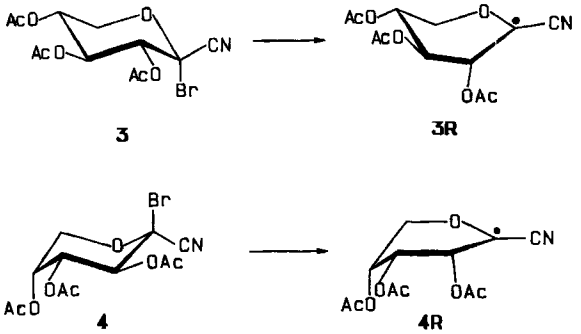


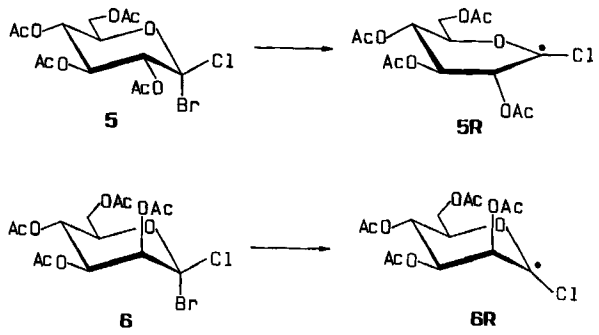
Figure 1. ESR spectrum of the 2,3,4,6-tetra-*O*-acetyl-1-cyano-D-galactopyranosyl radical (**2R**) in fluorobenzene at +37°C (top) and simulation (bottom)

The xylosyl derivative **3R** displays a slight increase in the β-H coupling constant compared to the C-1-unsubstituted radical **C** (R^1 = Ac, R^2 = H). The 1.630-mT splitting, compared to 1.221 mT in **C**, indicates a slightly less pronounced $B_{2,5}$ boat character. This could be regarded as a manifestation of the influence of the cyano group. In terms of simple PMO rationalizations it could be argued that the captodatively substituted radical center gains less from the interaction with the LUMO of the β-C–O bond than the C-1-unsubstituted radical.

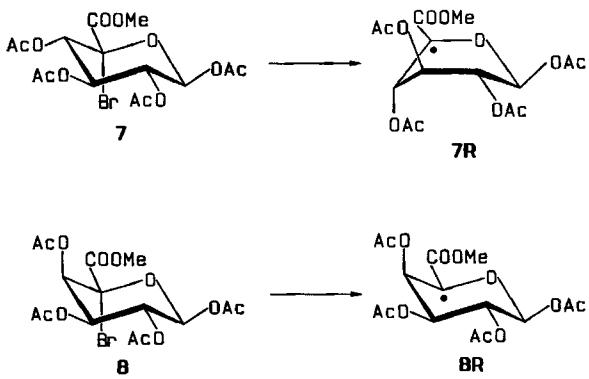
Radicals **3R** and **4R** differ in the configuration at C-4 in that the substituent in the D-arabinosyl compound **4** is in an axial position, whereas it is equatorially oriented in **3**. This change causes an increase in the β-H coupling constant from 1.630 mT in **3R** to 2.266 mT in **4R**, corresponding to a more axial position of the β-H in **4R** than in **3R**. This is presumably the consequence of an unfavorable 2,4-steric interaction of the acetoxy groups, thus preventing the development of a fully evolved boat conformation. Similar behavior has been observed in the galactosyl radical **2R**. An H_4 half-chair conformation is in closest agreement with the observed hyperfine splittings.



Radicals **5R** and **6R** differ from the previous ones by the presence of a chlorine atom at C-1 instead of a cyano group. Chlorine is a radical-stabilizing group but can not be classified as a captor substituent. The increase of the β-H coupling from 1.407 mT in the C-1-unsubstituted radical to 2.333 mT in **5R** could be the consequence of a conformational change and/or of a pyramidalization at C-1. The latter might be indicated by the increase in the *g* value. The small difference between the coupling constants of **6R** and the corresponding C-1-unsubstituted mannosyl radical **G** (R^1 = Ac, R^2 = CH_2OAc) could also be the consequence of a change in hybridization at C-1 rather than a significant conformational change. Chlorine and an oxygen substituent, both electronegative elements, at a radical center should induce pyramidalization. It should be remembered that two oxygen atoms alone suffice to make a radical center essentially nonplanar[12].

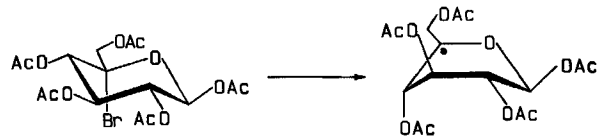


In structures **7R**–**10R** we encounter peracetylated deoxypyranosan-5-yl radicals. Their conformation is of interest, because the immediate surroundings of the radical center are equivalent to that of the pyranos-1-yl radicals **1R**–**4R**, except for the replacement of the cyano group by hydrogen, methoxycarbonyl, and acetoxymethyl, respectively. Thus, this is a situation where the quasi-anomeric effect should operate and provoke conformational changes. Furthermore, in **7R** and **8R** a captodative substitution pattern of the radical center can be recognized.



The radical precursors **7**–**10** assume a $^4C_1$ chair conformation and, if the radical conformation remains the same, distinct values for the β-H coupling constants would be expected. Thus, a large β-H coupling should be observed in **7R**. The experimental result [a(β-H) = 0.587 mT] suggests that β-H is not in an axial position as in **7** but in a more equatorial arrangement. The γ couplings resemble those in the peracetylated glucosyl radical **C** (R^1 = Ac, R^2 =

CH_2OAc). It is, therefore, proposed that **7R** undergoes a similar conformational change to a boat structure. In this way it can take advantage of the proposed quasi-anomeric stabilization. The small coupling of 0.587 mT indicates the β-hydrogen atom to be even more oriented in the nodal plane of the SOMO than in the glucosyl radical **C** [R^1 = Ac, R^2 = CH_2OAc; a(β-H) = 1.407 mT]. The situation is close to that in **8R** where this coupling constant is 0.547 mT at 24°C. Due to the axial position of the acetoxy group in **8** there is already an equatorial/axial relationship between the unpaired spin orbital and the hydrogen atom. Therefore, **8R** remains in a $^4C_1$ chair conformation, a situation that has been encountered for the tetraacetoxy-mannosyl radical **G** (R^1 = Ac, R^2 = CH_2OAc). As in **1R**–**6R** the additional captor group in **7R** and **8R** does not have consequences for the conformation of the radicals. This, in turn, is further supported by radicals **9R** and **10R**, where boat conformations analogous to the glucosyl system **C** are suggested by the ESR data.



Discussion

The primary result of our study is that a captor substituent at the radical center in pyranosan-5-yl radicals and in pyranosyl radicals does not influence the conformation of these radicals; they adopt a more or less pronounced boat conformation which is also assumed in the absence of the additional radical stabilizing substituent. This fact raises questions as to the completeness of the FMO interpretation of the preferred boat conformation in some acylated or alkylated glucosyl and pyranosan-5-yl radicals. The switch from a $^4C_1$ conformation in the radical precursor **A** to the $B_{2,5}$ conformation in the radical **C** was originally explained to derive mainly from a gain in stabilization through the interaction of the SOMO with the σ* orbital of the β-C–O bond in an ecliptic arrangement[4,5]. The oxygen lone pair does enhance this interaction, because its interaction with the unpaired electron at C-1 raises the energy of the unpaired electron orbital rendering it more favorable for the interaction with the σ* orbital. The resulting stabilization, now strong enough to overcompensate the steric interactions connected with the conformational change, was called a "quasi-anomeric" effect as it resembles in character the normal anomeric effect[13]. There, a lone-pair orbital is stabilized by the interaction with the σ* orbital of an axial C–O bond at C-1 of the carbohydrate.

The additional cyano group at C-1 in **1R** does not seem to affect this interpretation. The cyano group is a good radical-stabilizing group[14], and should therefore contribute to the stability of **1R**. The question is whether such a stabilizing effect should increase, decrease, or leave unaffected the tendency to form a $B_{2,5}$ boat conformation. The nitrogen coupling constant in **1R** is similar to that of the *tert*-butoxy(cyano)methyl radical[10b] (a_N = 0.310 mT), i.e. from this point of view **1R** could be considered a typical captodatively substituted radical. Regardless of the controversy about the amount of captodative stabilization it is a fact that the radical center gains stabilization through this substitution pattern. In terms of FMO theory this results from a stabilization of the SOMO by the interaction with the π and π* orbitals of the acceptor. The lowering of the SOMO, however, should lead to a *reduced* interaction with the σ* orbital of the β-C–O bond. Their separation now has been increased. In fact, HMO analysis of a captodatively substituted radical by Klessinger[15] shows that energetically the SOMO resembles that of a normal unsubstituted carbon radical. However, a high-lying SOMO, resulting from the interaction with the oxygen lone-pair in the carbohydrate radical, was considered essential for the ability to take advantage from the interaction with the σ* orbital of the β-C–O bond. Support for this interpretation came from the observation that deoxypyranosan-2-,-3-, and -4-yl radicals do not undergo conformational changes even if this would introduce an interaction with a σ* orbital of a β-C–O bond[6]. Thus, a contradiction seems to exist in the proposed explanation for the preferred conformations.

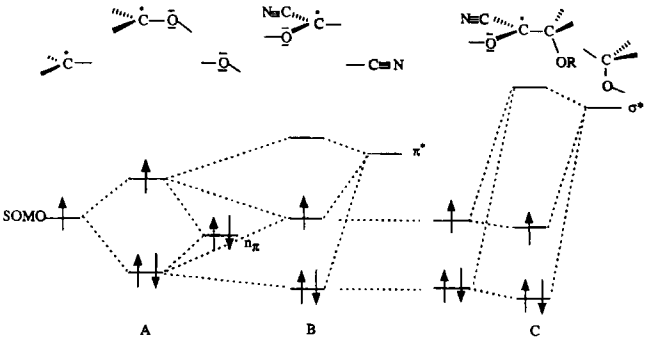
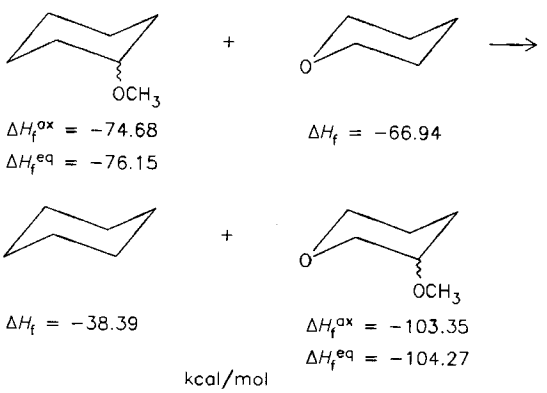


Figure 2. FMO scheme for the quasi-homo-anomeric interaction

We propose that the FMO picture is incomplete and has to be modified in order to be consistent with the observed conformational effects. In Figure 2, the FMO diagram is shown for successive interaction of a SOMO with a donor and an acceptor substituent (A and B), leading to an orbital arrangement of a captodatively substituted radical. The net stabilization of this system is mainly due to a lowering of the n_π orbital, with the SOMO barely involved. The arrangement B now interacts with the σ* orbital of the β-C–O bond. Both the SOMO and the n_π orbital will be affected. The latter contribution could be considered the result of a "homo-anomeric" effect between the lone-pair at

oxygen and the β-C–O bond at C-2. The combination of both stabilizations supplies the driving force for the change from a $^4C_1$ to a $B_{2,5}$ conformation. Consequently, the effect may be termed "quasi-homo-anomeric". As was pointed out above, the SOMO–LUMO interaction alone does not suffice to cause the conformational change. A similar situation can be found in open-chain β-heteroatom-substituted ethyl radicals[12,16]. Whereas β-alkoxyethyl radicals. $^{\cdot}CH_2CH_2OR$, adopt a staggered minimum conformation with the β-C–O bond oriented orthogonally to the SOMO, 1,2-dialkoxyethyl radicals, $RO\dot{C}HCH_2OR'$, prefer an ecliptic arrangement of the SOMO and the β-C–O bond, as can be deduced from the small β-H splittings[17]. In fact, effects which might be called "homo-anomeric", i.e. 1,3-interaction of an oxygen n_π orbital and a σ^*_{C-O} orbital, have been observed in 1,3-dioxane systems[18]. Here, several electronegative substituents, e.g. F, OAc, NO_2, SO_2R, etc. were actually found to prefer the axial position.

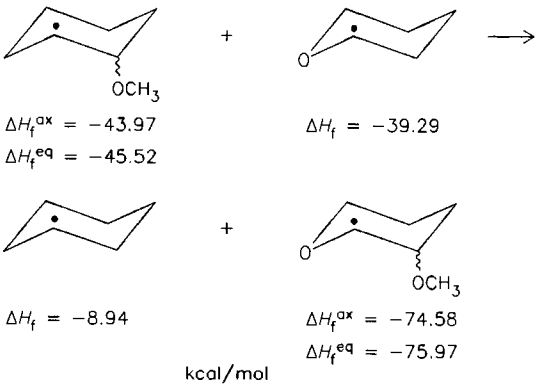
In order to test the proposal of a quasi-homo-anomeric effect, we carried out semiempirical calculations on the AM 1 level[19]. Two isodesmic reactions, where the ΔH_f values of the components are those of the energy-minimized structures, were considered. This approach minimizes effects from differences in correlation energies of the molecules and has been used in ab initio calculations by Schleyer et al.[20].



(2)

In eq. (2) equatorial or axial methoxycyclohexane was treated with tetrahydropyran to give cyclohexane and 3-methoxytetrahydropyran, with either an equatorial or an axial arrangement of the methoxy group. As can be calculated from the heats of formation, the equatorial position of the substituent is favored in both methoxycyclohexane ($\Delta\Delta H_f$ = 1.47 kcal/mol) and in 3-methoxytetrahydropyran ($\Delta\Delta H_f$ = 0.92 kcal/mol). In the latter case, the preference for the equatorial form is reduced by ca. 0.5 kcal/mol. The total heats of reaction are ΔH^{ax} = −0.12 and ΔH^{eq} = +0.43 kcal/mol. The negative ΔH^{ax} and the positive ΔH^{eq} value may be interpreted in terms of a small stabilizing homo-anomeric interaction in the saturated system. Indeed, it is not expected that the amount of this stabilization should be large, and so the actual numbers should not be overinterpreted[21].

In eq. (3) a comparable isodesmic reaction is shown for the radicals. ΔH^{ax} = −0.26 kcal/mol is about twice as exothermic as in the saturated system. In the radical case, ΔH^{eq} is also negative (−0.1 kcal/mol) indicating that the radical is stabilized by the interaction with an equatorial methoxy group. Although one should be careful with the interpretation of this result, we tend to see here an increase in the homo-anomeric stabilization as the consequence of an increased transmission of the interaction of the n_O orbital with the β-C–O bond by the SOMO. It could be stated that the radical center acts as a better mediator for the homo-anomeric interaction than the CH_2 group.



(3)

Conclusion

In summary, it is proposed that the lowering of the n_O orbital due to the "quasi-homo-anomeric" stabilization is the dominant stabilizing interaction causing the observed conformational change in glucosyl-type radicals. So far the lowering of this orbital was considered the result of interaction primarily with the SOMO. The presence of captor subtituents at the radical center made it necessary to reformulate slightly the original FMO interpretation of the conformational effects in carbohydrate-derived radicals.

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Experimental

Materials: 2,3,4,6-Tetra-*O*-acetyl-1-bromo-D-glucosyl cyanide[22] (**1**), 2,3,4,6-tetra-*O*-acetyl-1-bromo-D-galactosyl cyanide[23] (**2**), 2,3,4-tri-*O*-acetyl-1-bromo-D-xylosyl cyanide[23] (**3**), 2,3,4-tri-*O*-acetyl-1-bromo-D-arabinosyl cyanide[23] (**4**), 2,3,4,6-tetra-*O*-acetyl-1-chloro-D-glucosyl bromide[24] (**5**), 2,3,4,6-tetra-*O*-acetyl-1-chloro-D-mannosyl bromide[24] (**6**), 1,2,3,4-*O*-acetyl-5-bromo-β-D-xylopyranose[25] (**9**), 1,2,3,4,6-penta-*O*-acetyl-5-bromo-β-D-glucopyranose[26] (**10**), and methyl 1,2,3,4-tetra-*O*-acetyl-5-bromo-β-D-glucopyranuronate[27] (**7**) were prepared according to literature methods.

Methyl 1,2,3,4-Tetra-O-acetyl-5-bromo-β-D-galacto-pyranuronate (**8**): Methyl 1,2,3,4-tetra-*O*-acetyl-β-D-galactopyranuronate[28] (0.40 g, 0.9 mmol) was dissolved in absolute tetrachloromethane (15 ml), and barium carbonate (0.5 g), then bromine (0.2 ml) were added. The reaction mixture was heated at reflux and irradiated with a 200-W lamp for 1 h. After cooling to room temp., the solids were filtered off and washed with small portions of tetrachloromethane. The filtrate was washed with satd. aqueous sodium bicarbonate and 10% aqueous sodium hydrogen sulfite solutions, then dried with anhydrous magnesium sulfate. Evaporation of the solution yielded 0.48 g of a syrup which was purified by column chromatography on silica gel in benzene/ether/hexane (4:2:4). For TLC monitoring of the fractions benzene/ether/hexane (6:3:1) was

used. – Fraction A (R_f = 0.58) contained about 5 mg of an unidentified by-product. – Fraction B (R_f = 0.51) contained 22 mg of a substance assumed to be a mixture of over-brominated products containing bromine also in the acetyl moieties as deduced from the ^{1}H-NMR spectrum, which was very similar to that of fraction C except that an additional singlet appeared at δ = 3.82 (CH_2BrCO) and only three acetyl resonance lines were present. – Fraction C (R_f = 0.42) contained 370 mg (76%) of **8**. – $[\alpha]_D^{20}$ = −6 (*c* = 1.24, $CHCl_3$). – ^{1}H NMR ($CDCl_3$): δ = 6.22 (d, $J_{1,2}$ = 9 Hz, 1H, 1-H), 5.92 (d, $J_{3,4}$ = 3 Hz, 1H, 4-H), 5.78 (dd, $J_{2,3}$ = 10 Hz, 1H, 3-H), 5.43 (dd, 1H, 2-H), 3.87 (s, 3H, CO_2CH_3), 2.00–2.20 (4 s, 12H, 4 OAc).

$C_{15}H_{19}BrO_{11}$ (455.2) Calcd. Br 17.55 Found Br 17.43

ESR Measurements: A detailed description is given in ref.[1,5].

CAS Registry Numbers

1: 82469-74-7 / **1R**: 124856-33-3 / **2**: 83497-42-1 / **2R**: 124856-34-4 / **3**: 83497-43-2 / **3R**: 124856-35-5 / **4**: 89158-09-8 / **4R**: 124856-36-6 / **5**: 112290-59-2 / **5R**: 124856-37-7 / **6**: 125072-55-1 / **6R**: 124856-38-8 / **7**: 65615-69-2 / **7R**: 124856-39-9 / **8**: 124856-32-2 / **8R**: 124856-40-2 / **9**: 69534-64-1 / **9R**: 124856-41-3 / **10**: 69534-61-8 / **10R**: 124856-42-4 / methyl 1,2,3,4-tetra-*O*-acetyl-β-D-galactopyranuronate: 30628-06-9

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