



Structure of C-1 substituted glycopyranosyl azides: new insights based on CD measurements

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Abstract

CD spectra have been recorded for a series of peracetylated D-glycopyranosyl azides (D-*gluco*, D-*galacto*, D-*xylo*, D-*arabino* configuration) substituted at the anomeric position by various groups: amido, azido, cyano, ethoxy, methoxy. Application of the azide octant rule for the interpretation of the sign for the long-wavelength azide band allowed conformation of the azido group in each mono azido derivative investigated to be established. In each 1-cyano derivative, the azido group was in a *gauche*-like arrangement with respect to the C-1–O^{ring} bond, which is considered as a manifestation of the *exo*-anomeric effect of the azido group. For the 1-alkoxy derivatives, an antiparallel orientation of the azido group with respect to the C-1–O^{ring} bond was found in solution by CD measurement analysis, as already observed for methoxyazide **5** in the solid state. For azidoamide derivatives, intramolecularly (N–H–N^{azide}) H-bonded conformers are believed to prevail in methanol, in contrast to the situation in DMSO. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Initiated by pioneering observations by Edward¹ and Lemieux,² continuing interest towards stereo-electronic effects at the anomeric carbon of sugars^{3–6} is mainly explained by the need to closely control the selectivities of synthetic reactions, in particular glycosylation, and to get reliable structural data from the resulting oligosaccharides. Such knowledge was shown to be essential in order to precisely

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investigate their binding abilities with proteins, e.g. lectins⁷ as an example of supramolecular interactions. However, although *O*-glycosides are primarily concerned with these effects, a large array of glycosyl derivatives have contributed to the development of this field, feeding ongoing controversies.⁸ The nature of the stereoelectronic effects in tetrahydropyran/carbohydrate derivatives bearing one substituent at the anomeric carbon is more or less understood on the basis of generally accepted models (dipolar interaction, delocalization, lone-pair repulsion) that can rationalize one or more aspects of the anomeric effects. There is, however, no unified theory which could explain all the phenomena from the same simple basis.^{3–6}

While practically all types of substituent groups at the anomeric centre have been investigated as to their participation in exerting stereoelectronic effects,^{3–6} there is only a little data, mainly on a phenomenological level, which describe manifestations of stereoelectronic effects in anomerically bifunctional derivatives. The more documented examples comprise monosaccharide derivatives with the following pairs of substituents at the anomeric carbon: CN–Br,⁹ CN–Cl,¹⁰ CN–F,¹¹ CN–OAc,¹² CN–N₃,¹⁰ CN–SCN,¹³ CONH₂–Br,¹⁴ CONH₂–OH,¹⁴ CONH₂–N₃,¹⁴ N₃–OR (R=Me, Et),¹⁵ N₃–N₃,¹⁶ OMe–SMe,¹⁷ Cl–Br,¹⁸ F–F,¹⁸ Cl–NO₂,¹⁹ as well as ulose²⁰ and ulosonic acid derivatives.²¹ Anomeric configurational and/or ring conformational equilibria of some of these derivatives were studied mainly by NMR methods.^{9–11,14,15} In some cases, CD measurements were also performed; however, only with those compounds which had no classical chromophores (CN–Br, CN–OAc).²² X-Ray analyses of anomerically disubstituted monosaccharide derivatives having CN–Br,²³ CN–OAc,²³ CN–SCN,¹³ and N₃–OMe¹⁵ groups were also published. Photolytic transformation of 1-alkoxy-D-glucopyranosyl azides clearly exhibited different product ratios depending on the anomeric configuration of the substrates.²⁴ This was in contrast to results for 1-cyano-D-glucopyranosyl azides^{25,26} and D-fructopyranosyl azides²⁰ which gave the same products on photolysis, whatever the anomeric configuration of the substrate. These differences in product distribution are considered as manifestations of stereoelectronic effects. Besides these sporadic data, neither systematic investigations of such compounds nor attempts to theoretically rationalize these phenomena have been done so far.

As a result of recent synthetic work, we gathered a series of anomerically substituted D-glycosyl azides. These compounds, possessing a well studied chromophore^{27–29} at the doubly substituted anomeric position, offered themselves for CD investigations.³⁰ Since the anomeric configuration of each of these compounds was ascertained by either X-ray analysis¹⁵ or heteronuclear ³J_{H,CN} coupling,^{9–11,14} the conformation of the azido group was the only variable which was expected to account for the observed sign of the Cotton effects due to the azide chromophore. In fact, thorough spectroscopic studies of glycopyranosyl azides were first carried out by Paulsen et al. who resorted to CD measurements²⁷ and X-ray crystal structure analysis.^{31–33} Both methods showed that, in both the solid^{31–33} and liquid state,²⁷ the azido group was oriented towards the ring oxygen atom (Fig. 1) in a *gauche*-orientation with respect to the C-1–O^{ring} bond. This conformational preference observed for peracetylated α - and β -glycopyranosyl azides was interpreted as a manifestation of the *exo*-anomeric effect of the azido group.²⁷ A detailed study of the photolysis of acyclic azidoethers also led to the conclusion that the azido and the alkoxy groups were in an almost eclipsed orientation in the preferred ground state conformation.³⁴

Herein, we present application of the azide octant rule^{27,28} to draw structural conclusions from the observed CD spectra of the anomerically substituted glycosyl azides. Throughout this report, the anomeric carbon of the substituted glycosyl azides investigated is referred to as C-1 for the sake of clarity since application of systematic nomenclature would lead to two different numberings.

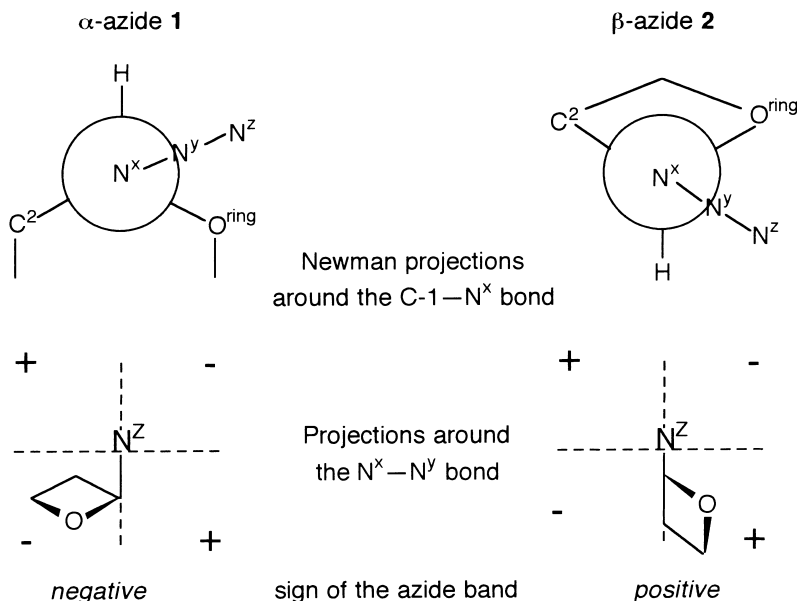


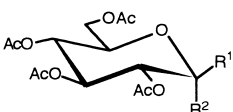
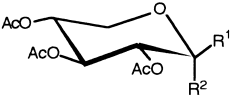
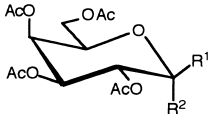
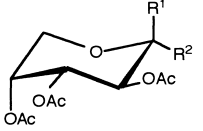
Figure 1. Preferred conformation of the azido group and the projections used for prediction of the sign for the long-wavelength CD band in α - and β -D-glycopyranosyl azides **1** and **2** in the 4C_1 conformation.²⁷ The same is true for the 1C_4 conformers which are not shown

2. Results and discussion

Investigated were per-*O*-acetylated 1-alkoxy- **3–6**,¹⁵ 1-cyano- **8–11,13**,^{10,25} 1-carboxamido- **12,14**,^{10,13} 1-azido- **7**¹⁶ D-glycopyranosyl azides (Table 1). From the point of view of the stereoelectronic effects the additional anomeric substituents belong to different categories: the alkoxy,^{3–6} cyano,^{9,35–39} and azido⁴⁰ groups are known to exert normal (*endo*-)anomeric effects; the alkoxy^{3–6} and the azido²⁷ groups may also participate in *exo*-anomeric effects; the carboxamido group has been shown to have a *reverse* anomeric effect;^{3–6,41} the cyano and the carboxamido groups, having no lone pairs on the atom attaching them to the anomeric carbon, cannot participate in *exo*-anomeric effects: for the former no rotamers can be defined while for the latter, to the best of our knowledge, conformational preferences along the C-1–CONH₂ bond have not been determined as yet.

The azide octant rule²⁸ predicts a *negative* sign of the azide band for the acetylated α -D-glucopyranosyl azide **1** and a *positive* one for the β form **2**²⁷ (Table 1; Fig. 1). This rule applies for both the 4C_1 and 1C_4 chair forms.²⁷ As seen in Table 1, the sign of molecular ellipticities [Θ] recorded for each of the cyano azides **8–11, 13** matched the sign found for **1** and **2**: a positive Cotton effect was associated with a β -oriented azido chromophore and vice versa. Therefore, a *gauche*-arrangement of the azido group with respect to the ring oxygen seems the most probable conformation in each of these molecules, as already found for **1** and **2**.²⁷ However, replacing 1-H by a cyano group introduces perturbing atoms in sectors opposite the sugar ring in both staggered positions (Fig. 2, conformers *a, b*) as well as in eclipsed arrangements (Fig. 2, conformers *d, e*) which should reduce the azide band intensity. Note that in conformers *c* and *f* (Fig. 2), the cyano group does not appear in any sector, whereas the pyranosyl ring occupies two sectors, so that the location of the ring oxygen atom is expected to determine the sign of the azide band. Only conformers *a, d* and *f* can be expected, on the basis of the projections, to give rise to a positive sign of the azide band of 1-cyano- β -D-glycopyranosyl azides. Since the intensities of the Cotton effect for α -azides **8, 10** and **13** and β -azides **9** and **11** are not very different from those of **1**

Table 1
CD spectral data of peracetylated D-glycopyranosyl azides **1–14**

Compound		R ¹	R ²	[Θ]/λ ^a
 <p>D-gluco</p>	1	H	N ₃	-1600/268 ^b
	2	N ₃	H	+1100/269 ^c
	3	OMe	N ₃	+690/274
	4	OEt	N ₃	+630/272
	5	N ₃	OMe	-2200/272
	6	N ₃	OEt	-2700/273
	7	N ₃	N ₃	+510/282
 <p>D-xyllo</p>	8	CN	N ₃	-1500/267
	9	N ₃	CN	+1900/269
 <p>D-galacto</p>	10	CN	N ₃	-1600/266
	11	N ₃	CN	+1900/268
	12	N ₃	CONH ₂	-670/274 -200/272 ^d
 <p>D-arabino</p>	13	CN	N ₃	-1700/270
	14	CONH ₂	N ₃	+580/290 +460/291 ^d

^a Molar ellipticities measured for methanolic solutions at concentration 3–4 mmol·L⁻¹ with a 0.2 cm cell ([Θ]; deg·cm²·dm⁻¹·mol⁻¹; λ; nm).

^b Lit.²⁷ values: -1485/266 (for dioxane solution).

^c Lit.²⁷ values: +1138/271 (for dioxane solution).

^d Measured in DMSO at concentration ~2 mmol·L⁻¹.

and **2**, respectively, the position of the CN group should be in (Fig. 2, conformers *c* and *f*), or close to (Fig. 2, conformers *d* and *e*), a symmetry plane where its contribution to the Cotton effect can be equal, or close, to none. Conformer *c* would have a weak steric interaction between H-2 and N₃²⁷ and a strong electrostatic repulsion between the parallel dipoles of N₃²⁷ and CN. Conformer *f* is practically free of steric interactions (that between N₃ and CN should be insignificant) and the dipolar interactions are more favourable between the N₃ and the CN groups; however, less so between the N₃ group and the O^{ring} atom. Therefore, as a compromise, the azide group may be in a position between the staggered *a* and eclipsed *f* conformations with respect to the CN substituent, giving rise for **9** and **11** to CD spectra similar to that of the unsubstituted β-D-glycosyl azide **2** with an equatorial azido group. For the α-anomers **8**, **10** and **13**, having a negative sign of the azide band as found for **1**, similar considerations lead to the conclusion that

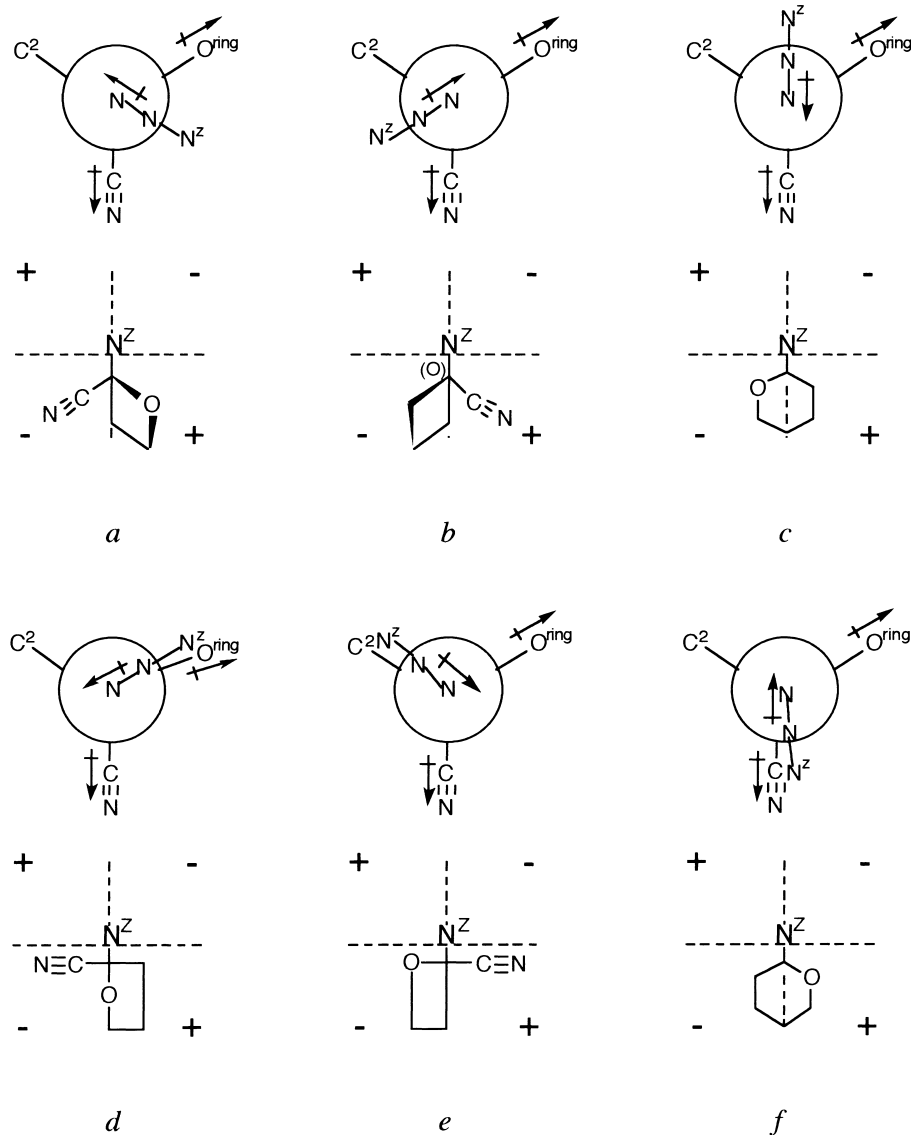


Figure 2. Application of the azide octant rule to 1-cyano-1-deoxy- β -D-glycopyranosyl azides (e.g. **9** and **11**) in the 4C_1 conformation: Newman projections around the C-1-N^x bond and projections used for predicting the sign of the azide long-wavelength band

the azide group may be between a *gauche*-position with respect to the C-1-O^{ring} bond and the eclipsed position with respect to the cyano group.

As compared to the aforementioned azido derivatives, a sign reversal of the CD band associated to the azide group was found for 1-alkoxy-glycosyl azides **3–6**, thus suggesting shifts of the conformational equilibria. Viewing conformers **3a–3c** in Fig. 3, representing α -azide **3** with the methoxy group adopting a *gauche*-orientation to the C-1-O^{ring} bond, it is only **3b** and **3c** which give rise to a positive CD band. Rotamer **3a** would give a weak negative contribution because of the presence of the glycosidic oxygen in the rear-right-bottom positive sector and some probable front sector occupancy by the CH₃ group. However, this structure is most probably a minor component in the conformer population because of

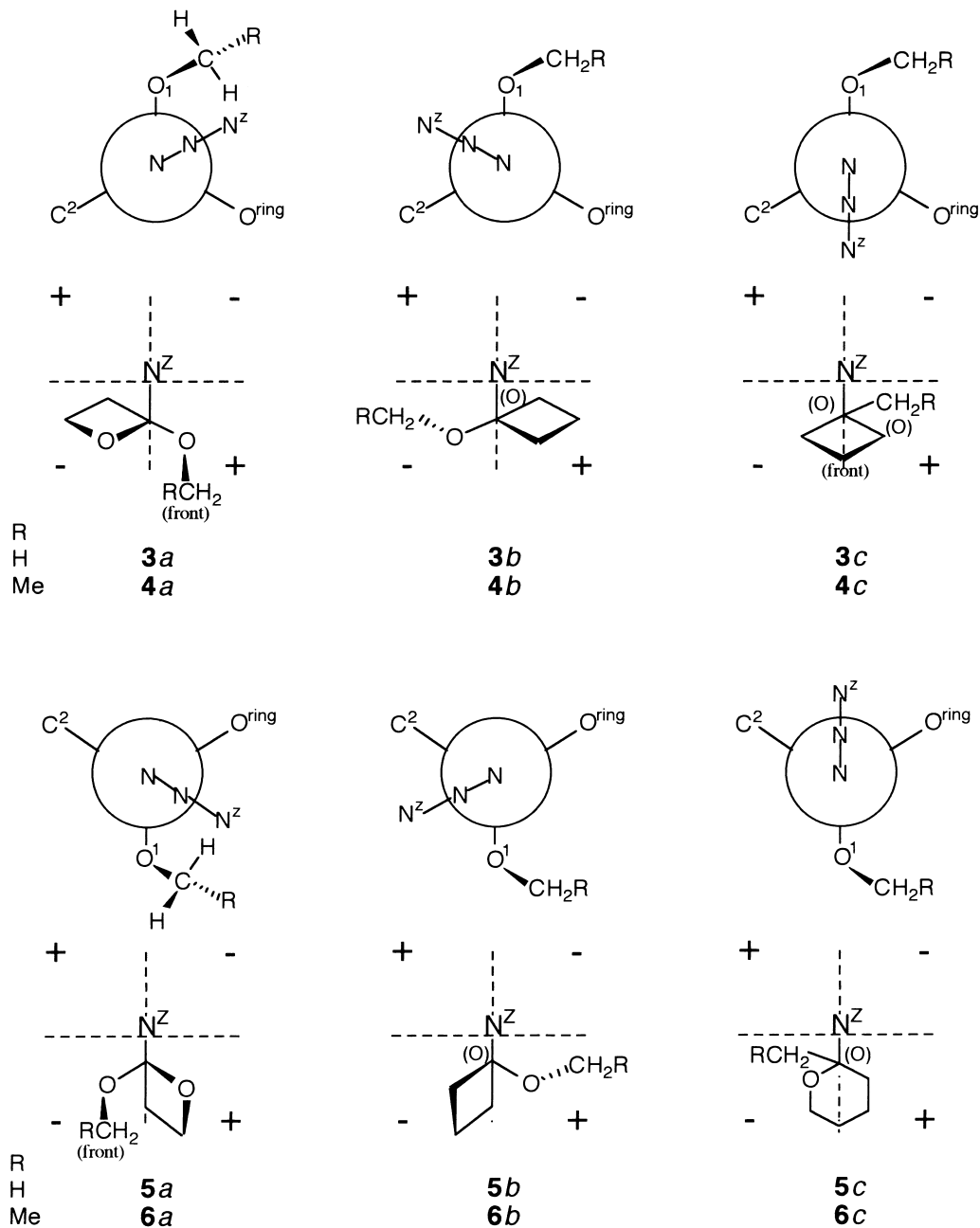


Figure 3. Application of the azide octant rule to 1-alkoxy- α - and β -D-glucopyranosyl azides **3/4** and **5/6** in the 4C_1 conformation: Newman projections around the C-1–N^x bond and projections used for predicting the sign of the azide long-wavelength band

steric hindrance, due to 1,3-*diaxial* hydrogen–azide interaction²⁸ with the methyl C–H bonds in the aglycone. Participation of **3c** may be diminished by steric interactions with the H-3 and H-5 protons. The same arguments apply to the ethoxy derivative **4**. Therefore, compounds **3** and **4** appear to prefer conformation *b* in solution.

Similar consideration may be extended to β -azides **5** and **6** (Fig. 3, conformers **5a–c** and **6a–c**),

suggesting the preponderance of rotamers **5b** and **5c**, giving rise to a negative CD band. The **5c** arrangement suffers from a weak steric interaction between H-2 and the azido moiety²⁷ which may diminish its participation in the conformational equilibrium. For compound **5**, evidence has been obtained by NMR spectroscopy and X-ray crystal analysis showing that the methoxy group was in a *gauche*-orientation to the C-1–O^{ring} bond, in both the liquid (CDCl₃) and solid state.¹⁵ Consideration of other C-1–OCH₂R rotamers in both series does not alter the above conclusions since the OCH₂R group would remain in the same sectors for the more populated conformers *a* and *b* in **3–6**. It follows from the sign found for the azide band that in the preferred conformers of the alkoxy azides, the azido group is antiparallel to the C-1–O^{ring} bond, in an opposite direction as compared to the unsubstituted azides **1** and **2** where this group is *gauche* relative to the same bond. An X-ray structure determination showed that in the solid state the azido group in **5** was also antiparallel to the C-1–O^{ring} bond.¹⁵ The preferred conformation found for alkoxyazides **3–6** correspond in fact to an optimized situation compatible with a full development of stereoelectronic effects. In α -azides **3** and **4** with a β -oriented OCH₂R group, the aglycone moiety can exert the *exo*-anomeric effect ($n_{O-1} \rightarrow \sigma^* \text{C-1-O}^{\text{ring}}$ delocalization), whereas the azido group in a *gauche*-orientation with respect to the *O*-glycosidic bond is suitably placed to achieve delocalization towards the $\sigma^* \text{C-1-O-1}$ orbital. The same is true for compounds **5** and **6** which allow, in addition, electronic delocalization through the *endo*-anomeric effect ($n_{O^{\text{ring}}} \rightarrow \sigma^* \text{C-1-O-1}$ delocalization). This could account for the fact that compounds **5** and **6** were found to correspond with the thermodynamically favoured epimers.¹⁵

It is worth noting that the intensities in the Cotton effects increase for **5** and **6** and decrease for **3** and **4**, as compared to those of the unsubstituted glycosyl azides **1** and **2**. Weakening of the azide band intensities in the spectra of **3** and **4** might be attributed to the glycosidic oxygen occupying the rear-left-bottom negative octant (Fig. 3, conformers *b* in **3** and **4**). On the other hand, in the case of **5** and **6**, an essentially similar arrangement corresponding to conformer *b* (Fig. 3) results in an enhancement of intensity in the CD band. A reason for the variation of intensities can be that the conformational rigidity of the two anomers differs from one another. In β -azides **5** and **6**, the rotational position of the α -alkoxy group is mainly restricted to the one shown in Fig. 3 (conformers *a–c* in **5** and **6**). Other positions for the α -alkoxy groups are much more unfavourable due to the steric interactions with the ring as well as loss of *exo*-anomeric stabilization (calculated rotational barrier in *axial* 2-methoxy-tetrahydropyran:⁴² ~10.5 kcal/mol). In α -azides **3** and **4**, the β -alkoxy group may rotate more freely (calculated rotational barriers in *equatorial* 2-methoxy-tetrahydropyran:⁴² 4.5 and 7.5 kcal/mol). The more tightly fixed position of the α -OR group in **5** and **6** may more strongly limit the motion of the azido group as compared to the more flexible β -OMe/OEt groups in **3** and **4**. Consequently, the population of the most probable rotameric states (*a–c*) is different in the α - and β -azides. In the case of alkoxy- β -azides **5** and **6**, the dominant rotamer is *b*, giving rise to a more intense CD band. Note that the highest band amplitude (–2700 at 273 nm) is observed for the more sterically demanding ethoxy derivative **6**, as compared to **5** (–2200 at 272 nm). In accordance with these considerations, the difference in the intensities of the CD bands for **3** and **4** is negligible.

For the azido-amides **12** and **14**, again a reversal of the sign for the Cotton effect as compared to the unsubstituted glycosyl azides **1** and **2** was observed. It follows that, from the azide octant rule, conformers of type *b* and *c* (CONH₂ instead of OCH₃) in Fig. 3 should preponderate. The azido moiety may rotate rather freely in these compounds since the intensities of the CD bands are in the same range as those for **3** and **4** although for such azidoamide derivatives it is reasonable to consider the existence of intramolecular hydrogen bondings in the vicinity of the anomeric centre. They could involve an amide hydrogen atom as the hydrogen donor and an oxygen atom as the acceptor (either O-2 or O^{ring}). There is experimental evidence supporting intramolecular H-bonding involving the endocyclic ring oxygen

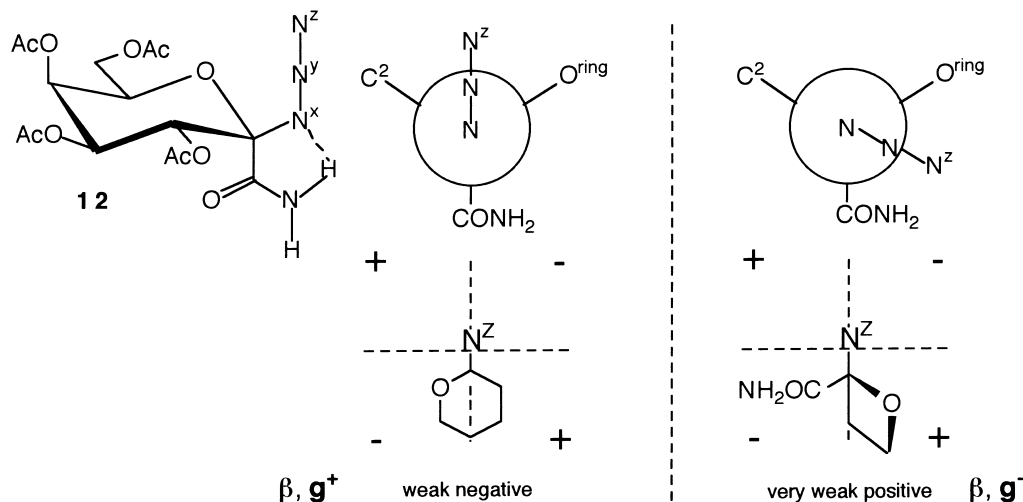
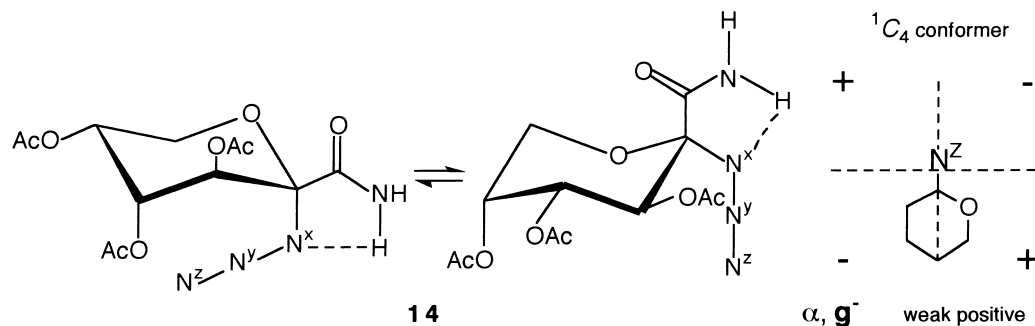


Figure 4. Proposed predominant conformer of compound **12** with an H-bond between the amide group and the N^x atom. The dihedral angle N^y–N^x–C1–O^{ring} corresponds to $\pm 60^\circ$ noted g^+/g^-

atom in tetrahydropyran⁴³ and pyranoside⁴⁴ derivatives. However, in the present case, such H-bonding would place the carbonyl group in a roughly parallel orientation with either the C-1–O^{ring} or C-2–O-2 bond so that the corresponding conformers should be destabilized by the occurrence of unfavourable dipolar interactions. In the azido group, the N^x atom has a high electronic density which accounts for its basic properties⁴⁵ and its possible involvement in H-bonding, as put forward to account for the reactivity of azidohydrins⁴⁶ and that of acyl derivatives in 1-amino-8-azidonaphthalene.⁴⁷ The decreased intensity found for the azide band when the spectra of **12** and **14** were obtained from solutions in DMSO suggests that the population of conformers is more equally distributed as compared to the situation in methanol, maybe due to the weakening of a probable hydrogen-bonding between an amide hydrogen and the negatively polarized N^x nitrogen atom of the azido group (Figs. 4 and 5). It is proposed that for **12** the predominant conformer in methanol is type *c* (see Fig. 3); also noted g^+ (Fig. 4), in accordance with the weak negative CD band observed, while contribution of conformer g^- (Fig. 4), having a weak positive effect, could be enhanced in DMSO. The same argument is in favour of **14** g^- as the main conformer in methanol (Fig. 5) with an enhanced contribution of **14** g^+ (azido group *gauche* to the C-1–O^{ring} bond) in DMSO. However, **14** showed a red-shift of the azide band and a less expressed solvent sensitivity (+580/290 and +460/291 in MeOH and DMSO, respectively) as compared to **12** (–670/274 and –200/272) (Table 1). Being a pentopyranose derivative, **14** exists in a conformational equilibrium (Fig. 5) in which the ⁴C₁ chair form is highly represented due to the reverse and the normal (*endo*-)anomeric effect of the amido⁴¹ and azido⁴⁰ groups, respectively. In the g^- conformer of the ⁴C₁ form, the sugar ring can also occupy front sectors which would render its positive contribution uncertain. On the other hand, this H-bonded azide rotamer can be disfavoured in the ⁴C₁ form because of the probably very significant 1,3-*syn*-diaxial interactions of the azido group (Fig. 5). Therefore, the H-bridged conformers are less preponderant in **14** and, consequently, the effect of the H-bond breaking DMSO is less pronounced.

Diazide **7** showed a weak positive CD which is just the opposite of what would be expected by simple addition of values of band amplitudes measured for the α -azide **1** and its β -anomer **2**. It is a question, however, whether the azide sector rule can be applied for **7** having two azide chromophores in geminal position where an electronic interaction between them cannot be excluded.⁴⁹ It is reasonable to assume that **7** with an anomeric centre linked to three heteroatoms would prefer conformations which accommodate the highest number of electronic delocalizations, as noted for compounds **3–6**. This could



	4C_1	:	1C_4 (%) ^a		$J_{4,5}, J_{4,5'} (Hz)$
CDCl ₃	52	:	48		~5.2, ~6.8
DMSO- <i>d</i> ₆	61	:	39		4.0, 7.7
CD ₃ OD	50	:	50		6.2, 6.6
acetone- <i>d</i> ₆ ^b	59	:	41		4.4, 7.5

Figure 5. Conformational equilibrium of compound **14** and application of the azide octant rule to the 1C_4 conformer. ^aCalculated on the basis of $J_{4,5}$ couplings using $J_{4a,5a}=11.6$ Hz and $J_{4e,5e}=1.5$ Hz as limiting values for the 4C_1 and 1C_4 conformers, respectively.^{48b} The ${}^1C_4: {}^4C_1$ ratio for compound **14** was erroneously published¹⁴ to be 60:40 in acetone-*d*₆.

occur when one azido group (either α or β) is *gauche* to the C-1-O^{ring} bond, the other being antiparallel to avoid unfavourable steric/dipolar interactions. These two conformers could exert *endo*- and *exo*-anomeric effects as well as an additional delocalization from the N^x atom of the antiparallel azido group towards the σ^*C1-N^x orbital of the *gauche* azido group. Therefore, both conformers should have comparable energies and could participate to a comparable extent to the conformational equilibrium of **7**. Hence, the occurrence of several conformers for **7** could account for the low intensity of its CD band.

3. Conclusion

Application of the azide octant rule for the interpretation of CD data recorded for a series of peracetylated anomerically substituted D-glycopyranosyl azides allowed the conformation of the azido group in each mono azido derivative investigated to be established. For those derivatives having a 1-cyano group, the azido group was found to be in a *gauche*-arrangement with respect to the C-1-O^{ring} bond, whatever the anomeric configuration. This conformational preference was shown to be a manifestation of the *exo*-anomeric effect. For the 1-alkoxy derivatives studied, an antiparallel orientation of the azido group with respect to the C-1-O^{ring} bond was found in solution by CD measurement analysis, as similarly observed for methoxyazide **5** in the solid state. Such arrangements appear to be compatible with an extensive expression of stereoelectronic effects in a mixed (*O,O,N*)-orthoester-type segment. The solvent-dependent CD spectra obtained for two azidoamides support the existence of H-bonded conformers with a hydrogen bond between the amide hydrogen atom and the N^x atom of the azido group in methanol. In such conformers, probably less tightly fixed for a conformationally labile D-*arabino* derivative, both the azido and the amido groups are lying in a plane orthogonal to the pyranose ring mean plane.

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