Synthesis of tetrazoles bearing a sugar moiety (sugar tetrazoles). X-Ray molecular structure of '(7*R*,8*R*,9*S*,10*R*)-8,9,10-tribenzyloxy-7-benzyloxymethyl-6-oxa-1,5-pentamethylenetetrazole'

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Thermolysis of perbenzylated D-glucopyranosediyl diazide **1** and D-galactopyranosediyl diazide **4** afforded, respectively, the corresponding 6-oxa-1,5-pentamethylenetetrazoles **2** and **5** *via* the sugar azido nitrenes, while, photolysis of diazides **1** and **4** gave, respectively, compounds **2** and **5** together with the corresponding by-products, 10-oxa-1,5-pentamethylenetetrazoles **3** and **6**. Similarly, 5-(sugar chain)-substituted tetrazole **9** was obtained by the thermolysis of perbenzylated 1,1-diazido acyclic sugar **8**, while compound **9** and 1-(sugar chain)-substituted tetrazole **10** were formed by the photolysis of compound **8**. Interestingly, the thermolysis and photolysis of 1,1-diazido-2,3-di-*O*-benzyl-D,L-glyceraldehyde **8f** gave both the corresponding **9f** and **10f**.

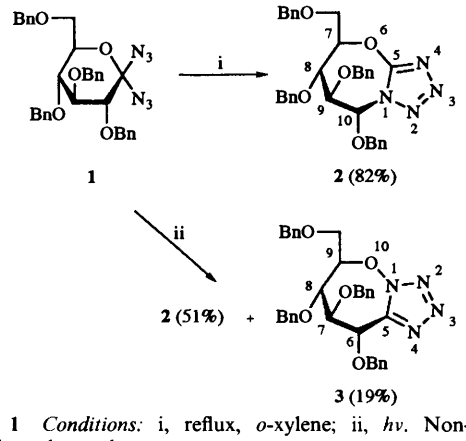
Introduction

Some tetrazoles having a sugar moiety (sugar tetrazoles) were synthesized in order to allow a study of analogues of biologically active tetrazoles such as 1,5-pentamethylenetetrazole† (leptazol or metrazole).[1]

Results and discussion

From pyranosediyl diazides

For this project, we employed the photolysis of perbenzylated D-glucopyranosediyl diazide **1**,[2] because the *gem*-dialkyl azides are known to afford the corresponding tetrazoles *via* azido nitrenes upon photolysis.[3] Then, compound **1** was irradiated in dry benzene under argon with a high-pressure Hg lamp for 2 h to give the desired (7*R*,8*R*,9*S*,10*R*)-8,9,10-tribenzyloxy-7-benzyloxymethyl-6-oxa-1,5-pentamethylenetetrazole **2** and its isomer **3** in 51 and 20% yield, respectively (Scheme 1).



Scheme 1 *Conditions:* i, reflux, *o*-xylene; ii, *hv*. Non-systematic numbering scheme shown.

The structure of compound **2** was determined unequivocally by X-ray crystallography, while compound **3** was assigned tentatively as 10*S*-epimer of **2** mainly by NMR data[4] (Fig. 1).

† Throughout this paper, the fused tetrazolo-oxazepines are numbered as bicyclic systems, with the numbering schemes shown in Scheme 1.

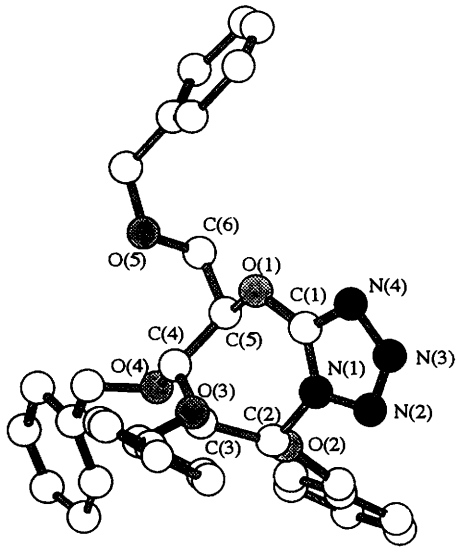
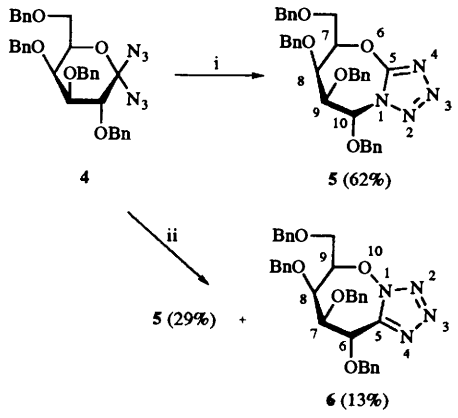


Fig. 1 X-Ray molecular structure of compound **2** with crystallographic numbering scheme (hydrogen atoms omitted)

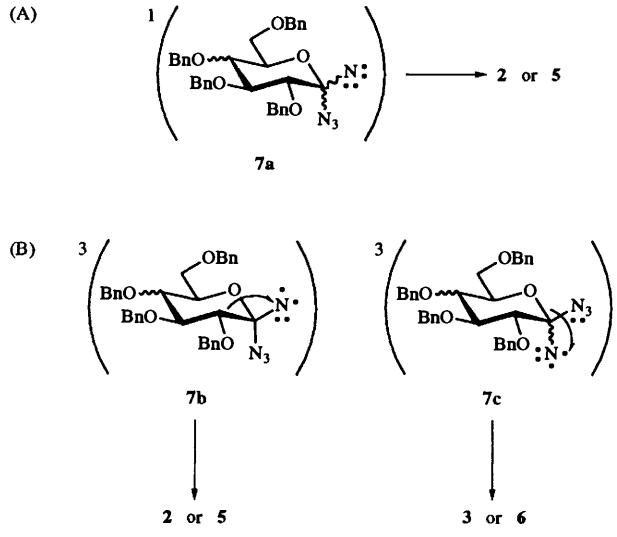
Later, a study of the NMR and X-ray crystallographic data by Descotes and co-workers[5] revealed that **3** is not the 10*S* epimer of compound **2** but, surprisingly, is the *O*-rearranged product, (6*S*,7*R*,8*S*,9*R*)-6,7,8-tribenzyloxy-9-benzyloxymethyl-10-oxa-1,5-pentamethylenetetrazole. On the other hand, refluxing of diazide **1** in *o*-xylene for 17 h under argon afforded only compound **2** as needles in 82% yield.

Further, thermolysis of the perbenzylated D-galactopyranosediyl diazide **4** gave (7*R*,8*S*,9*S*,10*R*)-8,9,10-tribenzyloxy-7-benzyloxymethyl-6-oxa-1,5-pentamethylenetetrazole **5** in 62% yield, while photolysis of compound **4** gave compound **5** and (6*S*,7*R*,8*R*,9*R*)-6,7,8-tribenzyloxy-9-benzyloxymethyl-10-oxa-1,5-pentamethylenetetrazole **6** in 29 and 17% yield, respectively (Scheme 2).

Judging from the results of a photochemical study on peracetylated methyl 1-azido-α- or β-D-glucopyranosides,[6] the formation of compounds **2**, **3**, **5** and **6** can be reasonably explained as shown in Scheme 3. That is, thermolysis of substrates **1** and **4** gives, respectively, products **2** and **5** *via*



Scheme 2 *Conditions:* i, reflux, *o*-xylene; ii, *hv*. Non-systematic numbering scheme shown.



Scheme 3 (A) Thermolysis; (B) photolysis

singlet azido nitrene **7a**, as is reported for simple azides.[7] On the other hand, photolysis of substrates **1** and **4** gives, respectively, **2**, **3** and **5**, **6** perhaps *via* triplet azido nitrenes **7b** and **7c**, because the addition of acetophenone as a triplet sensitizer has no effect on the product distribution (**2** and **3** or **5** and **6**).

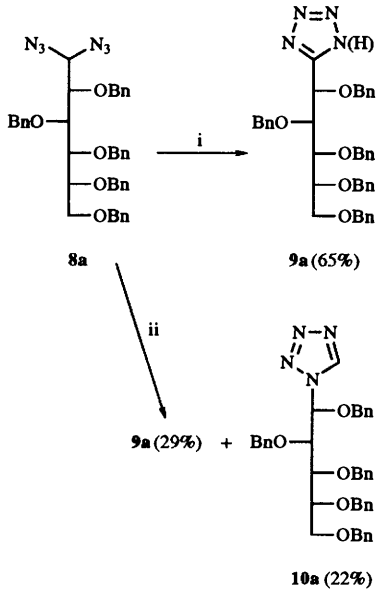
From acyclic sugar diazides

Next, we intended to synthesize tetrazoles bearing an acyclic sugar moiety by using the corresponding acyclic diazides. The starting material, 1,1-diazido-2,3,4,5,6-penta-*O*-benzyl-1,1-dideoxy-D-glucose hydrate **8a**, was prepared by the following four steps: formation of a dithioacetal,[8] benzylation, cleavage of dithioacetal,[9] and formation of diazide of perbenzylated D-glucose.

When diazide **8a** was refluxed in *o*-xylene for 6 h under argon, tetrazole **9a** was obtained in 65% yield, while photolysis of diazide **8a** afforded tetrazoles **9a** and **10a** in 29 and 22% yield, respectively (Scheme 4).

The present reaction was also observed in the case of perbenzylated D-mannose, D-arabinose, D-ribose, D-erythrose and DL-glyceraldehyde. The results are summarized in Table 1.

A plausible mechanism for this reaction is considered in Scheme 5. Thermolysis of sugar diazide **8** gives a singlet sugar azido nitrene **11**, which is inserted between the C(1)–H bond to give an azido imino sugar **13**, followed by cyclization to the sugar tetrazoles **9**. Photolysis of diazide **8** gives at first an excited singlet sugar diazide **8***, which is immediately converted into



Scheme 4 *Conditions:* i, reflux, *o*-xylene; ii, *hv*

Table 1 Thermolysis and photolysis of acyclic sugar diazides **8**

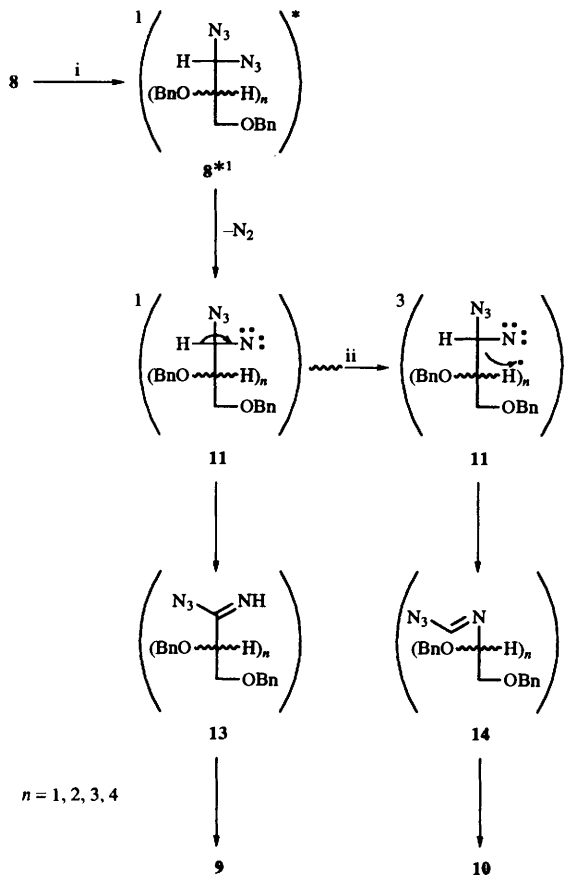
Sugar moiety of diazide	Thermolysis (%)	*hv* (%)
D-Glucose **8a**	65 (**9a**)	29 (**9a**); 22 (**10b**)
D-Mannose **8b**	43 (**9b**)	23 (**9b**); 9 (**10b**)
D-Arabinose **8c**	61 (**9c**)	21 (**9c**); 19 (**10c**)
D-Ribose **8d**	30 (**9d**)	14 (**9d**); 14 (**10d**)
D-Erythrose **8e**	61 (**9e**)	16 (**9e**); 16 (**10e**)
(±)-Glyceraldehyde **8f**	11 (**9f**); 6 (**10f**)	14 (**9f**); 21 (**10f**)

nitrene **11** with the evolution of nitrogen to form tetrazole **9** *via* imine **13**. A part of nitrene **11** is changed to a triplet azido nitrene **12** *via* intersystem crossing (ISC) and then triplet **12** gives tetrazole **10** *via* an azido imino intermediate **14**. This mechanism is supported reasonably by the fact that when compound **8c** is irradiated with acetophenone (3 mol equiv.; 0.15 mol dm^{-3}) as a triplet sensitizer with a high-pressure Hg lamp only **10c** is produced, in 14–18% yield. It was interesting that the thermolysis of (±)-1,1-diazido-2,3-di-*O*-benzyl-1,1-dideoxyglyceraldehyde hydrate **8f** gave compound **10f** (21%) *via* triplet **12** along with tetrazole **9f** (14%). In this case, the ponderous effect[10] appears to play a role in the readily occurring ISC.

The structures of products **9** and **10** were determined by ^{1}H NMR (HH-COSY and NOESY), ^{13}C NMR (COM, DEPT and HC-COSY), and mass (FAB) spectroscopy together with elemental analysis. Their characteristic NMR and MS data are summarized in Table 2.

Furthermore, the structure of compounds **9** was confirmed by the fact that compound **9c** could also be synthesized from the known reaction of tetra-*O*-benzyl-D-arabinononitrile with ammonium azide.[11]

In order to determine exactly the position of the sugar chain on the tetrazole ring in species **10**, several NMR techniques were examined by using two model compounds, 1-(benzyloxymethyl)-1*H*-tetrazole **15** and 2-(benzyloxymethyl)-2*H*-tetrazole **16**, which were prepared by the reaction of tetrazole with benzyl chloromethyl ether. Although usual NMR techniques such as COLOC (correlation spectroscopy *via* long-range couplings) and HMBC (^{1}H-detected heteronuclear multiple-bond connectivity) could not distinguish between isomers **15** and **16** owing to the small value of ^3J[C(5)–CH_2OBn] (2.7 Hz), the selective



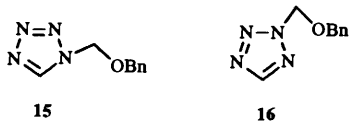
Scheme 5 *Conditions:* i, reflux or *hv*; ii, ISC = intersystem crossing

Table 2 Characteristic NMR and MS data of compounds **9** and **10**

Compound	δ of C-5 (ppm)	δ of NH[a] (ppm)	MS (FAB) *m/z* (M + 1)$^+$
9a	153.8	*b*	671
9b	154.0	12.71	671
9c	155.3	12.66	551
9d	153.5	12.35	551
9e	153.8	12.62	431
9f	154.5	*b*	311
10a	142.4		671
10b	142.8		671
10c	142.4		551
10d	142.6		551
10e	142.5		431
10f	141.8		311

[a] The signal disappeared upon shaking with D_2O. [b] Not observed.

INEPT technique[12] was found to be effective for this purpose (Table 3). That is, compounds **10** can be assigned as 1-(sugar chain)-substituted tetrazoles when both differential NOE and selective INEPT are observed. Based on this method, the structures of compounds **10** were determined clearly.



15 16

Experimental

Microanalyses were performed with Perkin-Elmer 240B and 2400 elemental analysers at the Chemical Analysis Center of Chiba University. IR and ^1H NMR were measured with Hitachi-215, JEOL-JNM-FX270, JEOL-GSX-400 and JEOL-GSX-500 spectrometers. *J* Values are given in Hz. ^{13}C NMR spectra was measured with a JEOL-JNM-FX270 spectrometer. Mass spectra (FAB) were measured using 3-nitrobenzyl alcohol (NBA) matrix on a JEOL-HX110 spectrometer (KI or NaCl was added when M$^+$ didn't appear). Wakogel C-200 was used for column chromatography, Kieselgel 60 F_{254} (Merck) for TLC, and Wakogel B-5F for preparative TLC (PLC). Columns JAIGEL-GS 320 (methanol) and J-53-4F13 (chloroform) were used for recycling preparative HPLC (Japan Analytical Industry Co. HPLC-908).

Table 3 Comparison of several NMR techniques for C-5 in compounds **15** and **16**

Technique	**15**	**16**
Differential NOE (5-H and CH_2OBn)	○	×
^1H–^{13}C Coupling constants (Gate-decoupling method)	^1J = 216 Hz ^3J = 2.7 Hz	^1J = 214 Hz ^4J ~ 0
COLOC (4 Hz) and HMBC (4 Hz)	×	×
Selective INEPT (3 Hz)	○	×

○: Observed; ×: not observed.

(7*R*,8*R*,9*S*,10*R*)-8,9,10-Tribenzyloxy-7-benzyloxymethyl-6-oxa-1,5-pentamethylenetetrazole 2

Compound **1** (173 mg, 0.23 mmol) was dissolved in *o*-xylene (3 cm^3) and the mixture was heated at reflux for 17 h under argon. After cooling, the solvent was evaporated off. The resulting reaction mixture was purified by PLC [hexane–ethyl acetate (3:1)] to give *title compound* **2** (135 mg, 82%) as needles, mp 114–115 °C (from hexane–ethyl acetate) (Found: C, 70.8; H, 6.1; N, 9.7. $C_{34}H_{34}N_4O_5$ requires C, 70.57; H, 5.92; N, 9.68%); ν_{max}(KBr)/cm^{-1} 3000 and 2850; δ_H(400 MHz; $CDCl_3$) 3.86 (2 H, d, *J* 2.9, 7-CH_2O), 3.99 (1 H, dd, *J* 4.6 and 1.3, 9-H), 4.15 (1 H, dd, *J* 1.3 and 10.3, 8-H), 4.24 (1 H, d, *J* 12.3, PhCH_2), 4.31 (1 H, d, *J* 12.3, PhCH_2), 4.41 (1 H, d, *J* 11.5, PhCH_2), 4.46 (1 H, d, *J* 11.5, PhCH_2), 4.58 (1 H, d, *J* 12.1, PhCH_2), 4.66 (1 H, d, *J* 12.3, PhCH_2), 4.67 (1 H d, *J* 12.1, PhCH_2), 4.83 (1 H, d, *J* 12.3, PhCH_2), 4.96 (1 H, dd, *J* 10.3 and 2.9, 7-H), 5.83 (1 H, d, *J* 4.6, 10-H), 7.00–7.02 (2 H, m, Ph) and 7.20–7.37 (18 H, m, Ph); δ_C(100 MHz; $CDCl_3$) 68.7 (7-CH_2O) 71.5, 72.1, 72.8 and 73.7 (4 × PhCH_2), 76.9, 77.4, 83.6 and 84.4 (C-8, -9, -7 and -10), 127.8–128.6 (Ph), 135.5, 136.2, 137.1 and 137.7 (4 × C-*ipso* of Ph) and 162.4 (C-5); *m/z* (FAB) 579 (M + 1)$^+$.

(7*R*,8*S*,9*S*,10*R*)-8,9,10-Tribenzyloxy-7-benzyloxymethyl-6-oxa-1,5-pentamethylenetetrazole 5

This compound was obtained from the galactone diazide **4** (291 mg, 0.48 mmol) in a similar manner to that described for compound **2**. Starting compound **4** was prepared by the same method as the preparation of its gluco epimer **1**. *Compound* **5** was obtained as an oil (117 mg, 42%) [Found: *m/z* (FAB) 579.2609. $C_{34}H_{35}N_4O_5$ (M + 1)$^+$ requires *m/z*, 579.2607]; ν_{max}(neat)/cm^{-1} 3000 and 2850; δ_H(500 MHz; $CDCl_3$) 3.63 (1 H, dd, *J* 8.4 and 12.0, 7-CH_2O), 3.85 (1 H, dd, *J* 3.2 and 12.0, 7-CH_2), 4.07 (1 H, dd, *J* 4.7 and 3.0, 9-H), 4.33 (1 H, dd, *J* 3.0 and 4.1, 8-H), 4.43–4.73 (8 H, m, 4 × PhCH_2), 4.93 (1 H, m, 7-H), 5.74 (1 H, d, *J* 4.7, 10-H), 7.04–7.06 (2 H, m, Ph) and 7.17–7.40 (18 H, m, Ph); δ_C(100 MHz; $CDCl_3$) 67.4 (7-CH_2O), 71.5, 73.0, 73.6 and 73.8 (4 × PhCH_2), 75.6, 75.7, 84.1 and 84.3 (C-7, -8, -9 and -10), 127.8–128.7 (Ph), 135.1, 136.4, 137.0 and 137.7 (4 × C-*ipso* of Ph) and 160.5 (C-5).

(6*S*,7*R*,8*S*,9*R*)-6,7,8-Tribenzyloxy-9-benzyloxymethyl-10-oxa-1,5-pentamethylenetetrazole 3

Compound **1** (69 mg, 0.11 mmol) was dissolved in benzene (7 cm^3) and the solution was irradiated with a high-pressure mercury lamp (400 W) for 2 h. The reaction mixture was concentrated and the residue was purified by PLC [hexane–ethyl acetate (3:1)] to give compound **2** (33 mg, 51%) and title compound **3** (13 mg, 19%) as an oil, ν_{max}(neat)/cm^{-1} 3000 and 2840; δ_H(500 MHz; $CDCl_3$) 3.68 (1 H, dd, *J* 5.2 and 11.6, 9-CH_2O), 3.78 (1 H, dd, *J* 2.8 and 11.6, 9-CH_2O), 3.91 (1 H, dd, *J* 6.6 and 6.9, 8-H), 4.12 (1 H, dd, *J* 6.6 and 6.6, 7-H), 4.42 (1 H, d, *J* 11.3, PhCH_2), 4.49 (2 H, s, PhCH_2), 4.57 (2 H, d, *J* 11.3, PhCH_2), 4.61 (1 H, m, 9-H), 4.65–4.68 (2 H, m, PhCH_2), 4.86 (1 H, d, *J* 11.8, PhCH_2), 5.04 (1 H, d, *J* 6.6, 6-H) and 7.12–7.36 (20 H, m, Ph); δ_C(100 MHz; $CDCl_3$) 60.4 (9-CH_2O), 67.4, 72.6, 73.6 and 74.1 (4 × PhCH_2), 71.5, 76.7, 78.9 and 89.4 (C-9, -8, -7 and -6), 127.5–128.5 (Ph), 136.4, 137.0, 137.1 and 137.2 (4 × C-*ipso* of Ph) and 146.4 (C-5); *m/z* (FAB) 579 $(M + 1)^+$.

(6*S*,7*R*,8*R*,9*R*)-6,7,8-Tribenzyloxy-9-benzyloxymethyl-10-oxa-1,5-pentamethylenetetrazole 6

This compound (12 mg, 17%) was obtained from galacto diazide **4** (103 mg, 0.17 mmol) in a similar manner to that described for compound **3**, together with regioisomer **5** (29 mg, 29%). Compound **6** was obtained as an oil [Found: *m/z* (FAB), 579.2605. $C_{34}H_{35}N_4O_5$ $(M + 1)^+$ requires *m/z*, 579.2607]; ν_{max}(neat)/cm^{-1} 3000 and 2840; δ_H(500 MHz; $CDCl_3$) 3.32 (1 H, dd, *J* 3.1 and 9.1, 9-CH_2O), 3.70 (1 H, dd, *J* 5.5 and 9.1, 9-CH_2O), 4.19 (1 H, dd, *J* 6.0 and 2.2, 7-H), 4.38 (2 H, d, *J* 11.7, PhCH_2), 4.47 (1 H, dd, *J* 7.1 and 2.2, 8-H), 4.51–4.63 (6 H, m, 3 × PhCH_2), 4.82 (1 H, ddd, *J* 3.1, 5.5 and 7.1, 9-H), 5.06 (1 H, d, *J* 6.0, 6-H) and 7.15–7.36 (20 H, m, Ph); δ_C(100 MHz; $CDCl_3$) 65.0 (9-CH_2O), 67.7, 72.3, 73.6 and 73.7 (4 × PhCH_2), 76.4, 78.3, 80.2 and 80.5 (C-9, -8, -7 and -6), 126.5–128.6 (Ph), 136.2, 136.9, 136.9 and 137.5 (4 × C-*ipso* of Ph) and 147.4 (C-5).

General method for the preparation of perbenzylated 1,1-diazido acyclic sugars

1,1-Diazido-2,3,4,5,6-penta-*O*-benzyl-1,1-dideoxy-D-glucose hydrate 8a. To a solution of 2,3,4,5,6-penta-*O*-benzyl-D-glucose (1.00 g, 1.59 mmol) in dichloromethane (10 cm^3) under argon was added dropwise azidotrimethylsilane (0.84 cm^3, 6.34 mmol) and boron trifluoride–diethyl ether (0.18 cm^3, 1.59 mmol). The resulting mixture was stirred for 3 h at room temp. and then was quenched with aq. sodium hydrogen carbonate, and extracted with chloroform (3 × 20 cm^3). The combined extracts were dried over Na_2SO_4 and concentrated. The residue was purified by both PLC [hexane–ethyl acetate (4:1)] and recycling preparative HPLC with chloroform to give *compound* **8a** (83.2 mg, 8%) as an oil [Found: *m/z* (FAB), 699.3298. $C_{41}H_{43}N_6O_5$ $(M + 1)^+$ requires *m/z*, 699.3295]; ν_{max}(neat)/cm^{-1} 3000, 2840 and 2100; δ_H(500 MHz; $CDCl_3$) 3.66–3.70 (2 H, m, 6-H_2), 3.73–3.90 (4 H, m, 2-, 3-, 4- and 5-H), 4.42–4.76 (10 H, m, PhCH_2), 4.79 (1 H, d, *J* 5.8, 1-H) and 7.12–7.34 (25 H, m, Ph); δ_C(100 MHz; $CDCl_3$) 69.7 (C-6), 72.5, 73.2, 73.4, 75.2 and 75.5 (5 × PhCH_2), 76.8, 77.4, 79.3, 79.4 and 81.6 (C-1, -2, -3, -4 and -5), 127.6–128.4 (Ph) and 137.8, 137.9, 138.1, 138.1 and 138.3 (5 × C-*ipso* of Ph).

1,1-Diazido-2,3,4,5,6-penta-*O*-benzyl-1,1-dideoxy-D-mannose hydrate 8b. This *compound* was obtained, in 7% yield from 2,3,4,5,6-penta-*O*-benzyl-D-mannose by a similar manner to that described for epimer **8a**, as an oil [Found: *m/z* (FAB; KI added), 737.2858. $C_{41}H_{42}KN_6O_5$ $(M + K)^+$ requires *m/z*, 737.2854]; ν_{max}(neat)/cm^{-1} 3000, 2840 and 2100; δ_H(500 MHz; $CDCl_3$) 3.69 (1 H, dd, *J* 4.7 and 10.2, 6-H), 3.82–3.93 (4 H, m, 2-, 3-, 5- and 6-H), 3.99 (1 H, dd, *J* 3.9 and 5.2, 4-H), 4.40 (1 H, d, *J* 11.3, PhCH_2), 4.47–4.51 (4 H, m, PhCH_2), 4.53 (1 H, d, *J* 11.8, PhCH_2), 4.58 (1 H, d, *J* 11.3, PhCH_2), 4.65 (1 H, d, *J* 13.2, PhCH_2), 4.67 (1 H, d, *J* 11.8, PhCH_2), 4.69 (1 H, d, *J* 11.3, PhCH_2), 4.94 (1 H, d, *J* 3.3, 1-H) and 7.21–7.32 (25 H, m, Ph); δ_C(100 MHz; $CDCl_3$) 69.7 (C-6), 72.5, 73.2, 73.4, 75.2 and 75.5 (5 × PhCH_2), 76.8, 77.4, 79.3, 79.4 and 81.6 (C-1, -2, -3, -4, -5), 127.6–128.4 (Ph) and 137.8, 138.0, 138.1, 138.1 and 138.3 (5 × C-*ipso* of Ph).

1,1-Diazido-2,3,4,5-tetra-*O*-benzyl-1,1-deoxy-D-arabinose hydrate 8c. This *compound* was obtained, in 30% yield from 2,3,4,5-tetra-*O*-benzyl-D-arabinose by a similar manner to that described for compound **8a**, as an oil [Found: *m/z* (FAB; KI added), 617.2285. $C_{33}H_{34}KN_6O_4$ requires *m/z*, 617.2279]; ν_{max}(neat)/cm^{-1} 3000, 2850, 2100, 1480 and 1440; δ_H(400 MHz; $CDCl_3$) 3.66 (1 H, dd, *J* 3.9 and 10.4, 5-H), 3.74 (1 H, dd, *J* 4.6 and 5.9, 2-H), 3.75 (1 H, dd, *J* 3.7 and 3.9, 4-H), 3.84 (1 H, dd, *J* 3.7 and 10.4, 5-H), 3.91 (1 H, dd, *J* 4.6 and 6.4, 3-H), 4.40–4.78 (8 H, m, PhCH_2), 4.79 (1 H, d, *J* 5.9, 1-H) and 7.23–7.36 (20 H, m, Ph); δ_C(100 MHz; $CDCl_3$) 68.1 (C-5), 71.6, 73.4, 74.6 and 75.4 (4 × PhCH_2), 77.4, 78.0, 78.1 and 81.1 (C-1, -2, -3, -4), 127.7–128.4 (Ph) and 137.8, 137.9, 138.0 and 138.1 (4 × C-*ipso* of Ph).

1,1-Diazido-2,3,4,5-tetra-*O*-benzyl-1,1-deoxy-D-ribose hydrate 8d. This *compound* was obtained, in 19% yield from 2,3,4,5-tetra-*O*-benzyl-D-ribose by a similar manner to that described for compound **8a**, as an oil [Found: *m/z* (FAB), 601.2518. $C_{33}H_{34}N_6NaO_4$ requires *m/z*, 601.2539]; ν_{max}(neat)/cm^{-1} 3040, 3000, 2850 and 2100; δ_H(400 MHz; $CDCl_3$) 3.64 (1 H, dd, *J* 5.3 and 10.3, 5-H), 3.71 (1 H, dd, *J* 4.2 and 10.3, 5-H), 3.87–3.81 (2 H, m, 2- and 3-H), 3.96 (1 H, m, 4-H), 4.47–4.80 (8 H, m, 4 × PhCH_2), 4.94 (1 H, d, *J* 3.9, 1-H) and 7.24–7.36 (20 H, m, 4 × Ph); δ_C(126 MHz; $CDCl_3$) 69.8 (C-5), 72.7, 73.5, 73.7 and 74.8 (4 × PhCH_2), 77.4, 78.2, 78.6 and 80.6 (C-1, -2, -3 and -4), 127.7–128.6 (Ph) and 137.5, 137.8, 138.2 and 138.2 (4 × C-*ipso* of Ph).

1,1-Diazido-2,3,4-tri-*O*-benzyl-1,1-deoxy-D-erythrose hydrate 8e. This *compound* was obtained, in 29% yield from 2,3,4-tri-*O*-benzyl-D-erythrose by a similar manner to that described for compound **8a**, as an oil [Found: *m/z* (FAB; NaCl added), 481.1958. $C_{25}H_{26}NaN_6O_3$ $(M + Na)^+$ requires *m/z*, 481.1964]; ν_{max}(neat)/cm^{-1} 3040, 3000, 2870, 2840 and 2100; δ_H(500 MHz; $CDCl_3$) 3.60 (1 H, dd, *J* 3.4 and 10.4, 4-H), 3.67 (1 H, ddd, *J* 3.0, 3.4 and 7.8, 3-H), 3.72 (1 H, dd, *J* 3.0 and 10.4, 4-H), 3.88 (1 H, dd, *J* 2.8 and 7.8, 2-H), 4.47–4.53 (3 H, m, PhCH_2), 4.57 (1 H, d, *J* 11.0, PhCH_2), 4.66 (1 H, d, *J* 11.6, PhCH_2), 4.83 (1 H, d, *J* 10.7, PhCH_2), 4.96 (1 H, d, *J* 2.8, 1-H) and 7.24–7.35 (15 H, m, Ph); δ_C(100 MHz; $CDCl_3$) 67.3 (C-4), 72.2, 73.4 and 75.3 (3 × PhCH_2), 76.9, 77.4 and 79.9 (C-1, -2 and -3), 127.8–128.5 (Ph) and 137.5, 137.7 and 137.9 (3 × C-*ipso* of Ph).

(±)-1,1-Diazido-2,3-di-*O*-benzyl-1,1-dideoxyglyceraldehyde hydrate 8f. This *compound* was obtained, in 29% yield from (±)-2,3-di-*O*-benzylglyceraldehyde by a similar manner to that described for compound **8a**, as an oil [Found: *m/z* (FAB; KI added), 337.1100. $C_{17}H_{18}KN_6O_2$ requires *m/z* 337.1128]; ν_{max}(neat)/cm^{-1} 3030, 3000, 2840 and 2100; δ_H(400 MHz; $CDCl_3$) 3.60 (2 H, dd, *J* 4.8 and 10.0, 3-H), 3.67 (1 H, td, *J* 4.6 and 4.8, 2-H), 4.52–4.80 (4 H, m, PhCH_2), 4.86 (1 H, d, *J* 4.6, 1-H) and 7.26–7.39 (10 H, m, Ph); δ_C(126 MHz; $CDCl_3$) 68.3 (C-3), 70.7, 73.5 (2 × PhCH_2), 76.6 and 79.4 (C-1 and -2), 127.8–128.6 (Ph) and 137.4 and 137.6 (2 × C-*ipso* of Ph).

General method for the thermolysis of acyclic sugar diazides

5-[(1′*S*,2′*R*,3′*R*,4′*R*)-1′,2′,3′,4′,5′-Pentabenzyloxypentyl]-1*H*-tetrazole 9a. A solution of diazide **8a** (60 mg, 0.085 mmol) in *o*-xylene (3 cm^3) was heated at reflux for 6 h under argon. After cooling, the solvent was evaporated off. The reaction mixture was purified by PLC [hexane–ethyl acetate (1:1)] to give *title compound* **9a** (37 mg, 65%) as an oil [Found: *m/z* (FAB), 671.3241. $C_{41}H_{43}N_4O_5$ $(M + 1)^+$ requires *m/z*, 671.3233];

ν_{max}(neat)/cm^{-1} 3000 and 2850; δ_H(500 MHz; $CDCl_3$) 3.73 (1 H, dd, *J* 3.9 and 10.5, 5'-H), 3.87 (1 H, dd, *J* 3.6 and 6.6, 4'-H), 3.90 (1 H, dd, *J* 3.0 and 10.5, 5'-H), 4.17–4.20 (2 H, m, PhCH_2 and 2'-H), 4.27 (1 H, dd, *J* 3.9 and 6.6, 3'-H), 4.40 (1 H, d, *J* 10.7, PhCH_2), 4.45 (1 H, d, *J* 11.8, PhCH_2), 4.52–4.58 (4 H, m, PhCH_2), 4.62 (1 H, d, *J* 11.8, PhCH_2), 4.68 (1 H, d, *J* 6.9, PhCH_2), 4.70 (1 H, d, *J* 8.0, PhCH_2), 5.28 (1 H, d, *J* 6.1, 1'-H) and 6.87–7.36 (25 H, m, Ph); δ_C(100 MHz; $CDCl_3$) 68.3 (C-5'), 70.9 (C-4'), 72.0, 72.6, 73.4 and 74.3 (4 × Ph*C*H_2), 77.9 (C-1'), 78.4 (C-2'), 78.6 (C-3'), 127.8–128.6 (Ph), 136.5, 136.7, 137.2, 137.9 and 138.1 (5 × C-*ipso* of Ph) and 153.5 (C-5).

5-[(1'*R*,2'*R*,3'*R*,4'*R*)-1',2',3',4',5'-Pentabenzyloxypentyl]-1*H*-tetrazole 9b. This *compound* was obtained, in 43% yield from substrate **8b** by a similar manner to that described for compound **9a**, as an oil [Found: *m*/*z* (FAB), 671.3232. $C_{41}H_{43}N_4O_5$ (M + 1)$^+$ requires *m*/*z*, 671.3233]; ν_{max}(neat)/cm^{-1} 3000 and 2850; δ_H(400 MHz; $CDCl_3$) 3.73 (1 H, dd, *J* 3.7 and 10.1, 5'-H), 3.85–3.91 (2 H, m, 5'-H and PhCH_2), 4.17–4.20 (2 H, m, 4'- and 2'-H), 4.25 (1 H, dd, *J* 4.2 and 6.4, 3'-H), 4.40–4.47 (2 H, m, PhCH_2), 4.52–4.55 (3 H, m, PhCH_2), 4.58–4.63 (2 H, m, PhCH_2), 4.66–4.70 (2 H, m, PhCH_2), 5.28 (1 H, d, *J* 5.9, 1'-H), 6.88–7.35 (25 H, m, Ph) and 12.71 (1 H, br, NH); δ_C(126 MHz; $CDCl_3$) 68.4 (C-5'), 71.1 (C-4'), 72.0, 72.6, 73.4, 74.4 and 74.6 (5 × Ph*C*H_2), 78.0, 78.5 and 78.7 (C-1', -2' and -3'), 127.7–128.6 (Ph), 136.5, 136.8, 137.2, 138.0 and 138.2 (5 × C-*ipso* of Ph) and 154.0 (C-5).

5-[(1'*R*,2'*S*,3'*R*)-1',2',3',4'-Tetrabenzyloxybutyl]-1*H*-tetrazole 9c. This *compound* was obtained, in 61% yield from compound **8c** by a similar manner to that described for compound **9a**, as a syrup (Found: C, 71.7; H, 6.2; N, 10.1. Calc. for $C_{33}H_{34}N_4O_4$ requires C, 71.98; H, 6.22; N, 10.17%); ν_{max}(neat)/cm^{-1} 3000 and 2850; δ_H(400 MHz; $CDCl_3$) 3.71 (1 H, dd, *J* 3.7 and 10.8, 4'-H), 3.85 (1 H, dd, *J* 2.8 and 10.8, 4'-H), 3.91–3.95 (2 H, m, 3'-H, PhCH_2), 4.04 (1 H, dd, *J* 3.1 and 7.5, 2'-H), 4.30–4.33 (2 H, m, PhCH_2), 4.38 (1 H, d, *J* 11.4, PhCH_2), 4.46 (1 H, d, *J* 11.0, PhCH_2), 4.53 (2 H, s, PhCH_2), 4.66 (1 H, d, *J* 11.5, PhCH_2), 5.36 (1 H, d, *J* 3.1, 1'-H), 7.00–7.02 (2 H, m, Ph), 7.14–7.17 (2 H, m, Ph), 7.25–7.34 (16 H, m, Ph) and 12.66 (1 H, br, NH); δ_C(100 MHz; $CDCl_3$) 67.8 (C-4'), 72.0, 72.9, 73.5 and 74.8 (4 × Ph*C*H_2), 72.4, 77.4 and 79.7 (C-1', -2' and -3'), 127.7–128.6 (Ph), 136.3, 136.7, 137.7 and 137.8 (4 × C-*ipso* of Ph) and 155.3 (C-5); *m*/*z* (FAB) 551 (M + 1)$^+$.

Preparation of compound 9c by the authentic method.[11] A mixture of 2,3,4,5-tetra-*O*-benzyl-D-arabinose (619 mg, 1.21 mmol), hydroxylamine hydrochloride (411 mg, 6.05 mmol), pyridine (5 cm^3), and ethanol (5 cm^3) was refluxed for 4.5 h. The resulting reaction mixture was evaporated to give an oil, which was then extracted with chloroform. The extract was washed successively with 0.1 mol dm^{-3} HCl and saturated aq. $NaHCO_3$. Usual work-up by PLC [hexane–ethyl acetate (2:1); R_f 0.6] gave 2,3,4,5-tetra-*O*-benzyl-D-arabinose oxime in 95% yield.

To a stirred mixture of the oxime obtained above (596 mg, 1.13 mmol), dry 1,4-dioxane (5 cm^3) and dry pyridine (0.18 cm^3, 2.27 mmol) was added dropwise trifluoroacetic anhydride (0.17 cm^3, 1.25 mmol) for 20 min. The resulting mixture was heated at 60–65 °C for 2.5 h. The reaction mixture was extracted with chloroform, and then the extract was washed with saturated aq. NaCl and evaporated to give an oil. Usual work-up by PLC [hexane–ethyl acetate (2:1); R_f 0.74] gave 2,3,4,5-tetra-*O*-benzyl-D-arabinononitrile in 86% yield as needles, mp 148–149 °C, ν_{max}(KBr)/cm^{-1} 3000, 2850 and 2240; δ_H(270 MHz; $CDCl_3$) 3.62 (1 H, dd, *J* 3.3 and 10.2, 5'-H), 3.74 (1 H, dd, *J* 3.0 and 10.2, 5'-H), 3.79 (1 H, ddd, *J* 3.0, 3.3 and 7.6, 4'-H), 4.02 (1 H, dd, *J* 3.0 and 7.6, 3'-H), 4.57 (1 H, d, *J* 3.0, 2'-H), 4.27–4.89 (8 H, m, PhCH_2) and 7.12–7.40 (20 H, m, Ph).

A mixture of the nitrile obtained above (437 mg, 0.86 mmol), sodium azide (71.6 mg, 1.10 mmol), ammonium bromide (108 mg, 1.10 mmol), and *N*,*N*-dimethylformamide (5 cm^3) was stirred for 18 days. The reaction mixture was extracted with benzene, which was purified by PLC [hexane–ethyl acetate (2:1); R_f 0.08] to afford compound **9c** in 16% yield.

5-[(1'*S*,2'*S*,3'*R*)-1',2',3',4'-Tetrabenzyloxybutyl]-1*H*-tetrazole 9d. This *compound* was obtained, in 30% yield from compound **8d** by a similar manner to that described for compound **9a**, as needles, mp 92–93 °C [Found: *m*/*z* (FAB), 551.2682. $C_{33}H_{35}N_4O_4$ (M + 1)$^+$ requires *m*/*z*, 551.2658]; ν_{max}(KBr)/cm^{-1} 3400, 3000 and 2850; δ_H(400 MHz; $CDCl_3$) 3.32 (1 H, m, 3'-H), 3.58 (1 H, dd, *J* 3.6 and 10.6, 4'-H), 3.63 (1 H, dd, *J* 3.0 and 10.6, 4'-H), 4.28 (1 H, dd, *J* 2.2 and 8.3, 2'-H), 4.83–4.38 (8 H, m, 4 × PhCH_2), 5.41 (1 H, d, *J* 2.2, 1'-H), 7.18–7.35 (20 H, m, 4 × Ph) and 12.35 (1 H, s, NH); δ_C(100 MHz; $CDCl_3$) 67.5 (C-4'), 72.2, 77.3 and 79.4 (C-1', -2' and -3'), 72.1, 72.5, 73.5 and 75.1 (4 × Ph*C*H_2), 127.8–128.7 (Ph), 136.7, 137.2, 137.4 and 137.8 (4 × C-*ipso* of Ph) and 153.5 (C-5).

5-[(1'*S*,2'*R*)-1',2',3'-Tribenzyloxypropyl]-1*H*-tetrazole 9e. This *compound* was obtained, in 61% yield from compound **8e** by a similar manner to that described for compound **9a**, as needles, mp 101–102 °C [Found: *m*/*z* (FAB), 431.2085. $C_{25}H_{27}N_4O_3$ (M + 1)$^+$ requires *m*/*z*, 431.2083]; ν_{max}(KBr)/cm^{-1} 3000, 2840, 1430 and 1080; δ_H(500 MHz; $CDCl_3$) 3.43 (1 H, dd, *J* 6.3 and 10.0, 3'-H), 3.50 (1 H, dd, *J* 5.0 and 10.0, 3'-H), 4.17 (1 H, ddd, *J* 2.9, 5.0 and 6.3, 2'-H), 4.40 (1 H, d, *J* 11.8, PhCH_2), 4.44 (1 H, d, *J* 11.8, PhCH_2), 4.50 (1 H, d, *J* 11.8, PhCH_2), 4.54 (1 H, d, *J* 11.8, PhCH_2), 4.69 (1 H, d, *J* 11.5, PhCH_2), 4.72 (1 H, d, *J* 11.3, PhCH_2), 5.17 (1 H, d, *J* 2.9, 1'-H), 7.19–7.29 (15 H, m, Ph) and 12.62 (1 H, s, NH); δ_C(126 MHz; $CDCl_3$) 68.4 (C-3'), 72.0 and 78.8 (C-1' and -2'), 72.1, 73.6 and 73.6 (3 × Ph*C*H_2), 127.7–128.6 (Ph), 136.6, 137.3 and 137.3 (3 × C-*ipso* of Ph) and 153.8 (C-5).

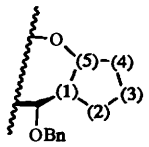
5-[(1',2'-Dibenzyloxy)ethyl]-1*H*-tetrazole 9f. This compound was obtained, in 11% yield from compound **8f** together with its isomer **10f** (6%), by a similar manner to that described for compound **9a**, as needles, mp 74–76 °C [Found: *m*/*z* (FAB), 311.1478. $C_{17}H_{19}N_4O_2$ (M + 1)$^+$ requires *m*/*z*, 311.1508]; ν_{max}(KBr)/cm^{-1} 2880 and 1560; δ_H(500 MHz; $CDCl_3$) 3.74 (1 H, dd, *J* 3.6 and 10.7, 2'-H), 3.99 (1 H, dd, *J* 3.0 and 10.7, 2'-H), 4.51 (2 H, dd, *J* 3.2 and 11.7, PhCH_2), 4.58 (2 H, dd, *J* 5.8 and 11.8, PhCH_2), 5.07 (1 H, dd, *J* 3.0 and 3.6, 1'-H) and 7.22–7.35 (10 H, m, Ph); δ_C(126 MHz; $CDCl_3$) 70.6 and 70.7 (C-1' and -2'), 72.2 and 74.0 (2 × Ph*C*H_2), 127.9–128.8 (Ph), 136.3 and 136.8 (2 × C-*ipso* of Ph) and 154.5 (C-5).

General method for the photolysis of acyclic sugar diazides

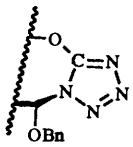
1-[(1'*R*,2'*S*,3'*R*,4'*R*)-1',2',3',4',5'-Pentabenzyloxypentyl]-1*H*-tetrazole 10a. Compound **8a** (130 mg, 0.19 mmol) was dissolved in dichloromethane (10 cm^3) and the resulting reaction mixture was irradiated by a high-pressure mercury lamp at 30 °C for 9 h. The mixture was then concentrated and the residue was purified by PLC [hexane–ethyl acetate (2:1)] to give compound **9a** (37 mg, 29%) together with *title compound* **10a** (28 mg, 22%) as an oil [Found: *m*/*z* (FAB), 671.3226. $C_{41}H_{43}N_4O_5$ (M + 1)$^+$ requires *m*/*z*, 671.3233]; ν_{max}(neat)/cm^{-1} 3010 and 2850; δ_H(270 MHz; $CDCl_3$) 3.59 (1 H, dd, *J* 4.1 and 9.9, 5'-H), 3.68 (1 H, dd, *J* 4.3 and 9.9, 5'-H), 3.80–3.88 (2 H, m, 3'- and 4'-H), 3.97 (1 H, dd, *J* 4.3 and 6.5, 2'-H), 4.18 (1 H, d, *J* 11.0, PhCH_2), 4.30 (1 H, d, *J* 11.8, PhCH_2), 4.41–4.48 (4 H, m, PhCH_2), 4.61 (1 H, d, *J* 11.6, PhCH_2), 4.64–4.67 (3 H, m, PhCH_2), 6.20 (1 H, d, *J* 4.3, 1'-H), 7.03–7.34 (25 H, m, Ph) and 8.56 (1 H, s, 5-H); δ_C(126 MHz; $CDCl_3$) 68.1 (C-5'), 72.0, 72.3, 73.4, 74.5, 75.7 (5 × Ph*C*H_2), 77.7 (C-1'), 78.6 (C-2'), 80.1 (C-3'), 87.9 (C-4'), 127.7–128.7 (Ph), 135.0, 136.9, 137.8, 137.8 and 138.1 (5 × C-*ipso* of Ph) and 142.4 (C-5). Differential NOE was observed between 1'-H and 5-H, and selective INEPT (3 Hz) was observed between 1'-H and C-5.

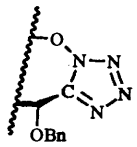
1-[(1'*S*,2'*S*,3'*R*,4'*R*)-1',2',3',4',5'-Pentabenzyloxypentyl]-1*H*-tetrazole 10b. This *compound* was obtained, in 9% yield from

Table 4



ring system A





ring system B

	Thermal parameters (Å²)		Bond length (Å)				
	B(1)	B(5)	(1)–(2)	(2)–(3)	(3)–(4)	(4)–(5)	(1)–(5)
Ring system **A**	5.2	5.0	1.357	1.298	1.374	1.307	1.336
Ring system **B**	3.2	8.0	1.340	1.296	1.368	1.336	1.323

compound **8b**, together with isomer **9b** (23%), by a similar manner to that described for compound **10a**, as an oil [Found: *m/z* (FAB; NaCl added), 693.3047. $C_{41}H_{42}N_4NaO_5$ (M + Na)$^+$ requires *m/z*, 693.3053]; ν_{max}(neat)/cm^{-1} 3000, 2840, 1490 and 1440; δ_H(500 MHz; $CDCl_3$) 3.64 (1 H, dd, *J* 3.0 and 9.6, 5'-H), 3.73 (1 H, dd, *J* 5.0 and 5.5, 3'-H), 3.82–3.88 (2 H, m, 4'- and 5'-H), 4.11–4.32 (2 H, m, PhCH_2), 4.33 (1 H, dd, *J* 4.7 and 5.0, 2'-H), 4.36–4.63 (8 H, m, PhCH_2), 6.09 (1 H, d, *J* 4.7, 2'-H), 7.06–7.34 (25 H, m, Ph) and 8.78 (1 H, s, 5-H); δ_C(126 MHz; $CDCl_3$) 68.0 (C-5'), 71.5, 71.7, 73.4, 74.6 and 75.5 (5 × Ph*C*H_2), 77.9, 78.0, 80.2 and 88.5 (C-1', -2', -3' and -4'), 127.6–128.7 (Ph), 135.3, 137.3, 137.9, 137.9 and 138.0 (5 × C-*ipso* of Ph) and 142.8 (C-5). Differential NOE was observed between 1'-H and 5-H, and selective INEPT (3 Hz) was observed between 1'-H and C-5.

1-[(1'*S*,2'*R*,3'*R*)-1',2',3',4'-Tetrabenzyloxybutyl]-1*H*-tetrazole 10c. This *compound* was obtained, in 19% yield from compound **8c** together with isomer **9c** (21%), by a similar manner to that described for compound **10a**, as an oil [Found: *m/z* (FAB; NaCl added), 573.2471. $C_{33}H_{34}N_4NaO_4$ (M + Na)$^+$ requires *m/z*, 573.2478]; ν_{max}(neat)/cm^{-1} 3000 and 2840; δ_H(400 MHz; $CDCl_3$) 3.62–3.80 (3 H, m, 3'-H and 4'-H_2), 4.06 (1 H, dd, *J* 3.3 and 7.7, 2'-H), 3.90–4.59 (8 H, m, 4 × PhCH_2), 6.29 (1 H, d, *J* 3.3, 1'-H), 7.02–7.45 (20 H, m, 4 × Ph) and 8.64 (1 H, s, 5-H); δ_C(100 MHz; $CDCl_3$) 67.1 (C-4'), 71.8, 72.5, 73.5 and 75.2 (4 × Ph*C*H_2), 67.1, 77.3, 79.0 and 88.2 (C-1', -2' and -3'), 127.6–128.7 (Ph), 135.0, 136.6, 137.6 and 137.8 (4 × C-*ipso* of Ph) and 142.4 (C-5). Differential NOE was observed between 1'-H and 5-H, and selective INEPT (3 Hz) was observed between 1'-H and C-5.

1-[(1'*R*,2'*R*,3'*R*)-1',2',3',4'-Tetrabenzyloxybutyl]-1*H*-tetrazole 10d. This *compound* was obtained, in 14% yield from compound **8d** together with isomer **9d** (14%), by a similar manner to that described for compound **10a**, as an oil [Found: *m/z* (FAB; NaCl added), 573.2471. $C_{33}H_{34}N_4NaO_4$ (M + Na)$^+$ requires *m/z*, 573.2478]; ν_{max}(neat)/cm^{-1} 3000 and 2840; δ_H(500 MHz; $CDCl_3$) 3.05 (1 H, ddd, *J* 3.3, 3.6 and 8.0, 3'-H), 3.55 (1 H, dd, *J* 3.6 and 10.5, 4'-H), 3.64 (1 H, dd, *J* 3.3 and 10.5, 4'-H), 4.29 (1 H, dd, *J* 3.0 and 8.0, 2'-H), 4.36–4.86 (8 H, m, PhCH_2), 6.39 (1 H, d, *J* 3.0, 1'-H), 7.13–7.38 (20 H, m, Ph) and 8.76 (1 H, s, 5-H); δ_C(126 MHz; $CDCl_3$) 67.2 (C-4'), 72.0, 72.4, 73.5 and 75.5 (4 × Ph*C*H_2), 76.9, 78.1 and 88.4 (C-1', -2' and -3'), 127.8–128.8 (Ph), 135.4, 137.2, 137.5 and 137.9 (4 × C-*ipso* of Ph) and 142.6 (C-5). Differential NOE was observed between 1'-H and 5-H, and selective INEPT was observed between 1'-H and C-5.

1-[(1'*R*,2'*R*)-1',2',3'-Tribenzyloxypropyl]-1*H*-tetrazole 10e. This *compound* was obtained, in 16% yield from compound **8e** together with isomer **9e** (16%), by a similar manner to that described for compound **10a**, as an oil [Found: *m/z* (FAB; KI added), 469.1622. $C_{25}H_{26}KN_4O_3$ (M + K)$^+$ requires *m/z*, 469.1642]; ν_{max}(neat)/cm^{-1} 3000 and 2840; δ_H(400 MHz; $CDCl_3$) 3.31 (1 H, dd, *J* 5.8 and 10.3, 3'-H), 3.56 (1 H, dd, *J* 4.4 and 10.3, 3'-H), 4.12 (1 H, ddd, *J* 4.4, 4.8 and 5.8, 2'-H), 4.41–4.52 (6 H, m, PhCH_2), 6.10 (1 H, d, *J* 4.8, 1'-H), 7.10–7.37 (15 H, m, Ph) and 8.69 (1 H, s, 5-H); δ_C(126 MHz; $CDCl_3$) 67.4 (C-3'), 71.9, 73.4 and 73.6 (3 × Ph*C*H_2), 77.5 and 87.3 (C-1', -2'), 127.7–128.8 (Ph), 135.2, 136.8 and 137.4 (3 × C-*ipso* of Ph) and 142.5 (C-5). Differential NOE was observed between 1'-H and 5-H, and selective INEPT was observed between 1'-H and C-5.

1-[(1',2'-Dibenzyloxy)ethyl]-1*H*-tetrazole 10f. This *compound* was obtained, in 21% yield from compound **8f**, together with isomer **9f** (14%), by a similar manner to that described for compound **10a**, as an oil [Found: *m/z* (FAB), 311.1490. $C_{17}H_{19}N_4O_2$ (M + 1)$^+$ requires *m/z*, 311.1508]; ν_{max}(neat)/cm^{-1} 3080, 3030, 3000, 2900 and 2840; δ_H(500 MHz; $CDCl_3$) 3.85 (1 H, dd, *J* 4.0 and 10.8, 2'-H), 3.93 (1 H, dd, *J* 5.2 and 10.8, 2'-H), 4.44 (1 H, d, *J* 11.8, PhCH_2), 4.54 (2 H, s, PhCH_2), 4.60 (1 H, d, *J* 11.8, PhCH_2), 5.99 (1 H, dd, *J* 4.0 and 5.2, 1'-H), 7.18–7.38 (10 H, m, Ph) and 8.80 (1 H, s, 5-H); δ_C(126 MHz; $CDCl_3$) 69.8 (C-2'), 71.7 and 73.9 (2 × Ph*C*H_2), 85.8 (C-1'), 127.9–128.9 (Ph), 135.0 and 136.6 (2 × C-*ipso* of Ph) and 141.8 (C-5). Differential NOE was observed between 1'-H and 5-H, and selective INEPT was observed between 1'-H and C-5.

1-Benzyloxymethyl-1*H*-tetrazole 15 and 2-benzyloxymethyl-2*H*-tetrazole 16. To a solution of KOH (272 mg, 4.8 mmol) and 1*H*-tetrazole (287 mg, 4.10 mmol) in methanol (5 cm^3) was added benzyl chloromethyl ether (0.56 cm^3, 4.04 mmol). The resulting mixture was stirred for 18 h at room temperature and was then concentrated. The residue was purified by PLC [hexane–ethyl acetate (4:1)] to give compounds **15** (93 mg, 12%) and **16** (76 mg, 10%).

1-Benzyloxymethyl-1*H*-tetrazole **15** was an oil, δ_H(400 MHz; $CDCl_3$) 4.60 (2 H, s, PhCH_2), 5.82 (2 H, s, NCH_2), 7.30–7.39 (5 H, m, Ph) and 8.77 (1 H, s, 5-H); δ_C(126 MHz; $CDCl_3$) 71.9 (Ph*C*H_2), 75.7 (NCH_2), 128.3–128.8 (Ph), 135.1 (C-*ipso* of Ph) and 142.7 (C-5).

2-Benzyloxymethyl-2*H*-tetrazole **16** was an oil, δ_H(400 MHz; $CDCl_3$) 4.67 (2 H, s, PhCH_2), 5.97 (2 H, s, NCH_2), 7.31–7.39 (5 H, m, Ph) and 8.60 (1 H, s, 5-H); δ_C(126 MHz; $CDCl_3$) 72.0 (Ph*C*H_2), 79.4 (NCH_2), 128.2–128.6 (Ph) 135.5 (C-*ipso* of Ph) and 153.3 (C-5).

X-Ray crystal determination of compound 2

A single crystal of **2** was obtained as needles from ethanol. Crystal size was 0.60 × 0.20 × 0.12 mm. The intensity data were measured at ambient temperature on a Rigaku AFC-5 four-circle diffractometer by using graphite-monochromatized Mo-Kα radiation; scan speed 4° min^{-1}. Three standard reflections (040, $\bar{9}\bar{1}1$, $20\bar{2}$) were measured for every 200 reflections and showed no significant variations throughout the data collection; 2629 reflections ($5° \leqslant 2\theta \leqslant 50°$) measured, 1595

Table 5 Selected bond lengths (Å) in compound **2**

C(2)–C(3)	1.528(17)	N(3)–N(4)	1.374(15)
C(3)–C(4)	1.526(16)	N(4)–C(1)	1.307(15)
C(4)–C(5)	1.525(16)	O(1)–C(1)	1.318(13)
C(5)–C(6)	1.498(17)	O(1)–C(5)	1.448(14)
N(1)–C(1)	1.336(14)	O(2)–C(2)	1.404(15)
N(1)–C(2)	1.465(15)	O(3)–C(3)	1.403(14)
N(1)–N(2)	1.357(15)	O(4)–C(4)	1.415(13)
N(2)–N(3)	1.298(16)	O(5)–C(6)	1.413(15)

Table 6 Selected bond angles (°) in compound **2**

C(1)–N(1)–C(2)	130.1(10)	O(1)–C(1)–N(1)	128.5(10)
C(1)–O(1)–C(5)	116.2(8)	O(1)–C(1)–N(4)	122.4(10)
C(2)–C(3)–C(4)	115.6(9)	O(1)–C(5)–C(4)	111.5(9)
C(3)–C(4)–C(5)	114.1(9)	O(1)–C(5)–C(6)	106.5(9)
C(4)–C(5)–C(6)	114.8(10)	O(2)–C(2)–C(3)	107.4(9)
N(1)–C(1)–N(4)	109.1(10)	O(2)–C(2)–N(1)	112.9(10)
N(1)–C(2)–C(3)	109.7(9)	O(3)–C(3)–C(2)	106.0(9)
N(1)–N(2)–N(3)	105.3(10)	O(3)–C(3)–C(4)	113.0(9)
N(2)–N(1)–C(1)	108.9(9)	O(4)–C(4)–C(3)	111.0(9)
N(2)–N(1)–C(2)	120.3(9)	O(4)–C(4)–C(5)	105.5(9)
N(2)–N(3)–N(4)	111.2(10)	O(5)–C(6)–C(5)	108.4(10)
N(3)–N(4)–C(1)	105.4(10)		

independent reflections [$F_o \geqslant 3\sigma(F_o)$] were used for analysis ($R_{int} = 0.020$).

The positions of all atoms were deduced by direct methods. Difference Fourier maps were used to locate the positions of benzylic C atoms. H-atom positions were calculated by the HYCO80 program in UNICS-III system.[13] Anisotropic thermal parameters for sugar skeleton atoms and isotropic thermal parameters for other carbon atoms were used; 249 parameters, $R = 0.085$; $S = 1.24$, max. and min. heights in final difference Fourier syntheses were 1.692, -0.754 e Å^{-3}, max. (shift/e.s.d.) = 0.113{χ of C[O(5)]5}.

Crystal data. $C_{34}H_{34}N_4O_5$, M = 578.64, monoclinic, space group $P2_1$, $a = 17.303(4)$, $b = 8.156(1)$, $c = 11.257(2)$ Å, $\beta = 90.97(2)°$, $V = 1588.3(6)$ Å^3, $Z = 2$, $D_c = 1.210$ g cm^{-3}, λ(Mo-Kα) = 0.710 73 Å, $F(000) = 612$. Final conventional R-factors: R 0.085 for 1595 observed reflections [$|F_o| \geqslant 3\sigma(|F_o|)$] and 249 parameters.

When N(1) and C(5) of the ring system A are interchanged in the structure refinement, the B factors, B(1) and B(5), of the resulting ring system B exhibit totally different values. Such a change should not be reasonable for the B factors of two adjacent atoms (C and N). Besides, bond alternation, which is reasonable for ring system A, exhibits unrealistic properties upon the interchanging of N(1) and C(5) as shown in Table 4. These results strongly suggest that the structure of the main photo-product should be asigned to structure **2** with the ring system A.

Tables 5 and 6 show bond lengths and bond angles, respectively, for compound **2**.

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