337 (22000), 357 (18000), 409 (5200), 421 (4800), 480 (110), 494 (110), 512 (110), 535(80), 554 nm (70); FAB-MS: *m/z* (%): 1417 (100) [M^+], 1300 (30) [M^+ – bzim].

2: As for **1** using benzimidazole (0.04 g, 0.33 mmol), excess NaH, and [nBu$_4$N][Pt(bzqn)Cl$_2$] (0.20 g, 0.29 mmol). A yellow precipitate was afforded after reflux for 12 h. Slow evaporation of an acetone/benzene solution yielded yellow crystals (yield 84%). Satisfactory elemental analysis was obtained; ^{1}H NMR (500 MHz, [D$_6$]DMSO, 27 °C, TMS): $\delta = 9.26$-6.91 (m); ^{13}C NMR (126 MHz, [D$_6$]DMSO, 27 °C, TMS): $\delta = 156.7$, 149.4 – 148.8, 144.2 – 138.4, 133.4 – 115.7, 110.5; IR (Nujol): $\tilde{\nu} = 1620$, 1610 cm^{-1} (C=N); UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 271 (70000), 278 (73000), 358 (14000), 372 (14000), 413 (4000), 469 nm (440); FAB-MS: *m/z* (%): 1471 (100) [M^+], 1354 (25) [M^+ – bzim].

Received: September 16, 1998 [Z12422IE]
German version: *Angew. Chem.* **1999**, *111*, 708 – 710

Keywords: luminescence · metallomacrocycles · N ligands · platinum · self-assembly

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A New Type of Glycosidic Linkage: An Open-Chain Acetal-Linked *N*-Acetylgalactosamine in the Core Part of the Lipopolysaccharides from *Proteus* Microorganisms**

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Monosaccharides in natural compounds are usually present in a cyclic hemiacetal form, in which the exocyclic hemiacetal oxygen atom is used for the connection to the aglycon. Herein we report the identification of a new type of linkage between monosaccharides found in the core part of the lipopolysaccharides (LPS) from two serotypes of *Proteus*. LPS is a component of the outer membrane of Gram-negative bacteria, and comprises three regions: the O-antigenic polysaccharide, the lipid A, and the core, a nonrepetitive oligosaccharide linking the O-antigenic polysaccharide to the lipid A.[1] Normally, core oligosaccharides have complex structures, relatively conserved for each type of bacteria. The biological

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[**] We thank Prof. Dr. W. Kaca, Prof. Dr. Z.Sidorczyk, and Prof. Dr. A.Rozalski from The Institute of Microbiology & Immunology of University of Lodz, Lodz, Poland, and Prof. Dr. E. S. Stanislavsky from I. I. Mechnikov Institute of Vaccine and Sera, Russian Academy of Medical Sciences, Moscow, Russia for supplying bacterial cells, and Dr. Jens Ø. Duus for helpful discussions.

functions of the particular core structures are as yet unknown. Partial structural analysis of the core region of LPS has been reported for several strains of *Proteus* bacteria.[2–7]

In the present work the core oligosaccharides were released from the LPS by mild acid hydrolysis and isolated using gel chromatography and anion exchange chromatography. Analysis of the NMR spectra of the core oligosaccharides from serotypes *Proteus mirabilis* O27 and *Proteus vulgaris* OX2 revealed spin systems of 2-aminoaldoses (units L and L′; lettering is assigned arbitrarily) with an unusual coupling constant pattern (Table 1). The coupling constants do not correspond to values normally observed for pyranosides in chair conformation or equilibria thereof. The absence of low-field carbon signals (Table 2) indicated that these sugars do not possess furanose structures. Intramolecular NOEs observed between either H1 and H3, or H3 and H5, but not from H1 to H5 of the sugar residue L are difficult to explain by a ring conformation or equilibria thereof. NOE data showed strong correlations between the anomeric L1 proton and protons 4 and 6b of the galactosamine residue M, and a weak signal between L1 and M6a (Table 1, Figure 1). The ^{13}C NMR signals of C4 and C6 of the galactosamine residue M were downfield shifted by $\Delta\delta \approx 6-7$ compared to the signals of a nonsubstituted α-galactosamine residue, whereas signals of C3 and C5 were upfield shifted by $\Delta\delta = 3$ and 8, respectively. This indicated simultaneous substitution at O4 and O6.

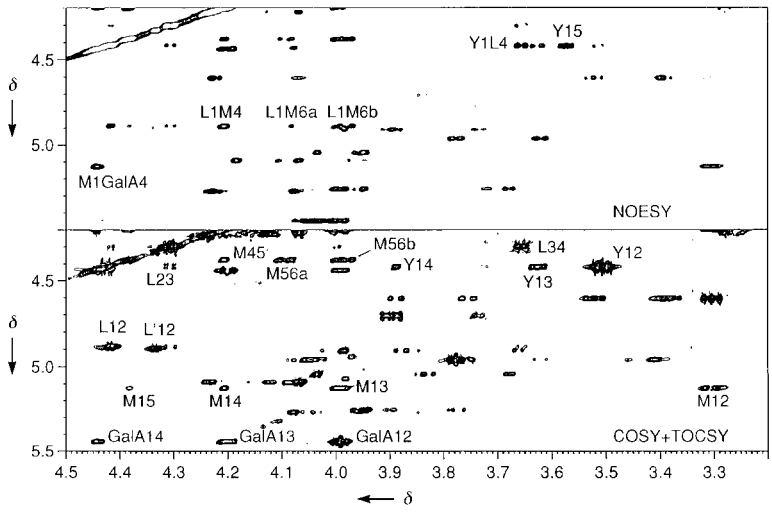

Figure 1. Parts of NOESY (upper trace) and COSY + TOCSY spectra of the core oligosaccharide from *P. vulgaris* OX2. Unit L′ is a nonsubstituted residue, which appears in a disaccharide **3** after deamination.

Table 1. ^{1}H NMR data.[a]

Unit, compound	H-1	H-2	H-3	H-4	H-5	H-6a	H-6b
S, **1**	4.58	3.40	3.49	3.39	3.42	3.94	3.69
S, core O27	4.52	3.28	3.44	3.32	3.41	3.89	3.62
S $J_{n,n+1}$ [Hz]	8	10	10	10	$J_{5,6b}$ 6	$J_{6a,6b}$ 12	$J_{5,6a}$ 2
Y, **2**	4.48	3.52	3.64	3.89	3.58	3.64	3.64
Y, core OX2	4.42	3.50	3.63	3.89	3.57	3.74	3.74
Y $J_{n,n+1}$ [Hz]	8	10	3.5	ca. 0	–	–	–
L, **1**	4.87	4.34	4.26	3.42	4.08	3.81	3.73
L, core O27	4.84	4.27	4.19	3.36	4.02	3.76	3.67
L, **2**	4.87	4.44	4.28	3.67	4.00	3.80	3.66
L, core OX2	4.88	4.41	4.30	3.65	3.99	3.79	3.66
L, **3**	4.89	4.36	4.12	3.36	3.93	3.66	3.66
L′, core OX2	4.89	4.33	–	–	–	–	–
L $J_{n,n+1}$ [Hz]	5.5	1.5	10	2	$J_{5,6b}$ 6	$J_{6a,6b}$ 12	$J_{5,6a}$ 7
dM, **1**	5.09	3.93	4.39	4.38	4.00	4.16	4.03
M, core O27	5.22	3.58	4.15	4.20	4.39	4.07	3.97
dM, **2**	5.09	3.95	4.40	4.40	4.00	4.15	4.02
M, core OX2	5.13	3.30	3.99	4.20	4.38	4.09	3.98
dM, **3**	5.09	3.94	4.41	4.40	4.01	4.16	4.03
dM $J_{n,n+1}$ [Hz]	3.5	8	–	–	$J_{5,6b}$ 2	$J_{6a,6b}$ 13	$J_{5,6a} < 1$

[a] Interresidual NOE: **1**: S1-L5s,6am, L1-dM4s,6bs; core O27: S1-L5s,6am, L1-M4s,5w,6aw,6bs; **2**: Y1-L1w,2m,3w,4s, L1-dM4s,6aw,6bs; core OX2: Y1-L4m, L1-dM4s,6aw,6bs; **3**: L1-M4s,6aw,6bs.

Table 2. ^{13}C NMR data.

Unit, compound	C1	C2	C3	C4	C5	C6
S, **1**	102.8	73.9	76.2	70.4	76.2	61.7
S, core O27	102.9	73.7	75.9	70.1	76.0	61.7
Y, **2**	103.6	71.4	73.1	69.0	75.5	61.3
Y, core OX2	103.5	71.3	73.0	68.9	75.4	61.3
L, **1**	98.8	52.5	67.9	69.4	78.5	62.0
L, core O27	100.6	52.3	67.8	69.2	78.4	62.2
L, **2**	99.1	51.8	67.6	77.1	69.8	62.6
L, core OX2	100.6	51.2	67.4	77.0	69.8	62.5
L, **3**	99.0	52.3	68.4	69.7	70.1	63.6
L′, core OX2	100.6	51.8	–	–	–	–
dM, **1**	90.4	84.0	73.8	76.6	73.4	67.4
M, core O27	96.9	51.2	65.2	75.0	64.1	69.0
dM, **2**	90.4	83.8	73.8	76.5	73.3	67.2
M, core OX2	99.6	51.0	67.2	75.3	64.0	69.0
dM, **3**	90.5	84.0	73.8	76.5	73.3	67.2

Fragments containing the sugar residue L (compound **1** from O27 serotype, compounds **2** and **3** from OX2 serotype) were isolated after deamination of the core oligosaccharides with sodium nitrite in acetic acid (Scheme 1). MALDI mass spectra of compounds **1** and **2** contained signals of ions $[M+H]^+$ at m/z 528.5 (minor), $[M+H_2O+H]^+$ at m/z 546.5 (major), and $[M+H_2O+Na]^+$ at m/z 568.4. These ions corresponded to trisaccharides built up of two hexoses and one acetamidohexose with an aldehyde group of the reducing 2,5-anhydrotalose (deamination product of galactosamine) present predominantly in the hydrated form.

NMR analysis of compounds **1**–**3** (Tables 1 and 2) showed that they all contain the above-described fragment L. All coupling constants and other features of the spectra of this residue remained unchanged compared to those of the starting core oligosaccharides. HMBC spectra showed cross peaks from L1 to dM4 and dM6 (Figure 2). Taken together, NOE and HMBC spectra indicated that residue L was linked to both positions 4 and 6 of the 2,5-anhydrotalose residue. Compound **1** contained additionally a β-glucopyranose residue S, attached, according to NOE and HMBC spectra, to O5 of the sugar residue L. In oligosaccharide **2**, the sugar residue L was glycosylated at O4 with a β-galactopyranose residue Y, and a minor product **3** contained only sugar residues L and dM.

The oligosaccharides **1**–**3** were hydrolyzed (4 M HCl, 100 °C, 4 h) and analyzed by using an amino acid analyzer

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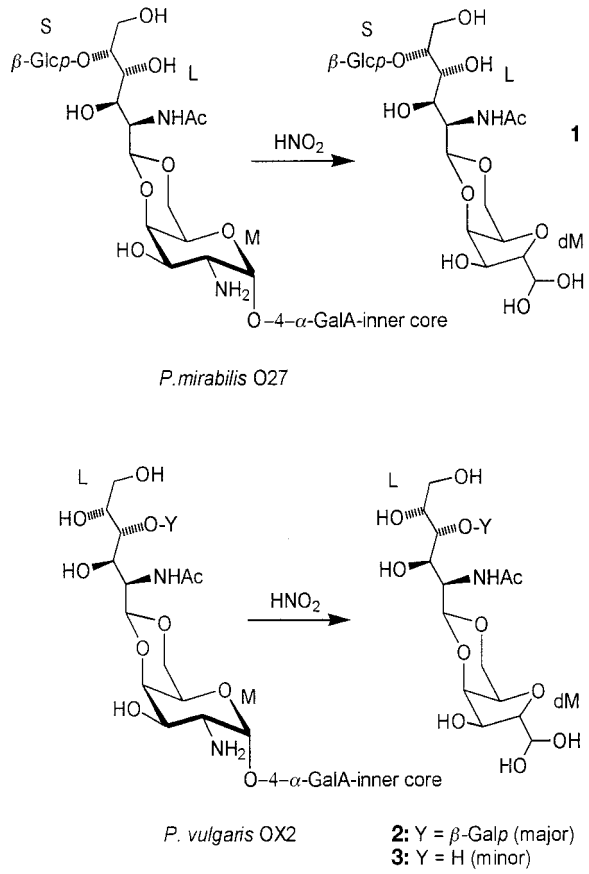

Scheme 1.

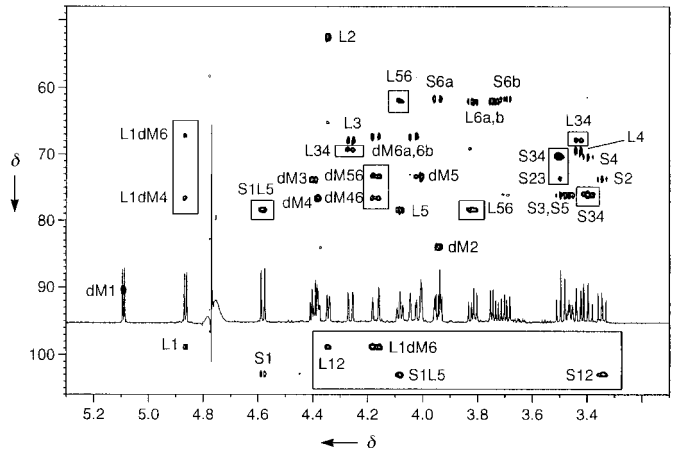

Figure 2. Overlap of ^{1}H, HSQC, and HMBC (signals in boxes) spectra of the oligosaccharide **1**.

and GC (as alditol acetates). In all cases, galactosamine was detected as well as 2,5-anhydrotalose and glucose (in **1**) or galactose (in **2**). Methylation analysis of oligosaccharides **1**–**3** (after borohydride reduction) with the identification of the products as alditol acetates by GC-MS confirmed the proposed structures.

Combined together, these data suggest a new type of glycosidic structure with an open-chain *N*-acetylgalactosamine linked as cyclic acetal to positions 4 and 6 of the galactosamine in the α-pyranoside form. NOE correlations between protons L1 and M4,6 indicate axial orientation of the proton L1, and therefore carbon L1 possesses an (*S*)-configuration. In order to prove that this structure was not an artifact from LPS cleavage under the mild acidic conditions during work-up, the LPS of *P. vulgaris* OX2 was deacylated with anhydrous hydrazine and the product studied by NMR spectroscopy. The fragments Y-L-M and L′-M were identified (differing from the above-described substances by the absence of the N-acetyl group in L), and showed the same coupling constants and substitution pattern as for the compounds described here.

The novel type of linkage between sugar residues—open-chain cyclic acetal linkage—is no surprise from a chemical point of view. Nevertheless, it has not been previously reported in natural products and has not even been discussed as a theoretical possibility.[8] In contrast, cyclic acetals built up of non-sugar oxo compounds, such as pyruvic acid, are common components of bacterial polysaccharides.[1, 9] The chemical stability of the acetal linkage formed by an *N*-acetylgalactosamine residue does not differ substantially from that of a normal glycosidic linkage, as it survives hydrolysis with acetic acid and methylation analysis, but can be cleaved under the hydrolytic conditions normally used in monosaccharide analysis (2 M HCl, 100 °C). It may therefore be more widely occurring in natural poly- or oligosaccharides but not detected, since conventional analysis of *Proteus* serotype O27 core (monosaccharide analysis, methylation, mass spectrometry) would lead to the identification of terminal glucose, terminal *N*-acetylgalactosamine and 4,6-disubstituted galactosamine instead of the structural fragment described here. We propose the use of the symbol "*o*" (for "open") to identify this type of sugar form in abbreviated formulas, thus the formula of the disaccharide **3** could be written as (1*S*)-Gal*o*NAc-(1 →4,6)-2,5-anh-Tal. Detailed analysis of the LPS core structures will be reported elsewhere.

Experimental Section

Bacteria were cultivated and lipopolysaccharide was isolated as described previously.[10, 11]

NMR spectroscopy and general methods: ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-600 spectrometer in D_2O at 25 °C with acetone as standard ($\delta = 2.225$ for ^{1}H, $\delta = 31.5$ for ^{13}C) using standard pulse sequences. NOESY spectra were recorded for core oligosaccharides, and ROESY (mixing time 250 ms) for compounds **1**–**3**. NMR spectra were assigned by using the program Pronto[12] and NMR, GC, GC-MS, methylation and monosaccharide analysis was performed as previously described.[13, 14]

Preparation of core oligosaccharides and oligosaccharides **1**–**3**: LPSs from serotypes O27 and OX2 (200 mg each) were hydrolyzed with 2% acetic acid (100 °C, 5 h). The resulting precipitate removed by centrifugation, and the supernatant separated on a Sephadex G50 SF gel (Pharmacia) column (2.5 × 80) using pyridine/acetic acid buffer (4 and 10 mL in 1 L water) and monitoring by Waters differential refractometer. Core fractions were further separated on a TSK-DEAE column (1.5 × 20 cm) in water, monitored by refractometer, to give several fractions. For the analysis the last fraction eluted was used. Core oligosaccharides (20 mg each) were dissolved in water (2 mL), and $NaNO_2$ (5 mg) and AcOH (30 μL) were added. After 1 h at 20 °C, the mixtures were desalted by gel filtration chromatography on a TSK HW40(S) gel (Merck) column (1.6 × 80 cm). Fractions containing oligosaccharides **1**–**3** (detected by NMR spectroscopy) were separated by ascending paper chromatography (Whatman No

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1 paper) in pyridine/butanol/acetic acid/water (1:1:1:1), with alkaline silver nitrate detection. Compounds **1**–**3** were eluted from paper with water.

Received: October 5, 1998 [Z12485IE]
German version: *Angew. Chem.* **1999**, *111*, 712–715

Keywords: carbohydrates · glycosides · natural products · NMR spectroscopy

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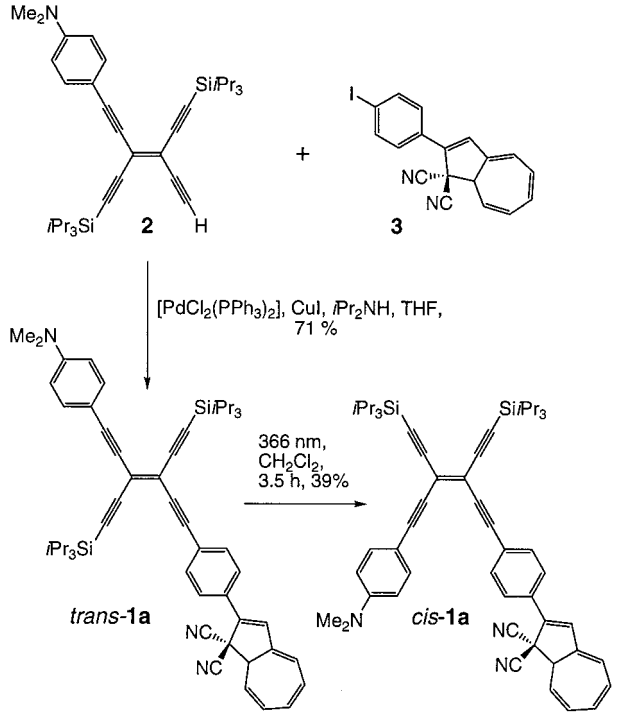
A Novel Three-Way Chromophoric Molecular Switch: pH and Light Controllable Switching Cycles**

Luca Gobbi, Paul Seiler, and François Diederich*

Dedicated to Professor Fritz Vögtle on the occasion of his 60th birthday

The field of molecular switches has received much attention in recent years.[1] Of particular interest are photoresponsive systems since the use of light as an external stimulus for the interconversion of two states allows for rapid and clean processes.[2] Herein we report a molecule with three addressable subunits that can undergo individual, reversible switching cycles.[3] Compound **1a** (Scheme 1) consists of a) a tetraethynylethene (TEE, 3,4-diethynylhex-3-ene-1,5-diyne)[4] core, which can be reversibly photoisomerized between its *cis* and *trans* forms,[5] b) a dihydroazulene (DHA) unit, which can be transformed into a vinylheptafulvene (VHF) moiety upon irradiation,[6] and c) a proton sensitive *N*,*N*-dimethylanilino (DMA) group.

The target compound *trans*-**1a** (Scheme 1) was prepared by Sonogashira cross-coupling[7] of TEE **2**[8] with the aryl iodide **3**.[9] The X-ray crystal structure analysis of *trans*-**1a**[10] (Figure 1) shows only minor deviations (ca. 0.1 Å) from



Scheme 1. Synthesis of *trans*-**1a** and *cis*-**1a**.

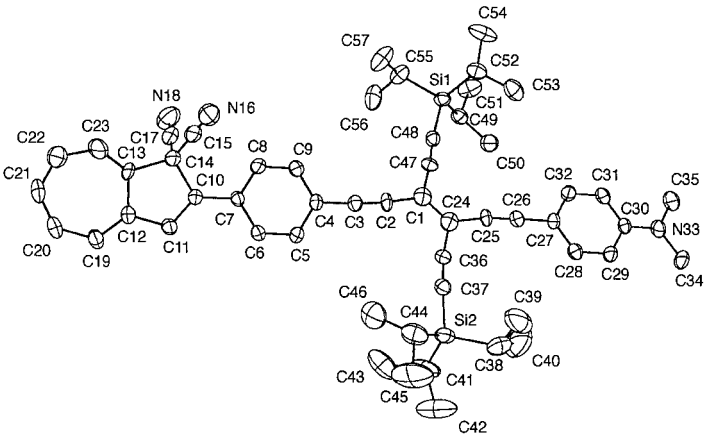


Figure 1. ORTEP plot of *trans*-**1a** in the crystal. The vibrational ellipsoids shown are at the 30% level.

planarity in the diarylated TEE core. The dihydroazulene moiety is slightly turned out of this plane, with the dihedral angle C14-C10-C7-C8 amounting to 13°. The diastereoisomeric *cis*-**1a** was obtained in 39% yield upon photolysis of *trans*-**1a** in CH_2Cl_2 at $\lambda = 366$ nm.

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[**] This work was supported by the ETH Research Council and a Varon Visiting Professorship at the Weizmann Institute of Science (to F.D.). We thank Dr. M. Gómez-López for useful discussions.

  1433-7851/99/3805-0674 $ 17.50+.50/0