4: Crude Na_3[**2**] was prepared from $(Me_3NH)_3$[**1**] (2.00 g, 4.64 mmol) as described above. The crude Na_3[**2**] was dissolved in water (50 mL), and the solution was acidified to pH 2 with HCl (2 N). The mixture was stirred for 5 min and filtered. Aqueous Me_4NCl (5 N) was added until precipitation was complete. The brown precipitate was collected by filtration, the solid dissolved in acetone/chloroform (40 mL, 1/1), and the resulting solution passed through silica gel column (3×45 cm, elution with the same solvent mixture). The yellow solution was collected, and the solvent was removed in vacuo. The residue was dissolved in H_2O (20 mL), and aqueous Me_4NCl (5 mL, 1 N) was added to precipitate crude $(Me_4N)_2$[**4**]. The product was purified by recrystallization from acetone/ether and dried in vacuo to yield (Me_4N)[**4**] (0.42 g, 25%) as bright yellow crystals. $^{11}B\{^1H\}$ NMR (H_2O): $\delta =$ 31.3 (2B, apical B–H); 15.6 (2B, B–B); −0.5 (2B, B–N); −4.4, −12.5, −16.7, −19.0 (total of 12B, equatorial B–H); −29.1 (2B, apical B–H); ESI-MS: m/z: 289.3 [$\{(CH_3C(NH)_2B_{20}H_{16}\}^-$]; ^1H NMR (CD_3CN): $\delta = 5.9$ (s, NH); 1.7 (s, CH_3); ^{13}C NMR (CD_3CN): $\delta = 169.1$ (CCH_3), 24.2 (CH_3).

5: Dry (Me_4N)[**4**] (1.00 g, 2.75 mmol) was refluxed in water (30 mL) for 2 h. An aqueous solution of $[Ph_3PMe]Br$ was added until precipitation was complete. The white powder was filtered and purified by recrystallization from CH_3CN/ether. The resulting solid was dried in vacuo to yield $[Ph_3PMe]$[**5**] (0.37 g, 33%) as a white powder. The product was identified by its $^{11}B\{^1H\}$ NMR[10] and ESI mass spectra (m/z: 136.4 [$(B_{10}H_9NH_3)^-$]).

7: Dry $[(Me_3NH)_4]$[**6**][11] (2.00 g, 4.08 mmol) was added to a stirred suspension of NaH (0.50 g, 20.8 mmol) in dry CH_3CN; hydrogen gas was evolved. The mixture was stirred at room temperature for 1 h and filtered, and then the CH_3CN was removed in vacuo. The residue was dissolved in dry CH_3CN (100 mL). Benzoquinone (1.50 g, 14.1 mmol) was added, and the solution was stirred for 3 h. The solution was filtered, and CH_3CN was removed in vacuo. The residue was dissolved in water (50 mL), and the solution was filtered again. The ion **7** in the solution was identified from its $^{11}B\{^1H\}$ NMR spectrum.[2]

8: The solution of ion **7** obtained above was acidified with HCl (1 N) to pH 3, stirred for 5 min, and filtered. Aqueous Me_4NCl (1 N) was added until precipitation was complete. The resulting white solid was collected by filtration and purified by recrystalization from CH_3CN/EtOH. It was dried in vacuo to yield $[Me_4N]_2$[**8**] (1.17 g, 72%). The product was identified by its $^{11}B\{^1H\}$ NMR and ESI mass spectra.[2]

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[7] Crystal structure analysis of $[Me_4N]$[**4**]. Yellow crystals obtained by recrystallization from acetone/ether: $B_{20}C_6H_{33}N_3$, $M_r = 363.6$, crystal dimensions $0.15 \times 0.4 \times 0.4$ mm^3, Syntex $P\bar{1}$ diffractometer, Cu$_{K\alpha}$ radiation, $\lambda = 1.5418$ Å, 298 K; θ-2θ scan mode to $2\theta_{max} = 115°$. The unit-cell parameters were determined from 51 accurately centered reflections ($17.4° < 2\theta < 40.3°$): orthorhomic, space group $P2_12_12_1$, $a =$ 15.404(8), $b = 9.544(5)$, $c = 19.647(10)$ Å, $V = 2889$ Å^3, $Z = 4$, $\rho_{calcd} =$ 1.01 g cm^{-3}, $\mu = 3.36$ cm^{-1}. Of the 2131 unique reflections measured ($+h$, $+k$, $\pm l$), 1620 were considered observed ($I > 3\sigma(I)$), and the structure was solved by direct methods; 212 refined parameters, maximum residual electron density 0.1 e Å^{-3}, least-square refinement against $|F^2|$, $R = 0.075$ for the observed reflections, $R_w = 0.092$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101300. Copies of the data can be obtained free of charge on application to: CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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A New Isomer of the $[B_{20}H_{18}]^{2-}$ Ion: Synthesis, Structure, and Reactivity of *cis*-$[B_{20}H_{18}]^{2-}$ and *cis*-$[B_{20}H_{17}NH_3]^{-}$**

Fangbiao Li, Kenneth Shelly, Carolyn B. Knobler, and M. Frederick Hawthorne*

Dedicated to Professor Heinrich Nöth
on the occasion of his 70th birthday

The well-known polyhedral borane anion $[B_{20}H_{18}]^{2-}$ (**1**),[1] hereafter referred to as *trans*-$[B_{20}H_{18}]^{2-}$, and its photoisomer *iso*-$[B_{20}H_{18}]^{2-}$ (**2**)[2] were first synthesized in the 1960s, soon after the genesis of polyhedral borane chemistry. The electrophilic polyhedral boranes **1** and **2** (Scheme 1 A) have great potential as precursors in reductive substitution reactions which lead to new derivatives for possible employment in boron neutron capture therapy (BNCT).[3] The two $[B_{10}H_9]^-$ cage fragments in **1** are connected by a pair of three-center two-electron (3c–2e) bonds, while the two $[B_{10}H_9]^-$ cages in **2** are linked by a pair of B-H-B bridges. These bonds are electron deficient and are therefore susceptible to reactions with nucleophiles. In the facile reaction of **1** with hydroxide ion, the initially formed product is *ae*-$[B_{20}H_{17}OH]^{4-}$ (**3**), which is stable under basic conditions. In neutral aqueous media, **3** slowly isomerizes to a^2-$[B_{20}H_{17}OH]^{4-}$ (**4**, Scheme 1 B).[4] Although other isomers of $[B_{20}H_{18}]^{2-}$ have been proposed,[5] none have been detected other than the photoisomer **2**.[2]

The reduction of **1** with sodium in liquid ammonia produced a kinetically controlled product, the e^2-$[B_{20}H_{18}]^{4-}$ ion (**5**), which could be isomerized to the *ae*-$[B_{20}H_{18}]^{4-}$ ion (**6**, Scheme 1 C).[1] Oxidation of **5** with iron(III) ions under aqueous, acidic conditions at high temperature regenerates **1**.[1] However, recent studies of the low-temperature oxidation

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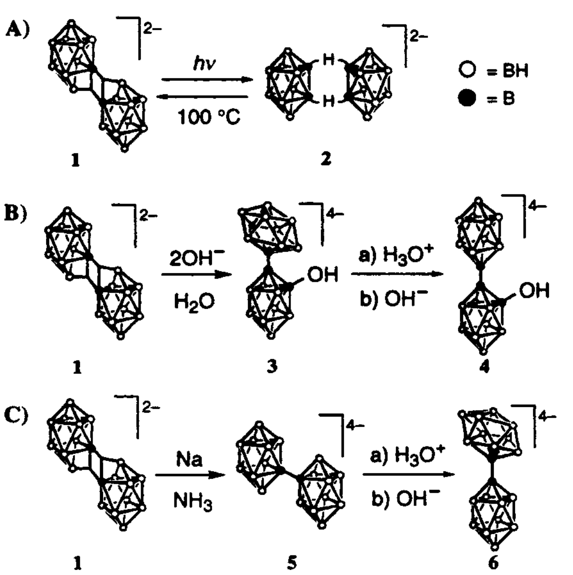
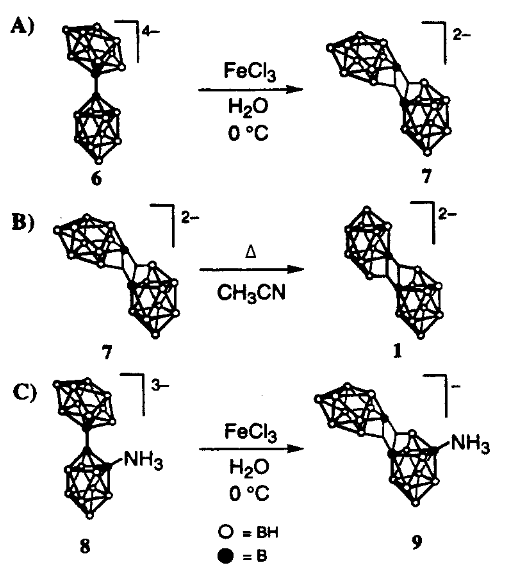
[**] This work was supported by the U.S. Department of Energy (DE-FG02-95ER61975). The following prefixes are used as isomer designations: *ae* = apical–equatorial isomers of $[B_{20}H_{18}]^{4-}$ derivatives ($[1\text{-}(2\text{-}B_{10}H_9)\text{-}B_{10}H_9]^{4-}$), a^2 = apical–apical isomers of $[B_{20}H_{18}]^{4-}$ derivatives ($[1\text{-}(1\text{-}B_{10}H_9)\text{-}B_{10}H_9]^{4-}$), e^2 = equatorial–equatorial isomers of $[B_{20}H_{18}]^{4-}$ derivatives ($[2\text{-}(2\text{-}B_{10}H_9)\text{-}B_{10}H_9]^{4-}$).



Scheme 1. Reactions of **1**. A) Photoisomerization to **2**. B) Reaction with OH^- ions to **3** and the isomerization of **3** to **4**. C) Reduction to **5** and the isomerization of **5** to **6**.

of **6** did not result in the expected *trans*-$[B_{20}H_{18}]^{2-}$ ion (**1**). Instead, the product obtained was the unprecedented polyhedral borane anion **7** (designated *cis*-$[B_{20}H_{18}]^{2-}$, Scheme 2 A) which is a new isomer of **1**. The two $[B_{10}H_9]^-$ fragments in **7** are arranged in a cisoid configuration, in contrast to the transoid configuration of **1**. With a similar synthetic strategy we also produced the novel anion **9** (designated here as *cis*-$[B_{20}H_{17}NH_3]^-$), which is the ammonio derivative of **7**. We report here the syntheses, structures, and reactions of **7** and **9**.



Scheme 2. A) Synthesis of **7** by oxidation of **6** at low temperature. B) Thermal isomerization of **7** to **1**. C) Oxidation of **8** to **9**.

The addition of an aqueous $FeCl_3$ solution to an aqueous solution of K_4[**6**] at 0 °C resulted in the rapid formation of **7** in high yield (Scheme 2 A). The product was immediately precipitated as $[Me_4N]_2$[**7**] to prevent further reaction or rearrangement. It was characterized by ^{11}B NMR spectroscopy and electrospray ionization mass spectrometry (ESI-MS). The structure of $[Me_4N]_2$[**7**] was determined by single-crystal X-ray diffraction.[6]

An ORTEP drawing of the structure of **7** is shown in Figure 1.[6] The polyhedral borane anion consists of two intact $[B_{10}H_9]^-$ cages linked by two 3c–2e bonds. The bond lengths within the two decaborate cages are normal and similar to those found in other structures derived from $[B_{10}H_{10}]^{2-}$. The three apical boron atoms B10′, B1′, and B1 exhibit essentially linear geometry, with a B10′-B1′-B1 angle of 178.9°. Similar 3c–2e bonds were first structurally characterized in **1**,[7] whose structure differs markedly from that of **7**. The two $[B_{10}H_9]^-$ cages in **1** are equivalent and arranged in a transoid configuration, while those in **7** are nonequivalent and cisoid.

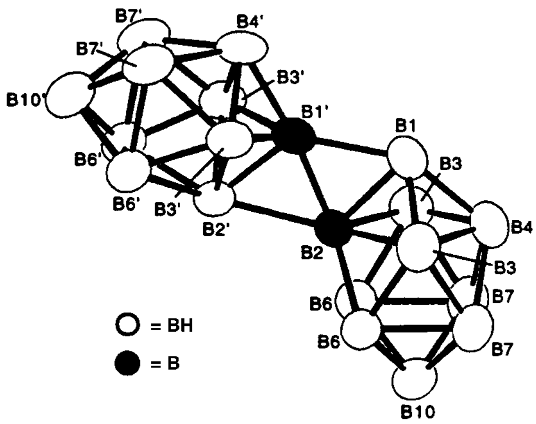
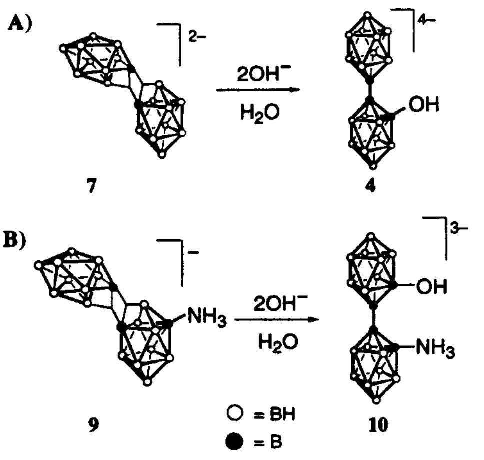


Figure 1. ORTEP representation of the structure of anion **7**, and the atom numbering scheme. For clarity the terminal B–H hydrogen atoms have been omitted. Selected bond lengths [Å] and angles [°] (estimated standard deviations in parentheses): B1′–B2′ 1.670(7), B1′–B1 1.853(8), B1–B2 1.683(7), B2–B2′ 1.974(7), B1′–B2 1.692(7); B10′-B1′-B1 178.9(2), B2′-B1′-B1 128.4(3), B1′-B2′-B2 54.6(2), B1′-B1-B2 56.9(2), B1-B2-B2′ 120.1(2).

Solutions of **7** in acetonitrile are unstable even at room temperature, and slowly rearrange to the more stable ion **1**. When a solution of $[Me_4N]_2$[**7**] in acetonitrile is heated for 1 h, almost complete conversion of **7** into **1** is observed in the ^{11}B NMR spectra (Scheme 2B). When **1** was subjected to the same conditions, **7** was not observed, demonstrating that the rearrangement is irreversible.

The UV spectrum of anion **7** in acetonitrile displays two electronic transitions in the near-UV region ($\lambda_{max} = 277$ nm, $\varepsilon = 1.44 \times 10^4$; $\lambda_{max} = 229$ nm, $\varepsilon = 3.29 \times 10^4$), which are similar to those the UV spectrum of **1** in the same solvent ($\lambda_{max} = 292$ nm, $\varepsilon = 1.08 \times 10^4$; $\lambda_{max} = 232$ nm, $\varepsilon = 2.38 \times 10^4$).[5] The similarity of the UV spectra of **7** and **1** presumably results from the similarity of the intercage bonding of these two species.

As in the case of **1**, the two 3c–2e bonds of **7** are electron deficient and susceptible to nucleophilic attack. The reaction of **7** with an aqueous solution of sodium hydroxide at room temperature led to the direct formation of the stable ion **4** in 77 % yield (Scheme 3 A). The anion **4** was previously reported to arise from the isomerization of **3**.[4] The reductive substitution of **7** represents a new method for the direct synthesis of stable a^2-$[B_{20}H_{18}]^{4-}$ derivatives.[2]



Scheme 3. A) Reaction of **7** with OH^- ions to **4**. B) Reaction of **9** with OH^- ions to **10**.

As in the synthesis of **7**, the oxidation of **8**[3] (the ammonio derivative of **6**) with iron(III) ions in aqueous solution at 0 °C afforded **9** (designated as *cis*-$[B_{20}H_{17}NH_3]^-$, Scheme 2C), which was isolated in 61% yield as the trimethylammonium salt. $[Me_3NH]$[**9**] was characterized by ^{11}B NMR spectroscopy and ESI mass spectrometry.

The structure of the anion **9** was determined by single-crystal X-ray structure analysis.[8] An ORTEP drawing is shown in Figure 2. The structure of **9** exhibits the same borane cage configuration as in **7**. The bond lengths within the two $[B_{10}H_9]^-$ cages are normal and similar to those in **7**.

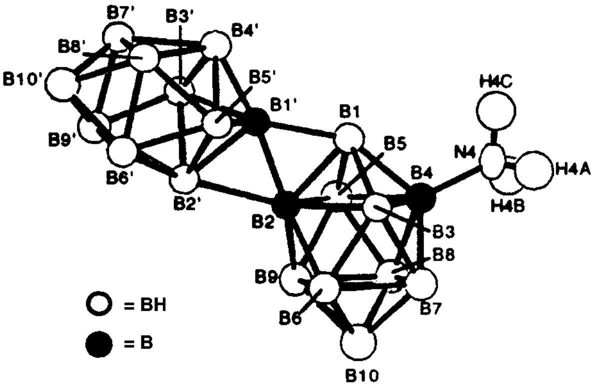


Figure 2. ORTEP representation of the structure of anion **9**, and the atom numbering scheme. For clarity the terminal B–H hydrogen atoms have been omitted. Selected bond lengths [Å] and angles [°] (estimated standard deviations in parentheses): B1–B2 1.716(8), B1–B1′ 1.814(8), B1′–B2′ 1.680(8), B2′–B2 1.952(8), B1′–B2 1.688(7), B4–N4 1.537(7); B10′-B1′-B1 176.8(3), B2-B1-B1′ 57.1(3), B1-B2-B2′ 118.5(4), B1-B1′-B2′ 129.0(4), B2-B2′-B1′ 54.8(3).

Owing to the reduced negative charge of anion **9** compared to ion **7**, **9** is much more reactive with nucleophiles than **1** or **7**, and it will react with weak nucleophiles (such as water) even at room temperature. While solutions of **9** in acetonitrile are relatively stable at room temperature, rearrangement to another as yet unidentified isomer is observed upon heating.

When $[Me_3NH]$[**9**] was treated with an aqueous solution of sodium hydroxide at room temperature (Scheme 3B), the disubstituted anion *a*²-$[B_{20}H_{16}(OH)NH_3]^{3-}$ (**10**, Scheme 3B) was isolated in 89% yield. The structure of the ion **10** was established by its ^{11}B NMR and ESI mass spectra although the mechanism leading to **10** is not yet entirely clear. However, the ^{11}B and 2D-COSY NMR spectra of **10** clearly establish that it is a disubstituted $[B_{20}H_{18}]^{4-}$ derivative with a different substituent on each $[B_{10}H_9]^-$ cage. This reaction provides a convenient route to disubstituted derivatives of *a*²-$[B_{20}H_{18}]^{4-}$ and may easily afford other disubstituted derivatives suitable for BNCT.

The synthesis of the anion **7** has not only revealed the existence of a new isomer of $[B_{20}H_{18}]^{2-}$, but has also provided a simple and direct route to stable *a*² derivatives of the polyhedral borane anion $[B_{20}H_{18}]^{4-}$. The new anion *cis*-$[B_{20}H_{17}NH_3]^-$ (**9**) may also have considerable potential in the synthesis of disubstituted derivatives of these polyhedral borane anions.

Experimental Section

7: An aqueous solution of iron(III) chloride (0.5 N, 30 mL, 15 mmol) was added to a solution of K_4[**6**][4] (2.00 g, 5.1 mmol) in water (100 mL) at 0 °C. An aqueous solution of Me_4NCl was immediately added to precipitate $[Me_4N]_2$[**7**]. The precipitate was isolated by filtration. The solid was dissolved in CH_3CN (50 mL), and the resulting solution was passed through a small plug of silica gel. The bright yellow solution was collected, and the solvent was removed under reduced pressure. The residue was stirred with water (20 mL), aqueous Me_4NCl solution (5 mL, 1 N) was added, and the mixture was cooled to 0 °C to produce a yellow precipitate. The precipitate was isolated by filtration and dried under vacuum to yield $[Me_4N]_2$[**7**] (1.33 g, 3.5 mmol, 69%). $^{11}B\{^1H\}$ NMR (160 MHz, H_2O): $\delta = 26.9$ (2B, apical B–H), –11.7 and –19.9 (total of 18B); ESI-MS: (*m/z*): 117.0 $[(B_{20}H_{18})^{2-}]$, 235.0 $[(B_{20}H_{18}+H)^-]$.

9: An aqueous solution of iron(III) chloride (0.5 N, 30 mL, 15 mmol) was added to a solution of $[Me_3NH]_3$[**8**][9] (2.00 g, 4.6 mmol) in water (100 mL) at 0 °C to produce a precipitate immediately. The reaction mixture was stirred for 1 h. The precipitate was collected by filtration, the solid was dissolved in CH_3CN (50 mL), and the resulting solution was passed through a small plug of silica gel. The bright yellow solution was collected, and the solvent was removed under reduced pressure. The residue was dissolved in water (20 mL), aqueous $[Me_3NH]Cl$ (5 mL, 1 N) was added, and the mixture was cooled to 0 °C to produce a bright yellow solid. The solid was separated by filtration and dried under vacuum to yield $[Me_3NH]$[**9**] (0.87 g, 2.8 mmol, 61%). $^{11}B\{^1H\}$ NMR (H_2O): $\delta = 26.8$ (2B, apical B–H), –1.5 (1B, B–N), –13.2, –17.2, –20.8, and –22.2 (total of 17B); ESI-MS: (*m/z*): 250.7 $[(B_{20}H_{17}NH_3)^-]$.

4: Dry $[Me_4N]_2$[**7**] (0.50 g, 1.3 mmol) was added to a solution of sodium hydroxide (0.50 g, 12.5 mmol) in water (10 mL) at room temperature. The solution was stirred for 4 h. A saturated solution of Me_4NCl in EtOH was added until the solution became turbid. Upon cooling of the solution to 0 °C, a fine white powder separated. The solid was collected by filtration, washed with ethanol, and dried in vacuo to yield $[Me_4N]_3$[**4**] (0.55 g, 1.0 mmol, 77%). The product was identified by $^{11}B\{^1H\}$ NMR spectroscopy.[4] ESI-MS: (*m/z*): 253.0 $[(B_{20}H_{17}OH+3H)^-]$, 326.1 $[\{Me_4N(B_{20}H_{17}OH+2H)\}^-]$.

10: Dry $[Me_3NH]$[**9**] (1.00 g, 3.3 mmol) was added to a solution of sodium hydroxide (1.00 g, 25.0 mmol) in water (10 mL) at room temperature. The solution was stirred for 4 h. A saturated solution of Me_4NCl in EtOH was added until the solution became turbid. Upon cooling of the solution to 0 °C, a fine white powder separated. The solid was collected by filtration, washed with ethanol, and dried in vacuo to yield $[Me_4N]_3$[**10**] (1.40 g, 2.9 mmol, 89%). The product was identified by ^{11}B NMR spectroscopy. $^{11}B\{^1H\}$ NMR (H_2O): $\delta = 8.3$ (2B, B–B), –2.5 (1B, B–O), –6.2 (1B, apical B–H), –7.4 (1B, apical B–H), –14.1 (1B, B–N), –23.5, –24.9,

−26.3, −29.3, −31.4 and −34.8 (total of 14B); ESI-MS: (*m/z*): 268.3 $[(\{B_{20}H_{16}(OH)NH_3)\}+2H)^-]$.

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[6] a) Crystal structure analysis of $[Me_4N]_2$[**7**]: colorless crystals from ethanol/acetonitrile: $C_8H_{42}B_{20}N_2$, $M_r = 382.7$; crystal dimensions $0.18 \times 0.38 \times 0.5$ mm³; Syntex $P\bar{1}$ diffractometer, $Cu_{K\alpha}$ radiation, $\lambda = 1.5418$ Å, 298 K; $\theta-2\theta$ scan mode to $2\theta_{max} = 120°$. The unit-cell parameters were determined from 25 accurately centered reflections ($18.9° < 2\theta < 26.6°$): orthorhombic, space group *Pnam* (no. 62), $a = 10.279(2)$, $b = 34.000(5)$, $c = 8.310(2)$ Å, $V = 2904$ Å³, $Z = 4$, $\rho_{calcd} = 0.97$ g cm^{-3}, $\mu = 2.94$ cm^{-1}. Of the 2330 unique reflections measured ($+h$, $+k$, $+l$), 1680 were considered observed ($I > 2\sigma(I)$), and the structure was solved by direct methods; 239 refined parameters, maximum residual electron density 0.13 e Å^{-3}, least-square refinement against $|F^2|$; $R = 0.078$ for the observed reflections, $R_w = 0.113$. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101302. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[8] Crystal structure analysis of $[Me_3NH]$[**9**]: colorless crystals from an aqueous solution, $C_3H_{30}B_{20}N_2$, $M_r = 310.5$, crystal dimensions $0.48 \times 0.05 \times 0.55$ mm³, Syntex $P\bar{1}$ diffractometer, $Cu_{K\alpha}$ radiation, $\lambda = 1.5418$ Å, 298 K; $\theta-2\theta$ scan mode to $2\theta_{max} = 115°$. The unit-cell parameters were determined from 41 accurately centered reflections ($19.7° < 2\theta < 40.1°$): orthorhombic, space group $P2_12_12_1$, $a = 10.334(7)$, $b = 10.873(8)$, $c = 17.523(12)$ Å, $V = 1969$ Å³, $Z = 4$, $\rho_{calcd} = 1.05$ g cm^{-3}, $\mu = 2.79$ cm^{-1}. Of the 1519 unique reflections measured ($+h$, $+k$, $+l$), 1318 were considered observed ($I > 2\sigma(I)$), and the structure was solved by direct methods; 156 refined parameters, maximum residual electron density 0.1 e Å^{-3}, least-square refinement against $|F^2|$; $R = 0.064$ for the observed reflections, $R_w = 0.082$.[6b]

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Expeditious Routes to Evernitrose and Vancosamine Derivatives and Synthesis of a Model Vancomycin Aryl Glycoside**

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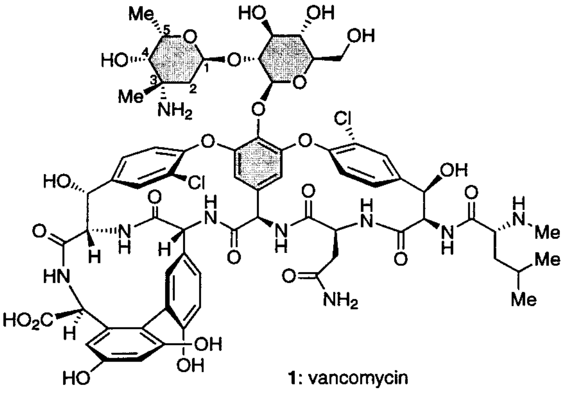
The antibiotics vancomycin[1] (**1**) and everninomicin 13,384-1[2] (for the structure, see following contribution)[3] include in their structures C3-branched 2,6-dideoxy-L-sugars containing an amino[4] or a nitro group,[5] respectively. Our interest in the total synthesis of vancomycin[6] and everninomicin 13,384-1[7] dictated new synthetic routes to these unique sugars and methods for their attachment onto their respective target molecules. Here we report the successful attainment of both goals, culminating in the construction of key intermediates **11** and **16** (see Scheme 1) and the assembly of vancomycin disaccharide **22** (see Scheme 2). In the following communication[3] we describe the synthesis of an advanced everninomicin 13,384-1 segment incorporating the nitrosugar.



1: vancomycin

A key objective of our strategy toward the nitrogen-containing sugar units of these antibiotics was the construction of an intermediate (**7**), from which both compounds **11** and **16** could be generated (Scheme 1). Towards this goal, we envisioned a stereocontrolled *anti* addition[8] of an acyl anion equivalent to an aldehyde derived from L-lactic acid as a means to install the C4 stereocenter (the numbering is based on the final carbohydrate), where the functionality at C3 was projected to arise by nucleophilic chain extension of an

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