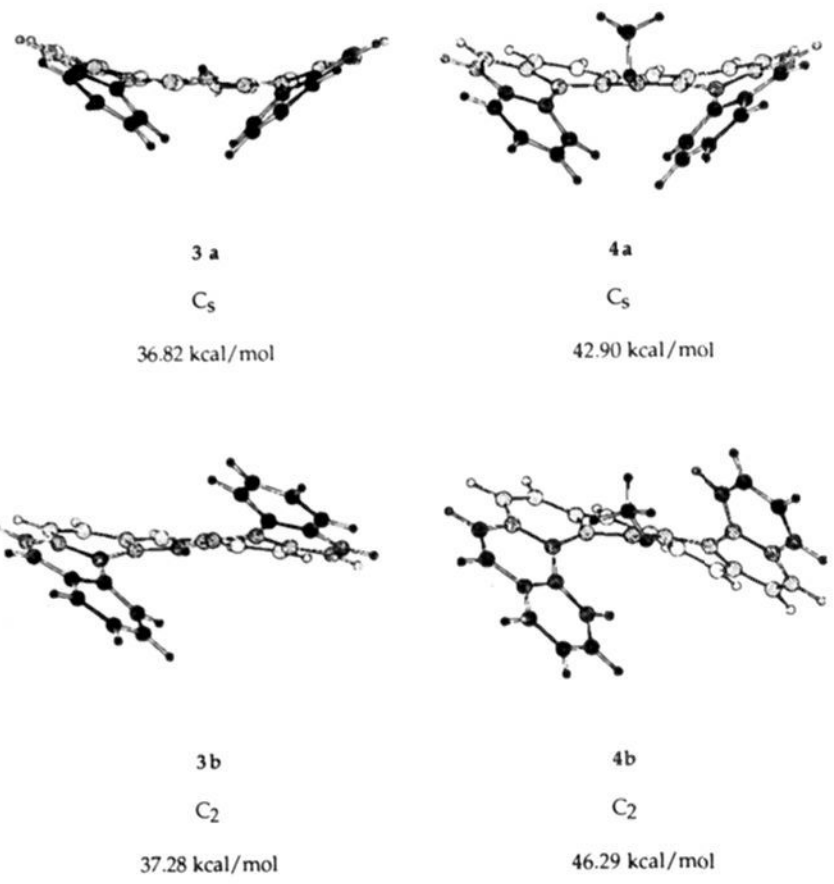


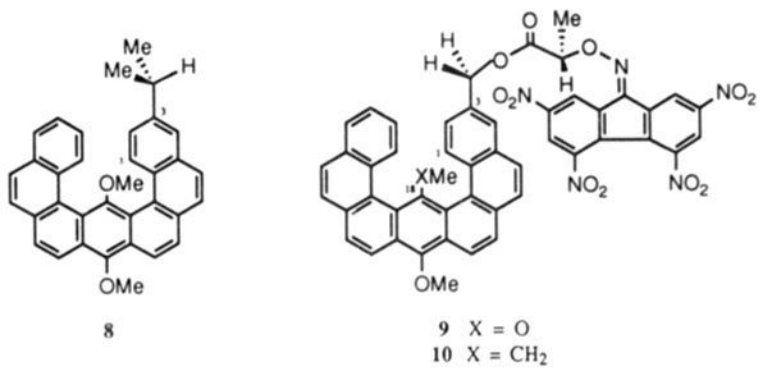

**Figure 2**. Calculated conformations and corresponding energies of dinaphtho[*a,j*]anthracene (**3a**, **3b**) and 18-methoxydinaphtho[*a,j*]-anthracene (**4a**, **4b**).

the $C_s$ (in contradistinction to $C_2$)[18] symmetry of the dinaphthoanthracene framework (Figure 1).

Interestingly, molecular mechanics calculations[19] show the energies (Figure 2; the calculated globally minimized energies are given under each structure) of the butterfly ($C_s$) and the helical ($C_2$) conformations to favor slightly (0.46 kcal/mol) the $C_s$ state **3a** of the parent system, but more so (3.39 kcal/mol) the $C_s$ state **4a** of the C-18 methoxy derivative.[20]

Interconversion of two such (pseudoenantiomeric) homomeric $C_s$ states of **1**, by a hoped-for linear inversion at C-18 methoxy oxygen, or by some other process, would, on a time-averaged basis, yield a planar molecule of effective $C_{2v}$ symmetry. Such an interconversion could be monitored through the coalescence of either diastereotopic $CH_3$ groups (enantiomerization) in 3-isopropyl-9,18-dimethoxydinaphtho[*a,j*]anthracene (**8**) or diastereotopic benzylic hydrogens (diastereomerization) in ester **9** derived from (−)-TAPA and 3-hydroxymethyl-9,18-dimethoxydinaphtho[*a,j*]anthracene:[21]

Dynamic studies[22] on **8** and **9**, in DMSO-$d_6$, yielded the following free energies of activation: 18.1 ± 0.2 kcal/mol ($T_{coal}$ 330 K) for **8** and 18.8 ± 0.3 kcal/mol ($T_{coal}$ 341 K) for **9**. For a control we also synthesized and studied **10** (no inversion is possible at $sp^3$ C of the C-18 $CH_2CH_3$ group). Coalescence in the spectrum of **10** was also observed at 393 K, leading *surprisingly* to a free energy of activation of 21.5 ± 0.3 kcal/mol. The close similarity of the coalescence barriers of **8** and **9** on the one hand, and **10**, on the other, strongly suggests that the coalescence is due to a motion other than oxygen inversion. It must be the case that a complex process of distortions of the aromatic carbon framework, not revealed by molecular models, coupled with C–O (for **8** and **9**) and C–C (for **10**) rotations, occurs in preference to linear inversion.[23] Therefore, *the barrier for linear oxygen inversion in* **1**, *and presumably also in other aryl methyl ethers, must be greater than 18.1 kcal/mol.*




**Acknowledgment**. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also thank Dr. A. Gordon (Pfizer Corp.) for inducing our interest in linear inversion of oxygen, Prof. F. Mallory, for fruitful discussions, and Prof. W. C. Still for the gift of his MacroModel program, version 2.5. NMR facilities at Yale University and Hunter College were used to obtain variable-temperature data; MS data were obtained at Pennsylvania State University.

**Supplementary Material Available:** Listing of final atomic parameters, anisotropic thermal parameters, bond lengths, bond angles, and least-squares planes through rings A–G for **1** (10 pages). Ordering information is given on any current masthead page.

(17) The crystals were monoclinic, space group $I2/a$, with $a$ = 39.035 (4), $b$ = 7.157 (1), $c$ = 35.497 (3) Å; $\beta$ = 113.91 (1)°; and $d_{calcd}$ = 1.285 g cm$^{-3}$ for $Z$ = 16 ($C_{32}H_{22}O_2$, $M_r$ = 438.53). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu K$\alpha$ radiation, $\theta$–$2\theta$ scans, pulse-height discrimination). The size of the crystal used for data collection was approximately 0.15 × 0.40 × 0.65 mm. A total of 6126 independent reflections were measured for $\theta$ <57°, of which 4412 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by a multiple-solution procedure (Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr.* **1971**, *A27*, 368) and was refined by block-diagonal least-squares procedures in which the matrix was partitioned into two blocks. In the final refinement, anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations but their parameters were not refined. The final discrepancy indexes are $R$ = 0.048 and $R_w$ = 0.049 for the 4412 observed reflections. The final difference map has no peaks greater than ±0.2 e A$^{-3}$.

(18) The $C_s$ symmetry conformation has been dubbed the *butterfly* conformation; whereas the $C_2$ symmetry conformation is termed the *helical* conformation.

(19) The molecular mechanics calculations were done with Macromodel version 2.5 using MM2 parameters on a microVAX II.

(20) See: Pascal, R. A., Jr.; McMillan, W. D.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 5652.

(21) The rotations about the Ar–*i*-Pr and 9-MeO–Ar bonds are assumed to be substantially faster.

(22) Details of the syntheses, analogous to that outlined for **1**, will be given in the full paper.

(23) This motion involving extreme distortion of the dinaphthoanthracene framework would take place in compound **4** as well.

## A Stable Crystalline Carbene

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We report the synthesis, structure, and characterization of the first crystalline carbene. Carbene **1**, 1,3-di-1-adamantylimidazol-2-ylidene, forms colorless crystals with sufficient kinetic and thermodynamic stability to be easily isolated and characterized. The deprotonation of 1,3-di-1-adamantylimidazolium chloride (**2**) in THF at room temperature with catalytic dimsyl anion ($^-CH_2S(O)CH_3$) in the presence of 1 equiv of sodium hydride produces carbene **1** (eq 1). This deprotonation can also be accomplished with potassium *tert*-butoxide in THF to give a 96% yield of **1**.

Carbene **1** is stable in the absence of oxygen and moisture. Recrystallization of **1** from toluene affords clear, colorless rectangular prisms with a melting point of 240–241 °C. A sample of **1** that had been melted could be remelted without depression of the melting point. A previously melted sample of **1** showed

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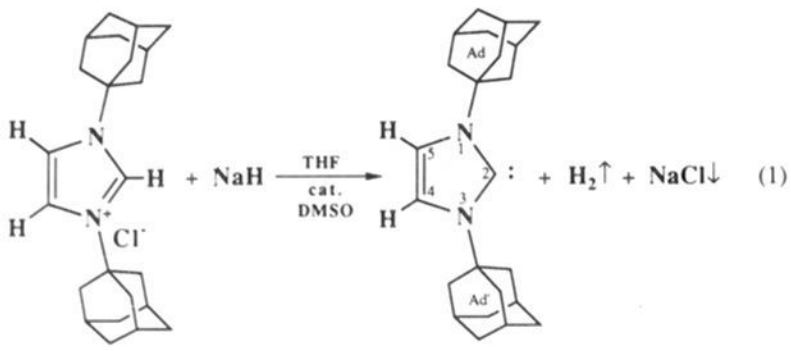


(1)

2 1

a $^1$H NMR spectrum identical with that of the initially isolated carbene. The NMR spectral data of **1** in benzene-$d_6$ are as follows: $^1$H NMR $\delta$ 1.58 ppm (s, $Ad_{4,6,10}$, 12 H), 2.01 (s, $Ad_{3,5,7}$, 6 H), 2.29 (s, $Ad_{2,8,9}$, 12 H), 6.91 (s, NC*H*, 2 H); $^{13}$C NMR [$^1$H] $\delta$ 211.43 (s, $C_2$), 113.88 (dd, $^1J_{CH}$ = 185.6 Hz, $^2J_{CH}$ = 13.4 Hz, $C_{4,5}$), 55.99 (s, $Ad_1$), 44.8 (tm, $^1J_{CH}$ = 131.3 Hz, $Ad_{2,8,9}$), 37.7 (tm, $^1J_{CH}$ = 126.8 Hz, $Ad_{4,6,10}$), 30.3 (dm, $^1J_{CH}$ = 128.9 Hz, $Ad_{3,5,7}$): $^{15}$N NMR $\delta$ −160.5 (ref $NH_4NO_3$). The electron-impact mass spectrum of **1** gave a base peak at $m/z$ = 336.26, corresponding to the molecular ion. The elemental analysis of **1** gave C, 82.13; H, 9.64; N, 8.36 (theory C, 82.09; H, 9.58; N, 8.32). The IR spectrum (KBr) of **1** shows absorbances at 2920, 1504, 1448, 1378, 1350, 1303, 1213, 1291, 833, 695, and 495 cm$^{-1}$.

A single crystal suitable for X-ray diffraction studies was grown by cooling a toluene solution of **1**. The X-ray crystal structure of **1** is depicted in Figure 1. Selected bond lengths and angles are given in Table I. The final $R$ factors were $R$ = 0.038 and $R_w$ = 0.034. The largest residual electron density in the final difference Fouier map was 0.20 e/Å$^3$ just outside the imidazole ring near $C_2$. An attempt to refine a hydrogen in this position resulted in an increase in the $R$ values until the isotropic thermal parameter increased beyond $B$ = 70 for the hydrogen.

Several striking features are revealed in the X-ray structure of **1**. One is the small N–C–N angle at the carbene center. This angle is significantly reduced from the typical range of values (108.5–109.7°) for the corresponding angle in imidazolium salts.[2] This carbenic angle is in agreement with theoretical studies on singlet ($^1$A′) carbenes bearing $\pi$-donor substituents.[3] The lengths of the $C_2$–$N_{1(3)}$ bonds are significantly increased from the value of 132 pm found in imidazolium salts.[2] The lengths of the $N_1$–$C_5$ and $N_3$–$C_4$ bonds are slightly longer than the corresponding bonds in typical imidazolium salts.[2] The largest structural changes are fairly well localized at the carbene center of **1**. These changes suggest a diminished $\pi$-delocalization in **1** as compared to imidazolium salts. This change in $\pi$-delocalization is also supported by the upfield shift in the imidazole ring proton in **1** versus **2** ($\delta$ 7.92 → 6.91).[4]

Carbene **1** enjoys both steric and electronic stabilization. The electronic stabilization factors include a $\pi$-donation into the carbene out-of-plane p orbital by the electron-rich $\pi$-system (N̈—C═C—N̈) and a $\sigma$-electronegativity effect. The $\pi$-interactions lead to several good resonance contributors for **1** in which positive charge is delocalized in the imidazole ring with the $C_2$ represented as a $\pi$-bonded carbanionic center (like phenyl anion). Wanzlick has suggested that this type of interaction might be useful in stabilizing nucleophilic carbenes.[5] Recent results from our laboratories have shown that the carbene position should not be solely represented as carbanionic since the calculated charge on carbon is only −0.08$e$.[6] Additional electronic stability for the carbene electron pair may be gained from the $\sigma$-electronegativity effects of the nitrogens on the carbene center. Although important, these electronic factors have not proven sufficient to allow the isolation of nucleophilic carbenes by previous workers.[7] The additional steric hindrance offered by the adamantyl substituents in **1** undoubtedly contributes to the kinetic stability. The hindrance offered by the adamantyls is evident both in the direct view in Figure 1 and in the shadowed plane which bears the ball and stick skeleton in addition to the space-filling outline. In spite of the bulk of the adamantyl substituents, the direct view of **1** looks as if there is sufficient room at the carbene center for chemical reaction to take place.

Carbenes have long been recognized as important reaction intermediates.[8] The aggressive study of carbenes as reactive intermediates has provided much fundamental knowledge for chemical science. Until now there have not been any "bottle-able" carbenes, and we hope that the production of these stable nucleophilic carbenes will allow for convenient study of this class of compounds. We are currently investigating both the electronic

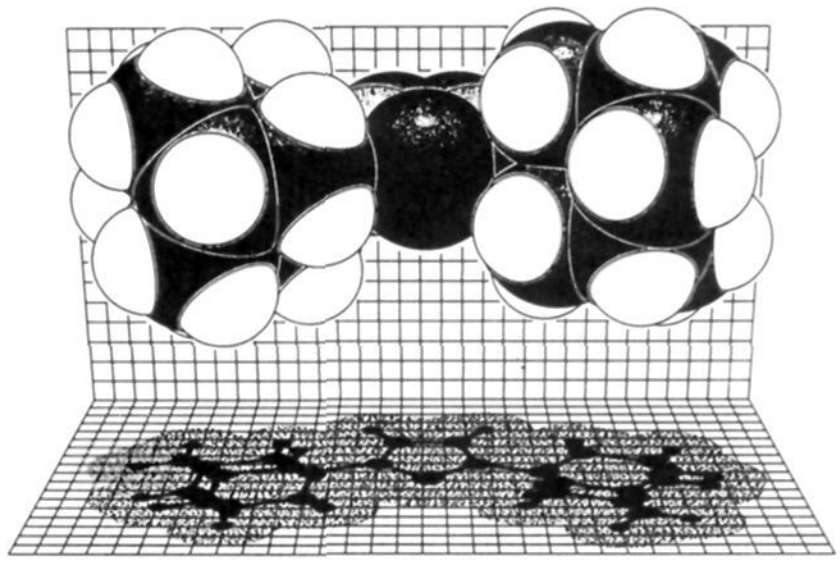

**Figure 1**. Space-filling KANVAS[1] drawing of the X-ray structure of **1**.

**Table I**. Selected Bond Lengths (pm) and Angles (deg) in **1**

| | bond length | | bond angle |
|---|---|---|---|
| $C_2$–$N_1$ | 136.7 (2) | $N_1$–$C_2$–$N_3$ | 102.2 (2) |
| $C_2$–$N_3$ | 137.3 (2) | $C_5$–$N_1$–$C_2$ | 112.1 (2) |
| $C_4$–$C_5$ | 133.8 (3) | $C_4$–$N_3$–$C_2$ | 112.3 (2) |
| $N_1$–$C_5$ | 138.2 (2) | $N_1$–$C_5$–$C_4$ | 107.2 (2) |
| $N_3$–$C_4$ | 138.6 (2) | $N_3$–$C_4$–$C_5$ | 106.2 (2) |
| $N_1$–$C_{1\text{-Ad}}$ | 148.2 (2) | $C_2$–$N_1$–$C_{1\text{-Ad}}$ | 123.4 (2) |
| $N_3$–$C_{1\text{-Ad}'}$ | 148.5 (2) | $C_2$–$N_3$–$C_{1\text{-Ad}'}$ | 122.1 (2) |

(1) This drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institut der Universitat Freiburg, FRG), which was modified by A. J. Arduengo, III (E. I. du Pont de Nemours & Co., Wilmington, DE), to produce the back and shadowed planes. The planes bear a 50-pm grid, and the lighting source is at infinity so that shadow size is meaningful.

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(3) For $CF_2$, see: (a) Bauschlicher, C. W., Jr.; Schaefer, H. F., III; Bagus, P. S. *J. Am. Chem. Soc.* **1977**, *99*, 7106. (b) Dixon, D. A. *J. Phys. Chem.* **1986**, *90*, 54. For $C(OH)_2$, see: (c) Feller, D.; Borden, W. T.; Davidson, E. R. *J. Chem. Phys.* **1979**, *71*, 4987. For CHF, CH(OH), and $CH(NH_2)$, see: (d) Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M.-B.; Apeloig, A.; Karni, M.; Chandrasekhar, J.; Schleyer, P. von R. *J. Am. Chem. Soc.* **1986**, *108*, 270.

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(7) There is a 21-paper series published by H.-W. Wanzlick which describes considerable chemistry of nucleophilic carbenes and work directed toward synthesis of a stable derivative. For paper number 21, see: Lachmannn, B.; Steinmaus, H.; Wanzlick, H.-W. *Tetrahedron* **1971**, *27*, 4085.

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structure and chemical reactivity of **1** and related isolable carbenes.

**Acknowledgment.** We are indebted to F. Davidson for his work on the NMR spectroscopy and Dr. D. A. Dixon for helpful discussions.

**Supplementary Material Available:** A complete description of the X-ray crystallographic determinations of **1** and 1,3-di-1-adamantylimidazolium tetraphenylborate, including tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, and bond angles (17 pages); tables of structure factor amplitudes for **1** and 1,3-di-1-adamantylimidazolium tetraphenylborate (16 pages). Ordering information is given on any current masthead page.

## Nuclear Magnetic Resonance of Hydroxyl and Amido Protons of Oligosaccharides in Aqueous Solution: Evidence for a Strong Intramolecular Hydrogen Bond in Sialic Acid Residues

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NMR studies of exchangeable protons of carbohydrates in aqueous solution are severely hampered by fast chemical exchange in conjunction with short relaxation times. Ten years after the first report[1a] of hydroxyl (OH) proton resonances for carbohydrates in aqueous solution at different pH values, studying OH protons of oligosaccharides in $H_2O$ at or near ambient temperature to extract three-dimensional structural information from their resonances is still far from routine.[1b] A number of investigators have used DMSO as the solvent to circumvent chemical exchange of OH and NH protons with residual water.[2a-h] In this communication we present a new approach to the NMR study of OH and NH protons in aqueous solution. The OH protons and their spatial neighbors are observed in pre-steady-state NOE experiments[3] with careful water suppression. This approach largely overcomes the problem of fast exchange. We demonstrate that the OH proton at C8 of sialic acid (the terminal monosaccharide residue in many biologically active glycoprotein and glycolipid carbohydrate chains) is involved in a strong, specific intramolecular hydrogen bond that is independent of the type of linkage in which the sialic acid is involved.

The oligosaccharides studied are NeuAc$\alpha$(2→3)Gal$\beta$(1→4)Glc (3′-sialyllactose) (**1**) and NeuAc$\alpha$(2→6)Gal$\beta$(1→4)Glc (6′-sialyllactose) (**2**). They were dissolved in 85% $H_2O$/15% $(CD_3)_2CO$ and analyzed in 5-mm NMR tubes at 261 K with a Bruker AM 500 spectrometer. Chemical shifts are referenced to internal DSS, by setting the chemical shift of the $^1H$ signal of residual $(CD_3)CO(CD_2H)$ to $\delta$ 2.204 ppm. The pulse sequences used in the $H_2O$-suppressed one-dimensional (1D) TOCSY[4a,b] (total correlation spectroscopy, also known as homonuclear Hartmann-Hahn spectroscopy), ROESY[5a,b] (rotating-frame NOESY), and NOESY[6] (nuclear Overhauser enhancement spectroscopy) experiments are shown in Figure 1. Spectra of compounds **1** and **2** are shown in Figures 2 and 3, respectively. The signals of the nonexchangeable (CH) protons of **1** and **2** were assigned by means of 1D TOCSY[4b] in $D_2O$ solution. The assignments for **1** were in agreement with those in the literature.[10,11] The complete assignment of the protons of **2** will be published elsewhere. The spectra of **1** and **2** (see Figures 2a and 3a) show NH and OH signals at $\delta$ 8-9 ppm and 5.6-7.6 ppm, respectively. The NH protons exchange with solvent protons at rates <0.1 $s^{-1}$; thus, they are readily observed as relatively narrow lined doublets. However, the exchange rates of OH protons with the solvent are greater than the HO-CH coupling constants, even at 261 K; consequently, any observable OH signals are broad, which makes their assignment by tracing $J$ connectivities impossible.

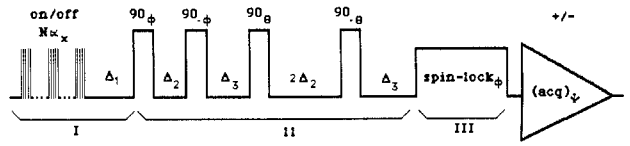


Figure 1. Pulse sequence for 1D $^1H$ NMR experiments in aqueous solution with $H_2O$ suppression utilizing the 1-1 echo technique[7] (stage II), followed by a short trim pulse. Normal 1D spectra were obtained without stage I and with a short trim pulse (about 3 ms) in stage III. Stage I consisted of a DANTE pulse train[8] which was used for selective inversion (180° pulse) in TOCSY and ROESY experiments, or for presaturation in the NOE experiments. The delay $\Delta_1$ is the mixing time for 1D pre-steady-state NOE experiments.[3,6] For other types of experiments, $\Delta_1$ was set just long enough to allow for a change of decoupler power. In 1D ROESY[5a,b] experiments, stage III consisted of a long spin-lock pulse or a train of short pulses;[9] for 1D TOCSY[4a,b] experiments, stage III consisted of the MLEV-17 pulse sequence sandwiched between two trim pulses. The phases of pulses and receiver were as follows: $\phi$ = 4$x$, 4(−$x$), 4$y$, 4(−$y$), $\theta$ = $x$, $y$, −$x$, −$y$, −$x$, −$y$, $x$, $y$, $y$, −$x$, −$y$, $x$, −$y$, $x$, $y$, −$x$, $\psi$ = $x$, −$x$, $x$, −$x$, −$x$, $x$, −$x$, $x$, $y$, −$y$, $y$, −$y$, −$y$, $y$, −$y$, $y$. The first pulse in the MLEV-17 sequence had a phase $\phi$ + 90°.

The subspectrum of the sialic acid residue of **1**, including its NH signal, was obtained by 1D TOCSY upon selective inversion of the NeuAc H3eq signal (Figure 2b). The H3ax, H4, H5, NH, and H6 signals are readily assigned from their multiplet structure and $J$ signature. Figure 2c shows a 1D ROESY spectrum of **1** recorded with irradiation of the NeuAc NH proton. Several spatial connectivities to the NeuAc ring protons identified in trace 2b are clearly observable; the strongest NOE is visible between NH and H6. Traces d and e in Figure 2 show 1D NOE difference spectra recorded with irradiation of OH protons at $\delta$ 6.23 and 6.44 ppm. The strong NOE interaction between the proton at $\delta$ 6.23 and the ring proton H6 (trace d) is reminiscent of that observed for $G_{M1}$ in DMSO solution;[2h] it identifies[13] the proton that

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