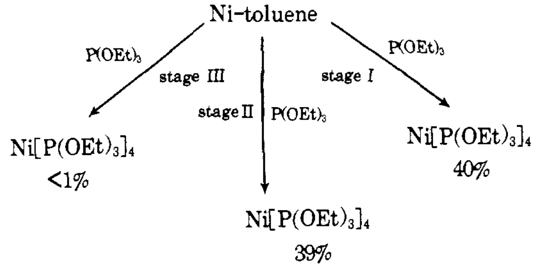
fairly low temperature (about −50 °C) in the reaction chamber. With Al_2O_3 the Ni was completely adsorbed (1-2% Ni loading) but did not change the overall surface area of the Al_2O_3 sample. On heating the Al_2O_3-Ni powder in stages with a small flame, its surface area decreased after each heating until finally the area had fallen from 120 to 70 m^2/g. Apparently the small Ni crystallites sintered upon heating and blocked some of the pores in the Al_2O_3 sample.

When stage II Ni-toluene is allowed to warm to room temperature, stage III, a Ni-toluene slurry is formed. This clustered form of the Ni is not reactive with triethyl phosphite under the same conditions as stage I and II were, thus showing that solvated atoms are probably present both in stage I and II. Vacuum pumpoff of solvent leaves stage IV, pyrophoric, reactive Ni-toluene clusters (cf. Table I for properties).



Ni-THF. A yellow matrix forms upon codeposition that consists of a reactive, low temperature stable Ni(0)-etherate. This etherate is quite reactive with such things as alkyl halides causing reduction and coupling. Warming of the Ni-THF complex results in black streams of Ni-THF flowing to the bottom of the reactor. The resulting Ni-THF slurry is very finely divided and totally syringeable. It is also reactive with alkyl halides. After removal of THF under high vacuum pumping for several hours at room temperature, a very fine Ni-THF powder is formed that is a fairly unreactive hydrogenation catalyst, but a very good catalyst for cyclohexene disproportionation to benzene and cyclohexane. A great deal of residual THF is very strongly bound, which can only be displaced by strong ligands such as triethyl phosphite, but not by excess amines, alkenes, or ethers. The particles are surprisingly uniform as tiny spheres which upon strong heating release organics (THF (45%), butyraldehyde (20%), 1-butanal (30%), furan (5%)) with formation of larger Ni crystals, as shown by the SEM studies illustrated.

The process for producing these solvated metal atoms and clusters is very versatile since many metal-solvent combinations can be employed. Each stage (I-IV) in the clustering process can be useful in further chemical reactions.[7,8] Furthermore, this method points toward wide extentions of Sinfelt's "bimetallic cluster" principle[9] since two different metals could be clustered in the zero-valent state in a host of different matrices and then deposited on catalyst supports.

Acknowledgments. The generous support of the National Science Foundation (GP-42376) is greatly appreciated. We also are grateful for helpful discussions with Dr. Lewis Radonovich and the UND Medical School for the use of SEM equipment.

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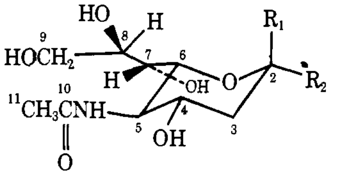
^{13}C Spin Lattice Relaxation in the Neuraminic Acids. Evidence for an Unusual Intramolecular Hydrogen Bonding Network[1]

Sir:

N-Acetylneuraminic acid (NANA) and its derivatives play an important role in the chemical and physical interactions of the glycoproteins and glycolipids associated with biomembranes, where it is bound ketosidically in the α anomeric form.[2] Therefore, we have decided to explore in some detail the structures and conformations of the neuraminic acids. Several recent reports have shown the utility of ^1H NMR and ^{13}C NMR in the study of NANA and NANA containing molecules.[3] We wish to report the first ^{13}C spin lattice relaxation (T_1) study of NANA and its derivatives and to demonstrate the potential of this parameter to provide unique insight into the structural understanding of these important biomolecules.

NANA (**1a**) was prepared from edible birds nest substance using a modification of existing published procedures.[4] Methyl β-D-*N*-acetylneuraminidate (**1b**) and 2-*O*-methyl-β-D-*N*-acetylneuraminic acid (**1c**) were prepared by the method of Kuhn et al.[5] The modified Koenigs-Knorr synthesis of Meindl and Tuppy was used to prepare 2-*O*-methyl-α-D-*N*-acetylneuraminic acid (**1d**).[6] Free acids were converted to their sodium salts by titration with NaOH solution followed by lyophilization. In order to minimize the effects of paramagnetic impurities, that seem especially prevalent in D_2O solutions, the sample preparation techniques suggested by Roberts and co-workers[7] were used.



1a, R_1 = OH; R_2 = $-CO_2H$
b, R_1 = OH; R_2 = $-CO_2CH_3$
c, R_1 = OCH_3; R_2 = $-CO_2H$
d, R_1 = $-CO_2H$; R_2 = OCH_3

We have examined the ^{13}C NMR of the four neuraminic acid derivatives. The T_{1obsd} values and corresponding nuclear Overhauser enhancements (η) are presented in Table I. Chemical shift values and assignments, which correspond closely to previously published data,[3a,b] have been omitted due to space limitations. All values represent the mean of three-five individual determinations, for which the standard deviations were ±10-15%. The values for T_{1DD}, which represent the contribution to the total relaxation from the direct dipole-dipole mechanism, were calculated from the

Table I. ^{13}C T_1's (s)[a] and η values[b] of Neuraminic Acid Derivatives Measured in 0.68 M D_2O Solutions[c]

	1a			1b			1c			1d		
C	T_{1obsd}	η	T_{1DD}	T_{1obsd}	η	T_{1DD}	T_{1obsd}	η	T_{1DD}	T_{1obsd}	η	T_{1DD}
1	15[d]	1.3	23	14[e]	1.4	20	13[d]	1.4	19	14[d]	1.3	22
2	5.0	1.7	5.9	5.5	1.9	5.8	4.3	1.7	5.1	6.0	2.0	6.0
3	0.13	2.0	0.13	0.17	2.0	0.17	0.12	2.0	0.12	0.15	2.0	0.15
4	0.32	2.0	0.32	0.30	1.9	0.32	0.25	1.9	0.26	0.28	2.0	0.28
5	0.29	2.0	0.29	0.30	2.0	0.30	0.27	2.0	0.27	0.30	2.0	0.30
6	0.29	2.0	0.29	0.32	2.0	0.32	0.25	2.0	0.25	0.32	2.0	0.32
7	0.27	2.0	0.27	0.30	2.0	0.30	0.23	2.0	0.23	0.28	2.0	0.28
8	0.31	2.0	0.31	0.30	2.0	0.30	0.25	2.0	0.25	0.31	2.0	0.31
9	0.22	2.0	0.22	0.20	1.9	0.21	0.18	1.9	0.19	0.20	2.0	0.20
10	6.6	1.7	7.8	7.0	1.4	10	4.8	1.3	7.4	6.3	1.6	7.9
11	1.4	1.6	1.8	1.7	1.7	2.0	1.4	1.6	1.8	1.4	1.7	1.6
12				1.4[f]	1.8	1.6	1.0[g]	1.6	1.3	1.3[g]	1.5	1.7

[a] Measured at 25.03 MHz on a JEOL PFT-100 NMR spectrometer by the fast inversion recovery sequence (FIRFT),[11] using 8K data points over a spectral width of 4000 Hz. The 90° pulse was 20 μs. [b] Measured by the gated decoupling technique.[12] [c] Temperature was maintained at 28.0 ± 0.5°; samples were degassed by purging with N_2 for 15 min or longer. [d] Carboxylate carbon. [e] Ester carboxyl carbon. [f] Ester methyl carbon. [g] Ketoside methoxy carbon.

$T_{1\,obsd}$ and the η value for each carbon atom.[8]

The value NT_{1DD}, where N is the number of directly bonded hydrogens, can be interpreted as an internal molecular mobility parameter for protonated carbons.[9] Thus increased mobility resulting from anisotropic molecular tumbling, internal rotation, or segmental motion is paralleled by an increase in the value of NT_{1DD}.[10] Examination of T_{1DD} for the molecules under study yields the following conclusions. (1) The similarity of values for the ring carbons, T_{1DD} for methines (C-4, C-5, C-6) and $2T_{1DD}$ for the methylene (C-3), is consistent with a rigid ring that tumbles isotropically in solution, i.e., demonstrates no preferred axis of rotation. (2) Methyl groups experience considerable free rotation, independent of the overall molecular motion. The value $3T_{1DD}$ for these carbons greatly exceeds NT_{1DD} for the carbons in the ring. (3) Since $2T_{1DD}$ for C-9 consistently exceeds NT_{1DD} for the ring carbons, C-9 experiences extra mobility relative to the ring.[13] (4) The motions of C-7 and C-8 are isotropic with the ring as evidenced by the substantial equality of these T_{1DD}'s with those of the ring methines (C-4, C-5, C-6). (5) Freedom of motion at C-9 is not substantially hindered upon transposition of the carboxylate moiety from the β anomers (**1a–c**) to the α anomer (**1d**), despite the intuitively attractive hydrogen bonding interaction that might be possible between the -OH at C-9 and the negatively charged carboxylate in the α anomer.

Brown and co-workers have examined the conformation of the glycerol side chain through the evaluation of vicinal coupling constants in the 270-MHz NMR of NANA (**1a**), and have proposed that hydrogen bonding occurs between the -OH at C-7 and the ring oxygen and between the -OH at C-8 and the oxygen at C-9.[3c] This model, however, is not supported by our measurements since it would require that *only* C-7 be isotropic with the ring. Additionally, motional coupling between C-8 and C-9 would predict equivalent NT_{1DD} values. Moreover, this hydrogen bonding scheme involves two comparatively unfavorable five-membered ring interactions.

Therefore, we wish to propose the following model that is both supported by our results and yet still completely consistent with the conformational relationships derived from the ^1H NMR. In this model (Figure 1) the amido N-H is hydrogen bonded to the oxygen at C-7 and the -OH at C-8 is hydrogen bonded to the ring oxygen, thus linking the motion of C-7 and C-8 to the ring through highly favorable six-membered ring (chair form) interactions. The motion of C-9, though, since it would be unencumbered by intramolecular hydrogen bonds, would be relatively freer than that of C-7 and C-8. It is interesting to note that, as a result of the hydrogen bond formed with the glycerol side chain, the acetamido carbonyl is favorably placed to form a third intramolecular hydrogen bond, between the carbonyl and the -OH at C-4. The proposed hydrogen bonding network would lock the ring very strongly into its favorable conformation. In the absence of this effect, it is conceivable that a small population of a less stable conformation could, with unfortunate results, bind to an improper biological receptor site.

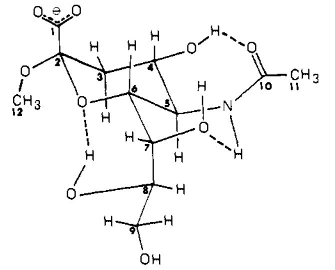


Figure 1. Conformational model of anion of **1d** showing the proposed hydrogen bonds and preferred conformation of the glycerol side chain. Although shown here only for the α anomer, this conformation is independent of anomeric configuration. Construction of CPK models indicates the preferential nature of these hydrogen bonds as well as the lack of unfavorable steric interactions. As measured in D_2O solution the exchangeable protons of the hydroxyls and the amido group would be replaced by deuterons.

Further studies relating to the ^{13}C NMR properties of the neuraminic acids and related biomolecules are currently being pursued.

Acknowledgments. Support of this research by the National Science Foundation is gratefully acknowledged. We also wish to thank the National Science Foundation for a grant to purchase the FT-NMR spectrometer used in this work.

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(10) This is strictly true only when the extreme narrowing condition is satisfied; in our experiments this can be confirmed by the observation of $\eta_{max} = 2.0$ for certain carbon atoms. A discussion of this topic can be found in: J. Schaefer, *Top. Carbon-13 NMR Spectrosc.*, **1**, Chapter 4 (1974).

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(13) Anisotropy in the absence of extra mobility could in principle account for the C-9 result, if the required number of linearly independent C–H vectors to detect anisotropic motion were not present at C-3 to C-8, but the requirement was met by the C-9 protons. However, it appears that in all reasonable conformations the requirement will be satisfied by C-7 or C-8 protons, so that very probably there is rotational mobility around the C-8–C-9 bond.

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Stability of Some C_7 Tertiary Alkyl Carbonium Ions

Sir:

The stabilities of gaseous carbonium ions have been investigated in this laboratory by pulsed, high-pressure mass spectrometric equilibrium measurements.[1,2] The temperature variation of the equilibria

$$t\text{-}C_4H_9^+ + RH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^+ + i\text{-}C_4H_{10} \quad (RH = \text{tertiary } C_4\text{–}C_7 \text{ alkanes}) \qquad (1)$$

were used to obtain the enthalpies of formation of C_4–C_7 carbonium ions. The values obtained for the C_7 ion derived from 2,4-dimethylpentane showed unexpected stability and an unexpectedly large negative entropy of formation. Similar results for C_7 alkyl ions have been obtained by Goren and Munson[3] using a continuous ionization mass spectrometric method.

We report here that C_7 alkyl carbonium ions undergo thermal decomposition at temperatures >480 K, and this decomposition caused the previously reported enthalpy and relative entropy for the carbonium ion derived from 2,4-dimethylpentane to be seriously in error. New and more accurate values for C_7 ions have been obtained and are given in this communication.

The decomposition reaction is

$$t\text{-}C_7H_{15}^+ \xrightarrow{k_2} t\text{-}C_4H_9^+ + C_3H_6 \qquad (2)$$

The occurrence of this reaction is masked by reaction (−1) when the t-C_7H_{15} ion is produced from t-$C_4H_9^+$, but it is readily apparent when $C_3H_7^+$ from propane serves as the reactant ion. However, we confirm that eq 2 also occurs with isobutane as reactant gas, for when deuterated 2-methylhexane was used as the C_7 hydrocarbon, deuterated butyl ions were observed.

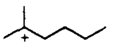
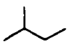
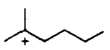
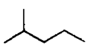
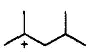
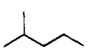
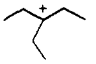
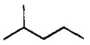
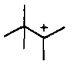
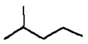
Both (2) and (−1) lead from the $C_7H_{15}^+$ to the $C_4H_9^+$ ion. The rates r_2 (= k_2) for eq 2 have been investigated in a study which will be reported separately, and the values of k_2 generally fall in the range (1-20) × $10^3\ s^{-1}$. The rate for (−1) is usually much smaller than $10^3\ s^{-1}$ under our conditions. For example, for RH = 2,4-dimethylpentane we find k_{-1} at 500 K from the values of k_1[4] and the value of the equilibrium constant for eq 1 to be 3.0×10^{-15} $cm^3/(mol\ s)$. With a typical values of $(i\text{-}C_4H_{10}) = 2 \times 10^{16}$ mol/cm^3 this gives for the rate $r_{-1} = 0.6\ s^{-1}$, which is $\ll(1\text{-}20) \times 10^3\ s^{-1}$. Consequently, in the system of reactions 1 and 2, a constant ion ratio is established by the steady-state situation $r_1 = r_{-1} + r_2$ and

$$1 \equiv \left(\frac{r_{-1} + r_2}{r_1}\right)_{ss} = \frac{k_{-1}[t\text{-}C_7H_{15}^+][i\text{-}C_4H_{10}] + k_2[t\text{-}C_7H_{15}^+]}{k_1[t\text{-}C_4H_9^+][C_7H_{16}]} \cong \frac{k_2}{k_1}\frac{[t\text{-}C_7H_{15}^+]}{[t\text{-}C_4H_9^+][C_7H_{16}]};\ K_a = \frac{[t\text{-}C_7H_{15}^+]}{[t\text{-}C_4H_9^+][C_7H_{16}]} \qquad (3)$$

where the apparent equilibrium constant K_a is defined as $K_a = k_2/k_1$ and is the quantity experimentally determined when $r_2 \gg r_{-1}$. In our previous work[2] $K_a[i\text{-}C_4H_{10}]$ was taken as the true equilibrium constant for eq 1. The temperature dependence of K_a is determined mainly by the activation energy of k_2 and is not related to the enthalpy change of eq 1. The unexpected thermochemical behavior of the 2,4-dimethylpentyl ion found previously appears to be an artifact caused by the unexpected and previously unknown thermal pyrolysis reaction (2).

Table I. Thermodynamic Values[a] from

$$R' + RH \rightleftharpoons R^+ + R'H$$

R^+	$R'H$	ΔH_f (R^+), kcal/mol	$\Delta\Delta S_f$ (R^+)[b] eu	$D(R^+\text{–}H^-)$, kcal/mol
		150.5	32.7	231.8
		151.5	37.1	232.7
		148.4	29.3	231.2
		150.6	33.8	230.5
		144.5	15.8	228.1

[a] ΔH_f and ΔS_f values for neutral reactants from D. W. Scott, *J. Chem. Phys.*, **60**, 3144 (1974). $\Delta H_f(H^-)$ = 34.7 kcal/mol calculated from R. S. Berry, *Chem. Rev.*, **60**, 533 (1969). [b] $\Delta\Delta S_f(R^+) = \Delta S_f(R^+) - \Delta S_f(t\text{-}C_4H_9^+)$.

In our kinetic studies we observed that eq 2 does not proceed at observable rates below 450 K. We therefore measured thermodynamic values for several tertiary carbonium ions by the equilibrium method between 300 and 450 K. In these measurements mixtures of ~15% of the appropriate heptane in 2-methylpentane (2-MP) were used, at a total particle density of ≈1.5 × 10^6 mol/cm^3. These conditions assured that the reactant to product ion ratios in the equilibrium constant

$$K = \frac{I_{C_7H_{15}^+}}{I_{C_6H_{13}^+}}\frac{P_{2\text{-MP}}}{P_{(C_7H_{16})}} \qquad (4)$$

remained within the dynamic range of the mass spectrometer throughout our experiments.

At least duplicate sets of equilibrium measurements at several temperatures were made for each system. The van't Hoff plots from each set of data exhibited an acceptably small amount of scatter. The reproducibility of the thermodynamic values was found to be within ±0.3 kcal/mol and ±3 eu except for the values for 2,4-dimethylpentyl ion, where differences of ±0.6 kcal/mol and 6 eu between four repetitive runs occurred for unknown reasons. The stability