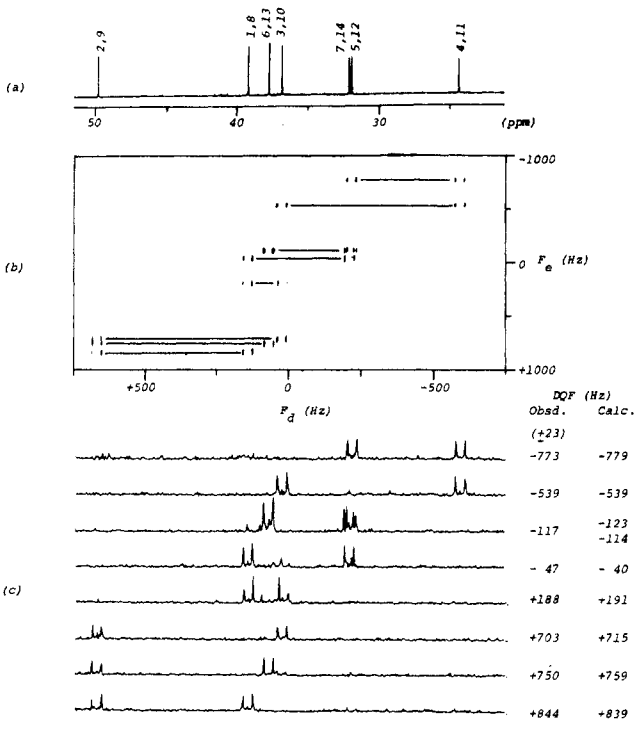

Figure 1. (a) ^{13}C NMR spectrum of tetrahydrobinor-S in $CDCl_3$. (b) Contour plot of the CCC2D NMR spectrum. The horizontal lines indicate the connectivities between the various AX (or AB) carbon doublets. (c) F_d traces at the calculated double quantum frequencies more clearly showing the connectivities between various carbon centers and the agreement between the calculated and observed DQF's.

frequencies. Thus, the CCC2D NMR spectrum should be clearly able to differentiate between the two possible structures for tetrahydrobinor-S.

Figure 1 summarizes the results. Figure 1a is the regular ^{13}C spectrum in $CDCl_3$ at room temperature. The multiplicity of each peak was assigned on the basis of APT experiment (attached proton test or spin echo Fourier transform).[11] Figure 1b is the contour plot of the CCC2D NMR spectrum (see Experimental Section for details). The horizontal lines show the connectivity between the carbon sites. The methine carbon resonances at $\delta_{^{13}C}$ 49.8, 39.3, and 37.0 clearly show three connectivities each at the corresponding double quantum frequencies (frequencies at the F_e domain, which is the algebraic sum of the single quantum frequencies of the two carbon resonances in the F_d domain measured with respect to the transmitter frequency). Similarly the methylene carbons at $\delta_{^{13}C}$ 32.4, 32.2, and 24.1 show two connectivities each. The methine carbon at $\delta_{^{13}C}$ 37.8 shows one connectivity with the methine carbon at $\delta_{^{13}C}$ 49.8 and connectivities to two methylenes at $\delta_{^{13}C}$ 32.4 and 32.2, appearing approximately at the same double quantum frequency. Figure 1c shows F_d traces at specific double quantum frequencies again clearly indicating the connectivities between the various carbon centers.

The analysis of the CCC2D NMR spectrum of tetrahydrobinor-S clearly shows that the structure of this pentacyclic hydrocarbon is **3** (pentacyclo-[8.4.0.0^{2,6}.0^{3,8}.0^{9,13}]tetradecane) and not **2** (pentacyclo-[9.3.0.0^{2,6}.0^{3,8}.0^{9,14}]tetradecane). Our results support Schleyer's earlier prediction based on molecular mechanics calculations.[5] Carbon–carbon connectivity 2D NMR is clearly a powerful method in structure determination, allowing one to differentiate even closely related structures that otherwise cannot be distinguished by NMR spectroscopy. The present study on the structure of tetrahydrobinor-S serves well to demonstrate the utility of this method.

Experimental Section

Tetrahydrobinor-S was prepared according to literature procedure.[2] The ^{13}C NMR spectrum (Figure 1a) and the CCC2D NMR spectrum (Figure 1b,c) were recorded at 50.3 MHz ^{13}C resonance frequency in $CDCl_3$ (~30% solution) at ambient temperature on a Varian XL-200 spectrometer equipped with a Nicolet Model Zeta 8 plotter. The pulse sequence used[9] is 90°–τ–180°–τ–90°–t_1–135°–acquisition (t_2), where t_1 is the evolution period, t_2 is the detection period, and τ = 7 ms ($\approx 1/4J_{CC}$). J_{CC}). The 135° read pulse was used to provide a high discrimination ratio between echo and antiecho and still retain ~20% signal-to-noise ratio improvement.[9] Phase cycling[8,9] of the read pulse provides quadrature detection in both domains, and the sign of the double quantum frequency can also be determined. Broad-band proton decoupling was performed throughout the experiment. The data were obtained by using a 1500-Hz spectral width for the detection (F_d) domain and a 3000-Hz spectral width for the evolution (F_e) domain. Data were collected for 160 transients for each of the 128 different values of the evolution period, with a 5-s delay between transients. A 1K Fourier number was used for the detection domain transformation and a 256 Fourier number for the evolution domain transformation. The accuracy of the double quantum frequencies measured is ~23 Hz (spectral width in the evolution domain divded by the number of different values of the evolution period). The observed and the calculated (from the resonance frequencies of the individual carbons) double quantum frequencies are given in Figure 1c.

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

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Methyl(4-diazoniophenyl)oxonium Dication: A Diazonium Oxonium Dication[1]

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The ambient character of benzenediazonium ions has been firmly established by ^{13}C and ^{15}N NMR spectroscopic studies and by IR spectroscopy.[2-4] All attempts to observe a C-protonated benzenediazonium dication under stable ion conditions proved unsuccessful. For example, even 2,6-dialkyl-substituted benzenediazonium ions show no ^1H NMR evidence for protonation in magic acid at low temperature, only small solvent shifts were observed.[5] This reinforces that charge delocalization into the aromatic ring plays a significant role.

We have found now that *p*-methoxybenzenediazonium tetrafluoroborate (**1**) is O-protonated in FSO_3H–SbF_5 (1:4)

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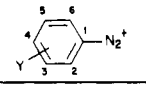
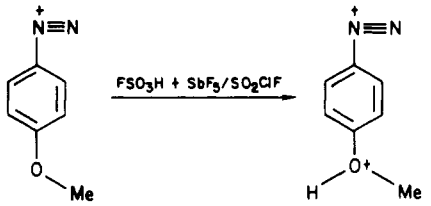
Table I. Carbon-13 Chemical Shifts[a] of Benzenediazonium Salts in Superacid Solvents[b] and SO_2[c]



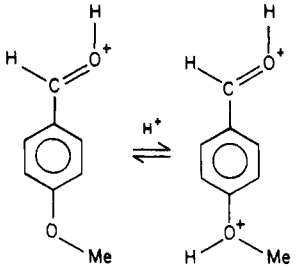
Y	solvent system	C-1	C-2	C-3	C-4	C-5	C-6	CH_3
H	SO_2	112.2	131.9	131.5	141.9	131.5	131.9	
	FSO_3H–SbF_5 (1:4)/SO_2ClF	111.6	131.8	131.3	142.4	131.3	131.8	
4-OMe	SO_2	100.1	135.2	117.6	169.8	117.6	135.2	56.8
4-OMe	FSO_3H–SbF_5 (1:4)/SO_2ClF	114.9	136.4	120.9	157.9	120.9	136.4	75.3
4-OMe	FSO_3H–SbF_5 (1:1)/SO_2ClF	112.8	135.8	119.6	158.4	119.6	135.8	70.6
2-OMe	SO_2	98.3	162.8	114.1	144.6	122.7	131.1	57.8
2-OMe	FSO_3H–SbF_5 (1:4)/SO_2ClF	98.1	162.8	114.1	144.6	122.7	131.1	58.2

[a] In ppm from external capillary Me_4Si. [b] At −75 °C. [c] At −30 °C.

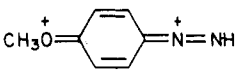
at low temperature (−75 °C) in SO_2ClF, $\delta_{^{13}C(OMe)}$ 75.3 ($\Delta\delta$ = 18.5). Whereas the C_1, $C_{2,6}$, and $C_{3,5}$ are expectedly deshielded as compared to the spectrum of 1 in SO_2, the C_4 absorption shows a small shielding effect (see Table I). In FSO_3H–SbF_5 (1:1)/SO_2ClF superacid system at −75 °C, the methoxy absorption is less deshielded at $\delta_{^{13}C(OMe)}$ 70.6 ($\Delta\delta$ = 13.8) and indicates somewhat faster exchange with the solvent acid due to a decrease in acidity.[6] No demethylation or demethoxylation was observed.



The ^1H NMR spectrum of 1 in FSO_3H–SbF_5 (1:4)/SO_2ClF shows a deshielded methoxy $\delta_{^1H}$ 4.42 and two aromatic singlet absorptions at $\delta_{^1H}$ 7.25 and 7.93 for the $H_{3,5}$ and $H_{2,6}$ with an integral ratio of 3:2:2, respectively. The acidic $HOMe^+$ signal could not be observed as a separate distinct signal in the ^1H NMR spectrum even at −75 °C as it is still exchanging on the NMR time scale with the solvent acid. Similar observations were made in HF–SbF_5/SO_2ClF solvent. This is analogous to the behavior of diprotonated *p*-methoxybenzaldehyde in HF–SbF_5 or FSO_3H–SbF_5, studied by Sommer et al.,[7] which resulted in a general deshielding of the ^1H NMR signals and a decrease in rotational barrier for phenyl–carbonyl bond on diprotonation. Similarly, deshielding of the methoxy carbon and shielding of the C_4 ring carbon was observed in the ^{13}C NMR spectrum upon diprotonation.



Protonation of the β-^{15}N labeled 1 ($\delta_{^{15}N}$ 321 from NH_3) in FSO_3H–SbF_5 (1:4)/SO_2ClF resulted in an upfield shift of the $^{15}N_\beta$ signal ($\delta_{^{15}N}$ 313.2; $\Delta\delta_{^{15}N}$ 7.8). This indicates that the para substituent is strongly electron withdrawing[8] and is in accord with the formation of a dication. In a coupled spectrum the β-^{15}N remained a singlet, ruling out possible N-protonation of the tautomeric form, i.e.,



Attempts to O-methylate 1 with $MeF/SbF_5/SO_2$ or with $MeI/AgSbF_6/SO_2$ at low temperature were unsuccessful.

Unlike the 4-methoxybenzenediazonium ion, 2-methoxybenzenediazonium ion is not O-protonated under similar conditions due to the proximity of the developing positive charge with the N_2^+.

Experimental Section

3,5-Dimethylbenzene- and β-^{15}N labeled *p*-methoxybenzenediazonium ion tetrafluoroborate were prepared by diazotization of their anilines with $NaNO_2$ and $Na^{15}NO_2$, respectively, and were precipitated from CH_3NO_2/ether. All other diazonium ion salts were commercially available (Ozark-Mahoning or Aldrich) and were purified by precipitation from CH_3NO_2/ether and repeated washing with dry ether and drying under vacuum.

^1H, ^{13}C and ^{15}N NMR spectra were recorded on Varian FT-80 and XL-200 spectrometers.

Preparation of the Ions. To the diazonium ion salt (50–70 mg) stirred in SO_2ClF and cooled to −75 °C was added the superacid (ca. 1 mL) diluted in SO_2ClF (1 mL) with Vortex mixing until homogeneous.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

Registry No. 1, 459-64-3; 1-β-^{15}N, 96845-60-2; *p*-$MeOC_6H_4N_2^+ \cdot H^+$, 96845-61-3; *p*-$MeOC_6H_4N{\equiv}{}^{15}N^3 \cdot H^+$, 96845-62-4; *o*-$MeOC_6H_4N_2^+$, 17356-93-3; PhN_2^+, 2684-02-8.

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Facile Synthesis of Chiral Glycine from D-Ribose

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The development of the general synthetic method of hexoses and pentoses with chirally deuterated hydroxymethyl groups[1] prompted us to utilize these monosaccharides as the synthetic starting materials of other biologically important, chirally deuterated compounds. We selected chiral glycine as our first synthetic target. As the

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