2: mp 102–104 °C; IR (KBr) 3405, 3012, 2937, 1457, 1321, 1284, 1268, 1211, 1000, 980, 905, 854, 833, 750, 653; ^{1}H NMR ($CDCl_3$) δ 7.2 (s, 4 H), 5.45 (d, 1 H), 5.2 (s, 1 H), 4.1 (m, 1 H), 1.9 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 146.72, 141.78, 127.37, 126.76, 120.66, 118.96, 86.18, 78.7, 72.68, 39.98; mass spectrum, CI, m/e 163 (M + 1, 22%), 145 (100%), 118 (15%), 117 (9%), EI, m/e 133 (2%), 119 (7%), 118 (100%), 103 (2%), 90 (12%). Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.06; H, 6.22. Found: C, 73.76; H, 6.28.

Acknowledgment. We gratefully acknowledge support from the National Institutes of Health (Grant GM 10937-22) in this research.

Registry No. 1, 573-57-9; 2, 96898-07-6; 3, 37480-22-1; BMS, 13292-87-0; 9-BBN, 280-64-8; Chx_2BH, 1568-65-6; Sia_2BH, 1069-54-1.

The Structure of Tetrahydrobinor-S (Pentacyclo[8.4.0.0^{2,6}.0^{3,8}.0^{9,13}]tetradecane) Based on C–C Connectivity Two-Dimensional NMR Study

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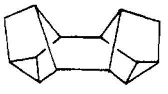
Diamantane, the second member of the adamantanoid hydrocarbons, became readily available after a convenient high-yield preparation was reported independently by Schleyer[1] and McKervey.[2] The chemistry of this interesting cage hydrocarbon and its derivatives has been extensively studied since then. The preparation involves acid-catalyzed rearrangement of the isomeric pentacyclic hydrocarbon tetrahydrobinor-S. Tetrahydrobinor-S is the product of hydrogenation of binor-S[3,4] (1) (heptacyclo[8.4.0.0^{2,12}.0^{3,7}.0^{4,9}.0^{6,8}.0^{11,13}]tetradecane) over PtO_2 in AcOH at 40 atm H_2 pressure.[1,2] Hydrogenation of binor-S, in principle, can give rise to four products (**2**–**5**) corresponding to the hydrogenolysis of the cyclopropane rings in various fashion.



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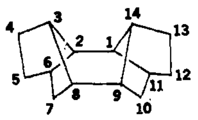

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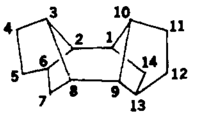

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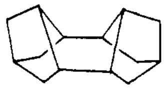

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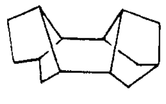

5

In fact only one product is formed when binor-S is hydrogenated with H_2 over PtO_2 catalyst. However, the structure of tetrahydrobinor-S remained elusive. Structures **4** and **5** can be ruled out on the basis of the ^{13}C NMR[5,6] spectrum. The ^{13}C NMR spectrum shows seven carbon resonances at $\delta_{^{13}C}$ 49.8 (d), 39.3 (d), 37.8 (d), 37.0 (d), 32.4 (t), 32.2 (t), and 24.1 (t). Structure **4** (C_{2h} symmetry) should have five carbon resonances, while structure **5** (C_1 symmetry) should have 14 carbon resonances. Thus, these two structures obviously will not fit the observed ^{13}C spectrum. However, both structure **2** (C_s symmetry) and structure **3** (C_2 symmetry) contain seven distinct carbons of the same general type in accord with the observed ^{13}C spectrum. The significant difference between structures **2** and **3** is that **2** is achiral while **3** is chiral. On the basis of molecular mechanics calculation Schleyer et al. suggested **3** as the structure of the compound.[5]

We now wish to report our study using carbon–carbon connectivity 2D (CCC2D) NMR spectroscopy[7] unequivocally proving the structure of tetrahydrobinor-S to be **3**, i.e. pentacyclo[8.4.0.0^{2,6}.0^{3,8}.0^{9,13}]tetradecane.

Results and Discussion

The carbon–carbon connectivity 2D NMR developed by Freeman et al.[7] and the later modifications of the technique[8,9] are based on the INADEQUQTE[10] pulse sequence (see Experimental Section for the details of the pulse sequence). The INADEQUATE pulse sequence generates a double quantum coherence in molecules containing two scalar coupled ^{13}C spins. The CCC2D NMR experiment uses the frequency of the double quantum coherence itself as the criterion for connectivity. The double quantum coherence, generated by the 90°–τ–180°–τ–90° sequence, is allowed to "evolve" during the evolution period at the double quantum frequency, which is the sum of the resonance frequencies of the coupled spins (measured with respect to the transmitter frequency). A proper choice of τ ($\approx 1/4J_{CC}$, where J_{CC} is the one-bond ^{13}C–^{13}C coupling constant) would generate double quantum coherence only from molecules containing two scalar coupled ^{13}C spins adjacent to each other. After two-dimensional Fourier transformation, a spectrum is obtained with the conventional carbon-13 satellite lines in the F_d dimension and the corresponding double quantum frequencies in the F_e dimension (see Experimental Section for details).

An examination of structures **2** and **3** reveals that the two molecules differ in their connectivities. In fact, if **2** were the correct structure, one would predict two double quantum frequencies each for the methylene carbons (C_4, C_5, and C_7) and for two of the four methine carbons (C_1 and C_8) as they each are attached to two other "nonequivalent" carbons. However, the other two methine carbons (C_3 and C_6) are attached to three nonequivalent carbons, and thus one would observe three double quantum frequencies for each of these two CH's. In contrast in structure **3**, all the methine carbons are attached to three nonequivalents carbons, and thus each one should show three double quantum frequencies. For the methylenes, as in structure **2**, one would predict two double quantum

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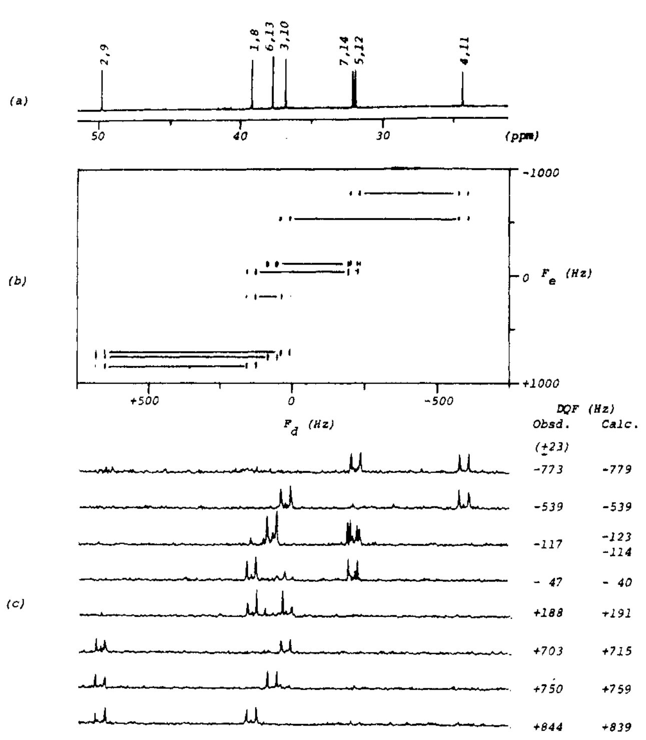

Figure 1. (a) ^{13}C NMR spectrum of tetrahydrobinor-S in $CDCl_3$. (b) Contour plot of the CCC2D NMR spectrum. The horizontal lines indicate the connectivities between the various AX (or AB) carbon doublets. (c) F_d traces at the calculated double quantum frequencies more clearly showing the connectivities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

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Registry No. 3, 51966-18-8.

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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 ^{1}H 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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