Table X. Calculated (6-31G*) and Predicted Experimental Vibrational Frequencies (cm^{-1}) for Ethynamine

description	symmetry	calcd (6-31G*)	corrn factor[a]	pred exptl
NH$_2$ asym. stretch	a″	3868	0.865	3346
NH$_2$ sym. stretch	a′	3771	0.864	3258
C—H stretch	a′	3675	0.910	3344
C≡C stretch	a′	2432	0.885	2152
NH$_2$ sciss	a′	1815	0.88	1597
NH$_2$ rock	a″	1330	0.95	1264
C—N stretch	a′	1138	0.97	1104
CCH bend	a″	831	0.795	661
NH$_2$ wag	a′	754	0.80	603
CCH bend	a′	645	0.795	513
NCC bend	a′	506	0.89	450
NCC bend	a″	426	0.87	371

[a] From data in Table IX; see text.

quencies. For some modes, values of the ratio $\nu_{\text{exptl}}/\nu_{\text{calcd}}$, lie close together (e.g., those for C≡C or ≡C—H stretch), but for others the ratio may vary widely from molecule to molecule. As we have at most four values for comparison and in some cases only two, we are unable to assess magnitudes of probable error. Instead, we show in Table X the calculated (6-31G*) vibrational frequencies for ethynamine along with a correction factor obtained for each mode by judicious selection and/or weighting of those shown in Table IX. We suggest that the resulting "predicted" experimental vibrational frequencies for ethynamine be regarded as midpoints of ranges of up to 100 cm^{-1} within which the corresponding experimental frequency is likely to lie; for the favorable cases noted above (e.g., C≡C and ≡C—H stretch), we believe the experimental frequency may lie within 10 cm^{-1} of that predicted, but in other cases predicted frequencies are subject to much greater uncertainties.

Concluding Remarks

Ethynamine has yet to be synthesized in the laboratory or observed in interstellar space. Theory has the opportunity of contributing to its discovery. We hope that the present predictions of the structure, rotational constants, microwave frequencies, and vibrational frequencies for ethynamine will facilitate its identification, both in the laboratory and in interstellar space.

Acknowledgment. We thank Professor W. M. Irvine for helpful correspondence.

Registry No. NH$_2$—C≡CH, 52324-04-6; NH$_2$—C≡N, 420-04-2.

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Nuclear Spin–Spin Coupling via Nonbonded Interactions. 6. The Importance of Bridgehead Interactions on ^{1}H–^{1}H, ^{1}H–^{13}C, and ^{13}C–^{13}C Coupling Constants in Bicycloalkanes

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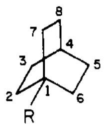
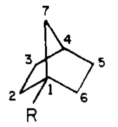
Abstract: Experimental and theoretical methods are used to investigate the importance of the nonbonded interactions associated with the bridgehead carbon atoms (C$_{1b}$ and C$_{nb}$) of a series of bicycloalkanes and their 1-substituted methyl and carboxylic acid derivatives. Within the H$_1$–C$_{1b}$···C$_{nb}$–H$_n$ and C$_1$–C$_{1b}$···C$_{nb}$–H$_n$ moieties of these compounds, the long-range ^{1}H$_1$–^{1}H$_n$, ^{13}C$_1$–^{1}H$_n$, vicinal ^{1}H$_1$–^{13}C$_{nb}$, ^{13}C$_1$–^{13}C$_{nb}$, and interbridgehead ^{13}C$_{1b}$–^{13}C$_{nb}$ coupling constants were measured. The trends within these series of compounds are reproduced quite well by the INDO-FPT molecular orbital results; for example, the experimental (calculated) results for coupling between the bridgehead carbon atoms in bicyclo[2.2.2]octane-1-carboxylic acid and bicyclo[1.1.1]pentane-1-carboxylic acid are (+)13.2 (14.2) and (−)25.2 (−24.8) Hz, respectively; the pattern of experimental coupling constants in the series is consistent with the calculated sign change. In contrast to all of the other coupling constants in these series, contributions of nonbonded interactions to the bridgehead coupling constants are small and relatively constant for this type of coupling.

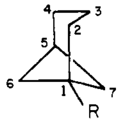
Previous papers from these laboratories[2-5] have demonstrated the importance of nonbonded interactions (NBI), which involve the bridgehead carbon atoms in the series of bicycloalkanes **1**–**5**, to the ^{13}C–^{1}H,[2] ^{13}C–^{13}C,[2,5] and ^{13}C–^{19}F[3,4] coupling constants involving the bridgehead carbons (C4 in **1**, **2**, and **4**, C5 in **3**, and C3 in **5**) and the substituent X bonded to the C1 carbon atom. All couplings measured so far increase in magnitude in the series **1** to **5**. However, depending on the number of intervening bonds and which nuclei are coupled, the magnitude of the increase is substantially greater or substantially less than would be expected on the basis of simple additivity of coupling contributions over "equivalent" two- or three-bond paths. Moreover, the long-range ^{1}H–^{19}F coupling constants in the series of compounds **1d**–**5d** range



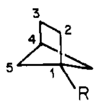
1a–d



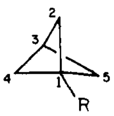
2a–d



3a–d



4a–d



5a–d

a, R = ^{1}H, ^{2}H; b, R = ^{13}CH$_3$- c, R = ^{13}CO$_2$H; d, R = ^{19}F

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Table I. Experimental Data for ^{1}H–^{1}H and ^{13}C–^{1}H Coupling Constants in the Bicycloalkanes **1a–5a** Compared with INDO-FPT Molecular Orbital Results[a]

	$J_{HH'}$[b]			J_{CH}[c]		
compd	exptl[d]	INDO-FPT	NBI[e]	exptl[d]	INDO-FPT	NBI[e]
1a	[f]	0.81	−2.65	<1[g]	0.34	−0.45
2a	1.0–1.6[h]	1.20	1.88	8.75[i]	8.57	−3.46
3a	5.4 (8)[j]	7.06	7.78	8.5 (5)[j]	10.01	−8.19
4a	6.23 (7)[j]	7.95	7.32	12.7 (5)[j]	13.76	−7.52
5a	18.2 (1)[j,k]	28.52	25.02	12.1 (1)[j]	17.50	−30.31

[a] All values in hertz. [b] Coupling between the bridgehead protons. [c] Coupling between a bridgehead carbon and a bridgehead hydrogen. [d] Values in parentheses are the uncertainties in the last figure reported. [e] Molecular orbital results obtained on subtracting the NNBI results from the values in the preceding column as described in the text and in ref 2. [f] Value too small to be detected. [g] Walter, S. R. Ph.D. Thesis, University of Arizona, 1982. [h] Ramey, K. C.; Lini, D. C.; Moriarty, R. M.; Gopal, H.; Welsh, H. G. *J. Am. Chem. Soc.* **1967**, *89*, 2401. [i] Aydin, R.; Loux, J.-P.; Günther, H. *Angew. Chem.* **1982**, *94*, 451. [j] This work. [k] A value of 18 Hz was reported by Wiberg et al.: Wiberg, K. B.; Lampman, G. M.; Ciula, R. P.; Connor, D. S.; Schertler, P.; Lavanish, J. *Tetrahedron* **1965**, *21*, 2749.

from 5.6 to 70.6 Hz. By means of modified molecular orbital (MO) calculations in which certain interactions are deleted from the computations, it was demonstrated that the magnitudes of the nonbonded interactions (NBI) increase exponentially in the series.[2,4] Moreover, it was demonstrated that the NBI are *positive* in sign for $J(^{13}C-^{19}F)$ and $J(^1H-^{19}F)$ but are *negative* in sign for ^{1}H–^{13}C and ^{13}C–^{13}C coupling constants. In the present study the experimental data in the series of compounds are extended to include the long-range ^{1}H–^{1}H coupling constants in the parent hydrocarbons **1a–5a**, the ^{13}C–^{1}H coupling constants in the series of methyl-substituted compounds **1b–5b**, and the ^{13}C–^{13}C coupling constants between the bridgehead carbon atoms in the series **1c–5c**. Experimental results in the latter series of compounds[6] were based on natural-abundance measurements via ^{13}C satellites and double quantum coherence techniques.[7]

Results and Discussion

1. Long-Range ^{1}H–^{1}H and Vicinal ^{13}C–^{1}H Coupling Constants in the Series of Bicycloalkanes 1a–5a. Entered in Table I are the experimental values of the long-range interproton coupling constants (see Experimental Section) between the protons, which are bonded to the bridgehead carbon atoms in the H_1–$C_{1b}\cdots C_{nb}$–H_n moiety. Also included are the $^{13}C_{1b}$–^1H_n coupling constants between the bridgehead carbon atom and the proton bonded to the second bridgehead carbon atom in the series of parent bicycloalkane compounds **1a–5a**. Data for the long-range ^{1}H–^{1}H coupling constants show the typical dramatic increase noted for ^{13}C–^{19}F and ^{1}H–^{19}F coupling constants as the bridgehead carbon atoms become closer together in the series.[2–5] On the other hand, the ^{13}C–^{1}H coupling constants for **1a–5a** make a big jump in going from the three four-bond paths in **1a** to increasing numbers of three-bond paths in **2a–5a**. This is similar to the pattern observed for $^{13}C_1$–$^{13}C_{nb}$ coupling constants for the C_1–$C_{1b}\cdots C_{nb}$–H_n moieties of the 1-methyl-substituted **1b–4b**[5] and 1-carboxylic acid **1c–5c**[2] compounds.

For a better understanding of these results, a series of molecular orbital calculations were performed for the Fermi contact contributions, and the results are also entered in Table I. All calculations were based on the finite perturbation theory (FPT) formulation in the INDO (intermediate neglect of differential overlap) approximation of the self-consistent-field (SCF) MO theory.[8–10] Molecular geometries were based on the electron-diffraction results,[11] with substituent geometries from the compilation of Sutton.[12] Calculations were performed on Control Data Corp. CYBER 175 or Digital Equipment Corp. DEC-10 digital computers.

Table II. Experimental Data for ^{13}C–^{1}H and ^{13}C–^{13}C Coupling Constants in the Series of 1-Methylbicycloalkanes **1b–5b** Compared with INDO-FPT Molecular Orbital Results[a]

	J_{CH}[b]			$J_{CC'}$[c]		
compd	exptl[d]	INDO-FPT	NBI[e]	exptl[d]	INDO-FPT	NBI[e]
1b	[f]	0.53	−1.45	0.31[g]	−0.17	0.03
2b	[f]	0.22	0.59	3.96[g]	3.84	−1.31
3b	3.0 (1)[h]	2.80	3.36	5.82[g]	5.36	−3.05
4b	3.2 (1)[h]	2.82	2.91	7.50[g]	5.71	−2.33
5b	11.7 (1)[h]	12.40	10.70	9.71[g]	8.95	−13.10

[a] All values in hertz. [b] Long-range ^{13}C–^{1}H coupling between the $^{13}CH_3$ and the hydrogen at the bridgehead. [c] Intercarbon coupling between the $^{13}CH_3$ and the nonbonded bridgehead carbon. [d] Values in parentheses are the uncertainties in the last figure cited. [e] Molecular orbital results obtained on subtracting the NNBI calculated results from the results in the preceding column. [f] This value was too small to be detected; probably less than 1 Hz. [g] Reference 5. [h] This study.

The calculated INDO-FPT MO results in Table I are in reasonably good agreement with the experimental data. Even though the calculated values of ^{1}H–^{1}H and ^{13}C–^{1}H coupling constants in bicyclo[1.1.1]pentane (**5a**) are substantially overestimated, the trends in the two series of coupling constants are adequately reproduced.

Because of the quite different trends in the two series of coupling constants, it was of interest to investigate the importance of the nonbonded interactions between the bridgehead carbon atoms; a modified MO procedure[2,4,13] was used wherein elements of the Fock matrices associated with the bridgehead carbon atoms were set equal to zero in each SCF cycle. These recalculated values (NNBI) provide a qualitative estimate of the importance of the nonbonded interactions (NBI). Entered in Table I are the differences $\Delta J_{HH'}$ and ΔJ_{CH} (designated NBI in Table I), which were obtained on subtracting the NNBI results from the usual INDO-FPT-MO results, $\Delta J_{NN'} = J_{NN'}(\text{INDO}) - J_{NN'}(\text{NNBI})$. Clearly, the very large magnitudes of the NBI indicate the quite different behavior for the two types of coupling; in both types of coupling constants the NBI became increasingly large in magnitude in the series **1a–5a** corresponding to the decreased distance between the bridgehead carbon atoms. However, the signs of the NBI are opposite for the two types of coupling. As a consequence, the long-range H–H coupling constants are almost entirely due to the NBI, whereas the J_{CH} result from a cancellation between the negative NBI and the positive vicinal contributions, i.e., no vicinal paths in **1a**, one in **2a**, two in both **3a** and **4a**, and three in **5a**. As discussed in a previous paper[4] in this series, the sign of the NBI for coupling over *n* formal bonds in the bicycloalkanes follows those for the type of coupling expected over *n* − 1 bonds in the corresponding saturated hydrocarbon. Moreover, the bicyclo[2.2.2]octane compounds are unique in the series because one more formal bond is involved.[4]

2. Long-Range ^{1}H–^{13}C and Vicinal ^{13}C–^{13}C Coupling Constants in the 1-Methylbicycloalkanes 1b–5b. Entered in Table II are the experimental results for long-range ^{1}H–$^{13}C_1$ (see Experimental Section) and the vicinal $^{13}C_1$–$^{13}C_{nb}$ coupling constants C_1–$C_{1b}\cdots C_{nb}$–H_n moiety of **1b–5b**.[5] The trends in the experimental data closely parallel those for ^{1}H–^{1}H and ^{1}H–^{13}C coupling constants in Table I. Furthermore, the INDO-FPT-MO results, which are also included in Table II, are in good agreement with the experimental data. The nonbonded contributions, which are designated NBI in Table II, follow a similar pattern in terms of increasing magnitudes and different signs for the two types of nonbonded interactions.

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Table III. Experimental Data for ^{13}C–^{13}C Coupling Constants between the Bridgehead Carbons in the Series of Bicycloalkane-1-carboxylic Acids **1c**–**5c** Compared with the INDO-FPT Molecular Orbital Results[a]

compd	exptl[b]	INDO-FPT	NBI[c]
1c	(+)13.21 (5)	14.24	−1.02
2c	(+)7.38 (9)	2.50	−1.89
3c	(−)8.74 (9)	−9.63	−1.02
4c	(−)4.48 (9)	−3.90	−0.38
5c	(−)25.16 (9)	−24.83[d]	−0.96

[a] All values in hertz. [b] Values in parentheses are signs assumed on the basis of trends within the series and estimated errors in the last figure reported. [c] Calculated contributions arising from nonbonded interactions. These were obtained by subtracting the NNBI results from the INDO-FPT-MO results. [d] Using a somewhat different geometry, a value of −17.6 Hz was calculated by Schulman and Newton: Schulman, J. M.; Newton, M. D. *J. Am. Chem. Soc.* **1974**, *96*, 6295.

3. ^{13}C–^{13}C Coupling between the Bridgehead Carbon Atoms in the Series of Bicycloalkane-1-carboxylic Acids 1c–5c. Entered in Table III are the experimentally determined and the calculated INDO-FPT-MO values for intercarbon coupling constants between the bridgehead carbon atoms C_{1b} and C_{nb} in the $C_1-C_{1b}\cdots C_{nb}-H_n$ moiety of bicycloalkane-1-carboxylic acids **1c**–**5c**. Experimental ^{13}C–^{13}C coupling constants were measured in natural abundance from the ^{13}C satellite spectra and/or by double quantum coherence techniques.[7] The experimental details are reported in a separate study[6] which emphasizes the substituent dependencies of directly bonded and vicinal ^{13}C–^{13}C coupling constants in a number of 1-substituted bicyclo[2.2.2]octanes as well as the series of bicycloalkane-1-carboxylic acids.

The pattern of the experimental coupling constants and the agreement of the calculated MO results in Table III provide strong support for a change of sign of the bridgehead ^{13}C–^{13}C coupling constants in progressing from the bicyclo[2.2.1]heptane-1-carboxylic acid (**2c**) to either bicyclo[3.1.1]heptane-1-carboxylic acid (**3c**) or bicyclo[2.1.1]hexane-1-carboxylic acid (**4c**).[6] These results are consistent with contributions of 4–5 Hz along the vicinal paths, contributions of −1 to −4 Hz along the two bond paths, and negligible coupling along the four-bond paths. Except for the calculated value for the ^{13}C–^{13}C coupling constant in **2c**, the agreement with experimental values is remarkable because the INDO-FPT method typically gives very poor agreement for geminal ^{1}H–^{1}H, ^{1}H–^{13}C, and ^{13}C–^{13}C coupling constants. For example, the experimental and calculated values of $^1J_{CC'}$ in **5c** are (−)25.2 Hz and −24.8 Hz, respectively. Also included in the table are the calculated values of the nonbonded contributions to the coupling between the bridgehead carbons. The very small magnitude and the essential constancy of the values of the nonbonded contributions (NBI) in Table III are surprising, as all previous calculated and experimental data obtained in these laboratories have indicated an exponential increase for the NBI in proceeding from the bicyclo[2.2.2]octane to the bicyclo[1.1.1]pentane. This is a quite unexpected result, and an alternative scheme of delineating coupling pathways[14] would be of interest. If the z axis is taken along the $C_{1b}\cdots C_{3b}$ internuclear axis in **5**, interactions between the $2p_z$ and $2p_y$ atomic orbitals on the bridgehead carbons make negligible contributions to the vicinal and long-range couplings. However, elimination of only the 2s and $2p_z$ interactions leads to an NBI of +1.9 Hz for $J(^{13}C_{1b}-^{13}C_{3b})$ in **5c**. This suggests that some cancellation is taking place in this procedure, but at least qualitatively, the nonbonded interactions are small for this type of coupling.

Conclusions

As noted in previous studies the nonbonded interaction associated with long-range and vicinal coupling constants follows an exponential decrease in magnitude with bridgehead separation. Some interesting trends occur for the coupling between the bridgehead carbon atoms in the series of bicycloalkane-1-carboxylic acids. There is almost certainly a change in sign as one proceeds from a positive coupling over three equivalent vicinal paths (+13.2 Hz) in the bicyclo[2.2.2]octane compound to one of three equivalent geminal paths for which the experimental magnitude of 25.2 Hz is probably negative and in very good agreement with the INDO-FPT-MO value of −24.8 Hz. In contrast to all of the other types of coupling investigated in these laboratories, the NNBI procedure suggests small, essentially constant contributions for this type of coupling.

Experimental Section

Spectra. Proton and ^{13}C NMR spectra were recorded at 250.13 and 62.90 MHz, respectively, on a Bruker Instruments WM-250 FT-NMR spectrometer. Unless noted otherwise, chloroform-*d* was used as solvent and provided the internal lock. Proton NMR spectra were measured in sealed 5-mm sample tubes, which had been degassed by the freeze–pump–thaw method, and ^{13}C NMR spectra were obtained in 10-mm sample tubes. Digital resolution, as determined by spectral widths and computer memory size, was better than the estimated errors.

The long-range H–H coupling constants in bicyclo[2.1.1]hexane (**4a**) and bicyclo[1.1.1]pentane (**5a**) were obtained from the ^{13}C satellite spectra with ^{1}H-{^{1}H} homodecoupling. The vicinal coupling constant ^{13}C–^{1}H of **4a** was also implicit in the satellite spectra and is entered in Table I. The long-range coupling constant between the proton at the bridgehead of bicyclo[3.1.1]heptane (**3a**) was estimated from the value of $^4J_{HD}$ in the 1-deuterio derivative. Decoupling of the six protons of the parent compound at δ 1.79 gave a triplet for the two bridgehead protons. In the 1-deuteriobicyclo[3.1.1]heptane each of these lines was further split into 1:1:1 triplets by the deuterium. The vicinal ^{13}C–^{1}H coupling constant of 8.5 Hz in **3a** was inferred from the ^{13}C–^{2}H coupling constant with multiplication by the ratio of the magnetogyric ratio of deuterium to hydrogen (6.214).

The long-range ^{13}C–^{1}H coupling constants between the methyl carbon and the bridgehead hydrogens of the 1-methylbicyclo[3.1.1]heptane (**3b**), 1-methylbicyclo[2.1.1]hexane (**4b**), and 1-methylbicyclo[1.1.1]pentane (**5b**) were measured from the additional splitting of the ^{1}H resonances in the ^{13}C-labeled compounds with homonuclear ^{1}H-{^{1}H} decoupling.

The proton NMR spectra of **1a** and **2a** have been discussed primarily in terms of substituted compounds,[15,16] whereas ^{1}H chemical shift and some coupling constant data have been reported for **3a**,[17] **4a**,[17,18] **5a**,[17,19] and **1b**–**5b**.[20]

Carbon-13 chemical shift data have been reported for the 1-substituted bicyclo[2.2.2]octanes **1a**–**d**,[2,5,21] bicyclo[2.2.1]heptanes **2a**–**d**,[3,22] bicyclo[3.1.1]heptanes **3a**–**3d**,[3,5,6,23] bicyclo[2.1.1]hexanes **4a**–**d**,[2,3,24] and bicyclo[1.1.1]pentanes **1a**,[23] **1b**,[5] **1c**,[6] and **1d**.[3]

Intercarbon coupling constants in the bicycloalkane-1-carboxylic acids **1c**–**4c** were measured in natural abundance from the ^{13}C satellite and double quantum coherence spectra.[6]

Synthesis. 1-Methylbicyclo[2.2.2]octane (**1a**), -[2.2.1]heptane (**2a**), -[3.1.1]heptane (**3a**), -[2.1.1]hexane (**4a**), and -[1.1.1]pentane (**5a**) were prepared as described.[25]

1-Deuteriobicyclo[2.1.1]hexane (4a). A mixture of 1-bromobicyclo[2.1.1]hexane[26] (130 mg, 0.8 mmol), tri-*n*-butyltin deuteride (260 mg, 0.9 mmol), and *N*,*N*′-azabis(isobutyronitrile) (5 mg) in a stoppered Pyrex test tube was irradiated with a 450 W Hanovia mercury lamp for 6 h. The product was removed under reduced pressure and collected at −80 °C (60 mg, 90%).

5-Deuteriobicyclo[3.1.1]heptane-1-carboxylic Acid (3a). A mixture of methyl 5-bromobicyclo[3.1.1]heptane-1-carboxylate[20] (0.75 g, 3.2 mmol), tri-*n*-butyltin deuteride (1.0 g, 3.4 mmol), and *N*,*N*′-azabis(isobutyro-

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nitrile) (10 mg) was irradiated as described above. The mixture was cooled in ice and treated with bromine until the latter was in slight excess, which was then removed by washing with aqueous sodium metabisulfite. After being diluted with pentane (5 mL) the mixture was chromatographed on silica gel. Elution with pentane removed the tin compounds, and the deuterated ester (0.45 g, 90%) was obtained essentially pure upon elution with ether/pentane (1:4): ^{1}H NMR δ (CCl_4) 3.63 (s, 3 H), 2.42–2.12 (m, 2 H), 2.12–1.67 (m, 6 H), 1.67–1.43 (m, 2 H). Hydrolysis of the ester to 5-deuteriobicyclo[3.1.1]heptane-1-carboxylic acid (0.35 g, 85%) was effected by methanolic potassium hydroxide at 50 °C for 2 h. The acid had spectral data in accord with those observed for the protio isomer.[20]

1-Deuteriobicyclo[3.1.1]heptane (3a). 5-Deuteriobicyclo[3.1.1]heptane-1-carboxylic acid (0.34 g, 2.5 mmol) and freshly distilled thionyl chloride (2.5 mL) were heated under reflux for 2 h. Excess reagent was removed in vacuo and the crude acid chloride was dissolved in a mixture of dichloromethane (1 mL) and anhydrous pyridine (0.5 mL) and cooled in an ice bath. *tert*-Butyl hydroperoxide (1.5 mL, 4.3 mmol) in 1,2-dichloroethane was added dropwise to the stirred mixture maintained at 0 °C. After 3 h the contents were poured on to ice–water and extracted with dichloromethane. The combined organic fractions were washed with cold, dilute sulfuric acid, water, and finally cold aqueous sodium carbonate, before being dried ($MgSO_4$). Filtration through Florisil followed by evaporation of solvent yielded *tert*-butyl 5-deuteriobicyclo[3.1.1]heptane-1-peroxycarboxylate (0.42 g, 79%); ^{1}H NMR δ (CCl_4) 2.50–2.13 (m, 2 H), 2.13–1.88 (m, 6 H), 1.88–1.47 (m, 2 H), 1.27 (s, 9 H). The peroxy ester was added to triisopropylbenzene (2 mL) and the mixture heated at 110 °C for 2 h. Volatile products were swept into a cold trap by a gentle stream of nitrogen, and the byproducts contaminating the hydrocarbon were removed by washing with water. 1-Deuteriobicyclo[3.1.1]heptane (0.11 g, 58%) had physical properties consistent with those of the unlabeled hydrocarbon.[17]

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Registry No. **1a** (unlabeled), 280-33-1; **1b** (unlabeled), 19074-26-1; **1c** (unlabeled), 699-55-8; **2a** (unlabeled), 279-23-2; **2b** (unlabeled), 10052-18-3; **2c** (unlabeled), 18720-30-4; **3a** (unlabeled), 286-34-0; **3a** (labeled), 91239-73-5; **3b** (unlabeled), 87969-60-6; **3c** (unlabeled), 91239-72-4; **4a** (unlabeled), 285-86-9; **4a** (labeled), 91239-74-6; **4b** (unlabeled), 17065-20-2; **4c** (unlabeled), 64725-77-5; **5a** (unlabeled), 311-75-1; **5b** (unlabeled), 10555-48-3; **5c** (unlabeled), 22287-28-1; 5-deuteriobicyclo[3.1.1]heptane-1-carboxylic acid, 91239-75-7; 1-bromobicyclo[2.1.1]hexane, 77379-00-1; methyl 5-bromobicyclo[3.1.1]heptane-1-carboxylate, 91239-76-8; methyl 5-deuteriobicyclo[3.1.1]heptane-1-carboxylate, 91239-77-9; 5-deuteriobicyclo[3.1.1]heptane-1-carbonyl chloride, 91239-78-0; *tert*-butyl hydroperoxide, 75-91-2; *tert*-butyl 5-deuteriobicyclo[3.1.1]heptane-1-peroxycarboxylate, 91265-45-1.

Carbon Kinetic Isotope Effects on the Hydration of Carbon Dioxide and the Dehydration of Bicarbonate Ion

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Abstract: ^{13}C kinetic isotope effects on the hydration of CO_2 and the dehydration of HCO_3^- in aqueous solution have been measured by rapid removal of the product and conversion to an isotopically stable form, followed by isotope-ratio analysis. The isotope effect on hydration is $k^{12}/k^{13} = 1.0069 \pm 0.0003$ at 24 °C. The isotope effect on dehydration is 1.0147 ± 0.0007. The ratio of these two values gives an equilibrium isotope effect of $K^{12}/K^{13} = 1.0077$, in good agreement with previously measured values. The small magnitudes of the kinetic isotope effects indicate that the transition state for conversion of HCO_3^- to CO_2 is very similar to that of HCO_3^-. This information together with previously measured solvent isotope effects indicates that the mechanism of HCO_3^- dehydration probably involves general-acid-catalyzed donation of a proton from H_3O^+ to the departing oxygen, rather than unimolecular decomposition of the zwitterion $H_2O^+{-}CO_2^-$ in the rate-determining step.

The isotopic chemistry of processes involving carbon dioxide is important in connection with studies in chemistry, biochemistry, geochemistry, and plant physiology. Equilibrium isotope fractionations have been measured for the liquefication of CO_2,[1] the dissolution of gaseous CO_2 in water,[2,3] the conversion of CO_2 into HCO_3^- (ref 4), and the incorporation of CO_2 into the carboxyl groups of organic compounds.[5] Kinetic isotope fractionations have been reported for chemical decarboxylations,[6] enzymatic decarboxylations,[7] enzymatic carboxylations,[8] and diffusion processes.[3] However, isotope effects have not yet been measured for one of the very simplest and potentially most important reactions involving CO_2, namely, the hydration of CO_2 and its reverse, the dehydration of HCO_3^-.

Carbon isotope fractionation accompanying the hydration of CO_2 is potentially of importance in plants, particularly in C4 plants and in CAM plants during nocturnal CO_2 fixation, wherein atmospheric CO_2 must be converted to HCO_3^- prior to fixation by phosphoenolpyruvate (PEP) carboxylase.[9] Although it is generally assumed that carbonic anhydrase levels in plants are high and that

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