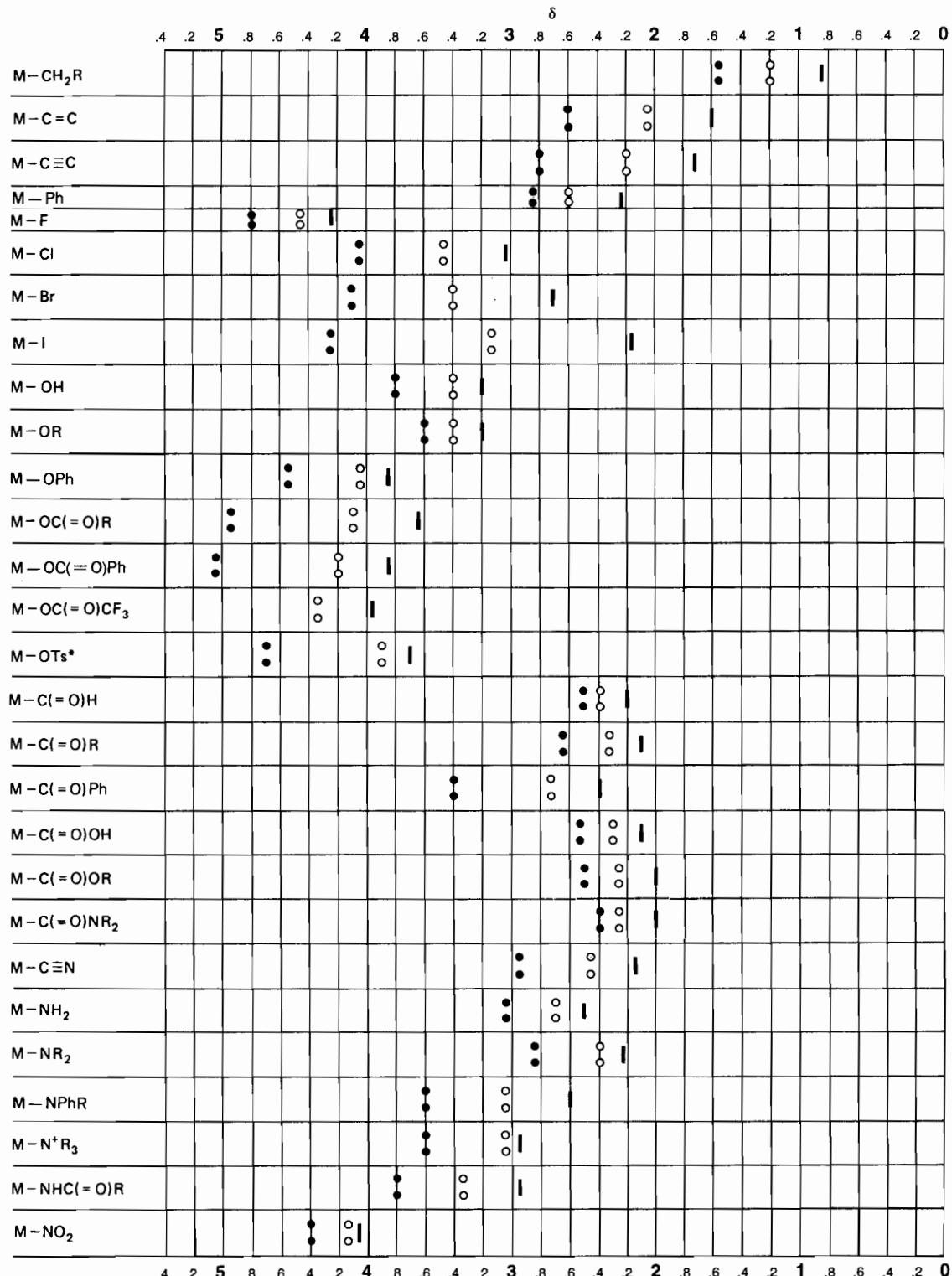
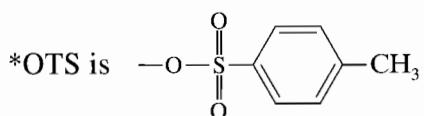
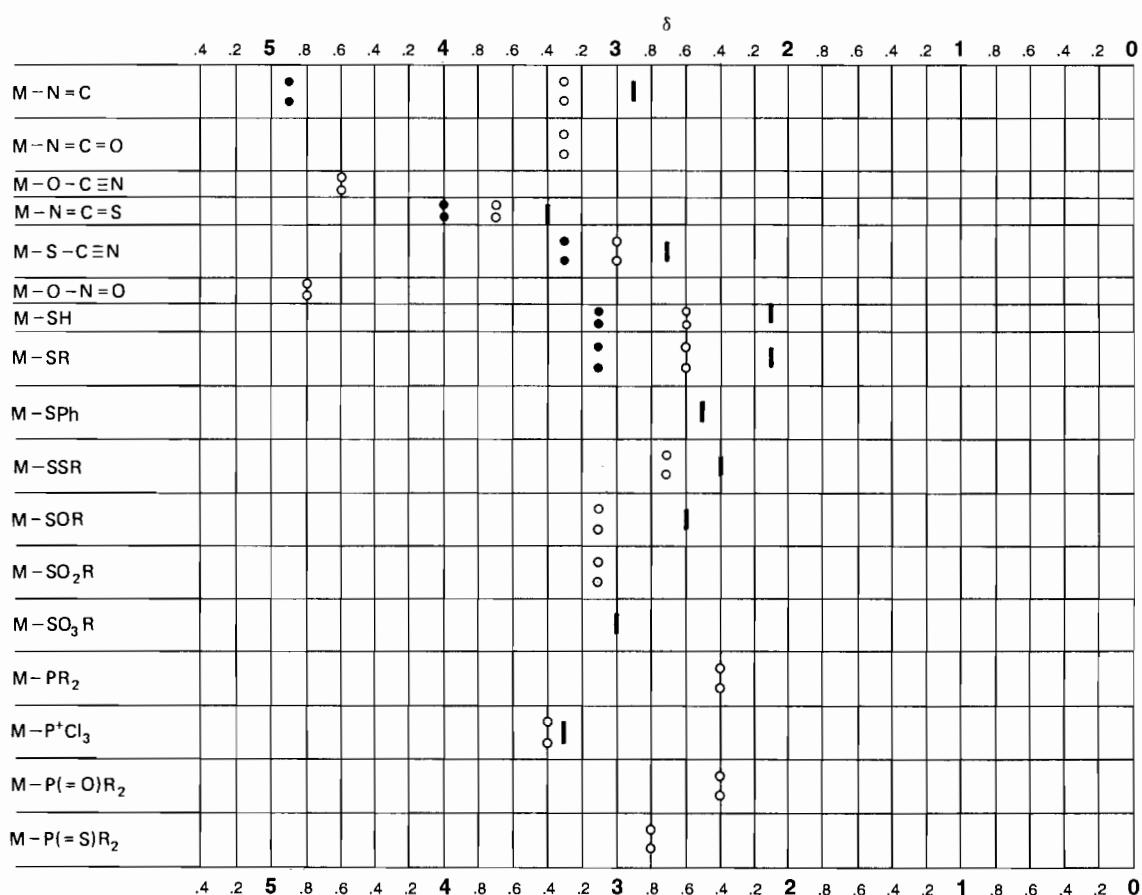


**CHART A.1 CHEMICAL SHIFTS OF PROTONS ON A CARBON
ATOM ADJACENT (α POSITION) TO A FUNCTIONAL GROUP**
APPENDIX A IN ALIPHATIC COMPOUNDS (M—Y)

- M = methyl
- M = methylene
- M = methine

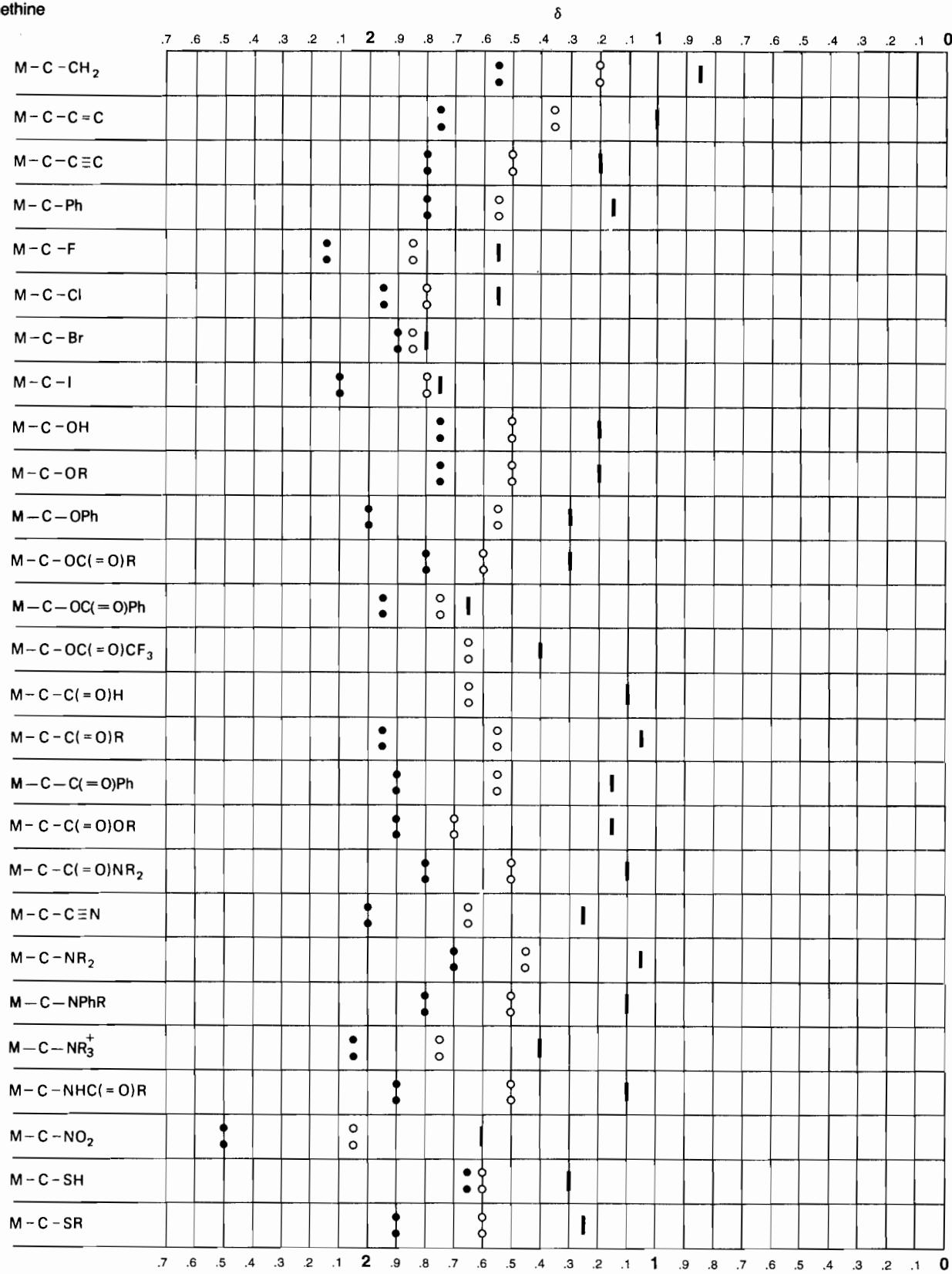


APPENDIX A (Continued)

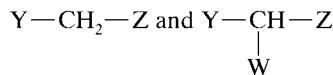
APPENDIX A

CHART A.2 CHEMICAL SHIFTS OF PROTONS ON A CARBON ATOM ONCE REMOVED (β POSITION) FROM A FUNCTIONAL GROUP IN ALIPHATIC COMPOUNDS (M—C—Y)

- M = methyl
- M = methylene
- M = methine



EFFECT ON CHEMICAL SHIFTS BY TWO OR THREE DIRECTLY ATTACHED FUNCTIONAL GROUPS



The chemical shift of a methylene group attached to two functional groups can be calculated by means of the substituent constants (σ values) in Table B.1. Shoolery's rule* states that the sum of the constants for the attached functional groups is added to δ 0.23, the chemical shift for CH_4 :

$$\delta(Y-\text{CH}_2-Z) = 0.23 + \sigma_Y + \sigma_Z$$

The chemical shift for the methylene protons, of $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$, for example, is calculated from the σ values in Table B.1.

$$\begin{array}{r} 0.23 \\ \sigma_{\text{Ph}} = 1.85 \\ \sigma_{\text{Br}} = 2.33 \\ \hline \delta = 4.41 \text{ Found, } \delta 4.43 \end{array}$$

Shoolery's original constants have been revised and extended in Table B.1. The observed and calculated chemical shifts for 62% of the samples tested were within ± 0.2 ppm, 92% within ± 0.3 ppm, 96% within 0.4 ppm, and 99% within ± 0.5 ppm.[†] Table B.1 contains substituent constants (Friedrich and Runkle, 1984) for the more common functional

* Shoolery, J.N. (1959). *Varian Technical Information Bulletin*, Vol 2, No. 3. Palo Alto, CA: Varian Associates.

[†] Data from Friedrich, E.C., and Runkle, K.G. (1984). *J. Chem. Educ.* **61**, 830; (1986) **63**, 127.

TABLE B.1 Substituent Constants for Alkyl Methylenes (and Methyl) Protons.

| Y or Z | Substituent Constants (σ) | Y or Z | Substituent Constants (σ) |
|------------------|------------------------------------|-----------------------------------------|------------------------------------|
| —H | 0.34 | —OC(=O)R | 3.01 |
| —CH ₃ | 0.68 | —OC(=O)Ph | 3.27 |
| —C—C | 1.32 | —C(=O)R | 1.50 |
| —C≡C | 1.44 | —C(=O)Ph | 1.90 |
| —Ph | 1.83 | —C(=O)OR | 1.46 |
| —CF ₂ | 1.12 | —C(=O)NR ₂ (H ₂) | 1.47 |
| —CF ₃ | 1.14 | —C≡N | 1.59 |
| —F | 3.30 | —NR ₂ (H ₂) | 1.57 |
| —Cl | 2.53 | —NHPh | 2.04 |
| —Br | 2.33 | —NHC(=O)R | 2.27 |
| —I | 2.19 | —N ₃ | 1.97 |
| —OH | 2.56 | —NO ₂ | 3.36 |
| —OR | 2.36 | —SR(H) | 1.64 |
| —OPh | 2.94 | —OSO ₂ R | 3.13 |

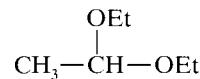
groups. Note that chemical shifts of methyl protons can be calculated by using the constant for H (0.34). For example $\text{H}-\text{CH}_2-\text{Br}$ is equivalent to CH_3Br .

Tables B.2a, B.2b, and B.2c: Chemical Shift Correlations for Methine Protons

Table B.2a gives the substituent constants* to be used with the formulation

$$\delta \text{CHXYZ} = 2.50 + \sigma_X + \sigma_Y + \sigma_Z$$

which is satisfactory if at least two of the substituents are electron-withdrawing groups. In other words, only a single substituent may be an alkyl group (R). Within these limits, the standard error of estimate is 0.20 ppm. For example, the chemical shift of the methine proton in



is calculated from Table B.2a as follows:

$$\delta = 2.50 + 1.14 + 1.14 + 0.00 = 4.78$$

The found value is 4.72.

Tables B.2b and B.2c are used jointly for methine protons that are substituted by at least two alkyl groups

* Bell, H.M., Bowles, D.B. and Senese, F. (1981). *Org. Magn. Reson.*, **16**, 285. With permission.

TABLE B.2a Substituent Constants for Methine Protons.

| Group | (σ) |
|-------------------------------|--------------|
| —F | 1.59 |
| —Cl | 1.56 |
| —Br | 1.53 |
| —NO ₂ | 1.84 |
| —NH ₂ | 0.64 |
| —NH ₃ ⁺ | 1.34 |
| —NHCOR | 1.80 |
| —OH, —OR | 1.14 |
| —OAr | 1.79 |
| —OCOR | 2.07 |
| —Ar | 0.99 |
| —C=C | 0.46 |
| —C≡C | 0.79 |
| —C≡N | 0.66 |
| —COR, —COOR, —COOH | 0.47 |
| —CONH ₂ | 0.60 |
| —COAr | 1.22 |
| —SH, —SR | 0.61 |
| —SO ₂ R | 0.94 |
| —R | 0 |

TABLE B.2b Observed Methine Proton Chemical Shifts of Isopropyl Derivatives.

| (CH ₃) ₂ CHZ | | (CH ₃) ₂ CHZ | |
|-----------------------------------------|----------------|--------------------------------------|----------------|
| Z | δ (ppm) obs | Z | δ (ppm) obs |
| H | 1.33 | HO | 3.94 |
| H ₃ C | 1.56 | RO | 3.55 |
| R | 1.50 | C ₆ H ₅ O | 4.51 |
| XCH ₂ | 1.85 | R(H)C(=O)O | 4.94 |
| R(H)C(=O) | 2.54 | C ₆ H ₅ C(=O)O | 5.22 |
| C ₆ H ₅ C(=O) | 3.58 | F ₃ CC(=O)O | 5.20 |
| R(H)OC(=O) | 2.52 | ArSO ₂ O | 4.70 |
| R ₂ (H ₂)NC(=O) | 2.44 | | |
| C ₆ H ₅ | 2.89 | R(H)S | 3.16 |
| R ₂ (H ₂)C=CR(H) | 2.62 | RSS | 2.63 |
| R(H)C≡C | 2.59 | | |
| N≡C | 2.67 | F | 4.50 |
| | | Cl | 4.14 |
| R ₂ (H ₂)N | 3.07 | Br | 4.21 |
| R(H)C(=O)NH | 4.01 | I | 4.24 |
| O ₂ N | 4.67 | | |

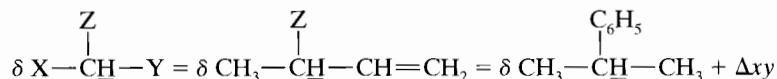
(or other groups of low polarity). Friedrich and Runkle proposed the relationship

$$\delta_{\text{CHXYZ}} = \delta_{(\text{CH}_3)_2\text{CHZ}} = \Delta xy$$

in which the X and Y substituents are alkyl groups or other groups of low polarity. The Z substituent covers a range of polarities. Δxy is a correction factor. The relationship states that the chemical shift of a methine proton with at least two low-polarity groups is equivalent to the chemical shift of an isopropyl methine proton plus correction factor.

The substituent constants for a Z substituent on an isopropyl methine proton are given in Table B.2b. The Δxy correction factors are given in Table B.2c.

The following example illustrates the joint use of Tables B.2b and B.2c, with CH₃, CH=CH₂, and C₆H₅ as substituents. The most polar substituent is always designated Z.

**TABLE B.2c** Correction Factors for Methine Substituents of Low Polarity.

| Open-Chain Methine Proton Systems | Δxy | Cyclic Methine Proton Systems | Δxy |
|-----------------------------------------|-------------|----------------------------------------|----------------|
| | 0.00 | | -1.0 |
| | -0.20 | | +0.40 |
| | -0.40 | | +0.20 |
| | +0.20 | | monosub. -0.20 |
| | +0.40 | | axial H +0.25 |
| | +1.15 | | 0.00 |
| | +0.90 | | 0.00 |

From Table B.2b, $\delta = 2.89$ for $\text{CH}_3-\overset{\text{C}_6\text{H}_5}{\underset{|}{\text{CH}}}-\text{CH}_3$.

From Table B.2c, $\Delta xy = 0.00$ for CH₃. $\Delta xy = 0.40$ for CH=CH₂.

Therefore, $\delta \text{CH}_3-\overset{\text{C}_6\text{H}_5}{\underset{|}{\text{CH}}}-\text{CH}=\text{CH}_2 = 2.89 + 0.00 + 0.40 = 3.29$ (Found: $\delta = 3.44$).

APPENDIX C CHEMICAL SHIFTS IN ALICYCLIC AND HETEROCYCLIC RINGS**TABLE C.1** Chemical Shifts in Alicyclic Rings.

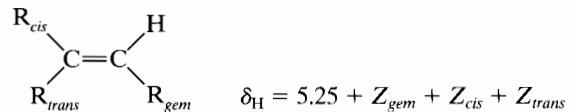
| | | | | | | | | | | | |
|--|------|--|-----------|--|--------------|--|--------------|--|------|--|---------------------|
| | 0.22 | | 1.96 | | 1.51 | | 1.44 | | 1.54 | | 1.78 |
| | 1.65 | | 1.96 3.03 | | 2.06 2.02 | | 2.22 ~1.8 | | 2.38 | | 2.30 ~1.52 ~1.94 |

TABLE C.2 Chemical Shifts in Heterocyclic Rings.

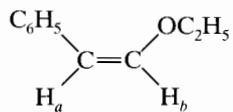
| | | | | | | | |
|--|----------------------|--|-------------------|--|------------------------|--|--------------------------------|
| | 2.54 | | 2.72 4.73 | | 1.85 3.75 | | 1.51 3.52 |
| | 1.62 H 0.03 | | 2.23 2.38 3.54 | | 1.59 2.75 H 2.01 | | 1.50 1.50 2.74 H 1.84 |
| | 2.27 | | 3.17 3.43 | | 1.93 2.82 | | 2.23 3.00 |
| | 3.9–4.1 4.75–4.90 | | 5.90 | | 1.68 4.70 3.80 | | 1.90 3.70 |
| | 3.01 | | 2.08 4.38 2.31 | | 1.62 2.27 4.06 | | |

CHEMICAL SHIFTS IN UNSATURATED APPENDIX D AND AROMATIC SYSTEMS

(See Table D.1)



For example, the chemical shifts of the alkene protons in



are calculated:

| | | | | |
|--|----------------|------------------------------------------------|-------|-------|
| | H _a | C ₆ H ₅ _{gem} | 1.35 | 5.25 |
| | | OR _{trans} | -1.28 | 0.07 |
| | | | 0.07 | 8.532 |
| | H _b | OR _{gem} | 1.18 | 5.25 |
| | | C ₆ H ₅ _{trans} | -0.10 | 1.08 |
| | | | 1.08 | 8.633 |

TABLE D.1 Substituent Constants (*Z*) for Chemical Shifts of Substituted Ethylenes.

| Substituent R | Z | | | Substituent R | Z | | |
|------------------------------------------|------|-------|-------|---------------|------|-------|-------|
| | gem | cis | trans | | gem | cis | trans |
| -H | 0 | 0 | 0 | | 1.03 | 0.97 | 1.21 |
| -Alkyl | 0.44 | -0.26 | -0.29 | | | | |
| -Alkyl-ring ^a | 0.71 | -0.33 | -0.30 | | | | |
| -CH ₂ O, -CH ₂ I | 0.67 | -0.02 | -0.07 | | 1.37 | 0.93 | 0.35 |
| -CH ₂ S | 0.53 | -0.15 | -0.15 | | 1.10 | 1.41 | 0.99 |
| -CH ₂ Cl, -CH ₂ Br | 0.72 | 0.12 | 0.07 | | 0.50 | 0.35 | 0.10 |
| -CH ₂ N | 0.66 | -0.05 | -0.23 | | 0.23 | 0.78 | 0.58 |
| -C≡C | 0.98 | -0.04 | -0.21 | | 1.18 | -1.06 | -1.28 |
| -C≡N | 1.26 | 0.08 | -0.01 | | 1.14 | -0.65 | -1.05 |
| -C=C conj ^b | 1.10 | 1.13 | 0.81 | | 2.09 | -0.40 | -0.67 |
| -C=O | 1.06 | 1.01 | 0.95 | | 1.35 | 0.37 | -0.10 |
| -C=O conj ^b | 1.00 | 1.35 | 0.74 | | 1.00 | 0.19 | 0.03 |
| -COOH | | | | | 1.04 | 0.40 | 0.55 |
| -COOH conj ^b | 0.69 | 0.97 | 0.39 | | 0.69 | -1.19 | -1.31 |
| -COOR | 0.84 | 1.15 | 0.56 | | 2.30 | -0.73 | -0.81 |
| -COOR conj ^b | 0.68 | 1.02 | 0.33 | | 1.00 | -0.24 | -0.04 |
| | | | | | 1.58 | 1.15 | 0.95 |

^a Alkyl ring indicates that the double bond is part of the ring

^b The Z factor for the conjugated substituent is used when either the substituent or the double bond is further conjugated with other groups.

Source: Pascual C., Meier, J., and Simon, W. (1966) *Helv. Chim. Acta*, **49**, 164.

TABLE D.2 Chemical Shifts of Miscellaneous Alkenes

| $\text{R} = \text{C}(=\text{O})\text{OCH}_3$ | $\text{R} = \text{C}(=\text{O})\text{CH}_3$ | $\text{R} = \text{OC}(=\text{O})\text{CH}_3$ |
|----------------------------------------------|---------------------------------------------|----------------------------------------------|
| | | |
| | | |
| | | |
| | | |
| | | |

TABLE D.3 Chemical Shifts of Alkyne Protons

| | | | |
|---------------------------------------------------|-----------|-------------------------------------------------|-----------|
| $\text{HC}\equiv\text{CR}$ | 1.73–1.88 | $\text{HC}\equiv\text{C}-\text{COH}$ | 2.23 |
| $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CR}$ | 1.95 | $\text{HC}\equiv\text{CH}$ | 1.80 |
| $\text{HC}\equiv\text{C}-\text{Ph}$ | 2.71–3.37 | $\text{HC}\equiv\text{C}-\text{CH}=\text{CR}_2$ | 2.60–3.10 |

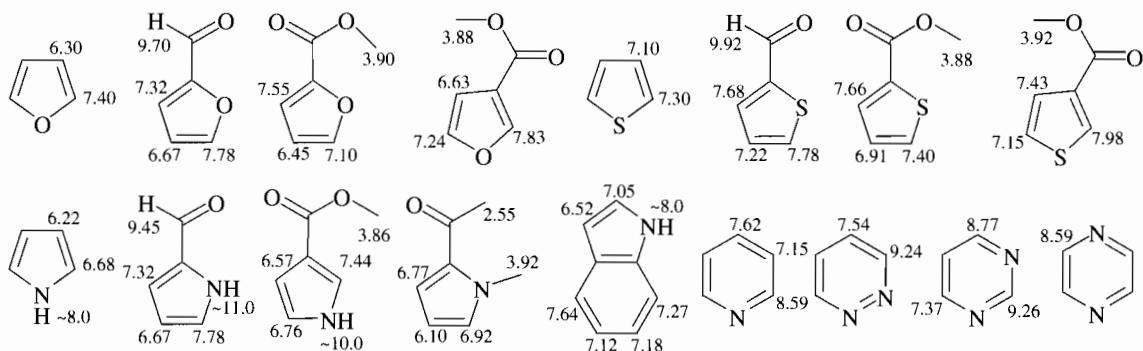
TABLE D.4 Chemical Shifts of Protons on Fused Aromatic Rings

| | | | | |
|--|--|--|--|--|
| | | | | |
|--|--|--|--|--|

CHEMICAL SHIFTS OF PROTONS ON MONOSUBSTITUTED BENZENE RINGS

| | 9 | .8 | .6 | .4 | .2 | 8 | .8 | .6 | .4 | .2 | 7 | .8 | .6 | .4 | .2 | 6 | |
|---------------------------------------------|---|----|----|----|----|---|----|----|----|----|---|----|----|----|----|----------|--|
| | | | | | | | | | | | | | | | | δ | |
| Benzene ^a | | | | | | | | | : | | | | | | | | |
| CH ₃ (omp) | | | | | | | | | : | | | | | | | | |
| CH ₃ CH ₂ (omp) | | | | | | | | | : | | | | | | | | |
| (CH ₃) ₂ CH (omp) | | | | | | | | | : | | | | | | | | |
| (CH ₃) ₃ C o,m,p | | | | | | | | | : | : | : | | | | | | |
| C=CH ₂ (omp) | | | | | | | | | : | | | | | | | | |
| C≡CH o, (mp) | | | | | | | | | : | : | | | | | | | |
| Phenyl o, m, p | | | | | | | | | : | : | : | | | | | | |
| CF ₃ (omp) | | | | | | | | | : | | | | | | | | |
| CH ₂ Cl (omp) | | | | | | | | | : | | | | | | | | |
| CHCl ₂ (omp) | | | | | | | | | : | | | | | | | | |
| CCl ₃ o, (mp) | | | | | | | : | | : | | | | | | | | |
| CH ₂ OH (omp) | | | | | | | | | | : | | | | | | | |
| CH ₂ OR (omp) | | | | | | | | | | : | | | | | | | |
| CH ₂ OC(=O)CH ₃ (omp) | | | | | | | | | | : | | | | | | | |
| CH ₂ NH ₂ (omp) | | | | | | | | | | : | | | | | | | |
| F m,p,o | | | | | | | | | | : | : | : | | | | | |
| Cl (omp) | | | | | | | | | | : | | | | | | | |
| Br o, (pm) | | | | | | | | | : | : | | | | | | | |
| I o,p,m | | | | | | | | : | | : | : | : | | | | | |
| OH m,p,o | | | | | | | | | | | : | : | : | : | | | |
| OR m, (op) | | | | | | | | | | : | | : | | | | | |
| OC(=O)CH ₃ m,p,o | | | | | | | | | | : | : | : | | | | | |
| OTs ^b (mp), o | | | | | | | | | | | : | : | | | | | |
| CH(=O)o,p,m | | | | | | | | : | | : | : | | | | | | |
| C(=O)CH ₃ o, (mp) | | | | | | | | : | | : | | | | | | | |
| C(=O)OH o, p, m | | | | | | | | : | | : | : | | | | | | |
| C(=O)OR o, p, m | | | | | | | : | | | : | : | | | | | | |
| C(=O)Cl o, p, m | | | | | | | : | | | : | : | | | | | | |
| C≡N (omp) | | | | | | | | | | : | | | | | | | |
| NH ₂ m,p,o | | | | | | | | | | | : | : | : | | | | |
| N(CH ₃) ₂ m(op) | | | | | | | | | | | : | | : | | | | |
| NHC(=O)R o,m,p | | | | | | | | | : | | : | : | | | | | |
| NH ₃ ⁺ o (mp) | | | | | | | | | : | : | | | | | | | |
| NO ₂ o,p,m | | | | | | | : | | | : | : | | | | | | |
| SR (omp) | | | | | | | | | | | : | | | | | | |
| N=C=O (omp) | | | | | | | | | | | : | | | | | | |

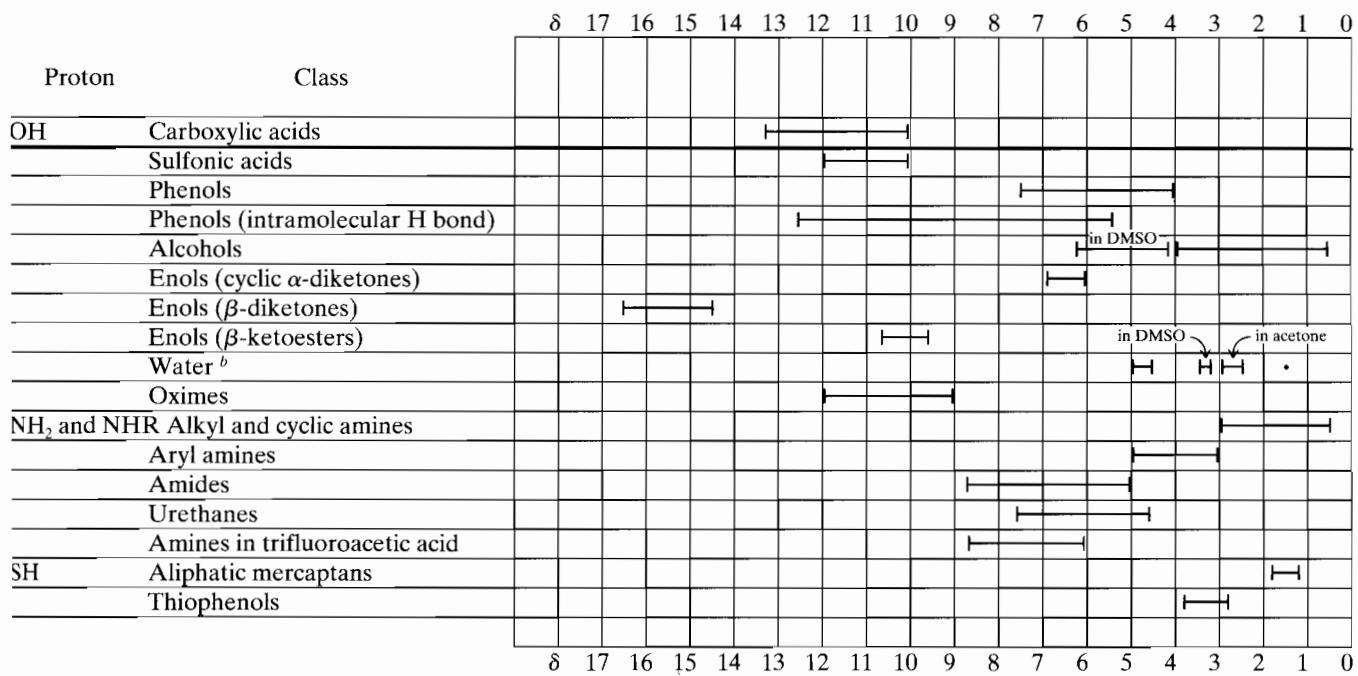
^a The benzene ring proton is at δ 7.27, from which the shift increments are calculated as shown at the end of Section 3.4.^b OTS = *p*-toluenesulfonyloxy group.

TABLE D.5 Chemical Shifts of Protons on Heteroaromatic Rings**TABLE D.6** Chemical Shifts of $\text{HC}=\text{O}$, $\text{HC}=\text{N}$, and HC(O)_3 Protons

| | | | | | |
|---------------------|------|---------------------|------|------------------------|------|
| RCH=O | 9.70 | HC(=O)OR | 8.05 | RCH=NOH cis | 7.25 |
| PhCH=O | 9.98 | HC(=O)NR_2 | 8.05 | RCH=NOH trans | 6.65 |
| RCH=CHCH=O | 9.78 | HC(OR)_3 | 5.00 | | 6.05 |

PROTONS SUBJECT TO HYDROGEN-BONDING EFFECTS

APPENDIX E (PROTONS ON HETEROATOMS)^a



^a Solvent CDCl_3 . Chemical shifts within a range are a function of concentration.

^b See Section 3.6.1.2.

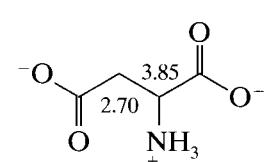
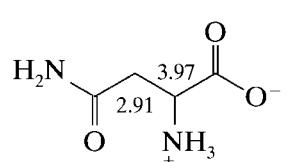
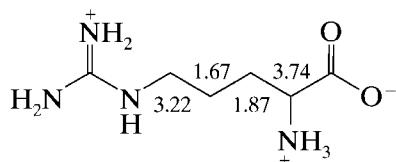
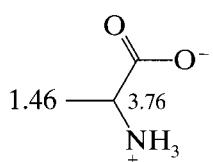
APPENDIX F PROTON SPIN-COUPLING CONSTANTS

| Type | J_{ab} (Hz) | J_{ab} Typical | Type | J_{ab} (Hz) | J_{ab} Typical |
|-----------------------------------------------------------------------------|--------------------------------------|------------------|-----------------------------------------------------------------------------------------------|----------------------------------------------------------------------------|------------------------------------------------------------|
| | 0–30 | 12–15 | | 6–12 | 10 |
| CH_a-CH_b (free rotation) | 6–8 | 7 | | 0–3 | 1–2 |
| $\text{CH}_a-\overset{\text{ }}{\underset{\text{ }}{\text{C}}}-\text{CH}_b$ | 0–1 | 0 | | 4–10 | 7 |
| | | | | 0–3 | 1.5 |
| ax-ax | 6–14 | 8–10 | | 0–3 | 2 |
| ax-eq | 0–5 | 2–3 | $\text{C}=\text{CH}_a-\text{CH}_b=\text{C}$ | 9–13 | 10 |
| eq-eq | 0–5 | 2–3 | | 3 member 4 member 5 member 6 member 7 member 8 member | 0.5–2.0 2.5–4.0 5.1–7.0 8.8–11.0 9–13 10–13 |
| | <i>cis</i> 5–10 <i>trans</i> 5–10 | | | | |
| | <i>cis</i> 4–12 <i>trans</i> 2–10 | | $\text{CH}_a-\text{C}\equiv\text{CH}_b$ $-\text{CH}_a-\text{C}\equiv\text{C}-\text{CH}_b-$ | 2–3 2–3 | |
| | <i>cis</i> 7–13 <i>trans</i> 4–9 | | | 6 | |
| CH_a-OH_b (no exchange) | 4–10 | 5 | | 4 | |
| | 1–3 | 2–3 | | J (ortho) J (meta) J (para) | 6–10 1–3 0–1 |
| $\text{C}=\text{CH}_a-\text{CH}_b$ | 5–8 | 6 | | J (2–3) J (3–4) J (2–4) J (3–5) J (2–5) J (2–6) | 5–6 7–9 1–2 1–2 0–1 0–1 |
| | 12–18 | 17 | | J (2–3) J (3–4) J (2–4) J (3–5) J (2–5) J (2–6) | 5 8 1.5 1.5 1 ~0 |
| | 0–3 | 0–2 | | J (2–3) J (3–4) J (2–4) J (2–5) | 1.3–2.0 3.1–3.8 0–1 1–2 |
| | | | | | 1.8 3.6 ~0 1.5 |

APPENDIX F (Continued)

| Type | J_{ab} (Hz) | J_{ab} Typical | Type | J_{ab} (Hz) | J_{ab} Typical |
|--------------------------|----------------------------------------------------------|------------------------------------------|--------------------------|---------------------------------------------|---------------------------------------------|
| | $J(2-3)$ $J(3-4)$ $J(2-4)$ $J(2-5)$ | 4.9–6.2 3.4–5.0 1.2–1.7 3.2–3.7 | 5.4 4.0 1.5 3.4 | Proton–Carbon-13 (See Tables 5.17, 5.18) | |
| | $J(1-3)$ $J(2-3)$ $J(3-4)$ $J(2-4)$ $J(2-5)$ | 2–3 2–3 3–4 1–2 1.5–2.5 | | | 44–81 |
| | $J(4-5)$ $J(2-5)$ $J(2-4)$ $J(4-6)$ | 4–6 1–2 0–1 2–3 | | | 3–25 0–4 |
| | $J(4-5)$ $J(2-4)$ $J(2-5)$ | 3–4 ~0 1–2 | | | 1–8 |
| | | | | | 12–40 |
| | | | | | <i>o</i> 6–10 <i>m</i> 5–6 <i>p</i> 2 |
| | | | | | $\alpha\gamma$ 4.3 $\beta\gamma$ 48 |
| Proton–Phosphorus | | | | | |
| | | 630–707 | | | |
| | $(CH_3)_3P$ | 2.7 | | | |
| | $(CH_3)_3P=O$ | 13.4 | | | |
| | $(CH_3CH_2)_3P$ | 0.5 (HCCP) 13.7 (HCP) | | | |
| | $(CH_3CH_2)_3P=O$ | 11.9 (HCCP) 16.3 (HCP) | | | |
| | | 10–13 | | | |
| | | 15–20 | | | |
| | $CH_3OP(OR)_2$ | 10.5–12 | | | |
| | $P[N(CH_3)_2]_3$ | 8.8 | | | |
| | $O=P[N(CH_3)_2]_3$ | 9.5 | | | |

Source: Complied by Varian Associates. Absolute values. Reproduced with permission.

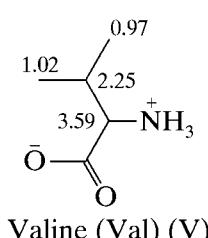
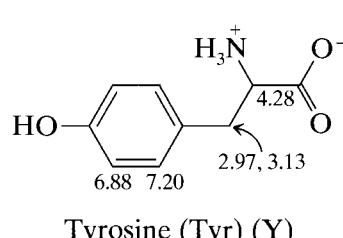
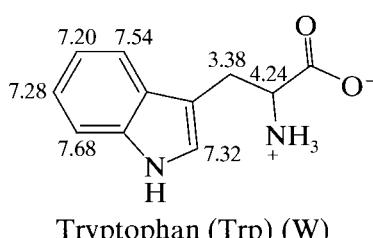
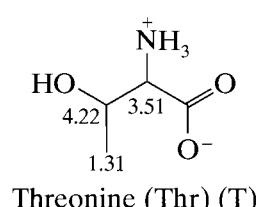
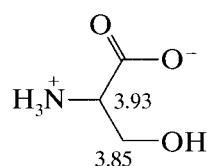
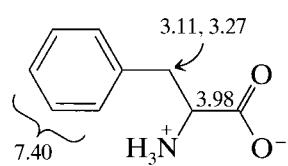
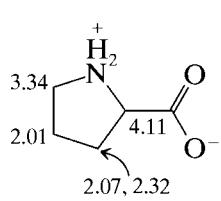
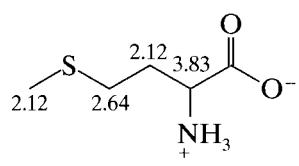
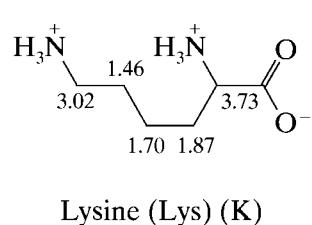
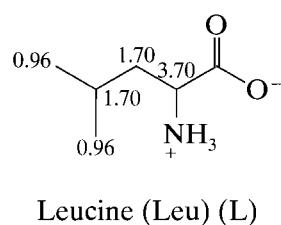
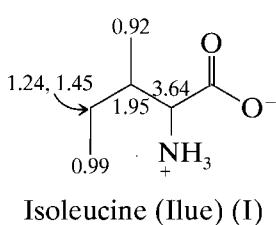
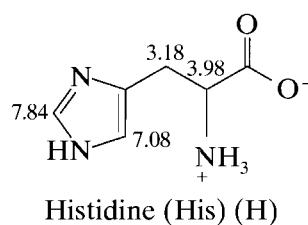
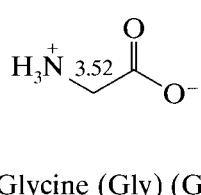
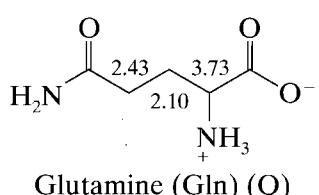
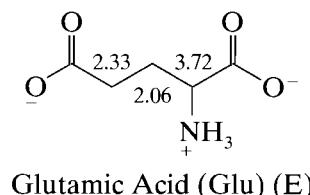
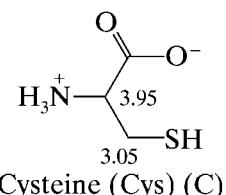
APPENDIX I PROTON NMR CHEMICAL SHIFTS OF AMINO ACIDS IN D₂O

Alanine (Ala) (A)

Arginine (Arg) (R)

Asparagine (Asn) (N)

Aspartic Acid (Asp) (D)



**CHEMICAL SHIFTS AND MULTIPLICITIES OF RESIDUAL
PROTONS IN COMMERCIALLY AVAILABLE DEUTERATED
APPENDIX G SOLVENTS (MERCK & CO., INC.)**

| Compound ^a | Molecular Weight | δ_H (multiplet) | Compound ^a | Molecular Weight | δ_H (multiplet) |
|------------------------------------------------------|------------------|------------------------------|-----------------------------------------------------|------------------|------------------------|
| Acetic acid- <i>d</i> ₄ | | 11.53 (1) | Nitromethane- <i>d</i> ₃ | | 4.33 (5) |
| 64.078 | | 2.03 (5) | 64.059 | | |
| Acetone- <i>d</i> ₆ | | 2.04 (5) | Isopropyl alcohol- <i>d</i> ₈ | | 5.12 (1) |
| 64.117 | | | 68.146 | | 3.89 (br) |
| Acetonitrile- <i>d</i> ₃ | | 1.93 (5) | | | 1.10 (br) |
| 44.071 | | | | | 8.71 (br) |
| Benzene- <i>d</i> ₆ | | 7.15 (br) | Pyridine- <i>d</i> ₅ | | 7.55 (br) |
| 84.152 | | | 84.133 | | 7.19 (br) |
| Chloroform- <i>d</i> | | 7.26 (1) | Tetrahydrofuran- <i>d</i> ₈ | | 3.58 (br) |
| 120.384 | | | 80.157 | | 1.73 (br) |
| Cyclohexane- <i>d</i> ₁₂ | | 1.38 (br) | Toluene- <i>d</i> ₈ | | 7.09 (m) |
| 96.236 | | | 100.191 | | 7.00 (br) |
| Deuterium oxide | | 4.63 (ref. DSS) ^c | | | 6.98 (m) |
| 20.028 | | 4.67 (ref. TSP) ^c | | | 2.09 (5) |
| 1,2-Dichloroethane- <i>d</i> ₄ | | 3.72 (br) | Trifluoroacetic acid- <i>d</i> | | 11.50 (1) |
| 102.985 | | | 115.030 | | |
| Diethyl- <i>d</i> ₁₀ ether | | 3.34 (m) | 2,2,2-Trifluoroethyl alcohol- <i>d</i> ₃ | | 5.02 (1) |
| 84.185 | | 1.07 (m) | 103.059 | | 3.88 (4 × 3) |
| Diglyme- <i>d</i> ₁₄ | | 3.49 (br) | | | |
| 148.263 | | 3.40 (br) | | | |
| | | 3.22 (5) | | | |
| <i>N,N</i> -Dimethylformamide- <i>d</i> ₇ | | 8.01 (br) | | | |
| 80.138 | | 2.91 (5) | | | |
| | | 2.74 (5) | | | |
| Dimethyl- <i>d</i> ₆ sulphoxide | | 2.49 (5) | | | |
| 84.170 | | | | | |
| <i>p</i> -Dioxane- <i>d</i> ₈ | | 3.53 (m) | | | |
| 96.156 | | | | | |
| Ethyl alcohol- <i>d</i> ₆ (anh) | | 5.19 (1) | | | |
| 52.106 | | 3.55 (br) | | | |
| | | 1.11 (m) | | | |
| Glyme- <i>d</i> ₁₀ | | 3.40 (m) | | | |
| 100.184 | | 3.22 (5) | | | |
| Hexafluoroacetone deuterate | | 5.26 (1) | | | |
| 198.067 | | | | | |
| HMPT- <i>d</i> ₁₈ | | 2.53 (2 × 5) | | | |
| 197.314 | | | | | |
| Methyl alcohol- <i>d</i> ₄ | | 4.78 (1) | | | |
| 36.067 | | 3.30 (5) | | | |
| Methylene chloride- <i>d</i> ₂ | | 5.32 (3) | | | |
| 86.945 | | | | | |
| Nitrobenzene- <i>d</i> ₅ | | 8.11 (br) | | | |
| 128.143 | | 7.67 (br) | | | |
| | | 7.50 (br) | | | |

^a Purity (Atom % D) up to 99.96 % ("100 %") for several solvents.

^b The residual proton consists of one proton of each kind in an otherwise completely deuterated molecule. For example, deuterated acetic acid has two different kinds of residual protons: CD₂H—COOD and CD₃—COOH. The CD₂H proton, coupled to two D nuclei is at δ 2.03 with a multiplicity of 5 (i.e., 2nI + 1 = 2 × 2 × 1 + 1 = 5). The carboxylic proton is a singlet at δ 11.53.

^c DSS is 3-trimethylsilyl)-1-propane sulfonic acid, sodium salt. TSP is sodium-3-trimethylpropionate-2,2,3,3-d₄. Both are reference standards used in aqueous solutions.

Table 1. ^1H NMR Data^a

| | proton | mult | THF- <i>d</i> ₈ | CD ₂ Cl ₂ | CDCl ₃ | toluene- <i>d</i> ₈ | C ₆ D ₆ | C ₆ D ₅ Cl | (CD ₃) ₂ CO | (CD ₃) ₂ SO | CD ₃ CN | TFE- <i>d</i> ₃ | CD ₃ OD | D ₂ O | |
|----------------------------|---------------------------------|-------------------|----------------------------|---------------------------------|-------------------|--------------------------------|-------------------------------|----------------------------------|------------------------------------|------------------------------------|--------------------|----------------------------|--------------------|------------------|------|
| solvent residual signals | | | 1.72 3.58 | 5.32 | 7.26 | 2.08 6.97 7.01 7.09 | 7.16 6.99 7.14 | 6.96 6.99 | 2.05 | 2.50 | 1.94 | 5.02 3.88 | 3.31 | 4.79 | |
| water | OH | s | 2.46 | 1.52 | 1.56 | 0.43 | 0.40 | 1.03 | 2.84 ^b | 3.33 ^b | 2.13 | 3.66 | 4.87 | | |
| acetic acid | CH ₃ | s | 1.89 | 2.06 | 2.10 | 1.57 | 1.52 | 1.76 | 1.96 | 1.91 | 1.96 | 2.06 | 1.99 | 2.08 | |
| acetone | CH ₃ | s | 2.05 | 2.12 | 2.17 | 1.57 | 1.55 | 1.77 | 2.09 | 2.09 | 2.08 | 2.19 | 2.15 | 2.22 | |
| acetonitrile | CH ₃ | s | 1.95 | 1.97 | 2.10 | 0.69 | 0.58 | 1.21 | 2.05 | 2.07 | 1.96 | 1.95 | 2.03 | 2.06 | |
| benzene | CH | s | 7.31 | 7.35 | 7.36 | 7.12 | 7.15 | 7.20 | 7.36 | 7.37 | 7.37 | 7.36 | 7.33 | | |
| <i>tert</i> -butyl alcohol | CH ₃ | s | 1.15 | 1.24 | 1.28 | 1.03 | 1.05 | 1.12 | 1.18 | 1.11 | 1.16 | 1.28 | 1.40 | 1.24 | |
| | OH | s ^c | 3.16 | | | 0.58 | 0.63 | 1.30 | | 4.19 | 2.18 | | 2.20 | | |
| chloroform | CH | s | 7.89 | 7.32 | 7.26 | 6.10 | 6.15 | 6.74 | 8.02 | 8.32 | 7.58 | 7.33 | 7.90 | | |
| 18-crown-6 | CH ₂ | s | 3.57 | 3.59 | 3.67 | 3.36 | 3.39 | 3.41 | 3.59 | 3.51 | 3.51 | 3.64 | 3.64 | 3.80 | |
| cyclohexane | CH ₂ | s | 1.44 | 1.44 | 1.43 | 1.40 | 1.40 | 1.37 | 1.43 | 1.40 | 1.44 | 1.47 | 1.45 | | |
| 1,2-dichloroethane | CH ₂ | s | 3.77 | 3.76 | 3.73 | 2.91 | 2.90 | 3.26 | 3.87 | 3.90 | 3.81 | 3.71 | 3.78 | | |
| dichloromethane | CH ₂ | s | 5.51 | 5.33 | 5.30 | 4.32 | 4.27 | 4.77 | 5.63 | 5.76 | 5.44 | 5.24 | 5.49 | | |
| diethyl ether | CH ₃ | t, 7 | 1.12 | 1.15 | 1.21 | 1.10 | 1.11 | 1.10 | 1.11 | 1.09 | 1.12 | 1.20 | 1.18 | 1.17 | |
| | CH ₂ | q, 7 | 3.38 | 3.43 | 3.48 | 3.25 | 3.26 | 3.31 | 3.41 | 3.38 | 3.42 | 3.58 | 3.49 | 3.56 | |
| diglyme | CH ₂ | m | 3.43 | 3.57 | 3.65 | 3.43 | 3.46 | 3.49 | 3.56 | 3.51 | 3.53 | 3.67 | 3.61 | 3.67 | |
| | CH ₂ | m | 3.53 | 3.50 | 3.57 | 3.31 | 3.34 | 3.37 | 3.47 | 3.38 | 3.45 | 3.62 | 3.58 | 3.61 | |
| | OCH ₃ | s | 3.28 | 3.33 | 3.39 | 3.12 | 3.11 | 3.16 | 3.28 | 3.24 | 3.29 | 3.41 | 3.35 | 3.37 | |
| dimethylformamide | CH | s | 7.91 | 7.96 | 8.02 | 7.57 | 7.63 | 7.73 | 7.96 | 7.95 | 7.92 | 7.86 | 7.97 | 7.92 | |
| | CH ₃ | s | 2.88 | 2.91 | 2.96 | 2.37 | 2.36 | 2.51 | 2.94 | 2.89 | 2.89 | 2.98 | 2.99 | 3.01 | |
| | CH ₃ | s | 2.76 | 2.82 | 2.88 | 1.96 | 1.86 | 2.30 | 2.78 | 2.73 | 2.77 | 2.88 | 2.86 | 2.85 | |
| 1,4-dioxane | CH ₂ | s | 3.56 | 3.65 | 3.71 | 3.33 | 3.35 | 3.45 | 3.59 | 3.57 | 3.60 | 3.76 | 3.66 | 3.75 | |
| DME | CH ₃ | s | 3.28 | 3.34 | 3.40 | 3.12 | 3.12 | 3.17 | 3.28 | 3.24 | 3.28 | 3.40 | 3.35 | 3.37 | |
| ethane | CH ₃ | s | 0.85 | 0.85 | 0.87 | 0.81 | 0.80 | 0.79 | 0.83 | 0.82 | 0.85 | 0.85 | 0.85 | 0.82 | |
| ethanol | CH ₃ | t, 7 | 1.10 | 1.19 | 1.25 | 0.97 | 0.96 | 1.06 | 1.12 | 1.06 | 1.12 | 1.22 | 1.19 | 1.17 | |
| | CH ₂ | q, 7 ^d | 3.51 | 3.66 | 3.72 | 3.36 | 3.34 | 3.51 | 3.57 | 3.44 | 3.54 | 3.71 | 3.60 | 3.65 | |
| | OH | s ^{c,d} | 3.30 | 1.33 | 1.32 | 0.83 | 0.50 | 1.39 | 3.39 | 4.63 | 2.47 | | | | |
| ethyl acetate | CH ₃ CO | s | 1.94 | 2.00 | 2.05 | 1.69 | 1.65 | 1.78 | 1.97 | 1.99 | 1.97 | 2.03 | 2.01 | 2.07 | |
| | CH ₂ CH ₃ | q, 7 | 4.04 | 4.08 | 4.12 | 3.87 | 3.89 | 3.96 | 4.05 | 4.03 | 4.06 | 4.14 | | | |
| | CH ₂ CH ₃ | t, 7 | 1.19 | 1.23 | 1.26 | 0.94 | 0.92 | 1.04 | 1.20 | 1.17 | 1.20 | 1.26 | 1.24 | 1.24 | |
| ethylene | CH ₂ | s | 5.36 | 5.40 | 5.40 | 5.25 | 5.25 | 5.29 | 5.38 | 5.41 | 5.41 | 5.40 | 5.39 | 5.44 | |
| ethylene glycol | CH ₂ | s ^e | 3.48 | 3.66 | 3.76 | 3.36 | 3.41 | 3.58 | 3.28 | 3.34 | 3.51 | 3.72 | 3.59 | 3.65 | |
| H grease ^f | CH ₃ | m | 0.85–0.91 | 0.84–0.90 | 0.84–0.87 | 0.89–0.96 | 0.90–0.98 | 0.86–0.92 | 0.90 | 0.82–0.88 | | 0.88–0.94 | 0.86–0.93 | | |
| | CH ₂ | br s | 1.29 | 1.27 | 1.25 | 1.33 | 1.32 | 1.30 | 1.29 | 1.24 | | 1.33 | 1.29 | | |
| hexamethylbenzene | CH ₃ | s | 2.18 | 2.20 | 2.24 | 2.10 | 2.13 | 2.10 | 2.17 | 2.14 | 2.19 | 2.24 | 2.19 | | |
| n-hexane | CH ₃ | t, 7 | 0.89 | 0.89 | 0.88 | 0.88 | 0.89 | 0.85 | 0.88 | 0.86 | 0.89 | 0.91 | 0.90 | | |
| | CH ₂ | m | 1.29 | 1.27 | 1.26 | 1.22 | 1.24 | 1.19 | 1.28 | 1.25 | 1.28 | 1.31 | 1.29 | | |
| HMDSO | CH ₃ | s | 0.07 | 0.07 | 0.07 | 0.10 | 0.12 | 0.10 | 0.07 | 0.06 | 0.07 | 0.08 | 0.07 | 0.08 | 0.28 |
| HMPA | CH ₃ | d,9.5 | 2.58 | 2.60 | 2.65 | 2.42 | 2.40 | 2.47 | 2.59 | 2.53 | 2.57 | 2.63 | 2.64 | 2.61 | |
| hydrogen | H ₂ | s | 4.55 | 4.59 | 4.62 | 4.50 | 4.47 | 4.49 | 4.54 | 4.61 | 4.57 | 4.53 | 4.56 | | |
| imidazole | CH(2) | s | 7.48 | 7.63 | 7.67 | 7.30 | 7.33 | 7.53 | 7.62 | 7.63 | 7.57 | 7.61 | 7.67 | 7.78 | |
| | CH(4,5) | s | 6.94 | 7.07 | 7.10 | 6.86 | 6.90 | 7.01 | 7.04 | 7.01 | 7.01 | 7.03 | 7.05 | 7.14 | |
| methane | CH ₄ | s | 0.19 | 0.21 | 0.22 | 0.17 | 0.16 | 0.15 | 0.17 | 0.20 | 0.20 | 0.18 | 0.20 | 0.18 | |
| methanol | CH ₃ | s ^g | 3.27 | 3.42 | 3.49 | 3.03 | 3.07 | 3.25 | 3.31 | 3.16 | 3.28 | 3.44 | 3.34 | 3.34 | |
| | OH | s ^{c,g} | 3.02 | 1.09 | 1.09 | | | 1.30 | 3.12 | 4.01 | 2.16 | | | | |
| nitromethane | CH ₃ | s | 4.31 | 4.31 | 4.33 | 3.01 | 2.94 | 3.59 | 4.43 | 4.42 | 4.31 | 4.28 | 4.34 | 4.40 | |
| n-pentane | CH ₃ | t, 7 | 0.89 | 0.89 | 0.88 | 0.87 | 0.87 | 0.84 | 0.88 | 0.86 | 0.89 | 0.90 | | | |
| | CH ₂ | m | 1.31 | 1.30 | 1.27 | 1.25 | 1.23 | 1.23 | 1.27 | 1.27 | 1.29 | 1.33 | 1.29 | | |
| propane | CH ₃ | t, 7.3 | 0.90 | 0.90 | 0.90 | 0.89 | 0.86 | 0.84 | 0.88 | 0.87 | 0.90 | 0.90 | 0.91 | 0.88 | |
| 2-propanol | CH ₃ | sept, 7.3 | 1.33 | 1.32 | 1.32 | 1.32 | 1.26 | 1.26 | 1.31 | 1.29 | 1.33 | 1.33 | 1.34 | 1.30 | |
| | CH ₂ | d, 6 | 1.08 | 1.17 | 1.22 | 0.95 | 0.95 | 1.04 | 1.10 | 1.04 | 1.09 | 1.20 | 1.50 | 1.17 | |
| propylene | CH ₃ | dt, 6, 1.5 | 1.69 | 1.71 | 1.73 | 1.55 | 1.55 | 1.58 | 1.68 | 1.68 | 1.70 | 1.70 | 1.70 | | |
| | CH ₂ (1) | dm, 10 | 4.89 | 4.93 | 4.94 | 4.92 | 4.95 | 4.91 | 4.90 | 4.94 | 4.93 | 4.93 | 4.91 | 4.95 | |
| | CH ₂ (2) | dm, 17 | 4.99 | 5.03 | 4.98 | 5.01 | 4.98 | 5.00 | 5.03 | 5.04 | 5.03 | 5.01 | 5.06 | | |
| | CH | m | 5.79 | 5.84 | 5.83 | 5.70 | 5.72 | 5.72 | 5.81 | 5.80 | 5.85 | 5.87 | 5.82 | 5.90 | |
| pyridine | CH(2,6) | m | 8.54 | 8.59 | 8.62 | 8.47 | 8.53 | 8.51 | 8.58 | 8.58 | 8.57 | 8.45 | 8.53 | 8.52 | |
| | CH(3,5) | m | 7.25 | 7.28 | 7.29 | 6.67 | 6.66 | 6.90 | 7.35 | 7.39 | 7.33 | 7.40 | 7.44 | 7.45 | |
| | CH(4) | m | 7.65 | 7.68 | 7.68 | 6.99 | 6.98 | 7.25 | 7.76 | 7.79 | 7.73 | 7.82 | 7.85 | 7.87 | |
| pyrrole | NH | br t | 9.96 | 8.69 | 8.40 | 7.71 | 7.80 | 8.61 | 10.02 | 10.75 | 9.27 | | | | |
| | CH(2,5) | m | 6.66 | 6.79 | 6.83 | 6.43 | 6.48 | 6.62 | 6.77 | 6.73 | 6.75 | 6.84 | 6.72 | 6.93 | |
| | CH(3,4) | m | 6.02 | 6.19 | 6.26 | 6.27 | 6.37 | 6.27 | 6.07 | 6.01 | 6.10 | 6.24 | 6.08 | 6.26 | |
| pyrrolidine ^h | CH ₂ (2,5) | m | 2.75 | 2.82 | 2.87 | 2.54 | 2.54 | 2.64 | | 2.67 | 2.75 | 3.11 | 2.80 | 3.07 | |
| | CH ₂ (3,4) | m | 1.59 | 1.67 | 1.68 | 1.36 | 1.33 | 1.43 | | 1.55 | 1.61 | 1.93 | 1.72 | 1.87 | |
| silicone grease | CH ₃ | s | 0.11 | 0.09 | 0.07 | 0.26 | 0.29 | 0.14 | 0.13 | −0.06 | 0.08 | 0.16 | 0.10 | | |
| tetrahydrofuran | CH ₂ (2,5) | m | 3.62 | 3.69 | 3.76 | 3.54 | 3.57 | 3.59 | 3.63 | 3.60 | 3.64 | 3.78 | 3.71 | 3.74 | |
| | CH ₂ (3,4) | m | 1.79 | 1.82 | 1.85 | 1.43 | 1.40 | 1.55 | 1.79 | 1.76 | 1.80 | 1.91 | 1.87 | 1.88 | |
| toluene | CH ₃ | s | 2.31 | 2.34 | 2.36 | 2.11 | 2.11 | 2.16 | 2.32 | 2.30 | 2.33 | 2.33 | 2.32 | | |
| | CH ₂ (2,4,6) | m | 7.10 | 7.15 | 7.17 | 6.96–7.01 | 7.02 | 7.01–7.08 | 7.10–7.20 | 7.18 | 7.10–7.30 | 7.10–7.30 | 7.16 | | |
| | CH(3,5) | m | 7.19 | 7.24 | 7.25 | 7.09 | 7.13 | 7.10–7.17 | 7.10–7.20 | 7.25 | 7.10–7.30 | 7.10–7.30 | 7.16 | | |
| triethylamine | CH ₃ | t, 7 | 0.97 | 0.99 | 1.03 | 0.95 | 0.96 | 0.93 | 0.96 | 0.93 | 0.96 | 1.31 | 1.05 | 0.99 | |
| | CH ₂ | q,7 | 2.46 | 2.48 | 2.53 | 2.39 | 2.40 | 2.39 | 2.45 | 2.43 | 2.45 | 3.12 | 2.58 | 2.57 | |

^a Except for the compounds in solutions 8–10, as well as the gas samples, hexamethylbenzene, and the corrected values mentioned in the Supporting Information, all data for the solvents CDCl₃, C₆D₆, (CD₃)₂CO, (CD₃)₂SO, CD₃CN, CD₃OD, and D₂O were previously reported in ref 2. ^b A signal for HDO is also observed in (CD₃)₂SO (3.30 ppm) and (CD₃)₂CO (2.81 ppm), often seen as a 1:1:1 triplet ($J_{H,D} = 1$ Hz). ^c Not all OH signals were observable. ^d In some solvents, the coupling interaction between the CH₂ and the OH protons may be observed ($J = 5$ Hz). ^e In CD₃CN, the OH proton was seen as a multiplet at 2.69 ppm, as well as extra coupling to the CH₂ resonance. ^f Apiezon brand H grease. ^g In some solvents, a coupling interaction between the CH₃ and the OH protons may be observed ($J = 5.5$ Hz). ^h Pyrrolidine was observed to react with (CD₃)₂CO.