# Deuterium Isotope Effects on the Protolytic Dissociation of Organic Acids in Electronically Excited States

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**Abstract:** The deuterium isotope effect upon the acid strength of a series of phenols and aromatic carboxylic acids and their ground and first excited singlet states has been studied. Quantitative descriptions of equilibrium isotope perturbations for ground-state acids are shown to be applicable to electronically excited compounds. For all compounds investigated, the equilibrium isotope effect decreased with increasing strength of the protium acid, in both ground and excited states. The isotope effect in an excited phenol is smaller than that in the ground state of the same compound, whereas the effect increases upon excitation for aromatic carboxylic acids, indicating that the magnitude of the isotope effect is principally a function of acid strength in both the ground and excited states of an aromatic acid.

Protolytic dissociation constants of weak acids are almost always larger in water than in deuterium oxide. Although the existence of this effect has been known for more than 30 years, few of its details are understood. The lower acidity of a deuterium acid, compared with that of the corresponding protium acid, has been related to differences in zero-point energy of the proton and deuteron when covalently bonded to an acidic species[2] and to differences in zero-point energy of hydrogen bonds between the acidic or basic species and solvent molecules.[3]

The difference in acidity between a protium acid and its deuterium counterpart tends to increase as the strength of the hydrogen acid decreases. Various investigators have noted approximately linear relations between $pK_H - pK_D$ (hereafter denoted $\Delta pK$) and $pK_H$.[4] Bell and Kuhn[5] noted such a linear relation for a series of alcohols, but observed large deviations from linearity when carboxylic acids were studied. They presumed[5] that charge effects were responsible for the deviations observed with carboxylic acids; a similar opinion has been advanced by Martin.[6] It is, however, not clear why charge effects should be significantly more important for carboxylic acids than for phenols. Despite the several studies mentioned above, it remains uncertain whether the value of $\Delta pK$ obtained for a given acid is primarily a function of the strength of the acid or of its "type" and charge.

The present investigation is concerned with the measurement of isotope effects upon the strengths of electronically excited acids. By exciting a dissociable compound, its acidity is changed greatly[7] but its charge and "type" presumably remain essentially unchanged. Thus, if $\Delta pK$ values obtained for an acid in its excited and ground states were essentially identical, the significance of acid-type or charge effects would be indicated. However, if the observed $\Delta pK$ values in excited and ground states could be predicted with reasonable precision from a knowledge of the acidities of the two states, excellent evidence would be provided for the concept that acid strength is the predominant contributory factor to $\Delta pK$. Hence, an investigation of excited-state protolytic dissociation, in water and deuterium oxide, of a number of aromatic acids was undertaken.

## Experimental Section

Preparation and purification procedures for the organic compounds have been described.[8] Water was purified by distillation from alkaline permanganate. Deuterium oxide, obtained from Columbia Organic Chemicals (Columbia, S. C.) and Merck, Sharpe and Dohme of Canada (Montreal), was stated to be not less than 99.5% isotopically pure, a fact which was verified by pycnometry.[9] All glassware used in the preparation and/or storage of $D_2O$ solutions was conditioned by drying at 120° for at least 3 days. All deuterium oxide solutions were stored in glass-stoppered containers and desiccators over Drierite.

Ground-state $pK_a$ values were determined spectrophotometrically,[10] using buffers of constant ionic strength (0.01) described by Biggs[11] and Perrin.[12] In order to utilize the spectrophotometric technique in $D_2O$, it was necessary to obtain pL values (L denoting lyonium ion) in $D_2O$ solutions and $D_2O$–$H_2O$ mixtures. As shown by Long and co-workers[13] pL values can be obtained from ordinary glass-electrode pH meter readings by use of the equation

$$\mathrm{pL} = \text{meter reading} + 0.3314n + 0.0766n^2 \quad (1)$$

where $n$ denotes the atom fraction of hydrogen present in the solution. For buffers prepared in $D_2O$, it was assumed that the same activity coefficients obtained as those for the comparable buffers in $H_2O$. Although this assumption is of uncertain validity, the activity corrections[10–12] are sufficiently small that the assumption should not introduce significant error into $pK_a$ values determined in $D_2O$.

Procedures used for measuring absorption and emission spectra have been reported.[8]

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[1] (a) National Science Foundation Predoctoral Fellow, 1962–1965. Financial support from the Purdue Research Foundation is acknowledged.

[2] G. N. Lewis and P. W. Schutz, *J. Am. Chem. Soc.*, **56**, 1913 (1934).

[3] C. A. Bunton and V. J. Shiner, Jr., *ibid.*, **83**, 42 (1961).

[4] See, for example, C. K. Rule and V. K. La Mer, *ibid.*, **60**, 1974 (1938); and N. C. Li, P. Tang, and R. Mathur, *J. Phys. Chem.*, **65**, 1074 (1961).

[5] R. P. Bell and A. T. Kuhn, *Trans. Faraday Soc.*, **59**, 1789 (1963).

[6] R. B. Martin, *Science*, **139**, 1198 (1963).

[7] For a review, see A. Weller, *Progr. Reaction Kinetics*, **1**, 189 (1961).

[8] E. L. Wehry and L. B. Rogers, *J. Am. Chem. Soc.*, **87**, 4234 (1965).

[9] C. J. Rodden, "Analysis of Essential Nuclear Reactor Materials," U. S. Atomic Energy Commission, Washington, D. C., 1964, p. 642.

[10] R. A. Robinson, in "Structure of Electrolytic Solutions," W. J. Hamer, Ed., John Wiley and Sons, Inc., New York, N. Y., 1959, Chapter 16.

[11] A. I. Biggs, *Trans. Faraday Soc.*, **52**, 35 (1956).

[12] D. D. Perrin, *Australian J. Chem.*, **16**, 572 (1963).

[13] P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, **64**, 188 (1960); P. Salomaa, L. L. Schalenger, and F. A. Long, *J. Am, Chem. Soc.*, **86**, 1 (1964).

**Table I.** Ground-State $pK_H$ and $pK_D$ Values for Phenols

| Compound | $pK_H$ | Ref. | $pK_D$ | Ref. | $\Delta pK$ |
|---|---|---|---|---|---|
| Phenol | 10.00 | This work | 10.62 | This work | +0.62 |
| | 9.97 | *a* | | | |
| 4-Phenolsulfonate | 8.97 | This work | 9.52 | This work | +0.55 |
| | 9.03 | *b* | | | |
| 4-Nitrophenol | 7.22 | This work | 7.77 | This work | +0.55 |
| | 7.24 | *c* | 7.79 | *c* | +0.55 |
| | 7.26 | *d* | 7.74 | *d* | +0.48 |
| 2,4-Dinitrophenol | 4.06 | This work | 4.55 | This work | +0.49 |
| | 4.07 | *e* | 4.59 | *e* | +0.52 |
| | 4.12 | *d* | 4.82 | *d* | +0.70 |
| 2,5-Dinitrophenol | 5.19 | This work | 5.70 | This work | +0.51 |
| | 5.20 | *e* | 5.73 | *e* | +0.53 |
| 4-Bromophenol | 9.35 | This work | 9.94 | This work | +0.59 |
| | 9.36 | *a* | | | |
| 3-Methoxyphenol | 9.62 | This work | 10.20 | This work | +0.58 |
| | 9.65 | *a* | | | |
| 4-Methoxyphenol | 10.24 | This work | 10.85 | This work | +0.61 |
| | 10.21 | *a* | | | |
| 4-Hydroxyphenyltrimethyl-ammonium chloride | 8.34 | This work | 8.90 | This work | +0.56 |
| | 8.35 | *f* | | | |
| 2-Naphthol | 9.47 | This work | 10.06 | This work | +0.59 |
| | 9.46 | *g* | | | |
| | 9.63 | *h* | | | |

[a] A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 388 (1961). [b] E. E. Sager, M. R. Schooley, A. S. Carr, and S. F. Acree, *J. Res. Natl. Bur. Std.*, **35**, 521 (1945). [c] D. C. Martin and J. A. V. Butler, *J. Chem. Soc.*, 1366 (1939). [d] Ref. 16. [e] Ref. 5. [f] H. C. Ko, W. F. O'Hara, and L. G. Hepler, *J. Am. Chem. Soc.*, **86**, 1003 (1964). [g] Ref. 7. [h] A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Methuen and Co., Ltd., London, 1962.

Excited-state dissociation constants were calculated by the Förster cycle.[14]

$$pK_a - pK_a^* = (2.10 \times 10^{-3})(\Delta\bar{\nu}) \text{ at } 298^\circ\text{K}. \qquad (2)$$

In eq. 2, $K_a$ and $K_a^*$ are the protolytic dissociation constants in the ground and excited states, respectively, and $\Delta\bar{\nu}$ is the frequency difference (in cm.$^{-1}$) of the 0–0 bands of the electronic transition in the acid and conjugate base. In the case of the lowest singlet → singlet transition, the 0–0 frequency cannot be obtained directly from room-temperature absorption or fluorescence spectra, due to spectral overlap; the 0–0 frequency for a given species was, therefore, estimated by averaging the frequencies of absorption and fluorescence maxima of that species.[14]

## Results and Discussion

For the various phenols studied, the ground-state $pK_H$ and $pK_D$ values obtained in the present work are compared with literature results in Table I. Where literature data are available, agreement between the present results and the various literature values is generally satisfactory.[15] The excited singlet-state $pK$ values (denoted $pK^*$) are listed in Table II for all compounds except the nitrophenols, which do not fluoresce. As expected, electronic excitation greatly enhanced the acidity of these compounds.[7]

In Figure 1, $\Delta pK$ is plotted against $pK_H$ for all phenols investigated. Both ground- and excited singlet-state points are plotted. For the ground-state points, an approximately linear relation was noted between $\Delta pK$ and $pK_H$; the equation of the least-squares line is

$$pK_D - pK_H = \Delta pK = 0.41 + 0.018pK_H \qquad (3)$$

The slope of the line, 0.018, is in good agreement with that predicted for such linear plots.[6] It should be noted that no ground-state point, even those for positively or negatively charged phenols, deviated from the line by more than 0.02 $pK$ unit. Thus, charge effects appear of relatively minor importance in determining the magnitude of isotope effects in ground-state phenols, as previously reported by Bell and Kuhn[5] and Martin.[6]

**Table II.** Excited Singlet-State $pK_H$ and $pK_D$ Values for Phenols

| Compound | $pK_H^*$ | $pK_D^*$ | $\Delta pK^*$ |
|---|---|---|---|
| Phenol | 4.1 | 4.6 | +0.5 |
| 4-Phenolsulfonate | 2.3 | 2.7 | +0.4 |
| 4-Bromophenol | 2.9 | 3.4 | +0.5 |
| 3-Methoxyphenol | 4.6 | 5.1 | +0.5 |
| 4-Methoxyphenol | 5.7 | 6.2 | +0.5 |
| 4-Hydroxyphenyltrimethyl-ammonium chloride | 1.6 | 2.0 | +0.4 |
| 2-Naphthol | 3.0 | 3.5 | +0.5 |

Excited-state acidities cannot generally be specified to a precision greater than 0.1 $pK$ unit. Hence, a consideration of Figure 1 reveals that, within experimental error, *the isotope effect in an excited phenol can be predicted from the equation describing the effect in the ground state* (eq. 3). This interesting result appears to indicate that acid strength is indeed the predominant factor contributing to $\Delta pK$. It will be noted that no unusual deviations from this statement were observed for positively or negatively charged phenols, implying that charge effects are negligible in excited, as well as ground state, phenols.

While good linear plots of $\Delta pK$ *vs.* $pK_H$ are often obtained for phenols, such plots for carboxylic acids usually are characterized by a high degree of scatter.[5,16]

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(14) A. Weller, *Z. Elektrochem.*, **56**, 662 (1952).

(15) An exception is $pK_D$ for 2,4-dinitrophenol; McDougall and Long[16] obtained 4.82 by a glass-electrode potentiometric titration, while Bell and Kuhn[5] obtained 4.59 by a spectrophotometric technique involving no glass-electrode measurements in heavy water. The discrepancy caused Bell and Kuhn to express skepticism regarding the accuracy of glass-electrode measurements in $D_2O$. The present value (4.55) agrees well with that obtained by Bell and Kuhn, even though glass-electrode $pK$ values were used. Hence, it is assumed that the glass electrode is reliable in $D_2O$, as reported by Long and co-workers,[13] and that the apparent error of $pK_D$ for 2,4-dinitrophenol as reported by McDougall and Long[16] is due to some other factor.

(16) A. C. McDougall and F. A. Long, *J. Phys. Chem.*, **66**, 429 (1962).

**Table III.** Ground-State $pK_H$ and $pK_D$ Values for Carboxylic Acids

| Compound | $pK_H$ | Ref. | $pK_D$ | Ref. | $pK_{obsd}$ | $pK_{prepd}$[a] |
|---|---|---|---|---|---|---|
| Benzoic acid | 4.16<br>4.17 | This work<br>*b* | 4.65 | This work | +0.49 | +0.51 |
| 2-Chlorobenzoic acid | 2.91<br>2.94 | This work<br>*c* | 3.38 | This work | +0.47 | +0.49 |
| 2-Nitrobenzoic acid | 2.17<br>2.17 | This work<br>*d* | 2.60 | This work | +0.43 | +0.48 |
| 4-Sulfobenzoic acid | 3.65<br>3.72 | This work<br>*f* | 4.12 | This work | +0.47 | +0.62<br>(+0.50)[e] |
| 1-Naphthoic acid | 3.73<br>3.70 | This work<br>*g* | 4.27 | This work | +0.54 | +0.51 |
| 2-Naphthoic acid | 4.21<br>4.16 | This work<br>*g* | 4.68 | This work | +0.47 | +0.51 |

[a] As calculated from eq. 4. [b] I. M. Kolthoff and W. Bosch, *J. Phys. Chem.*, **36**, 1695 (1932). [c] J. F. J. Dippy, F. R. Williams, and R. H. Lewis, *J. Chem. Soc.*, 343 (1935). [d] J. F. J. Dippy and R. H. Lewis, *ibid.*, 1426 (1937). [e] The $Z$ term in eq. 4 was neglected in calculating the value in parentheses. [f] H. Zollinger, W. Büchler, and C. Wittwer, *Helv. Chim. Acta*, **36**, 1711 (1953). [g] J. F. J. Dippy, J. R. C. Hughes, and J. W. Laxton, *J. Chem. Soc.*, 1470 (1954).

This fact is often rationalized on the basis of charge effects,[5] and Martin[6] proposed an equation, used to predict $\Delta pK$ from $pK_H$, in which a term for charge effects is included. This equation is

$$pK_D - pK_H = 0.45 + 0.015pK_H - 0.12Z \quad (4)$$

where $Z$ denotes the net charge on the acid form of the conjugate acid–base pair being considered. In Table III, values of $pK_H$ and $pK_D$ for six ground-state aromatic carboxylic acids are presented, and the experimental $\Delta pK$ values are compared with those predicted from eq. 4. Agreement between predicted and observed $\Delta pK$ values is moderately good, except in the case of 4-sulfobenzoic acid, for which $Z = -1$. If the $Z$ term is eliminated from eq. 4, the agreement between predicted and observed $\Delta pK$ values is considerably enhanced. This interesting result implies that charge effects may not always be highly significant for carboxylic acids.

Experimental values for $pK_H$ and $pK_D$ in the first excited singlet state of five carboxylic acids are listed in Table IV. Experimental $\Delta pK^*$ values are compared with those predicted from eq. 4. With the exception of 2-naphthoic acid, agreement is surprisingly good, especially if the $Z$ term is dropped in the case of 4-sulfobenzoic acid. It is thus concluded that quantitative descriptions of isotope effects in the ground states of aromatic alcohols and carboxylic acids can be applied with reasonable precision to electronically excited states of the compounds. It was previously demonstrated that a similar statement obtains for substituent effects upon the acidity of excited phenols.[8] It therefore is concluded that ground-state parameters often may be of considerable utility in predicting the chemical properties of electronically excited species.

**Table IV.** Excited Singlet-State $pK_H$ and $pK_D$ Values for Carboxylic Acids

| Compound | $pK_H^*$ | $pK_D^*$ | $pK_{obsd}^*$ | $pK_{prepd}^{*a}$ |
|---|---|---|---|---|
| Benzoic acid | 9.5 | 10.1 | +0.6 | +0.59 |
| 2-Chlorobenzoic acid | 8.1 | 8.7 | +0.6 | +0.57 |
| 4-Sulfobenzoic acid | 9.1 | 9.7 | +0.6 | +0.71<br>(+0.59)[b] |
| 1-Naphthoic acid | 10.0 | 10.6 | +0.6 | +0.60 |
| 2-Naphthoic acid | 11.5 | 12.3 | +0.8 | +0.62 |

[a] As calculated from eq. 4. [b] The $Z$ term in eq. 4 was neglected in calculating the value in parentheses.

It is interesting to note that the magnitude of the isotope effect in an excited phenol was smaller than that in the ground state of the same compound, whereas the isotope perturbation for an excited aromatic carboxylic acid was larger. This is exactly the result which would be predicted from the assumption that acid strength, rather than charge or "acid type" effects, is the predominant factor in determining the magnitude of the isotope effect. Since the acidity of a phenol increases upon excitation, whereas that of a carboxylic acid decreases, the study of isotope effects upon the protolytic dissociation of organic acids in excited states provides a unique tool for demonstrating the dependence of $\Delta pK$ on $pK_H$.

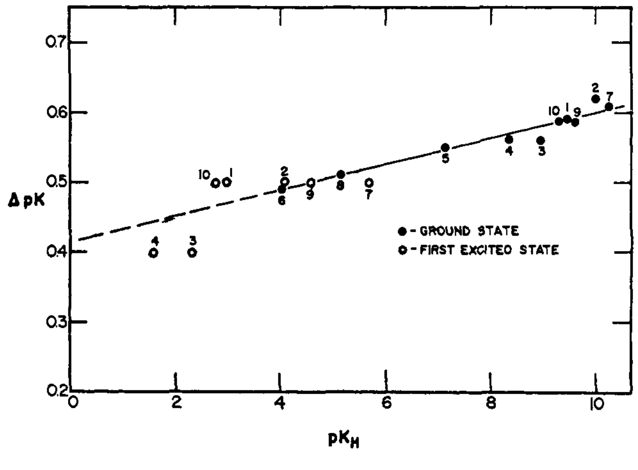

Figure 1. Plot of $pK_D - pK_H$ *vs.* $pK_H$ in ground and first excited singlet states of 2-naphthol (**1**), phenol (**2**), 4-phenolsulfonate (**3**), 4-hydroxyphenyltrimethylammonium chloride (**4**), 4-nitrophenol (**5**), 2,4-dinitrophenol (**6**), 4-methoxyphenol (**7**), 2,5-dinitrophenol (**8**), 3-methoxyphenol (**9**), and 4-bromophenol (**10**).

Thus far, the discussion has been restricted to "pure" water and deuterium oxide. In the past, acid strengths in mixed $H_2O$–$D_2O$ solvents have been the subject of several investigations. The earliest quantitative treatment in that regard was reported by Gross and coworkers.[17] The mathematical relationship developed

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(17) P. Gross, H. Steiner, and F. Krauss, *Trans. Faraday Soc.*, **32**, 877 (1936); P. Gross, H. Steiner, and H. Suess, *ibid.*, **32**, 883 (1936).

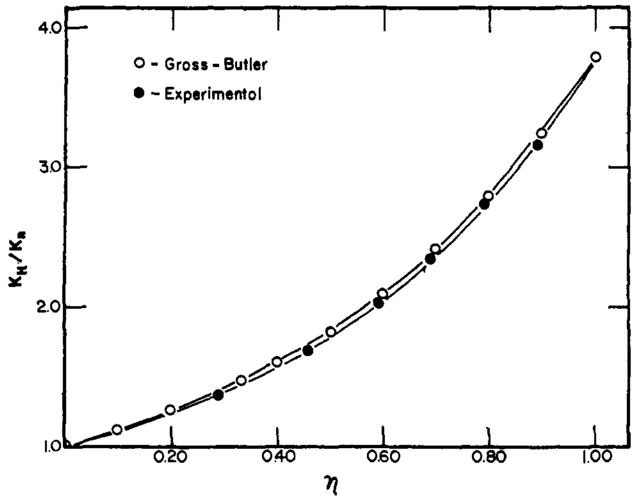

Figure 2. Variation of $K_H/K_n$ with $n$ for 2-naphthol in the ground state.

from this theory is now usually called the "Gross–Butler equation," which may be written

$$\frac{K_H}{K_n} = \frac{1 - n + n\phi}{(1 - n + nl)^3}$$

$$\phi = l^3(K_H/K_D) \qquad (5)$$

where $K_n$ is the acidity constant in a water–heavy water solvent mixture of $n$ atom fraction deuterium, and $l$ is a parameter, usually assumed to equal 0.67.[13,18] Generally, the Gross–Butler equation fits experimental data very well for weak, monobasic acids; more refined equations must be used for strong acids.[13,19]

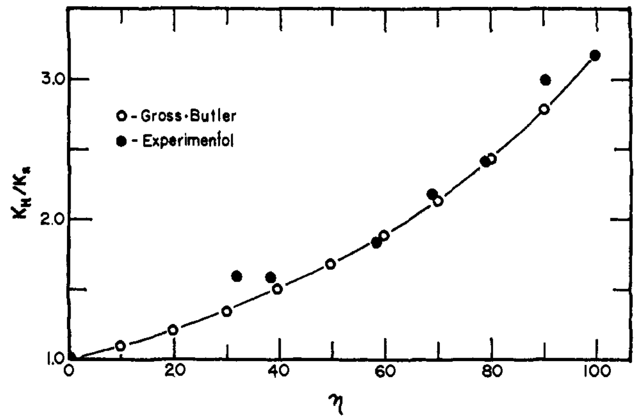

Figure 3. Variation of $K_H/K_n$ with $n$ for 2-naphthol in the first excited singlet state.

In the present study, the variation of $K_H/K_n$ was measured as a function of $n$ for 2-naphthol in its ground and first excited singlet states; the experimental results are compared with the curves predicted from the Gross–Butler equation in Figures 2 and 3. Agreement between theory and experiment is excellent for the ground state, and, considering the uncertainties involved in measuring excited-state acidities, the agreement is surprisingly good for the first excited singlet. To a first approximation, it is concluded that the Gross–Butler equation adequately predicts $pK_n$ values in mixed $D_2O$–$H_2O$ solvents, provided that $pK_H{}^*$ is fairly large. This observation lends further support to the observation that magnitudes of equilibrium isotope effects in electronically excited aromatic compounds can be predicted, with a surprising degree of accuracy, from ground-state equations and parameters.

[18] A. J. Kresge and A. L. Allred, *J. Am. Chem. Soc.*, **85**, 1541 (1963).

[19] E. L. Purlee, *ibid.*, **81**, 263 (1959); V. Gold, *Trans. Faraday Soc.*, **56**, 255 (1960).

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# Substituent Effects. V.[1,2] Further Evidence Concerning the Nature of the Inductive Effect

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**Abstract:** The ultraviolet absorption spectra of *m*- and *p*-aminophenyltrimethylammonium ions, of *m*- and *p*-trifluoromethylaniline, and of β- and γ-aminopyridine have been compared with that of aniline; the results suggest that the "inductive" substituent $CF_3$ operates mainly by a field effect rather than by a π-inductive effect. This conclusion was also supported by comparisons of the proton n.m.r. spectra of *p*-tolyl- and *p*-methylbenzyltrimethylammonium ions, of *p*-trifluoromethyltoluene, and of γ-picoline in various solvents.

There are a number of different ways in which a substituent can influence a distant reaction center; the purpose of the work described in this series of papers is to assess the relative importance of the possible modes of action of substituents, and to establish some procedure for estimating the effects of given substituents in arbitrary molecules. The first four papers of this series described a study of substituent effects in naphthalene; in them it was concluded that the so-called "inductive effect" of classical organic theory is in fact a direct field

[1] This work was supported by the Army Research Office through Grant DA-ARO-D-31-124-G496.

[2] Part IV: M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.*, **84**, 3548 (1962).

[3] N.A.S.A. Predoctoral Fellow, 1962–1964; National Institutes of Health Predoctoral Fellow, 1964–1965.