to be remarkably stable and possesses rather unexpected properties.

The synthesis was accomplished by adding dinitrogen tetroxide to solid [Me$_4$N][BCl$_4$] at −78° (mole ratio $N_2O_4/BCl_4^- > 8:1$); the system was then allowed to warm to 0° over a period of approximately 2 hr. The removal of the excess dinitrogen tetroxide, along with the nitrosyl chloride produced in the reaction, was effected at room temperature, leaving a white, crystalline solid with the approximate composition for the desired product. Prolonged contact with dinitrogen tetroxide, or carrying out the reaction at room temperature, increased the oxynitrate or boric oxide content. Extraction with ammonia removed the complex nitrate, leaving the oxide behind. The solid recovered from the filtrate was analyzed. *Anal.* Calcd for [Me$_4$N][B(NO$_3$)$_4$]: C, 14.41; H, 3.69; B, 3.30; Me$_4$N$^+$, 22.22; N (Devarda), 16.81. Found: C, 14.6; H, 4.8; B, 3.32; Me$_4$N$^+$, 22.42; N (Devarda), 16.94.[4]

The X-ray powder pattern of the solid was obtained by using Cu Kα radiation and is shown in Table I. The pattern shows no reflections for tetramethylammonium nitrate, a likely impurity.

Table I

d, A	RI[a]	*d*, A	RI	*d*, A	RI
7.25	s	3.39	s	2.35	w
5.70	m	3.29	w	2.32	w
5.15	s	3.19	w	2.20	vw
4.90	vw	3.15	w	2.15	vw
4.70	vw	3.05	m	2.02	w
4.40	m	2.82	w	1.98	w
3.90	vw	2.64	w	1.94	w
3.80	vs	2.60	w	1.91	w
3.60	w	2.49	w	1.88	w
3.45	w	2.45	w		

[a] Relative intensity.

The infrared spectrum in Nujol and KBr shows lines at 669, 743, 755, 767, 887, 950, 1007, 1297, 1311, 1356, 1385, 1416, 1489, 1582, 1612, and 1626 cm.$^{-1}$ The absorptions for ν_4 at 1582 to 1626 cm^{-1} and for ν_1 at 1297 and 1311 cm^{-1} are the two prominent bands. The 1582- and 1626-cm^{-1} lines appear as shoulders on the 1612-cm^{-1} lines. This splitting of the ν_4 and ν_1 absorptions together with the (ν_4–ν_1) separation of 271 to 339 cm^{-1} are expected for unidentate nitrato bonding.[5,6] Ionic nitrate vibrations at ~1330 cm^{-1} for tetramethylammonium nitrate were absent from the spectrum.

Molecular weight determinations in acetonitrile in a concentration range of 0.045 to 0.288 *m* gave a value of 185 ± 15. The theory for [Me$_4$N][B(NO$_3$)$_4$], assuming complete dissociation into two ions, is 166.5. Conductance measurements support dissociation. Equivalent conductance values obtained in acetonitrile at 18° are listed in Table II. A plot of Λ against the square root of the concentration is linear and extrapolates to an equivalent conductance of 210 ohm^{-1} cm^{-2} at infinite dilution. Berns and Fuoss[7] report an equivalent conductance for [Me$_4$N]NO$_3$ in acetonitrile at 25° of 200.5 ohm^{-1} cm^{-2} at infinite dilution. Thus dissociation into two ions is clearly indicated. If the conductivity data are used to calculate the measured molecular weight in the concentration range indicated, a value of about 205 is obtained which checks well with the measured value of 185 ± 15. A preliminary ^{11}B nmr spectrum shows the single expected peak with a chemical shift value of 44.0 ppm relative to NaBH$_4$ in acetonitrile. If the δ value for NaBH$_4$ in acetonitrile is comparable to its value in H$_2$O, [Me$_4$N][B(NO$_3$)$_4$] has a chemical shift value comparable to NaB(C$_6$H$_5$)$_4$ and NaB(OMe)$_4$.

Table II

Concn[a]	Λ[b]	Concn	Λ
0.123	135	0.012	157
0.06	132	0.006	170
0.024	157	0.0024	184

[a] Molal. [b] In ohm^{-1} cm^{-2}.

The complex is not noticeably soluble in, nor hydrolyzed by cold water. Some solubility is indicated in hot water. It is readily soluble in methanol, acetonitrile, ammonia, and dimethylformamide from which it can be recovered unchanged. Reaction occurs with sulfur dioxide to give products as yet unknown. As mentioned previously, a slow reaction occurs in dinitrogen tetroxide producing the boron oxide linkage.

[Me$_4$N][B(NO$_3$)$_4$] is stable at room temperature; samples have been stored for periods of more than 2 months without noticeable decomposition. The compound is insensitive to shock when struck sharply with a hammer.

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(4) The total nitrogen by the Dumas method was 19.6% *vs.* the theoretical value of 21.02%. It has been our experience, however, with tetramethylammonium compounds and complex nitrates in general, that values slightly lower than theoretical are to be expected. The nitrogen balance obtained by adding Devarda (NO$_3^-$) and tetramethylammonium analyses was 21.18%, or nearly theoretical (21.02%).

(5) K. W. Bagnell, D. Brown, and J. G. H. duPreez, *J. Chem. Soc.*, 5523 (1964).

(6) B. O. Field and C. J. Hardy, *Quart. Rev.* (London), **18**, 385 (1964).

(7) D. S. Berns and R. M. Fuoss, *J. Am. Chem. Soc.*, **83**, 1321 (1961).

C. R. Guibert, M. D. Marshall
Callery Chemical Company
Callery, Pennsylvania

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Spin–Spin Coupling in Primary Alcohols

Sir:

We have measured the spin–spin coupling constant, J_{HCOH}, for a wide variety of primary alcohols in CCl$_4$ solution[1] and have found that J_{HCOH} for 0.22 *M* solutions (see Table I) increases as the electronegativity of the hydroxyl carbon is increased.[2] This conclusion

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(1) Measurements were made at 23° on a Varian HR-100 nmr spectrometer, using calibration by the usual audio side-band technique and CCl$_4$ dried over Linde Type 13-X molecular sieve. When the hydroxyl proton failed to show sharp splitting initially, the alcohol was purified by distillation, or by drying over molecular sieve, or by passing through a column of alumina or silica gel–molecular sieve; for troublesome cases a small amount of activated alumina was added to the nmr sample tube.

(2) A positive sign for J_{HCOH} has been established for 2-methyl-2-

is justified by the good fit (correlation coefficient of 0.95) of our data to the equation $J_{\mathrm{HCOH}} = 5.6 + 1.9\sigma^*$, where σ^* is Taft's polar substituent constant for RCH_2 in RCH_2OH.[3] Our correlation is indeed unusual because all reported correlations of vicinal proton–proton coupling constants with electronegativity require that *J decrease* with increasing electronegativity.[4] An increase in the vicinal coupling constant with an increase in electronegativity of the substituent(s) on the β-carbon atom occurs in some cases in which either the substituent variation was not sufficiently extensive or the change in *J* was not large enough to justify a definitive correlation.[5,6] Also, in none of these cases does the coupling occur across a bond containing an oxygen atom.

Table I also gives J_{HCOH} for 0.22 *M* solutions in dimethyl sulfoxide (DMSO),[7] including J_{HCOH} for Cl_3CCH_2OH and $NCCH_2CH_2OH$. Traynham and Knesel[8] failed to observe methylene–hydroxyl coupling for the latter alcohols in DMSO and concluded that alcohols with electron-withdrawing substituents close to the hydroxyl function do not show coupling, or do so only after extensive purification. In contrast to the difficulties which we experienced with CCl_4 solutions and which Traynham reported for DMSO solutions, we found that no special treatment was required to obtain splitting of the hydroxyl resonance in DMSO dried over Linde Type 13-X molecular sieve. It is possible that the high alcohol concentrations used by Traynham and Knesel (10–30 vol. %) were responsible for the absence of observable coupling.

Finally, the data in Table I show that replacement of CCl_4 by DMSO causes J_{HCOH} for a particular alcohol to decrease, and a "leveling effect" on the total range of J_{HCOH} values. However, the correlation of J_{HCOH} with σ^* is still qualitatively preserved in DMSO.

Table I. Observed Spin–Spin Coupling Constants for Some Primary Alcohols

	Spin–Spin Coupling Constant, J_{HCOH}, cps[a]	
R in RCH_2OH	CCl_4 solvent	DMSO solvent
$(NO_2)_3C$	8.3 ± 0.2	6.9 ± 0.2[b]
$CH_3C(NO_2)_2$	7.4 ± 0.2	6.2 ± 0.2
$(CH_3)_2C(NO_2)$	6.7 ± 0.2	5.7 ± 0.1
NO_2CH_2	6.6 ± 0.2[c]	5.2 ± 0.2
Br_3C	8.0 ± 0.2	6.6 ± 0.2
Cl_3C	7.8 ± 0.2	6.8 ± 0.2
F_3C	7.4 ± 0.2	6.7 ± 0.2
Cl_2HC	7.4 ± 0.2	6.4 ± 0.1
$BrCH_2$	6.6 ± 0.1	5.5 ± 0.1
$ClCH_2$	6.4 ± 0.1	*d*
$HC{\equiv}C$	6.1 ± 0.2	6.0 ± 0.2
$H_2C{=}CH$	5.9 ± 0.1	5.5 ± 0.1
C_6H_5	5.9 ± 0.1	5.6 ± 0.2
CH_3	5.1 ± 0.1	5.0 ± 0.1
H	5.3 ± 0.2	5.2 ± 0.1
$(CH_3)_3C$	5.7 ± 0.2	5.4 ± 0.3
$CH_3CH_2OCH_2$	6.0 ± 0.2	5.2 ± 0.2
CH_3OCH_2	6.1 ± 0.1	5.2 ± 0.1
$C_6H_5OCH_2$	6.1 ± 0.1	5.5 ± 0.1
$C_6H_5CH_2OCH_2$	6.0 ± 0.1	4.9 ± 0.2
$NCCH_2$	6.2 ± 0.2[c]	5.3 ± 0.1
$C_6H_5CH_2$	*e*	5.1 ± 0.1

[a] Measured at 23° on 0.22 *M* solutions with a Varian HR-100 nmr spectrometer. Standard deviation follows each J_{HCOH} value. [b] Acetone solvent. This alcohol is degraded rapidly by DMSO. [c] Saturation concentration, *ca.* 0.05 *M.* [d] A split hydroxyl peak is superimposed on the methylene resonance, making interpretation difficult. A similar degeneracy also has been observed at 60 Mc (R. W. King, private communication). [e] Splitting could not be observed.

We can rationalize the decrease in J_{HCOH} when CCl_4 is replaced by DMSO in terms of hydrogen bonding of the hydroxyl groups by DMSO: (i) The observed coupling constant is a weighted average of the coupling constants of the conformational isomers—in the case of primary alcohols the treatment is analogous to that for H–F coupling in the hindered rotator, $CHCl_2CF_2Cl$.[9] From the temperature dependence of J_{HCOH} for methyl and ethyl alcohols (50% in acetone) it was concluded that the barrier to rotation about the C–O bond of these alcohols is <100 cal/mole (see Abraham, ref. 7). Our results for DMSO indicate that the C–O bond may be hindered to a greater extent in the bulkier alcohols. Hydrogen bonding with the solvent should increase the preference of the O–H bond for a position *trans* to the R group or *gauche* to the methylene protons. If the angular dependence of spin–spin coupling through the C–O bond is similar to that of the C–C bond,[10] J_{HCOH} would be smaller in a good hydrogen-bonding solvent (DMSO) than in a poor hydrogen-bonding solvent (CCl_4). Molecular models show that most of the alcohols in Table I are at least somewhat hindered, and so it is possible that their *J* values, even for CCl_4, are weighted in favor of J_{gauche}. (ii) The electron density in the C–O or O–H bond may be altered significantly by hydrogen bonding. We have found that replacement of CCl_4 by DMSO causes an upfield shift of 0.04 to 0.27 ppm in the methylene proton resonance as well as downfield shifts to τ values between 3 and 6 in the hydroxyl resonance.[11]

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nitro-1,3-propanediol by F. Hruska, T. Schaefer, and C. A. Reilly, *Can. J. Chem.*, **42**, 697 (1964). Since all of our J_{HCOH} values are greater than 5 cps, it is likely that there is no reversal in the sign of J_{HCOH} in our series and that all our J_{HCOH} values are positive. We are attempting to confirm the sign of J_{HCOH} by multiple irradiation experiments.

(3) The methylene carbon in RCH_2 has roughly the same degree of hybridization for all the alcohols in our series, and so a good measure of the electronegativity of this carbon can be taken as σ^* for RCH_2. See R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 616.

(4) References to these correlations are given by T. Schaefer, F. Hruska, and G. Kotowycz, *Can. J. Chem.*, **43**, 75 (1965).

(5) For example: (a) monosubstituted cyclopropanes *vs.* the corresponding *gem*-dichlorocyclopropanes (see reference cited in footnote 4); (b) protonated vs. unprotonated 2-substituted thiazoles (G. M. Clarke and D. H. Williams, *J. Chem Soc.*, 4597 (1965)); (c) disubstituted thiophenes (K. Takahashi, T. Sone, Y. Matsuki, and G. Hazato, *Bull. Chem. Soc. Japan*, **36**, 108 (1963)); (d) disubstituted benzenes (J. Martin and B. P. Dailey, *J. Chem. Phys.*, **37**, 2594 (1962); D. M. Grant, R. C. Hirst, and H. S. Gutowsky, *ibid.*, **38**, 470 (1963); R. Freeman, N. S. Bhacca, and C. A. Reilly, *ibid.*, **38**, 293 (1963); S. Clough, *Mol. Phys.*, **2**, 349 (1959)); (e) coupling between the methyl and olefinic protons in 1-halopropenes (R. A. Beaudet and J. D. Baldeschwieler, *J. Mol. Spectry.*, **9**, 30 (1962); M. Y. DeWolf and J. D. Baldeschwieler, *ibid.*, **13**, 344 (1964)); (f) five-membered rings (K. W. Buck, A. B. Foster, A. R. Perry, and J. M. Webber, *Chem. Commun.*, 433 (1965)); (g) 3-fluoropropenes (A. A. Bothner-By, S. Castellano, and H. Günther, *J. Am. Chem. Soc.*, **87**, 2439 (1965)).

(6) We thank a referee for bringing to our attention ref 5c–e,g. We were first made aware of the trends in substituted propenes by Dr. T. Schaefer (private communication).

(7) The use of hydrogen-bonding solvents facilitates the study of the hydroxyl resonance of alcohols by nmr. For the use of acetone see R. J. Abraham, *Proc. Colloq. AMPERE*, **11**, 589 (1962). For the use of DMSO see D. E. McGreer and M. M. Mocek, *J. Chem. Educ.*, **40**, 358 (1963), and O. L. Chapman and R. W. King, *J. Am. Chem. Soc.*, **86**, 1256 (1964).

(8) J. G. Traynham and G. A. Knesel, *ibid.*, **87**, 4220 (1965).

(9) R. W. Fessenden and J. Waugh, *J. Chem. Phys.*, **37**, 1466 (1962).

(10) M. Karplus, *ibid.*, **30**, 11 (1959).

(11) Chapman and King[7] have also noted this effect.

Other factors may cause J to decrease when CCl_4 is replaced by DMSO, but we consider them to be of secondary importance to those already mentioned. For example, intramolecular hydrogen bonding in the nitro- and halo-substituted alcohols[12] and modification of the electron-withdrawing power of R by solvation might be considered.

W. B. Moniz, C. F. Poranski, Jr.
U. S. Naval Research Laboratory
Washington, D. C. 20390

T. N. Hall
U. S. Naval Ordnance Laboratory
White Oak, Silver Spring, Maryland 20910

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(12) Evidence for such bonding is given by P. J. Krueger and H. D. Mettee, *Can. J. Chem.*, 42, 340 (1964), and by W. F. Baitinger, P. von R. Schleyer, T. S. S. R. Murty, and L. Robinson, *Tetrahedron*, 20, 1635 (1964).

Book Reviews

Phase Transitions. By Robert Brout, University of Brussels. W. A. Benjamin, Inc., 1 Park Ave., New York, N. Y. 1965. xiii + 202 pp. 16 × 23.5 cm. $9.00.

The molecular theory of phase transitions, under investigation since the earliest days of statistical mechanics, is still largely not understood. Only for highly idealized models (two-dimensional Ising lattice, ideal Bose gas, Kac-Uhlenbeck model) can one give anything like a complete and rigorous discussion based on the principles of statistical thermodynamics. Realistic models (even as simple as a collection of atoms interacting by Lennard-Jones potentials) are presently out of reach by exact methods. Over the years, a number of approximation schemes have been developed: one particularly attractive one is based on the idea of a self-consistent field. (An illustration is the Bragg–Williams method in the theory of order–disorder transitions.)

"Phase Transitions" surveys formulations and applications of the self-consistent field method. The formulations are sometimes based on simple physical pictures (as in the original molecular field theory of ferromagnetism) and sometimes on rather highbrow techniques of many-body theory. In particular, about one-third of the book deals with "graphology," essentially a set of variations on the theme of the classic Ursell-Mayer virial expansion. Self-consistent field arguments are used in connection with the Ising lattice, the liquid–gas transition, freezing, ferromagnetism, superconductivity, and superfluidity. It seems to this reviewer that the results obtained from self-consistent field arguments are seldom quantitatively correct in the neighborhood of phase transitions, and sometimes not even qualitatively correct. Nevertheless, one often learns more from failure than from success.

The book grew out of sets of lecture notes, and the general style is relaxed and chatty. It was up-to-date in March 1964, as indicated by the many footnotes and other comments Added In Proof. The reader will surely be charmed by the modest way in which the author calls attention to, and corrects, mistakes in the text and in his earlier articles. It can be recommended to serious students of statistical mechanics, both as a survey of applications of the self-consistent field method, and as an introduction to "graphology."

Robert Zwanzig
Physical Chemistry Division, Institute for Basic Standards
National Bureau of Standards, Washington, D. C.

BOOKS RECEIVED, *November 1965*

E. J. Ambrose, Editor. "Cell Electrophoresis. A Symposium Convened by the British Biophysical Society." Little Brown and Co., 34 Beacon St., Boston, Mass. 1965. 204 pp. $10.00.

Vladimír Bažant, Václav Chvalovský, and Jiří Rathouský. "Organosilicon Compounds." Volume 1. Chemistry of Organosilicon Compounds." Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1965. 616 pp. $25.00.

Vladimír Bažant, Václav Chvalovský, and Jiří Rathouský. "Organosilicon Compounds." Volume 2. Part 1. "Register of Organosilicon Compounds." Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1965. 699 pp. $25.00.

Vladimír Bažant, Václav Chvalovský, and Jiří Rathouský. "Organosilicon Compounds." Volume 2. Part 2. "Register of Organosilicon Compounds." Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1965. 544 pp. $25.00.

Ronald Breslow. "Organic Reaction Mechanisms. An Introduction." W. A. Benjamin, Inc., 1 Park Ave., New York, N. Y. 1965. 232 pp. $7.00.

Paul A. D. de Maine. "Digital Computer Programs for Physical Chemistry." Volume II. "Autoplotter, Expansion, Self-Judgment, Spectral, Polarization, Conductance, Kinetic, and Special Iterative Programs." The Macmillan Co., 60 Fifth Ave., New York, N. Y. 1965. 493 pp. $19.95.

Bodie E. Douglas and Darl H. McDaniel. "Concepts and Models of Inorganic Chemistry." Blaisdell Publishing Co., 35 West 50th St., New York, N. Y. 1965. 510 pp. $10.50.

Roderick P. Kernan. "Cell K." Butterworth Inc., 7235 Wisconsin Ave., Washington, D. C. 1965. 152 pp. $5.75.

G. Kortüm. "Treatise on Electrochemistry." American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 1965. 637 pp. $30.00.

K. Macek and I. M. Hais, Editors. "Stationary Phase in Paper and Thin-Layer Chromatography. Proceedings of the 2nd Symposium Held at Liblice, June 10–12, 1964." American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 1965. 358 pp. $16.00.

R. A. Morton, Editor. "Biochemistry of Quinones." Academic Press Inc., Ltd., Berkeley Square House, Berkeley Square, London, W1, England. 1965. 585 pp. $18.00.

Eugene Müller, Editor. With O. Bayer, H. Meerwein, and K. Ziegler. "Methoden der Organischen Chemie (Houben-Weyl). Vierte, Völlig neu Gestaltete Auflage." Band X/3. "Stickstoff-Verbindungen I." Teil 3. Georg Thieme Verlag, Pastfach 732, Herdweg 63, Stuttgart 1, Germany. 1965. 971 pp. DM 255.

D. D. Perrin. "Dissociation Constants of Organic Bases in Aqueous Solution." Butterworth Inc., 7235 Wisconsin Ave., Washington, D. C. 1965. 473 pp. $28.00.

Eberhard Schröeder and Klaus Lübke. Translated by Erhard Gross. "The Peptides." Volume I. "Methods of Peptide Synthesis." Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1965. 481 pp. $20.00.

Rolf Strohecker and Heinz M. Henning. Translated by D. D. Libman. "Vitamin Assay. Tested Methods." Verlag Chemie, G.m.b.H., Weinheim/Bergstr., Germany. 1965. 360 pp. $12.00.