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Monthly  
Ecumenical  
Letters from  
Laboratories  
Of  
N-M-R

No. 3

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AN APPEAL

The ASTM group (v.i.) considering referencing techniques and reference compounds for all nuclei has the following members:

Paul C. Lauterbur, Chairman  
Donald P. Ames  
Harlan Foster  
George V. D. Tiers  
John R. Zimmerman

Ideas and suggestions concerning any phase of the group's work are invited. For example, if you have experience in any of the following areas, we would like to hear from you.

1. Use of external and/or internal standards for correlating large volumes of data.
2. Construction of spherical sample cells, or use of other special referencing apparatus and techniques.
3. Standards and referencing methods for nuclei other than protons.

Communications on these matters may be addressed to me personally or to AAB or BLS for inclusion in this Newsletter.

Paul C. Lauterbur  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh 13, Pa.

## Minutes of the Meeting

ASTM Committee E-13 Subcommittee VII on NMR Spectroscopy

New York, November 6, 1958

## Subcommittee Members in Attendance:

N. F. Chamberlain, Chairman  
S. Brownstein, Secretary  
D. P. Ames  
H. Foster  
B. Jones, in place of J. N. Shoolery  
J. E. Lancaster  
P. C. Lauterbur  
H. Rubin, in place of A. R. Aikman  
R. E. Swarbrick  
G. V. D. Tiers  
J. R. Zimmerman

## In addition

E. J. Rosenbaum, Chairman Committee E-13  
R. F. Robey, Secretary Committee E-13  
A. D. Turissini  
I. Weinberg

were present and interested in the work of the committee.

The meeting was called to order by Mr. Chamberlain at 2:00 p.m. Dr. Brownstein was elected secretary for this meeting. Suggested areas of investigation, derived from suggestions made by subcommittee members before the meeting, were outlined by Mr. Chamberlain as follows:

1. Nomenclature to be used in discussing details of NMR spectra.
2. Referencing techniques and reference compounds.
3. Resonance spectra of nuclei other than protons.
4. Presentation of data obtained from NMR spectra.
5. Instrument performance and specifications.
6. Effects of sample temperature
7. Spin decoupling procedures.
8. Exchange of information.

Items 1 through 4 were selected by vote of those present as being the most important and promising problems for immediate attack. Chairmen were selected for work groups to work on these problems. Each chairman is responsible for recruiting his own work group and directing its activities. After a work group has reached agreement on a convenient segment of its work, its recommendations are to be circulated to the entire NMR subcommittee for comments. When the subcommittee has reached agreement, its recommendations will be circulated to other subcommittees of Committee E-13 which are concerned with broadly similar types of work to reduce conflict and duplication within the broad field of absorption spectroscopy. Then follows the job of selling these recommendations to the workers and editors, a problem which the ASTM organization has handled successfully for many years.

Dr. G. V. D. Tiers was selected chairman of the group to study the problem of nomenclature. After conclusions on nomenclature have been reached, they are to be submitted to the Nomenclature Subcommittee of E-13 to insure compatibility with the overall approach of Committee E-13.

Since the problem of referencing and of the consideration of spectra of nuclei other than protons overlap considerably, it was decided that one group should consider both problems. Dr. P. C. Lauterbur was chosen chairman of this group. No chairman has yet been chosen for the data presentation group.

It was decided that items 5, 6 and 7 need not be given detailed study at the present time; however, some opinions were expressed on these topics.

The question of the necessity for precision cells for external referencing was raised by Mr. Chamberlain and a plea was made for some experimental data. Dr. Zimmerman commented that this is being investigated by the API project on nuclear magnetic resonance\*. It was mentioned that measurement of peak separations should be done by the sideband method unless a resonance-stabilized magnetic field is used. Dr. Rosenbaum said that care should be taken in setting up performance specifications to insure that the requirements are consistent with the purpose for which the spectra are to be used.

With respect to item 8, it was announced that the NMR research group at Mellon Institute has started circulation of a monthly news-letter of current information in NMR spectroscopy. This is an informal letter, and circulation will be held to those active in the field.

It was announced that the ASTM will be holding a Pacific Coast Regional Meeting in San Francisco on October 11-16, 1959. There will be a half-day symposium on NMR with Emery Rogers of Varian Associates as chairman.

There were varying opinions on when the next meeting of the group should be held. It was tentatively decided to meet at the Pittsburgh Meeting on Applied Spectroscopy, the first week of March, 1959.

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\*See M.E.L.L.O.N.M.R. No. 2 p. 12.

4.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY  
DEPARTMENT OF CHEMISTRY  
CAMBRIDGE 39, MASSACHUSETTS

December 8, 1958

Dr. A. A. Bothner-By,  
Mellon Institute,  
Pittsburgh.

Dear Aksel:

I promised Barry some time ago that I would send him the enclosed material, but only the arrival of the second issue of the Journal of Unpublished Research has finally prompted me to do it.

Historically this came about as a result of my surprise at seeing Tiers' account of the "isotope effect" on the  $F^{19}$  resonance of 1-hydropropoforane (!). Since then the reasons for surprise have largely evaporated, but at the time I asked a Senior thesis student, Harvey Notarius, to repeat Tiers' measurements in order to see the effect at first hand. As you see, Notarius' measurements corroborate Tiers' statement. There are however a few points which Tiers' note does not state or else does not make clear, videlicet:

1. This is another case in which the coupling between the most distant  $F^{19}$  groups is larger (7 cps) than either of the shorter-range F-F couplings ( $4\frac{1}{2}$  and about zero).


2. The proton resonance is a very pretty triplet of triplets of quartets (!) with couplings to the fluorines of 52,  $4\frac{1}{2}$  and 0.8 cps, respectively.

3. The  $\alpha-F^{19}$  resonance of the deuterated compound agrees exactly with that calculated from that of the nondeuterated compound and the gyromagnetic ratio of D. It contains 36 lines, of which most are cleanly resolved.

For those who read Tier's note in reprint form, it should be pointed out that the texts of the original note and of the reprint are not the same, apparently through a printer's error.

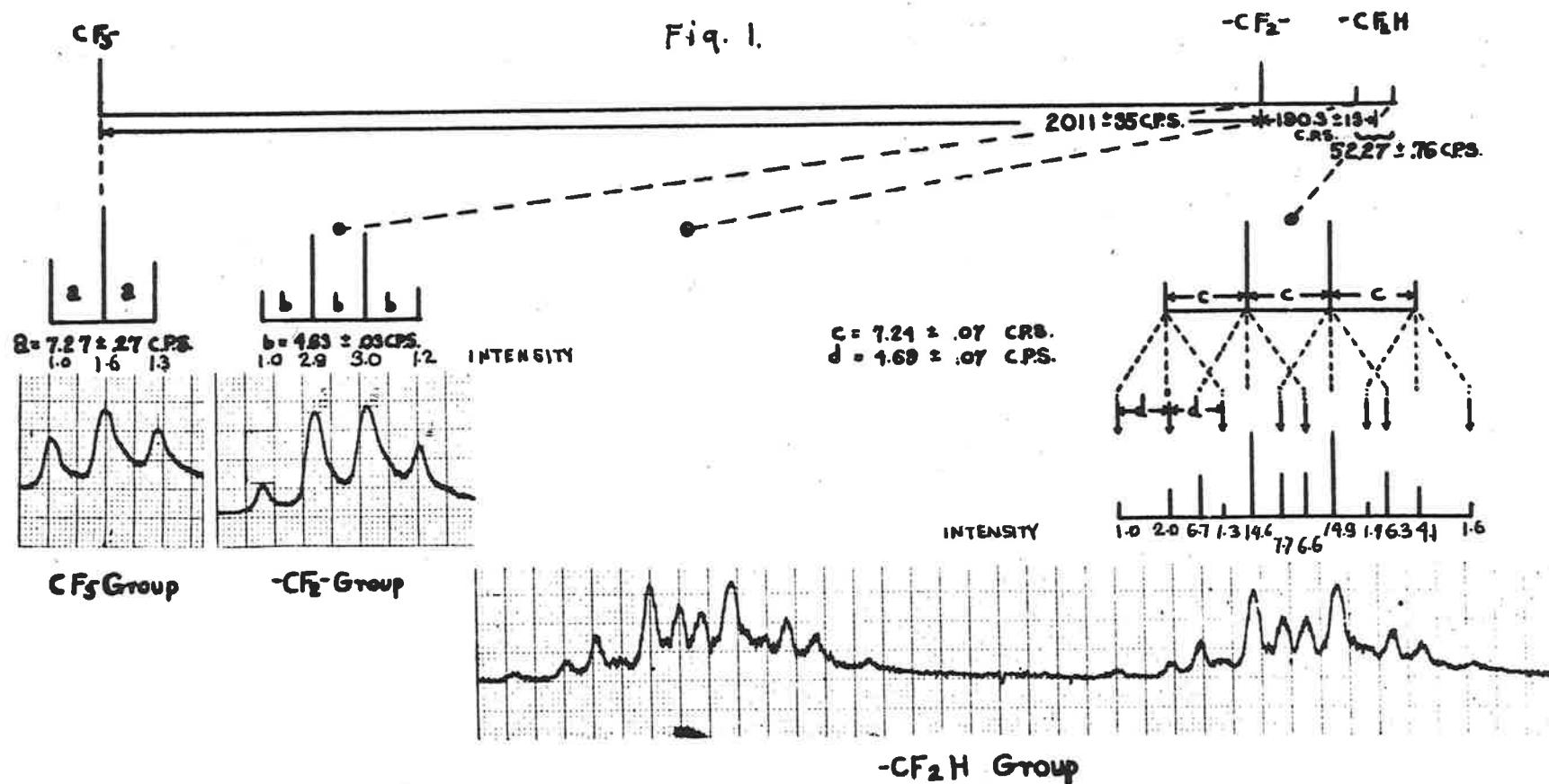
Please feel free to file this in the wastebasket if you like, but return the enclosed figure to me.

Yours,

  
John S. Waugh

Spectrum of the  $F^{19}$  Resonance in  $CF_3-CF_2-CF_2H$  Shown under increasing degrees of Resolution  
 Values are those experimentally observed.

P.5.



5.

## A METHOD OF ESTIMATING CHEMICAL SHIFTS IN SUBSTITUTED METHANES

One of the problems encountered in interpreting High-Resolution NMR spectra is that of making assignments of the lines to specific chemical groups. Although the integrated intensities are of some value, it is often very important to be able to estimate fairly closely where the resonance of a particular group should fall. Since any carbon atom in a chain can be considered as a substituted methane, it seemed worthwhile to investigate the "additivity" of the shielding effects of various possible substituent groups.

In this work it is very important to eliminate as far as possible all solvent effects; therefore, only data from G.V.D. Tiers' "Table of Characteristic NMR Shielding Values" plus a few measurements made in our own laboratory using dilute solutions in  $\text{CDCl}_3$  were used.

No effort was made to consider whether the shielding effect of a group arises from diamagnetic or paramagnetic effects. All of the groups considered turned out to exert a net paramagnetic shielding on the remaining protons when they replaced a proton in methane. Surprisingly good "additivity" was found for the average values finally chosen to represent each group. The serious departures from "additivity" occurred in the case of substituents with strong magnetic anisotropy. In such cases, even small molecular distortions may become important.

Since electron withdrawing effects are known to be important<sup>1</sup>, it is necessary to take into account the fact that it becomes progressively harder to extract electrons from a carbon atom as one attaches additional electronegative groups. This was done by taking an average for several successive substitutions, as, for example,  $\text{CH}_4$  to  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Cl}$  to  $\text{CH}_2\text{Cl}_2$ , and  $\text{CH}_2\text{Cl}_2$  to  $\text{CHCl}_3$ . Similar series for other substituents were considered wherever the data were available. The number finally chosen for each substituent usually represented the average of the first and second substitutions, weighted a little more heavily in favor of the first substitution. Therefore, the shielding "constants" cannot be used to predict

(1) B.P. Dailey and J.N. Shoolery, J.A.C.S. 77, 3977 (1955)

the shifts of mono-substituted methanes accurately, but these are already measured very precisely and recorded in Tiers' Table.

The shifts of the methyl protons in  $\text{CCl}_4$  solutions of methane, ethane, propane, and butane are 375.5, 337.5, 335.1, and 335.9 cps, respectively, at 60 mc relative to benzene in a concentric cell. The value for methane was taken as the constant in the empirical equation for estimating the shift of the protons in a substituted methane with substituents  $i$ .

$$\delta \text{ (cps)} = 375.5 - \sum_i \sigma_i^{\text{eff}} \text{ (cps) relative to external benzene at 60 mc}$$

or

$$\delta \text{ (ppm)} = 9.767 - \sum_i \sigma_i^{\text{eff}} \text{ (ppm) relative to internal } (\text{CH}_3)_4\text{Si} = 10.00 \text{ at any frequency}$$

Values of  $\sigma_i^{\text{eff}}$ , the effective shielding constants for various groups, are listed in Table I in cps at 60 mc and also in parts per million. The shifts of the mono-substituted methanes are listed in the last column for comparison and easy reference.

Table II demonstrates the rather surprisingly good estimates of chemical shifts which can be made with the assumption of "additivity" of effective shielding constants for a wide variety of substituted methanes. Most of the predictions are correct to within 0.1 ppm. At the bottom of the Table are listed five compounds for which fairly large discrepancies arise. These have been discussed earlier.

It is hardly necessary to point out that since the data were derived from molecules in which the substituents rotate about single bonds, resulting in some average shielding effect, one should not ordinarily try to apply these empirical equations to protons on carbon atoms which are members of rings. The fixed orientations of substituents in such compounds can result in shieldings markedly different from the average values of Table I. For compounds of the proper type, however, the method of estimating chemical shifts described here has been found to be of considerable value in assigning and interpreting spectra of compounds for which no closely similar, authentic models are available.



TABLE I. Effective shielding constants,  $\sigma^{\text{eff}}$ , for various groups in substituted methanes.

Group, X	$\sigma^{\text{eff}}$ (cps at 60 mc)	$\sigma^{\text{eff}}$ (ppm)	Shift of $\text{CH}_3\text{X}$ from $\text{CH}_4$ (cps at 60 mc)
Cl	152	2.53	169
OR	142	2.36	ca 180 <sup>a</sup>
Br	140	2.33	147
$\text{C}_6\text{H}_5$	110	1.832	126
I	109	1.818	115
$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C} = \text{O} \\ \diagup \end{array}$	102	1.700	ca 111 <sup>a</sup>
-S	98	1.638	111
$\begin{array}{c} \text{R} \\ \diagup \\ \text{N} \\ \diagdown \\ \text{R}' \end{array}$	94	1.568	ca 115 <sup>a</sup>
$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \quad \text{R}' \quad \text{R}'' \end{array}$	79	1.318	ca 85 <sup>a</sup>
$\text{CH}_3$	28	0.466	38

a. depends upon R, R', and R''.

TABLE II. Comparison of predicted and observed shielding values in substituted methanes, based on group shielding constants,  $\sigma_{\text{eff}}$ .

Compound Type	Predicted	Observed	$\Delta$ (cps at 60 mc)
Br-CH <sub>2</sub> -Cl	83 <i>81.5</i>	80	-3
C <sub>6</sub> H <sub>5</sub> -CH <sub>2</sub> -Cl	113 <i>v</i>	119	+6
C <sub>6</sub> H <sub>5</sub> -CH <sub>2</sub> -OR	123	125	+2
C <sub>6</sub> H <sub>5</sub> -CH <sub>2</sub> -Br	125	124	-1
(Cl-CH <sub>2</sub> -C=) <sub>2</sub>	144	147	+3
-CH-CH-CH <sub>2</sub> -OH	154	155	+1
CH <sub>2</sub> =CH-CH <sub>2</sub> -Br	156	158	+2
C <sub>6</sub> H <sub>5</sub> -CH <sub>2</sub> -C(=O)	163	162	-1
C <sub>6</sub> H <sub>5</sub> -CH <sub>2</sub> -N<	171	176	+5
=C-CH <sub>2</sub> -C(=O)	194	200	+6
CH <sub>3</sub> -CH <sub>2</sub> -OR	200	188	-12
CH <sub>3</sub> -CH <sub>2</sub> -C <sub>6</sub> H <sub>5</sub>	232	232	0
CH <sub>3</sub> -CH <sub>2</sub> -C(=O)	240	246	+6
CH <sub>3</sub> -CH <sub>2</sub> -S	244	246	+2
CH <sub>3</sub> -CH <sub>2</sub> -N<	248	244	-4
(CH <sub>3</sub> ) <sub>3</sub> -CH	291 <i>v</i>	296	+5

TABLE II. Contd.

Compound Type	Predicted	Observed	$\Delta$ (cps at 60 mc)
$C_6H_5-CH-(CH_3)_2$	211	217	+6
$(C_6H_5)_2-CH-CH_3$	127	138	+11
$I-CH_2-I$	155	155	0
$Cl-CH_2-Cl$	71	69	-2
$Br-CH_2-Br$	95	93	-2
$C_6H_5-CH_2-C_6H_5$	155	154	-1
$=C-CH_2-C=$	217	215 <sup>a</sup>	-2
$Cl-CH_2-I$	114	90	-24
$(CH_3)_2-CH-Cl$	167	142	-25
$(CH_3)_2-CH-Br$	179	138	-41
$(CH_3)_2-CH-I$	210	135	-75
$C_6H_5-CH-Cl_2$	-39	-7	+32
$CH_3-CH_2-CH_3$	319.5	331.5	+22

(a) Measured in cyclopentadiene

J. N. Shoolery  
 Varian Associates  
 Palo Alto, California

Errata: M.E.L.L.O.N.M.R. No. 2 page 16. The entries under  $A_{2X_4}$  should read

$$(J_{AX} + J_{AX'})/2 \quad 32$$

and

$$\{(J_{AX} + J_{AX'} - J_{AA})/2\} + R_1 \quad 8 \mu_{01}$$

instead of

$$(J_{AX} + J_{AX'})/2 \quad 30$$

and

$$\{J_{AX} + J_{AX'} - (J_{AA}/2)\} + R_1 \quad 8 \mu_{01}$$

MAILING LIST FOR M.E.L.L.O.N.M.R. No. 3

Prof. A. L. Allred  
Department of Chemistry  
Northwestern University  
Evanston, Illinois

Dr. Weston Anderson  
Varian Associates  
Instrument Division  
611 Hansen Way  
Palo Alto, California

Dr. S. Brownstein  
Department of Chemistry  
Cornell University  
Ithaca, New York

Prof. George Büchi  
Department of Chemistry  
Massachusetts Institute of Tech.  
Cambridge 39, Massachusetts

Mr. N. F. Chamberlain  
Research and Development Div.  
Humble Oil and Refining Company  
Baytown, Texas

Dr. V. M. Clark  
University Chemical Laboratory  
Lensfield Road  
Cambridge, England

Prof. H. Conroy  
Department of Chemistry  
Yale University  
New Haven, Connecticut

Prof. E. J. Corey  
Department of Chemistry  
University of Illinois  
Urbana, Illinois

Prof. D. J. Cram  
Department of Chemistry  
University of California  
Los Angeles 24, California

Dr. L. Crombie  
Department of Chemistry  
University of London  
King's College  
London, W.C. 2, England

Mr. T. J. Curphey  
Department of Chemistry  
Harvard University  
12 Oxford Street  
Cambridge 38, Massachusetts

Prof. William G. Dauben  
Department of Chemistry  
University of California  
Berkeley 4, California

Dr. J. B. Dickey  
Director of Research  
Tennessee Eastman Company  
Kingsport, Tennessee

Dr. R. J. Gillespie  
Department of Chemistry  
McMasters University  
Hamilton, Ontario, Canada

Prof. R. E. Glick  
Department of Chemistry  
Whitmore Laboratory  
The Pennsylvania State University  
University Park, Pennsylvania

Prof. H. S. Gutowsky  
Department of Chemistry  
University of Illinois  
Urbana, Illinois

Dr. L. M. Jackman  
Department of Organic Chemistry  
Imperial College of Science and  
Technology  
London, S.W. 7, England

Dr. Charles M. Judson  
Research Service Department  
American Cyanamid Company  
1937 W. Main Street  
Stamford, Connecticut

Mr. P. C. Lauterbur  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh 13, Pa.

Prof. L. Mandell  
Department of Chemistry  
Emory University  
Emory University, Georgia

Dr. S. Meiboom  
Department of Applied Mathematics  
The Weizmann Institute of Science  
Rehovot, Israel

Dr. C. Naar  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh 13, Pa.

Dr. W. D. Phillips  
Chemical Department  
Experimental Station  
E. I. duPont de Nemours and Co.  
Wilmington, Delaware

Dr. L. Pratt  
Department of Inorganic Chemistry  
Imperial College of Science and  
Technology  
London, S.W. 7, England

Herrn. H. Primas  
Laboratorium für Organische Chemie  
Eidgenössische Technische Hochschule  
Universitätsstrasse, 6  
Zürich 6, Switzerland

Dr. W. E. Putnam  
Houston Research Laboratory  
Shell Oil Company  
P. O. Box 2527  
Houston 1, Texas

Dr. C. A. Reilly  
Shell Development Company  
Emeryville, California

Prof. R. E. Richards  
Lincoln College  
Oxford, England

Prof. J. D. Roberts  
Department of Chemistry  
California Institute of Tech.  
Pasadena, California

Prof. Max T. Rogers  
Department of Chemistry  
Michigan State University  
East Lansing, Michigan

Dr. M. Saunders  
Department of Chemistry  
Yale University  
New Haven, Connecticut

Dr. W. G. Schneider  
Division of Pure Chemistry  
National Research Council  
Ottawa, Ontario, Canada

Dr. N. Sheppard  
University Chemical Laboratory  
Lensfield Road  
Cambridge, England

Dr. J. N. Shoolery  
Varian Associates  
611 Hansen Way  
Palo Alto, California

Dr. F. Sondheimer  
Daniel Sieff Research Institute  
The Weizmann Institute of Science  
Rehovot, Israel

Prof. G. H. Stout  
Department of Chemistry  
University of Washington  
Seattle 5, Washington

Dr. L. H. Sutcliffe  
Dept. of Inorganic and Physical Chem.  
Vine Street  
Liverpool 7, England

Dr. L. F. Thomas  
Department of Chemistry  
University of Birmingham  
Edgbaston, Birmingham 15  
England

Dr. G. V. D. Tiers  
Minnesota Mining & Mfg. Co.  
Central Research Laboratory  
2301 Hudson Road  
St. Paul 9, Minnesota

Prof. J. S. Waugh  
Department of Chemistry  
Massachusetts Institute of Tech.  
Cambridge 39, Massachusetts

Prof. K. B. Wiberg  
Department of Chemistry  
University of Washington  
Seattle 5, Washington

Prof. R. H. Wiley  
Department of Chemistry  
University of Louisville  
Louisville 8, Kentucky

Prof. R. B. Woodward  
Department of Chemistry  
Harvard University  
12 Oxford Street  
Cambridge 38, Massachusetts

Dr. J. R. Zimmerman  
Magnolia Petroleum Company  
Field Research Laboratories  
Dallas, Texas