Monthly
Ecumenical
Letters from
Laboratories
Of
N-M-R
No. 4

MINNESOTA MINING AND MANUFACTURING COMPANY

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CENTRAL RESEARCH DEPARTMENT

2301 HUDSON ROAD

ST. PAUL 9, MINNESOTA

January 24, 1959

AIRMAIL

Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Shapiro:

There exists some misunderstanding of the "tau-system" for which I, as the author, am undoubtedly responsible. At your and Dr. Bothner-By's suggestion, I have prepared this letter in an attempt to clarify "τ" for the NSR enthusiasts who receive MELLONMR.

(1) The definition of τ (J. Phys. Chem. 62 1151 (1958)) makes it identical with the "δ" thus far used by MELLONMR to indicate spectral position. (And I will seize this opportunity to urge that MELLONMR use the symbol τ, rather than δ, when τ is meant!)

(2) τ-values are defined and may be obtained in any medium in which Me_4Si is sufficiently soluble to be detected by NSR spectroscopy. This is explicitly stated in my J.P.C. note, and sample numerical values are given, but nevertheless the belief has been expressed (by some) that τ-values are restricted to dilute CCl_4 solutions.

(3) There has been objection to the symbol τ based on the fact that τ has also been used for the correlation time; to me it seems improbable that much confusion would result. Trouble arises when a symbol (such as δ) is used according to two or more conflicting definitions. (For example, the definition of δ in MELLONMR No. 1 is not the same as that in MELLONMR No. 2, p. 4 or 14-16.) Obviously, if there is to be no re-use of the Greek alphabet, new ones must be invented or old ones exhumed!

(4) The compound symbol, δ_L^m, mentioned by Dr. Bothner-By, allows great flexibility of definition. It is accordingly of value for the symbolic representation of the many possible position-relationships currently being reported in the scientific literature. This fact may be both a strength and a weakness. Chemists will not enjoy subscripts and superscripts, as may be deduced from their reaction to thermodynamic symbolism. I would press for the use of a symbol other than δ (historically used to represent differences) if the quantity is thought of as a position

rather than a difference; I am satisfied with the "J/δ" usage. In any event the notation, however cumbersome, does call attention to the real problems inherent in referencing!

(5) An appreciable part of the merit of the τ-system is that it provides a simple, easily remembered spectral scale, analogous to the familiar infrared scale, which permits at least equally good correlations to be made. I suspect that the τ-system represents a very good (though largely fortuitous) balance of simplicity and precision for the chemist which should not be set aside in the attempt to make nomenclature entirely descriptive.

Sincerely,

George Van Dyke Tiers

G. V. D. Tiers

GVDT:js

P.S. Congratulations to John Waugh, MELLONMR No.3, for doing n-C_3F_7H right! Incidentally, the discrepancy between article and reprints resulted from the Journal failing to make the changes requested in proof.

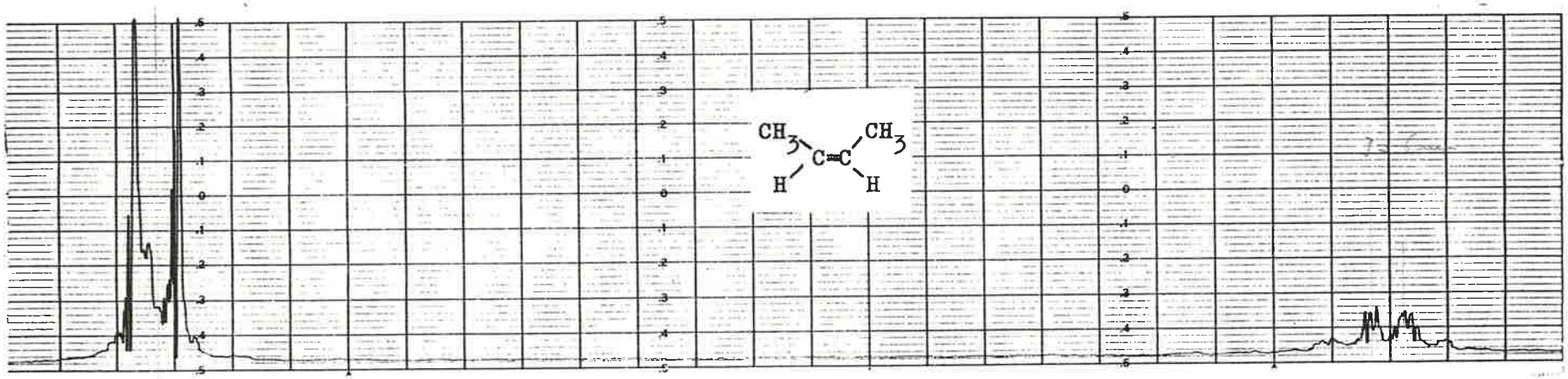
MELLON INSTITUTE
4400 FIFTH AVENUE
PITTSBURGH 13, PA.

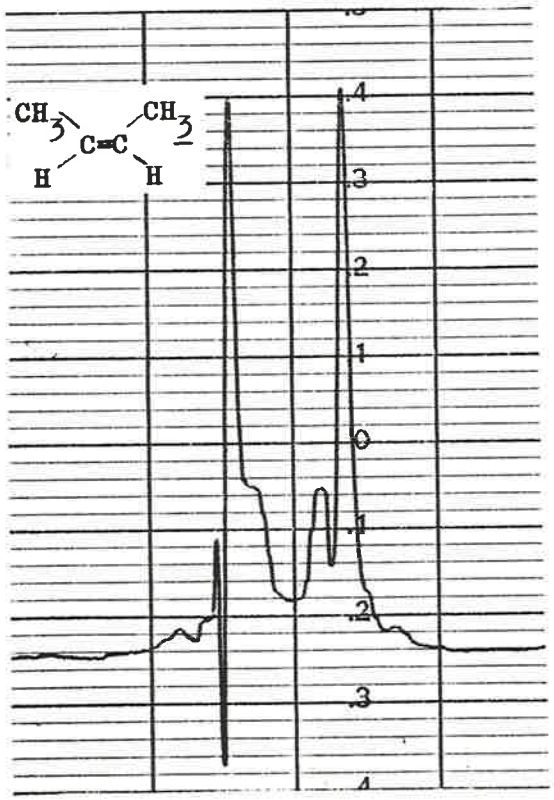
Utilizing Johnson and Bovey's table of chemical shift values arising from aromatic rings, one can calculate the average anomalous solution shift for proton resonances in aromatic solvents, on the basis of the model of the "proton skating randomly on the surface of a circumscribed cylinder" {(J. Chem. Phys., 26, 1657 (1957)}. The formula is:

$$\langle \sigma \rangle = \frac{\sum_{p=0.1}^{p=a} (0.2p - 0.01)\,\sigma_{p,(\ell/2)} + \sum_{z=0}^{z=\ell/2} 0.2a\,\sigma_{a,z}}{a(a+\ell)}$$

where the summation is taken for every increment of 0.1 in p or z, and a and ℓ are respectively the radius and altitude of the circumscribed cylinder. For a = 2.1 ring radii and ℓ = 2.2 ring radii, $\langle \sigma \rangle$ comes out to be 0.439, in reasonable agreement with ~0.5 (experimentally observed).

A. Bothner-By





H_0

cis-Butene-2

(neat, degassed)

60 mc.

See data on

page 6

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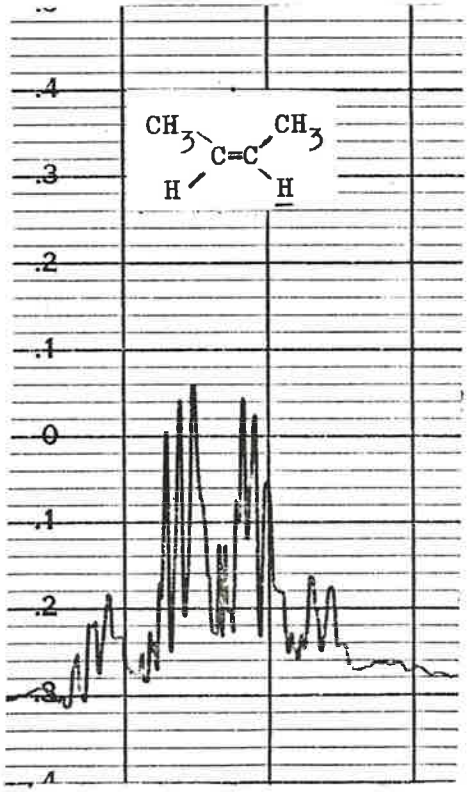
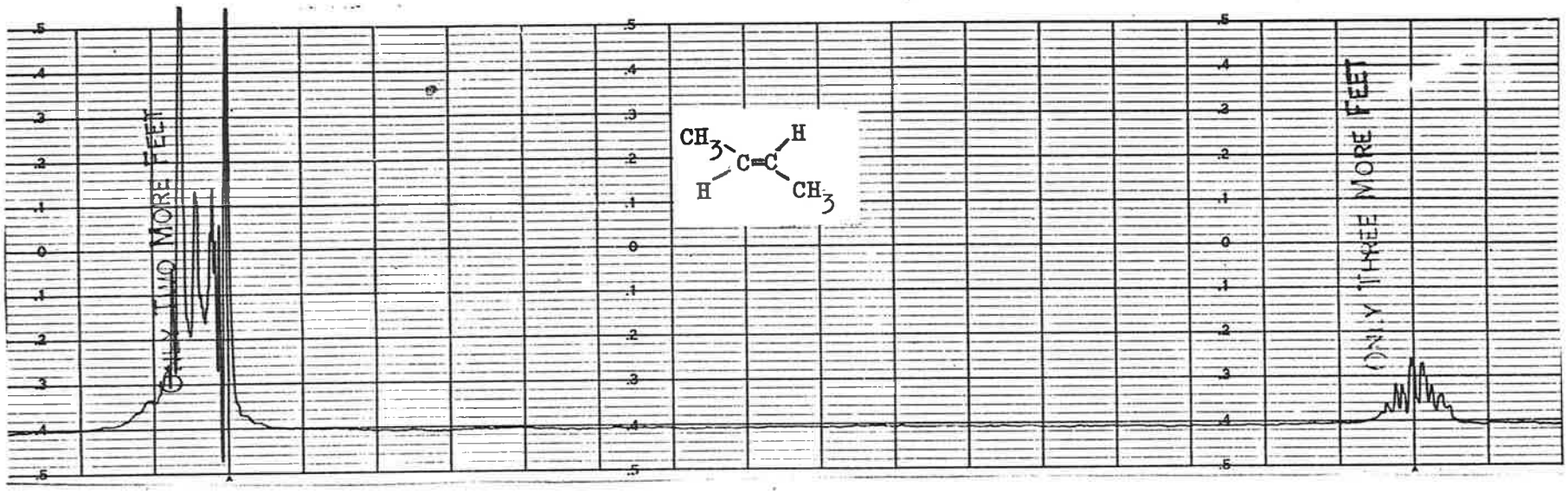
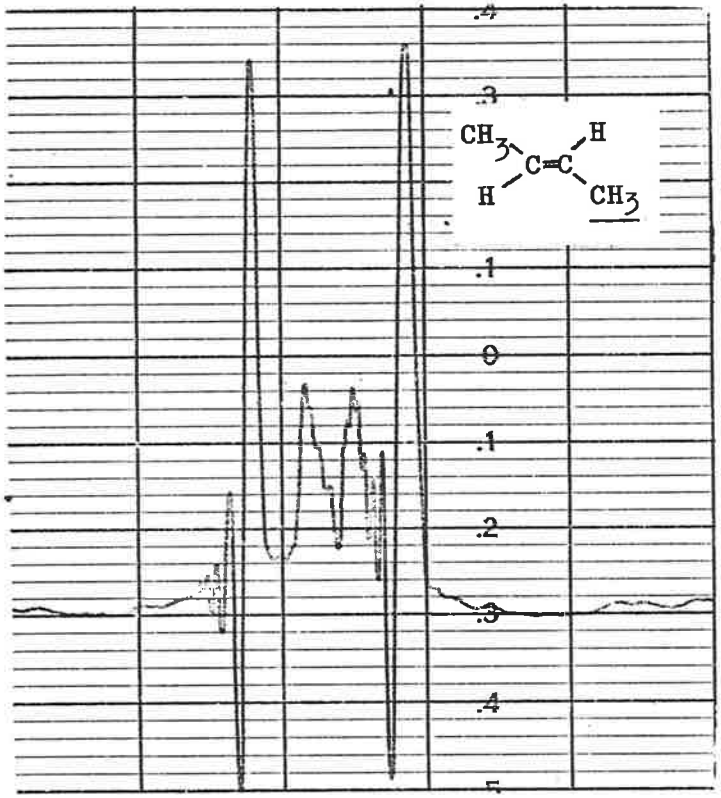




H_0



trans-Butene-2

(neat, degassed)

60 mc.

See data on

page 6

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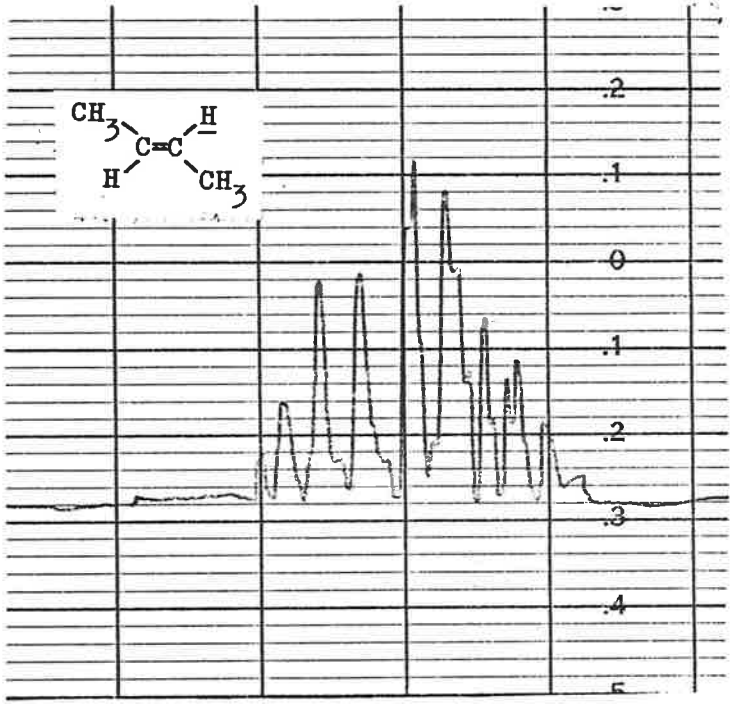


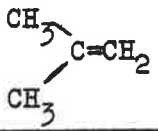
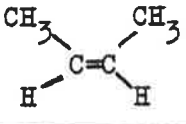
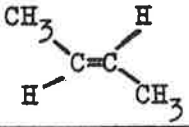
Isobutylene, cis and trans-Butene-2

(All Phillips Petroleum Company Pure Grade)

Solutions: All as neat liquid + 1% Me_4Si as internal reference (δ_{Me_4Si} = +10.00); samples degassed; no external reference.

Measurements on dilute solutions in CCl_4 (referenced internally and externally) are in progress, as well as relevant theoretical calculations.

R.F. = 60 mc.

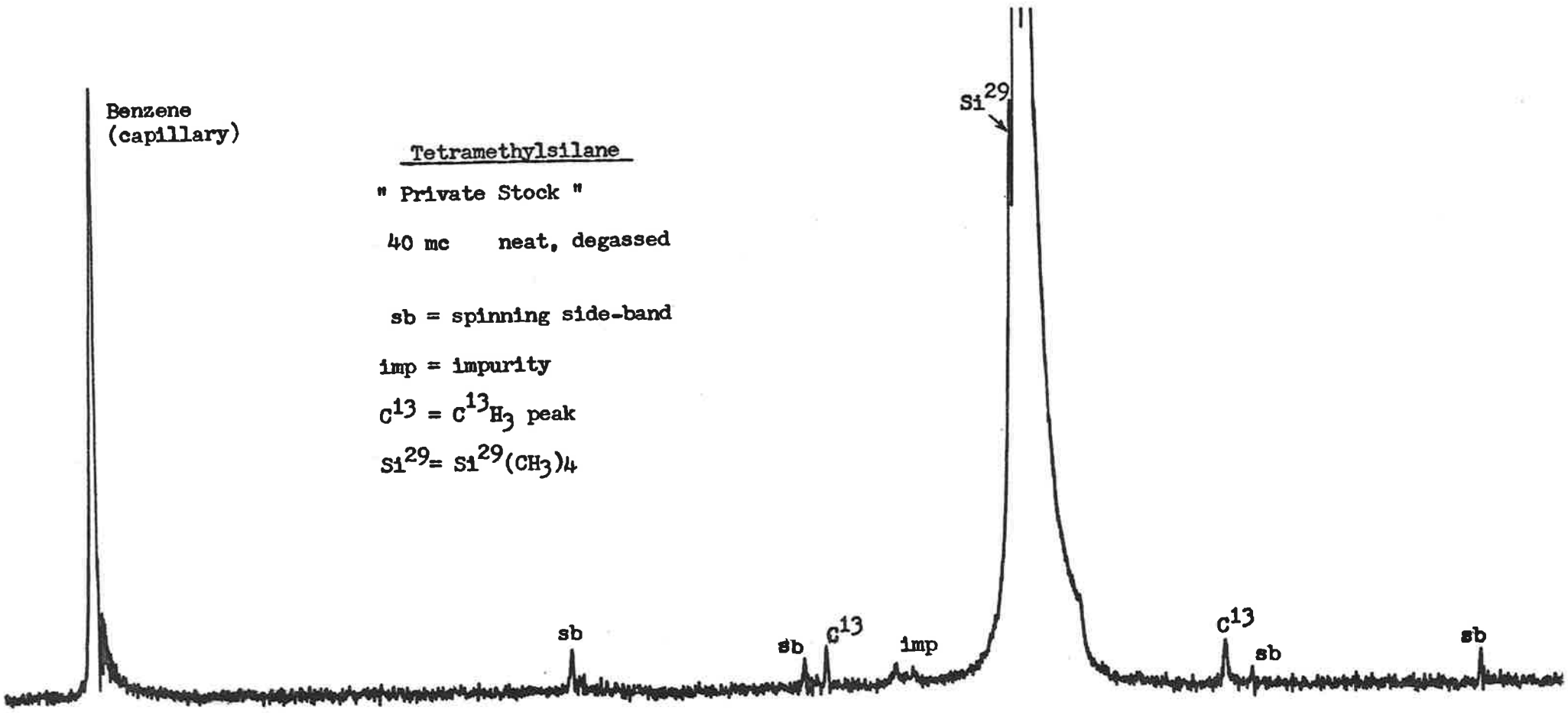
			
δ_{C-CH_3}	8.32_3	8.44_0	8.41_9
δ_{C-H}	5.36_7	4.59_4	4.62_3

3.84

(1) All values $\pm 0.00_8$

(2) For $Me_2C=CH_2$, $|\delta_{C-CH_3} - \delta_{C-H}|$ is the same for the neat liquid with and without the 1% Me_4Si (cf. M.E.L.L.O.N.M.R. No. 1, p. 7).

A. A. Bothner-By, C. Naar-Colin
Mellon Institute



PCL BLS

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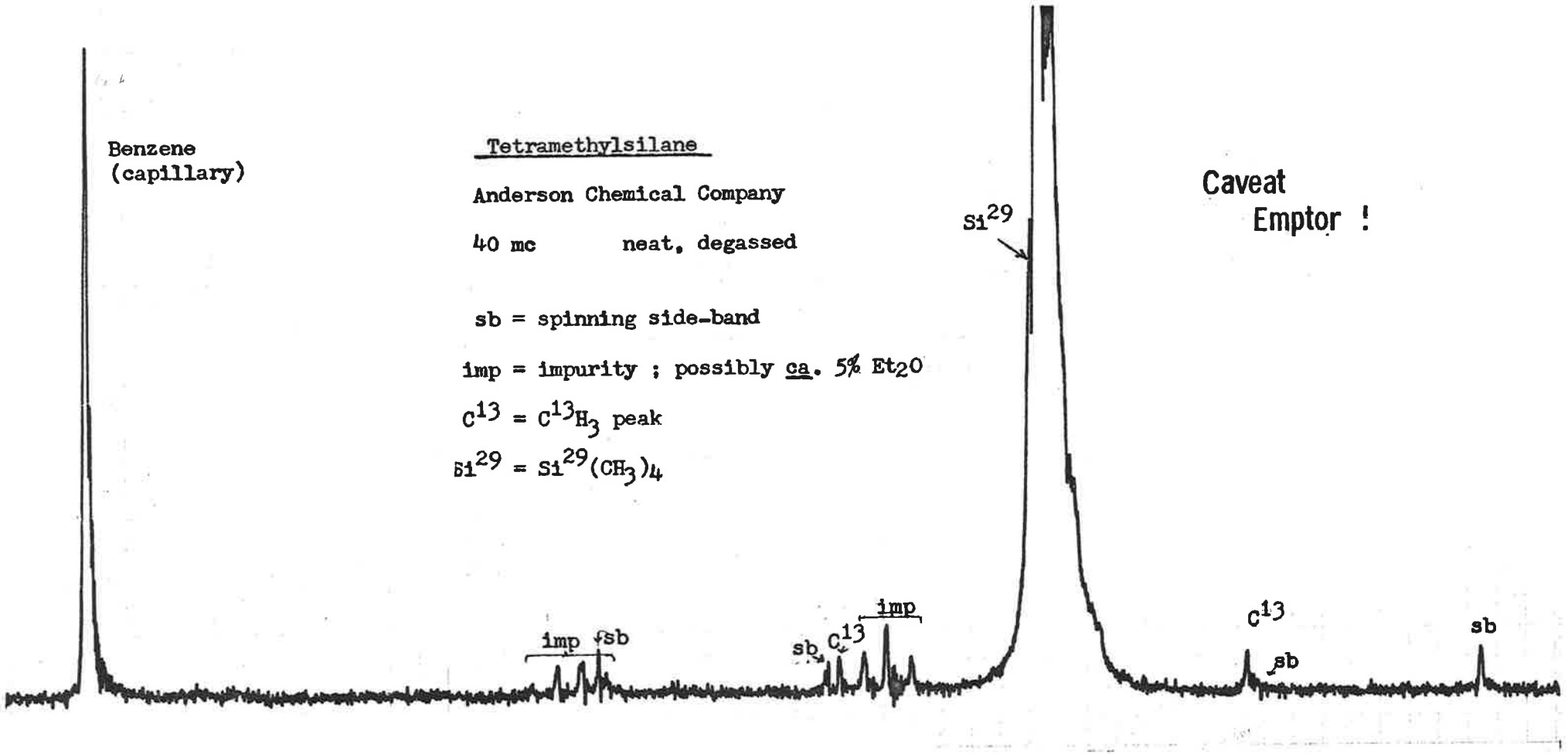

PCL BLS

Mellon Institute
Pittsburgh, Pa.

MAILING LIST FOR M.E.L.L.O.N.M.R. No.4

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. Richard Hughes
Gulf Research & Development Co.
P. O. Drawer 2038
Pittsburgh 30, Pennsylvania

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-Colin
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 fur 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 & 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

Dr. R. F. M. White
Chemistry Department
University College London
Gower Street
London W.C. 1, England

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