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No. 9

# $C^{13}$ Splittings in Proton Magnetic Resonance Spectra.

## I. Hydrocarbons<sup>x</sup>

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(Received )

Indirect spin-spin couplings between protons and  $C^{13}$  nuclei have been measured for a number of hydrocarbons. The results are interpreted on the basis of a simple semiempirical equation relating the coupling constants with the amount of  $s$ -character of the carbon-atomic orbitals involved in the bonds. No evidence is found for a dependence of the coupling constants on supposed changes in ionic character of the bonds.

An equation is also presented relating the coupling constants and the C-H internuclear distances. This provides a new indirect means of evaluating C-H distances, with a reliability apparently at least comparable with that of methods in current use.

<sup>x</sup> This work was made possible by grants from the Purdue Research Foundation, E. I. du Pont de Nemours and Company, and the National Science Foundation.

Table 2

Observed values of the  $C^{13}$ -H coupling constants,  $J_{C-H}$

Compound	$J_{C-H}$ (sec <sup>-1</sup> )	
	This work	Ref. 5
Cyclohexane	123	140
$(CH_3)_2C=C(CH_3)_2$	124	-
CH <sub>4</sub>	125	-
$(CH_3)_4C$	124	120
Mesitylene (CH <sub>3</sub> groups)	126	126
Cyclopentane	128	-
CH <sub>3</sub> -C≡C-CH <sub>3</sub>	131	-
$C^{13}H_3-C≡C-H$	132	-
Mesitylene (ring C <sup>13</sup> H)	154	160
Benzene	159	159
Cyclopropane	161	-
CH <sub>3</sub> -C≡C <sup>13</sup> -H	248	-
$C_6H_5-C≡C^{13}-H$	251	-
Ethylene	157	

Table 3

Observed values of long-range proton-proton coupling constants,  $J_{H-H}$

Compound	$J_{H-H}$ (sec <sup>-1</sup> )
CH <sub>3</sub> -C≡C-H	2.8 ± .3
CH <sub>3</sub> -C≡C-CH <sub>3</sub>	2.7 ± .5
Cyclopropane	7.5 ± .5
Ethylene	{ 11 ± 2 18 ± 2

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II. Bonding in Substituted Methanes\*

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We have measured indirect spin-spin couplings between protons and  $C^{13}$  nuclei in a variety of substituted methanes. As found earlier for hydrocarbons, the coupling constants,  $J_{C-H}$ , appear to be linearly related both to the percent  $s$  character of the carbon atomic orbital participating in the C-H bond and to the bond length. On the basis of the large variations of the  $J_{C-H}$  values and of the C-H bond lengths in these compounds we conclude that the state of hybridization of the carbon atom cannot be reliably inferred from the observed, essentially tetrahedral valence angles. This means that the bonds must in many cases be considered as somewhat bent.

We investigated the dependence of the C-H bond hybridization in compounds of type  $CH_3X$  upon the properties of the substituent group. The results can be correlated on the assumption that the effective electronegativity and the size of the atom directly attached to the methyl carbon primarily determine the hybridization.

Table I

$C^{13}$ -H Coupling Constants for Substituted Methanes

Compound	$J_{C-H}$ (Sec <sup>-1</sup> )	Compound	$J_{C-H}$ (Sec <sup>-1</sup> )
(CH <sub>3</sub> ) <sub>3</sub> SiCN	122	(CH <sub>3</sub> ) <sub>2</sub> NH(BH <sub>3</sub> )	139
(CH <sub>3</sub> ) <sub>2</sub> C=CH <sub>2</sub>	126 <sup>a</sup>	CH <sub>3</sub> OH	141
C <sub>2</sub> H <sub>6</sub>	126 <sup>b</sup>	CH <sub>3</sub> OC <sub>6</sub> H <sub>5</sub>	143
(CH <sub>3</sub> ) <sub>2</sub> C=O	126	H <sub>2</sub> C(CN) <sub>2</sub>	145
CH <sub>3</sub> -C <sub>6</sub> H <sub>5</sub>	126 <sup>c</sup>	p-CH <sub>3</sub> O-C <sub>6</sub> H <sub>5</sub> -CHO	145
CH <sub>3</sub> -CHO	127 <sup>d</sup>	CH <sub>3</sub> NO <sub>2</sub>	147
p-CH <sub>3</sub> -C <sub>6</sub> H <sub>5</sub> -NO <sub>2</sub>	127	(CH <sub>3</sub> -O-C(O)CH <sub>2</sub> ) <sub>2</sub>	147 <sup>f</sup>
(CH <sub>3</sub> ) <sub>4</sub> Sn	128 <sup>e</sup>	CH <sub>3</sub> F	149 <sup>g</sup>
(CH <sub>3</sub> ) <sub>3</sub> C-CN	129	CH <sub>3</sub> Cl	150
CH <sub>3</sub> -COOH	130	CH <sub>3</sub> I	151
(CH <sub>3</sub> ) <sub>3</sub> N	131	CH <sub>3</sub> Br	152
(CH <sub>3</sub> ) <sub>2</sub> NH	132	CH <sub>2</sub> I <sub>2</sub>	173
CH <sub>3</sub> NH <sub>2</sub>	133	CH <sub>2</sub> Cl <sub>2</sub>	178
CH <sub>3</sub> CCL <sub>3</sub>	134	CHBr <sub>3</sub>	206
CH <sub>3</sub> CN	136	CHCl <sub>3</sub>	209
(CH <sub>3</sub> ) <sub>2</sub> SO	138		

a.  $J_{C-H}$  (ethylenic) = 155;  $J_{H-H} = 1.2 \pm 0.1$

b.  $J_{H-H} = 7.7 \pm 0.2$

c.  $J_{C-H}$  (ring)ave = 155

d.  $J_{C-H}$  (aldehyde) = 173

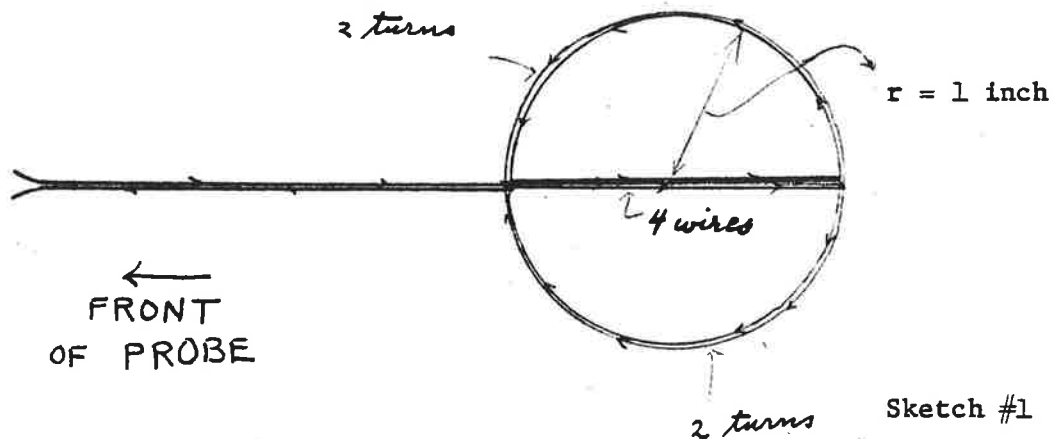
e.  $J_{H-Sn} = 53$  (Sidebands due to Sn<sup>117</sup> and Sn<sup>119</sup> overlap)

f.  $J_{C-H}$  (CH<sub>2</sub> groups) = 155;  $J_{H-H}$  (-CH<sub>2</sub>-CH<sub>2</sub>-) = 7.1  $\pm$  0.4

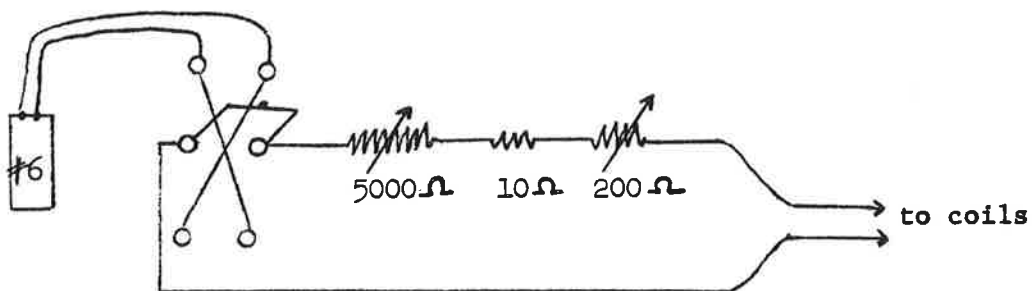
g.  $J_{H-F} = 45.8 \pm 0.5$

Field gradient coils.

In order to obtain a degree of facile control over the magnetic field gradient in the vertical direction, we have mounted a pair of gradient adjusting coils on the sides of the Varian high resolution probe. The coils are wound from enameled copper magnet wire (28 gauge), and are wound according to sketch #1. (one coil only shown). The coils are easily centered using the Helmholtz coil groove as a guide.



Current is supplied from a #6 dry cell, using the circuit shown in sketch #2



Sketch #2

The coils are simple to construct, and may be affixed to the probe with cement or scotch tape. A rapid, smooth and convenient adjustment of the vertical gradient is possible thereby.

Concerning External Referencing;

A Preliminary Report

The problem of external referencing has been re-examined with a view to

- (i) determining the limits of precision obtainable using the 'capillary technique'.
- (ii) evaluating the relative merits of the capillary technique and the method using Wilmad precision coaxial cells.
- (iii) discovering other factors, including instrumental ones, which can affect the precision of line separation measurements.

A number of sets of sample tubes were prepared; within a given set (e.g., tubes No. 61-68 inc.) there were four tubes of substance A with a capillary of substance B (e.g., 61-64) and four tubes of substance B with a capillary of substance A (e.g., 65-68). The substances were all pure liquids (at least 99.5 mole % pure by VPC analysis) each giving rise to a single, sharp resonance line (The latter consideration precluded the use of toluene - cf. M.E.L.L.O.N.M.R. No. 7, p. 2.). Where possible the pairs of substances were chosen so that their magnetic susceptibilities were as different as possible. All tubes and capillaries were filled on the vacuum line with degassed substances and were sealed off in vacuo.

Precision-bore tubing and capillary stock were not used.\*

Within a given set of tubes there were different liquid column heights in both tubes and capillaries and differing tube and capillary lengths as well as varying capillary diameters.

Line separation data obtained here at Mellon Institute were determined and processed as follows:

(i) Separations were determined by the side-band technique by visually determining exact superposition of 'real' and 'image' peaks on the oscilloscope, as judged by perfection in the pattern of the ringing decay.

(ii) A non-resettable, capacitor tuned (v.i.) audio-oscillator was employed.

(iii) The audio-oscillator frequencies were counted by a frequency counter, and were read and recorded by a second person to avoid operator prejudice. Readings once made were irrevocable.

(iv) Five readings were taken on each tube, and five 10-second frequency counts made for each reading.

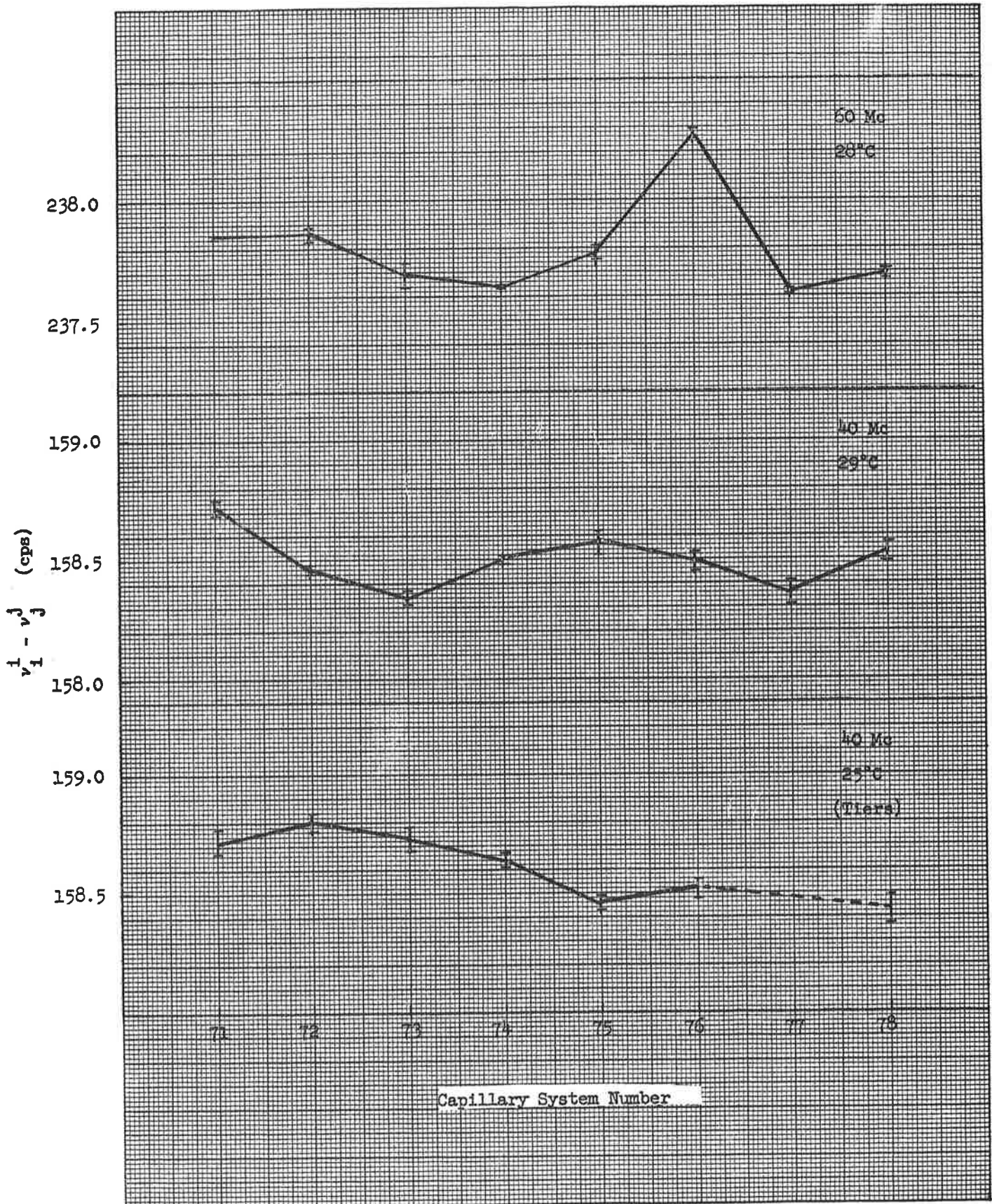
Measurements on one set of tubes were run by Dr. G. V. D. Tiers, who used a graphical method to determine the separations. His data are included below, with our preliminary results on two sets of tubes.

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\* The tedious and costly selection of lengths of "5 mm O.D." Pyrex tubing can be avoided readily by ordering sample tube stock directly from Corning (No. 7740 tubing, 4.8 mm O.D.  $\pm$  0.004" x 0.032 wall  $\pm$  0.005" (in 36" lengths) at \$13.53 per lb.). This cost is essentially the same as that of using that part of stock 5 mm. tubing which is actually of the correct size. Convenient capillary stock is Corning No. 9530 melting point tubes, capillary, 12" length, 1.5 mm O.D.

Line Separation Measurements ( in cps. )

Tube No. R. F.	51	52	53	54	55	56	57	58	Average, 51 - 58
60 mc. (t = 28°C)	128.10	128.24	128.22	128.12	128.26	128.30	128.38	128.28	128.27 ± 0.02
	.16	.20	.24	.28	.26	.38	.24	.38	
	.22	.26	.20	.12	.30	.36	.24	.32	
	.24	.30	.32	.14	.38	.36	.50	.04	
	.04	.28	.38	.38	.38	.34	.30	.20	
	128.15 ± 0.02	128.26 ± 0.01	128.27 ± 0.02	128.21 ± 0.03	128.32 ± 0.02	128.35 ± 0.01	128.33 ± 0.03	128.24 ± 0.04	
		128.22 ± 0.02				128.31 ± 0.02			
	71	72	73	74	75	76	77	78	Average, 71 - 78
60 mc. (t = 28°C)	237.80	237.86	237.72	237.68	237.68	238.22	237.60	237.60	237.80 ± 0.05  x 2/3 = 158.53 ± 0.03
	.86	.90	.96	.60	.72	.36	.60	.72	
	.90	.96	.70	.62	.80	.18	.60	.72	
	.84	.72	.54	.70	.80	.28	.60	.72	
	.86	.88	.52	.60	.92	.30	.68	.70	
	237.85 ± 0.01	237.86 ± 0.03	237.69 ± 0.05	237.64 ± 0.01	237.78 ± 0.03	238.27 ± 0.02	237.62 ± 0.01	237.69 ± 0.02	
		237.76 ± 0.05				237.84 ± 0.10			
	158.84	158.50	158.32	158.46	158.80	158.44	158.40	158.42	158.50 ± 0.03
40 mc. (t = 29°C)	.64	.40	.32	.58	.64	.42	.22	.44	
	.60	.50	.30	.40	.42	.70	.22	.62	
	.72	.52	.50	.56	.40	.50	.60	.70	
	.80	.40	.26	.50	.60	.40	.36	.48	
		158.72 ± 0.03	158.46 ± 0.02	158.34 ± 0.03	158.50 ± 0.02	158.57 ± 0.05	158.49 ± 0.04	158.36 ± 0.05	158.53 ± 0.04
		158.50 ± 0.05				158.49 ± 0.03			
40 mc. (t = 25°C) G.V.D. Tiers	<u>Incr.</u> <u>Decr.</u>	<u>Incr.</u> <u>Decr.</u>	<u>Incr.</u> <u>Decr.</u>	<u>Incr.</u> <u>Decr.</u>	<u>Incr.</u> <u>Decr.</u>	<u>Incr.</u> <u>Decr.</u>	<u>Incr.</u> <u>Decr.</u>	<u>Incr.</u> <u>Decr.</u>	(not available - tube broken)
	158.54 158.43	158.84 158.90	158.74 158.93	158.72 158.52	158.55 158.48	158.37 158.46	158.29 158.61		
	.78 159.06	.94 .71	.75 .50	.62 .72	.34 .49	.71 .39	.57 .51		
	.74 158.77	.64 .76	.90 .56	.73 .50	.55 .38	.54 .65	.07 .54		
		158.72 ± 0.05	158.80 ± 0.04	158.73 ± 0.05	158.64 ± 0.03	158.46 ± 0.03	158.52 ± 0.04	158.43 ± 0.06	
		158.72 ± 0.02				158.47 ± 0.02			





Conclusions.

(1) The capillary technique of external referencing is highly precise, even without recourse to the use of precision tubing and capillary stock.

(2) Other factors than possible perturbations caused by imperfect capillary system geometry are probably of greater importance in determining the precision of separation measurements. These factors include:

(i) The presence of dissolved oxygen in both the sample and the reference. (v.i.)

(ii) The resolution at the moment the separation measurement is made. It is found that a very small, temporary deterioration of resolution prevents the possibility of an unequivocal choice between (say) 237.1 and 237.2 cps settings of the modulation frequency.

(iii) The widths of both sample and reference lines.

(3) No systematic error is introduced in changing from a capillary of A in a tube of B to a capillary of B in a tube of A.

(4) There is no perceptible dependence of precision on uniformity in length of the capillary or of the column of reference substance contained therein. Capillaries of lengths as in the present study (at least two inches) are sufficiently cylindrical and parallel to the axis of the sample tube so that errors do not arise from this source. In practice, it is found that if a capillary is inadequately constructed, filled or sealed, its unsuitability is readily apparent, and is manifested by major

perturbations in the appearance of the spectrum, e.g., spinning side-bands, split or distorted lines, etc.

(5) External referencing by the Wilmad precision coaxial cell technique suffers from the following disadvantages:

(i) It is expensive, particularly for the often highly desirable maintenance of a sizeable 'library' of sample tubes over periods of time.

(ii) It is very difficult, if feasible at all, to degas the reference substance in the annulus. An un-degassed reference substance gives rise to a signal broader than, and shifted with respect to, that from a degassed sample. In addition to Evans' findings (Chem. and Ind., 526 (1958)), the following data, obtained using Wilmad tubes and the measuring techniques described above, may be cited: ( $t = 28^{\circ}\text{C}$ ; R. F. = 60 mc.)

Tube (a): Degassed cyclohexane tube, annulus of air-equilibrated benzene:  
line separation =  $317.52 \pm 0.02$  cps.

Tube (b): Degassed benzene tube, annulus of air-equilibrated cyclohexane:  
line separation =  $318.90 \pm 0.02$  cps.


Difference = 1.38 cps.


(6) When peak separations are measured by the superposition of a modulation side-band, it is necessary to use an audio-oscillator with a continuously variable frequency. Capacitor-tuned oscillators (e.g., HP 200AB) satisfy this requirement, but the one resistor-tuned oscillator tested (HP 202A) jumped several tenths of a cycle as the wire-wound variable


resistor was turned. Such oscillators can be used if a small "vernier" resistor is added for fine tuning.

(7) Errors can also be introduced by the use of sine waves (or other broad waveforms) to trigger a frequency counter. For example, when measuring a frequency of 100.24 cps with a ten-second gate, the counter will most often read 100.3 cps, with an occasional 100.2. The results are a bunching of the average readings around the tenth-cycle points and an upward shift of the average by as much as one-tenth of a cycle, depending on the amplitude of the sine wave. Thus, in addition to introducing an error in the frequency, the statistics of the measurement are badly distorted. These effects will, of course, be ten times worse if a one-second gate is used. Triggering of the counter gate by a narrow pulse eliminates all of these troubles.

We would welcome collaborations with other laboratories in pursuing this investigation. We are prepared to furnish (on loan) these tubes or additional sets for the purpose of cross-checking the measurements thus far made. We would also welcome further suggestions on more stringent tests which might be applied.

  
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