

FOREWORD

This report was prepared by Southern Research Institute, Birmingham, Alabama, under Contract No. AF 33(616)-8205, Project No. 7360, Task No. 736005. This work was a continuation of that performed under Contract No. AF 33(616)-5855, a study of the relationship between the wavenumbers and intensities of far infrared absorption bands of mono- and disubstituted benzenes and the structure of these molecules. This is the final report. The work was administered under the direction of the Directorate of Materials and Processes, Deputy Commander/Technology, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio, with Lt. Neil T. McDevitt as project engineer.

This report describes work conducted from April 15, 1961, through April 14, 1962.

ACKNOWLEDGMENTS

The purifications of compounds described in this report were performed by the Institute's Organic Preparations Section under the supervision of Mr. W. E. Fitzgibbon. Analyses were performed by the Analytical Chemistry Section under the supervision of Dr. W. J. Barrett.

Contrails

ABSTRACT

Attempts have been made to correlate the intensities of far infrared absorption bands of mono- and disubstituted benzenes with physical properties of the molecules or of their substituents. The intensities of ν_{18}' and ν_{19}' were measured for monosubstituted benzenes having these substituents: -F, -Cl, -Br, -I, -CN, -CH₃, -CF₃, -CCl₃, -NO₂, and -OCH₃. Some second-degree correlations but no useful simple correlations were found. Correlations were sought for the intensity of ν_4 of symmetrical 1,4-disubstituted benzenes, a vibration probably not as likely to mix with other modes of its symmetry species as ν_{18}' and ν_{19}' . However, the intensities of ν_4 did not correlate well either.

Complete infrared spectra of all 38 compounds studied are cataloged from 4000 to 265 cm⁻¹.

This technical documentary report has been reviewed and is approved.

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TABLE OF CONTENTS

	<u>PAGE</u>
I. INTRODUCTION.....	1
II. RESULTS OF INTENSITY MEASUREMENTS.....	3
A. Intensity of ν_{19}' of Monosubstituted Benzenes.....	3
B. Intensity of ν_{18}' of Monosubstituted Benzenes.....	4
C. Intensity of ν_4 of Symmetrical 1,4-Disubstituted Benzenes.....	5
III. INTENSITY CORRELATIONS.....	5
A. Treatment of Data.....	5
B. Physical Properties.....	6
C. Correlation of A_{19}' with Physical Properties for Monosubstituted Benzenes.....	6
D. Correlation of A_{18}' with Physical Properties for Monosubstituted Benzenes.....	8
E. Correlation of A_4 with Physical Properties for Symmetrical 1,4-Disubstituted Benzenes.....	12
IV. WAVENUMBER CORRELATIONS.....	17
V. SUMMARY AND CONCLUSIONS.....	20
VI. EXPERIMENTAL SECTION.....	21
A. Materials.....	21
1. Toluene.....	21
2. Fluorobenzene.....	21
3. Benzonitrile.....	22

TABLE OF CONTENTS (continued)

	<u>PAGE</u>
VI. EXPERIMENTAL SECTION (continued)	
A. Materials (continued)	
4. Anisole	22
5. Chlorobenzene	22
6. Nitrobenzene	22
7. Benzotrifluoride	23
8. Bromobenzene	23
9. Benzotrichloride	23
10. Iodobenzene	23
11. <u>o</u> -Xylene	24
12. <u>o</u> -Difluorobenzene	24
13. <u>o</u> -Phthalonitrile	24
14. Veratrole (1,2-dimethoxybenzene)	24
15. <u>o</u> -Dichlorobenzene	25
16. <u>o</u> -Dinitrobenzene	25
17. <u>o</u> -Dibromobenzene	25
18. <u>o</u> -Diiodobenzene	25
19. <u>m</u> -Xylene	26
20. <u>m</u> -Difluorobenzene	26
21. <u>o</u> -Isophthalonitrile	26
22. <u>m</u> -Dimethoxybenzene	26
23. <u>m</u> -Dichlorobenzene	26
24. <u>m</u> -Dinitrobenzene	27
25. <u>1,3</u> -Bis(trifluoromethyl)benzene	27
26. <u>m</u> -Dibromobenzene	27
27. <u>1,3</u> -Bis(trichloromethyl)benzene	27
28. <u>m</u> -Diiodobenzene	28
29. <u>p</u> -Xylene	28
30. <u>p</u> -Difluorobenzene	28
31. <u>o</u> -Terephthalonitrile	28
32. <u>p</u> -Dimethoxybenzene	29
33. <u>p</u> -Dichlorobenzene	29
34. <u>p</u> -Dinitrobenzene	29
35. <u>1,4</u> -Bis(trifluoromethyl)benzene	29
36. <u>p</u> -Dibromobenzene	29
37. <u>1,4</u> -Bis(trichloromethyl)benzene	30
38. <u>p</u> -Diiodobenzene	30

TABLE OF CONTENTS (continued)

	<u>PAGE</u>
VI. EXPERIMENTAL SECTION (continued)	
B. Intensity Measurements.....	30
C. NMR Measurements.....	38
VII. REFERENCES	42
APPENDIX—Atlas of Spectra of Mono- and Disubstituted Benzenes	44

LIST OF FIGURES

<u>FIGURE</u>		<u>PAGE</u>
1.	Monosubstituted benzenes: intensity of ν_{19}' vs. Sanderson's charge withdrawal from the ring	9
2.	Monosubstituted benzenes: intensity of ν_{19}' vs. NMR chemical shift of the <u>para</u> proton from benzene.....	10
3.	Monosubstituted benzenes: intensity of ν_{18}' vs. Sanderson's charge on the substituent atom next to the ring.....	11
4.	Monosubstituted benzenes: intensity of ν_{18}' vs. $\sqrt{(\delta_A + 0.18)^2 + (0.011)^2}$	13
5.	Symmetrical 1, 4-disubstituted benzenes: intensity of ν_4 vs. Sanderson's charge on the substituent atom next to the ring.....	15
6.	Symmetrical 1, 4-disubstituted benzenes: intensity of ν_4 vs. $\sqrt{(\delta_A + 0.83)^2 - (0.275)^2}$	16
7.	Symmetrical 1, 4-disubstituted benzenes: wavenumber of ν_4 vs. $\sqrt{(\delta_A + 0.83)^2 - (0.275)^2}$	18
8.	Symmetrical 1, 4-disubstituted benzenes: wavenumber of ν_4 vs. Sanderson's partial charge on hydrogen.....	19
9.	Refractive index of cesium bromide as a function of wavenumber	32
10.	Dispersion of cesium bromide as a function of wavelength	33
11.	Computed spectral slit width in the cesium bromide region as a function of wavenumber.....	34
12.	Computed spectral slit width in the sodium chloride region as a function of wavenumber	39
13.	Infrared spectrum of toluene. Liquid: 0.016 mm cell	45
14.	Infrared spectrum of fluorobenzene. Liquid: 0.016 mm cell	46
15.	Infrared spectrum of benzonitrile. Liquid: 0.018 mm cell.....	47

LIST OF FIGURES (continued)

<u>FIGURE</u>		<u>PAGE</u>
16.	Infrared spectrum of anisole. Liquid; 0.016 mm cell	48
17.	Infrared spectrum of chlorobenzene. Liquid; 0.016 mm cell	49
18.	Infrared spectrum of nitrobenzene. Liquid; 0.016 mm cell	50
19.	Infrared spectrum of benzotrifluoride. Liquid; 0.016 mm cell	51
20.	Infrared spectrum of bromobenzene. Liquid; 0.016 mm cell	52
21.	Infrared spectrum of benzotrichloride. Liquid; 0.016 mm cell and capillary film	53
22.	Infrared spectrum of iodobenzene. Liquid; 0.016 mm cell	54
23.	Infrared spectrum of <u>o</u> -xylene. Liquid; 0.018 mm cell	55
24.	Infrared spectrum of <u>o</u> -difluorobenzene. Liquid; 0.018 mm cell	56
25.	Infrared spectrum of phthalonitrile. Solid in pressed disks: near infrared, 1 mg/650 mg KBr; far infrared, 2 mg/350 mg KI	57
26.	Infrared spectrum of veratrole. Liquid; 0.018 mm cell	58
27.	Infrared spectrum of <u>o</u> -dichlorobenzene. Liquid; 0.016 mm cell	59
28.	Infrared spectrum of <u>o</u> -dinitrobenzene. Solid in pressed disks: near infrared, 1 mg/650 mg KBr; far infrared, 2 mg/350 mg KI	60
29.	Infrared spectrum of <u>o</u> -dibromobenzene. Liquid; 0.016 mm cell	61
30.	Infrared spectrum of <u>o</u> -diiodobenzene. Liquid; 0.018 mm cell	62
31.	Infrared spectrum of <u>m</u> -xylene. Liquid; 0.018 mm cell	63
32.	Infrared spectrum of <u>m</u> -difluorobenzene. Liquid; 0.018 mm cell	64

LIST OF FIGURES (continued)

<u>FIGURE</u>	<u>PAGE</u>
33. Infrared spectrum of isophthalonitrile. Solid in pressed disks: near infrared, 1 mg/650 mg KBr; far infrared, 2 mg/350 mg KI	65
34. Infrared spectrum of <u>m</u> -dimethoxybenzene. Liquid: 0.018 mm cell .	66
35. Infrared spectrum of <u>m</u> -dichlorobenzene. Liquid: 0.016 mm cell . . .	67
36. Infrared spectrum of <u>m</u> -dinitrobenzene. Solid in pressed disks: near infrared, 1 mg/650 mg KBr; far infrared, 2 mg/350 mg KI	68
37. Infrared spectrum of 1,3- <u>bis</u> (trifluoromethyl)benzene. Liquid: 0.013 mm cell	69
38. Infrared spectrum of <u>m</u> -dibromobenzene. Liquid: 0.016 mm cell . . .	70
39. Infrared spectrum of 1,3- <u>bis</u> (trichloromethyl)benzene. Solid in pressed disks: near infrared, 1 mg/650 mg KBr; far infrared, 2 mg/350 mg KI	71
40. Infrared spectrum of <u>m</u> -diiodobenzene. Liquid: capillary film	72
41. Infrared spectrum of <u>p</u> -xylene. Liquid: 0.018 mm cell	73
42. Infrared spectrum of <u>p</u> -difluorobenzene. Liquid: 0.016 mm cell	74
43. Infrared spectrum of terephthalonitrile. Solid in pressed disks: near infrared, 1 mg/650 mg KBr; far infrared, 2 mg/350 mg KI	75
44. Infrared spectrum of <u>p</u> -dimethoxybenzene. Solid in pressed disks: near infrared, 1 mg/650 mg KBr; far infrared, 2 mg/350 mg KI	76
45. Infrared spectrum of <u>p</u> -dichlorobenzene. Solid: near infrared, capillary film; far infrared, pressed disk, 2 mg/350 mg KI	77
46. Infrared spectrum of <u>p</u> -dinitrobenzene. Solid in pressed disks: near infrared, 1 mg/650 mg KBr; far infrared, 2 mg/350 mg KI	78

LIST OF FIGURES (continued)

<u>FIGURE</u>	<u>PAGE</u>
47. Infrared spectrum of <u>1,4-bis</u> (trifluoromethyl)benzene: Liquid: 0.016 mm cell.....	79
48. Infrared spectrum of <u>p</u> -dibromobenzene. Solid in pressed disks: near infrared, 1 mg/650 mg KBr; far infrared, 2 mg/350 mg KI	80
49. Infrared spectrum of <u>1,4-bis</u> (trichloromethyl)benzene. Solid in pressed disks: near infrared, 1 mg/650 mg KBr; far infrared, 2 mg/350 mg KI	81
50. Infrared spectrum of <u>p</u> -diiodobenzene. Solid: capillary film.....	82

LIST OF TABLES

<u>TABLE NO.</u>	<u>PAGE</u>
1. Summary of Intensities of ν_{19}' for Monosubstituted Benzenes	4
2. Summary of Intensities of ν_{18}' for Monosubstituted Benzenes	4
3. Summary of Intensities of ν_4 for Symmetrical 1,4-Disubstituted Benzenes	5
4. List of Physical Properties	7
5. Sanderson's Partial Charge Data for Symmetrical 1,4-Disubstituted Benzenes	14
6. Tentative Assignments for ν_{19}' of Symmetrical Disubstituted Benzenes	20
7. Refractive Indexes of Fluorobenzene	22
8. Summary of Intensity Data for ν_{19}' of Monosubstituted Benzenes in Cyclohexane Solution	36
9. Summary of Intensity Data for ν_{18}' of Monosubstituted Benzenes in Cyclohexane Solution	37
10. Summary of Intensity Data for ν_4 of Symmetrical 1,4-Disubstituted Benzenes in Cyclohexane Solution	40
11. NMR Chemical Shifts of Monosubstituted Benzenes in ppm from Benzene	41
12. NMR Chemical Shifts of 1,4-Disubstituted Benzenes in ppm from Benzene	41

Contrails

A FUNDAMENTAL STUDY OF THE INFRARED SPECTRA OF
SUBSTITUTED AROMATIC COMPOUNDS

I. INTRODUCTION

The purpose of the research is to explore the possibility of correlating the wavenumbers and intensities of the far infrared absorption bands of mono- and disubstituted benzenes with physical properties of their substituents. The background for this study and our initial results have been reported previously in detail.^{1,2} However, in our earlier work we did not attempt any correlations of band intensities with physical properties. As a consequence, this aspect of the problem has been emphasized in this report.

The subject of the measurement of absolute intensities of infrared absorption bands and the attempts to relate such "integrated intensities" to molecular structure has been adequately reviewed recently.^{3,4,5} and will not be repeated in detail here. Theoretically, the absolute intensity of the *i*th fundamental infrared absorption band, A_i , may be expressed as in equation 1.

$$A_i = \frac{\pi g_i}{3c} \left| \frac{\partial \mu_e}{\partial Q_i} \right|^2 \quad (1)$$

Here, c is the velocity of light, g_i is the degeneracy of the *i*th mode, $\partial \mu_e / \partial Q_i$ is the variation of the molecular electric dipole moment with the normal coordinate. In terms of observable quantities, A_i may be expressed as in equation 2.

$$A_i = \int \alpha_\nu d\nu = \frac{1}{nl} \int \ln(I_0/I)_\nu d\nu \quad (2)$$

Here, α is the Lambert-law absorption coefficient, κ , [$\kappa = (1/l) \ln(I_0/I)$] divided by the concentration of the absorbing species, \underline{n} , I_0 is the light intensity incident upon the sample, I is the transmitted intensity, and l is the pathlength. If \underline{n} is in molecules/cm³, l in cm, and ν the frequency in sec⁻¹, then A_i will have the units cm² molecules⁻¹ sec⁻¹ (ln). In this report all intensity measurements are given in Thompson Units,⁶ T. U., where

$$1 \text{ T. U.} = 1 \times 10^{-7} \text{ cm}^2 \text{ molecules}^{-1} \text{ sec}^{-1} (\ln).$$

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The techniques employed here in measuring \underline{A} are given below in the Experimental Section.

As was the case with the correlation of wavenumbers of vibrations with physical properties,¹ previous work on the correlation of band intensities with physical properties has been limited to characteristic functional group vibrations.^{3, 4, 7, 8} For example, Brown⁷ discusses substituted benzenes of the form $X-C_6H_4-S$, where S is the absorbing functional group and X is the meta or para substituent. S may be a group such as -OH, -NH₂, or -CN, and the vibration of interest is the corresponding O-H, N-H, or C≡N stretching frequency. Brown proposes, on the basis of theoretical considerations, that for such vibrations, $A^{1/2}$ should be linearly related to Hammett's substituent constants, σ . Rao and Venkataraghavan⁸ find equally good correlations of $\log A$ with σ . These authors point out that although wavenumber is mainly determined by bond force constants, intensity is determined by dipole moment changes during the vibration, as may be seen from equation 1, above. Substituent groups generally change both ν and \underline{A} but not necessarily in the same direction or to the same degree.

In this work, however, we have been primarily interested in low-wavenumber vibrations of substituted benzenes. Such vibrations are not localized in a single pair of atoms, as in a simple stretching vibration, but involve motions of most or all of the atoms in the molecule. The intensities of such modes are not to be expected to be simple functions of a single physical property, but are undoubtedly affected by the mass of the substituent and by the influence of the substituent upon the force constants and electron distribution in the ring. Properties which presumably measure these latter effects are Hammett's substituent constants, σ_p and σ_m ; Taft's substituent constants, σ_I and σ_R ; and group electronegativities, X. Thus we have stressed these particular properties in our attempts to correlate intensities with physical properties.

The compounds selected for study were mono- and disubstituted benzenes substituted with the following ten representative substituents: -F, -Cl, -Br, -I, -CN, -CH₃, -CF₃, -CCl₃, -NO₂, and -OCH₃. They were selected both because they represent a wide range of physical properties—mass and electron-withdrawing power—and because they are simple. Simplicity is desirable in order that they do not too seriously alter the symmetry of the substituted ring. The hydroxyl and amino groups were not included because their strong tendency to hydrogen bonding leads to undesirable intermolecular interaction with consequent wavenumber and intensity shifts of their infrared bands.

We commenced our intensity measurements with ν_{19}' (γ CX) b_1 of mono-substituted benzenes. * ν_{19}' was selected for initial study both because it is normally the most intense band in the 650- to 265- cm^{-1} region and because its assignment is fairly certain in most of the molecules studied. We next measured the intensity ν_{18}' (α CCC) a_1 of monosubstituted benzenes and then ν_4 (γ CH) b_1 of symmetrical 1,4-disubstituted benzenes.

The spectra from 4000 to 265 cm^{-1} of all 38 compounds initially selected for study were recorded and are appended to this report. Two additional compounds (1,2-bis(trifluoromethyl)benzene and 1,2-bis(trichloromethyl)benzene) that would have completed the series of disubstituted benzenes were not obtainable.

II. RESULTS OF INTENSITY MEASUREMENTS

A. Intensity of ν_{19}' of Monosubstituted Benzenes

We have measured the integrated intensities of ν_{19}' (γ CX) b_1 for all ten mono-substituted benzenes. Table 1 summarizes the results. Column one lists the substituents, columns two and three the wavenumbers and intensities.

Each intensity value is the mean of two or more determinations. The technique and details of measurement are given in the Experimental Section, below. For convenience the substituents are arranged in order of increasing mass.

The intensity of ν_{19}' varies only slightly, discounting the three values for $-\text{NO}_2$, $-\text{CF}_3$, and $-\text{CCl}_3$. These last three are an order of magnitude lower than the remaining seven. The mean value of \underline{A} for ν_{19}' for these seven is 0.57 T. U. with a standard deviation of ± 0.09 T. U. Since the error in \underline{A} is estimated as about 5% or ± 0.03 T. U., there is still a significant variation in \underline{A} for ν_{19}' .

* The numbering system employed is the same as that described previously.^{1,2} However, we are now following the recommendations of the Joint Commission on Spectroscopy with regard to species notation.⁹ For monosubstituted benzenes with C_{2v} symmetry this means choosing the x -axis perpendicular to the ring and the z -axis through the 1- and 4-carbon atoms of the ring. The in-plane species are A_1 and B_2 , and the out-of-plane species are A_2 and B_1 . This change reverses the B_1 and B_2 species designations compared to our former notation.

Table 1. Summary of Intensities of ν_{19}' for Monosubstituted Benzenes

<u>Substituent</u>	<u>$\nu_0(\text{cm}^{-1})^*$</u>	<u>A(T. U.)</u>
-CH ₃	463	0.49
-F	498	0.62
-CN	545	0.71
-OCH ₃	509	0.64
-Cl	467	0.49
-NO ₂	510	0.012
-CF ₃	485	0.065
-Br	457	0.54
-CCl ₃	507	0.056
-I	448	0.48

* The wavenumber assignments listed are in general the same as given in reference 1. However, the different value for ν_{19}' for benzonitrile follows the recent assignment of this molecule by Green.¹⁰

B. Intensity of ν_{18}' of Monosubstituted Benzenes

The intensities of ν_{18}' for the selected monosubstituted benzenes are tabulated in Table 2. The data are arranged in order of increasing substituent mass. Only mean values are reported here. The solvent was cyclohexane, n-hexane, or 2,2,4-trimethylpentane. The technique and details of measurement are given in the Experimental Section, below.

Table 2. Summary of Intensities of ν_{18}' for Monosubstituted Benzenes

<u>Substituent</u>	<u>$\nu_0(\text{cm}^{-1})$</u>	<u>A(T. U.)</u>
-CH ₃	521	0.024
-F	519	0.28
-CN	461	0.0077
-OCH ₃	441	0.053
-Cl	418	0.14
-NO ₂	396	0.14
-CF ₃	339	0.22
-Br	315	0.080
-CCl ₃	308	0.040
-I	266	-**

** Wavenumber too low to measure.

C. Intensity of ν_4 of Symmetrical 1,4-Disubstituted Benzenes

Table 3 summarizes the intensities of ν_4 for symmetrical 1,4-disubstituted benzenes. Again the substituents are arranged in order of increasing mass. The solvents employed were cyclohexane, n-hexane, or benzene.

Table 3. Summary of Intensities of ν_4 for Symmetrical 1,4-Disubstituted Benzenes

<u>Substituent</u>	<u>$\nu_0(\text{cm}^{-1})$</u>	<u>A(T. U.)</u>
-CH ₃	795	2.7
-F	834	4.9
-CN	842	2.8
-OCH ₃	825	3.6
-Cl	820	3.1
-NO ₂	837	3.2
-CF ₃	848	3.9
-Br	811	3.0
-CCl ₃	851	6.6
-I	802	2.5

ν_4 for this series of compounds is considerably more intense than are ν_{18}' or ν_{19}' for the corresponding monosubstituted compounds. However, A_4 varies by only a little more than a factor of two for the series. No mass dependence of either ν_4 or A_4 is apparent from Table 3.

III. INTENSITY CORRELATIONS

A. Treatment of Data

The intensity data were first hand-plotted against the various physical properties to look for obvious simple correlations. When it became obvious that no such correlations were to be found, we attempted multiple linear correlations of the form shown in equation 3.

$$A = b_0 + \sum_{i=1}^n b_i x_i \quad (3)$$

Here \bar{A} is intensity, the x_i are various physical properties, and b_0 and b_i are parameters to be determined by the method of least squares. The calculations were programmed for a Royal-McBee LGP-30 digital computer. The advantage of the particular program employed is that four or five of the x_i can be treated simultaneously, and not only is a correlation coefficient, \bar{r} , computed for the entire set taken together, but also for \bar{A} with x_1 , \bar{A} with x_2 , etc. The correlation coefficient,¹¹ \bar{r} , was used as a criterion of the degree of correlation obtained. Although \bar{r} can have the range 0 to 1, 1 being perfect correlation, we accepted $\bar{r} > 0.9$ as sign of a good correlation here. For comparison, Rao and Venkataraghavan⁹ quote an average value of \bar{r} of 0.923 for the correlations of the intensities of carbonyl, hydroxyl, amine, and nitrile stretching bands of substituted benzenes with Hammett's σ , and the correlation we found earlier¹ between ν_{18}' and the reciprocal of the square root of the reduced mass of the phenyl-X system gives an \bar{r} of 0.98.

B. Physical Properties

Physical properties which were tested for possible correlation with intensities are listed in Table 4. The sources for most of these data were the same as given in reference 1; others were measured in the course of this work and are described in the Experimental Section.

C. Correlation of A_{19}' with Physical Properties for Monosubstituted Benzenes

The best correlations we have found with the intensity of ν_{19}' have been with Sanderson's partial charge data. Correlation coefficients are listed below for a linear relation:

<u>Sanderson's Data</u>	<u>Correlation Coefficient</u>
δ_X (charge withdrawal from ring)	0.80
δ_H (partial charge on hydrogen)	0.83
δ_C (partial charge on carbon)	0.83
δ_A (charge on the substituent atom next to the ring)	0.51

Table 4. List of Physical Properties

Symbol	Description	Source Reference
σ_p	Hammett's <u>para</u> substituent constant	1
σ_m	Hammett's <u>meta</u> substituent constant	1
σ_p^+	Electrophilic <u>para</u> substituent constant	12
σ_m^+	Electrophilic <u>meta</u> substituent constant	12
σ_I	Taft's inductive substituent constant	1
σ_R	Taft's resonance substituent constant	1
X	Group electronegativity	1
μ_e	Electric dipole moment	1
m	Substituent mass	1
μ_s	Platt's spectroscopic moment	1
μ_m	Mesomeric dipole moment	1
δ_X	Sanderson's charge withdrawal from the ring	1
δ_A	Sanderson's charge on the atom of X next to the ring	1
δ_C	Sanderson's partial charge on carbon	1
δ_H	Sanderson's partial charge on hydrogen	1
MR _D	Molar refraction	13
$\Delta S_V^{b.p.}$	Entropy of vaporization at the boiling point	13, 14
δ_r	NMR chemical shift of ring protons from benzene	15 and this work
ν	Wavenumber of the absorption band	This work

As seen from Figure 1, showing the intensity of ν_{19}' vs. Sanderson's charge withdrawal from the ring, δ_X , these relations are not linear. The true form of the function is not simple to determine from the available data. If calculated as an ellipse with center at $\delta_X = 0.82$, $A_{19}' = 0.53$ T. U., the correlation coefficient improves to 0.86.

In addition, we found a correlation coefficient of 0.81 for the intensity of ν_{19}' with the NMR chemical shift of the para proton from benzene. This relation appears linear and is shown in Figure 2.

D. Correlation of A_{18}' with Physical Properties for Monosubstituted Benzenes

Correlations for the intensity of ν_{18}' were sought with the same physical properties tried for the intensity of ν_{19}' . No property shows good linear correlation with the intensity of ν_{18}' .

The largest correlation coefficients obtained were for the partial charge data of Sanderson. Correlation coefficients for these are tabulated below, again for a linear relation:

<u>Sanderson's Data</u>	<u>Correlation Coefficient</u>
δ_X (charge withdrawal from the ring)	0.54
δ_C (partial charge on carbon)	0.54
δ_H (partial charge on hydrogen)	0.53
δ_A (charge on the substituent atom next to the ring)	0.39

As is seen from Figure 3, showing the plot of A_{18}' vs. Sanderson's charge on the substituent atom next to the ring, δ_A , these relations are not linear. Figure 3 appears to be a hyperbola; therefore, the axes and foci were determined graphically in order to evaluate a and b in the equation for a hyperbola with foci on the y axis:

$$\frac{y^2}{a^2} = \frac{x^2}{b^2} + 1$$

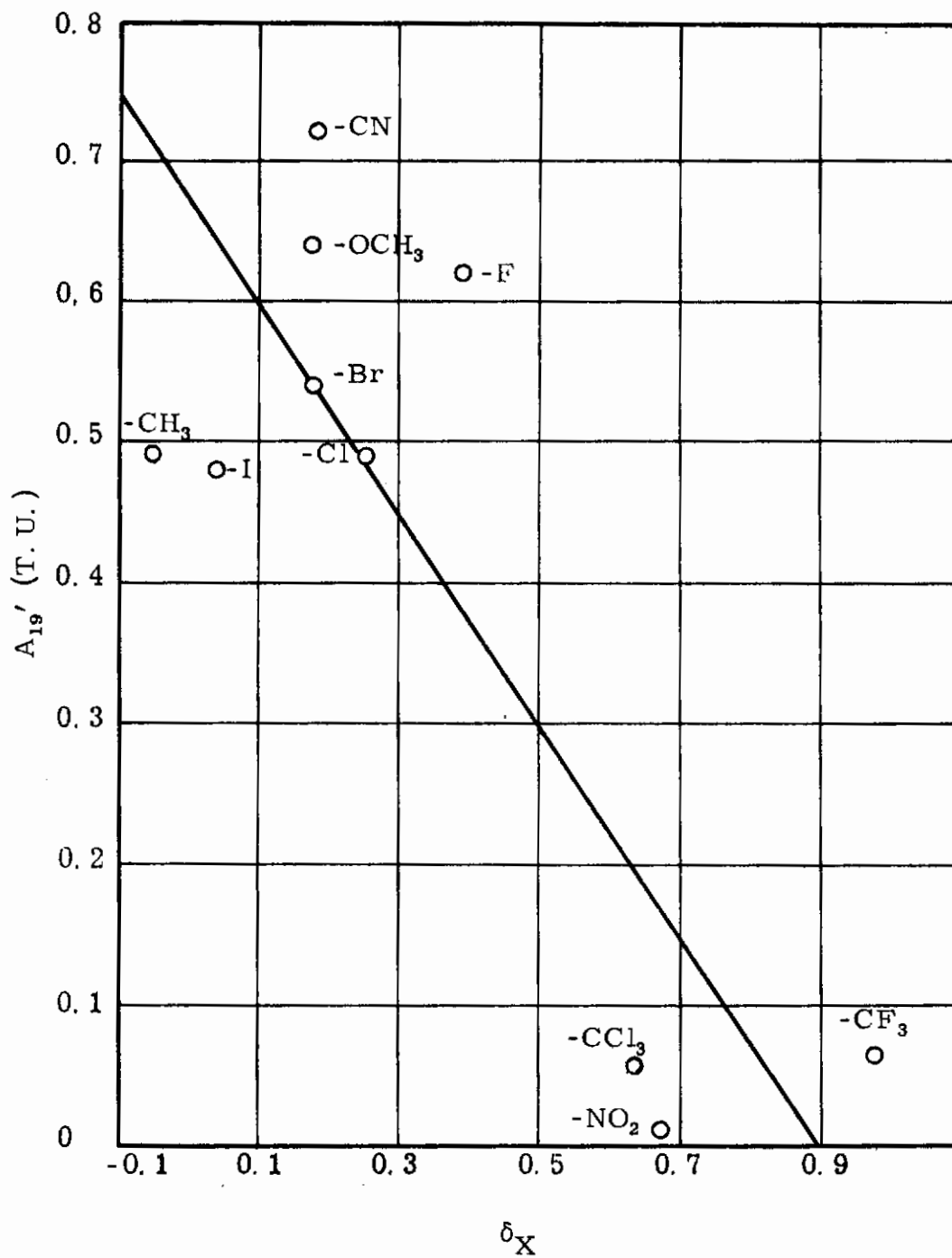


Figure 1. Monosubstituted benzenes: intensity of ν_{19}' vs. Sanderson's charge withdrawal from the ring.

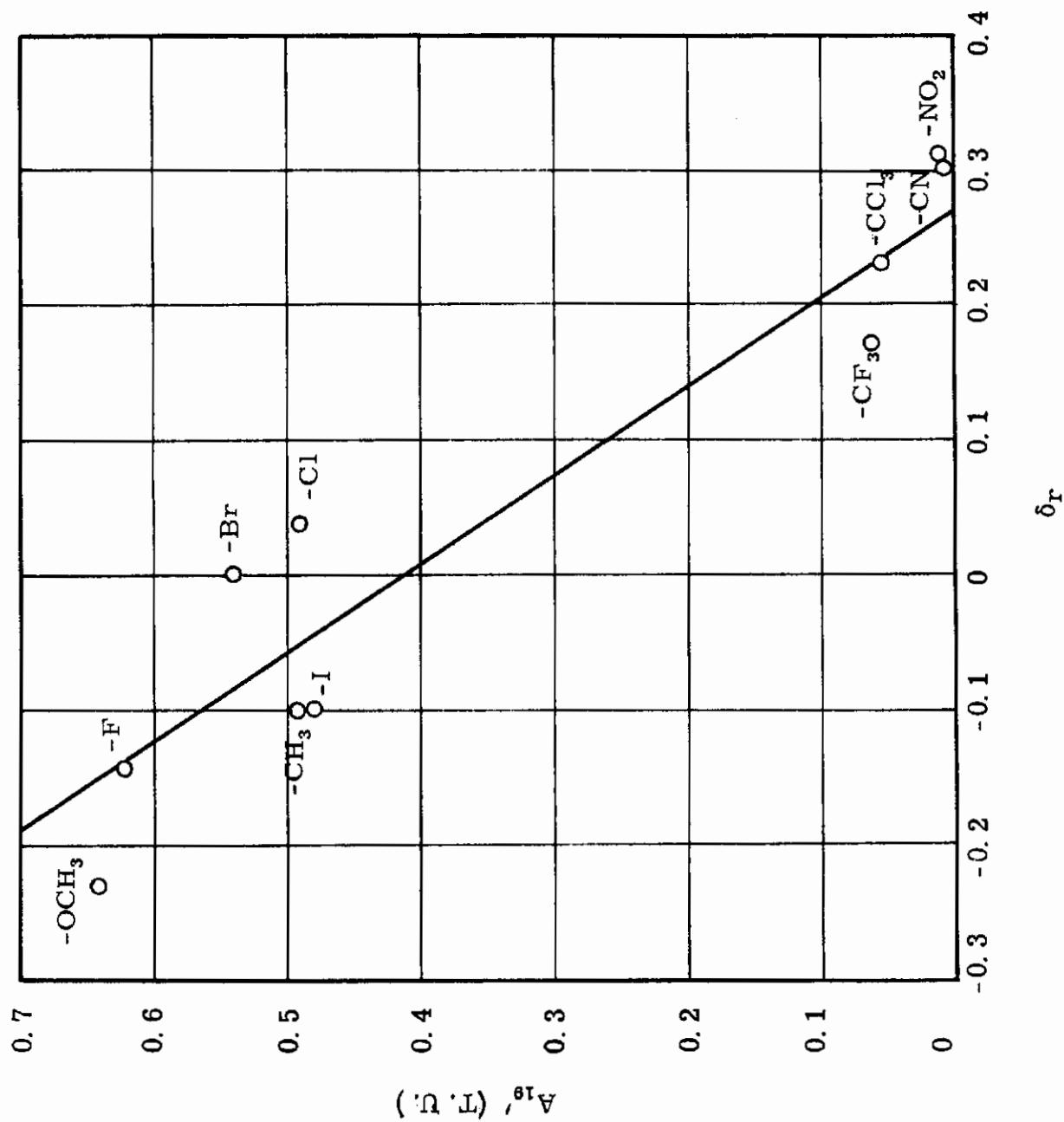


Figure 2. Monosubstituted benzenes: intensity of $\nu_{19'}$ vs. NMR chemical shift of the para proton from benzene.

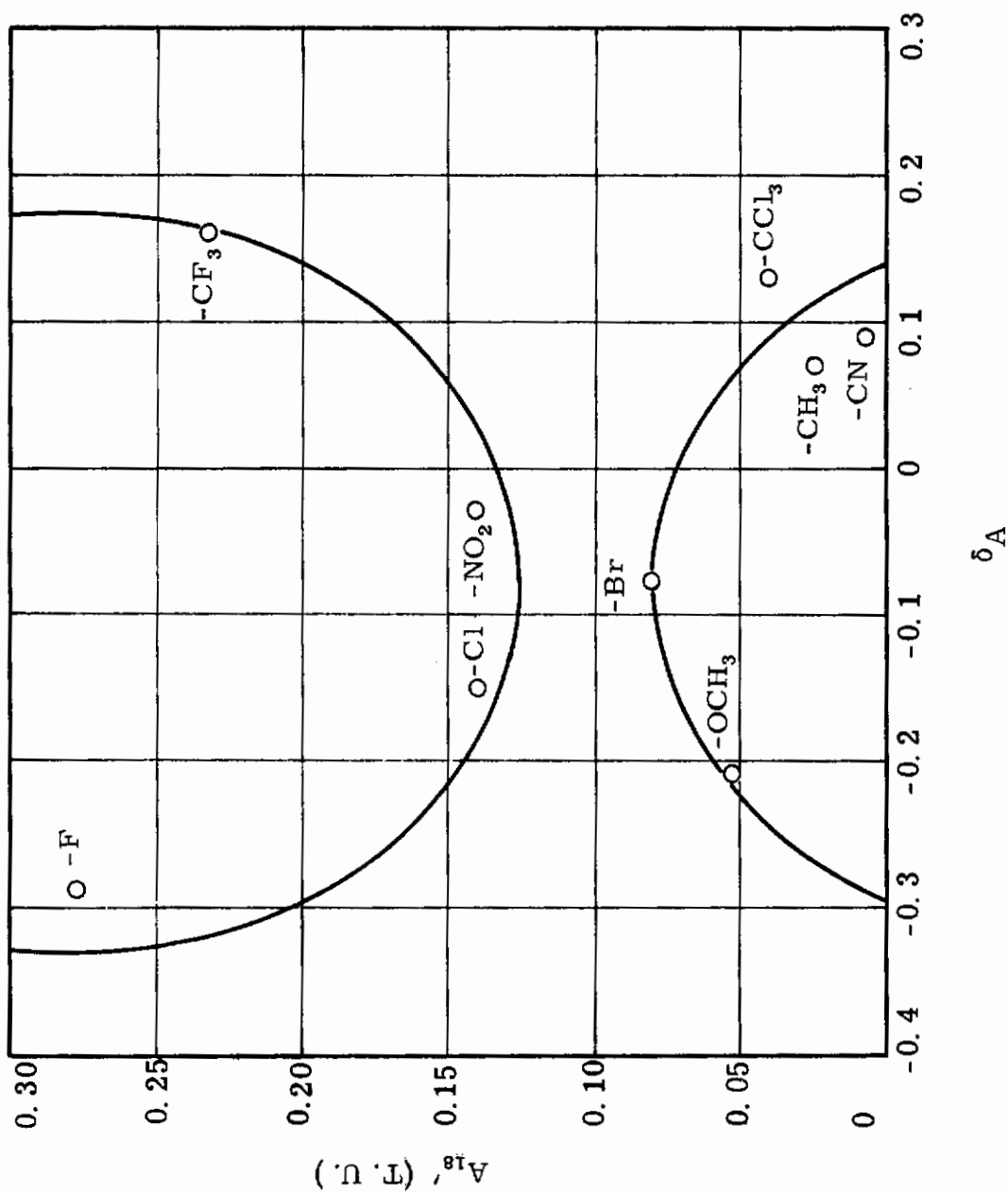


Figure 3. Monosubstituted benzenes; intensity of ν_{18} vs. Sanderson's charge on the substituent atom next to the ring.

The independent variable, \underline{x} , was adjusted to be $\delta_A + 0.18$ in order to make the foci fall on the \underline{y} axis.

A quantity \underline{x}' was then introduced: $x' = \pm\sqrt{x^2 + b^2}$ with $b = 0.011$, as determined graphically.

If negative values of \underline{x}' are taken for points lying on the lower branch of the hyperbola shown in Figure 3, and positive values of \underline{x}' are taken for those on the upper branch, a linear relation should now exist between \underline{x}' and the intensity of ν_{18}' . Solving the least-squares equation for our values of \underline{x}' and A_{18}' , and determining the correlation coefficient, we found such a linear relation with a correlation coefficient of 0.95. This relation is shown in Figure 4.

E. Correlation of A_4 with Physical Properties for Symmetrical 1,4-Disubstituted Benzenes

Sanderson's data were not available for symmetrical 1,4-disubstituted benzenes, and so these quantities were calculated by his method in order to attempt correlations with them. These values are shown in Table 5.

Correlation coefficients obtained for the correlation of A_4 with these quantities, using a linear least-squares program, are listed below:

<u>Data by Sanderson's Method</u>	<u>Correlation Coefficient</u>
δ_X (charge withdrawal from ring)	0.54
δ_C (partial charge on carbon)	0.54
δ_H (partial charge on hydrogen)	0.53
δ_A (charge on the substituent atom next to the ring)	0.067

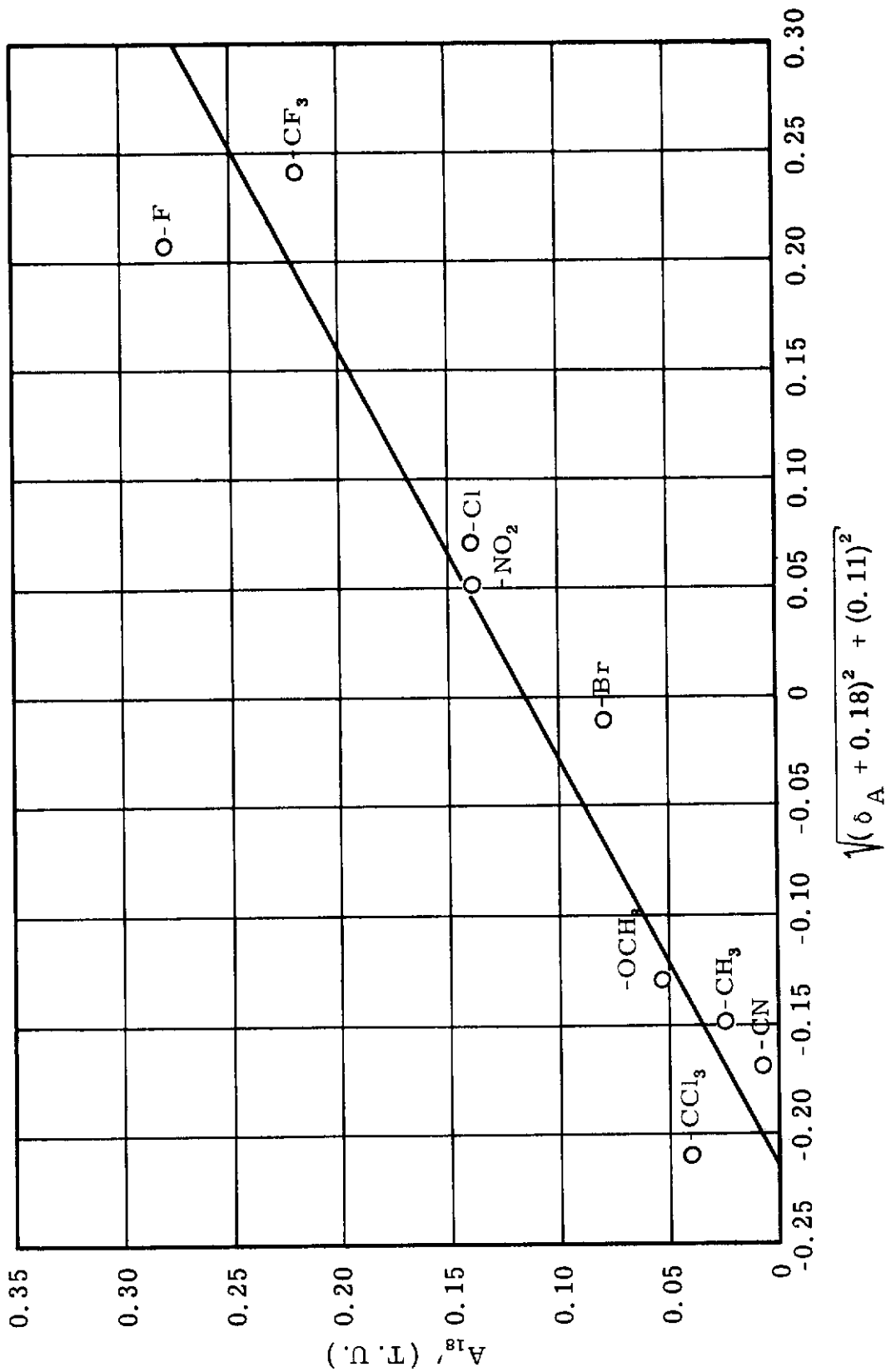


Figure 4. Monosubstituted benzenes: intensity of ν_{18} vs.

$$\sqrt{(\delta_A + 0.18)^2 + (0.11)^2}$$

Table 5. Partial Charge Data for Symmetrical 1,4-Disubstituted Benzenes
Calculated by the Method of Sanderson

Substituent	δ_X^*	δ_C^*	δ_H^*	δ_A^*
-CH ₃	-0.088	-0.034	0.026	-0.034
-F	0.712	0.046	0.108	-0.358
-CN	0.298	0.005	0.066	0.005
-OCH ₃	0.242	-0.001	0.060	-0.300
-Cl	0.457	0.021	0.083	-0.229
-NO ₂	1.082	0.082	0.146	-0.083
-CF ₃	1.504	0.124	0.189	0.124
-Br	0.320	0.007	0.069	-0.160
-CCl ₃	0.968	0.071	0.134	0.071
-I	0.060	-0.018	0.042	-0.030

* δ_X = Charge withdrawal from the ring.

δ_C = Partial charge on carbon.

δ_H = Partial charge on hydrogen.

δ_A = Charge on the atom of the substituent next to the ring.

Plots of the intensity of ν_4 vs. these quantities show that the relations are not linear. The plot of A_4 vs. the charge on the substituent atom next to the ring, δ_A , shown in Figure 5, is apparently elliptical and was treated accordingly.

The axes of the ellipse were determined graphically, and " \underline{x} " was adjusted to be $\delta_A + 0.83$, in order to make the center of the ellipse fall on the " \underline{y} " axis.

In order to use a linear least-squares program, a quantity \underline{x}' , equal to $\pm\sqrt{\underline{x}^2 - a^2}$, was introduced (a = the semi-major axis = 0.275). Positive values for \underline{x}' were used for points above the major axis of the ellipse, negative values for points below this axis.

The intensity of ν_4 gives a correlation coefficient of 0.98 with \underline{x}' so determined. This relation is shown in Figure 6.

The only other quantity showing any semblance of correlation with A_4 is wavenumber. The linear correlation of A_4 with ν_4 gave an r of 0.66. No satisfactory multiple correlations were found.

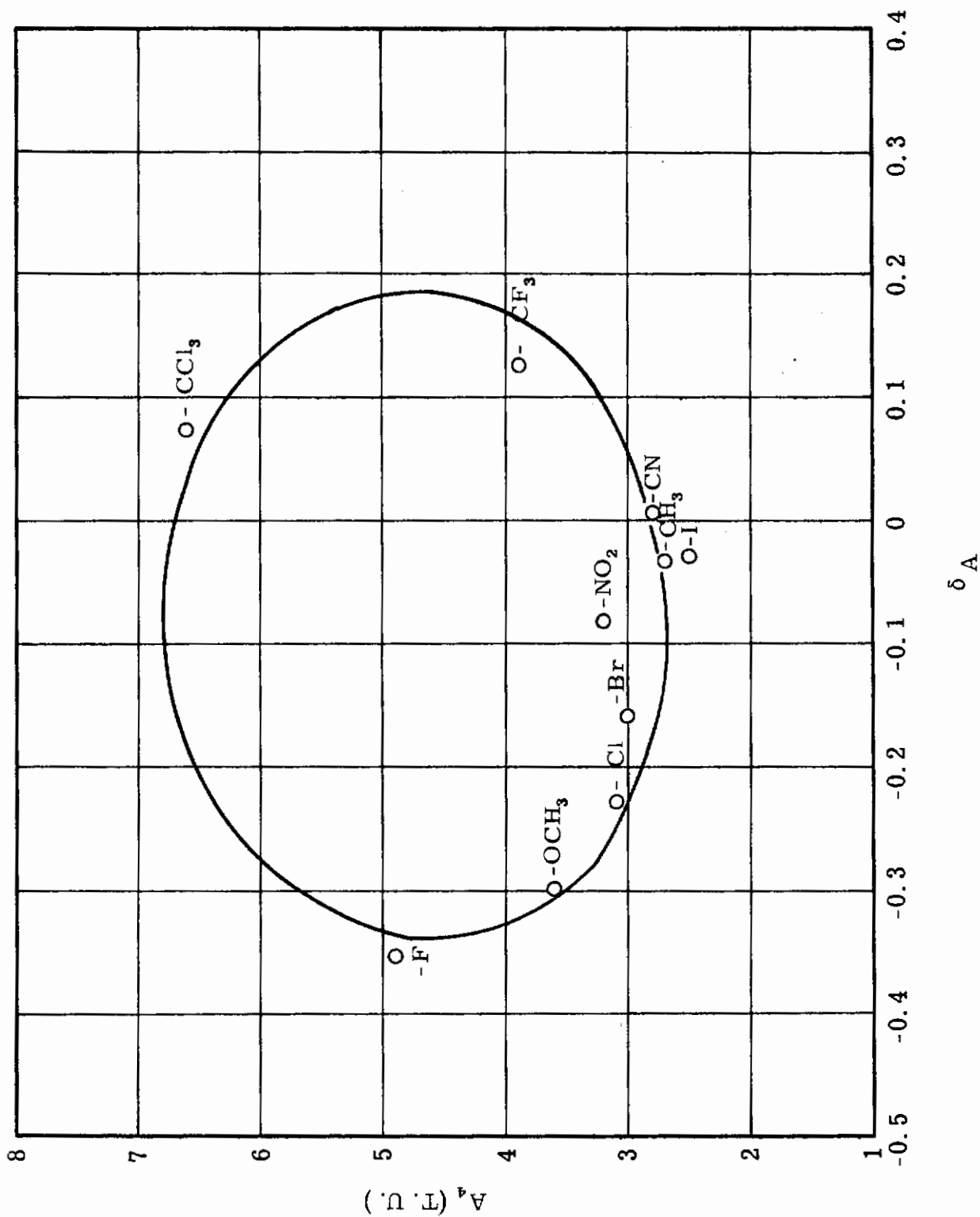


Figure 5. Symmetrical 1,4-disubstituted benzenes: intensity of ν_4 vs. Sanderson's charge on the substituent atom next to the ring.

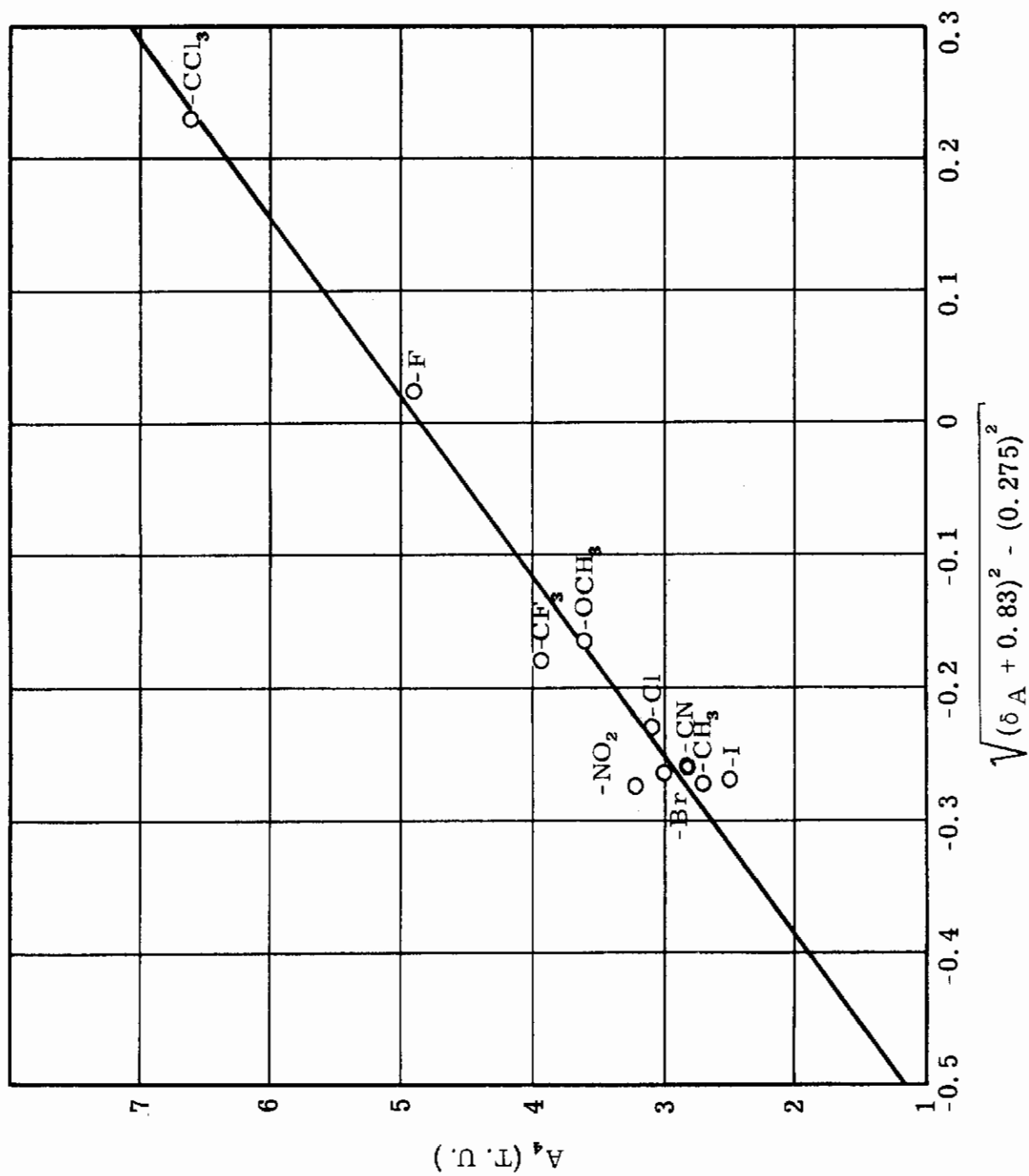


Figure 6. Symmetrical 1,4-disubstituted benzenes: intensity of ν_4 vs.

$$\sqrt{(\delta_A + 0.83)^2 - (0.275)^2}$$

$$\sqrt{(\delta_A + 0.83)^2 - (0.275)^2}$$

IV. WAVENUMBER CORRELATIONS

No satisfactory correlations were found for the wavenumber of ν_{19}' of monosubstituted benzenes with physical properties, nor were any new correlations discovered for the wavenumber of ν_{18}' . As previously reported¹ the relations of Sanderson's partial charge data with the wavenumber of these vibrations is not linear, though there may be some second degree relation.

The largest correlation coefficients obtained with the wavenumber of ν_4 for symmetrical 1,4-disubstituted benzenes were with partial charge data calculated by the method of Sanderson. These are listed below:

<u>Data Calculated by the Method of Sanderson</u>	<u>Correlation Coefficients*</u>
δ_X (charge withdrawal)	0.81
δ_C (partial charge on carbon)	0.81
δ_H (partial charge on hydrogen)	0.81
δ_A (charge on the atom of the substituent next to the ring)	0.26
$1/\delta_H$	0.84

* Treating the relation as though linear.

As with other correlations found using Sanderson's partial charges, these relations are not linear, generally appearing to be hyperbolas. By plotting x' , described in Section III E, against wavenumber of ν_4 , a clearly-defined hyperbola is obtained. This is shown in Figure 7.

The simplest curve obtained was for the wavenumber of ν_4 vs. the partial charge on hydrogen, shown in Figure 8.

We made tentative assignments for ν_{19}' for the ortho-, meta-, and para-disubstituted benzenes, as shown in Table 6, and attempted correlations of these data with physical properties. None was successful.

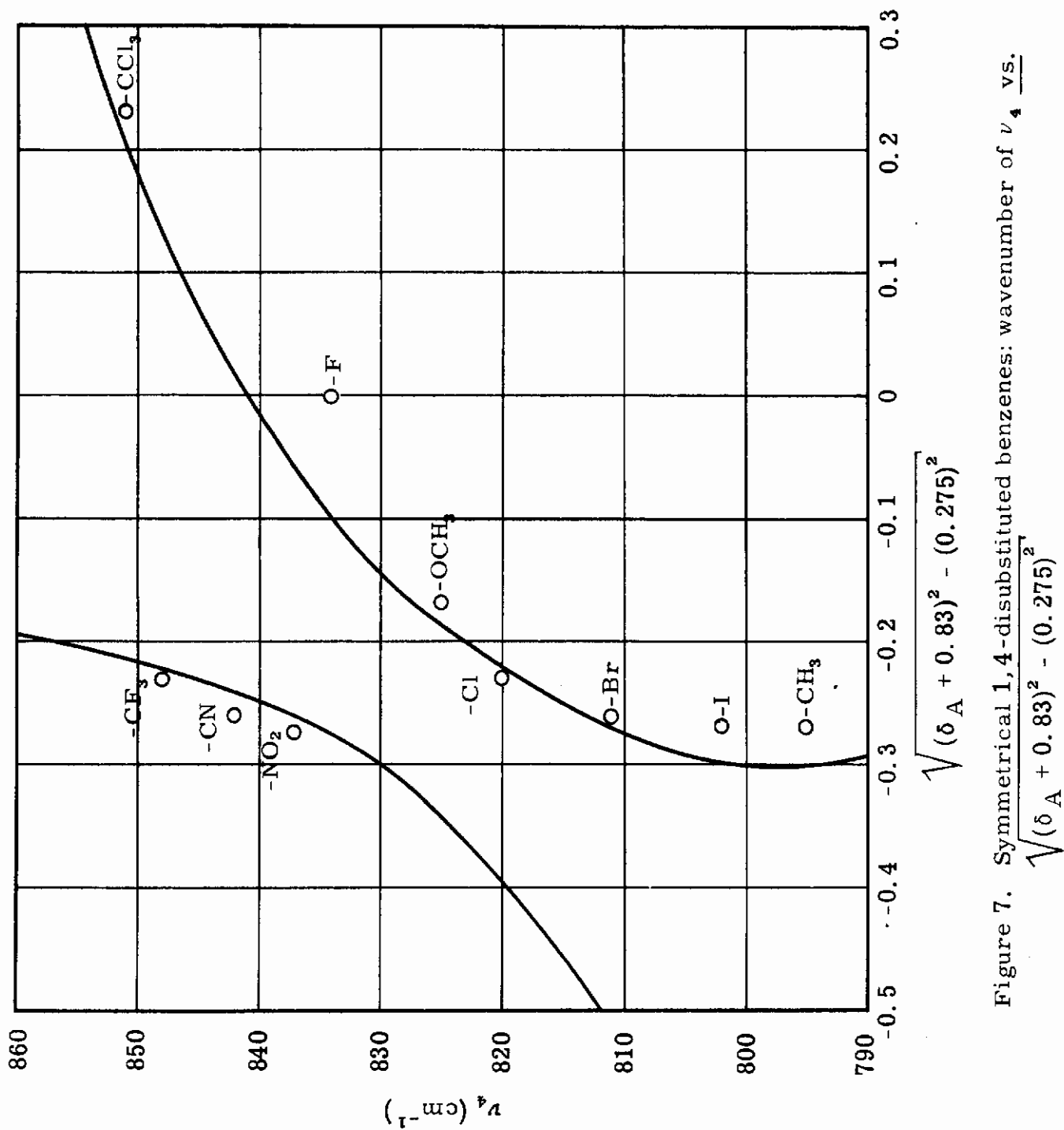


Figure 7. Symmetrical 1,4-disubstituted benzenes: wavenumber of ν_4 vs. $\sqrt{(\delta_A + 0.83)^2 - (0.275)^2}$

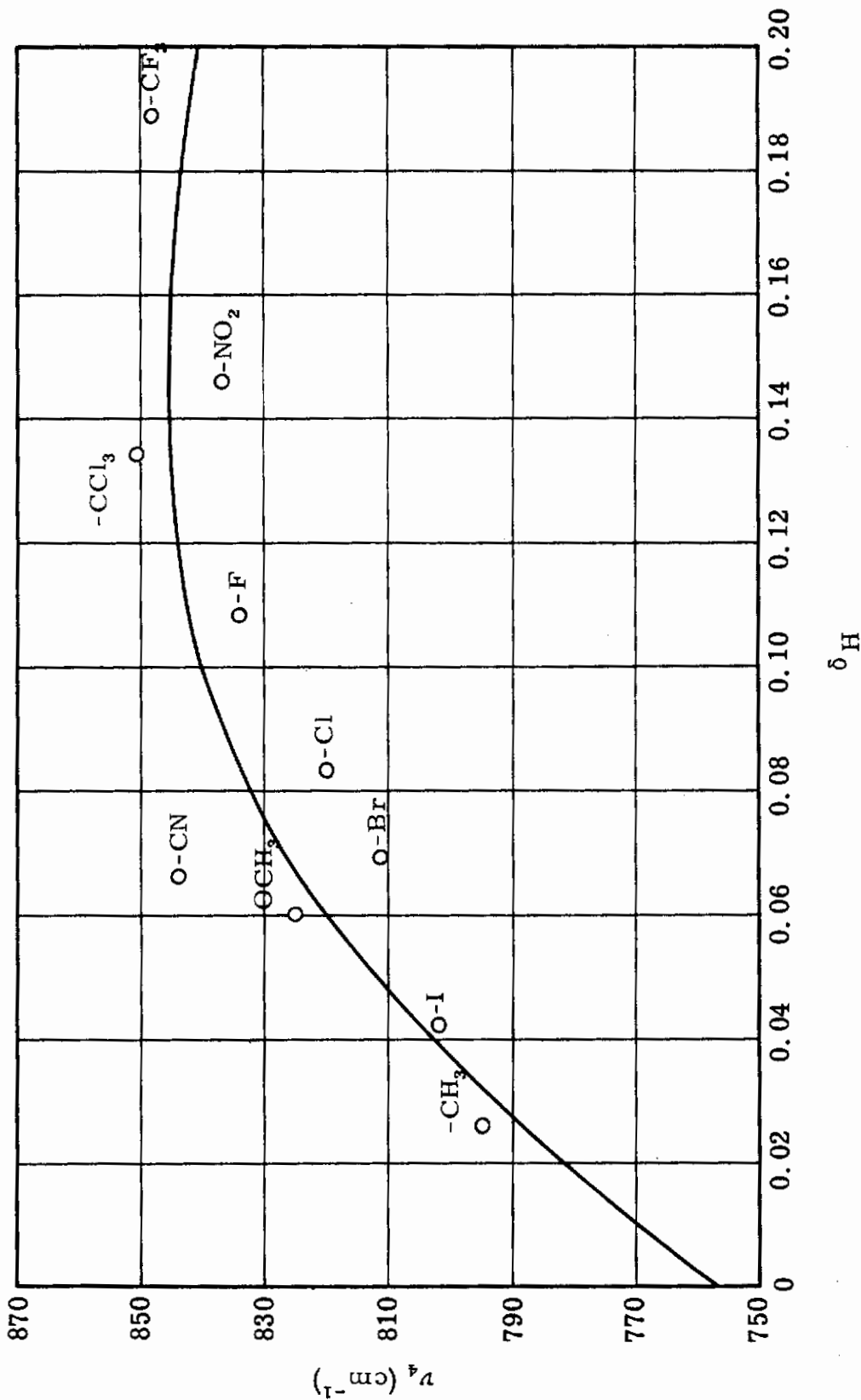


Figure 8. Symmetrical 1,4-disubstituted benzenes: wavenumber of ν_4 vs. Sanderson's partial charge on hydrogen.

Table 6. Tentative Assignments for ν_{19}' of Symmetrical Disubstituted Benzenes

Substituents	Wavenumber in cm^{-1}		
	Ortho	Meta	Para
-CH ₃	435	431	483
-F	450	457	508
-CN	474	461	-
-OCH ₃	465	459	470
-Cl	437	431	481
-NO ₂	425	405	442
-CF ₃	-	437	448
-Br	431	425	472
-CCl ₃	-	433	442
-I	420	417	463

V. SUMMARY AND CONCLUSIONS

Although correlations of the intensities of ν_{18}' and ν_{19}' for monosubstituted benzenes were attempted with a wide variety of physical properties, no simple relation between intensity and physical properties was uncovered. One reason for our not finding any correlation of A_{19}' with physical properties may be that it is mixing with other modes of its symmetry species, in particular with ν_{20}' .¹ However, since ν_{20}' occurs below the range of the cesium bromide prism (in the range 150 to 250 cm^{-1}), we could not measure its intensity with our present equipment. We could not, then, try to correlate ($A_{19}' + A_{20}'$) with physical properties. We felt that it might be possible to test this notion for symmetrical 1,4-disubstituted benzenes, however. Since there are only three modes in the species B_{3u} to which ν_{19}' and ν_{20}' belong, one should be able to measure the intensity of the third mode, ν_4 , and correlate it with physical properties if ν_{19}' and ν_{20}' are not mixing with ν_4 . We presumed this to be so since the wavenumbers of ν_{19}' and ν_{20}' are substituent sensitive, whereas the wavenumber of ν_4 is far less so. ν_4 remains near 800 cm^{-1} . We, therefore, measured the intensities of ν_4 for the ten 1,4-disubstituted benzenes previously selected for study and attempted to correlate A_4 with physical properties. However, no useful correlations were found for A_4 .

As was reported in the wavenumber correlation work earlier,¹ Sanderson's partial charge data gave non-linear correlations. Most of these relations appeared to be homogeneous equations of the second degree, that is, ellipses or hyperbolas. Even supposing these correlations are significant, they are not useful in a practical sense as they are double-valued; that is, a single value of a physical property would lead to a prediction of two different values of intensity, or vice versa.

We may thus conclude that, assuming our assignments for the various bands in each series are correct, the degree of mixing of these types of vibrations is probably variable within a series. That is, ν_{19}' may be mixing with ν_{20}' in chlorobenzene to a far different extent than it is mixing with ν_{20}' in, say, nitrobenzene. Their intensities would thus not be capable of being simply related to physical properties.

VI. EXPERIMENTAL SECTION

A. Materials

1. Toluene

Toluene was a reagent grade product of General Chemical Division of Allied Chemical Corporation. Gas chromatography showed it to be of 99.9% purity. Its index of refraction was determined as $n_D^{25} = 1.4941$, which agrees with a literature value of 1.4941.¹³

2. Fluorobenzene

Fluorobenzene was an Eastman Kodak product. Analysis by gas chromatography showed 99.9% fluorobenzene; $n_D^{25} = 1.4632$. Dreisbach¹³ gives $n_D^{25} = 1.46553$. This large discrepancy led us to investigate the source of Dreisbach's data. He apparently employed the value given by Timmermans¹⁶ of $n_D^{15} = 1.46837$. However, he listed this value as n_D^{20} and proceeded to calculate n_D^{25} and n_D^{30} from it. That this is so is confirmed by Vogel's¹⁷ value of $n_D^{20} = 1.46573$ which corrects to $n_D^{25} = 1.4632$ in good agreement with our result. These values are summarized for clarity in Table 7.

Table 7. Refractive Indexes of Fluorobenzene

Source	n_D^t			
	15	20	25	30
Dreisbach ¹³		1.46837	1.46553	1.46256
Timmermans ¹⁶	1.46837		1.4634*	
Vogel ¹⁷		1.46573	1.4632*	
This work			1.4632	

* These values were calculated from $\frac{dn_D}{dt} = -0.00050^\circ\text{C}^{-1}$

3. Benzonitrile

Benzonitrile was a compound from Matheson, Coleman, and Bell. Gas chromatography showed its purity as 99.9%. Determination of index of refraction gave $n_D^{25} = 1.5253$. According to Jeffery and Vogel,¹⁸ $n_D^{20} = 1.52823$, which would give a value of approximately 1.5257 for 25°C.

4. Anisole

Anisole was an Eastman Kodak product which has been described previously.¹ Gas chromatographic analysis showed it to be 99.9% anisole; $n_D^{25} = 1.5143$, which agrees with the value according to Timmermans¹⁶ ($n_D^{25} = 1.51430$), and compares well with the value given by Vogel,¹⁹ if the value is corrected to 25°C, ($n_D^{20} = 1.51779$).

5. Chlorobenzene

Chlorobenzene was obtained from Matheson, Coleman, and Bell. Analysis by gas chromatography showed it to be 99.7% chlorobenzene; $n_D^{25} = 1.5216$. Dreisbach¹³ quotes $n_D^{25} = 1.52138$.

6. Nitrobenzene

Nitrobenzene was an Eastman Kodak compound, previously described.¹ Gas chromatography showed its purity as 100%; $n_D^{25} = 1.5498$, as compared to a value according to Dreisbach¹³ of 1.55006.

7. Benzotrifluoride

This compound was purified by distillation. Gas chromatographic analysis showed 99.9% benzotrifluoride; $n_D^{25} = 1.4124$, compared with Dreisbach's¹³ value of 1.41225.

8. Bromobenzene

Bromobenzene was an Eastman Kodak product. Gas chromatography showed 99.2% bromobenzene; $n_D^{25} = 1.5573$, compared with Dreisbach's¹³ value of 1.55709.

9. Benzotrichloride

This compound was an Eastman Kodak product. It was purified by bubbling with dry nitrogen to remove all fumes, extracting three times with 100 ml of a saturated solution of NaHCO_3 , drying with MgSO_4 , and distilling. The distillation was carried out at atmospheric pressure (749.7 mm), using a twenty-inch, vacuum jacketed column packed with glass helices. The fraction collected boiled at 218°C.

Elemental analyses gave the following results:

	<u>Found</u>	<u>Theory</u>
% C	43.2, 43.3	43.00
% H	2.7, 2.8	2.58
% Cl	54.3, 54.3	54.42

A determination of index of refraction gave $n_D^{25} = 1.5563$.

10. Iodobenzene

Three samples of iodobenzene have been used. All three were Eastman Kodak products. Gas chromatographic analysis showed all three to be 99.7% iodobenzene. For Sample 1, $n_D^{25} = 1.6171$; Samples 2 and 3, $n_D^{25} = 1.6175$. Dreisbach¹³ lists this value as 1.6172.

11. o-Xylene

o-Xylene was obtained from Phillips Petroleum Company (99 mol % minimum). Gas chromatography indicated that it was 99.3% o-xylene; $n_D^{25} = 1.5025$, compared with Dreisbach's¹³ value of 1.5030.

12. o-Difluorobenzene

This compound was obtained from Pierce Chemical Company. It was purified by distillation at atmospheric pressure using the column described in 9 above. The product was collected at 92°C.

Gas chromatographic analysis showed that it was 99.9% o-difluorobenzene; $n_D^{25} = 1.4471$.

13. Phthalonitrile

Phthalonitrile was a product of Eastman Kodak, practical grade. It was purified by recrystallizing twice from ethanol, after which elemental analyses gave the following results:

	<u>Found</u>	<u>Theory</u>
% C	75.1, 74.9	74.98
% H	3.4, 3.3	3.15
% N	21.7, 21.9	21.87

14. Veratrole (1,2-dimethoxybenzene)

Veratrole was obtained from Eastman Kodak, and purified by distillation at 10-mm pressure using the column described in 9 above. The sample was collected at 91°C.

After distillation, gas chromatography gave an analysis of 100% veratrole; $n_D^{25} = 1.5323$.

15. o-Dichlorobenzene

o-Dichlorobenzene was another product from Eastman Kodak. Gas chromatographic analysis showed the percent o-dichlorobenzene to be 99.9%; $n_D^{25} = 1.5490$. Dreisbach¹³ lists $n_D^{25} = 1.54920$.

16. o-Dinitrobenzene

This compound was obtained from K. and K. Laboratories, Inc. It was purified by two successive recrystallizations from ethanol, using charcoal in the first.

After purification, elemental analyses gave the following results:

	<u>Found</u>	<u>Theory</u>
% C	43.0, 43.1	42.86
% H	2.4, 2.5	2.40
% N	16.5, 16.5	16.67

17. o-Dibromobenzene

o-Dibromobenzene was a product from Eastman Kodak. Analysis by gas chromatography showed it to be 99.3% o-dibromobenzene; $n_D^{25} = 1.6084$; Dreisbach's¹³ value is $n_D^{25} = 1.60909$.

18. o-Diiodobenzene

This compound was purchased from Eastman Kodak. It was purified by distillation using a spinning-band column.

Subsequent elemental analyses gave the following results:

	<u>Found</u>	<u>Theory</u>
% C	22.1, 22.0	21.84
% H	1.2, 1.2	1.22

19. m-Xylene

m-Xylene was a product of Phillips Petroleum Company which gas chromatography showed to be 99.5% m-xylene; $n_D^{25} = 1.4945$. The value from Dreisbach¹³ is $n_D^{25} = 1.49464$.

20. m-Difluorobenzene

This compound was obtained from Eastman Kodak. Analysis by gas chromatography showed it to be 99.7% m-difluorobenzene; $n_D^{25} = 1.4356$. A value calculated using data from Timmermans¹⁶ is $n_D^{25} = 1.4347$.

21. Isophthalonitrile

Isophthalonitrile was prepared at Southern Research Institute from isophthalic acid obtained from Oronite Chemical Company.

Determinations of carbon, hydrogen, and nitrogen gave the following results:

	Found	Theory
% C	75.0	74.98
% H	3.2	3.15
% N	22.0	21.87

22. m-Dimethoxybenzene

m-Dimethoxybenzene was purchased from Eastman Kodak. It was redistilled using the column described under 9 above at 84.2° and 7 mm pressure. Later it was distilled again using a spinning-band column, at 86° and 9 mm pressure.

Gas chromatography showed this product to be 99.6% m-dimethoxybenzene; $n_D^{25} = 1.5233$.

23. m-Dichlorobenzene

This compound was obtained from Eastman Kodak. Gas chromatographic analysis showed 99.8% m-dichlorobenzene; $n_D^{25} = 1.5437$, compared to a value from Dreisbach¹³ of $n_D^{25} = 1.54337$.

24. m-Dinitrobenzene

m-Dinitrobenzene was another Eastman Kodak product. Elemental analyses gave the following results:

	Found	Theory
% C	42.9, 43.0	42.86
% H	2.5, 2.6	2.40
% N	16.5	16.67

25. 1,3-Bis(trifluoromethyl)benzene

This compound was purchased from Columbia Organic Chemicals Company, Inc. It was distilled at 114-114.5°C and atmospheric pressure. It was then redistilled using a spinning band column, and a center portion was collected.

Analysis by gas chromatography showed this portion to be 99.7% pure; $n_D^{25} = 1.3787$.

26. m-Dibromobenzene

m-Dibromobenzene was a product of Eastman Kodak. Gas chromatographic analysis showed it to be 99.7% m-dibromobenzene; $n_D^{25} = 1.6052$.

27. 1,3-Bis(trichloromethyl)benzene

This compound was obtained from K. and K. Laboratories, Inc. Elemental analyses gave the following results:

	Found	Theory
% C	30.8	30.71
% H	1.4	1.29
% N	68.3	68.00

28. m-Diodobenzene

m-Diodobenzene was another product of Eastman Kodak. It was purified by two recrystallizations from ethanol.

Subsequent elemental analyses gave the results below:

	Found	Theory
% C	21.8	21.84
% H	1.3	1.22

29. p-Xylene

p-Xylene was obtained from Phillips Petroleum Company. Gas chromatography showed it to be 99.9+% p-xylene; $n_D^{25} = 1.4933$. The Dreisbach¹³ value is $n_D^{25} = 1.49325$.

30. p-Difluorobenzene

This compound was purchased from K. and K. Laboratories, Inc. Analysis by gas chromatography showed it to be 99.8% p-difluorobenzene; $n_D^{25} = 1.4390$. A calculated value, based on data from Timmermans,¹⁶ is $n_D^{25} = 1.4391$.

31. Terephthalonitrile

Terephthalonitrile was a product of Eastman Kodak. It was purified by two successive crystallizations from benzene; it was then dried for two hours at 78°C.

The purified product gave the following results for elemental analyses:

	Found	Theory
% C	74.9, 75.2	74.99
% H	3.0, 3.3	3.15
% N	21.8, 21.6	21.87

32. p-Dimethoxybenzene

p-Dimethoxybenzene was a product of Eastman Kodak. Gas chromatographic analysis showed that it was 99.4% p-dimethoxybenzene.

33. p-Dichlorobenzene

This compound was also obtained from Eastman Kodak. Analysis by gas chromatography showed 100% p-dichlorobenzene.

34. p-Dinitrobenzene

This compound was prepared at Southern Research Institute, and its preparation was described in a previous report.¹ Current elemental analyses gave the following results:

	<u>Found</u>	<u>Theory</u>
% C	42.7, 43.1	42.86
% H	2.6, 2.3	2.40
% N	16.4	16.67

35. 1,4-Bis(trifluoromethyl)benzene

Columbia Organic Chemicals Company, Inc. was the source of this compound. It was purified by distillation at atmospheric pressure employing the column described under 9 above, and the product collected at 115°C.

Analysis by gas chromatography showed it to be 99.4% pure; $n_D^{25} = 1.3777$.

36. p-Dibromobenzene

p-Dibromobenzene was a product of Brothers Chemical Company. Gas chromatography showed that it was 99.7% p-dibromobenzene.

37. 1, 4-Bis(trichloromethyl)benzene

We purchased this compound from K. and K. Laboratories. Elemental analyses gave the following results:

	<u>Found</u>	<u>Theory</u>
% C	30.9	30.71
% H	1.3	1.29
% N	68.1	68.00

38. p-Diodobenzene

p-Diodobenzene was obtained from Eastman Kodak. It was purified by two recrystallizations from ethanol.

Elemental analyses on the purified compound gave the following results:

	<u>Found</u>	<u>Theory</u>
% C	21.8	21.84
% H	1.2	1.22

B. Intensity Measurements

The absorption bands, ν_{18}' and ν_{19}' , were recorded with a Perkin-Elmer Model 21 double-beam spectrophotometer equipped with cesium bromide optics. The standard thermocouple has been replaced with one manufactured by the Charles Reeder Company. This thermocouple has about twice the sensitivity of the detector normally used.

The wavelength scale was calibrated against atmospheric carbon dioxide and water-vapor bands. Wavelength accuracy is estimated as ± 0.06 microns. To reduce the loss of energy owing to atmospheric absorption, the entire instrument, including the sampling area, was purged with dry nitrogen at all times.

The wavelength drive was adjusted to present 0.1 microns per centimeter in place of the normal 0.5 microns per centimeter. With this setting, the absorption band is spread out to a more suitable shape from which to obtain the necessary data for intensity calculations. The recording speed was about 0.15 microns per minute. The mechanical slit width chosen was a compromise between the spectral slit width desired, the available energy, and the signal-to-noise ratio.

Computed spectral slit widths, S' , were calculated according to the formula of Jones and Sandorfy²⁰ for prism spectrometers

$$S' = \frac{\nu^2 [1 - n^2 \sin^2 \frac{\alpha}{2}]^{\frac{1}{2}}}{4 \sin \frac{\alpha}{2} \frac{dn}{d\lambda}} (s/f) + \frac{\nu}{2b \frac{dn}{d\lambda}}$$

in which ν is the wavenumber in cm^{-1} , n is the refractive index of the prism at ν , α is the apex angle of the prism, s is the width of the entrance or exit slit (whichever is greater), f is the focal length in the same units as s , b is the prism base in cm, and $\frac{dn}{d\lambda}$ is the dispersion of the prism at ν .

The dispersion of the CsBr prism used in our calculations, as $\frac{\Delta n}{\Delta \lambda}$, was computed from published data for the refractive index of CsBr.^{21, 22} Plots of n vs. ν , and of $\frac{\Delta n}{\Delta \lambda}$ vs. λ were constructed and are shown in Figures 9 and 10.

The calculations for the computed slit width were programmed for a Royal McBee LGP-30 digital computer, and computed at intervals of 50 cm^{-1} from $700\text{-}275 \text{ cm}^{-1}$ for each of 16 slit programs. Values for S' were then plotted against ν for each slit program. Eight of these curves are shown in Figure 11.

These values of S' , the computed spectral slit widths, are to be considered as the minimum values of S , the true spectral slit width of our instrument at any wavenumber.

All of the compounds were measured in solution. The most suitable solvent found was cyclohexane. In a few cases it was necessary to switch to 2,2,4-trimethylpentane or n-hexane because of strong solvent absorption in the vicinity of the sample absorption band. No solvent effect on intensity was found. Most measurements were made at a concentration of around 1 M. Little concentration dependence of A was noted where lower concentrations (down to 0.04 M) were tried. Both fixed-thickness CsBr cells and a variable space cell were employed. Cells were calibrated by the interference fringe technique.

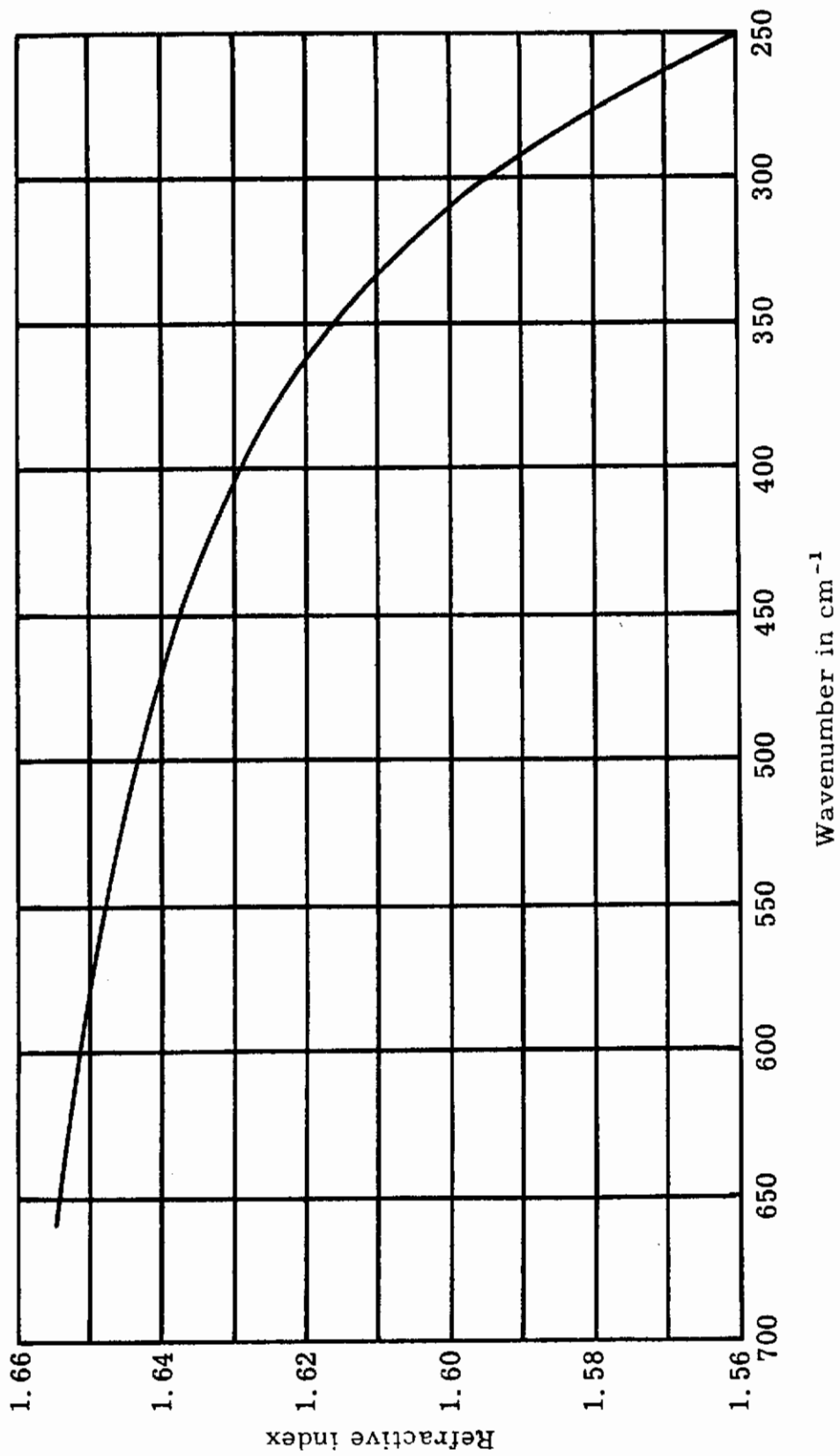


Figure 9. Refractive index of cesium bromide as a function of wavenumber.

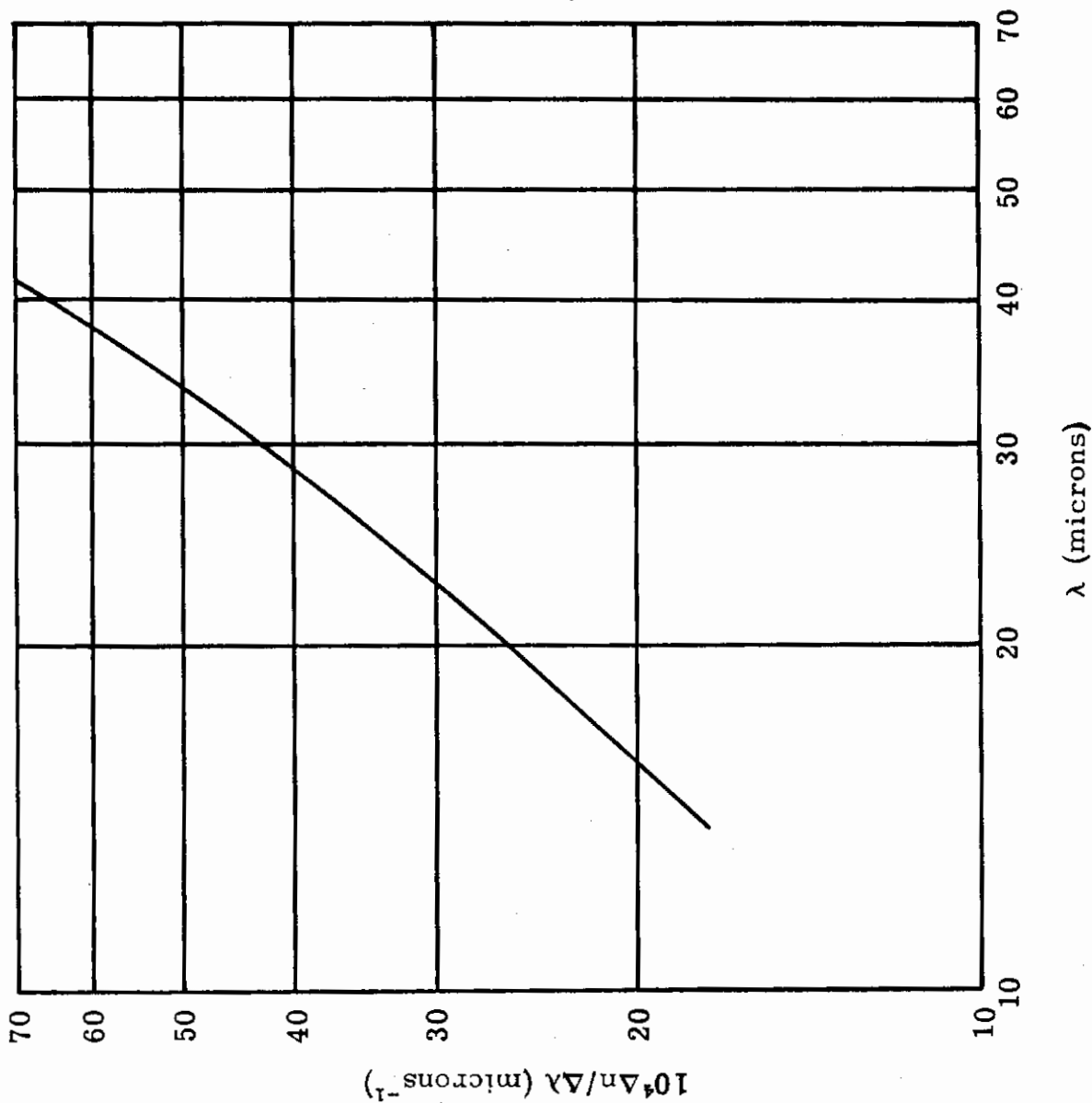


Figure 10. Dispersion of cesium bromide as a function of wavelength.

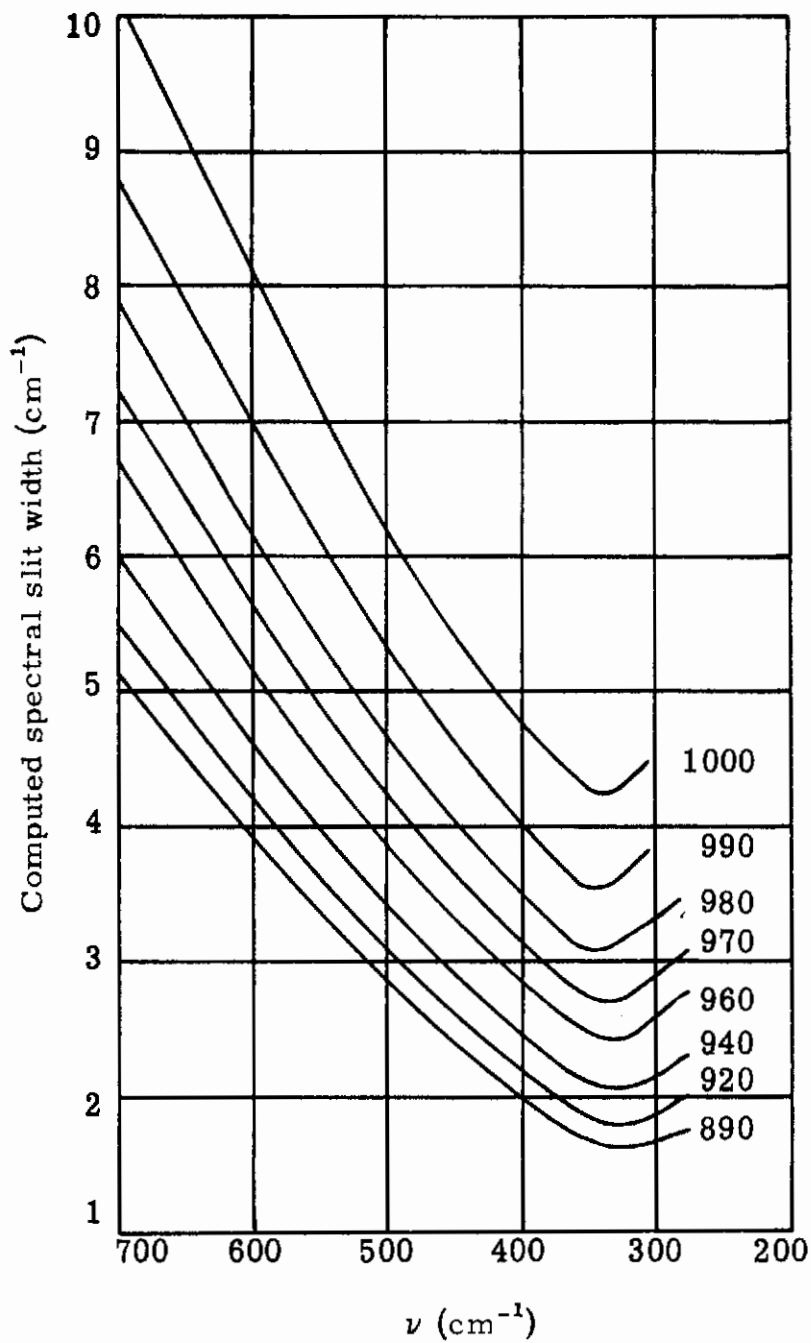


Figure 11. Computed spectral slit width in the cesium bromide region as a function of wavenumber; the number on each curve is the corresponding Perkin-Elmer Model 21 slit program designation.

Integrated intensities were obtained by the method of Cabana and Sandorfy.²³ This method is an extension of that of Ramsay²⁴ which is based on the assumption that the absorption band has the shape of a normal distribution or Lorentz curve. Ramsay's method employs as parameters the absorbance at the band maximum, $\log \left(\frac{T_0}{T} \right)_{\nu_0}$; the apparent half-band width, $\Delta \nu_{1/2}^a$; and $\underline{K}_{1/2}$, a dimensionless factor which depends upon the ratio of $\Delta \nu_{1/2}^a$ to \underline{S}' and to a lesser extent on peak intensity. Cabana and Sandorfy's method is analogous but depends upon band widths and \underline{K} values determined for 3/4, 1/2, 1/4, and 1/8 of the peak maximum. In addition, $\Delta \nu_{1/4}^a$, for example, is split into two parts, $\delta' \nu_{1/4}^a$ and $\delta'' \nu_{1/4}^a$ in order to take into account any dissymmetry in the band. Their complete equation is:

$$\begin{aligned}
 A = (1/c_l) \ln \left(\frac{T_0}{T} \right)_{\nu_0} \{ & 0.5498 [\delta' \nu_{1/8}^a] (K'_{1/8}) + (\delta'' \nu_{1/8}^a) (K''_{1/8}) \} \\
 & + 0.1569 [\delta' \nu_{1/4}^a] (K'_{1/4}) + (\delta'' \nu_{1/4}^a) (K''_{1/4}) \} \\
 & + 0.1693 [\delta' \nu_{1/2}^a] (K'_{1/2}) + (\delta'' \nu_{1/2}^a) (K''_{1/2}) \} \\
 & + 0.1240 [\delta' \nu_{3/4}^a] (K'_{3/4}) + (\delta'' \nu_{3/4}^a) (K''_{3/4}) \} \}
 \end{aligned}$$

In this equation \underline{c} is the concentration, \underline{l} is the pathlength, $\ln(T_0/T)_{\nu_0}$ is the apparent absorbance in terms of natural logarithms, and $\delta \nu$ and \underline{K} are discussed above.

Tables 8 and 9 summarize the results obtained on ν_{19}' and ν_{18}' of mono-substituted benzenes. The precision of our measurements in cases where a large number of runs have been made indicates a relative error of $\pm 5\%$ in \underline{A} . In both tables column one lists the substituent, column two the wavenumber at the band maximum, column three the molarity, column four the path length, column five the apparent absorbance at ν_0 , column six the apparent half-band width, column seven the computed spectral slit width, and column eight the absolute integrated intensity determined by the method of Cabana and Sandorfy.²³

In one case, ν_{19}' of iodobenzene, we replotted the observed data on a linear absorbance-linear wavenumber basis and measured the area with a planimeter. After applying "wing" corrections after Ramsay,²⁴ the value of \underline{A} obtained was 0.523 T. U. This compares very well with the value of 0.521 T. U. calculated for the same band by the method of Cabana and Sandorfy, which is far less time consuming.

Table 8. Summary of Intensity Data for ν_{19}' of Monosubstituted Benzenes in Cyclohexane Solution

Substituent	$\nu_0(\text{cm}^{-1})$	$c(\text{M})$	$l(\text{cm})$	$\log\left(\frac{T_0}{T}\right)/\nu_0$	$\Delta\nu_{\frac{1}{2}}^a(\text{cm}^{-1})$	$S'(\text{cm}^{-1})$	$A(\text{T. U.})$
-CH ₃	463	1.002	0.0107	0.546	5.22	2.50	0.49
		0.966	0.0107	0.519	5.19	2.50	0.49
		Mean = 0.49					
-F	498	1.006	0.0107	0.547	6.60	3.23	0.61
		1.074	0.0107	0.592	6.50	3.23	0.62
		Mean = 0.62					
-CN*	545	1.047	0.0107	0.603	7.90	3.25	0.71
		1.063	0.0107	0.627	7.32	3.25	0.71
		Mean = 0.71					
-OCH ₃ *	509	1.523	0.0107	0.393	13.24	3.33	0.65
		1.550	0.0107	0.400	13.38	3.06	0.62
		Mean = 0.64					
-Cl	467	0.969	0.0107	0.575	4.52	2.90	0.48
		0.969	0.0107	0.603	4.54	2.90	0.49
		0.969	0.0107	0.575	4.75	2.90	0.48
		0.969	0.0107	0.600	4.65	2.90	0.49
		0.965	0.0107	0.558	4.80	2.38	0.47
		0.965	0.0107	0.565	4.98	2.38	0.51
		0.965	0.0107	0.583	4.58	2.38	0.49
		Mean = 0.49					
-NO ₂ *	510	1.061	0.105	0.057	-	2.92	0.012**
		0.987	0.105	0.057	-	2.92	0.012**
		Mean = 0.012					
-CF ₃	485	0.841	0.105	0.293	9.86	2.70	0.066
		0.860	0.105	0.300	9.52	2.70	0.064
		Mean = 0.065					
-Br	457	1.021	0.0107	0.644	4.99	2.78	0.56
		0.745	0.0107	0.488	4.50	2.78	0.51
		Mean = 0.54					
-CCl ₃ *	507	0.811	0.1052	0.246	9.02	2.92	0.055
		0.867	0.1052	0.265	8.52	2.92	0.056
		Mean = 0.056					
-I	448	0.958	0.0107	0.556	4.82	2.70	0.47
		0.976	0.0107	0.580	4.64	2.70	0.47
		0.930	0.0107	0.536	4.68	2.70	0.47
		0.945	0.0107	0.585	4.51	2.70	0.50
		0.938	0.0107	0.582	4.76	2.70	0.52
		0.824	0.0107	0.511	4.72	2.70	0.51
		0.793	0.0107	0.442	4.76	2.70	0.46
		0.823	0.0107	0.431	4.94	2.70	0.43
		Mean = 0.48					

* Anisole, benzonitrile, and nitrobenzene were run in 2,2,4-trimethylpentane. Benzotrichloride was run in n-hexane.

** Area estimated with a planimeter after graphical resolution of overlapping band system.

Table 9. Summary of Intensity Data for ν_{18}' of Monosubstituted Benzenes in Cyclohexane Solution

Substituent	ν_0 (cm ⁻¹)	c(M)	l(cm)	$\log\left(\frac{T_0}{T}\right)\nu_0$	$\Delta\nu_{\frac{1}{2}}^a$ (cm ⁻¹)	S' (cm ⁻¹)	A(T. U.)
-CH ₃ *	521	1.08	0.150	0.264	8.70	3.30	0.025
		1.12	0.150	0.289	7.90	3.30	0.024
							Mean = 0.024
-F*	518	1.06	0.0250	0.568	7.84	3.30	0.28
		1.03	0.0250	0.546	7.94	3.30	0.28
							Mean = 0.28
-CN	460	1.29	0.200	0.148	8.58	3.38	0.0072
		1.37	0.100	0.088	7.91	3.38	0.0082
							Mean = 0.0077
-OCH ₃ **	442	2.70	0.100	0.379	20.79	2.50	0.053
-Cl	418	0.445	0.105	0.641	5.68	2.46	0.15
		0.673	0.070	0.563	6.46	2.46	0.13
		0.445	0.100	0.610	5.42	2.46	0.14
							Mean = 0.14
-NO ₂	394	0.93	0.0500	0.457	7.24	2.79	0.14
		0.85	0.0500	0.430	7.48	2.79	0.14
							Mean = 0.14
-CF ₃	338	1.02	0.0300	0.538	6.38	2.71	0.21
		0.97	0.0250	0.415	6.48	2.71	0.22
							Mean = 0.22
-Br	315	0.516	0.150	0.583	6.18	1.95	0.080
		1.02	0.105	0.758	6.62	1.95	0.080
							Mean = 0.080
-CCl ₃ †	307	1.69	0.100	0.363	10.18	2.82	0.039
		1.58	0.100	0.342	10.80	2.82	0.042
							Mean = 0.040
-I††	266						

* Toluene was run in n-hexane, and fluorobenzene was run in 2,2,4-trimethylpentane.

** Anisole's band was so broad and diffuse that only an estimate of its intensity was made, employing Ramsay's method.

† Ramsay's method was used for benzotrichloride also.

†† The wavenumber of ν_{18}' for iodobenzene is too low to measure on our instrument.

The absorptions of ν_4 were recorded with a Perkin-Elmer Model 221-G double-beam spectrophotometer equipped with a sodium chloride prism and a 240 line-per-mm grating. This combination under normal survey conditions, gives a relatively constant spectral slit width of about 3 cm^{-1} throughout the 4000- to 650-cm^{-1} region.

The wavenumber scale was calibrated against atmospheric carbon dioxide and water-vapor bands. Wavenumber accuracy is estimated as $\pm 1 \text{ cm}^{-1}$. To reduce the loss of energy owing to atmospheric absorption, the entire instrument, including the sampling area, was purged with dry nitrogen at all times.

Intensities were calculated by the method of Cabana and Sandorfy, and the computed spectral slit widths, S' , were calculated according to the formula of Jones and Sandorfy.²⁰ The curves are shown in Figure 12.

All of the compounds were measured in solution. In most cases the solvent used was cyclohexane. *o*-Dinitrobenzene and terephthalonitrile were insoluble in cyclohexane, so the solvent used for these measurements was benzene. The solvent for 1,4-bis(trichloromethyl)benzene was *n*-hexane, since the wavenumber of ν_4 of this compound was coincident with absorption of cyclohexane. Most measurements were made at a concentration of around 0.1 M. Fixed-thickness sodium chloride cells were employed. Calibration was by the interference-fringe technique.

Table 10 summarizes the results obtained on ν_4 of symmetrical 1,4-disubstituted benzenes.

C. NMR Measurements

Nuclear magnetic resonance spectra were recorded with a Varian Associates model A-60 NMR spectrometer with a magnetic field of 14,092 oersteds at a frequency of 60 Mc/sec. The solvents used were cyclohexane for the mono-substituted benzenes and acetone for the 1,4-disubstituted benzenes. The chemical shift, δ_r , is measured in ppm downfield from benzene.

Table 11 lists the data for monosubstituted benzenes and Table 12 the data for the symmetrical 1,4-disubstituted benzenes.

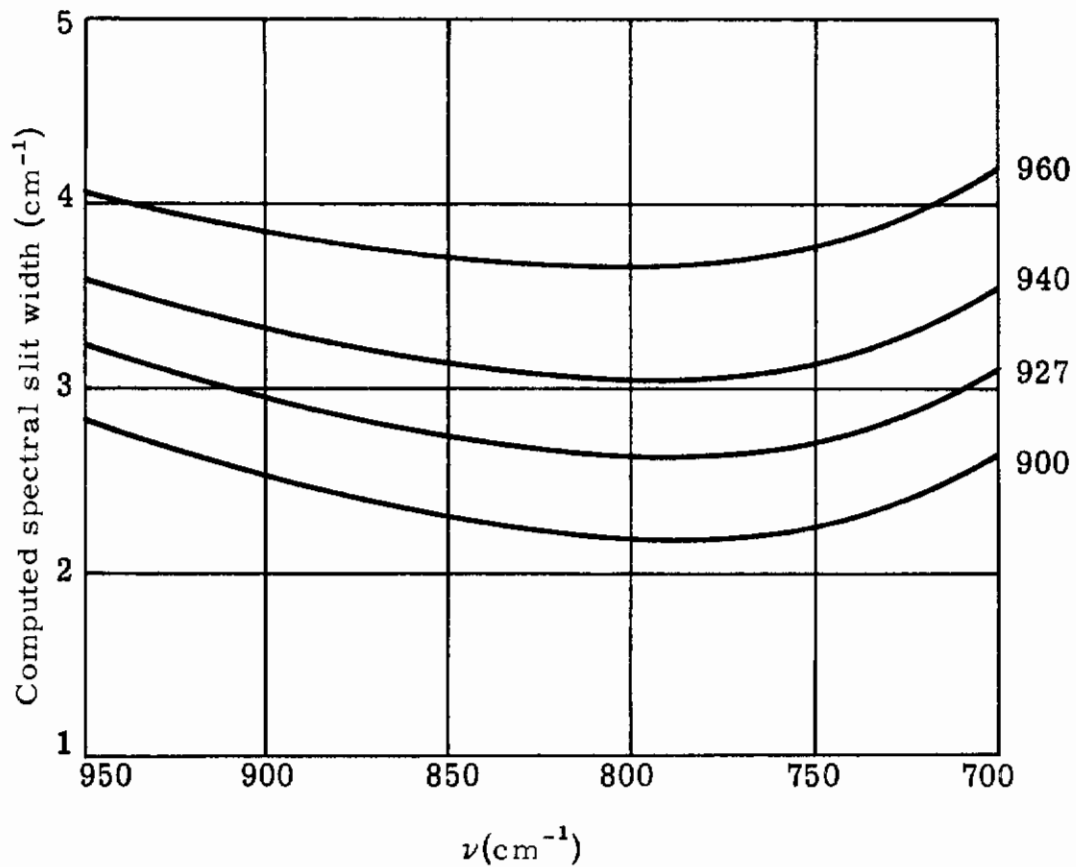


Figure 12. Computed spectral slit width in the sodium chloride region as a function of wavenumber; the number on each curve is the corresponding Perkin-Elmer Model 221-G slit program designation.

Table 10. Summary of Intensity Data for ν_4 of Symmetrical 1,4-Disubstituted Benzenes in Cyclohexane Solution.

Substituent	$\nu_0(\text{cm}^{-1})$	$c(\text{M})$	$l(\text{cm})$	$\log\left(\frac{T_0}{T}\right)\nu_0$	$\Delta\nu_{\frac{1}{2}}^a(\text{cm}^{-1})$	$S'(\text{cm}^{-1})$	$A(\text{T. U.})$
-CH ₃	795	0.105	0.0100	0.300	5.6	2.73	2.63
		0.142	0.0100	0.405	5.5	2.73	2.68
Mean = 2.7							
-F	834	0.113	0.0100	0.564	6.0	2.80	4.91
		0.121	0.0100	0.594	6.2	2.80	4.98
Mean = 4.9							
-CN*	842	0.0552	0.0100	0.102	8.7	2.82	2.84
		0.0784	0.0100	0.143	8.9	2.82	2.82
Mean = 2.8							
-OCH ₃	825	0.116	0.0100	0.303	7.2	2.79	3.50
		0.115	0.0100	0.302	7.8	2.79	3.72
Mean = 3.6							
-Cl	820	0.110	0.0100	0.474	4.0	2.78	3.06
		0.113	0.0100	0.485	4.0	2.78	3.08
Mean = 3.1							
-NO ₂ *	837	0.0601	0.0100	0.281	4.1	2.82	3.20
		0.0748	0.0100	0.343	3.9	2.82	3.18
Mean = 3.2							
-CF ₃	848	0.121	0.0100	0.628	4.0	2.86	3.86
		0.136	0.0100	0.701	4.0	2.86	4.04
Mean = 3.9							
-Br	811	0.128	0.0100	0.483	4.8	2.62	3.05
		0.144	0.0100	0.560	3.8	2.62	2.90
Mean = 3.0							
-CCl ₃ [†]	851	0.0385	0.0100	0.165	9.0	2.87	6.77
		0.0572	0.0100	0.240	8.6	2.87	6.33
Mean = 6.6							
-I	802	0.0635	0.0100	0.252	3.6	2.74	2.47
		0.0911	0.0100	0.367	3.7	2.74	2.50
Mean = 2.5							

* Solvent was benzene.

† Solvent was n-hexane.

Table 11. NMR Chemical Shift of the *para* Proton of Monosubstituted Benzenes Measured in 50% Solution in Cyclohexane

<u>Substituent</u>	<u>Chemical Shift (ppm from benzene)</u>	<u>Source</u>
-CH ₃	-0.10	1
-F	-0.143	2
-CN	+0.30	1
-OCH ₃	-0.23	1
-Cl	+0.037	2
-NO ₂	+0.312	2
-CF ₃	+0.170	2
-Br	0.00	1
-CCl ₃	+0.23	1
-I	-0.10	1

1. Reference 15
2. This work

Table 12. NMR Chemical Shift of the Ring Protons in Symmetrical 1,4-Disubstituted Benzenes, Measured in 1% Solution in Acetone

<u>Substituent</u>	<u>Chemical Shift (ppm from benzene)</u>
-CH ₃	-0.31
-F	-0.18
-CN	+0.69
-OCH ₃	-0.51
-Cl	+0.07
-NO ₂	+1.18
-CF ₃	+0.64
-Br	+0.19
-CCl ₃	+0.84
-I	+0.19

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APPENDIX

Atlas of Spectra of Mono- and Disubstituted Benzenes

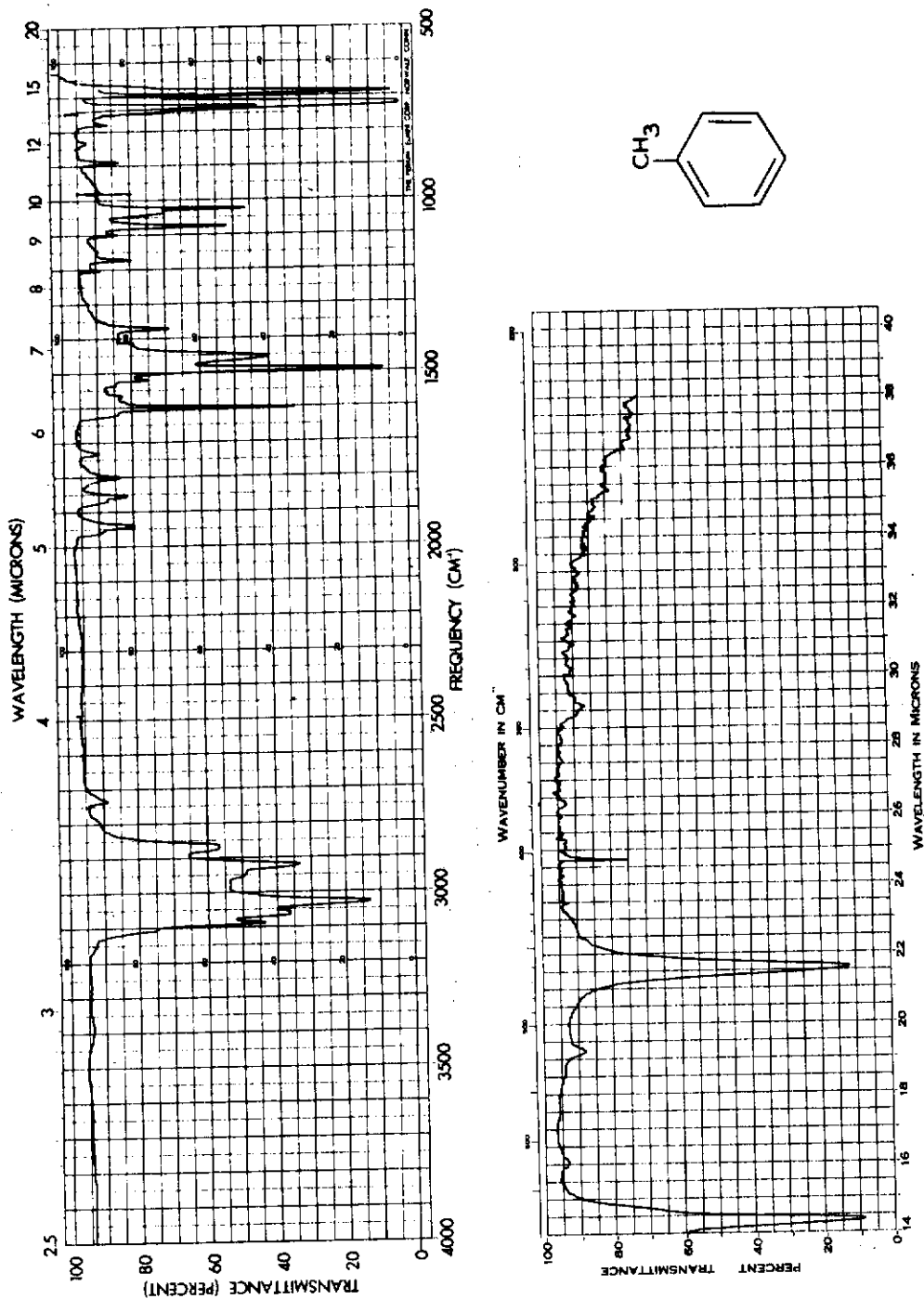


Figure 13. Infrared spectrum of toluene. Liquid: 0.016 mm cell.

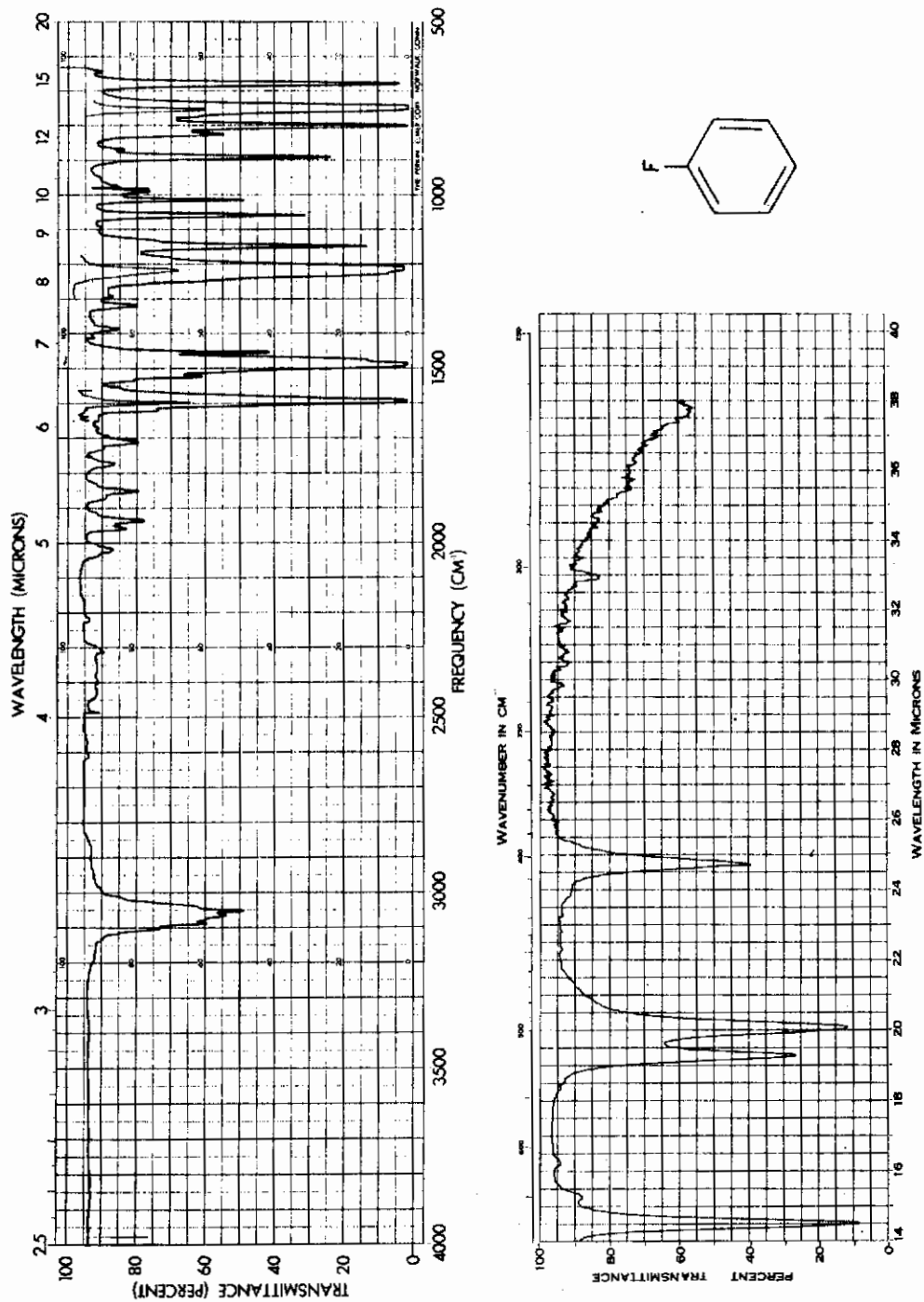


Figure 14. Infrared spectrum of fluorobenzene. Liquid; 0.016 mm cell.

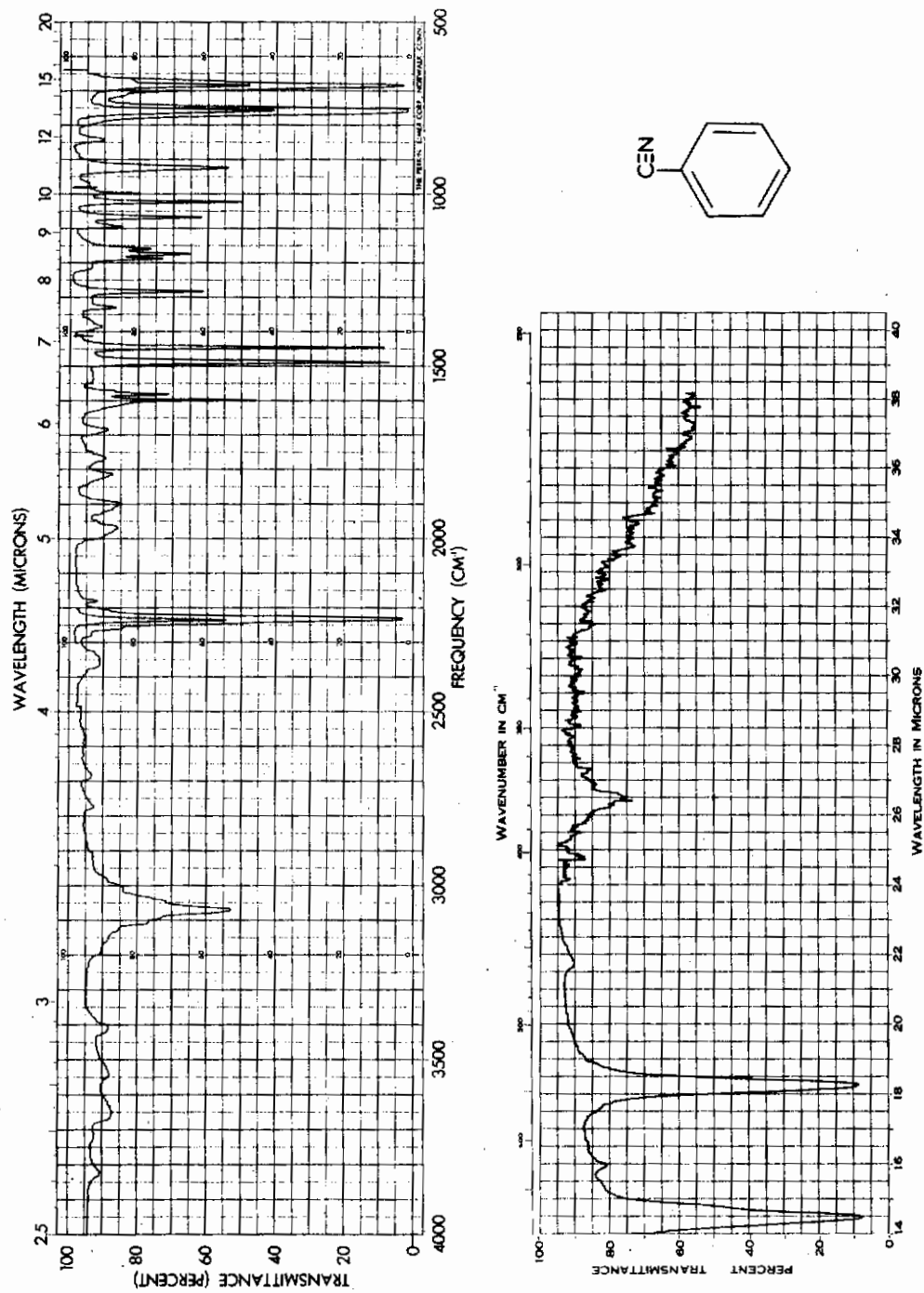


Figure 15. Infrared spectrum of benzonitrile. Liquid; 0.018 mm cell.

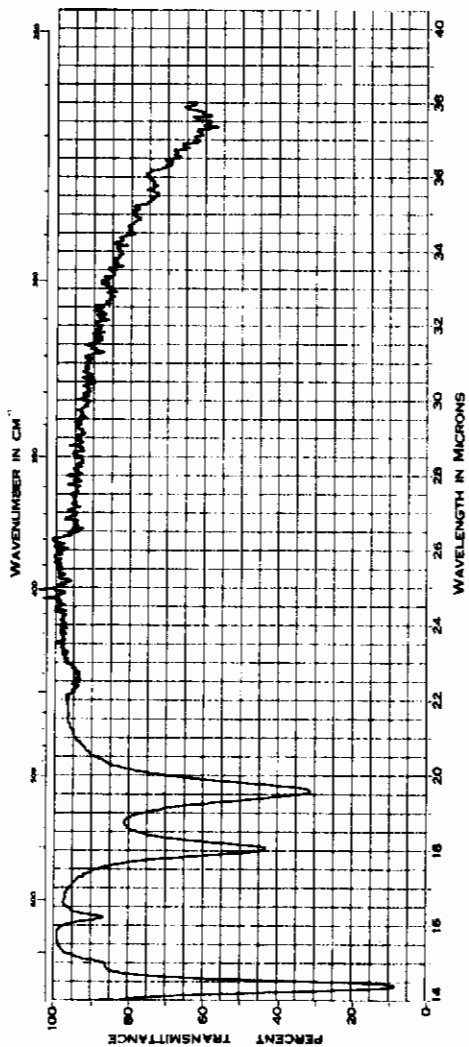
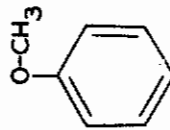
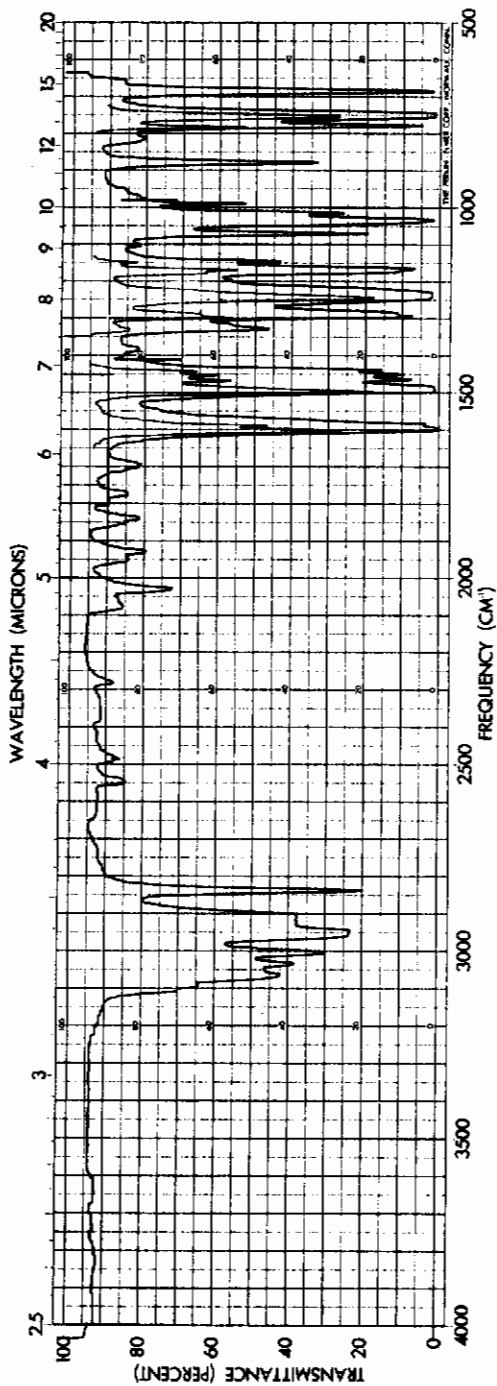


Figure 16. Infrared spectrum of anisole. Liquid: 0.016 mm cell.

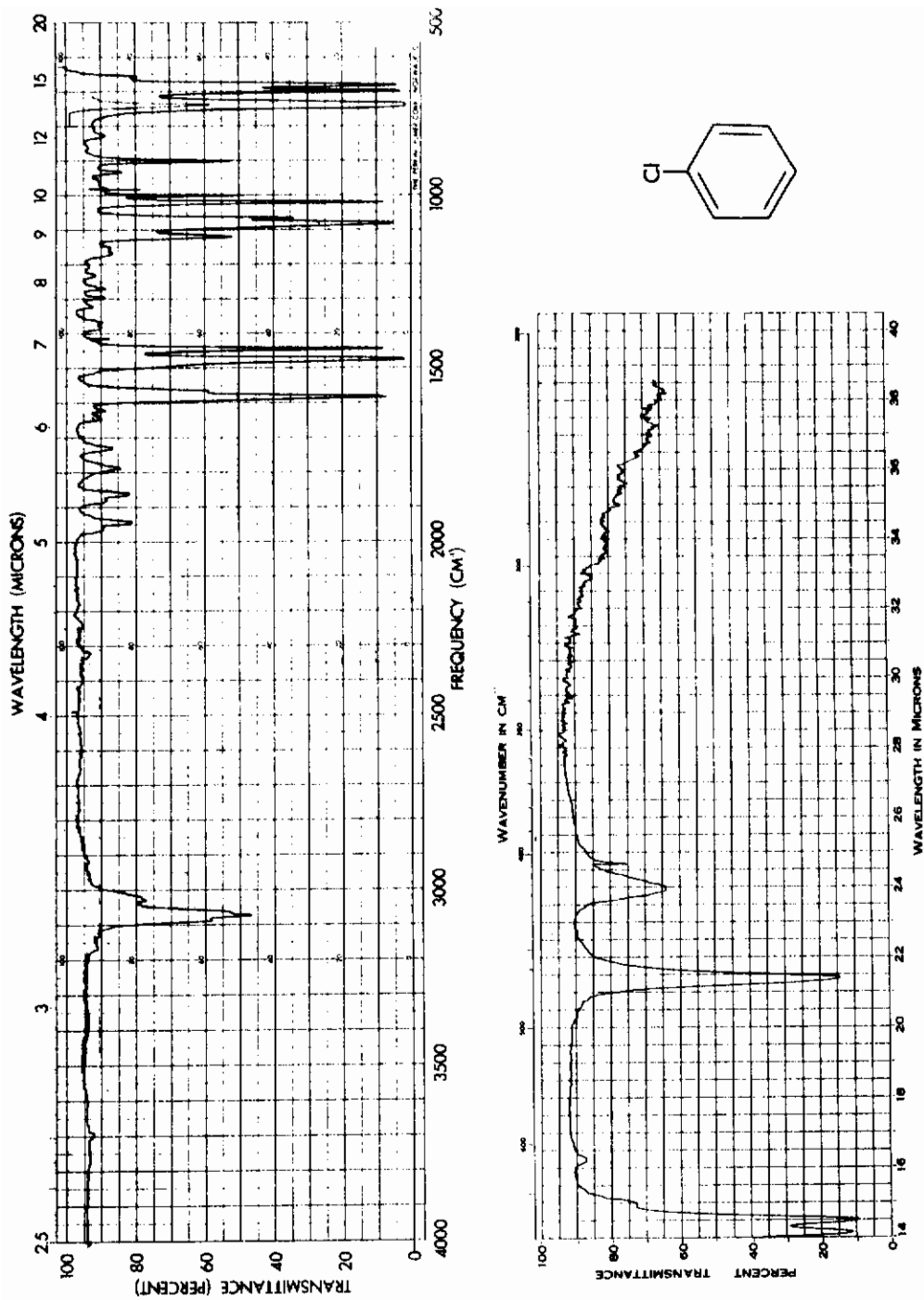


Figure 17. Infrared spectrum of chlorobenzene. Liquid; 0.016 mm cell.

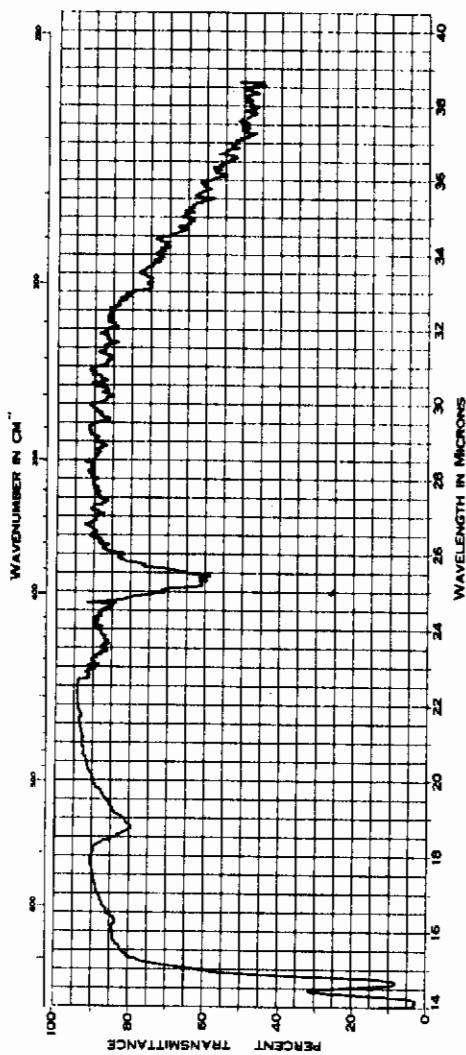
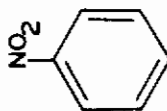
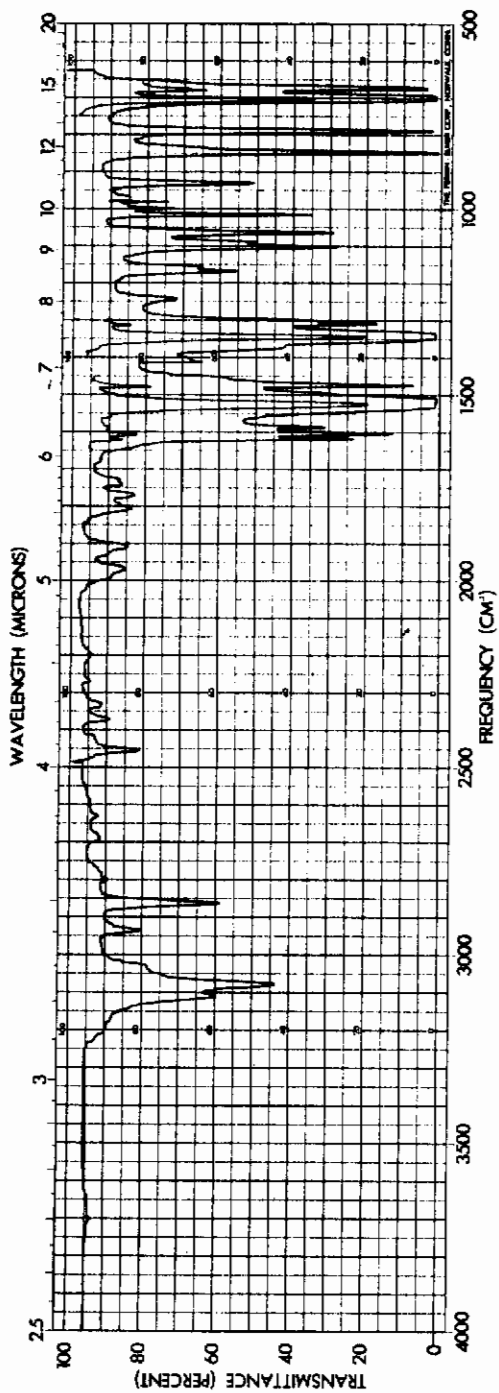


Figure 18. Infrared spectrum of nitrobenzene. Liquid; 0.016 mm cell.

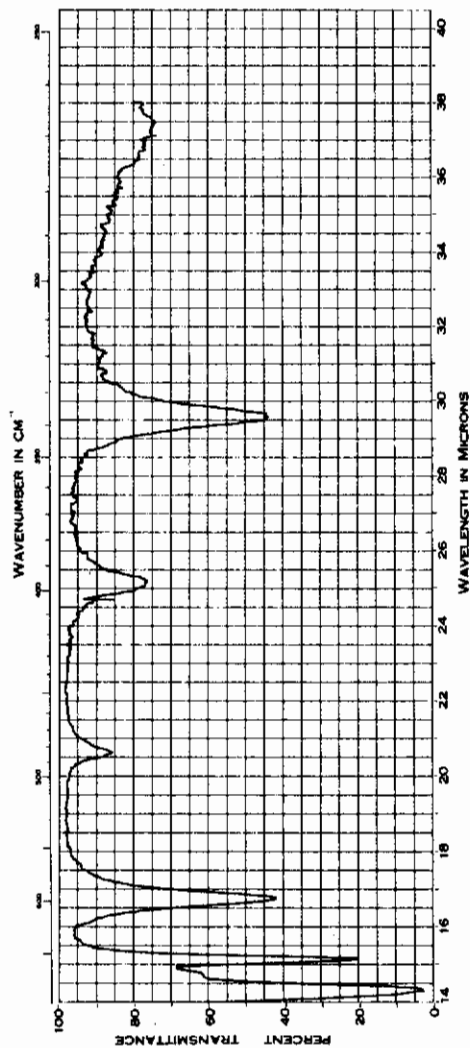
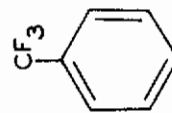
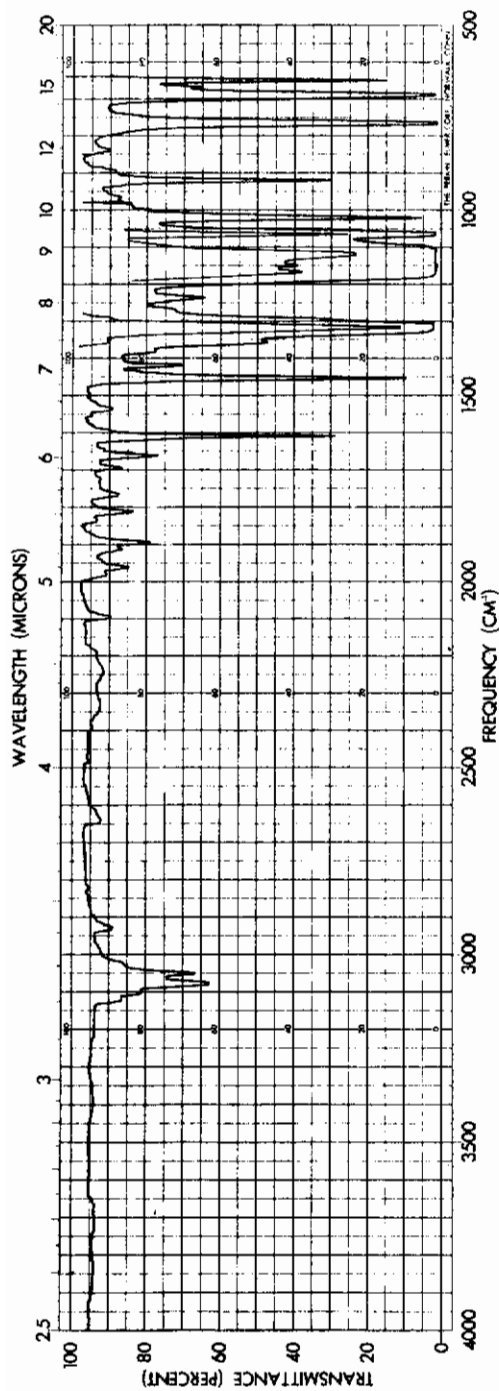


Figure 19. Infrared spectrum of benzotrifluoride. Liquid: 0.016 mm cell.

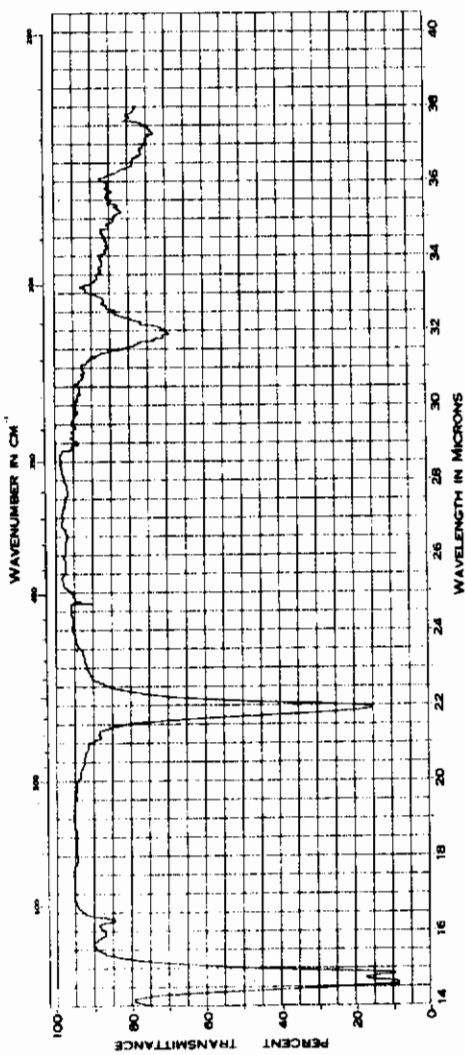
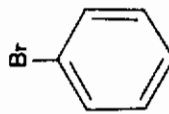
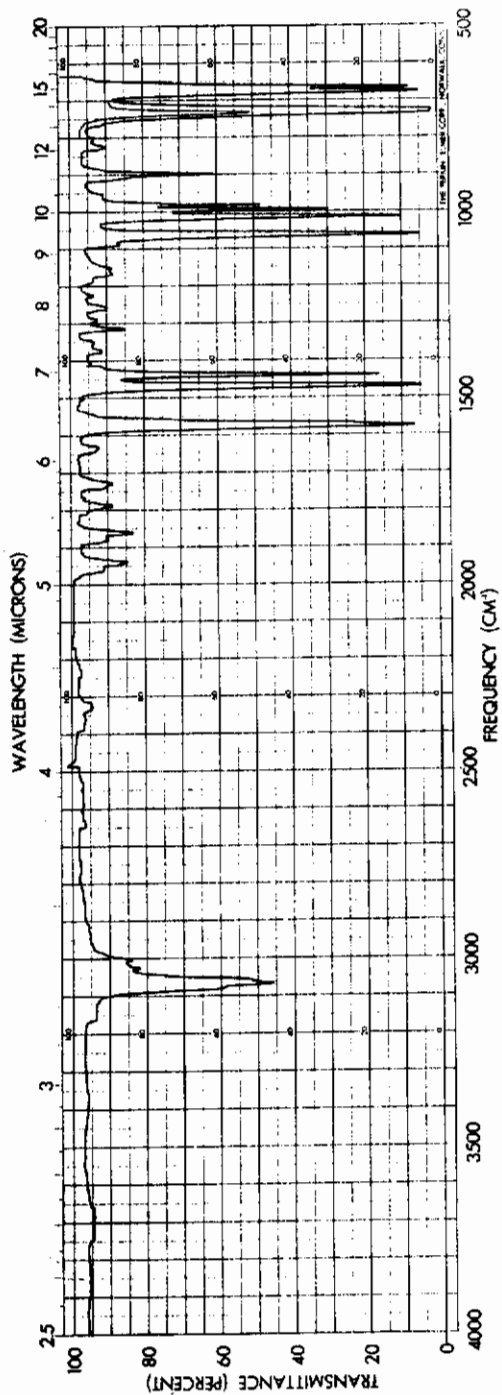


Figure 20. Infrared spectrum of bromobenzene. Liquid; 0.016 mm cell.

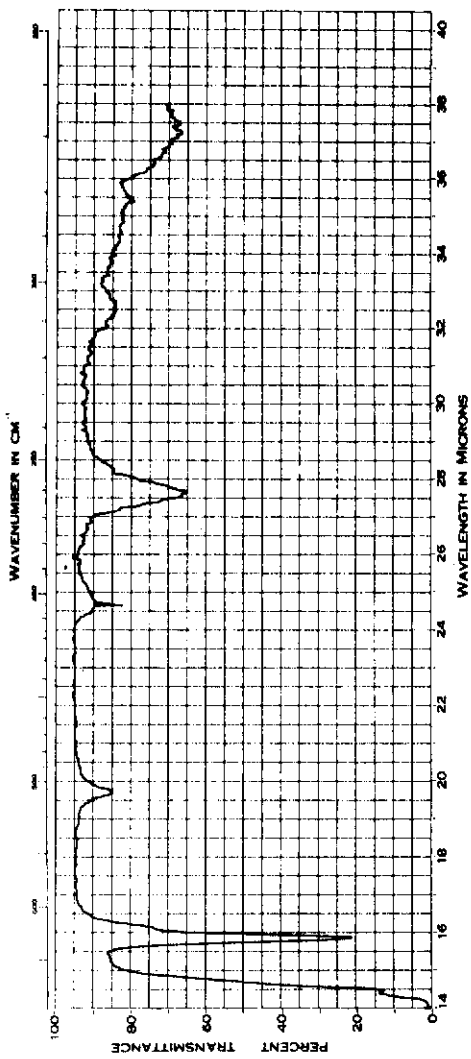
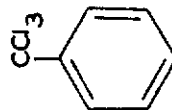
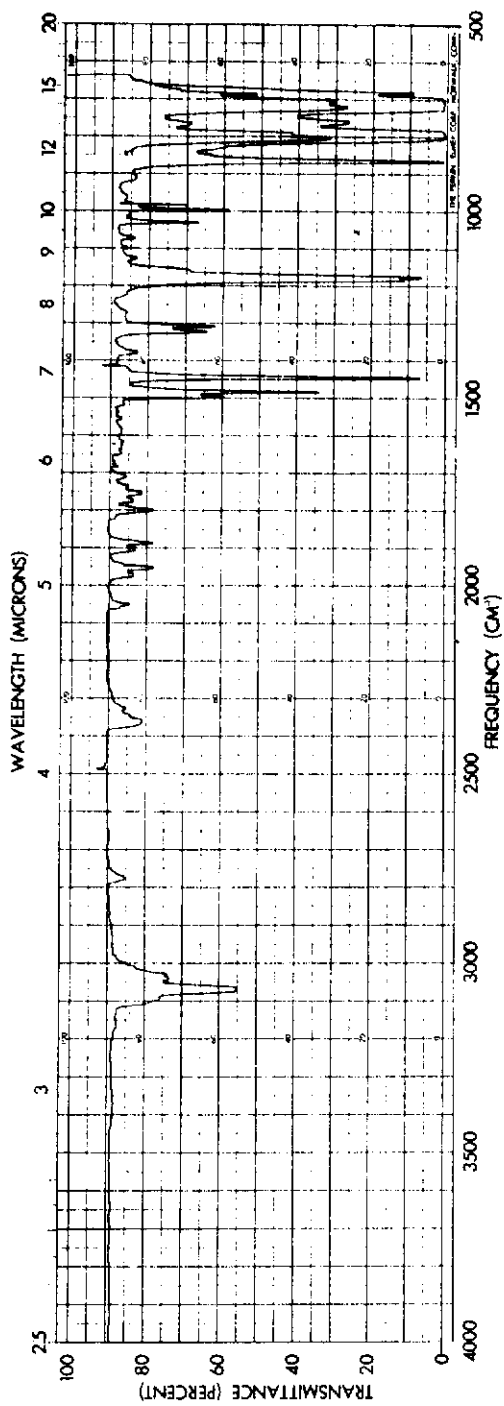


Figure 21. Infrared spectrum of benzotrichloride. Liquid: 0.016 mm cell and capillary film.

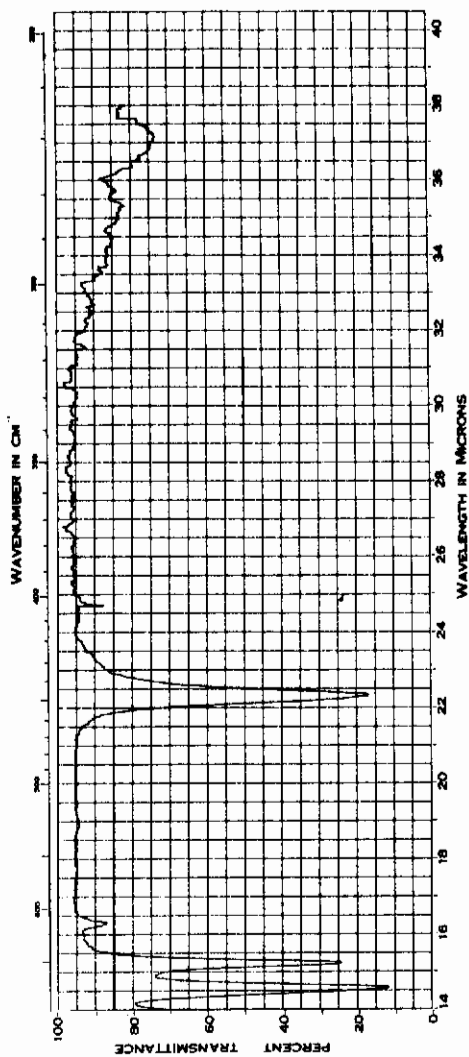
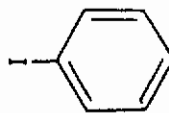
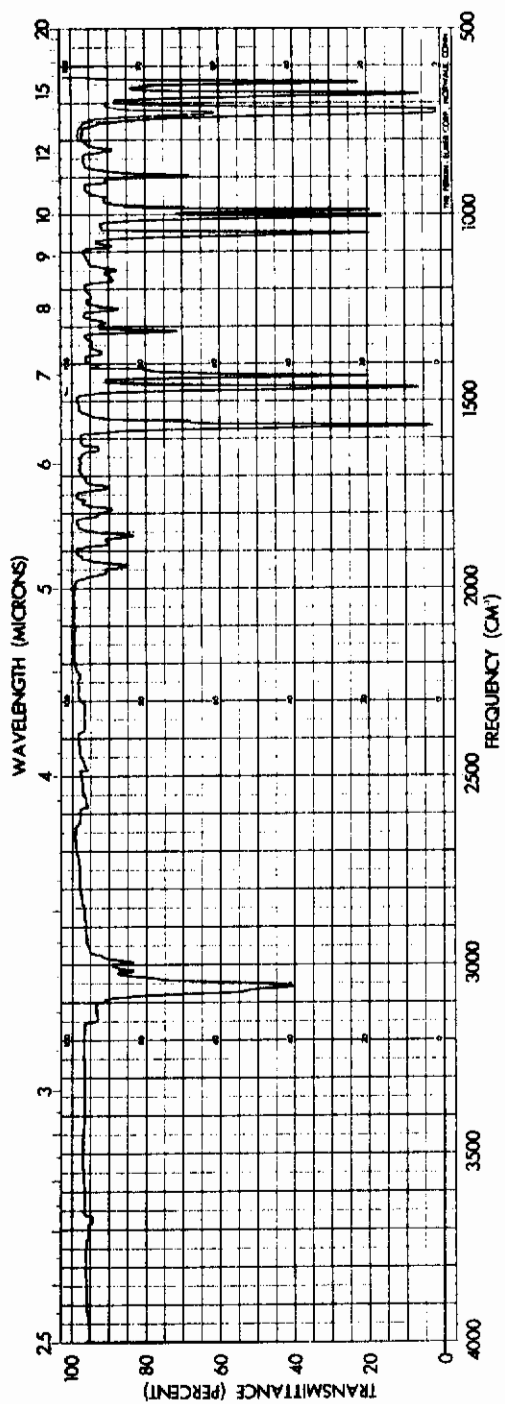


Figure 22. Infrared spectrum of iodobenzene. Liquid: 0.016 mm cell.

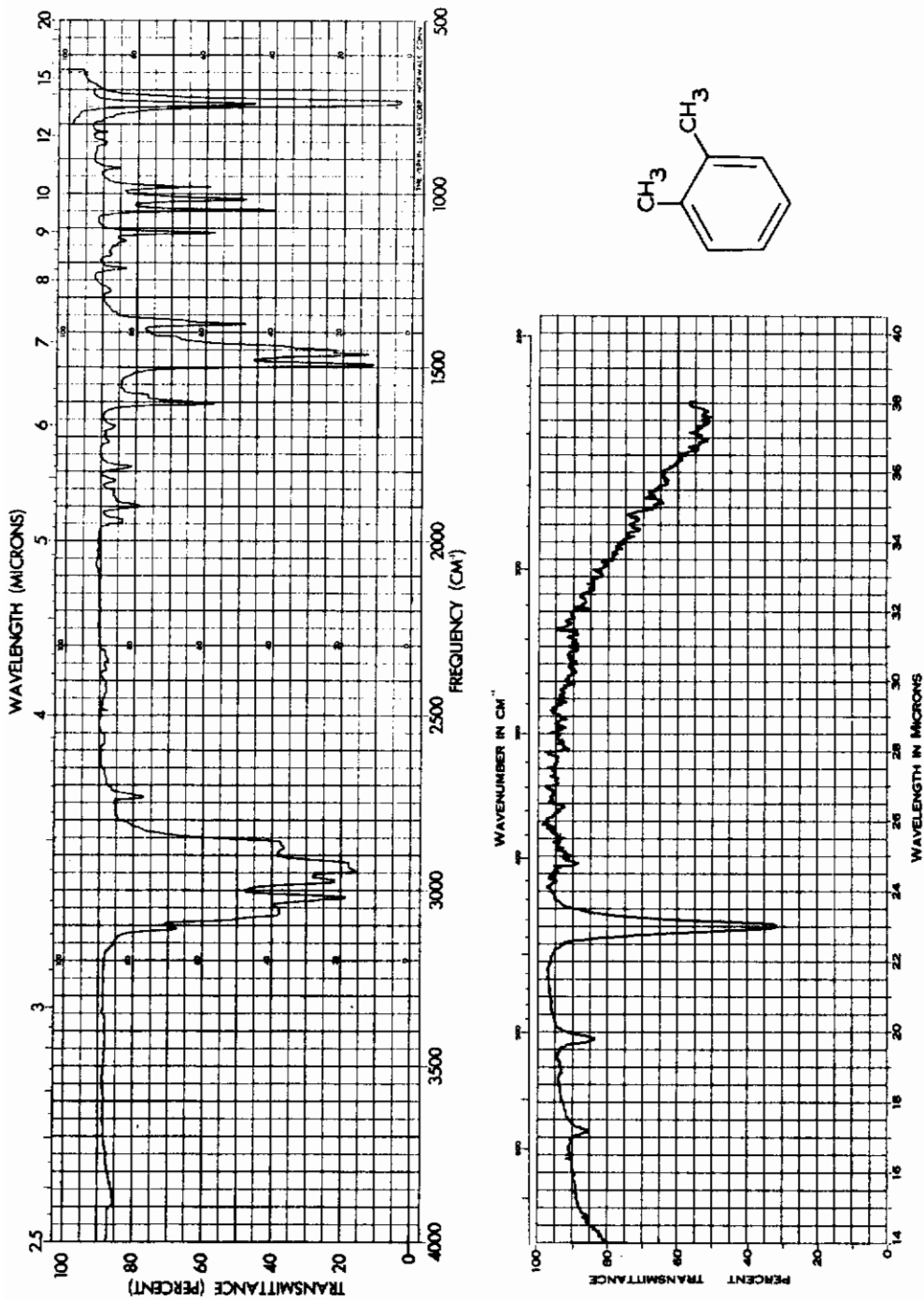


Figure 23. Infrared spectrum of o-xylene. Liquid: 0.018 mm cell.

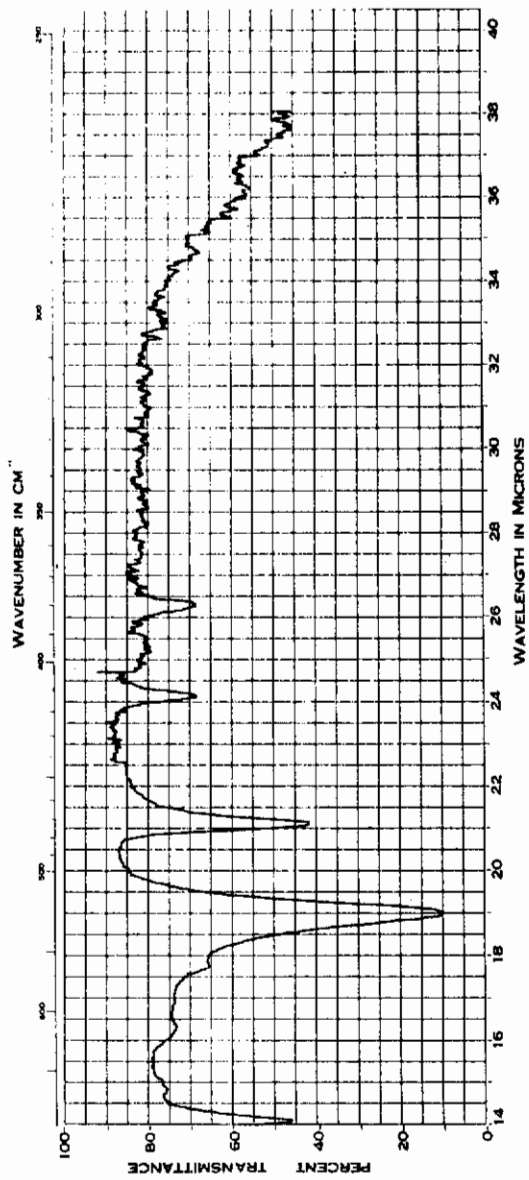
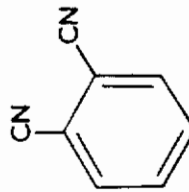
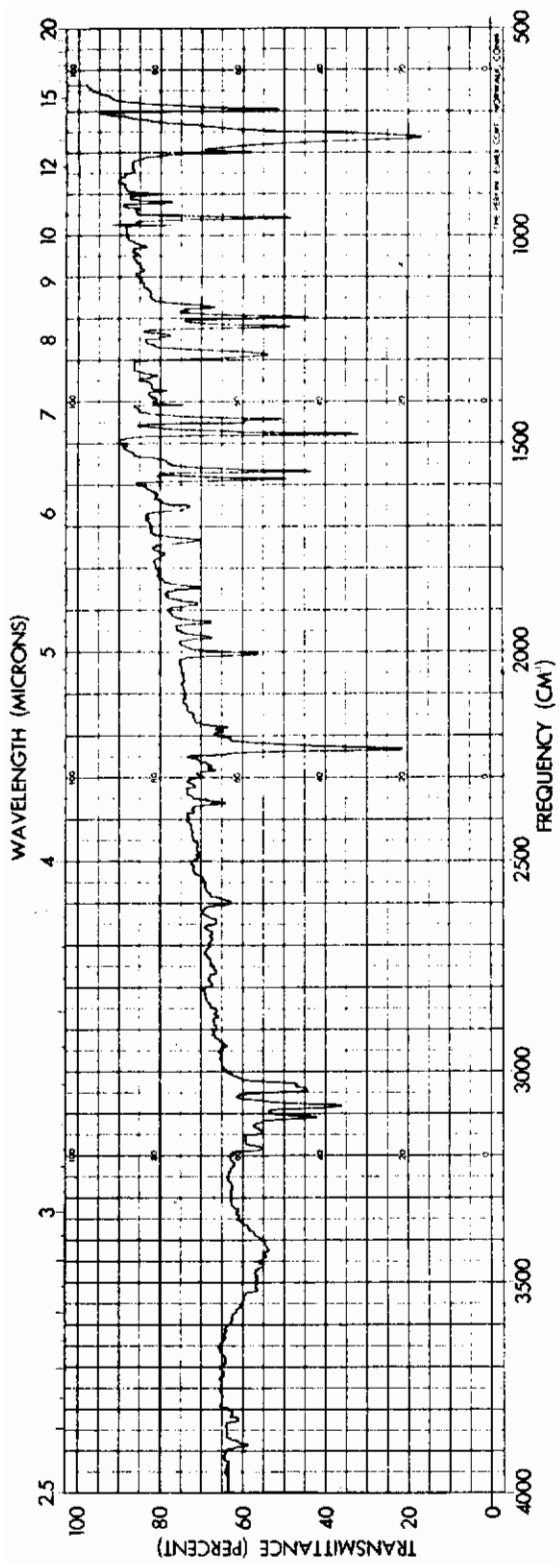


Figure 25. Infrared spectrum of phthalonitrile. Solid in pressed disks: near infrared, 1 mg/650 mg KBr; far infrared, 2 mg/350 mg KI.

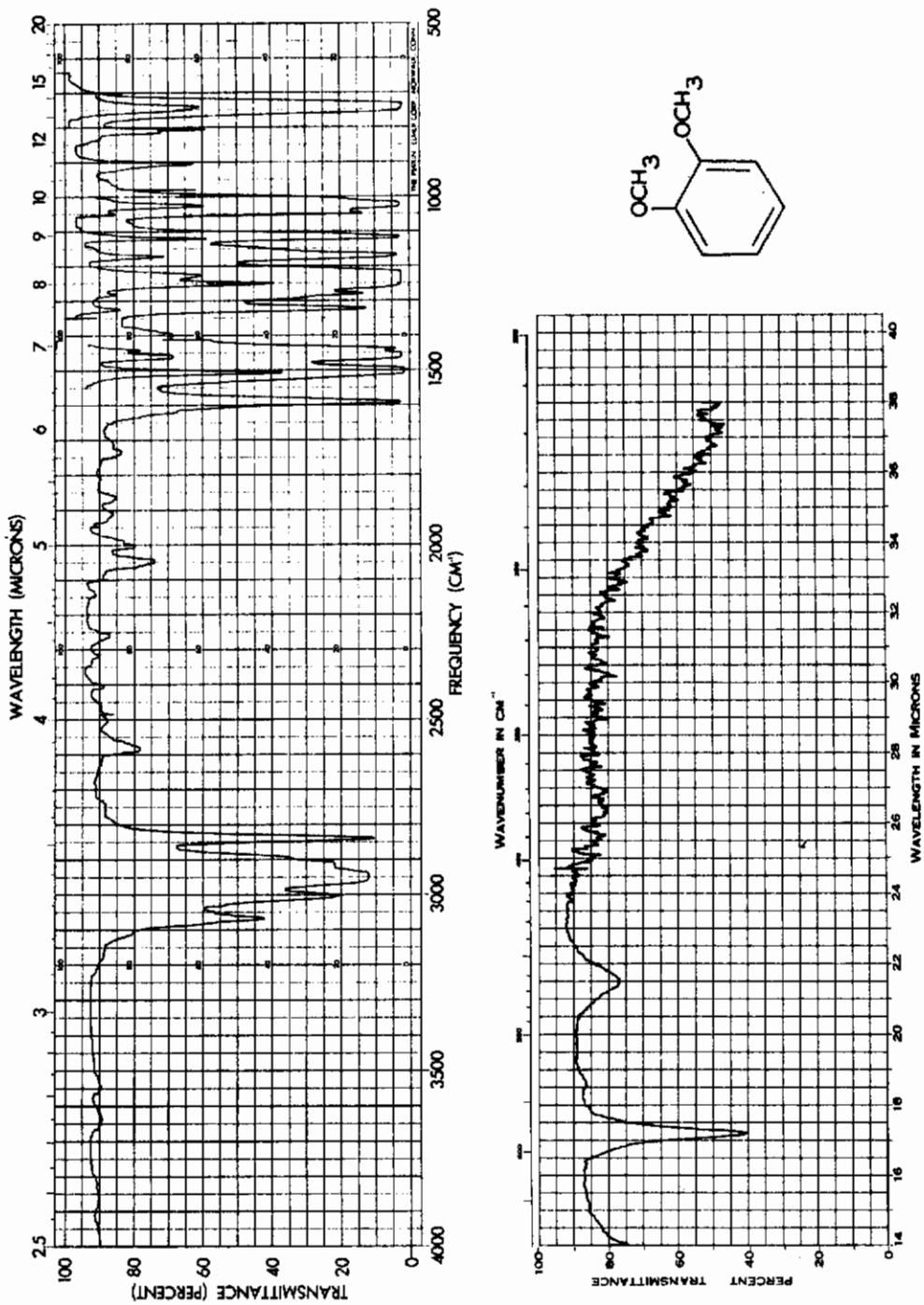


Figure 26. Infrared spectrum of veratrole. Liquid: 0.018 mm cell.

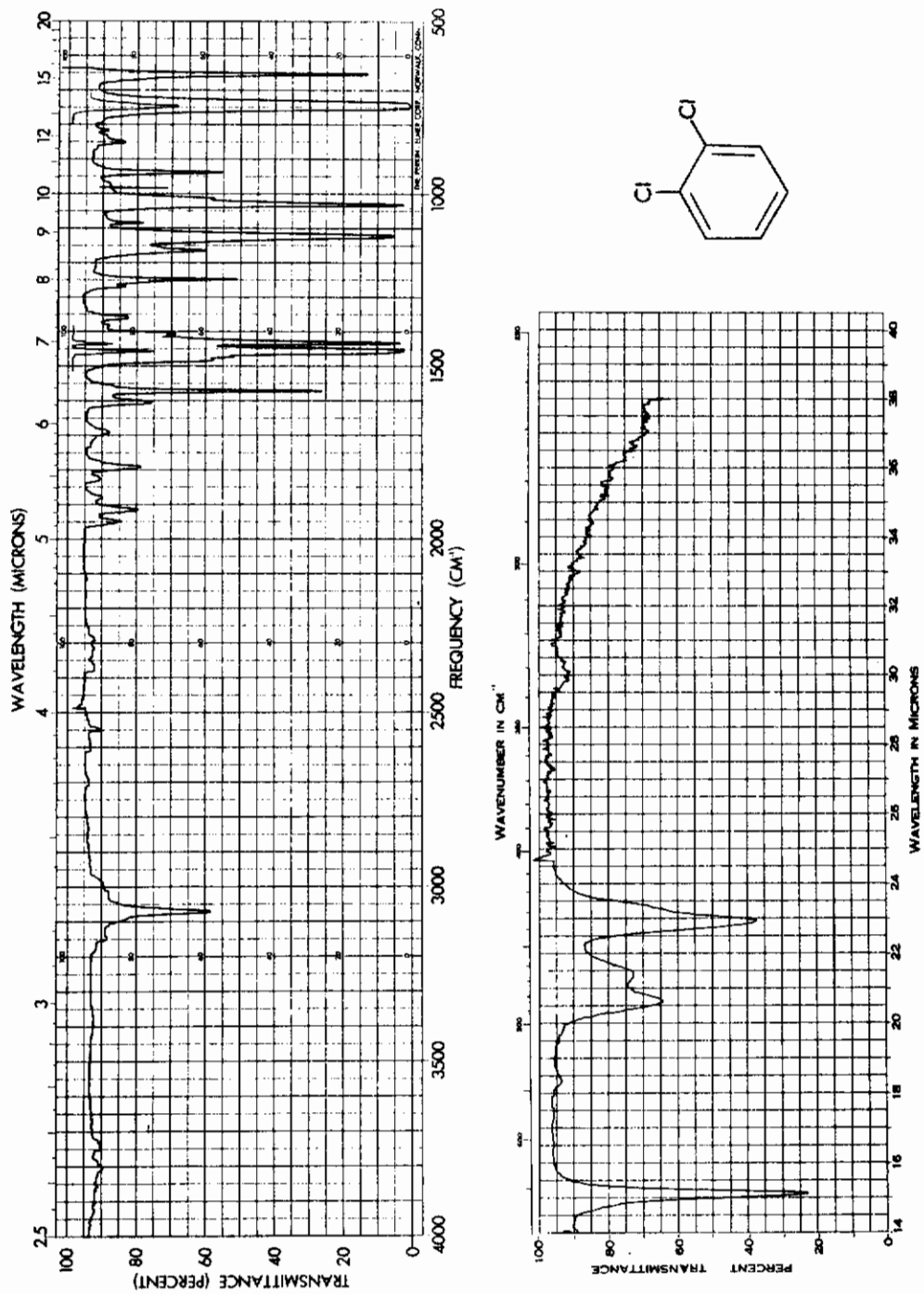


Figure 27. Infrared spectrum of *o*-dichlorobenzene. Liquid; 0.016 mm cell.

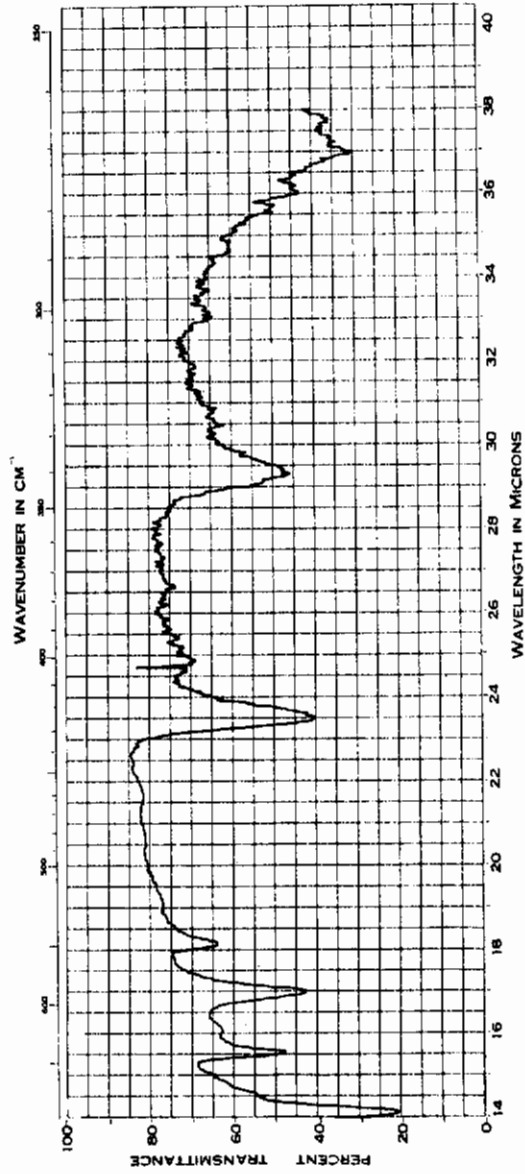
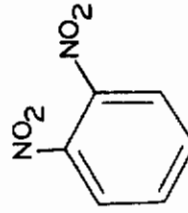
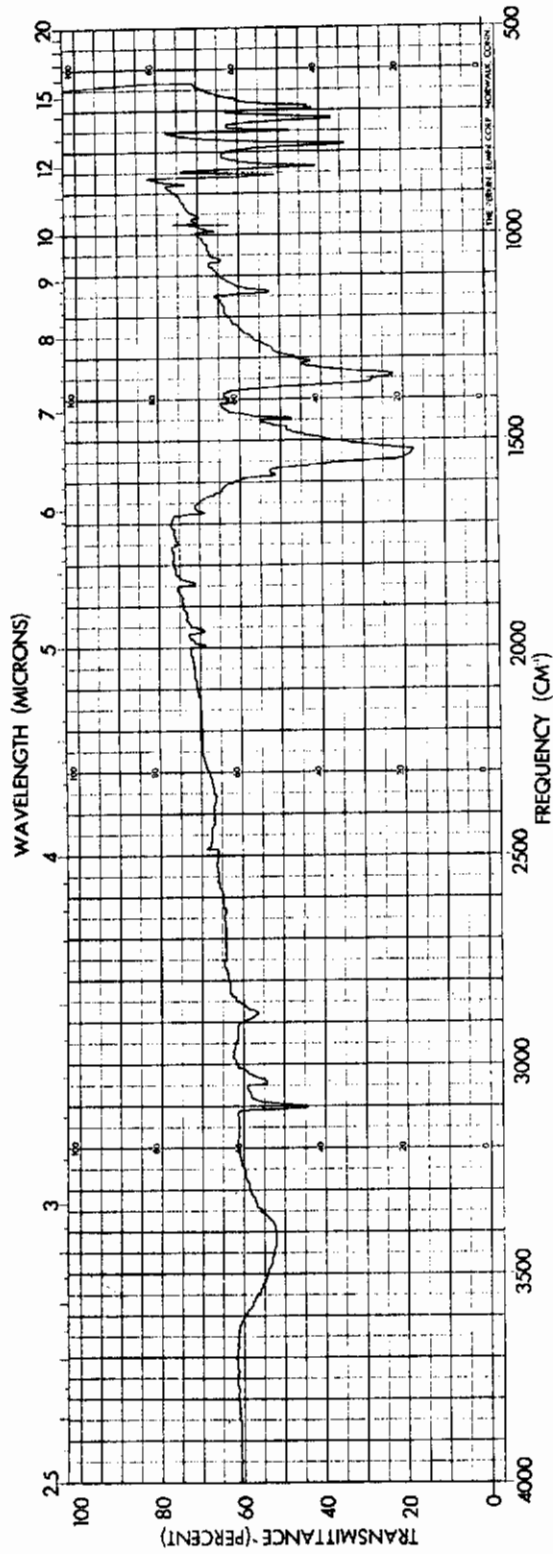


Figure 28. Infrared spectrum of o-dinitrobenzene. Solid in pressed disks: near infrared, 1 mg/650 mg KBr; far infrared, 2 mg/350 mg KI.

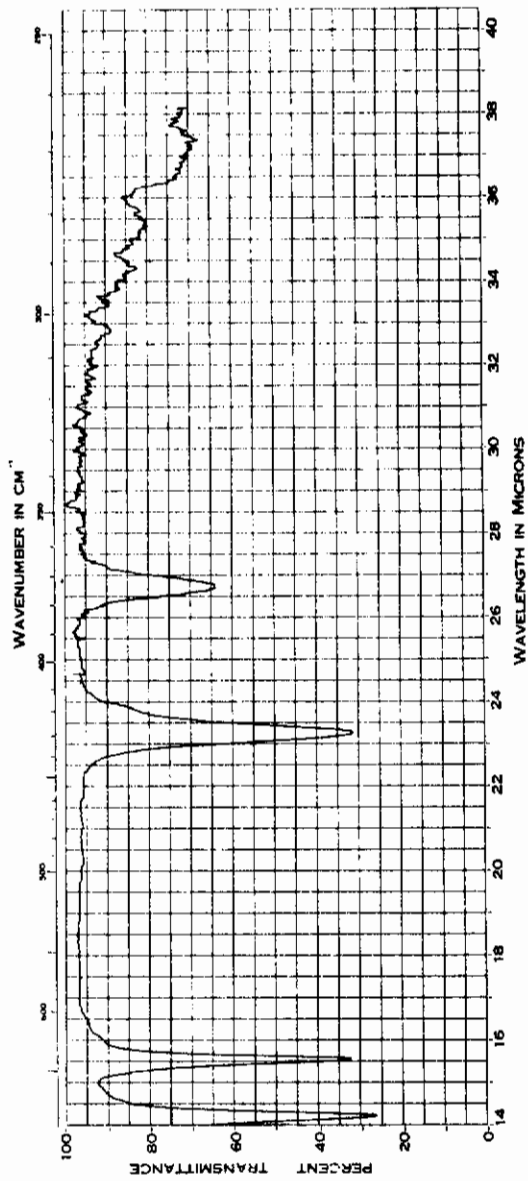
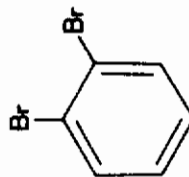
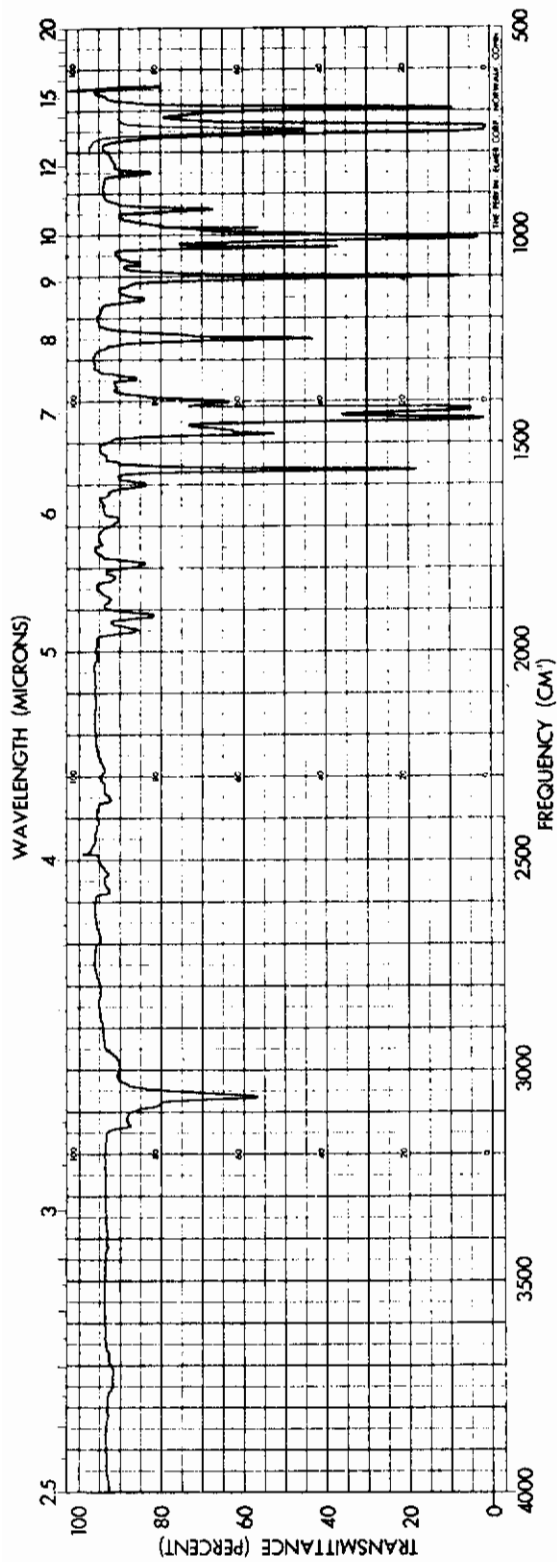


Figure 29. Infrared spectrum of o-dibromobenzene. Liquid; 0.016 mm cell.

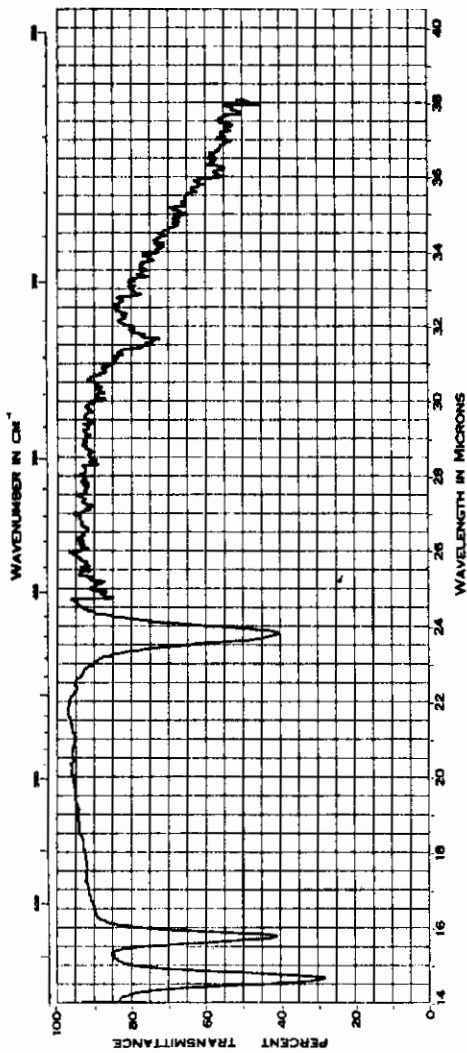
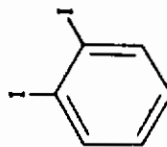
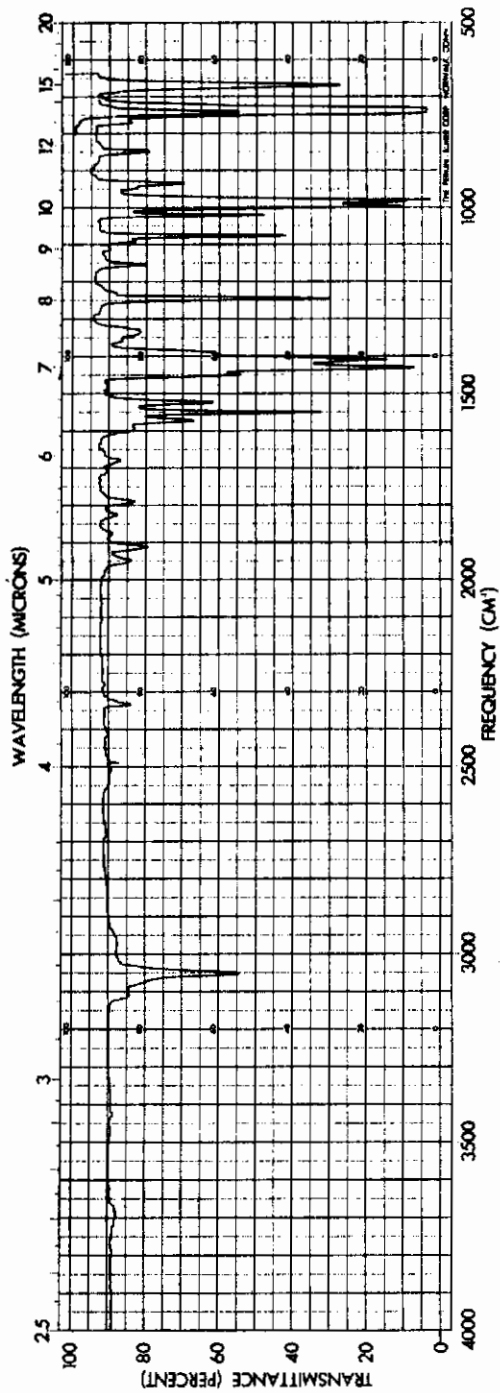


Figure 30. Infrared spectrum of o-diiodobenzene. Liquid: 0.018 mm cell.

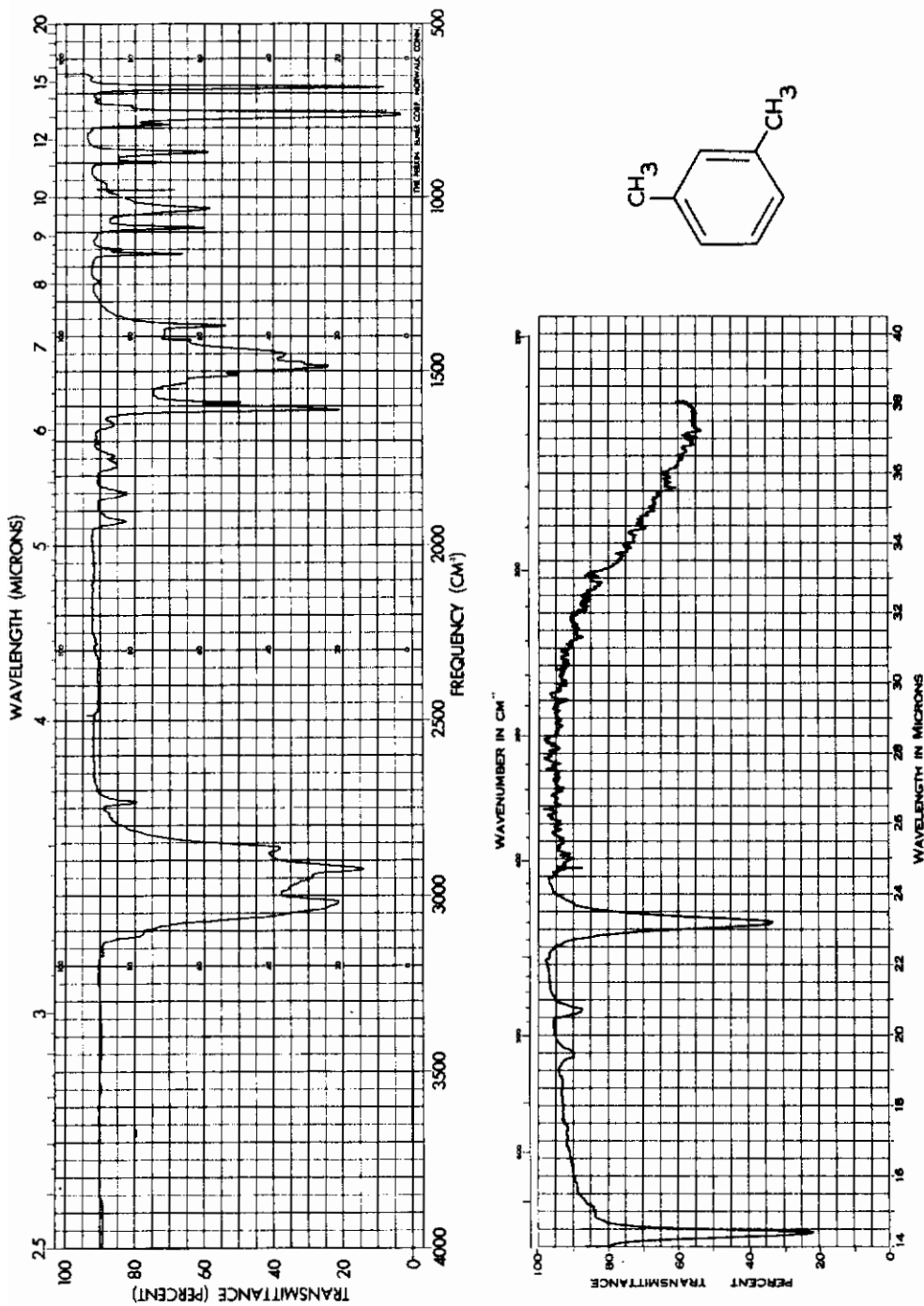


Figure 31. Infrared spectrum of m-xylene. Liquid; 0.018 mm cell.

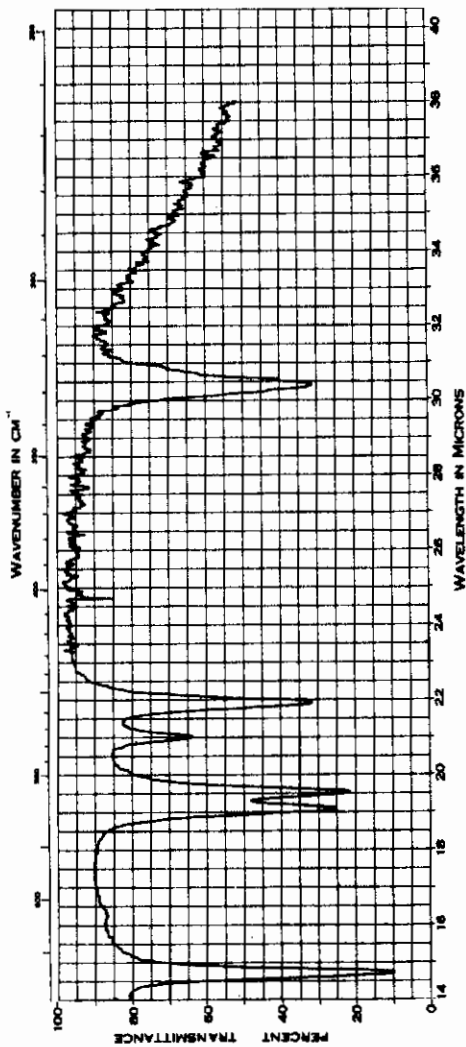
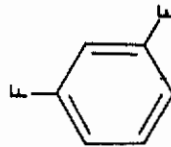
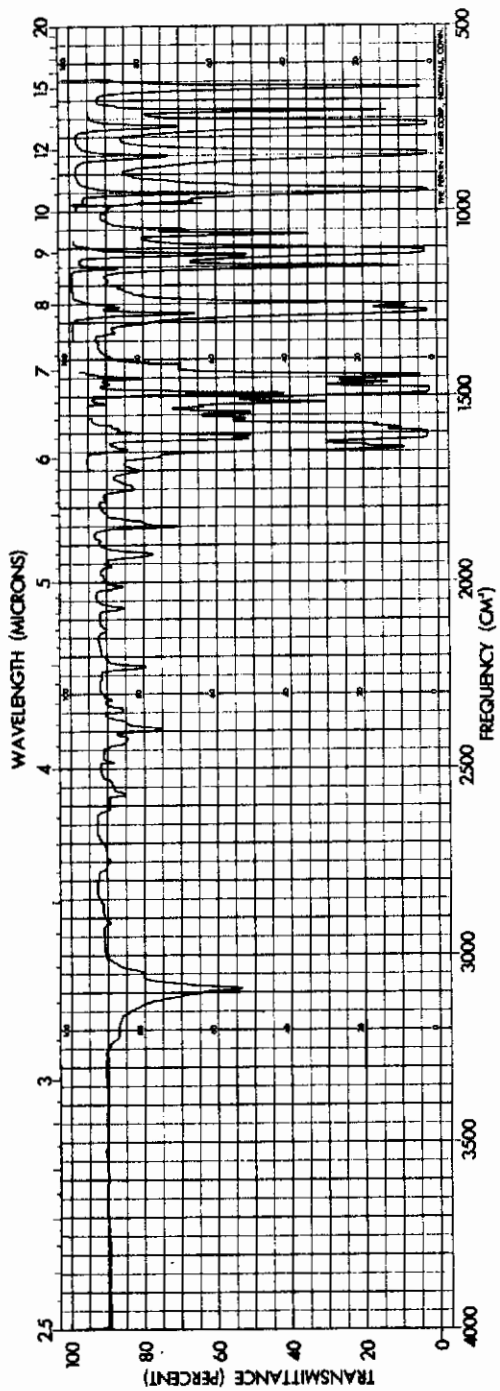


Figure 32. Infrared spectrum of m-difluorobenzene. Liquid; 0.018 mm cell.

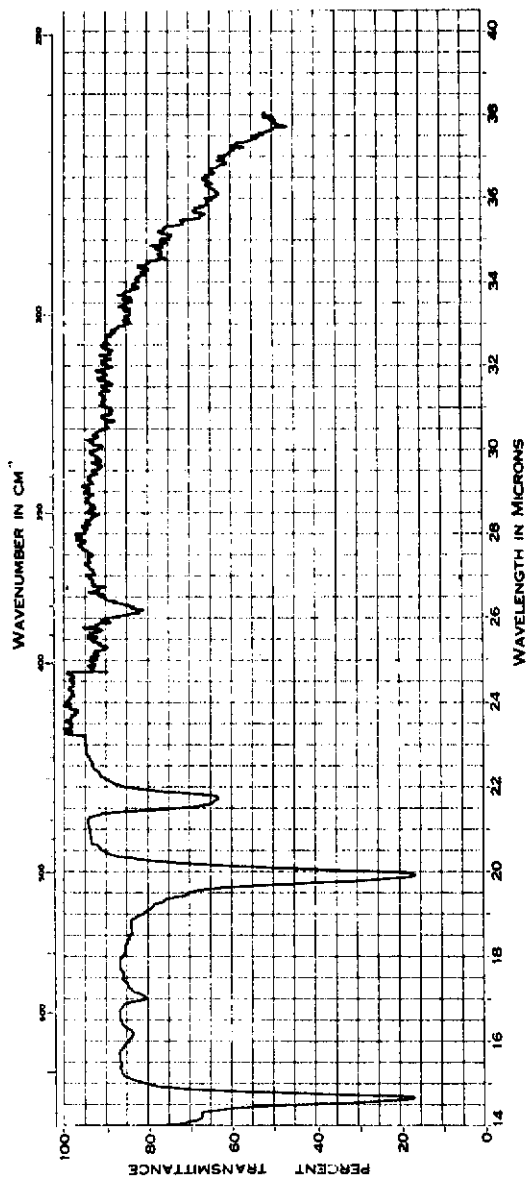
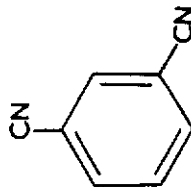
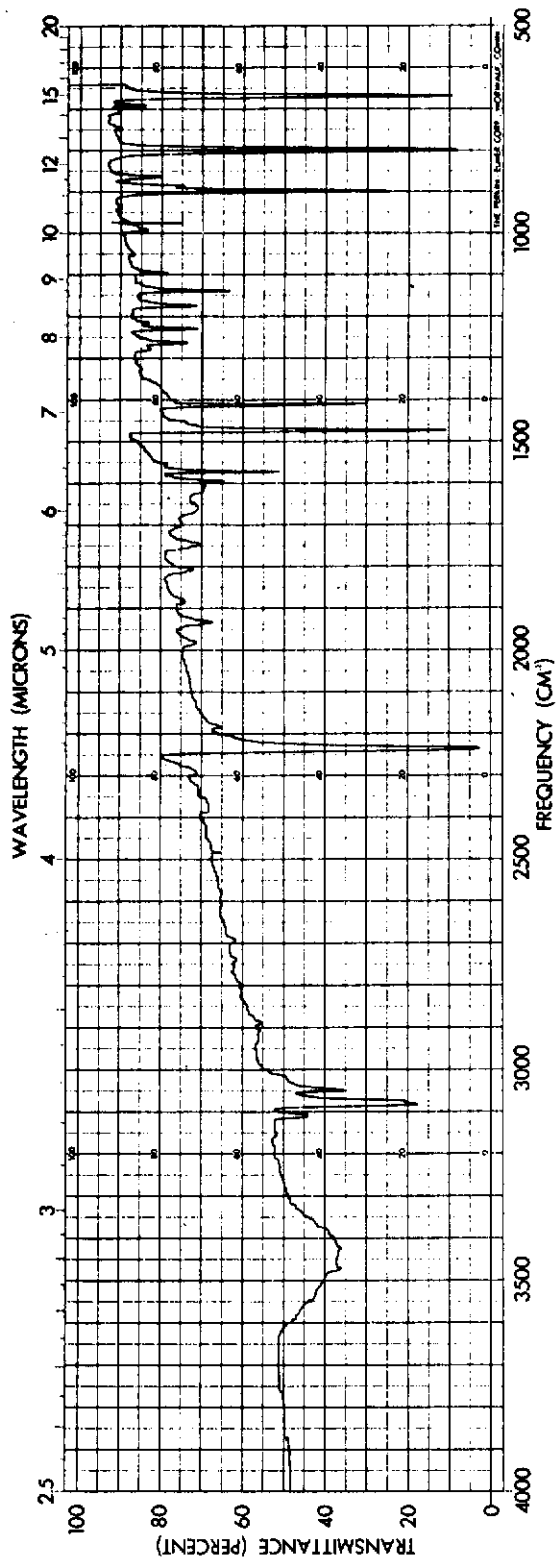


Figure 33. Infrared spectrum of isophthalonitrile. Solid in pressed disks; near infrared, 1 mg/650 mg KBr; far infrared, 2 mg/350 mg KI.

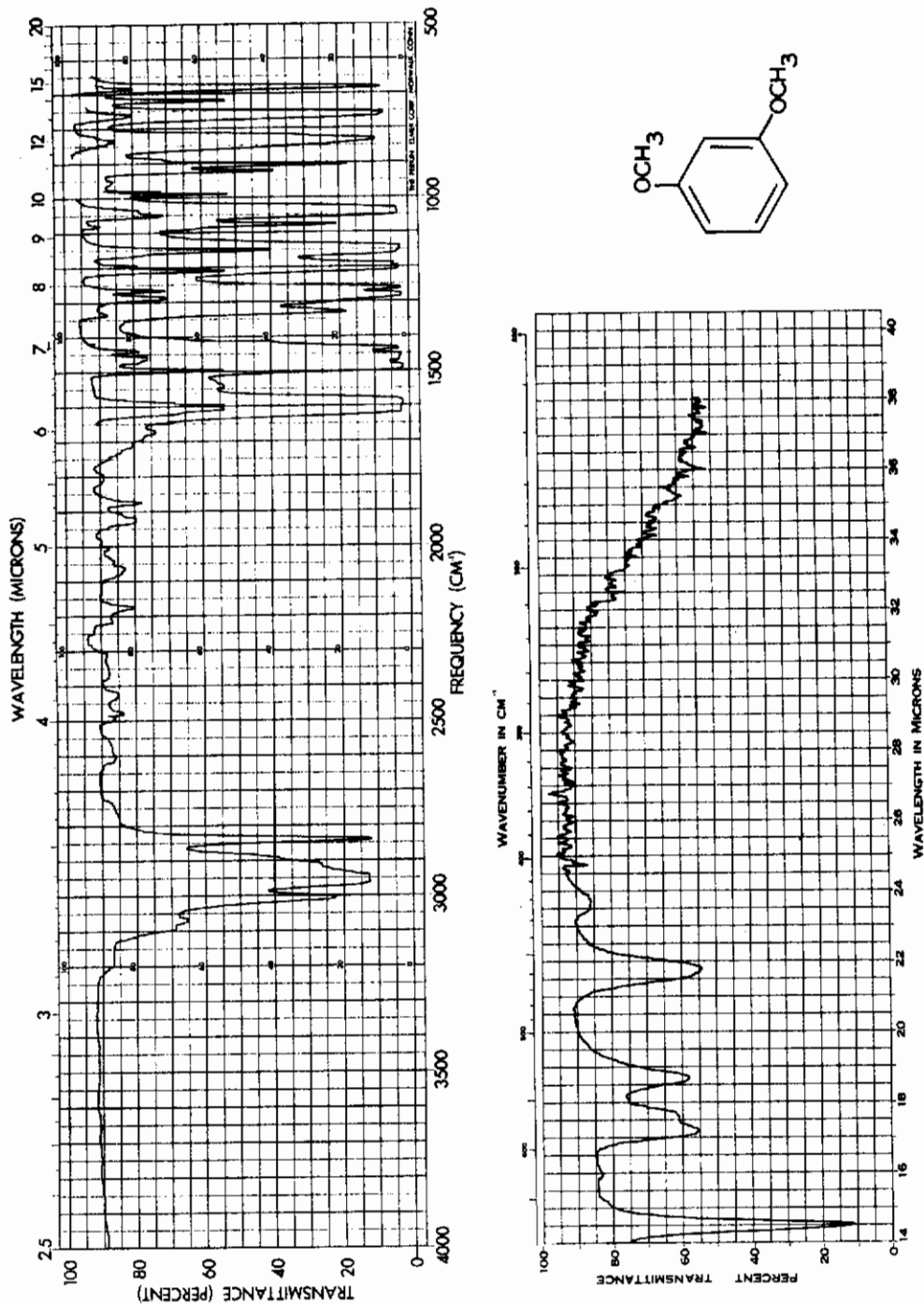


Figure 34. Infrared spectrum of m-dimethoxybenzene. Liquid: 0.018 mm cell.

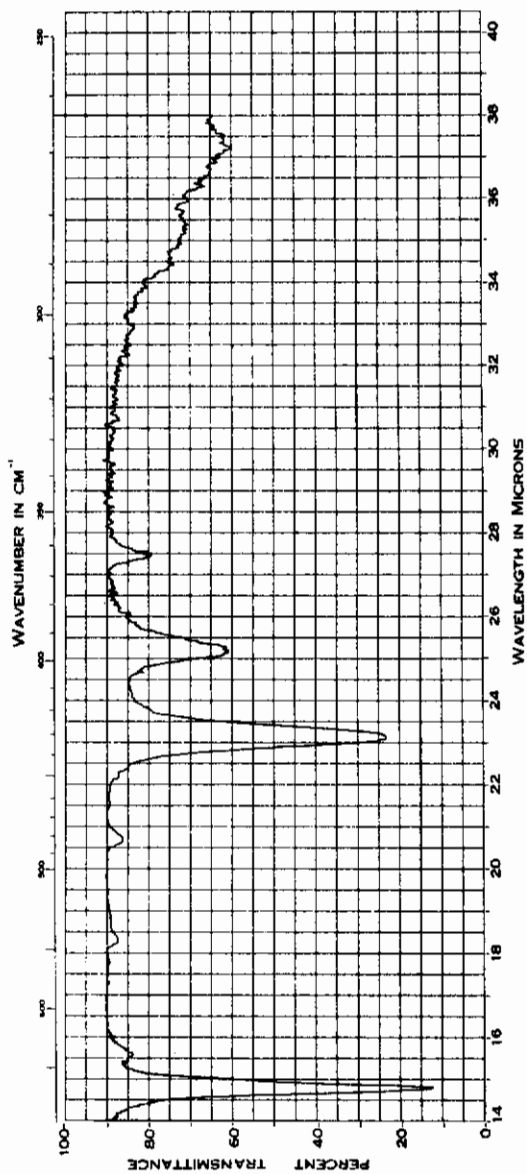
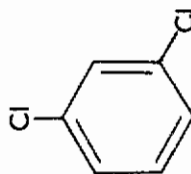
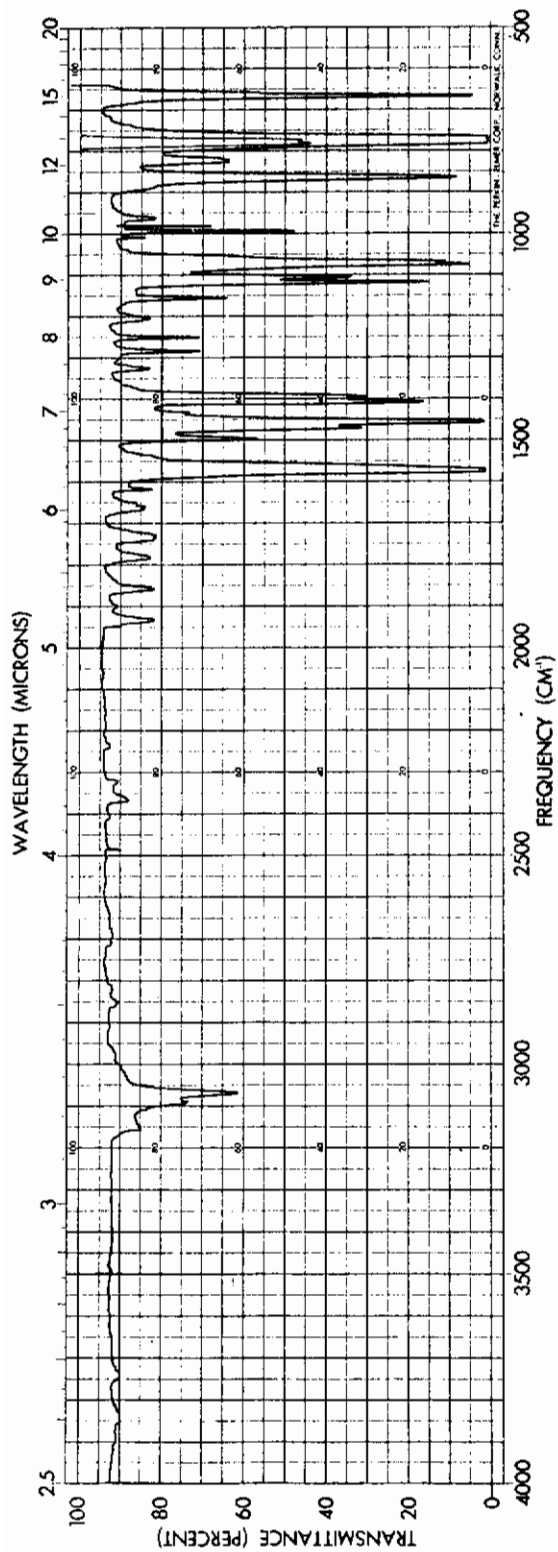


Figure 35. Infrared spectrum of *m*-dichlorobenzene. Liquid; 0.016 mm cell.

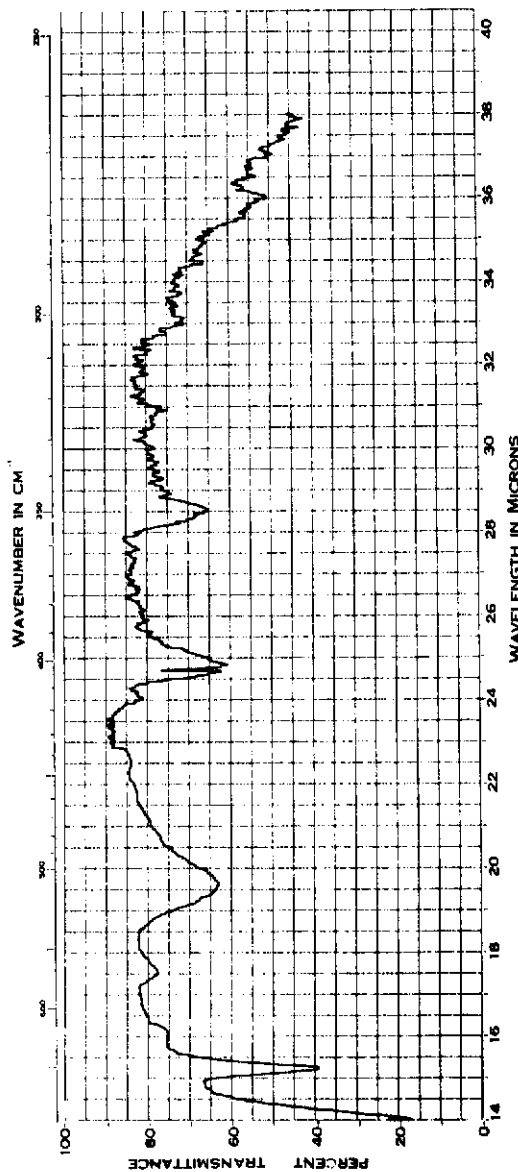
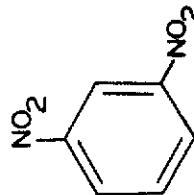
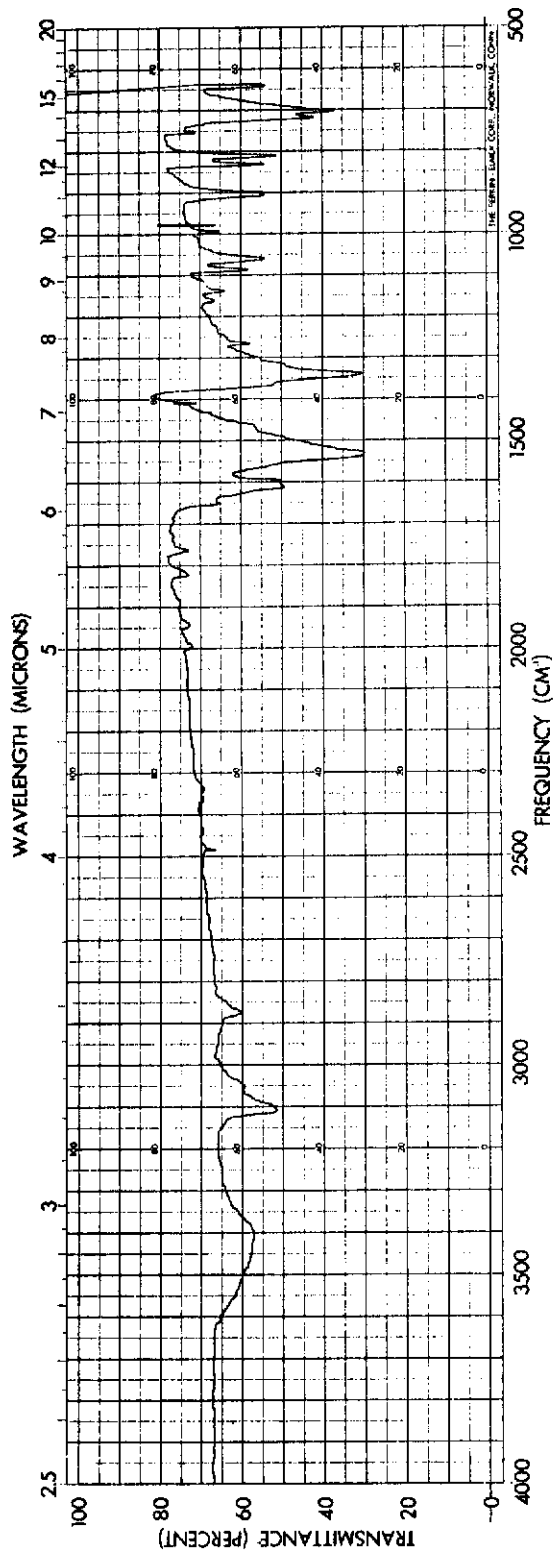


Figure 36. Infrared spectrum of m-dinitrobenzene. Solid in pressed disks: near infrared, 1 mg/650 mg KBr; far infrared, 2 mg/350 mg KI.

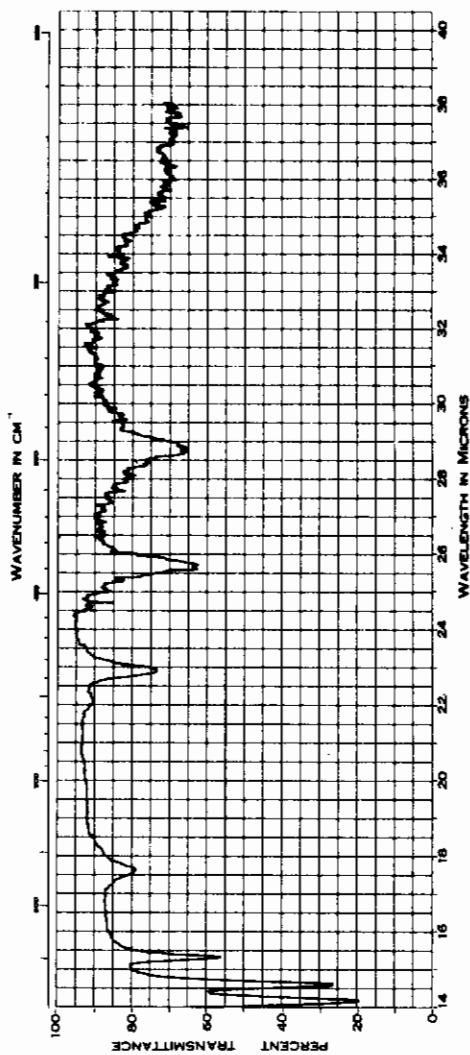
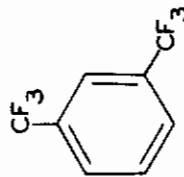
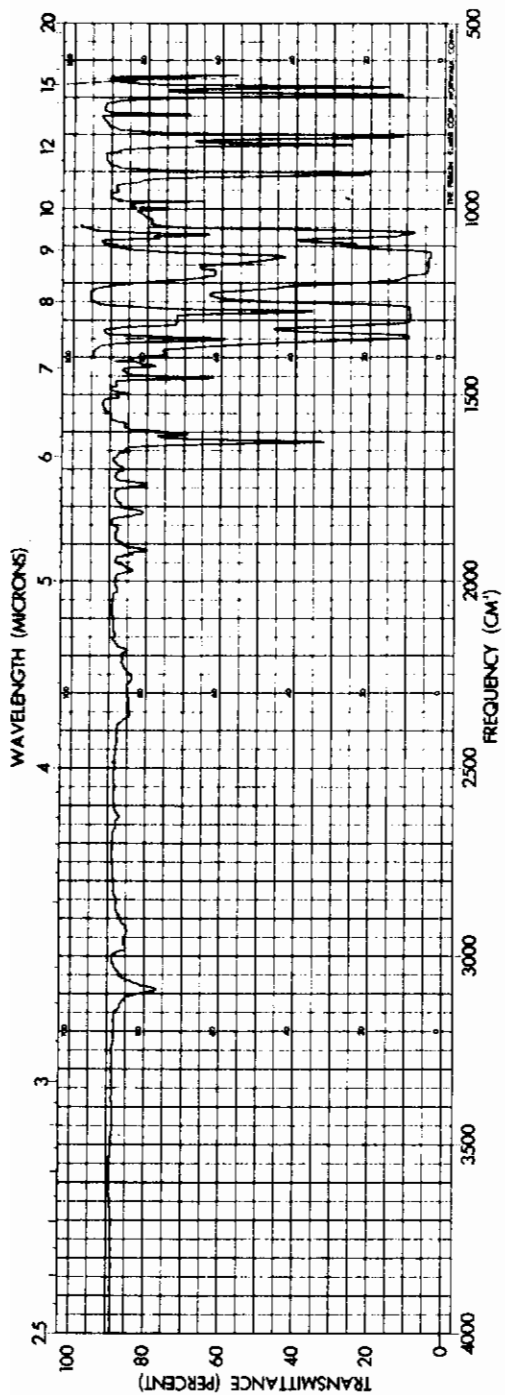


Figure 37. Infrared spectrum of 1,3-bis(trifluoromethyl) benzene.
Liquid: 0.013 mm cell.

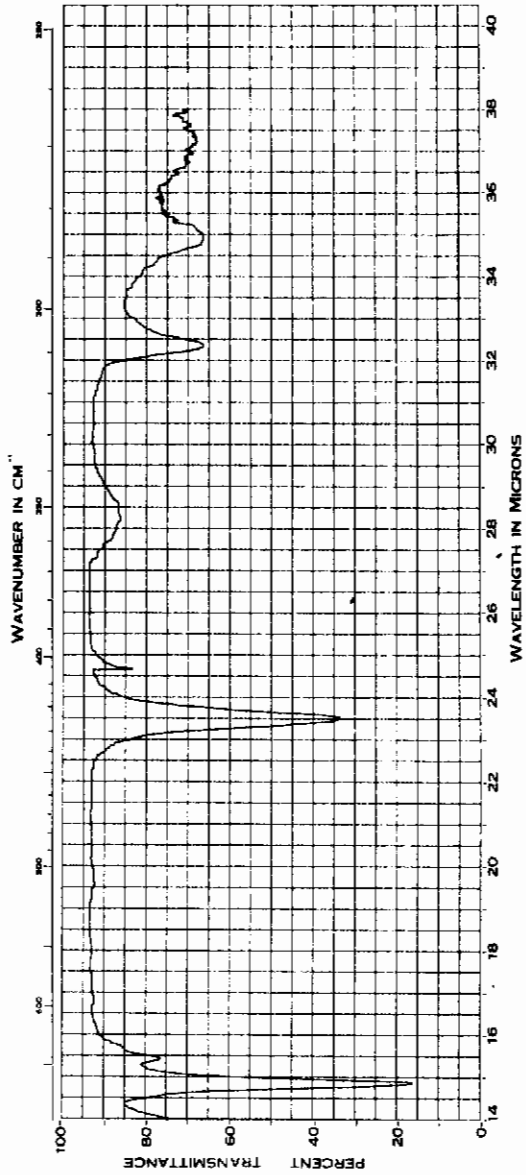
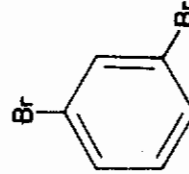
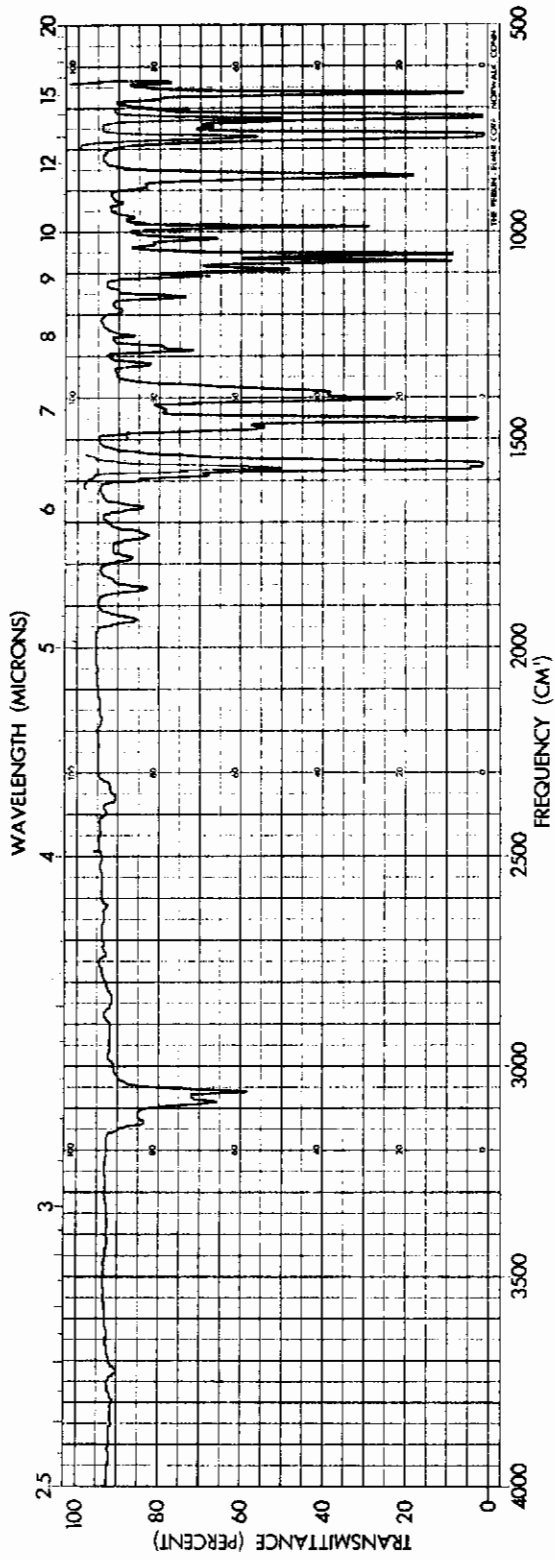


Figure 38. Infrared spectrum of m-dibromobenzene. Liquid; 0.016 mm cell.

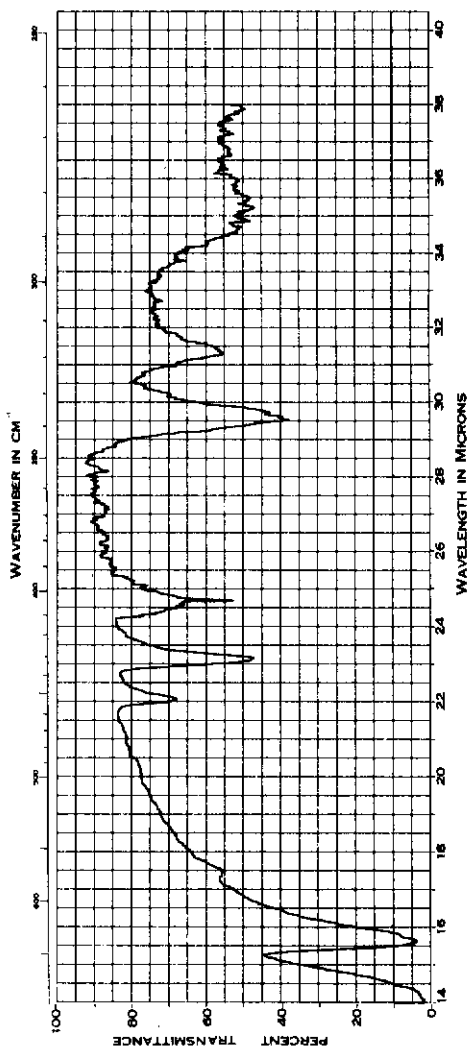
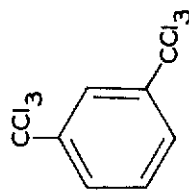
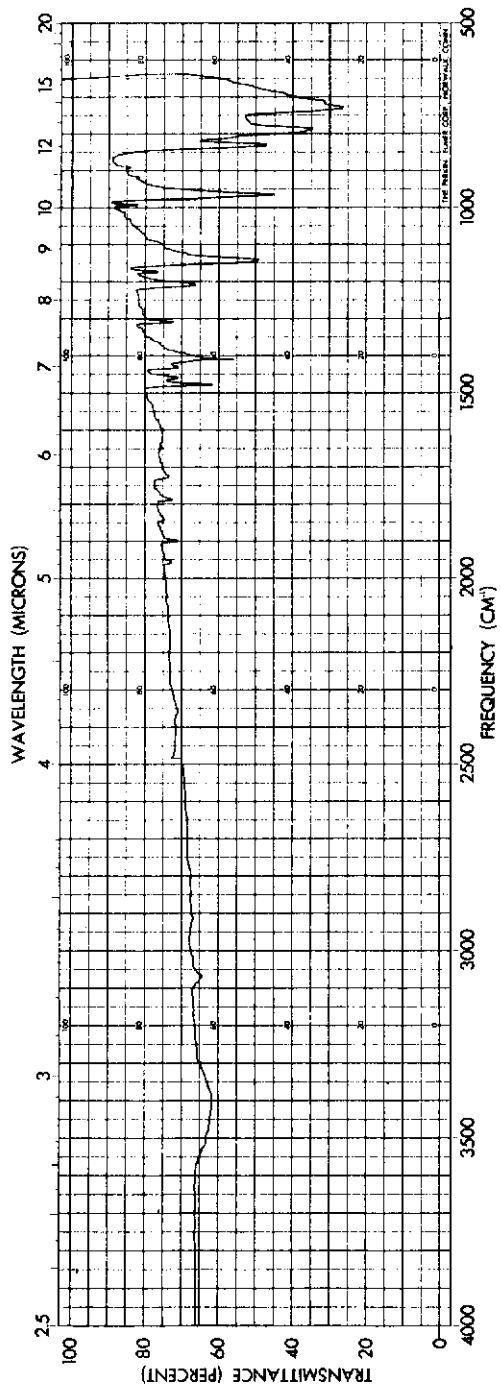


Figure 39. Infrared spectrum of 1,3-bis(trichloromethyl)benzene. Solid in pressed disks: near infrared, 1 mg/650 mg KBr; far infrared, 2 mg/350 mg KI.

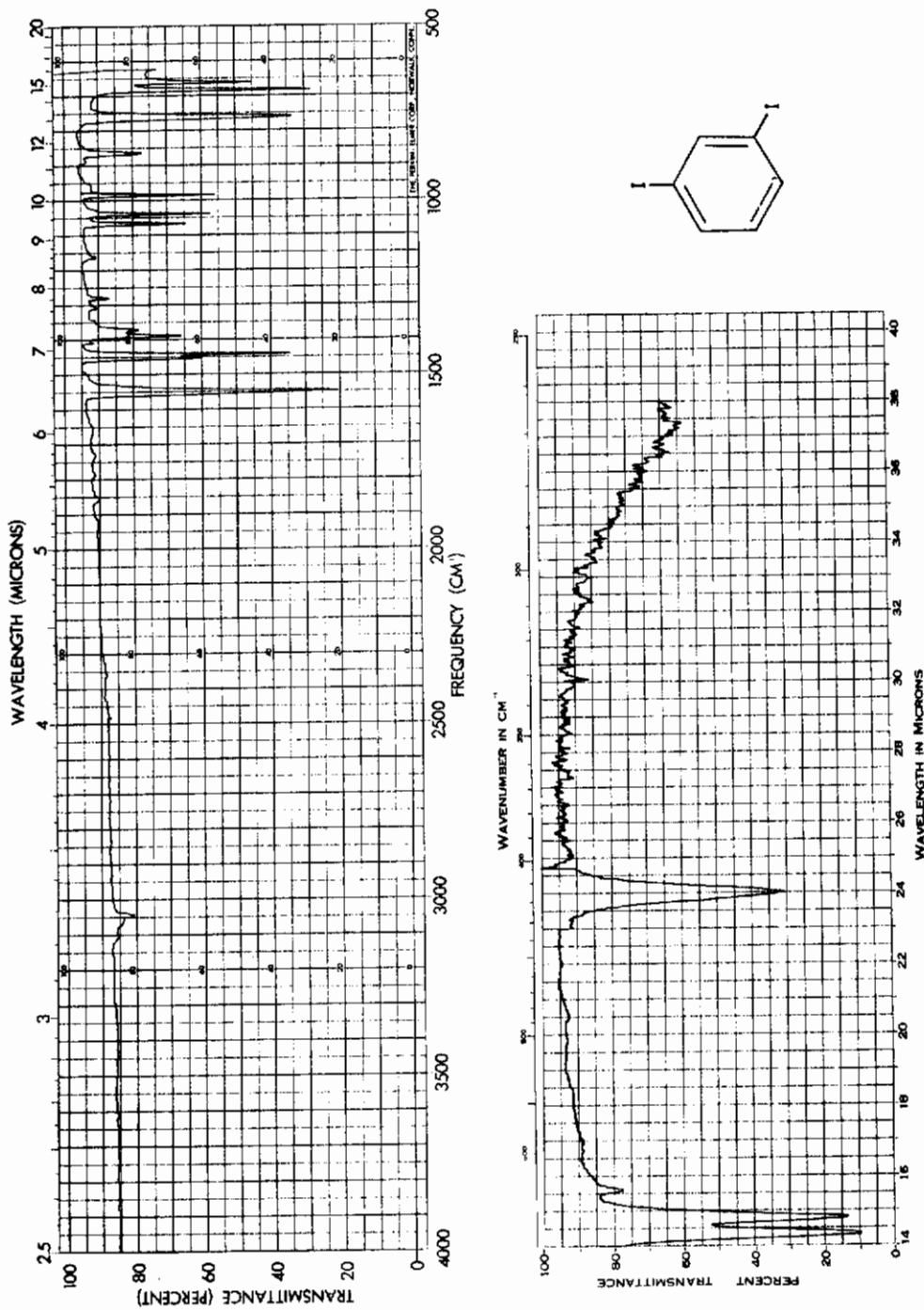


Figure 40. Infrared spectrum of *m*-diiodobenzene. Liquid; capillary film.

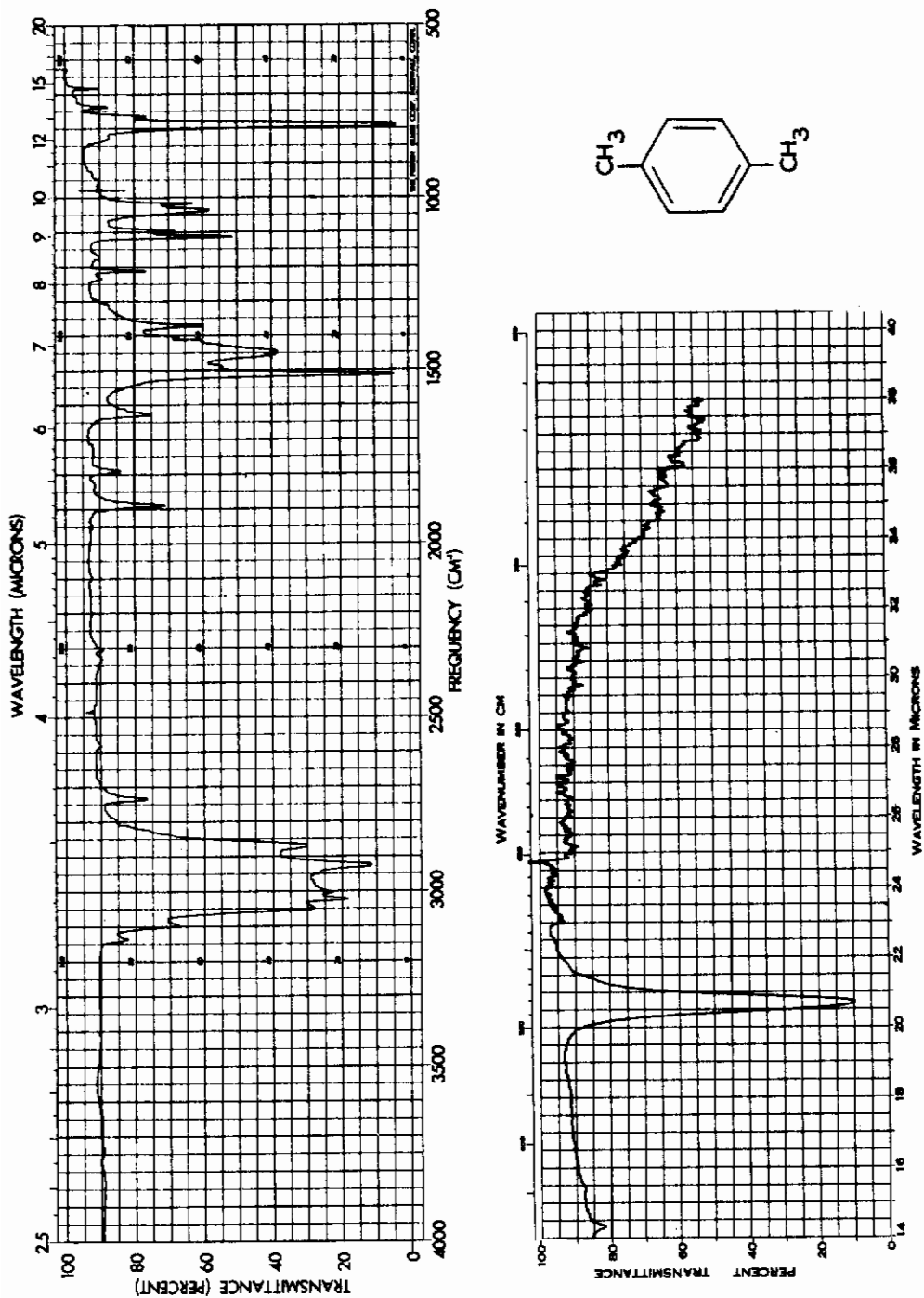


Figure 41. Infrared spectrum of p-xylene. Liquid: 0.018 mm cell.

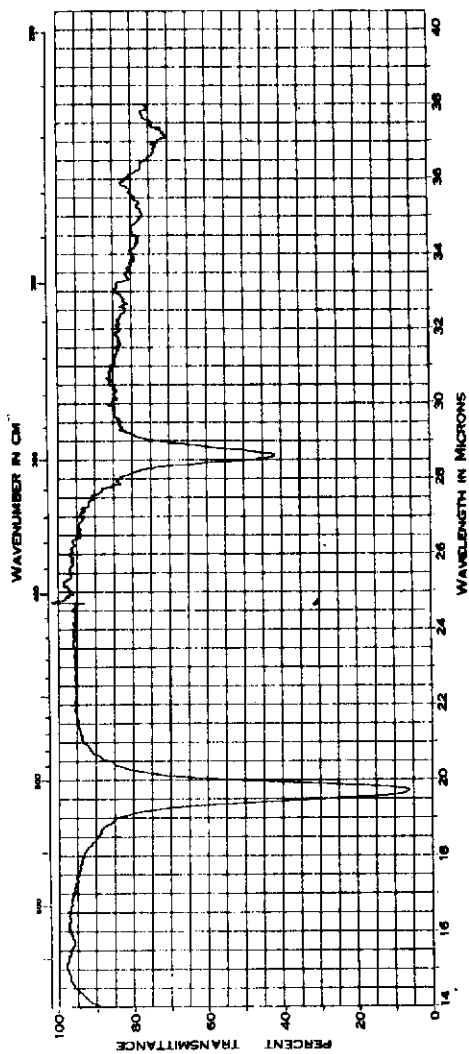
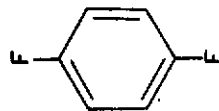
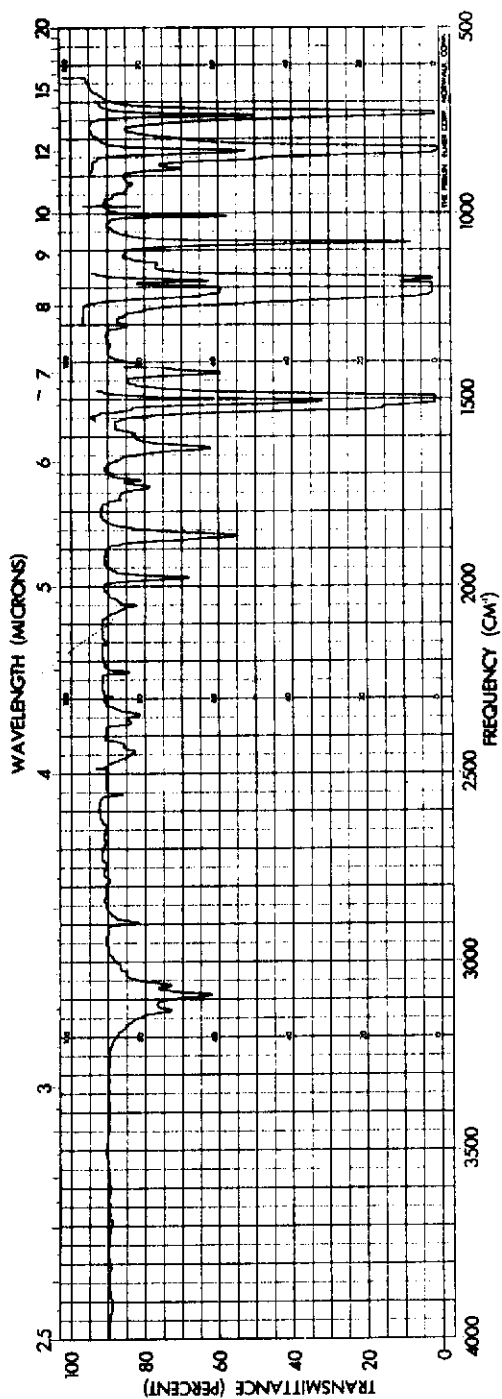


Figure 42. Infrared spectrum of p-difluorobenzene. Liquid: 0.016 mm cell.

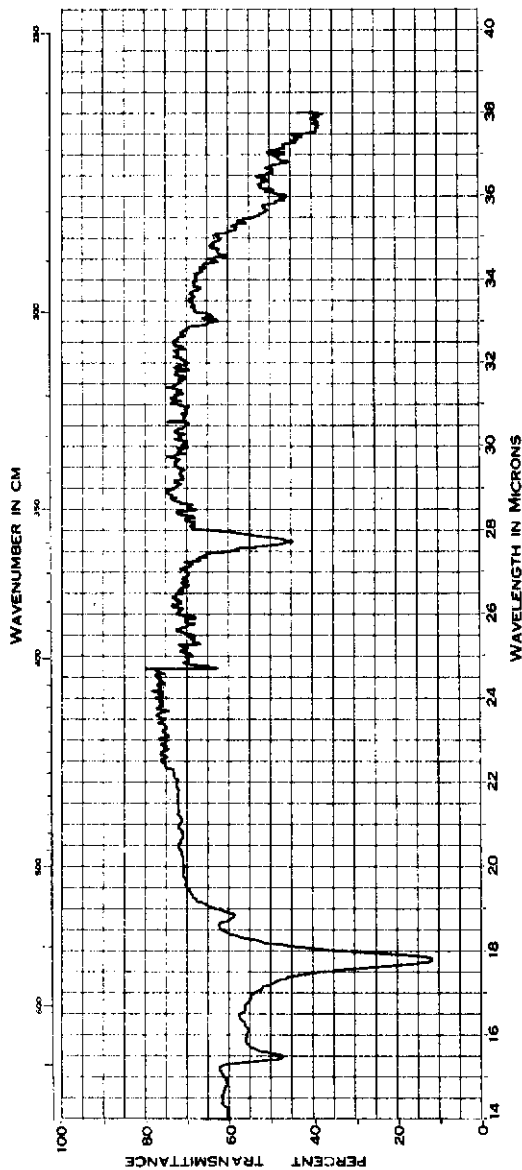
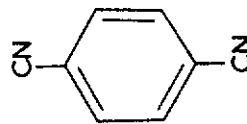
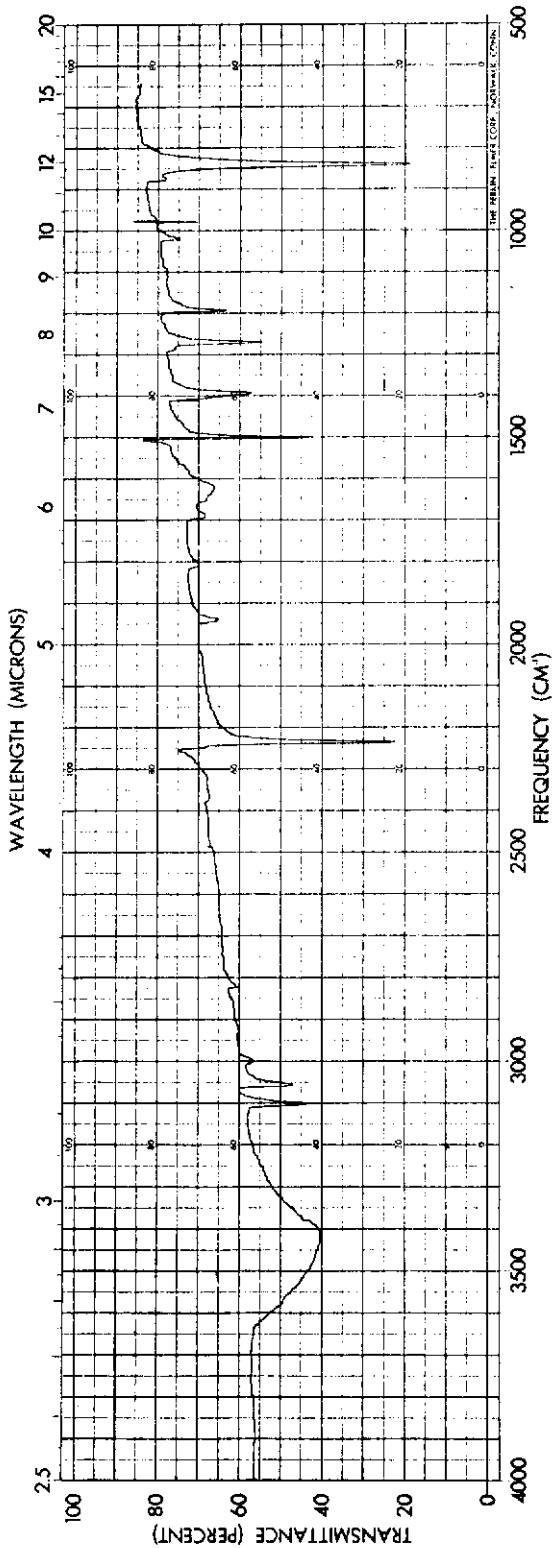


Figure 43. Infrared spectrum of terephthalonitrile. Solid in pressed disks; near infrared, 1 mg/650 mg KBr; far infrared, 2 mg/350 mg KI.

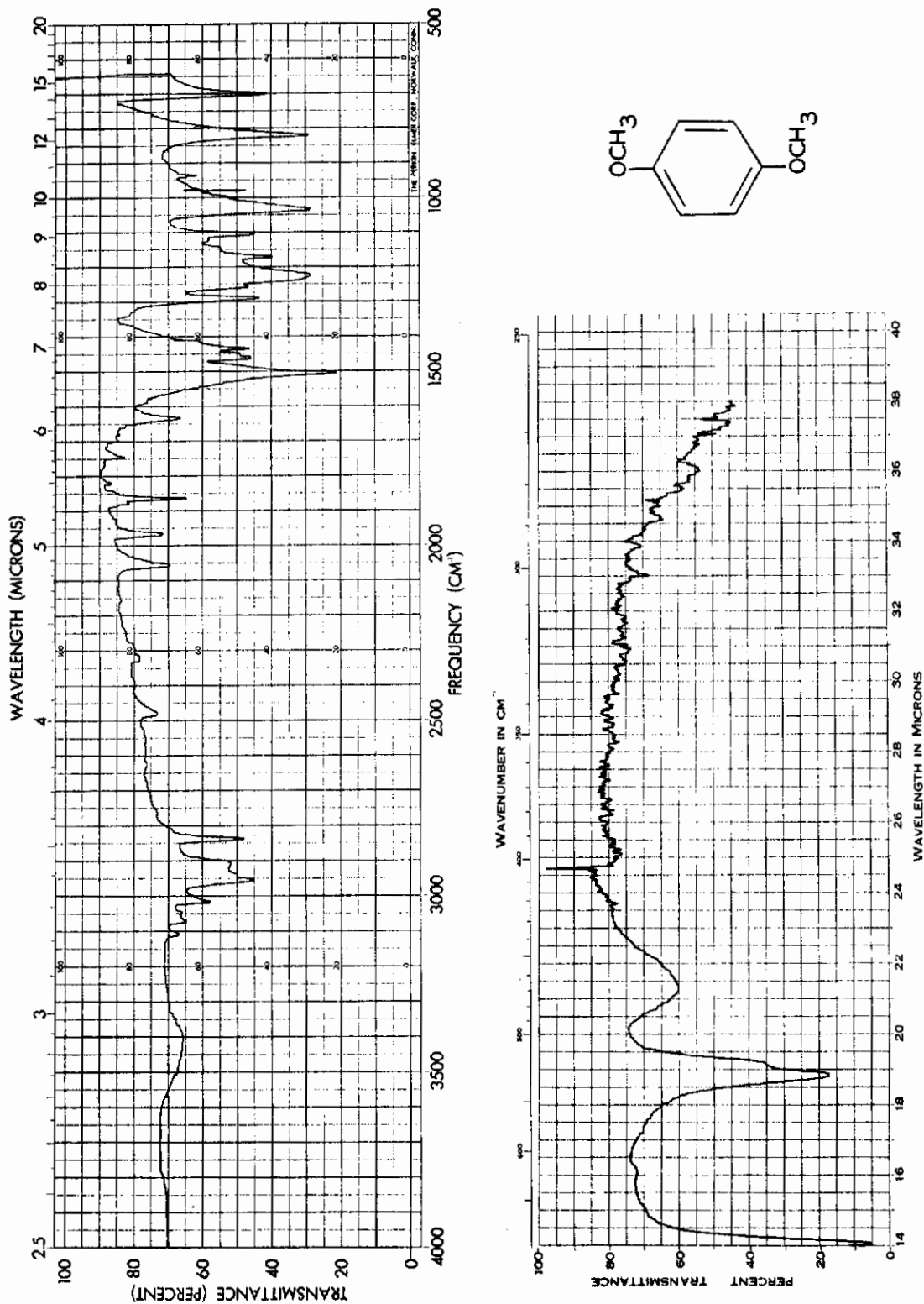


Figure 44. Infrared spectrum of p-dimethoxybenzene. Solid in pressed disks: near infrared, 1 mg/650 mg KBr; far infrared, 2 mg/350 mg KI.

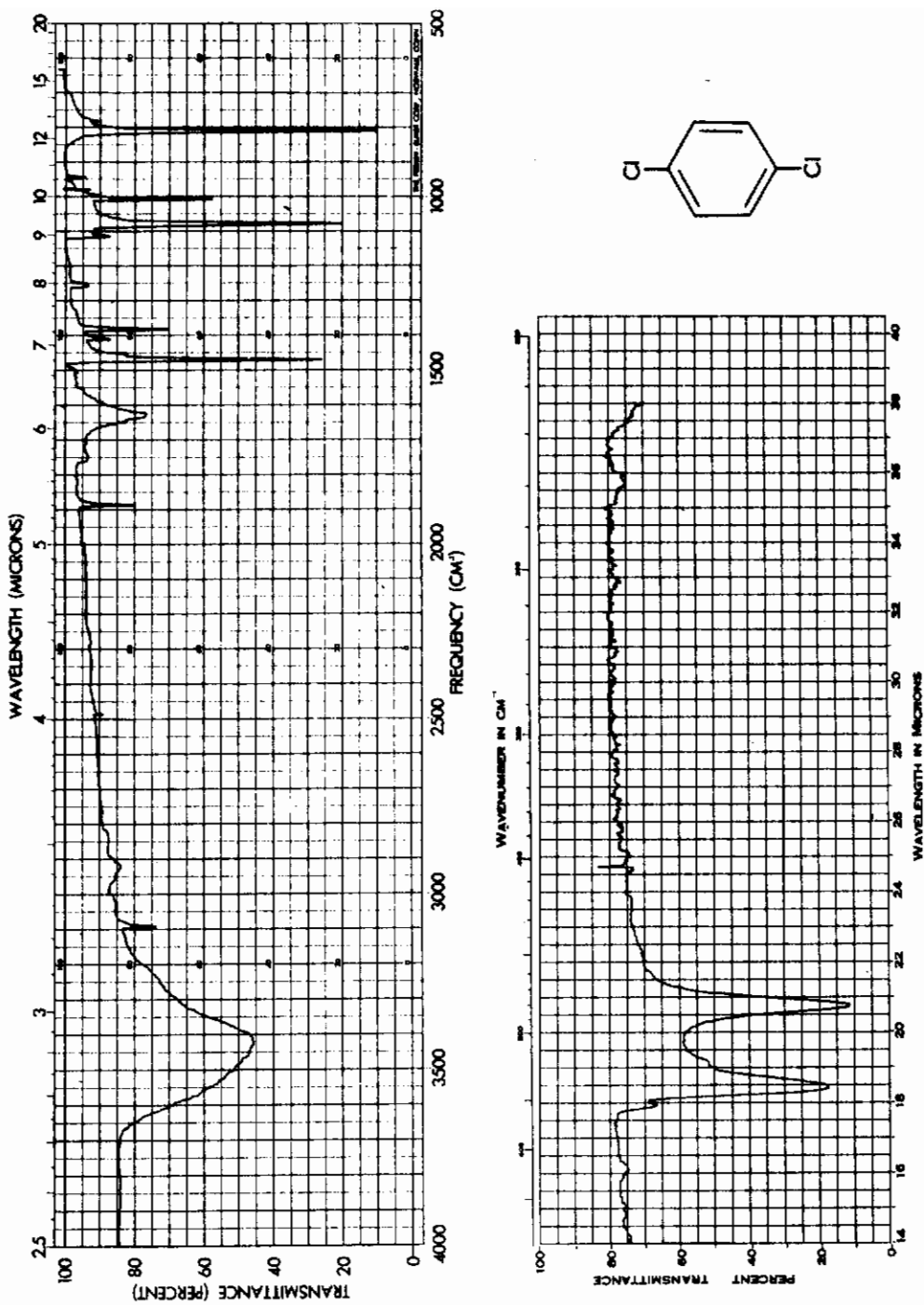


Figure 45. Infrared spectrum of p-dichlorobenzene. Solid: near infrared, capillary film; far infrared, pressed disk—2 mg/350 mg KI.

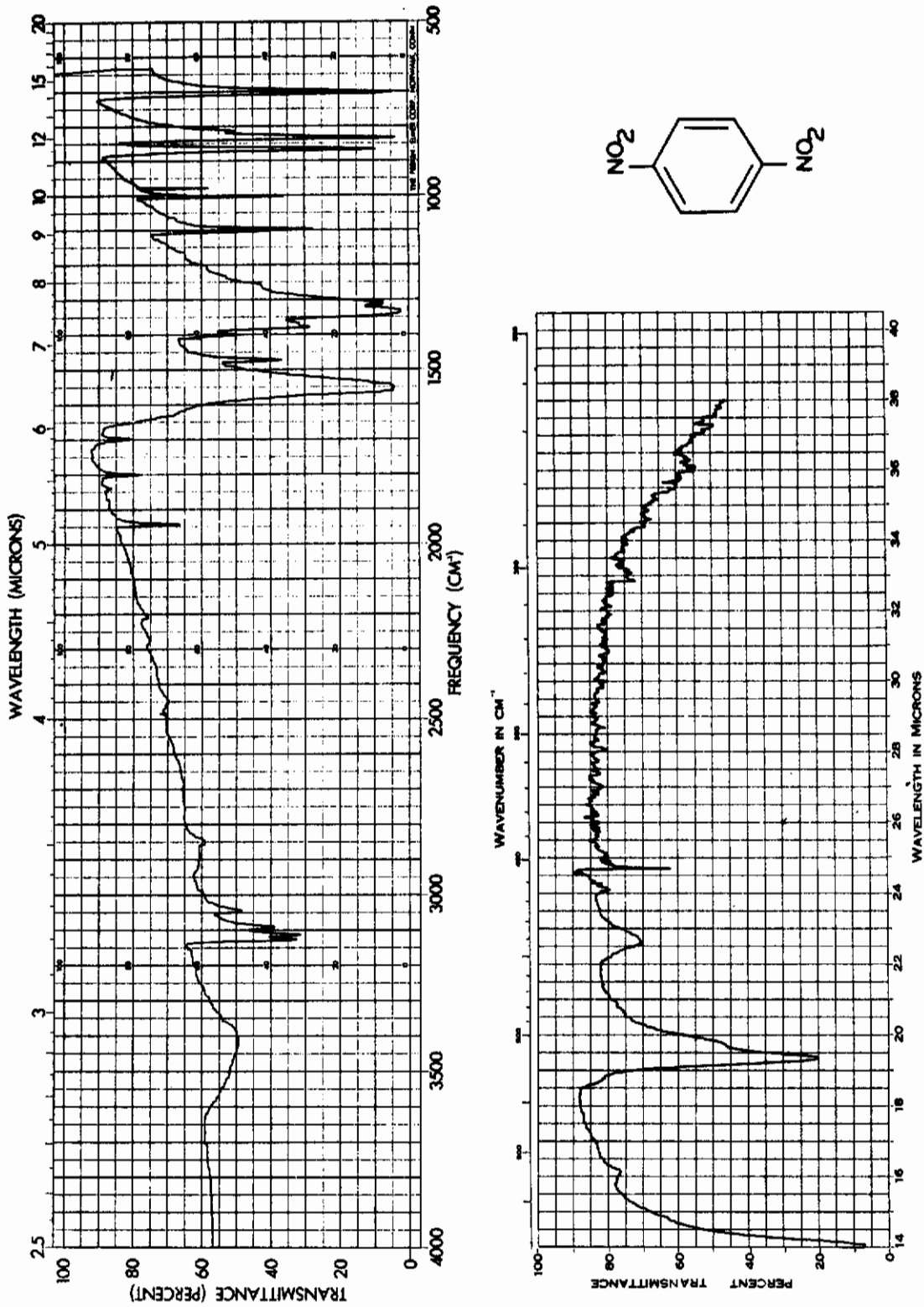


Figure 46. Infrared spectrum of p-dinitrobenzene. Solid in pressed disks: near infrared, 1 mg/650 mg KBr; far infrared, 2 mg/350 mg KI.

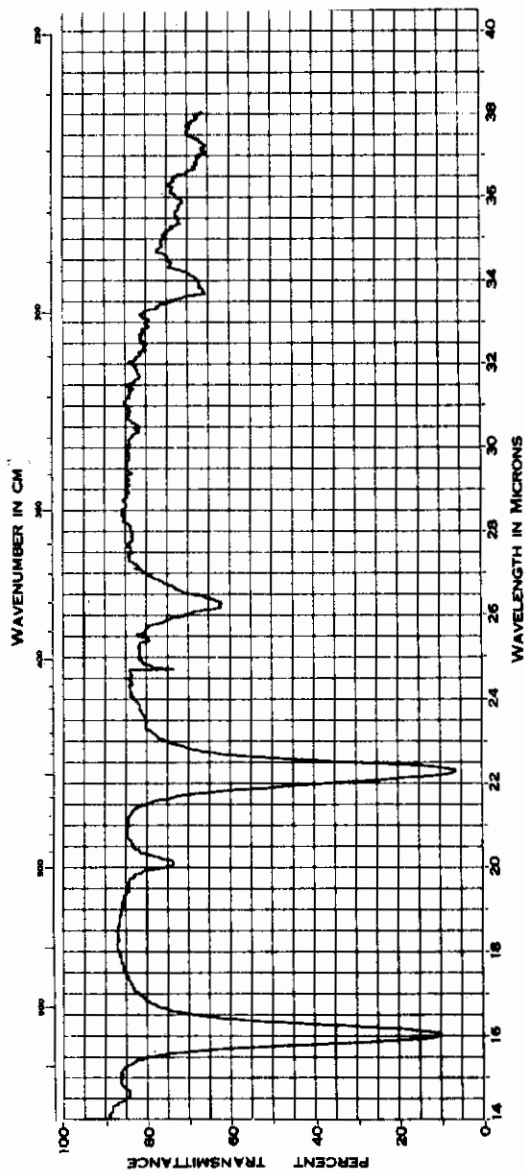
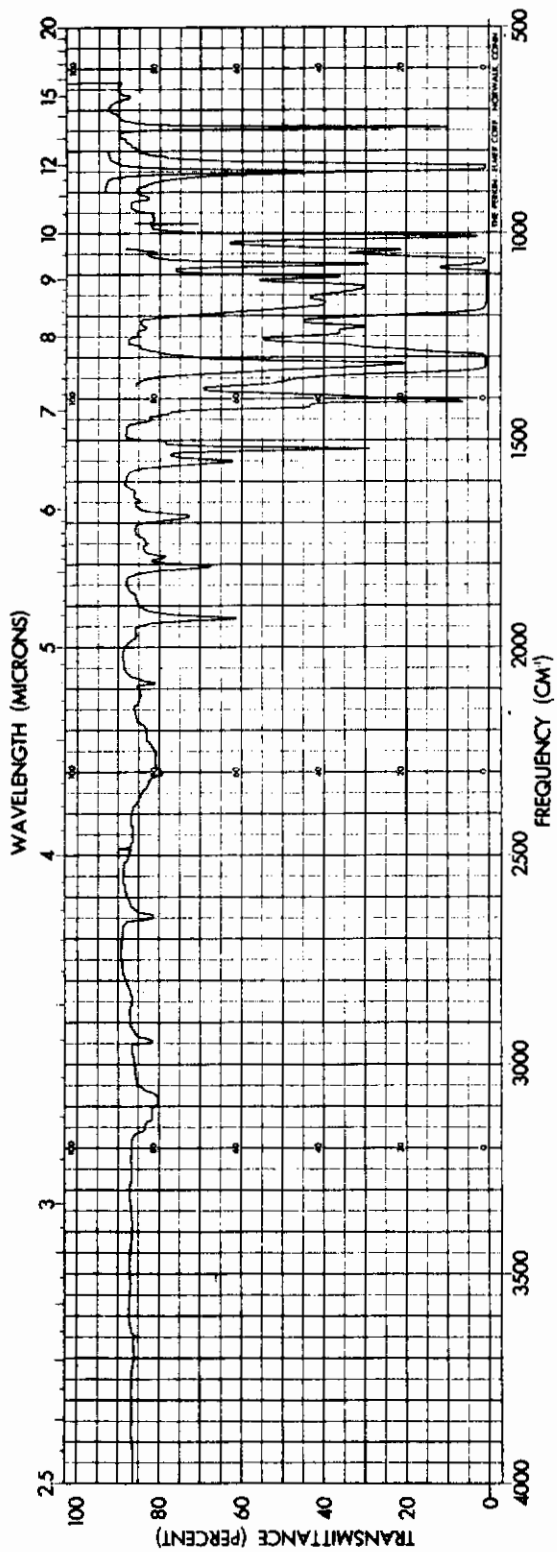


Figure 47. Infrared spectrum of 1,4-bis(trifluoromethyl)benzene.
Liquid: 0.016 mm cell.

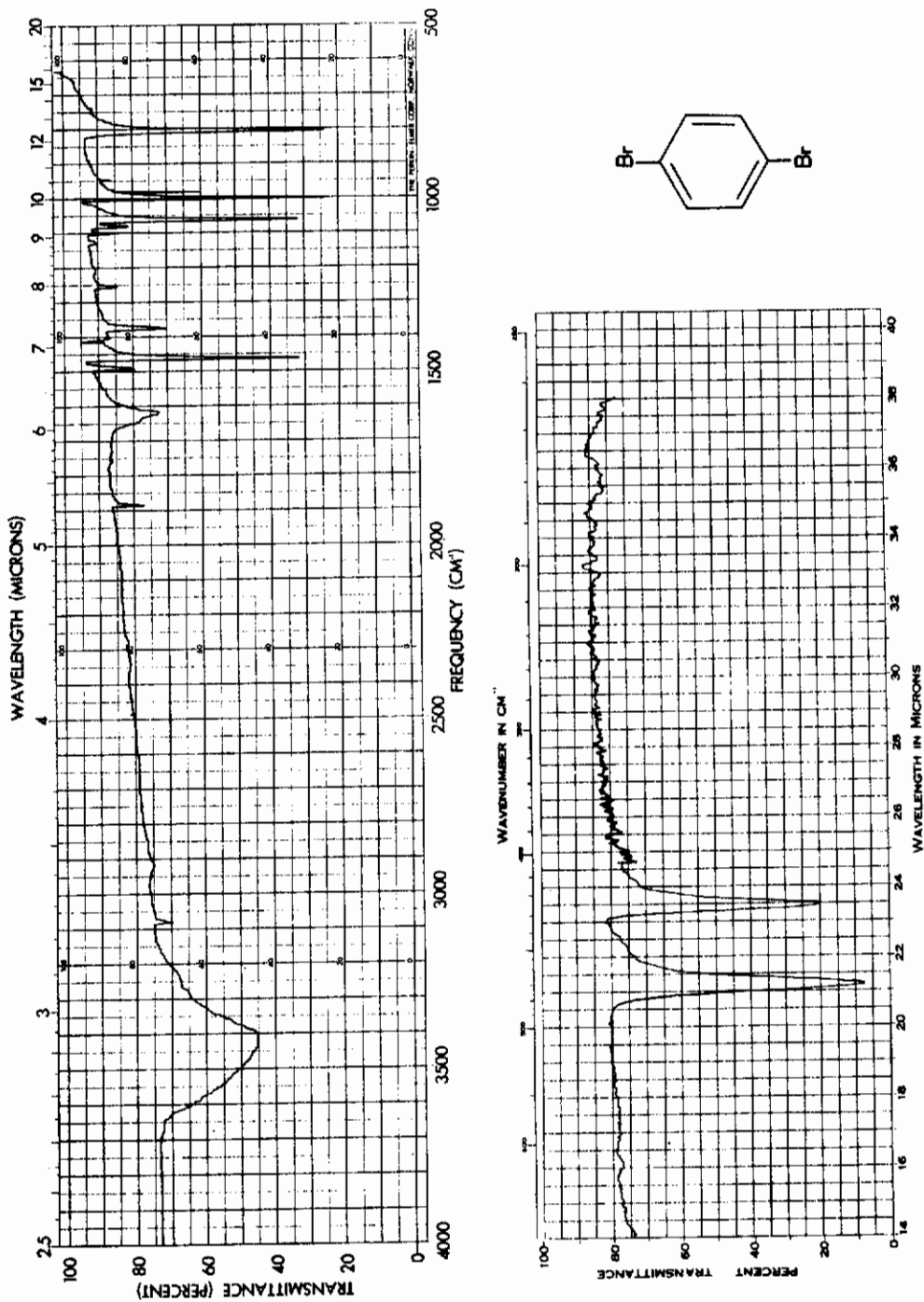


Figure 48. Infrared spectrum of p-dibromobenzene. Solid in pressed disks; near infrared 1 mg/650 mg KBr; far infrared, 2 mg/350 mg KI.

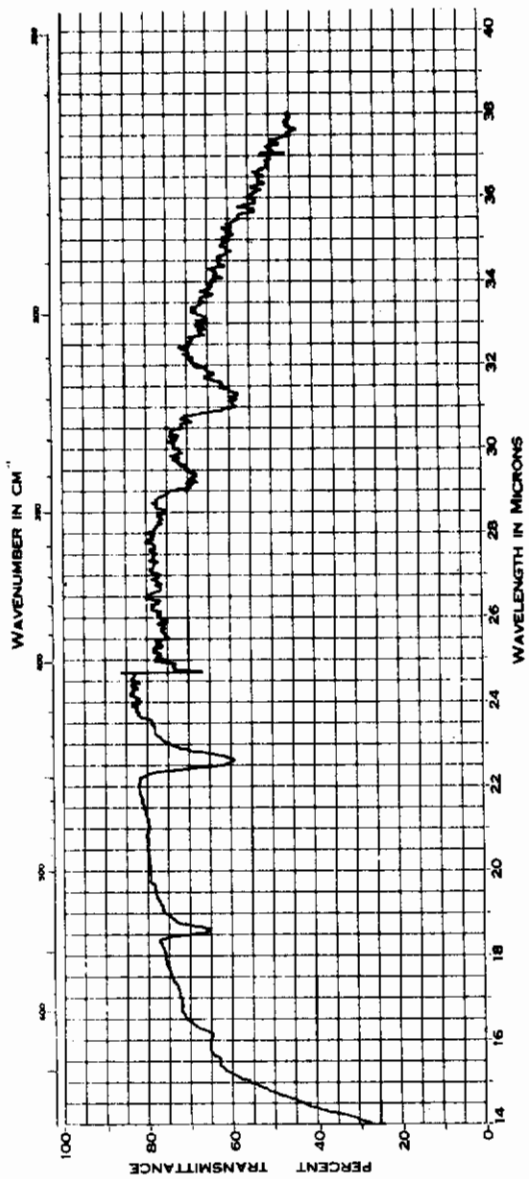
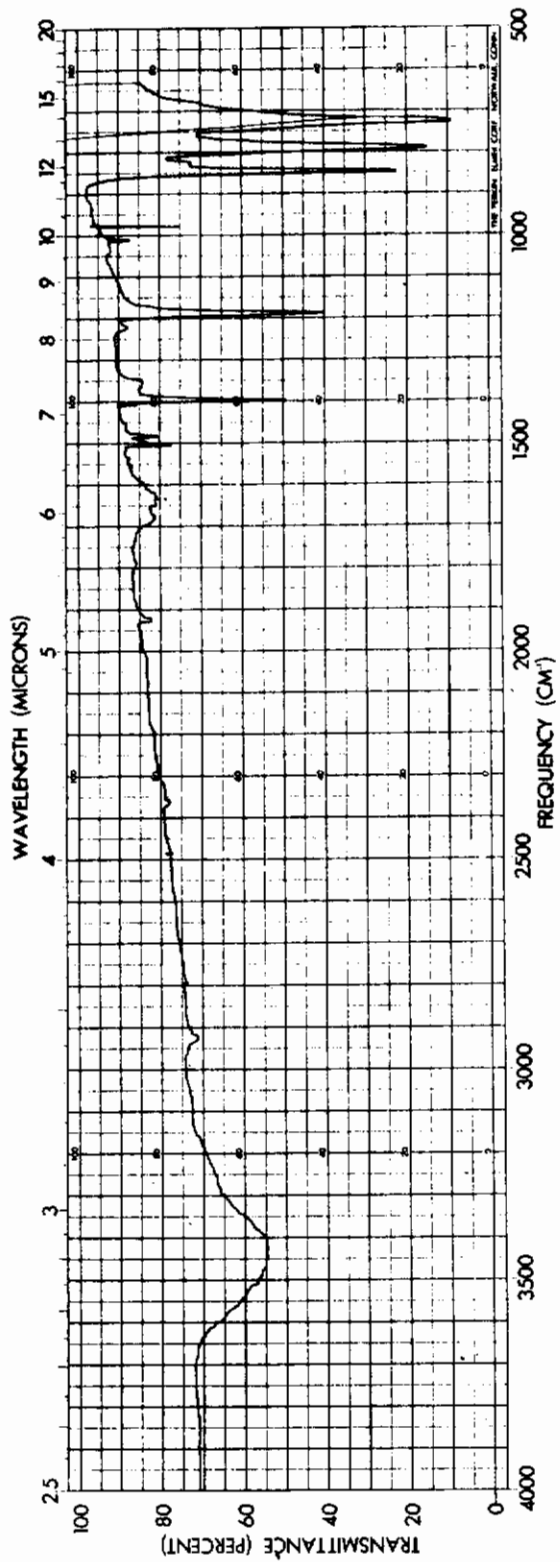


Figure 49. Infrared spectrum of 1,4-bis(trichloromethyl)benzene. Solid in pressed disks; near infrared, 1 mg/650 mg KBr; far infrared, 2 mg/350 mg KI.

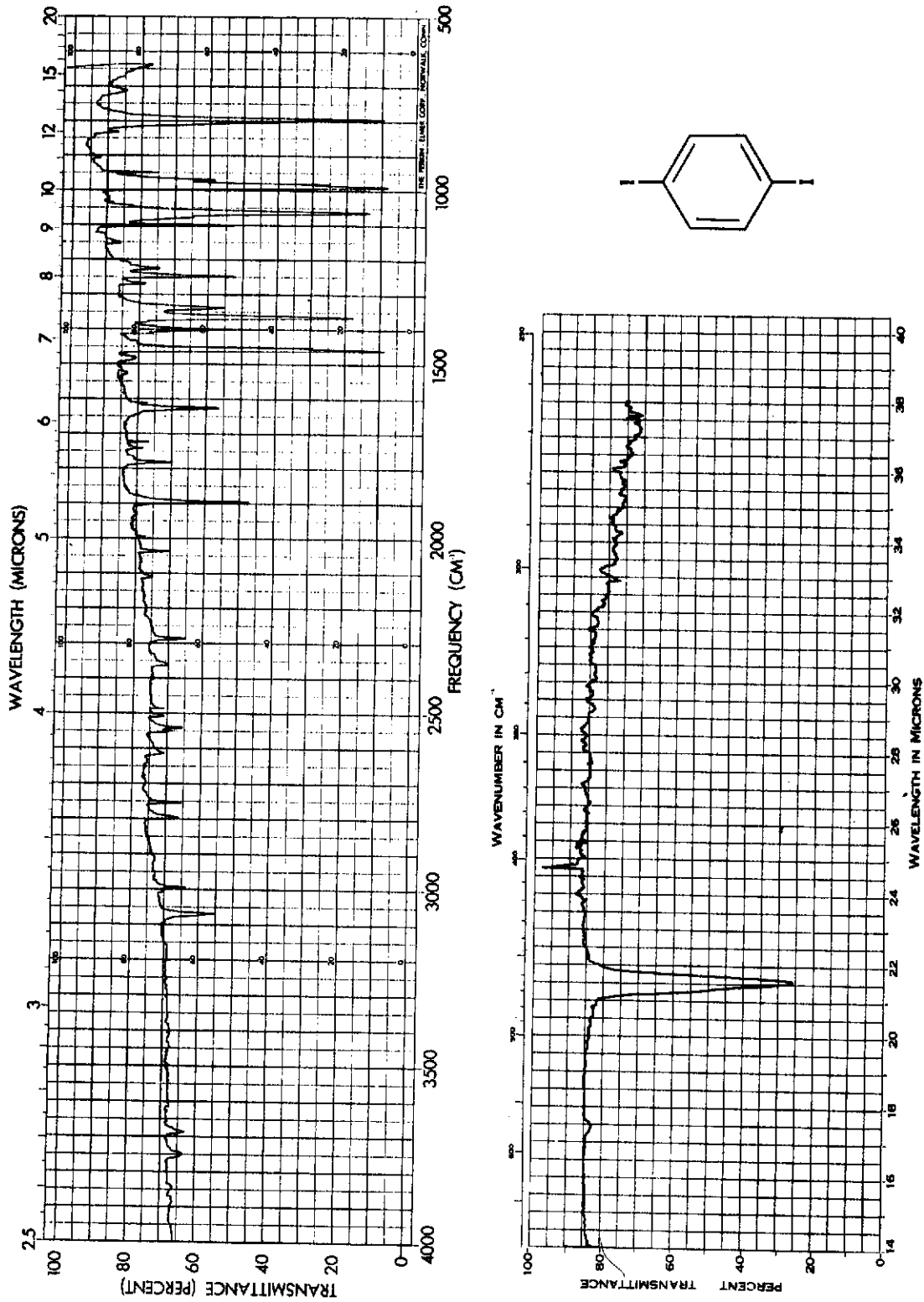


Figure 50. Infrared spectrum of p-diiodobenzene. Solid: capillary film.