

Aromatic Ring Proton Determination by Infrared Intensity
Measurement in the 1650-2000 Wavenumber Region

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The infrared absorption spectra of aromatic compounds in the 1650-2000 cm^{-1} region are well known to be characteristic of ring substitution pattern (5). The observed frequencies in benzene derivatives have been assigned to overtones and combinations of $=\text{CH}$ out-of-plane deformations (4). The absorption in this region has been employed for the determination of total aromatics in petroleum distillates (2). Most compounds with $=\text{CH}$ out-of-plane deformation vibrations in the 750-1000 cm^{-1} region may also be expected to exhibit absorption bands due to overtones and combination tones in the 1650-2000 cm^{-1} region and such is the case for polynuclear hydrocarbons (3) and olefinics (1). In the course of a survey of the absorption of aromatics at equimolar concentration in carbon tetrachloride, it was observed that the integrated intensity over the entire absorption band complex in the 1650-2000 cm^{-1} region appeared to be a monotonic function of number of aromatic ring protons. This observation prompted a detailed study of the relationship between integrated intensity and aromatic structure which is reported in this paper.

Experimental

All compounds were apparently of sufficient purity so as to be used as is, without purification. Spectra were obtained, where solubility permitted, at 0.5 molar concentration in carbon tetrachloride, in path lengths of 0.5 to 2 mm., with solvent compensation in the reference beam. A few samples were run "neat" in 0.1 or 0.2 mm. cell paths. Compounds of limited solubility were analyzed at a path length of 5 mm. Spectra were obtained in all cases on a Beckman IR-12 infrared spectrophotometer flushed with dry air to remove all but traces of water vapor. Spectra were run in absorbance on a 2x abscissa scale at moderately high resolving power to permit resolution of closely overlapping bands. Areas under the absorption bands were measured with a planimeter. Baselines were usually drawn parallel to the abscissa to intercept the absorption at 2000 cm^{-1} . Integrated intensities were calculated in practical units, $\text{cm}^{-1} \ell \text{ mole}^{-1}$, log 10 basis.

Results

Spectra in the 1650-2000 cm^{-1} region of aromatic hydrocarbons (0.5 molar, 0.5 mm path), selected to illustrate the characteristic absorption intensities as a function of ring type and substitution, are shown in Figure 1. These spectra are facsimile presentations which also can be used as a guide to determination of ring type or substitution. Obviously the total absorption varies markedly with degree of substitution. Integrated intensities for a group of aromatic hydrocarbons, selected to represent all the twelve possible classes of substituted benzenes, along with values for some dinuclear, trinuclear and condensed ring systems, are listed in Table I by individuals, and in Table II by averages for ring type. The most obvious variable appears to be the ring proton concentration, or number of $=\text{CH}$ oscillators per ring. The relationship between integrated intensity and ring proton concentration appears to be monotonic, as shown in Figure 2. A linear relationship between intensity and ring proton concentration was observed for phenyl rings (benzene derivatives and polyphenyls), as shown in Figure 3. The plot for phenyls does not run into the origin, which suggests that some other type of vibration is making a constant contribution per phenyl ring to the total intensity in the combination band region. Polynuclear hydrocarbons fall on a line with a steeper slope, which does

extrapolate to the origin. Substituted naphthalenes and dinuclear heterocyclics appear to fall on a line of intermediate slope, but there are insufficient data on this group at the present to justify a strictly linear plot. Assuming that the absorption in hexasubstituted benzenes is a constant measure of skeletal or other phenyl ring vibrations, a fairly constant intensity of about 100 ($\text{cm}^{-2} \text{ l mole}^{-1}$) per proton in pendent phenyl rings and 75 per proton in interior rings is obtained in the polyphenyls as shown in Table III. In the polyphenyls only the terminal phenyl rings are considered to be pendent while the remaining interior phenyl rings are assumed to contribute only combination tones of $=\text{CH}$ oscillators in the 1650-2000 cm^{-1} region.

The effects of some polar and other ring substituents on the aromatic absorption intensity in this region are listed in Table IV. Olefinic double bonds display overtones in this region, as exemplified by the spectrum of styrene with an increased absorption at 1820 cm^{-1} compared with its brominated derivative, shown in Figure 4. The intensity per olefinic $=\text{CH}$ oscillator is approximately equal to an aromatic $=\text{CH}$ oscillator.

Additional bands are observed in the spectra of monosubstituted benzenes in solution in an inert solvent, as shown in Figure 5, for pure tert. butylbenzene and for a 10-fold dilution in carbon tetrachloride run at equivalent pathlengths times concentration. The two highest frequency bands split into doublets. A suggested assignment for each of these doublets (which were observed in the spectra of nearly all monosubstituted benzenes) as combinations of fundamentals is given for a few cases in Table V. At sufficiently high resolution some splitting can be observed even in undiluted compounds (dotted line of Figure 5).

Discussion

There appears to be little doubt that the integrated absorption intensity of aromatic hydrocarbons in the 1650-2000 cm^{-1} region is a monotonic function of the ring proton concentration, as depicted in Figure 2. This observation is at variance with the apparent constancy per ring, independent of degree of substitution, reported by Bomstein (2) for a number of alkylbenzenes. Bomstein's data, however, does show a significant variation of intensity with substitution. His K values for benzene/mono/di/trialkylbenzenes are in the ratio of 1.6/1.2/1.06/1.0, compared with ratios of integrated intensities in this paper of 1.7/1.35/1.15/1.0. (Differences between the two sets may reflect differences in integration range, background assumptions, types of compounds and instrument performance.) Bomstein stated that naphthalenes have different, presumably higher, K values, reflecting perhaps a higher ring proton concentration. Therefore, the apparent constancy observed by Bomstein for absorption in the 1700-2000 cm^{-1} region independent of degree of substitution holds only because his data were restricted to a relatively narrow range of ring proton concentration, perhaps 1.5 to 2 fold, compared with the 12-fold range explored in this study.

There also appears to be little doubt that the absorption due to phenyl rings is a linear function of ring proton content in both mononuclear hydrocarbons and polyphenyls, as shown in Figure 3. The intersection of this plot above zero on the ordinate can be interpreted as evidence of a background absorption of about 130 $\text{cm}^{-2} \text{ l mole}^{-1}$, associated with ring skeletal vibrations in pendent phenyl rings. The total 1650-2000 cm^{-2} absorption in m-quinquephenyl, for example, consists of a contribution of 260 $\text{cm}^{-2} \text{ l mole}^{-1}$ for the two pendent rings, plus a contribution of approximately 75 $\text{cm}^{-2} \text{ l mole}^{-1}$ for each ring proton, or a total intensity of 1910 $\text{cm}^{-2} \text{ l mole}^{-1}$, compared with an observed value of 2080. A linear plot of the 1650-2000 cm^{-1} absorption intensity against ring proton concentration which extrapolates to zero (Figure 3) was observed for polynuclear hydrocarbons and condensed ring systems, which suggests that all the intensity in this region in constrained ring systems is due to ring protons, with an average

intensity per proton of about $130 \text{ cm}^{-2} \text{ l mole}^{-1}$. For example the integrated absorption intensity of 20-methylcholanthrene in the $1650\text{-}2000 \text{ cm}^{-1}$ region was found to be $1168 \text{ cm}^{-2} \text{ l mole}^{-1}$ (Table I), equivalent to a value of 8.9 aromatic protons per molecule, compared with a formula value of 9.

Rubrene would present a complex case, since it contains 4 phenyl rings attached to a naphthalene skeleton. If the intensity relations in Table II apply to this compound (not yet measured) the lower and upper limits of numbers of aromatic protons per molecule would be estimated by infrared to be 24 to 30, compared with a formula value of 28. A reasonable expectation is the determination of aromatic protons (provided the molecular weight is known) to within $\pm 10\%$ of the formula value of the infrared technique of this paper.

On the basis of integrated intensity measurements, it appears reasonable to include a band near $1620\text{-}1640$ in para alkylbenzenes with the combination tones. Its inclusion on a frequency basis has already been justified by Whiffen(4).

Sharpening of peaks and splitting of bands were observed for monoalkylbenzenes and other aromatics, as depicted in Figures 1 and 5. The total $1650\text{-}2000 \text{ cm}^{-1}$ intensity was found to be essentially constant in the range 0.5 molar to 6 molar (approximately 10 times diluted, and undiluted). In the monosubstituted benzenes the two highest frequency bands of the $1650\text{-}2000 \text{ cm}^{-1}$ set, near 1860 and 1945 cm^{-1} , have been designated as i+h and h+j, summation tones by Whiffen (4). Under sufficiently high resolution partial splitting of one or both of these bands can be observed. More complete splitting was observed in non-interacting solvents such as hexane, carbon tetrachloride and carbon disulfide and the peaks were found to be narrower. The 1865 cm^{-1} peak of monoalkylbenzenes apparently is an i+h summation band but the three remaining peaks at 1880 , 1938 and 1955 cm^{-1} appear to be, respectively, i+j, 2h and 2j bands. Little or no splitting was observed in solutions in chloroform and methylene chloride. Presumably the acidic hydrogen in these solvents (and the ring proton of undiluted aromatics) is able to complex with the π electron orbitals of the monosubstituted benzene ring in such a way as to cause the split bands to overlap and merge into broader bands.

It is possible to estimate the aromatic proton content of compounds (benzenoid and heterocyclics) from the infrared absorption intensity in the $1650\text{-}2000 \text{ cm}^{-1}$ region using average intensities ($\text{cm}^{-2} \text{ l mole}^{-1}$) for each ring proton of 100 for mononuclear, 120 for dinuclear, and 130 for polynuclear hydrocarbons. The number of ring protons is then the total $1650\text{-}2000 \text{ cm}^{-1}$ intensity divided by the appropriate unit value. As in any spectroscopic measurement, the molecular weight must be known to carry out the analysis. Interference by olefins can be handled by selective bromination or hydrogenation. The intensity of styrene (which contains a conjugated double bond) in this region was found to be equivalent to 7 protons. After bromination (cf. Figure 4) the intensity was observed to be equivalent to 5 protons, demonstrating selective disappearance of an interfering group without disturbing the ring proton contribution.

Literature Cited

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- (2) Bomstein, J., Anal. Chem. 25 1770 (1953).
- (3) Fuson, H. and Josien, M. L., J. Am. Chem. Soc. 78 3049 (1946).
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Table I. Integrated Intensities ($\text{cm}^{-2} \text{ mole}^{-1}$) of Aromatic Hydrocarbons in the 1650-2000 cm^{-1} Region.

Compound	Proton #	Intensity	Compound	Proton #	Intensity
Hexamethylbenzene	0	140	tert-Butylbenzene	5	525
Hexethylbenzene	0	120	1-Phenylpentane	5	445
Pentamethylbenzene	1	180	1,1-Dimethylpropylbenzene	5	510
1,2,4,5-Tetramethylbenzene	2	350	n-Hexylbenzene	5	435
1,2,4,5-Tetraisopropylbenzene	2	310	n-Octylbenzene	5	530
2,5-Diisopropyl-p-Xylene	2	300	Cyclohexylbenzene	5	455
2-Bromomesitylene	2	260	1-Phenyldecane	5	450
1,2,3,4-Tetramethylbenzene	2	300	3-Phenyldecane	5	510
1,2,3,5-Tetramethylbenzene	2	300	Chlorobenzene	5	457
1,2,3-Trimethylbenzene	3	300	Pyridine	5	465
1,2,4-Trimethylbenzene	3	305	2,4,6-Trimethylnaphthalene	5	560
1,2,4-Trichlorobenzene	3	360	Benzene	6	610
2,5-Dibromotoluene	3	355	1,2-Dimethylnaphthalene	6	740
1,3,5-Trimethylbenzene	3	385	1,3-Dimethylnaphthalene	6	648
1,3,5-Trisopropylbenzene	3	385	1,4-Dimethylnaphthalene	6	710
3-tert-Butyl-m-Xylene	3	400	1,5-Dimethylnaphthalene	6	830
3-tert-Butyl-5-ethyltoluene	3	365	1,6-Dimethylnaphthalene	6	762
o-Ethyltoluene	4	409	2,3-Dimethylnaphthalene	6	725
o-Dimethylbenzene	4	399	2,6-Dimethylnaphthalene	6	687
o-Xylene	4	406	Quinoline	7	760
o-Dichlorobenzene	4	376	iso-Quinoline	7	800
m-Ethyltoluene	4	420	1-Methylnaphthalene	7	815
m-Diethylbenzene	4	401	2-Methylnaphthalene	7	795
m-Xylene	4	412	Naphthalene	8	1030
m-Diisopropylbenzene	4	345	9,10-Dimethylantracene	8	1130
m-Chlorotoluene	4	406	Retene	8	1000
m-Dichlorobenzene	4	439	20-Methylcholanthrene	9	1168
p-Ethyltoluene	4	425	2-Methylphenanthrene	9	1028
p-Diethylbenzene	4	415	2-Methylantracene	9	1280
p-Xylene	4	432	9-Methylantracene	9	1158
p-Cymene	4	452	Phenanthrene	10	1214
p-Diisopropylbenzene	4	478	Anthracene	10	1295
p-tert-Butyltoluene	4	427	Diphenylmethane	10	1100
o-Picoline	4	384	Biphenyl	10	1070
o-Picoline	4	424	Pyrene	10	1330
o-Picoline	4	428	Chrysene	12	1600
Toluene	5	478	3,4-Benzopyrene	12	1630
Ethylbenzene	5	525	1,2-Benzanthracene	12	1430
n-Propylbenzene	5	440	Perylene	12	1900
iso-Propylbenzene	5	495	Triphenylene	12	1420
n-Butylbenzene	5	415	m-Quaterphenyl	18	1845
iso-Butylbenzene	5	490	o-Quaterphenyl	18	1575
sec-Butylbenzene	5	520	m-Quinquephenyl	22	2080

Table II. Average Intensities by Ring Type of Aromatic Hydrocarbons in the 1650-2000 cm^{-1} region.

Compound Type (and Number)	No. of Ring Protons	Total Intensity	Intensity per Ring Proton	Average
Hexa-alkylbenzene (2)	0	130	---	
Penta-alkylbenzene (1)	1	180	180	
Tetra-alkylbenzene (6)	2	295	147	
Trialkylbenzene (8)	3	360	119	
Dialkylbenzene (19) ^a	4	415	104	104
Monoalkylbenzene (8)	5	485	97	(Mononuclear)
Dialkylnaphthalene (7)	6	725	121	
Dinuclear (4) ^a	7	790	113	118 (Dinuclear)
Polynuclear (3)	8	1055	132	
Polynuclear (4)	9	1160	129	
Polynuclear (3)	10	1290	129	
Polynuclear (5)	12	1610	134	131
Polyphenyls (4)	10-22	(Table I)	98	(Polynuclear)

^aIncluding some heterocyclics.

Table III. Intensities of Mononuclear Aromatics and Polyphenyls in the 1650-2000 cm^{-1} Region.

Number of Ring Protons	Total Intensity	Net Intensity ^a	Intensity per Ring Proton
1	180	50	50
2	295	165	83
3	300	230	77
4	415	285	71
5	485	355	71
6	610	480	80
10	1070	810	81
18	1710	1450	81
22	2080	1825	83

^aNet intensity equals total intensity minus a background or skeletal vibration value of $130 \text{ cm}^{-2} \text{ l mole}^{-1}$ for each pendent aromatic ring.

Table IV. Intensity Effects of Polar and Olefinic Substituents on the Aromatic Absorption in the 1650-2000 cm^{-1} Region.

Substituent	Ring Proton Equivalent
Electron Donating Group	+ 1.5 to 2 protons
Chlorine	Little Change
Nitro	+ 2 protons
Side chains conjugated double bond	+ 1.5 to 2 protons
Isolated olefinic double bond	+ 1.5 to 2 protons

Table V. Frequencies of Absorption Bands of Monosubstituted Benzenes in =CH Out-of-Plane Deformation and Summation Regions.

	<u>Average</u>	<u>Toluene</u>	<u>Chlorobenzene</u>
Fundamentals ^a			
f	751	728	740
g	837	844	830
i	908	895	902
h	962	966	965
j	982	982	985
Summation Bands			
o	1742	1731	1731
g+i	1745	1739	1732
o	1797	1797	1788
g+h	1819	1810	1795
o	1865	1853	1861.5
i+h	1870	1861	1867
o	1880	1869	1882
i+j	1890	1877	1887
o	1938	1937	1941.5
2h	1924	1932	1930
o	1955	1955	1962
2j	1964	1964	1970

^aFundamentals from Reference 4.

o = Observed frequencies in carbon tetrachloride solution, 0.5 molar.

Captions for Figures

- Figure 1. Spectra of aromatic hydrocarbons in 1650-2000 cm^{-1} region at 0.5 molar concentration in carbon tetrachloride, 0.5 mm. path length, compensated with solvent in reference beam.
- Figure 2. Integrated intensities ($\text{cm}^{-2} \ell \text{mole}^{-1}$) of aromatic hydrocarbons in the 1650-2000 cm^{-1} region as a function of ring proton concentration.
- Figure 3. Integrated intensities ($\text{cm}^{-2} \ell \text{mole}^{-1}$) of mono and polynuclear aromatic hydrocarbons in 1650-2000 cm^{-1} region as a function of ring proton concentration.
- Polynuclear
 - x Dinuclear
 - Mononuclear and Polyphenyls
- Figure 4. Spectra of styrene — and brominated derivative --- in 1650-2000 cm^{-1} region at 10% v/v in carbon tetrachloride, 1 mm. path length.
- Figure 5. Spectra of tert. butylbenzene in 1650-2000 cm^{-1} region.
- undiluted, 0.1 mm. path, run at 9 cm^{-1} resolution
 - ⋯ (offset) undiluted, 0.1 mm. path, run at 1.5 cm^{-1} resolution
 - 10% v/v in carbon tetrachloride, compensated, 1 mm. path, run at 1.5 cm^{-1} resolution.

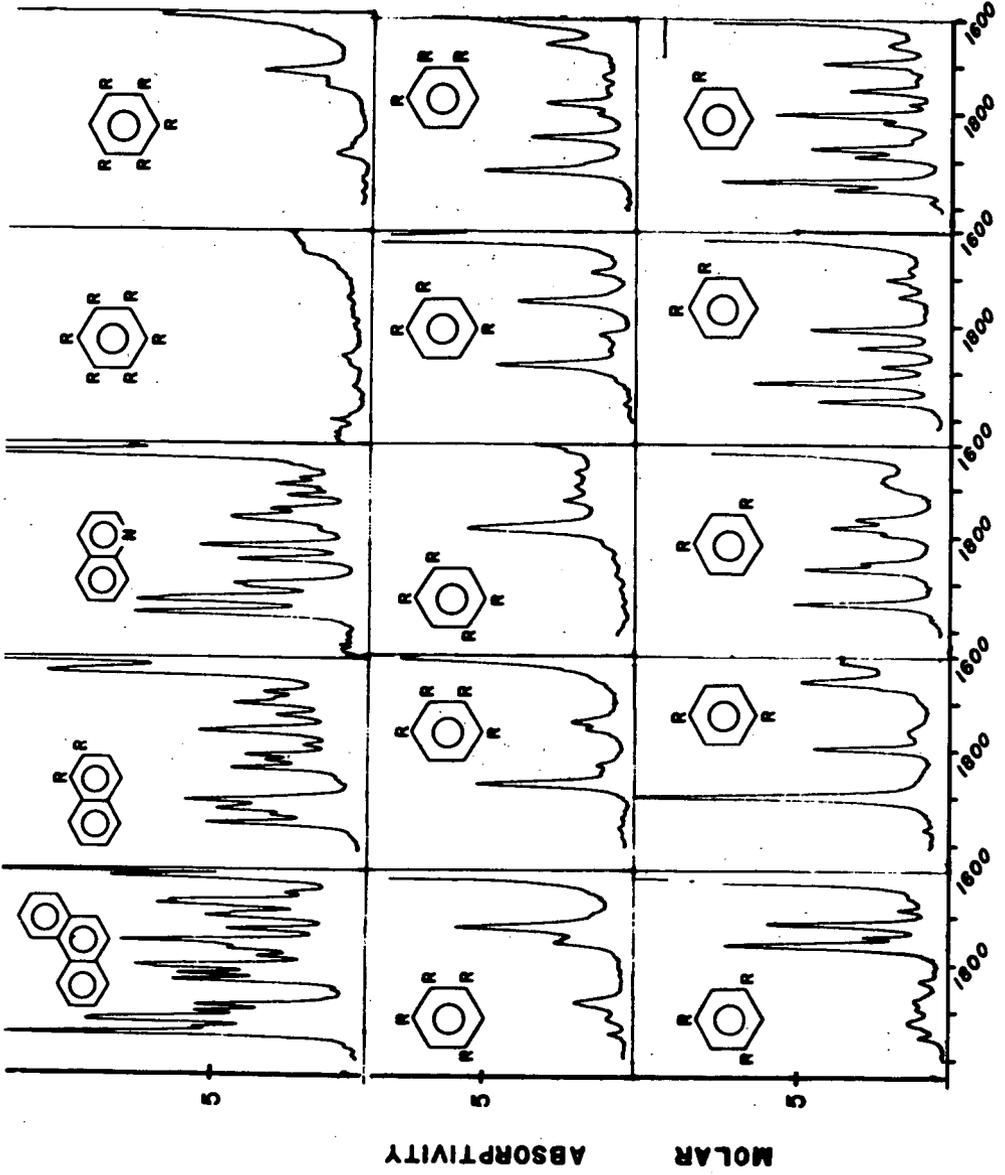


Figure 1.

