**72.   *Infra-red Spectra in the 3μ Region of Naphthalene, α- and β-Methylnaphthalenes, Quinoline, and isoQuinoline : An Aid to Analysis.***

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Absorption spectra of naphthalene, quinoline, *iso*quinoline, and α- and β-methylnaphthalenes, in carbon tetrachloride solution, have been examined in the region 2·6—3·8μ, with sufficient resolution to give all details of the bands.   The first three compounds have a region of absorption, with somewhat complex structure, at about 3·27μ, arising from CH groups, and the remaining two compounds have in addition, at longer wave-lengths up to 3·5μ, a set of bands attributable to the CH_3 group.   The spectra of quinoline and *iso*quinoline differ sufficiently to be used as a means of identification and estimation.   Quinoline and α-methylnaphthalene have spectra which in some ways resemble those of simple benzene derivatives in the 3·27μ region, while *iso*quinoline and β-methylnaphthalene are more like naphthalene.   It is pointed out that the m. p.'s of these β-substituted compounds, although lower than that of naphthalene, are considerably higher than those of the α-substituted compounds, and this appears to be general.
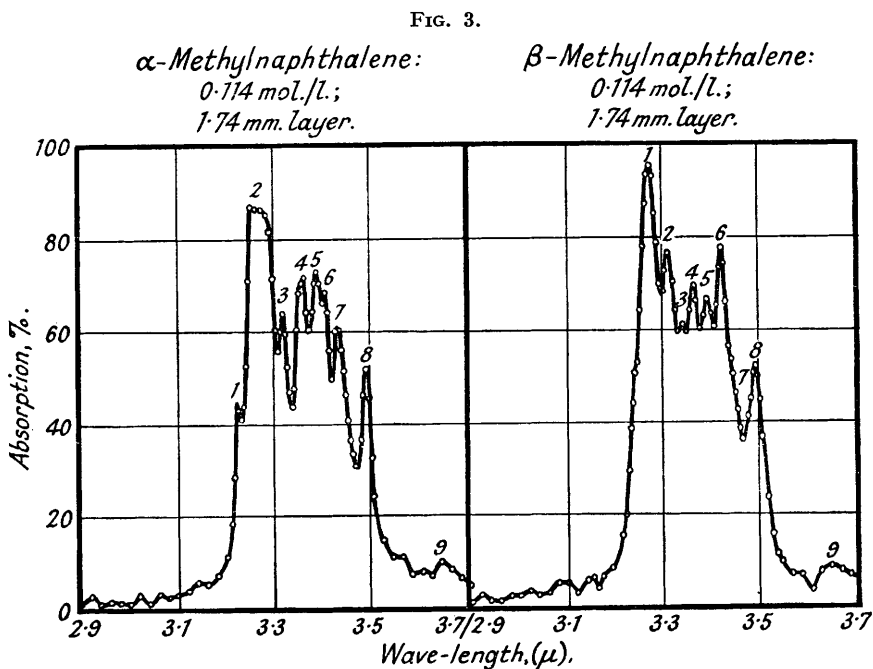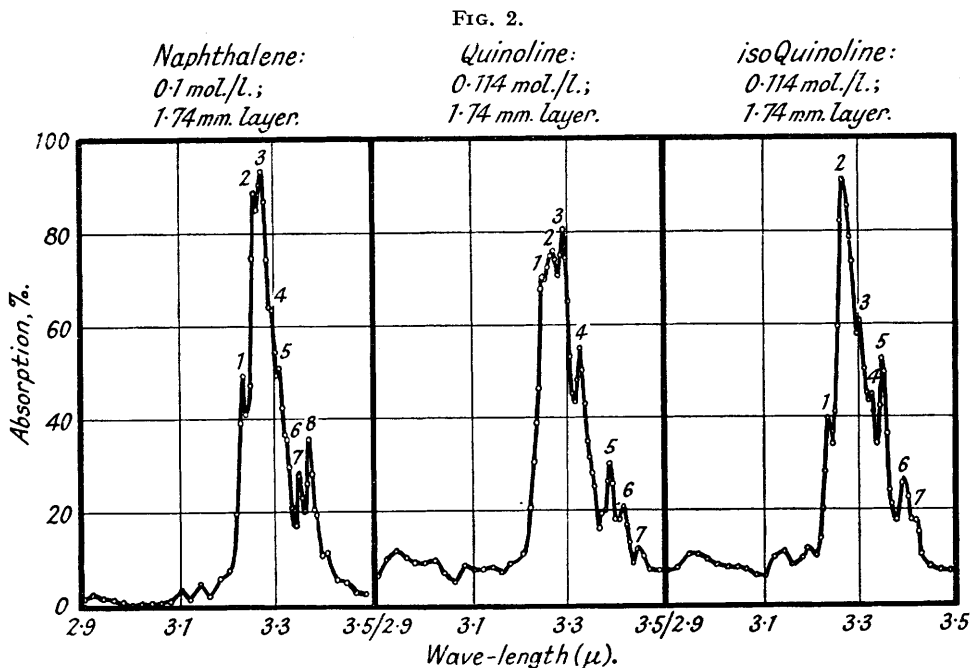
IT is not well known that infra-red absorption spectra may be employed as a practical method for the identification and frequently for the determination of certain substances,

FIG. 1.
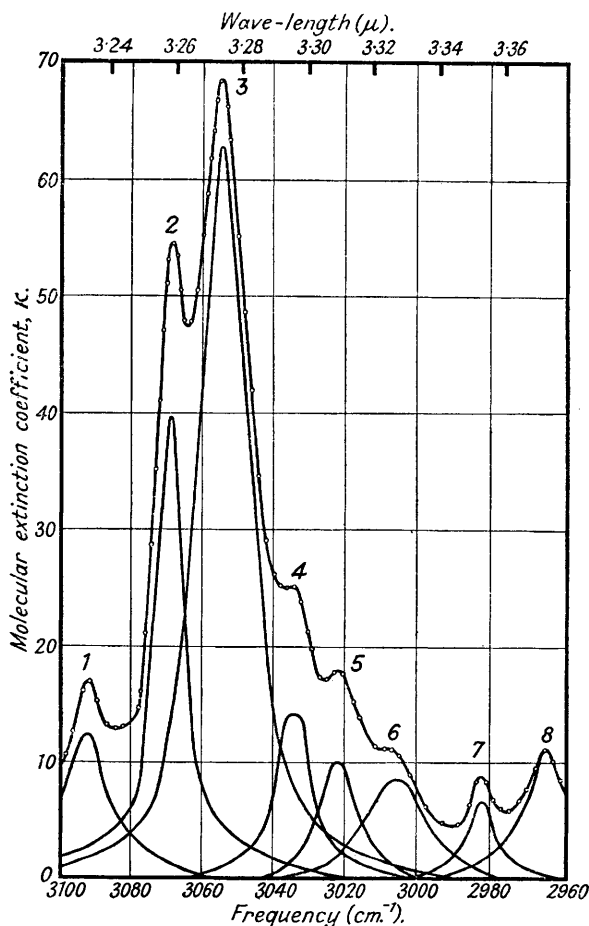
Graphical separation of the absorption bands of naphthalene in carbon tetrachloride (cf. Fig. 2).

alone or in admixture, provided that instruments of sufficient resolving power are available. The ordinary rock-salt prism apparatus is not generally suitable for the purpose.

FIG. 2.

Naphthalene: 0·1 mol./l.; 1·74 mm. layer.

Quinoline: 0·114 mol./l.; 1·74 mm. layer.

isoQuinoline: 0·114 mol./l.; 1·74 mm. layer.

FIG. 3.

α-Methylnaphthalene: 0·114 mol./l.; 1·74 mm. layer.

β-Methylnaphthalene: 0·114 mol./l.; 1·74 mm. layer.

The present communication deals, amongst other matters, with a method for determining the proportion of *iso*quinoline present in quinoline, an impurity which may be found in small proportion in quinoline prepared from coal tar. Essentially, the method depends upon the fact that with infra-red spectrometers of adequate resolving power the funda-

TABLE I.

Infra-red Frequencies in the Region of 3000 cm.⁻¹.

Naphthalene				Quinoline				isoQuinoline				α-Methylnaphthalene				β-Methylnaphthalene			
freq	No.	κ	f	freq	No.	κ	f	freq	No.	κ	f	freq	No.	κ	f	freq	No.	κ	f
3092	1	12·4	17·1					3091	1	6·7	11·9	3099	1	8·1	11·1				
				3078	1	18·8	19·5												
3068	2	39·7	10·9																
								3060	2	53·1	26·6	3055	2	43·3	~50	3053	1	68·2	26·8
3053	3	63	17·7	3058	2	20·3	25·3												
3034	4	14·1	11·4	3038	3	28·6	19·9	3027	3	13·6	16·8								
3022	5	10·0	13·9													3018	2	22·6	22·1
3005	6	8·5	20·0	3003	4	13·2	18·5	3007	4	9·1	18·6	3009	3	11·0	20·8				
2982	7	6·7	9·1					2986	5	15·8	16·1					2990	3	15·3	24·0
												2974	4	25·0	23·4	2970	4	23·6	19·7
2965	8	11·0	14·1	2953	5	7·5	18·5	2948	6	6·7	19·4	2948	5	22·6	21·5	2948	5	17·3	20·3
												2931	6	17·1	18·0	2921	6	31·9	24·3
				2927	6	5·0	22·0	2928	7	3·9	23·4	2908	7	18·3	19·2				
				2899	7	2·9	14·9					~2890		(weak)		2896	7	6·8	25·6
												2862	8	16·0	19·2	2862	8	16·1	31·7
												~2740	9	(weak)		~2740	9	(weak)	

Raman frequencies in the region of 3000 cm.⁻¹ (intensities in parenthesis).

3001 (1)	3011 (1)			
3025 (0)		3020 (3)		
3054 (12)	3062 (3)	3058 (3)	3062 (0)	3057 (0)

CH₃ frequencies are underlined. The frequencies ~2740 cm.⁻¹ for α- and β-methylnaphthalene often appear for compounds with methyl groups; the bands are weak, however, and cannot be fundamentals. Frequency ~2920 of the CH₃ appears split (2931, 2908) in the α-compound.

Under each infra-red frequency in Table I are figures which refer respectively to the number of the band in the figure, the molecular extinction coefficient at the maximum of the band (see Fig. 1), and the band width, f (in cm.⁻¹), at half extinction. The integrated area of a band is approximately $1·4 f\kappa_{max}$. (*loc. cit.*, 1938).

Naphthalene, *iso*quinoline, and β-methylnaphthalene have for their region of maximum absorption a sharp peak (split in the case of naphthalene) with centre about 3057 cm.⁻¹. Quinoline has a triple-headed band in the same region, somewhat like the triple band characteristic of simple benzene derivatives. The centre of the band is about 3058 cm.⁻¹ (3·27μ), and this frequency is close to the centre of the group of bands of benzene. α-Methylnaphthalene has a broad band with centre 3055 cm.⁻¹; its width is comparable with that of the benzene group.

The Raman frequencies are due to the following authors :

Naphthalene (cryst.). Ananthakrishnan, *Proc. Indian Acad. Sci.*, 1937, **5**, A, 200. Other workers give only one line (for solid, liquid, and solutions); mean value for liquid is 3061, Gockel, *Z. physikal. Chem.*, 1935, B, **29**, 79.

Quinoline and isoquinoline. Bonino and Manzoni-Ansidei, *Mem. Accad. sci. Inst. Bologna, Classe sci. fis.*, 1934, **9**, 3. Other workers give only one line for the quinolines : 3054 for quinoline, Bonino and Cella, *Atti R. Accad. Lincei*, 1932, **15**, 385; 3056 (5) for quinoline and 3047 (8) for *iso*quinoline, Jatkar, *Indian J. Physics*, 1936, **10**, 23.

α- and β-Methylnaphthalene. Gockel (*loc. cit.*). Earlier values by Ziemecki, *Z. Physik*, 1932, **78**, 123, 3059 (4) for both substances.

The Raman data are rather discordant, but broadly, the most important line in the region 2700—3100 cm.⁻¹ corresponds, within a few cm.⁻¹, to the main infra-red absorption band (~3060 cm.⁻¹) for the five compounds examined. Similarly, the weaker Raman lines are quite close to infra-red frequencies.

mental C–H vibrations in the 3μ region of the spectrum may exhibit considerable changes in character and shape on passing from one compound to another.

A study of C–H vibrations in organic molecules has been reported in some detail in the special case of CH_2 groups in varied types of molecule (*Proc. Roy. Soc.*, 1938, *A*, **167**, 257). It has been shown (*ibid.*, 1937, *A*, **162**, 419) that, generally, in solution in carbon tetrachloride, compounds containing a phenyl group are characterised by three bands at about 3·27μ, well separated from the aliphatic CH bands which are found at longer wavelengths extending to 3·5μ. In the present work we desired to see in what way the spectra of polycyclic compounds differed from the simple benzene derivatives. Five compounds are here reported : naphthalene, α- and β-methylnaphthalene, quinoline, and *iso*quinoline.

EXPERIMENTAL.

The grating apparatus and technique have already been described (*loc. cit.*). A wavelength range from 2·6 to 3·8μ was covered, and where a part of this region is omitted in the absorption curves it may be taken that the absorption under our conditions of measurement is negligible. The substances were all examined in carbon tetrachloride solution at a concentration of approximately 0·1M, with a cell length of 1·74 mm., and temperature of 18—20°. Positions of the maxima of the sharper bands could be determined accurately to 1 cm.$^{-1}$, and the method of graphical separation of bands and intensity estimation already described (*loc. cit.*, 1938) was employed. Fig. 1 illustrates this and gives some idea of the precision obtainable.

The methylnaphthalenes were purified and checked by their picrates (α-picrate, m. p. 141·5°; β-picrate, m. p. 117·5°; Heilbron gives 141—142° and 115—116° respectively). Synthetic quinoline was used in preference to the coal-tar product as a standard since it was found that, in addition to *iso*quinoline, the latter was liable to contain methylnaphthalenes.

Figs. 2 and 3 show the results obtained. All the compounds have an intense absorption band in the region of 3·27μ, as have benzene derivatives; but the structure of the band is more complex for the polycyclic compounds of Fig. 2, and several bands appear in the region 3·3—3·5μ which normally contains aliphatic C–H frequencies. A general examination of the curves indicates that the 3·27μ band has roughly the same shape for naphthalene, *iso*quinoline, and β-methylnaphthalene on the one hand, and for α-methylnaphthalene and quinoline on the other. Table I emphasises this and gives full details of the bands. A significant point is that for α-methylnaphthalene and quinoline the band is wider and more like the bands obtained with benzene derivatives. The implication is that substituents in the α-position disturb the typical naphthalene vibrations more than do substituents in the β-position, and that in some ways the former compounds are akin to a benzene ring with a side chain. Consideration of the m. p.'s of many α- and β-substituted compounds strengthens this view, and by reference to Table II it will be seen that the m. p. of the β- is higher than that of the α-compound. This table can

TABLE II.

Naphthalene, m. p. 80·3°.

Substituted in α-position.	Substituted in β-position.
Quinoline, m. p. ∼ − 20°	*iso*Quinoline, m. p. 24·6°
α-Methylnaphthalene, m. p. − 22°	β-Methylnaphthalene, m. p. 37—38°
α-Chloronaphthalene (liquid at room temp.)	β-Chloronaphthalene, m. p. 61°
α-Naphthylamine, m. p. 50°	β-Naphthylamine, m. p. 113°

be considerably extended from recorded data, and it may be noted also that the observation regarding m. p.'s extends to derivatives of anthracene (m. p. 217°) to an even greater degree; thus 1-methylanthracene has m. p. 85—86° and the 2-methylanthracene has m. p. 207° (9-methylanthracene has m. p. 81·5°). In the case of the methylnaphthalenes, the β-compound is a solid at ordinary temperature, not unlike naphthalene in appearance and smell, but melting at a lower temperature; the α-compound is a liquid at the ordinary temperature. Similarly *iso*quinoline more closely resembles naphthalene in general physical properties (including infrared absorption) than does quinoline. The characteristic smell of quinoline is absent in *iso*quinoline, which has a modified naphthalene odour.

Determination of iso*Quinoline in Quinoline or vice versa.*—For this purpose, a wave-length is chosen where the spectra of the two compounds differ as much as possible. Convenient wave-lengths are those corresponding to the maxima of bands 2 and 3 in quinoline (Fig. 2). Admixture of *iso*quinoline has the effect of increasing band 2 and reducing band 3, and a simple calculation enables the proportion of *iso*quinoline to be determined, it being assumed, of course,

that no other substances are present with absorption in this region. The apparatus should be calibrated by means of solutions of known concentration; differences of 1% in the content of *iso*quinoline should be detectable.

The optical density of a solution is defined as $d = \log_{10} I_0/I$, where I_0 is the intensity of the light passing through a cell containing solvent alone at a given wave-length, and I is the light transmitted through the solution; d is proportional to the amount of absorbing material in the light path, *i.e.*, proportional to the concentration provided that the cell length is kept constant. The molecular extinction coefficient κ is obtained from d by the relation $\kappa = d/cl$, where c is the concentration of the solution in mol./l. and l is the cell length in cm. To determine the constituents of the binary mixture, advantage is taken of the variation of the optical density at a chosen wave-length, and of the fact that the optical density is additive in the conditions of the experiment. If the wave-lengths corresponding to the maxima of bands 2 and 3 of quinoline are λ_1 and λ_2, the measurements under the conditions of Fig. 2 can be summarised as follows :

	Absorption at λ_1.	Absorption at λ_2.
Quinoline	76·3% ($d = 0·625$)	81·0% ($d = 0·721$)
*iso*Quinoline	90·5% ($d = 1·022$)	63·2% ($d = 0·434$)
$\begin{cases} (1-x) \text{ Quinoline and} \\ x \text{ } iso\text{quinoline} \end{cases}$	$d = 0·625 + 0·397x$	$d = 0·721 - 0·287x$

CH_3 *Bands.*—In another connexion we have examined a variety of hydrocarbons containing methyl groups, and we can state that, in general, four bands between 3·33 and 3·50μ are attributable to methyl groups, and moreover, the four frequencies vary but little from one compound to another. With α- and β-methylnaphthalene the methyl bands are mixed up with small bands in the same region of the spectrum, similar to those which appear in naphthalene and the quinolines. A fairly satisfactory separation of the bands can be made, and details are given in Table I.