The Characteristic Infrared Absorption of the Methyl Rocking Vibrations of Aromatic Methyl Groups.

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Evidence is presented that the CH_3 rocking modes of isolated aromatic methyl groups absorb near 1042 cm.$^{-1}$ and that the vibration is probably degenerate. For two adjacent methyl groups frequencies near 990 and 1021 cm.$^{-1}$ are suggested, and the more highly methylated compounds are considered.

SOME of the more troublesome frequencies to assign in many molecules are the CH_3 rocking frequencies which are external group vibrations in Sheppard and Simpson's sense (*Quart. Rev.*, 1953, **7**, 19) and are therefore liable to vary with the nature of the residue to which the methyl group is attached. The range 950—1150 cm.$^{-1}$ covers the majority of assignments (Torkington, *J. Chem. Phys.*, 1950, **18**, 768; Brown and Sheppard, *Trans. Faraday Soc.*, 1954, **50**, 1164, etc.), and a characteristic methyl frequency near 967 cm.$^{-1}$, when the group is attached to a *cyclo*hexane or to a sugar ring, has been assigned to this mode (Barker, Bourne, Stephens, and Whiffen, *J.*, 1954, 4211).

In toluene derivatives in which the methyl group is attached to a more rigid skeleton than in aliphatic compounds, there is a greater probability that the group frequency will be more constant. Pitzer and Scott (*J. Amer. Chem. Soc.*, 1943, **65**, 803) have tentatively assigned frequencies in the range 1000—1200 cm.$^{-1}$ to the rocking vibrations, but admit that the evidence for the detailed assignments is weak. The frequencies to be expected for benzene derivatives in general have recently been discussed (Randle and Whiffen, " Molecular Spectroscopy," Report on the conference held in London in October 1954 by the Institute of Petroleum) and relevant spectra have been examined to see what extra infrared absorption appears when methyl groups are present.

In compounds with a methyl group and no substituent in either of the adjacent *ortho*-positions in the ring, a band of moderate intensity appears near 1042 cm.$^{-1}$ and some examples are given in Table 1. *meta*-Disubstituted benzenes are excluded as these have a

TABLE 1. *Isolated methyl groups: Table of frequency of absorption (in cm.$^{-1}$), maximum extinction coefficient (in cm.^{2} molecule^{-1} log$_e$), and band width at half height (in cm.$^{-1}$).*

	ν (cm.$^{-1}$) *	$10^{20}E_{max.}$	$\Delta\nu_{1/2}$		ν (cm.$^{-1}$) *	$10^{20}E_{max.}$	$\Delta\nu_{1/2}$
Toluene	1041	4·0	22	*p*-Chlorotoluene...	1042	6·1	16
p-Xylene	1042	7·4	18	*p*-Bromotoluene...	1041	5·8	*ca.* 17
Mesitylene *a*	1037 †	—	—	*p*-Iodotoluene ...	1040	5·5	*ca.* 17
p-Fluorotoluene ...	1042	4·0	18				

* In CS$_2$ solution, except † which is for liquid.
a A.P.I. project No. 44, " Catalogue of Infrared Spectra."

ring C–H deformation expected near 1045 cm.$^{-1}$ (Randle and Whiffen, *loc. cit.*) which masks the methyl absorption.

There is no evidence to show whether this is the in-plane or the out-of-plane methyl rocking; indeed, it is by no means certain that the six-fold potential-energy barrier opposing internal rotation of the methyl group relative to the phenyl ring is large enough to remove the degeneracy which is present in such compounds as methyl chloride in which the attached group is cylindrically symmetrical. Pitzer (*Discuss. Faraday Soc.*, 1951, **10**, 66) quotes 500 ± 500 cal. as the best value for toluene, though this may well be many times too high in view of the observed value of only 6 cal. for nitromethane (Tannenbaum, Johnson, Myers, and Gwinn, *J. Chem. Phys.*, 1954, **22**, 949) which has a similar six-fold barrier. A search failed to reveal any possibilities for a second methyl rocking frequency although it is difficult to be satisfied of its absence since in most of the spectra the range 900—1150 cm.$^{-1}$ contains many absorption bands. In mesitylene (1 : 3 : 5-trimethylbenzene), whose symmetry reduces the number of absorption bands considerably, there is no unassigned absorption band of comparable intensity to that at 1037 cm.$^{-1}$, although it might be expected that one in-plane (degenerate) and one out-of-plane rocking mode should be active in the infrared and that the dipole-moment gradients, which govern the intensity, should be similar. Some of the compounds of Table 1 have been measured in carbon disulphide solution and their peak intensities and band widths are given. They are only approximate, as overlapping by neighbouring bands is serious in some cases. The band widths are exceptionally large and must be compared with the many neighbouring bands for these same solutions which are seldom over 10 cm.$^{-1}$ wide at half intensity. This is perhaps further evidence that the degeneracy is not quite lifted by the phenyl group.

ortho-Substituents are likely to raise the potential barrier (Pitzer, *loc. cit.*, quotes 2000 cal. for *o*-xylene), and if the substituent is a second methyl group symmetric and anti-symmetric rocking vibrations will arise. Table 2 gives some further compounds and

TABLE 2. *Adjacent methyl groups.*

Two adjacent Me groups	Frequency (cm.$^{-1}$)
o-Xylene *a*	985, 1022, 1053
1 : 2 : 4-Trimethylbenzene *a*	999, 1021, 1038
1 : 2 : 4 : 5-Tetramethylbenzene *a*	1000, 1022

More than two adjacent Me groups	
1 : 2 : 3-Trimethylbenzene *a*	988, 1010
1 : 2 : 3 : 4-Tetramethylbenzene *a*	1005, 1040, 1065
1 : 2 : 3 : 5-Tetramethylbenzene *a*	990, 1010, 1035, 1076
Pentamethylbenzene *b*	997, 1011, 1031, 1072
Hexamethylbenzene *b*	989, 1063

a A.P.I. project No. 44, " Catalogue of Infrared Spectra." *b* In CS$_2$ (Whiffen, Thesis, Oxford, 1946).

their absorption frequencies in this region although some of these may be due to in-plane ring C–H deformations. Although it is unwise to generalize on three cases, there is evidence for absorption near 995 and 1022 cm.$^{-1}$ for *ortho*-dimethyl compounds without further substituents adjacent to the methyl groups.

Hexamethylbenzene has three strong infrared bands between 500 and 1300 cm.$^{-1}$,

viz., at 1063, 988, and 793 cm.$^{-1}$, which can reasonably be attributed to the in-plane and the out-of-plane methyl rocking and the E_{1u} C–CH$_3$ stretching. An approximate calculation, treating the methyl group as a point mass of 15 with a C–CH$_3$ stretching constant of 4·5 × 10^5 dynes/cm. (Herzberg, " Infra-red and Raman Spectra," van Nostrand, 1945, p. 193) and with other constants transferred from benzene, led to E_{1u} frequencies of 1490 cm.$^{-1}$ (ring C–C stretching), 850 cm.$^{-1}$ (C–CH$_3$ stretching), and less than 350 cm.$^{-1}$ (C–CH$_3$ deformation). It seems reasonable to suppose that the observed band at 793 cm.$^{-1}$ is the C–CH$_3$ stretching, that at 988 cm.$^{-1}$ the out-of-plane methyl rocking, and that at 1063 cm.$^{-1}$ is the in-plane methyl rocking, which is taken to be the higher since it will involve greater van der Waals repulsion. The arguments of this paragraph are fully supported by the assignment by Mann and Thompson (*Proc. Roy. Soc.*, 1952, *A*, **211**, 168), who used oriented crystals of hexamethylbenzene and polarised radiation.

Experimental.—The carbon disulphide solutions were measured on a Grubb-Parsons single-beam spectrometer with slits of 0·12 mm., cell length 1·1 mm., and concentrations of 2% v/v or less.

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