Vibrational Spectra of Some Substituted Benzene Derivatives

V. N. Verma[ab]

[a] Department of Physics, Banaras Hindu University, Varanasi, India [b] Department of Chemistry, The University of Southampton, United Kingdom

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V.N.Verma*
Department of Physics
Banaras Hindu University
Varanasi-221005
India

ABSTRACT

The infrared spectra of 1,2,3-; 1,2,4- and 1,3,5-trimethylbenzenes have been recorded in the liquid phase in the region 250-4000 cm^{-1} on a Perkin Elmer Grating Spectrophotometer model 521. Under the general symmetry considerations, the molecule 1,2,4- belongs to C_{2v} point group, the 1,2,3-isomer belongs to Cs and the 1,3,5-isomer to D_{3h} point group. The observed bands have been assigned to different modes of vibrations.

INTRODUCTION

The vibrational spectra of methylbenzene and dimethyl-

benzenes have been analysed and reported by many workers (1-9). The

work on trisubstituted benzenes where substituents are the same are

limited. The vibrational spectra of 1,3,5-trichlorobenzene have been

reported by Daviev et al.(10) and of 1,2,4-trichlorobenzene by Deb

and Banerjee (11). Similarly the vibrational analyses of sym-trifluoro-

benzene and sym-trichlorobenzene have been presented by several

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* Present Address: Department of Chemistry, The University of Southampton, United Kingdom.

workers (12—16). The spectra of trimethylbenzenes have however been studied to a very limited extent. Bentley and Walforth (17) have recorded the infrared spectra of several alkylbenzenes but no analysis was proposed. Theoretical estimates of several fundamental frequencies of 1,3,5- trimethylbenzene and 1,2,4- trimethylbenzene have been made by Nonnenmacher and Mecke (18) and by Bogomolov (19). Banerjee and Medhi (20) have observed the effects of changes due to phase on the spectra of 1,2,4- and 1,3,5- isomers in the region 600-3100 cm^{-1}. Raman spectra of these isomers are available from the earlier work of Venktashwaran (21) and Kohlrausch and Pongratz (22). In this article a complete vibrational analysis of 1,2,3-; 1,2,4- and 1,3,5- trimethyl-benzenes spectra has been presented.

EXPERIMENTAL

The liquid samples of these isomers were obtained from Koch-Light Laboratories, U.K. and were further purified by redist-illation under reduced pressure before use. The infrared spectra have been recorded in the liquid phase in the range 250-4000 cm^{-1} on a Perkin Elmer Grating Spectrophotometer Model 521. The spectra are reproduced in Figs. 1,2 and 3.

RESULTS AND DISCUSSION

Under the usual approximations to methyl group, the 1,2,3- isomer may be classified under C_{2v} point group and the 1,2,4- isomer under C_s point group while the symmetrically substituted 1,3,5- isomer would belong to D_{3h} point group. The choice of axes are in the confirmity with the choice of axes of the Joint Commission for Spectroscopy. The 30 benzene like modes can therefore be classified into different symmetry species as follows:

C_s Point group   : $21a' + 9a''$

C_{2v} Point group   : $11a_1 + 10b_2 + 3a_2 + 6b_1$

D_{3h} Point group   : $4a_1' + 3a_2' + 7e' + 3a_2'' + 3e''$

INFRARED ABSORPTION SPECTRUM OF 1,2,4—TRIMETHYLBENZENE IN LIQUID PHASE.

Fig. 1

INFRARED ABSORPTION SPECTRUM OF 1,2,3—TRIMETHYLBENZENE IN LIQUID PHASE

Fig. 2

INFRARED ABSORPTION SPECTRUM OF 1,3,5—TRIMETHYLBENZENE IN LIQUID PHASE
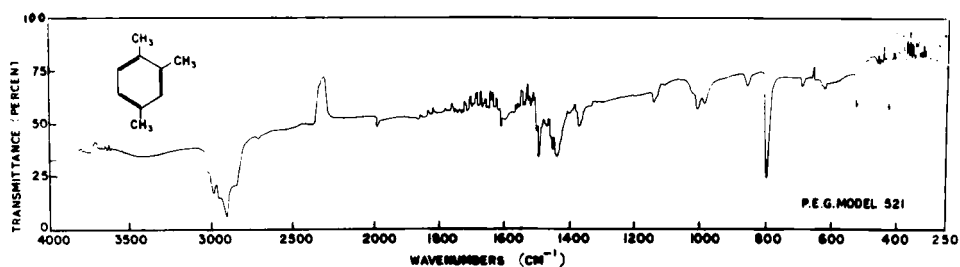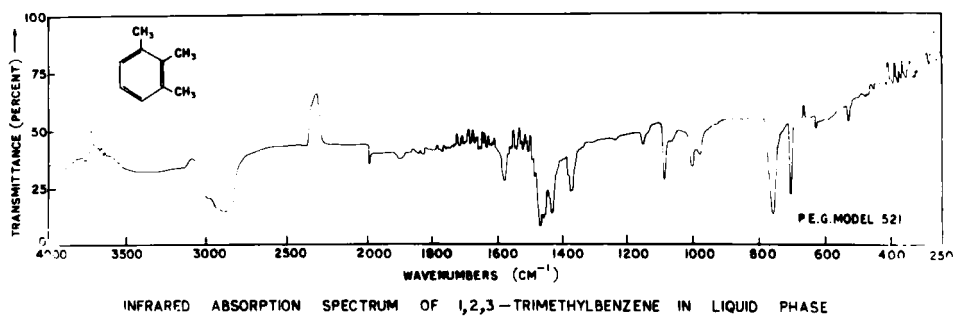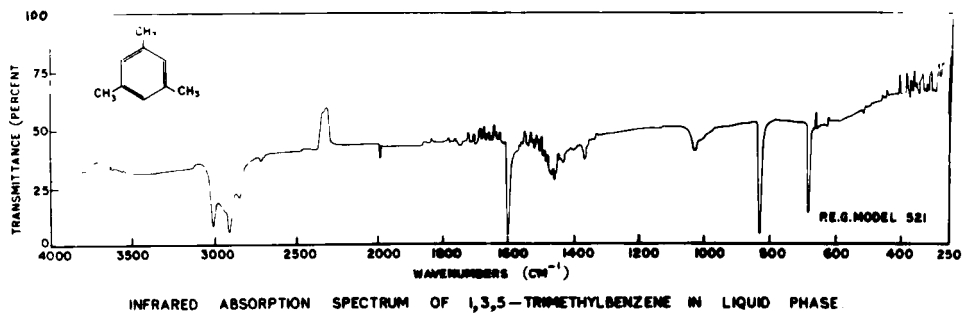
Fig. 3

351

In C_s point group all the fundamental vibrations are allowed in Raman as well as in the infrared spectra. For the C_{2v} point group the vibrations for a_2 species will be inactive in the infrared but active in the Raman and the vibrations of a_1, b_1, and b_2 species are active in both spectra. In the case of D_{3h} symmetry, fundamentals of species a_2'' and e'' are infrared active and a_1', e' and e'' are Raman active while the fundamentals belonging to a_2' type would not appear in any of these spectra. In the Raman spectrum the a_1' vibrations will give rise to polarised lines while the e' and e'' vibrations will result in unpolarised lines. In addition to these 30 benzene-like vibrations several additional vibrations due to the different CH_3 groups would also appear in the spectrum. The observed vibrational frequencies and their proposed assignments to different modes of vibrations are given in Tables I,II and III.

It has been established (26) that as the number of methyl group attached to the benzene ring increases the infrared spectrum gradually loses its aromatic character and in extreme cases the vibrations of the methyl groups dominate in the infrared spectrum.

The magnitudes of the C-C stretching vibrations corresponding to the e_{2g}(1595) and e_{1u}(1485) vibrations of benzene are affected by the addition of substituents in the ring. But as the symmetry of the molecule is lowered from D_{6h}, both vibrations split into two components, one having an appreciably lower frequency and the other a slightly higher frequency than the parent frequency. The e_{1u} (1485 cm^{-1}) mode of benzene is commonly called a skeletal mode or ring stretching, but is in reality the result of a coupling between C-H deformation and C-C stretching mode. As the number of substitutions is increased the contribution of the C-H mode of this vibration becomes less pronounced and it becomes a nearly pure ring stretching vibration. The frequencies observed at 1612,1567, 1498 and 1462 cm^{-1} in 1,2,4-TMB (trimethylbenzene), at 1608, 1579, 1503 and 1450 cm^{-1} in 1,2,3-TMB and at 1601, 1572, 1508 and 1488 cm^{-1} in 1,3,5-TMB have been assigned to the C-C stretching modes arising from these two benzene modes(The degenerate vibrations of benzene would not split into two components in this molecule of D_{3h} symmetry. The assumption of D_{3h} symmetry for 1,3,5-

TABLE I

Vibrational Frequencies and their Assignments for
1,2,4-Trimethylbenzene

Raman Frequencies(cm^{-1}) Ref.(22)	Infrared Frequencies(cm^{-1})	Assignments
210(4b)		C-CH$_3$ o.p.bending
285(2)		C-CH$_3$ o.p.bending
	298(3)	C-CH$_3$ i.p.bending
321(6)	329(3)	C-CH$_3$ i.p.bemding
	354(3)	
	363(3)	
	372(3)	
	380(3)	
	392(3)	
	410(3)	
432(2)	430(6)	C-C-C o.p.bending
471(3)	466(1)	C-C-C O.p.bending
	528(4)	C-C-C o.p.bending
557(8)		C-C stretching (ring breathing)
	624(2)	C-H o.p.bending
715(5)	696(2)	C-H o.p.bending
744(8)		CH$_3$ wagging
807(1b)	804(10)	CH$_3$ wagging
	860(2)	C-H o.p.bending
928(3)		CH$_3$ rocking
	990(3)	CH$_3$ rocking
	1012(4)	CH$_3$ rocking
1125(2)	1116(sh)	C-H i.p.bending
1150(1)	1148(3)	C-CH$_3$ sym.stretching
1205($\frac{1}{2}$)		C-CH$_3$ asym.stretching
1239(10)		C-CH$_3$ asym.stretching

TABLE I   (continued)

1377(10)	1378(6)	C-H sym.def.in CH_3group
	1404(3)	528+860
1444(5b)	1444(7)	C-H asym.def.in CH_3group
	1456(6)	C-H asym.def.in CH_3group
	1462(sh)	C-C stretching
	1473(4)	C-H asym.def. in CH_3group
	1498(7)	C-C stretching
	1521(2)	990+1148-624
	1560(2)	990+1012-430
1571(4)	1567(2)	C-C stretching
1615(7)	1612(4)	C-C stretching
	1634(2)	1473+1148-990
	1650(2)	2x329+990
	1682(2)	2x528+2x624
	1717(2)	466+624
	1728(2)	286+1444
	1736(2)	329+1404
	1744(2)	286+1456
	1827(2)	329+1493
2731(1)	2716(1)	2(C-H sym.def.in CH_3)
2857(3)	2840(sh)	C-H sym.stretching in CH_3
2912(6b)	2908(9)	C-H sym.stretching in CH_3
	2946(sh)	C-H asym.stretching in CH_3
	2983(7)	C-H asym.stretching in CH_3
3038(3)	3028(sh,b)	C-H stretching(aromatic)

N.B. : The intensity is given in the parenthesis.

i.p.=in-plane; o.p.=out-of-plane; def.=deformation; sym.=
symmetrical; asym.=asymmetrical; sh=shoulder and b=broad.

TABLE II

Vibrational Frequencies and their Assignments for

1,2,3-Trimethylbenzene

Raman Frequencies(cm^{-1}) Ref.(22)	Infrared Frequencies(cm^{-1})	Assignments
228		$C-CH_3$ o.p.bending
269	264(3)	$C-CH_3$ o.p.bending
	286(3)	$C-CH_3$ i.p.bending
	313(4)	$C-CH_3$ i.p.bending
	370(3)	
	391(3)	
	443(1)	C-C-C o.p.ring def.
	469(1)	C-C-C o.p. ring def.
484	492(1)	C-C-C o.p.ring def.
509		
536	521(1)	C-C-C o.p. ring def.
654	648(1b)	C-C stretching (ring breathing)
	700(9)	C-H o.p.bending
744	753(10)	CH_3 wagging
810		CH_3 wagging
888		C-H o.p.bending
	976(4)	CH_3 rocking
990	997(6)	CH_3 rocking
1090	1084(7)	C-H i.p.bending
1163	1153(3)	$C-CH_3$ sym.stretching
1240	1236(1b)	$C-CH_3$ asym.stretching
1317		
	1368(8b)	C-H sym.def.in CH_3
	1432(9)	C-H asym.def.in CH_3
	1450(sh)	C-C stretching

TABLE II (continued)

	1455(9)	C-H asym. def.in CH_3
1468	1466(10)	C-H asym. def.in CH_3
	1503(4)	C-C stretching
	1537(4)	443+1084
1589	1579(7)	C-C stretching
	1608(2)	C-C stretching
	1630(2)	264+1368
	1642(2)	648+997
	1649(2)	286+1368
	1668(2)	700+976
	1681(2)	443+1236
	1701(2)	264+1432
	1716(2)	264+1455
	1764(2)	286+1466
	1824(2)	313+2×753
	1837(2)	753+1084
	1900(2)	443+1455
	2829(9)	2(C-H sym.def.in CH_3)
2866		C-H asym.stretching in CH_3
	2983(sh)	C-H asym.stretching in CH_3
3045		C-H stretching(aromatic)
	3710(2)	2×264+2×1579

N.B. : As in the footnote of Table I.

trimethylbenzene is justified only as long as the CH_3 group is taken as a point mass. For the assignments of the ring vibrations this is to some extent justified. However, as CH_3 is not really a point mass the actual symmetry of the molecule is not exactly D_{3h} and the degenerate vibrations may show a splitting as assumed inthe present case. Ofcourse, one can not be completely certain on this point). This shows that shifts in the components of 1485 cm^{-1} from the parent frequency are much less in 1,3,5-TMB as compared to the other isomers. This seems to be a general result for trisubstituted benzenes, as corresponding mode is

TABLE III

Vibrational Frequencies and their Assignments for
1,3,5-Trimethylbenzene

Raman Frequencies(cm^{-1}) Ref.(21)	Infrared Frequencies(cm^{-1})	Assignments
233		C-CH$_3$ o.p.bending
275	273(sh)	C-CH$_3$ i.p.bending
	300(2)	C-CH$_3$ o.p.bending
	322(2)	C-CH$_3$ i.p.bending
	330(2)	
	338(2)	
	353(2)	
	378(3)	
	400(3b)	
	456(3b)	C-C-C o.p.bendimg
519		C-C-C o.p.ring def.
578		C-C stretching (ring breathing)
	662(sh)	C-C-C o.p. ring def.
	687(8)	C-C-C o.p. ring def.
847	835(10)	C-H o.p. bending
976	980(sh)	CH$_3$ rocking
998		CH$_3$ rocking
1036	1033(2)	C-H i.p.bending
1255		C-CH$_3$ sym. stretching
1301	1337(sh,b)	C-CH$_3$ asym.stretching
1357		C-CH$_3$ asym.stretching
1380	1372(3)	C-H sym.def.in CH$_3$
	1464(4)	C-H asym.def. in CH$_3$
	1472(4)	C-H asym. def. in CH$_3$
	1488(3)	C-C stretching
(1438)	1508(2)	C-C stretching
	1525(2)	
	1541(2)	

TABLE III   (continued)

	1572(sh)	C-C stretching
1611	1601(10)	C-C stretching
2724		2(C-H sym. def.in CH_3)
2857	2852(4)	C-H sym.stretching in CH_3
2917	2912(8)	C-H sym.stretching in CH_3
	2924(sh)	C-H asym.stretching in CH_3
	2964(sh)	C-H asym.stretching in CH_3
	3012(8)	C-H stretching(aromatic)

N.B. : As in the footnote of Table I.

  ( ) value taken from Ref.(22).

reported at 1475 cm^{-1} in the vibrational spectrum of symmetrical
trifluorobenzene (27). In contrast to the above four C-C vibrations,
the C-C stretching mode (ring breathing) arising from the a_{1g}(992 cm^{-1})
of benzene mode is considerably affected by the substitution. Taking
inot account the views from Varaanyi (28), the observed bands at 557 cm^{-}
in 1,2,4-TMB, and at 648 cm^{-1} in 1,2,3-TMB are assigned to this mode. No
such band is observed in the infrared spectrum of 1,3,5-TMB, but
a band observed at 578 cm^{-1} in the Raman spectrum may be assigned to thi
C-C stretching vibration. A frequency of magnitude 575 cm^{-1} observed
in the fluorescence spectrum of 1,3,5-TMB has been assigned to this
mode by Dirum and Sveshnikov (29). It has not been possible to correlate
any of the observed frequencies with the C-C stretching mode observed
at 1309 cm^{-1} in benzene. In the case of D_{3h} symmetry, this mode
belong to the a_2' symmetry species and is forbidden both in infrared
and in Raman spectra. Normal Coordinate Analyses using UVFF have
indicated that the magnitude of this vibration for trisubtituted benzene
would be lower that 1300 cm^{-1}(30).

  The two vibrations in the substituted benzenes corr-
esponding to the e_{2u}(404 cm^{-1}) of benzene are highly substituent
sensitive. The two component vibrations generally lie in the region
420-600 cm^{-1} in the spectra of trisubstituted benzenes (31). Taking
these facts and the expected frequency ranges for these vibrations,

the two components of this mode have been assigned to the bands observed at 430 and 466 cm^{-1} in 1,2,4-TMB, at 492 and 521 cm^{-1} in 1,2,3-TMB and only one band at 456 cm^{-1} in 1,3,5-TMB.

The C-H asymmetrical stretching mode in the methyl groups are expected to give rise to strong bands in the neighbourhood of 2900 cm^{-1}. Two such bands are observed at 2946 and at 2983 cm^{-1} in the infrared spectrum of 1,2,4-TMB and at 2944 and 2968 cm^{-1} in the spectrum of 1,3,5- TMB, but only one band is observed in the spectrum of 1,2,3-TMB at 2983 cm^{-1}. All are assigned to C-H assymmetrical stretching mode of vibration in the CH_3 group. The corresponding vibrations in o-, m- and p-xylenes have been reported at 2950 cm^{-1} and 2970 cm^{-1} (5,6,9). The C-H symmetrical stretching modes have been identified as being involved in the bands observed at 2840 and 2908 cm^{-1} for 1,2,4-TMB and at 2852 and 2912 cm^{-1} for 1,3,5-TMB. The corresponding bands are not observed in the infrared spectrum of 1,2,3-TMB, but appear in its Raman spectrum at 2866 and 2914 cm^{-1}. The vibrations arising from the C-H deformation in the methyl group are very characteristics of the group and appear in the region 1475-1340 cm^{-1}. The asymmetrical deformation modes are found to have the higher frequency i.e. in the neighbourhood of 1460 cm^{-1}. These bands positions remain unaffected by the substitution unless a strongly electronegatively element or unsaturated group is substituted in the neighbourhood. The identification of these bands is therefore correspondingly easy and medium strong prominent bands observed at 1473, 1455 and 1444 cm^{-1} for 1,2,4-TMB, at 1466,1455 and 1432 cm^{-1} for 1,2,3-TMB and at 1472, and 1464 cm^{-1} for 1,3,5-TMB are assigned to the asymmetrical C-H deformation modes. The symmetrical deformation modes of the CH_3 group lie towards the lower limit of the above mentioned range of 1385-1370 cm^{-1} (32). These positions are more affected by other substituents attached to the ring. The band observed at 1378 cm^{-1} for 1,2,4-TMB, at 1368 cm^{-1} for 1,2,3-TMB, and at 1372 cm^{-1} for 1,3,5-TMC have been assigned to the C-H symmetrical deformation.

The rocking modes of methyl groups have been reported to have the magnitudes below 1000 cm^{-1} in the methyl substituted

benzenes on the basis of theoretical calculation by Kovner (33) and by Kovner and Peregudov (34). The bands observed at 928 cm^{-1} in the Raman spectrum of 1,2,4-TMB as well as to two bands at 990 and at 1012 cm^{-1} observed in the infrared spectrum of this molecule are assigned to this mode. For 1,2,3-TMB only two bands observed at 976 and 997 cm^{-1} in the infrared spectrum could be identified to this mode whereas for 1,3,5-TMB one infrared band at 980 cm^{-1} and a Raman band at 998 cm^{-1} have been assigned to the rocking mode of methyl groups. In toluene this mode has been reported at 1041 cm^{-1} while in p-cresol a value of 1045 cm^{-1} has been reported.

ACKNOWLEDGEMENTS

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