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ON THE RAMAN SPECTRUM AND STRUCTURE OF 1.3.5-TRIPHENYL BENZENE

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Plate XII

ABSTRACT. The Raman spectra of *s*-triphenyl benzene in various solutions have been studied for the first time The spectrum of this substance resembles that of other substances of the diphenyl benzene family The Raman frequencies obtained for this substance agree in most cases with those of diphenyl and of the ortho-, meta- and para-diphenyl benzene of this series investigated by previous authors

The frequencies observed and found in all these various solutions are at 3046(1), 2987(4), 1603(8), 1406(1). 1458(5), 1350(6 bd), 1238(4), 1045(3), 1003(10 603(1), 406(1), 384(5), 234(1), 170(5), 146(5) and 87(4) cm^{-1} respectively

The results have been discussed with reference to the Raman spectra of diphenyl and of ortho-, meta- and para- diphenyl benzene. A comparative study of the spectra observed in all these substances lends support to the view that the substituent rings of this compound cannot be very appreciably tilted from the plane of the central ring.

INTRODUCTION

In a previous communication to 'Nature' two of us (Mukerji and Singh, 1942) submitted a preliminary report giving the Raman frequencies obtained for *s*-triphenyl benzene in various solutions. During the last war this substances was practically unavailable, but now in the present investigation it has been possible to make a thorough study of the Raman spectra of this subtance in various solutions. Discussions regarding the structures of the substances of this family of compounds with particular reference to 1, 3, 5-triphenyl benzene have also been incorporated in the present paper.

EXPERIMENTAL

1, 3, 5-Triphenyl benzene obtained from the research laboratory of Eastman Kodak Company was further purified by crystallisation from absolute alcohol. The pure crystals thus formed were found opaque to light and hence were not studied for their Raman spectra in the solid state. The melting point of the substance is high (being 170° C) and it tends to decompose at that high temperature. It was, therefore, studied in solutions in carbon-disulphide, carbon tetrachloride, acetic acid and chloroform respectively. The frequencies due to *s*-triphenyl benzene found common in all the above solutions are recorded here.

Wood's method was used to photograph the Raman spectra. With mercury arc as the exciting light, very intense scattering was obtained, but there was also evidence of a very intense flourescence spectrum on the plate. In order to reduce it considerably and to obtain a clean background a filter of concentrated solution of sodium nitrite was used which cut off the ultra violet portions of the mercury arc and suppressed λ 4046 Å line considerably. The excitation was, therefore, only due to λ 4358 Å mercury line which gave fairly good and intense spectra. The plates were exposed for a period of 40 hours.

The spectrograms were taken on Agfa Isochrome plates which were previously backed, speed H and D 4400, with a Fuess glass spectrograph having a dispersion of about 21 Å in the region of λ 4358 Å. Measurements were made on a new accurate photo measuring micrometer. The wavelengths were calculated in the usual manner. The results for 1.3.5-triphenyl benzene have been tabulated in Table I in which the frequencies due to diphenyl, ortho-, meta- and para-diphenyl benzene have also been given for comparison.

TABLE I

Number	Diphenyl benzene (molten state) Mukerji and Aziz (1938)	*o*-diphenyl benzene (molten state) Mukerji and Aziz (1939).	*m*-diphenyl benzene (molten state) Mukerji and Aziz (1941).	*p*-diphenyl benzene Mukerji and Singh (1946).	1.2.3tri-phenyl benzene in solutions (Authors).
1	—	Meltg. Pt. 57^0 Boilg. Pt. 332^0	—	42(5) solid	—
2	—	73(5) (bd)	80(4) (diff.)	85(5) solid	87(4)
3	—	—	—	93(3) molten	—
4	—	112(5) (bd)	—	—	—
5	140(4) (bd)	114(6) (bd)	151(2) (diff.)	—	146(6)
6	193(0)	—	—	—	170(5)
7	—	238(6) (bd)	238(3) (diff.)	—	234(1)
8	267(4) (bd)	253(1)	275(3) (diff.)	—	—
9	313(4) (bd)	319(3)	—	—	—
10	368(0)	359(5)	—	—	384(5)*
11	408(5) (bd)	406(6)	406(3)	—	406(1)
12	—	—	—	409(1) molten	—
13	449(0)	—	—	—	—
14	—	501(1)	—	—	—
15	—	521(2)	—	—	—
16	548(1)	558(3)	—	—	—
17	614(4)	615(5) (bd)	611(3)	508(½) solid	603(1)
18	—	—	—	593(0) molten	—
19	—	708(6)	707(3)	—	—
20	740(5)	744(2)	—	—	—
21	779(4)	774(5)	766(1)	773(5) solid	—
22	—	—	—	761(2) molten	—
23	—	—	801(½)	811(0) solid	—
24	838(4) (bd)	839(4)	838(1)	—	—
25	—	874(½)	—	—	—
26	898(½)	—	901(1)	—	—
27	—	—	—	940 molten	—
28	964(1)	—	964(½)	—	—
29	980(1)	993(8)	—	981(4) solid	—
30	1003(10)	1005(8)	1000(10)	1008(4) solid	1003(10)
31	—	—	—	1007(5) molten	—
32	1032(5)	1032(7)	1039(1)	1039(1)	1045(½)
33	—	1059(2)	—	—	—
34	1090(½)	—	1098(½)	—	—
35	1157(4)	1158(6)	1153(2)	1148(0) solid	—

TABLE I (contd.)

Number	Diphenyl benzene (molten state) Mukerji and Aziz (1938).	o-diphenyl benzene (molten state) Mukerji and Aziz (1939).	m-diphenyl benzene (molten state) Mukerji and Aziz (1941).	p-diphenyl benzene Mukerji and L Singh (1946).	1,2,3-Triphenyl benzene in solutions (Authors).
36	1189(3)	1180(2)	—	—	—
37	—	—	—	1219(6) solid	—
38	1241(1)	1247(4)	—	1223(4) molten	1238(4)
39	1283(10)	1288(10)	1279(2)	1274(10) solid	—
40	—	—	—	1283(10) molten	—
41	1318(½)	—	1309(10)	—	—
42	—	—	1345(0)	—	1350(6) (bd)
43	1376(0)	—	—	1372(0) solid	—
44	—	—	—	1350(1) molten	—
45	—	—	1403(½)	—	—
46	1452(1)	1430(½)	1453(½)	—	1458(5)*
47	—	1471(½)	—	—	—
48	1506(4)	1503(5)	1494(4)	1503(1) solid	1496(1)
49	—	—	—	1523(2) diff. molten	—
50	—	—	—	1549(3)	—
51	—	1577(1)	1566(1)	—	—
52	1590(8)	1595(10)	1597(10)	1592(10) solid	
53	—	—	—	1600(10) molten	—
54	1610(10)	1608(5)	1607(4)	1605(10)	—
55	—	—	—	1673(0) solid	1603(8)
56	—	—	—	1760(1) solid	—
57	—	—	—	2029(3) solid	2036(4)
58	—	—	—	2095(3) solid	—
59	—	—	—	2140(½) solid	—
60	—	—	—	2205(½) solid	—
91	—	—	—	2824(0) solid	—
62	2961(0)	—	—	—	—
63	—	—	—	—	—
64	3047(1)	3041(3)	—	3041(3) solid	2987(4)*
65	—	—	—	3043(2) molten	3046(1)
66	3063(5)	3059(6)	3062(2)	—	—
67	3192(0)	3196(0)	—	—	—

(bd) = broad (diff.) = diffuse.

* The three frequencies marked with asterisk were found only in acetic ether and chloroform solutions.

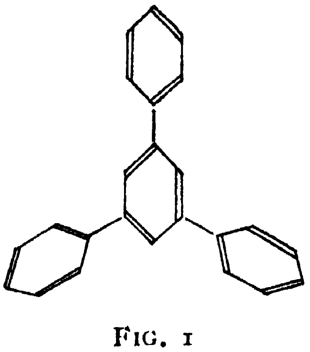


FIG. 1

s-Triphenylbenzene

RESULTS AND DISCUSSION

Raman spectrum of diphenyl and of the ortho-, meta- and para- diphenyl benzene have been studied and reported by two of us (Mukerji and Aziz, 1938, 39, 41) and Mukerji and L. Singh (1946) previously. In this investigation we have studied the Raman spectra of *s*-triphenyl benzene. We can now compare the spectra of the substances of the diphenyl benzene family with those of symmetrical triphenyl benzene, as given in the foregoing table.

We know that in benzene there is a single ring with all the six carbon atoms free. In diphenyl one of the carbon atoms is loaded with a phenyl group. In the case of ortho- and meta- diphenyl benzene two of the carbon atoms are loaded with phenyl groups in the ortho- and meta- positions respectively. In *p*-diphenyl benzene two of the carbon atoms are also loaded with phenyl groups in the para position. The ortho, meta and para compounds have three benzene rings and in the para compound these benzene rings are joined end on in the para position.

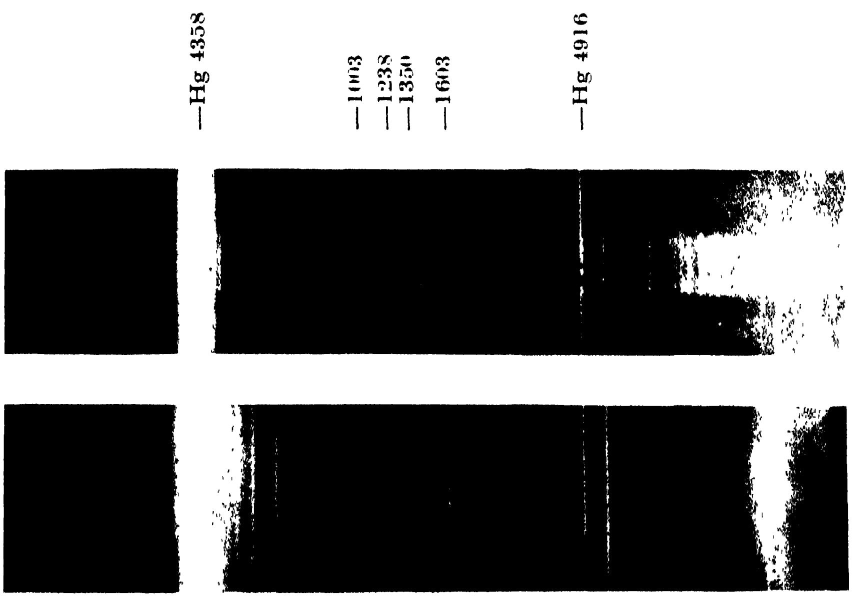
s-triphenyl benzene consists of four benzene rings, three of which are substituted in the fourth in positions 1, 3 and 5. Loss of any one of these benzene rings converts the substance into *m*-diphenyl benzene. It is, therefore, worthwhile to compare the frequencies of this substance with those of *m*-diphenyl benzene. It will be found, as given in Table I, that there is a close agreement between the majority of triphenyl benzene frequencies and those of *m*-diphenyl benzene The strongest frequency of triphenyl benzene observed at 1003 cm^{-1} is found equally strong by in *m*-diphenyl benzene and is also present in all the other compounds of this series. It may be observed here that in the case of the ortho- and para-diphenyl benzene, as will be seen in Table I, two strong lines are observed, in place of a single one, at 1003 cm^{-1}, as observed in *s*-triphenyl benzene. This agrees remarkably well with the fact that the other line of this doublet has also completely disappeared in *m*-diphenyl benzene.

But the marked dissimilarity is that very strong line at 1309 cm^{-1} observed in *m*-diphenyl benzene and also equally strongly in diphenyl and ortho and para compounds of this series with slightly lower frequencies is found to be completely missing in this compound.

It appears, therefore, that the addition of the extra benzene ring in position 5 of the central benzene ring of *m*-diphenyl benzene which makes *s*-triphenyl benzene a perfectly symmetrical compound is responsible for the disappearance of this line in the latter compound.

The other very marked difference is that the stronger frequency of the doublet at 1597 cm^{-1}, also found in all the compounds of this series, is not observed in *s*-triphenyl benzene, although the other frequency of this doublet at 1603 cm^{-1} appears in *s*-triphenyl benzene very strongly. It is possible that the two frequencies of this doublet have merged into one without being separated in *s*-triphenyl benzene, unless ethylene linkage C=C in the benzene rings of this compound has not been considerably weakened in the solution.

If we compare the frequencies of diphenyl with those of *s*-triphenyl benzene, which is obtained by the addition of two more benzene rings



Raman spectra of 1, 3, 5-triphenyl benzene

(a) In CS_2 solution
(b) ,, CCl_4 ,,

to diphenyl in the positions 3 and 5 of the central benzene ring, we find that many of the frequencies due to diphenyl are also present in *s*-triphenyl benzene. The two most prominent frequencies of diphenyl observed at 1003 cm^{-1} and 1610 cm^{-1} respectively appear almost equally strong in *s*-triphenyl benzene Amongst the other frequencies common to these two compounds are 3046, 1496, 1458, 1238, 614 and 146 cm^{-1} respectively, which are fairly strong in both these compounds.

It will be seen from Table I that many of the frequencies observed in ortho- diphenyl benzene have not appeared in *s*-triphenyl benzene. It is possible that since the Raman spectra of this substance were obtained in various solvents that many of the frequencies due to the ortho compound which are fairly weak have not appeared on the triphenyl benzene plate, being too feeble to be detected.

The frequency observed at 3084 cm^{-1} as a weak line in *s*-triphenyl benzene evidently represents the C-H stretching vibration.

The line at 1458 cm^{-1} which is also observed in other compounds of the series evidently corresponds to the transverse oscillation of hydrogen. The frequency at 1350 cm^{-1} which appears as a broad band in *s*-triphenyl benzene is also observed as a very weak line at 1345 cm^{-1} in *m*-diphenyl benzene. Similarly the line at 1238 cm^{-1} is also observed with slightly varying frequencies in diphenyl and *o*-diphenyl benzene.

There are two other frequencies, one at 603 cm^{-1} and the other at 406 cm^{-1} observed in *s*-triphenyl benzene, are also found, as Table I will show, in all the other compounds of this series. The frequency at 603 cm^{-1} then represents a carbon bending motion arising from the elongation and narrowing of the hexagonal configurations in this compound. The frequencies at 384 cm^{-1} and 234 cm^{-1} respectively due to *s*-triphenyl benzene are probably due to deformation oscillations of the molecule.

The frequency at 146 cm^{-1} observed in *s*-triyhenyl benzene as a fairly strong line is also found common to all other compounds of this series except *p*-diphenyl benzene. As it has not appeared in solid *p*-diphenyl benzene, although fairly strong, so it cannot possibly be due to lattice oscilliations which is expected in the solid state. It may probably be due to the deformation oscillations of the molecule.

The frequency at 73 cm^{-1} observed as a broad band in molten ortho-diphenyl benzen which has shifted to 80 cm^{-1} as a diffuse band in molten *m*-diphenyl benzene and to 93 cm^{-1} in molten *p*-diphenyl benzene, has appeared at 87 cm^{-1} in *s*-triphenyl benzene, in solution. *p*-diphenyl benzene in the solid state gives this frequency as a strong line at 85 cm^{-1}. This frequency appears, therefore, to be the lattice oscillation in the solid state of these compounds, which becomes weak and diffused when these compounds are in the molten state or in solution. The very low frequency at 42 cm^{-1} also observed in solid *p*-diphenyl benzene, as Table I will show, does not appear in *s*-triphenyl benzene in solution. This frequency evidently is due to lattice oscillations in the solid state.

It will be seen from Table I that there are hardly any frequencies observed in *s*-triphenyl benzene, in various solutions, which are not also present in one or the other compounds of this series, nor is there any strong frequency observed in this substance which can be said to be characteristic of this compound. There is not also much marked variation in the frequencies of this compound from those observed in other compounds of this series.

Diphenyl and *p*-diphenyl benzene have already been shown to be planer in structure. As regards ortho-diphenyl benzene, according to X-ray investigations of Clews and Lonsdale (1937), its most likely structure is one in which the two phenyl groups have their planes turned in the same direction out of the plane of the parent nucleus.

As regards *s*-triphenyl benzene its structure was studied by Orelkin and Lonsdale (1934) by X-ray investigation, who gave some priliminary data leading to its approximate structure. Their results are still inconclusive. In this investigation we have already pointed out that many of the frequencies of this substance agree remarkably well with those of diphenyl and also in many cases with those of the other compounds of the diphenyl benzene family. Diphenyl and *p*-diphenyl benzene have already been shown to be planer in structure, and as there is no marked dissimilarity between the frequencies of *s*-triphenyl benzene and those of the other compounds of the series, it is quite likely that the deviation from the planer configuration of this compound, if at all, cannot be very marked. Our results, therefore, lend support to the view that *s*-triphenyl benzene is planer in structure.

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