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The Raman Spectra of Ring Compounds. II. Poly-Substituted Benzene Compounds

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The Raman spectra of: fluorobenzene, 1,2,4-trichlorobenzene, 1,2,4,5-tetrachlorobenzene, pentachlorobenzene, hexachlorobenzene, and hexamethylbenzene have been studied. Their relation to the vibrations of the benzene ring is discussed.

IN a previous paper,[1] the Raman spectra of chlorobenzene, bromobenzene and iodobenzene were discussed. The data on this series have now been extended by the study of fluorobenzene, the Raman spectrum of which has not been reported hitherto. The spectrum of this compound is of particular interest in that it serves as a valuable link between the spectra of the three heavier halogen derivatives which are visibly similar to each other, and that of benzene. The Raman spectra of the three dichlorobenzenes have recently been re-examined by one of us and J. W. Swaine.[2] It is the purpose of this paper to describe the results of studies undertaken to investigate the effect of further replacement of the hydrogen atoms of benzene by heavier atoms or groups, especially chlorine, upon the Raman spectrum of the benzene ring.

For this purpose, we have photographed the Raman spectrum of one compound from each of the further stages of chlorination of benzene, and that of hexamethylbenzene. While this work was in progress, a paper by Dadieu, Kohlrausch and Pongratz[3] appeared in which results were given for the entire series of chlorine derivatives of benzene and one line for hexamethylbenzene. However, as several new lines have been found for each of the compounds studied in this investigation, the description of the results at this time appears warranted.

I. EXPERIMENTAL

The apparatus and technique used in this work were described in an earlier paper.[1] All of the work was done with filtered light from capillary mercury arcs. The blue light was used in all cases, the violet when possible, and the green in a few cases. Lines of low displacement excited by the green mercury line appear in some of the plates taken primarily for the blue excitation.

All of the substances except pentachlorobenzene were obtained from the Eastman Kodak Company. Fluorobenzene was used without further purification. It is a stable liquid and required no unusual precautions. It was studied with blue and violet excitation separately. The 1,2,4-trichlorobenzene was distilled once before using, a one degree cut being taken at the reported boiling point. It was studied with blue and violet excitation separately. It is also a stable liquid but exhibits slight fluorescence which was largely eliminated by the use of a sodium nitrite filter. The 1,2,4,5-tetrachlorobenzene was distilled into the Raman tube from a small bulb without further purification. It was studied in the molten state with continuous distillation. Blue and violet excitation were used separately. Strong fluorescence was observed.

Pentachlorobenzene was prepared by the chlorination of technical tetrachlorobenzene obtained from the Dow Chemical Co. The product was purified by fractional distillation and frac-

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[1] Murray and Andrews, J. Chem. Phys. 1, 406 (1933).

[2] Swaine and Murray, J. Chem. Phys. 1, 512 (1933).

[3] Dadieu, Kohlrausch and Pongratz, Monats. f. Chem. 61, 426 (1932).

tional crystallization from alcohol. Because of the small yield obtained, the purification was not complete and the purity of the resultant product was estimated to be about 93 percent. Because of the strong fluorescence and decomposition by short waves, this substance was studied only with blue excitation. It was investigated in the molten state. Hexachlorobenzene was purified by sublimation. It was studied in the molten state with continuous distillation, in the solid state and in solution in carbon tetrachloride. In the latter work, the method of High and Pool[4] was applied. Mixtures of hexachlorobenzene and carbon tetrachloride with about 1 percent of nitrobenzene or metadinitrobenzene to suppress fluorescence, were sealed into a Raman tube and the temperature raised to bring the solids into solution. The best results were obtained from the molten material, with rapid distillation to remove the colored and fluorescent decomposition products. Blue and green excitation were used separately. Hexamethylbenzene was distilled into the Raman tube without further purification and was studied in the molten state with continuous distillation. Only blue excitation was used. The

fluorescence was very strong. Attempts to obtain the Raman spectrum of hexaethylbenzene were unsuccessful due to the extreme fluorescence.

II. RESULTS

The results obtained are presented in Tables I–VI. The wave numbers of observed Raman lines in cm^{-1}, letters indicating the mercury exciting line, visually estimated relative intensities, and the Raman displacements are given. The wave numbers of the mercury lines indicated by the letters are as follows: d, 24,705; e, 24,516; f, 23,039; g, 22,995; h, 22,938; and k, 18,308. Letters following the intensities signify as follows; b, broad; v, shaded to the violet; and r, shaded to the red. Wave-number values enclosed in parentheses refer to doubtful lines. Most of the values reported are averages from several plates. The probable error is believed to be about 3 cm^{-1} for average lines, slightly less for very sharp lines, and about 10 cm^{-1} for extremely weak lines.

TABLE I. *Fluorobenzene.*

$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$
24,465	d	3	240	23,358	e	2	1158	(21,788)	d	1b	(2917)
24,276	e	1	240	23,293	e	1	1223	21,780	h	3	1158
24,185	d	2	520	23,207	d	1	1498	(21,719)	d	1b	(2986)
24,090	d	2	615	23,104	d	3b	1601	21,717	h	3	1221
24,000	$\{$ d / e	1	(705) / 516	22,694	h	8	244	21,678	d	1	3027
				22,436	h	0	502	21,636	h	0	1302
23,950	d	1	755	22,417	h	3	521	21,630	d	10b	3075
23,898	$\{$ d / e	6	807 / 618	22,325	h	2	613	21,515	d	1	3190
				22,235	f	0	804	21,441	$\{$ f / h	0	1598 / 1497
23,875	d	1	830	22,185	g	1	810				
23,822	d	0	883	22,131	h	9	807	21,439	e	3b	3077
23,706	$\{$ d / e	2	999 / 810	22,108	h	1	830	21,395	g	0	1600
				22,090	d	1	2615	21,337	h	4b	1601
23,692	d	10	1013	22,031	f	0	1008	(21,313)	h	0	(1625)
23,680	$\{$ d / e	1	(1025) / 836	21,984	g	1	1011	19,857	h	2	3081
				21,944	h	2	994	18,062	k	5	246
23,635	d	1b	1070	21,927	h	10	1011	17,503	k	3	805
23,546	d	3	1159	21,869	h	0	1069	17,302	k	3	1006
23,502	e	2	1014	21,836	g	0	1159	17,164	k	0	1144
23,483	d	3	1222								

244 (8), 502 (0), 520 (3), 615 (2), (705) (1), 755 (1), 807 (9), 830 (1), 883 (0), 997 (2), 1013 (10), (1025) (1), 1070 (1b), 1159 (3), 1222 (3), 1302 (0), 1498 (1), 1601 (4b), (1625) (0), 2615 (1), (2917) (1b), (2986) (1b), 3027 (1), 3075 (10), 3090 (1).

4 High and Pool, Phys. Rev. **38**, 374 (1931).

TABLE II. *1,2,4-trichlorobenzene.*

$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$
24,399	d	2	306	23,387	e	0	1129	22,261	h	6	677
24,376	d	3	329	23,356	e	2	1160	22,182	d	$2v$	2523
24,249	d	3	456	23,332	$\{d$	0	1373 $\}$	22,122	h	2	816
24,223	d	$1b$	482		h		-394	22,070	h	0	868
24,191	$\{d$	$2b$	514 $\}$	23,251	h	$0b$	-313	21,902	h	4	1036
	e		325	23,136	d	5	1569	21,886	h	1	(1052)
24,060	e	1	456	22,756	h	2	182	21,840	h	$2b$	1098
24,029	d	5	675	22,740	h	4	198	21,807	h	$3b$	1131
23,891	d	2	814	22,722	h	1	216	21,780	h	5	1158
23,840	$\{d$	2	865 $\}$	22,628	h	2	310	21,677	h	1	1261
	e		676	22,608	h	5	330	21,634	d	10	3071
23,668	d	4	1037	22,540	h	2	398	21,590	d	1	3115
23,611	d	$2b$	1094	22,479	h	2	459	21,573	d	$1b$	3132
23,609	h	1	-671	22,449	h	0	489	21,563	h	0	1375
23,575	d	$4b$	1130	22,423	h	0	515	21,445	e	2	3071
23,548	d	6	1157	22,363	$\{h$	0	575 $\}$	21,367	h	$5b$	1571
23,481	e	2	1035		f		676	19,860	h	1	3078
23,445	$\{d$	$1b$	1260 $\}$	22,318	g	0	677				
	e		1071								

182 (2), 198 (4), 216 (1), 310 (2), 330 (5), 398 (2), 459 (2), 489 (0), 515 (0), 677 (6), 816 (2), 868 (0), 1036 (4), (1052) (1), 1098 (2), 1131 (3), 1158 (5), 1261 (1), 1375 (2), 1571 (3), 2523 (2v), 3071 (10), 3115 (1), 3132 (1).

TABLE III. *1,2,4,5-tetrachlorobenzene.*

$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$
24,350	d	2	355	22,642	g	1	353	21,775	h	8	1163
24,194	d	0	511	22,625	h	3	313	21,745	h	1	1193
24,150	e	1	366	22,583	h	$10v$	355	21,727	h	1	1211
24,018	d	3	687	22,432	h	2	506	21,696	h	0	1242
23,827	$\{d$	$1b$	878 $\}$	22,363	$\{h$	$1b$	575 $\}$	21,640	d	3	3065
	e		689		f		676	21,601	h	1	1337
23,615	h	1	-677	22,315	g	1	680	21,557	d	1	3148
23,538	d	$4r$	1167	22,297	h	1	641	21,518	d	0	3187
23,355	e	1	1161	22,253	h	10	685	21,463	$\{f$	1	1576
23,289	h	2	-351	22,059	h	$0b$	879		h		1475
23,253	h	1	-215	22,014	h	0	924	21,455	e	0	3061
23,133	d	2	1572	21,921	h	0	1017	21,370	h	5	1568
22,747	h	5	191	21,872	f	0	1167	21,345	h	0	1593
22,708	h	3	230	21,833	g	0	1162	19,860	h	1	3078
22,683	f	1	356								

191 (5), 220 (3), 313 (3), 355 (10), 506 (2), 641 (1), 685 (10), 879 (0), 924 (0), 1017 (0), 1163 (8), 1193 (1), 1211 (1), 1242 (0), 1337 (1), (1475) (1), 1568 (2), 1593 (0), 3065 (3), 3148 (1), 3187 (0).

TABLE IV. *Pentachlorobenzene.*

$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$
23,280	h	0	-342	22,376	h	3	562	21,726	h	3	1212
22,738	h	2	200	22,308	h	0	630	21,701	h	0	1237
22,710	h	1	228	22,251	h	2	687	21,592	h	1	1346
22,661	h	1	277	21,985	h	1	953	21,545	h	0	1393
22,643	g	0	352	21,943	h	0	995	21,477	h	0	1461
22,617	h	2	321	21,851	h	1	1087	21,380	h	$3b$	1558
22,588	h	$5b$	350	21,772	h	3	1166	21,343	h	0	1595
22,551	h	3	387	21,749	h	2	1189	21,265	h	1	1673
22,427	h	0	511								

200 (2), 228 (1), 277 (1), 321 (2), 350 (5b), (387) (3), (511) (0), 562 (3), 630 (0), (687) (2), 953 (1), 995 (0), 1087 (1), (1166) (3), 1189 (2), 1212 (3), 1237 (0), 1346 (1), 1393 (0), 1461 (0), 1558 (3), 1595 (0), 1673 (1).

TABLE V. *Hexachlorobenzene.*

$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$
23,309	h	3	−371	22,534	h	0	404	21,366	h	0	1572
23,260	h	1	−322	22,001	h	0	937	21,321	h	0	1617
22,772	h	1	166	21,968	h	0	970	18,673	k	1	−365
22,717	h	2	221	21,924	h	0	1014	18,086	k	0	222
22,663	h	0b	275	21,754	h	1	1184	17,976	k	1	332
22,614	h	3b	324	21,712	h	3	1226	17,933	k	5	375
22,594	h	0	344	21,505	h	0b	1433	17,884	k	0	424
22,566	h	10	372	21,423	h	2	1515				

166 (1), 221 (2), 275 (0b), 324 (3b), 344 (0), 372 (10), 414 (0), 937 (0), 970 (0), 1014 (0), 1184 (1), 1226 (3), 1433 (0b), 1515 (2), 1572 (0), 1617 (0).

TABLE VI. *Hexamethylbenzene.*

$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$
23,488	h	2	−550	22,385	h	2	553	21,615	h	0	1323
22,625	h	0	313	22,363	h	1	575	21,553	h	0	1385
22,595	h	1	343	22,155	h	1	783	21,355	h	0	1583
(22,560)	h	0b	(378)	21,785	h	1	1153	19,999	h	1	2939
22,488	h	1	450	(21,687)	h	0	(1251)	(19,953)	h	0	(2985)
22,441	g	0	553	21,643	h	1	1295				

313 (0), 343 (1), (378) (0b), 450 (1), 553 (2), 575 (1), 783 (1), 1153 (1), (1251) (0), 1295 (1), 1323 (0), 1385 (1b), 1583 (0), 2939 (1), (2985) (0).

III. DISCUSSION

The Raman spectra of the substances studied are represented graphically in Figs. 1 and 2 together with the spectra of the other members of the series as obtained from the literature cited above. The data for benzene have been summarized, from the numerous papers which have appeared on this substance. The data for the heavier mono-derivatives are taken from our previous paper.[1] The data for the dichlorobenzenes are taken from the paper cited above.[2]
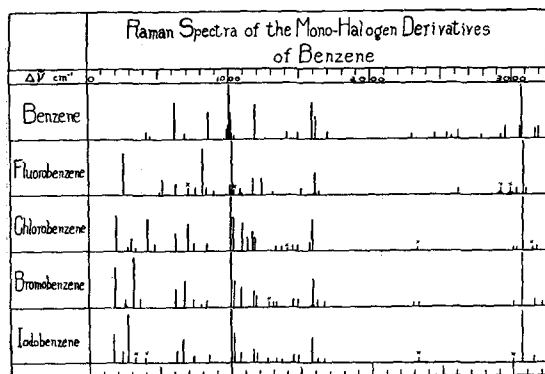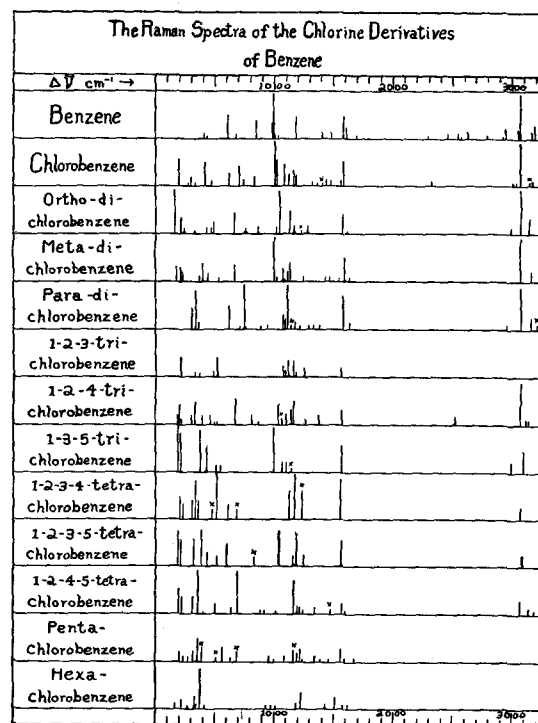

FIG. 1.

FIG. 2.

The data for the poly-substituted benzene compounds not studied in this investigation are taken from Dadieu, Kohlrausch and Pongratz.[3] The lengths of the lines represent the estimated relative intensities while a triangle at the base of the line signifies that it is broad. Cross marks above the lines designate those considered doubtful.

The Raman spectrum of fluorobenzene has not been investigated previously. The lines reported at 705 and 1025 are assumed to have been excited by the 24,705 mercury line. They coincide with the lines at 516 and 836 excited by the 24,516 mercury line but are stronger than would be expected if such were the origins. The lines reported at 2917 and 2986 coincide with the lines 1159 and 1222 excited by the 22,938 mercury line, which was not completely removed by the filter, but are assigned to the 24,705 exciting line on account of their intensity relative to lines known to have been excited by the blue mercury line.

1,2,4-trichlorobenzene has been studied by Morris[5] and by Dadieu, Kohlrausch and Pongratz.[3] The line reported at 575 and characterized as uncertain by the latter authors was not found in this investigation. All other previously reported lines were confirmed. New lines were found at 216, 489, 515, 868, (1052), 1375, 2523, 3115 and 3132. The assignment of a line to 1052 is doubtful on account of its proximity to the line 1163 excited by the 23,039 mercury line.

1,2,4,5-tetrachlorobenzene has been studied by Dadieu, Kohlrausch and Pongratz.[3] All lines reported by them have been confirmed. New lines have been found at 506, 641, 879, 924, 1017, 1211, 1242, 1337, (1475), 1593, 3148 and 3187. The assignment of the line at 21,463 cm^{-1} to 1475 as excited by the 22,938 mercury line is based on relative intensity.

Pentachlorobenzene has been studied by Dadieu, Kohlrausch and Pongratz.[3] The lines reported by them at 817 and 1028 and characterized as uncertain were not found. New lines were found at (387), (511), 630, 953, 995, (1166), 1346, 1393, 1461, 1595 and 1673. The lines listed as uncertain are those which correspond to the positions of strong lines of probable impurities

[5] Morris, Phys. Rev. **38**, 141 (1931).

and which were not found by Dadieu, Kohlrausch and Pongratz.

Hexachlorobenzene has been studied by Dadieu, Kohlrausch and Pongratz.[3] All lines reported by them have been confirmed. New lines have been found at 166, 275, 344, 414, 937, 970, 1014, 1572 and 1617.

Hexamethylbenzene has been studied by Dadieu, Kohlrausch and Pongratz.[3] These authors did not give a complete report on this substance but merely mentioned one line which corresponds to the one found at 1583. The results obtained are probably incomplete due to the very strong fluorescence.

The Raman spectrum of fluorobenzene resembles those of the heavier mono-halogen derivatives in many respects but shows certain very marked differences. It is very similar to the spectrum of toluene whose side chain has nearly the mass of the fluorine atom. All of the stronger lines below the region of 1000 cm^{-1} and some of the weaker ones are obviously analogous to lines in chlorobenzene. The group of lines near 1000 cm^{-1} resembles that in benzene rather than the grouping found in the heavier mono-halogen derivatives. The spectrum of fluorobenzene in the region of 1200 cm^{-1} is very different from those of the other derivatives. It is of interest to note that several of the lines which appear in benzene as well as in the mono-derivatives have higher values in fluorobenzene than in benzene itself while the values for the lines of the heavier derivatives are lower than those of benzene. This would appear to indicate that the introduction of the halogen has the effect of raising the force constants involved and that this effect predominates over the effect of the increased mass in the case of the fluorine compound but is overcome by the heavier masses of the chlorine, bromine, and iodine atoms.

Upon substituting additional chlorine atoms, especially in positions of low symmetry, the spectrum becomes increasingly complex. The differences between isomeric compounds of this series are marked. Little can be done at present to interpret these spectra by direct comparison. As would be expected, many lines appear in the low regions which are associated with the bending and stretching of the carbon-halogen bonds.

Coincident with this is a decrease in intensity of the lines in the region of 3000 cm^{-1} associated with the C−H bond. At the same time there is a splitting up of lines due to ring vibrations caused by the loss of symmetry. As pointed out by Dadieu, Kohlrausch and Pongratz,[3] the appearance of the lines in the region of 1600 cm^{-1} in hexachlorobenzene shows that these lines cannot be accounted for by bending motions of the C−H bond. It does not, however, eliminate the possibility of lines from these motions in this region for there are several lines in this region and their inter-relations in the different compounds has not yet been traced out. The appearance of ring motions in this region would appear to indicate the presence of the double bond in the ring as pointed out by the above authors. This cannot be regarded as certain, however, for there is a possibility that such lines may be due to ring motions without double bonds and these have been observed in the mechanical models.

Dadieu, Kohlrausch and Pongratz have also pointed out the fact that the 992 line of benzene only appears in the poly-substituted derivatives in which the substituents are oriented in the meta positions with respect to each other. Lines have been found at approximately this position in the spectra of 1,2,4,5-tetrachlorobenzene, pentachlorobenzene and hexachlorobenzene but they are very weak. It is hoped that further interpretation of these spectra will be possible when studies of the mechanical models of the molecules are completed. The praseodymium nitrate used as a filter was obtained from a mixture of praseodymium and lanthanum salts kindly supplied by Mr. Mark Eichelberger of the Lindsay Light Company.