Studies with Vibrating Mechanical Models II. The Series: C6H5Cl–C6Cl6

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FIG. 5.

The results were quite unsatisfactory. As found in the earlier model studies,[1] it is very difficult to get vibration in a steady state at a sharp resonance frequency if the molecule is what may be called the "floppy" type such as a long hydrocarbon chain. The model of the centric formula was compact enough to avoid this difficulty, the cross bonds acting to stabilize the vibration, but the models representing the Kekulé and Pauling resonance formulas were very unstable and yielded results that appeared to be incomplete and unreliable.

From this we may conclude that the usefulness of the models will be restricted largely to the study of certain relatively simple and stable types of vibration such as the X, Y and H movements where one can expect to get qualitative evidence of the effect of a change of mass on the frequency.
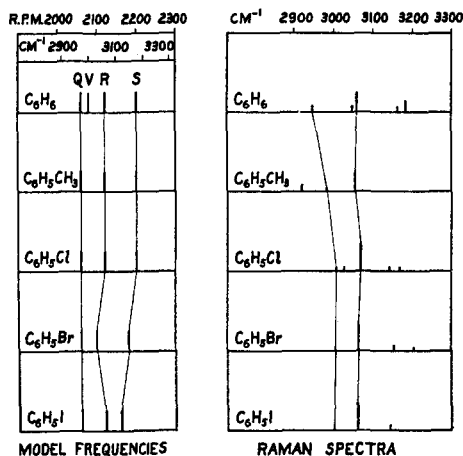
series of compounds with two other sets of models in which the springs representing the benzene ring correspond, respectively, to the Kekulé and to the Pauling resonance formulas.

The authors wish to thank Mr. Charles F. Squire for the study which he made of the resonance and Kekulé models in connection with the work reported here.

Studies with Vibrating Mechanical Models
II. The Series: $C_6H_5Cl - C_6Cl_6$

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Mechanical models have been constructed for the following molecules based on the Pauling resonance formula for benzene: C_6H_6; C_6H_5Cl; o-, m-, p-$C_6H_4Cl_2$; (1, 2, 3)-, (1, 2, 4)-, (1, 3, 5)-$C_6H_3Cl_3$; C_6Cl_6. The mechanical spectra of these models have been observed and compared with the Raman spectra. The shifts in frequency observed in passing down the series are the same in both mechanical and Raman spectra in a number of cases. This makes possible the identification of several of the lines connected with the motions of the chlorine atoms and of the line at 992 cm⁻¹ associated with the symmetrical expansion of the benzene ring. The types of motion show an evolution from the symmetrical group of C_6H_6, which can be correlated with group theory, through the various doublets and triplets associated with the less symmetrical intermediate compounds, to the group connected with C_6Cl_6 which is similar to that of C_6H_6 except for the inversion of frequency order due to the increased mass of the substituent atoms

I N studying the variation of characteristic frequencies with structure, some of the most interesting shifts in frequencies are those associated with the change in position of substitution in the benzene ring. Since a rather complete series of Raman spectra are available for the various chloro-derivatives of benzene, this group of compounds was selected as the basis for an extension of the work with the vibrating mechanical models.

The atoms and bonds were represented by the same types of ball and spring used in work by Teets and Andrews[1] reported in the previous article of this series. The procedure followed for

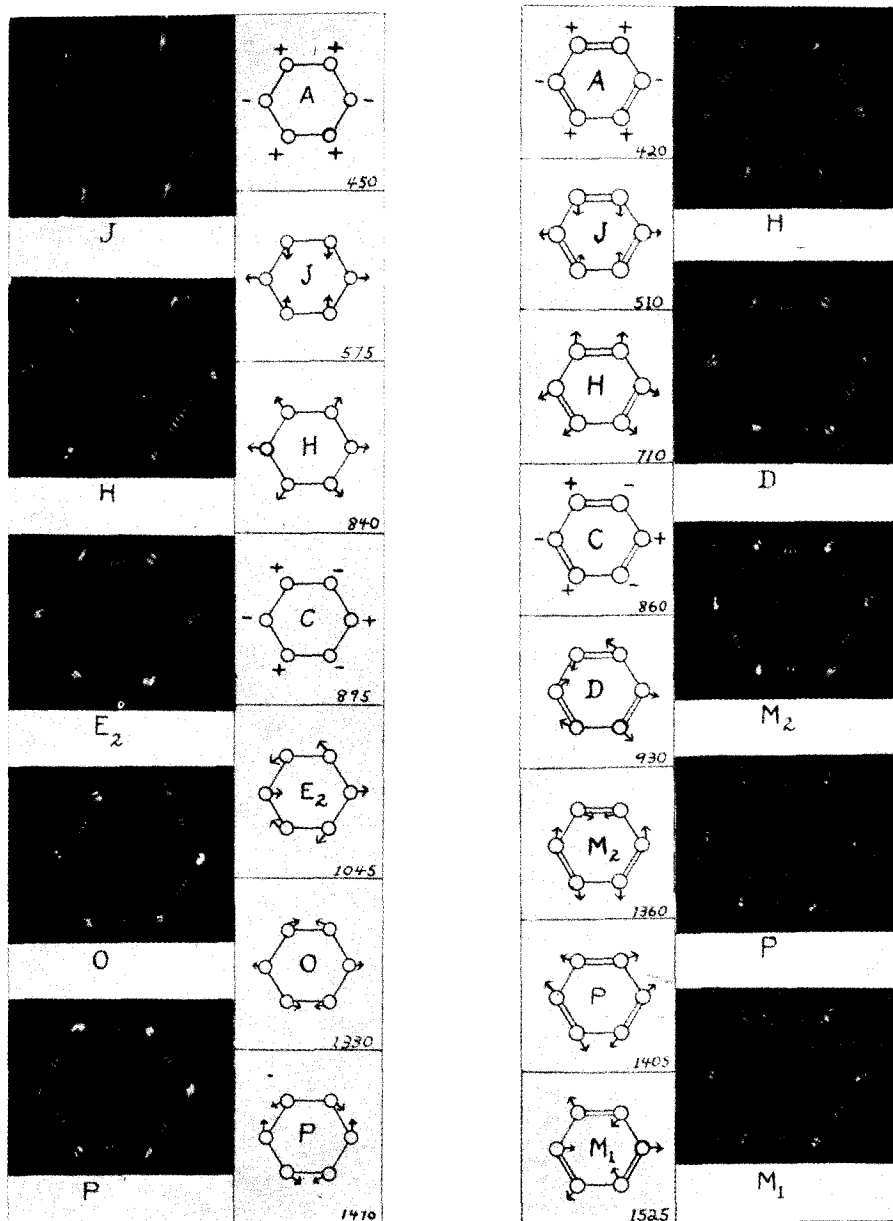[1] D. Teets and D. H. Andrews, J. Chem. Phys. **3**, 175 (1935).

FIG. 1. Photographs of model motions in benzene. (a) Resonance formula; (b) Kekulé formula.

observing the vibrations of the models was also the same, with the addition in some cases of the photographic method described by Andrews and Murray.[2]

A change was made in the structure of the benzene ring used in the models. The recent work of Pauling[3] and Wheland has supported a structure for the benzene ring in which adjacent carbon atoms in the ring are joined by bonds about one and one-half times as strong as the normal carbon – carbon bond. It appears that the forces between atoms *meta* or *para* to one another are negligible. On the basis of these considerations the model used in this work was constructed with springs, joining adjacent carbon atoms, of a strength roughly one and one-half times that of the springs previously used to represent the normal C – C bond.

Although the previous investigations with the models indicated that there was great instability in the type of model representing the resonance formula for benzene, there appeared to be some hope that the addition of several heavy substituents around the ring would act as a stabilizing influence. This was found to be the case and fairly satisfactory results were obtained for most of the modes of motion. It was necessary, however, to leave off the balls representing the hydrogen atoms in order to avoid the complications of harmonics.

The first step in the investigation was therefore the study of the model of the "resonance" ring without hydrogens. This was carried out with the help of the photographic method[2] and since a model of the Kekulé formula for benzene was available it was studied at the same time. The results are shown in Figs. 1a and 1b. Photographs are included to show the motions which take place in the plane of the ring. The figures in the lower right-hand corner of each diagram are the r.p.m. at which the motion in question is observed.

More or less by chance the values of the r.p.m. correspond roughly to the values of the wave numbers in cm^{-1} so that comparison with the spectra is quite easy. One notes immediately that the frequencies of the two models cover

[2] D. H. Andrews and J. W. Murray, J. Chem. Phys. 2, 634 (1934).
[3] L. Pauling and G. W. Wheland, J. Chem. Phys. 1, 362 (1933).

about the same range, 400–1500. This is the range to which the vibrations of the ring have been assigned on the basis of the Raman and infrared spectra of benzene.

It is interesting to note that the frequency of the P type of vibration undergoes a change of less than five percent when the bonds are changed from the "one and one-half" type to alternate single and double. This weakens the argument that double bonds must be necessary to produce a frequency as high as the 1585–1606 cm^{-1} doublet in benzene, a hypothesis that certain authors have advanced. In fact the general distribution of frequencies for the two models is so nearly the same that it is useless to try to distinguish between them with the present accuracy of observation.
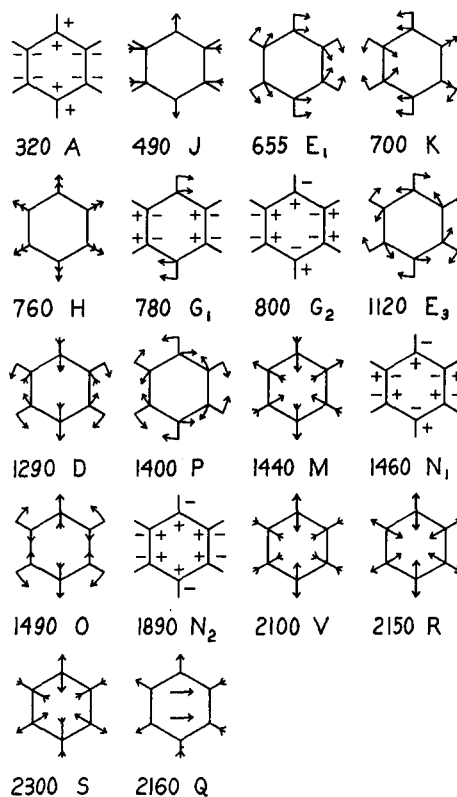
Fig. 2 shows the results obtained with the

FIG. 2. Benzene, resonance formula.

200 X   260 W   365 Y   460 A₁

490 A₂   595 J₁   675 J₂   790 C

825 K   900 H   1050 E₂   1130 M

1400 O

FIG. 3. Chlorobenzene.

120 X₁   205 W₁   230 W₂   245 X₂

375 Y₂   390 A₁   500 A₂   615 J

750 C   800 K   915 H   1150 M₁

1145 M₂   1355 O

FIG. 5. m-Dichlorobenzene.

105 X₁   185 W₂   240 X₂   265 W₁

345 Y₂   400 Y₁   490 A   630 J

765 C   800 K   930 H   1110 E₂

1130 M₁   1215 M₂   1390 O

FIG. 4. o-Dichlorobenzene.

140 X₁   155 W₁   240 X₂   285 Y₂

295 W₂   375 A₂   485 A₁   505 J₀

600 J₂   705 J₁   790 K   995 H

1095 E₂   1175 C   1230 M   1360 O
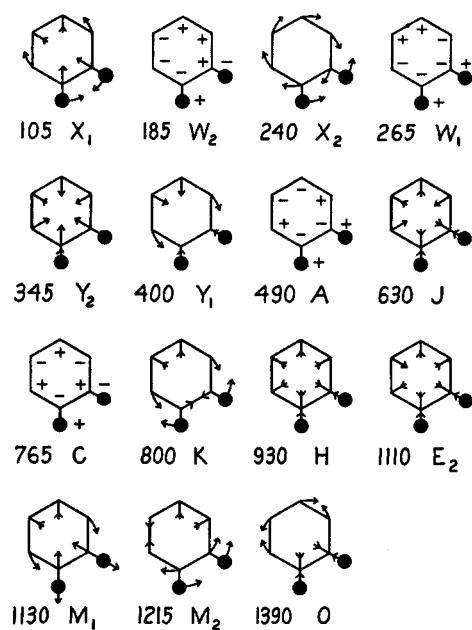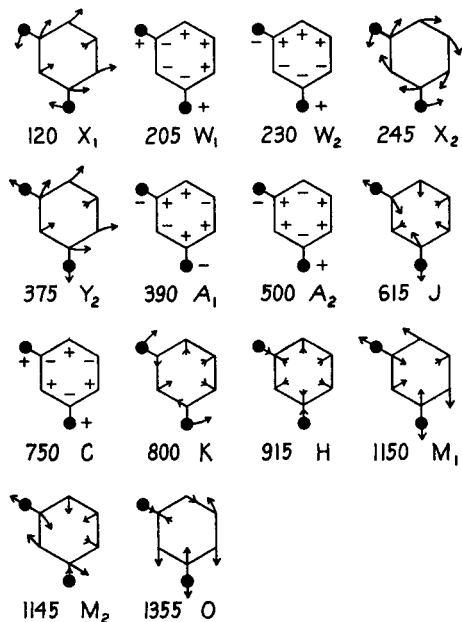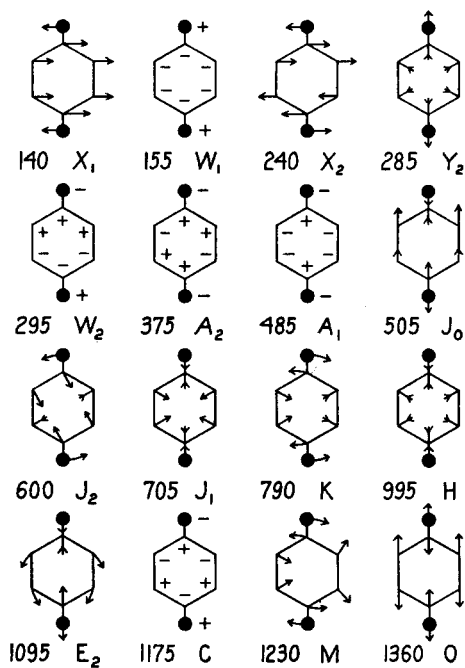
FIG. 6. p-Dichlorobenzene.

Pauling formula for benzene when balls and springs are added to represent the hydrogen atoms and $C-H$ bonds. We do not believe these results are complete. From the mechanical point of view the Pauling ring structure is much less compact than the centric formula on which the earlier model was based.[1] As a result, there is much greater difficulty in getting clear-cut resonance in a steady state. Interference develops with harmonics and with types of motion possessing nearly similar frequencies and the results for that reason are much less certain.

On the whole the accuracy is again not great enough so that one can come out positively in favor of this Pauling formula. It is clear, however, that the change from the diagonal cross-bond structure to the Pauling formula shifts the frequencies for various types of motion very markedly. We may be able to identify these types of motion with certain lines in the spectrum by the shifts which take place upon substitution and also by the polarization and intensity of the lines. If this can be done, then the value of the frequency will give a clear-cut answer regarding the nature of the formula. For example, the J type of motion has a frequency corresponding to about 1100 cm^{-1} in the diagonal cross-bond formula and 675 cm^{-1} in the Pauling formula (provided we accept the identification of the H motion with the 992 cm^{-1} frequency). If the J motion can be positively correlated with the 606 cm^{-1} Raman line, then it will be quite certain that there are no forces comparable to cross bonds.

The study of the various chloro-derivatives of benzene was carried out with the model of the ring based on the Pauling formula, leaving off the balls and springs representing the hydrogen atoms and $C-H$ bonds. This was done to avoid the difficulties of harmonic interference previously mentioned.

The results are shown in Figs. 3 to 10. The value of the mechanical frequency in r.p.m. is given under each figure. These values are plotted in Fig. 11. A scale has been added for converting them to cm^{-1}, based on the correlation of the 992 cm^{-1} line in benzene with the II type of motion. The Raman spectra are shown by the customary graphical plot in Fig. 12. The values
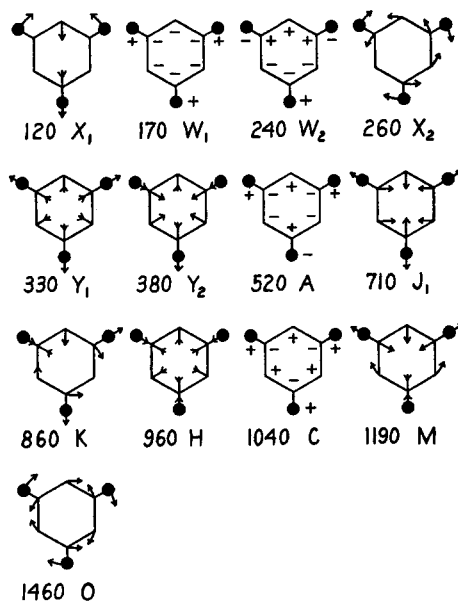
FIG. 7. 1,3,5-Trichlorobenzene.

for benzene are taken from the work of Grassmann and Weiler;[4] for C_6H_5Cl from Murray and Andrews;[5] for o, m, p-$C_6H_4Cl_2$ from Swaine and Murray;[6] for 1, 2, 3- and 1, 3, 5-$C_6H_3Cl_3$ from Kohlrausch;[7] and for 1, 2, 4-$C_6H_3Cl_3$ and C_6Cl_6 from Murray and Andrews.[8]

In comparing the model and Raman spectra one notes first of all the general similarity in the spectral region covered and in the number of lines for each compound. At least this is true for the compounds where it has been possible to get fairly complete Raman spectra. In the case of the higher melting compounds the fluorescence at high temperatures and the comparative insolubility have prevented the obtaining of satisfactory photographs. In the figure one notes the comparative paucity of lines in the spectra of

[4] P. Grassmann and J. Weiler, Zeits. f. Physik 86, 321 (1933).
[5] J. W. Murray and D. H. Andrews, J. Chem. Phys. 1, 406 (1933).
[6] J. W. Swaine and J. W. Murray, J. Chem. Phys. 1, 512 (1933).
[7] K. W. F. Kohlrausch, *Die Smekal-Raman Effekt*, Julius Springer, Berlin (1931).
[8] J. W. Murray and D. H. Andrews, J. Chem. Phys. 2, 119 (1934).
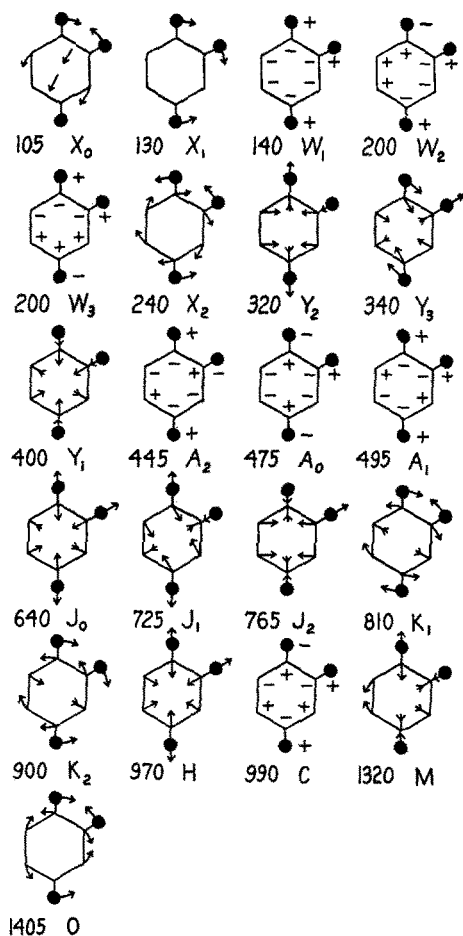
FIG. 8. 1,2,4-Trichlorobenzene.

FIG. 9. 1,2,3-Trichlorobenzene.

1, 2, 3- and 1, 3, 5-$C_6H_3Cl_3$ and C_6Cl_6. Considerations of this sort led us to omit $C_6H_2Cl_4$ and C_6HCl_5 from the study.

As mentioned previously, the scale for comparing the model spectra with values of the frequency in cm^{-1} was calculated so that the line for the H type of motion in benzene falls at 992 cm^{-1}, the position of the strongest Raman line in benzene. There are two reasons for doing this. First, this line has been identified with the H type of motion by E. B. Wilson, Jr.,[9] on the basis
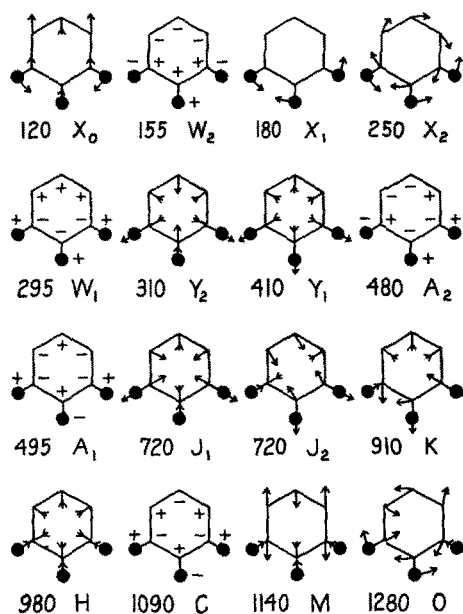
of Placzek's selection rules for Raman spectra. In the second place, the series of model frequencies, associated with the H motion as we pass from C_6H_6 to C_6Cl_6, bears a striking resemblance to the series of lines in the Raman spectra which we obtain by selecting for each compound the strongest line found in the 1000 cm^{-1} region. The shifts in the model spectrum correspond to the shifts in the Raman spectrum, not only in sign but in magnitude.

This assignment of the 992 cm^{-1}·line to the H motion does not correspond with the conclusions previously drawn by other authors. Kohlrausch[10] and his associates have attributed this line to a motion resembling the M_1 type in Fig. 1b. Bhagavantam[11] ascribes it to a type of motion like P in Fig. 1a. One notes, however, that neither the shifts of the M_1 line, nor those of P line in the model spectrum bear any resemblance at all to the shifts of the series of strong lines in the 1000 cm^{-1} region of the Raman spectrum. The

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[9] E. B. Wilson, Jr., Phys. Rev. 46, 146 (1934).

[10] A. Dadieu, A. Pongratz and K. W. F. Kohlrausch, Sitzungsber. Akad. Wissensch. Wien [II b] 141, 751 (1932).
[11] S. Bhagavantam, Ind. J. Phys. 5, 615 (1930).

100 X₀ (D) 115 W₂ (C) 130 X₁ (K) 130 W₃ (G)

205 W₁ (N₂) 270 Y₂ (J) 295 Y₃ (H) 310 X₂ (E₃)

355 Y₄ (M) 475 Y₁ (Q) 530 A (I) 655 C (N)

860 J (V) 940 E (P) 1080 H (R) 1650 K (L)
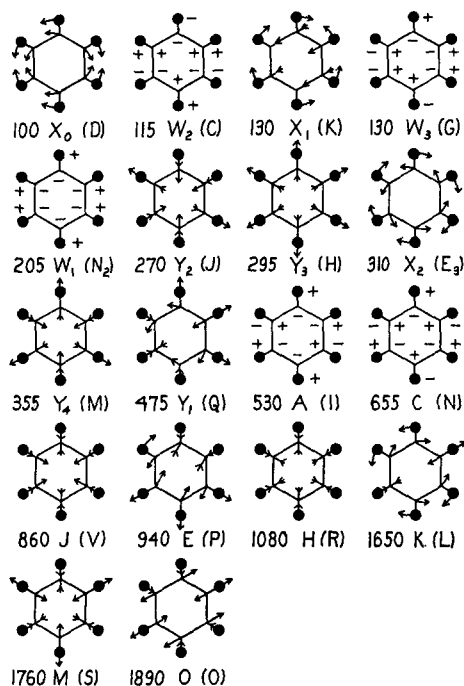
1760 M (S) 1890 O (O)

FIG. 10. Hexachlorobenzene.

striking resemblance of this series to the H frequencies and the lack of resemblance to any other set of frequencies make a strong argument in favor of this correlation. This is also in accord with the results found in the series of compounds studied by Teets and Andrews.[1] It agrees with the results obtained by Murray, Squire and Andrews[12] in their study of the shift of the 992 cm⁻¹ line in passing from benzene to deuteriobenzene (C_6D_6).

Let us consider next the relations between the model and Raman spectra in the low frequency region where we find the motions associated with the substituent chlorine atoms. Quite apart from any arbitrary arrangement of the lines in series, we note the resemblance between the left-hand boundaries of the two figures. Except in the case of p-$C_6H_4Cl_2$ there is almost quantitative agreement between the lowest frequency found in the

[12] J. W. Murray, C. F. Squire and D. H. Andrews, J. Chem. Phys. 2, 714 (1934).

model spectrum of each molecule and the lowest line in the corresponding Raman spectrum.

The X, Y and W frequencies lying just to the right of the boundary also show some correlation between the two figures. As may be seen from Figs. 3–10, the X and W frequencies are associated with motions of the chlorine atoms bending the C – Cl bonds, in the plane of the ring for the X motion and perpendicular to the plane for the W motion. The Y motion takes place in the plane of the ring along the line of the C – Cl bond. In the case of C_6H_5Cl the correlation is quite good, if one neglects the two weak lines of zero intensity lying at 275 and 333 cm⁻¹ which were not found by Dadieu, Pongratz and Kohlrausch.[10] In the other compounds it is much less certain. Lines have been drawn in, however, to indicate a few of the possible series relations in the Raman spectra.

Proceeding up the scale of frequency in the model spectrum we meet next the motions of type A, in which there is a bending of the ring perpendicular to its plane. This is the motion of lowest frequency in benzene. It is a type of motion that may be expected to have a very weak line according to the selection rules. As yet we cannot positively identify this series in the Raman spectra, although the "halogen" lines are in about the right place for this type of motion.

There seems to be more evidence for the next higher series, the one originating in the J motion in benzene. As previously mentioned, this series is important because it gives a clue to the strength of the forces between carbon atoms lying *para* to each other in the ring. In passing from benzene to chlorobenzene in the models the J motion which has a multiplicity of two in benzene, breaks down into two types of motion, in one of which the axis of symmetry includes the chlorine atom, while in the other it does not. At the same time the E_1 motion loses its identity and becomes coupled with one of these J motions. This is indicated by the dotted line in Fig. 11. Although the classification throughout the remaining members of the series is rather difficult, one finds some basis in the shifts in this region for assigning the lines to the J motions.

With the exception of the H motions which have already been discussed, there do not appear to be any other significant relations between the
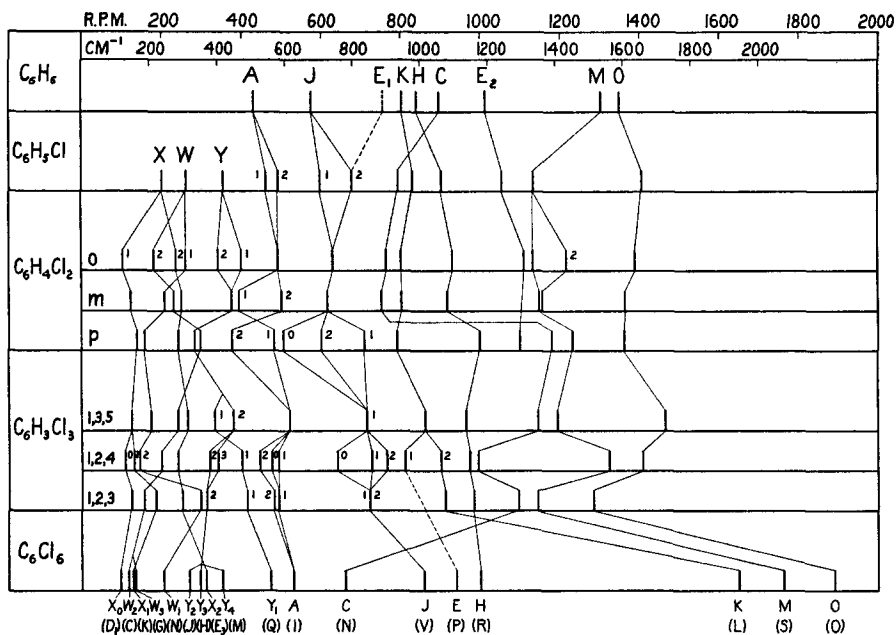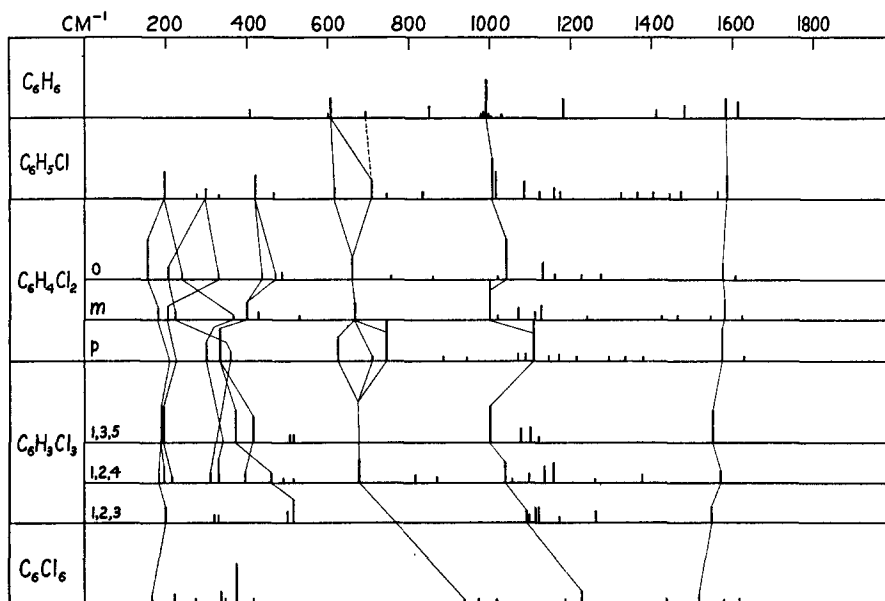
FIG. 11. Model frequencies.

FIG. 12. Raman spectra.

models and the Raman spectra. The only lines in the spectra which appear to form a series are those lying beneath the 1600 cm^{-1} doublet in benzene. These lines form a kind of upper limit to the so-called "ring" region of the Raman spectrum. The O-series of model frequencies also forms the upper limit for the mechanical spectrum but the shifts in the two series are not at all the same. It will undoubtedly be necessary to have a very detailed knowledge of the ring forces and of the bending forces for the $C-H$ bond before this region of the spectrum can be interpreted.

In closing we wish to call attention to the relation which the types of motion in C_6Cl_6 bear to the motions in C_6H_6. From the point of view of symmetry these two compounds are identical. Mechanically they differ in that benzene has the heavier of its two kinds of atoms in the ring while in C_6Cl_6 the substituent atoms are the heavier. We thus find two sets of relations between the motions in C_6Cl_6 and those in benzene. For example, the II motion, when traced through the series, ends up in a motion which generically speaking should be labeled "II," but is actually mechanically identical with the R motion in benzene. These two sets of relations are indicated by placing the generic symbol directly below the line in Fig. 11 while the symbol indicating the true mechanical counterpart of the motion in benzene is placed in parenthesis.

Because of these relations the motions in C_6Cl_6 may be compared with the motions deduced by E. Bright Wilson, Jr., for this symmetry class.[13] A diagram showing the character of these motions has been included in the preceding article of this series.[1] A comparison of these with the motions observed in C_6Cl_6 shows that in this model many of the predictions from group theory are confirmed.

[13] E. Bright Wilson, Jr., Phys. Rev. **45**, 707 (1934).

Finally let us sum up the evidence from these studies for or against the various formulas for benzene. The general agreement of the mechanical and Raman spectra indicates that the six carbon atoms in benzene are arranged in a flat ring and not in some other form such as a prism. The agreement of the positions and shifts of the J frequencies with the Raman spectra in the 600 cm^{-1} region indicates that there are no effective forces acting between carbon atoms para to one another in the ring, and is therefore evidence against the centric formula.

The 992 cm^{-1} series in the Raman spectra is identified with the II type of motion, from the shifts in the series of halogenated compounds and in deuterio-benzene. From this identification it is possible to calculate the average force constant of the $C-C$ bond in the ring, obtaining a value of 7.55×10^5 dynes cm^{-1}, roughly one and one-half times the average value for the normal homopolar single bond. These facts are in accord with the resonance formula of Pauling or with the Kekulé formula.

The lack of extra lines in the Raman spectrum of the ortho-disubstituted compounds as compared with the para and meta is evidence that there are no isomers of the type to be expected on the basis of the stable Kekulé formula. One must conclude that, if molecules of the Kekulé formula exist, the transformation between the two isomeric forms is rapid compared with the frequency of 1000 cm^{-1}. It must be so rapid that the force effective in vibration of the ring is evenly distributed around the ring, so that the result is really the Pauling formula. The weight of evidence therefore seems to be in favor of the Pauling resonance formula for benzene.