286. *Force Constants and Molecular Structure. Part V. The Relation between Force Constant and Bond Length.*

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The results of earlier calculations are collated with a view to examining the relationship between force constant and bond length for the linkages C–O, C–C, and C–H. In particular, the results are used to test the empirical relationships recently suggested by Badger and by Clark, which relate the force constant to the bond length. In the case of all three bond types, both sets of formulæ fit the data fairly well, but minor corrections are apparently necessary. The constants involved in each of the empirical equations are calculated. The results suggest the possibility of calculating bond lengths in some cases at least as accurately as they can be measured by the method of electron diffraction.

ATTEMPTS to obtain a relationship between the force constant of a linkage and its length have been made by several workers, notably by Badger (*J. Chem. Physics*, 1934, **2**, 128; 1935, **3**, 710), and by Clark (*Phil. Mag.*, 1935, **19**, 476; 1936, **22**, 1137). Badger found that the relationship $r_e = (C_{ij}/k_e)^{1/3} + d_{ij}$, whilst primarily designed for use with diatomic molecules (in all electronic states), could be applied with some success to the bonds in polyatomic molecules. In this relationship r_e is the bond length, and k_e the force constant; C_{ij} is a quantity which is almost constant, but varies slightly with different bonds according to the nature of the atom-pair forming the bond; d_{ij} is a quantity which varies more markedly for different bonds and depends on the position of the component atoms in the Periodic Table. Clark's formula, which was for use with frequencies, can be written so as to involve the force constant, in the form $k_e r_e^6 = 5{\cdot}863 \times 10^{-2} K^2 \mu/n$, in which μ is the reduced mass of the two nuclei forming the link, and n and K are quantities determined by the special type of link. Clark has attempted to make allowances for the specific factors involved in each particular link, *e.g.*, *ss* or *pp* binding, etc., these factors not being controlled in Badger's expression. Clark's relationship appears to be rather more satisfactory than Badger's for certain diatomic molecules, but has not so far been carried over to the case of polyatomic molecules.

In Part IV (preceding paper) and in Part VI (following paper) we have calculated the force constants of linkages in a series of polyatomic molecules. The resulting data make it possible to test the applicability of the above relations with respect to the bonds C–O, C–H, and C–C.

(i) *The Carbon–Oxygen Bond.*—Table I summarises the relevant data on this case, values of r_e being in A. The figures for carbon monoxide are due to Sponer ("Molekulspektren," Vol. I, pp. 32, 33). The force constants for the remaining molecules are those found in the

other papers of this series. The link lengths for keten and for carbon suboxide are given by Brockway (*Rev. Mod. Physics,* 1936, **8**, 261); those of carbon dioxide are the spectroscopic values; and that for formaldehyde is obtained from the measured moments of inertia by the considerations given in Part III.

TABLE I.

Molecule.	$k_e \times 10^{-6}$, dynes/cm.	$(1/k_e)^{1/3}$.	r_e, obs.	r_e, calc., Badger.	$(k_e)^{1/6} r_e$.	$(1/k_e)^{1/6}$	r_e, calc., Clark.
CO $^1\Pi^+$	1·891	0·81	1·13	1·143	1·257	0·899	1·122
CO $^1\Sigma$	1·915	0·805	1·12	1·141	1·248	0·897	1·119
CO $^3\Sigma$	1·971	0·798	1·14	1·137	1·276	0·893	1·114
CO $^1\Pi$	0·923	1·026	1·232	1·266	1·216	1·0135	1·264
CO $^3\Pi$	1·217	0·939	1·205	1·216	1·245	0·968	1·207
CH$_2$O	1·23	0·933	(1·197)	1·213	1·239	0·966	1·204
CH$_2$·CO	1·23	0·933	—	1·213	—	0·966	1·204
CO$_2$	1·524	0·868	1·16	1·176	1·245	0·932	1·162
C$_3$O$_2$	1·415	0·89	1·20 ± 0·02	1·188	1·271	0·944	1·177

For the C–O bond we should have, according to Badger, $r_e = 0·571/k_e^{1/3} + 0·680$ in which r_e is expressed in A. units and k_e is in the units 10^6 dynes/cm., *i.e.*, $C_{ij} = 0·1861$ and $d_{ij} = 0·680$. In Fig. 1 $(1/k_e)^{1/3}$ is plotted against r_e. It is seen that a fairly satisfactory
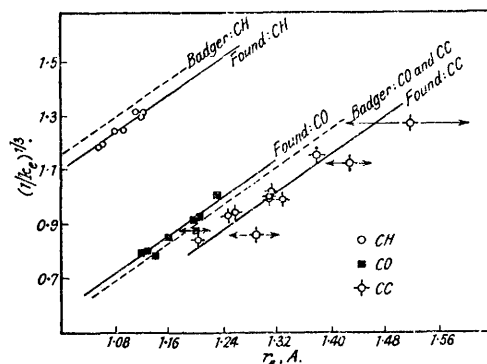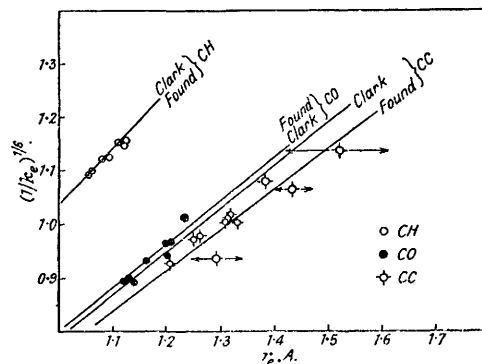

FIG. 1.

FIG. 2.

straight line can be drawn through the points, but this line does not coincide with that represented by Badger's equation; however, the slope of both lines is roughly the same. Assuming the slopes to be identical, we obtain for d_{ij} the value 0·667. This difference is well within the possible errors of Badger's empirical quantities.

According to Clark, for the C–O bond with pp binding, $n = 10$, $\mu = 48/7$, and $K = 9680$, so that $r_e k_e^{1/6} = 1·247$ in the same units as above. To test this relationship, in Fig. 2 r_e is plotted against $(1/k_e)^{1/6}$. Clark's equation actually represents the most satisfactory line that could be drawn through the points, if it were to pass through the origin. The values of $k_e^{1/6} r_e$ given in Table I are seen to agree well with the equation, the mean value for all the points being 1·250.

If the force constants are assumed, and distances calculated, it is found that Clark's method gives remarkably good results, which are better than those obtained from the Badger relationship. Better results would of course be obtained with the latter if the value of d_{ij} found, *viz.*, 0·667, were taken.

(ii) *The Carbon–Hydrogen Bond.*—Table II summarises the data for the carbon–hydrogen bonds, r_e being given in A. The figures for the CH molecule are taken from Sponer (*op. cit.*, pp. 26, 27). The force constants for the other molecules are as found in the other papers of this series. The link length for methane is that given by Ginsburg and Barker (*J. Chem. Physics,* 1935, **3**, 668), that for hydrogen cyanide by Bartunek and Barker (*Physical Rev.,* 1935, **48**, 516), that for acetylene by Herzberg, Patat, and Spinks (*Z. Physik,* 1934, **92**, 87), and for the other molecules the lengths are given in the other papers of this series.

TABLE II.

Molecule.	$k_e \times 10^{-6}$, dynes/cm.	$(1/k_e)^{1/3}$.	r_e, obs.	r_e, calc., Badger.	$(k_e)^{1/6}r_e$.	$(1/k_e)^{1/6}$.	r_e, calc., Clark.
CH $^2\Pi$	0·442	1·313	1·12	1·084	0·977	1·146	1·108
CH $^2\Delta$	0·424	1·331	1·11	1·095	0·961	1·154	1·116
CH$_4$	0·498	1·261	1·093	1·055	0·974	1·123	1·086
C$_2$H$_2$	0·58	1·199	1·058	1·02	0·965	1·095	1·058
C$_2$H$_4$	0·502	1·258	1·08	1·053	0·962	1·122	1·085
CH$_2$O	0·43	1·325	(1·122)	1·091	0·971	1·151	1·113
HCN	0·57	1·206	1·06	1·059	0·965	1·098	1·062

According to Badger we should have $r_e = 0.571/k_e^{1/3} + 0.335$, *i.e.*, $C_{ij} = 0.1861$ and $d_{ij} = 0.335$. In Fig. 1 $1/k_e^{1/3}$ is plotted against r_e. It is seen that a fairly satisfactory straight line can be drawn through the points, but as in the case of the carbon–oxygen bond, the line is again not coincident with that represented by Badger's equation. As far as can be seen, the slopes are the same, and the facts can be interpreted satisfactorily by supposing that d_{ij} has the value 0·303. For the light atoms Badger's values of d_{ij} are somewhat unsatisfactory and the difference found is not at all unreasonable. For a bond M–H, M being an atom of the first short period of the Periodic Table, Clark gives 8050. It is clear that this value must vary slightly for the different atoms in the period, but he makes no allowance for this. If we plot (Fig. 2) $(1/k_e)^{1/6}$ against r_e, the points lie on a fairly good straight line. If we now take the mean of the calculated values of the product $k_e^{1/6}r_e$ (0·9665) and use the relationship $k_e^{1/6}r_e = 0.9665$ to plot the line $1/k_e^{1/6}$ against r_e, it is seen that this line (which it must be remembered passes through the origin) is as nearly as could have been drawn coincident with the best line through the experimental points. The value of K deduced is 8680.

As in the case of the carbon–oxygen bond, calculation of the distances from the force constants is more satisfactory with Clark's relation than with Badger's, although again of course Badger's relationship would be more satisfactory with the modified value of d_{ij}. It should be noted, too, that the form of Clark's equation used here was determined for this special case.

(iii) *The Carbon–Carbon Bond.*—Table III summarises the relevant data for this case. The figures for the diatomic molecules are taken from Sponer. The force constants of the link in the remaining molecules are those found in the papers of this series. The link length in ethylene is that taken by Penney (*Proc. Roy. Soc.*, 1937, **158**, *A*, 306), in allene, cyanogen, carbon suboxide, and tetrachloroethylene from Brockway (*loc. cit.*), and in acetylene from the data of Herzberg, Patat, and Spinks (*loc. cit.*). The bond length in ethane is that quoted by Brockway, but it will be seen that the limits of error claimed are large.

TABLE III.

Molecule.	$k_e \times 10^{-6}$, dynes/cm.	$(1/k_e)^{1/3}$.	r_e, obs.	r_e, calc., Badger.	$(k_e)^{1/6}r_e$.	$(1/k_e)^{1/6}$.	r_e, calc., Clark.
C$_2$ $^3\Pi_u$	0·948	1·018	1·31	1·26	1·321	1·009	1·32
C$_2$ $^1\Pi_u$	0·910	1·032	1·315	1·27	1·335	1·016	1·328
C$_2$ $^3\Pi_g$	1·13	0·960	1·26	1·23	1·235	0·980	1·284
C$_2$ $^1\Pi_g$	1·181	0·946	1·25	1·22	1·217	0·9725	1·275
C$_2$H$_4$	0·98	1·007	1·33	1·255	1·334	1·003	1·31
C$_2$H$_6$	0·46 *	1·295	1·52 ± 0·1	1·42	?	1·138	1·49
CH$_2$:C:CH$_2$	0·973	1·010	1·31 ± 0·05	1·255	1·313	1·005	1·315
C$_3$O$_2$	1·487	0·876	1·29 ± 0·03	1·185	1·207	0·936	1·23
C$_2$H$_2$	1·58	0·858	1·205	1·18	1·116	0·9265	1·217
C$_2$Cl$_4$	0·62	1·173	1·38	1·35	1·492	1·083	1·417
C$_2$N$_2$	0·669	1·143	1·43 ± 0·03	1·335	1·529	1·069	1·40

* Mean value.

For this bond, we should have, taking Badger's figures, $r_e = 0.571/k_e^{1/3} + 0.680$, *i.e.*, $C_{ij} = 0.1861$ and $d_{ij} = 0.680$. In Fig. 1, it is seen that although a fairly satisfactory line can be drawn through the points, this line again does not coincide with that to be expected from Badger's equation. Again, it is seen that the slope of the lines is roughly the same, and assuming the slopes to be identical, we obtain for d_{ij} the value 0·735. The difference is well within the possible errors in Badger's quantities.

According to Clark, for the carbon–carbon bond with pp binding, $n = 8$, $\mu = 6$, and $K = 9680$. Then $r_e k_e^{1/6} = 1\cdot266$. The line obtained from this equation by plotting $(1/k_e)^{1/6}$ against r_e, does not pass satisfactorily through the points shown in Fig. 2. Taking the mean value of $k_e^{1/6}r_e$ from Table III to be $1\cdot31$, and assuming the equation $k_e^{1/6}r_e = 1\cdot31$, we see that in addition to passing through the origin this line passes satisfactorily through the points. This result would imply a value of K of 10,800.

As in the previous cases, the distances obtained from the force constants by using Clark's relation are more in accord with the observed values than are those obtained from Badger's equation.

<div align="center">DISCUSSION.</div>

It is seen in each of the above cases that the formulæ of Badger and of Clark can be carried over with fair success to a consideration of bonds in polyatomic molecules. If it were possible to obtain linkages of the atom-pairs with more widely differing force constants, as in the case of the diatomic molecules used by Badger, the agreement might appear very close. When applied to Badger's relationship, however, the results clearly indicate the specific nature of d_{ij}, and this quantity would appear to require more detailed specification than so far given by Badger, who makes no allowance for the peculiar nature of the atoms involved, apart from their horizontal row in the Periodic Table. In so far as the calculation of the distances from the force constants is concerned, Clark's method is strikingly successful. It seems indeed possible that this may in many cases provide a means of determining a bond length more accurately than is allowed by measurements of electron diffraction. This is especially the case with lighter atoms which are less suitable in diffraction work.

It is interesting to notice how this has been applied in the study of the vibrations of formaldehyde in the previous paper. In order to calculate the bond lengths from the measured moments of inertia, it is necessary to assume θ, the $\widehat{\text{HCH}}$ angle. The value assumed for θ gives bond lengths (for both C–H and C–O) which are related to the force constants in such a way as to agree closely with either of the above relationships. This is a separate justification for the assumption of the particular value of θ.

The figures for carbon suboxide are not entirely satisfactory, particularly as regards the C–C bond. This may arise from uncertain values of the bond lengths found by electron-diffraction measurements, although reference to a previous paper will show that minor errors in the values of the force constants may arise from lack of certain knowledge of the interaction terms of the potential function.

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