

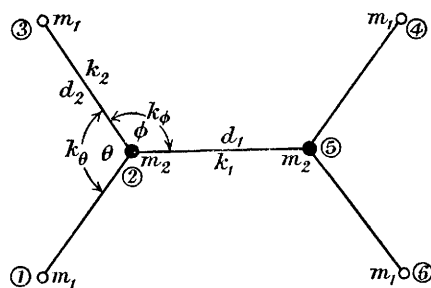
### 285. Force Constants and Molecular Structure. Part IV. Ethylene and Tetrachloroethylene.

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With a view to comparison with the corresponding data for ethylene, which have been previously determined, the force constants of the linkages in tetrachloroethylene are calculated from the normal vibration frequencies, a simple but apparently adequate potential function being used. The C-C link force constant in tetrachloroethylene appears to have a value between the normal values for a single and a double bond, and there are indications that the molecule is a resonance hybrid. The form of the vibrations is discussed.

In Part II of this series (this vol., p. 1376) we have determined the force constants of the linkages in ethylene, and in Parts I and III (this vol., pp. 1291 and 1384) we have shown how variations of force constants can be related to problems of molecular structure. In the present paper the relationships with tetrachloroethylene are examined, and a comparison is made between the force constants of the C-C bond in ethylene and tetrachloroethylene. A preliminary note on these data has already been published (*Nature*, 1937, 139, 509). The figures then given are here slightly amended as a result of small improvements in the mathematical treatment.

1. *Molecular Form and Assignment of Vibration Frequencies.*—Suppose the masses of



carbon are  $m_2$  and of chlorine  $m_1$ , and let the angles  $\widehat{\text{C}}\widehat{\text{C}}\widehat{\text{C}}\text{Cl}$  and  $\widehat{\text{C}}\widehat{\text{C}}\widehat{\text{C}}$  be  $\theta$  and  $\phi$  respectively. Let the C-C and C-Cl bond lengths be  $d_1$  and  $d_2$ , and the force constants of these links for stretching  $k_1$  and  $k_2$ . This nomenclature is the same as previously used for ethylene (see figure).

Electron-diffraction measurements have been made by Brockway, Beach, and Pauling (*J. Chem. Physics*, 1935, 57, 2693), and by de Laszlo (*Nature*, 1935, 135, 474). It is found that the shape of the molecule is determined by  $\phi = 123^\circ 45'$ , *i.e.*,  $\theta = 112^\circ 30'$ ,  $d_1 = 1.38 \text{ \AA}$ ., and  $d_2 = 1.73 \pm 0.02 \text{ \AA}$ . The moments of inertia are too large for spectral determination, and the figures just given will therefore be taken.

Measurements of both the Raman spectrum and the infra-red spectrum have been described. The data on the Raman spectrum are summarised in Landolt-Börnstein (*Ergänzungsband*, pp. 992, 995), the values for the shifts being 1569(6), 509(2), 445(6), 345(3), 236(5). The infra-red spectrum was analysed by Ta-You Wu (*Physical Rev.*, 1934, 46,

465), who found bands at 913 (strong), 802 (strong), 782 (strong), 755 (medium). As in the case of ethylene, the nine planar vibrations of the molecule fall into four symmetry groups. Class A contains the three totally symmetric oscillations  $\nu_1, \nu_2, \nu_3$ ; class B contains two vibrations ( $\nu_4, \nu_5$ ) symmetric to the  $x-x$  plane and antisymmetric to the  $y-y$  plane. The three totally symmetric frequencies will be intense in the Raman effect. They can therefore be assigned to 1569 ( $\nu_1$ ), 445 ( $\nu_2$ ), and 236 ( $\nu_3$ ). The assignment of the other frequencies is less certain. The class B frequencies should be found as fundamentals in the infra-red, and it seems probable that  $\nu_4 = 913$ . This assignment of  $\nu_1, \nu_2, \nu_3, \nu_4$  agrees with that suggested by Ta-You Wu and by Duchesne (*Nature*, 1937, **139**, 288). It is likely that the frequency  $\nu_5$  occurs in a region of the infra-red not yet explored, and the value taken for it is 345. Reasons for choosing this weak Raman frequency will be explained below. That the frequency  $\nu_5 = 345$  should appear feebly in the Raman effect is perhaps understandable, since the measurements were made with liquid tetrachloroethylene.

2. *Calculation of the Force Constants.*—In the light of previous work by Urey and Bradley (*Physical Rev.*, 1931, **38**, 1969), Rosenthal (*ibid.*, 1934, **46**, 730), and others (see Sutherland, *Ann. Reports*, 1936, **33**, 59) on carbon tetrachloride and similar halogenated compounds, we should not expect the vibrations of tetrachloroethylene to comply at all closely with a potential function of the form of simple valency force field. The data confirm this supposition, and we have to explore the nature of the cross terms necessary to interpret the results satisfactorily. As with ethylene we must also, if possible, be able to account for the special importance of the particular cross terms used.

For any molecule of the ethylene type, it was shown in the previous paper that a potential function which involves no interaction between the two methylene groups, or between one methylene group and the C-C bond, leads to a relation between the frequencies  $\nu_1, \nu_2, \nu_3, \nu_4, \nu_5$  of the form

$$\nu_4^2 + \nu_5^2 + \frac{m_2 + 2m_1}{m_2} \cdot \frac{\nu_1^2 \nu_2^2 \nu_3^2}{\nu_4^2 \nu_5^2} = \nu_1^2 + \nu_2^2 + \nu_3^2$$

This relationship was derived earlier by Mecke (*Z. physikal. Chem.*, 1932, **17**, B, 1), and by Sutherland and Dennison (*Proc. Roy. Soc.*, 1935, **148**, A, 250), whose method was more general. If we insert the values  $\nu_1 = 1569$ ,  $\nu_2 = 445$ ,  $\nu_3 = 236$ ,  $\nu_4 = 913$ , and  $\nu_5 = 345$ , the left-hand side almost exactly balances the right. This is, in part, a justification for the assignment of  $\nu_5$  to 345. That such close agreement is found indicates that the potential function desired need not at any rate involve interaction terms between the opposite  $\text{CCl}_2$  groups or between one of these and the C-C bond. In the case of ethylene the magnitudes of the frequencies suggested a possible interaction between  $\nu_2$  and  $\nu_3$ . This clearly does not arise in the present case. On the other hand, the nature of the large chlorine atoms suggests the possibility of three types of interaction term,  $k\Delta_{12}\Delta\theta$ ,  $k\Delta_{12}\Delta_{23}$ , and  $k\Delta\phi_1\Delta\phi_2$ . The first of these can be imagined as arising from the fact that when the link 1,2 is compressed, the approach of the two chlorine atoms may result in a widening of the  $\widehat{\text{ClCCl}}$  angle. Alternatively, a decrease in  $\theta$  might lengthen the C-Cl bonds. In the same way for the second cross term a decrease in the link length 1,2 might bring about an increase in the length 2,3. Again, expansion of  $\phi_1$  might result in a compression of  $\phi_2$  giving the third cross term.

We shall therefore assume a potential function of the form

$$2V = k_1\Delta_{25}^2 + 4k_2\Delta_{12}^2 + 2k_0\Delta\theta^2 + 4k_\phi\Delta\phi^2 + 2k_3\Delta_{12}\Delta_{23} + 2k_\mu\Delta_{12}\Delta\theta + 2k_4\Delta\phi_1\Delta\phi_2.$$

For the totally symmetric oscillations this reduces to

$$2V = 4k_a\Delta_{12}^2 + k_b\Delta_{25}^2 + 4k_c\Delta\phi^2 + 2k_d\Delta_{12}\Delta\theta$$

in which  $k_a = (k_2 + \frac{1}{2}k_3)$ ;  $k_b = k_1$ ;  $k_c = (2k_0 + k_\phi) + \frac{1}{2}k_4$ , and  $k_d = k_\mu$ .

Thus the number of independent constants is reduced to four. The equations for the three totally symmetric frequencies are then

$$\nu_1^2 + \nu_2^2 + \nu_3^2 = k_a \left[ P \right] + k_b \left[ Q \right] + \frac{k_c}{d_2^2} \left[ R \right] + \frac{k_d}{d_2} \left[ S \right]$$

$$\nu_1^2\nu_2^2 + \nu_2^2\nu_3^2 + \nu_1^2\nu_3^2 = k_a k_b \left[ \frac{Q}{m_1} \right] + \frac{k_b k_c}{d_2^2} \left[ \frac{Q}{m_1} \right] + \frac{k_a k_c}{d_2^2} [T] - \frac{k_d^2}{d_2^2} \left[ \frac{T}{4} \right]$$

$$\nu_1^2\nu_2^2\nu_3^2 = \frac{k_a k_b k_c}{d_2^2} \left[ \frac{Q}{m_1^2} \right] - \frac{k_b k_d^2}{d_2^2} \left[ \frac{Q}{4m_1^2} \right]$$

in which  $P = \left[ \frac{1}{m_1} + \frac{2 \cos^2 \frac{1}{2} \theta}{m_2} \right]$ ,  $Q = \left[ \frac{2}{m_2} \right]$ ,  $R = \left[ \frac{1}{m_1} + \frac{2 \sin^2 \frac{1}{2} \theta}{m_2} \right]$ ,

$$S = \left[ \frac{2 \sin \frac{1}{2} \theta \cos \frac{1}{2} \theta}{m_2} \right], \quad T = \frac{1}{m_1} \left\{ \frac{1}{m_1} + \frac{2}{m_2} \right\}$$

Using the same potential function, for the pair of class B frequencies, *i.e.*, symmetric to the  $x$ - $x$  axis, we find

$$\nu_4^2 + \nu_5^2 = k_a P + \frac{k_c}{d_2^2} R + \frac{k_d}{d_2} S$$

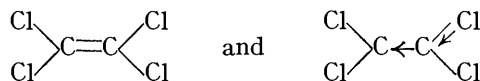
$$\nu_4^2\nu_5^2 = \frac{k_a k_c}{d_2^2} T - \frac{k_d^2}{d_2^2} \frac{T}{4}$$

With the values  $k_a = 4.9 \times 10^5$ ,  $k_b = 6.188 \times 10^5$ ,  $k_c = 3.891 \times 10^{11}$ ,  $k_d = -0.33 \times 10^{-3}$ , the frequencies calculated are  $\nu_1 = 1571$ ,  $\nu_2 = 443$ ,  $\nu_3 = 231$ ,  $\nu_4 = 915$ ,  $\nu_5 = 347$ , the errors being +2, -2, -5, +2, +2. The approximate relative amplitudes of the nuclei in the different vibrations are given below.

Totally symmetric.	$\nu$ .	$x_1$ .	$x_2$ .	$y_1$ .				
$x_1 = -x_6 = -x_4 = x_3$	1571	+1.0	-24.5	+0.90				
$y_1 = y_6 = -y_3 = -y_4$					443	+1.0	+0.65	+1.95
$x_2 = -x_5; y_2 = y_5 = 0$					231	+1.0	+0.2	-0.47
Class [B]								
$x_1 = x_6 = x_3 = x_4$	915	+1.0	-5.83	+0.86				
$y_1 = y_4 = -y_3 = -y_6$					347	+1.0	-5.83	-8.3
$x_2 = x_5; y_2 = y_5 = 0$								

#### DISCUSSION.

The potential function used above must be regarded as satisfactory, since with four independent constants it reproduces five frequencies very well. The main point of the calculation was to obtain a value for the force constant of the C-C bond in tetrachloroethylene, and to compare the value with that found for ethylene. The result shows that in tetrachloroethylene there is a marked fall in this constant ( $9.8$  to  $6.2 \times 10^5$ ). Using a different potential function, Duchesne has recently also arrived at this conclusion. It suggests that the molecule is a hybrid structure, formed from such possible types as



The value of the force constant of a carbon-carbon single bond is about  $4.5 \times 10^5$ . On the other hand, as pointed out by Badger (*J. Chem. Physics*, 1934, **2**, 128; 1935, **3**, 710), the mutual repulsion of the halogen atoms in a molecule of this type may result in a stretching of the linkages in the molecule.\* This may to some extent be involved in the case of tetrachloroethylene, but we do not regard it as entirely responsible for the effect observed. It is interesting to notice that the decrease in the C-C bond constant in tetrachloroethylene goes parallel with an increase in the bond length. In ethylene  $r_e = 1.33$  A. and in tetrachloroethylene, the electron-diffraction measurements give  $r_e = 1.38$  A. Reference is made to this in the following paper. Assuming simple valency force field to apply to carbon tetrachloride, we find  $k_{\text{CCl}} = 4.38 \times 10^5$ . That this value is not, however, satisfactory has been shown by Rosenthal (*Physical Rev.*, 1934, **46**, 730), since a complex potential function is really necessary. The value given by Sutherland (*loc. cit.*, p. 64) for  $k_{\text{CCl}}$  is

\* Our attention was drawn to this point by Dr. G. B. B. M. Sutherland.

$3.5 \times 10^5$ . Thus it seems that in tetrachloroethylene the value for  $k_{\text{CCl}}$  is really greater than that of a normal single bond. Electron-diffraction measurements of the distance tend to confirm this conclusion.

It will be noticed that the constant for the bending of the  $\widehat{\text{ClCCl}}$  angle in tetrachloroethylene is rather higher than the value usually found for such a constant. This may be connected with the large nature of the chlorine atoms. It should also be mentioned that the results found in the previous paper suggest that if tetrachloroethylene is really a resonance hybrid, we might then expect cross interaction terms of the form  $k\Delta_{\text{CCl}}\Delta_{\text{CC}}$ . Actually, adequate agreement is obtained without them.

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