287. *Force Constants and Molecular Structure. Part VI. Compounds containing the Cyanide Link.*

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The force constant of the C–N link in a series of molecules and ions is calculated from the known vibration frequencies, each case being examined separately. The results show that the molecule of cyanogen exhibits well-defined mesomerism, and this may also apply to the cyanogen halides. The thiocyanate ion may be regarded either as a resonance structure or as a structure involving links of $1\frac{1}{2}$ or $2\frac{1}{2}$ units respectively. The relationships between force constant and bond length are discussed.

In continuation of the previous papers of this series, we have calculated the force constants of the linkages in some linear polyatomic molecules each containing the carbon–nitrogen bond. Owing to the increased complications in the consideration of these molecules com-

pared with those previously studied, we have considered for the present only linear " parallel " vibrations, in order to exclude the force constants for the bending of angles and other related factors. Despite these simplifications, lack of experimental data and also in some cases the nature of the specific problems themselves frequently introduce ambiguities into the cases examined, but as shown below, it may be possible, as in the earlier cases, by a consideration of a related series of molecules to decide between two or more possible solutions in any given case.

(i) *The* CN *Diatomic Molecule.*—Regarding the molecule as m_1m_2 with a force constant k, we have $\nu^2 = k\{1/m_1 + 1/m_2\}$. Taking the data from Sponer (" Molekülspektren," pp. 38, 39) for three states, we obtain the results of Table I.

TABLE I

State.	ν.	$k \times 10^{-5}$, dynes/cm.	r, A.
$^2\Sigma^+$	2164	17·74	1·148
$^2\Pi$	1789	12·11	1·236
$^2\Sigma^+$	2069	16·21	1·169

(ii) *The Cyanide Ion.*—Taking the Raman frequencies for alkali cyanides (Kohlrausch, " Der Smekal–Raman Effekt," p. 321), we find $\bar{\nu} = 2085$. This gives, as in (i), $k = 16{\cdot}38 \times 10^5$.

(iii) *Hydrogen Cyanide and Deuterium Cyanide.*—There are two parallel frequencies of each of these molecules $m_1m_2m_3$. Unfortunately, as shown by the calculations of Penney and Sutherland (*Proc. Roy. Soc.*, 1936, **156**, *A*, 654), it may be necessary to introduce an interaction term into the potential function. Writing

$$2V = k_1\Delta_{12}^2 + k_2\Delta_{23}^2 + k_3\Delta_{12}\Delta_{23}$$

we find

$$\nu_1^2 + \nu_2^2 = k_1\{1/m_1 + 1/m_2\} + k_2\{1/m_2 + 1/m_3\} - k_3\{1/m_2\}$$

$$\nu_1^2\nu_2^2 = k_1k_2\{(m_1 + m_2 + m_3)/m_1m_2m_3\} - \tfrac{1}{4}k_3^2\{(m_1 + m_2 + m_3)/m_1m_2m_3\}$$

Thus for hydrogen cyanide, there are three independent constants but only two frequencies. We can, however, take a third frequency from the isotopic molecule deuterium cyanide, and solve for the constants, assuming the cross-term constant to be the same in each case. Taking the data of Bartunek and Barker (*Physical Rev.*, 1935, **48**, 516) for hydrogen cyanide, we have $\nu_1 = 3313$, $\nu_2 = 2089$, and for deuterium cyanide $\nu_1 = 2630$. From these we find $k_{CN} = 18{\cdot}10 \times 10^5$, $k_{CH} = 5{\cdot}665 \times 10^5$, and $k_3 = -0{\cdot}65 \times 10^5$. For the bond lengths we have $r_{CN} = 1{\cdot}15$ and $r_{CH} = 1{\cdot}06$ A.

(iv) *Cyanogen.*—There are three linear vibrations of this molecule. Two are symmetrical, (ν_1, ν_2) and one is antisymmetrical (ν_3). The assignment and magnitudes are discussed by Sponer (*op. cit.*, p. 77) and by Mecke (" Hand- und Jahrbuch der Chem. Physik," Vol. 9, ii). We have $\nu_1 = 2335$, $\nu_2 = 860$, and $\nu_3 = 2150$.

If the masses 1, 2, 3, 4, are m_1, m_2, m_2, m_1, the force constants of the C–N and C–C bonds k_2 and k_1, and the cross-term constant k_3 (NCC),

$$2V = k_1\Delta_{23}^2 + k_2\Delta_{12}^2 + k_2\Delta_{34}^2 + k_3\Delta_{12}\Delta_{23} + k_3\Delta_{34}\Delta_{23}$$

and

$$\nu_1^2 + \nu_2^2 = k_2\{1/m_1 + 1/m_2\} + k_1\{2/m_2\} - k_3\{2/m_2\}$$

$$\nu_1^2\nu_2^2 = 2k_1k_2\{1/m_1m_2\} - k_3^2\{1/m_1m_2\}$$

$$\nu_3^2 = k_2\{1/m_1 + 1/m_2\}$$

We thus find $k_{CC} = 6{\cdot}69 \times 10^5$, $k_{CN} = 17{\cdot}51 \times 10^5$, and $k_{NCC} = 1{\cdot}17 \times 10^5$. The distances measured by electron diffraction are $r_{CC} = 1{\cdot}43 \pm 0{\cdot}03$ A. and r_{CN} $1{\cdot}16 \pm 0{\cdot}02$ A.

(v) *Cyanogen Halides.*—The vibration frequencies of the cyanogen halides have been considered by Penney and Sutherland (*loc. cit.*) and by West and Farnsworth (*J. Chem. Physics*, 1933, **1**, 402). Each of the molecules of the chloride, bromide, and iodide has two frequencies for linear vibration; for CNCl, $\nu_1 = 2201$, $\nu_2 = 729$; for CNBr, $\nu_1 = 2187$, $\bar{\nu}_2 = 580$; for CNI, $\bar{\nu}_1 = 2158$, $\bar{\nu}_2 = 470$. The potential above of simple valency force

field being assumed for this type of molecule, *i.e.*, with no cross term, the force constants can be calculated as in case (iii) above, with $k_3 = 0$. We find

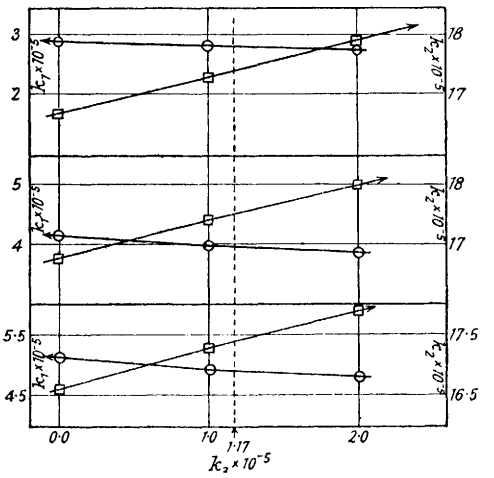
Molecule	NCCl	NCBr	NCI
$k_{CN} \times 10^{-5}$	16·65	16·81	16·75
$k_{CX} \times 10^{-5}$	5·15	4·17	2·94

These values have also been calculated by Penney and Sutherland and by West and Farnsworth, with results close to the values just given. It is clear, however, that we should make allowance for the relatively small interaction term in the potential function represented in (iii) by $k_3\Delta_{12}\Delta_{23}$. Unfortunately, we have no means of ascertaining with certainty the magnitude of k_3. We can proceed as follows. We assume successively values of $k_3 \times 10^{-5}$ of 0, + 1, + 2, and calculate k_1 and k_2. The results are summarised in Table II, and represented graphically in the figure.

TABLE II.

		Cyanogen chloride.	Cyanogen bromide.	Cyanogen iodide.
$k_3 = 0$	$k_1 \times 10^{-5}$	5·15	4·17	2·945
	k_2	16·65	16·81	16·75
$k_3 = 1 \times 10^5$	k_1	4·965	4·03	2·86
	k_2	17·33	17·45	17·33
$k_3 = 2 \times 10^5$	k_1	4·845	3·94	2·81
	k_2	17·92	18·04	17·91

In hydrogen cyanide the cross-term constant $k_3 = -0{\cdot}65 \times 10^5$. In cyanogen it is $+ 1{\cdot}17 \times 10^5$. *A priori* considerations would suggest that in the cyanogen halides the value of k_3 should be rather more like that in cyanogen. From the curves of the figure we notice that on putting $k_3 = 1{\cdot}17 \times 10^5$ as in cyanogen, the values of k_1 and k_2 are: for CNCl 4·94 and 17·43; for CNBr 4·01 and 17·55; for CNI 2·85 and 17·43; *i.e.*, the values of k_{CN} are in each case very close to the value in cyanogen. For this reason, as well as for others, it seems probable that k_3 really has the value *ca.* $1{\cdot}17 \times 10^5$.



(vi) *The Thiocyanate Ion.*—The frequencies of this ion were determined by Langseth, Nielsen, and Sørensen (*Z. physikal. Chem.*, 1934, **27**, *B*, 100), who give $\nu_1 = 750$, $\nu_2 = 2066$. Again we write a potential function involving k_{CS}, k_{CN}, and k_x, the cross-term constant. We then have three constants and only two frequencies. For different assumed values of k_x we find:

$k_x \times 10^{-5}$	−2	−1	0	+1	+2
k_{CS} ,,	5·86	5·60	5·33	5·09	4·93
k_{CN} ,,	12·89	13·61	14·36	15·08	15·73

It is certain that k_x lies between the limits + 2 and − 2, and probably it is positive. This means that k_{CS} must lie between the limits 5·9 and $4{\cdot}9 \times 10^5$, and k_{CN} between 12·9 and $15{\cdot}7 \times 10^5$. In carbon disulphide and carbonyl sulphide, according to Penney and Sutherland (*loc. cit.*), $k_{CS} = 7{\cdot}6$ and $8{\cdot}0 \times 10^5$, corresponding to the C–S double link. According to Sidgwick ("The Covalent Link," p. 123) the value of k_{CS} in methylthiol is $3{\cdot}01 \times 10^5$ (single C–S link). Thus the value of k_{CS} in the thiocyanate ion for any plausible value of the cross term k_x will be intermediate between those for a single and a double bond. In the same way the value of k_{CN} is higher than would be expected for a double bond and lower than would apply to a triple bond. This is discussed further below.

(vii) *Mercuric Cyanide and the Argentocyanide Ion*, $Ag(CN)_2^-$.—Taking these structures to be $m_1m_2m_3m_2m_1$ and numbering the atoms 1, 2, 3, 4, 5, we can write in general

$$2V = k_2\Delta_{12}^2 + k_2\Delta_{45}^2 + k_1\Delta_{23}^2 + k_1\Delta_{34}^2 + k_3\Delta_{12}\Delta_{23} + k_3\Delta_{34}\Delta_{45} + k_4\Delta_{23}\Delta_{34}$$

The two symmetric frequencies are then given by

$$\nu_1^2 + \nu_2^2 = k_2\{1/m_1 + 1/m_2\} + (k_1 + \tfrac{1}{2}k_4)\{1/m_2\} - k_3\{1/m_2\}$$

$$\nu_1^2\nu_2^2 = k_2\{k_1 + \tfrac{1}{2}k_4\}\{1/m_1m_2\} - \tfrac{1}{4}k_3^2\{1/m_1m_2\}.$$

Since only the two symmetrical frequencies are known, we need only consider this pair. Again, there are here three independent constants with only two frequencies. For mercuric cyanide $\nu_1 = 260$, $\nu_2 = 2197$, and for the argentocyanide ion $\nu_1 = 239$ and $\nu_2 = 2130$ (Kohlrausch, " Der Smekal–Raman Effekt," p. 321). By assuming values of k_3 over a plausible range (-2 to $+2 \times 10^5$) the following values of the other constants are obtained :

$k_3 \times 10^{-5}$		$-2.$	$-1.$	0.	$+1.$	$+2.$
$Hg(CN)_2$	k_{HgC}	1·06	1·07	1·05	1·03	1·04
	k_{CN}	16·89	17·43	17·98	18·52	19·05
$[Ag(CN)_2]^-$	k_{AgC}	0·88	0·90	0·88	0·87	0·89
	k_{CN}	15·85	16·38	16·93	17·47	18·00

It is not possible to select a satisfactory value for k_3 on *a priori* grounds. If we choose $k_{CN} = 18{\cdot}1$, as in hydrogen cyanide, we should find for mercuric cyanide $k_{HgC} \cong 1{\cdot}2$ and $k_3 \cong +0{\cdot}2 \times 10^5$, and for the argentocyanide ion $k_{AgC} \cong 0{\cdot}89$ and $k_3 \cong +2{\cdot}2 \times 10^5$. The value of the cross-term constant in the latter ion seems very large. If we take k_{CN} as in cyanogen and in the cyanogen halides (17·5) we should obtain for mercuric cyanide $k_3 \cong -0{\cdot}9$ and for the argentocyanide ion $k_3 \sim +1{\cdot}05 \times 10^5$. The contrast between the last two cases may arise in some way either from the anomalous nature of the mercury atom, previously noticed, or from the ionic nature of the argentocyanide ion.

Discussion.

There seems little doubt that the " normal " value of the force constant of the C–N triple bond is *ca.* $18{\cdot}1 \times 10^5$. In cyanogen the value of k_{CN} is 17·51, *i.e.*, low. It is also seen that in cyanogen the value of the carbon–carbon force constant lies well intermediate between the values of a single carbon–carbon bond (*ca.* 4·5) and a double carbon–carbon bond (9·8) (previous paper). These facts suggest that cyanogen is a mesomeric structure, a fact which has already been suggested by measurements of the bond length.

The relationships are similar in the case of the cyanogen halides. The value of k_{CN} in each case is *ca.* $17{\cdot}5 \times 10^5$, and in the case of cyanogen chloride k_{CCl} ($4{\cdot}94 \times 10^5$) is noticeably higher than in the halogenated methanes, where its value is " normal." The structure of the cyanogen halides might then be written $N \leftarrow C \leftarrow X$. It should be pointed out that in calculating the value of $k_{C\,Hal.}$ in these compounds, values higher than the " normal " would be obtained for any plausible value of the cross-term constant.

The thiocyanate ion is also found to have values for the force constants which correspond to non-integral bonds. We could write two possible mesomeric structures : $[\bar{S} - C \equiv N]$ and $[S = C = \bar{N}]$.

Actually the structure of the ion may be a hybrid of these possibilities. On the other hand, in this molecule the facts could be explained equally well by the assumption of one single electronic structure $[\cdot\ddot{S}{:}C{:}\dot{N}\cdot]$, which implies the existence of bonds of $1\frac{1}{2}$ and $2\frac{1}{2}$ units.

Another point to which attention should be drawn is the result that in hydrogen cyanide the value of k_{CH} ($5{\cdot}66 \times 10^5$) is higher than that usually associated with a single C–H bond ($5{\cdot}0 \times 10^5$ in ethylene and methane). The result is parallel to that found with acetylene and deuteroacetylene, where the C–H bond force constant is *ca.* $5{\cdot}8 \times 10^5$. This variation in C–H force constants has been discussed in the previous paper.

In calculating the cross-term constant in the above molecules and in previous cases, data have been accumulated which reveal a possibly general rule regarding the magnitudes of these constants. With molecules showing the phenomenon of a hybrid structure, the value of the interaction constant seems to be positive and relatively large, whereas in the

case of simpler structures the values are small and may be positive or negative. A possible interpretation of this for the special case of carbon dioxide was referred to in Part III. In the present cases the peculiarity is again noticed.

It is possible to test the empirical equations of Badger (*J. Chem. Physics*, 1934, **2**, 128; 1935, **3**, 710) and of Clark (*Phil. Mag.*, 1934, **18**, 459; 1936, **22**, 1137) relating the force constant of the C–N link with its length. The data are summarised below, values of r being in A.

Molecule.	$k \times 10^{-6}$, dynes/cm.	r, obs.	$(1/k)^{1/3}$.	r, calc., Badger.	$(1/k)^{1/6}$.	$k^{1/6} . r$.	r, calc., Clark.
CN $^2\Sigma^+$	1·774	1·148	0·826	1·152	0·909	1·263	1·142
CN $^2\Pi$	1·211	1·236	0·938	1·216	0·969	1·276	1·218
CN $^2\Sigma^+$	1·621	1·169	0·851	1·166	0·923	1·267	1·160
HCN	1·810	1·15	0·821	1·149	0·906	1·270	1·138
C_2N_2	1·751	1·16 ± 0·02	0·830	1·154	0·911	1·273	1·145

Badger's equation would be written in the form $r_e = 0{\cdot}571/k_e^{1/3} + 0{\cdot}680$. This represents a straight line plot of $(1/k)^{1/3}$ against r_e. The data given are in fairly good agreement with this line, and the distances determined from the force constants are frequently close to the values found experimentally.

Clark's equation would be $k_e^{1/6} r_e = 1{\cdot}257$. This represents a straight line through the origin if $(1/k)^{1/6}$ is plotted against r_e, but the line does not pass through the points observed at all. On the other hand, if we write $k_e^{1/6} r_e = 1{\cdot}270$ (the mean observed value), a very adequate agreement is obtained. If, as in the previous paper, $k_e r_e^6 = 5{\cdot}863 \times 10^{-2} \times K^2\mu/n$, we have, since $n = 9$ and $\mu = 84/13$, $K = 9982$.

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