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Normal Coordinate Treatment and Force Constants of Alkanonitriles

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Force constants of the Urey-Bradley type are calculated for a series of alkanonitriles. The calculation covers the mononitriles: CH_3CN, CH_3CH_2CN, $(CH_3)_2CHCN$, $(CH_3)_3CCN$, and the dinitriles: $NCCH_2CN$, $NCCHDCN$, $NCCD_2CN$, *trans*-$NCCH_2CH_2CN$, *gauche*-$NCCH_2CH_2CN$. The results show that the force constants can be transferred from molecule to molecule as a group. It is also shown that a group of force constants is characteristic of a corresponding chemical structure or a substituent.

One of the most important problems in the field of vibration spectroscopy is to find a reliable set of force constants which may explain the frequencies of many molecules with similar chemical structures. For the purpose of finding transferrable force constants of alkyl cyanides, a series of stadies have been made.

There exist some difficulties in the normal coordinate treatment of rather complicated molecules which are composed of many different atoms or substituents. The most important problem, from the viewpoint of force field, is that the number of force constants which should be considered in calculations often exceeds that of information obtained from vibration spectra. Consequently, the force constants obtained from the calculation are somewhat ambiguous and sometimes cause an erroneous conclusion when they are transferred to other molecules.

In the case of molecules consisting of a few atoms or of many but similar atoms or chemical bonds, the problem is easily settled or does not exist at all, because the number of force constants which should be determined is small, while many pieces of information can be obtained not only from the vibrational frequencies themselves but also from the other experimental results. One solution for this problem may be obtained by carrying out the normal coordinate treatment of many molecules having similar chemical structures. However, there still remain doubts as to whether the method can also be applied to the case in which two or more chemical structures are combined in one molecule.

In the present report the result of the normal coordinate treatment of some basic alkanonitriles will be discussed.

Calculation of Force Constants and Results

The infrared spectra and their frequency assignment necessary for the present work will be found in the references,[1–3] and are not discussed here. The method of calculation exactly follows that of the reference[4]

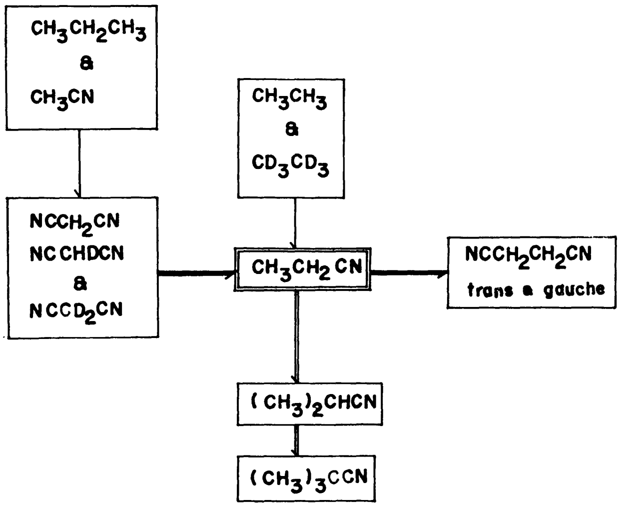

Fig. 1. The Diagram of the Determination of Force Constants of Alkylnitriles.

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[1] T. Fujiyama, the MA-thesis submitted to the University of Tokyo (1963).

[2] T. Fujiyama and T. Shimanouchi, *Spectrochim. Acta*, **20**, 829 (1964).

[3] T. Fujiyama, K. Tokumaru, and T. Shimanouchi, *ibid.*, **20**, 415 (1964).

[4] T. Shimanouchi, *J. Chem. Phys.*, **17**, 245, 734, 848 (1949).

and is not repeated here.5)

The process for the determination of the force constants is illustrated in Fig. 1. Prior to the explanation of the process, it is convenient to classify the force constants of alkanonitriles into three groups: a hydrocarbon group, an α-carbon group, and a cyanide group. The significance of these groups is illustrated in Fig. 2.

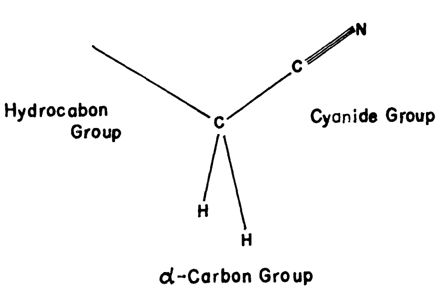

Fig. 2. Classification of Force Constants.

The α-carbon group is composed of the force constants associated with the α-carbon to any extent and the other two groups are composed of those associated with the β-carbon or with the cyanide radical. The force constants of acetonitrile obtained by Nakagawa9) and those of normal hydrocarbons obtained by Takahashi10) are a good starting set for the present calculation.

First, malononitrile and its deuterated compounds are treated using the force constants obtained from acetonitrile and propane. In this process, it was found necessary to make essential changes in the values of some force constants. The molecules studied next was ethylcyanide. The force constants determined for malononitrile were directly transferred to those associated with α-carbon and cyanide groups, while those for a methyl part were transferred from ethane. These two processes were designed for finding the force constants of alkanonitriles associated with the cyanide group and the α-carbon group. A little refinement of the force constants was necessary in the process from malononitrile to ethyl cyanide in order to obtain a good agreement between the observed and the calculated frequencies. However, the force constants of the hydrocarbon group and of the cyanide group remain unchanged.

Then the study was extended to larger molecules by two routes. One route was for succinonitrile in order to confirm the reliability of the force constants for the α-carbon and the cyanide groups. The results obtained were satisfactory both for the *trans* and the *gauche* conformations of succinonitrile. The other route was designed for finding the force constants associated with the secondary and the tertiary α-carbons. In this case also, the force constants were transferred from ethylcyanide. It must be emphasized here that in the treatment of the last three molecules, $NCCH_2CH_2CN$, $(CH_3)_2CHCN$, and $(CH_3)_3CCN$, the force constants of the hydrocarbon and the cyanide groups were not changed essentially.

The final set of force constants thus obtained are summarized in Table 1 and in Table 2. The calculated frequencies are compared with the observed frequencies in Figs. 3(a) and 3(b).

Interpretation

In the previous section, the difficulty of the normal coordinate treatment of rather complicated molecules has been emphasized. The alkyl cyanides are just such molecules which are composed of many chemically different atoms, H, C, and N. As easily be understood from many chemical phenomena, the chemical properties of the atoms associated with the α-carbon atoms are much different from those of the β-carbon atom. The effect of the substituent, the –CN radical, extends not only to the α-carbon but also to the atoms attached to the α-carbon atom.

One of the main object of this calculation is to see whether we can obtain a set of force constants which may be transferred as a group from one molecule to another. If the force constants of the hydrocarbon

Table 1. Force constants for the cyanide and the hydrocarbon groups

Molecule	Cyanide		Hydrocarbon				
	K(C≡N)	F(CCN) H(CCN)	K(C–H)	K(C–C)	F(HCH) H(HCH)	F(CCC) H(CCC)	κ(CH_3)
$NCCH_2CN$	18.159	0.501 0.141	—	—	— —	— —	—
$NCCH_2CH_2CN$	18.30	0.50 0.14	—	2.50	— —	— —	—
CH_3CH_2CN	18.47	0.50 0.15	4.48	2.00	0.07 0.44	— —	0.01
$(CH_3)_2CHCN$	18.47	0.55 0.15		2.00	0.07 0.44	0.33_5 0.27_5	0.01
$(CH_3)_3CCN$	18.47	0.50 0.15	4.48	2.00	0.07 0.44	0.33_5 0.27_5	0.01

The κ's are expressed in the unit of md · A. All the other parameters are in md/A.

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5) After the completion of this work, a few papers were reported in which a few of the alkylnitriles of the present topics are discussed.6-8) It is important to notice that their spectral assignments are often inconsistent with ours.1)

6) J. J. Lucier, E. C. Tuazon, and F. F. Bentley, *Spectrochim. Acta*, **24**, 771 (1968).

7) P. Klaboe, *ibid.*, **26**, 87 (1970).

8) R. Yamadera and S. Krimm, *ibid.*, **24**, 1677 (1968).

9) I. Nakagawa and T. Shimanouchi, *ibid.*, **18**, 513 (1962).

10) H. Takahashi, *Nippon Kagaku Zasshi*, **82**, 1304 (1961).

TABLE 2. FORCE CONSTANTS FOR THE α-CARBON GROUP

Molecule	K(C–H)	K(C–CN)	F(HCH) H(HCH)	F(CCH)^{CH_3} H(CCH)	F(CCH)^{CN} H(CCH)	F(CCC) H(CCC)	F(CCH) H(CCH)	$\kappa(C_\alpha)$
$NCCH_2CN$	4.200	3.202	0.101	—	0.507	0.300	—	0.05
			0.342	—	0.210	0.430	—	
$NCCH_2CH_2CN$	4.20	3.10	0.10	0.54	0.51	0.32	—	0.025
			0.34	0.16	0.21	0.36	—	
CH_3CH_2CN	4.34	2.60	0.10	0.54	0.51	0.34	0.48	0.05
			0.36	0.19	0.21	0.38	0.14	
$(CH_3)_2CHCN$	4.20	2.60	—	0.54	0.51	0.44	0.48	0.11
			—	0.19	0.21	9.35	0.14	
$(CH_3)_3CCN$	—	2.60	—	—	—	0.34	0.48	0.11
			—	—	—	0.38	0.14	

The κ's are expressed in the unit of md·A. All the other parameters are in md/A.

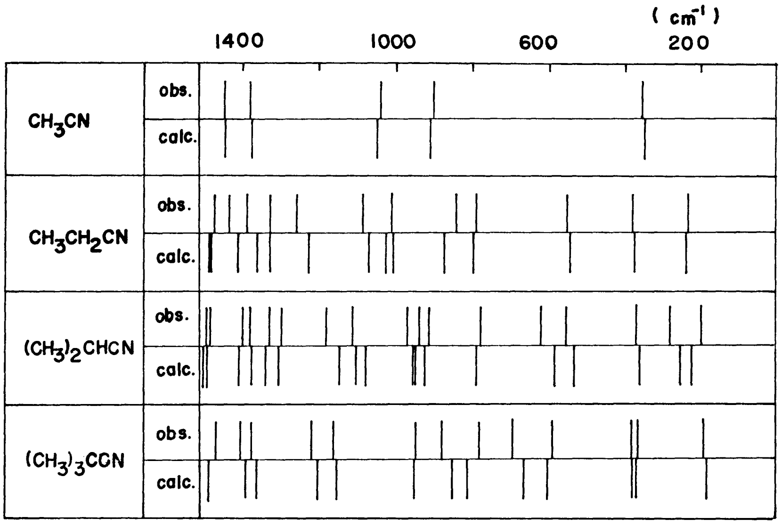

Fig. 3(a). Vibrational Frequencies for Alkanomononitriles.

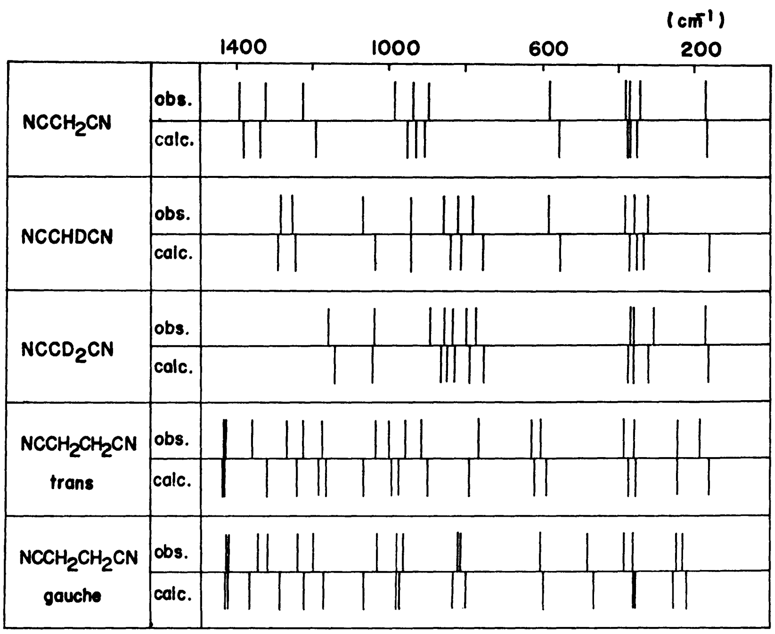

Fig. 3(b). Vibrational Frequencies for Alkanodinitriles.

group and the cyanide group are to be transferred unchanged from one molecule to the other, then the force constants which should be refined through the series of calculations are limited to those of the α-carbon group.

The Cyanide Group (see Table 1). The C≡N stretching vibration has little effect upon the other frequencies because it is an almost completely localized vibration. Consequently, the stretching force constants, K(C≡N), can be determined with good accuracy. The K(C≡N) changes its magnitude from the dinitriles to the mononitriles as is shown in Table 1. The tendency is interesting if the K(C≡N)'s are compared with the values of K(C–CN) of Table 2. The magnitude of K(C–CN) decreases from the dinitriles to the mononitriles, while that of K(C≡N) increases its magnitude. This implies that there exist some interactions between the C–CN and the C≡N bonds. As will be found elsewhere, this is also confirmed by the change of the bond length of the C–CN.

The force constants of the linear part, C–C≡N, are transferred quite successfully from one molecule to another in this series of calculations.

The Hydrocarbon Groups (see Table 1). The force constants belonging to this group have the same values as those of normal hydrocarbons. The K(C–H) of isobutylonitrile is not given in Table 1 because the high frequency separation has been made in the normal coordinate treatment of this molecule.

It may seem rather curious that the K(C–C) of succinonitrile has the value of 2.50 md/A, while the other K(C–C)'s have the values of 2.00 md/A. However the superposed effect from two adjacent α-carbon atoms on the C–C bond of succinonitrile certainly explains the relatively large value of the obtained force constant. The C–C bond of succinonitrile is sandwiched between two α-carbons, so that the effect of the substituents is supposed to be very large. Therefore, it should rather be classified into the cyanide group. Actually, some specific characters of the C–C bond have been reported and a hyperconjugation between the C–C and the C–N bonds has been proposed. Consequently, the anomalous value of this force constant does not spoil the transferability of this group force constants.

The α-Carbon Group (see Table 2). The stretching force constants, K(C–C)'s, are a little smaller than those of hydrocarbon group. This may suggest that the effect of the substituent extends to the nature of the bond between the α-carbon and the hydrogen atoms. A similar conclusion can be obtained from the values of F(H··H) and H(H·C·H). As the correlation between these two force constants is large, we cannot compare the magnitudes of these force constants separately. As a pair, however, an apparent decrease in the magnitude can be recognized for the F(H··H) and the H(H·C·H) values when they are compared with those of normal hydrocarbons.[11] The result is related with the fact that the CH_2 scissoring vibrations occur relatively lower frequencies for the alkanonitriles than for normal hydrocarbons.[12]

The molecular tension around the α-carbon atom does not satisfy the transferability in this group. In the case of a methyl group, the values of 0.01 md·A are commonly used for all the methyl parts of the molecules. According to the discussion of our laboratory, the reliable values are hardly be found as for the molecular tension of the skeletal part. For the purpose of finding reliable and transferable parameters, the result is not desirable (see the last column of Table 2).

In the 7th column of Table 2 the repulsive and the bending force constants, F(C··H) and H(CCH), are given. At first, they were expected to behave just like those for hydrocarbon molecules and were readily transferred from ethane. However, it was found through the calculation of ethylcyanide that their values must be reduced considerably in magnitude so as to obtain the reasonable frequencies for the C–C stretching, the C–CN stretching, and the methyl rocking vibrations. The force constants thus settled must be quite different from those for the simple hydrocarbon group. Nevertheless, they exhibit good transferability as the components of the α-carbon group (see Table 2). This result suggests that the effect of the substituent extends to the α-carbon or to the bond between α- and β-carbon atoms.

Discussion

Reliability of the Force Constants Obtained. The force constants obtained for each group may be quite reliable, because they show good transferability among the eight molecules treated in the present work. Moreover, the force constants of the hydrocarbon group are consistent with those of normal hydrocarbons. The cyanide group force constants are rather consistent with the results for acetonitrile. The agreement of the calculated frequencies with the observed frequencies given in Figs. 3(a) and 3(b) is very satisfactory. This gives ultimate supports for the reliability of the force constants obtained in this calculation.

Determination of the Force Field of a Complicated Molecule. The conclusions we have drawn from the present analysis of the force constants are itemized as follows:

1) Transferability of force constants is satisfied as a group.

2) Let there be two sets of force constants, one for a group A and another for a group B which is chemically different from A. If both sets of force constants are well determined, there is a reasonable hope of calculating the normal vibrations of such a molecule as A-B satisfactorily.

3) Moreover, the force constants of such molecules as A-C-B can be obtained rather definitely. We may well transfer the sets of force constants associated with the groups A and B, while the refinement should be made only for the set which is associated with C.

4) In this process, the number of force constants to be determined is rather small despite the com-

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[11] After this work was finished, quite different values were reported for the force constants of normal hydrocarbons. However, the magnitude of the F-matrix element does not change at all.

[12] It was found later that the CH_2 scissoring vibration decreases its frequency in accordance with the magnitude of the electronegativity of the substituents.

plexities of the molecules.

5) If the force constants obtained from A and B are accurate, then the accuracy of the force constants obtained from the A-C-B will be confirmed. Thus, we can obtain the force constants associated with the C part with little ambiguity and the force constants thus obtained will be able to become good measures for considering the specific character of the C part.

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