1117. *Spectroscopic Studies: Part IV.*[1] *The Prediction of Conformation from Bond Stretching Frequencies.*

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A study on $XCH_2 \cdot CH_2Y$ molecules shows that the C–X bond stretching frequency depends upon the electronegativity of Y, χ (Y), when X and Y are in the *trans*-position. This correlation is used to demonstrate that the *gauche*-isomer is the more stable conformer for $ClCH_2 \cdot CH_2 \cdot CN$ and $BrCH_2 \cdot CH_2 \cdot CN$.

IT is the purpose of this paper to put forward simple relationships between electronegativities and carbon–halogen bond stretching frequencies that have proved useful in conformational analysis. Physical methods useful for conformational analysis are of extreme importance,[2] for example infrared studies have been used[3] and recently, nuclear magnetic resonance spectroscopy has been applied.[4]

Rotational Isomerism and Bond Stretching Vibrations.—Molecules of the type $XCH_2 \cdot CH_2X$ and $XCH_2 \cdot CH_2Y$ can exist as rotational isomers. The most probable stable conformations for these molecules are the "staggered" *trans*- and *gauche*-forms (Fig. 1).
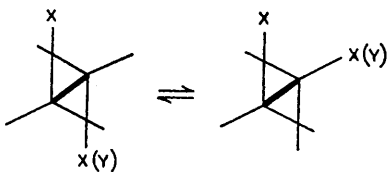

FIG. 1. *trans*- and *gauche*-conformers.

In molecules of the type $XCH_2 \cdot CH_2X$ (X = Br, Cl) it has been shown[5] from symmetry considerations, infrared and Raman spectroscopy, and dipole-moment figures, that the *trans*-isomer is the more stable. Similarly, for the dicyano-compound (X = CN), it has been shown[6] that the *gauche*-isomer is the more stable. For molecules of the type $XCH_2 \cdot CH_2Y$ (X = halogen, Y = CN), it is difficult, owing to the lack of symmetry, to determine directly from spectroscopic evidence which is the more stable isomer, since all the vibrations are infrared- and Raman-active. An exhaustive study on molecules of the type $ClCH_2 \cdot CXYZ$, where X, Y, and Z can be a combination of H, Me, and halogen, by Mizushima *et al.* has shown that the value of the $\nu(CCl)$ frequency depends upon the particular conformation. It was found that $\nu(CCl)$ depends upon which atom or group, Y, is *trans* to the chlorine atom, being higher in frequency when Y is Me or Cl than when Y is a hydrogen atom.

[1] Part III, Ladd and Orville-Thomas, *J.*, 1964, 2689.
[2] Huckel, *Bull. Soc. chim. France*, 1963, 1.
[3] Braude and Waight, "Progress in Stereochemistry," Butterworths, London, 1954, Vol. 1, p. 167.
[4] Eliel, Gianni, Williams, and Stothers, *Tetrahedron Letters*, 1962, 741.
[5] Brown and Sheppard, *Trans. Faraday Soc.*, 1952, **48**, 128.
[6] Fitzgerald and Janz, *J. Mol. Spectroscopy*, 1957, **1**, 49.

Values for carbon–halogen bond stretching frequencies in the molecules studied by Mizushima and other authors are collected in Tables 1 and 2.

Bond Stretching Vibrations and Electronegativity.—The $\nu(CX)$ vibrational frequency in molecules with the *trans*-conformation is dependent upon the character of the CX bond. This, in turn, is certainly influenced by the inductive effect exerted by the CY bond, which depends upon the character of the CY bond. Now a convenient measure of the character of a bond is its bond stretching force constant, f. It seems reasonable, therefore, to postulate that $\nu(CX)$ is dependent both upon $f(CX)$ and $f(CY)$, and hence upon the product $f(CX)f(CY)$.

TABLE 1.

$\nu(CCl)$ Frequencies in substituted aliphatic hydrocarbons.

Molecule	$\nu(CCl)$ (cm.$^{-1}$)	A*	Ref.	Molecule	$\nu(CCl)$ (cm.$^{-1}$)	A*	Ref.
$CH_3 \cdot CH_2 \cdot CH_2Cl$	651	H	7	$BrCH_2 \cdot CH_2Cl$	721	Br	5
$ClCH_2 \cdot CH_2Cl$	709	Cl	7		665	H	
	754	Cl		$ICH_2 \cdot CH_2Cl$	707	I	8
	654	H			660	H	
	677	H		$ClCH_2 \cdot CH_2 \cdot OH$	749	OH	9
$(CH_3)_2CH \cdot CH_2Cl$	689	Cl	7		662	H	
$CH_3 \cdot ClHC \cdot CH_2Cl$	734	Cl	7	$CF_3 \cdot CHCl_2$	834, 734	F	10
	666	H		$CF_3 \cdot CH_2Cl$	801	F	10

* Atom or group *trans* to chlorine atom.

TABLE 2.

$\nu(CBr)$ Frequencies in substituted aliphatic hydrocarbons.

Molecule	$\nu(CBr)$ (cm.$^{-1}$)	A*	Ref.	Molecule	$\nu(CBr)$ (cm.$^{-1}$)	A*	Ref.
$CH_3(CH_2)_2Br$	564	H	7	$ClCH_2 \cdot CH_2Br$	629	Cl	7
$(CH_3)_2CH \cdot CH_2Br$	619	H	7		583	H	
$BrCH_2 \cdot CH_2Br$	586	Br	7	$BrCH_2 \cdot CH_2 \cdot OH$	681	OH	11
	657	Br			589	H	
	568	H		$CF_3 \cdot CH_2Br$	750	F	12
	551	H		$CF_3 \cdot CHBr_2$	721, 714	F	13

* Atom or group *trans* to bromine atom.

Gordy[14] has obtained an empirical relationship in which force constants are found to be proportional to the electronegativity product of the bound atoms. By using this stepping stone, it seems reasonable to suppose that $\nu(CX)$ will depend in some fashion on the electronegativity product $\chi(X)\chi(Y)$. For a series of similar bonds, such as CCl where X = Cl, it is seen that $\nu(CCl)$ will depend upon $\chi(Y)$ alone.

When the average $\nu(CCl)$ frequencies of molecules of the type $CH_2Cl \cdot CXYZ$ are plotted against $\chi(Y)$, where Y is the group *trans* to Cl, a straight-line relationship is found (Fig. 2); a similar relationship is found for the corresponding bromo-compounds. A value of 3·51 was used[15] for $\chi(OH)$.

The straight-line relationships found indicate that the frequencies increase as the electronegativity of Y increases. In addition, since the slopes of the two plots are approximately parallel, the effect is roughly the same in both cases.

Prediction of $\nu(Carbon–Halogen)$ Frequencies.—A great deal of interest has been aroused by the anomalous properties of the lower members of the nitrile family, $XCH_2 \cdot CN$ and

[7] Mizushima, Shimanouti, Nakamura, Hayashi, and Tsuchiya, *J. Chem. Phys.*, 1957, **26**, 970.
[8] Mizushima, Shimanouti, Nakagawa, and Miyake, *J. Chem. Phys.*, 1953, **21**, 215.
[9] Mizushima, Shimanouti, Miyagawa, Ake, and Yasumi, *J. Chem. Phys.*, 1951, **19**, 1471.
[10] Nielsen, Liang, and Smith, *J. Chem. Phys.*, 1953, **21**, 1060.
[11] E. W. Jones, Ph.D. Thesis, University of Wales, 1963.
[12] Nielsen and Theimer, *J. Chem. Phys.*, 1957, **27**, 891.
[13] Klaboe and Nielsen, *J. Chem. Phys.*, 1959, **30**, 1335.
[14] Gordy, *J. Chem. Phys.*, 1946, **14**, 305.
[15] Dailey and Shoolery, *J. Amer. Chem. Soc.*, 1955, **77**, 3977.

$XCH_2 \cdot CH_2 \cdot CN$. They have not been extensively studied spectroscopically, and frequency assignment is difficult for both series. As an aid to frequency assignment in the methyl nitriles, R. G. Jones and Orville-Thomas[16] made use of a relationship found for the methylene deformation frequencies in CH_2XY molecules and the electronegativity product, $\chi(X)\,\chi(Y)$.
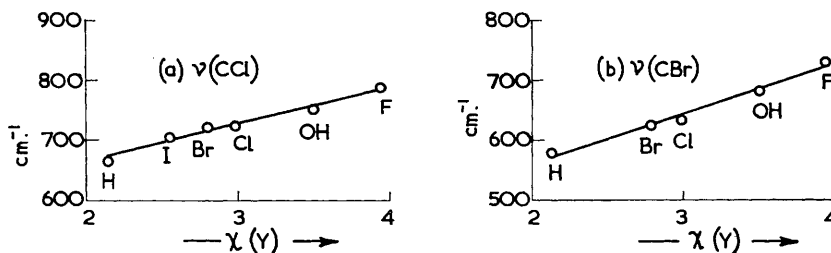

FIG. 2.

These correlations predicted an effective electronegativity value of 3·20 for the CN group. With this value and the generally accepted value of 2·15 for hydrogen, the carbon–halogen stretching frequencies given in Table 3 were predicted; also included in Table 3 are the observed frequencies. Considering the simplicity of these correlations, the agreement between observed and calculated frequencies for $ClCH_2 \cdot CH_2 \cdot CN$ and $BrCH_2 \cdot CH_2 \cdot CN$ is satisfactory.

TABLE 3.

Observed and calculated $\nu(C-Hal)$ frequencies for $ClCH_2 \cdot CH_2 \cdot CN$ and $BrCH_2 \cdot CH_2 \cdot CN$.

Molecule	A*	ν(C–Hal) (Calc.)	ν(C–Hal) (Obs.)
$ClCH_2 \cdot CH_2 \cdot CN$	CN	740	754
	H	673	666
$BrCH_2 \cdot CH_2 \cdot CN$	CN	660	677
	H	574	577

* Atom or group *trans* to halogen.

Stability of Conformers.—When a substance can exist as rotational isomers, it is found that the liquid- and solid-state spectra of a particular molecule differ. The spectrum of the liquid is richer, since it contains an equilibrium mixture of the various isomers, whereas the solid-state spectrum is usually that for one single conformer, the most stable one. When the liquid- and solid-state spectra for $ClCH_2 \cdot CH_2 \cdot CN$ and $BrCH_2 \cdot CH_2 \cdot CN$ are examined it is found that the band at 754 cm.$^{-1}$ disappears in the solid state of the chloro-derivative and that at 677 cm.$^{-1}$ disappears for the bromo-derivative. This indicates that in the solid state these molecules assume the *gauche*-form.

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[16] R. G. Jones and Orville-Thomas, *Spectrochim. Acta*, 1964, **20**, 291.