Tetrahedron Letters No.19, pp. 2325-2330, 1968. Pergamon Press. Printed in Great Britain.

STRUCTURE-FREQUENCY CORRELATIONS AND CONFORMATION OF ALKYL AND CYCLOALKYL HALOGENIDES

C. Altona*

Laboratory of Organic Chemistry, The University, Leiden, The Netherlands

(Received in UK 1 November 1967; accepted for publication 8 February 1968)

It is found that a small set of empirically determined frequencies suffices to predict with fair accuracy the C-Hal "stretching" frequencies displayed by many types of organic mono- and dihalogenides.

The convenient P, S, T system of notation utilized here was suggested by Mizushima et al. (1), following certain observations by Brown and Sheppard (2). Until recently, its use was restricted to studies (1,3-6) of the C-Hal frequencies in aliphatic and polymeric monochlorides, which efforts aimed at the correlation of IR absorption bands in narrow spectral regions with particular conformations.

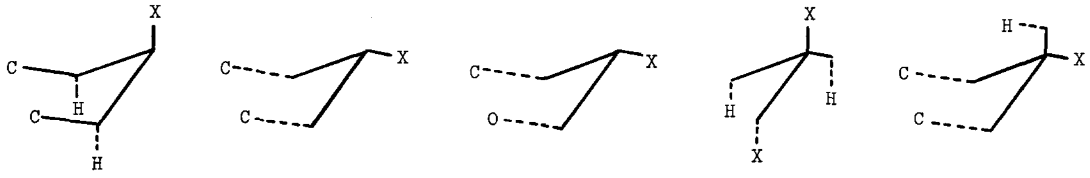
In this laboratory the method was extended to cover bromides and iodides as well. It proved to be of wide applicability and a valuable tool in conformational analysis of cyclic and non-cyclic molecules (7-9). It can now be stated that IR and Raman active stretching frequencies of many types of C-X bond (X = Cl, Br, I) are predictable within ±20 cm^{-1} provided a few authentic examples of the sought type are available. An extension of the method to aliphatic molecules where X = CN was recently reported (10). Model studies (11) and force-field calculations (5) seem to indicate that the extreme sensitivity of the C-Hal frequency to chemical and geometrical environment is due, at least in part, to different interactions with the C-C-Hal bending motion.

The chemical/geometrical arrangement in the vicinity of the C-Hal bond is classified (1,3) according to three main types: P (primary), S (secondary), T (tertiary); the atom or atoms in antiperiplanar position are indicated by a subscript. A prime indicates configurations where a C-Hal bond projects between two α-β C-C bonds (P'_H) or an α-β C-C bond projects between a C-Hal and a C-C bond (S'_{HH}). Some common arrangements or "types" are shown in

---

*Present address: Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, U.S.A.

Fig. 1*.



S''_{HH} S_{CC} S_{CO} T_{XHH} (T_{CHH}) T_{CCH}

FIG. 1. Examples of Some Chemical/Geometrical Combinations (X = halogen)

Each type, e.g. S_{CC}, is assigned a frequency, or "stretching parameter", which is a "best value" obtained by examining the infrared and Raman spectra of the greatest possible number of compounds in which the type occurs. Further work on the correlation between chemical environment and stretching frequency is in progress.

Monohalogenides

In Table I a more complete list of stretching parameters is reported (cf. 7-9). The numbers represent the average of the observed type frequency in at least 3 compounds, although in many cases 10-17 examples have been utilized. A few parameters were obtained from one or two systems only; these are indicated by $\sim$.

The data are derived in part from the literature (3,13,14) and in part from our collection of IR and Raman spectra (15,16,17). The examples serve to illustrate the scope of the present method (note that these observed values have not been used to derive the parameters). The mean difference, $\nu_{obs} - \nu_{pred}$ is of the order of $\pm 5 - \pm 10$ cm^{-1} in several large series (each *ca.* 40 samples) of homologous compounds. In only a few cases the difference amounts to ± 20 cm^{-1} or more.

Several symbols are added to the original set (1,3,4): O = oxygen; p = oxygen lone

---

*A modified representation, recently introduced (12), is specifically aimed at describing all possible rotamers, regardless of the existence of an observable effect on C-Hal frequency. Note that the present notation intends to describe the correlation between chemical/geometrical arrangement and C-Hal stretching frequency, not rotational isomerism. The use of terms like P_H form (3,4,12) seems less fortunate from the standpoint of conformation nomenclature.

pair or π orbital; q = preceding the type symbol signifies that the C-Hal bond is flanked by one quaternary carbon atom; S''_{HH} (see Fig. 1). In a few cases (S_{CH} and qT_{CHH}) aliphatic and cyclic systems show slightly different frequencies and it might prove advantageous then to specify the ring size by adding a superscript. For example, the C-Br frequencies of type S_{CH} occur near 613 cm^{-1} in the spectra of aliphatic bromides and near 596 cm^{-1} in those of cyclohexanoid systems (S^6_{CH}). Sec. cyclohexyl halogenides substituted in position 4 show a slight increase in C-X frequency (4R effect) for several S types (Table I).

Example I shows an interesting application to the conformational analysis of a molecule that would be difficult to study by other methods.

TABLE I. C-Cl, C-Br and C-I Stretching Parameters (cm^{-1}) for Various Chemical/Geometrical Combinations (see text)

Type	C-Cl	C-Br	C-I	Type	C-Cl	C-Br	C-I
P_H	653	562	503	S_{HO}	700	660	---
P'_H	683	614	580	S_{CO}	767	728	---
P_C	726	646	594	S_{Hp}	575	534	---
P_X	726	624	576	S_{Xp}	708	632	---
P_O	$\sim$750	$\sim$665	$\sim$617	T_{HHH}	560	505	487
S_{HH}	611	535	486	T_{CHH}	612	588	573
S'_{HH}	632	578	548	qT_{CHH}	$\sim$607	$\sim$548	---
S''_{HH}*	685	660	---	qT^6_{CHH}	$\sim$585	$\sim$530	---
S_{CH}	666	613	577	T_{CCH}	$\sim$650	$\sim$640	---
S^6_{CH}*	650	596	---	*4R	+18	+6	---
S_{CC}*(a)	742	686	---				

(a) Our values for S_{CC}, obtained from equatorial halogenocyclohexanes, differ substantially from those suggested in ref. 12.

Gem-dihalogenides

Systematic investigations of the spectra of these compounds are apparently lacking but the available data (13) show that two C-Hal frequencies occur; the one at lower wavenumber (ν_s) having the greater intensity in the Raman effect, the other (ν_{as}) being the stronger in the IR spectrum. The frequency difference, $\Delta\nu = \nu_{as} - \nu_s$, increases with increasing mass of the halogen; it also increases on passing from $-CHX_2$ to $-CX_2-$ groups. It is suggested that the average frequency, $\nu_{av} = 1/2(\nu_{as} + \nu_s)$, can be predicted by the following procedure: replace each halogen in its turn by hydrogen, take the corresponding type frequency and average the resulting values. Example II illustrates this point.

Vic-dihalogenides

A study of vic-dihalogeno compounds in the cyclic (7,15) and open-chain (8) series reveals that the two C-Hal stretching frequencies of the anti configuration usually occur as a strongly coupled pair: an intense Raman band is observed at the higher frequency (ν_s), whereas ν_{as} is found as a strong IR active mode of vibration at lower wavenumber.

There is practically no frequency shift when a halogen is substituted for a carbon atom, i.e., the subscripts C and X are interchangeable (with the exception of P_C and P_X for X = Br and X = I). Hence, ν_{av} can be predicted easily from Table I by taking the average of the appropriate stretching parameters.

The frequency difference $\Delta\nu$ increases in the series $\Delta\nu TT$ (0-40 cm^{-1}, both halogens tertiary) < $\Delta\nu PP$ (40-70 cm^{-1}) < $\Delta\nu SS \cong \Delta\nu ST$ (60-125 cm^{-1}) with $\Delta\nu$ (C-Cl) < $\Delta\nu$ (C-Br). As a rule, $\Delta\nu_{obs} >> \Delta\nu_{pred}$ in the above cases, notably when $\Delta\nu_{pred}$ is relatively small (<50 cm^{-1}). Where $\Delta\nu_{pred}$ amounts to 80 cm^{-1} or more, one usually finds $\Delta\nu_{obs} \approx \Delta\nu_{pred}$. This situation often occurs in PS and PT systems.

The vibrations of vic-dihalogenides in gauche configuration are treated similarly. The coupling ($\Delta\nu$) is much weaker than in anti systems. Two medium-intensity bands are found in the IR as well as in the Raman spectra. In PP and SS systems, $\Delta\nu_{obs} \approx$ 10-40 cm^{-1} when $\Delta\nu_{pred} = 0$. Examples III-IV show some common situations.

1,3- and 1,4-dihalogenides

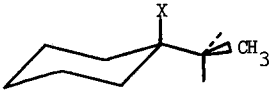
The two C-X frequencies appear to be more or less coupled for certain conformations of the carbon-carbon chain. As with vic-dihalogenides, it is found necessary to study the IR as well as the Raman spectra in order to make an unambiguous assignment, notably in the cyclohexane series (examples V-VII).

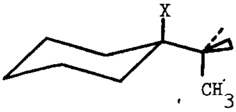
Experimental

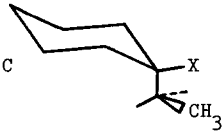
The infrared spectra of refs. 7-9 and 15-17 were recorded on a Unicam SP100 spectrometer. The wavenumbers listed in the examples pertain to solutions (30 mg/ml) in carbon disulphide, unless indicated otherwise (ref. 13). The Raman spectra (neat liquids) were obtained on a Hilger and Watts Ramanspectrometer with photoelectric scanning attachment.

Examples

I. 1-halogeno-1-ethylcyclohexanes (8)

A


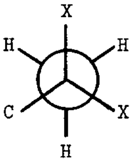
B


C


X	T_{HHH}	ν_{obs}	T_{CHH}	ν_{obs}	T_{CCH}	ν_{obs}
Cl	560	548(vs)	612	602(w)	~650	642(w)
Br	505	499(s)	588	590(vw)	~640	628(w)

The <u>gauche</u> conformation A appears to predominate.

II. 2,2-dihalogenopropanes (13)



ν_{av}(obs)	S_{HH}	$\Delta\nu$(obs)
605	611	96
533	535	104
499	486	103

III. 1,2-dihalogenopropanes (anti form) (8)

X_1	X_2	ν_{as}	ν_s	ν_{av}(obs)	$(S_{XH},P_X)_{av}$	$\Delta\nu$(obs)	$\Delta\nu$(pred)
Cl	Cl	670	722	691	692	52	60
Br	Br	568	649	608	618	81	11
Cl	Br	602	721	664	670	119	113

IV. <u>cis</u>-2,3-dichlorodioxane (ae $\rightleftharpoons$ ea equilibrium) (17)

X_2	X_3	ν_1	ν_2	ν_{av}(obs)	$(S_{Hp},S_{CO})_{av}$	$\Delta\nu$(obs)	$\Delta\nu$(pred)
Cl	Cl	582	778	680	671	196	193

V. <u>cis</u>-1,3-dihalogenocyclohexanes (ae $\rightleftharpoons$ ea equilibrium) (16)

X_1	X_3	ν_{as}	ν_s	ν_{av}(obs)	$(S''_{HH},S_{CC})_{av}$	$\Delta\nu$(obs)	$\Delta\nu$(pred)
Cl	Cl	668	747	707	714	79	57
Br	Br	613	725	669	673	112	26
Cl(a)	Br(e)	640	732	686	686	92	1
Br(a)	Cl(e)	630	747	689	701	117	82

VI. <u>trans</u>-1,3-dihalogenocyclohexanes (ee form) (16)

X_1	X_3	ν_{as}	ν_s	ν_{av}(obs)	S_{CC}	$\Delta\nu$(obs)	$\Delta\nu$(pred)
Cl	Cl	719	758	739	742	39	0
Br	Br	643	732	688	686	89	0
Cl	Br	666	751	708	714	85	56

VII. cis-1,4-dihalogenocyclohexanes (ae $\rightleftharpoons$ ea equilibrium) (16)

X_1	X_4	ν_{as}	ν_s	ν_{av}(obs)	$(S_{HH}, S_{CC}, 2\times 4R)_{av}$	$\Delta\nu$(obs)	$\Delta\nu$(pred)
Cl	Cl	690	777	734	731	87	57
Br	Br	642	735	689	679	93	26
Cl(a)	Br(e)	660	750	705	698	90	11
Br(a)	Cl(e)	660	770	715	713	110	94

Acknowledgment

The author is indebted to Prof. Dr. E. Havinga for his stimulating interest. Part of this study was carried out in collaboration with Dr. H. J. Hageman and Drs. H. R. Buys, whose contributions are gratefully acknowledged.

References

1. S. Mizushima, T. Shimanouchi, K. Nakamura, M. Hayashi, and T. Tsuchiya, *J. Chem. Phys.*, **26**, 970 (1957).
2. J. K. Brown and N. Sheppard, *Trans. Faraday Soc.*, **48**, 128 (1952); **50**, 535, 1164 (1954); *Proc. Roy. Soc.*, **A231**, 555 (1955).
3. J. J. Shipman, V. L. Folt, and S. Krimm, *Spectrochim. Acta*, **18**, 1603 (1962).
4. S. Krimm, *Infrared Spectroscopy and Molecular Structure*, p. 305, M. Davies, ed., Elsevier, Amsterdam (1963).
5. J. Stökr, B. Schneider, and J. Jakes, *9th Eur. Congress Mol. Spectry.*, 10-15 Sept. 1967, Madrid, Spain, Abstr. 78.
6. N. L. Allinger and C. D. Liang, *J. Org. Chem.*, **32**, 2391 (1967).
7. C. Altona, H. J. Hageman, and E. Havinga, *Spectrochim. Acta*, in press.
8. C. Altona and H. J. Hageman, *Rec. Trav. Chim.*, in press.
9. H. R. Buys, C. Altona, and E. Havinga, *Tetrahedron*, to be published; *Rec. Trav. Chim.*, in press.
10. J. J. Lucier and E. C. Tuazon, *9th Eur. Congress Mol. Spectry.*, 10-15 Sept. 1967, Madrid, Spain, Abstr. 77.
11. N. B. Colthup, *Spectrochim. Acta*, **20**, 105 (1964).
12. E. F. Mooney and M. Goldstein, *Bromine and Its Compounds*, p. 837, Z. E. Jolles, ed., Academic Press, London (1966).
13. K. W. F. Kohlrausch, *Ramanspectren*, Leipzig (1943).
14. F. F. Bentley, N. T. McDevitt, and A. L. Rozek, *Spectrochim. Acta*, **20**, 105 (1964).
15. H. J. Hageman, *Thesis Leiden* (1965).
16. H. M. van Dort, *Thesis Leiden* (1963).
17. Spectral data were also taken from the following *Theses Leiden*: E. C. Wessels (1960); C. Altona (1964); H. J. Geise (1964); M. C. Planje (1966); A. Adriaanse (1967); H. R. Buys (1968).