

438. *Infrared Solvent Shifts and Molecular Interactions. Part VII.¹
Conformational Isomers of Halogenocyclohexanes.*

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The influence of solvent environment on the C-Hal frequencies of the axial and equatorial forms of chloro- and bromo-cyclohexane, and 3 α - and 3 β -chlorocopropane is examined. No significant changes are found for the intensity ratio of each isomeric pair but in each case the relative shifts of the equatorial form are greater than those of the axial. This effect can be utilised in the differentiation of conformational isomers. The results are discussed in the light of theories of infrared solvent shifts.

Of the several physical techniques available for the structural investigation of conformational isomers of cyclohexane derivatives, infrared (i.r.) spectroscopy has been particularly valuable. A monosubstituted derivative can occur in two conformations with the substituent X either equatorial (*eq*) or axial (*ax*). Both forms can coexist and it appears quite general that the C-X stretching frequency of an equatorial bond occurs at a higher value than that of the corresponding axial bond. If the two forms differ sufficiently in stability their relative abundance may be altered on changing the polarity of the solvent and several *intensity* studies² on C-X absorptions have shown this to be so. No detailed study as that reported here, however, has been made of the effect of solvent environment on *frequencies*.

In the two previous Parts^{1,3} of this series it was shown that solvent-induced frequency shifts could be utilized to determine the configuration of rotational isomers of halogenoethanes. It was considered that the solvent-variation method might be extended to other flexible molecules and this Part describes studies on conformational isomers of halogenated derivatives of cyclohexane.

EXPERIMENTAL

Spectra were recorded on Grubb-Parsons double-beam G.S. 2A grating and G.S. 3A KBr-prism spectrometers, standard techniques being used. Spectra of solutions were measured with a 0.13-mm. cell in most instances and concentrations were the minimum required for accurate band measurement and no case exceeded 0.2M. Special care was exercised over solvent compensation by employing a variable pathlength cell in the reference beam. Spectra of vapours were recorded by using a 10-cm gas cell. Frequency values of sharp bands have a precision of ± 1 cm.⁻¹ and relative shifts, ± 0.5 cm.⁻¹.

All solvents and cyclohexyl chloride and bromide were commercial products purified by recommended procedures until their boiling points agreed with literature values, and all were rigorously dried. The samples of 3 α - and 3 β -chlorocopropane and 3 β -chlorocholestane were kindly provided by Dr. G. H. R. Summers from the Swansea steroid collection.⁴

RESULTS AND DISCUSSION

It has been shown⁵ that chloro- and bromo-cyclohexane each exhibit two C-Hal stretching frequencies arising from the axial and equatorial forms; in agreement with the general pattern for $\nu(\text{C-X})$, the higher frequency is assigned to the vibration of the equatorial C-Hal bond.

Table 1 lists these two pairs of bands, measured in a wide variety of solvents. No changes in relative intensities of either pair of bands were observed, throughout the solvent range. All four bands exhibit the pattern of solvent shifts typical of $\nu(\text{C-Hal})$

¹ Part VI, Hallam and Ray, *J. Mol. Spectroscopy*, 1964, **12**, 69.

² Le Fèvre, *Proc. Chem. Soc.*, 1960, 117.

³ Hallam and Ray, *J.*, 1964, 318.

⁴ Barton, Page, and Shoppee, *J.*, 1956, 331.

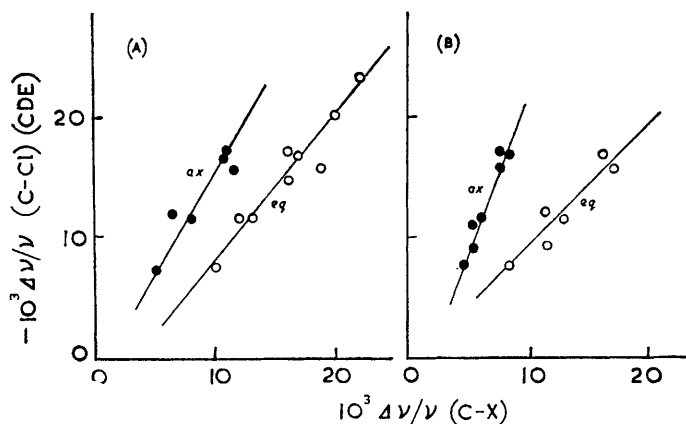
⁵ Larnoudie, *Compt. rend.*, 1952, **235**, 154.

absorptions⁶ and yield straight lines⁷ when their relative shifts are plotted (Figure) against the corresponding shifts of $\nu_a(\text{C-Cl})$ of *cis*-dichloroethylene, the "standard" C-Hal absorption. This fully confirms that they all arise from C-Hal vibrations and contrasts

TABLE I.
The effect of solvent on C-Hal stretching frequencies (cm^{-1}) of mono halogeno-cyclohexanes.

Solvent	$\text{C}_6\text{H}_{11}\text{Cl}$				$\text{C}_6\text{H}_{11}\text{Br}$			
	ν_{eq}	$10^3 \cdot \Delta\nu/\nu$	ν_{ax}	$10^3 \cdot \Delta\nu/\nu$	ν_{eq}	$10^3 \cdot \Delta\nu/\nu$	ν_{ax}	$10^3 \cdot \Delta\nu/\nu$
Vapour	741		689.5		696br		662vw	
Liquid	730.5	14.2	683	9.4	686	14.3	657.5	6.8
Solid	728	17.5	abs.		685.5	15.1	abs.	
n-Hexane	733.5	10.1	686	5.1				
Cyclohexane	734	9.4	686	5.1	690	8.6	659	4.5
Carbon tetrachloride					688	11.5	658.5	5.3
Carbon disulphide ...	732	12.1	684	8.0	687	12.9	658	6.0
Di-n-butyl ether	731	13.5	685	6.5	688	11.5	658.5	5.3
Tetrachloroethylene...					688	11.5	658.5	5.3
Benzene	729	16.2						
Methyl iodide	729	16.2	682	10.9				
Dioxan	729	16.2	682	10.9	685	15.8	657	7.6
Acetone	728.5	16.9	682	10.9	684.5	16.5	656.5	8.3
Nitromethane	727	18.9						
Acetonitrile	727	18.9	681.5	11.6	684	17.2	657	7.6
Methylene bromide ...	727	18.9	680	13.8	682	20.1		
Dimethyl formamide	726	20.2						
Dimethyl sulphoxide	724.5	22.3						

markedly with the behaviour of other bands in this region which remain constant to within $\pm 1 \text{ cm}^{-1}$ throughout the same solvent range. If we compare the solvent sensitivities of the vibrational modes of the two isomers, in terms of these slopes,⁷ S , we find that the response of the equatorial bond is appreciably greater than that of the axial (Table 2).



Relative shifts of $\nu(\text{C-Hal})$ bands of (A) chlorocyclohexane, (B) bromocyclohexane, plotted against the corresponding shifts of *cis*-dichloroethylene (CDE).⁶

Since we are still far from a complete understanding of the mechanism of solvent-induced frequency shifts it is of interest to examine the significance of these sensitivities in connection with theories of solvent shifts. It is generally recognised that the major

⁶ Hallam and Ray, *Trans. Faraday Soc.*, 1962, **58**, 1299.

⁷ Cutmore and Hallam, *Trans. Faraday Soc.*, 1962, **58**, 40.

contributions to the shifts arise from (i) solute-solvent dipolar association effects, and (ii) dielectric effects. All the studies^{1,3,6} to date suggest that dielectric factors play the dominant role in $\nu(\text{C-Hal})$ shifts. Since the dipole moments of the equatorial and axial forms of halogenocyclohexanes probably differ very little² the dielectric contributions to the shifts will be comparable and the differences in solvent-response between the two isomers must arise in the dipolar interaction term. Considerable chemical evidence exists that an axial group is sterically hindered by the proximity of the two adjacent axial hydrogen atoms, compared with the same group in the equatorial position. Thus the equatorial halogen atom is more susceptible to solvation, an effect which should become more pronounced as the size of

TABLE 2.

S Values for some conformational isomers.

Compound	S_{eq}	S_{ax}	S_{eq}/S_{ax}
Chlorocyclohexane	1.04 ± 0.05	1.5 ± 0.06	0.69
Bromocyclohexane	1.0 ± 0.09	2.7 ± 0.3	0.37
3α -Chlorocopropane	1.0 ± 0.2	—	} 0.7
3β -Chlorocopropane	—	1.4	
3β -Chlorocholestane	1.1 ± 0.2	—	—

the substituent is increased. This is borne out by the ratio S_{eq}/S_{ax} , which is 0.69 for the chloride compared with 0.37 for the bromide. Further evidence for the importance of the steric factor comes from the data of Chiurdoglu and Reisse⁸ for cyclohexyl iodide. Since they employed only three solvents, a satisfactory S_{eq}/S_{ax} ratio cannot be obtained for the iodo-compound, but by using $\Delta\nu = \nu(\text{cyclohexane}) - \nu(\text{acetone})$ $\Delta\nu_{eq}/\Delta\nu_{ax} \simeq 3$, which confirms that as the halogen atom becomes larger, solvent approach to the axial conformer is further hindered.

To ascertain whether this enhanced solvent response of the equatorial form is a general behaviour of conformational isomers, the polycyclic systems 3α - and 3β -chlorocopropane were also studied (Table 3). Although the $\nu(\text{C-Cl})$ of the axial conformer (3β) could only

TABLE 3.

The effect of solvent on C-Cl stretching frequencies (cm^{-1}) of chloro-steroids.

Solvent	Chlorocopropane				Chlorocholestane	
	$3\alpha(eq)$		$3\beta(ax)$		$3\beta(eq)$	
	ν	$10^3 \cdot \Delta\nu/\nu$	ν	$10^3 \cdot \Delta\nu/\nu$	ν	$10^3 \cdot \Delta\nu/\nu$
n-Hexane					757.5	3.3
Cyclohexane	755	6.6	712.5	4.9	758.5	2.0
Carbon disulphide	751	11.8	710	8.4	755.5	6.0
Bromoform	745.5	19.1				
Benzene	748	15.8	709	9.8	753	9.2
Acetone	747.5	16.4			755	6.6
Dioxan	748.5	15.1			753.5	8.6
Methylene bromide					751.5	11.2

Note. To provide a convenient reference point in calculating relative shifts, vapour frequencies have been assumed.

be followed in a limited range of three solvents it is quite clear that the equatorial form is the more solvent-sensitive. We had planned to study the corresponding derivatives of cholestane, whose C-Cl orientations are the opposite of the copropane pair, but unfortunately the 3α -compound was unavailable. The 3β -compound, however, shows a response (Table 3) similar to that of 3α -chlorocopropane from which we would predict that 3β -chlorocholestane should have an S value of about 1.4.

The results further emphasize the complexity of the mechanism of $\nu(\text{C-Hal})$ solvent shifts. However, correlations between these shifts and isomeric conformations may be of considerable use in ascertaining molecular configurations, particularly for those isomeric pairs which show only minor intensity variations on change of physical state or solvent.

⁸ Chiurdoglu and Reisse, *Bull. Soc. chim. belges*, 1961, **70**, 472.

S-values may possibly provide a quantitative measure of the relative reactivities of equatorial and axial groups.

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