

54. *Infrared Solvent Shifts and Molecular Interactions. Part V.<sup>1</sup>  
Rotational Isomers of Halogenated Compounds.*

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The effect of solvent on the carbon-halogen and carbonyl stretching frequencies of halogenated ethanes and chloroacetone has been studied. For each pair of isomers the solvent response, in terms of the relative shifts of the absorptions bands, as distinct from changes in relative band intensities, is greater for the more polar form. These findings throw some light on the mechanism of solvent shifts and can be utilised in the differentiation of rotational isomers.

STUDIES<sup>2</sup> of the influence of solvent on carbon-halogen vibrational frequencies suggest that the solvent-variation technique provides a useful guide to the assignment of these frequencies, particularly for molecules which possess more than one type of such link and for those which exist in several conformations giving rise to different vibrational frequencies. The present paper reports the use of this technique in elucidating the configuration of rotational isomers.

<sup>1</sup> Part IV, Hallam and Ray, *Trans. Faraday Soc.*, 1963, **59**, 1983.

<sup>2</sup> Hallam and Ray, *Trans. Faraday Soc.*, 1962, **58**, 1299.

One of the methods commonly used to identify such isomers is to follow the changes in intensity which occur on dissolution in solvents of different polarity since the more polar form is favoured in solvents of high dielectric constant.<sup>3</sup> The technique described here, however, involves measurement of the relative solvent shifts: these are then compared with the corresponding shifts of a reference molecule which does not possess different rotational configurations.

#### EXPERIMENTAL

The spectra were recorded on Grubb-Parsons double-beam G.S. 2A grating and G.S. 3A (potassium bromide prism) instruments, by standard techniques. Solution spectra were measured with use of a 0.13 mm. cell in most instances, and concentrations were the minimum required for accurate band measurement and in no instance exceeded 0.2M. Vapour spectra were recorded with use of a 10-cm. gas cell. Frequency values of sharp bands have a precision of  $\pm 1$  cm.<sup>-1</sup> and relative shifts one of  $\pm 0.5$  cm.<sup>-1</sup>.

Solvents and solutes were commercial products purified by recommended procedures until their b. p.s agreed with recorded values and were rigorously dried. Special care was exercised over solvent compensation by employing a cell of variable path length in the reference beam.

#### RESULTS AND DISCUSSION

The behaviour of the carbon-halogen absorptions of 1,2-dichloro- and 1,2-dibromoethane were studied first, since the C-X stretching modes for the *trans*- and *gauche*-forms of these molecules have been unequivocally assigned.<sup>3</sup>



$\nu_a$ C-X (cm. <sup>-1</sup> )	709 (liq.)	675	} X = Cl
$\nu_s$ C-X (cm. <sup>-1</sup> )	Inactive	655	
$\mu$ (D)	0.17	2.54	} X = Br
$\nu_a$ C-X (cm. <sup>-1</sup> )	587	551	
$\mu$ (D)	0	2.2	

Table 1 lists these frequencies measured for a wide variety of solvents. All exhibit the pattern of solvent shifts found for  $\nu$ C-Hal absorptions and yield straight lines (B.H.W. plots)

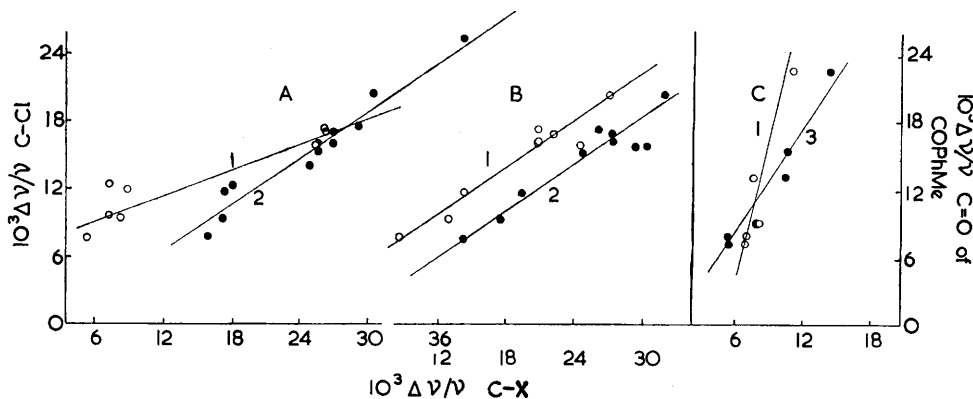
TABLE I.  
Effect of solvent on C-Hal stretching frequencies (cm.<sup>-1</sup>) of 1,2-dihaloethanes.

Solvent	(CH <sub>2</sub> Cl) <sub>2</sub>				(CH <sub>2</sub> Br) <sub>2</sub>	
	$\nu_a$ (I)	$\nu_a$ (II)	$\nu_s$ (II)	$A_I/A_{II}$ *	$\nu_a$ (I)	$\nu_a$ (II)
Vapour .....	727					
n-Hexane .....		686.5	662		591.5	557.5
Cyclohexane .....	715.5	686	662	~1.9		
CCl <sub>4</sub> .....		684.5	660.5		590.5	556
(CCl <sub>2</sub> ) <sub>2</sub> .....	714.5	685				
CS <sub>2</sub> .....	714.5	684	659	~2.1	589.5	555.5
Bu <sup>n</sup> O .....	714	~685	660			
CH <sub>2</sub> Br <sub>2</sub> .....	709					
C <sub>2</sub> H <sub>6</sub> .....	708.5				588	553.5
MeCN .....	708.5	672.5	653.5	1.4		
Me·NO <sub>2</sub> .....	707.5					
COMe <sub>2</sub> .....	707.5	672	654		588	
Dioxan .....	706	~672	653			
H·CO·NMe <sub>2</sub> .....	705				583.5	548.5
Me <sub>2</sub> SO .....					582	548
PO(NMe <sub>2</sub> ) <sub>3</sub> .....	697.5					

\* Ratio of [peak intensity of  $\nu_a$ (I)]/[peak intensity of  $\nu_a$ (II)].

<sup>3</sup> Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, 1954.

when their relative shifts are plotted (*e.g.*, Fig. A) against the corresponding shifts of  $\nu_a\text{C-Cl}$  of *cis*-dichloroethylene, the "standard" C-Hal absorption.<sup>2</sup> This confirms the view that they all arise from C-Hal vibrations, and contrasts with the behaviour of the other absorptions in this region (1032, 944, 881  $\text{cm}^{-1}$ ) which remain constant within  $\pm 1 \text{ cm}^{-1}$  throughout the solvent range. If we compare the solvent sensitivities of the antisymmetric modes of the two isomers of dichloroethane, in terms either of the B.H.W. slopes,  $S$ , or the shift  $\Delta\nu = [\nu(\text{cyclohexane}) - \nu(\text{acetone})]$ , we find that the *gauche*-form ( $S = 0.42 \pm 0.05$ ;  $\Delta\nu = 14 \text{ cm}^{-1}$ ) has double the response of the *trans*-form ( $S = 0.78 \pm 0.07$ ;  $\Delta\nu = 8 \text{ cm}^{-1}$ ). The lower band is intensified on passing into a more polar environment, but



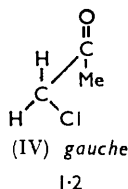
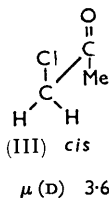
Relative shifts of  $\nu\text{C-Cl}$  bands of (A) 1,2-dichloroethane, (B) isobutyl chloride, plotted against the corresponding shifts of *cis*-dichloroethylene;<sup>2</sup> (C)  $\nu\text{C=O}$  bands of chloroacetone plotted against the corresponding shifts of acetophenone.<sup>6</sup>

1 = *gauche*; 2 = *trans*; 3 = *cis*.

only in a few solvents can the intensity of both bands be measured with reasonable accuracy, and the resultant ratio does not show such a large variation as  $S$ . A similar comparison of the corresponding symmetric modes is not possible since that for the *trans*-molecule is infrared-inactive; the  $S$  value for the *gauche*-form is  $0.65 \pm 0.05$  and  $\Delta\nu = 8 \text{ cm}^{-1}$ .

Carbon-bromine bonds are less sensitive to solvent influences<sup>2</sup> than are carbon-chlorine bonds, so that comparison of these modes is not on such a firm footing. However, what little difference in sensitivity there is for the dibromoethane isomers is also in favour of the *gauche*-configuration:  $S = 0.87 \pm 0.06$ ;  $\Delta\nu = [\nu(\text{hexane}) - \nu(\text{H}\cdot\text{CO}\cdot\text{NMe}_2)] = 9 \text{ cm}^{-1}$ ; *trans*:  $S = 0.97 \pm 0.06$ ;  $\Delta\nu = 8 \text{ cm}^{-1}$ .

To ascertain whether this enhanced solvent response of the more polar form is general for rotational isomers, the more complex compound, monochloroacetone was studied. This has two negative dipole sites susceptible to solvation interactions and has been shown to exhibit rotational isomerism which gives rise to two carbonyl and two C-Cl frequencies.



Dipole-moment and spectroscopic studies<sup>4</sup> have shown that the more polar *cis*-form (III) is the more stable in the liquid and the solid state, whereas the *gauche*-form (IV) becomes

<sup>4</sup> Mizushima, Shimanouchi, Miyazawa, Ichishima, Kuratani, Nakagawa, and Shida, *J. Chem. Phys.*, 1953, **21**, 815.

more abundant in the vapour. Mizushima *et al.*<sup>4</sup> assigned the upper of the pair of C=O, and the lower of the C-Cl frequencies to form (IV), but Bellamy and Williams<sup>5</sup> reversed the carbonyl assignments and identify the 1745 cm.<sup>-1</sup> absorption of the liquid with the *cis*-form (III). This revised assignment was based on intensification of the higher-frequency carbonyl band in acetonitrile solution compared with that in carbon tetrachloride solution, and the intensification of the lower band with increased temperature.

TABLE 2.

Effect of solvent on the C=O and C-Cl stretching frequencies (cm.<sup>-1</sup>) of chloroacetone.

Solvent	(III)		(IV)		$A_{III}/A_{IV}$ *	
	$\nu$ C=O	$\nu$ C-Cl	$\nu$ C=O	$\nu$ C-Cl	C=O	C-Cl
Vapour .....		760	1743	731		
n-Hexane .....	1754	765	1731.5			
Cyclohexane .....	1754	763.5	1731	728.5		
Bu <sup>n</sup> <sub>2</sub> O .....	1751.5	763	1729	727	0.89	0.93
C <sub>6</sub> H <sub>6</sub> .....		762.5		726		1.05
Dioxan .....		762.5		727		1.05
MeCN .....	1747	762.5	1730	727		1.46
Me·NO <sub>2</sub> .....		763		727.5		~1.4
CH <sub>2</sub> Br <sub>2</sub> .....	1746.5	763		728	0.93	1.04
COMe <sub>2</sub> .....		762		726		1.27
Me <sub>2</sub> SO .....		757		726		
CCl <sub>4</sub> ·CH <sub>2</sub> ·OH .....	1740		1724			

\* Ratio of [peak intensity of  $\nu$ (III)]/[peak intensity of  $\nu$ (IV)] for carbonyl and for C-Cl absorptions.

Table 2 presents the carbonyl and C-Cl doublets measured in an extended solvent range. The C=O shifts follow the pattern established for carbonyl dipoles<sup>6</sup> and give straight lines when plotted (Fig. C) against the corresponding shifts of  $\nu$ C=O of acetophenone. The slopes (*cis*:  $S = 1.6 \pm 0.1$ , *gauche*:  $S = 3.6 \pm 0.3$ ) show that the more polar *cis*-isomer is considerably more sensitive to solvents than the *gauche*-form. The C-Cl absorptions are somewhat less sensitive than usual but again the response of the higher frequency band is greater than the lower {*cis*:  $\Delta\nu = [\nu(\text{cyclohexane}) - \nu(\text{Me}_2\text{SO})] = 6.5 \text{ cm.}^{-1}$ , *gauche*:  $\Delta\nu = 2.5 \text{ cm.}^{-1}$ }. Like the carbonyl doublet the C-Cl shifts are accompanied by a slight intensification of the higher-frequency band in the more polar solvents. These results, therefore, confirm the assignments of Mizushima *et al.*<sup>4</sup> for the C-Cl frequencies and Bellamy and Williams's reassignment for the carbonyl frequencies.

It is of special interest to examine the significance of these different sensitivities in connection with theories of solvent shifts. Although we are still far from a complete understanding of the mechanism of solvent-induced frequency shifts, it is generally recognised<sup>7</sup> that the major contributions arise from (i) solute-solvent dipolar association effects and (ii) dielectric effects. Whilst association effects are undoubtedly predominant in determining  $\nu$ X-H shifts, dielectric factors become significant in  $\nu$ C-O shifts and possibly dominant in  $\nu$ C-Hal shifts.<sup>2</sup> The results for monochloroacetone substantiate this since, if dipolar association governed these shifts, it might reasonably be expected that the isomeric configuration which possesses the more polar bonds would exhibit the greatest shifts. If, in the absence of quantitative assessments, we accept the vapour frequencies as being a reasonable measure of bond polarities, we see that the observed displacements are contrary to the above expectation. That is, they support the claim that dielectric factors play a determining role, since the *cis*-form, being the more polar, might conceivably be influenced more than the *gauche*-form by changes in the macroscopic dielectric constant of the medium. The reduced sensitivity of the C-Cl absorptions of the two forms probably

<sup>5</sup> Bellamy and Williams, *J.*, 1957, 4294.

<sup>6</sup> Bellamy and Williams, *Trans. Faraday Soc.*, 1959, 55, 14.

<sup>7</sup> Hallam, "Molecular Spectroscopy," Proc. Third Conference Institute of Petroleum Hydrocarbon Research Group, London, 1962, p. 245.

TABLE 3.

Effect of solvent on the C-Cl stretching frequencies of isobutyl chloride, and the  $\nu_a$ C-Cl and carbonyl stretching frequency ( $\text{cm}^{-1}$ ) of carbonyl chloride.

Solvent	Bu <sup>t</sup> Cl			Cl <sub>2</sub> C=O	
	$\nu$ C-Cl (V)	$\nu$ C-Cl (VI)	$A_V/A_{VI}$ *	$\nu$ (C=O)	$\nu_a$ C-Cl
Vapour .....	745.5	698		1830	850
n-Hexane .....	735	692	~1.9	1814	836.5
Cyclohexane .....	734.5	691.5	2.1	1814	835
(CCl <sub>2</sub> ) <sub>2</sub> .....	732.5	689			
CCl <sub>4</sub> .....		689		1813	841
CS <sub>2</sub> .....	731	688	2.2	1808	835
C <sub>6</sub> H <sub>6</sub> .....	727				835
(CH <sub>2</sub> Br) <sub>2</sub> .....	725	683.5	1.8		
MeCN .....	723.5	681	2.1	1810	849
Me·NO <sub>2</sub> .....	723		~2.2	1810	849
CHCl <sub>3</sub> .....				1773	843
COMe <sub>2</sub> .....	725	682.5	~2.1		
Dioxan .....	726	683.5			
H·CO·NMe <sub>2</sub> .....	721.5	679	1.8		

\* Ratio of [peak intensity of  $\nu$ (V)]/[peak intensity of  $\nu$ (VI)].

arises because of the competing effect of the neighbouring carbonyl dipole. The dipolar association factor, which must still be operative, is a competitive feature and the oxygen atom is a much more favourable site than chlorine for solvent attachment. Moreover, any specific solvent association with oxygen, weakens the C=O bond and probably causes



some internal electron redistribution which leads to a strengthening of the C-Cl bond. This raising of the C-Cl frequency partially compensates the solvent lowering of this frequency. The results for dichloroethane, although conclusive in showing that the *gauche*-form is the more solvent-sensitive, give no lead as to origin of the shifts, since the more polar *gauche*-form also possesses the more polar C-Cl links, according to the frequency values.

To clarify this, further studies were initiated which uphold the interpretation of these shifts. First, isobutyl chloride was studied (Table 3) as an example of a molecule which exhibits rotational isomerism<sup>8</sup> but has only one active dipole. The two stable conformations are represented by (V) and (VI). On the basis of their vapour frequencies the individual C-Cl links differ slightly in polarity, but the overall molecular dipole moments are not so significantly different as for chloroacetone. In the absence of a competing oxygen group, therefore, the solvent sensitivity of both  $\nu$ C-Cl bands might be expected to be normal and of the same magnitude. That this is so can be seen from the Table and Fig. B, which yields *S*-values, *trans*  $0.70 \pm 0.05$ , *gauche*  $0.72 \pm 0.05$ . The relative intensities of the two bands also remain fairly constant throughout these solvents.

Secondly, a solvent study was made of carbonyl chloride, chosen since it has two active centres attached to the same carbon atom, whereby the competitive effect of solvents ought to be most pronounced. The results (Table 3) indicate that whilst the downward shift of  $\nu$ C=O has the magnitude and pattern of  $\nu$ C=O of acetyl chloride,<sup>6</sup> a link of similar polarity, the antisymmetric  $\nu$ C-Cl is shifted upwards. Here apparently, preferential association at the carbonyl dipole raises the C-Cl frequency by an amount which outweighs the lowering of this frequency by dielectric effects.

<sup>8</sup> Brown and Sheppard, *Trans. Faraday Soc.*, 1954, **50**, 1164.

*Conclusions.*—These results support the view that dielectric factors are important in determining C-Hal frequency shifts. Correlations between solvent-induced shifts and isomeric conformations, of the type considered above, may prove of use in determining the configurations of flexible molecules, particularly for configurational isomers which show only minor intensity variations on change of physical state or solvent.

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