

These equations are linear in α and β . The derivatives in the coefficients are obtained from eq 4A; R_i is the difference between f_i in eq 4A and y_i^{exptl} . Equations 7A are solved⁵⁷ to give the corrections α and β , and these are then added to A_0 and B_0 to give A_1 and B_1 . The next

(57) The set of linear equations (7A) was solved by a standard subroutine MATRIX in the University's CDC 6400 computer. However, it can be handled by any specially written subroutine for solution of linear equations.

iteration uses A_1 and B_1 in eq 4A and 7A to obtain another set of the corrections α and β , and the process is repeated until the standard deviations of two successive iterations differ by less than a predetermined value (in this case 10^{-5}). Once the best values of A and B have been found, all the experimental times are changed by a small increment and the iteration is repeated as above. The time increment, Δt , which gives a minimum standard deviation is taken to be the "zero-time correction."

Nature and Effect of Solute-Solvent Interactions on Vibrational Spectra of Rotational Isomers

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Abstract: Infrared spectra have been measured for solutions of 1,2-dichloroethane, 1,2-dibromoethane, 1-fluoro-2-haloethanes, and β -halopropionitriles in a range of solvents having different dielectric constants. The relative intensity changes and carbon-halogen frequency shifts are correlated with the dielectric constant function $(\epsilon - 1)/(2\epsilon + 1)$. It is concluded that the nature of the solute-solvent interactions is mainly electrostatic. The usefulness of the reported correlations as aids to conformational and vibrational frequency analysis is critically assessed.

A considerable number of studies have been made of the general effect of solvent media on vibrational frequencies and intensities and of the comparative effects on rotational isomers. In the general case frequency shifts have been explained in terms of the Kirkwood-Bauer-Magat equation

$$\Delta\nu/\nu = C(\epsilon - 1)/(2\epsilon + 1) \quad (1)$$

where $\Delta\nu$ is frequency difference between vapor and solution phases, ϵ is the dielectric constant of the solvent, and C is a constant characteristic of the solute. This relationship has subsequently been modified by a number of workers^{1,2} and although the treatments are satisfactory for nonpolar solvents, the shifts in polar solvents are generally greater than those predicted and empirical corrections to account for specific or localized interactions have been made.³ At best there is still only a semiquantitative understanding of solvent effects, and clearly the use of solutes which have rotational isomers will contribute little to a clarification of this particular problem. The purpose of this paper is more to evaluate the use which may be made of solvent effects in establishing the various conformations of rotational isomers.

Experimental Section

Infrared studies were made using a Grubb-Parsons GS2A spectrometer.

All solutes and solvents were dried and purified by standard techniques until their boiling points agreed with generally accepted values.

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(1) R. L. Williams, *Annu. Rept. Progr. Chem.*, **58**, 34 (1961).

(2) A. D. Buckingham, *Proc. Roy. Soc., Ser. A*, **248**, 169 (1958).

(3) G. L. Caldow and H. W. Thompson, *ibid.*, *Ser. A*, **254** (1960).

Solutions were run in standard 0.1-mm cells equipped with sodium chloride or potassium bromide windows. The solution concentrations were as low as practicable, and in all cases were less than 0.5 M.

Results and Discussion

Solvent effects can be conveniently subdivided into frequency shifts and intensity variations. These will be considered independently.

(1) Frequency Shifts. The main purpose of previous studies has been to attempt to differentiate between effects due to specific interactions and bulk dielectric solvent effects.^{4,5} Additionally, a correct assignment of the bands to a particular conformation can sometimes be made. The need for this latter type of information is seen by considering compounds of the type XCH_2-CH_2Y . When $X = Y$ in, for example, 1,2-dichloroethane, the problem is trivial since the trans conformer has a center of symmetry and the mutual exclusion principle for infrared and Raman activity applies. However, in the cases where there is not a center of symmetry, the assignment of bands to a particular conformer is not so straightforward. The usual method is to consider the solid-state spectrum of the compound, since it is often found that only the more stable conformer is present in this phase. However, there are many examples where such simplification of the spectrum does not occur on changing phase. Hence there is a need for an alternative method.

It has been established that in the case of 1,2-dichloroethane, the relative shifts of the $\nu(C-Cl)$ absorption bands are greater for the more polar conformer.⁴ The so-called Bellamy-Hallam-Williams (BHW) plots of

(4) H. E. Hallam and T. C. Ray, *J. Chem. Soc.*, 318 (1964).

(5) N. Oi and J. F. Coetzee, *J. Amer. Chem. Soc.*, **91**, 2478 (1969).

$\Delta\nu/\nu$ in a range of solvents,⁶ against the corresponding values for a different compound containing the same grouping, are found to be approximately linear. In order to test the applicability of this approach to other 1,2-disubstituted ethanes, we have carried out similar experiments using the β -halopropionitriles and the 1-fluoro-2-haloethanes for which the vibrational spectra have been studied in some detail.⁷⁻⁹

The results for 1-chloro-2-fluoroethane and 1-bromo-2-fluoroethane are given in Table I. It is possible to make reasonable BHW plots using *cis*-dichloroethylene or *n*-propyl chloride as a standard, but for the present purposes we prefer to plot the relative shifts as a function of $(\epsilon - 1)/(2\epsilon + 1)$. The plots are shown in Figure 1, and with the exception of the aromatic-type solvents, reasonable straight lines are obtained. This may be taken as an indication that the KBM equation (1) gives a fair interpretation of the solvent shifts. It is remarkable, when one considers the magnitude of the frequency shifts, that such reasonable plots are obtained. Any error in measurement of band positions may cause large discrepancies in the plots.

In the case of the β -halopropionitriles the data present additional difficulties. The chloro compound shows shifts of up to 10 cm^{-1} for both isomers compared with that observed in cyclohexane. If $\Delta\nu$ values are measured with respect to the recently determined vapor-phase values,¹⁰ then shifts of up to 17 cm^{-1} are obtained. The vapor-state spectra for the bromo and iodo derivatives have not been obtained and, although in the present work these two compounds were thoroughly investigated using a variety of solvents, the $\Delta\nu$ values relative to cyclohexane were never greater than 4 cm^{-1} . No useful purpose would be served by presenting these data, although the general point, that the larger shifts are associated with the gauche isomer, was evident. The data for the chloro compound are given in Table I and Figure 1.

We feel that it is worth presenting these data in full in order to show that they may be used to obtain apparently reasonable straight-line plots. Although it is certainly clear that the greater shifts, *i.e.*, $\Delta\nu/\nu$ values, are associated with the more polar isomer, the fact that the bond stretching frequency of this isomer is always less than that of the trans contributes quite markedly to the observed effect. Clearly any experimental studies require meticulous care since often the shifts are only a few reciprocal centimeters. Although such studies are useful in showing qualitatively the nature of solvent effects, *i.e.*, the applicability or otherwise of the KBM relationship (aromatic-type solvents behave as though their dielectric constants are considerably higher than the known values), and, in specialized instances, for identification of group frequencies of polar groups,^{11, 12} we consider that the method is not normally a profitable one by which to assign bands to a particular isomer.

(6) L. J. Bellamy, H. E. Hallam, and R. L. Williams, *Trans. Faraday Soc.*, **54**, 1120 (1958).

(7) E. Wyn-Jones and W. J. Orville-Thomas, *J. Chem. Soc. A*, 101 (1966).

(8) M. F. El Bermami and N. Jonathan, *ibid.*, **A**, 1711, (1968).

(9) M. F. El Bermami and N. Jonathan, *J. Chem. Phys.*, **49**, 340 (1968).

(10) P. Klabeo and J. Grundnes, *Spectrochim. Acta, Part A*, **48**, 1905 (1968).

(11) L. J. Bellamy and P. E. Rogasch, *J. Chem. Soc.*, 2218 (1960).

(12) H. Gotz, E. Heilbronner, A. R. Katritzky, and R. A. Jones, *Helv. Chim. Acta*, **44**, 387 (1961).

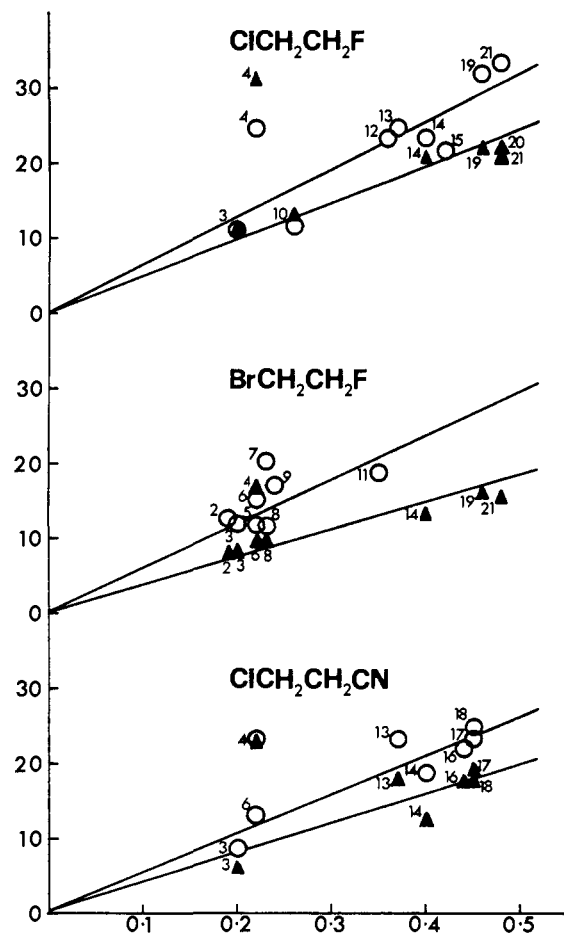


Figure 1. Relative frequency shifts of $\nu(\text{C-Cl})$ and $\nu(\text{C-Br})$ bands of 1-chloro-2-fluoroethane, 1-bromo-2-fluoroethane, and β -chloropropionitrile vs. the dielectric constant function, $(\epsilon - 1)/(2\epsilon + 1)$: Δ , trans; \circ , gauche; ordinate, $10^3 \Delta\nu/\nu$; abscissa, $(\epsilon - 1)/(2\epsilon + 1)$.

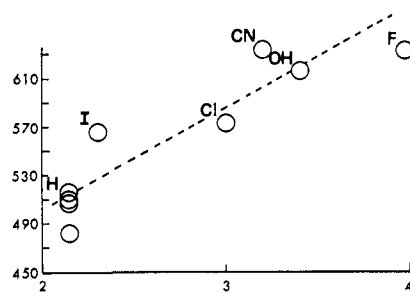


Figure 2. Plot of $\nu(\text{C-I})$ of 1,2-disubstituted ethanes against the electronegativity of the atom or group in the trans position.

Although their approach did not involve solvent effect studies, it is worth noting that Jones and Orville-Thomas¹³ developed an interesting method using $\nu(\text{C-X})$ shifts to assign these bands to particular conformers. The method is based on an empirical relationship which gives the force constant of a band as being proportional to the electronegativity product of the bound atoms.¹⁴ When this method was applied to 1,2-disubstituted ethanes of the type $\text{XCH}_2\text{CH}_2\text{Y}$, reasonable straight-line plots were obtained when $\nu(\text{C-Cl})$ and $\nu(\text{C-Br})$ were plotted against the electronegativity of the atom or group in the corresponding trans position. As may be seen from Figure 2, it has been found

(13) E. W. Jones and W. J. Orville-Thomas, *J. Chem. Soc., Suppl.*, **1**, 5853 (1964).

(14) W. Gordy, *J. Chem. Phys.*, **14**, 305 (1946).

Table I. Solvent Effects on Frequencies of C-X Stretching Absorption Bands

Solvent	$\frac{\epsilon - 1}{2\epsilon + 1}$	FCH ₂ CH ₂ Cl					
		$\nu(\text{C-Cl})$ gauche	$\Delta\nu$	$\frac{10^3\Delta\nu}{\nu}$	$\nu(\text{C-Cl})$ trans	$\Delta\nu$	$\frac{10^3\Delta\nu}{\nu}$
1. Vapor	0	685	0	0	775	0	0
2. <i>n</i> -Butane	0.19						
3. Cyclohexane	0.20	677	8	11.7	766	9	11.6
4. Dioxane	0.22	688	17	24.8	751	24	31.0
5. Cyclohexene	0.22						
6. Carbon tetrachloride	0.22						
7. Benzene	0.23						
8. Tetrachloroethylene	0.23						
9. Toluene	0.24						
10. Carbon disulfide	0.26	677	8	11.7	765	10	12.9
11. Bromoform	0.35						
12. Dibromoethane	0.36	669	16	23.4			
13. Diiodomethane	0.37	668	17	24.8			
14. Iodomethane	0.40	669	16	23.4	759	16	20.6
15. Bromoethane	0.42	670	15	21.9			
16. Methyl isobutyl ketone	0.44						
17. Diethyl ketone	0.45 ^a						
18. Methyl isopropyl ketone	0.45 ^a						
19. Acetone	0.46	663	22	32.1	758	17	21.9
20. Nitromethane	0.48				758	17	21.9
21. Acetonitrile	0.48	662	23	33.6	759	16	20.6

^a Estimated value. ^b Reference 10.

possible to make a similar straight-line plot for $\nu(\text{C-I})$ using the data given in Table II. Rather surprisingly, a similar result may be obtained for $\nu(\text{C-F})$, but in this case the strong coupling of several vibrations must make the result extremely suspect. Normal coordinate cal-

Table II. $\nu(\text{C-I})$ Frequencies (cm⁻¹) in Substituted Ethanes

Molecule	Atom trans to I	$\nu(\text{C-I})$	Ref
ICH ₂ CH ₂ OH	H	517	<i>a</i>
	OH	617	
ICH ₂ CH ₂ F	H	517	9
	F	631	
ICH ₂ CH ₂ Cl	H	511	<i>b</i>
	Cl	576	
ICH ₂ CH ₂ I	H	483	<i>c</i>
	I	568	
ICH ₂ CH ₂ CN	H	498	8
	CN	634	

^a M. Kuhn, W. Luttke, and R. Mecke, *Z. Anal. Chem.*, **170**, 106 (1959). ^b S. Mizushima, T. Shimanouchi, I. Nakagawa, and A. Miyake, *J. Chem. Phys.*, **21**, 215 (1953). ^c K. W. Kohlrausch and G. P. Ypsilanti, *Z. Phys. Chem., Abt. B*, **29**, 274 (1935).

culations clearly show that the $\nu(\text{C-X})$ vibrations are sensitive to the azimuthal angle θ and in all cases deviations from a straight-line relationship are to be expected since the degree of sensitivity depends on the substituent Y. Nevertheless, the fact that reasonable correlations between frequency shifts and electronegativities are obtained makes the method of some specialized use in distinguishing between carbon-halogen stretching vibrations of different conformers. An analogy may be drawn between this approach and the "additional field effects" invoked by Bellamy and Williams¹⁵ to explain the difference between the $\nu(\text{C=O})$ frequencies for the conformers of α -chloro acid halides. This behavior, in which the frequency related to the staggered conformation is higher than that associated with the trans, is general for all monohalogenoacetyl halides.^{16,17}

(15) L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 3465 (1958).

(2) **Intensity Variations.** The energy difference between rotational isomers in solution varies with the polarity of the solvent. Hence one has the general well-known rule that the more polar conformer is relatively more favored in solvents having high dielectric constants. The solvation energy of a nonpolarizable molecule in a solvent of dielectric constant ϵ is given by

$$E^v = E^s = \frac{\epsilon - 1}{2\epsilon - 1} \mu^2/a^3 \quad (2)$$

where E^v and E^s are the energies in the vapor and solution phases, respectively, μ is the solute dipole moment, and a is the molecular radius. Abraham and co-workers¹⁸ have modified this equation to include contributions from polarization of the molecule by its own reaction field. The change in energy difference between rotational isomers A and B on passing from the vapor to solution phase is then given by

$$\Delta E^v - \Delta E^s = \frac{\mu_A^2 - \mu_B^2}{a^3} \frac{x}{1 - 2\alpha x/a^3} \quad (3)$$

where $x = (\epsilon - 1)/(2\epsilon + 1)$ and α is the molecular polarizability. Equation 3 predicts energy difference changes which are considerably greater than those determined experimentally, and it was found necessary to include a quadrupole term in order to obtain satisfactory agreement.

Very little use has been made of infrared spectroscopy to study energy differences between rotational isomers in various solvents. Direct measurements over an extended temperature range are theoretically feasible but experimentally impracticable because of the high volatility of most suitable solvents and the difficulties of making sufficiently reproducible intensity measurements in solution. However, the ratio of the number of molecules in the trans conformation compared with the gauche is related to the optical densities A_t and A_g of a band unique to each isomer. If ΔE is defined as ($E_g -$

(16) A. Y. Khan and N. Jonathan, *J. Chem. Phys.*, **50**, 1801 (1969).

(17) A. Y. Khan and N. Jonathan, *ibid.*, **52**, 147 (1970).

FCH ₂ CH ₂ Br						ClCH ₂ CH ₂ CN					
$\nu(\text{C-Br})$		$10^3\Delta\nu$	$\nu(\text{C-Br})$	$\Delta\nu$	$10^3\Delta\nu$	$\nu(\text{C-Cl})$		$10^3\Delta\nu$	$\nu(\text{C-Cl})$	$\Delta\nu$	$10^3\Delta\nu$
gauche	$\Delta\nu$	ν	trans			gauche	$\Delta\nu$	ν	trans		ν
588	0	0	689.5	0	0	686 ^b	0	0	771.5	0	0
580.5	7.5	12.7	684	5.5	7.9						
582	6	10.2	684	5.5	7.9	680	6	8.7	767	4.5	5.8
			678	11.5	16.6	670	16	23.3	754	17.5	22.7
581	7	11.9									
579	9	15.3	683	6.5	9.4	677	9	13.1			
576	12	20.4									
581	7	11.9	683	6.5	9.4						
578	10	17.0									
577	11	18.7									
			680.5	9	13.0	670	16	23.3	758	13.5	17.5
						673	13	18.9	762	9.5	12.3
						671	15	21.9	758	13.5	17.5
						670	16	23.3	757	14.5	18.8
			678.5	11	15.9	669	17	24.8	758	13.5	17.5
			679	10.5	15.2						

E_t), one can, by making the usual assumptions, arrive at the relationship

$$\Delta E = X - Y \log A_g/A_t \quad (4)$$

where X and Y are constants. This equation may be used to estimate energy difference variations in a range of solvents, provided that one accepts the reasonable first-order approximation that extinction coefficients are not solvent dependent.

A comprehensive study of the intensity variation of 1,2-dichloroethane in various solvents⁵ was published after this work was completed. That investigation showed that there was a reasonable straight-line relationship between the intensity ratio A_t/A_g and the relative frequency shifts for n -propyl chloride. Our values for A_t/A_g in the same solvents were in reasonable agreement with this work for the ν_{17} bands at 727 (trans) and 694 cm^{-1} (gauche). For the sake of completeness we have included the published values in the present Table III together with some additional data and new data for 1,2-dibromoethane and 1-chloro-2-fluoroethane. The bands in question were due to the ν_{16} vibration at 1192 (trans) and 1236 cm^{-1} (gauche) for the dibromo compound and the $\nu(\text{C-Cl})$ at 775 (trans) and 685 cm^{-1} (gauche) for the fluorinated ethane. For the present purposes we prefer to plot $\log A_t/A_g$ (or sometimes, for convenience $\log 10A_t/A_g$) against the quantity $(\epsilon - 1)/(2\epsilon + 1)$. The results are shown in Figure 3. It is clear from this figure that there is a reasonable smooth relationship between the energy difference and $(\epsilon - 1)/(2\epsilon + 1)$ except for the aromatic solvents. If eq 2 were an adequate representation of the influence of dielectric constant on energy difference, then a straight-line plot would be expected. However, the modified form of eq 3 used by Abraham, *et al.*,¹⁸ predicts a convex curve. There is perhaps just sufficient evidence in these plots to show that this is in fact the case. If the energy difference is known in both the vapor and the liquid

phases then it is straightforward to estimate the corresponding value in any of the other solvents given. It is interesting to apply this approach to the data given in Table IV and Figure 4 for the β -halopropionitriles.

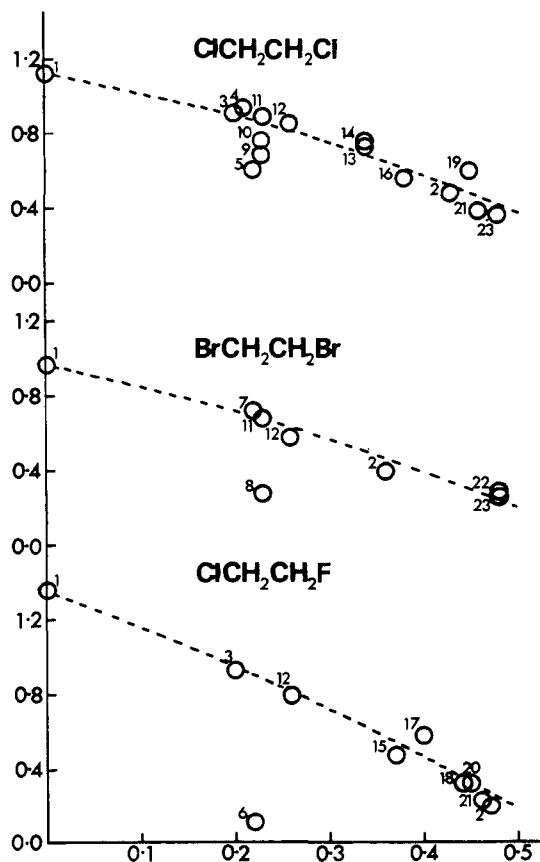


Figure 3. Plot of the logarithm of the intensity ratio of bands unique to trans and gauche isomers of 1,2-dichloroethane, 1,2-dibromoethane, and 1-chloro-2-fluoroethane against the dielectric constant function, $(\epsilon - 1)/(2\epsilon + 1)$: ordinate, $\log A_t/A_g$; abscissa, $(\epsilon - 1)/(2\epsilon + 1)$.

(18) R. J. Abraham, L. Cavalli, and K. G. R. Pachler, *Mol. Phys.*, **11**, 471 (1966).

Table III. Solvent Effects on Intensities of (C-X) Stretching Absorption Bands in 1,2-Dihaloethanes

Solvent	ϵ^a	$\frac{\epsilon - 1}{2\epsilon + 1}$	—1,2-Dichloroethane ^c —		—1,2-Dibromoethane ^d —		—Chloro-2-fluoroethane ^d —	
			$\frac{A_t(\text{C-Cl})}{A_g(\text{C-Cl})}$	Log $\frac{A_t(\text{C-Cl})}{A_g(\text{C-Cl})}$	$\frac{A_t(\text{C-Br})}{A_g(\text{C-Br})}$	Log $\frac{A_t(\text{C-Br})}{A_g(\text{C-Br})}$	$\frac{10A_t(\text{C-Cl})}{A_g(\text{C-Cl})}$	Log $\frac{10A_t(\text{C-Cl})}{A_g(\text{C-Cl})}$
1. Vapor	1	0	13.4 ^d	1.127	9.4	0.973	23.1	1.362
	10.7	0.43						
	(C ₂ H ₄ Cl ₂)	(C ₂ H ₄ Cl ₂)						
2. Liquid	4.9	0.36	3.0 ^d	0.477	2.5	0.398	1.6	0.204
	(C ₂ H ₄ Br ₂)	(C ₂ H ₄ Br ₂)						
	21.1	0.47						
	(C ₂ H ₄ FCl)	(C ₂ H ₄ FCl)						
3. Cyclohexane	2.0	0.20	8.2	0.914			8.5	0.929
4. Pentene	2.1	0.21	8.7	0.940				
5. 1,4-Dioxane	2.2	0.22	4.0	0.602				
6. Dioxane	2.2	0.22					1.3	0.114
7. Carbon tetrachloride	2.2	0.22			5.4	0.732		
8. Benzene	2.3	0.23			1.9	0.279		
9. Benzene- <i>d</i>	2.3	0.23	4.9	0.690				
10. <i>p</i> -Xylene	2.3	0.23	5.8	0.763				
11. Tetrachloroethylene	2.3	0.23	7.9	0.898	4.8	0.681		
12. Carbon disulfide	2.6	0.26	7.2	0.857	3.8	0.580	6.3	0.799
13. Diisopropyl ether	4.1	0.34	5.5 ^d	0.740				
14. Diethyl ether	4.3	0.34	5.7	0.756				
15. Diiodomethane	5.3	0.37					3.0	0.477
16. Ethyl acetate	6.0	0.38	3.6	0.556				
17. Iodomethane	7.0	0.40					3.8	0.580
18. Methyl isobutyl ketone	13.1	0.44					2.1	0.322
19. Mesityl oxide	15.0	0.45	3.9 ^d	0.591				
20. Methyl isopropyl ketone	15 ^b	0.45					2.1	0.322
21. Acetone	20.7	0.46	2.4	0.380			1.7	0.230
22. Methyl thiocyanate	35.0	0.48			1.9	0.279		
23. Acetonitrile	36.0	0.48	2.3	0.362	1.8	0.255		

^a Dielectric constant values taken mainly from A. A. Maryott and E. R. Smith, "Table of Dielectric Constants for Pure Liquids," National Bureau of Standards Circular 514, U. S. Government Printing Office, Washington, D. C., 1951. ^b Estimated value. ^c N. Oi and J. F. Coetzee, *J. Amer. Chem. Soc.*, **91**, 2473 (1969). ^d Present work.

Table IV. Solvent Effects on Intensities of C-X Stretching Absorption Bands^b in β -Halopropionitriles

Solvent	ϵ	$\frac{\epsilon - 1}{2\epsilon + 1}$	— β -Chloropropionitrile—		— β -Bromopropionitrile—		— β -Iodopropionitrile—	
			$\frac{A_t(\text{C-Cl})}{A_g(\text{C-Cl})}$	Log $\frac{10A_t(\text{C-Cl})}{A_g(\text{C-Cl})}$	$\frac{A_t(\text{C-Br})}{A_g(\text{C-Br})}$	Log $\frac{10A_t(\text{C-Br})}{A_g(\text{C-Br})}$	$\frac{A_t(\text{C-I})}{A_g(\text{C-I})}$	Log $\frac{10A_t(\text{C-I})}{A_g(\text{C-I})}$
1. Liquid		0.47 ^a	0.29	0.46	0.53	0.72	0.57	0.76
2. Cyclohexane	2.0	0.20	1.49	1.17	2.21	1.34	1.52	1.18
3. Carbon tetrachloride	2.2	0.22			1.52	1.18	2.05	1.31
4. Dioxane	2.2	0.22	0.68	0.83	1.22	1.09		
5. Tetrachloroethylene	2.3	0.23			1.47	1.17	2.14	1.33
6. Toluene	2.4	0.24					1.40	1.15
7. Diiodomethane	5.3	0.37	0.51	0.71			1.53	1.19
8. Chlorobenzene	5.7	0.38					1.03	1.01
9. Iodomethane	7.0	0.40	0.68	0.83	1.12	1.05	0.91	0.96
10. Methyl isobutyl ketone	13.1	0.44	0.35	0.54				
11. Methyl isopropyl ketone	15 ^a	0.45	0.30	0.48				
12. Diethyl ketone	16 ^a	0.45	0.30	0.48				
13. Acetonitrile	36.0	0.48					0.78	0.89

^a Estimated value. ^b Values for the carbon-halogen stretching vibrations are given in ref 8.

Vapor-phase energy difference measurements for these compounds have not been made because of their low volatility. The liquid-phase values are approximately 0.4, 0.5, and 0.8 kcal/mol, respectively,⁸ for the chloro, bromo, and iodo derivatives. In each case the gauche conformer is the more stable. Dipole moment measurements¹⁰ on the chloro and bromo compounds in carbon tetrachloride solution were inconclusive, but suggested that the gauche isomer was slightly the more stable. Figure 4 then may be taken as good evidence that the trans conformer is the more stable in the vapor

phase. This series and the 1-fluoro-2-haloethanes are thus examples of stability inversion on change of phase. This is not surprising, since both series have the gauche conformer as the more stable in the liquid phase and, as we have emphasized previously,^{8,9} there is no obvious reason why in the absence of specific internal association, such compounds should have this form as the more stable in the vapor state. It is also worth noting that Figures 3 and 4 give a warning against correlating liquid-state energy differences with intramolecular properties. Additionally, liquid-state energy difference values are often suspect because they are made over an extended temperature range and correc-

(19) M. F. El Bermani and N. Jonathan, unpublished data.

tions are not applied for the associated changes in density and dielectric constant.

The results given in Tables III and IV are evidence that, in agreement with the frequency shift data discussed earlier, the solute-solvent interaction is basically electrostatic in nature. The aromatic-type solvents show the usual anomalous behavior. Our data, like those of Oi and Coetzee,⁵ are not consistent with the concept of hydrogen bonding, since ethers behave normally. However, we see no need to invoke the hydrogen-bonding concept and prefer to suggest that the reason for these solvents being "more polar locally than their macroscopic properties indicate" is essentially due to dipole-induced dipole interaction. Such a model has been invoked to explain aromatic-solvent-induced shifts in nuclear magnetic resonance.²⁰ Indeed, it is the basis of a method which has been used for determining solute dipole moments.²¹ The finding that the frequency shifts for *n*-propyl chloride and isobutyl chloride in benzene > toluene > mesitylene⁵ is compatible with this theory because the increasing solvent bulk should progressively inhibit the arrangement of solvent molecules around solute.

The final point to be made from the intensity data is that there is a considerable change in the relative intensity of a band unique to one conformer on passing from low to high dielectric constants. This may be used as the basis of a most useful method for determining the conformations of the isomers, provided that there is a reasonable difference in their dipole moments. One can also use solvent-induced intensity changes as an aid to vibrational frequency analysis, since, unlike the frequency shift method, it is not only applicable to the C-X stretching vibrations. The solvent-induced intensity changes are the same for all bands unique to a

(20) W. G. Schneider, *J. Phys. Chem.*, **66**, 2653 (1962).

(21) T. L. Brown and K. Stark, *ibid.*, **69**, 2679 (1965).

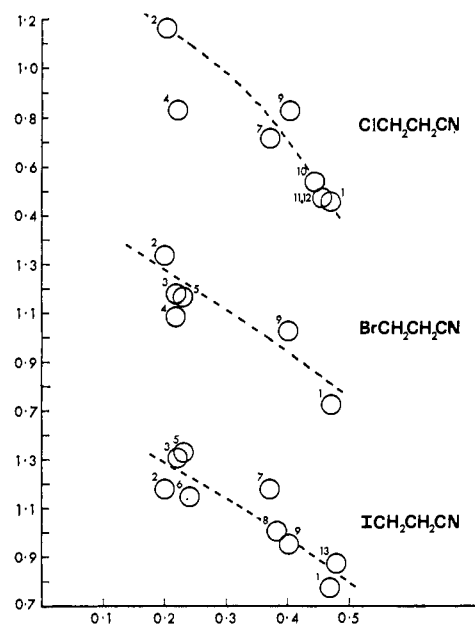


Figure 4. Plots of the logarithm of intensity ratios of $\nu(\text{C-X})$ bands of the trans and gauche isomers of the β -halopropionitriles against the dielectric constant function, $(\epsilon - 1)/(2\epsilon + 1)$, for β -chloropropionitrile, β -bromopropionitrile, and β -iodopropionitrile: ordinate, $\log 10A_t/A_g$; abscissa, $(\epsilon - 1)/(2\epsilon + 1)$.

particular isomer. In many cases "mixed bands can be readily recognized because of intermediate intensity changes. Although a variety of solvents may be employed for such measurements, it will frequently be found that the most extreme variations will be on passing from the vapor to the liquid phase.

Acknowledgments. We wish to thank the Science Research Council for the award of a studentship (to A. J. W.).