

THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 50, 1980

EFFECT OF PRESSURE ON THE CONFORMATION
OF MOLECULES*

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In general, pressure affects the sizes and shapes of molecules, and the purpose of this paper is to review what is known about the effect of pressure on the shapes of small molecules, as described by internal rotation angles. The principal investigations made so far are on the effect of freezing induced by pressure changes, the equilibria between conformational isomers in fluids, and the changes in the structure of molecules due to changes in internal rotation angle in both solids and liquids.

1. Introduction

This paper is offered in celebration of the fiftieth volume of The Review of Physical Chemistry of Japan, and as a contribution to the Commemoration Volume. I send with it my congratulations on its previous successes and my best wishes for its continuing success in the future.

In general, pressure affects the sizes and shapes of molecules. If a molecule is symmetric enough and is subject to symmetric enough forces, as, for example, a diamond crystal subjected to hydrostatic pressure, pressure changes only the interatomic distances, and changes them uniformly until a catastrophic change to a new structure occurs. In diamond, the rate of decrease of all interatomic distances with increasing pressure is one third the compressibility, or $0.12 \text{ \AA Mbar}^{-1}$ at low pressures. In less symmetric molecules, where the interatomic angles are not determined by symmetry, or in symmetric molecules that are distorted by an environment of lower symmetry, the interatomic angles are also affected by pressure. The interatomic angles can be divided into two kinds, namely, bond angles that are determined by two atoms next to a third, and internal rotation angles, *i.e.* the dihedral angle between the planes ABC and BCD of the non-linear chain of atoms A-B-C-D. The purpose of this paper is to review what is known about the effect of pressure on the equilibrium between conformational isomers and on the internal rotation angles.

Although it is known by general symmetry arguments that bond angles change with pressure unless they are determined by symmetry, almost nothing quantitative is known. An example is the distortion of the ZnCl_4^{2-} ion in Cs_2ZnCl_4 . The ion is on a plane of symmetry, and is therefore distorted by the crystal forces from the tetrahedral symmetry it presumably has when isolated. In the isolated ZnCl_4^{2-} ion one of the stretching vibrations is triply

(Received November 7, 1980)

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degenerate. In the Cs_2ZnCl_4 crystal, it splits into 3 non-degenerate vibrations, and the splitting is a measure of the distortion from tetrahedral. The splitting increases with increasing pressure¹⁹ and so the distortion increases. Unfortunately, there are four independent Cl-Zn-Cl angles and three independent Zn-Cl bonds, and the nature of the distortion cannot be determined even if the change of bond length is neglected.

It is in general easier to distort internal rotation angles than bond angles because they are weaker. In addition, some molecules that can change their internal rotation angles have two or more conformational isomers. The equilibrium between these isomers changes with pressure, and this changing equilibrium constitutes another aspect of the effect of pressure on internal rotation angles. The purpose of this paper is to review the current state of knowledge about small molecules in these areas.

The effect of hydrostatic pressure on molecular conformations is of course part of the larger subject, the effect of stress on molecular conformations. One of the more spectacular examples of this subject is the rubberiness of rubber. In rubber, the polymer chains are irregularly coiled and are pinned to one another at rare cross links. When the rubber is strained, the chains uncoil by changing the rotation about the bonds to new equilibrium positions. Related effects occur in crystalline polymers. For example, the Young's moduli of highly ordered polyoxymethylene and polypropylene are much smaller than those of highly ordered polyethylene. In polyoxymethylene and polypropylene, the molecules are coiled, and the moduli at low strains are determined by the resistance to internal rotation, whereas in polyethylene the molecules are extended chains, and it is the C-C-C angle bending that determines the modulus.²⁰ Although these effects are very important, they will not be discussed here because this review is restricted to small molecules.

For the same reason, the effects of pressure on the conformation of proteins and polypeptides, the radius of gyration of polymer molecules²¹, and the structure of polymer crystals will be omitted, and so also will the effect of pressure on order-disorder transitions in lipid bilayers and related materials. Nevertheless, the results reviewed should be relevant to all these topics.

2. Effect of Pressure on the Equilibrium between Conformers

2-1. *Effect of freezing on molecular conformations*

Many fluids are composed of two or more conformers in equilibrium, and when they freeze one of the conformers is usually preferred in the crystal. The effect of freezing by cooling and by squeezing on the conformer present in the crystal has been studied by Brasch⁴⁰ and by Klaeboe and coworkers⁵⁻¹⁴⁰ in a number of papers. The results are summarized in Table 1. In most cases, cooling and squeezing form the same solid, but occasionally form a different one. Often one of them is metastable, but occasionally two stable solids containing different conformers occur. Little is known about the causes of these effects except in general terms.

Table 1. Conformations in the solid state of molecules having more than one conformational isomer

Molecule	State ^a in solid formed by		Ref. for pressure experiment
	cooling	squeezing at ~22°C	
1, 2-dichloroethane	<i>trans</i>	<i>trans</i>	Brasch ⁽⁴⁾
1, 2-dibromoethane	<i>trans</i>	<i>trans</i>	Brasch ⁽⁴⁾
1, 1, 2-trichloroethane	less polar	either either	Brasch ⁽⁴⁾ Christian <i>et al.</i> ⁽⁵⁾
1, 1, 2, 2-tetrachloroethane	<i>gauche</i>	<i>trans</i>	Brasch ⁽⁴⁾
1, 1, 2, 2-tetrabromoethane	usually <i>gauche</i> ^b	usually <i>trans</i> ^b	Brasch ⁽⁴⁾
1, 2-dibromopropane	<i>trans</i> ^c	<i>trans</i> ^c	Thorbjørnsrud <i>et al.</i> ⁽⁶⁾
1, 3-dibromopropane	<i>gg</i>	<i>gg</i>	Thorbjørnsrud <i>et al.</i> ⁽⁷⁾
1, 3-diiodopropane	<i>gg</i>	<i>tt</i> ^d	Thorbjørnsrud <i>et al.</i> ⁽⁷⁾
methylcyclohexane	—	<i>e</i>	Lauer and Peterkin ⁽⁸⁾
chlorocyclohexane	<i>e</i> + <i>a</i> at high temp. <i>e</i> at low temp.	<i>e</i> ^e	Klaeboe ⁽⁹⁾
bromocyclohexane	<i>e</i> at low temp.	<i>e</i> ^e	Klaeboe ⁽⁹⁾
iodocyclohexane	<i>e</i>	<i>e</i> ^e	Klaeboe ⁽⁹⁾
cyanocyclohexane	? ^f	<i>a</i>	Hornqvist and Klaeboe ⁽¹⁰⁾
isocyanatocyclohexane	<i>e</i>	<i>a</i>	Hornqvist and Klaeboe ⁽¹⁰⁾
<i>trans</i> -1, 2-dichlorocyclohexane	<i>ee</i>	<i>ee</i>	Klaeboe ⁽¹¹⁾
<i>trans</i> -1, 2-dibromocyclohexane	<i>aa</i>	<i>aa</i>	Klaeboe ⁽¹¹⁾
<i>trans</i> -1, 2-chlorobromocyclohexane	<i>ee</i>	<i>aa</i>	Hornqvist and Klaeboe ⁽¹²⁾
<i>trans</i> -1, 2-dimethylcyclohexane	—	<i>ee</i> or <i>ee</i> + <i>aa</i>	Lauer and Peterkin ⁽⁸⁾
<i>cis</i> -1, 3-dimethylcyclohexane	—	<i>ee</i>	Lauer and Peterkin ⁽⁸⁾
<i>trans</i> -1, 4-dichlorocyclohexane	<i>ee</i> ^g	<i>aa</i> ^h	Ellestad and Klaeboe ⁽¹³⁾
<i>trans</i> -1, 4-dibromocyclohexane	<i>ee</i> ⁱ	<i>aa</i> ^h	Ellestad and Klaeboe ⁽¹³⁾
<i>trans</i> -1, 4-diiodocyclohexane	<i>ee</i>	<i>aa</i>	Klaeboe ⁽¹⁴⁾
<i>trans</i> -1, 4-bromochlorocyclohexane	<i>ee</i>	<i>aa</i>	Klaeboe ⁽¹⁴⁾
<i>trans</i> -1, 4-chloriodocyclohexane	<i>ee</i>	<i>aa</i>	Klaeboe ⁽¹⁴⁾
<i>trans</i> -1, 4-bromiodocyclohexane	<i>ee</i>	<i>aa</i>	Klaeboe ⁽¹⁴⁾
<i>trans</i> -1, 4-dimethylcyclohexane	—	<i>a</i> ^j	Lauer and Peterkin ⁽⁸⁾

^a *a*=axial, *e*=equatorial, *g*=*gauche*, *t*=*trans*.^b The other conformer could also be obtained.^c The C-Br bonds are *trans*.^d Of *C*_{2v} symmetry.^e A small amount of the *a* conformer remained in the polycrystalline solids.^f Probably formed a glass.^g At room temperature. Either *ee* or *aa* crystals could be obtained by annealing at >10°C an amorphous solid formed from the vapor.^h Obtained by squeezing the ordinary solid.ⁱ At room temperature.^j Probable conclusion.

2-2. Equilibrium between conformers in solution

Until recently, the only method of measuring the difference of volume of conformers has been by measuring the attenuation of sound waves by the fluid. The maximum acoustic loss μ_{\max} per wavelength due to an interchange between conformers is related to the difference ΔV of partial volume between the conformers by the equation

$$\mu_{\max} = A \left[1 - \frac{\Delta V}{V} - \frac{C_p}{\alpha_T \Delta H^\circ} \right],$$

where A is a constant depending on the concentrations of the conformers at equilibrium and the standard difference between them of the enthalpy ΔH° and the Gibbs function, and C_p and α_T the heat capacity and thermal expansivity of the solution respectively.¹⁵⁾ It often happens, however, that

$$\frac{\Delta V}{V} - \frac{C_p}{\alpha_T \Delta H^\circ} \ll 1,$$

and then μ_{\max} is insensitive to ΔV . Nevertheless, over thirty volumes of conformational isomerism have been measured by this technique and are summarized by North and Pethrick,¹⁵⁾ but the uncertainties of most of them are high.

The effect of pressure P on the equilibrium constant K of two conformers,

$$K = a_1/a_2,$$

where a_1 and a_2 are the activities of the conformers, is directly related to the difference ΔV° of volume between them in the standard states used to define the activities. The relation is

$$\left[\frac{\partial \ln K}{\partial P} \right]_T = -\frac{\Delta V^\circ}{RT},$$

where R is the gas constant and T the temperature. Usually, the activities are replaced by mole fractions, so that the standard states are the actual states in the solution, and if the conformers are in dilute solution, the equilibrium constant is often written as the ratio of their concentrations. The effect of pressure on conformational equilibria can, therefore, be used to determine the difference of volume between the conformers.

Several measurements have been reported recently of the effect of pressure on the relative proportions of conformers, and they are summarized in Table 2. Both the infrared and Raman spectra have been used to analyze the mixtures, using either diamond anvils or steel pressure vessels fitted with windows.

The simplest compound that has been measured is *n*-heptane,¹⁶⁾ and the concentrations were measured by the Raman spectra of the longitudinal compression, or acoustic, vibrations. The all *trans* conformer, *tttt*, could be distinguished from the single *gauche*, *tggt*, as they have bands at 309 and 507 cm⁻¹ respectively, and the single *gauche* and the double *gauche*, *gggt*, conformers contribute to the band at 312 cm⁻¹. It was assumed that the normal coordinates of these vibrations were unaffected by pressure. From the data of Fig. 3 of Schoen *et al.*¹⁶⁾

Effect of Pressure on the Conformation of Molecules

Table 2. Volume differences between conformational isomers

Compound and isomers ^a	Solvent	Temp. °C	Pressure range, kbar	Pressure vessel ^b	Analytical method	ΔV , ml ^c	Ref.
<i>n</i> -heptane <i>tgtr</i> , <i>tttt</i>	neat	~21	0-16	d. a.	Raman	~-1.8	Schoen <i>et al.</i> ¹⁶⁾
<i>n</i> -heptane <i>gttt</i> and <i>ggtt</i> , <i>tttt</i>	neat	~21	0-16	d. a.	Raman	~-1.3	Schoen <i>et al.</i> ¹⁶⁾
1,2-dichloroethane <i>gauche</i> , <i>trans</i>	<i>n</i> -hexane 20% v/v	~21	0-5	s. v.	aniso. Raman ^c	-3.8 ± 0.2	Taniguchi <i>et al.</i> ¹⁷⁾
	<i>n</i> -hexane 30% v/v	~21	0-4	s. v.	aniso. Raman	-3.5 ± 0.2	Taniguchi <i>et al.</i> ¹⁷⁾
1,2-dibromoethane <i>gauche</i> , <i>trans</i>	2-methylbutane 10% v/v	~21	0-2.5	s. v.	aniso. Raman	-4.5 ± 0.5	Taniguchi <i>et al.</i> ¹⁷⁾
	acetonitrile 10% v/v	~21	0-3.5	s. v.	aniso. Raman	-2.0 ± 0.5	Taniguchi <i>et al.</i> ¹⁷⁾
1,1,2-trichloroethane more polar, less polar	neat	~45	0-4	d. a.	infrared	-3.8 ± 1	Christian <i>et al.</i> ¹⁸⁾
	CS ₂ 20% v/v	~45	0-7	d. a.	infrared	-1.8 ± 0.4	Christian <i>et al.</i> ¹⁸⁾
Chlorocyclohexane axial, equatorial	CS ₂	~50	0-10	d. a.	infrared	-1.9 ± 0.1	Christian <i>et al.</i> ¹⁸⁾
<i>trans</i> -1,4-dichlorocyclohexane axial, equatorial	CS ₂	~50	0-10	d. a.	infrared	-2.8 ± 0.2	Christian <i>et al.</i> ¹⁸⁾
<i>trans</i> -1,4-dibromocyclohexane axial, equatorial	CS ₂ 0.12 M	~50	0-10	d. a.	infrared	-3.8 ± 0.2	Christian <i>et al.</i> ¹⁹⁾

^a The volume change is the volume of the first-named less that of the second-named conformer.^b d. a. represents a diamond anvil, and s. v. a steel pressure vessel with glass windows.^c aniso Raman is the anisotropic Raman spectrum.

the volume change on transforming the *trans* to the single *gauche* is $\sim -1.8 \text{ cm}^3 \text{ mol}^{-1}$, and for transforming it to the mixture of the single and double *gauche* is $\sim -1.3 \text{ cm}^3 \text{ mol}^{-1}$.

The effect of pressure on the equilibrium between *trans* and *gauche* 1, 2-dichloroethane and 1, 2-dibromoethane, which are almost the archetypes of conformational isomerism, was measured by Taniguchi *et al.*¹⁷⁾ using a steel pressure vessel with glass windows. The concentrations were determined by means of the anisotropic Raman spectrum of the carbon-halogen stretching vibrations, as they appear to be sufficiently uncoupled from the other bands to be used for this purpose. The ratio of the integrated intensities of the two *gauche* bands to that of the *trans* symmetric bands was taken as the ratio of the concentrations. The logarithm of the ratio was linear in the pressure and gave volume changes at the *trans*-to-*gauche* transformation of 1, 2-dichloroethane in 20% and 30% v/v solution in *n*-hexane of -3.8 and $-3.5 \text{ cm}^3 \text{ mol}^{-1}$ respectively. For 1, 2-dibromoethane in 10% v/v solution in 2-methylbutane and acetonitrile, the volume change was -4.5 and $-2.0 \text{ cm}^3 \text{ mol}^{-1}$ respectively.

The remaining compounds in Table 2 were studied by Christian *et al.*^{18,19)} by infrared spectroscopy using a diamond anvil cell. There are more problems in using infrared than in using Raman spectroscopy, particularly the bending of the anvil faces, which would cause a non-uniform sample thickness. However, at the small pressure ranges used, this may not be important.

At least three effects contribute to these volume changes, namely, the overlap of the methyl groups, the change of local packing of the solvent and solute, and the change of the long-range electrostatic interaction with the solvent.

Only the first two effects contribute significantly to the equilibria in *n*-heptane. The distance between the methyl groups in the *gauche* conformer is $\sim 3.1 \text{ \AA}$, which is much shorter than the distance 4.0 \AA which is a typical methyl-methyl distance in crystals.²⁰⁾ The overlap volume is, therefore, of the magnitude of a few $\text{cm}^3 \text{ mol}^{-1}$.

The intermolecular packing effect has been discussed theoretically for *n*-butane by Pratt *et al.*²¹⁾ using as a model rigid methyl and methylene groups in a molecule whose only degree of freedom was the internal rotation angle. For *n*-butane dissolved in carbon tetrachloride and in *n*-butane the volume change for the *trans*-to-*gauche* transformation was calculated as -4.7 and $\sim -2 \text{ cm}^3 \text{ mol}^{-1}$ respectively. On the basis of Schoen *et al.*'s¹⁶⁾ results on *n*-heptane, and taking account of the contraction due to the overlap of the methyl groups, these values may be somewhat high, but are of the right magnitude. A semiquantitative discussion of the same effect was given by Schoen *et al.*¹⁶⁾

As the two *gauche*-1, 2-dihaloethanes are polar molecules, having dipole moments of about 3 D, and the *trans* conformers have no dipole moment, the volume difference between them is determined partly by electrostatic effects, as well as by the internal and intermolecular steric effects that dominate the volume change in *n*-heptane. Electrostatic effects can often be represented crudely by a model in which the molecule is represented as a spherical distribution

of charge that is characterized by dipole and quadrupole moments, and the solvent is represented by a continuous dielectric having a low-frequency permittivity ϵ . The difference ΔG between the conformers of the change of Gibbs function on transferring the molecule from vacuum to the dielectric is readily calculated.²²⁾ The electrostatic contribution to the volume difference between the conformers can be obtained by differentiating it with respect to pressure.¹⁷⁾

The electrostatic dipole and quadrupole moments of 1, 2-dichloroethane and 1, 2-dibromoethane were calculated assuming that they could be represented by carbon-halogen point dipoles directed along the bonds and situated at their centers. The calculated electrostatic volume differences are $-3.3 \text{ cm}^3 \text{ mol}^{-1}$ for 1, 2-dichloroethane in *n*-hexane solution and -1.5 and $-1.9 \text{ cm}^3 \text{ mol}^{-1}$ for 1, 2-dibromoethane in 2-methylbutane and acetonitrile solution respectively. These values, when -1.3 and $-2.5 \text{ cm}^3 \text{ mol}^{-1}$ are added for halogen overlap in the *gauche* conformers, agree reasonably well with the measured values listed in Table 2, but fail to represent the difference between 1, 2-dibromoethane in 2-methylbutane and acetonitrile.

The existence of an electrostatic effect on the volume change seems to be demonstrated by the differences between *n*-heptane and the dihaloethanes, but the effects of the internal overlap and intermolecular packing are not experimentally differentiated.

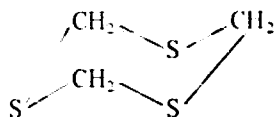
3. Effect of Pressure on Internal Rotation Angles

If an internal rotation angle is determined by symmetry, as in ethane, small changes of pressure will not affect it. However, if the *cis* conformation of ethane has the smaller volume, it will be preferred, and at a high enough pressure, a transformation will occur from the staggered to the *cis* conformation. No example of this kind of conformational change is yet known.

If an internal rotation angle is not determined by symmetry, it will depend on the pressure. Two molecules are now known whose change of internal rotation angle with pressure has been measured. They are 1, 2-dichloroethane and trithiane.

There are no general ways of measuring the effect of pressure on internal rotation angles, and each case must be treated as a separate problem. Nmr spectroscopy may be useful if there are no conformers interconverting faster than the nmr time scale, but no measurements have been reported. Two methods have been used so far, both using Raman spectroscopy. In one (trithiane) the intensity of a vibration could be expanded in an empirical power series in the deviation from the *eclipsed* conformation, where it has zero intensity. If the first term is taken, there is only one parameter, which can be eliminated by comparing intensities at high and low pressure. In the other (1, 2-dichloroethane) a simplified model of the two coupled oscillators was treated, which yielded the relative intensities of two bands as a function of the internal rotation angle. Each will be treated in turn.

Trithiane is a puckered six-membered ring compound $(\text{CH}_2\text{S})_3$,



Its conformation is not determined by symmetry, and so it should depend on the pressure, as well as on the solvent, phase, and other aspects of its environment. It is not immediately obvious whether pressure will tend to flatten or to pucker the molecule further. The first evidence that the molecule might flatten under pressure was reported by Brasch *et al.*²³⁾ and Hamann *et al.*²⁴⁾ Several bands in the infrared spectrum of the solid, and also in the spectrum of trioxane, were greatly reduced in intensity relative to the rest of the spectrum at pressures estimated to be of the magnitude of 50 kbar. The authors speculated that the changes in the spectrum might be due to a flattening of the molecule. It turns out, however, that the observed effects and the assumed^{23,24)} vibrational assignments are not consistent with flattening, but the assignment could be changed in a plausible way to make it so for trithiane,²⁵⁾ but trioxane appears not to flatten significantly.²⁶⁾

The puckered trithiane ring has symmetry C_{2v} , and the vibrations belong to species A_1 and E , which are active in both the infrared and Raman, and A_2 , which is inactive in both. The flattened ring has symmetry D_{3h} . The A_1 vibrations that become symmetric to the horizontal plane in the flat molecule lose infrared activity, as do also the E vibrations that become antisymmetric to the horizontal plane. The A_1 vibrations that become antisymmetric to the horizontal plane lose their Raman activity. Although the changes in the infrared spectrum,²³⁾ after some reassignment,²⁵⁾ agreed with flattening, they were purely qualitative and cannot be further analyzed.

The only readily measurable Raman band that loses its intensity in the planar molecule is

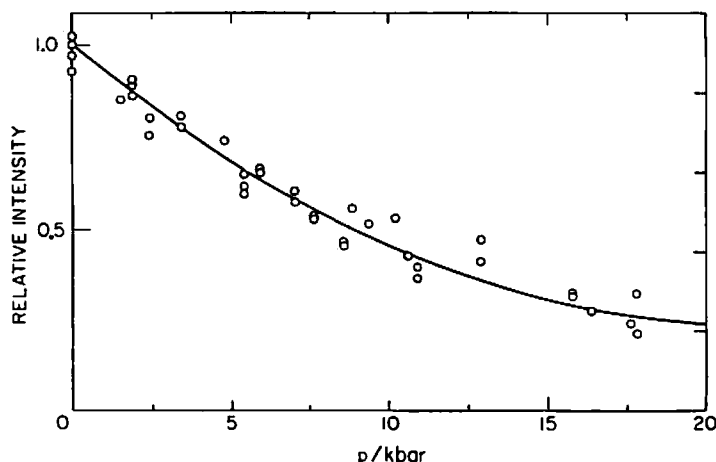


Fig. 1. The relative intensity of the 309 cm^{-1} ring-flattening vibration of trithiane and its neighbors as a function of pressure.²⁵⁾ The scale of the ordinate is arbitrary.

the ring-flattening or internal rotational vibration at 309 cm^{-1} . Its Raman intensity²³⁾ relative to its neighboring bands, is plotted on an arbitrary scale in Fig. 1. By 18 kbar it has decreased to about a quarter of its value at zero pressure.

This result can be analyzed as follows. Symmetry requires that the Raman intensity be even in x , where x is the distance between the carbon and sulphur planes, and to be zero at the flat conformation, for which $x=0$. It also requires it to be zero in the (unrealizable) fully puckered conformation, in which all the carbon atoms are superimposed, and so are the sulphur atoms. For this conformation, $x=a$, the C-S bond length. The simplest formula for the Raman intensity $I(x)$ as a function of the equilibrium interplanar distance x that meets these conditions is

$$I(x) \propto x^2(a^2 - x^2).$$

The intensity as a function of pressure is, then,

$$\frac{I(P)}{I(P=0)} = \frac{x^2}{x_0^2} \frac{1 - x^2/a^2}{1 - x_0^2/a^2}, \quad (1)$$

where P is the pressure, x the equilibrium value of x at pressure P , and x_0 the value of x at $P=0$. From the structure of the trithiane crystal,^{28,29)} $a=1.818\text{ \AA}$ for all bonds and x_0 is 0.652 \AA . To be formally accurate, the C-S bond length ought to be treated as a function of pressure. To the accuracy of the theory, however, it can be taken as constant. From these values, the intensities of Fig. 1, and Eq. (1), the value of x/x_0 as a function of pressure can be obtained. It is plotted in Fig. 2. Within experimental error it is linear in the pressure

$$x/x_0 = 1 - 26P/\text{Mbar},$$

and if an extrapolation is valid, trithiane would become planar at $\sim 38\text{ kbar}$.

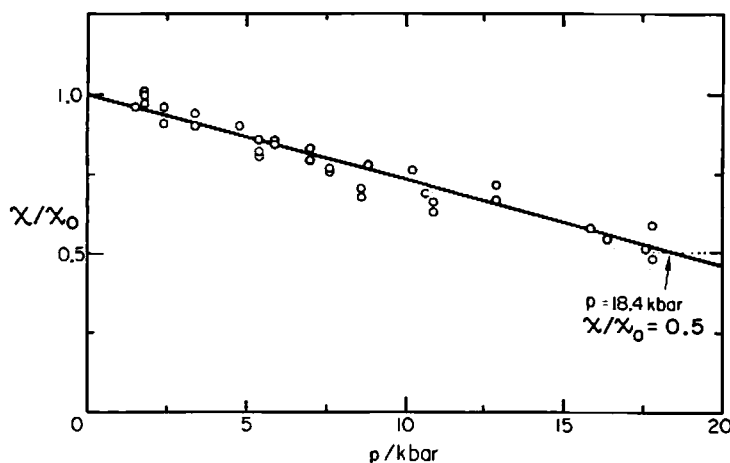


Fig. 2. The equilibrium value of x/x_0 of trithiane as a function of pressure.²⁵⁾

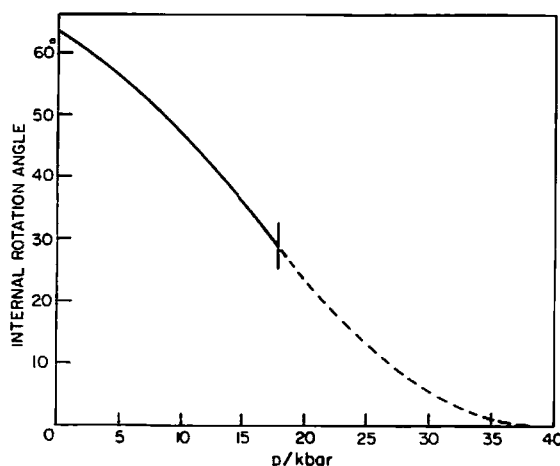


Fig. 3. The internal rotation angle θ of trithiane as a function of pressure.²⁵⁾

The internal rotation angle at zero pressure is about 66° .^{27,28)} The S-C-S and C-S-C angles are not related to one another by symmetry, but by assuming that the difference of their cosines is independent of the pressure, the internal rotation angle θ , measured from the *cis* conformation, changes with x/x_0 at the rate

$$\frac{d\theta}{d(x/x_0)} = -50^\circ,$$

and so the rate of change of θ with pressure is²⁵⁾

$$\frac{d\theta}{dp} = -1.3^\circ \text{ kbar}^{-1}.$$

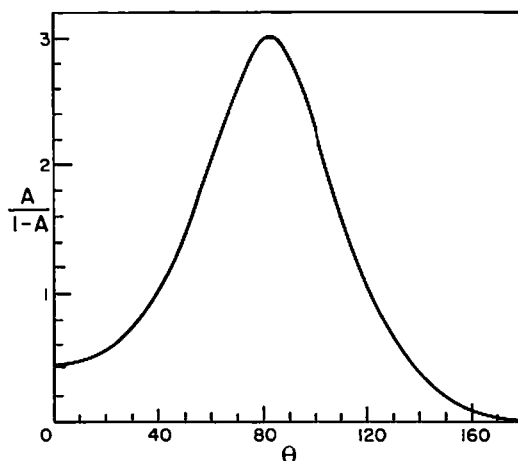
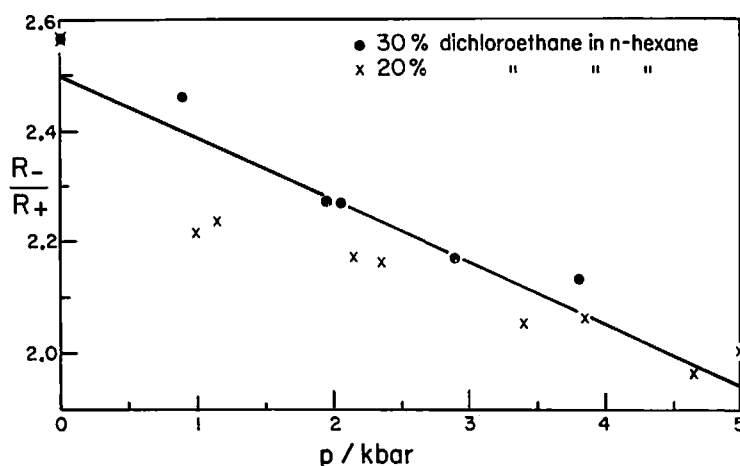
With the same assumption, the internal rotation angle can be calculated as a function of pressure, and the results are shown in Fig. 3.

The first step in determining how the internal rotation angles of the 1, 2-dihaloethanes change with pressure is to determine how the Raman intensities change with internal rotation angle. A model is assumed in which the two carbon-halogen stretching motions are not significantly coupled to the other vibrations, and the polarizabilities of the carbon-halogen bonds change in a cylindrically symmetric manner when the bond is stretched. Then it can be shown that ratio of the integrated anisotropic Raman intensities of the out-of-phase and in-phase carbon-halogen stretching vibrations is²⁹⁾

$$\frac{R_-(\text{aniso})}{R_+(\text{aniso})} = \frac{\nu_-}{\nu_+} \frac{A}{1-A}, \quad (2)$$

where ν_- and ν_+ are the frequencies of the asymmetric and symmetric vibrations respectively,

$$A = 3 \left(\sin^2 \alpha \cos^2 \frac{1}{2} \theta - \sin^4 \alpha \cos^4 \frac{1}{2} \theta \right),$$

Fig. 4. The quantity $A/(1-A)$ of Eq. (2).²⁹⁾Fig. 5. The ratio of the anisotropic Raman intensities of the asymmetric and symmetric carbon-chlorine stretching vibrations of *gauche*-1,2-dichloroethane.²⁹⁾

α the C-C-halogen angle, and θ the internal rotation angle from the *cis* conformation. The factor $A/(1-A)$, which is plotted in Fig. 4, is, therefore, a unique function of the internal rotation angle, and so the angle can be determined from the measured relative intensities and frequencies.

The experimental measurements of the ratio of the anisotropic Raman intensities of the carbon-halogen stretching vibrations of 1, 2-dichloroethane dissolved in *n*-hexane are shown as a function of pressure in Fig. 5. They are somewhat scattered, but are consistent with a slope of -0.12 kbar^{-1} , which corresponds to a change of internal rotation angle of about $-2^\circ \text{ kbar}^{-1}$. This is of the same magnitude as the rate of change of the internal rotation angle in trithiane. Its value implies that if the slope were independent of pressure, the *cis*

conformation would become the stable one at ~ 15 kbar. The transition state between the two *gauche* conformers would have become a stable state.³⁰¹

In liquids, each molecule is, of course, being continually bombarded by its neighbors and so undergoing continuous distortion. Under certain circumstances, the mean square value of this distortion and the effect of pressure can be measured by the Raman spectrum. The underlying theory of the method is obtained by specializing Eq. (2) to small deviations ϕ from the *trans* conformation $\theta = \pi$. It then becomes

$$\frac{R_{-}(\text{aniso})}{R_{+}(\text{aniso})} = \frac{3}{4} \frac{\nu_{-}}{\nu_{+}} \sin^2 \alpha \phi^2.$$

Of course, any distortion that removes the center of symmetry will make the asymmetric stretch of the *trans* conformer Raman active. However, the internal rotation coordinate is much the weakest coordinate, and might be expected to be the most distorted. Then the Raman activity induced by the distortion may be attributed in a first approximation to the distortion of the internal rotation angle. If this is so, the mean value of the intensity ratio averaged over a time that is long compared to the time of the significant fluctuations of the internal rotation angle gives the mean square value of the angle.

The asymmetric band of *trans*-1, 2-dibromoethane,²⁹¹ which is the only substance for which measurements have been made so far, is overlapped by the symmetric band of the *gauche* conformer, and so its exact intensity is uncertain. It is about 0.02 and 0.04 respectively in 2-methylbutane and acetonitrile,²⁹¹ which correspond to root mean square deviations from the *trans* conformation of ~ 10 and $\sim 15^\circ$ respectively. The resolution of the two bands is sufficiently uncertain that the effect of pressure on the distortion cannot at present be obtained accurately, but the method will be applied in more favorable cases.

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