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DIELECTRIC STUDIES—III

CONFORMATIONAL STUDIES OF 1,4-DIOXAN,1,4-DITHIAN AND 1,4-THIOXAN

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Abstract—By the employment of a microwave procedure of improved accuracy, the weak dielectric absorption of 1,4-dioxan,1,4-dithian and 1,4-thioxan has been studied. 1,4-Dioxan and 1,4-thioxan have been examined in the liquid state, 1,4-dithian in *p*-xylene and 1,4-thioxan in cyclohexane and in nujol. All have been studied at four microwave frequencies and the static dielectric constant at one megacycle has also been measured. The data have been analysed to yield apparent dipole moments and, in the case of 1,4-thioxan two relaxation times. Speculations have been made as to the identities of the species present. The potential of this type of approach to conformational isomer studies of ring systems is considered, particularly with reference to determination of energy barriers between two such isomers.

INTRODUCTION

NUMEROUS dipole moment determinations have been carried out on 1,4-dioxan and a few on 1,4-dithian. Calderbank and Le Fèvre[1] summarized the position in 1949 to be that, in the gaseous state, 1,4-dioxan is nonpolar and that in the liquid state both had either very small or zero moments. However, even the gaseous state value of zero is uncertain since values of 0 and 0·49D have been reported.[2] The nonmicrowave procedure in dipole moment (μ) evaluation of a solute in a solvent employs the equation:

$$\mu = 0{\cdot}01281\{({}_2P_\infty - xR_D)T\}^{1/2} \qquad (1)$$

where R_D is the molar fraction for the sodium D line, ${}_2P_\infty$ is the polarization of the solute at infinite dilution, and the correction factor (x taken to be 1·0, 1·05 or 1·1) to allow for the fact that:

$$P_A + P_E \neq R_D \qquad (2)$$

For substances with a very low moment the uncertain allowance to be made for the excess atomic polarization over the contribution in R_D makes it impossible to decide whether the compound has a genuine moment, especially if a high value for the atomic polarization might be anticipated in connection with a particular bending mode. However, the microwave technique does not suffer from such approximations.

Cumper and Vogel[3] have recently examined 1,4-thioxan in benzene solution employing Eq. (1) in the evaluation and obtained a moment of 0·42D but pointed out that a large atomic polarization term could result in a significant error in the dipole moment.

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[1] K. E. Calderbank and R. J. W. Févre, *J. Chem. Soc.* 199 (1949).

[2] A. L. McClellan, *Tables of Experimental Dipole Moments*, W. H. Freeman, U.S.A. (1963).

[3] C. W. N. Cumper and A. I. Vogel, *J. Chem. Soc.* 3521 (1959).

Although we have studied the dipole moments of these three compounds by a dielectric absorption technique at microwave frequencies, our major aim was to examine the energy barriers between conformational isomers in such ring systems. No such data appears to be available in the literature and, indeed, is quite sparse for any saturated ring systems. If the energy barrier lies between about 1 to 3·5 kcal/mole, our method would seem to be well suited to such studies for systems which may be analysed in terms of two or three relaxation times. However, to achieve such analyses on weakly polar liquids or very dilute solutions, it is necessary to have a greater accuracy of measurement than most of the dielectric absorption methods have employed in the past and it is desirable to measure at three or more microwave frequencies.

RESULTS AND BASIC THEORY

The apparatus and techniques employed have been described previously.[4] A bridge method is employed and the attenuation and phase shift are measured for

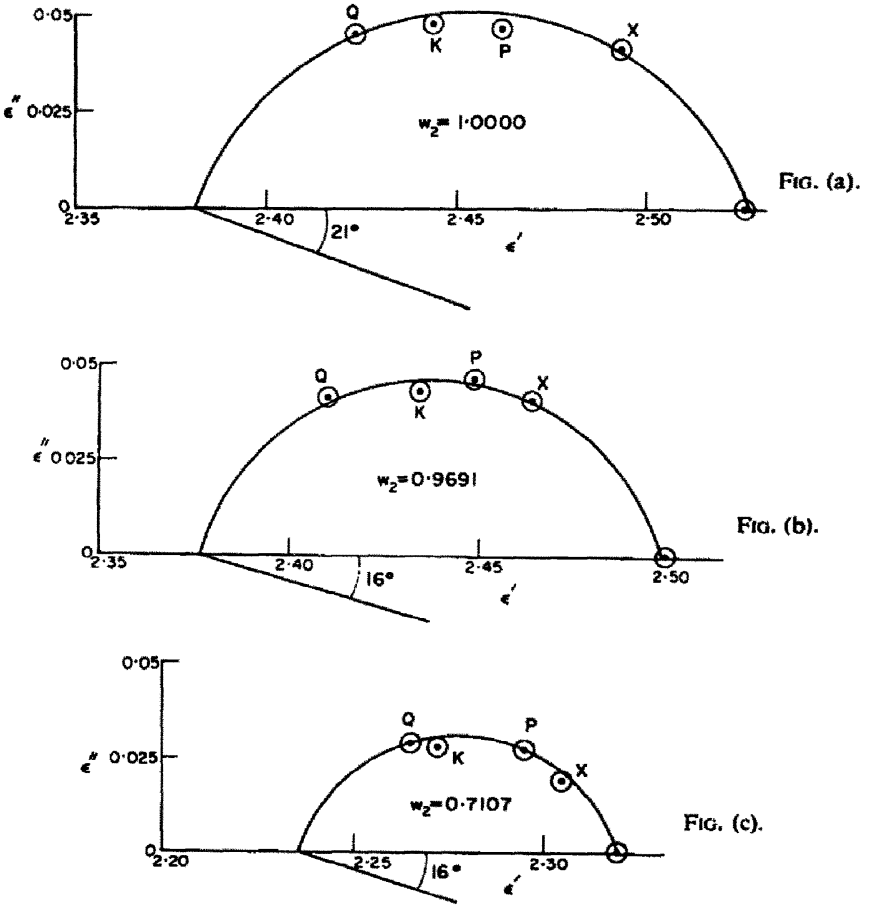

FIG. (a).

FIG. (b).

FIG. (c).

FIG. 1. Cole-Cole plots of various weight fractions of 1,4-thioxan in cyclohexane and nujol at 25°.

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[4] W. F. Hassell, M. D. Magee, Miss S. W. Tucker and S. Walker, *Tetrahedron* **20**, 2137 (1964).

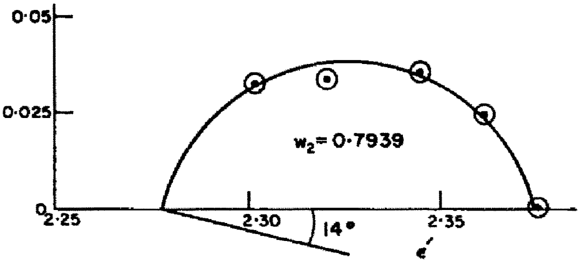

Fig. (d).

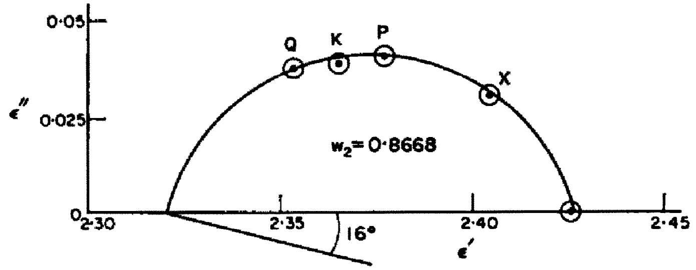

Fig. (e).

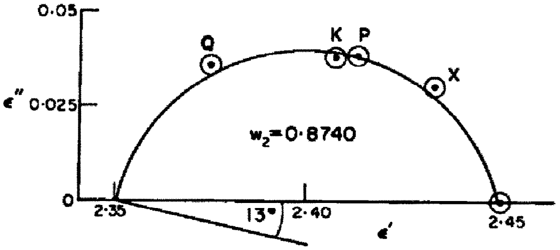

Fig. (f).

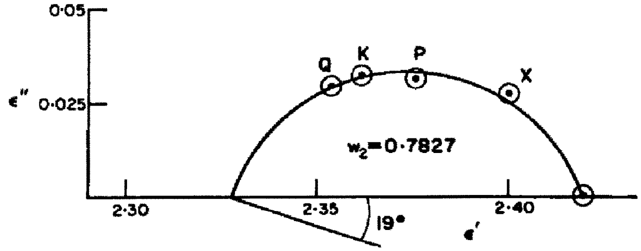

Fig. (g).

various pathlengths of liquid or solution and the dielectric constant (ε') and loss factor (ε'') are evaluated for each wavelength; ε' may be identified with the usual picture of dielectric constant, whereas ε'' measured the ability of the medium to dissipate energy; ε' and ε'' are related to the relaxation time (τ) and the angular frequency ω by the equations:

$$\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \frac{\omega\tau}{1 + \omega^2\tau^2} \tag{3}$$

$$\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{1 + \omega^2\tau^2} \tag{4}$$

where ε_0 is the static dielectric constant (e.g. the value measured at 1 Mc/s frequency) and ε_∞ is the dielectric constant at very high frequencies.

On elimination of $\omega\tau$ from Eqs. (3) and (4) the equation of a circle is obtained:

$$\left\{\varepsilon' - \frac{(\varepsilon_0 + \varepsilon_\infty)}{2}\right\}^2 + \varepsilon''^2 = \left[\frac{(\varepsilon_0 - \varepsilon_\infty)}{2}\right]^2 \tag{5}$$

from which a plot of ε'' (ordinate axis) against ε' in the complex plane gives what is known as the Cole-Cole plot.[5] If the diameter of the semi-circle lies along the abscissa, then the dielectric data may be explained in terms of one relaxation time. If, however, this diameter has been displaced by angle $\alpha(\pi/2)$ in a clockwise direction from the ε_∞ point, then this suggests the presence of more than one relaxation time.

From the ε'' and ε' data for each frequency and the ε_0 value the best semi-circle is fitted by computer analysis. In addition, the radius, the centre and the angle $\alpha(\pi/2)$ are so obtained. The resulting data for 1,4-thioxan are presented graphically in Fig. 1 since their inadequacies may be readily assessed in such a plot.

The loss factors of 1,4-dioxan and 1,4-dithian were so small that Cole-Cole plots were not feasible and the data are given in Table 1.

Table 1. Dielectric absorption data for 1,4-dithian in *p*-xylene, 1,4-dioxan and *p*-xylene. μ_a and μ_b are the apparent dipole moments (in D) corresponding to mean relaxation times of 3×10^{-12} and 7×10^{-12} sec respectively as calculated from equation 6. The loss of the solvent was subtracted in the case of 1,4-dithian

Solute	Solvent	Wt. Fraction	Band†	ε'	ε''	μ_a	μ_b
1,4-dithian	*p*-xylene	0·0635	Q	2·263	0·0056	0·13	0·13
			K	2·272	0·0043	0·17	0·14
			X	2·282	0·0025	0·17	0·13
	p-xylene	1·000000	Q	2·255	0·0052		
			K	2·256	0·0037		
			X	2·264	0·0022		
1,4-dioxan		1·000000	Q	2·213	0·0079	0·11	0·11
			K	2·214	0·0043	0·09	0·08
			X	2·219	0·0028	0·11	0·08

† The letters Q, K, P and X refer to measurements at 0·86, 1·25, 1·85 and 3·22 cm respectively.

The apparent dipole moments of 1,4-dioxan and 1,4-dithian were evaluated from the equation:

$$\mu = \left\{\frac{27\text{kT}}{4\pi\text{N}c} \times \frac{\varepsilon''}{(\varepsilon_1 + 2)^2} \times \frac{(1 + \omega^2\tau^2)}{\omega\tau}\right\}^{1/2} \tag{6}$$

in which c is the concentration in moles/cc and ε_1 is the dielectric constant of the solution.

For a system with two mutually independent relaxation times (τ_1 and τ_2) Bergmann[6] developed the following method of analysis. For such a system Eqs. (3) and (4) are modified to include contributions from each of the re-orienting dipoles as follows:

$$\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = C_1 \frac{\omega\tau_1}{1 + (\omega\tau_1)^2} + C_2 \frac{\omega\tau_2}{1 + (\omega\tau_2)^2} = Y \tag{7}$$

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[5] K. S. Cole and R. H. Cole, *J. Chem. Phys.* **9**, 341 (1941).

[6] K. Bergmann, *Doctoral Dissertation*, Freiburg/Breisgau, West Germany (1957).

$$\frac{\varepsilon^1 - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{C_1}{1 + (\omega\tau_1)^2} + \frac{C_2}{1 + (\omega\tau_2)^2} = Z \tag{8}$$

in which C_1 and C_2 are the relative weights of each relaxation term and

$$C_1 + C_2 = 1 \tag{9}$$

The relaxation times and their relative weights may be evaluated by a graphical procedure and for this Y and Z are divided into two contributions:

$$Y = C_1Y_1 + C_2Y_2 \tag{10}$$

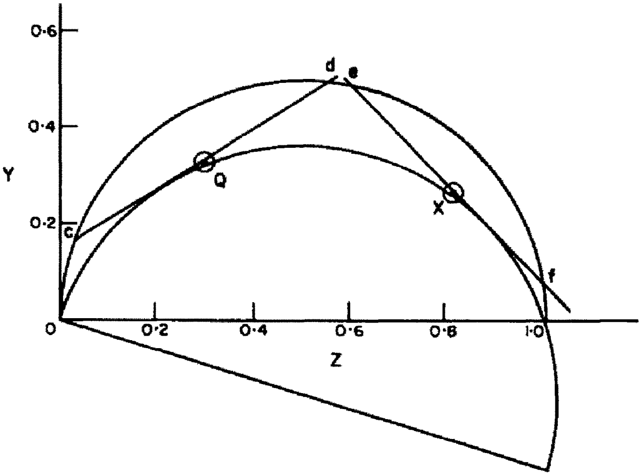

Fig. 2. Semi-circles employed in the Bergmann analysis. The two chords are drawn to pass through the Q and K band points so that the ratio of cQ and Qd is the same as eX to Xf.

$$Z = C_1Z_1 + C_2Z_2 \tag{11}$$

in which the values of Y and Z are assessed from the experimental data since

$$Y = \frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} \qquad Z = \frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} \tag{12}$$

where the ε_∞ value may be obtained from the high frequency intercept of the Cole-Cole plot with the abscissa. When Y is plotted against Z for the data at different frequencies, as in Fig. 2, the result is a semicircle, the diameter of which is inclined at the angle $\alpha(\pi/2)$ to the abscissa. Plotted also in this figure is the normalized Debye semi-circle with the diameter on the abscissa. A chord of the outer semi-circle is chosen so that it passes through the point (Y,Z) which has been calculated from the data for one particular microwave frequency. Similarly, the procedure is repeated for each of the microwave frequencies. The choice of chords is guided by the fact that the ratios such as cQ/Qd have to be equal for all the wavebands. This ratio is equal to C_2/C_1. Hence, from this and Eqs. (7) to (11), C_1 and C_2, τ_1 and τ_2 may be evaluated. These initial estimates are then fed to a computer programmed to solve equation 7.

From the relaxation times so evaluated the free energy barrier ($\Delta G^{\neq}$) separating two equilibrium positions of the relaxing dipole may be evaluated from transition state theory[7] to be:

$$\frac{1}{\tau} = \kappa \frac{kT}{h} \exp\left(-\Delta G^{\neq}/RT\right) \tag{13}$$

where h is Plank's constant, k the Boltzmann constant, T the absolute temperature and κ the transmission coefficient and is normally taken to be 1; this corresponds with the case that each time a molecule is excited to the top of the energy barrier it continues to move in the same direction to the next minimum position. Thus, the process is one of relaxation between two equilibrium positions but is commonly referred to as rotation.

The dipole moment from the dielectric approach of 1,4-thioxan was evaluated from ε_0 and ε_∞ values obtained at each concentration by employing the equation:

$$\mu = 0{\cdot}012812 \left\{\frac{3T(\varepsilon_0 - \varepsilon_\infty)}{c(\varepsilon_0 + 2)(\varepsilon_\infty + 2)}\right\}^{1/2} \tag{14}$$

in which c is the concentration in moles/cc.

In Table 2 dipole moment values, the two relaxation times, α values and the viscosity (η_{12}) of certain solutions are given.

For 1,4-thioxan the dipole moment was also evaluated by the Guggenheim approach in the weight fraction range (w_2) 0·7 to 1·0 and the essential data are as follows:

$$\left(\frac{\varepsilon - \varepsilon_1}{w_2}\right)_{w_2 \to 0} = 0{\cdot}2321 \qquad \left(\frac{n^2 - n_1^2}{w_2}\right)_{w_2 \to 0} = 0{\cdot}1233$$

with $R_D = 27{\cdot}84\ \text{cm}^3$, $P_0 = 2{\cdot}719\ \text{cm}^3$ and the dipole moment 0·36D and employing Smith's correction[8,9] 0·35D.

Table 2. Data obtained from solutions of 1,4-thioxan in cyclohexane and nujol at 25°

Wt. fraction of thioxan	Solvent	η_{12} c.p.s.	μ (D)	τ_1	τ_2	α
1·0000		2·18	0·31	15	2·2	0·23
0·9691	cyclohexane	2·03	0·30	14	2·4	0·18
0·8668	cyclohexane	1·75	0·31	14	2·7	0·18
0·7939	cyclohexane	1·59	0·31	10	2·0	0·15
0·7107	cyclohexane	1·44	0·31	12	2·3	0·18
0·8740	nujol	2·94	0·29	13	2·8	0·14
0·7827	nujol	3·73	0·30	14	2·2	0·21

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[7] S. Glasstone, K. Laidler and H. Eyring, *The Theory of Rate Processes*. McGraw-Hill, New York (1941).

[8] R. P. Young, A. Holt and S. Walker, *Tetrahedron* **20**, 2351 (1964).

[9] J. W. Smith, *Electric Dipole Moments*. Butterworths, London (1955).

DISCUSSION

Since 1,4-dioxan, 1,4-dithian and 1,4-thioxan have measurable loss factors, this establishes that these systems contain contributions from polar species. From the data in the Cole–Cole plots the apparent dipole moment of 1,4-thioxan was obtained from Eq. 14 and is 0·31D in cyclohexane and 0·30D ± 0·01D in a mixture of 1,4-thioxan and nujol. For 1,4-dithian and 1,4-dioxan, largely as a result of the low loss factors and small dielectric constant variation at the different wavebands, the mean or the individual relaxation times cannot be deduced. Fortunately, the resulting dipole moments are fairly insensitive to the relaxation times assumed in the calculation (Table 1) and it would seem that the moments of 1,4-dithian and 1,4-dioxan are about 0·15D and 0·1D respectively.

Calderbank and Le Fèvre considered the best value for the total molar polarization of 1,4-dioxan at 25° was 24·6 cc. From atomic-electronic polarization data from dielectric constant sources,[9] it then becomes possible to estimate the dipole moment to be 0·16D. If, however, the molar refraction of 21·7 c.c. for the sodium-D line is taken to equal the sum of the atomic and electronic polarization, then the corresponding moment is 0·38D. Our microwave value thus bears out a high atomic polarization contribution in 1,4-dioxan. For both 1,4-dithian and 1,4-dioxan it would seem likely that in addition to a chair isomer, which has a zero moment, there is also some polar boat form present. An alternative explanation could be that the moment results from the dipole–dipole interaction of the type visualized by Whiffen.[10]

For 1,4-dioxan the atomic polarization is about 15% of the electronic polarization[9] which is quite high relative to the majority of molecules. Such data are not available for 1,4-dithian and 1,4-thioxan. To gain an appreciation as to whether the latter had a large atomic polarization term the moment in cyclohexane of 0·31D obtained by the microwave technique may be compared with that of 0·35D deduced from the Guggenheim approach. Thus, on comparison of these values with those of 1,4-dioxan, the atomic polarization contribution would appear significantly less for 1,4-thioxan.

The dielectric loss of 1,4-thioxan was appreciably greater than that of the other two and consequently was chosen for a more detailed study. In Table 2 the apparent dipole moment in cyclohexane and also in the nujol-1,4-thioxan mixture is virtually constant. Such consistency is not, however, to be anticipated for the individual relaxation times, which may be obtained by the Bergmann method. For a most favourable case the accuracy would not be expected to be better than ±10%. The lower relaxation time of $\sim 2{\cdot}5 \times 10^{-12}$ sec may be compared with that of tetrahydrothiophen and pyridine in cyclohexane at 25° of $\sim 2 \times 10^{-12}$ (to be published) and $2{\cdot}7 \times 10^{-12}$ sec at 20° respectively.[11] In fact, the closest parallel is sym-trioxan which is known to exist predominantly in the chair form[12] and the relaxation time of which in benzene is just less than that of pyridine in the same solvent. Thus, our τ_2 value can be identified with the relaxation of the chair form of 1,4-thioxan which from the dipole moment value must be the form predominantly present. Even bigger molecules such as chlorocyclohexane[11] and camphor,[13] which are roughly of a similar shape to 1,4-thioxan, have relaxation times of only $7{\cdot}4 \times 10^{-12}$ sec and $7{\cdot}1 \times 10^{-12}$

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[10] D. W. Whiffen, *Trans. Far. Soc.* **46**, 124 (1950).

[11] Von F. Hufnagel, H. Kilp, *Z. Naturforschung* **18a**, 770.

[12] R. C. Miller and C. P. Smyth, *J. Amer. Chem. Soc.* **79**, 308 (1963).

[13] Von A. Spernol and K. Wirtz, *Z. Naturforschung* **8a**, 522 (1953).

sec respectively in cyclohexane at 20°. One candidate for the higher relaxation time of $\sim 15 \times 10^{-12}$ sec is the overall rotation of another conformational isomer. However, the difference in volume and shape amongst the possible forms would seem insufficient to account for this. Nevertheless, it must be noted that in the case of a chair form the re-orientation of the dipole could be analysed in terms of rotation about two axes whereas with a skew boat the resultant dipole would be almost perpendicular to the long axis of this roughly ellipsoidal molecule and the re-orientation would be largely about this axis. As judged in terms of the volume swept out by such a species the relaxation time might be expected to be similar to that of the chair form. However, little is known regarding the relative magnitude of such relaxation times.

Its being related to the existence of an associated species of the type $(OC_4H_8S)_n$ would seem extremely improbable since the dipole moment value remains sensibly constant both in cyclohexane and nujol solutions of different concentration and in the pure liquid. In addition, the dipole–dipole relaxation mechanism as visualized by Whiffen[10] would hardly account for the τ_1 value since that type of interaction leads to relaxation times $\sim 1 \times 10^{-12}$ sec. A more likely interpretation is that τ_1 corresponds with a relaxation process involving the inter-conversion of two conformational isomers, that is an intramolecular re-orientation between two positions of equilibrium.

If only the chair and skew boat forms are present, then from the bond angles and bond moment data summarized by Cumper and Vogel[3] and the measured moment, the proportions of chair and boat may be estimated as approximately 99 to 1 respectively. This may be compared with the IR and Raman results of 1,4-dioxan which have shown that those molecules in the boat form are present in almost a negligible amount.[14] Calculation shows that an asymmetrical boat form of 1,4-thioxan with a moment of about 0·5D would correspond to an appreciable contribution from that form—sufficient to be readily detected by other spectroscopic methods.

It is interesting to note that each process is giving similar contributions (i.e. $C_1 \sim C_2$) to the dielectric loss. Two of the factors which determine these values are the:

(a) relative magnitude of the dipole moments involved in the relaxation processes, that is μ_1 and μ_2 corresponding respectively to τ_1 and τ_2, since the dielectric loss is directly proportional to the square of the relevant dipole moment.

(b) relative populations of the re-orienting species.

Since $C_1 \sim C_2$, it follows that if only two forms are present and C_2 corresponds to the relaxation contribution from the chair form with the low dipole moment, which is present to the extent of about 99%, then $\mu_1^2 \gg \mu_2^2$. This large C_1 contribution could result from the re-orientation of the appreciable COC or the CSC dipoles where the μ_{CO} and μ_{CS} bond moments are about 1·7 and 1·6D respectively and the $C\hat{O}C$ and $C\hat{S}C$ angles of inclination to the mean plane of the carbon atoms in the chair forms are about 60° and 55° respectively. The normal boat form which involves eclipsed hydrogen atoms would seem unlikely whereas the transformation:

$$\text{Skew boat} \rightarrow \text{chair}$$

may be achieved by "rotation" about the C—S or C—O bonds without introducing interactions due to eclipsed hydrogen atoms, and such a transformation would be consistent with the C_1/C_2 ratio. Little is known of potential energy or free energy

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[14] S. I. Mizushima, *Structure of Molecules and Internal Rotation.* Academic Press, New York (1954).

barriers relating to conformational changes in such heterocyclic six-membered ring compounds and no appropriate comparison can be made with our experimental free energy value of 2·9 kcal/mole. Such a comparison is desirable for a more definite identification that the τ_1 relaxation process is to be associated with a conformational change and that the transformation is of this type.

CONCLUSION

Both the dipole moment and the relaxation time data indicate the presence of more than one conformational isomer for 1,4-thioxan in the liquid state, in cyclohexane and in a 1,4-thioxan–nujol mixture. The dielectric data may be analysed in terms of two relaxation times—one corresponding with the re-orientation of the chair form (τ_2) while a strong candidate for the other τ_1 is an interconversion between two conformational isomers in equilibrium. A less likely explanation is that τ_1 is the relaxation time for the re-orientation of the skew boat form. The τ_2 value of $2{\cdot}5 \times 10^{-12}$ sec and the τ_1 of 15×10^{-12} sec by means of transition state theory lead to free energies of activation for these relaxation processes of 1·6 and 2·7 kcal/mole respectively. Even if the relaxation time errors were of the order of ±20%, the corresponding errors in the energy barriers would be only about ±0·1 kcal/mole. This compares most favourably with the values quoted by other methods. The potential of this procedure in the study of suitable energy barriers between conformational isomers would seem considerable.

EXPERIMENTAL

Materials. The purification of cyclohexane and *p*-xylene has been described earlier.[8] 1,4-Dioxan—Analar grade was purified by Eigenberger's method.[15] 1,4-Dithian was prepared from Na_2S and ethylene dibromide;[16] the product was twice recrystallized from EtOH and dried in vacuum over P_2O_5. The m.p. was 111·5°. 1,4-Thioxan—Analar grade was refluxed with and then distilled from Na through a 30 theoretical plate spinning band column and the second fraction at 147° was collected. To ensure that all the materials were dry, the liquids were stored in dark bottles over Na whilst 1,4-dithian was kept in a desiccator over P_2O_5. Samples of each were analysed by gas chromatography to confirm purity and dryness.

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[15] E. Eigenberger, *J. Prakt. Chem.* **75**, 130 (1931).

[16] R. C. Fusan, R. D. Lipscomb, B. C. McKusick and L. S. Reed, *J. Org. Chem.* **11**, 513 (1946).