

**A P P E N D I X**

**List of publications**

**Reprints of published papers**

### List of publications

1. Dielectric studies of ortho and para bromoanisoles and  $\beta$ -bromophenetole in the liquid state, Bulletin of the Chemical Society of Japan, 47, 2315 (1974).
2. Microwave absorption and relaxation processes in thioanisole in the liquid state, Indian Journal of Physics, 49, 133 (1976).
3. Dielectric relaxation in substituted propanes in the liquid state, The Journal of Chemical Physics, 65 No.9, 3595 (1976).
4. Dielectric relaxation in p-substituted thiophenols in the liquid state, Bulletin of the Chemical Society of Japan, 49, 663 (1976).
5. Microwave absorption and internal rotation in some dicyano alkanes in benzene solution, Indian Journal of Physics, 51 B, 34 (1977).
6. Microwave absorption and dielectric relaxation in some substituted propanes in the liquid state, Advances in Molecular Relaxation and interaction processes, 10, 273 (1977).
7. Microwave absorption and relaxation processes in some halogenated esters in the liquid state, Indian Journal of Physics, 51 B, 42 (1977).
8. Internal rotation of multibonded groups attached to phenyl ring and their possible geometrical structure, Advances in Molecular Relaxation and interaction process, Vol. 12, No.3 (1978) (in press).
9. Relaxation mechanisms in 4-bromo-3-methylthiophenol and 4-chloro- $\alpha$ -toluolthiol in the liquid state (communicated).
10. Relaxation processes in some halogenated esters in the liquid state (communicated).

MICROWAVE ABSORPTION AND DIELECTRIC RELAXATION IN SOME SUBSTITUTED  
PROPANES IN THE LIQUID STATE

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(Received 30 March 1976)

ABSTRACT

The dielectric absorption in 1-phenyl-propyl-bromide, 1-phenyl-propyl-mercaptan and 1-phenyl-propyl-amine in the liquid state has been studied at different microwave frequencies. The dielectric data were analysed in terms of molecular and end-group  $\text{CH}_2\text{X}$  relaxation time ( $\text{X} = \text{Br}$ ,  $\text{SH}$  and  $\text{NH}_2$ ) and their relative weight factors, heat of activation, dipole moments have been determined.

INTRODUCTION

Aromatic compounds with rotatable small polar groups are found to be characterized by two discrete relaxation processes [1] intramolecular relaxation having a shorter relaxation time and molecular relaxation with a relatively larger relaxation time. In contrast to this, aliphatic molecules such as *n*-alkylhalides [2], cyanides [3], ketones [4], in which group rotation occurs about the C-C bond only, show a distribution of relaxation times between two limits - the lower limit corresponding to the rotation of the end-group about its bond with the rest of the molecule and the upper limit corresponding to the largest orienting unit i.e. molecular end-over-end rotation. In the case of aliphatic ethers [5] and sulphides [6], in which group rotation occurs about a bond other than the C-C bond, two discrete relaxation processes have been reported. In the case of  $\alpha$ ,  $\omega$ -diholoalkanes [7,8] the dielectric data were represented by Davidson-Cole skewed arc plots which are associated with co-operative orientations.

It would be interesting to study the dielectric behaviour of long chain aliphatic molecules with a phenyl ring attached to one terminal. The results of microwave investigations on the dielectric absorption of 1-phenyl-propyl-bromide, 1-phenyl-propyl-mercaptan and 1-phenyl-propyl-amine are now presented.

## EXPERIMENTAL

Chemicals: Pure samples of 1-phenyl-propyl-bromide, 1-phenyl-propyl-mercaptan and 1-phenyl-propyl-amine, obtained from 'Ega Chemie' (Germany), were dried and distilled under reduced pressure before use in the investigations. The boiling points in all the liquids were in agreement with literature values.

Apparatus: The apparatus for the measurements of dielectric permittivity  $\epsilon'$ , dielectric loss  $\epsilon''$ , in the region 0.8, 1.25, 1.62 and 3.49 cm microwaves were described earlier [9]. The static dielectric permittivity  $\epsilon_0$  was measured at 1 MHz, the refractive index  $n_D$  was determined with an 'Abbe refractometer', the viscosity  $\eta$  was measured with an Ostwald viscometer and the density  $d$  with a pycnometer. The temperature in each experiment was kept constant within  $\pm 1^\circ\text{C}$  by means of a thermostat. The estimated errors in the determination of  $\epsilon'$  and  $\epsilon''$  are about 2% and 4% respectively.

## RESULTS

The experimental values of dielectric permittivity  $\epsilon'$  and dielectric loss  $\epsilon''$  at different microwave frequencies and at different temperatures are given in Table 1, which also includes the static dielectric permittivity  $\epsilon_0$  at different temperatures. Complex plane plots (Fig. 1) of the dielectric loss  $\epsilon''$  and dielectric permittivity  $\epsilon'$  shows a symmetric distribution with a depressed centre, unlike the asymmetric distribution in aliphatic ethers [5,6] and haloalkanes [7]. The distribution parameter obtained from the arc plots in all the liquids studied were appreciably large at all temperatures, indicating the presence of more than one relaxation process in them.

Attempts were then made to analyse the dielectric data in terms of two relaxation processes making use of Bergmann equations [10]

$$a = \frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{c_1}{1 + \omega^2 \tau_1^2} + \frac{(1 - c_1)}{1 + \omega^2 \tau_2^2} \quad (1)$$

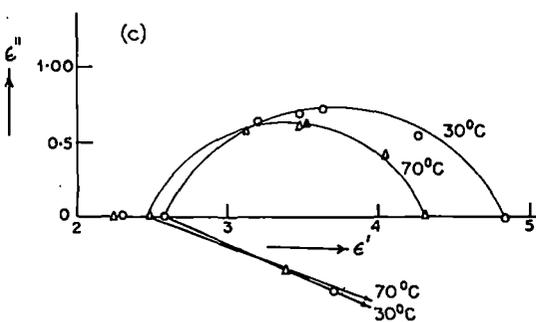
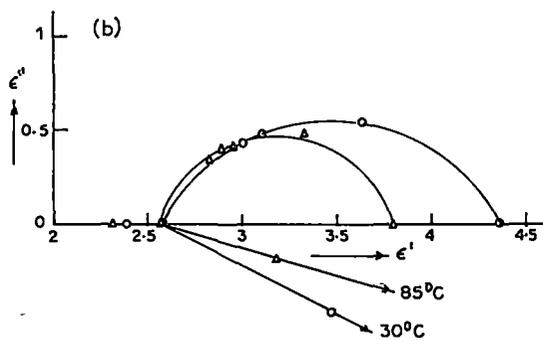
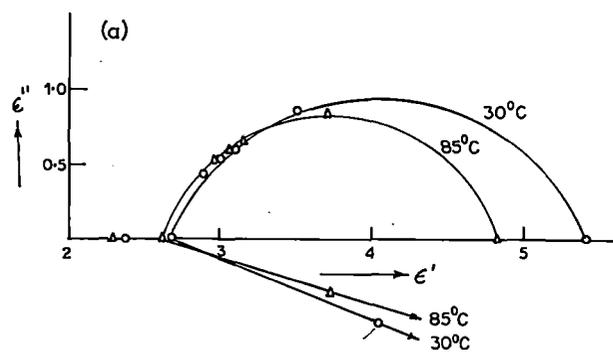


Fig.1.(a) Cole-Cole arc plot-3 phenyl-propyl-bromide; (b) Cole-Cole arc plot-3 phenyl-propyl-mercaptan; (c) Cole-Cole arc plot-3 phenyl-propylamine.

Table 1. Observed and calculated values of dielectric permittivity and dielectric loss

3-phenyl-propyl-bromide										
T°C	f = 1 MHz		f = 8.6 GHz				f = 18.5 GHz			
	$\epsilon_0$	$\epsilon'_{\text{obs}}$	$\epsilon'_{\text{cal}}$	$\epsilon''_{\text{obs}}$	$\epsilon''_{\text{cal}}$	$\epsilon'_{\text{obs}}$	$\epsilon'_{\text{cal}}$	$\epsilon''_{\text{obs}}$	$\epsilon''_{\text{cal}}$	
30	5.41	3.50	3.43	.85	.85	3.10	3.12	.60	.61	
50	5.18	3.60	3.50	.86	.87	3.14	3.15	.62	.62	
70	4.96	3.68	3.57	.85	.88	3.16	3.18	.64	.66	
85	4.83	3.71	3.62	.85	.87	3.16	3.20	.65	.66	
3-phenyl-propyl-mercaptan										
T°C	$\epsilon_0$	f = 24.03 GHz				f = 35.13 GHz				
		$\epsilon'_{\text{obs}}$	$\epsilon'_{\text{cal}}$	$\epsilon''_{\text{obs}}$	$\epsilon''_{\text{cal}}$	$\epsilon'_{\text{obs}}$	$\epsilon'_{\text{cal}}$	$\epsilon''_{\text{obs}}$	$\epsilon''_{\text{cal}}$	
30	5.41	3.00	3.03	.53	.55	2.88	2.91	.43	.46	
50	5.18	3.02	3.05	.54	.56	2.87	2.93	.41	.46	
70	4.96	3.05	3.08	.57	.58	2.90	2.97	.46	.50	
85	4.83	3.07	3.10	.59	.60	2.96	2.97	.52	.52	
3-phenyl-propyl-mercaptan										
T°C	$\epsilon_0$	f = 8.6 GHz				f = 18.5 GHz				
		$\epsilon'_{\text{obs}}$	$\epsilon'_{\text{cal}}$	$\epsilon''_{\text{obs}}$	$\epsilon''_{\text{cal}}$	$\epsilon'_{\text{obs}}$	$\epsilon'_{\text{cal}}$	$\epsilon''_{\text{obs}}$	$\epsilon''_{\text{cal}}$	
30	4.36	3.64	3.42	.54	.59	3.11	3.16	.47	.49	
50	4.15	3.58	3.38	.50	.56	3.06	3.11	.45	.46	
70	3.95	3.46	3.31	.47	.53	2.99	3.03	.43	.44	
85	3.80	3.34	3.29	.48	.51	2.96	2.99	.42	.43	
3-phenyl-propyl-mercaptan										
T°C	$\epsilon_0$	f = 24.03 GHz				f = 35.13 GHz				
		$\epsilon'_{\text{obs}}$	$\epsilon'_{\text{cal}}$	$\epsilon''_{\text{obs}}$	$\epsilon''_{\text{cal}}$	$\epsilon'_{\text{obs}}$	$\epsilon'_{\text{cal}}$	$\epsilon''_{\text{obs}}$	$\epsilon''_{\text{cal}}$	
30	4.36	3.01	3.09	.44	.47	2.89	2.97	.40	.44	
50	4.15	2.97	3.04	.42	.44	2.86	2.93	.38	.41	
70	3.95	2.92	2.96	.40	.41	2.81	2.87	.35	.37	
85	3.80	2.90	2.92	.40	.39	2.83	2.83	.34	.34	
3-phenyl-propyl-amine										
T°C	$\epsilon_0$	f = 8.6 GHz				f = 18.5 GHz				
		$\epsilon'_{\text{obs}}$	$\epsilon'_{\text{cal}}$	$\epsilon''_{\text{obs}}$	$\epsilon''_{\text{cal}}$	$\epsilon'_{\text{obs}}$	$\epsilon'_{\text{cal}}$	$\epsilon''_{\text{obs}}$	$\epsilon''_{\text{cal}}$	
30	4.83	4.27	4.00	.53	.68	3.63	3.68	.71	.68	
50	4.57	4.15	3.88	.48	.61	3.53	3.58	.62	.61	
70	4.32	4.05	3.88	.42	.54	3.52	3.56	.62	.59	

Table 1. Continued

3-phenyl-propyl-amine										
	f = 1 MHz		f = 24.03 GHz				f = 35.13 GHz			
T°C	$\epsilon_o$	$\epsilon'_{obs}$	$\epsilon'_{cal}$	$\epsilon''_{obs}$	$\epsilon''_{cal}$	$\epsilon'_{obs}$	$\epsilon'_{cal}$	$\epsilon''_{obs}$	$\epsilon''_{cal}$	
30	4.83	3.48	3.56	.68	.70	3.20	3.36	.63	.72	
50	4.57	3.45	3.48	.63	.62	3.12	3.30	.56	.65	
70	4.32	3.48	3.45	.61	.60	3.12	3.28	.58	.62	

$$b = \frac{\epsilon''}{\epsilon_o - \epsilon_\infty} = \frac{c_1 \omega \tau_1}{1 + \omega^2 \tau_1^2} + \frac{(1 - c_1) \omega \tau_2}{1 + \omega^2 \tau_2^2} \quad (2)$$

and the simplified equation [11] is

$$\frac{1-a}{b\omega} = \tau_1 + \tau_2 - \frac{a\omega}{b} \tau_1 \tau_2 \quad (3)$$

The equation (3), with the dielectric data at several microwave frequencies can be put in the form

$$\sum_{i=1}^n Sx_i - Py_i - 1 = 0 \quad (4)$$

where,  $S = \tau_1 + \tau_2$ ,  $P = \tau_1 \tau_2$ ,  $x = \frac{b\omega}{1-a}$ ,  $y = \frac{a\omega^2}{1-a}$

This is a linear equation and is solved by the least squares method [12].

For ready reference the working equations are

$$S = \frac{\sum_{i=1}^n y_i \sum_{i=1}^n x_i y_i - \sum_{i=1}^n x_i \sum_{i=1}^n y_i^2}{\left(\sum_{i=1}^n x_i y_i\right)^2 - \sum_{i=1}^n x_i^2 \sum_{i=1}^n y_i^2} \quad (5)$$

$$P = \frac{\sum_{i=1}^n y_i \sum_{i=1}^n x_i^2 - \sum_{i=1}^n x_i \sum_{i=1}^n x_i y_i}{\left(\sum_{i=1}^n x_i y_i\right)^2 - \sum_{i=1}^n x_i^2 \sum_{i=1}^n y_i^2} \quad (6)$$

$$C_1 = \frac{\sum_{i=1}^n a_i f_i + \sum_{i=1}^n b_i g_i - \sum_{i=1}^n f_i f'_i - \sum_{i=1}^n g_i g'_i}{\sum_{i=1}^n f_i^2 + \sum_{i=1}^n g_i^2} \quad (7)$$

$$f_i = (f_1 - f'), \quad f_1 = \frac{1}{1 + \omega \tau_1^2}, \quad f' = \frac{1}{1 + \omega^2 \tau_2^2}$$

$$g_i = (g_1 - g'), \quad g_1 = \frac{\omega \tau_1}{1 + \omega \tau_1^2}, \quad g' = \frac{1}{1 + \omega^2 \tau_2^2}$$

The value of  $t_\infty$  was adjusted and  $\tau_1$ ,  $\tau_2$  and  $C_1$  are determined from equations 5, 6 and 7 until the mean square deviation given by the relation

$$A = \sum (\epsilon''_{\text{obs}} - \epsilon''_{\text{cal}})^2 + \left\{ \frac{\epsilon'_{\text{obs}} - \epsilon'_{\text{cal}}}{n} \right\}^2$$

is found to be a minimum. The calculations were carried out on the IBM1130 computer. The values of  $\tau_1$ ,  $\tau_2$ ,  $C_1$  and  $\epsilon_\infty$  are given in Table 2.

Table 2. Values of  $\epsilon_\infty$ ,  $\alpha$ ,  $\tau_1$ ,  $\tau_2$ ,  $C_1$  and  $n_D^2$

$T^\circ\text{C}$	$\epsilon_\infty$	$\alpha$	$\tau_1 \times 10^{12} \text{sec}$	$\tau_2 \times 10^{12} \text{sec}$	$C_1$	$n_D^2$
1 phenyl-propyl-bromide						
30	2.68	.25	51.35	5.77	.80	2.37
50	2.69	.24	41.07	5.21	.79	2.34
70	2.65	.24	32.81	4.27	.78	2.32
85	2.62	.20	28.56	3.89	.76	2.30
1-phenyl-propyl-mercaptan						
30	2.58	.31	35.51	3.66	.65	2.39
50	2.56	.29	29.27	3.32	.66	2.36
70	2.54	.23	24.81	3.07	.69	2.33
85	2.54	.19	19.87	2.62	.73	2.31
1-phenyl-propyl-amine						
30	2.58	.27	30.32	3.34	.48	2.31
50	2.53	.27	27.00	3.00	.47	2.28
70	2.48	.23	19.50	2.83	.44	2.26

The calculated values of  $\epsilon'$  and  $\epsilon''$  with these values of  $\tau_1$ ,  $\tau_2$ ,  $C_1$  and  $\epsilon_\infty$  from equation (1) and (2) are included in Table 1 for comparison.

The heat of activation for dielectric relaxation for molecular reorientation  $\Delta H\tau_1$  and for group rotation  $\Delta H\tau_2$  are determined from the plots of  $\log \tau_1 T$  vs  $\frac{1}{T}$  and  $\log \tau_2 T$  vs  $\frac{1}{T}$  respectively. The heat of activation for viscous flow  $\Delta H\eta$  was determined from the plot of  $\log \eta$  vs  $\frac{1}{T}$ . The dipole moment  $\mu$  for all the liquids at different temperatures were determined from the values of density  $d$ , static dielectric permittivity using the Onsager equation. The values of  $\Delta H\tau_1$ ,  $\Delta H\tau_2$ ,  $\Delta H\eta$  and  $\mu$  are given in Table 3.

Table 3. Values of  $\Delta H\eta$ ,  $\Delta H\tau_1$ ,  $\Delta H\tau_2$ ,  $\eta$ ,  $d$  and  $\mu$

$T^\circ\text{C}$	$\Delta H\eta$ kcal/mole	$\Delta H\tau_1$ kcal/mole	$\Delta H\tau_2$ kcal/mole	$\eta_{cp}$	$d$ gm/cc	$\mu$ Debye
1-phenyl-propyl-bromide						
30				1.97	1.31	1.53
50	3.34	1.74	1.06	1.35	1.29	1.53
70				1.01	1.26	1.55
85				0.85	1.25	1.57
1-phenyl-propyl-mercaptan						
30				1.67	1.001	1.29
50	3.03	1.88	0.95	1.19	0.98	1.28
70				0.92	0.97	1.26
85				0.77	0.96	1.23
1-phenyl-propyl-amine						
30				1.70	1.02	1.34
50	3.34	1.79	-	1.18	1.00	1.34
70				0.89	0.99	1.34

## DISCUSSION

It can be seen from Table 2 that the shorter relaxation time in the case of 1-phenyl-propyl-bromide at  $30^\circ\text{C}$  is 5.8 ps, which is a little larger than the  $-\text{CH}_2\text{Cl}$  group relaxation time of 4.9 ps at  $30^\circ\text{C}$  in the liquid

benzylchloride [13], and compares well with the  $-\text{CH}_2\text{Br}$  relaxation time of 6.3 ps in benzyl bromide [14] in the liquid state. So it is concluded that the shorter relaxation time in 1-phenyl-propyl-bromide is due to rotation of the  $-\text{CH}_2\text{Br}$  end-group. Similarly the shorter relaxation time of 3.7 ps at  $30^\circ$ , which compares well with the  $-\text{CH}_2\text{SH}$  group relaxation time of 3.35 ps at  $30^\circ\text{C}$  in benzylthiol [15] in the liquid state, is attributed to rotation of the  $-\text{CH}_2\text{SH}$  end-group in 1-phenyl-propyl-mercaptan. From similar considerations for 1-phenyl-propyl-amine the shorter relaxation time of 3.3 ps is accounted for by the rotation of the  $-\text{CH}_2\text{NH}_2$  group.

The larger relaxation times of 35.5 and 30.3 ps at  $30^\circ\text{C}$  for 1-phenyl-propyl-mercaptan and 1-phenyl-propyl-amine respectively, have a similar order of magnitude and may be due to molecular end-over-end rotation. The larger relaxation time of 51.3 ps at  $30^\circ\text{C}$  in phenyl-propyl-bromide which is appreciably larger than the other liquids, is due to higher viscosity in this liquid. Thus it is found that the dielectric data in the three 1-phenyl substituted propanes may be analysed in terms of molecular end-over-end and the end-group rotation, in contrast to the n-alkyl halides where a distribution of relaxation time has been reported.

It may be seen from Table 2 that both the molecular and end-group rotation in all the liquids decrease with increase of temperature as is usually observed in polar liquids.

Weight factors: From the value of  $C_1$  in Table 2, it is seen that molecular reorientation is the major relaxation process in 1-phenyl-propyl-bromide ( $C_1 \simeq .8$ ) which is similar to that ( $C_1 \simeq .8$ ) in benzyl bromide [14] in the liquid state. In 1-phenyl-propyl-mercaptan the molecular reorientation is the major relaxation process ( $C_1 \simeq .65$ ), while in benzylthiol, the group rotation ( $C_2 \simeq .73$ ) is the major relaxation process. Similarly in 1-propyl propylamine, contributions from molecular and end-group rotation are almost equal, whereas group relaxation is the major contributing factor ( $C_2 = .85$ ) in benzylamine [14] in the liquid state. The lowering of the contribution from the end-group rotation in 1-phenyl-propyl-mercaptan and 1-phenyl-propyl-amine, compared to benzylthiol and benzylamine, may be due to the fact that the rotational axis is less rigidly fixed in the former compounds compared to that in benzyl compounds, as a result of which the moment components responsible for group rotation in them becomes less.

Dipole moment: From Table 3, it can be seen that the dipole moment in 1-phenyl-propyl-bromide is about 1.53 D which is about the bond moment of  $\text{CH}_2\text{Br}$  end-group. The dipole moment in this liquid is found to increase with increase of temperature which is an indication of the existence of

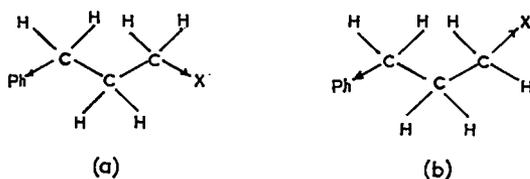


Fig.2. Ph-phenyl ring. X = Br, SH, NH<sub>2</sub>.

more than one rotational isomer (fig. 2). The proportion of isomers with higher dipole moment increases at higher temperatures.

In the case of 1-phenyl-propyl-mercaptan, the dipole moment is 1.29 D which compares with benzylthiol ( $\mu = 1.33$  D). In this liquid the dipole moment decreases with increase of temperature showing that isomers with less moment are abundant at lower temperature.

The dipole moment in 1-phenyl-propyl-amine is 1.34 D and is independent of temperature. This means that the isomers if any, will be of similar moments.

**Activation energy:** The heat of activation for molecular reorientation in the three liquids are of similar magnitude ( $\approx 1.8$  kcal/mole) and is about half as much as the heat of activation for viscous flow in them. The barrier for end-group rotation  $\Delta H\tau_2$  in 1-phenyl-propyl-bromide and 1-phenyl-propyl-mercaptan is about 1 kcal/mole. The potential barrier for internal rotation in 1-phenyl propyl-amine is about 120 Cal/mole only, which means that there is almost free rotation of the  $-\text{CH}_2\text{NH}_2$  group in this liquid.

The difference in the values of  $t_\infty$  and  $n^2D$  in all the liquids, suggests the possibility of the presence of a third high frequency absorption region in the liquids.

#### ACKNOWLEDGEMENT

We thank Professor G. S. Kastha for his kind interest.

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## Microwave absorption and relaxation processes in thioanisole in the liquid state

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(Received 17 September 1974)

Complex dielectric permittivities in thioanisole in the liquid state have been measured at different microwave frequency regions. The dielectric data have been analysed in terms of molecular and intramolecular relaxation processes.

### 1. INTRODUCTION

Molecular and intramolecular relaxation have been reported in the case of anisole in the liquid state (Vaughan *et al* 1963, Garg & Smyth 1967) as well as in dilute solution in benzene (Forest & Smyth 1964, Farmer & Walker 1969, Klages & Krauss 1971). Though the molecular relaxation time  $\tau_1$  in the pure liquid and in dilute solution are almost the same ( $\tau_1 = 15$  p.sec. at 20°C), the methoxy group relaxation time  $\tau_2 = 3$  p.sec at 20°C and its contribution  $C_2(0.2)$  to total polarization in the liquid state differs considerably from the values of  $\tau_2 = 7$  p.sec at 20°C and  $C_2 = 0.8$  in dilute benzene solution. The drastic reduction of the weight factor  $C_2(0.2)$  for methoxy group rotation in the liquid anisole from its value ( $C_2 = 0.8$ ) in the dilute benzene solution has been attributed by Garg & Smyth (1967) to some restraint in the C-O bond as a result the methoxy group rotation is not completely free but hindered. The increase in the methoxy group relaxation time ( $\tau_2 = 7$  p.sec) in dilute benzene solution was suggested by Ghatak *et al* (1974) as due to the formation of weak bond between  $\pi$ -electron of the ring and hydrogen atom of the methoxy group.

The -S-CH<sub>3</sub> group in thioanisole is similar to the -O-CH<sub>3</sub> group in anisole. It will be interesting to compare the dielectric behaviour of the two molecules in the pure liquid state. With this object in view, investigations on microwave absorption in thioanisole in the liquid state were carried out in the wavelength regions 3.49 cm., 3.17 cm., 1.62 cm., 1.25 cm. and 8 mm. The results are presented and discussed in the present communication.

*Chemical*: A pure sample of thioanisole was obtained from EGA Chemie (West Germany). It was distilled under reduced pressure before use in the investigations.

## 2. EXPERIMENTAL

The dielectric permittivity  $\epsilon'$  and dielectric loss  $\epsilon''$  at different microwave frequencies were measured by Suber's (1948) method.

The static dielectric constant  $\epsilon_0$  was measured at 1 MHz/sec obtained from an crystal controlled oscillator, the refractive index  $n_D$  was determined with an Abbe refractometer and the viscosity  $\eta$  and density  $d$  were measured with an Ostwald viscometer and a pycnometer respectively.

All the dielectric data were obtained at temperatures 30, 50 and 70°C. The temperature of each experiment was controlled within  $\pm 1^\circ\text{C}$  by a thermostat.

## 3. RESULTS

The values of  $\epsilon'$  and  $\epsilon''$  obtained at different microwave regions and at different temperatures together with the values of  $\epsilon_0$  and viscosity ( $\eta$ ) and density ( $d$ ) at different temperatures are given in table 1.

Table 1. Values of  $\epsilon_0$ ,  $\epsilon'$ ,  $\epsilon''$ ,  $\eta$  and  $d$  for thioanisole at different temperatures

$\lambda\text{cm}$	3.49		3.17		1.626		1.249		0.83				
Temp. °C	$\epsilon_0$	$\epsilon'$	$\epsilon''$	$\eta$	$d$ gm/cc								
30	4.88	4.41	0.57	4.39	0.58	3.83	0.64	3.63	0.61	3.37	0.53	1.05	1.05
50	4.65	4.30	0.51	4.28	0.52	3.80	0.61	3.65	0.60	3.38	0.53	0.80	1.03
70	4.53	4.20	0.50	4.17	0.51	3.80	0.58	3.67	0.57	3.40	0.51	0.54	1.01

The Cole-Cole arc plots (shown in figure 1) were drawn in the complex plane and the high frequency dielectric constant  $\epsilon_\infty$  and the distribution parameter  $\alpha$  were obtained from the arc plots as usual. Appreciable value of the distribution parameter at all temperatures as also the curvature in the plot of  $\epsilon'$  vs  $\epsilon''w$  indicated the presence of more than one relaxation mechanism.

So the dielectric data were analysed in terms of two relaxation processes by straight forward calculations using equations due to Kastha (1968) and used successfully by others (Ghatak *et al* 1974, Bhattacharyya *et al* 1970, Kastha *et al* 1969, Hasan *et al* 1971). The values of  $\tau_1$  and  $\tau_2$  at different temperatures together with the weight factor  $C_2$  are given in table 2. The activation energies for dielectric relaxation for the molecular orientation  $\Delta H\tau_1$  and for group rotation  $\Delta H\tau_2$  were obtained from the straight line plots of  $\log \tau_1 T$  vs  $1/T$  and  $\log \tau_2 T$  vs  $1/T$  respectively. The activation energy for viscous flow  $\Delta H\eta$  was obtained

from the plots of  $\log \eta$  vs  $1/T$ . The values of  $\Delta H\tau_1$ ,  $\Delta H\tau_2$ ,  $\Delta H\eta$ ,  $\alpha$ ,  $n_D^2$  and dipole moment ( $m$ ) are included in table 2.

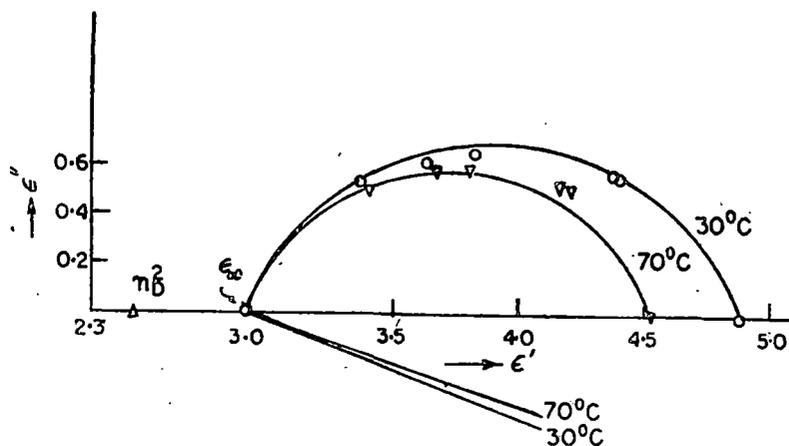


Fig. 1. Cole-Cole arc plot of thioanisole

#### 4. DISCUSSIONS

From table 2 it can be seen that both the molecular and intramolecular relaxation times decrease with the increase of temperature as is generally observed. The intramolecular relaxation time  $\tau_2$  is found to be much less dependent on temperature and consequently on viscosity than the molecular relaxation time. This shows that the groups are well shielded from the influence of neighbouring molecules. The molecular relaxation time  $\tau_1$  of about 22 p.sec at 30°C in the liquid thioanisole obtained in the present investigations is larger than the value of  $\tau_1 = 15$  p.sec at 20°C either in the liquid anisole (Garg & Smyth 1967) or its solution in benzene (Forest & Smyth 1964, Farmer & Walker 1969, Klages & Krauss 1971). This is consistent with the sizes of the molecules. The  $-S-CH_3$  group relaxation time  $\tau_2 = 3$  p.sec at 30°C in the present case compares well with the  $-O-CH_3$  group relaxation time of 3 p.sec at 20°C in the liquid anisole.

Table 2. Values of  $\alpha$ ,  $\epsilon_\infty$ ,  $n_D^2$ ,  $\tau_1$ ,  $\tau_2$ ,  $\Delta H\tau_1$ ,  $\Delta H\tau_2$ ,  $\Delta H\eta$  and moment  $m$

Temp °C	$\alpha$	$\epsilon_\infty$	$n_D^2$	$\tau_1 \times 10^{12}$ in sec.	$\tau_2 \times 10^{12}$ in sec.	$C_2$	$\Delta H\tau_1$ in k.cal/mole	$\Delta H\tau_2$ in k.cal/mole	$\Delta H\eta$ in k.cal/mole	Mean moment $m$ in $D$
30	0.24	2.91	2.50	22.7	3.0					
50	0.23	2.90	2.46	16.7	2.7	0.63	2.01	0.77	2.54	1.32
70	0.22	2.91	2.43	13.1	2.2					

It is interesting to note that the weight factor  $C_2$  for group rotation in thioanisole (table 2) is about 0.63 which is much larger than the  $C_2 = 0.2$  in the case of liquid anisole. So it appears that the  $-S-CH_3$  group rotation in thioanisole in the liquid state is much less hindered than the  $-O-CH_3$  group rotation in anisole in the liquid state.

This is also supported by the fact that the activation energy for  $-O-CH_3$  group rotation in the liquid anisole is about 1.5 k.cal/mole (Garg & Smyth 1967) which is much larger compared to the  $\Delta H\tau_2 = 0.770$  k.cal./mole for  $-S-CH_3$  group rotation in thioanisole in the liquid state. The weight factor  $C_2$  for group rotation in thioanisole can be estimated from dipole moment considerations. For this purpose the dipole moment of thioanisole in the liquid state was calculated by using Onsager equation (Smyth 1955) from the measured values of static dielectric constant  $\epsilon_0$ , refractive index  $n_D$  and density ( $d$ ) of the liquid. It is found to be 1.32  $D$ , which compares well with the literature value (Smyth 1955) of 1.27  $D$ . The weight factor  $C_2$  is given by the ratio of the square of dipole moment component perpendicular to the axis of rotation (C-S axis) to the square of the total moment of the molecule i.e.,

$$C_2 = \frac{(1.32 \sin 57^\circ)^2}{(1.32)^2} = 0.70,$$

where  $57^\circ$  (Smyth 1955) is the angle made by the group moment with the C-S axis.

Thus the theoretical values of  $C_2 = 0.7$  for  $-S-CH_3$  group rotation agrees well with the experimentally obtained value of 0.63.

This supports the earlier conclusion that the  $-S-CH_3$  group rotation in the liquid thioanisole is more or less free unlike the case of  $-O-CH_3$  group rotation in anisole in the liquid state.

The appreciable difference between the values of  $\epsilon_\infty$  and  $n_D^2$  (table 2) indicates the presence of a third absorption region in mm. wavelength region of the type of *Poley absorption* (Poley 1955).

#### ACKNOWLEDGMENT

Authors' thanks are due to Dr. S. B. Roy for guidance. They are grateful to Professor G. S. Kastha for his interest in the work.

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## Microwave absorption and internal rotation in some dicyanoalkanes in benzene solution. part-I.

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In order to understand the dipole reorientation processes in flexible chain molecules, the dielectric permittivities and dielectric losses of three dicyanoalkanes in benzene solution have been measured at wave lengths 0.8, 1.25, 1.65 and 3.49 cm at different temperatures. The dielectric data could be represented by cole cole are plots and were analysed in terms molecular reorientation and internal rotation of the  $-\text{CH}_2\text{CN}$  groups. The potential barriers to molecular reorientation  $\Delta H_{\tau_1}$  and to internal rotation  $\Delta H_{\tau_2}$  have been determined. The temperature dependence of the apparent dipole moment was attributed to the presence of more than one conformer in each of the compounds. The increase in the distribution parameter  $\alpha$  with increase in temperature in 1, 3 dicyanopropane has been explained.

### 1. INTRODUCTION

Studies on the dielectric absorption of microwaves in a number of alkylhalides (Higasi *et al* 1960, Vaughan *et al* 1962) showed that the results could be analysed in terms of relaxation times between two limits, the lower limit being determined by the segmental orientation of the terminal  $-\text{CH}_2\text{Br}$  group and the upper limit corresponding to the end-over-end rotation of the entire molecule. Similar studies in the case of  $\alpha,\omega$ - dihaloalkanes (Garg *et al* 1973, Suresh Chandra *et al* 1972) with the two dipoles attached to the two terminals, showed that the results would be equally represented by Davidson-Cole skewed arc plots and also by the assumption of two independent Debye type absorption processes. In order to have a clear understanding of the dipole reorientation processes in flexible chain molecules, a programme was undertaken to extend similar studies in the case of a number dicyano-alkanes. In the present paper is reported the results obtained from the microwave absorption in 1, 2 dicyanoethane, 1, 3 dicyanopropane and 1, 4 dicyanobutane in benzene solution together with a discussion of the results.

## 2. EXPERIMENTAL

*Chemicals*: Pure samples of 1, 2 dicyanoethane, 1, 3 dicyanopropane and 1, 4 dicyanobutane were procured from Schuchardt (Germany). These were dried and distilled under reduced pressure before use in the investigations. The boiling points and refractive indices in all the liquids were in agreement with the literature values.

*Apparatus*: The apparatus for the measurement of dielectric permittivity  $\epsilon'$  dielectric loss  $\epsilon''$  in the region 0.8, 1.25, 1.62 and 3.49 cm microwaves were described in an earlier paper (Das et al 1973). The static dielectric permittivity  $\epsilon_0$  was measured at 1 MHz, the refractive index  $n_D$  was determined with an Abbe refractometer. The viscosity  $\eta$  and density  $d$  were measured with a Ostwald viscometer and a pycnometer respectively. The temperature in each experiment was kept constant within  $\pm 1^\circ\text{C}$  by means of a thermostat. The estimated errors in the determination of  $\epsilon'$  and  $\epsilon''$  were about 2% and 4% respectively.

## 3. RESULTS

The experimental values of  $\epsilon'$  and  $\epsilon''$  at different microwave frequencies and at different temperatures are given in table 1. The values of  $\epsilon_0$ ,  $n_D^2$ , density ( $d$ ) and viscosity  $\eta$  at different temperatures are given in table 2. Complex plane plots (figure 1) of the dielectric permittivity  $\epsilon'$  and

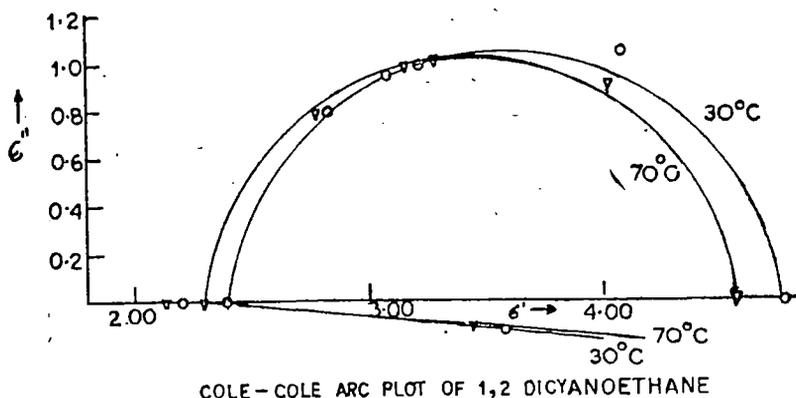
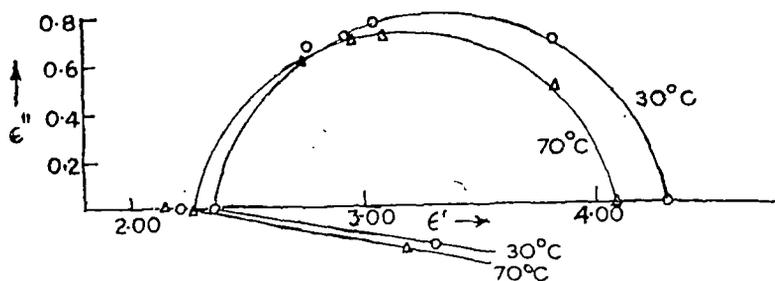
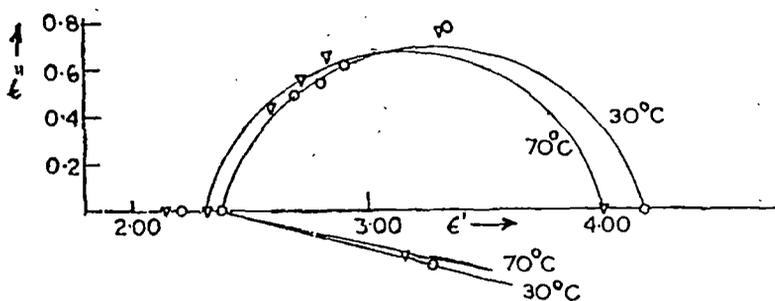


Fig. 1

dielectric loss  $\epsilon''$  show a symmetric distribution with a depressed centre in each of the dicyanoalkanes at all temperatures, unlike the case in  $n$  alkylhalides (Vaughan *et al* 1962),  $\alpha,\omega$ - dihaloalkanes (Garg *et al* 1973, Suresh Chandra 1972) etc. where such plots showed assymmetric distribution. The distri-



COLE-COLE ARC PLOT OF 1,3 DICYANOPROPANE



COLE-COLE ARC PLOT OF 1,4 DICYANOBUTANE

Fig. 1

bution parameters  $\alpha$  from the arc plots in the present dicyanoalkanes, were found appreciable at all temperatures, which is an indication of the presence of more than one relaxation processes in them. Attempts were then made to analyse the dielectric data in terms of two relaxation processes, making use of Bergmanns equations (1960)

$$a = \frac{\epsilon' - \epsilon_{\infty}}{\epsilon_0 - \epsilon_{\infty}} = \frac{c_1}{1 + \omega^2 \tau_1^2} + \frac{c_2}{1 + \omega^2 \tau_2^2} \quad \dots\dots(1)$$

$$b = \frac{\epsilon''}{\epsilon_0 - \epsilon_{\infty}} = \frac{c_1 \omega \tau_1}{1 + \omega^2 \tau_1^2} + \frac{c_2 \omega \tau_2}{1 + \omega^2 \tau_2^2} \quad \dots\dots(2)$$

from which was derived a simplified linear equation.

$$Sx - Py - 1 = 0 \quad \dots\dots\dots(3)$$

where  $S = \tau_1 + \tau_2$ ,  $P = \tau_1 \tau_2$ ,  $x = \frac{b\omega}{1-a}$  and  $y = \frac{a\omega^2}{1-a}$

Table 1. Observed and calculated values of dielectric permittivities and dielectric losses in benzene solution. Concentrations are in mole fractions

.098 1, 2 dicyanoethane in benzene

t°C	f = 8.6 GHz				f = 24.05 GHz				f = 24.05 GHz				f = 36.2 GHz			
	$\epsilon'_{\text{Obs}}$	$\epsilon'_{\text{Cal}}$	$\epsilon''_{\text{Obs}}$	$\epsilon''_{\text{Cal}}$												
30	4.05	4.04	1.06	1.03	3.22	3.28	1.00	1.04	3.08	3.05	.96	.95	2.82	2.78	.80	.77
45	4.04	4.04	.98	.97	3.25	3.31	1.02	1.03	3.12	3.07	.98	.96	2.81	2.80	.79	.79
60	4.02	4.02	.90	.89	3.28	3.33	1.00	1.01	3.15	3.09	.98	.95	2.78	2.80	.79	.81
.085 1, 3 dicyanopropane in benzene																
30	3.81	3.66	.70	.77	3.05	3.16	.78	.80	2.92	2.98	.73	.76	2.76	2.74	.68	.66
45	3.80	3.65	.61	.72	3.08	3.16	.76	.76	2.94	3.00	.72	.72	2.75	2.77	.63	.64
60	3.82	3.61	.50	.66	3.08	3.16	.72	.72	2.95	3.01	.70	.70	2.74	2.79	.62	.65
.073 1, 4 dicyasobutane in benzene																
30	3.34	3.34	.78	.76	2.91	2.92	.62	.61	2.75	2.75	.52	.55	2.70	2.68	.48	.47
45	3.31	3.32	.76	.77	2.85	2.85	.60	.61	2.75	2.75	.52	.52	.65	2.64	.42	.41
60	3.32	3.33	.76	.76	2.84	2.83	.64	.64	2.73	2.72	.56	.55	2.60	2.60	.43	.42

The equation (3) was solved by the method of least squares described in an earlier paper (Roy *et al* 1976). The calculations for the determination of  $\tau_1$ ,  $\tau_2$ ,  $c_1$  were carried out on IBM computer 1130. The calculated values  $\epsilon'$ ,  $\epsilon''$  are included in table 1 for comparison with the observed values. The values of  $\tau_1$ ,  $\tau_2$ ,  $c_1$  at different temperatures are given in table 3 and those of  $\epsilon_\infty$  are included in table 2. The barriers to molecular reorientation

Table 2. Values of  $\epsilon_0$ ,  $n^2_D$ ,  $\epsilon_\infty$ ,  $d$ ,  $\eta$  of the dicyanoalkanes in benzene solution.

$t^\circ\text{C}$	$\epsilon_0$	$n^2_D$	$\epsilon_\infty$	$d_{\text{gm/cc}}$	$\eta_{\text{c.p.}}$
1, 2 dicyanoethane in benzene.					
30	4.78	2.20	2.40	.878	.47
45	4.68	2.18	2.36	.867	.42
60	4.55	2.15	2.30	.850	.36
1, 3 dicyanopropane in benzene.					
30	4.30	2.21	2.35	.880	.50
45	4.20	2.17	2.35	.865	.42
60	4.08	2.15	2.27	.850	.36
1, 4 dicyanobutane in benzene.					
30	4.20	2.21	2.38	.874	.50
45	4.10	2.19	2.38	.864	.44
60	4.02	2.15	2.32	.850	.38

$\Delta H\tau_1$  and to internal rotation  $\Delta H\tau_2$  were obtained from the straight line plots of  $\log \log \tau_1 T$  vs  $\frac{1}{T}$  and  $\log T \tau_2$  vs  $\frac{1}{T}$  respectively. The heat of activation for viscous flow was obtained from the plot of  $\log \eta$  vs  $\frac{1}{T}$ . The dipole moment  $\mu$  was calculated from the equation (Tay and Crossley 1972)

$$\mu^2 = \frac{9 k T (\epsilon_0 - \epsilon_\infty) (2 \epsilon_0 + \epsilon_\infty)}{4 \pi N \epsilon_0 (\epsilon_\infty + 2)^2} \quad (4)$$

where  $N$  is the number of solute molecules per ml of the solution.

The values of  $\Delta H\tau_1$ ,  $\Delta H\tau_2$ ,  $\Delta H\eta$  and  $\mu$  are included in table 3.

#### 4. DISCUSSION

*Molecular and internal relaxation time.* It can be seen from table 3 that the larger relaxation times  $\tau_1$  at any temperature in 1, 2-, 1, 3- and 1, 4- dicyanoalkanes respectively are consistent with the increasing sizes of the molecules

and are evidently the molecular relaxation times. The molecular relaxation time  $\tau_1$  of 22.6 p.s at 30°C in 1, 4 dicyanobutane is comparable with the molecular relaxation time of 23 p sec. at 25°C in 1, 4 dibromobutane (Grag *et al* 1973).

Table 3. Values of  $\alpha$ ,  $\tau_1$ ,  $\tau_2$ ,  $C_1$ ,  $\Delta H_{\tau_1}$ ,  $\Delta H_{\tau_2}$ ,  $\Delta H_{\eta}$  and  $\mu$  in the dicyanoalkanes in benzene solution, conc. in mole fraction

t°C	$\alpha$	$\tau_1 \times 10^{12} \text{Sec}$	$\tau_2 \times 10^{12} \text{Sec}$	$C_1$	$\Delta H_{\tau_1}$ kcal/mol	$\Delta H_{\tau_2}$ kcal/mol	$\Delta H_{\eta}$ kcal/mol	$\mu$ (Debye)
.098 1, 2 dicyanoethane.								
30	.070	14.3	4.8	.80				3.50
45	.065	13.1	4.1	.80	0.64	1.20	2.09	3.57
60	.060	11.8	3.6	.79				3.65
.085 1, 3 dicyanopropane.								
30	.10	20.6	5.8	.51				3.56
45	.11	17.0	4.6	.60	1.34	2.42	2.06	3.68
60	.13	15.8	3.7	.57				3.79
.073 1, 4 dicyanobutane.								
30	.16	22.6	3.6	.79				3.86
45	.14	19.8	2.3	.84	1.24	3.69	2.02	3.88
60	.13	17.1	1.8	.85				3.98

The shorter relaxation time  $\tau_2$  lying in the range 4-5.8 p s at 30°C, compare well with the relaxation time 6.5 p.sc. at 30°C of the acetonitril ( $\text{CH}_3\text{CN}$ ) (Eloranta & Kadaba 1971) molecule in benzene solution and is most probably due to the rotation of the  $\text{CH}_2\text{CN}$  groups in each of the dicyanoalkanes. It may be noted that both the molecular and intramolecular relaxation times decrease with increase of temperature of the solutions as is usually observed in polar liquids.

*Distribution parameter.* The distribution parameter  $\alpha$  (table 2) in 1, 2 - and 1, 4 - dicyanoalkane, decreases as usual with increase of temperature, but in the case of 1, 3 dicyanopropane, the  $\alpha$ -value increases with increase in temperature. Similar increase in the value in 1, 3 propane dithiol (Roy

*et al* 1976) at higher temperatures was attributed to the increase in the proportion of the higher energy TT conformer which, being more extended than the other conformers GG and TG, has got a larger relaxation time than the other two forms, so the same explanation is applicable for the increase in  $\alpha$ -value at higher temperature in the 1, 3 dicyanopropane which also has three conformers in the liquid state (Matsubara 1961, Yamadera 1958, Thorjornsrud 1972). Further it can be seen that at any temperature, the  $\alpha$ -value is in the increasing order from 1, 2 dicyanoethane to 1, 4 dicyanobutane, probably due to the number of segmental oscillation around the various C-C bonds increase, with the increase in number of such bonds.

*Weight factors.* The molecular reorientation is found to be (table 2) the major relaxation process in 1, 2 - and 1, 4 - dicyanoalkanes, whereas in 1, 3 dicyanopropane the contribution from the internal rotation ( $C_2 \approx .45$ ) is only a little less than that of the molecular relaxation.

*Barrier to molecular and internal rotation.* The barrier to molecular reorientation ( $\Delta H\tau_1$ ) in 1, 2 dicyanoethane and 1, 3 dicyanopropane in benzene solution are about 0.64 and 1.34 kcal/mol respectively and are about half the value of the barrier to internal rotation of (1.2 and 2.42 kcal/mol) the  $-\text{CH}_2\text{CN}$  groups in the respective molecules. In the case of 1, 4 dicyanobutane the barrier to internal rotation ( $\Delta H\tau_2 \approx 3.69$  kcal/mol) is about three times as large as that due to the molecular reorientation. It is also noted that the barrier to internal rotation increases with the increase in the number of C-C rotational axes.

*Dipole moment.* In all the three dicyanoalkanes in benzene solution, the apparent dipole moment (table 3) is found to increase with increase of temperature of the solution indicating thereby the presence of more than one conformer in each of them and that the conformer with higher moment is of higher energy form. From spectroscopic studies it is reported that in 1, 2 dicyanoethane in the pure liquid state there exist two conformers trans and gauche, the latter being of the lower energy form but having higher dipole moment. In the present studies, in 1, 2 dicyanoethane in benzene solution, the conformer having higher dipole moment is of higher energy form, which is just opposite to that in pure liquid. The difference in behavior in pure liquid and in solution, may be explained as due to the molecular association in the pure liquid but in solution such association does not exist.

In the case of 1, 3 dicyanopropane (Thorjornsrud 1972) in the liquid state, three forms GG, TG and TT are present, the former two forms are in comparable proportion while the TT form present in minute proportion. From the bond moment and bond angle calculations, the dipole moment of GG

( $\mu \approx 3.8D$ ) and TG ( $\mu \approx 4.0D$ ) (Fig. 2) are nearly the same and that of TT form ( $\mu \approx 4.5D$ ) is appreciably highr.

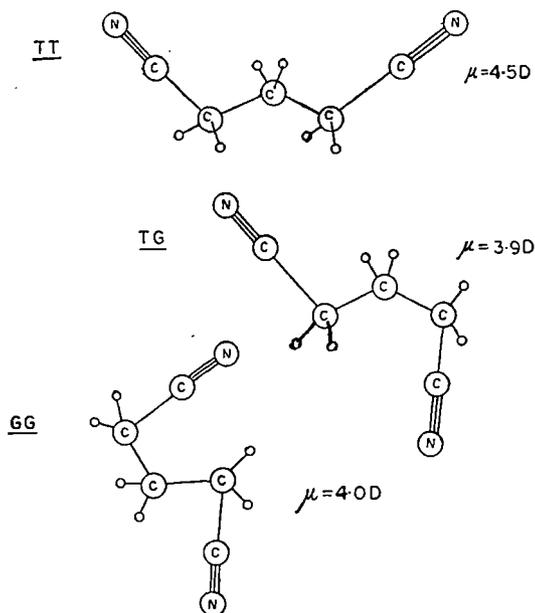


Fig. 2. Molecular configurations of 1, 3 dicyanopropane.

So the increase in the apparent dipole moment with increase in temperature in this liquid may be attributed to the increase in the proportion of the TT form at higher temperature. This is also supported by the increase in the distribution parameter  $\alpha$  at higher temperatures as mentioned earlier.

#### ACKNOWLEDGMENT

We thank Prof. G. S. Kastha for his kind interest in the work.

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## Microwave absorption and relaxation processes in some halogenated esters in the liquid state.

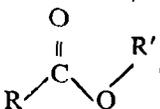
S. K. ROY, K. SENGUPTA AND S. B. ROY

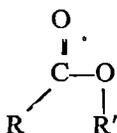
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In order to study the possibility of internal rotation and ascertain molecular configurations in halogenated esters, complex dielectric permittivities have been measured at different frequencies and at different temperatures in the esters of ethyl 3-chloropropionate, methyl 3 bromopropionate and methyl-4 chlorobutyrate in the liquid state. The dielectric data were analysed in terms of two relaxation processes. The larger relaxation time  $\tau_1$  was attributed to molecular reorientation and the shorter one  $\tau_2$  to the rotation of  $\text{CH}_2\text{X}$  ( $\text{X} = \text{halogen}$ ) group. The potential barriers to molecular orientation  $\Delta H\tau_1$  and to internal rotation  $\Delta H\tau_2$  have been determined. The molecular reorientation ( $c_1 = .7$ ) was found to be the major relaxation process in all the esters. The observed values of the dipole moment was about 2.2-2.3 D and was almost temperature independent. From a comparison of the observed dipole moment and the moments estimated from bond moments and bond angles for possible conformers, the conformers present in the esters have been indicated.

### 1. INTRODUCTION

The general predominance of the trans conformer  over the cis

conformer  in aliphatic esters such as formates and acetates has

been attributed to the rigid coupling of alkyl radical of the ester group with carbonyl oxygen (Kaprovich 1954, Nozdrev 1965, Piercy and Subrahmanyam 1965, Oki and Nakanishi 1970). As a result the alkoxy group is not free to rotate about the C-O bond in formates and acetates. Dielectric relaxation

studies in these esters (Rajyam and Murty 1973) have shown that molecular reorientation is the only relaxation mechanism in these esters. In substituted esters however, though the basic ester skeleton of the compounds retains the cis configuration, the internal rotation about the C-C bond is possible and such rotation has been reported in methyl chloroacetate (Mizushima 1954), ethyl bromoacetate, halo-brutyrate (Srivastava and Dinanath 1974) etc. In order to study the possibility of internal rotation and ascertain the molecular configurations in some halogenated esters, dielectric absorption measurements at different microwave frequencies, have been carried out in ethyl 3 chloropropionate, methyl 3 bromo-propionate and methyl 4-chlorobutyrate in the liquid state at different temperatures. The results of the investigations are reported and discussed in this paper.

## 2. EXPERIMENTAL

Pure samples of ethyl 3 chloropropionate, methyl 3 bromo propionate procured from Fluka (Switzerland) were distilled under reduced pressure before use in the investigations.

*Apparatus*: The apparatus for the dielectric measurements at microwave frequencies and static frequency were the same as described in an earlier paper (Das et al, 1973). The refractive index was measured with an Abbe refractometer, the density with a Pycnometer and the viscosity with a viscometer. Thermostat was used for maintaining the temperature of the experiment constant within  $\pm 1^\circ\text{C}$ . Estimated errors in the determination of  $\epsilon'$  and  $\epsilon''$  are about 2% and 4% respectively.

## 3. RESULTS

The experimental values of  $\epsilon'$  and  $\epsilon''$  are given in table 1. Cole—Cole plots (Fig 1) of the dielectric data showed high value of distribution  $\alpha$  in all the cases indicating more than one relaxation processes in each case. The method of analysis of the data in terms of two relaxation processes was described earlier (Roy *et al*, 1976). The Calculated values of  $\epsilon'$  and  $\epsilon''$  are included in Table 1 for comparison. The values of  $\epsilon_0$ ,  $n_D^2$ ,  $\epsilon_\infty$ ,  $d$  and  $\eta$  are given in table 2. The barriers to molecular orientation and internal rotation were obtained from the plots of  $\log \tau_1 T$  vs  $\frac{1}{T}$  and  $\log \tau_2 T$  vs  $\frac{1}{T}$  respectively. The activation energy for viscous flow was obtained from the graph  $\log \eta$  vs  $\frac{1}{T}$ . The dipole moment was calculated from  $\epsilon_0$  and density, by using Onsager's equation. The values of  $\tau_1$ ,  $\tau_2$ ,  $c_1$ ,  $\Delta H\tau_1$ ,  $\Delta H\tau_2$ ,  $\Delta H\eta$  and  $\mu$  are given in table 3.

Table 1. Observed and calculated values of dielectric permittivity  $\epsilon'$  and dielectric loss  $\epsilon''$ 

T.°C	f = 8.59 GHz				f = 18.43 GHz				f = 23.96 GHz				f = 35.12 GHz			
	$\epsilon'_{\text{obs}}$	$\epsilon'_{\text{Cal}}$	$\epsilon''_{\text{obs}}$	$\epsilon''_{\text{Cal}}$	$\epsilon'_{\text{obs}}$	$\epsilon'_{\text{Cal}}$	$\epsilon''_{\text{obs}}$	$\epsilon''_{\text{Cal}}$	$\epsilon'_{\text{obs}}$	$\epsilon'_{\text{Cal}}$	$\epsilon''_{\text{obs}}$	$\epsilon''_{\text{Cal}}$	$\epsilon'_{\text{obs}}$	$\epsilon'_{\text{Cal}}$	$\epsilon''_{\text{obs}}$	$\epsilon''_{\text{Cal}}$
	Ethyl 3 chloropropionate.															
30	5.84	5.83	2.82	2.81	4.54	4.53	2.24	2.24	4.16	4.15	2.08	2.07	3.60	3.63	1.77	1.79
50	6.00	5.99	2.85	2.85	4.47	4.46	2.29	2.29	4.08	4.09	2.08	2.08	3.59	3.59	1.78	1.77
70	6.08	6.09	2.48	2.47	4.64	4.64	2.09	2.08	4.29	4.29	1.91	1.91	3.86	3.84	1.68	1.67
	methyl 3 bromopropionate.															
30	5.80	5.60	2.78	2.80	4.20	4.37	2.15	2.21	3.96	3.99	1.98	2.01	3.48	3.49	1.64	1.66
50	5.92	5.71	2.60	2.67	4.45	4.57	2.18	2.16	4.20	4.13	2.02	2.00	3.40	3.61	1.51	1.70
70	6.10	5.68	2.40	2.48	4.58	4.55	2.04	2.06	4.15	4.19	1.98	1.97	3.30	3.68	1.42	1.76
	methyl 4 chlorobutyrate.															
30	6.55	6.11	2.21	2.38	4.85	5.00	1.95	1.94	4.59	4.70	1.80	1.84	4.05	4.23	1.58	1.69
50	6.65	6.10	2.00	2.32	4.80	4.98	1.89	1.89	4.54	4.70	1.80	1.79	4.08	4.29	1.60	1.70
70	6.72	6.33	1.72	2.08	5.25	5.20	1.92	1.85	4.74	4.91	1.80	1.77	4.20	4.50	1.60	1.72

Table 2. Values of  $\epsilon_0$ ,  $n_D^2$ ,  $\epsilon_\infty$ ,  $d$  and  $\eta$

T°C	$\epsilon_0$	$n_D^2$	$\epsilon_\infty$	$d_{gm\ cc}$	$\eta_{cp.}$
ethyl 3 chloropropionate.					
30	10.19	2.02	2.56	1.09	1.21
50	9.45	1.99	2.52	1.07	.91
70	8.64	1.97	2.60	1.04	.74
methyl 3 promopropionate.					
30	5.81	2.11	2.72	1.6	1.49
50	5.92	2.08	2.68	1.48	.99
70	6.10	2.06	2.50	1.45	.82
methyl 4 chlorobutyrate					
30	9.51	2.04	2.88	1.11	.89
50	9.12	2.01	2.56	1.08	.70
70	8.51	1.99	2.44	1.07	.55

Table 3. Values of  $\alpha$ ,  $\tau_1$ ,  $\tau_2$ ,  $C_1$ ,  $\Delta H\tau_1$ ,  $\Delta H\tau_2$ ,  $\Delta H\eta$  and  $\mu$

T°C	$\alpha$	$\tau_1 \times 10^{12} \text{Sec.}$	$\tau_2 \times 10^{12} \text{Sec.}$	$C_1$	$\Delta H\tau_1$	$\Delta H\tau_2$	$\Delta H\eta$	$\mu$ (Debye)
Ethyl 3 chloropropionate.								
30	.22	34.6	5.1	.71	1.87	2.68	2.65	2.27
50	.18	25.5	4.4	.72	—	—	—	2.88
70	.18	21.1	3.3	.73	—	—	—	2.23
methyl 3 bromopropionate.								
30	.20	48.2	6.8	.72	0.9	1.11	3.11	2.15
50	.21	40.7	5.9	.70	—	—	—	2.17
70	.24	36.0	4.8	.65	—	—	—	2.26
methyl 4 chlorobutyrate								
30	.24	31.3	3.8	.67	1.13	1.74	2.44	2.17
50	.29	27.7	2.9	.65	—	—	—	2.20
70	.29	22.4	2.4	.59	—	—	—	2.25

#### 4. DISCUSSION

It can be seen from Table 3 that the reduced molecular relaxation time ( $\tau_1/\eta$ ) in the three esters, ethyl 3 chloropropionate, methyl 3 bromopropionate and methyl 4 chlorobutyrate at 30°C are 28.6, 32.0 and 35 p.Sec. respectively and are consistent with the increasing sizes of the molecules.

The values of these relaxation times compare well with the molecular relaxation time  $\tau_1 \approx 34$  p.sec. at  $30^\circ\text{C}$  in ethylchloroacetate reported by Srivastava and Dinanath (1973). The shorter relaxation time  $\tau_2$  lying in the range

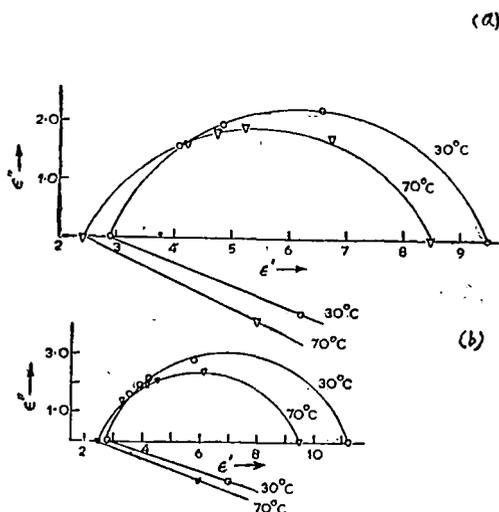


Fig. 1. Cole Cole plots of (a) me- 4 chl. butyrate (b) ethyl-3 chl propionate

4-5 ps at  $30^\circ\text{C}$  in the present esters compares well with the  $\text{CH}_2\text{Cl}$  group rotation (4.4 p.s) in benzylchloride in the liquid state (Turner et al 1970) and is therefore attributed to the relaxation time of  $\text{CH}_2\text{Cl}$  group rotation in ethyl 3-chloropropionate and methyl 4-chlorobutyrate. Similarly the shorter relaxation time  $\tau_2$  of 6.8 p.sec. at  $30^\circ\text{C}$  in methyl 3 bromopropionate which comparable to the of  $\text{CH}_2$  Br group rotation (6.3 p.Sec.) in benzyl bromide (Hasan et al 1971), is evidently due to the rotation of  $\text{CH}_2$  Br group in the methyl bromopropionate. It may be noted here that both molecular and group relaxation times decrease with increase of temperature, though the rate of their decrease is quite different.

**Weight factors:** As can be seen from table 3, that the value of weight factor  $C_1 \approx .65-.7$  in all the esters, indicating that molecular reorientation is the major relaxation process in all of them. This value of  $C_1$  is in conformity with the value of  $C_1 \approx .65$  in halobutyrate reported by Srivastava and Dinanath (1974).

**Distribution Parameter:** The value of the distribution parameter (table 2) is found to be appreciably large in all the esters and it is the highest in the methyl 4-chlorobutyrate. This indicates that the number of relaxation processes in the methyl 4-chlorobutyrate is larger than the other two esters.

It is quite plausible because there are two axes of internal rotation in the propionates, while, in the chlorobutyrate there are three such rotational axes.

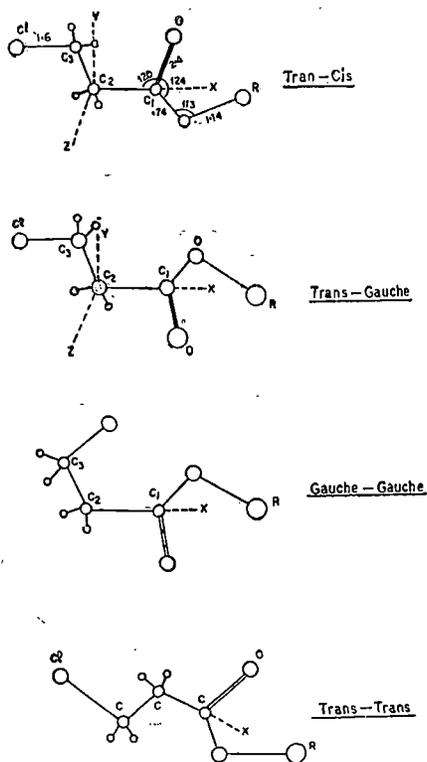


Fig. 2a. Conformers of methyl 3 bromopropionate

*Potential barriers to molecular and internal rotation*: The barrier to molecular reorientation  $\Delta H\tau_1$  (Table 3) in the case of ethyl-3 chloropropionate is highest ( $\Delta H\tau_1 \approx 1.87$  kcal/mole) and is lowest in methyl 3-bromopropionate ( $\Delta H\tau_1 \approx 1$  kcal/mole). The barrier to internal rotation ( $\Delta H\tau_2$ ) in each case is found to be higher than the corresponding value for the barrier to molecular reorientation.

*Dipole moment and molecular configurations*: The experimentally obtained values of the dipole moment is found to lie in the range 2.2-2.3D (table 3) in all the three esters and is almost temperature independent. The existence of the internal rotation in each of the esters, as discussed above, suggests that the possibility of several rotamers in each esters having two/three axes of internal rotation. Assuming there are a few forms (Fig 2) trans-cis, trans-gauche and trans-trans, (Fig 2a) present in the ethyl 3-chloropropionate

and methyl 3-bromopropionate, the dipole moment of each form was calculated from the bond moments and bond angles by vector addition. The values of the calculated moment for TC, TG and TT are about 1.9D and is nearly

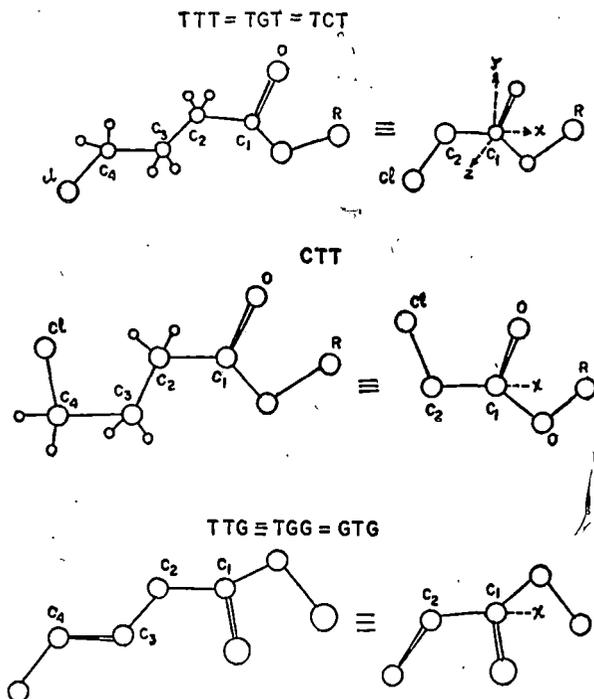


Fig. 2b. Conformers of methyl 4 chlorobutyrate

equal to the observed dipole moment. The calculated moment for the GG form is about 3.24D which is much larger than the observed value of 2.2D. So it is concluded that the esters of ethyl 3 chloropropionate and methyl 3 bromopropionate consist of TC, TG and TT forms, which having similar moments, the apparent moment does not change with temperature. It may be noted here that Som *et al* (1976) reported the presence of at least two forms of rotamers in these esters of which TC is more stable than the other. The ester of methyl 4-chlorobutyrate has three internal axes of rotation and has about eight possible rotamers of which TTC, TTG, TGG, TGT and TTT (Fig 2b) are considered for calculation.

The observed moment of 2.2D agrees well with the calculated moment of 2.4D for TTG and TGG forms, but differ much from that of TTC (3.2D) and TGT & TTT ( $\mu \approx .3D$ ). It is therefore concluded that the major constituents of methyl 4-chlorobutyrate are TTG and TGG conformers.

#### ACKNOWLEDGMENT

We thank Prof. G. S. Kashya for his kind interest.

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# Dielectric relaxation in substituted propanes in the liquid state

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(Received 10 September 1975)

Complex dielectric permittivities of 1,3-propanedithiol and 1,2,3-tribromopropane in the liquid state have been evaluated at 0.85, 1.25, 1.62, 3.17, and 3.49 cm in the microwave regions at different temperatures. The activation energies for dielectric relaxation and viscous flow have been determined. The dipole moments of both molecules have been calculated. The distribution parameter in 1,3-propanedithiol was found to increase with increase in temperature, and a possible explanation is given.

## INTRODUCTION

Recently it has been reported from studies of dielectric relaxation in some rotational isomeric molecules,<sup>1-4</sup> that the distribution parameter  $\alpha$ , in the case of 1, 2-propanedithiol,<sup>1</sup> increases with increase in temperature, while it decreases in 1, 2-dihaloethanes,<sup>3,4</sup> 1, 2-dihalopropanes,<sup>2</sup> and 1, 2-ethanedithiol.<sup>1</sup> The increase in the distribution parameter  $\alpha$  in 1, 2-propanedithiol was accredited to the increase in the relative concentration of the *gauche* 2 conformer, which at lower temperatures is present only in minute proportion.

Similar investigations in the cases of 1, 3-propanedithiol and 1, 2, 3-tribromopropane in the liquid state have been made with a view to study how the distribution parameter  $\alpha$  in these liquids behaves with change of temperatures. The results obtained, have been presented and discussed in this paper.

## EXPERIMENTAL

### Chemicals

Samples of 1, 3-propanedithiol and 1, 2, 3-tribromopropane of 98% purity were procured from Ega Chemie (Germany). These were dried and then distilled under reduced pressure before use in the investigations. The boiling points in the two cases were 170 and 220°C, respectively, which are in agreement with literature values.

## Apparatus

The dielectric permittivity  $\epsilon'$  and dielectric loss  $\epsilon''$  in the 0.85, 1.25, 1.62, 3.17, and 3.49 cm microwave regions were measured by Surber's method.<sup>5</sup> The static dielectric permittivity  $\epsilon_0$  was measured at 1 MHz obtained from a crystal controlled oscillator. The refractive index  $n_D$  was determined with an Abbe refractometer. The viscosity  $\eta$  and density  $d$  were measured by an Oswald viscometer and a pycnometer, respectively. The temperature in all the experiments was controlled within  $\pm 1^\circ\text{C}$  by means of a thermostat.

## RESULTS

The values of  $\epsilon'$ ,  $\epsilon''$ , and  $\epsilon_0$  at different temperatures for the two liquids are given in Table I. The dielectric data were fitted in Cole-Cole arcs (Fig. 1). The high frequency dielectric permittivity  $\epsilon_\infty$  and the distribution parameter  $\alpha$  were obtained from the arc plots in the usual manner. The effective relaxation time  $\tau$  was determined from the relation  $v/u = (\omega\tau)^{1-\alpha}$ , where  $v$  is the distance on the Cole-Cole plot between  $\epsilon_0$  and the experimental point and  $u$  is the distance between the point and  $\epsilon_\infty$ . The heats of activation for dielectric relaxation  $\Delta H_\tau$  and viscous flow  $\Delta H_\eta$  were obtained from the plots of  $\log\tau$  vs  $1/T$  and  $\log\eta$  vs  $1/T$ , respectively. The dipole moment  $\mu$  of each molecule was calculated from the static dielectric permittivity  $\epsilon_0$ , density  $d$ , and high frequency dielectric permittivity  $\epsilon_\infty$  using Onsager's equation.

TABLE I. Values of  $\epsilon'$ ,  $\epsilon''$ , and  $\epsilon_0$  at different temperatures.

Temp °C	$\lambda = 0.85$ cm		$\lambda = 1.25$ cm		$\lambda = 1.62$ cm		$\lambda = 3.17$ cm		$\lambda = 3.49$ cm		$\lambda = 300$ m $\epsilon_0$
	$\epsilon'$	$\epsilon''$									
1, 3-propanedithiol											
30	5.56	1.40	5.96	1.40	6.27	1.41	7.00	1.26	7.06	1.09	8.11
50	5.46	1.29	5.84	1.20	6.10	1.20	6.63	1.00	6.72	0.97	7.64
70	5.36	1.08	5.64	0.96	5.82	0.95	6.24	0.80	6.32	0.79	7.16
1, 2, 3-tribromopropane											
30	2.81	0.49	2.92	0.58	3.04	0.68			3.48	0.95	6.00
50	2.77	0.56	2.93	0.71	3.08	0.79			3.56	1.08	5.66
70	2.76	0.60	2.95	0.78	3.13	0.90			3.72	1.10	5.30
85	2.83	0.69	3.04	0.84	3.23	0.94			3.88	1.04	5.10

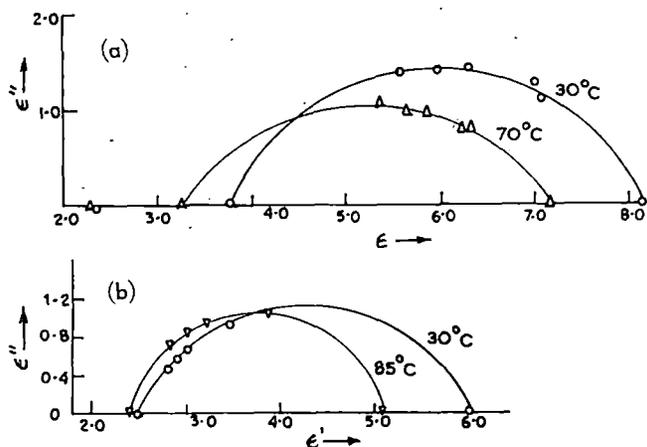


FIG. 1. (a) Cole-Cole arc plots of 1,3-propanedithiol. (b) Cole-Cole arc plot of 1,2,3-tribromopropane.

The values of  $n_D^2$ ,  $\epsilon_\infty$ ,  $\alpha$ ,  $\eta$ ,  $d$ ,  $\Delta H_\tau$ ,  $\Delta H_\eta$ , and  $\mu$  are given in Table II. The accuracy in the determination of  $\epsilon'$  and  $\epsilon''$  is about 2% and 4%, respectively.

## DISCUSSION

### 1,3-propanedithiol

It can be seen from Table II that the value of the relaxation time  $\tau$  in 1,3-propanedithiol is about 6.3 psec at 30°C, which compares well with the value of 6.2 psec at 20°C in 1,2-propanedithiol.<sup>1</sup> This shows that the molecules are of similar sizes.

The heat of activation for viscous flow  $\Delta H_\eta$  in the 1,3-propanedithiol is about 2.5 kcal/mole which compares well with the corresponding value of  $\Delta H_\eta = 2.3$  kcal/mole in 1,2-propanedithiol. But the heat of activation for dielectric relaxation  $\Delta H_\tau \approx 2.2$  kcal/mole in the former is much larger than the value of  $\Delta H_\tau = 1.15$  kcal/mole in the latter.

The distribution parameter  $\alpha$  in 1,3-propanedithiol (Table II) is found to increase with increase in temperature. This is similar to the case of 1,2-propanedithiol but unlike that in 1,2-ethanedithiol, or 1,2-disubstituted ethanes<sup>2,3</sup> and propanes.<sup>1,4</sup>

It is also seen from Table II that the apparent dipole moment  $\mu$  of 1,3-propanedithiol in the liquid state in-

creases with increase in temperature indicating that there is more than one conformer present in the liquid and the relative proportion of the conformer with higher dipole moment increases with increase in temperature.

Spectroscopic studies have shown that three conformers *GG*, *TG*, and *TT* are present in 1,3-propanedithiol<sup>6</sup> as in the case of 1,3-dihalopropanes<sup>7,8</sup> and the relative proportion of the three forms<sup>6</sup> are in the diminishing order of *GG* 65%, *TG* 35%, and *TT* 5%. So it is probable that in 1,3-propanedithiol, the conformers are in similar proportion, i.e., *TT* form is present in very small quantity. From an approximate calculation of the dipole moment (see Appendix and Fig. 3), it is found that the moment of the *TT* form is larger than that of *GG* form, while the moment of the *TG* form is intermediate between them. So from the increase in the apparent dipole moment with increase in temperature, it is concluded that the relative proportions of the *TT* and/or *TG* conformers, which are present in smaller proportion at lower temperature, increase at higher temperature. The *TT* form, being more extended than the *TG* and *GG* forms, should have larger relaxation time, which causes an increase in the value of the distribution parameter  $\alpha$  at higher temperatures. In this respect, the dielectric behavior of this liquid is similar to the case of 1,2-propanedithiol.

### 1,2,3-tribromopropane

Since the viscosity  $\eta$  of this liquid (3.9 cP at 30°C) is much larger than that of 1,2-dibromopropane<sup>4</sup> (1.26 cP at 20°C), it would be convenient to compare the reduced relaxation time ( $\tau/\eta$ ) of the two liquids. The reduced relaxation time in the present liquid is 12 psec cP<sup>-1</sup> at 30°C, which is a little larger than that of 10 psec cP<sup>-1</sup> at 20°C in 1,2-dibromopropane. This shows that the 1,2,3-tribromopropane molecule is a little larger in size than the 1,2-dibromopropane molecule.

The heat of activation for dielectric relaxation  $\Delta H_\tau \approx 3.3$  kcal/mole in 1,2,3-tribromopropane is much larger than the  $\Delta H_\tau \approx 1.5$  kcal/mole in 1,2-dibromopropane. This is probably due to a third bromine atom in the former molecule.

The heat of activation for viscous flow  $\Delta H_\eta \approx 3.65$

TABLE II. Values of  $n_D^2$ ,  $\epsilon_\infty$ ,  $d$ ,  $\eta$ ,  $\alpha$ ,  $\tau$ ,  $\Delta H_\tau$ ,  $\Delta H_\eta$ , and  $\mu$ .

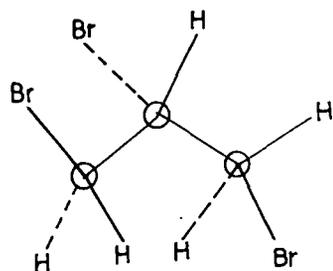
Temp °C	$n_D^2$	$\epsilon_\infty$	$d$ g/cc	$\eta$ cP	$\alpha$	$\tau$ $\times 10^{12}$ sec	$\Delta H_\tau$ kcal/mole	$\Delta H_\eta$ cal/mole	$\mu_D$
1,3-propanedithiol									
30	2.37	3.76	1.07	1.07	0.26	6.3			1.26
50	2.34	3.42	1.06	0.85	0.31	4.8	2.2	2.5	1.37
70	2.30	3.24	1.03	0.70	0.39	3.6			1.44
1,2,3-tribromopropane									
30	2.49	2.49	2.39	3.92	0.28	48.2			1.56
50	2.46	2.46	2.35	2.59	0.22	30.9	3.3	3.7	1.57
70	2.43	2.43	2.31	1.86	0.17	22.0			1.57
85	2.41	2.41	2.29	1.50	0.15	16.1			1.57

kcal/mole in 1, 2, 3-tribromopropane is larger than the activation energy of dielectric relaxation  $\Delta H_r = 3.3$  kcal/mole as is generally observed.

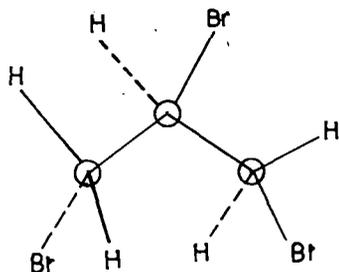
The distribution parameter  $\alpha$  in this liquid, in contrast to that in 1, 3-propanedithiol, decreases with increase in temperature as observed in other polar molecules.

The apparent dipole moment of 1, 2, 3-tribromopropane in the liquid state (Table II), is found to be temperature independent.

From spectroscopic studies<sup>9</sup> it has been reported that, of the nine possible conformers in 1, 2, 3-trichloropropane, only two conformers (Fig. 3) are present in the liquid, the major form III being more abundant than the minor form I. Similar results have been reported in 1, 2, 3-tribromopropane<sup>10</sup> also. The dipole moment of these conformers arises mainly from the C-Br bond moment attached to the three carbon atoms, the CH<sub>2</sub> moment being negligible. From Fig. 2, it can be easily seen that in each conformer, the moment of one C-Br bond attached to one carbon atom, cancels that in another carbon atom, the moments being in opposite direction. Only one C-Br bond moment ( $\approx 1.6$  D) remains, which is the moment of each conformer. This explains that any increase in the relative proportion of the less stable conformer, with increase in temperature, does not affect the apparent di-



Major form III



Minor form I

FIG. 2. Two conformers in 1, 2, 3-tribromopropane.

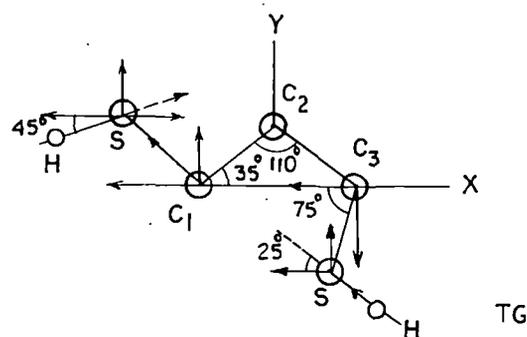
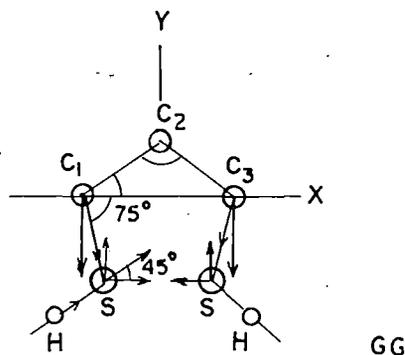
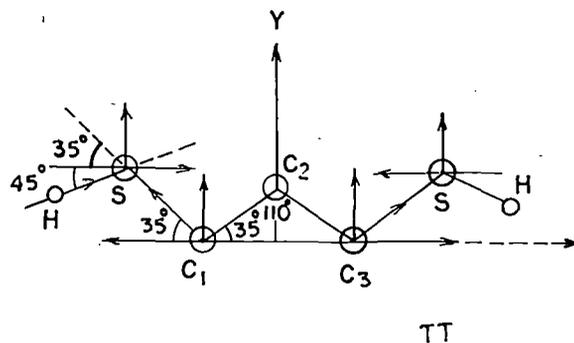


FIG. 3. Three conformers in 1, 3-propanedithiol.

pole moment in the liquid. Moreover, since the conformers are of similar sizes the distribution parameter  $\alpha$  does not increase with increase of temperature.

Finally, it should be noted that the large difference in the values of  $n_D^2$  and  $\epsilon_\infty$  in 1, 3-propanedithiol, indicates the presence of a Poley type absorption in the high frequency region. Such adsorption is absent in 1, 2, 3-tribromopropane in the liquid state, since the  $n_D^2$  and  $\epsilon_\infty$  values in this case are almost the same.

#### ACKNOWLEDGMENTS

The authors are thankful to Dr. S. B. Roy for guidance and to Professor G. S. Kastha for his kind interest in this work

## APPENDIX

Approximate calculation of the dipole moments of the three conformers of 1, 3-propanedithiol from the bond moments and bond angles, the  $\text{CH}_2$  moment being small, is neglected.  $\mu_1 = \mu_{\text{C-S}} = 0.9 \text{ D}$ ,  $\mu_2 = \mu_{\text{H-S}} = 0.7 \text{ D}$ ,  $\angle \text{CCC} = 110^\circ$  (Minkin *et al.*<sup>11</sup>) and  $\angle \text{CSH} = 100^\circ$  (Shaw *et al.*<sup>12</sup>).

## TT conformer

$$x \text{ component of } \mu_{\text{C-S}} \text{ attached to two carbon atoms} = \mu_1 \cos 35^\circ - \mu_1 \cos 35^\circ = 0$$

$$x \text{ component of } \mu_{\text{H-S}} \text{ attached to two sulfur atoms} = \mu_2 \cos 45^\circ - \mu_2 \cos 45^\circ = 0$$

$$y \text{ component of } \mu_{\text{C-S}} \text{ attached to two carbon atoms} = \mu_1 \sin 35^\circ + \mu_1 \sin 35^\circ = 2\mu_1 \sin 35^\circ$$

$$y \text{ component of } \mu_{\text{H-S}} \text{ attached to two sulfur atoms} = \mu_2 \sin 45^\circ + \mu_2 \sin 45^\circ = 2\mu_2 \sin 45^\circ$$

$$\text{Total moment of TT form} = 2\mu_1 \sin 35^\circ + 2\mu_2 \sin 45^\circ = 2.006 \text{ D}$$

## GG conformer

$$x \text{ component of } \mu_{\text{C-S}} \text{ attached to two carbon atoms} = \mu_1 \cos 75^\circ - \mu_1 \cos 75^\circ = 0$$

$$x \text{ component of } \mu_{\text{H-S}} \text{ attached to two sulfur atoms} = \mu_2 \cos 25^\circ - \mu_2 \cos 25^\circ = 0$$

$$y \text{ component of } \mu_{\text{C-S}} \text{ attached to two carbon atoms} = -\mu_1 \sin 75^\circ - \mu_1 \sin 75^\circ = -2\mu_1 \sin 75^\circ$$

$$y \text{ component of } \mu_{\text{H-S}} \text{ attached to two sulfur atoms} = \mu_2 \sin 25^\circ + \mu_2 \sin 25^\circ = 2\mu_2 \sin 25^\circ$$

$$\text{Total moment of the GG form} = -2\mu_1 \sin 75^\circ + 2\mu_2 \sin 25^\circ = -1.14 \text{ D}$$

## TG conformer

$$x \text{ component of } \mu_{\text{C-S}} \text{ attached to the two carbon atoms} = -\mu_1 \cos 35^\circ - \mu_1 \cos 75^\circ = -0.97 \text{ D}$$

$$x \text{ component of } \mu_{\text{H-S}} \text{ attached to the two sulfur atoms} = \mu_2 \cos 45^\circ - \mu_2 \cos 25^\circ = -0.20 \text{ D}$$

$$\text{Total } x \text{ component} = -(0.97 + 0.20) = -1.17 \text{ D}$$

$$y \text{ component of } \mu_{\text{C-S}} \text{ attached to the two carbon atoms} = \mu_1 \sin 35^\circ - \mu_1 \sin 75^\circ = -0.39 \text{ D}$$

$$y \text{ component of } \mu_{\text{H-S}} \text{ attached to the two sulfur atoms} = \mu_2 \sin 45^\circ + \mu_2 \sin 25^\circ = 1.12 \text{ D}$$

$$\text{Total } y \text{ component} = 1.12 - 0.39 = 0.73 \text{ D}$$

$$\text{Total moment of the TG form} = \sqrt{x^2 + y^2} = 1.4 \text{ D}$$

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REPRINTED FROM

# BULLETIN

OF THE

CHEMICAL SOCIETY  
OF JAPAN

VOL. 49, NO. 3, MARCH 1976

THE CHEMICAL SOCIETY OF JAPAN

## Dielectric Relaxation in *p*-Substituted Thiophenols in the Liquid State

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(Received April 21, 1975)

The dielectric absorption in 4-methylthiophenol and 4-chlorothiophenol in the liquid state has been studied in 0.8, 1.25, 1.62 and 3.49 cm microwave regions. Molecular and intramolecular relaxation times, their relative weight factors and the heats of activation have been determined. The results have been discussed and compared with other related molecules.

Intramolecular rotation of various polar groups in aromatic molecules<sup>1-3)</sup> in dilute solutions and in pure liquids has been studied extensively. Such studies of intramolecular rotation of SH group in organic molecules are rather few. Fong and Smyth<sup>4)</sup> reported the intramolecular rotation of SH group in naphthalenethiol in dilute benzene solution. Recently, Hasan *et al.*,<sup>5)</sup> from studies of dielectric relaxation in benzenethiol and benzylthiol in the liquid state reported that intramolecular rotation of the SH group was the main relaxation process in both the thiophenols. From a comparison of the values of SH group relaxation time  $\tau_2$  and its weight factor  $C_2$  in the thiophenols, with the corresponding  $\tau_2$  and  $C_2$  values for OH group rotation in phenols and substituted phenols reported by Aihara and Davies,<sup>6)</sup> Hasan *et al.*<sup>5)</sup> concluded that the intermolecular hydrogen bonding S-H...S are negligible in the thiophenols even in the liquid state.

The object of the present investigations was to extend similar studies in the case of *p*-substituted thiophenols in the liquid state and compare the results with the corresponding *p*-substituted phenols. The results obtained in the case of 4-methylthiophenol and 4-chlorothiophenol are presented and discussed in this paper.

### Experimental

The apparatus for the measurements of dielectric permittivity  $\epsilon'$ , dielectric loss  $\epsilon''$  in the region 0.8, 1.25, 1.62 and 3.49 cm microwaves were described earlier.<sup>7)</sup> The static dielectric constant  $\epsilon_0$  was measured at 1 MHz, the refractive index  $n_D$  was determined with an Abbe refractometer, the viscosity  $\eta$  was measured with an Ostwald viscometer and the density  $d$  with a pycnometer. The temperature in each experiment was kept constant within  $\pm 1^\circ\text{C}$  by means of a thermostat. The estimated errors in  $\epsilon'$  and  $\epsilon''$  are about 2% and 4% respectively.

### Results

The experimental values of  $\epsilon'$  and  $\epsilon''$  at different microwave frequencies together with the values of  $\epsilon_0$  at different temperatures are given in Table 1. These data were then fitted in Cole-Cole arc plots (Fig. 1). The high frequency dielectric constant  $\epsilon_\infty$  and the distribution parameter  $\alpha$  were obtained as usual from the arc plots. The values of  $\epsilon_\infty$  in each case was found much higher than that of  $n_D^2$ . The values of the distribution parameter were appreciably high at all temperatures, indicating the presence of more than one relaxation process. This was confirmed by the non-linear plots of  $\epsilon'$  vs  $\epsilon''\omega$ . The dielectric data were

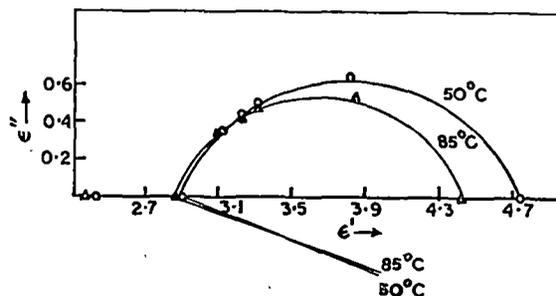


Fig. 1. Cole-Cole arc plot of 4-thiocresol.

then analysed in terms of two relaxation processes following the equations of Bergmann *et al.*<sup>8)</sup> and as simplified by Bhattacharyya *et al.*<sup>9)</sup> for straightforward calculations.

Bergmann's equations are

$$a = \frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{C_1}{1 + \omega^2\tau_1^2} + \frac{(1 - C_1)}{1 + \omega^2\tau_2^2} \quad (1)$$

and

$$b = \frac{\epsilon''}{\epsilon_0 - \epsilon_\infty} = \frac{C_1\omega\tau_1}{1 + \omega^2\tau_1^2} + \frac{(1 - C_1)\omega\tau_2}{1 + \omega^2\tau_2^2} \quad (2)$$

The simplified equation<sup>9)</sup> is

$$\frac{1 - a}{b\omega} = \tau_1 + \tau_2 - \frac{a\omega}{b}\tau_1\tau_2 \quad (3)$$

which can be written in the form

$$\sum_{i=1}^n Sx_i - Py_i - 1 = 0 \quad (4)$$

where

$$S = \tau_1 + \tau_2, P = \tau_1\tau_2, x = \frac{b\omega}{1 - a} \text{ and } y = \frac{a\omega^2}{1 - a}$$

Eq. (4) is a linear equation and can be solved by the method of least squares. From the principle of least square, it can be easily shown from Eq. (4) that

$$S = \frac{\sum_{i=1}^n y_i \sum_{i=1}^n x_i y_i - \sum_{i=1}^n x_i \sum_{i=1}^n y_i^2}{\left(\sum_{i=1}^n x_i y_i\right)^2 - \sum_{i=1}^n x_i^2 \sum_{i=1}^n y_i^2} \quad (5)$$

$$P = \frac{\sum_{i=1}^n y_i \sum_{i=1}^n x_i^2 - \sum_{i=1}^n x_i \sum_{i=1}^n x_i y_i}{\left(\sum_{i=1}^n x_i y_i\right)^2 - \sum_{i=1}^n x_i^2 \sum_{i=1}^n y_i^2} \quad (6)$$

Solving Eqs. (5) and (6),  $\tau_1$  and  $\tau_2$  can be calculated. The value of  $C_1$  is then determined from the equation given below, obtained from Eqs. (1) and (2) by applying the least square principle.

TABLE 1. OBSERVED AND CALCULATED VALUES OF DIELECTRIC PERMITTIVITY  $\epsilon'$  AND DIELECTRIC LOSS  $\epsilon''$ 

$T^\circ\text{C}$	Freq. = 8.60 GHz				Freq. = 18.50 GHz				Freq. = 24.03 GHz				Freq. = 35.13 GHz				1MHz $\epsilon_0$
	$\epsilon'_{\text{obsd}}$	$\epsilon'_{\text{calcd}}$	$\epsilon''_{\text{obsd}}$	$\epsilon''_{\text{calcd}}$													
4-Methylthiophenol																	
50	3.83	3.68	0.66	0.70	3.32	3.35	0.50	0.51	3.24	3.28	0.44	0.45	3.13	3.20	0.36	0.39	4.74
70	3.85	3.68	0.59	0.66	3.31	3.34	0.48	0.50	3.23	3.27	0.42	0.43	3.12	3.19	0.34	0.36	4.56
85	3.85	3.70	0.54	0.63	3.32	3.37	0.47	0.47	3.24	3.25	0.41	0.41	3.09	3.19	0.32	0.33	4.43
4-Chlorothiophenol																	
65	3.43	3.40	0.20	0.22	3.27	3.27	0.21	0.21	3.22	3.23	0.20	0.20	3.16	3.18	0.18	0.18	3.59
85	3.40	3.39	0.18	0.18	3.26	3.27	0.20	0.20	3.23	3.23	0.19	0.19	3.18	3.18	0.18	0.18	3.52

TABLE 2. VALUES OF  $\alpha$ ,  $\epsilon_\infty$ ,  $\tau_1$ ,  $\tau_2$ ,  $\Delta H\tau_1$ ,  $\Delta H\eta$  and  $\mu$ 

$T^\circ\text{C}$	$\alpha$	$n_D^2$	$\epsilon_\infty$	$\tau_1 \times 10^{12}$ s	$\tau_2 \times 10^{12}$ s	$C_1$	$\Delta H\tau_1$ kcal/mol	$\Delta H\eta$ kcal/mol	$\mu_D$
4-methylthiophenol									
50	0.23	2.43	2.91	29.7	3.1	0.79	1.31	2.03	1.4
70	0.22	2.40	2.92	25.8	2.6	0.79			
85	0.22	2.38	2.92	22.2	1.9	0.82			
4-Chlorothiophenol									
65	0.21	2.50	3.00	17.7	2.8	0.63	2.00	—	—
85	0.19	2.47	2.99	14.2	2.4	0.62			

$$C_1 = \frac{\sum_{i=1}^n a_i f_i + \sum_{i=1}^n b_i g_i - \sum_{i=1}^n f_i f_i' - \sum_{i=1}^n g_i g_i'}{\sum_{i=1}^n f_i^2 + \sum_{i=1}^n g_i^2} \quad (7)$$

where

$$f_i = (f_1 - f_i'), \quad f_1 = \frac{1}{1 + \omega^2 \tau_1^2}, \quad f_i' = \frac{1}{1 + \omega^2 \tau_2^2}$$

$$g_i = (g_1 - g_i'), \quad g_1 = \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2}, \quad g_i' = \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2}$$

The value of  $\epsilon_\infty$  as obtained from Cole-Cole plot may not coincide with the actual value in Eqs. (1) and (2), but it will lie between the  $n_D^2$ -value and  $\epsilon'$ -value obtained at the highest microwave frequency used. So, to start with, any value for  $\epsilon_\infty$  within the above limit is assumed and  $\tau_1$ ,  $\tau_2$  and  $C_1$  values are determined. With these values of  $\tau_1$ ,  $\tau_2$  and  $C_1$ , the values of  $\epsilon'$  and  $\epsilon''$  are calculated from Eqs. (1) and (2). The value of  $\epsilon_\infty$  is then varied and the process is repeated till the mean square deviation  $A$ , from the relation

$$A = \sum (\epsilon''_{\text{obsd}} - \epsilon''_{\text{calcd}})^2 + \left\{ \frac{\epsilon'_{\text{obsd}} - \epsilon'_{\text{calcd}}}{n} \right\}^2,$$

is found to be minimum. The ' $n$ ' is a scaling factor to reduce the error in  $\epsilon'$ , to the same magnitude of the error in  $\epsilon''$ . A value of  $n=3$  is used in the present case. The values of  $\epsilon_\infty$ ,  $\tau_1$ ,  $\tau_2$  and  $C_1$  are given in Table 2. All the calculations were carried on the IBM Computer 1130. The calculated values of  $\epsilon'$  and  $\epsilon''$  are included in Table 1.

The activation energies for dielectric relaxation and viscous flow were obtained from the straight line plots of  $\log \tau T$  vs.  $1/T$  and  $\log \eta$  vs.  $1/T$  respectively. The dipole moment in the case of 4-methylthiophenol was calculated from  $\epsilon_0$  and density  $d$  using Onsager's equation. The values of  $\alpha$ ,  $n_D^2$ ,  $\Delta H\tau_1$ ,  $\Delta H\eta$  and  $\mu$  are

included in Table 2.

### Discussion

It can be seen from Table 2 that the molecular and intramolecular relaxation times in both the *para* substituted thiophenols, decrease with increase in temperature as is generally observed in polar liquids, so also the distribution parameter  $\alpha$  decreases with increase of temperature.

The intramolecular relaxation time  $\tau_2$  for SH group rotation in both the liquids are of the same order ( $\approx 3$ ps) and compares well with the  $\tau_2$ -values in thiophenol (2.6 ps) and in benzylthiol (3.1 ps) in the liquid state reported earlier<sup>5)</sup> as also in naphthalenethiol (2.5 ps) in dilute solution in benzene reported by Fong and Smyth.<sup>4)</sup> Thus it is found that the SH group relaxation times in pure liquids as also in dilute benzene solution are almost the same, showing thereby that the intermolecular hydrogen bondings S-H...S of the type hydroxyl hydrogen bonding, observed in phenol and substituted phenols,<sup>10)</sup> are negligible in the thiophenols even in the liquid state.

It would be interesting to compare the  $\tau_1$  and  $\tau_2$  values of the present liquids, with those of *p*-substituted phenols reported by Magee and Walker.<sup>10)</sup> Though the molecular relaxation time  $\tau_1$  of 29.7 ps at 50 °C in 4-methylthiophenol compares well with the value of  $\tau_1=32$  ps at 25 °C in 4-methylphenol in *p*-xylene solution, the SH group relaxation time of 2.85 ps in the former, is definitely much smaller than the OH group relaxation time  $\tau_2=8.4$  ps in the latter. The molecular relaxation time  $\tau_1=17.7$  ps at 65 °C in 4-chlorothiophenol in the liquid state is almost half the value of  $\tau_1=39$  ps in 4-chlorophenol in *p*-xylene solution and the  $\tau_2$ -value of 2.8 ps for SH group rotation in the former is about our fourth the  $\tau_2$ -value of 12.7 ps

for OH group rotation in the latter. The unusual lengthening of the OH group relaxation of *p*-substituted phenols in *p*-xylene solution was attributed by Magee and Walker<sup>10</sup>) to association among the solute molecules, in addition to the effects of solvents. The lengthening of molecular relaxation time ( $\tau_1=39$  ps) in 4-chlorophenol in dilute *p*-xylene solution to double the  $\tau_1$ -value of 17.7 ps in 4-chlorothiophenol, seems to suggest that a dimer has been formed in *p*-chlorophenol molecule by association with other solute molecule probably through H-Cl hydrogen bond. Similar bond formation is not observed in 4-methylphenol in the *p*-xylene solution.

**Weight factors:** It is seen from Table 2 that the weight factor  $C_1$  for 4-methylthiophenol and 4-chlorothiophenol are about 0.79 and 0.63 respectively. An estimate for the weight factors for both the thiophenols can be made from consideration of bond moments. Assuming the moments of  $\mu_{\text{CH}_3}=0.37\text{D}$ ,  $\mu_{\text{C-S}}=0.9\text{D}$ ,  $\mu_{\text{H-S}}=0.7\text{D}$ ,  $\mu_{\text{C-Cl}}=1.5\text{D}$  and  $\angle\text{CSH}=135^\circ$ ,<sup>11)</sup> and remembering that the  $\text{CH}_3$  group moment is directed towards the benzene ring, the moment components responsible for SH group rotation are  $\mu_2=0.49\text{D}$  in both the molecules, while the moment components responsible for molecular reorientations are  $\mu_1=0.8\text{D}$  in methyl thiophenol and  $\mu_1=1.1\text{D}$  in 4-chlorothiophenol. From the above values of  $\mu_1$  and  $\mu_2$ , the ratio of the weight factors in the two cases are,

$$\frac{C_2}{C_1} = \left( \frac{0.49}{0.8} \right)^2 = \frac{0.24}{0.64} \text{ or } C_1 = 0.73$$

in 4-methylthiophenol and

$$\frac{C_2}{C_1} = \left( \frac{0.49}{1.1} \right)^2 = \frac{0.24}{1.21} \text{ or } C_1 = 0.83$$

in 4-chlorothiophenol. Thus the weight factors  $C_1$  for molecular reorientation in both the liquids are larger than that for group rotation. This is in conformity with the values obtained experimentally. It may be noted here that some uncertainty may arise in the calculated value of the dipole moment in 4-chlorothiophenol, due to appreciable mesomeric charge shift occurring across the molecule.<sup>12)</sup>

The activation energy  $\Delta H\tau_1$  for molecular relaxation in 4-methylthiophenol is about 1.3 kcal/mol which, as usual, is less than the corresponding activation energy of  $\Delta H\dot{\eta}=2$  kcal/mol for viscous flow. In the

case of 4-chlorothiophenol, the dielectric data could be taken only for two temperatures and therefore activation energy  $\Delta H\tau_1$  may not be reliable in this case.

The values of  $\epsilon_\infty$  in both the *p*-substituted thiophenols are appreciably larger than the value of  $n_D^2$  at all temperatures. This indicates the presence of a third dispersion region of the 'Poley type' in the high frequency region.

The dipole moment of 4-methylthiophenol has been determined from  $\epsilon_0$  and density  $d$ , using Onsager's equation and is found to be 1.4D, which agrees well with the value of 1.46D obtained from bond moment calculation of the  $\text{CH}_3$  group in the *para* position of thiophenol ( $\mu=1.22\text{D}$ ).

The authors express their sincere thanks to Professor G. S. Kastha for helpful discussions and to Mr. D. Bhowmic for his help in making the computer programme.

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**Potassium  $\mu$ -(*trans*-Hyponitrito-*N,N'*)-bis{pentacyanocobaltate(III)}  
and Potassium  $\mu$ -(*Trans*-Hyponitrito-*O,O'*)-Bis-  
{Pentacyanocobaltate(III)}**

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(Received July 28 1975)

$K_6[Co_2(CN)_{10}(N_2O_2)] \cdot 2H_2O$  (orange salt) was prepared by reaction of  $[Co(NO)(NH_3)_5]Cl_2$  with an aqueous solution of potassium cyanide.  $K_6[Co_2(CN)_{10}(N_2O_2)] \cdot 4H_2O$  (yellow salt) was obtained by adding an aqueous solution of the orange salt to methanol. On the basis of IR and Raman spectra for their  $^{14}NO$ - and  $^{15}NO$ -salts, and of IR spectra for their gaseous decomposition products, the orange salt is considered to be a linkage isomer of the yellow salt with respect to the *trans*-hyponitrito bridge. It is presumed that the orange salt is potassium  $\mu$ -(*trans*-hyponitrito-*N,N'*)-bis{pentacyanocobaltate(III)}, the yellow salt being potassium  $\mu$ -(*trans*-hyponitrito-*O,O'*)-bis{pentacyanocobaltate(III)}.

Toyuki<sup>1)</sup> and Jezowska-Trzebiatowska *et al.*<sup>2)</sup> prepared  $K_6[Co_2(CN)_{10}(N_2O_2)] \cdot 4H_2O$  with a *cis*- or *skew*-hyponitrito bridge by the method given by Nast and Rohmer.<sup>3)</sup> On the other hand, Raynor<sup>4)</sup> prepared  $K_6[Co_2(CN)_{10}(N_2O_2)] \cdot 4H_2O$  with a *trans*-hyponitrito group, according to the method given by Nast, Mesche and Neubauer.<sup>5)</sup> While investigating the method of Nast and Rohmer,<sup>3)</sup> we prepared two new isomers with a *trans*-hyponitrito group,  $K_6[Co_2(CN)_{10}(N_2O_2)] \cdot nH_2O$  ( $n=2$  or  $4$  for orange and yellow salts, respectively).<sup>6)</sup>

This paper describes studies on the two isomers with respect to IR and Raman spectra, UV spectra, and thermal decomposition. The product prepared according to the method of Nast and Rohmer<sup>3)</sup> is also discussed by comparing its IR absorption bands with those of the two isomers.

### Experimental

**Preparation.** Synthetic procedures and elementary analyses for the orange and the yellow salts were reported in detail.<sup>6)</sup> From 1 to 3 g of  $[Co(NO)(NH_3)_5]Cl_2$  was used for preparing the orange salt. Powdered  $[Co(NO)(NH_3)_5]Cl_2$  was added little by little to a 30% aqueous solution of potassium cyanide with stirring in order to keep the reaction vessel at constant temperature ( $-10^\circ C$ ). The procedure differs from that reported by Nast and Rohmer.<sup>3)</sup> Yield, 0.6—2 g.  $\chi_g$  (at 293K) =  $-0.45 \times 10^{-6}$  (c.g.s.). One gram of the orange salt was used for preparing the yellow salt. Yield, 0.8 g.  $\chi_g$  (at 293K) =  $-0.36 \times 10^{-6}$  (c.g.s.).

**Thermal Decomposition and Decomposition with 10% Potassium Cyanide Aqueous Solution.** Decomposition was carried out in a vacuum line. A reaction vessel containing the salt (*ca.* 0.5 g) was heated *in vacuo* in an electric furnace at a rate of *ca.* 1—2  $^\circ C \text{ min}^{-1}$ . Both the orange and the yellow salts decomposed violently at *ca.* 155 and 116  $^\circ C$ , respectively, to give gray powders. About 0.5 g of the salt was added in a reaction vessel containing 5 ml of 10% KCN solution frozen with the aid of liquid nitrogen, and the reaction vessel was evacuated. When the frozen solution was melted, both the salts decom-

posed by contact with the aqueous solution. The gaseous products thus obtained were dehydrated with  $P_4O_{10}$  and transferred to a gas cell with windows of calcium difluoride.

**Measurements.** The magnetic susceptibility was measured by the Gouy method. The IR spectra of the salts were measured as Nujol and hexachlorobutadiene mulls in the region 200—4000  $cm^{-1}$  on JASCO 402G and JASCO model IR-F spectrometers. The Raman spectra of the powdered samples were recorded in the region 100—1500  $cm^{-1}$  on a JASCO R-300 spectrometer equipped with He-Ne laser. The gaseous products were identified by means of their IR spectra.<sup>7)</sup> The mole ratio of the liberated NO to  $N_2O$  was determined.<sup>8)</sup> The diffuse reflection spectra of the salts were measured with a Hitachi EPS-3T spectrometer. The UV spectra in aqueous solution were recorded with a Hitachi 124 spectrometer.

### Results and Discussion

#### *Raman and IR Spectra for the Orange and Yellow Salts.*

Wave numbers of the IR and Raman bands and their assignments are summarized in Table 1.

**Raman Spectra:** Upon  $^{15}NO$ -substitution ( $^{15}N$  atom% = 95), the bands at 1257 and 1165  $cm^{-1}$  for the orange salt shifted downwards by 31 and 39  $cm^{-1}$ , respectively and, the bands at 1412 and 1070  $cm^{-1}$  for the yellow salt shifted downwards by 43 and 18  $cm^{-1}$ , respectively. Upon  $^{15}NO$ -substitution ( $^{15}N$  atom % = 50), the 1257  $cm^{-1}$  band for the orange salt shifted and split into three peaks at 1253, 1242, and 1226  $cm^{-1}$  (their intensity ratio 1:2:1). The same phenomenon was observed with the yellow salt; the 1412  $cm^{-1}$  band shifted and split into three peaks, 1414, 1392, and 1369  $cm^{-1}$  (their intensity ratio 1:2:1). This indicates that N-N bond is present in both the orange and yellow salts. For other bands, no isotopic shifts upon  $^{15}NO$ -substitution could be observed. The bands in the region *ca.* 400—550  $cm^{-1}$  are considered to be due to the  $Co(CN)_5$  group.<sup>9)</sup>

**IR Spectra:** The bands at 1157, 609, and 299  $cm^{-1}$  for the orange salt shifted downwards by 21, 14, and 2  $cm^{-1}$  upon  $^{15}NO$ -substitution ( $^{15}N$  atom % = 95), respectively, while the bands at 987, 630, and 329  $cm^{-1}$  for the yellow salt shifted downwards by 15, 6, and 6  $cm^{-1}$ , respectively.

The 1630 and 3580  $cm^{-1}$  bands for the orange salt

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REPRINTED FROM

# BULLETIN

OF THE

CHEMICAL SOCIETY  
OF JAPAN

VOL. 47, NO. 9, SEPTEMBER, 1974

THE CHEMICAL SOCIETY OF JAPAN

# Dielectric Studies of *ortho*- and *para*-Bromoanisoles and $\beta$ -Bromophenetole in the Liquid State

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(Received February 8, 1974)

Complex dielectric permittivities in *ortho*- and *para*-bromoanisoles and  $\beta$ -bromophenetole in the liquid state have been measured in 1.6, 3.17, and 3.49 cm microwave regions at different temperatures. The dielectric data were analysed in terms of molecular and intramolecular relaxation times. The values of methoxy group relaxation times and its contribution to total polarization obtained in the liquid bromoanisoles have been compared to the corresponding values in dilute solutions reported in literatures. Activation energy for dielectric relaxation and viscous flow in all the cases have also been obtained in all the liquids.

From studies of dielectric relaxation in anisole and dimethoxy benzenes in the liquid state Vaughan *et al.*<sup>1)</sup> reported that the relaxation time of methoxy group rotation  $\tau_2$  and its contribution  $C_2$  to total polarization are about 3 ps at 20 °C and 0.2 respectively excepting in the case of *o*-dimethoxy benzene where  $C_2=0.7$ . Garg and Smyth<sup>2)</sup> extended the investigation in liquid anisole at still higher frequency region and reported the similar values of  $\tau_2$  and  $C_2$ . These values of  $\tau_2$  and  $C_2$  in anisole and *p*-dimethoxy benzene in dilute solutions reported by different workers<sup>3-5)</sup> are found to be 7—9 ps at 20 °C and 0.7 respectively, while in *p*-bromoanisole in dilute solution though the  $\tau_2$  value is 9 ps at 20 °C, the  $C_2$  is only 0.2 as reported by Farmer and Walker.<sup>4)</sup> So it appears that the methoxy group relaxation time and its contribution  $C_2$  in anisole or dimethoxy benzene in dilute solution are larger than their values in pure liquids. Garg and Smyth<sup>2)</sup> suggested that the reduction in the contribution of  $C_2$  of the methoxy group rotation from its value in solution to the liquid state might be due to some restraint in the C—O bond as a result the methoxy group rotation in anisole is not completely free but hindered.

It will be interesting to study how the methoxy group rotation  $\tau_2$  and its contribution  $C_2$  in haloanisoles in the liquid state, compare with the corresponding values in dilute solutions published in literatures. The present paper reports the results of investigation on dielectric relaxation of *o*-bromo and *p*-bromoanisoles and  $\beta$ -bromophenetole in the liquid state together with a discussion of the results.

## Experimental

Pure samples of *o*-bromoanisole, *p*-bromoanisole and  $\beta$ -bromophenetole were dried with fused calcium chloride and then subjected to fractional distillation. The proper fraction was then distilled under reduced pressure before use in the investigation. The experimental arrangement for measurement of dielectric permittivity  $\epsilon'$ , dielectric loss  $\epsilon''$ , static dielectric constant  $\epsilon_0$ , refractive index  $n_D$ , viscosity  $\eta$ , and density  $d$  at different temperatures were the same as described in an earlier paper.<sup>6)</sup> The accuracy in the measurements of  $\epsilon'$  and  $\epsilon''$  were about 2 and 5% respectively.

## Results

The experimentally obtained values of  $\epsilon'$  and  $\epsilon''$  at different wave lengths and at different temperatures together with  $\epsilon_0$  at 1 MHz at different temperatures are given in Table 1 and the viscosity  $\eta$ , density  $d$  and refractive index  $n_D$  at different temperatures are given in Table 2. Cole-Cole arc plots (some shown in Fig. 1) were drawn with the dielectric data. The high frequency dielectric constant  $\epsilon_\infty$  and the distribution parameter  $\alpha$  were obtained as usual from the arc plots. The large values of distribution parameter and also the nonlinear plots of  $\epsilon'$  vs.  $\epsilon''/\omega$  indicated the presence of more than one relaxation mechanism in all the liquids. The dielectric data were therefore analysed in terms of two relaxation processes by a straightforward analytical method developed by Kastha<sup>7)</sup> and applied successfully by others.<sup>8-10)</sup> The values of relaxation times for

TABLE 1. VALUES OF  $\epsilon'$ ,  $\epsilon''$  AND  $\epsilon_0$

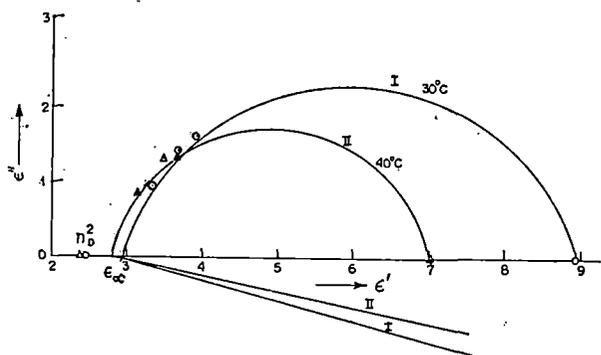
Compound	Temp. °C	$\lambda=1.62$ cm		$\lambda=3.17$ cm		$\lambda=3.49$ cm		$\epsilon_0$
		$\epsilon'$	$\epsilon''$	$\epsilon'$	$\epsilon''$	$\epsilon'$	$\epsilon''$	
<i>o</i> -Bromoanisole	30	3.27	0.97	3.68	1.41	3.91	1.62	8.96
	50	3.35	1.11	3.79	1.55	4.18	1.82	8.68
	70	3.42	1.28	3.96	1.76	4.20	1.91	8.36
	85	3.45	1.33	4.01	1.91	4.39	2.04	8.14
<i>p</i> -Bromoanisole	30	2.97	0.67	3.32	1.16	3.46	1.27	7.40
	50	2.99	0.89	3.35	1.43	3.47	1.53	7.12
	70	3.05	0.90	3.53	1.44	3.67	1.52	6.82
	85	3.04	0.99	3.63	1.54	3.73	1.62	6.56
$\beta$ -Bromophenetole	40	3.12	0.84	3.48	1.30	3.66	1.34	7.04
	55	3.23	0.95	3.69	1.34	3.86	1.42	6.69
	70	3.32	1.04	3.88	1.40	4.00	1.45	6.28
	85	3.44	1.06	4.02	1.34	4.19	1.37	6.00

TABLE 2. VALUES OF  $\alpha$ ,  $\eta$ ,  $d$ ,  $n_D^2$  AND  $\epsilon_\infty$ 

Compound	Temp. °C	Distribution parameter $\alpha$	Viscosity $\eta$ (cP)	Density $d$ (g/cm <sup>3</sup> )	Square of refractive index $n_D^2$	$\epsilon_\infty$
<i>o</i> -Bromoanisole	30	0.175	1.998	1.500	2.46	2.94
	50	0.159	1.353	1.481	2.43	2.88
	70	0.140	1.002	1.455	2.40	2.84
	85	0.059	0.839	1.437	2.37	2.80
<i>p</i> -Bromoanisole	30	0.095	1.499	1.482	2.43	2.76
	50	0.090	1.150	1.457	2.40	2.66
	70	0.084	0.910	1.438	2.37	2.64
	85	0.080	0.769	1.421	2.35	2.56
$\beta$ -Bromophenetole	40	0.126	2.420	1.409	2.39	2.82
	55	0.116	1.726	1.392	2.37	2.81
	70	0.115	1.325	1.372	2.35	2.77
	85	0.112	1.003	1.356	2.32	2.74

TABLE 3. VALUES OF  $\tau_1$ ,  $\tau_2$ ,  $C_1$ ,  $\Delta H\tau_1$ ,  $\Delta H\tau_2$ ,  $\Delta H\eta$  AND  $\mu$ 

Compound	Temp. °C	$\tau_1 \times 10^{12}$ (s)	$\tau_2 \times 10^{12}$ (s)	$C_1$	$\Delta H\tau_1$ (kcal/mol)	$\Delta H\tau_2$ (kcal/mol)	$\Delta H\eta$ (kcal/mol)	Dipole moment $\mu$ (D)
<i>o</i> -Bromoanisole	30	48.9	10.9	0.63	2.28	2.22	3.45	2.15
	50	37.2	8.7					
	70	28.7	7.7					
	85	22.6	6.2					
<i>p</i> -Bromoanisole	30	33.7	7.3	0.85	2.02	2.72	2.70	1.98
	50	24.9	5.6					
	70	23.5	4.2					
	85	19.2	3.2					
$\beta$ -Bromophenetole	40	33.0	9.8	0.65	2.01	2.16	3.54	2.02
	55	28.5	8.5					
	70	22.8	7.1					
	85	20.6	5.6					

Fig. 1. Cole-Cole plot of *o*-bromoanisole at 30 °C (Curve I,  $\odot$ ) and  $\beta$ -bromophenetole at 40 °C (Curve II,  $\triangle$ ).

molecular orientation  $\tau_1$  and group rotation  $\tau_2$  and weight factor  $C_1$  for molecular orientation are included in Table 3. The activation energies for dielectric relaxation by molecular orientation  $\Delta H\tau_1$  and group rotation  $\Delta H\tau_2$  were obtained from the slopes of the straight line plots of  $\log T\tau$  vs.  $1/T$  and the activation energy for viscous flow  $\Delta H\eta$  were obtained from the graphs of  $\log \eta$  vs.  $1/T$ . The values of  $\Delta H\tau_1$ ,  $\Delta H\tau_2$ , and  $\Delta H\eta$  are included in Table 3.

### Discussion

It can be seen from Table 3 that the molecular and

intramolecular relaxation times as also the distribution parameter  $\alpha$  in all the liquids decrease with increase of temperature as is generally observed.

The value of molecular relaxation time  $\tau_1=49$  ps at 30 °C in *o*-bromoanisole appears much larger than the value of  $\tau_1=33.7$  ps at the same temperature in *p*-bromoanisole. But the reduced relaxation time  $\tau_1/\eta$  of the two molecules are of the same order ( $\approx 23$  ps) of magnitude, showing thereby that the two isomeric molecules are of the same size.

*o*-Bromoanisole. A comparison of molecular relaxation time  $\tau_1$  of *o*-bromoanisole and *o*-dimethoxy benzene both in the liquid state, shows that the molecular relaxation time  $\tau_1 \approx 49$  ps at 30 °C in the former molecule obtained in the present investigation is almost the same as that of 48.5 ps at 25 °C in the latter reported by Vaughan *et al.*<sup>11</sup> This is consistent with the sizes of the two molecules.

The contribution of methoxy group rotation  $C_2$  in *o*-bromoanisole in the liquid state is only about 0.37 as against the value 0.7 in the case of *o*-dimethoxy benzene in the liquid state. The former molecule having C-Br bond moment of about 1.55 D as against O-CH<sub>3</sub> bond moment of  $\approx 1.3$  D in the latter molecule, has total moment larger than the latter molecule. So the ratio of group moment component to the total moment which is a measure of  $C_2$  is expected to be larger in the latter molecule.

The contribution of the methoxy group rotation  $C_2$  in *o*-bromoanisole can be calculated from the consideration of total moment and methoxy group moment of the molecule. The O-CH<sub>3</sub> bond has a moment of about 1.3 D making an angle 55° with the direction of C-O bond in the benzene ring. The component of the O-CH<sub>3</sub> bond moment perpendicular to the direction of C-O bond, which is responsible for methoxy group rotation is

$$\mu_2 = 1.3D \times \sin 55^\circ = 1.06D$$

and the total moment of the molecule  $\mu_1$  can be obtained by the vector sum of C-Br bond moment and component of O-CH<sub>3</sub> bond moment along the C-O axis and is given by

$$\begin{aligned} \mu_1^2 &= (1.55)^2 + (1.3 \cos 55^\circ)^2 \\ &+ 2 \times 1.55 \times 1.3 \cos 55^\circ \cdot \cos 60^\circ \\ &= 3.92 \\ \mu_1 &= 1.99D \end{aligned}$$

This value of 1.99 D agrees fairly well with the experimentally obtained value of 2.15 D.

$$\text{Now } C_2 = \left( \frac{\mu_2}{\mu_1} \right)^2 = \left( \frac{1.06}{1.99} \right)^2 = 0.30$$

So theoretically calculated value of  $C_2=0.30$  compares reasonably well with the experimentally obtained value of  $C_2=0.37$ .

***p*-Bromoanisole.** The value of molecular relaxation time  $\tau_1=33.7$  ps and group relaxation time  $\tau_2=7.3$  ps at 30 °C as also the contribution from methoxy group rotation  $C_2=0.15$  obtained in the liquid *p*-bromoanisole, agree fairly well with the values of  $\tau_1=31$  ps  $\tau_2=7$  ps at 25 °C and  $C_2=0.2$  in *p*-bromoanisole in dilute solution of *p*-xylene reported by Farmer and Walker.<sup>4)</sup> The similarity in dielectric behaviour of *p*-bromoanisole in pure liquid and dilute solution suggests that the dipole-dipole interaction is not very effective in the liquid state of the molecule.

**Comparison of the Relaxation Time of Methoxy Group Rotation in Pure Liquid and Dilute Solution.** The relaxation time of methoxy group rotation in *o*-bromo- and *p*-bromoanisole in the liquid state obtained in the present investigation are of the same order of methoxy group rotation (7–9) ps reported in anisole and substituted anisoles in dilute solutions reported by Farmer and Walker<sup>4)</sup> and Klages and Krauss<sup>5)</sup> but larger than the value of about 3 ps of the methoxy group rotation in anisole and dimethoxy benzenes in liquid state reported by Vaughan *et al.*<sup>1)</sup> and Garg and Smyth.<sup>2)</sup> So it appears that the methoxy group rotation in molecules containing only methoxy group as substituent is less hindered in the liquid state than in anisole in dilute solution or in haloanisoles either in the liquid state or in solutions. This is supported by the fact that the activation energy of methoxy group rotation in anisole in liquid state as reported by Garg and Smyth<sup>2)</sup> is only 1.5 kcal/mol which is much smaller than the value of 2.6 kcal/mol for methoxy group rotation in anisole in dilute solution in *p*-xylene calculated from the data of Farmer and Walker<sup>4)</sup> and also from the values of 2.2–2.6 kcal/mol (Table 3) for

methoxy group rotation in the bromo-anisoles in liquid state obtained in the present investigation.

The larger value of the methoxy group rotation of anisole in benzene or *p*-xylene solution than in the pure liquid may be due to the formation of a weak bond between the  $\pi$ -electron of the solvent molecule and hydrogen atom of the methoxy group. Similar bond formation in 1,2-dichloroethane and benzene has been reported by Chitoku and Higasi.<sup>11)</sup>

**$\beta$ -Bromophenetole.** The reduced molecular relaxation time  $\tau_1/\eta$  of  $\beta$ -bromophenetole at 40 °C is about 14 ps which is smaller than the value  $\tau_1/\eta=23$  ps at 30 °C in bromoanisoles. Thus the  $\beta$ -bromophenetole molecule appears to be a little bit smaller than the molecules of bromoanisoles.

The group relaxation time  $\tau_2=9.8$  ps at 40 °C in this case is larger than the methoxy group rotation in anisole in dilute solution or haloanisoles in liquid state. This value of  $\tau_2=9.8$  ps at 40 °C is also larger than the relaxation time of ethoxy group rotation  $\tau_2=4$  ps at 40 °C in the liquid state reported by Bhattacharyya *et al.*<sup>8)</sup> which is consistent with their sizes.

The contribution of group rotation  $C_2$  here is only –0.32 as against the value of  $C_2=0.63$  in ethoxy group rotation in phenetole. The substitution of Br-atom in the ethoxy group might increase hindrance and thus reduces the value of  $C_2$  in the present case.

**Activation Energy.** The activation energy of dielectric relaxation by molecular orientation in all the liquids are of the same order (2.1 kcal/mol) and each is smaller than the corresponding activation energy for viscous flow as usually observed.

The activation energy for molecular relaxation  $\Delta H\tau_1=2.1$  kcal/mol in *p*-bromoanisole in liquid state obtained in the present investigation is about the same as the value of  $\Delta H\tau_1=2.07$  kcal/mol obtained for *p*-bromoanisole in dilute solution, calculated from the data of Farmer and Walker.<sup>4)</sup> This shows that the dipolar interaction are almost the same in the liquid *p*-bromoanisole and its solution in *p*-xylene as mentioned earlier.

The activation energy of group rotation in the liquid ( $\Delta H\tau_2=2.2$  kcal/mol) and in solution ( $\Delta H\tau_2=1.9$  kcal/mol) calculated from the data of Farmer and Walker<sup>4)</sup> are also compatible.

It can be seen from Table 2 that the values of  $n_D^2$  in all the liquids are less than the respective values of  $\epsilon_\infty$ . This indicates the presence of a high frequency absorption region as suggested by Poley.<sup>12)</sup> This 'Poley absorption' has been generally explained as due to torsional molecular librations in potential minima of fluctuating interaction field of the neighbouring molecules.<sup>13)</sup>

The authors wish to express their sincere thanks to Dr. S. B. Roy for his guidance and to Professor G. S. Kastha for his keen interest.

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