

## CHAPTER 7

### MICROWAVE ABSORPTION AND DIELECTRIC RELAXATION IN SOME SUBSTITUTED PROPANES WITH A PHENYL RING ATTACHED TO ONE END

#### 7.1 Introduction

Relaxation mechanisms in aromatic molecules with small rotatable polar groups such as  $-SH$ ,  $-CH_2SH$ ,  $O-CH_3$ ,  $O-C_6H_4Br$ ,  $-SCH_3$  and  $-NCS$ ,  $-NCO$ ,  $-NSO$  were discussed in Chapters 3 - 6. Such studies in aromatic molecules with large rotatable polar groups such as  $-CH_2CH_2CH_2Br$ ,  $-CH_2CH_2CH_2SH$  and  $-CH_2CH_2CH_2NH_2$  have not been reported in literature. It will be interesting to study the possibility of internal rotation in these molecules and to ascertain if the internal rotation occurs by the rotation of the whole group or by a part of it. The results of investigations on the absorption of microwaves in 1-phenyl propylbromide, 1-phenylpropylmercaptan and 1-phenylpropylamine in the liquid state are presented and discussed in this chapter.

#### 7.2 Results

The experimental values of dielectric permittivity  $\epsilon'$  and dielectric loss  $\epsilon''$  at different microwave frequencies and at different temperatures are given in Tables 7.1 - 7.3 which also includes the static dielectric permittivity  $\epsilon_0$  at different temperatures. Complex plane plots (Fig.7.1) of the dielectric loss  $\epsilon''$  and dielectric permittivity  $\epsilon'$  shows a symmetric distribution with a depressed centre unlike the asymmetric

Table 7.1

Observed and calculated values of dielectric permittivity and dielectric loss

1-Phenylpropyl bromide										
T°C	f = 1 MHz		f = 8.6 GHz				f = 18.5 GHz			
	$\epsilon_0$	$\epsilon'_{obs}$	$\epsilon'_{cal}$	$\epsilon''_{obs}$	$\epsilon''_{cal}$	$\epsilon'_{obs}$	$\epsilon'_{cal}$	$\epsilon''_{obs}$	$\epsilon''_{cal}$	
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	3.62	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	
f = 24.03 GHz										
f = 35.13 GHz										
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	

distribution in aliphatic ethers<sup>1,2</sup> and haloalkanes<sup>3,4</sup>. 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.

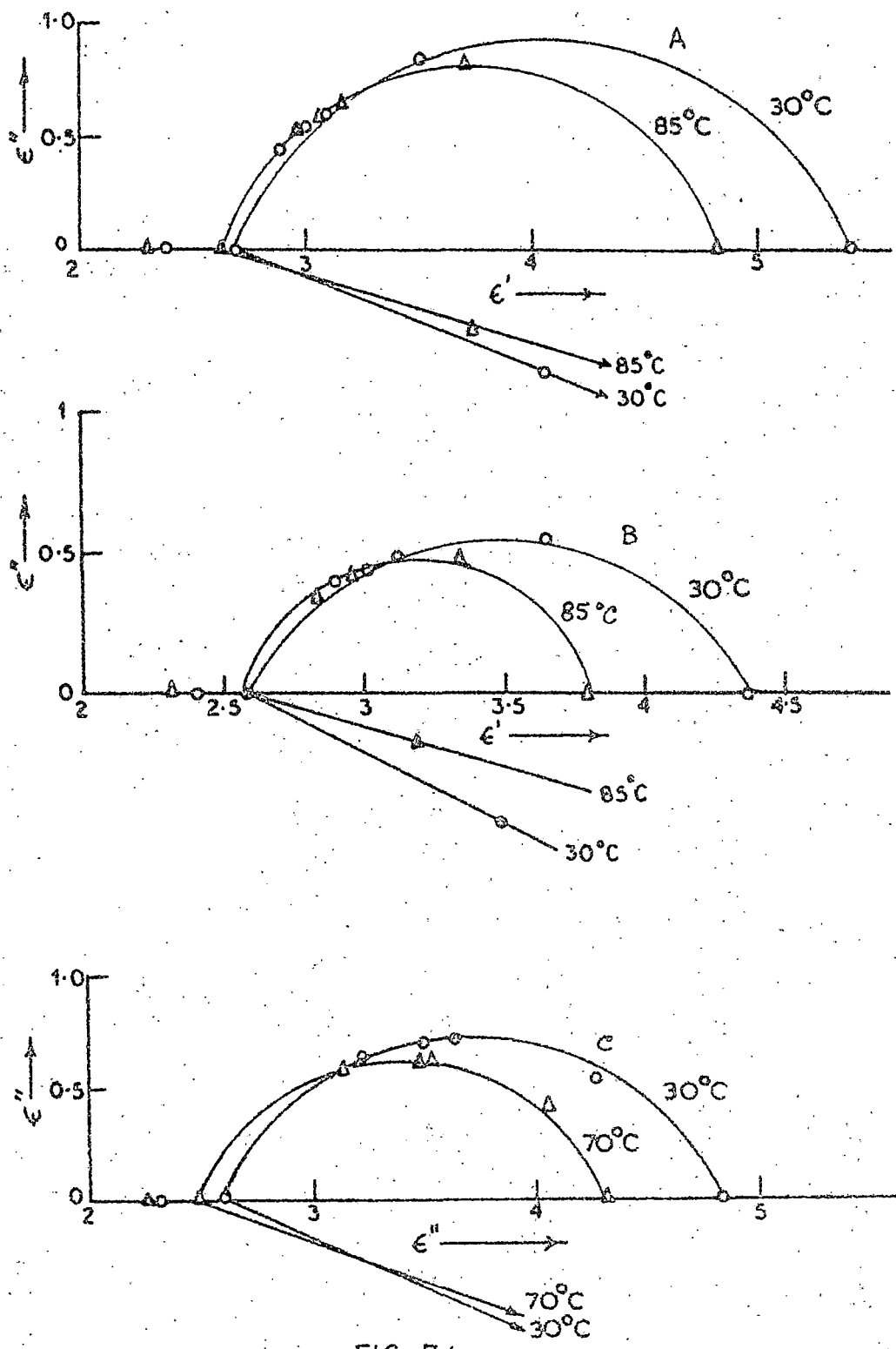


FIG. 7.1

- A. Cole-Cole arc plot of 1-phenylpropylbromide
- B. Cole-Cole arc plot of 1-phenylpropyl mercaptan
- C. Cole-Cole arc plot of 1-phenylpropylamine

Table 7.2

Observed and calculated values of dielectric permittivity and dielectric loss

1-phenylpropylmercaptan										
T°C	f = 1 MHz		f = 8.6 GHz				f = 18.5 GHz			
	$\epsilon_0$	$\epsilon'_{obs}$	$\epsilon'_{cal}$	$\epsilon''_{obs}$	$\epsilon''_{cal}$	$\epsilon'_{obs}$	$\epsilon'_{cal}$	$\epsilon''_{obs}$	$\epsilon''_{cal}$	
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	.43	.51	2.96	2.99	.42	.43	
f = 24.03 GHz										
f = 35.13 GHz										
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	

Attempts were then made to analyse the dielectric data in terms of two relaxation processes by the method of least square presented in Chapter 3. The calculations were carried out on the IBM 1130 computer. The values of  $\tau_1$   $\tau_2$   $C_1$   $\epsilon_\infty$   $\eta_D^2$  are given in Table 7.4. The calculated values of  $\epsilon'$  and  $\epsilon''$  with the values of  $\tau_1$   $\tau_2$   $C_1$  and  $\epsilon_\infty$  obtained from the least square analysis are included in Tables 7.1 - 7.3 for comparison.

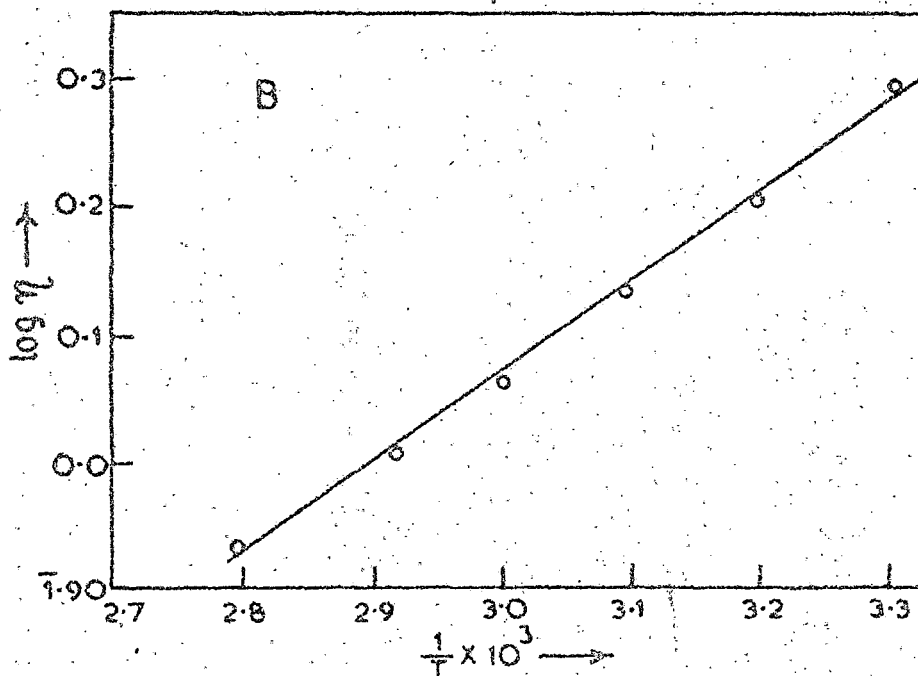
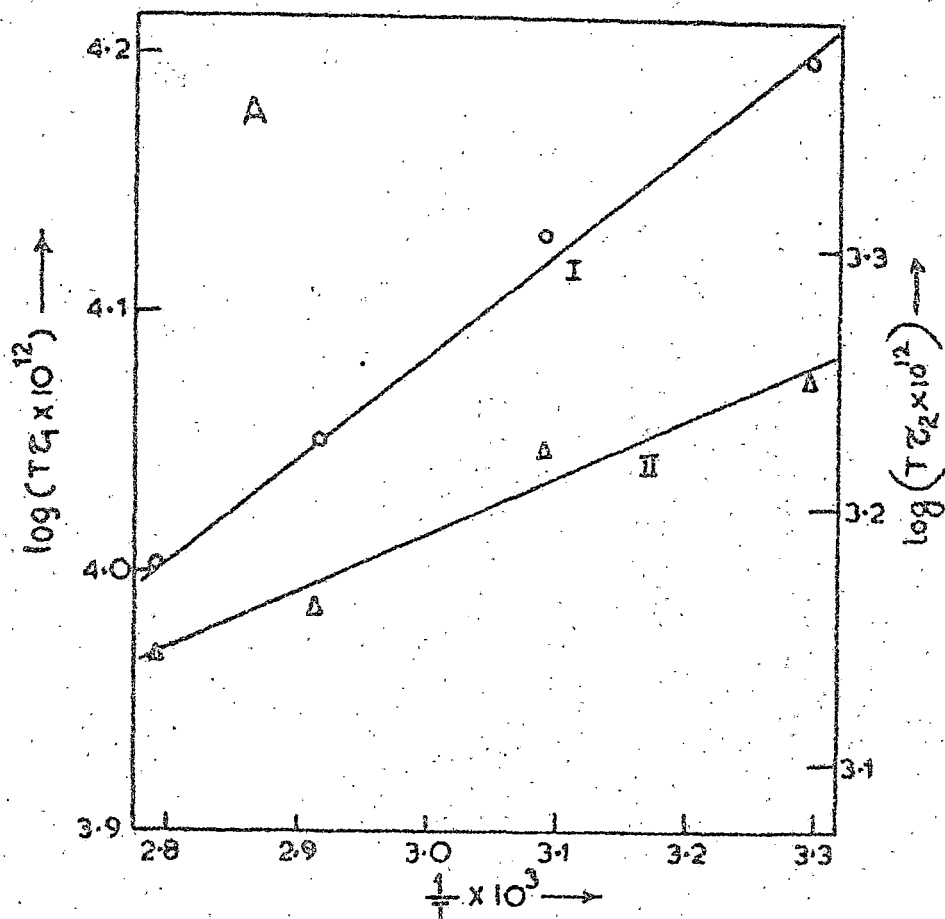


FIG. 7.2

- A. I. Plot of  $\log(\tau c_1)$  vs.  $1/T$  for 1-phenylpropylbromide  
 II. Plot of  $\log(\tau c_2)$  vs.  $1/T$  for 1-phenylpropylbromide  
 B. Plot of  $\log \eta$  vs.  $1/T$  for 1-phenylpropylbromide

The energy barriers for molecular reorientation  $\Delta Hc_1$  and group rotation  $\Delta Hc_2$  were determined from the plots of  $\log(\tau c_1)$  vs  $1/T$  and  $\log(\tau c_2)$  vs  $1/T$  (Figs. 7.2 - 7.4) respectively. The energy barrier for viscous flow was also determined from the plots of

Table 7.3

Observed and calculated values of dielectric permittivity and dielectric loss

1-phenylpropylamine										
T°C	f = 1 MHz		f = 8.6 GHz				f = 18.5 GHz			
	$\epsilon_0$	$\epsilon'_{obs}$	$\epsilon'_{cal}$	$\epsilon''_{obs}$	$\epsilon''_{cal}$	$\epsilon'_{obs}$	$\epsilon'_{cal}$	$\epsilon''_{obs}$	$\epsilon''_{cal}$	
30	4.83	4.27	4.00	.53	.68	3.63	3.63	.71	.68	
50	4.57	4.15	3.88	.48	.61	3.53	3.53	.62	.61	
70	4.32	4.05	3.88	.42	.54	3.52	3.56	.62	.59	
f = 24.03 GHz										
f = 35.13 GHz										
30	4.83	3.48	3.56	.68	.70	3.20	3.36	.68	.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	

$\log \eta$  vs  $1/T$  (Figs. 7.2 - 7.4). The values of dipole moment  $\mu_D$ , density (d), viscosity ( $\eta$ ) and the distribution parameter ( $\alpha$ ) are given in Table 7.5. The values of  $\Delta Hc_1$ ,  $\Delta Hc_2$  and  $\Delta H\eta$  are given in Table 7.6.

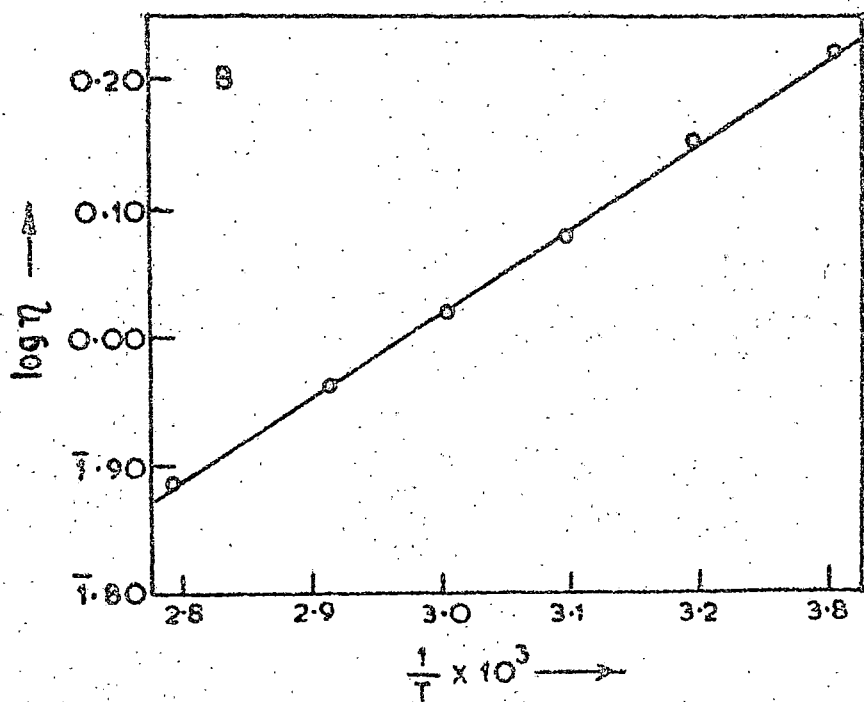
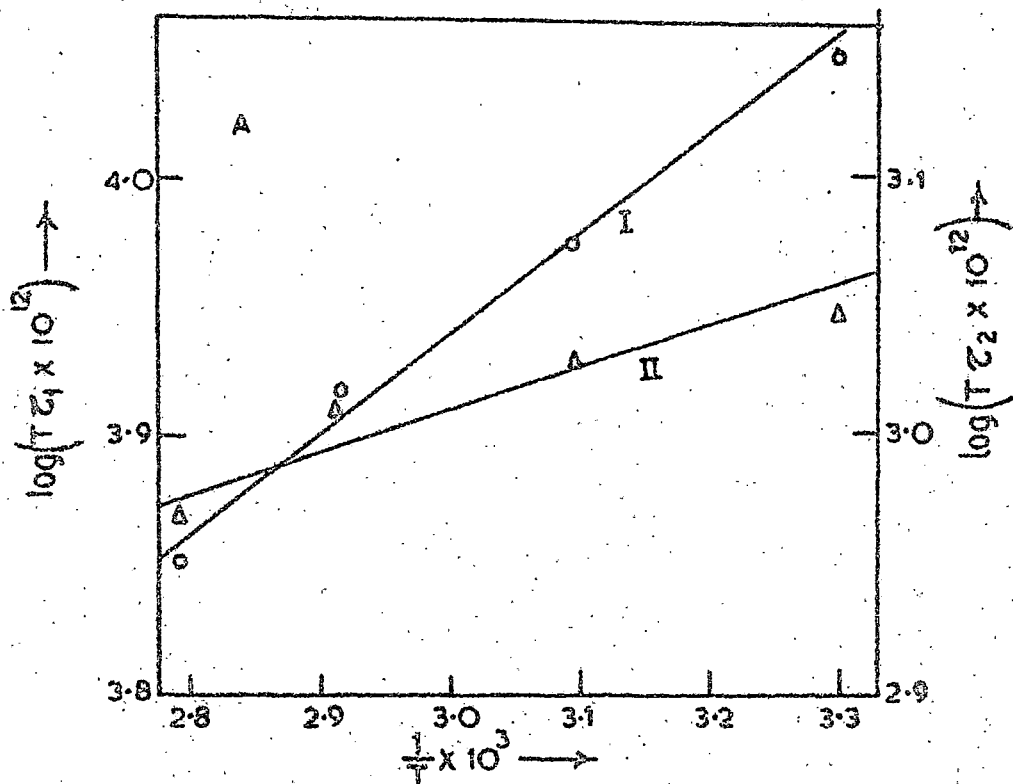


FIG. 7-3

- A. I. Plot of  $\log(\tau_1)$  vs.  $1/T$  for 1-phenylpropyl mercaptan  
 II. Plot of  $\log(\tau_2)$  vs.  $1/T$  for 1-phenylpropyl mercaptan  
 B. Plot of  $\log \eta$  vs.  $1/T$  for 1-phenylpropyl mercaptan

### 7.3 Discussion

It can be seen from Table 7.4 that the shorter relaxation time in the case of 1-phenylpropylbromide at 30°C is 5.8 p.sec which is a little larger than the CH<sub>2</sub>Cl group relaxation time of 4.9 p.sec at 30°C in the liquid benzylchloride<sup>5</sup> and compares well with the CH<sub>2</sub>Br relaxation time of 6.3 p.sec in benzylbromide<sup>6</sup> in the liquid state. So it is concluded that the shorter relaxation time in 1-phenylpropylbromide is due to rotation of the CH<sub>2</sub>Br end group. Similarly the shorter relaxation time of 3.7 p.sec at 30°C, compares well with the CH<sub>2</sub>SH group relaxation time of 3.35 p.sec at 30°C in benzylthiol<sup>7</sup> both in the liquid state is attributed to rotation of the CH<sub>2</sub>SH end group in 1-phenylpropylmercaptan. From similar consideration the shorter relaxation time of about 9 p.sec at 30°C (Table 7.4), compares well with the CH<sub>2</sub>NH<sub>2</sub> group relaxation time of 2-3 p.sec in benzylamine<sup>8</sup> in dilute benzene solution and is accounted for by the rotation of CH<sub>2</sub>NH<sub>2</sub> end group in 1-phenylpropylamine.

The larger relaxation times of 35.5 and 30.3 p.sec at 30°C for 1-phenylpropyl mercaptan (  $\eta = 1.67 \text{ c.p.}$  ) and 1-phenylpropyl amino (  $\eta = 1.70 \text{ c.p.}$  ) respectively, have a similar order of magnitude and may be due to molecular end-over-end rotation. The larger relaxation time of 51.3 p.sec at 30°C in 1-phenylpropyl bromide (  $\eta = 1.97 \text{ c.p.}$  ) which is



Table 7.4

Values of  $\epsilon_{\infty}$ ,  $n_D^2$ ,  $\tau_1$ ,  $\tau_2$  and  $C_1$

$T^{\circ}C$	$n_D^2$	$\epsilon_{\infty}$	$C_1$	$\tau_1 \times 10^{12}$ Sec	$\tau_2 \times 10^{12}$ Sec.
<u>1-phenylpropylbromide</u>					
30	2.37	2.68	0.80	51.35	5.77
50	2.34	2.69	0.79	41.07	5.21
70	2.32	2.65	0.78	32.81	4.27
85	2.30	2.62	0.76	28.56	3.89
<u>1-phenylpropylmercaptan</u>					
30	2.39	2.53	0.65	35.61	3.66
50	2.36	2.56	0.66	29.27	3.32
70	2.33	2.54	0.69	24.81	3.07
85	2.31	2.54	0.73	19.87	2.62
<u>1-phenylpropylamine</u>					
30	2.31	2.58	0.48	30.32	3.34
50	2.28	2.53	0.47	27.00	3.00
70	2.26	2.43	0.44	19.50	2.83

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, similar to the case in  $\alpha, \omega$  dihaloalkanes<sup>3,4</sup>, but unlike the case of alkylcyanides<sup>9</sup>, alkylketones<sup>10</sup> where distribution of relaxation times have been reported.

Table 7.5

Values of  $d, \eta, \mu$  and  $\alpha$ .

$T^{\circ}C$	$\alpha$	$\eta$ c.p.	$d$ gm/cc	$\mu$ Debye
<u>1-phenylpropylbromide</u>				
30	.25	1.97	1.31	1.53
50	.24	1.35	1.29	1.53
70	.24	1.01	1.26	1.55
85	.20	0.85	1.25	1.57
<u>1-phenylpropylmercaptan</u>				
30	.31	1.67	1.00	1.29
50	.29	1.19	0.98	1.28
70	.23	0.92	0.97	1.26
85	.19	0.77	0.96	1.28
<u>1-phenylpropylamine</u>				
30	.27	1.70	1.02	1.34
50	.27	1.18	1.00	1.34
70	.23	0.89	0.99	1.34

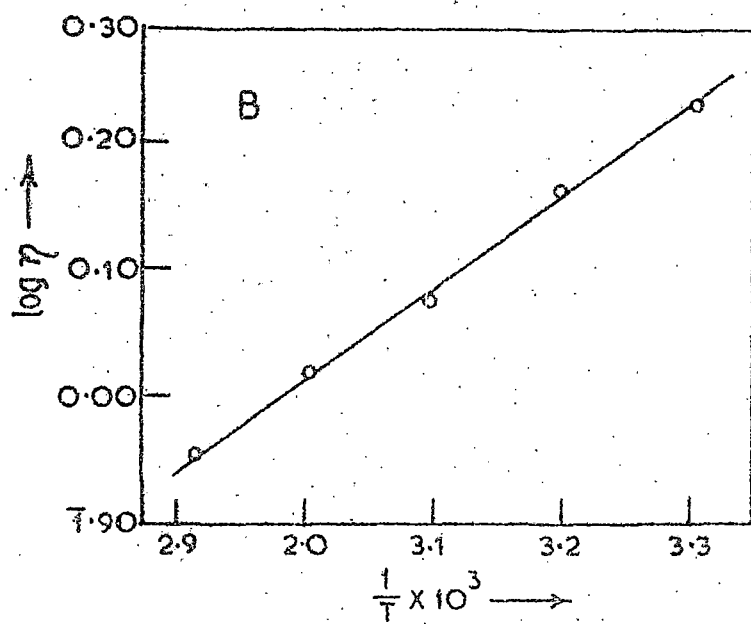
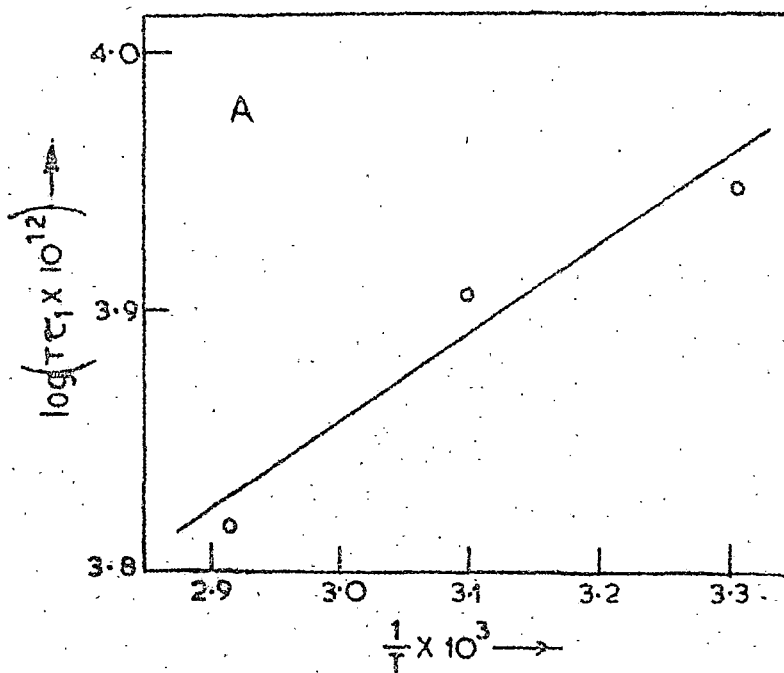


FIG 7-4

- A. Plot of  $\log(\tau c_1)$  vs.  $1/T$  for 1-phenylpropylamine  
 B. Plot of  $\log \eta$  vs.  $1/T$  for 1-phenylpropylamine

It may be seen from Table 7.4 that both the molecular and end group rotation in all the liquids decrease with increase temperature as is usually observed in polar liquids.

#### Weight factors

From the value of  $C_1$  in Table 7.4, it is seen that molecular reorientation is the major relaxation process in 1-phenylpropylbromide ( $C_1 \approx 0.8$ ) which is similar to that ( $C_1 \approx 0.8$ ) in benzyl bromide<sup>6</sup> in the liquid state. In 1-phenylpropyl mercaptan the molecular reorientation is the major relaxation process ( $C_1 = 0.65$ ), while in benzylthiol, the group rotation ( $C_2 = 0.73$ ) is the major relaxation process. Similarly in 1-phenylpropylamine, contributions from molecular and end group rotation are almost equal, whereas group relaxation is the major contributing factor ( $C_2 = 0.85$ ) in benzylamine<sup>6</sup> in the liquid state. The lowering of the contribution from the end-group rotation in 1-phenylpropylmercaptan and 1-phenylpropylamine, compared to benzylthiol and benzylamine respectively 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, the moment components responsible for group rotation in them becomes less.

#### Dipole moment

From Table 7.5, it can be seen that the dipole moment in 1-phenylpropylbromide 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 more than one rotational isomer (Fig.7.5).

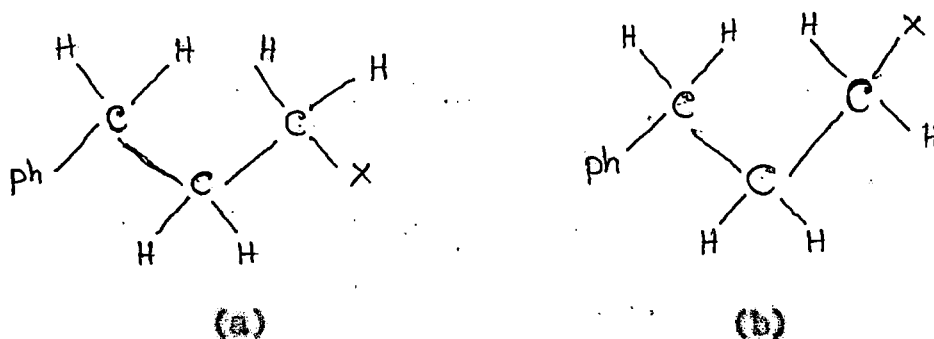


Fig.7.5

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

The proportion of isomers with higher dipole moment increases at higher temperatures.

Table 7.6

Values of  $\Delta H_{\eta}$   $\Delta H_{\epsilon_1}$  and  $\Delta H_{\epsilon_2}$

	$\Delta H_{\eta}$ Kcal/ mole	$\Delta H_{\epsilon_1}$ Kcal/ mole	$\Delta H_{\epsilon_2}$ Kcal/ mole
1-phenylpropylbromide	3.34	1.74	1.06
1-phenylpropylmercaptan	3.03	1.38	0.95
1-phenylpropylamine	3.34	1.79	0.12

In the case of 1-phenylpropylmercaptan the dipole moment is 1.29 D which compares with benzylthiol ( $\mu = 1.23\text{D}$ ). In this

liquid the dipole moment decreases with increase of temperature showing that isomers with less moment are abundant at higher temperature.

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

Potential barriers for molecular, intramolecular and viscous flow (  $\Delta H_c$ ,  $\Delta H_c$  and  $\Delta H_r$  )

The potential barrier for molecular reorientation in the three liquids are of similar magnitude ( 1.8 Kcal/mole) and is about half as much as the energy barrier for viscous flow in them. The barrier for end group rotation  $\Delta H_c$  in 1-phenyl propylbromide and 1-phenylpropylmercaptan is about 1 Kcal/mole. The potential barrier for internal rotation in 1-phenylpropyl 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 molecule.

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

References

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## STUDIES ON ALIPHATIC MOLECULES

The Chapters 3 - 7 were devoted with the results of dielectric absorption of microwaves in aromatic molecules with various rotatable polar groups attached to them and their interpretations in terms of molecular and intramolecular reorientations and other structural parameters of the molecules.

In the following three chapters (Chapters 8 - 10) the results of investigations obtained in the case of aliphatic molecules will be presented and interpretation of the results will be given.