

CHAPTER 8

DIELECTRIC RELAXATION IN SUBSTITUTED PROPANES IN THE LIQUID STATE

8.1 Introduction

From studies of dielectric relaxation in some rotational isomeric molecules¹⁻⁴, it was reported that the distribution parameter α in the case of 1,2-propanedithiol¹ increase with increase in temperature, while it decreases in 1,2-dihaloethanes^{3,4}, 1,2-dihalo propane³ and 1,2-ethanedithiol¹. The increase on the distribution parameter α 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 have been made in the case of 1,3-propanedithiol and 1,2,3-tribromopropane with a view to studying how the distribution parameter α in these liquids behave with change of temperature and how it could be interpreted in terms of conformers, if any.

8.2 Results

The values of ϵ' and ϵ'' at different microwave frequencies together with ϵ_0 at different temperature are presented in Tables 8.1 and 8.2. The dielectric data were fitted in Cole-Cole arcs (Fig. 8.1). The high frequency dielectric

permittivity ϵ_∞ and the distribution parameter α were obtained from the arc plots in the usual manner.

Table 8.1

Observed values of dielectric permittivity and dielectric loss

1,3-propanedithiol							
T°C	f = 1MHz	f = 8.6 GHz		f = 9.5 GHz		f = 18.5 GHz	
	ϵ_0	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
30	8.11	7.06	1.09	7.00	1.26	6.27	1.41
50	7.64	6.72	0.97	6.63	1.00	6.10	1.20
70	7.16	6.32	0.79	6.24	0.80	5.82	0.95
f = 24.0 GHz f = 35.3 GHz							
30	8.11	5.96	1.40	5.56	1.40		
50	7.64	5.54	1.20	5.46	1.29		
70	7.16	5.64	0.96	5.36	1.03		

The effective relaxation times τ was determined from the relation $v/u = (\omega\tau)^{1-\alpha}$ where v is the distance on the Cole-Cole plot between ϵ_0 and the experimental point and u is the distance between the point and ϵ_∞ . The heats of activation for dielectric relaxation ΔH_τ and viscous flow ΔH_η were obtained from the plots of $\log(\tau\omega)$ vs $1/T$ and $\log \eta$ vs $1/T$ (Figs. 8.2 and 8.3) respectively. The dipole moment μ of each molecule was calculated from the static dielectric permittivity

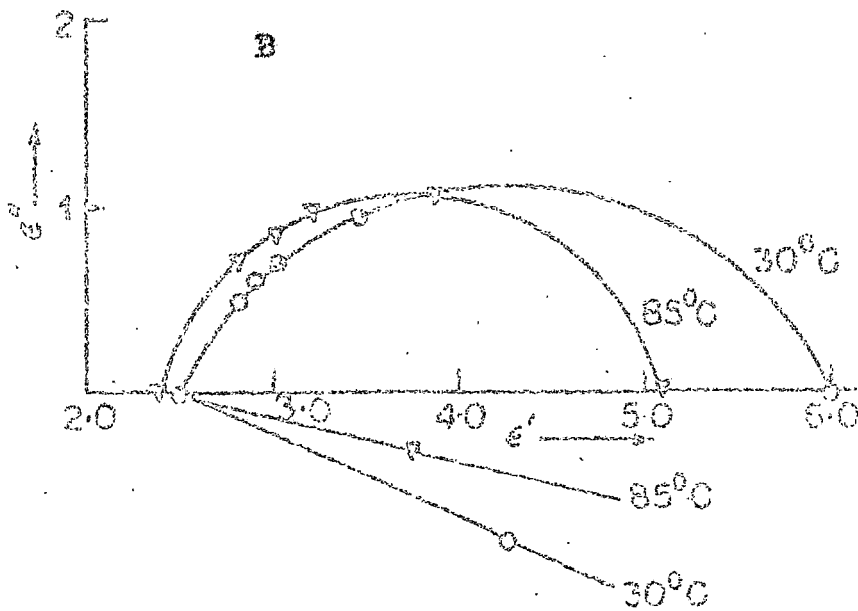
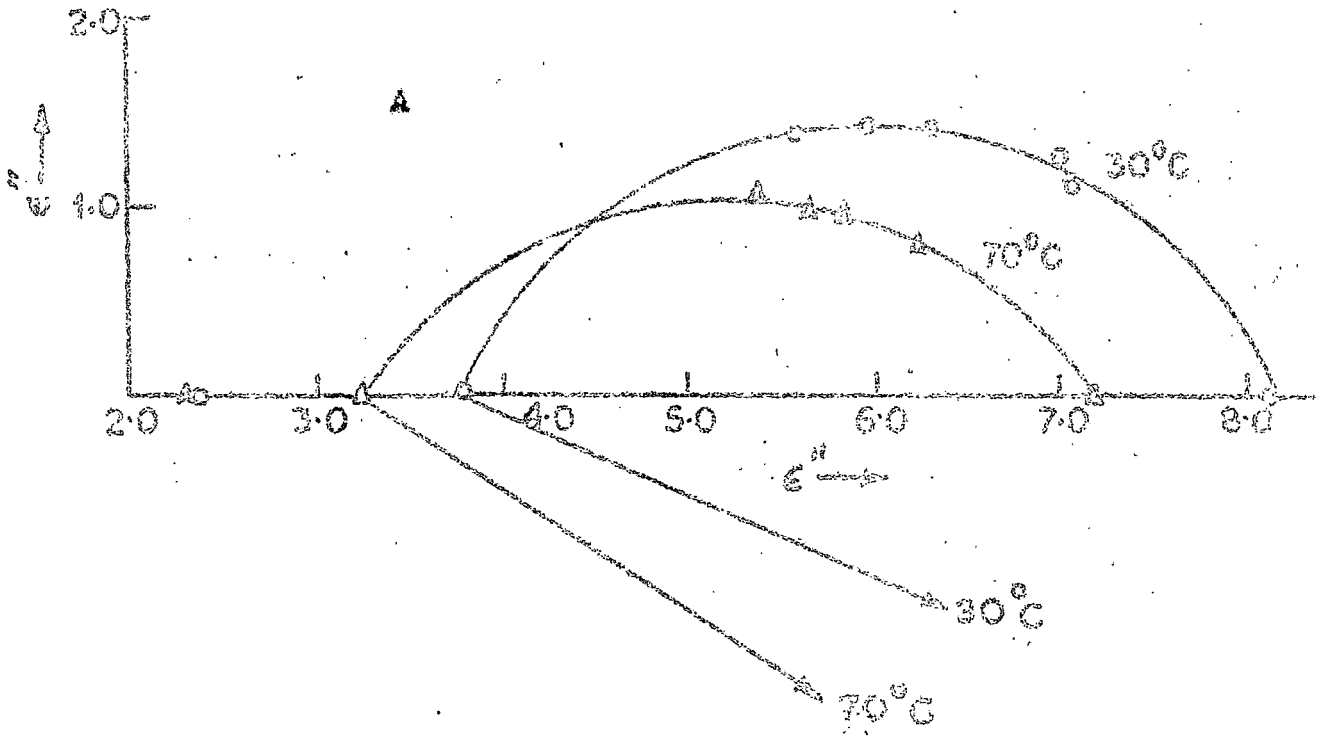


Fig.8.1

A. Cole-Cole are plot of 1,3-propanedithiol

B. Cole-Cole are plot of 1,2,3-tribromopropane

density and high frequency dielectric permittivity ϵ_{∞} using Onsager's equation. The values of τ_D^2 , ϵ_{∞} , τ and α are given in Table 8.3 and the values ΔH_D , ΔH_C , μ_D density (d) and viscosity (η) are included in Table 8.4.

Table 8.2

Observed values of dielectric permittivity and dielectric loss

1,2,3-tribromopropane						
	f = 1 MHz		f = 8.6 GHz		f = 18.5 GHz	
T°C	ϵ_0	ϵ'	ϵ''	ϵ'	ϵ''	
30	6.00	3.48	0.95	3.04	0.68	
50	5.66	3.56	1.03	3.08	0.79	
70	5.30	3.72	1.10	3.13	0.90	
85	5.10	3.88	1.04	3.23	0.94	
		f = 24.0 GHz		f = 35.3 GHz		
30	6.00	2.92	0.58	2.81	0.49	
50	5.66	2.93	0.71	2.77	0.56	
70	5.30	2.95	0.78	2.76	0.60	
85	5.10	3.04	0.84	2.83	0.69	

8.3 Discussion

1,3-propanedithiol

It can be seen from Table 8.3 that the value of relaxation time τ in 1,3-propanedithiol is about 6.3 p.sec at 30°C which

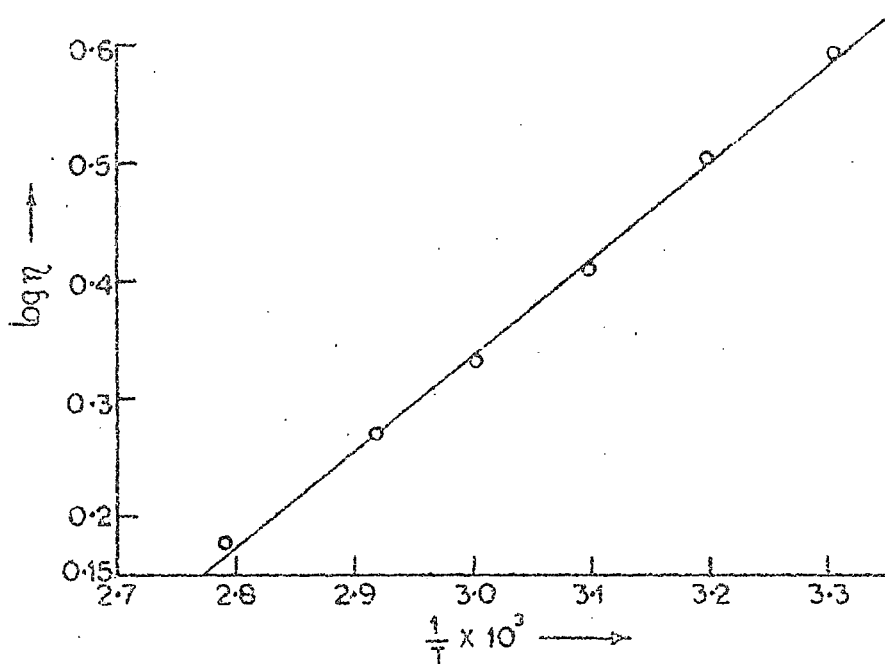
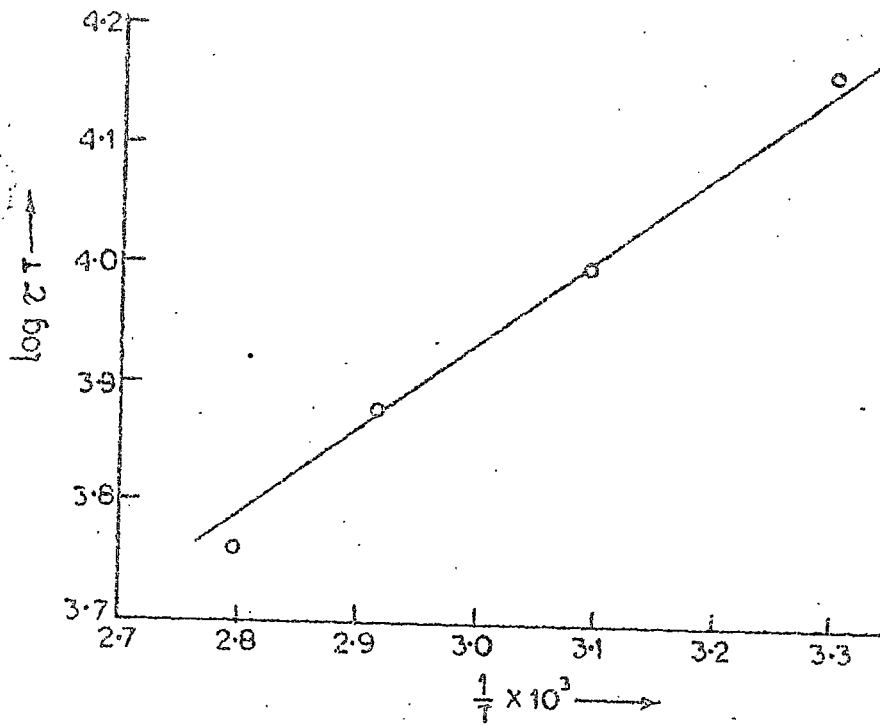


Fig. 8,2

Plot of $\log (\tau_c)$ vs. $1/T$ of 1,2,3-tribromopropane

Plot of $\log \eta$ vs. $1/T$ of 1,2,3-tribromopropane

compares well with the value of 6.2 p. sec at 20°C in 1,2-propanedithiol¹. This shows that the molecules are of similar sizes.

The heat of activation for viscous flow ΔH_{η} in the 1,3-propanedithiol is about 2.5 Kcal/mole which compares well with corresponding value of $\Delta H_{\eta} = 2.3$ Kcal/mole in 1,2-propanedithiol. But the heat of activation for dielectric relaxation

$\Delta H_{\tau} = 2.2$ 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 α in 1,3-propanedithiol 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^{2,3} and propanes^{1,4}. It is also seen from Table 8.4 that the apparent dipole moment μ of 1,3-propanedithiol in the liquid state increases 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-propanedithiol⁵ as in the case of 1,3-dihalopropanes^{6,7} and the relative proportion of the three forms⁷ 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 for different conformers (Fig.8.4) 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

Table 8.3

Values of n_D^2 ϵ_∞ α and τ

TC	n_D^2	ϵ_∞	$\tau \times 10^{12}$ Sec	α
1,3-propanedithiol				
30	2.97	3.76	6.3	0.26
50	2.94	3.42	4.8	0.31
70	2.90	3.24	3.6	0.39
1,2,3-tribromopropane				
30	2.49	2.49	48.2	0.23
50	2.46	2.46	30.9	0.22
70	2.43	2.43	22.0	0.17
85	2.41	2.41	16.1	0.15

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 α at higher temperatures.

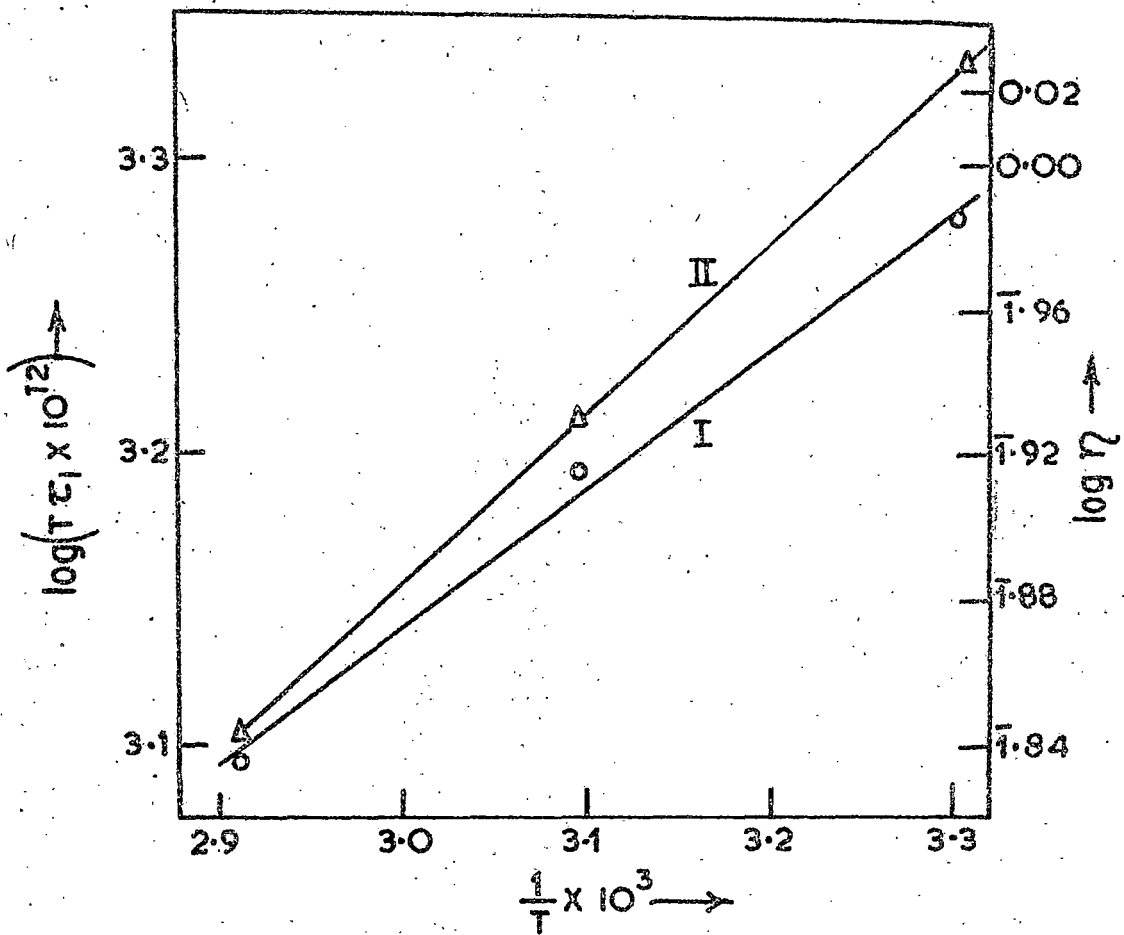


FIG. 8.3

- I. Plot of $\log(\tau_1)$ vs. $1/T$ for propanedithiol
 II. Plot of $\log \eta$ vs. $1/T$ for propanedithiol

1,2,3-tribromopropane

Since the viscosity η of this liquid (3.9 c.P at 30°C) is much larger than that of 1,2-dibromopropane⁴ (1.26 c.P at 20°C) it would be convenient to compare the reduced relaxation time (τ/η) of the two liquids. The reduced relaxation time (τ/η) in the present liquid is 12 p.sec c.P⁻¹ at 30°C which is a little larger than that of 10 p.sec c.P⁻¹ 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 $\Delta H_{\tau} = 3.3$ Kcal/mole in 1,2,3-tribromopropane is much larger than the

$\Delta H_{\tau} = 1.5$ 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 $\Delta H_{\eta} = 3.65$ Kcal/mole in 1,2,3-tribromopropane is larger than the activation energy of dielectric relaxation $\Delta H_{\tau} = 3.3$ Kcal/mole as is generally observed.

The distribution parameter α 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 8.4) is found to be temperature

independent.

From spectroscopic studies⁸ it has been reported that of the nine possible conformers in 1,2,3-trichloropropane, only two conformers (Fig.8.5) 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-tribromopropane⁹ also. The

Table 8.4

Values of density (d), viscosity (η) μ
 ΔH_c and ΔH_η

$T^\circ C$	d gm/cc	η c.P	μ_D	ΔH_c Kcal/mole	ΔH_η Kcal/mole
<u>1,3-propanedithiol</u>					
30	1.08	1.07	1.26		
50	1.05	0.85	1.37	2.2	2.5
70	1.03	0.70	1.44		
30	2.39	3.92	1.56		
50	2.35	2.59	1.57	3.3	3.7
70	2.31	1.86	1.57		
85	2.29	1.50	1.57		

dipole moments of these conformers arise mainly from the C-Br bond moment attached to the three carbon atoms, the CH_2 moment

being negligible. From Fig. 3.5, 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 moment being in opposite direction. Only one C-Br bond moment (≈ 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 dipole moment in the liquid. Moreover, since the conformers are of similar sizes, the distribution parameter does not increase with increase of temperature.

Finally it should be noted that the large difference in the values of n_D^2 and ϵ_∞ in 1,3-propanedithiol, indicates the presence of a 'Poley type' absorption in the high frequency region. Such absorption is absent in 1,2,3-tribromo propane in the liquid state, since the n_D^2 and ϵ_∞ values in this case are almost the same.

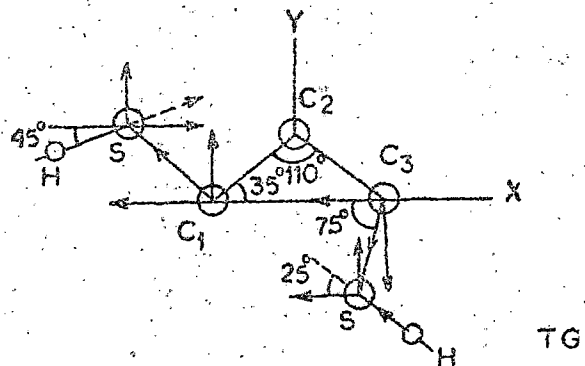
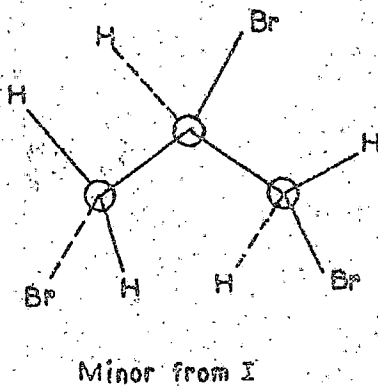
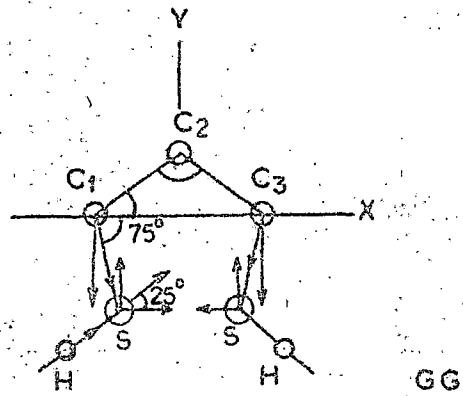
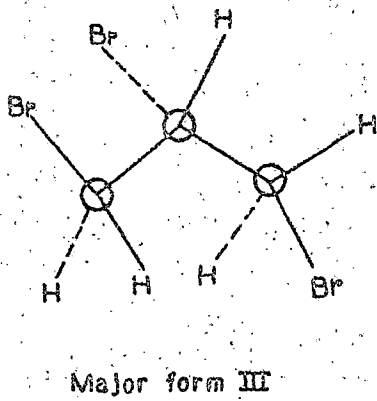
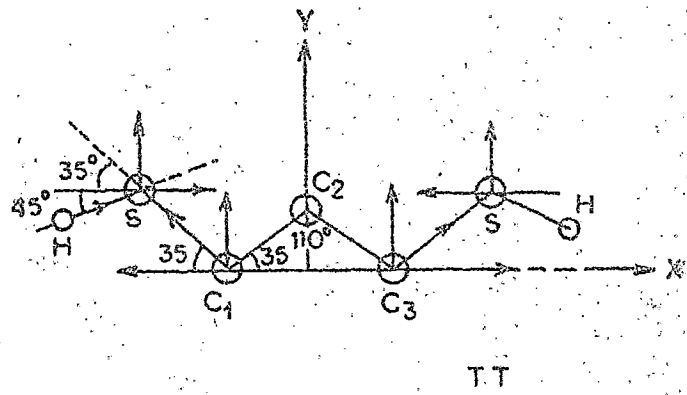


FIG. 8.5

FIG. 8.4

Fig.8.4 - Three conformers in 1,3-propanedithiol
 Fig.8.5 - Two conformers in 1,2,3-tribromopropane

Approximate calculations of dipole moment :

Approximate calculation of the dipole moments of the three conformers of 1,3-propanedithiol from the bond moments and bond angles, the CH_2 moment being small is neglected.

$$\mu_1 = \mu_{\text{C-S}} = 0.9 \text{ D}, \mu_2 = \mu_{\text{H-S}} = 0.7 \text{ D} \quad \angle \text{CCC} = 110^\circ \text{ (Minkin et al., }^{10}) \text{ and } \angle \text{CSH} = 100^\circ \text{ (Shaw et al., }^{11}).$$

TT conformer

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

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

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

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

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

GG conformer

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

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

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

y component of μ_{H-S} attached to two sulfur atoms

$$= \mu_2 \sin 25^\circ + \mu_2 \sin 25^\circ = 2\mu_2 \sin 25^\circ$$

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

IG conformer

x component of μ_{C-S} attached to the two carbon atoms

$$= -\mu_1 \cos 35^\circ - \mu_1 \cos 75^\circ = -0.97 \cdot D.$$

x component of μ_{H-S} attached to the two sulfur atoms

$$= \mu_2 \cos 45^\circ - \mu_2 \cos 25^\circ = -0.20 \cdot D$$

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

y component of μ_{C-S} attached to the two carbon atoms

$$= \mu_1 \sin 35^\circ - \mu_1 \sin 75^\circ = -0.39 \cdot D$$

y component of μ_{H-S} attached to the two sulfur atoms

$$= \mu_2 \sin 45^\circ + \mu_2 \sin 25^\circ = 1.12 \cdot D.$$

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

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

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