

CHAPTER 9

INTERNAL ROTATION IN α, ω DICYANOALKANES IN BENZENE SOLUTION

9.1 Introduction

Studies on the dielectric absorption of microwaves in a number of alkyl halides^{1,2} 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 α, ω dihaloalkanes^{3,4} with the two dipoles attached to the two terminals, showed that the results could 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 orientation processes in flexible chain molecules, a programme was undertaken to extend similar studies in the case of a number of α, ω dicyanoalkanes. In the present chapter dielectric absorption of 1,2-dicyanoethane, 1,3-dicyanopropane and 1,4-dicyanobutane at different microwave frequencies have been made and the results and the discussion are presented in this chapter.

9.2 Results

The experimental values of dielectric permittivity ϵ' and dielectric loss ϵ'' at different microwave frequencies and at different temperatures together with the values of static dielectric permittivity ϵ_0 at different temperatures are given in Tables 9.1 - 9.3. Complex plane plots (Fig.9.1) of the

Table 9.1

Observed and calculated values of dielectric permittivity and dielectric loss in benzene solution

Concentrations are in mole fraction

1,2-dicyanoethane (.098)										
	f = 1 MHz		f = 8.6 GHz				f = 18.3 GHz			
T°C	ϵ_0	ϵ'_{obs}	ϵ'_{cal}	ϵ''_{obs}	ϵ''_{cal}	ϵ'_{obs}	ϵ'_{cal}	ϵ''_{obs}	ϵ''_{cal}	
30	4.78	4.05	4.04	1.06	1.03	3.22	3.28	1.00	1.04	
45	4.68	4.04	4.04	0.98	0.97	3.25	3.31	1.02	1.03	
60	4.55	4.02	4.02	0.90	0.89	3.23	3.33	1.00	1.01	
	f = 24.05 GHz					f = 36.2 GHz				
30	4.78	3.03	3.05	0.96	0.95	2.82	2.78	0.80	0.77	
45	4.68	3.12	3.07	0.98	0.96	2.81	2.80	0.79	0.79	
60	4.55	3.15	3.09	0.98	0.95	2.78	2.80	0.79	0.81	

dielectric permittivity ϵ' and dielectric loss ϵ'' show a symmetric distribution with a depressed centre in each of the dicyanocalkanes at all temperatures, unlike the case in

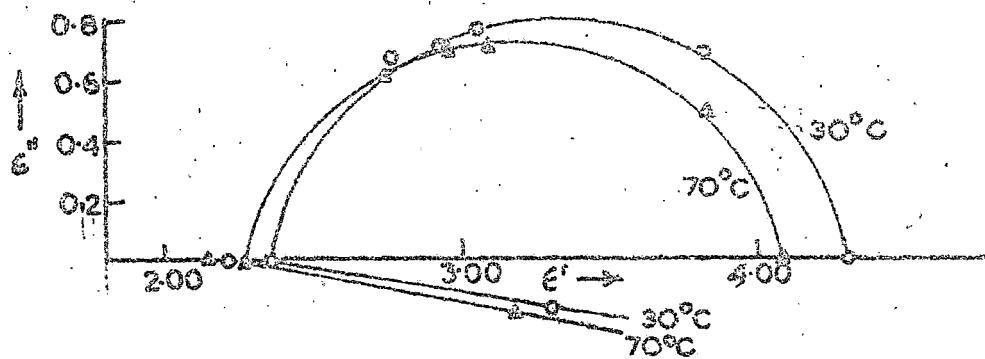
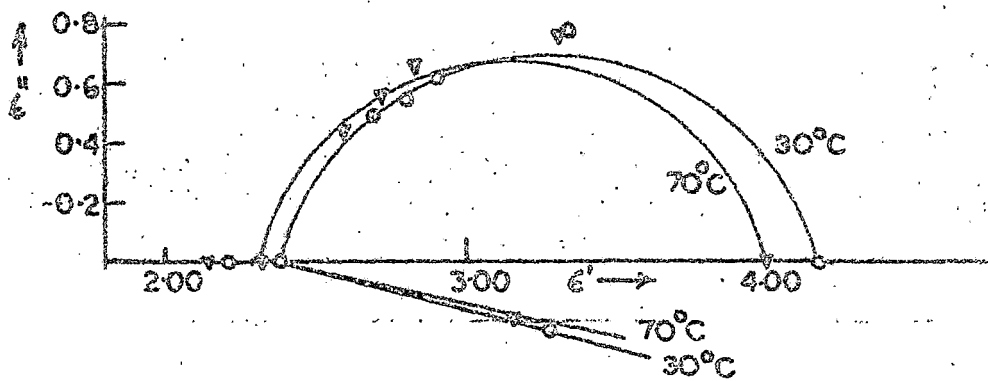
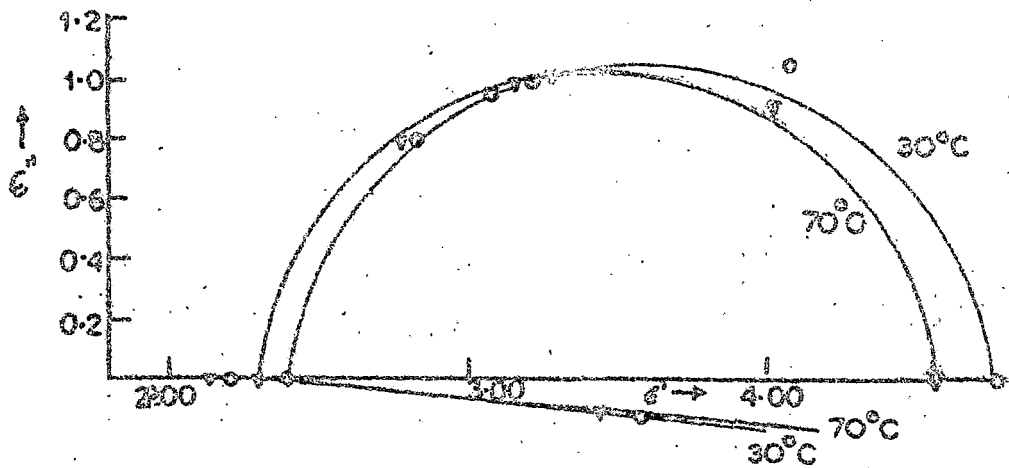


Fig. 9.1

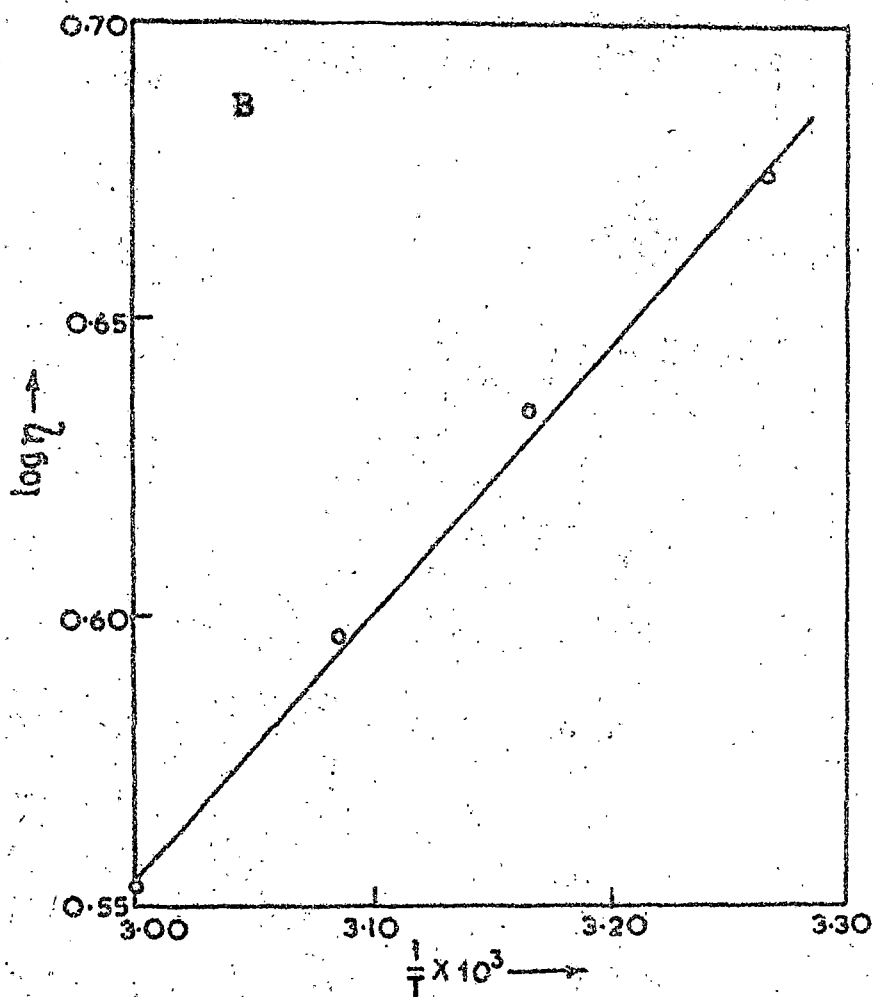
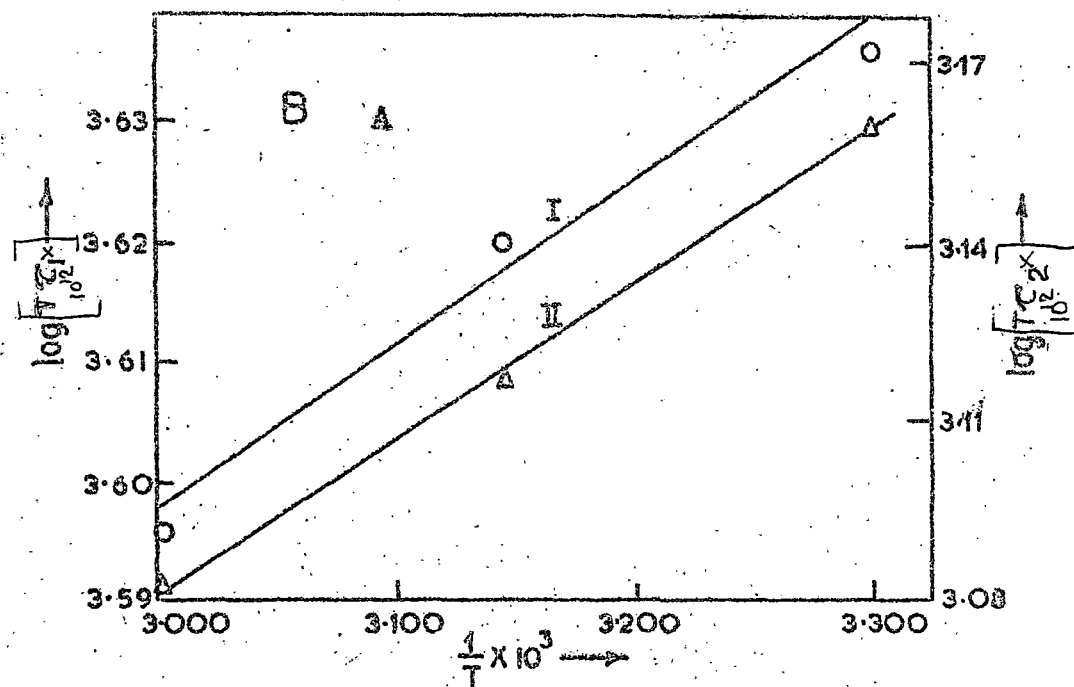
n-alkylhalides², α, ω dihaloalkanes^{3,4} etc. where such plots showed asymmetric distribution. The distribution parameter obtained from the arc plots in the present dicyanoalkanes, were found appreciable at all temperatures, which is an indication of the presence of more than one relaxation processes in them. Attempts are then made to analyse the dielectric data in terms of two relaxation processes by the least square method described in Chapter 3.

Table 2.2

Observed and calculated values of dielectric permittivity and dielectric loss in benzene solution

Concentrations are in mole fraction

1,3-dicyanopropane (.025)										
T°C	f = 1 MHz		f = 2.6 GHz		f = 18.3 GHz		f = 24.05 GHz		f = 36.2 GHz	
	ϵ_0	ϵ'_{obs}	ϵ'_{cal}	ϵ''_{obs}	ϵ''_{cal}	ϵ'_{obs}	ϵ'_{cal}	ϵ''_{obs}	ϵ''_{cal}	
30	4.30	3.81	3.66	.70	.77	3.05	3.16	.78	.80	
45	4.20	3.80	3.65	.61	.72	3.08	3.16	.76	.76	
60	4.08	3.82	3.61	.50	.66	3.08	3.16	.72	.72	
30	4.30	3.92	2.98	.78	.76	2.76	2.74	.68	.66	
45	4.20	2.94	3.00	.72	.72	2.75	2.77	.63	.64	
60	4.08	2.95	3.01	.70	.70	2.74	2.79	.62	.65	



1,2 DICYANOETHANE

Fig. 9.2 A. I. Plot of $\log(\tau c_1)$ vs. $1/T$
 II. Plot of $\log(\tau c_2)$ vs. $1/T$
 B. Plot of $\log \eta$ vs. $1/T$

The calculations for the determination of τ_1 , τ_2 , C_1 were carried out on IBM computer 1130. The calculated values of ϵ' and ϵ'' are also included in Tables 9.1 - 9.3. The values of n_D^2 , ϵ_∞ , α and η at different temperatures are given in Table 9.4 and the values of τ_1 , τ_2 , α and C_1 at different temperatures are given in Table 9.5. The barriers to molecular reorientation ΔH_{τ_1} and to internal rotation ΔH_{τ_2} were obtained from the straight line plots of $\log(\tau C_1)$ vs $1/T$ and $\log(\tau C_2)$ vs $1/T$ (Fig. 9.2 - 9.4) respectively. The energy barrier for viscous flow was obtained from the plot of $\log \eta$ vs $1/T$ (Figs. 9.2 - 9.4). The dipole moment μ was calculated from the equation⁵

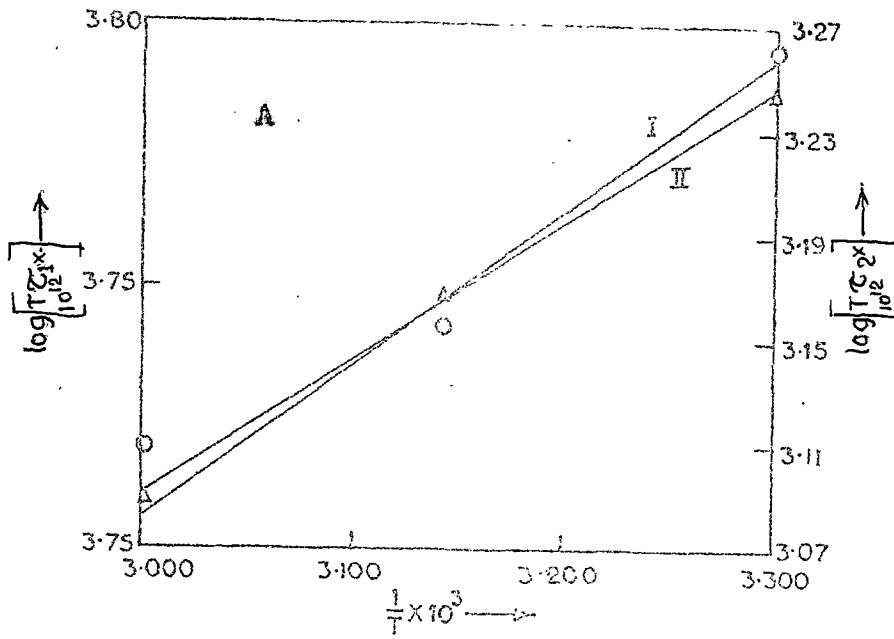
$$\mu^2 = \frac{9KT}{4\pi N} \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2}$$

where N is the number of solute molecules per ml. of the solution. The values of ΔH_{τ_1} , ΔH_{τ_2} , ΔH_η are included in Table 9.6 and the value of μ_D included in Table 9.5.

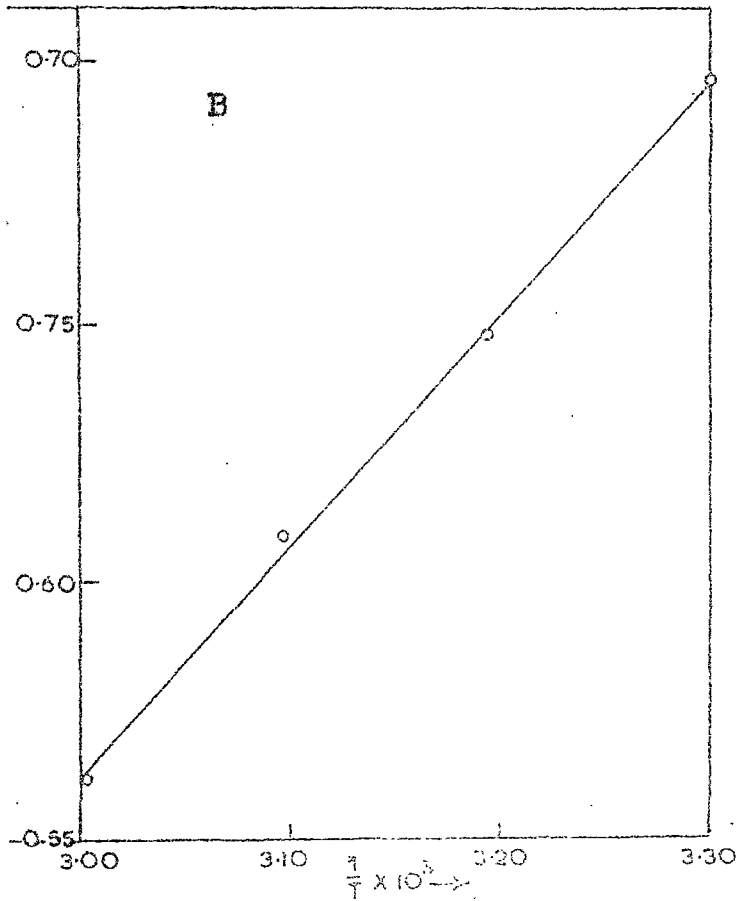
9.3 Discussion

Molecular and Intramolecular relaxation times ()

It can be seen from Table 9.5 that the larger relaxation time τ_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



1,3 DICYANOPROPANE



1,3 DICYANOPROPANE

Fig.9.3 A. I. Plot of $\log(Tc_2)$ vs. $1/T$
 II. Plot of $\log(T)$ vs. $1/T$
 B. Plot of \log vs. $1/T$

molecular relaxation time τ_1 of 22.6 p.sec at 30°C in 1,4-dicyanobutane is comparable with the molecular relaxation time of 23 p.sec at 25°C in 1,4-dibromobutane³.

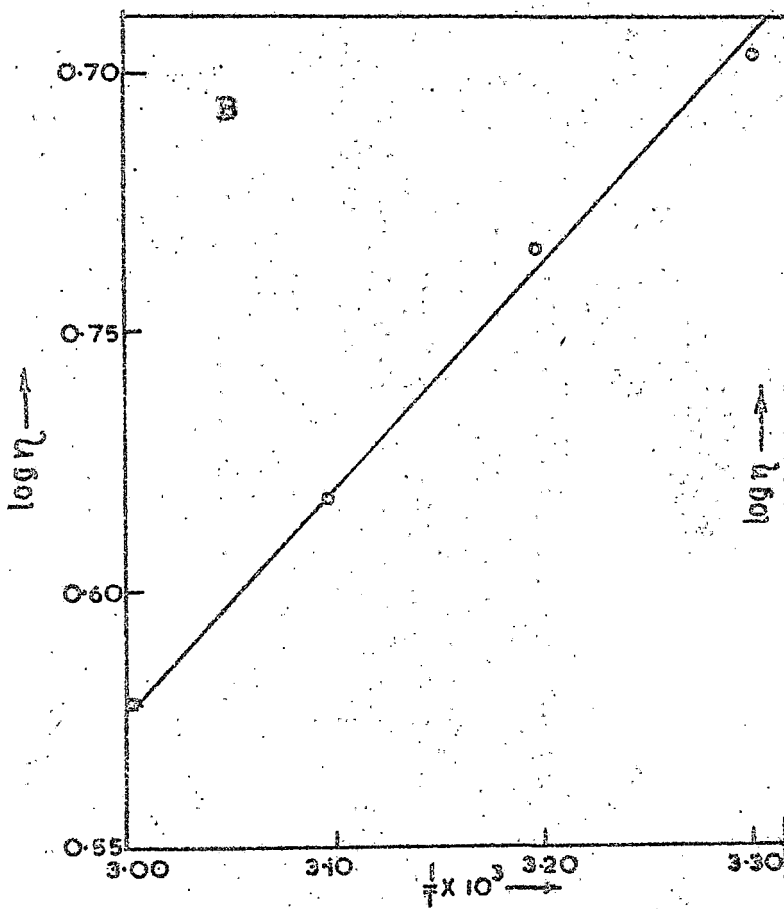
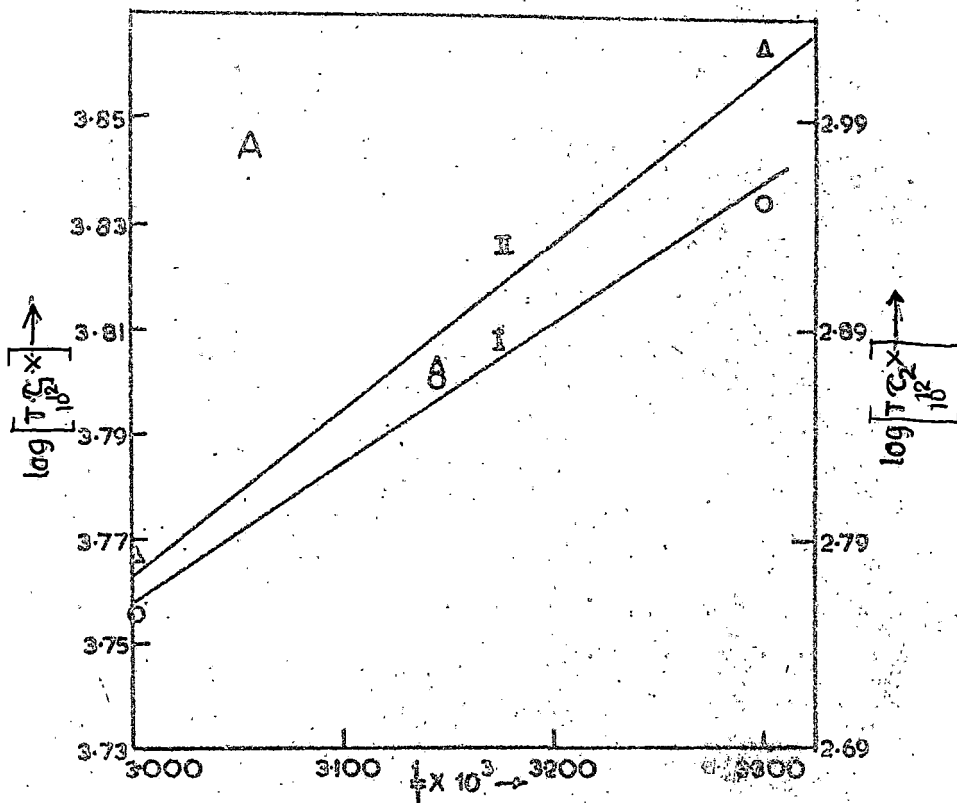
Table 9.3

Observed and calculated values of dielectric permittivity and dielectric loss in benzene solution

Concentrations are in mole fraction

1,4-dicyanobutane (.073)										
T°C	f = 1 MHz		f = 8.6 GHz				f = 18.3 GHz			
	ϵ_0	ϵ'_{obs}	ϵ'_{cal}	ϵ''_{obs}	ϵ''_{cal}	ϵ'_{obs}	ϵ'_{cal}	ϵ''_{obs}	ϵ''_{cal}	
30	4.20	3.34	3.34	.78	.76	2.91	2.92	.62	.61	
45	4.10	3.31	3.32	.76	.77	2.85	2.85	.60	.61	
60	4.02	3.32	3.33	.76	.76	2.84	2.83	.64	.64	
f = 24.0 GHz										
f = 36.2 GHz										
30	4.20	2.75	2.75	.52	.55	2.70	2.68	.49	.47	
45	4.10	2.75	2.75	.52	.52	2.65	2.64	.42	.41	
60	4.02	2.73	2.72	.55	.55	2.60	2.60	.43	.42	

The shorter relaxation time τ_2 in all the dicyanoalkanes lying in the range 4 - 5.8 p.sec at 30°C compare well with the relaxation time 6.5 p.sec at 30°C of the acetonitril (CH₃CN) molecule in benzene solution reported by Eloranta and Kadaba⁶ and is most probably due to the rotation of the -CH₂CN group



1,4 DICYANOBUTANE

Fig. 9.4 A. I. Plot of $\log(TC_1)$ vs. $1/T$
 II. Plot of $\log(TC_2)$ vs. $1/T$
 B. Plot of $\log \eta$ vs. $1/T$

in each of the dicyanoalkanes. It may be noted that both the molecular and intramolecular relaxation times decrease with increase of temperature of the solution as are generally observed in polar liquids.

Distribution parameter

The distribution parameter α in Table 9.5 in 1,2- and 1,4-dicyanoalkanes, decreases as usual with increase of temperature but in the case of 1,3-dicyanopropane, the α -value increases with the increase of temperature. Similar increase in the value of α in 1,3-propanedithiol at higher temperatures reported by Roy et al.⁷ 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 and consequently the larger value of the distribution parameter α than the other two forms. So the same explanation may be applicable for the increase in α -value at higher temperature in the 1,3-dicyanopropane, which is also has three conformers in the liquid state⁸⁻¹⁰. Further it can be seen that at any temperature, the α -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.

Table 9.4

Values of n_D^2 , ϵ_∞ , density (d) and viscosity (η)

T°C	n_D^2	ϵ_∞	d gm/cc	η c.P
<u>1,2-dicyanoethane</u>				
30	2.20	2.40	.878	0.47
45	2.18	2.36	.867	0.42
60	2.15	2.30	.850	0.36
<u>1,3-dicyanopropane</u>				
30	2.21	2.35	.830	0.50
45	2.17	2.35	.865	0.42
60	2.15	2.27	.850	0.36
<u>1,4-dicyanobutane</u>				
30	2.21	2.33	.874	0.50
45	2.19	2.33	.864	0.44
60	2.15	2.32	.850	0.38

The molecular orientation is found to be (Table 9.5) the major relaxation process in 1,2- and 1,4-dicyanoalkanes, whereas in 1,3-dicyanopropane the contribution from the internal rotation is only a little less than that of the molecular reorientation.

The barrier to molecular reorientation (ΔH_{c_1}) in 1,2-dicyanoethane and 1,3-dicyanopropane in benzene solution is about 0.64 and 1.34 Kcal/mole respectively and which is half

the value of the barrier to internal rotation of (1.2 and 2.42 Kcal/mole respectively) the $-\text{CH}_2\text{CN}$ group of the respective molecules. In the case of 1,4-dicyanobutane the barrier to internal rotation ($\Delta H_{e_2} = 3.69$ Kcal/mole) is about three times as large as that due to the molecular reorientation. It is also noted that the barrier to internal rotation increase as the number of C-C' rotational axes increase.

Table 9.5

Values of τ_1 τ_2 α C_1 and μ

$T^\circ\text{C}$	α	$\tau_1 \times 10^{12}$ Sec	$\tau_2 \times 10^{12}$ Sec	C_1	μ Debye
<u>1,2-dicyanoethane</u>					
30	.070	14.3	4.8	.80	3.50
45	.065	13.1	4.1	.80	3.57
60	.060	11.8	3.6	.79	3.65
<u>1,3-dicyanopropane</u>					
30	.10	20.6	5.2	.51	3.66
45	.11	17.0	4.6	.60	3.68
60	.13	15.8	3.7	.57	3.79
<u>1,4-dicyanobutane</u>					
30	.16	22.6	3.6	.79	3.86
45	.14	19.8	2.3	.84	3.88
60	.13	17.1	1.8	.85	3.93

Dipole moment

In all the three dicyanoalkanes in benzene solution the apparent dipole moment (Table 9.5) 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. This difference in behaviour 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.

Table 9.6

Values of ΔH_D , ΔH_{C_1} , ΔH_{C_2}

	ΔH_D Kcal/mole	ΔH_{C_1} Kcal/mole	ΔH_{C_2} Kcal/mole
1,2-dicyanoethane	2.09	0.64	1.20
1,3-dicyanopropane	2.06	1.34	2.42
1,4-dicyanobutane	2.02	1.24	3.09

Spectroscopic studies have shown that three conformers GG, TG and TT (Fig. 9.5) are present in 1,3-dicyanopropane¹⁰ and the former two forms are in comparable proportion while the TT form present in minute proportion. From the bond moments and bond angle calculations, it is found that the dipole moment of GG (≈ 3.8 D) and TG (≈ 4.0 D) are nearly the same and that of TT form (≈ 4.5 D) is appreciably higher and is more extended than the other two forms.

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, and an increase in the TT form at higher temperature causes an increase in the value of the distribution parameter α at higher temperature as mentioned earlier.

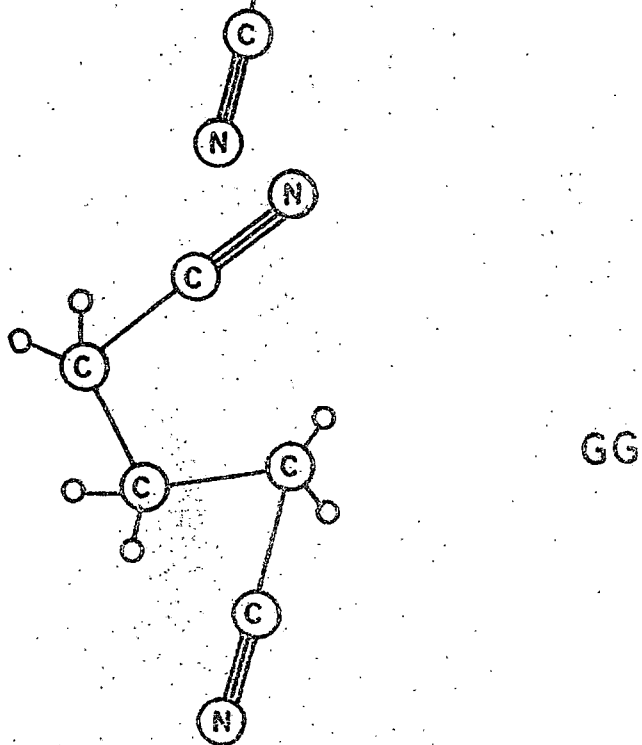
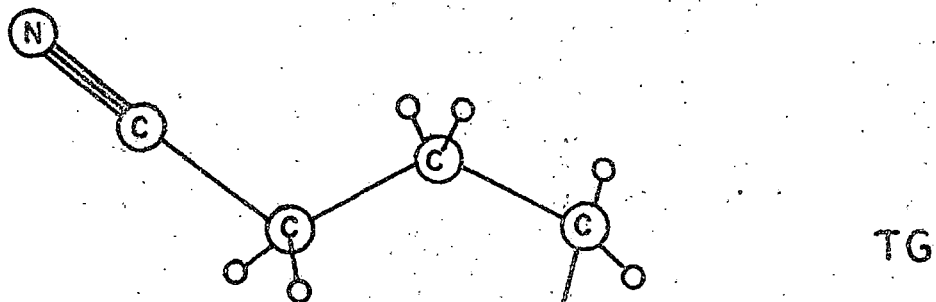
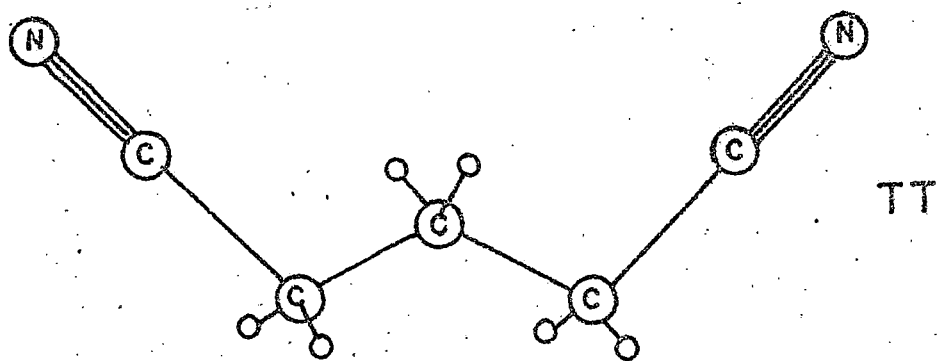


FIG. 9.5

Different conformers of 1,3-dicyanopropane

Approximate calculations of dipole moments of the three conformers of 1,3-dicyanopropane from bond angles and bond moments - $\mu_1 = \mu_{\text{C-N}} = 3.9 \text{ D}$

TT conformer

$$\mu^2 = 2\mu_1^2 = 2\mu_1^2 \sin 20^\circ$$

$$\mu = 4.48 \text{ D} \approx 4.5 \text{ D}$$

TC conformer

$$\mu_x = -\mu_1 \cos 35^\circ = \mu_1 \cos 60^\circ \cos 75^\circ + \mu_1 \sin 60^\circ \sin 20^\circ$$

$$\mu_y = \mu_1 \sin 35^\circ = \mu_1 \cos 60^\circ \sin 75^\circ$$

$$\mu_z = \mu_1 \sin 60^\circ \cos 20^\circ$$

$$\mu = 4.05 \text{ D} \approx 4.0 \text{ D}$$

CC conformer

$$\mu_x = \mu_1 \cos 60^\circ \cos 35^\circ = \mu_1 \cos 60^\circ \cos 35^\circ$$

$$= \mu_1 \cos 60^\circ \sin 75^\circ + \mu_1 \cos 60^\circ \sin 75^\circ$$

$$= 2\mu_1 \cos 60^\circ \sin 75^\circ$$

$$\mu = 3.77 \text{ D} \approx 3.80 \text{ D}$$

References

1. Higasi K., Bergmann K. and Smyth C.P., J. Phys. Chem., 64, 880 (1960).
2. Vaughan W.E., Lovell W.S. and Smyth C.P., J. Chem. Phys., 36, 753 (1962).
3. Garg S.K., Lovell W.S., Clementt C.J. and Smyth C.P., J. Phys. Chem., 77, 292 (1973).
4. Suresh Chandra, Jadav R.A. and Prakash J., J. Phys. Soc. Japan, 33, 175 (1972).
5. Fay S.P. and Crossley J., Canad. J. Chem., 50, 3031 (1972).
6. Eloranta J.K. and Kadaba P.K., Mat. Sc. Engg., 2, 203 (1971).
7. Roy S.K., Sengupta K. and Roy S.B., Bull. Chem. Soc. Japan, 49, 663 (1976).
8. Matsubara I., J. Chem. Phys., 35, 373 (1961).
9. Yamadera R. and Krinns, Spectrochim. Acta, A24, 1677 (1968).
10. Torbjornsrud J., Acta. Chem. Scand., 26, 3799 (1972).