

CHAPTER 6

INTERNAL ROTATION OF MULTIBONDED GROUPS ATTACHED TO PHENYL RING AND THEIR POSSIBLE GEOMETRICAL STRUCTURES

6.1 Introduction

In the previous Chapters 3 - 5 the intramolecular rotation of the polar groups such as $-SH$, $-CH_2SH$, $-O-CH_3$, $-OC_2H_5$ and $-SCH_3$ attached to phenyl ring were discussed. But the possibility of rotation of the multibonded groups like $-NCO$, $-NCS$, $-NSO$ etc. attached to the aromatic molecules has not been reported so far. As a knowledge of the flexibility of rotation of these groups will throw much light on the geometrical structure of the molecules, the results on the dielectric absorption of microwaves at different frequencies and at different temperatures in the case of phenylisocyanate, phenylisothiocyanate and N-sulfinylaniline in benzene solution, have been presented and discussed in this chapter.

6.2 Results

The experimental values of ϵ' and ϵ'' at different microwave frequencies at different temperatures together with static dielectric constant ϵ_0 at different temperatures are given in Tables 6.1 - 6.3. Cole-Cole arc plots (Fig.6.1) drawn with these data showed appreciable distribution in all the cases at all temperatures. Attempts were therefore made to analyse the

dielectric data in terms of two relaxation processes making use of Bergmann's¹ equations

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

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

From which was derived a simplified linear equation

$$Sx - \beta y - 1 = 0$$

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

The eqn.(3) for several microwave frequencies was solved by the method of least square² described in Chapter 3. The calculation was carried out on IBM computer 1130.

The calculated values of ϵ' and ϵ'' are also included in Tables 6.1 - 6.3 for comparison with observed values. The values of τ_1 , τ_2 , c_1 , α , τ_D^2 and ϵ_{∞} are given in Table 6.4. Activation energies for dielectric relaxation ΔH_c and for viscous flow ΔH_{η} were obtained from the plots of $\log(\tau c)$ vs $1/T$ and $\log \eta$ vs $1/T$ (Figs. 6.2 - 6.4) respectively. The dipole moment calculated from the relation³

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

where N is the number of the solute molecules per ml. of the solution. The values of ΔH_{c_1} , ΔH_{c_2} , ΔH_{η} , μ_D and η are

included in Table 6.5.

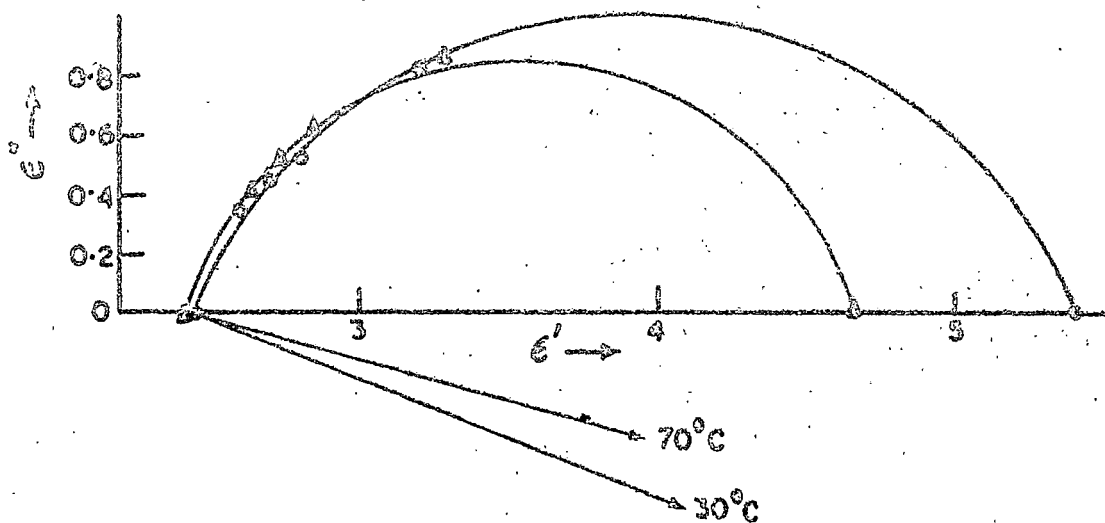
Table 6.1

Observed and calculated values of dielectric permittivity and dielectric loss

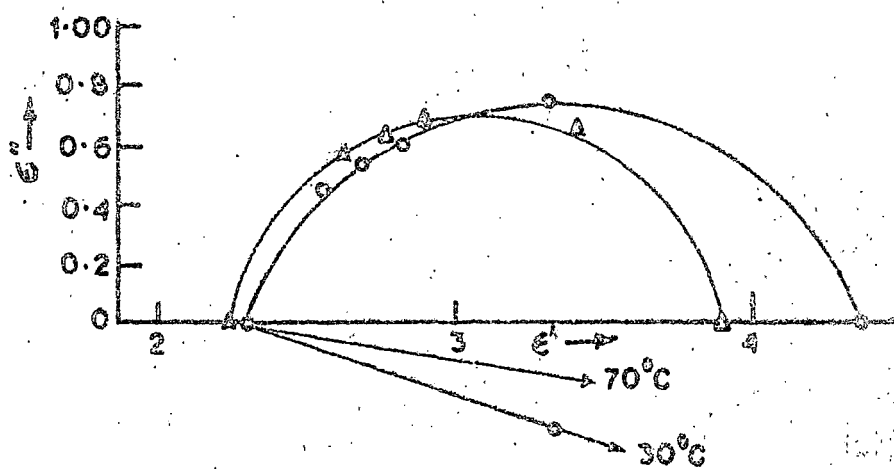
Phenylisothiocyanate									
T°C	f = 1 MHz		f = 8.6 GHz			f = 18.3 GHz			
	ϵ_0	ϵ'_{obs}	ϵ'_{cal}	ϵ''_{obs}	ϵ''_{cal}	ϵ'_{obs}	ϵ'_{cal}	ϵ''_{obs}	ϵ''_{cal}
30	5.40	3.20	3.06	.82	.83	2.81	2.82	.53	.54
50	5.05	3.25	3.13	.84	.87	2.82	2.83	.56	.56
70	4.70	3.29	3.22	.85	.88	2.85	2.84	.60	.59
Phenylisothiocyanate									
T°C	f = 24.4 GHz					f = 35.14 GHz			
	ϵ_0	ϵ'_{obs}	ϵ'_{cal}	ϵ''_{obs}	ϵ''_{cal}	ϵ'_{obs}	ϵ'_{cal}	ϵ''_{obs}	ϵ''_{cal}
30	5.40	2.70	2.75	.44	.47	2.60	2.67	.34	.40
50	5.05	2.70	2.76	.47	.49	2.63	2.68	.38	.41
70	4.70	2.74	2.77	.50	.51	2.64	2.68	.40	.43

6.3 Discussion

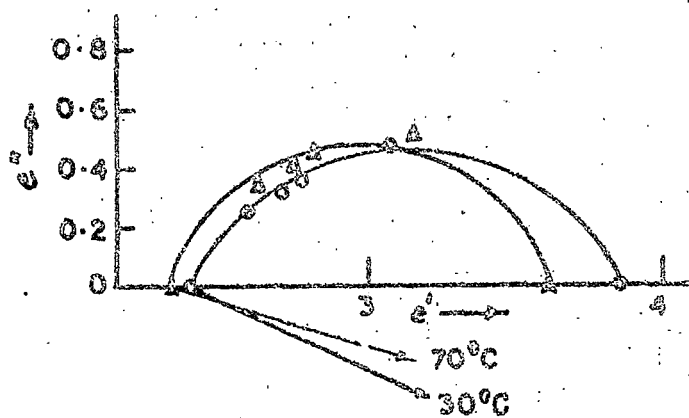
The fact that the dielectric data could be analysed in terms of two relaxation mechanisms in PhNCO, PhNCS and PhNSO shows that the shorter relaxation time τ_2 must be due to the rotation of the -NCO, -NCS and -NSO group rotation around the



COLE-COLE ARC PLOT OF PHENYL ISOTHIOCYANATE IN BENZENE SOLⁿ



COLE-COLE ARC PLOT OF PHENYLISOCYANATE IN BENZENE SOLⁿ



COLE-COLE ARC PLOT OF N-SULFINYLANILINE IN BENZENE SOLⁿ

Fig. 6.1

Table 6.2

Observed and calculated values of dielectric permittivity and dielectric loss

Phenylisocyanate									
T°C	f = 1 MHz		f = 26 GHz			f = 18.3 GHz			
	ϵ_0	ϵ'_{obs}	ϵ'_{cal}	ϵ''_{obs}	ϵ''_{cal}	ϵ'_{obs}	ϵ'_{cal}	ϵ''_{obs}	ϵ''_{cal}
30	4.36	3.32	3.20	.74	.77	2.83	2.86	.61	.61
50	4.03	3.39	3.33	.68	.72	2.87	2.89	.64	.64
70	3.92	3.42	3.38	.64	.66	2.90	2.93	.67	.67
f = 24.4 GHz									
f = 35.14 GHz									
30	4.36	2.69	2.74	.54	.56	2.55	2.60	.45	.49
50	4.03	2.73	2.76	.53	.60	2.59	2.61	.51	.53
70	3.92	2.77	2.78	.63	.63	2.63	2.62	.55	.55

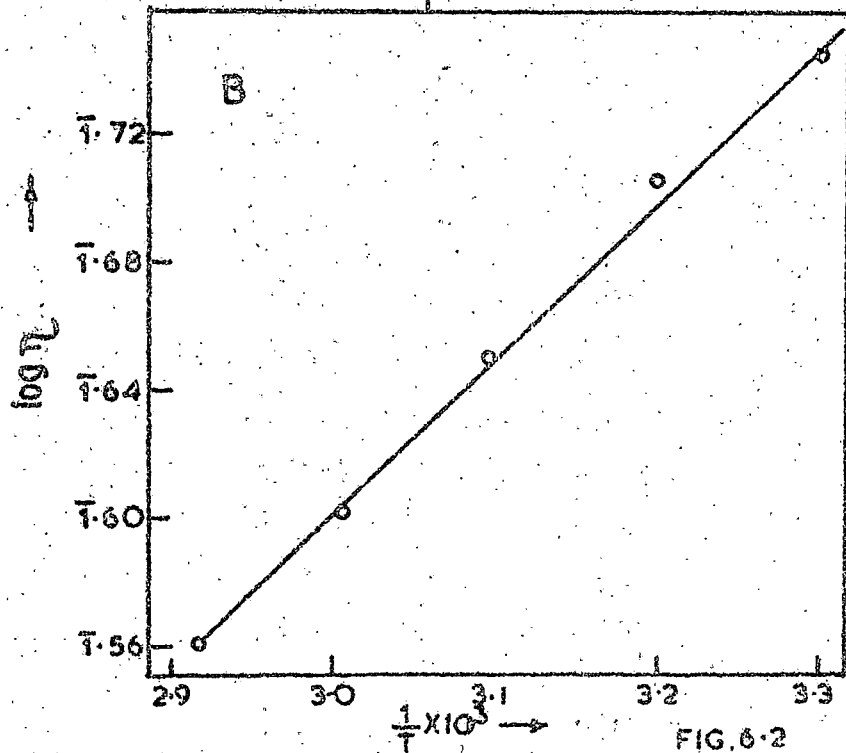
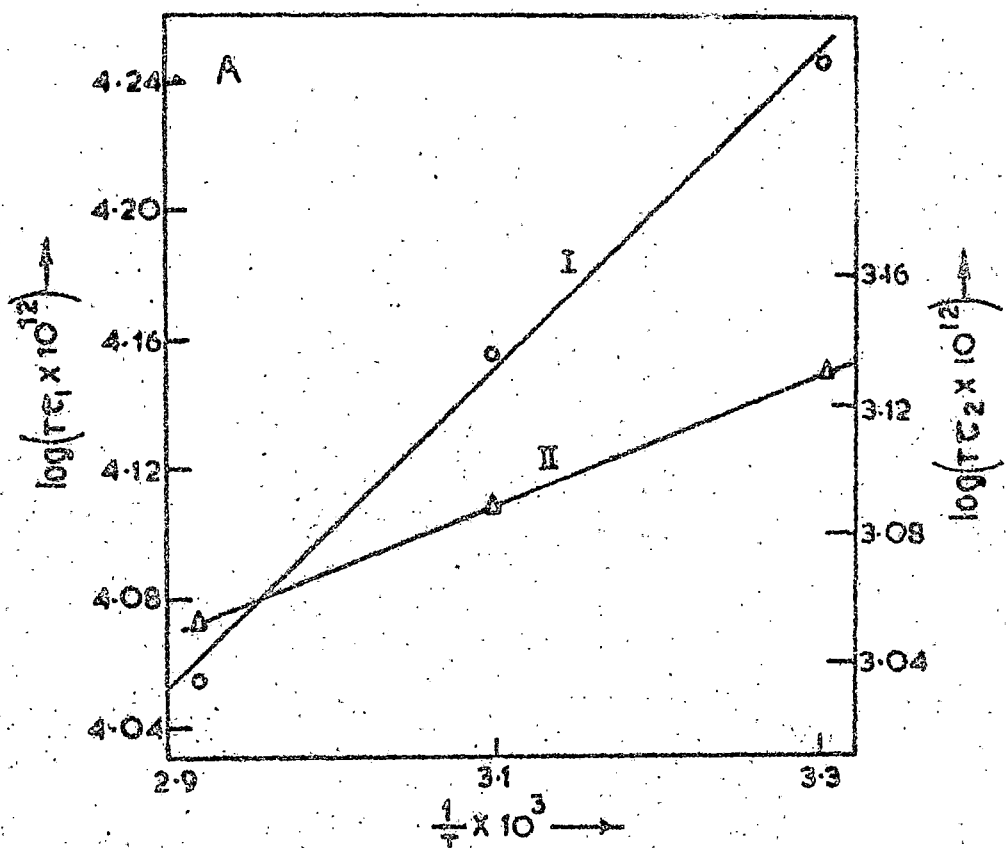


FIG. 6.2

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

Table 6.3

Observed and calculated values of dielectric
permittivity and dielectric loss

N-Sulfinylanilene										
	f = 1 MHz		f = 8.6 GHz				f = 18.3 GHz			
T°C	ϵ_0	ϵ'_{obs}	ϵ'_{cal}	ϵ''_{obs}	ϵ''_{obs}	ϵ'_{obs}	ϵ'_{cal}	ϵ''_{obs}	ϵ''_{cal}	
30	3.85	3.08	2.99	.48	.51	2.73	2.73	.36	.36	
50	3.76	3.13	3.08	.52	.56	2.80	2.80	.42	.42	
70	3.65	3.16	3.15	.52	.53	2.82	2.83	.46	.46	
	f = 24.4 GHz				f = 35.14 GHz					
30	3.85	2.72	2.73	.32	.32	2.60	2.67	.25	.29	
50	3.76	2.74	2.73	.37	.37	2.62	2.67	.31	.33	
70	3.65	2.76	2.74	.41	.41	2.64	2.66	.35	.35	

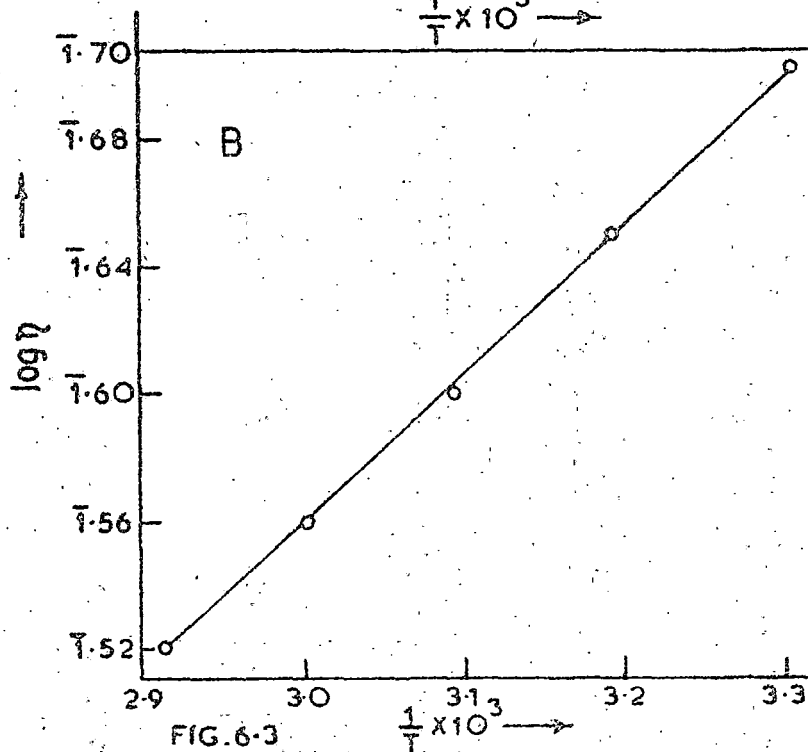
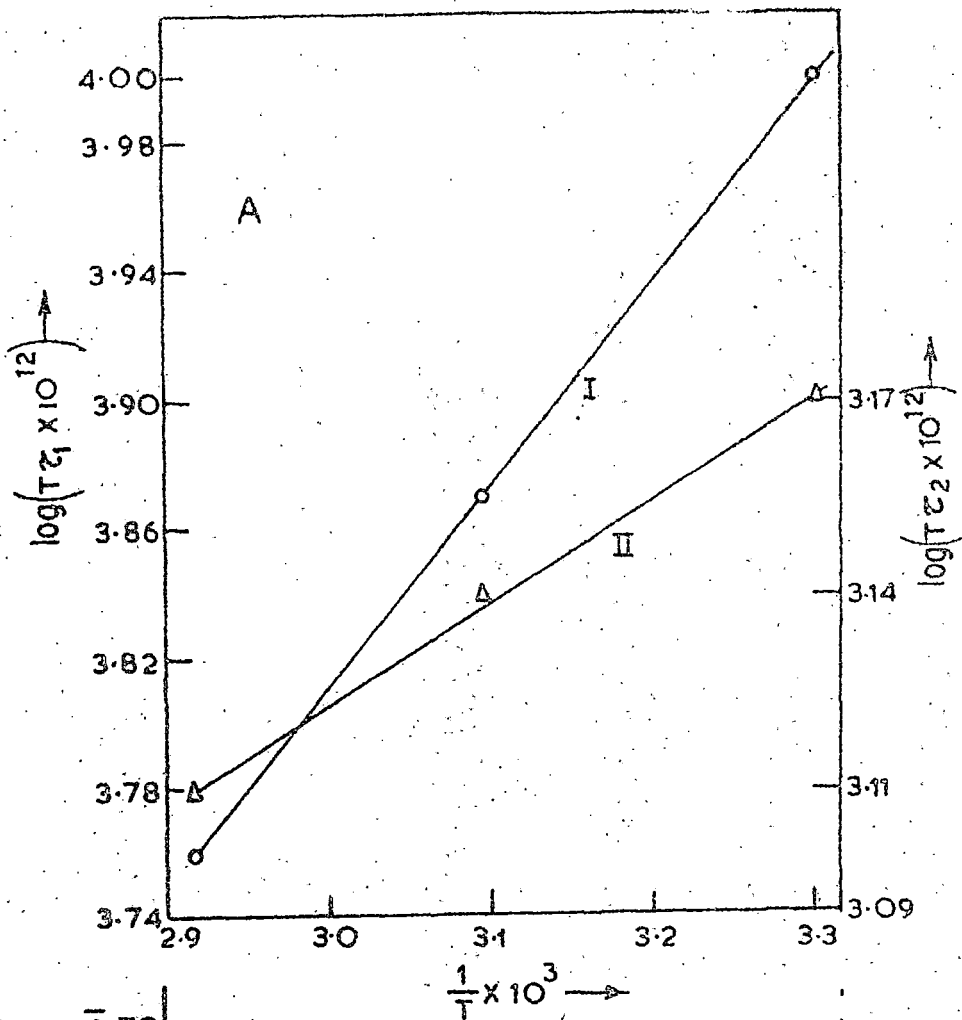


FIG. 6-3

- A. I. Plot of $\log(\tau_{c1})$ vs. $1/T$ for phenylisocyanate
 II. Plot of $\log(\tau_{c2})$ vs. $1/T$ for phenylisocyanate
 B. Plot of $\log \eta$ vs. $1/T$ for phenylisocyanate

the CN bond attached to the benzene ring. In the case of PhNCO and PhNCS, the -NCO and NCS group must be inclined with the $C_1 - C_4$ axis of the benzene ring either in plane or outside it. Such inclination of -NCS and -NCO groups with $C_1 - C_4$ axis of the benzene ring in PhNCS and PhNCO respectively has been reported by Kartritzky et al.⁴ from infrared studies and from u.v. absorption studies by Chakraborty et al.⁵. Beard and Dailey⁶ also reported from microwave spectroscopic studies that the C-N-C angle in CH_3NCS is 142° , while Ham and Willis⁷ asserted that C-N-C angle in PhNCS is 140° .

The three molecules of PhNCO, PhNCS and PhNSO are almost similar in sizes and their relaxation times expected to be similar in magnitude. Actually, the relaxation time τ_1 in PhNCO and PhNSO (Table 6.4) are almost the same ($\tau_1=33$ p.sec at $30^\circ C$) but the relaxation time τ_1 in PhNCS is 58 p.sec at $30^\circ C$, which is almost double the τ_1 -value in PhNCO and PhNSO. It is concluded that the relaxation time τ_1 of 33 p.sec is the molecular relaxation time in PhNCO and PhNSO and the τ_1 value of 58 p.sec in PhNCS might be the relaxation time of a dimeric molecule formed through association. Such tendency of formation of dimers in nitroso compound has been reported.⁴

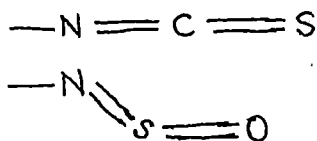
The shorter relaxation time τ_2 of the -NCS and -NCO groups are similar (about 4.5 p.sec at $30^\circ C$) and is much

Table 6.4

Values of ϵ_{∞} , α , τ_1 , τ_2 , C_1 and n_D^2

TC	n_D^2	ϵ_{∞}	$\tau_1 \times 10^{12}$ sec	$\tau_2 \times 10^{12}$ sec	α	C_1
Phenylisothiocyanate						
30	2.43	2.45	53.10	4.45	.25	.82
50	2.40	2.43	44.40	3.80	.21	.85
70	2.36	2.42	33.00	3.26	.13	.85
Phenylisocyanate						
30	2.27	2.30	33.13	4.87	.22	.70
50	2.25	2.26	23.00	4.28	.16	.68
70	2.22	2.25	16.50	3.70	.11	.68
N-Sulfinylaniline						
30	2.33	2.41	34.00	2.72	.30	.77
50	2.35	2.37	24.60	2.35	.25	.77
70	2.32	2.33	18.60	2.02	.20	.76

larger than the $\tau_2 = 2.7$ p.sec at 30°C due to the -NSO group rotation in PhNSO. This may be due to the fact that the size of the -NSO group in the bent position is smaller than the sizes of -NCO or -NCS groups which are linear.



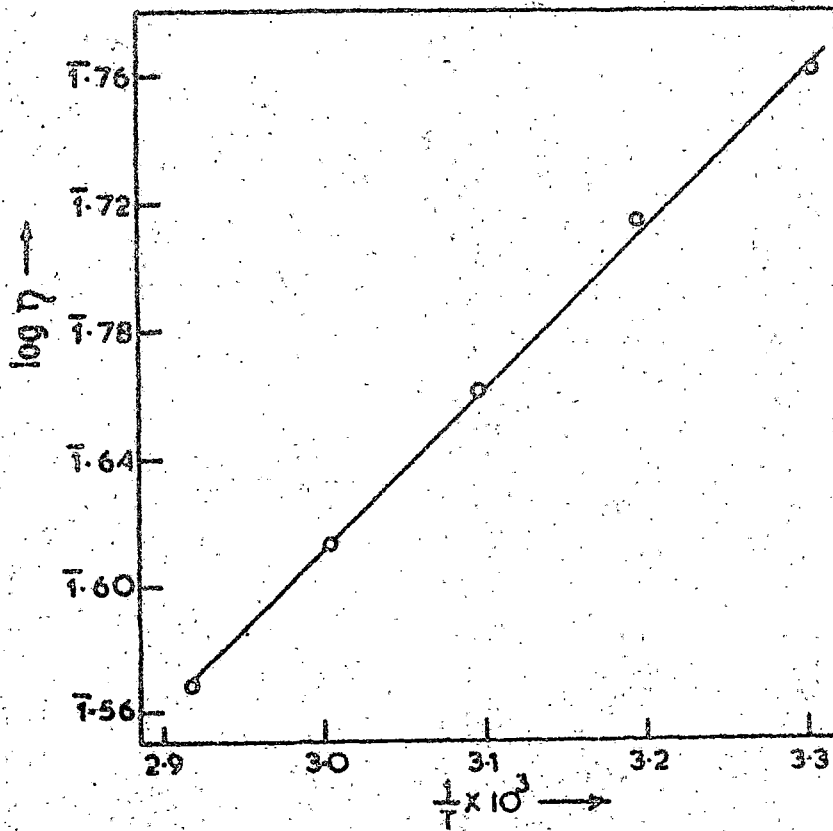
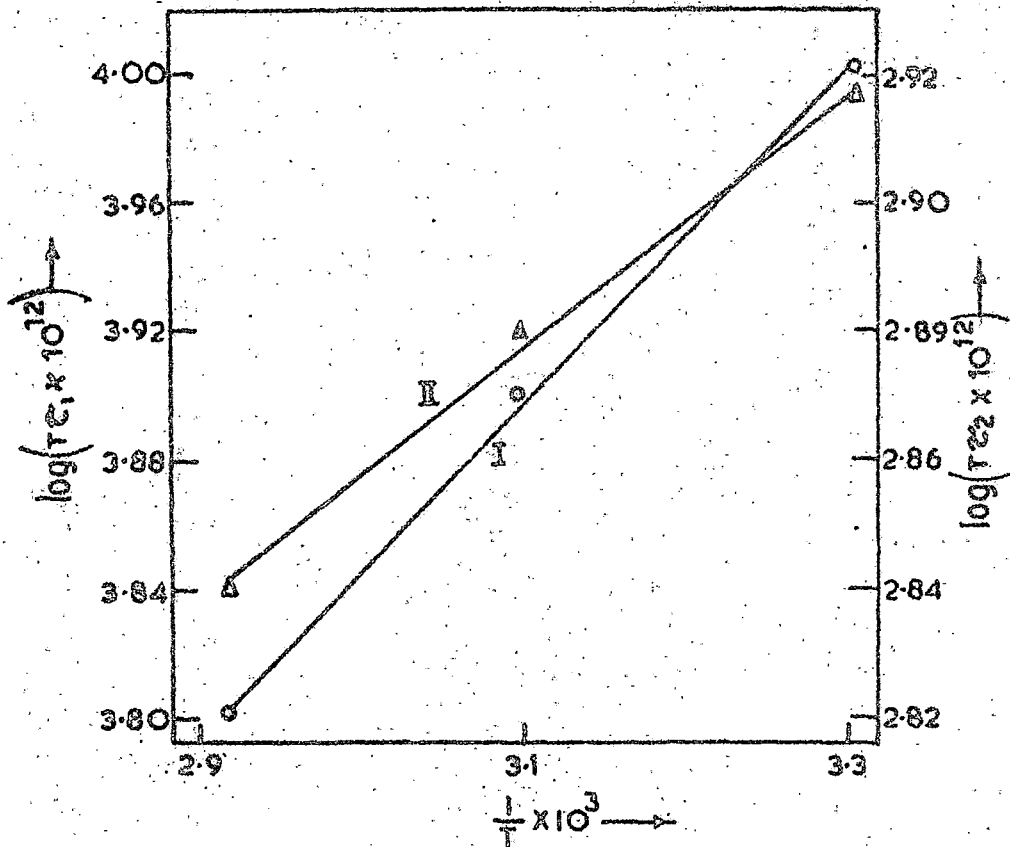


FIG. 6.4

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

Dipole moment

The experimentally obtained values of dipole moment of the three molecules in benzene solutions, as can be seen from Table 6.5 agree well with the μ -values reported in literature⁸ shown in the same table. It is also observed that the dipole moment is almost independent of temperature in all the cases, indicating thereby the presence of only one conformer in each of the compound. It may be noted that in the PhNSO molecule, of the two possible conformers trans and cis, only the trans form is favoured as reported by Benshan et al.⁹

Weight factor C_1

It is seen from the Table 6.4 that the weight factor C_1 for molecular orientation lying in the range .82 - .70 in the three cases, so the molecular reorientation is the major relaxation mechanism in each of the three compounds.

Structure of the -NCS and -NCO groups

As mentioned earlier, the NCS group is inclined to the C-N bond attached to the ring, the resultant moment μ of the molecule would make an angle θ with the C-N axis. Then the moment component responsible for molecular orientation is $\mu \cos \theta$

The weight factor for molecular orientation C_1 is given by

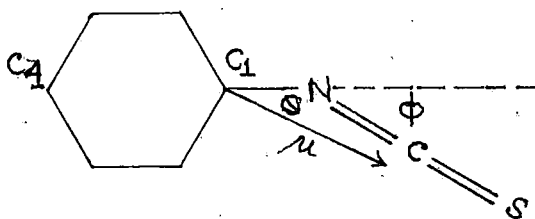
$$C_1 = \frac{(\mu \cos \theta)^2}{\mu^2} = .82 \quad (6.1)$$

$$\text{or } \theta = 25^\circ \quad (6.2)$$

Now if μ_1 is the moment of NCS group which makes an angle $\phi = 40^\circ$ with the C-N bond, then the moment component responsible for group rotation is $\mu_1 \sin \phi$. The weight factor for the group rotation C_2 is given by

$$C_2 = \frac{(\mu_1 \sin \phi)^2}{\mu^2} = .18$$

$$\text{or } \mu_1 = 1.8 \text{ D}$$



(6.3)

If the group -NCS is assumed double bonded.

$$\mu_{N=C=S} = -1.4 + 2 = 0.6 \text{ D} \quad (6.4)$$

and assuming the group as $\overset{+}{N} \equiv C - \overset{-}{S}$

$$\mu_{N \equiv C - S} = -3.1 + .9 = 2.2 \text{ D} \quad (6.5)$$

the latter μ -value for -NCS group fits better with the calculated value of $\mu_1 = 1.8 \text{ D}$, using the weight factor values C_1 and C_2 obtained experimentally. It is therefore concluded that the structure of -NCS group is $\overset{+}{N} \equiv C - \overset{-}{S}$ which is also suggested by Hibben¹⁰. Similarly in the case of PhNCO, the NCO group being inclined to the C-N bond, the resultant moment μ of the molecule

will be inclined to the C-N bond by an angle θ' which can be found out from the following relations. The weight factor for

Table 6.5

Values of ΔH_{η} , ΔH_{c_1} , ΔH_{c_2} , η and μ

$T^{\circ}C$	ΔH_{η} Kcal/mole	ΔH_{c_1} Kcal/mole	ΔH_{c_2} Kcal/mole	η c.p	μ Debye	μ (Literature) Debye
Phenylisothiocyanate						
30				.56	2.58	
50	2.35	2.20	0.98	.45	2.55	2.76
70				.33	2.50	
Phenylisocyanate						
30				.50	2.13	
50	2.30	2.10	0.80	.40	2.13	2.28
70				.33	2.13	
N-Sulfinylaniline						
30				.58	1.91	
50	2.36	2.25	0.92	.46	1.95	1.90
70				.37	1.97	

the molecular orientation C_1 is given by

$$C_1 = \frac{(\mu \cos \theta')^2}{\mu^2} = .70$$

$$\text{or } \theta' = 33^{\circ}$$

(6.6)

Now, the moment component responsible for molecular orientation

is $\mu \cos \theta'$ is given by

$$\mu \cos \theta' = 2.2 \cos 33^\circ = 1.95 D \quad (6.7)$$

and the moment component responsible for group rotation is

$$\mu \sin \theta' = 2.2 \sin 33^\circ \approx 1.2 D \quad (6.8)$$

Again, if μ_1 be the moment of the $-NCO$ group which makes an angle ϕ' with the C-N axis, then $\mu_1 \cos \phi'$ contributes to the molecular orientation and $\mu_1 \sin \phi'$ contributes to the group rotation. Therefore

$$\mu \cos \theta' = \mu_{CN} + \mu_1 \cos \phi' \quad (6.9)$$

or $\mu_1 \cos \phi' = 1.5 D \quad (6.10)$

and $\mu_1 \sin \phi' = \mu \sin \theta' = 1.2 D \quad (6.11)$

from eqns. (6.10) and (6.11)

$$\mu_1 = 1.92 D \text{ and } \phi' = 38^\circ$$

But $\mu_{N=C=O} = -1.4 + 2.4 = 1.0 D \quad (6.12)$

and $\mu_{N \equiv C - O} = -3.1 + 1.7 = 2.4 D \quad (6.13)$

Thus the moment of $\overset{+}{N} \equiv \overset{-}{C} - \overset{-}{O}$ group fits with the calculated value of $\mu_1 = 1.92$.

It is therefore concluded that the structure of the NCO group is $-N \equiv C - O$ and it makes an angle $\phi' = 38^\circ$ with the

C-N bond attached to the phenyl ring.

Potential barriers for molecular, intermolecular and viscous flow (ΔHc_1 , ΔHc_2 and $\Delta H\eta$)

The potential barrier ΔHc_1 for molecular orientation is as usual smaller than the energy barrier for viscous flow (Table 6.5). The energy barrier for internal rotation is less than 1 Kcal/mole in all the molecules and this is much smaller than the energy barrier for molecular reorientation.

References

1. Bergmann K., Roberti D.M. and Smyth C.P., J.Phys.Chem., 64, 665 (1960).
2. Roy S.K., Sengupta K. and Roy S.B., Advance Relaxation Processes, 10, 273 (1977).
3. Tay S.P. and Crossley J., Canad.J.Chem., 50, 2031 (1972).
4. Kartrizdy A.R., Keogh H.J., Ohlenrott S. and Topson R.D., J.Am.Chem.Soc., 92, 6855 (1970).
5. Chakraborti S., Sarkar A. and Banerjee S.B., Ind.J.Phys., (in press), (1977).
6. Beard C.J. and Bailey S.P., J.Am.Chem.Soc., 71, 929 (1949).
7. Ham N.S. and Willis J.B., Spectrochem.Acta., 16, 279 (1960).
8. Landolt Bornstein, Vol 1/3 Springer Verlag Berlin (1951).
9. Bonham J.S., Cheng C.L., Le Fevre R.J.W. and Milchere G.L.D., Australia J.Chem., 26, 421 (1973).
10. Hibben J.H., "Raman effect and its applications" (1939) P.282, Reinhold Publishing Corporation, New York.