TABLE 2 — NON-VANISHING β AND γ COMPONENTS IN PYRAZINE AND 1,3,5-TRIAZINE

(Values in esu)

$10^{+30}\,\beta_{xxx}$	$10^{+30}\,\beta_{xyy}$	$10^{+36}\,\gamma_{xxxx}$	$10^{+36}\,\gamma_{yyyy}$	$10^{+36}\,\gamma_{xxyy}$
		PYRAZINE		
0·0000	0·0000	−86·6236	−86·0165	−28·7723
		1,3,5-TRIAZINE		
−1·1688	−1·1688	−74·7640	−74·7640	−24·9207

$$\gamma = \sum_{i,j,k \neq 0} \frac{\langle \Psi_0|H'|\Psi_i\rangle \langle \Psi_i|H'|\Psi_j\rangle \langle \Psi_j|H'|\Psi_k\rangle \langle \Psi_k|H'|\Psi_0\rangle}{(W_i - W_0)^2 (W_j - W_0)} \qquad \dots(12)$$

In these expressions H' stands for ex, ey, ez. Like pyridine the first hyperpolarizability for pyrazine and 1,3,5-triazine also exist and is given by the second term of the expression (11). From our estimated[1] $\langle \Psi_I| x | \Psi_{I'}\rangle$ and $\langle \Psi_I | y | \Psi_{I'}\rangle$ the non-vanishing β and γ components for pyrazine and 1,3,5-triazine have been calculated and are given in Table 2.

Pi-electron susceptibility and pi-quadrupole moment — The pi-electron susceptibility[5] and the pi-quadrupole moments[6] calculated from the relations (13 and 14)

$$\chi_{mol} = -\frac{Ne^2}{6mC^2} \sum \bar{r}^2 + \frac{Ne^2}{6m^2C^2} \sum \frac{|P(n,n')|^2}{h\nu(n',n)} \qquad \dots(13)$$

and

$$Hzz = \sum_i e_i r_i^2 \; P_2 \, (z_i/r_i) \qquad \dots(14)$$

for pyrazine and 1,3,5-triazine are equal.

The dia- and paramagnetic terms obtained are $-57\cdot54 \times 10^{-6}$ and $35\cdot09 \times 10^{-6}$ respectively and the calculated value of the pi-quadrupole moment for the two moles is $11\cdot4784 \times 10^{-26}$ esu. These values are comparable with those calculated for pyridine[1]. As we have no experimental data to compare with these results it is difficult to say how far these results are correct.

The author is grateful to Prof. Sadhan Basu for his keen interest and guidance. The author also extends his cordial thanks to Dr Subir Bhattacharya, Dr P. N. Sen and Syed Sajjad Zaheer Adnan for their helpful suggestions and discussions.

References

1. ADHIKARI, SANAT K., SEN, P. N. & BASU, SADHAN, *J. chim. Phys.*, **9** (1972), 1282.
2. RUDENBERG, K. & PARR, R. G., *J. chim. Acta Phys*, **3** (1965), 1268,
3. SEN, P. N. & BASU, S. *Int. J. Quantum Chem.* **3**, (1969), 611.
4. SEN, P. N. & BASU, S., *Int. J. Quantum Chem.*, **2** (1968), 687.
5. BASU, S., *Theor. chim. Acta*, **3** (1965), 156.
6. SEN, P. N. & BASU, S., *J. chim. Phys.*, **48** (1968), 4075.

Liquid Crystalline Behaviour of Some Schiff Bases Derived from 4-*n*-Alkoxy-1-naphthaldehydes & *p*-(*n*-Amyloxy)aniline

J. S. DAVE, GEORGE KURIAN & N. R. PATEL

Chemistry Department, M.S. University, Baroda 390002

Five compounds of the homologous series 4-*n*-alkoxy-1-naphthylidene-*p*-(*n*-amyloxy)anilines have been synthesized and their liquid crystalline behaviour studied. The C_1-, C_3- and C_5-homologs are non-mesomorphic. The C_2-homolog is monotropic nematic in nature while the C_4-derivative exhibits enantiotropic nematic mesophase. The C_2- and C_3-homologs exhibit two solid modifications. The metastable modification has a transition temperature lower than that of the stable modification.

SYNTHESIS of low melting liquid crystalline compounds has aroused considerable interest recently in view of the potential applications of the compounds. Liquid crystalline substances comprise linear and rigid molecules. It is found that when molecular structure is varied, the liquid crystalline properties also change markedly. Dave *et al.* have observed that the introduction of a 1,4-substituted naphthalene moiety into a mesomorphic compound considerably reduces the liquid crystallinity of the compound[1,2]. Here we present the results of our studies on the mesomorphic behaviour of some members of the homologous series 4-*n*-alkoxy-1-naphthylidene-*p*-(*n*-amyloxy)anilines. Five Schiff base compounds (C_1-C_5) of the series were prepared by condensing various 4-*n*-alkoxy-1-naphthaldehydes[1] with *p*-(*n*-amyloxy)aniline[3]. The mesomorphic behaviour of these compounds was studied using a Leitz Ortholux II polarizing microscope equipped with a Leitz heating stage. The analysis for C, H and N for these compounds agreed well with the calculated values. The melting points and transition temperatures of these compounds are given in Table 1.

The C_1-, C_3- and C_5-homologs are non-mesomorphic. The C_2-member is monotropic nematic in nature while the C_4-derivative exhibits enantiotropic nematic mesophase. The C_2- and C_3-homologs exhibit two solid modifications C_I and C_{II}; the stable modification C_I has the higher transition point than

TABLE 1 — TRANSITION TEMPERATURES OF 4-*n*-ALKOXY-1-NAPHTHYLIDENE-*p*-(*n*-AMYLOXY)ANILINES

Alkyl group	Transition temp.* (°C)	
	Nematic	Isotropic
CH_3	—	86·5
C_2H_5	(61·5)	81·5[a], 74·5[b]
C_3H_7	—	78·0[a], 68·0[b]
C_4H_9	62·5	64·5
C_5H_{11}	—	68·5

*Figure in parenthesis indicates monotropy (a) stable modification, and (b) metastable modification.
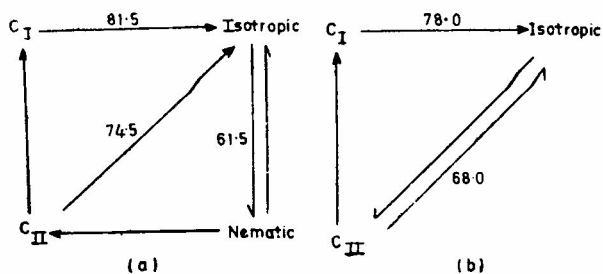
Fig. 1 — Liquid crystalline behaviour of 4-n-alkoxy-1-naphthylidene-p-(n-amyloxy)anilines

the metastable modification C_{II}. The C_{II} modification is obtained by rapid cooling of the isotropic liquid phase. In the case of the C_2-homolog both the solid forms give, on heating, the isotropic liquid which on cooling gives the monotropic nematic phase (Fig. 1a). In C_3-homolog no nematic phase is observed (Fig. 1b).

The absence of liquid crystallinity in C_1-, C_3- and C_5-homologs may be due to the high melting points of these compounds. The melting points and transition temperatures of these compounds are lower compared with those of the corresponding benzylidene compounds studied by Dave and Patel[4]. Further work is in progress.

The authors express their sincere thanks to Prof. S. M. Sethna and Prof. K. N. Trivedi for their interest in the work. One of them (N.R.P.) is thankful to the CSIR, New Delhi, for a research fellowship.

References

1. DAVE, J. S., KURIAN, G., PRAJAPATI, A. P. & VORA, R. A., *Molec. Cryst. Liq. Cryst.*, **14** (1971), 307; *Curr. Sci.*, **41** (1972), 415; *Indian J. Chem.*, **10** (1972), 754.
2. DAVE, J. S. & PRAJAPATI, A. P., *Pramana, Suppl. No. 1*, (1975), 435; *Curr. Sci.*, **45** (1976), 95.
3. GUTEKUNST, G. O. & GRAY, H. L., *J. Am. chem. Soc.*, **44** (1922), 1741.
4. DAVE, J. S. & PATEL, P. R., *Molec. Cryst.*, **2** (1966), 103.

Thiosemicarbazide as an Inhibitor in the Corrosion of Aluminium & Zinc

ABO EL-KHAIR B. MOSTAFA, KH. M. KAMEL & I. A. ABDEL-HAMID

Chemistry Department, University College for Women Ain Shams University, Cairo, A.R.E.

The effectiveness of thiosemicarbazide as an inhibitor in HCl and NaOH for the corrosion of aluminium has been investigated. The percentage inhibition increases up to 87% in acidic solution at [inhibitor]=$4.35 \times 10^{-3}M$. For the corrosion of aluminium, thiosemicarbazide (TSC) is a more effective inhibitor in acidic medium than in alkaline medium. This phenomenon has been attributed to the Zwitterion formation by TSC in alkaline medium. Similar behaviour is also observed for alkaline corrosion of zinc using TSC as inhibitor.

ORGANIC compounds are widely used as corrosion inhibitors[1,2]. The mechanism of the action of such inhibitors depends on their molecular structures[3], molecular area[4] and on their molecular weights[5,6]. The activity of cations as corrosion inhibitors rather than the molecules, has also been considered[7].

The activity of thiosemicarbazide (TSC) as an inhibitor in the corrosion of aluminium in both hydrochloric acid and sodium hydroxide solutions and of zinc metal in alkaline medium has now been evaluated.

Chemicals empolyed were of extra pure quality. The corrosion rate was determined using weight loss techniques. The percentage inhibition (P) was calculated from Eq. (1)

$$P = 100 \ (1 - W_2/W_1) \qquad \ldots(1)$$

where W_1 and W_2 are the corrosion rates in the absence and in presence of inhibitor respectively.

The rate of corrosion of aluminium is found to decrease with increase in [TSC] in $1N$ hydrochloric acid and $1N$ sodium hydroxide solutions, similar to the behaviour that observed in acid corrosion of iron in the presence of TSC[8]. It was found that the change in the percentage inhibition is not appreciably affected and lies within the experimental error in the temperature range 24-30°. The percentage inhibition at [inhibitor] = $4.39 \times 10^{-3}M$ is $\approx$ 87% in HCl and 61% in NaOH solutions, the corresponding values for thiourea inhibition of aluminium corrosion are 60% and 16% respectively[9]. It can be assumed that thiosemicarbazide acts as a more efficient inhibitor than thiourea at the same concentration in both media.

Fig. 1 represents the corrosion rate of zinc against log [inhibitor] in $1N$ sodium hydroxide solution. As in the case of aluminium, the corrosion rate in the zinc metal decreases with increasing [TSC]. The more efficient inhibition exhibited by TSC as compared to thiourea is probably due to the additional —NH— group in TSC molecule. Furthermore, the different charge distribution on TSC molecule increases its adsorption behaviour. However, due to the lower concentration of protons in alkaline medium, the inhibitor forms zwitterions[9] which decrease the corrosion rate in alkaline medium as compared to that in acidic medium.
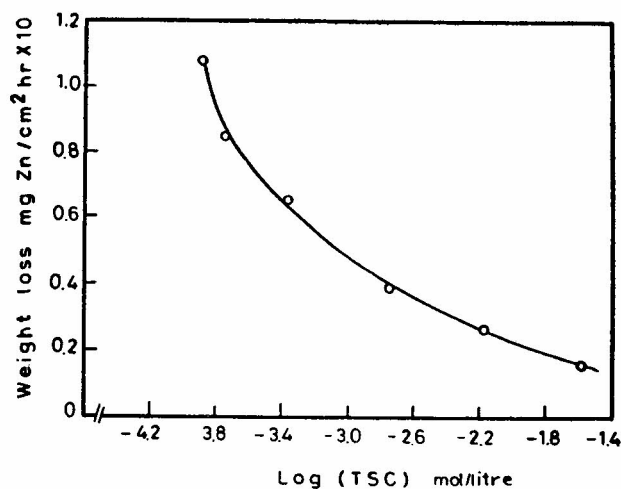

Fig. 1 — Effect of [thiosemicarbazide] on the corrosion rate of zinc in $0.1N$ NaOH at 25°