

24.0° C) was 100% but subsequently the entire stock of fry was wiped out in 3 hours (Fig. 4).

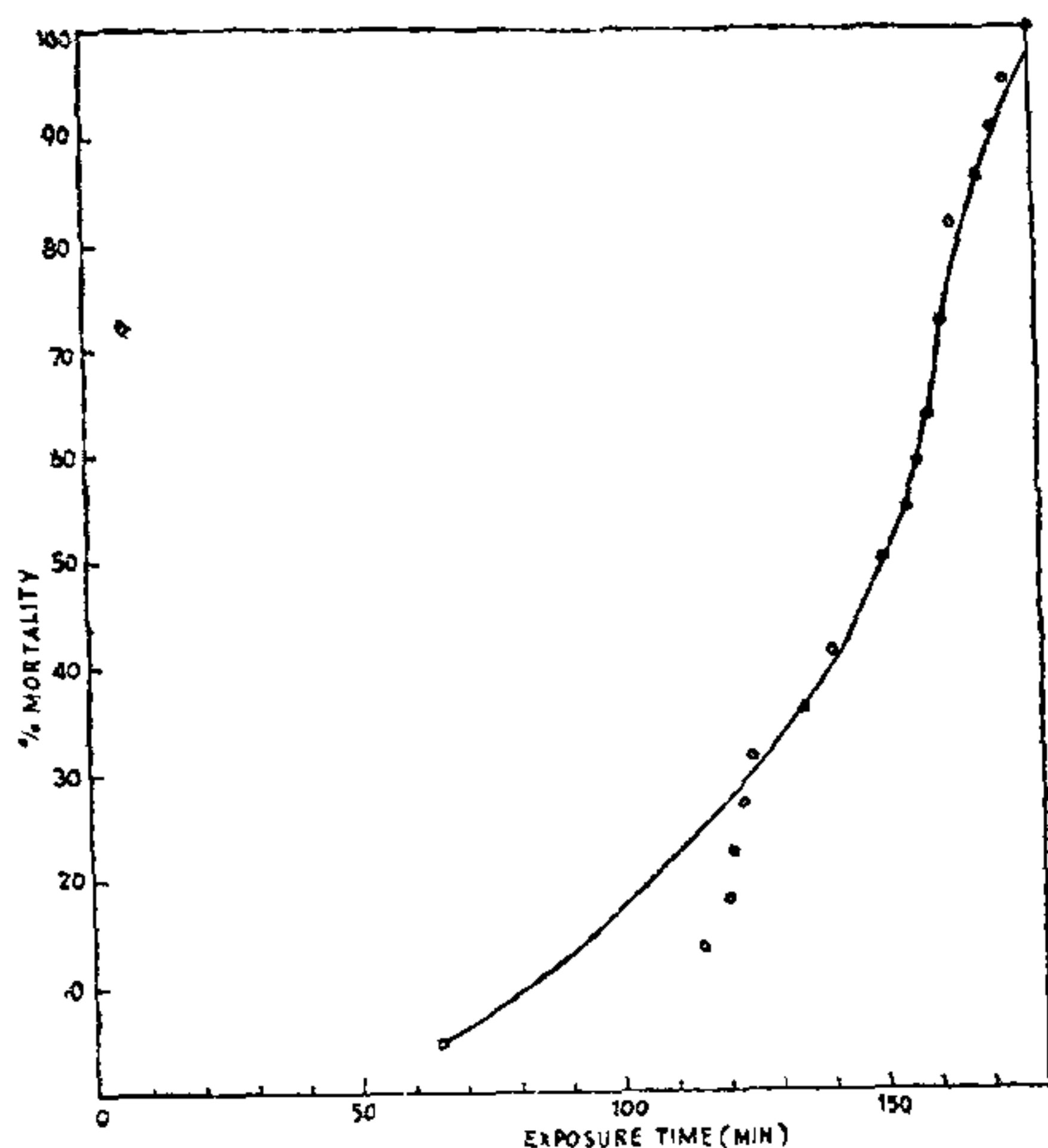


FIG. 4. Latent mortality of *Cirrhina mirgala* fry at 24° C after exposure to thermal shock at 39.2° C \pm 0.1 (30 seconds).

Prolonged exposure at 38.4° C can cause similar damage since the mortalities (at 23.5° C) after 6 and 8 minutes' exposure are markedly higher (12.5 and 25.0% in 24 hours) compared to the nil mortality when the exposure was limited to 4 minutes and less (Table II).

TABLE II

Responses of carp fry to test temperature of 38.4° C for various exposure periods

No. of Specimen	Duration of exposure (min.)	% Mortality	% Mortality observed on transfer to acclimated water	
			24 hrs	48 hrs
8	2	0	0	0
8	4	0	0	0
8	6	0	12.5	25
8	8	0	25	37.5

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SPECTROSCOPIC STUDIES OF PROPIONAMIDE, THIOPROPIONAMIDE, N, N-DEUTERATED PROPIONAMIDE AND N, N-DEUTERATED THIOPROPIONAMIDE

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SPECTROSCOPIC studies of amides received considerable attention since the structure of a secondary amide like N-methylacetamide is closely related to that of polypeptide. The studies of intermolecular associations in primary and secondary amides and of their deuterated species, dichroism studies of secondary amides and band contour studies of the absorption bands of secondary and tertiary amides in vapour phase are described by various workers and the assignments of the vibrational frequencies on the basis of these studies have been explained¹⁻⁷. We now report the Raman and infrared frequencies of propionamide, N, N-deuterated propionamide, thiopropionamide and N, N-

deuterated thiopropionamide and of them in solution of chloroform.

Propionamide and N, N-deuterated propionamide are solids and therefore their infrared spectra were recorded by mull technique with Perkin Elmer Model 21 and 337 spectrophotometers in the region 3,500 cm^{-1} to 400 cm^{-1} . Thiopropionamide and N, N-deuterated thiopropionamide are semi solids at room temperature and therefore their spectra were recorded by squeezing in a microfilm of unknown thickness of these substances between two plates of NaCl and KBr to cover the same range of 3,500 cm^{-1} to 400 cm^{-1} . The infrared spectra of the same amides in solution of chloroform

were recorded using matched cells of 0.1 mm thickness. The Raman spectrum of thiopropionamide was recorded on Coderg Raman spectrometer using a He-Ne laser source operating at 50 mW. The vibrational frequencies of propionamide and thiopropionamide and of them in solution of chloroform together with the assignments are given in Tables I and II. The Raman frequencies of propionamide are taken from Kohlrausch⁸.

The infrared frequencies of the functional groups and of the C-N stretching frequency of the amides and their deuterated species are given in Tables III and IV.

The functional groups responsible for hydrogen bonding in a primary amide like propionamide are the C=O and the NH₂ groups whereas in thioamides they are the C=S and the NH₂ groups. In solution of moderate concentration in a solvent, like

TABLE I
Raman and infrared frequencies of propionamide (in cm⁻¹)

Raman	Infrared		Assignment
	Pure Amide	In solution of CHCl ₃	
..	..	3510 (m)	ν_{as} (NH ₂) free
..	..	3400 (s)	ν_s (NH ₂) free
3346 (2b)	3356 (s)	3330 (w)	ν_{as} (NH ₂) bonded
3168 (1b)	3236 (s)	3226 (m)	ν_s (NH ₂) bonded
2986 (4s)	..	2975 (s)	ν_{as} (CH ₃)
2942 (5)	2930 (s)	2925 (sh)	ν_s (CH ₃)
2913 (5)	ν_{as} (CH ₂)
2848 (2)	2940 (ms)	2810 (sh)	ν_s (CH ₂)
1686 (2)	..	1675 (vs)	ν (C=O) free
1658 (4)	1658 (s)	..	ν (C=O) bonded
1602 (2b)	1629 (sh)	1580 (ms)	δ (NH ₂)
1457 (4b)	1466 (m)	1455 (ms)	ν_{as} (CH ₃)
1412 (4b)	1420 (m)	..	ν_s (CH ₃)
..	1380 (ms)	1380 (ms)	δ (CH ₂)
1291 (1)	..	1275 (w)	ν (C-N)
1244 (2b)	1297 (m)	1115 (w)	γ (NH ₂)
1125 (4b)	1139 (ms)	1080 (w)	ω (CH ₃)
1056 (3b)	1060 (m)	1000 (w)	ν (C-CH ₃)
991 (3b)	990 (w)	805 (m)	ν (C-CH ₂)
809 (8b)	809 (m)	665 (w)	δ (NH ₂) ₁
..	660 (w)	550 (ml br)	δ (O=C-N)
555 (2b)	555 (sh)	440 (w)	γ (C-CH ₂)
455 (3b)	470 (ms)	..	γ (C-CH ₃)
269 (2b)

TABLE II
Raman and infrared frequencies of thiopropionamide (in cm⁻¹)

Raman	Infrared		Assignment
	Pure Amide	In solution of CHCl ₃	
..	..	3486 (s)	ν_{as} (NH ₂) free
..	..	3435 (s)	ν_s (NH ₂) free
..	3292 (s)	3296 (vs)	ν_{as} (NH ₂) bonded
..	3180 (vs)	3176 (vs)	ν_s (NH ₂) bonded
..	2980 (m)	2980 (s)	ν_{as} (CH ₃)
..	2935 (m)	2935 (sh)	ν_s (CH ₃)
..	..	2870 (sh)	ν_{as} (CH ₂)
..	1635 (s)	1610 (vs)	δ (NH ₂)
1420 (m)	1435 (s)	1410 (vs)	ν (C-N)
..	1310 (ms)	1325 (ms)	δ (CH ₃)
1240 (m)	1240 (ms)	1240 (ms)	γ (NH ₂)
1040 (w)	1065 (ms)	1060 (m)	ω (CH ₃)
983 (w)	1010 (m)	1010 (m)	ν (C-CH ₃)
890 (w)	920 (s)	920 (s)	ν (C-CH ₂)
647 (vs)	690 (m)	660 (m)	ν (C=S)
..	625 (m)	..	δ (NH ₂) ₁
438 (w)	γ (C-CH ₃)
368 (s)	δ (S=C-N)
241 (ms)	γ (C-CH ₂)

TABLE III

Infrared frequencies of the functional groups and of C-N stretching frequency of propionamide and thiopropionamide and of their deuterated species

Mode of vibration	Propionamide	Thiopropionamide	Mode of vibration	N, N-deuterated propionamide	N, N-deuterated thiopropionamide
ν_{as} $\left(\begin{array}{c} \text{H} \\ \diagdown \text{N} \diagup \\ \text{H} \end{array} \right)$	3356	3292	ν_{as} $\left(\begin{array}{c} \text{D} \\ \diagdown \text{N} \diagup \\ \text{D} \end{array} \right)$	2519	2510
ν_s $\left(\begin{array}{c} \text{H} \\ \diagdown \text{N} \diagup \\ \text{H} \end{array} \right)$	3236	3180	ν_s $\left(\begin{array}{c} \text{D} \\ \diagdown \text{N} \diagup \\ \text{D} \end{array} \right)$	2370	2360
ν (C=O)/ ν (C=S)	1658	690	ν (C=O)/ ν (C=S)	1637	690
δ $\left(\begin{array}{c} \text{H} \\ \diagdown \text{N} \diagup \\ \text{H} \end{array} \right)$	1629	1635	δ $\left(\begin{array}{c} \text{D} \\ \diagdown \text{N} \diagup \\ \text{D} \end{array} \right)$	1080	1210
ν (C-N)	1297	1435	ν (C-N)	1316	1465
γ $\left(\begin{array}{c} \text{H} \\ \diagdown \text{N} \diagup \\ \text{H} \end{array} \right)$	1139	1240	γ $\left(\begin{array}{c} \text{D} \\ \diagdown \text{N} \diagup \\ \text{D} \end{array} \right)$	940	860
δ $\left(\begin{array}{c} \text{H} \\ \diagdown \text{N} \diagup \\ \text{H} \end{array} \right)_I$	660	625	δ $\left(\begin{array}{c} \text{D} \\ \diagdown \text{N} \diagup \\ \text{D} \end{array} \right)_I$	480	475

TABLE IV

Infrared frequencies of the functional groups and of C-N stretching frequency of propionamide and thiopropionamide and of their deuterated species in solution of chloroform

Mode of vibration	Propionamide	Thiopropionamide	Mode of vibration	Propionamide	Thiopropionamide
ν_{as} $\left(\begin{array}{c} \text{H} \\ \diagdown \text{N} \diagup \\ \text{H} \end{array} \right)$	3510	3486	ν_{as} $\left(\begin{array}{c} \text{D} \\ \diagdown \text{N} \diagup \\ \text{D} \end{array} \right)$	2584	2520
ν_s $\left(\begin{array}{c} \text{H} \\ \diagdown \text{N} \diagup \\ \text{H} \end{array} \right)$	3400	3435	ν_s $\left(\begin{array}{c} \text{D} \\ \diagdown \text{N} \diagup \\ \text{D} \end{array} \right)$	2415	2400
ν (C=O)/ ν (C=S)	1675	660	ν (C=O)/ ν (C=S)	1664	660
δ $\left(\begin{array}{c} \text{H} \\ \diagdown \text{N} \diagup \\ \text{H} \end{array} \right)$	1580	1610	δ $\left(\begin{array}{c} \text{D} \\ \diagdown \text{N} \diagup \\ \text{D} \end{array} \right)$	1074	1210
ν (C-N)	1275	1410	ν (C-N)	1307	1440
γ $\left(\begin{array}{c} \text{H} \\ \diagdown \text{N} \diagup \\ \text{H} \end{array} \right)$	1115	1240	γ $\left(\begin{array}{c} \text{D} \\ \diagdown \text{N} \diagup \\ \text{D} \end{array} \right)$	940	480
δ $\left(\begin{array}{c} \text{H} \\ \diagdown \text{N} \diagup \\ \text{H} \end{array} \right)_I$	δ $\left(\begin{array}{c} \text{D} \\ \diagdown \text{N} \diagup \\ \text{D} \end{array} \right)_I$

chloroform, the intermolecular associations break up progressively with the result that the spectra at these concentrations show absorption bands which are assigned to free as well as bonded NH_2 and $\text{C}=\text{O}$ vibrational frequencies in propionamide, or free and bonded NH_2 and $\text{C}=\text{S}$ vibrational frequencies of thiopropionamide. The observations in Tables III and IV indicate that the bands in the region of $3,300 \text{ cm}^{-1}$ and $3,200 \text{ cm}^{-1}$ are due to the asymmetric and symmetric stretching vibrations of the bonded NH_2 group while the bands in the region of $3,500 \text{ cm}^{-1}$ and $3,400 \text{ cm}^{-1}$ are due to the same modes of vibration of free NH_2 linkages. The difference between the stretching frequencies of

the free and the bonded NH_2 group is of the order of 200 cm^{-1} both in propionamide and thiopropionamide indicating that the intermolecular associations which are in these molecules of the type $\text{N}-\text{H} \dots \text{O}=\text{C}$ and $\text{N}-\text{H} \dots \text{S}=\text{C}$, are strong. While frequencies arising out of the NH_2 stretching vibrations of free molecules are higher than those of the bonded molecules, the deformation frequencies of the free NH_2 group are lower than those of the bonded NH_2 group. The infrared bands in the region of 1296 cm^{-1} in propionamide and 1435 cm^{-1} in thiopropionamide which are essentially due to C-N stretch, show a decrease in their frequency in solutions of chloroform.

The NH_2 stretching frequencies of propionamide and thiopropionamide occur in the region of $3,300\text{ cm}^{-1}$ and $3,200\text{ cm}^{-1}$. But the frequencies arising out of the same modes of vibration of the ND_2 group in N,N-deuterated propionamide and N,N-deuterated thiopropionamide occur in the region of $2,500\text{ cm}^{-1}$ and $2,400\text{ cm}^{-1}$. On deuteration, the $\text{C}=\text{O}$ stretching frequency in propionamide diminishes from 1658 cm^{-1} to 1637 cm^{-1} while the $\text{C}-\text{N}$ stretching frequency increases from 1297 cm^{-1} to 1316 cm^{-1} . The band at 1629 cm^{-1} which is assigned to $\delta(\text{NH}_2)$ in propionamide disappears on deuteration, and a new band appears at $1,080\text{ cm}^{-1}$ which is assigned to $\delta'(\text{ND}_2)$ deformation. The corresponding frequencies in this propionamide and N,N deuterated thiopropionamide are at $1,635\text{ cm}^{-1}$ and $1,210\text{ cm}^{-1}$. Similar results are obtained in the case of $\gamma(\text{NH}_2)$ and $\gamma(\text{ND}_2)$ vibrations of these amides.

The NH_2 stretching frequencies of thiopropionamide have lower values compared to those arising out of the same modes of vibration in propionamide. It is also significant to note that the $\text{C}-\text{N}$ stretching frequency in thiopropionamide is much higher than that of the same mode in propionamide.

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INFORMATION TO CONTRIBUTORS

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