Table I.

Compound	Yield %	M.p.°C
19a	36	180
b	30	176
c	40	170
d	80	144
e	50	181
f	60	170
g	50	178
h	57	132
i	75	204
j	60	156
k	75	190

Tritylisothiocyanate, also, afforded N-trityl-N'-diphenylthiourea (20), m.p. 134°, in about 50% yield.

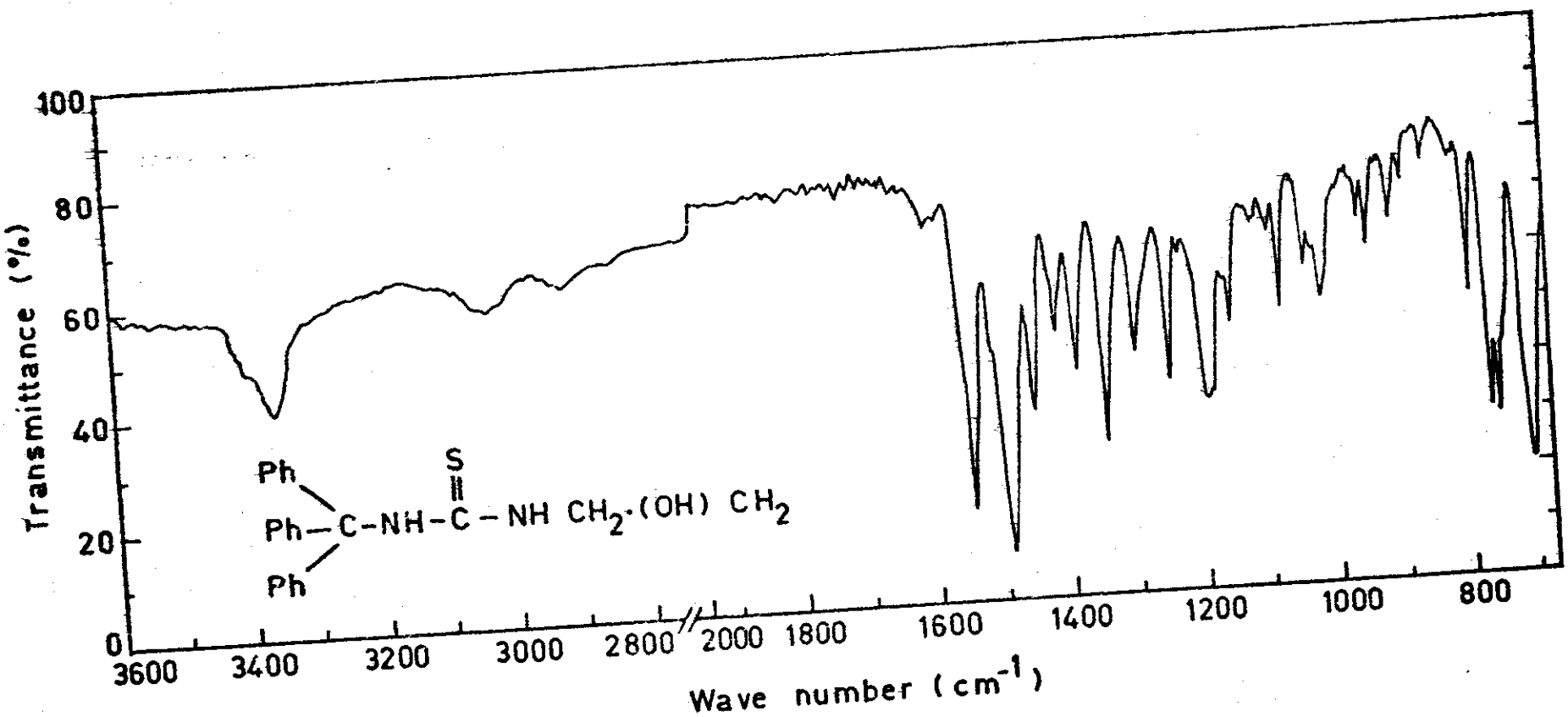

100
80
60
40
20
0
Transmittance (%)
Ph
Ph—C-NH-C-NH CH2·(OH) CH2
Ph
S
3600
3400
3200
3000
2800
2000
1800
1600
1400
1200
1000
800
Wave number (cm-1)

Fig. (1)

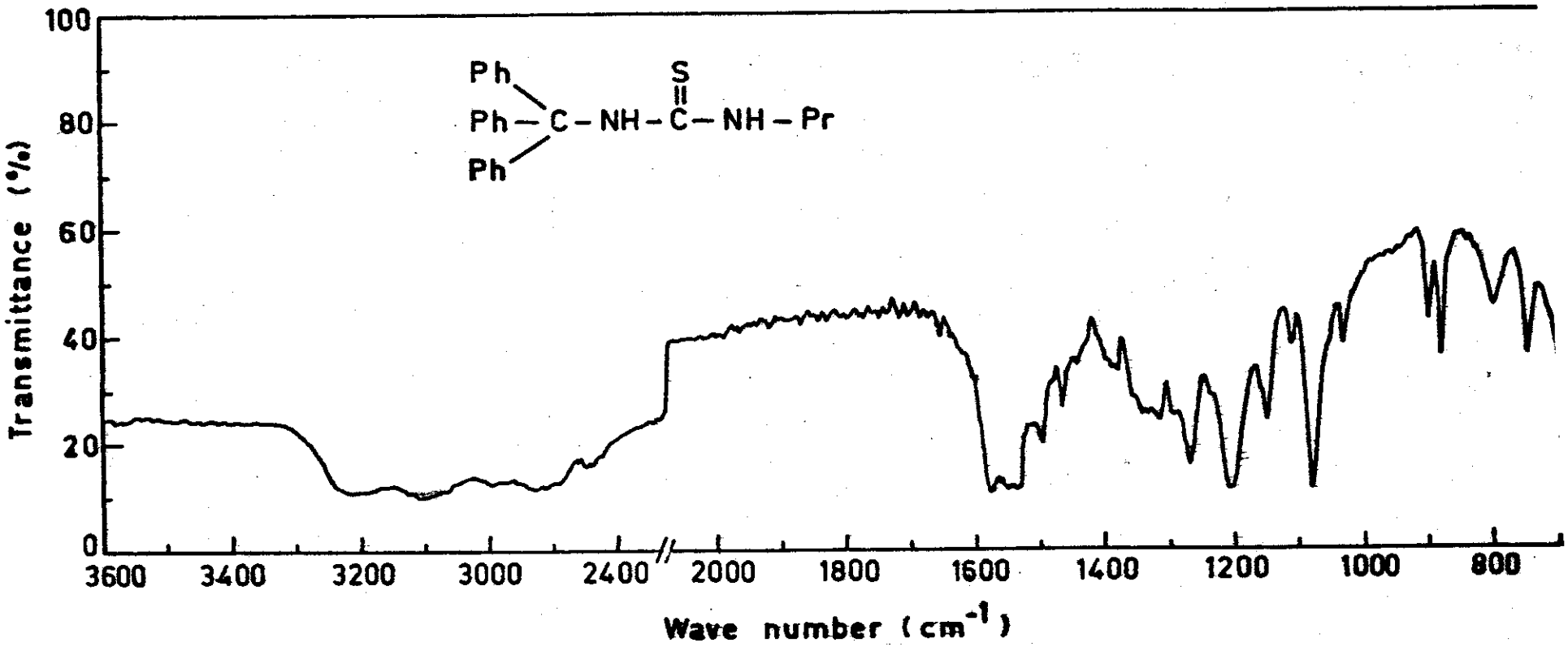

Ph
Ph — C — NH — C — NH — Pr
Ph
S
Transmittance (%)
100
80
60
40
20
0
3600
3400
3200
3000
2400
2000
1800
1600
1400
1200
1000
800
Wave number (cm⁻¹)

Fig. (2)

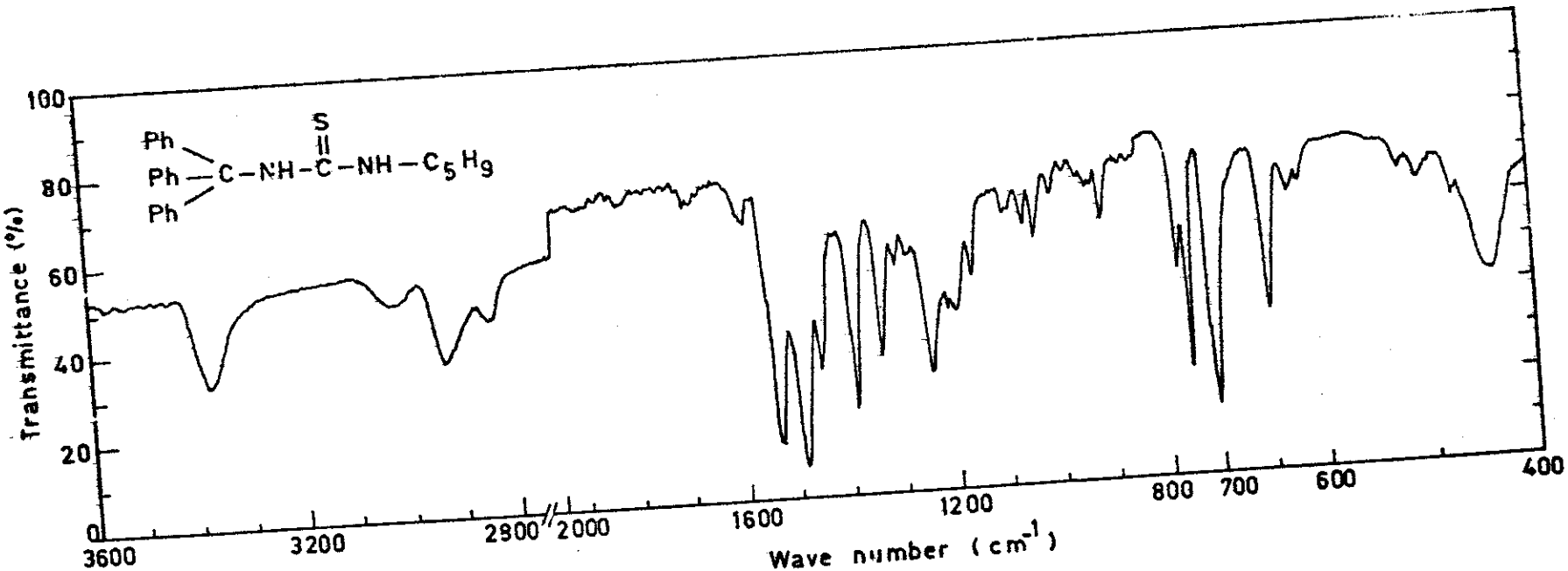

Ph
Ph—C–NH–C–NH–C5H9
Ph
S
100
80
60
40
20
0
Transmittance (%)
3600
3200
2800
2000
1600
1200
800
700
600
400
Wave number (cm-1)

Fig. (3)

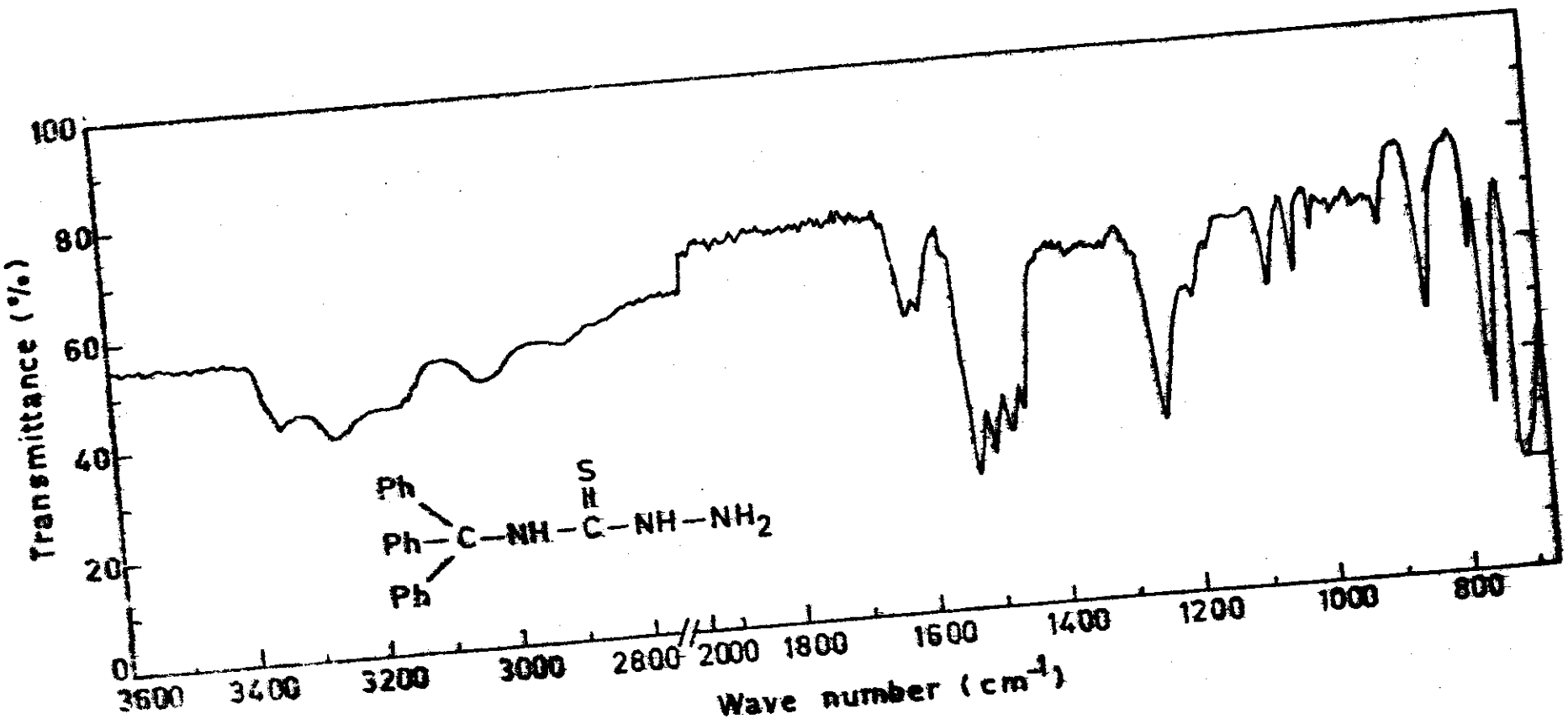

Transmittance (%)
100
80
60
40
20
0
3600
3400
3200
3000
2800
2000
1800
1600
1400
1200
1000
800
Wave number (cm⁻¹)
Ph
Ph—C—NH—C—NH—NH2
Ph
S

Fig. (4)

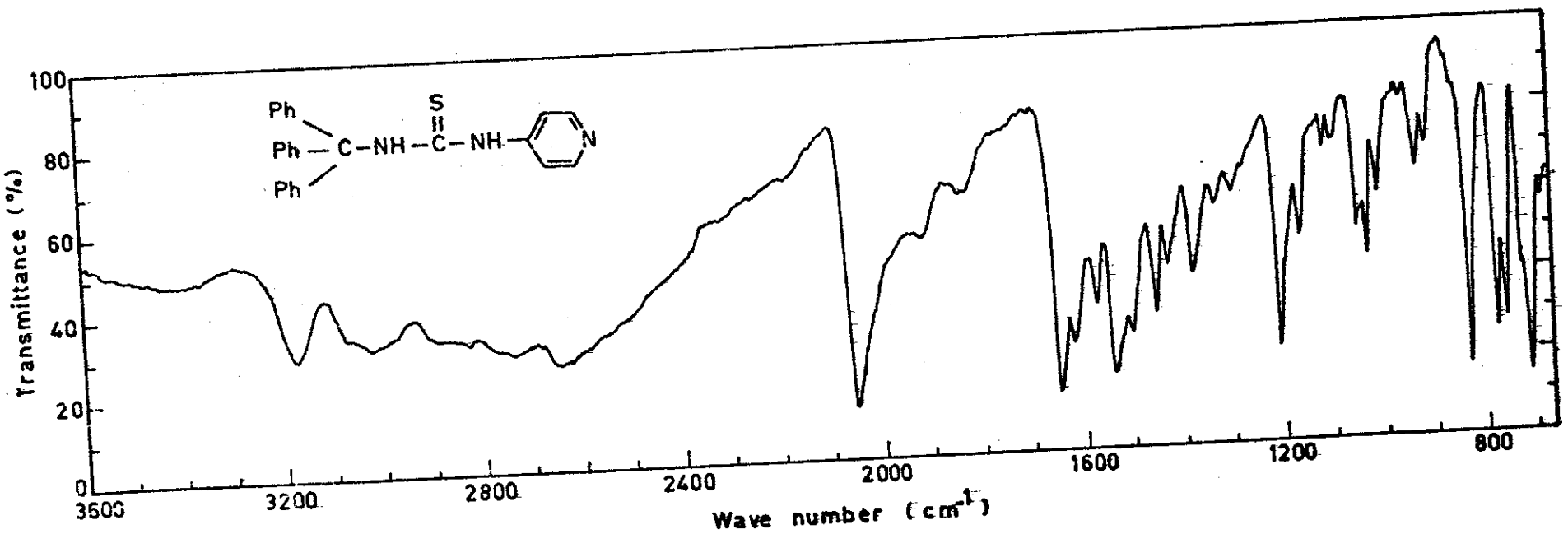
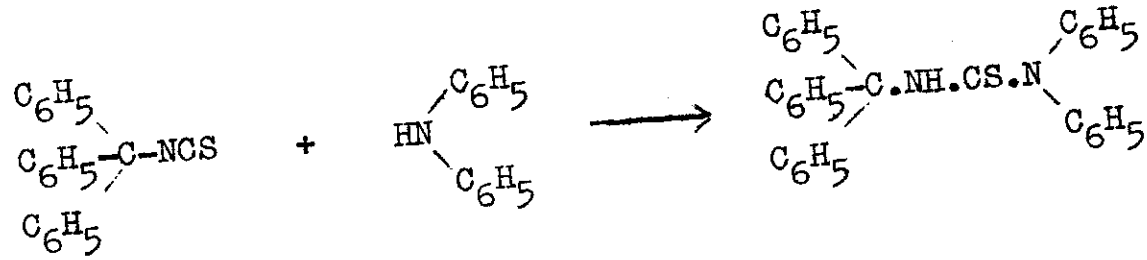
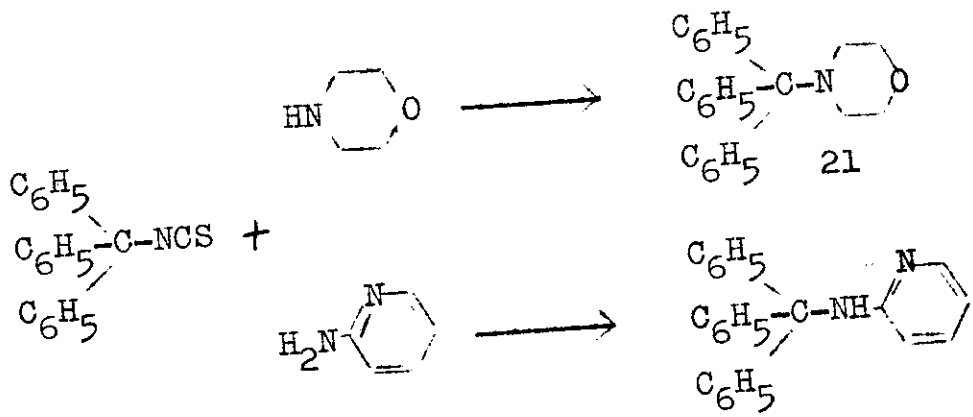

Ph
Ph — C–NH–C–NH
Ph
S
N
Transmittance (%)
100
80
60
40
20
0
3500
3200
2800
2400
2000
1600
1200
800
Wave number (cm⁻¹)

Fig. (5)



20

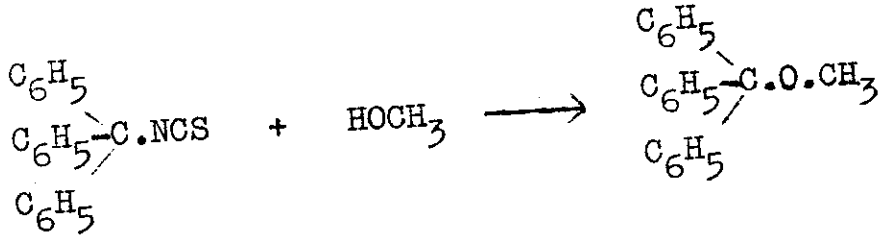
The reaction of tritylisothiocyanate with morpholine and/or 2-aminopyridine did not proceed in the usual way, and only N-tritylmorpholine (21) and trityl-2-aminopyridine (22) were obtained in 67% and 40% yields respectively as has been reported[169].



22

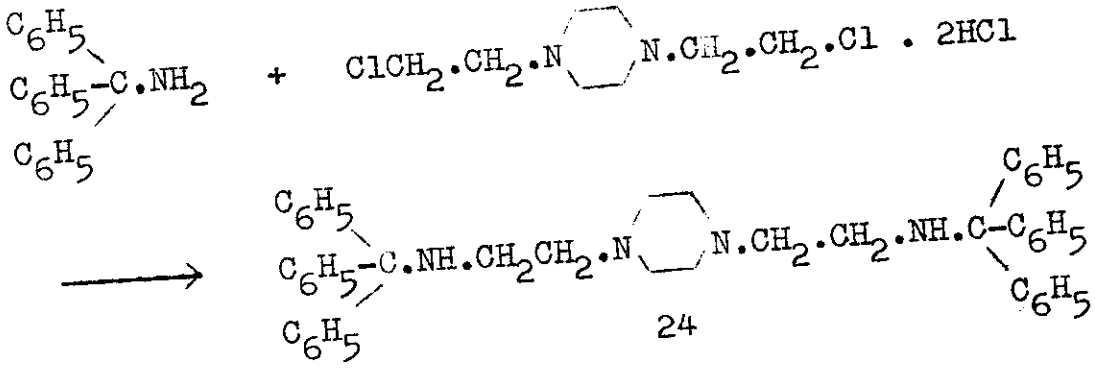
Attempted reaction of tritylisothiocyanate with aromatic and heterocyclic amines, such as o-toludine,

m-toludine, p-toludine and 3-aminopyridine did not give the respective thiourea derivatives. It seems that these amines did not enter into reaction with tritylisothiocyanate, like other amines, since attempted crystallisation of the reaction mixture from methanol, gave in all cases trityl-methyl ether (23), m.p. found identical with authentic sample prepared according to Bacon procedures[169,170].



23

The reaction of tritylamine with bis(β-chloroethyl) piperazine dihydrochloride[171-173], in methanol at refluxing temperature, for 15 hr., furnished the hitherto unreported bis(β-tritylaminoethyl)piperazine (24), m.p. 91° (60% yield).

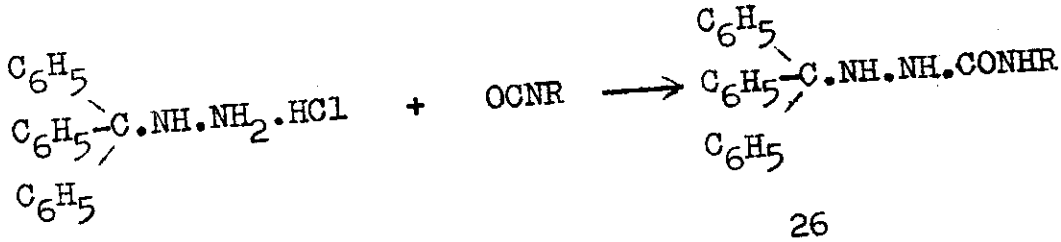


24

The IR spectrum of this compound (KBr) (Fig. 6) showed a broad band at 3300 cm^{-1} (NH).

Synthesis of Tritylsemicarbazides (26a,b):

The tritylsemicarbazides 26a,b have been prepared by reaction of tritylhydrazine hydrochloride (25), obtained from trityl chloride and hydrazine hydrate in dry ether[174], with the phenyl and cyclohexylisocyanates respectively. The reaction was conducted according to a procedure described by Petersen[175]. The semicarbazide 26a, m.p. 240°, and 26b, m.p. 236°, were obtained in 50% and 60% yields respectively. They showed in the IR (KBr) (Fig 7) absorption



25

26

26a, R= C_6H_5 *

b, R= C_6H_{11}

bands at 3260-3270 cm^{-1} and 1620 cm^{-1}, respectively.

* This compound was prepered using other procedure by J. Dennstedt, Ann., 452, 27 (1927).

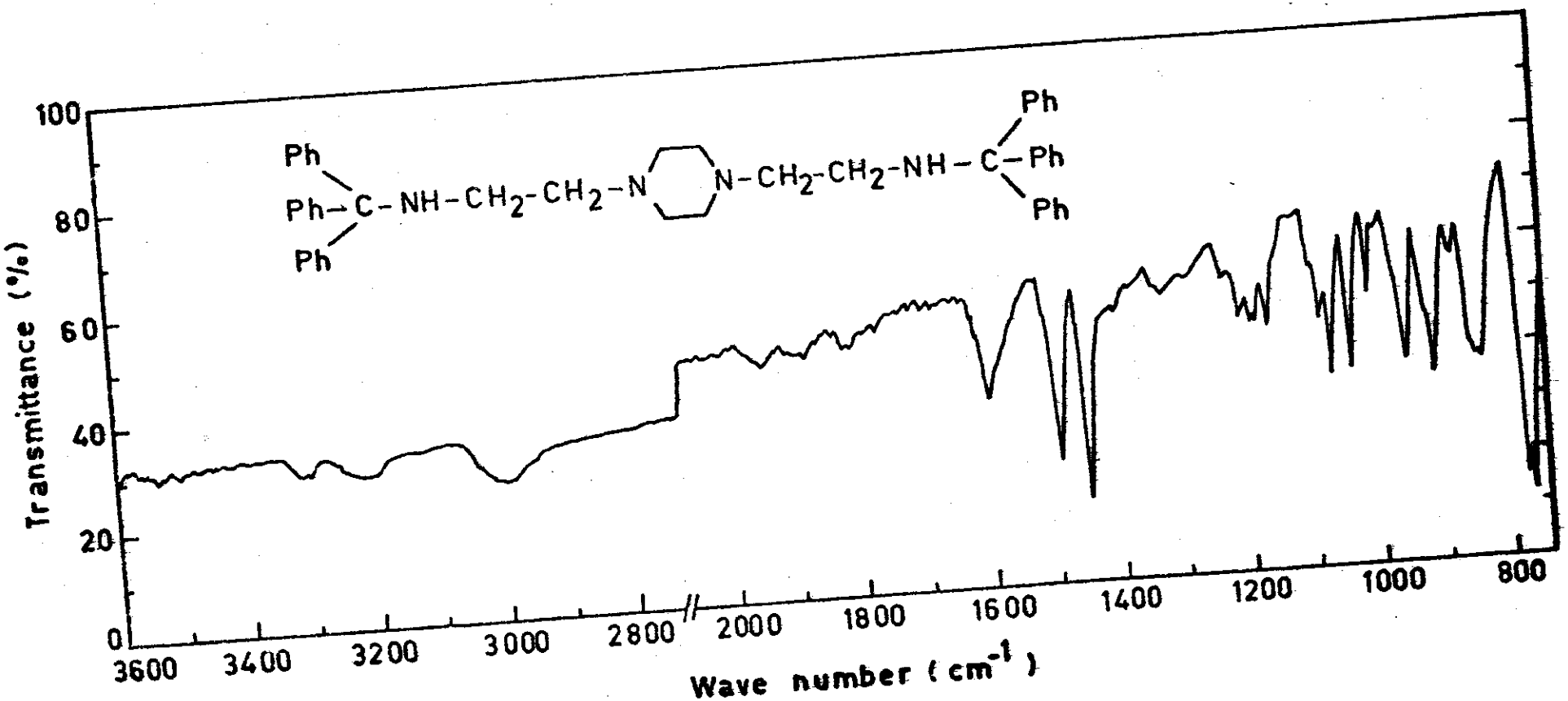

Ph
Ph–C–NH–CH2–CH2–N
Ph
N–CH2–CH2–NH–C–Ph
Ph
Ph
Transmittance (%)
100
80
60
40
20
0
3600
3400
3200
3000
2800
2000
1800
1600
1400
1200
1000
800
Wave number (cm-1)

Fig. (6)

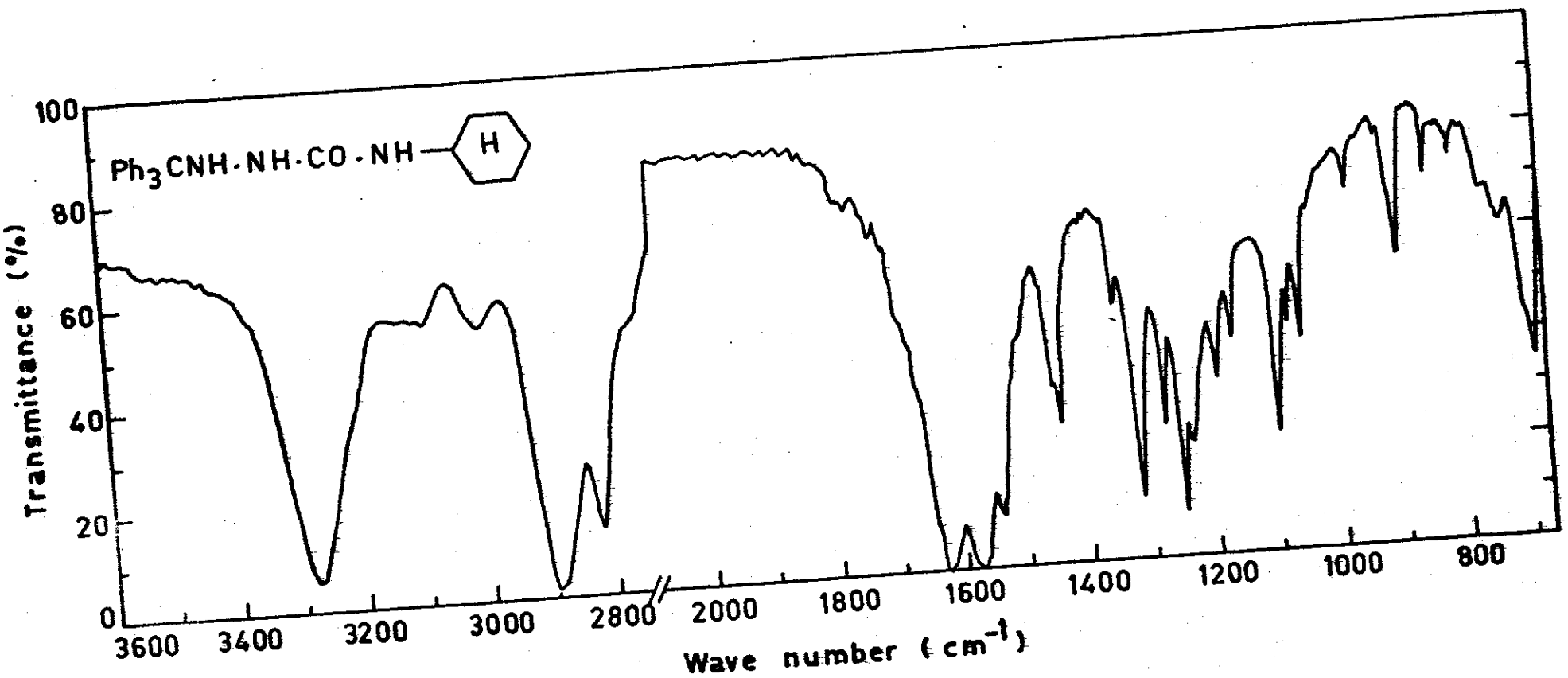
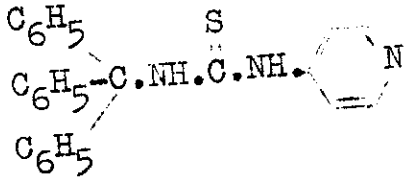

Ph3CNH-NH-CO-NH
H
Transmittance (%)
100
80
60
40
20
0
3600
3400
3200
3000
2800
2000
1800
1600
1400
1200
1000
800
Wave number (cm-1)

Fig. (7)

Biological evaluation of these compounds, for potential molluscicidal activity, revealed that all compounds are inactive with the exception of compound 19i, namely, N-trityl-N'-4-pyridylthiourea. It showed a 100% mortality for the fresh water snails, Bulinus truncatus and Biomphalaria alexandrina at concentration amounting to 1 and 1.5 ppm, respectively.

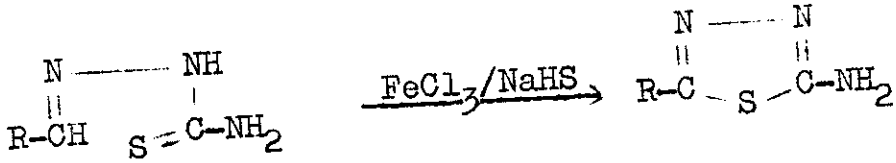


(19i)

These results indicates that the molluscicidal activity resides in the pyridine moiety of the molecule. It was not possible to evaluate the other position of substitution in the pyridine ring, since, the 2- and 3-substituted analogues of 19i could not be prepared by this method (cf. page 44).

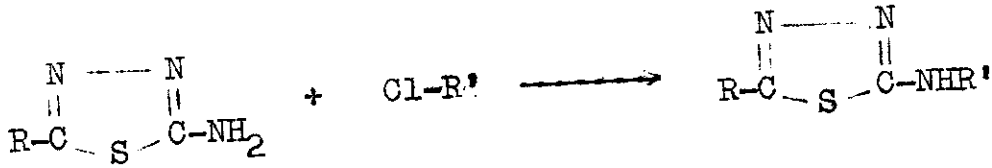
1,3,4-Thiadiazole Derivatives (28a-d):

The thiadiazole derivatives (28a;d) have been synthesised by condensation of 2-amino-5-substitutedthiadiazoles (27), obtained by oxidative cyclization of the respective thiosemicarbazone with ferric chloride, in the presence of sodium hydrogen sulphide[175], with the respective chloride.



27

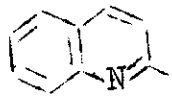
With trityl chloride, 2-amino-5-(α-furyl)thiadiazole derivative was obtained.

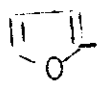
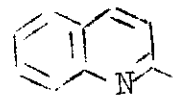


28

28a, R=  ;R'= CC_6H_5 (C_6H_5, C_6H_5)

b, R=  ;R'= CC_6H_5 (C_6H_5, C_6H_5)

28c, R=  ; R' = 

d, R=  ; R' = 

Physical data and percentage yields of compounds 28a–d are listed in Table II. Compounds 28b–d showed in the IR (KBr) (fig. 8-10) absorption bands at 3320-3315 cm^{-1} corresponding to the NH group.

Table II.

Compound	Yield %	M.p.°
28a	85	218
b	52	210
c	71	258
d	65	240

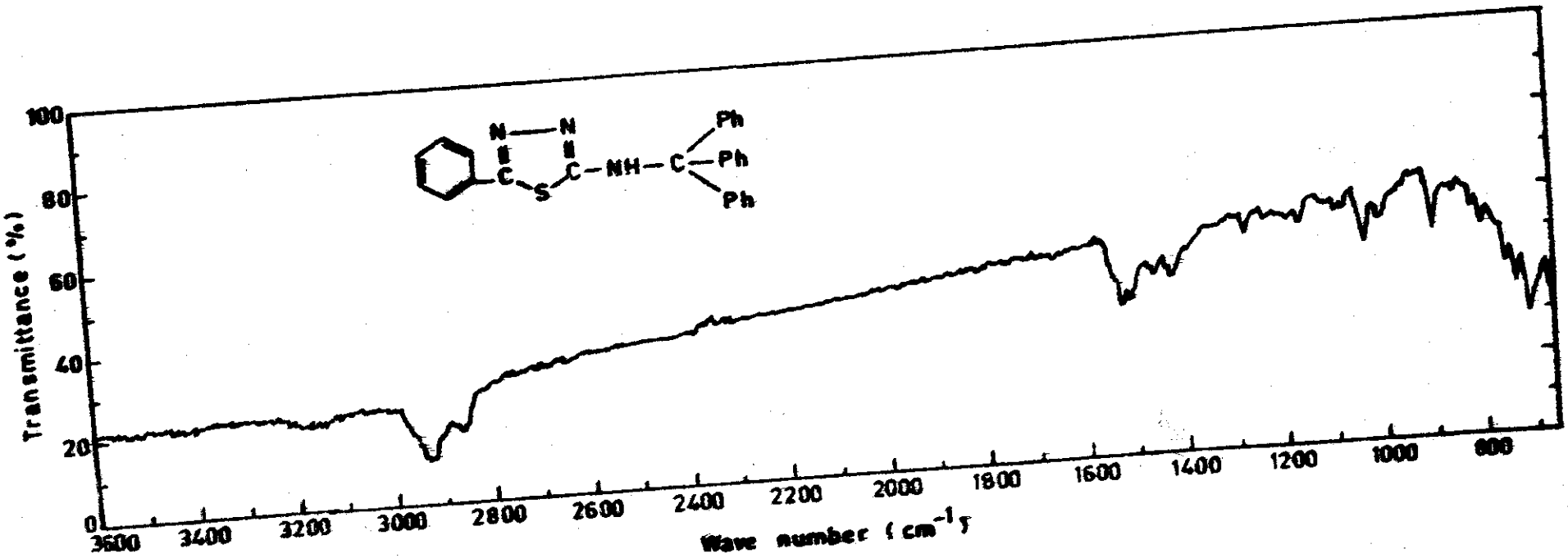

Transmittance (%)
100
80
60
40
20
0
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wave number (cm⁻¹)
N—N
C
S
C—NH—C
Ph
Ph
Ph

Fig. (8)

The NMR spectrum ($CDCl_3$) of compound 28b (Fig 11) as an example of this series, showed the following:
a broad band corresponding to 20 aromatic protons at 2.70 τ and a broad singlet of one proton (NH) at 1.17 τ .

Biological screening for molluscicidal activity of thiadiazoles 28a-d against Biomphalaria alexandrina and Bulinus trancatus showed an LC_{50} more than 250 ppm.

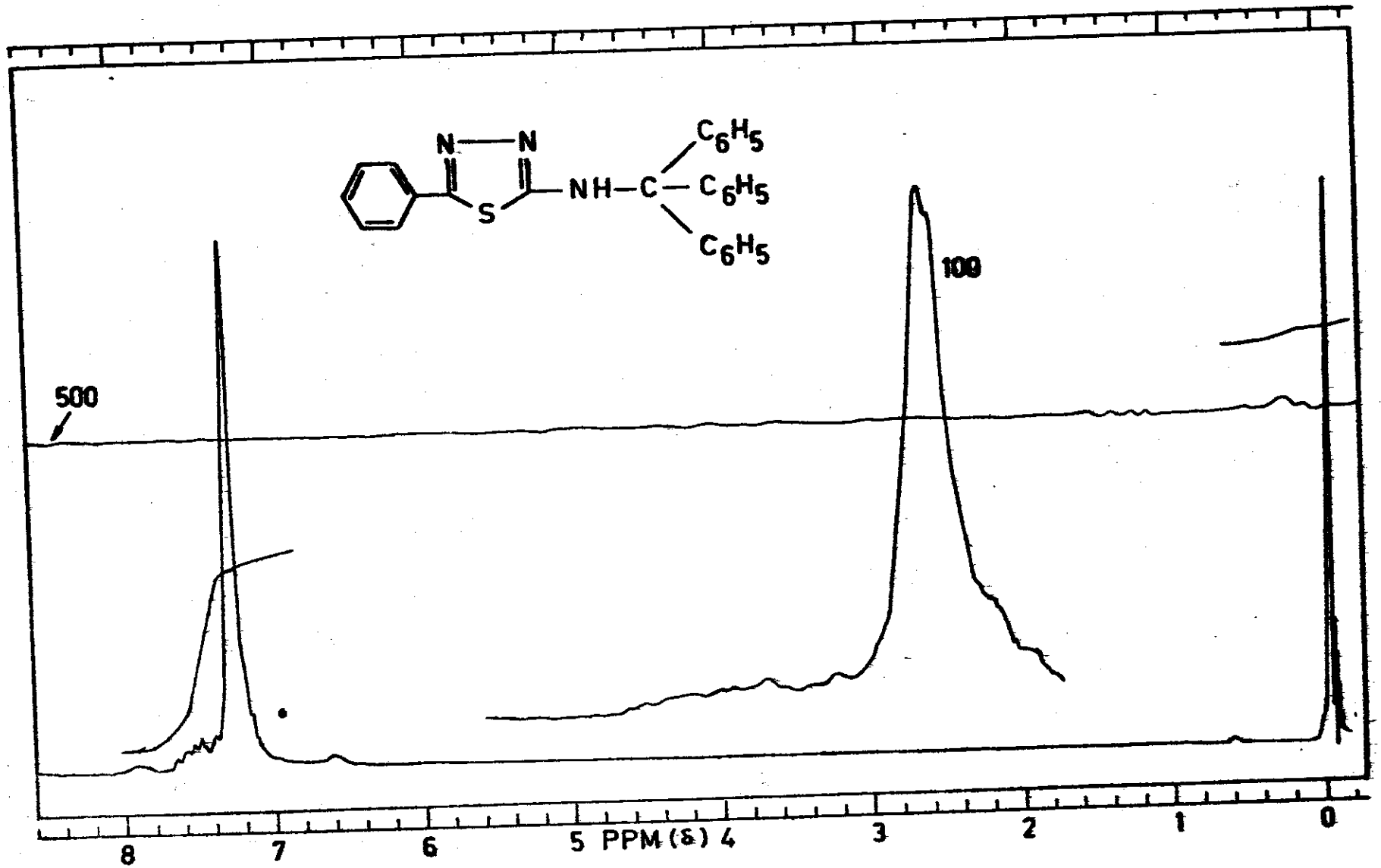


Fig. (11)