conditioned for several hours in pyridine; sample, about a milliequivalent; delivery rate: 1 ml/min with vigorous stirring.

Colorimetric tests: the well known colored reaction which takes place between ferric ions and hydroxamic function in acidic medium was adopted; for the iron solution 10 g of $Fe(ClO_4)_3 \cdot 9H_2O$ was dissolved in 95% ethyl alcohol into a 1 l. volumetric flask cautiously adding 250 ml of 70% perchloric acid and finally diluting with ethyl alcohol. Procedure: pipet a carefully measured volume of an hydroxamic acid solution (1–10 mmol) into a 25-ml volumetric flask. Add 5 ml of the iron perchlorate alcoholic solution and dilute with ethyl alcohol. Measure the absorbance at 520 mμ against the reagent blank. The concentration of hydroxamic acid may be deduced from a standard calibration curve.

For the *solubility* test saturated solutions of hydroxamic acids in different solvents were put in a thermostat at 26 °C for 2 h into glass tubes. On the centrifuged solution the amount of hydroxamic acid was determined by iron colorimetry.

The *thermal stability* was determined as follows: 250 μl of a 0.1 M solution of hydroxamic acid in chloroform was put into ten 25-ml volumetric flasks. After evaporation of chloroform by vacuum, the flasks were put into a thermostatic oven. At regular intervals the remaining hydroxamic acid was determined by iron colorimetry in order to control the variation of hydroxamic acid concentration as a function of the contact time.

The *chemical stability* was determined under different conditions. (a) In the same phase with 10 M $HClO_4$ in CH_3COOH at 50 °C: 0.1 M solutions of hydroxamic acids in 10 M $HClO_4$ in CH_3COOH were put into a thermostatic oven at 50 °C. At regular intervals the remaining hydroxamic acid was determined by iron colorimetry. (b) In the same phase in HNO_3, $HClO_4$, and HCl aqueous solutions: aqueous solutions contained hydroxamic acid (0.1 M) were maintained at 22 °C in glass tubes. At regular intervals colorimetric tests for hydroxamic acids were performed. (c) With HNO_3, $HClO_4$, and HCl in two phases: 20 ml of 0.1 M hydroxamic acid solution in chloroform were mechanically shaken with an equal volume of various acidic solutions in glass tubes. At regular intervals aliquots of the organic phases were submitted to colorimetric analysis in order to control the variation of hydroxamic acid concentration as a function of the contact time.

In all tests, urea (0.01 M) was added to HNO_3 to destroy nitrous acid. For *the extraction of* Fe^{3+} several 25-ml plastic stoppered tubes containing 10 ml of 2 M HNO_3, 10 ml of 0.1 M tributylacetohydroxamic acid chloroformic solution, and 250 μl of 0.01 M ferric nitrate aqueous solution were mechanically shaken. At regular intervals the optical density at 440 mμ of every solution was read against a reference of a chloroformic solution of 0.1 M hydroxamic acid equilibrated with the same volume of 2 M HNO_3.

The *extraction coefficients of* ^{59}Fe *and of* ^{239}Pu were determined as follow: 1 ml of 1 M HNO_3 (treated with urea), 2 ml of a 0.01 M hydroxamic acid choloformic solution and 250 μl of a 1 M nitric solution, containing ^{59}Fe and ^{239}Pu as tracers, were introduced in a plastic stoppered tube. The two phases were separated after 15 min of mechanical shaking and centrifugation. From every phase samples were prepared for α solid counting for ^{239}Pu and for liquid γ counting for ^{59}Fe (250/nl).

For α counting a Zn scintillation detector and for γ counting a NaI well detector were used.

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Received for review December 23, 1975. Accepted May 28, 1976.

Potential Antituberculous Agents. 3. *N*-Aryl-*N'*-2-(4-phenyl-5-arylazothiazolyl)thiocarbamides

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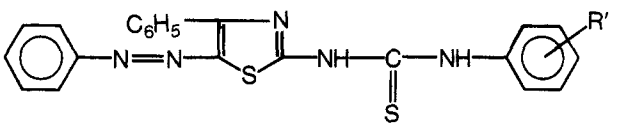
Various *N*-aryl-*N'*-2-(4-phenyl-5-arylazothiazolyl)thiocarbamides have been synthesized by the condensation of corresponding 2-amino-4-phenyl-5-arylazothiazoles with different arylisothiocyanates. The intermediates required in these syntheses were prepared according to the methods given in the literature.

There has been a growing interest, during the last few years, in the synthesis and biological evaluation of compounds containing the N*–N*–S* or O*–N*–S* tridentate ligand system (*3, 6–9*) or arylazo grouping (*10, 12*). This interest stems mainly from certain interesting antituberculous activities of disubstituted thiocarbamides (*1, 11*). As a part of a general study directed towards the development of antituberculous agents, the above mentioned rationale led to the examination of the synthesis and biological properties of *N*-aryl-*N'*-2-(4-phenyl-5-arylazothiazolyl)thiocarbamides having N*–N*–S* ligand and arylazo grouping and a modified azomethine linkage. Hopefully these potential antituberculous agents might afford compounds that would be less toxic to normal cells and have a better chemotherapeutic index. These compounds have been submitted for biological screening and the results will be reported elsewhere.

The present communication deals with the syntheses of *N*-aryl-*N'*-2-(4-phenyl-5-phenylazothiazolyl)-, *N*-aryl-*N'*-2-(4-phenyl-5-*o*-tolylazothiazolyl)-, *N*-aryl-*N'*-2-(4-phenyl-5-*m*-tolylazothiazolyl)-, and *N*-aryl-*N'*-2-(4-phenyl-5-*p*-tolylazothiazolyl)thiocarbamides by the condensation of corresponding 2-amino-4-phenyl-5-arylazothiazoles (II) with appropriate arylisothiocyanates.

The precursor 2-amino-4-phenylthiazole (I) was obtained by the condensation of acetophenone and thiourea in the presence

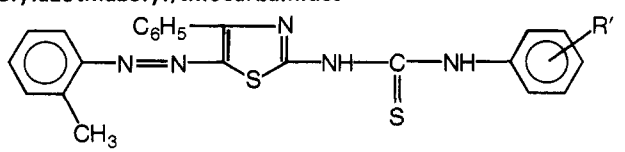
Table I. *N*-Aryl-*N'*-2-(4-phenyl-5-phenylazothiazolyl)thiocarbamides[a]



No.	R'	Mp, °C	% yield	Formula
1	H	243	75	$C_{22}H_{17}N_5S_2$
2	2-CH_3	285	80	$C_{23}H_{19}N_5S_2$
3	3-CH_3	255	74	$C_{23}N_{19}N_5S_2$
4	4-CH_3	195	82	$C_{23}N_{19}N_5S_2$
5	2-OCH_3	210	74	$C_{23}H_{19}N_5OS_2$
6	4-OCH_3	215	76	$C_{23}H_{19}N_5OS_2$
7	2-Cl	231	78	$C_{22}H_{16}ClN_5S_2$
8	3-Cl	199	72	$C_{22}H_{16}ClN_5S_2$
9	4-Cl	225	78	$C_{22}H_{16}ClN_5S_2$
10	2-OC_2H_5	208	75	$C_{24}H_{21}N_5OS_2$

[a] All of these compounds gave elemental analysis (C, H, N, S) within ±0.30 of the calculated values.

Table II. *N*-Aryl-*N'*-2-(4-phenyl-5-*o*-tolylazothiazolyl)thiocarbamides[a]



No.	R'	Mp, °C	% yield	Formula
1	H	215	78	$C_{23}H_{19}N_5S_2$
2	2-CH_3	192	72	$C_{24}H_{21}N_5S_2$
3	3-CH_3	195	80	$C_{24}H_{21}N_5S_2$
4	4-CH_3	197	75	$C_{24}H_{21}N_5S_2$
5	2-OCH_3	205	82	$C_{24}H_{21}N_5OS_2$
6	4-OCH_3	217	76	$C_{24}H_{21}N_5OS_2$
7	2-Cl	212	84	$C_{23}H_{18}ClN_5S_2$
8	3-Cl	200	72	$C_{23}H_{18}ClN_5S_2$
9	4-Cl	203	74	$C_{23}H_{18}ClN_5S_2$
10	2-OC_2H_5	209	70	$C_{25}H_{23}N_5OS_2$

[a] All of these compounds gave elemental analysis (C, H, N, S) within ±0.30 of the calculated values.

of iodine (*5*). The arylazo group at C-5 has been introduced by the coupling of different diazonium salts with I.

On boiling equimolar quantities of arylisothiocyanates (*4*) and II in benzene on a steam bath, high yields of the corresponding *N*-aryl-*N'*-2-(4-phenyl-5-phenylazothiazolyl)thiocarbamides (Table I) and *N*-aryl-*N'*-2-(4-phenyl-5-(*o,m,p*-tolyl)azothiazolyl)-thiocarbamides (Tables II, III, and IV) were obtained. The purification was achieved by recrystallization with DMF–ethanol (1:1).

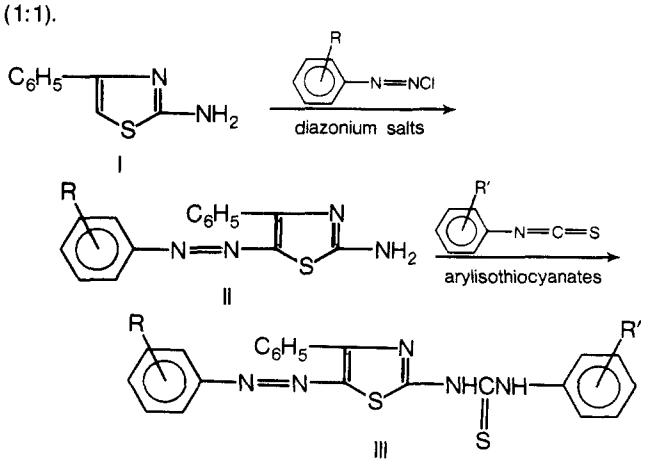
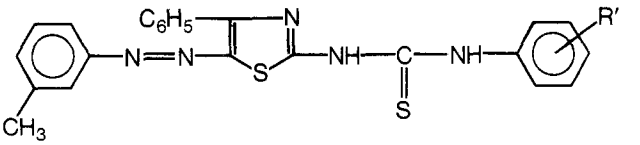


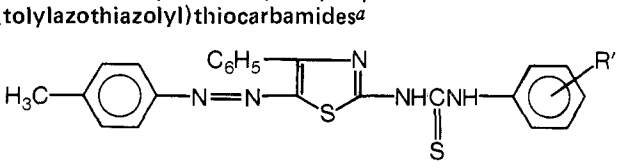
Table III. *N*-Aryl-*N'*-2-(4-phenyl-5-*m*-tolylazothiazolyl)thiocarbamides[a]



No.	R'	Mp, °C	% yield	Formula
1	H	232	85	$C_{23}H_{19}N_5S_2$
2	2-CH_3	214	82	$C_{24}H_{21}N_5S_2$
3	3-CH_3	209	80	$C_{24}H_{21}N_5S_2$
4	4-CH_3	227	84	$C_{24}H_{21}N_5S_2$
5	2-OCH_3	210	78	$C_{24}H_{21}N_5OS_2$
6	4-OCH_3	215	70	$C_{24}H_{21}N_5OS_2$
7	2-Cl	237	75	$C_{23}H_{18}ClN_5S_2$
8	3-Cl	220	78	$C_{23}H_{18}ClN_5S_2$
9	4-Cl	217	81	$C_{23}H_{18}ClN_5S_2$
10	2-OC_2H_5	213	80	$C_{25}H_{23}ClN_5S_2$

[a] All of these compounds gave elemental analysis (C, H, N, S) within ±0.30 of the calculated values.

Table IV. *N*-Aryl-*N'*-2-(4-phenyl-5-*p*-(tolylazothiazolyl)thiocarbamides[a]



No.	R'	Mp, °C	% yield	Formula
1	H	220	80	$C_{23}H_{19}N_5S_2$
2	2-CH_3	197	75	$C_{24}H_{21}N_5S_2$
3	3-CH_3	190	82	$C_{24}H_{21}N_5S_2$
4	4-CH_3	195	78	$C_{24}H_{21}N_5S_2$
5	2-OCH_3	212	72	$C_{24}N_{21}N_5OS_2$
6	4-OCH_3	217	74	$C_{24}H_{21}N_5OS_2$
7	2-Cl	222	70	$C_{23}H_{18}ClN_5S_2$
8	3-Cl	199	75	$C_{23}H_{18}ClN_5S_2$
9	4-Cl	205	78	$C_{23}H_{18}ClN_5S_2$
10	2-OC_2H_5	219	82	$C_{25}H_{23}N_5OS_2$

[a] All of these compounds gave elemental analysis (C, H, N, S) within ±0.30 of the calculated values.

where, R = H, 2-CH_3, 3-CH_3, or 4-CH_3 and R' = H, 2-CH_3, 3-CH_3, 4-CH_3, 2-OCH_3, 4-OCH_3, 2-Cl, 3-Cl, 4-Cl, 2-OC_2H_5, etc.

Experimental Section

Melting points were determined with a Kofler hot stage apparatus and are uncorrected.

2-Amino-4-phenylthiazole. It has been prepared according to the method given in the literature (*5*).

2-Amino-4-phenyl-5-phenylazothiazole. Sodium nitrite (1.4 g, 0.02 mol) dissolved in water (25 ml) was gradually added to a well-cooled solution of aniline (1.85 g, 0.02 mol) in 3 N HCl (2.5 ml). The diazonium salt solution was filtered to a cold suspension of 2-amino-4-phenylthiazole (3.52 g, 0.02 mol) and sodium acetate (5 g) in ethanol (50 ml). After 2 h, 2-amino-4-phenyl-5-phenylazothiazole was filtered and washed several times with water. It was recrystallized as red needles from a DMF–ethanol mixture (1:1), yield 4.5 g, 80%, mp 192 °C (lit. (*2*) mp 195 °C).

2-Amino-4-phenyl-5-(*o,m,p*)-tolylazothiazoles were prepared by adopting a similar procedure.

N-Phenyl-N'-2(4-phenyl-5-phenylazothiazolyl)thiocarbamide. A mixture of phenylisothiocyanate (1.35 g, 0.01 mol) and 2-amino-4-phenyl-5-phenylazothiazole (2.80 g, 0.01 mol) in benzene (15 ml) was refluxed for 6–8 h on a steam bath. The

solvent was removed under reduced pressure and the residue was repeatedly washed with petroleum ether (bp 40–60 °C). The crude thiocarbamide thus obtained was crystallized from a DMF–ethanol mixture (1:1) as deep red needles, yield 3.1 g, 75%, mp 243 °C.

Similarly other *N*-aryl-*N'*-2-(4-phenyl-5-phenylazothiazolyl)-thiocarbamides were prepared by the condensation of 2-amino-4-phenyl-5-phenylazothiazole and different arylisothiocyanates (Table I).

Using a similar procedure as above several *N*-aryl-*N'*-2-(4-phenyl-5-(*o,m,p*-tolyl)azothiazolyl)thiocarbamides (Tables II, III, and IV) were obtained.

Acknowledgment

We wish to thank Professor K. N. Udupa, Director, Institute of Medical Sciences, Banaras Hindu University, Varanasi, for providing necessary facilities for carrying out the work.

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Received for review February 24, 1976. Accepted June 24, 1976. The authors (J.S.U. and R.D.S.) are thankful to the Council of Scientific and Industrial Research, New Delhi (India), for the awards of research fellowships.

Correction

For the paper, "Liquid–Vapor Equilibria at 250.00 K for Systems Containing Methane, Ethane, and Carbon Dioxide," by Juan Davalos, Wayne R. Anderson, Robert E. Phelps, and Arthur J. Kidnay (*J. Chem. Eng. Data*, **21**, 81 (1976)), an error was made in transcribing the data from the laboratory notebooks to Table IV. The first five lines of Table IV should read as shown below. The error is also reflected in the respective points of Figure 4.

System press, atm	Y_{CH_4}	$Y_{C_2H_6}$	Y_{CO_2}	X_{CH_4}	$X_{C_2H_6}$	X_{CO_2}	K_{CH_4}	$K_{C_2H_6}$	K_{CO_2}
21.00	0.0265	0.4432	0.5303	—	—	—	—	—	—
	—	—	—	0.0033	0.4512	0.5455	—	—	—
	0.1728	0.5700	0.2572	—	—	—	—	—	—
	0.1602	0.5615	0.2783	0.0352	0.7898	0.1750	4.551	0.1711	1.5903
	0.2500	0.6200	0.1300	—	—	—	—	—	—