Table I. IR, Visible, and ^{1}H NMR Spectral Data for the Dyes[a]

R	X	ν(C=O)	ν(C=N) + ν(C=C)	λ, nm (ε)	^{1}H NMR chemical shifts (multiplicity, no. of protons)
CH_3CH_2	H	1680	1580	510 (17 200)	1.4 (t, 6), 2.10 (s, 6), 3.4 (m, 4), 7.4 (m, 10)
CH_3CH_2	CH_3	1688	1570	515 (16 000)	1.4 (t, 6), 2.4 (s, 6), 2.23 (s, 6), 3.4 (m, 4), 4.2 (q, 4), 7.1 (m, 8)
CH_3CH_2	OCH_3	1680	1575	510 (16 300)	1.4 (t, 6), 2.4 (s, 6), 3.4 (m, 4), 3.70 (s, 6), 4.30 (q, 4), 7.25 (q, 8)
CH_3CH_2	NO_2	1700	1595	534 (18 700)	1.40 (t, 6), 2.51 (s, 6), 3.5 (m, 4), 4.40 (q, 4), 7.62 (q, 8)
CH_3	NO_2	1700	1590	530 (19 100)	2.50 (s, 6), 3.4 (m, 4), 3.80 (s, 6), 7.00 (q, 8)

[a] Chemical shift represented in ppm, δ units. Key: s = singlet; t = triplet; q = quartet; m = multiplet.

the phenylazo derivatives of tricyclic tetradentate ligands (*2–4*). These molecules incorporate metal ions in their easily accessible cavities forming intensily colored stable pigments. We have found that similar metal complexes could be prepared from the phenylazo derivatives of the imine derived from β-ketoesters and ethylenediamine. The preparative route discussed in this report replaces the general method we adopted before, namely, the azo coupling reactions of the coordinated ligands by a simple recombination of the phenylazo derived ligands and the metal ions.

The preparation of the phenylazo derivatives of the imines derived from β-ketoesters and ethylenediamine was done by the procedure discussed below: 50 mmol of the imine was dissolved in 50 mL of 95% ethanol to which an excess of an aqueous saturated solution of sodium acetate was added. This solution was kept cooled at 0 °C. To this an aqueous solution of arenediazonium chloride (prepared from 100 mmol of an aromatic amine and neutralized with sodium acetate) was added slowly with gentle stirring. The reaction mixture was stirred at 0–5 °C till the coupling reaction was complete (10–15 min). The product formed was precipitated by adding about 100 mL of water. The precipitate was filtered, washed with water, and dried under vacuum. It was recrystallized from methanol.

A solution of 2 mmol of the ligand in 30 mL of methanol was stirred magnetically with 2 mmol of nickel(II) acetate in the same solvent for 2 h. A deep red dye was precipitated gradually. This was filtered and washed with a 1:1 water/methanol mixture and recrystallized from a 1:1 methanol/chloroform mixture. Yields were always more than 80% on the basis of the ligand.

All the isolated compounds gave elemental analysis for C, H, N, and Ni which were in good agreement with the represented structure. They are freely soluble in organic solvents but insoluble in aqueous media. They are nonelectrolytes in solution whereas magnetic susceptibility studies show them to be diamagnetic. The structure of these dyes was confirmed by IR, ^{1}H NMR, and electronic spectroscopic methods (Table I). In the IR spectra, all the compounds showed two strong absorption bands in the region 1550–1750 cm^{-1}, arising from the C=O, C=N, and C=C stretching vibrations (*2*, *3*).

The ^{1}H NMR spectra of these complexes (in $CDCl_3$) were consistent with the assigned structure. Detailed ^{1}H NMR assignments of the different protons in related compounds are discussed previously (*2–4*).

All the nickel compounds reported here were found to impart a reddish yellow color to cellulose which was reasonably stable toward light. The recombination method adopted here for the synthesis of metal dyes presents a wide choice of testing the properties of pigments with different azo functionalities and metal ions.

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Literature Cited

(1) R. Price in "The Chemistry of Synthetic Dyes", K. Venkataraman, Ed., Vol 3, Academic Press, New York, 1970.
(2) K. P. Balakrishnan and V. Krishnan, *Synth. React. Inorg. Met.-Org. Chem.*, **8**, 227 (1978); **9**, 109 (1979).
(3) K. P. Balakrishnan and V. Krishnan, *J. Inorg. Nucl. Chem.*, **41**, 37 (1979).
(4) K. P. Balakrishnan and V. Krishnan, *Transition Met. Chem.*, **3**, 337 (1978).

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Synthesis of *N*-Aryl-*N'*-2-(4-*p*-anisyl-5-arylazothiazolyl)thiocarbamides

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Different *N*-aryl-*N'*-2-(4-*p*-anisyl-5-arylazothiazolyl)thiocarbamides have been synthesized by the condensation of the corresponding 2-amino-4-*p*-anisyl-5-arylazothiazoles and appropriate aryl isothiocyanates. The intermediates required in these syntheses were prepared according to the methods reported in the literature.

In view of the little amount of work done on 5-arylazothiazoles and related compounds, and also in the pursuit of new potential antineoplastic drugs,[1-7] it was considered worthwhile to synthesize some title compounds and to study their antitumor properties. These compounds have been submitted for biological screening and results will be reported elsewhere.

The present communication deals with the syntheses of *N*-aryl-*N'*-2-(4-*p*-anisyl-5-phenylazothiazolyl)-, *N*-aryl-*N'*-2-(4-

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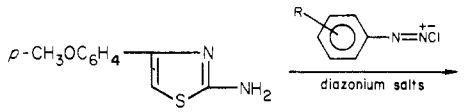
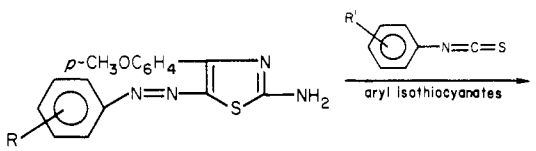
p-anisyl-5-*o*-tolylazothiazolyl)-, and *N*-aryl-*N'*-2-(4-*p*-anisyl-5-*o*-anisylazothiazolyl)thiocarbamides by the condensation of the corresponding 2-amino-4-*p*-anisyl-5-arylazothiazoles (II) with the appropriate aryl isothiocyanates.



I



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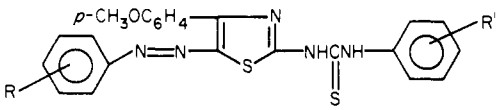


III

where R = H (I), R = 2-CH_3 (II), and R = 2-OCH_3 (III) and R' = H, 2-CH_3, 3-CH_3, 4-CH_3, 2-OCH_3, 2-Cl, 3-Cl, 4-Cl, 2-OC_2H_5, etc.

The precursor 2-amino-4-*p*-anisylthiazole (I) was obtained by the condensation of *p*-methoxyacetophenone and thiourea in the presence of iodine.[8] The arylazo group at position 5 has been introduced by the coupling effect as reported earlier.[9]

Experimental Section

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

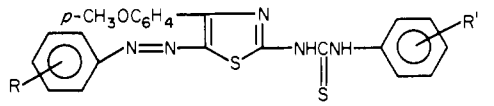
2-Amino-4-p-anisylthiazole. It has been prepared according to the method described in the literature.[8]

2-Amino-4-p-anisyl-5-arylazothiazoles (II). These were prepared by adopting a procedure already described.[9]

N-Phenyl-N'-2-(4-p-anisyl-5-phenylazothiazolyl)thiocarbamide. A mixture of phenyl isothiocyanate (1.35 g, 0.01 mol) and 2-amino-4-*p*-anisyl-5-phenylazothiazole (3.1 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 (1:1) mixture as deep red needles: yield 3.6 g (82%), mp 230 °C.

Similarly other *N*-aryl-*N'*-2-(4-*p*-anisyl-5-phenylazothiazolyl)thiocarbamides were prepared by the condensation of 2-amino-4-*p*-anisyl-5-phenylazothiazole with different aryl isothiocyanates (Table I).

Table I. *N*-Aryl-*N'*-2-(4-*p*-anisyl-5-arylazothiazolyl)-thiocarbamides[a]



R'	compd I (R = H) yield, %	compd I (R = H) mp, °C	compd II (R = 2-CH_3) yield, %	compd II (R = 2-CH_3) mp, °C	compd III (R = 2-OCH_3) yield, %	compd III (R = 2-OCH_3) mp, °C
H	82	230	78	255	80	214
2-CH_3	79	245	75	209	72	265
3-CH_3	75	239	70	291	70	254
4-CH_3	72	233	68	284	74	281
2-OCH_3	80	264	72	269	75	273
4-OCH_3	78	219	75	271	78	267
2-Cl	68	267	65	248	75	248
3-Cl	65	252	69	253	78	265
4-Cl	69	265	71	239	72	258
2-OC_2H_5	74	280	80	222	74	235

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

By use of a similar procedure as above, several *N*-aryl-*N'*-2-(4-*p*-anisyl-5-(*o*-tolyl and *o*-anisyl)azothiazolyl)thiocarbamides were prepared (Table I).

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Literature Cited

(1) Brockman, R. W.; Thomson, J. R.; Bell, M. J.; Skipper, H. E. *Cancer Res.* **1956**, *16*, 167.
(2) French, F. A.; Blanz, E. J., Jr. *Cancer Res.* **1963**, *23*, 9.
(3) French, F. A.; Blanz, E. J., Jr. *J. Med. Chem.* **1966**, *9*, 585.
(4) French, F. A.; Freedlander, B. L. *Cancer Res.* **1958**, *18*, 1920.
(5) French, F. A.; Freedlander, B. L. *Cancer Res.* **1960**, *20*, 505.
(6) Harmon, R. E.; Dutton, F. E.; Warren, H. D. *J. Med. Chem.* **1968**, *11*, 627.
(7) Modest, E. J.; Schlein, H. N.; Foley, G. E. *J. Pharm. Pharmacol.* **1957**, *9*, 68.
(8) Dodson, R. M.; King, L. C. *J. Am. Chem. Soc.* **1945**, *67*, 2242.
(9) Srivastava, P. K.; Upadhyaya, J. S.; Sharma, R. D. *J. Chem. Eng. Data*, **1976**, *21*, 508.
(10) Drains, F. B.; Brewstar, R. Q.; Olander, C. P. "Organic Synthesis", Collect Vol. 1; Wiley: New York, 1931; p 447.
(11) Beyer, H.; Walter, G. *Chem. Ber.* **1952**, *85*, 1077.

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