SYNTHESIS OF SOME SUBSTITUTED THIOUREAS

THIOUREA derivatives have attracted attention due to antitubercular[1], nematocidal[2] and fungicidal[3] activities, which are ascribed to the presence of N—C=S group. Many of these compounds are potential metal complexants and with a view to studying their complexing behaviour, 1, 4-phenylene-bis-, 4, 4'-biphenylene-bis-, 3, 3'-dimethoxyl-4, 4'-biphenylene-bis-, and N^1-N^3-benzyl allylthioureas have been synthesized for the first time and the structure of these compounds elucidated through a study of ir spectra.

Experimental

Materials : Benzidine, paraphenylenediamine, *o*-dianisidine, benzylamine, allylisothiocyanate and the solvents were of reagent grade.

Preparation : The substituted thioureas have been synthesized using the procedure adopted by Mandal[4]. Allyl isothiocyanate soution (0·2 M in 50 ml ethanol) was added dropwise to a solution of paraphenylenediamine (0·1 M in 50 ml ethanol), benzidine (0·1 M in 50 ml ethanol), *o*-dianisidine (0·1 M in 50 ml ethanol) or benzylamine (0·2 M in 80 ml ethanol). On refluxing the mixture for *ca* 1–3h (as necessary, in the different cases) reddish brown, dirty white and white solids were obtained for 1, 4-phenylene-bis-, 4, 4'-biphenylene-bis-, and 3, 3'-dimethoxyl-4, 4'-biphenylene-bis-allylthioureas respectively. N^1-N^3-benzylallylthiourea was obtained as a white solid on keeping the refluxed mixture at *ca* 5° overnight. The compounds were filtered, washed with ethanol and dried over calcium chloride under reduced pressure.

The compounds are insouble in water, ethanol, benzene, chloroform, tetrahydrofuran but soluble in acetone, dimethylformamide and dimethylsulphoxide. The purity of the compounds was checked by TLC. The compositions were obtained by elemental analysis (Table I).

TABLE I

Composition of the substituted thioureas

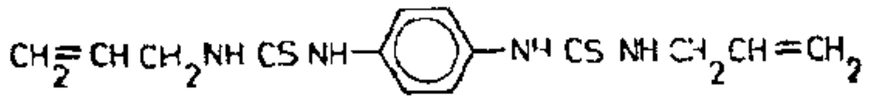
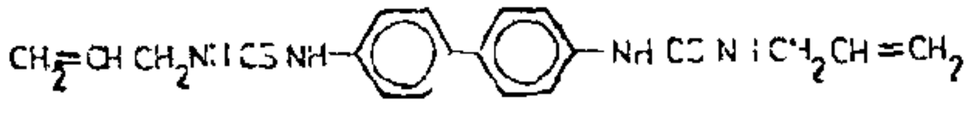
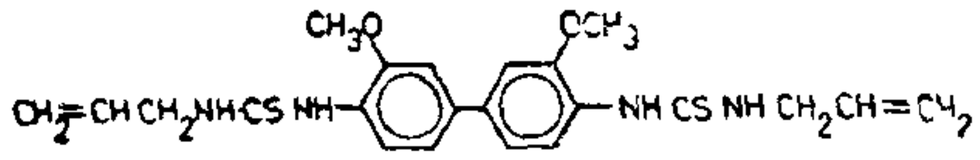
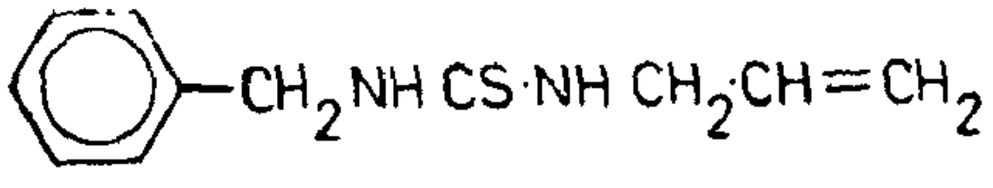
Compound	Yield %	Colour	Melting point	C% Calc. (found)	H% Calc. (found)	N% Calc. (found)
1, 4-phenylene-bis-(allylthiourea)	75	Reddish brown	210°	54·90 (54·63)	5·88 (6·02)	18·30 (18·17)
						
4, 4'-biphenylene-bis-(allylthiourea)	86	Dirty white	185°	62·83 (62·46)	5·76 (5·72)	14·48 (14·35)
						
3, 3'-dimethoxyl-4, 4'-biphenylene-bis-(allylthiourea)	85	White	222°	59·70 (59·45)	5·88 (5·82)	12·67 (12·58)
						
N^1-N^3-benzylallylthiourea	82	White	85°	64·04 (64·00)	6·80 (6·68)	13·59 (13·38)
						

TABLE II

Infra-red bonds (cm^{-1}) of 1, 4-*phenylene*-*bis*-(*allylthiourea*) (*PBAT*), 4, 4′-*biphenylene-bis*-(*allylthiourea*) (*BBAT*), 3, 3′-*dimethoxyl*-4, 4′-*biphenylene*-*bis*-(*allylthiourea*) (*DBBAT*) *and* N^1-N^3-*benzylallylthiourea* (*BAT*)

PBAT	BBAT	DBBAT	BAT	Band assignments
3240vs	3240vs	3310vs	3220s	N−H stretching
3090s	3030s	3020s	3040m	$CH = CH_2$ stretching
2940s	2940m	2960s	2950s	CH_2 stretching
1645vs	1640vs	1645vs	1640vs	C=C streching and S = C−N stretching
1550s	1550m	1540s	1530s	N−C−N stretching
1515m	1505m	1510m	1525m	N−H deformation (stretching)
1490s	1485s	1495s	1495s	N−C=S frequency
1450m	1460m	1455m	1450m	CH_2 deformation
1420w	1420w	1420w	1420w	C=S stretching
1400s	1390s	1400m	1395m	−C−N stretching of Ar–N type
1355	1385	1385	1390	NH−C=S stretching
1340	1350	1345	1340	
1250w	1240m	1260w	1240	C−N−H stretching
1220s	1225s	1210s	1200s	ring breathing + C−H deformation
1190s	1195m	1185m	1180s	
1115m	1140m	1140m	..	Absorption due to *o*- and *p*-substituted benzene ring
1075m	1055m	1055 m	..	
950	940	960	940	CH_2 wag

m = medium; s = strong; vs = very strong; w = weak.

Infra-red spectra : The ir spectra were recorded on a Perkin Elmer-577 infra-red spectrophotometer in the range 4000 to 400 cm^{-1} using KBr pellets. The main ir bands and their probable assignments are given in Table II. The presence of aromatic type structure is recognized by the presence of =C−H stretching[6], vibrations near 2960 cm^{-1} and C=C vibrations in the region 1645–1640 cm^{-1} in the infra-red spectra. The bands noted at 3310–3220 cm^{-1} correspond to N-H stretching[6], while C= S stretching[7] bands were noted at 1420 cm^{-1}. A strong and sharp band near 1400 cm^{-1} in all the ir spectra stands for C N stretching[8] of Ar–N type, and CH-N-R (R - aliphatic group) linkages[8] are expected from the ir bands near 1525 cm^{-1}. A very strong band near 3050 cm^{-1} confirms the presence of $-C=CH_2$[9] in ir spectra of all the substituted thioureas which is again confirmed by $-CH_2$ stretching[9] at 2980–2940 cm^{-1}, and $-CH_2$ deformation[9] at 1460–1450 cm^{-1} and CH_2 wag[9] at 960–940 cm^{-1}. The bands noted at 1140–1055 cm^{-1} in PBAT and BBAT are expected due to paresubstituted benzene ring absorption[10] while the bands at 1140 and 1055 cm^{-1} in ir spectra of PBAT show that the benzene ring is both *o*- and *p*-substituted[10]. The stretching frequencies due to N C -N[7], S−C−N[7] and C N- H[9] groups noted at 1515 1505 cm^{-1}, 1645-1640 cm^{-1} and 1240 1260 cm^{-1} respectively further support the structure.

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OCCURRENCE OF LEAD DEPOSITS IN THE JUTOGH FORMATION OF SIMLA HILLS, HIMACHAL PRADESH, INDIA

THIS communication puts on record the first report of occurrence of lead deposits (Galena) along with other sulphides in the Jutogh quartzites and metasemipelites exposed near Koti Ghat (31° 15′ 40″ N : 77° 23′ E) in Kumarsain Tehsil, Simla District, Himachal Pradesh, The area has previously been investigated by West[1] and recently in more detail by Srikantia and Sharma[2]. In the work done so far there is no report of mineralisation in the above-mentioned area.

During a detailed field mapping of the area along the Shali Thrust near Koti Ghat, the authors came across lead sulphide mineralisation. The occurrence is seen 100 m above the Shali Thrust in the Jutogh metamorphites. The samples from Koti Ghat show profuse development of galena with small amounts of chalcopyrite and pyrite. Galena is antimonial. The deposits occur as cavities and lenses up to 30 cm across. There is no basic intrusion in the area to suggest an igneous parentage for the sulphides. In such cases sulphides may have been deposited along with the rock in which they occur as found in the Daling Series at Rangpo, Sikkim by Sarkar and Bannerjee[3]. Later on, after the regional metamorphism, the rocks suffered thrusting and diaphthoresis during which the ore pockets have been disturbed. Mineralisation of chalcopyrite and pyrite has also been noticed in the Shali slate sequence of West (*op. cit.*) near Chamola (31° 18′ N : 77° 22′ 20″ E) and in Gauru Nala section just to the southeast of Kangar (31° 17′ 05″ N : 77° 21′ 45″ E).

The mineralisation is indicated by sulphurous smell given out by the rocks when broken. It was further confirmed by studying the recent cuttings and excavations being carried out by the Public Works Department for their project. It is too early to ascertain the economic potentials of these deposits. However, it is suspected that mineralisation continues perhaps along the bands into the hill as the quartzites dip into the hill at an angle of 35° in N 40° E.

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A NEW SPECIES OF *PHYLLOSTICTA* FROM INDIA

IN April, 1978, a leaf spotting coelomycete was collected on *Monstera deliciosa* Liebm, from North Gorakhpur Forest Division (U.P.). The present communication describes this collection as *Phyllosticta monsterae* sp. nov.

Phyllosticta monsterae sp. nov.

Maculae amphigenae, parvae, circulares vel irregulares, griseolae rufobrunneo-marginatae; pycnidia epiphylla, pauca vel multa, dipersa immersa, atrobrunnea, globosa vel subglobosa, crassitunicata, 50–90 μm diam.; ostiola distincta, singula, circularia, parva, ex hyphis obscurioribus crassitunicatis circumdata, 10–21·5 μm diam.; cellulae conidiferae a cellulis parietis interioris pycnicidici enatae, -elongatae, cylindricae, hyalinae; conidia solitaria, simplicia, hyalina, glabra, unicellularia, numerosa, plerumque plus minusve cylindrica, recta vel curvata, utrinque rotundata, tunica mucosa circumvallata ad apicem-