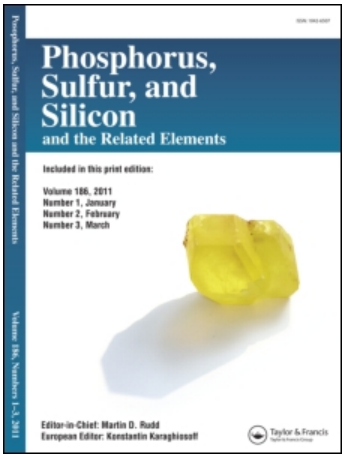

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

CHEMICAL INTERACTIONS BETWEEN TETRACYANOETHYLENE AND S-METHYLDITHIOCARBAZATE AS WELL AS AZOMETHINE DERIVATIVES

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To cite this Article Hassan, Alaa A.(1995) 'CHEMICAL INTERACTIONS BETWEEN TETRACYANOETHYLENE AND S-METHYLDITHIOCARBAZATE AS WELL AS AZOMETHINE DERIVATIVES', Phosphorus, Sulfur, and Silicon and the Related Elements, 101: 1, 189 — 196
To link to this Article: DOI: 10.1080/10426509508042516
URL: http://dx.doi.org/10.1080/10426509508042516

Phosphorus, Sulfur, and Silicon, 1995, Vol. 101, pp. 189–196
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CHEMICAL INTERACTIONS BETWEEN TETRACYANOETHYLENE AND S-METHYLDITHIOCARBAZATE AS WELL AS AZOMETHINE DERIVATIVES

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(Received September 26, 1994; in final form November 17, 1994)

The charge-transfer (CT) complexes of Schiff bases 2a–e derived from S-methyldithiocarbazate and tetracyanoethylene (TCNE) have been studied spectrophotometrically. S-methyldithiocarbazate 1 reacted with TCNE to yield 3-amino-4,5-dicyano-6-S-methyl-pyridazine 12 and 4,5-diamino-1,8-di-S-methylpyridazino[4,5-d]pyridazine 13 via CT-complexes, whereas 2a–e reacted with TCNE to afford 3-aryl-4-amino-5-cyano-6-S-methylpyridazines 22 and 3-aryl-5-S-methyl-1,2,4-thiadizaoles 16.

Key words: Schiff base, biological activity, methyldithiocarbazate, NMR spectra, IR spectra.

S-Methyldithiocarbazate and its derivatives 1 and 2 are considered as an interesting class of biologically active compounds.[1–4] A recent study indicated that S-methyldithiocarbazate has been utilized in the synthesis of several heterocyclic compounds such as amino- and arylazo-pyrazoles,[5–7] and unsymmetrical heterocyclic azines[8] as well as imidazotriazinethione.[9]

The chemical interactions between simple organic compounds (donors) and electron Π-acceptors to synthesize new heterocyclic compounds, were the target of our recent studies.[10–15] We recently reported that S-methyldithiocarbazate derivatives reacted with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to give thiadiazine, and bisazine as well as thidiazole derivatives via CT-complexation.[16] The aim of the present investigation is to study the behavior of S-methyldithiocarbazate and its derivatives 1 and 2a–e as electron donors towards TCNE as electron acceptor.

Table I contains the wavelengths of maximum absorption in the visible region attributable to neither component of the complex alone, but to a new molecular species. It is also apparent that, the λ_{max} values follow the order of decreasing basic character of the donors (OCH_3 > O—CH_2—O > CH_3 > H > Cl). Application of Job's[17] method for the continuous variation for the CT-complexes formed indicated 1:1 stoichiometry. The association constants (Kct) of formation and molar extinction coefficients (ε) of 1:1. CT-complexes studied (Table I) were determined by using Benesi-Hildebrand's method.[18] It is worth noting that the change in band intensities was slow to allow determination of the λ_{max} and (K_{ct}) values of the initially formed CT-complexes.

The transition energies (E) of the CT-complexes reported in Table I are another measure of the basic character of the electron donors 1a–c; and calculated according to the equation E[ev] = $h\nu_{max}$ for the complex.

TABLE I

Maximum absorption wavelengths λ_{max} [nm], association constants K [l mol^{-1}], molar extinction coefficients ε_{max} [l mol^{-1}] cm^{-1} and transition energies E[eV] of the CT-complexes of 2a-e with TCNE as well as ionization potentials i.p[e.v] of 2a–e in ethyl acetate at 15°C

Acceptor	Donor	λ_{max} [nm]	K_{ct} [l mol^{-1}]	ε_{max} [l.mol^{-1}cm^{-1}]	E [eV]	i.p. [eV]
TCNE	2a	482	3.02	182	2.57	8.63
TCNE	2b	525	4.10	122	2.36	8.35
TCNE	2c	548	5.03	286	2.26	8.22
TCNE	2d	sh (470)				
TCNE	2e	sh (530)				

The ionization potentials of the donors 1a–c were calculated from the frequencies of their complexes with TCNE using the following equation:

$$i.p[eV] = a + b\bar{\nu}cT$$

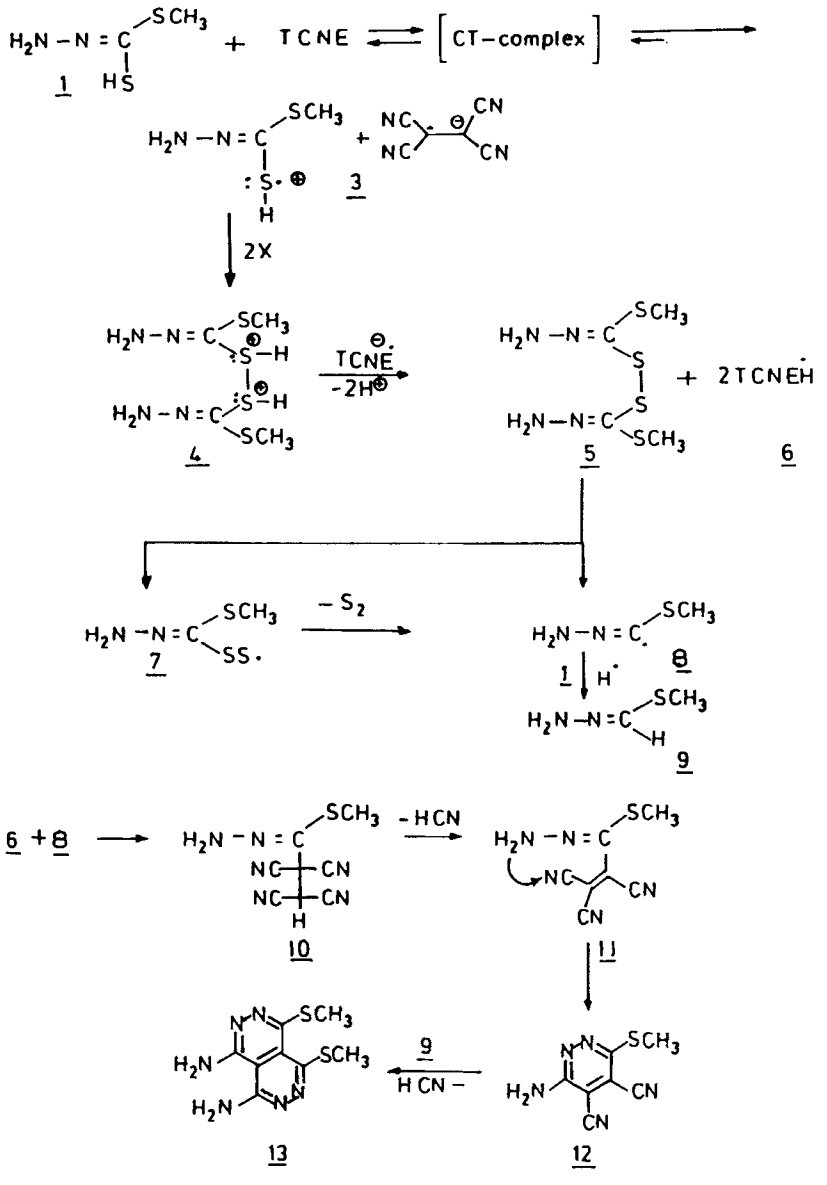
where a = 5.21 and b = 1650 are constants depending on the electron acceptor and their values are taken from Reference 19.

Mixing an ethyl acetate solution of 1 with twofold TCNE gave a green color with gradually disappeared to give a yellowish-brown color. This behavior may be explained as an initial formation of an unstable CT-complex, which is in equilibrium with the two components. As shown in the proposed mechanism illustrated in Scheme I, the CT-complex is followed by a complete electron transfer to form a radical ion pair 3. Recombination of the S-methyldithiocarbazate cation radical forms the dimer 4, which eliminates two protons by the TCNE anion radical to form the disulphide 5 and tetracyanoethane anion radical 6. The cleavage of the disulphide 5 may proceed unsymmetrically to yield 7 and 8. The anion radical 6 interacts with the cation radical 8 with elimination of one molecule of HCN to afford the tricyanovinylation product 11, which cyclizes through the attack of the amino group on the cyano one to give 3-amino-4,5-dicyano-6-S-methypyridazine 12 as the first product. Compound 12 reacted compound 9 with elimination of the HCN to give 4,5-diamino-1,8-di-S-methylpyridazino[4,5-d]pyridazine 13.

The proposed structures for 12 and 13 were supported by analytical data (Table III) as well as spectral data (Table II).

The molecular formulas were ascertained from elemental analysis as well as the mass spectra. The absence of NH/SH group and the presence of amino group attached to the pyridazine ring as well as the SME group are indicated from ^{1}H-NMR spectra. The presence of the cyano groups in 12 and absence of them in 13 are confirmed by IR spectra.

On the other hand, the Schiff bases derived from S-methyldithiocarbazate 2a–e reacted with TCNE in ethyl acetate to form transient CT-complexes (Table I). The ion pair 14 and the CT-complexes may be in equilibrium, but the chemical reaction depletes the complex. The formation of a cation radical is followed by a transfer of a hydrogen proton to TCNE to generate the radical 15 within a pair together with TCNE-H (6). The pyridazine and thiadiazole derivatives may be



SCHEME I

formed via two different routes based on the formation of the radical 15. The first one is the abstraction of a hydrogen radical from 15 by tetracyanoethylene to form 3-aryl-5-S-methyl-1,2,4-thiadiazole 16a–f. The other route is the dimerization of the radical 15 to form the disulfide 17, which undergoes unsymmetric cleavage to give 18 and 19. Furthermore, 18 may split off S_2 to yield also the radical 19. Combination of the radical 6 and 19 gave the adduct 20, followed by abstraction of one molecule of hydrogen from 2 and elimination of one molecule of malon-

TABLE II

The ^{1}H-NMR, IR and mass spectra of compounds 12, 13 and 16a–f as well as 22a–f

compound	^{*1}H-NMR (δ, TMS)	IR (KBr, cm^{-1})	MS m/z (rel. intensity %)
12	2.65 (s, 3H) SCH_3; 8.45 (s, br, 2H) NH_2	3380-3200 (NH_2); 2210 (CN); 1650, 1560 (Ar - C = C)	191 (M^+, 100); 190 (19); 174(44); 164(35); 158 (11); 139(15); 120(13); 66(28)
13	2.65 (s,6H) 2SCH_3 ; 8.10(s,br,4H) 2NH_2.	3420(NH_2); 2930(Ali-CH).	254(M^+,19);252(100);196(30);179(12);161(19); 91(79).
16a	2.80(s,3H) SCH_3; 7.50, 7.90(m,5H) Ar - H.	3050(Ar-CH); 2910(Ali-CH); 1570 (Ar - C = C).	208(M^+,100);176(3);175(13);161(7); 135(9); 121(25);77(14).
16b	2.35(s,3H)CH_3; 2.80(s,3H)SCH_3 7.30, 7.80(m,4H) Ar-H.	3060(Ar-CH); 2930(Ali-CH);1600 (Ar - C = C).	222(M^+,100); 190(3); 189(15); 135(28).
16c	2.80(s,3H)SCH_3; 3.85(s,3H)OCH_3; 6.95, 7.80(s,4H)Ar-H.	3100(Ar- CH); 2960(Ali-CH);1610(Ar - C = C).	238(M^+,100);206(6);205(43);151(33); 133(34); 105(15).
16d	2.76(s,3H)SCH_3; 7.45, 7.85(m,4H) Ar-H.	2840-2980(Ali-CH); 1600,1560 (Ar - C = C).	242(M^+,100); 209(21); 169(7); 155(29); 137(18); 105(21).
16e	2.78(s,3H)SCH_3; 4.20(s,2H) CH_2; 7.0, 7.50(m,3H)Ar-H.	3090(Ar-CH); 2920(Ali-CH); 1600(Ar - C = C).	252(M^+,100); 220(8); 219(44); 178(13); 165(40); 147(45).
16f	2.75(s,3H)SCH_3;2.90(s,6H);N$(CH_3)_2$; 6.60, 7.70(m,4H) Ar-H.	2890(Ali-CH); 1610, 1600 (Ar -C = C).	251(M^+,100);218(20);177(13); 164(30); 146(38); 145(25).
22a	2.70(s,3H)SCH_3; 7.40-7.75(m,5H) Ar-H; 8.63(s,br,2H)NH_2.	3410,3360(NH_2); 2890(Ali-CH); 2220(CN); 1645, 1600(Ar-C=C).	242(M^+,37);227(63);195(100); 179(19); 165(41); 153(32); 77(82).
22b	2.30(s,3H)CH_3; 2.72(s,3H)SCH_3; 7.30, 7.80(m,4H) Ar-H; 8.59(s,br,2H) NH_2.	3380, 3200(NH_2); 2890(Ali-CH); 2210(CN); 1650(Ar-C=C).	256(M^+,33);226(100);194(41); 168(51); 57(77).
22c	2.75(s,3H)SCH_3; 3.85(s,3H)OCH_3; 6.95, 7.85(m,4H) Ar -H; 8.65(s,br,2H) NH_2.	3400-3230(NH_2); 2920(Ali-CH); 2220(CN); 1650, 1600(Ar-C=C).	272(M^+,29);257(16);242(71); 227(100); 169(46); 153(22).
22d	2.80(s,3H)SCH_3; 7.60, 7.92(m,4H) Ar-H; 8.69(s,br,2H) NH_2.	3390, 3340(NH_2); 2960(Ali-CH); 2220(CN); 1630, 1600(Ar-C=C).	
22e	2.77(s,3H) SCH_3; 4.22(s,2H) CH_2; 7.00, 7.45(m,3H) Ar-H; 8.51(s,br,2H) NH_2.	3400, 3350,3200(NH_2); 2920(Ali-CH); 2210(CN); 1640, 1600(Ar-C=C).	286(M^+,22);271(100); 219(66); 193(93) 165(66); 147(77); 146(55); 73(71).
22f	2.70(s,CH_3)SCH_3;3.05(s,6H); N$(CH_3)_2$; 6.80, 7.75(m,4H) Ar-H;8.55 (s,br,2H) NH_2.	3410(NH_2); 3100(Ar-CH); 2980 (Ali-CH); 2210(CN); 1600(Ar-C=C).	

*All the compounds measured in DMSO-d_6 except compounds 16-a-d and 17f in $CDCl_3$.

onitrile to yield compound 21. Cyclization of 21 forms 4-amino-3-aryl-5-cyano-6-S-methyl-pyridazines 22.

The ^{1}H-NMR spectra of thiadiazole derivatives 16a–f indicated clearly the absence of any signals due to NH/SH or azomethine —CH and showed a singlet near 2.75 ppm, due to the SMe group attached to the thiadiazole ring. Also signals for aromatic protons and the substituents (OCH_3, O—CH_2—O, CH_3) were observed. The molecular formulas of thiadiazole derivatives are evidenced from the elemental analysis as well as mass spectra which gave the correct molecular ion peaks as base-peaks.

TABLE III

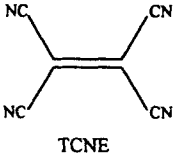
Analytical and physical data of compounds 12, 13 and 16a–f as well as 22a–f

Compound	Yield %	m.p. °C	Color of crystal	Solvent of recrystallization	Mol. Formula M. Wt	Analysis % C	H	N	Found (Calcd) S	Cl
12	56	253–55	Buff	Methanol	$C_7H_5N_5S$ (191.216)	44.19 (43.97	2.51 2.64	36.85 36.62	16.89 16.77)	
13	31	70–72	Brownish-yellow	Acetonitrile	$C_8H_{10}N_6S_2$ (254.339)	37.66 (37.78	4.14 3.96	32.91 33.04	25.37 25.22)	...
16a	51	57–59	Colorless	Cyclohexane	$C_9H_8N_2S_2$ (208.308)	51.72 (51.89	3.96 3.87	13.59 13.45	30.66 30.79)	
16b	62	53–55	Colorless	Cyclohexane	$C_{10}H_{10}N_2S_2$ (222.334)	54.18 (54.02	4.71 4.53	12.49 12.60	28.69 28.84)	
16c	55	91–93	Colorless	Cyclohexane	$C_{10}H_{10}N_2S_2O$ (238.333)	50.57 (50.40	4.41 4.23	11.92 11.75	27.07 26.91)	
16d	67	110–12	Colorless	Toluene	$C_9H_7N_2S_2Cl$ (242.753)	44.38 (44.53	2.77 2.91	11.63 11.54	26.55 26.42	14.73 14.60)
16e	49	88–90	Colorless	Ethanol	$C_{10}H_8N_2S_2O_2$ (252.317)	47.73 (47.60	3.36 3.20	11.28 11.10	25.33 25.42)	
16f	53	103–05	Pale Yellow	Ethanol	$C_{11}H_{13}N_3S_2$ (251.376)	52.41 (52.56	5.39 5.21	16.54 16.72	25.63 25.51	
22a	27	119–21	White	Ethanol	$C_{12}H_{10}N_4S$ (242.304)	59.64 (59.48	3.97 4.16	23.25 23.12	13.42 13.23)	
22b	21	138–40	Buff	Methanol	$C_{13}H_{12}N_4S$ (256.331)	61.11 (60.91	4.88 4.72	21.68 21.86	12.40 12.51)	
22c	24	125–27	Yellowish brown	Methanol	$C_{13}H_{12}N_4SO$ (272.330)	57.51 (57.34	4.49 4.44	20.46 20.57	11.92 11.77)	
22d	18	170–72	Pale brown	Acetonitrile	$C_{12}H_9N_4SCl$ (276.749)	51.89 (52.08	3.19 3.28	20.32 20.24	11.74 11.59	12.69 12.81)
22e	21	102–04	Buff	Ethanol	$C_{13}H_{10}N_4SO_2$ (286.314)	54.36 (54.54	3.48 3.52	19.71 19.57	11.41 11.20)	
22f	22	167–69	Yellow	Acetonitrile	$C_{14}H_{15}N_5S$ (285.372)	58.77 (58.92	5.21 5.30	24.65 24.54	11.33 11.24	

1

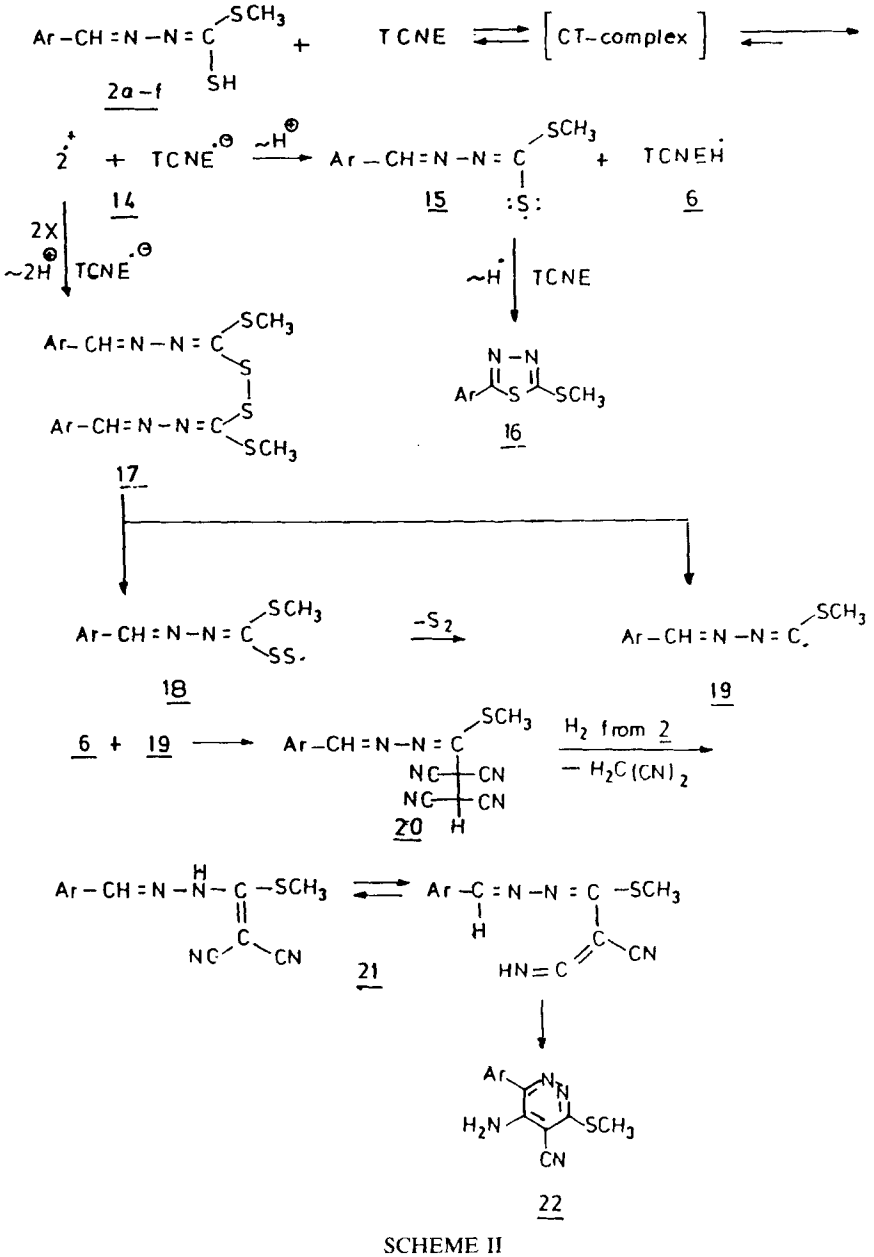
2a-f

a, Ar = C_6H_5 b, Ar = C_6H_4-p-CH_3
c, Ar = C_6H_4-p-OCH_3 d, Ar = C_6H_4-p-Cl
e, Ar = C_6H_3-3,4-O-CH_2-O f, Ar = C_6H_4-p-$N(CH_3)_2$



TCNE

FIGURE 1



SCHEME II

The proposed structure of pyridazine derivatives 22a–f were supported by analytical data (Table III) as well as spectral data (Table II).

EXPERIMENTAL

Melting points: Uncorrected. UV-vis spectra: Perkin Elmar Lambda 2 spectrophotometer; 1.0-cm stoppered silica cells, equipped with a thremostated cell holder. IR spectra: Shimadzu 470 spectropho-

tometer (KBr). ^{1}H-NMR spectra: Bruker WM 400 (400.1 MHz); chemical shifts in δ (ppm), TMS as internal standard. MS: Finnigan MAT 8430; 70 eV. Elemental analysis: Microanalytical unit at Cairo University.

Preparation of thin-layer chromatography: Air-dried 1.0-mm layers of silica gel, Merck pf 254 on plates were employed for preparative TLC and zones were detected by indicator fluorescence quenching exposure to 254 nm U.V. light.

Compounds

TCNE (EGA) was recrystallized from chlorobenzene and sublimed; S-methyldithiocarbazate 1 and Schiff bases 2a–f were prepared according to the literature.[20,21] Ethyl acetate used as solvent was purified following Vogel,[22] dried and distilled.

Reaction of S-methyldithiocarbazate 1 with TCNE: To a solution of 256 mg (0.002 mol) TCNE in 10 ml of dry ethyl acetate, S-methyldithiocarbazate 1 (0.001 mol) in 15 ml of dry ethyl acetate was added with stirring at room temperature. The color of the reaction mixture changed gradually during 45 min. from green to yellowish brown. The stirring was continued for 48 h. with admission of air to complete the reaction. The reaction mixture was chromatographed on thin-layer plates using toluene/ethyl acetate (10:1) as eluent, to give two zones. The fastest migrating zone contained compound 12, and the slowest migrating one contained compound 13. Extraction of the zones with acetone and recrystallization of the extracts from a suitable solvent afforded the pure compounds (Table III).

Reaction of Schiff bases derived from S-methyldithiocarbazate 2a–f with TCNE: To a stirred solution of 256 mg (0.002 mol) of TCNE in 10 ml of dry ethyl acetate, the Schiff bases 2a–f (0.001 mol) in 20 ml of dry ethyl acetate was added at room temperature. The color of the reaction mixture changed slowly within a few hours from green to yellowish-brown. After standing with stirring for 72 h, the reaction mixture was concentrated and the residue was then chromatographed on thin-layer plates using toluene/ethyl acetate (10:1) as eluent to give two zones; the first contained 3-aryl-5-S-methyl-1,2,4-thiadiazoles 16a–f and the second 4-amino-3-aryl-5-cyano-6-S-methyl-pyridazines 22a–f. Extraction of the zones with acetone and recrystallization of the extracts from a suitable solvent afforded the pure compounds (Table III).

ACKNOWLEDGEMENT

The author is indebted to Prof. Dr. H. Hopf, Institute of Organic Chemistry, Braunschweig University, for measuring ^{1}H-NMR as well as MS spectra.

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