Diheterocyclic Compounds from Dithiocarbamates and Derivatives Thereof. I. 2,2'-(Arylenediamino)bisbenzoazoles, 2,2'-(Arylenediamino)bis(imidazopyridines) and 8,8'-(Arylenediamino)bispurines

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A general method for the synthesis of the title compounds **5**, **6**, **10**, **14**, **15** and **16** is reported. All of them were prepared in one step from readily available dimethyl *N*,*N'*-(arylene)bisdithiocarbamates **1** and red mercury(II) oxide. The superiority of these reagents over the corresponding diisothiocyanates **7** and the synthetic utility of tetramethyl *N*,*N'*-(arylene)bisdithiocarbonimidates **2** are also discussed.

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Dithiocarbamic and dithiocarbonimidic acid esters derived from primary aromatic amines [1] were found to give rise to a great variety of five [2] and six-membered heterocyclic rings [3].

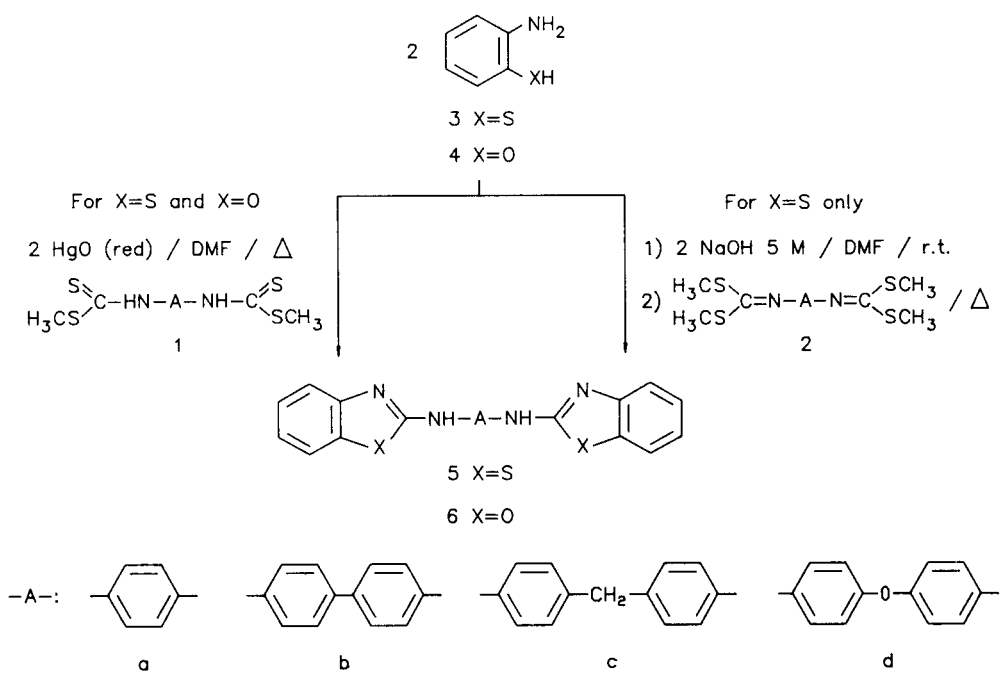
The versatility of these reagents led us to suppose that the corresponding difunctionalized derivatives would constitute suitable building blocks for the synthesis of bisheterocyclic compounds and of heterocyclic polymers, which have a great variety of useful properties [4].

In this paper we report the reactivity of bis(dithiocarbamic) and bis(dithiocarbonimidic) acid esters **1** and **2** with aromatic 1,2-dinucleophiles. Starting materials **1** and **2** are easily available from arylenediamines, as described in a previous communication [5].

Thus, the reaction of compounds **1** with 2-aminothiophenol **3** and 2-aminophenol **4** in refluxing dimethylformamide, in the presence of red mercury (II) oxide, afford **5** and **6** respectively, in good yields in a one-step procedure (Table 1).

On the other hand, when compounds **2** were made to react with dinucleophiles **3** and **4**, in the absence of the desulfurizing agent, no reaction was observed. In order to increase the nucleophilicity of **3** and **4**, two equivalents of sodium hydroxide were added to generate the corresponding anion. This allows compounds **5** to be prepared in good yields from 2-aminothiophenol **3**. The reaction of **2** with 2-aminophenol **4**, however, does not take place under similar conditions and even when reaction times are in-

Scheme I



Scheme II

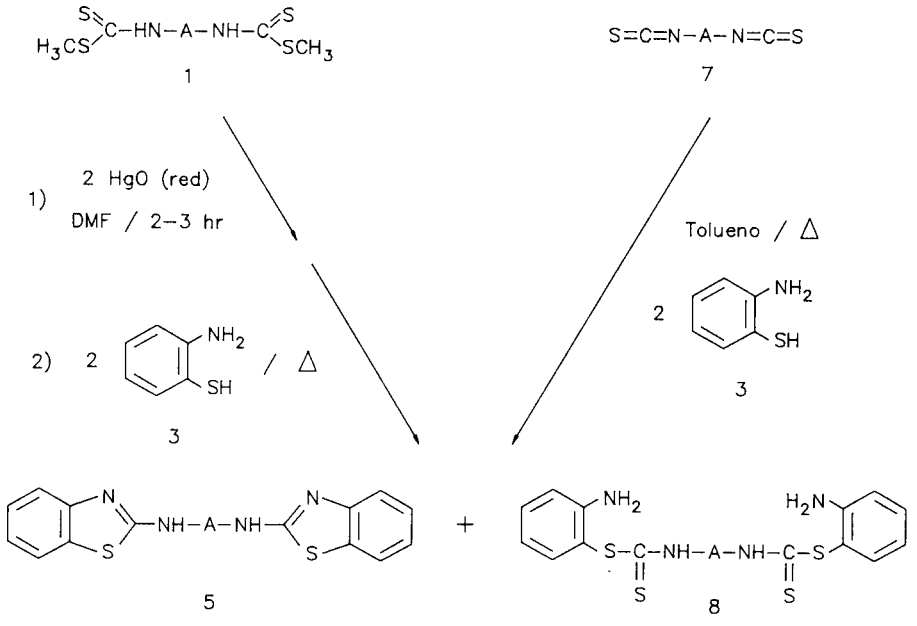


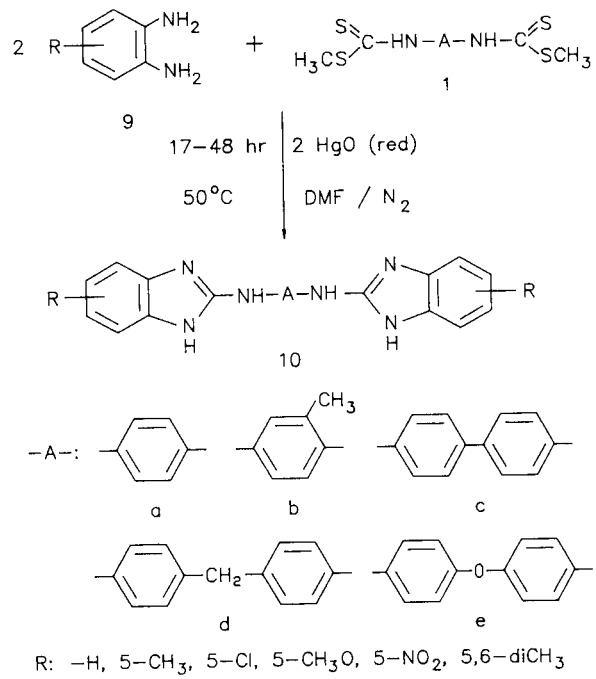
Table 1

Benzothiazoles and Benzoxazoles

Compound	mp (°C) (Recrystallization Solvent)	Yield (%) [a]
5a	276-278 (DMF/H_2O)	76 (63)
5b	>300 (DMF/H_2O)	75 (67)
5c	>300 (DMF/H_2O)	67 (60)
5d	258-260 (DMF/H_2O)	71 (62)
6a	>300 (DMF/H_2O)	79
6b	>300 (DMF/H_2O)	77
6c	286-288 (DMF/H_2O)	71
6d	264-266 (DMF/H_2O)	73

[a] Yield from bisdithiocarbonimidates (Method B) parentheses.

Scheme III



creased only decomposition products are obtained.

The reaction of compound **1** with **3** is specially noteworthy. We have recently reported that the treatment of **1** with red mercury (II) oxide in dimethylformamide affords arylenediisothiocyanates **7** [6]. As a consequence, it was thought that the reaction of **1** might take place *via* the corresponding diisothiocyanate **7**. In order to confirm this possibility **1** and red mercury (II) oxide were allowed to stand for 2-3 hours, **3** was then added and the mixture refluxed. The final product turned out to be a mixture of the expected product **5** and the bis(dithiocarbamate) **8**. Identical results were obtained from the reaction of **3** with pure products **7**, as might be expected from Tweit's work on monofunctionalized derivatives [7] (Scheme II).

In view of this, it now seems that the reaction of **1** with **3** takes place not only through isothiocyanates **7** but through **1** as well.

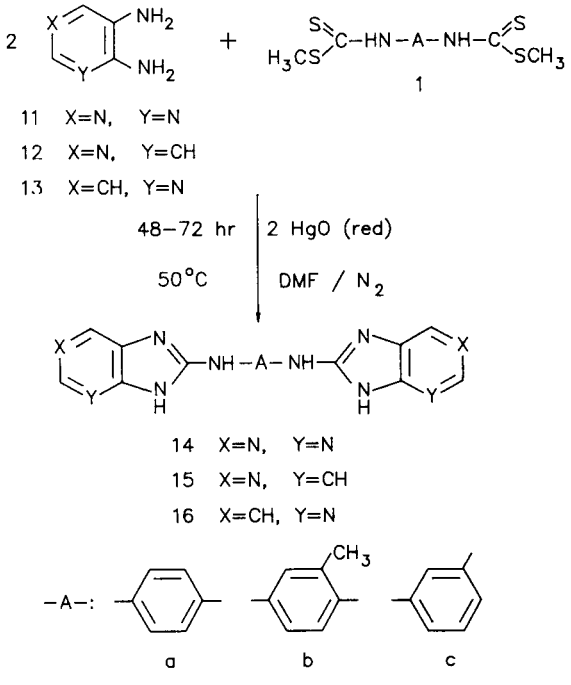
Finally, we would point out that in the synthesis of the bisbenzothiazoles **5**, a mixture of **1** and red mercury(II) oxide is a better reagent that the corresponding diisothiocyanate **7**, since no by-products were formed.

Table 2

Benzimidazoles

Compound	R	mp (°C) (Recrystallization Solvent)	Reaction time, hours	Yield (%)
10a	H	>300 (DMF/H_2O)	18	68
	5-CH_3	276-278 (DMF/H_2O)	24	54
	5-Cl	>300 (DMF/H_2O)	24	41
	5-NO_2	293-295 (DMF/H_2O)	48	69
	5-CH_3O	218-220 (DMF/H_2O)	24	63
	5,6-diCH_3	222-224 (DMF/H_2O)	48	57
10b	H	215-217 (DMF/H_2O)	30	71
	5-CH_3	196-198 (DMF/H_2O)	24	60
	5-Cl	216-218 (DMF/H_2O)	24	39
	5-NO_2	278-280 (DMF/H_2O)	48	42
	5-CH_3O	200-202 (DMF/H_2O)	24	72
	5,6-diCH_3	203-205 (DMF/H_2O)	48	53
10c	H	242-244 (DMF/H_2O)	18	61
10d	H	274-276 (DMF/H_2O)	18	57
10e	H	238-240 (DMF/H_2O)	18	62

Scheme IV



Bis(dithiocarbamates) **1** also show a high reactivity with aromatic and heteroaromatic *o*-diamines. Thus, benzimidazoles **10**, purines **14** and deazapurines **15** and **16** correctly named as imidazo[4,5-*c*]pyridines and imidazo[4,5-*b*]-pyridines, respectively result from the reaction of **1** with **9**, **11**, **12** and **13**, respectively, in the presence of red mercury(II) oxide in dimethylformamide under a nitrogen atmosphere (Schemes III and IV) (Tables 2 and 3).

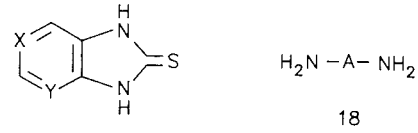
Reaction times depended on the nature of the *o*-diamine used (poorly nucleophilic amines required longer reaction times) and ranged from 17 to 22 hours. Lower temperatures than those used in the synthesis of compounds **5** and **6** were necessary in order to avoid the formation of the 2-thioxoimidazole derivatives **17** and diamines **18**, which were produced, among other products, when the reaction mixture was heated under reflux. This side-reaction bears a relation to the process described by Kiffer in the synthesis of 2-arylaminobenzimidazoles [8].

Table 3

Purines and their 1- and 3-Deaza Analogs

Compound	mp (°C) (Recrystallization Solvent)	Reaction time, hours	Yield (%)
14a	>300 (DMF/H_2O)	72	70
14b	>300 (DMF/H_2O)	72	71
14c	290-292 (DMF/H_2O)	48	70
15a	>300 (DMF/H_2O)	72	55
15b	260-262 (DMF/H_2O)	72	80
15c	>300 (DMF/H_2O)	48	88
16a	>300 (DMF/H_2O)	72	80
16b	>300 (DMF/H_2O)	72	65
16c	>300 (DMF/H_2O)	72	85

Figure



On the other hand, when bis(dithiocarbonimidates) **2** were heated with *o*-diamines **9**, **11**, **12** and **13**, no reaction was observed and, under tougher conditions, extensive decomposition occurred.

To sum up, the methods herein reported are extremely flexible, since a variety of heterazole-ring systems linked by different arylenediamino bridges can be prepared in a one-pot procedure from a common reagent. Apart from this the starting materials (*e.g.* **1**) are readily available in very good yields [5].

EXPERIMENTAL

Melting points were determined on a Büchi 510 apparatus and are uncorrected. The ir spectra were recorded on a Perkin-Elmer FT 1600 instrument. The nmr spectra were recorded on a Bruker WP 80 CW spectrometer with TMS as internal reference.

Synthesis of 2,2'-(Arylenediamino)dibenzothiazoles **5**.

General Procedures.

Method A.

To a suspension of 3.0 mmoles of 2-aminothiophenol **3** and 3.0 mmoles of red mercury(II) oxide in 10 ml of dimethylformamide was added 1.5 mmoles of the corresponding dimethyl *N,N'*-(arylene)bisdithiocarbamate **1** in 10 ml of dimethylformamide, at room temperature. Once **1** had been added, the mixture was refluxed for 8 hours and then the mixture was filtered hot. The filtrate was cooled in an ice-water bath and poured into water (100 ml). The precipitate thus obtained was filtered off, washed with water, ethanol and ether, dried and recrystallized.

Method B.

A solution of 2-aminothiophenol **3** (2.54 mmoles) in dimethylformamide (10 ml) was treated with aqueous 5 molar sodium hydroxide (0.5 ml, 2.5 mmoles), at room temperature and the mixture was stirred for 30 minutes. Then, a solution of the appropriate tetramethyl *N,N'*-(arylene)bisdithiocarbonimidate **2** (1.27 mmoles) in dimethylformamide (15 ml) was added dropwise and the reaction mixture was heated under reflux until no more methylmercaptan was evolved (6-8 hours).

After cooling, the mixture was poured into water (125 ml) in an ice-bath and the precipitate thus obtained was filtered, washed with water, ethanol and ether, dried *in vacuo* and recrystallized from the appropriate solvent.

2,2'-(1,4-Phenylenediamino)dibenzothiazole (**5a**).

This compound had ir: 1630 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 10.30 (s, 1H), 7.80 (s, 2H), 7.75-6.93 (m, 4H).

Anal. Calcd. for $C_{20}H_{14}N_4S_2$: C, 64.15; H, 3.77; N, 14.96. Found: C, 64.31; H, 3.63; N, 14.90.

2,2'-(4,4'-Biphenylylenediamino)dibenzothiazole (**5b**).

This compound had ir: 1635 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 10.67 (s, 1H), 8.02-7.49 (m, 6H), 7.45-7.00 (m, 2H).

Anal. Calcd. for $C_{26}H_{18}N_4S_2$: C, 69.31; H, 4.03; N, 12.44. Found: C, 69.36; H, 3.83; N, 12.33.

2,2'-(4,4'-Methylenediphenylenediamino)dibenzothiazole (**5c**).

This compound had ir: 1620 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 10.32 (s, 1H), 7.87-7.42 (m, 4H), 7.38-6.96 (m, 4H), 3.82 (s, 1H).

Anal. Calcd. for $C_{27}H_{20}N_4S_2$: C, 69.80; H, 4.34; N, 12.06. Found: C, 69.97; H, 4.01; N, 12.20.

2,2'-(4,4'-Oxydiphenylenediamino)dibenzothiazole (**5d**).

This compound had ir: 1620 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 10.43 (s, 1H), 7.93-6.85 (m, 8H).

Anal. Calcd. for $C_{26}H_{18}N_4OS_2$: C, 66.93; H, 3.89; N, 12.01. Found: C, 66.88; H, 3.86; N, 12.24.

Synthesis of 2,2'-(Arylenediamino)dibenzoxazoles **6**.

General Procedure.

These compounds were prepared in an identical manner as for compounds **5** by method A, the only difference being that 2-aminophenol **4** was used instead of 2-aminothiophenol **3**.

2,2'-(1,4-Phenylenediamino)dibenzoxazole (**6a**).

This compound had ir: 1660 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 10.42 (s, 1H), 7.73 (s, 2H), 7.59-6.96 (m, 4H).

Anal. Calcd. for $C_{20}H_{14}N_4O_2$: C, 70.17; H, 4.12; N, 16.37. Found: C, 70.10; H, 4.06; N, 16.33.

2,2'-(4,4'-Biphenylylenediamino)dibenzoxazole (**6b**).

This compound had ir: 1650 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 10.60 (s, 1H), 7.87 (d, 2H, J = 8); 7.66 (d, 2H, J = 8), 7.52-6.94 (m, 4H).

Anal. Calcd. for $C_{26}H_{18}N_4O_2$: C, 74.63; H, 4.34; N, 13.39. Found: C, 74.55; H, 4.10; N, 13.48.

2,2'-(4,4'-Methylenediphenylenediamino)dibenzoxazole (**6c**).

This compound had ir: 1660 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 11.40 (s, 1H), 7.84-6.85 (m, 8H), 3.82 (s, 1H).

Anal. Calcd. for $C_{27}H_{20}N_4O_2$: C, 74.99; H, 4.66; N, 12.95. Found: C, 74.75; H, 4.49; N, 13.09.

2,2'-(4,4'-Oxydiphenylenediamino)dibenzoxazole (**6d**).

This compound had ir: 1670 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 10.57 (s, 1H), 7.95-6.87 (m, 8H).

Anal. Calcd. for $C_{26}H_{18}N_4O_3$: C, 71.88; H, 4.18; N, 12.90. Found: C, 72.04; H, 4.19; N, 13.09.

Synthesis of 2,2'-(Arylenediamino)dibenzimidazoles **10**.

General Procedure.

To a suspension of 3.0 mmoles of the corresponding *o*-phenylenediamine **9** and 3.0 mmoles of red mercury(II) oxide in 10 ml of dimethylformamide was added 1.5 mmoles of the corresponding dimethyl *N,N'*-(arylene)bisdithiocarbamate **1** in 10 ml of dimethylformamide, at room temperature in a nitrogen atmosphere, which was maintained throughout. Once all **1** has been added, the mixture was heated at 50° for a time which depends on the *o*-phenylenediamine **9** used (see Table 2), and then the mixture was filtered hot. The filtrate was cooled in an ice-water bath and poured into water (150 ml). The precipitate thus obtained was filtered off, washed with water, ethanol and ether, dried and recrystallized.

2,2'-(1,4-Phenylenediamino)dibenzimidazole (**10a**, R = H).

This compound had ir: 1630 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 10.42 (s, 1H), 7.66 (s, 1H), 7.27-7.17 (m, 1H), 7.12-6.82 (m, 1H).

Anal. Calcd. for $C_{20}H_{16}N_6$: C, 70.57; H, 4.74; N, 24.69. Found: C, 70.76; H, 4.89; N, 24.63.

2,2'-(1,4-Phenylenediamino)bis(5-methylbenzimidazole) (**10a**, R = 5-CH_3).

This compound had ir: 1620 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 9.80 (s, 2H), 7.63 (s, 2H), 6.95-7.28 (m, 2H), 6.80-6.75 (m, 1H), 2.38 (s, 3H).

Anal. Calcd. for $C_{22}H_{20}N_6$: C, 71.72; H, 5.47; N, 22.81. Found: C, 71.68; H, 5.41; N, 23.04.

2,2'-(1,4-Phenylenediamino)bis(5-chlorobenzimidazole) (**10a**, R = 5-Cl).

This compound had ir: 1660 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 9.38 (s, 2H), 7.52 (s, 2H), 7.45-6.90 (m, 3H).

Anal. Calcd. for $C_{20}H_{14}Cl_2N_6$: C, 58.69; H, 3.45; N, 20.53. Found: C, 58.48; H, 3.65; N, 20.40.

2,2'-(1,4-Phenylenediamino)bis(5-nitrobenzimidazole) (**10a**, R = 5-NO_2).

This compound had ir: 1640 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 9.57 (s, 2H), 8.19-7.81 (m, 2H), 7.72 (s, 2H), 7.55-7.16 (m, 1H).

Anal. Calcd. for $C_{20}H_{14}N_8O_4$: C, 55.82; H, 3.28; N, 26.04. Found: C, 55.62; H, 3.52; N, 26.25.

2,2'-(1,4-Phenylenediamino)bis(5-methoxybenzimidazole) (**10a**, R = 5-CH_3O).

This compound had ir: 1625 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 9.62 (s, 2H), 7.65 (s, 2H), 7.32-7.18 (m, 1H), 6.96-6.88 (m, 1H), 6.75-6.59 (m, 1H), 3.78 (s, 3H).

Anal. Calcd. for $C_{22}H_{20}N_6O_2$: C, 65.99; H, 5.03; N, 20.99. Found: C, 65.88; H, 5.18; N, 21.12.

2,2'-(1,4-Phenylenediamino)bis(5,6-dimethylbenzimidazole) (**10a**, R = 5,6-diCH_3).

This compound had ir: 1670 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 9.46 (s, 1H), 7.50 (s, 1H); 7.18 (s, 1H), 2.18 (s, 3H).

Anal. Calcd. for $C_{24}H_{24}N_6$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.50; H, 6.28; N, 21.22.

2,2'-(2-Methyl-1,4-phenylenediamino)dibenzimidazole (**10b**, R = H).

This compound had ir: 1660 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 9.70 (s, 4H), 7.74-7.67 (m, 3H), 7.50-6.88 (m, 8H), 2.30 (s, 3H).

Anal. Calcd. for $C_{21}H_{18}N_6$: C, 71.17; H, 5.12; N, 23.71. Found: C, 71.23; H, 5.18; N, 23.83.

2,2'-(2-Methyl-1,4-phenylenediamino)bis(5-methylbenzimidazole) (**10b**, R = 5-CH_3).

This compound had ir: 1625 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 9.67 (s, 4H), 7.64-7.53 (m, 3H), 7.32-6.70 (m, 6H), 2.36 (s, 6H), 2.25 (s, 3H).

Anal. Calcd. for $C_{23}H_{22}N_6$: C, 72.23; H, 5.80; N, 21.97. Found: C, 72.48; H, 5.76; N, 21.74.

2,2'-(2-Methyl-1,4-phenylenediamino)bis(5-chlorobenzimidazole) (**10b**, R = 5-Cl).

This compound had ir: 1670 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 9.84 (s, 4H), 7.74-7.65 (m, 3H), 7.50-6.92 (m, 6H), 2.30 (s, 3H).

Anal. Calcd. for $C_{21}H_{16}Cl_2N_6$: C, 59.59; H, 3.81; N, 19.85. Found: C, 59.83; H, 3.99; N, 19.69.

2,2'-(2-Methyl-1,4-phenylenediamino)bis(5-nitrobenzimidazole) (**10b**, R = 5-NO_2).

This compound had ir: 1630 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 10.24 (s, 4H), 8.08-7.75 (m, 4H), 7.60-7.20 (m, 5H), 2.43 (s, 3H).

Anal. Calcd. for $C_{21}H_{16}N_8O_4$: C, 56.75; H, 3.63; N, 25.21. Found: C, 56.58; H, 3.51; N, 24.97.

2,2'-(2-Methyl-1,4-phenylenediamino)bis(5-methoxybenzimidazole) (**10b**, R = 5-CH_3O).

This compound had ir: 1620 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 9.26 (s, 4H), 7.70-6.69 (m, 9H), 3.75 (s, 6H), 2.88 (s, 3H).

Anal. Calcd. for $C_{23}H_{22}N_6O_2$: C, 66.65; H, 5.35; N, 20.28. Found: C, 66.57; H, 5.28; N, 20.22.

2,2'-(2-Methyl-1,4-phenylenediamino)bis(5,6-dimethylbenzimidazole) (**10b**, R = 5,6-diCH_3).

This compound had ir: 1670 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 9.87 (s, 4H), 7.83-7.38 (m, 3H), 7.08-6.97 (m, 4H), 2.25 (s, 12H), 2.08 (s, 3H).

Anal. Calcd. for $C_{25}H_{26}N_6$: C, 73.14; H, 6.38; N, 20.47. Found: C, 73.05; H, 6.32; N, 20.59.

2,2'-(4,4'-Biphenylylenediamino)dibenzimidazole (**10c**).

This compound had ir: 1640 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 9.46 (s, 1H), 7.84 (d, 1H, J = 8), 7.56 (d, 1H, J = 8), 7.42-7.13 (m, 1H), 7.07-6.78 (m, 1H).

Anal. Calcd. for $C_{26}H_{20}N_6$: C, 74.98; H, 4.84; N, 20.18. Found: C, 75.10; H, 4.96; N, 20.07.

2,2'-(4,4'-Methylenediphenylenediamino)dibenzimidazole (**10d**).

This compound had ir: 1630 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 9.00 (s, 2H), 7.10-6.00 (m, 8H), 3.14 (s, 1H).

Anal. Calcd. for $C_{27}H_{22}N_6O$: C, 75.33; H, 5.15; N, 19.52. Found: C, 75.25; H, 5.33; N, 19.56.

2,2'-(4,4'-Oxydiphenylenediamino)dibenzimidazole (**10e**).

This compound had ir: 1630 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 9.38 (s, 1H), 7.85-7.60 (m, 1H), 7.35-7.15 (m, 1H), 7.08-6.80 (m, 2H).

Anal. Calcd. for $C_{26}H_{20}N_6O$: C, 72.21; H, 4.66; N, 19.43. Found: C, 72.45; H, 4.72; N, 19.43.

Synthesis of 8,8'-(Arylenediamino)dipurines **14**.

General Procedure.

To a well stirred suspension of 3.0 mmoles of 4,5-diaminopyrimidine **11** and 3.0 mmoles of red mercury(II) oxide in 10 ml of dimethylformamide a solution of the corresponding dimethyl *N,N'*-(arylene)bisdithiocarbamate **1** (1.5 mmoles) in dimethylformamide (10 ml) was added dropwise at room temperature in a nitrogen atmosphere, which was maintained throughout. The mixture was heated at 50°C for a time which depends on the compounds used (see Table 3), cooled and poured into 3% hydrochloric acid (200 ml); the resulting suspension was boiled for 10 minutes and filtered while hot; the filtrate was made alkaline (*p*H = 8) with concentrated ammonium hydroxide and the precipitate thus obtained was filtered, dried and purified by recrystallization.

8,8'-(1,4-Phenylenediamino)dipurine (**14a**).

This compound had ir: 1700 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 9.22 (s, 2H), 8.25 (s, 1H), 8.00 (s, 1H), 6.82 (s, 2H).

Anal. Calcd. for $C_{16}H_{12}N_{10}$: C, 55.81; H, 3.51; N, 40.68. Found: C, 55.60; H, 3.74; N, 40.53.

8,8'-(2-Methyl-1,4-phenylenediamino)dipurine (**14b**).

This compound had ir: 1625 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 9.32 (s, 4H), 8.70-8.43 (m, 4H), 7.78-7.65 (m, 3H), 2.25 (s, 3H).

Anal. Calcd. for $C_{17}H_{14}N_{10}$: C, 56.98; H, 3.94; N, 39.08. Found: C, 56.91; H, 3.78; N, 39.12.

8,8'-(1,3-Phenylenediamino)dipurine (**14c**).

This compound had ir: 1650 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 9.17 (s, 2H), 8.19 (s, 1H), 7.96 (s, 1H), 7.12-6.78 (m, 2H).

Anal. Calcd. for $C_{16}H_{12}N_{10}$: C, 55.81; H, 3.51; N, 40.68. Found: C, 55.97; H, 3.46; N, 40.90.

Synthesis of 2,2'-(Arylenediamino)bis(imidazo[4,5-*c*]pyridines) **15**.

General Procedure.

These compounds were prepared in the same way as compounds **14**, the only difference being that 3,4-diaminopyridine **12** was used instead of 4,5-diaminopyrimidine **11**.

2,2'-(1,4-Phenylenediamino)bis(imidazo[4,5-*c*]pyridine) (**15a**).

This compound had ir: 1680 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 9.37 (s, 2H), 8.60 (s, 1H), 8.32-7.96 (m, 1H), 7.68-7.11 (m, 3H).

Anal. Calcd. for $C_{18}H_{14}N_8$: C, 63.15; H, 4.12; N, 32.73. Found: C, 62.95; H, 4.21; N, 32.60.

2,2'-(2-Methyl-1,4-phenylenediamino)bis(imidazo[4,5-*c*]pyridine) (**15b**).

This compound had ir: 1650 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 9.60 (s, 4H), 8.50 (s, 2H), 8.23-8.07 (m, 2H), 7.65-7.32 (m, 5H), 2.25 (s, 3H).

Anal. Calcd. for $C_{19}H_{16}N_8$: C, 64.03; H, 4.53; N, 31.44. Found: C, 63.80; H, 4.29; N, 31.32.

2,2'-(1,3-Phenylenediamino)bis(imidazo[4,5-*c*]pyridine) (**15c**).

This compound had ir: 1685 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 9.19 (s, 2H), 8.72 (s, 1H), 8.47-8.13 (m, 1H), 7.92-7.50 (m, 3H).

Anal. Calcd. for $C_{18}H_{14}N_8$: C, 63.15; H, 4.12; N, 32.73. Found: C, 63.32; H, 4.09; N, 32.95.

Synthesis of 2,2'-(Arylenediamino)bis(imidazo[4,5-*b*]pyridines) **16**.

General Procedure.

These compounds were prepared in the same way as compounds **14**, the only difference being that 2,3-diaminopyridine **13** was used instead of 4,5-diaminopyrimidine **11**.

2,2'-(1,4-Phenylenediamino)bis(imidazo[4,5-*b*]pyridine) (**16a**).

This compound had ir: 1625 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 9.42 (s, 2H), 8.56-8.43 (m, 2H), 7.79-7.61 (m, 3H).

Anal. Calcd. for $C_{18}H_{14}N_8$: C, 63.15; H, 4.12; N, 32.73. Found: C, 62.92; H, 4.02; N, 32.48.

2,2'-(2-Methyl-1,4-phenylenediamino)bis(imidazo[4,5-*b*]pyridine) (**16b**).

This compound had ir: 1625 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 9.79 (s, 4H), 8.23-8.05 (m, 4H), 7.56-7.28 (m, 5H), 2.26 (s, 3H).

Anal. Calcd. for $C_{19}H_{16}N_8$: C, 64.03; H, 4.53; N, 31.44. Found: C, 63.85; H, 4.70; N, 31.25.

2,2'-(1,3-Phenylenediamino)bis(imidazo[4,5-*b*]pyridine) (**16c**).

This compound had ir: 1640 cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 9.46 (s, 2H), 8.23-8.42 (m, 2H), 7.75-7.64 (m, 3H).

Anal. Calcd. for $C_{18}H_{14}N_8$: C, 63.15; H, 4.12; N, 32.73. Found: C, 63.03; H, 4.25; N, 32.59.

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