Synthesis of Unsymmetrical Diheteroarylbenzenes: Benzoazole and Quinazoline Derivatives

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Four different types of structures, namely **8**, **14**, **17** and **18** have been prepared for the first time. No more than five steps are needed to synthesize them using 4-nitroaniline as starting material. In order to confirm the proposed structures, some independent syntheses have been carried out.

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We have recently developed a method for the synthesis of diheterocyclic compounds such as arylenebis(azoles) [1] and arylenebis(quinazolines) [2], [3] among others.

Nevertheless, the synthetic routes used only led to symmetrically substituted derivatives. In this paper we report that similar unsymmetrical compounds with different azole and/or quinazoline rings can be prepared from a common precursor. At some stages of the synthetic scheme, use is made of alternative routes.

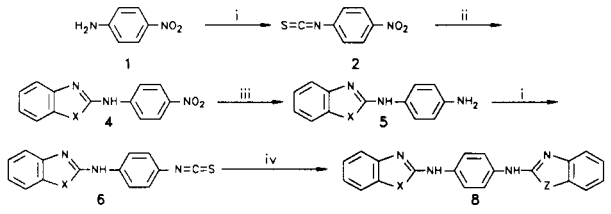
For the sake of simplicity the 1,4-phenylene group was chosen to test the validity of our approach, 4-nitroaniline being used as starting material.

Structures containing either two different azole rings, or two different quinazoline rings or one azole and one quinazoline ring have been synthesized after several steps, and hereafter they will be referred to as [5-5], [6-6] and [5-6] systems respectively.

Synthesis of [5-5] Systems.

These compounds of general structure **8** have been prepared in five steps from 4-nitroaniline according to Scheme I.

Scheme I



X	S	O	NH
3,4,5,6	a	b	c

X,Z	S,O	NH,S	O,NH
8	a	b	c

The scheme involves the stepwise formation of both azole rings starting from suitable difunctional derivative **2**. This compound turned out to be very well suited to our approach, the inert nitro group acting as a masked isothiocyanate, thus avoiding the problems which arise when *p*-phenylenediisothiocyanate is used for the synthesis of unsymmetrical compounds.

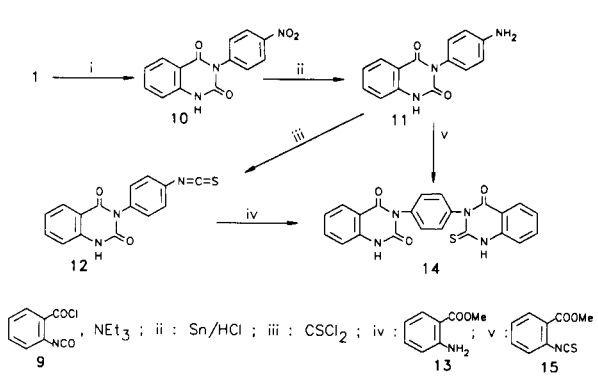
Treatment of **2** with dinucleophiles **3** in the presence of yellow mercury(II) oxide gave compounds **4** in very good yields (85-92%) which showed the expected absorptions in their ir and ^{1}H-nmr spectra. In every case the molecular ion was the base peak in the mass spectra.

Once the first azole ring had formed, the nitro group was converted into an isothiocyanato moiety in two steps: reduction to amino group followed by standard treatment with thiophosgene. Among the variety of methods which allow the first step, the typical system tin/hydrochloric acid was used since benzoazoles remain unaltered in these conditions [4] and final work up is very simple, yielding derivatives **5** in good yields (*ca* 70%).

Compounds **5** were treated with thiophosgene, giving isothiocyanates **6** in good yields (76-79%) except for **6c** (46%). This is due to an unavoidable reaction which takes place in the endocyclic -NH- groups and which leads to dimeric by-products, even when stoicheometric quantities of thiophosgene are used.

For compounds **5** and **6** the base peaks of the mass spectra were also the molecular ions. Condensation of **6** with dinucleophiles **7** in the presence of yellow mercuric oxide gave the mixed benzoazole derivatives **8** in good yields. In the case of compounds **8b-8c** it was better to use com-

Scheme II



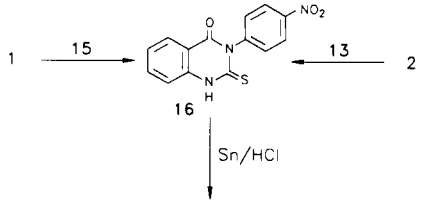
pounds **6a** and **6b** as starting materials than **6c**, due to the above-mentioned problems with the synthesis of the latter.

Synthesis of [6-6] System.

The synthesis of compound **14** was carried out from 4-nitroaniline, according to Scheme II. Thus quinazolinedione **10**, prepared in 83% yield from 2-isocyanatobenzoyl chloride **9** [5], was reduced to quinazoline **11** (74%) by tin/hydrochloric acid. This compound could be transformed into **14** by two different approaches: a) Reaction with thiophosgene and subsequently with methyl anthranilate (59%) or b) Reaction with methyl 2-isothiocyanatobenzoate **15** [6] (61%). In both cases the resulting product was the same and its structure was confirmed by its spectroscopical features.

In a different approach, the 4-oxo-2-thioxoquinazoline ring was the first to be synthesized either from **1** or from **2** (Scheme III), giving **16** which, nevertheless, could not be reduced to the corresponding amino derivative. The reaction gave a mixture of **11** and **10** instead, which indicated a preferential hydrolysis of the 2-thioxo [7] group in the reaction conditions. In consequence, this route had to be abandoned.

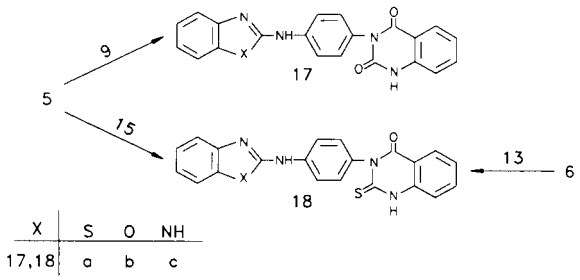
Scheme III



Synthesis of [5-6] Systems.

Two different approaches were used to synthesize the desired compounds. In the first, a precursor containing a preformed five membered ring was used, the most obvious candidates being **5** and **6** (Scheme IV). Thus, reaction of azole **5** with **9** gave the corresponding azolylaminoquinazolinediones **17** in nearly quantitative yield, while treatment of **5** with **15** gave the corresponding 2-thioxo analogues **18** (yield *ca* 60%) which were also available from compounds **6** and methyl anthranilate in similar yields.

Scheme IV



The second approach involved a precursor containing a quinazoline ring, namely **12** (Scheme V). This compound, when treated with suitable dinucleophiles **3** again gave structures **17** which were identical in every respect to those obtained according to Scheme IV, thus confirming the proposed structures.

Scheme V

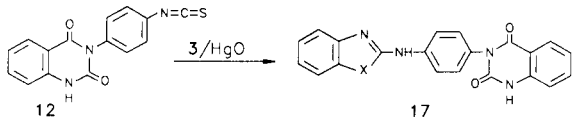


Table 1

[5-5] Systems and their Precursors

Compound	mp °C (Recrystallization solvent)	Yield (%)	MS m/z (%)
4a	214-216 (MeOH)	87	271 (M^+, 100)
4b	222-224 (MeOH)	85	255 (M^+, 100)
4c	282-284 (MeOH)	92	254 (M^+, 100)
5a	182-184 (MeOH)	71	241 (M^+, 100)
5b	200-202 (MeOH)	70	225 (M^+, 100)
5c	236-238 (MeOH)	68	224 (M^+, 100)
6a	204-206 (MeOH)	76	283 (M^+, 100)
6b	234-236 (AcOH) Lit [9] 242	79	267 (M^+, 100)
6c	282-284 (AcOH)	46	266 (M^+, 100)
8a	>300 (DMF/H_2O)	73 [a] 76 [b]	[d]
8b	266-268 (DMF/H_2O)	70 [a] 79 [c]	[d]
8c	254-256 (DMF/H_2O)	68 [b] 72 [c]	[d]

[a] From **6a**. [b] From **6b**. [c] From **6c**. [d] Not volatile.

Table 2

[6-6] System and its Precursors

Compound	mp °C (Recrystallization solvent)	Yield (%)	MS m/z (%)
10	>300 (MeOH) lit [10] 375	83	283 (M^+, 100)
11	>300 (MeOH)	74	253 (M^+, 100)
12	298-300 (AcOH)	78	295 (M^+, 100)
14	>300 (DMSO)	61 [a] 59 [b]	[c]

[a] From **15**. [b] From **13**. [c] Not Volatile.

Obviously, this second approach is only valid for quinazolinedione compounds, but not for their **18**-type analogues, since no adequate precursor could be synthesized.

In conclusion, we here report a simple method for the synthesis of 1,4-disubstituted benzenes with two different rings, either of benzoazole or quinazoline. Thus, this methodology successfully complements the one we have

Table 3
[5-6] Systems

Compound	mp ° C (Recrystallization solvent)	Yield (%)
17a	>300 ($DMSO/H_2O$)	72 [a] 91 [b]
17b	>300 ($DMSO/H_2O$)	68 [a] 92 [b]
17c	>300 ($DMSO/H_2O$)	74 [a] 94 [b]
18a	>300 ($DMSO/H_2O$)	63 [b] 62 [c]
18b	>300 ($DMSO/H_2O$)	60 [b] 62 [c]
18c	>300 ($DMSO/H_2O$)	58 [b] 56 [c]

[a] From **12**. [b] From **5**. [c] From **6**.

recently reported for the synthesis of several series of symmetrical diheterocyclic compounds linked by arylene units.

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 and a Varian VXR-300 spectrometer with TMS as internal reference. Mass spectra were obtained on a Hewlett-Packard 5995C spectrometer.

Synthesis of 2-(4-Nitrophenylamino)benzoazoles **4**.

General Procedure.

To a solution of 4-nitrophenylisothiocyanate **2** [8] (9 g, 0.05 mole) in toluene (150 ml) the corresponding 2-substituted aniline **3** (0.05 mole) in toluene (100 ml) was added. The solution was refluxed for 2 hours and then yellow mercuric oxide (10.8 g, 0.05 mole) was added. The mixture was refluxed for 4 hours (8 hours at 60° for **4c**), cooled at room temperature and filtered. The precipitate thus obtained was suspended in boiling methanol (750 ml) and filtered in hot. On cooling the filtrate pure compounds **4** precipitated.

2-(4-Nitrophenylamino)benzothiazole (**4a**).

This compound had ir: 3340, 1630 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 11.1 (s, 1H), 8.3 (d, 2H, J = 8), 8.0 (d, 2H, J = 8), 7.8-7.6 (m, 2H), 7.5-7.1 (m, 2H).

Anal. Calcd. for $C_{13}H_9N_3O_2S$: C, 57.55; H, 3.34; N, 15.49. Found: C, 57.47; H, 3.37; N, 15.63.

2-(4-Nitrophenylamino)benzoxazole (**4b**).

This compound had ir: 3250-3050, 1680 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 11.2 (s, 1H), 8.3 (d, 2H, J = 8), 7.9 (d, 2H, J = 8), 7.6-7.0 (m, 4H).

Anal. Calcd. for $C_{13}H_9N_3O_3$: C, 61.18; H, 3.55; N, 16.46. Found: C, 61.04; H, 3.63; N, 16.60.

2-(4-Nitrophenylamino)benzimidazole (**4c**).

This compound had ir: 3500-3050, 1660 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 11.2 (s, 1H), 10.2 (s, 1H), 8.2 (d, 2H, J = 8), 8.0 (d, 2H, J = 8), 7.5-7.2 (m, 2H), 7.1-6.9 (m, 2H).

Anal. Calcd. for $C_{13}H_{10}N_4O_2$: C, 61.41; H, 3.96; N, 22.04. Found: C, 61.23; H, 4.06; N, 21.86.

Synthesis of 2-(4-Aminophenylamino)benzoazoles **5**.

General Procedure.

To a suspension of the corresponding 2-(4-nitrophenylamino)-benzoazole **4** (0.02 mole) in boiling concentrated aqueous hydrochloric acid (120 ml) tin (11.9 g, 0.1 g-atom) was slowly added. The mixture was refluxed for 2 hours, filtered in hot and the filtrate poured into ice-cooled water (250 ml). Neutralization with aqueous 10 *M* sodium hydroxide precipitated 2-(4-aminophenylamino)benzoazoles **5** which were filtered, dried and recrystallized from methanol.

2-(4-Aminophenylamino)benzothiazole (**5a**).

This compound had ir: 3450-3050, 1630 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 8.9 (s, 1H), 7.8-7.5 (m, 2H), 7.4 (d, 2H, J = 8), 7.2-6.9 (m, 2H), 6.6 (d, 2H, J = 8), 3.8 (s, 2H).

Anal. Calcd. for $C_{13}H_{11}N_3S$: C, 64.71; H, 4.59; N, 17.41. Found: C, 64.53; H, 4.54; N, 17.60.

2-(4-Aminophenylamino)benzoxazole (**5b**).

This compound had ir: 3400, 3300-3100, 1640 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 9.9 (s, 1H), 7.5-6.9 (m, 6H), 6.6 (d, 2H, J = 8), 4.7 (d, 2H, J = 8).

Anal. Calcd. for $C_{13}H_{11}N_3O$: C, 69.32; H, 4.92; N, 18.65. Found: C, 69.38; H, 4.74; N, 18.58.

2-(4-Aminophenylamino)benzimidazole (**5c**).

This compound had ir: 3400, 3360-3300, 1660 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 7.4-7.1 (m, 2H), 7.0-6.8 (m, 1H), 6.6 (d, 1H, J = 8), 5.8 (s broad, 2H).

Anal. Calcd. for $C_{13}H_{12}N_4$: C, 69.62; H, 5.39; N, 24.98. Found: C, 69.84; H, 5.48; N, 25.12.

Synthesis of 2-(4-Isothiocyanatophenylamino)benzoazoles **6**.

General Procedure.

To a very well stirred suspension of calcium carbonate (5 g, 0.05 mole) and thiophosgene (2.3 g, 0.02 mole) in 1:1 water/chloroform (70 ml) in an ice bath, 2-(4-aminophenylamino)benzoazole **5** (0.02 mole) was slowly added. The mixture was stirred for 2 hours and then aqueous 10% hydrochloric acid was slowly added until no more carbon dioxide was evolved. The precipitate was filtered, washed with water, dried and finally recrystallized from a suitable solvent.

2-(4-Isothiocyanatophenylamino)benzothiazole (**6a**).

This compound had ir: 3200-3100, 2150, 1660 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 8.0-7.1 (m).

Anal. Calcd. for $C_{14}H_9N_3S_2$: C, 59.34; H, 3.20; N, 14.83. Found: C, 59.12; H, 3.10; N, 14.97.

2-(4-Isothiocyanatophenylamino)benzoxazole (**6b**).

This compound had ir: 3150-3050, 2100, 1640 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 11.1 (s, 1H), 7.8 (d, 2H, J = 8), 7.6-7.3 (m, 4H), 7.2-7.0 (m, 2H).

Anal. Calcd. for $C_{14}H_9N_3OS$: C, 62.91; H, 3.39; N, 15.72. Found: C, 62.97; H, 3.54; N, 15.68.

2-(4-Isothiocyanatophenylamino)benzimidazole (**6c**).

This compound had ir: 3200-3050, 2060, 1630 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 7.6-7.3 (m).

Anal. Calcd. for $C_{14}H_{10}N_4S$: C, 63.14; H, 3.78; N, 21.04. Found: C, 63.23; H, 3.87; N, 21.07.

Synthesis of Unsymmetrical *N,N'*-Dibenzoazolyl-1,4-diaminobenzenes **8**.

General Procedure.

To a suspension of **6** (2 mmoles) in toluene (12 ml), the corresponding 2-substituted aniline **7** (2 mmoles) in toluene (10 ml) and yellow mercuric oxide (0.43 g, 2 mmoles) were added. The mixture was refluxed for 6 hours (12 hours at 60° for **7**, Z = NH) and then filtered. The precipitate was suspended in boiling aqueous 5% hydrochloric acid and filtered in hot. The filtrate was cooled in an ice bath and neutralized with concentrated aqueous ammonium hydroxide to yield a solid which was filtered, washed with water, dried and finally recrystallized from a suitable solvent.

N-(2-Benzothiazolyl)-*N'*-(2-benzoxazolyl)-1,4-diaminobenzene (**8a**).

This compound had ir: 3180, 1678, 1623 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 10.4 (s, 1H), 7.9-7.0 (m, 6H).

Anal. Calcd. for $C_{20}H_{14}N_4OS$: C, 67.02; H, 3.94; N, 15.63. Found: C, 67.12; H, 4.03; N, 15.47.

N-(2-Benzimidazolyl)-*N'*-(2-benzothiazolyl)-1,4-diaminobenzene (**8b**).

This compound had ir: 3150-3050, 1654, 1629 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 10.2 (s, 3H), 7.8-7.4 (m, 5H), 7.3-6.8 (m, 7H).

Anal. Calcd. for $C_{20}H_{15}N_5S$: C, 67.21; H, 4.23; N, 19.59. Found: C, 67.08; H, 4.26; N, 19.72.

N-(2-Benzimidazolyl)-*N'*-(2-benzoxazolyl)-1,4-diaminobenzene (**8c**).

This compound had ir: 3160, 1648, 1640 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 10.4 (s, 1H), 7.8-6.8 (m, 4H).

Anal. Calcd. for $C_{20}H_{15}N_5O$: C, 70.37; H, 4.43; N, 20.52. Found: C, 70.44; H, 4.30; N, 20.54.

Synthesis of 3-(4-Nitrophenyl)-2,4-dioxo-1,2,3,4-tetrahydroquinazoline **10**.

This compound was prepared from 2-isocyanatobenzoyl chloride **9** and 4-nitroaniline **1** as described for compounds **17**, method A.

Synthesis of 3-(4-Aminophenyl)-2,4-dioxo-1,2,3,4-tetrahydroquinazoline (**11**).

The procedure was identical to that described for the synthesis of compounds **5** but with **10** instead of **4** as starting material.

This compound had ir: 3370, 3300-3100, 1730, 1670 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 11.4 (s, 1H), 8.0 (d, 1H, J = 8), 7.8-7.5 (m, 1H), 7.4-7.1 (m, 2H), 6.9 (d, 2H, J = 8), 6.6 (d, 2H, J = 8), 5.2 (s broad, 2H).

Anal. Calcd. for $C_{14}H_{11}N_3O_2$: C, 66.40; H, 4.38; N, 16.59. Found: C, 66.48; H, 4.37; N, 16.66.

Synthesis of 3-(4-Isothiocyanatophenyl)-2,4-dioxo-1,2,3,4-tetrahydroquinazoline (**12**).

The procedure was identical to that described for the synthesis of compounds **6**, but with **11** instead of **5** as starting material.

The compound had ir: 3230-3050, 2100, 1730, 1680 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 11.5 (s, 1H), 7.9 (d, 1H, J = 7), 7.8-7.0 (m, 7H).

Anal. Calcd. for $C_{15}H_9N_3O_2S$: C, 61.01; H, 3.07; N, 14.23. Found: C, 60.92; H, 2.99; N, 14.37.

Synthesis of 1-(2,4-Dioxo-1,2,3,4-tetrahydro-3-quinazolinyl)-4-(4-oxo-2-thioxo-1,2,3,4-tetrahydro-3-quinazolinyl)benzene (**14**).

Method A.

To a solution of methyl 2-isothiocyanatobenzoate **15** (0.38 g, 2 mmoles) in DMF (7 ml), **11** (0.5 g, 2 mmoles) in DMF (7 ml) was added. The mixture was heated at 60-80° for 2 hours and then refluxed for 24 hours. The mixture on cooling precipitated pure **14** which was filtered and washed with cold DMF and water.

A second fraction was obtained when water was added to the filtrate.

Method B.

To a solution of **12** (0.62 g, 2 mmoles) in DMF (8 ml) methyl anthranilate **13** (0.3 g, 2 mmoles) in DMF (8 ml) was added. The solution was heated at 60-80° for 2 hours and then refluxed for 24 hours. The work up procedure was identical to that described for method A.

This compound had ir: 3254, 3133, 1720, 1656 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 11.5 (s, 1H), 8.0-7.9 (m, 1H), 7.8-7.6 (m, 1H), 7.5-7.3 (m, 3H), 7.2-7.1 (m, 1H).

Anal. Calcd. for $C_{22}H_{14}N_4O_3S$: C, 63.76; H, 3.40; N, 13.52. Found: C, 63.69; H, 3.46; N, 13.59.

Synthesis of 1-(2-Benzoazolylamino)-4-(2,4-dioxo-1,2,3,4-tetrahydro-3-quinazolinyl)benzenes **17**.

General Procedures.

Method A.

To a suspension of 2-isocyanatobenzoyl chloride **9** (0.36 g, 2 mmoles) in anhydrous toluene (10 ml) placed in an ice bath, a suspension of 2-(4-aminophenylamino)benzoazole **5** (2 mmoles) and triethylamine (0.2 g, 2 mmoles) in anhydrous toluene (15 ml) was slowly added. The mixture was refluxed for 36 hours and then cooled at room temperature. The precipitated **17** was filtered and washed with boiling water and methanol.

Method B.

To a suspension of **12** (0.59 g, 2 mmoles) in toluene (12 ml), a solution of 2-substituted aniline **3** (2 mmoles) in toluene (10 ml) and yellow mercuric oxide (0.43 g, 2 mmoles) were added. The mixture was refluxed for 6 hours (12 hours at 60° for **3c**), cooled at room temperature and filtered. The precipitate was suspended in boiling 5% aqueous hydrochloric acid (40 ml), filtered in hot and the filtrate cooled in an ice bath. Neutralization with concentrated aqueous ammonium hydroxide precipitated products **17** which were filtered, washed with water, dried and finally recrystallized from a suitable solvent.

1-(2-Benzothiazolylamino)-4-(2,4-dioxo-1,2,3,4-tetrahydro-3-quinazolinyl)benzene (**17a**).

This compound had ir: 3306, 1716, 1652, 1621 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 11.6 (s, 1H), 10.7 (s, 1H), 8.0 (d, 1H, J = 7), 7.9-7.2 (m, 11H).

Anal. Calcd. for $C_{21}H_{14}N_4O_2S$: C, 65.27; H, 3.65; N, 14.50. Found: C, 65.07; H, 3.76; N, 14.47.

1-(2-Benzoxazolylamino)-4-(2,4-dioxo-1,2,3,4-tetrahydro-3-quinazolinyl)benzene (**17b**).

This compound had ir: 3288, 1722, 1658, 1636 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 11.5 (s, 1H), 10.7 (s, 1H), 7.9 (d, 1H, J = 8), 7.9 (d, 2H, J = 9), 7.7-7.6 (m, 2H), 7.5-7.4 (m, 2H), 7.3 (d, 2H, J = 9), 7.2-7.1 (m, 3H).

Anal. Calcd. for $C_{21}H_{14}N_4O_3$: C, 68.10; H, 3.81; N, 15.13. Found: C, 67.90; H, 3.89; N, 15.23.

1-(2-Benzimidazolylamino)-4-(2,4-dioxo-1,2,3,4-tetrahydro-3-quinazolinyl)benzene (**17c**).

This compound had ir: 3398, 1726, 1656, 1607 cm^{-1}; ^1H-nmr (DMSO-d_6): δ 11.6 (s, 1H), 9.8 (s, 2H), 8.0 (d, 1H, J = 9), 7.9 (d, 2H, J = 10), 7.8-7.7 (m, 1H), 7.4-7.3 (m, 2H), 7.25-7.2 (m, 4H), 7.1-7.0 (m, 2H).

Anal. Calcd. for $C_{21}H_{15}N_5O_2$: C, 68.28; H, 4.09; N, 18.96. Found: C, 68.42; H, 4.21; N, 18.87.

Synthesis of 1-(2-Benzoazolylamino)-4-(4-oxo-2-thioxo-1,2,3,4-tetrahydro-3-quinazolinyl)benzenes **18**.

General Procedures.

Method A.

To a solution of methyl 2-isothiocyanatobenzoate **15** (0.38 g, 2 mmoles) in DMF (7 ml), the corresponding 2-(4-aminophenylamino)benzoazole **5** (2 mmoles) in DMF (7 ml) was added. The solution was heated at 60-80° for 2 hours, refluxed for 24 hours and then cooled at room temperature to precipitate **15**. The precipitate was filtered, washed with cold DMF and methanol, dried and finally recrystallized from DMF/water.

Method B.

To a solution of the corresponding 2-(4-isothiocyanatophenylamino)benzoazole **6** (2 mmoles) in DMF (8 ml), methyl anthranilate **13** (0.3 g, 2 mmoles) in DMF (7 ml) was added. The mixture was heated for 2 hours at 60-80° and then refluxed for 24 hours. The work up procedure is identical to that described in method A.

1-(2-Benzothiazolylamino)-4-(4-oxo-2-thioxo-1,2,3,4-tetrahydro-3-quinazolinyl)benzene (**18a**).

This compound had ir: 3289, 3167, 1683, 1623 cm^{-1}; ^1H-nmr (TFA): δ 8.2 (d, 1H, J = 8), 8.0-7.3 (m, 11H).

Anal. Calcd. for $C_{21}H_{14}N_4OS_2$: C, 62.67; H, 3.51; N, 13.92. Found: C, 62.49; H, 3.61; N, 13.87.

1-(2-Benzoxazolylamino)-4-(4-oxo-2-thioxo-1,2,3,4-tetrahydro-3-quinazolinyl)benzene (**18b**).

This compound had ir: 3336, 3168, 1691, 1623 cm^{-1}; ^1H-nmr (TFA): δ 8.2 (d, 1H, J = 8), 8.0-7.1 (m, 11H).

Anal. Calcd. for $C_{21}H_{14}N_4O_2S$: C, 65.27; H, 3.65; N, 14.50. Found: C, 65.30; H, 3.82; N, 14.61.

1-(2-Benzimidazolylamino)-4-(4-oxo-2-thioxo-1,2,3,4-tetrahydro-3-quinazolinyl)benzene (**18c**).

This compound had ir: 3243, 1661, 1621 cm^{-1}; ^1H-nmr (TFA): δ 8.3 (d, 1H, J = 8), 8.1-7.5 (m, 11H).

Anal. Calcd. for $C_{21}H_{15}N_5OS$: C, 65.44; H, 3.92; N, 18.17. Found: C, 65.31; H, 3.88; N, 18.11.

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