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Preparation of [5,6,6] Tricyclic Guanidines from C,C-Bis(iminophosphoranes).

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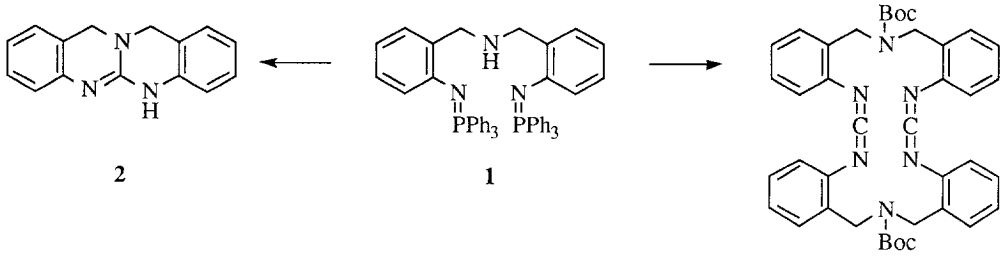
Abstract: Aza Wittig-type reaction of C,C-bis(iminophosphorane) **4**, derived from 2,5-bis(*o*-aminophenyl)pyrrole, with two equivalents of aryl isocyanates directly provided the tricyclic guanidines **9**, which underwent elimination of the corresponding diarylcarbodiimide by thermal treatment to give the parent [5,6,6] tricyclic guanidine **13**.

Recent years have witnessed a significant increase in the utilization of iminophosphoranes as valuable synthetic intermediates.[1] In particular, iminophosphoranes are versatile building blocks for the construction of azaheterocycles which constitute the backbone of various biologically active compounds such as lavendamycin,[2] aplysinopsin,[3] leucettamine B[4] and fascaplysin.[5] However, the chemistry of bis(iminophosphoranes) has been less studied. Bis(iminophosphoranes) have been shown to have high synthetic potential as a result of their ability to react with reagents having two functionalities or with two separate reagents with the same or different functionality.[6] In this context, we have reported that the C,C-bis(iminophosphorane) **1** reacted with aryl isocyanates or isothiocyanates to give rigid [6,6] guanidines[7] **2**, whereas with the system Boc_2O-DMAP provided the cyclic bis(carbodiimide) **3**.[8]

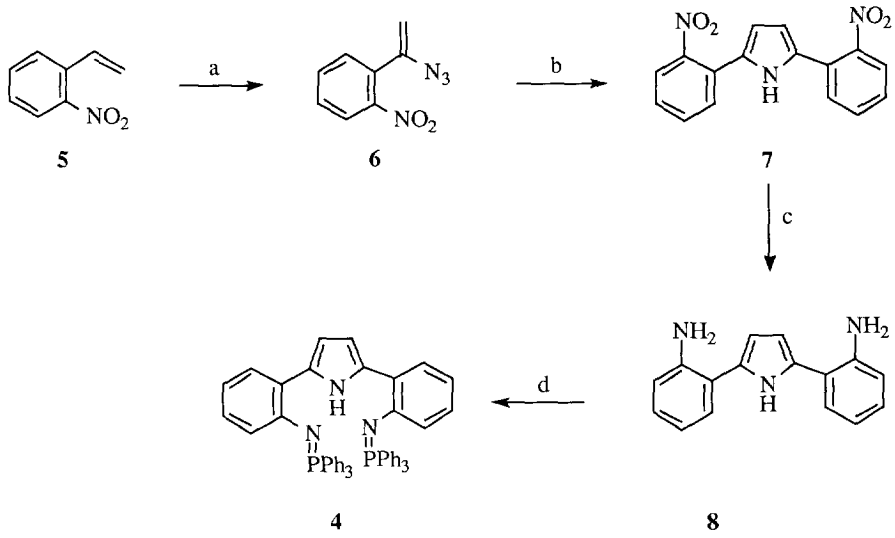


2 **1** **3**

As a further use of this type of C,C-bis(iminophosphoranes), it was decided that the next logical step would

be the preparation and chemical behaviour of the related C,C-bis(iminophosphorane) **4**, in which the amino group into the tether connecting the two aromatic rings is part of a pyrrole ring. At first it was of interest to see if the bis(iminophosphorane) **4** shows the same behaviour than the observed in bis(iminophosphorane) **1** with respect to aryl isocyanates. If this is so, aza Wittig-type reaction between **4** and isocyanates could provide the tricyclic BCD core found in the guanidino alkaloid ptilomycalin A, isolated from the sponge *Ptilocaulis spiculifer*, which have been shown to have antifungal, antiviral and antitumor activity and, for which only a few efforts toward its synthesis have been reported.[9]

To test our hypothesis the requisite bis(iminophosphorane) **4** was prepared by the four-step sequence: (a) conversion of the readily available *o*-nitrostyrene[10] **5** into the vinyl azide **6** by treatment with the system NaN_3-ICl and further basic treatment with potassium *t*-butoxide[11] (85%), (b) Staudinger reaction of **6** with triphenylphosphine and further treatment of the not isolated vinyliminophosphorane[12] with *o*-nitrophenacyl bromide to give 2,5-bis(*o*-nitrophenyl)pyrrole **7** in 40% yield, (c) hydrogenation of **7** in the presence of Pd on charcoal provided the expected triamino compound **8** in 76% yield, and (d) treatment of **8** with dibromotriphenylphosphorane in the presence of triethylamine afforded **4** in 68% yield (Scheme 1).

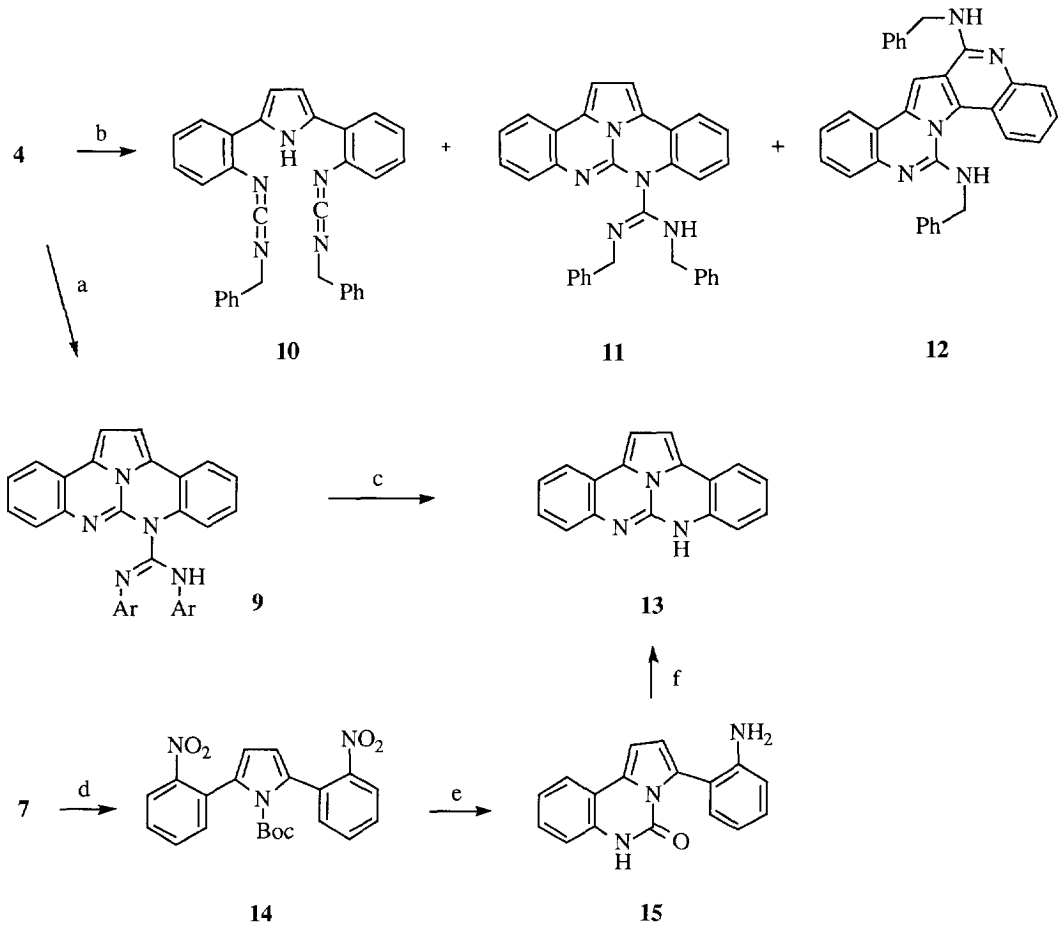


Reagents and Conditions (a) 1. NaN_3-ICl, CH_3CN, - 10 °C to r.t. 2. $KOBu^t$, Et_2O, 0 °C to r.t.; (b) 1. Ph_3P, C_6H_6, r.t. 2. *o*-nitrophenacyl bromide, Et_3N, C_6H_6, reflux; (c) H_2, Pd/C, EtOH, r.t.; (d) Ph_3PBr_2, Et_3N, C_6H_6, reflux.

Scheme 1

Aza Wittig-type reaction of bis(iminophosphorane) **4** with two equivalents of aryl isocyanates in benzene at reflux temperature gave directly the previously unreported pentacyclic compounds **9**, bearing two guanidine-type moieties, in 47-59% yield.The ^1H and ^{13}C n.m.r. spectra of compounds **9** indicated that the two aryl groups

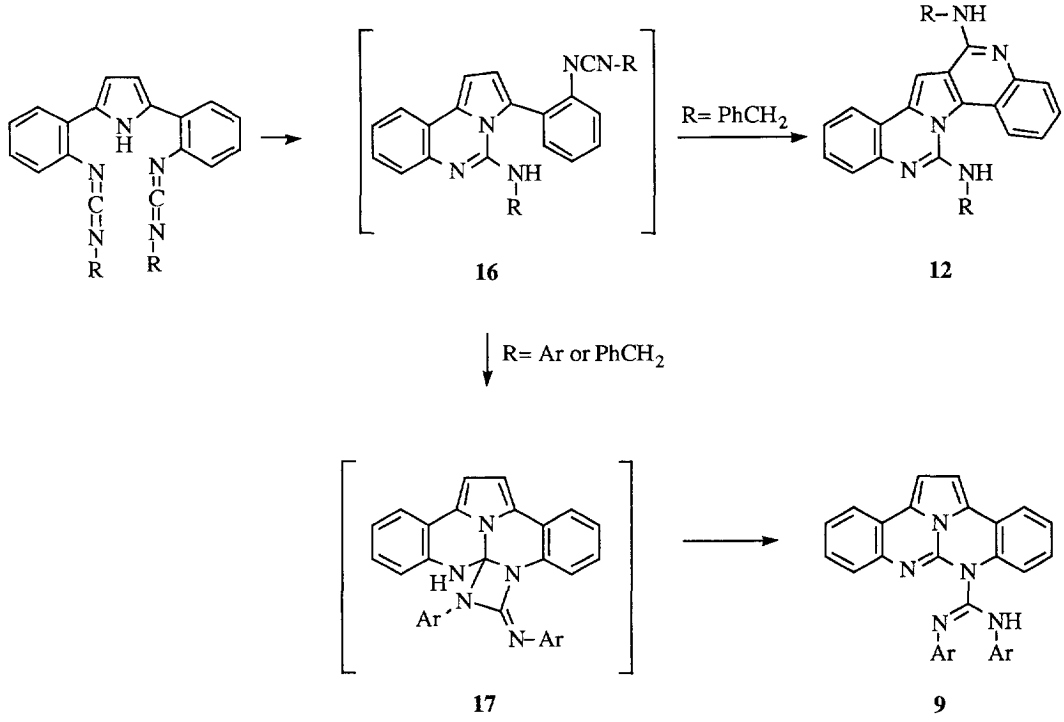
are nonequivalent. However, bis(iminophosphorane) **4** reacted with two equivalents of benzyl isocyanate under the same reaction conditions to give the corresponding bis(carbodiimide) **10** as the major product (39%), together with the tricyclic guanidine **11** (13%) and the compound **12** (22%). When compounds **9** were pyrolyzed at temperatures slightly higher than their melting points elimination of the corresponding diarylcarbodiimide took place, and the parent tricyclic guanidine **13** was isolated as a crystalline solid in fair yield. This compound can also be obtained in 52% overall yield by a three-step sequence: (a) reaction of 2,5-bis(*o*-nitrophenyl)pyrrole **7** with the system Boc_2O-DMAP in acetonitrile at room temperature furnished the *N*-protected pyrrole **14** in 92% yield, (b) hydrogenation in the presence of Pd on charcoal provided **15** in 70% yield, and (c) cyclization by the action of $POCl_3$ gave **13** in 81% yield (Scheme 2).



Reagents and Conditions (a) 2 Ar-NCO, C_6H_6, reflux; (b) 2 Ph-CH_2-NCO, C_6H_6, reflux; (c) Δ; (d) Boc_2O-DMAP, CH_3CN, r.t.; (e) H_2, Pd/C, EtOH, r.t.; (f) $POCl_3$, reflux.

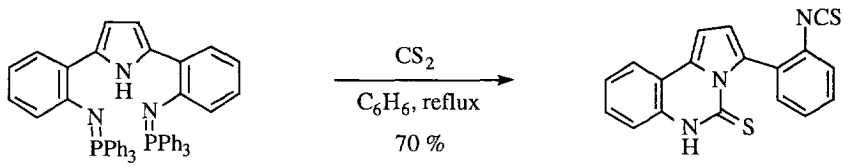
Scheme 2

Probably, formation of compounds **9**, **11** and **12** could involve an initial aza Wittig-type reaction between the bis(iminophosphorane) **4** and the two equivalents of isocyanate to give the corresponding bis(carbodiimide) type **10** which undergoes ring closure by nucleophilic attack of the nitrogen atom of the pyrrole ring on the central carbon atom of one of the two carbodiimide moieties to give the pyrroloquinazoline **16**, in which the remaining carbodiimide moiety could undergo either electrocyclic ring closure across the position 3 of the pyrrole ring to give **12** or an intramolecular [2+2] cycloaddition with the exocyclic carbon-nitrogen double bond, and subsequent opening of the four-membered ring of **17** affording **9** (Scheme 3). Support for this mechanism was found when bis(carbodiimide) **10** was converted into a mixture of **11** and **12** by heating in toluene at reflux temperature. All attempts to isolate the intermediate **16** met with failure. However, the closely related compound **18** was obtained in 80% yield when bis(iminophosphorane) **4** was treated with carbon disulfide in benzene at reflux temperature (Scheme 4).



Scheme 3

In conclusion, the work described here affords a simple but effective new and general route to [5,6,6] tricyclic guanidines derived from the pyrrolodiquinazoline ring system, bearing an additional exocyclic guanidino fragment. These relatively complex and unreported structures are assembled in a single one-pot procedure, under mild reaction conditions and from the readily available starting material C,C-bis(iminophosphorane) **4**.



4 **18**

Scheme 4

EXPERIMENTAL.

All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. IR spectra were obtained as nujol emulsions or films on a Nicolet 5DX spectrophotometer. NMR spectra were recorded on a Bruker AC-200 (200 MHz) or a Varian Unity 300 (300 MHz). Mass spectra were recorded on a Hewlett-Packard 5993C spectrometer. Microanalyses were performed on a Perkin-Elmer 240C instrument.

α-Azido-*o*-nitrostyrene 6.

To a cooled at -10 °C suspension of sodium azide (1.62 g, 25 mmol) in dry acetonitrile (10 ml) was added ICl (2.43 g, 15 mmol) in small portions and the mixture was stirred at that temperature for 10 min, and then *o*-nitrostyrene (1.49 g, 10 mmol) was added. The resultant mixture was allowed to warm at room temperature and stirring was continued for 20 h. The solution was poured into ice/water (200 ml) and then extracted with diethyl ether (3 x 75 ml). The combined organic layers were washed with a 5% aqueous solution of sodium thiosulfate (50 ml), water (4 x 50 ml) and dried over anhydrous magnesium sulfate. After filtration the filtrate was concentrated under reduced pressure and the residual oil was dissolved in diethyl ether (20 ml). The resultant solution was cooled at 0 °C and potassium *t*-butoxide (1.35 g, 12 mmol) was added. The solution was stirred at that temperature for 2 h and then at room temperature for 20 h. After pouring into water (100 ml) the solution was extracted with diethyl ether (3 x 50 ml) and the combined organic layers were washed with brine (2 x 50 ml) and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure an the residue was chromatographed on a silica gel column with *n*-hexane/diethyl ether (1:1) to give **6** in 85% yield as an oil. (Found: C, 50.25; H, 3.40; N, 29.22. $C_8H_6N_4O_2$ requires: C, 50.53; H, 3.28; N, 29.46); i.r. (neat): 2137, 2105, 1533, 1355, 1268 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 5.05 (d, 1 H, J = 2.15 Hz), 5.10 (d, 1 H, J = 2.15 Hz), 7.47-7.67 (m, 3 H), 7.90 (dd, 1 H, J = 1.53, 7.94 Hz); ^{13}C n.m.r. δ ($CDCl_3$): 102.8, 124.4, 130.2, 130.3, 131.3, 133.0, 143.0, 148.3; m/z (%): 190 (M^+, 5), 134 (51), 104 (100).

2,5-Bis(*o*-nitrophenyl)pyrrole 7.

To a cooled at 0 °C solution of **6** (1.90 g, 10 mmol) in dry benzene (25 ml) a solution of triphenylphosphine (2.62 g, 10 mmol) in the same solvent (10 ml) was added dropwise. The resultant solution was allowed to warm at room temperature and stirred for 4 h. Then, *o*-nitrophenacyl bromide (2.44 g, 10 mmol) and triethylamine (2.02

g, 20 mmol) were added and the resultant solution refluxed for 1.5 h. After cooling, the precipitated triethylammonium bromide was separated by filtration and the filtrate concentrated to dryness. The residual material was chromatographed on a silica gel column with *n*-hexane/ethyl acetate (3:2) to give **7** in 40% yield as orange prisms, m.p. 143-144 °C. (Found: C, 62.19; H, 3.76; N, 13.25. $C_{16}H_{11}N_3O_4$ requires: C, 62.14; H, 3.58; N, 13.58); i.r. (nujol): 3356, 1609, 1566, 1521, 1340, 1049, 808, 783, 745 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 6.49 (d, 2 H, J = 2.56 Hz), 7.33-7.41 (m, 2 H), 7.52-7.62 (m, 4 H), 7.73 (d, 2 H, J = 8.37 Hz), 9.46 (br s, 1 H); ^{13}C n.m.r. δ ($CDCl_3$): 112.4, 124.5, 126.3, 127.7, 128.5, 130.6, 132.5, 148.2; m/z (%): 309 (M^+, 41), 204 (63), 133 (43), 103 (100), 77 (63).

2,5-Bis(*o*-aminophenyl)pyrrole 8.

To a suspension of **7** (1.54 g, 5 mmol) in ethanol (30 ml) was added 10% Pd on charcoal (0.16 g), and the reaction mixture was stirred at room temperature under hydrogen at 2 atm for 4 h. The reaction mixture was heated at 50 °C and filtered on celite, which was washed with hot ethanol (2 x 10 ml). The filtrate and the ethanolic extracts were concentrated to dryness under reduced pressure and the residual material was recrystallized from ethanol to give **8** in 76% yield, as colourless needles, m.p. 175-176 °C. (Found: C, 77.00; H, 6.13; N, 16.80. $C_{16}H_{15}N_3$ requires: C; 77.08; H, 6.06; N, 16.85); i.r. (nujol): 3422, 3376, 3341, 3295, 3193, 3136, 1613, 1495, 1243, 765, 746 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 3.88 (br s, 4 H), 6.49 (s, 2 H), 6.75 (d, 2 H, J = 7.61 Hz), 6.82 (t, 2 H, J = 7.61 Hz), 7.08 (t, 2 H, J = 7.61 Hz), 7.27 (d, 2 H, J = 7.61 Hz), 9.02 (br s, 1 H); ^{13}C n.m.r. δ ($CDCl_3$): 108.6, 116.8, 119.4, 119.6, 127.9, 128.2, 129.9, 143.3; m/z (%): 249 (M^+, 72), 130 (100), 116 (16), 77 (11).

Bis(iminophosphorane) 4.

To a cooled at 0 °C solution of triphenylphosphine (2.62 g, 10 mmol) in dry benzene (70 ml), bromine (1.56 g, 10 mmol) in the same solvent (20 ml) was added dropwise. The mixture was allowed to warm at room temperature and then **8** (1.25 g, 5 mmol) and triethylamine (2.02 g, 20 mmol) were added. The resultant mixture was refluxed for 16 h. After cooling, the precipitated solid was separated by filtration, washed with cold water (250 ml) and air-dried to give **4** in 68% yield as colourless prisms, m.p. 318-320 °C; i.r. (nujol): 3363, 1589, 1435, 1325, 1276, 1107, 1021, 746, 717, 694 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$+CF_3COOH): 5.90 (d, 2 H, J = 2.62 Hz), 6.97 (d, 2 H, J = 7.87 Hz), 7.16 (td, 2 H, J = 1.57, 7.87 Hz), 7.24-7.60 (m, 28 H), 7.78-7.83 (m, 6 H), 10.11 (s, 1 H); ^{13}C n.m.r. δ ($CDCl_3$+CF_3COOH): 109.1, 119.7 (d, J = 102.8 Hz), 127.0 (d, J = 2.7 Hz), 127.9, 128.8, 129.8, 130.1 (d, J = 13.3 Hz), 130.7, 131.3 (d, J = 5.4 Hz), 132.4 (d, J = 2.4 Hz), 133.5 (d, J = 10.9 Hz), 135.7 (d, J = 2.7 Hz).

General Procedure for the Preparation of the Tricyclic Guanidines 9.

To a suspension of bis(iminophosphorane) **4** (0.38 g, 0.5 mmol) in dry benzene (15 ml) a solution of the appropriate aryl isocyanate (1 mmol) in the same solvent (10 ml) was added at once. The reaction mixture was heated at reflux temperature for 6 h. After cooling, the solvent was removed under reduced pressure and the residual material was chromatographed on a silica gel column with *n*-hexane/ethyl acetate (7:3) to give **9**.

9a (Ar = 3-CH_3.C_6H_4) (59%), m.p. 240-241 °C (from diethyl ether as colourless prisms). (Found: C, 80.25; H, 5.16; N, 14.49. $C_{32}H_{25}N_5$ requires: C, 80.14; H, 5.25; N, 14.60); i.r. (nujol): 3390, 1658, 1612, 1541, 1365, 769,

723 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 2.17 (s, 3 H), 2.18 (s, 3 H), 6.93-7.68 (m, 17 H), 8.13 (dd, 1 H, *J* = 1.99, 7.51 Hz), 9.75 (s, 1 H); ^{13}C n.m.r. δ (DMSO-d_6): 21.2, 103.1, 113.20, 116.4, 117.2, 118.0, 120.4, 120.5, 121.8, 121.9, 122.4, 123.3, 123.7, 124.0, 124.2, 126.9, 127.6, 128.1, 128.2, 128.7, 128.9, 132.8, 133.5, 137.6, 138.3, 139.2, 139.9, 140.5, 144.8, 146.7 (one methine carbon was not observed); m/z (%): 479 (M^+, 13), 348 (25), 258 (17), 257 (100).

9b (Ar = 4-CH_3.C_6H_4) (55%), m.p. 211-212 °C (from diethyl ether as colourless prisms). (Found: C, 80.27; H, 5.14; N, 14.51. $C_{32}H_{25}N_5$ requires: C, 80.14; H, 5.25; N, 14.60); i.r. (nujol): 3387, 1656, 1610, 1537, 1529, 1509, 1325, 1195, 811, 750 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 2.23 (s, 3 H), 2.27 (s, 3 H), 6.81 (d, 2 H, *J* = 4.20 Hz), 6.92-7.25 (m, 10 H), 7.38-7.50 (m, 5 H), 7.65 (dd, 1 H, *J* = 1.22, 7.81 Hz), 7.95 (dd, 1 H, *J* = 1.50, 8.11 Hz); ^{13}C n.m.r. δ ($CDCl_3$): 20.5, 20.8, 102.3, 115.8, 118.3, 119.3, 120.9, 121.5, 123.8, 124.3, 124.7, 126.9, 127.3, 127.4, 128.6, 129.3, 129.6, 131.4, 133.0, 133.1, 133.4, 136.5, 138.0, 138.4, 140.0, 144.2, 146.5 (one quaternary carbon was not observed); m/z (%): 479 (M^+, 5), 348 (19), 257 (100), 91 (20).

9c (Ar = 4-CH_3O.C_6H_4) (47%), m.p. 135-137 °C (from diethyl ether as colourless prisms). (Found: C, 75.21; H, 4.76; N, 13.60. $C_{32}H_{25}N_5O_2$ requires: C, 75.13; H, 4.92; N, 13.69); i.r. (nujol): 3394, 1655, 1616, 1547, 1506, 1298, 1247, 1181, 1036, 764, 752 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 3.68 (s, 3 H), 3.71 (s, 3 H), 6.68-7.56 (m, 18 H), 7.90 (d, 1 H, *J* = 7.50 Hz); ^{13}C n.m.r. δ ($CDCl_3$): 55.5, 102.4, 114.1, 114.5, 117.8, 118.4, 121.0, 121.1, 121.6, 123.8, 124.3, 124.9, 126.9, 127.4, 128.6, 128.8, 132.3, 133.2, 133.6, 134.2, 138.5, 140.4, 145.1, 146.8, 155.1, 155.9 (one methine carbon was not observed); m/z (%): 511 (M^+, 3), 364 (8), 257 (100), 239 (36), 77 (24).

9d (Ar = 4-Cl.C_6H_4) (52%), m.p. 162-163 °C (from diethyl ether as colourless prisms). (Found: C, 69.13; H, 3.61; N, 13.40. $C_{30}H_{19}Cl_2N_5$ requires: C, 69.24; H, 3.68; N, 13.46); i.r. (nujol): 3382, 1665, 1613, 1592, 1524, 1490, 1358, 1277, 1198, 830, 764, 753 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 6.81 (d, 1 H, *J* = 3.68 Hz), 6.89 (d, 2 H, *J* = 8.90 Hz), 7.02-7.61 (m, 15 H), 7.94 (dd, 1 H, *J* = 1.31, 7.61 Hz); ^{13}C n.m.r. δ ($CDCl_3$): 102.7, 116.8, 118.7, 120.6, 121.1, 121.7, 123.9, 124.3, 124.9, 127.0, 127.1, 127.6, 128.0, 128.4, 128.6, 128.9, 128.9, 129.3, 133.1, 133.7, 137.5, 138.1, 139.0, 139.2, 143.6, 146.0; m/z (%): 523 (M^++4, 1), 521 (M^++2, 5), 519 (M^+, 8), 370 (8), 368 (23), 257 (100).

Reaction of Bis(iminophosphorane) 4 with Benzyl Isocyanate.

To a suspension of bis(iminophosphorane) **4** (0.77 g, 1 mmol), in dry benzene (25 ml), a solution of benzyl isocyanate (0.27 g, 2 mmol) in the same solvent (5 ml) was added at once. The reaction mixture was refluxed for 7 h. After cooling, the solvent was removed under reduced pressure and the residual material was chromatographed on a silica gel column with *n*-hexane/ethyl acetate (4:1) to give **10** (R_f = 0.8), **11** (R_f = 0.6) and **12** (R_f = 0.2), which were recrystallized from *n*-hexane/diethyl ether.

10 (39%), m.p. 107-109 °C (colourless prisms). (Found: C, 80.02; H, 5.17; N, 14.47. $C_{32}H_{25}N_5$ requires: C, 80.14; H, 5.25; N, 14.60); i.r. (nujol): 3392, 3371, 2153, 1350, 1297, 1157, 1084, 919, 790, 694, 672, 635 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 4.54 (s, 4 H), 6.64 (d, 2 H, *J* = 2.63 Hz), 7.03-7.08 (m, 7 H), 7.29-7.43 (m, 9 H), 7.64 (d, 2 H, *J* = 7.34 Hz), 12.06 (br s, 1 H); ^{13}C n.m.r. δ ($CDCl_3$): 50.6, 107.9, 125.3, 125.5, 125.7, 126.4, 126.6, 127.4, 127.9, 128.8, 130.2, 133.9, 136.6, 137.7; m/z (%): 479 (M^+, 7), 257 (100), 91 (26).

11 (13%), m.p. 110-111 °C (colourless prisms). (Found: C, 80.25; H, 5.17; N, 14.76. $C_{32}H_{25}N_5$ requires: C,

80.14; H, 5.25; N, 14.60); i.r. (nujol): 3421, 1659, 1614, 1544, 1498, 1212, 752, 700 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 4.21 (dd, 1 H, *J* = 3.67, 14.43 Hz), 4.40 (d, 1 H, *J* = 13.64 Hz), 4.52 (dd, 1 H, *J* = 3.67, 14.43 Hz), 4.91 (d, 1 H, *J* = 13.64 Hz), 6.70-6.74 (m, 2 H), 6.84 (d, 2 H, *J* = 7.09 Hz), 6.98 (d, 1 H, *J* = 3.94 Hz), 7.07-7.37 (m, 14 H), 7.56 (dd, 1 H, *J* = 3.65, 5.77 Hz), 7.88 (dd, 1 H, *J* = 3.15, 6.03 Hz); ^{13}C n.m.r. δ ($CDCl_3$): 46.4, 53.4, 102.1, 117.5, 120.6, 121.4, 123.9, 124.1, 125.9, 126.2, 126.4, 127.1, 127.5, 127.6, 127.9, 128.1, 128.2, 128.6, 129.0, 129.3, 132.7, 132.9, 135.4, 137.9, 138.7, 143.2, 146.9, 149.0; m/z (%): 479 (M^+, 5), 257 (81), 91 (100).

12 (22%), m.p. 161-162 °C (colourless prisms). (Found: C, 80.23; H, 5.09; N, 14.75. $C_{32}H_{25}N_5$ requires: C, 80.14; H, 5.25; N, 14.60); i.r. (nujol): 3441, 3325, 1617, 1566, 1529, 1318, 1294, 752, 724, 703 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 4.89 (d, 2 H, *J* = 5.25 Hz), 4.93 (d, 2 H, *J* = 5.25 Hz), 5.29 (br s, 1 H), 5.50 (t, 1 H, *J* = 5.25 Hz), 6.97 (s, 1 H), 7.08-7.62 (m, 14 H), 7.81-7.95 (m, 4 H); ^{13}C n.m.r. δ ($CDCl_3$): 45.5, 46.3, 93.1, 115.2, 116.1, 117.8, 121.7, 122.4, 123.2, 123.7, 124.9, 126.4, 127.4, 127.6, 127.8, 128.3, 128.5, 128.6, 128.7, 128.8, 129.1, 137.1, 137.7, 139.6, 141.1, 144.1, 145.6, 151.3; m/z (%): 479 (M^+, 10), 283 (7), 106 (6), 91 (100), 65 (16).

N-(*t*-Butoxycarbonyl)- 2,5-bis(*o*-nitrophenyl)pyrrole 14.

To a solution of 2,5-bis(*o*-nitrophenyl)pyrrole **7** (0.62 g, 2 mmol) in dry acetonitrile (15 ml), Boc_2O (0.54 g, 2.5 mmol) and DMAP (0.24 g, 2 mmol) were added. The resultant solution was stirred at room temperature for 2 h, afterwards the solvent was removed under reduced pressure and the crude solid was chromatographed on a silica gel column with n-hexane/ethyl acetate (7:3) and further recrystallized from ethanol to give **14** in 92 % yield, as yellow prisms, m.p. 154-155 °C.(Found: C, 61.47; H, 4.78; N, 10.11. $C_{21}H_{19}N_3O_6$ requires: C, 61.61; H, 4.68; N, 10.26); i.r. (nujol): 1743, 1520, 1343, 1144, 1127, 983, 811, 746, 724, 655 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 1.02 (s, 9 H), 6.23 (s, 2 H), 7.52-7.67 (m, 6 H), 8.12 (d, 2 H, *J* = 8.13 Hz); ^{13}C n.m.r. δ ($CDCl_3$): 27.0, 84.2, 113.7, 124.3, 128.7, 130.6, 131.6, 132.9, 133.1, 148.1, 148.7; m/z (%): 409 (M^+, 11), 309 (38), 104 (17), 77 (12), 57 (100).

3-(*o*-Aminophenyl)-pyrrolo[1, 2-*c*]quinazolin-5(6*H*)-one 15.

To a solution of **14** (0.41 g, 1 mmol) in ethanol (30 ml) was added 10% Pd on charcoal (50 mg), and the mixture was stirred at room temperature under hydrogen at 2 atm for 4 h. The reaction mixture was filtered on celite and the filtrate was concentrated to dryness. The crude product was chromatographed on a silica gel column with n-hexane/ethyl acetate (1:1) and further recrystallized from ethanol to give **15** in 70% yield, as colourless prisms, m.p. 188-189 °C. (Found: C, 74.06; H, 4.85; N, 15.14. $C_{17}H_{13}N_3O$ requires: C, 74.17; H, 4.76; N, 15.26); i.r. (nujol): 3400, 3326, 3251, 3196, 1724, 1597, 1341, 1316, 1296, 1095, 1039, 940, 790, 750 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 4.69 (br s, 2 H), 6.47 (d, 1 H, *J* = 3.54 Hz), 6.53 (td, 1 H, *J* = 1.19, 7.36 Hz), 6.65 (dd, 1 H, *J* = 0.72, 7.85 Hz), 6.94-7.07 (m, 3 H), 7.12-7.33 (m, 3 H), 7.92 (d, 1 H, *J* = 7.71 Hz), 11.09 (s, 1 H); ^{13}C n.m.r. δ (DMSO-d_6): 103.7, 114.1, 114.7, 114.8, 115.1, 115.5, 119.3, 121.7, 122.6, 127.2, 128.2, 129.4, 130.3, 131.1, 132.8, 145.7, 147.3; m/z (%): 275 (M^+, 100), 274 (23), 258 (22), 257 (21), 130 (11).

Preparation of 7*H*-7,8,12c-triazacyclopenta[*fg*]naphtacene 13.

Method A: Compound **9** (0.25 mmol) was heated at 180-200 °C for 3 h. After cooling, the solid was extracted

with dichloromethane (2 x 5 ml) from which the corresponding diarylcarbodiimide was isolated. The remaining solid was slurried with ethanol and the precipitated solid was found to be **13** (77 %).

Method B: A mixture of **15** (0.1 g, 0.4 mmol) and phosphorus oxychloride (7 ml) was heated at reflux temperature for 8 h. After cooling, the clear solution was poured into ice/water (50 ml). Then 10% aqueous solution of sodium hydroxide was added dropwise until pH= 12. The mixture was stirred at room temperature for 2 h. The solid formed was separated by filtration, washed with water (3 x 15 ml), air-dried and a fraction of it was recrystallized from ethanol to give **13** in 81% yield, as yellow prisms, m.p. > 325 °C. (Found: C, 79.21; H, 4.21; N, 16.20. $C_{17}H_{11}N_3$ requires: C, 79.36; H, 4.31; N, 16.33); i.r. (nujol): 3113, 1644, 1626, 1612, 1588, 1549, 1529, 1301, 1156, 756, 742 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$+ CF_3COOH): 6.81 (s, 2 H), 7.01-7.05 (m, 2 H), 7.14-7.21 (m, 4 H), 7.44-7.49 (m, 2 H); ^{13}C n.m.r. δ ($CDCl_3$+ CF_3COOH): 107.8, 117.2, 117.5, 122.7, 125.8, 127.5, 129.9, 130.5, 143.5; m/z (%): 257 (M^+, 100), 203 (13), 128 (38), 114 (14), 75 (9).

Reaction of Bis(iminophosphorane) 4 with Carbon Disulfide.

A mixture of bis(iminophosphorane) **4** (0.38 g, 0.5 mmol), dry benzene (15 ml) and carbon disulfide (4 ml) was refluxed for 12 h. After cooling, the solvent was removed under reduced pressure and the crude product was chromatographed on a silica gel column with n-hexane/dichloromethane (1:4) to give **18** in 70% yield, as colourless prisms, m.p. 215-217 °C. (Found: C, 64.71; H, 3.21; N, 12.48. $C_{18}H_{11}N_3S_2$ requires: C, 64.84; H, 3.32; N, 12.60); i.r. (nujol): 3179, 3128, 2081, 1535, 1329, 1276, 1218, 1039, 931, 759, 714, cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 6.73 (d, 1 H, J = 3.93 Hz), 7.01 (d, 1 H, J = 3.93 Hz), 7.12-7.47 (m, 7 H), 7.88 (dd, 1 H, J = 1.83, 7.35 Hz), 10.11 (s, 1 H); ^{13}C n.m.r. δ (DMSO-d_6): 103.6, 114.7, 116.8, 120.1, 122.3, 123.8, 125.2, 126.3, 128.0, 129.1, 129.4, 130.4, 130.7, 131.4, 133.7, 133.9, 138.4, 169.6; m/z (%): 333 (M^+, 9), 276 (19), 275 (100), 243 (12), 138 (16), 137 (10).

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