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A SYNTHESIS AND TRANSFORMATIONS OF ALKYL 2-[2-CYANO-2-(2-PYRIDINYL)ETHENYL]AMINO-3-DIMETHYLAMINOPROPENOATES. A ONE-POT SYNTHESIS OF PYRROLO[3,2-*d*]PYRIMIDIN-4-ONES

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Abstract – Alkyl 2-[2-cyano-2-(2-pyridinyl)ethenyl]amino-3-dimethylaminopropenoates (**8**) and (**9**) were transformed by heating into alkyl 2-[2-cyano-2-(2-pyridinyl)ethenyl]amino-3-[2-methoxycabonyl-4-(2-pyridinyl)-1*H*-pyrrol-3-yl]aminopropenoates (**12**) and (**13**). Compounds (**8**) and (**9**) can be transformed in the presence of primary aliphatic amines into substituted pyrrolo[3,2-*d*]pyrimidines (**17**-**19**).

Recently, considerable interest has been manifested in the synthesis of pyrrole derivatives, since this heterocycle has been found in many natural products which possess biological properties and is the building block for porphyrins, chlorophylls, corrins and bile pigments.[1-6] In view of the importance of this heterocyclic systems for various applications, a large number of papers have been published on the preparation of this heterocyclic system.[5,7-9] Various substituted pyrroles have been prepared by condensation of α-aminocarbonyl compounds with 1,3-dicarbonyl compounds,[10-12] β-amino enones,[13,14] or 3-alkoxyacroleines,[15] by reaction of nitro compounds with isocyano acetates,[16-21] of α-chloroaldimines with KCN,[22] and α-acetoxy nitro compounds with isocyanatoacetonitrile.[23]

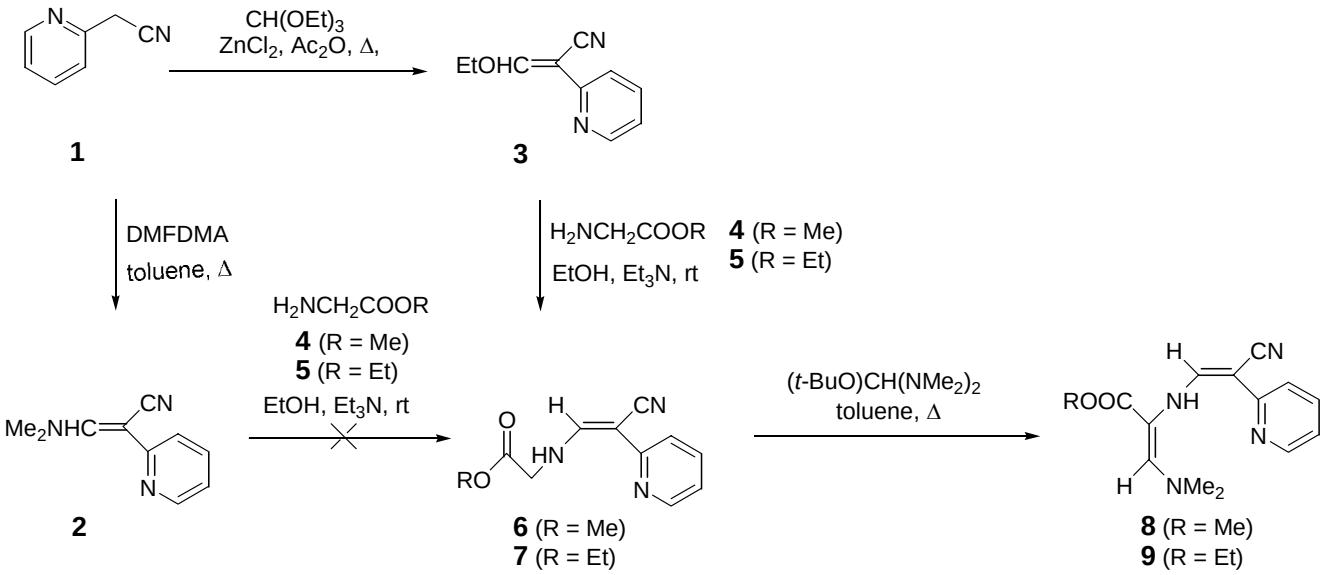
Only few examples of 3-aminopyrrole-2-carboxylates have been reported. They are: the condensation of α-amino-α-cyanoacetamides with ethyl acetoacetate followed by cyclization to ethyl 3-amino-2-carboxamido-5-methylpyrrole-4-carboxylate,[24] and the base-catalyzed cyclization of *N*-(2-cyano-ethenyl)glycine esters.[25] These 3-aminopyrrole-2-carboxylates have been used as intermediates in the synthesis of pyrrolo[3,2-*d*]pyrimidines (9-deazapurines), 9-deazaguanozines and other pyrrolo[3,2-*d*]pyrimidine *C*- nucleosides.[26]

Recently, substituted 2-(acylamino)- or 2-hydoxy-3-(dimethylamino)propenoates, masked α-formyl-α-amino- or α-formyl-α-hydroxy acids derivatives, and alkyl 2-[(2,2-disubstituted ethenyl)amino]-3-(dimethylamino)propenoates and related compounds have been used in our laboratory as reagents for preparation of several heterocyclic systems, such as 2*H*-pyran-2-ones and fused pyran-2-ones, fused pyridinones, pyrimidinones,[27-35] and imidazole-4-carboxylates,[36] including chiral α-heteroaryl-α-amino and -α-hydroxy acid derivatives[37,38] and other chiral heterocyclic systems.[39] Alkyl 2-(2,2,-disubstituted ethenyl)amino-3-dimethylamino)prop-2-enoates have been transformed into alkyl 3,4-disubstituted and alkyl 1-acyl-3,4-disubstituted pyrrole-2-carboxylates[40,41] and dialkyl 3-aminopyrrole-2,4-dicarboxylates[42] and further transformed into 5*H*-pyrrolo[3,2-*d*]pyrimidine derivatives (9-deazapurines).[43]

In continuation of our studies in this area, we report the synthesis of alkyl 2-[2-cyano-2-(2-pyridinyl)ethenyl]amino-3-[2-methoxycarbonyl-4-(2-pyridinyl)-1*H*-pyrrol-3-yl]aminopropenoates (**12**) and (**13**) and their further transformation into 3-substituted 7-(2-pyridinyl)-3,4-dihydro-5*H*-pyrrolo[3,2-*d*]pyrimidin-4-ones (**17**-**19**).

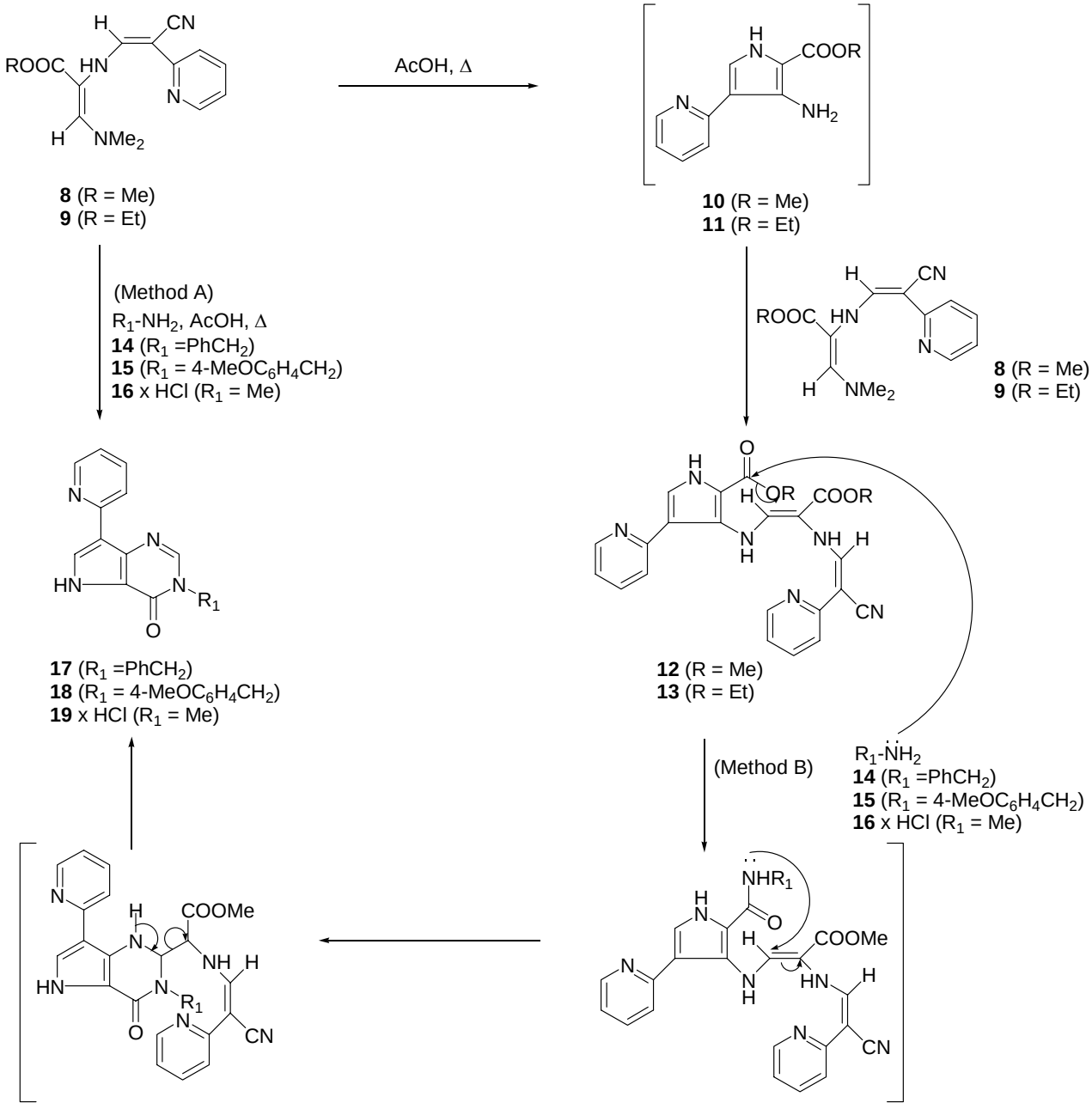
2-Pyridinylacetonitrile (**1**) was transformed with *N*,*N*-dimethylformamide dimethylacetal into 1-cyano-2-dimethylamino-1-(2-pyridinyl)ethene (**2**) by heating in anhydrous toluene for 1.5 h.[44] Since this compound did not react with alkyl glycinate hydrochlorides (**4**) and (**5**) in ethanol at room temperature, compound (**1**) was transformed with triethyl orthoformate in acetic anhydride in the presence of anhydrous $ZnCl_2$ by heating at 100-120°C for 3 h into 3-ethoxy-2-(2-pyridinyl)propenonitrile (**3**). This reacted with methyl (**4**) or ethyl glycinate hydrochloride (**5**) into methyl (**6**) and ethyl *N*-[2-cyano-2-(2-pyridinyl)ethenyl]glycinate (**7**) in 89% and 88% yields respectively and further converted with *tert*-butoxybis(dimethylamino)methane (Bredereck's reagent) into methyl (**8**) and ethyl (*Z*)-*N*-[(*E*)-2-cyano-2-(2-pyridinyl)-ethenyl]amino-3-dimethylaminopropenoate (**9**) in 94% and 72% yields, respectively. (Scheme 1).

Scheme 1



When compounds (**8**) and (**9**) were heated in acetic acid to boiling the corresponding methyl 2-[2-cyano-2-(2-pyridinyl)ethenyl]amino-3-[2-methoxycarbonyl-4-(2-pyridinyl)-1*H*-pyrrol-3-yl]aminopropenoate (**12**) and ethyl 2-[2-cyano-2-(2-pyridinyl)ethenyl]amino-3-[2-methoxycarbonyl-4-(2-pyridinyl)-1*H*-pyrrol-3-yl]aminopropenoate (**13**) were formed in 33% and 29% yields, respectively. The formation of the latter two compounds can be explained by cyclization of **8** and **9** into 3-amino-4-(2-pyridinyl)pyrrole-2-carboxylates (**10**) and (**11**), intermediates, according to the mechanism, which we have reported earlier for the formation of other 4-substituted 3-aminopyrrole-2-carboxylates,[42] followed by reaction with the starting compound in which dimethylamino group is substituted by aminopyrrole derivative to give products (**12**) and (**13**). (Scheme 2).

Scheme 2



When compound (**8**) was treated with aliphatic amines (**14-16**), the corresponding 3-substituted 7-(2-pyridinyl)-3,4-dihydro-5*H*-pyrrolo[3,2-*d*]pyrimidin-4-ones (**17-19**) were formed in 42%, 32% and 25% yields, respectively (Method A). The formation of pyrrolo[3,2-*d*]pyrimidine system can be explained in the following way. In the reaction (**8**→**17**), compound (**8**) changes into compound (**12**) and **12** reacts with an aliphatic amine to form pyrrole-2-carboxamide derivative followed by cyclization and elimination to give the final products, (Method B), according to the mechanism outlined on Scheme 2. This is supported experimentally, since the compound (**17**) was obtained also from compound (**12**) by heating with benzylamine (**14**) in acetic acid in 34% yield. (Scheme 2).

The structures of the new compounds were determined by ^{1}H NMR, ^{13}C NMR, and microanalyses. X-Ray analysis of compound (**8**), (Figure 1), shows (*Z*)-orientation of both substituted amino groups around the first double bond (C_2-C_3) and (*E*)-orientation of the substituted amino group and cyano group around the second double bond (C_7-C_8). The structure of compound (**18**) was also confirmed by X-Ray analysis. (Figure 2).

Figure 1. Ortep view of the asymmetric unit of **8**, showing the labeling of the non-hydrogen atoms. Ellipsoids are shown at 50% probability level.

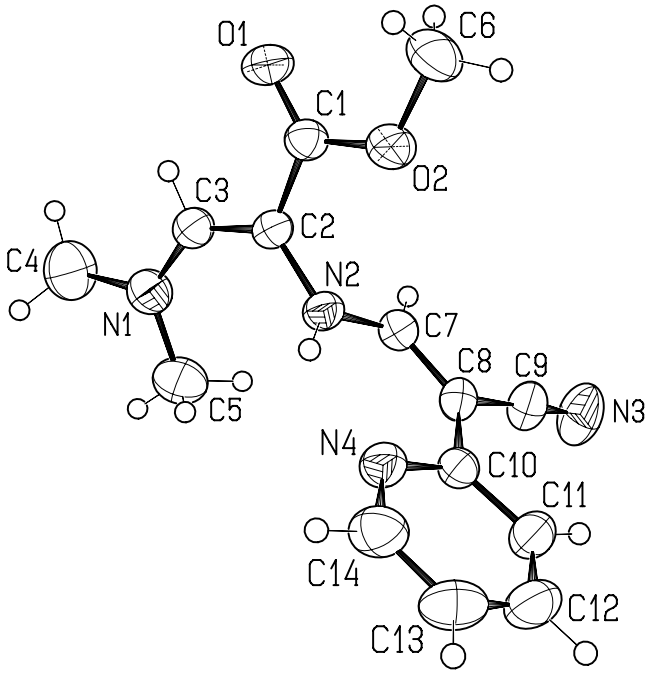
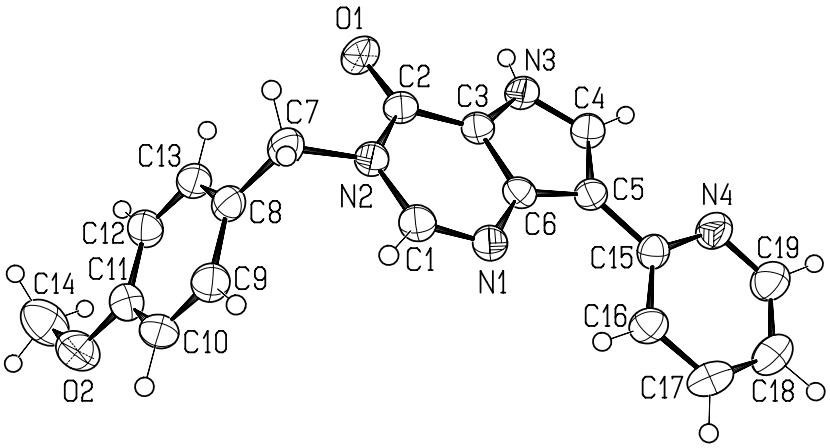


Figure 2. Ortep view of the asymmetric unit of **18**, showing the labeling of the non-hydrogen atoms. Ellipsoids are shown at 50% probability level.



EXPERIMENTAL

Melting points were taken on a Kofler micro hot stage. The ^{1}H NMR spectra and ^{13}C NMR spectra were obtained on a Bruker Avance DPX 300 spectrometer with TMS as the internal standard, MS spectra on an AutoSpecQ spectrometer, IR spectra on a Perkin-Elmer 1310 infrared spectrophotometer and microanalyses for C, H and N on a Perkin-Elmer CHN Analyser 2400. Compound (**2**) was prepared according to the procedure described in the literature.[44]

3-Ethoxy-2-(2-pyridinyl)propenonitrile (3). To the solution of 2-pyridinylacetonitrile (**1**) (3.0 g, 25.3 mmol) in acetic anhydride (25 mL) triethyl orthoformate (6.3 mL, 38 mmol) and catalytic amounts of anhydrous $ZnCl_2$ were added and the mixture was stirred in the oil bath at 100-120^{o}C for 2 h. The volatile compounds were evaporated *in vacuo*. The obtained oily residue was without further purification used for further transformations, IR 2160 cm^{-1} (CN), ^{1}H NMR ($CDCl_3$) δ: 1.44 (3H, t, $J_{CH\text{-}CH}$ = 7.2 Hz, CH_2CH_3), 4.29 (2H, q, $J_{CH\text{-}CH}$ = 7.2 Hz, CH_2CH_3), 7.13 (1H, ddd, $J_{H3\text{-}H5}$ = 1.1 Hz, $J_{H4\text{-}H5}$ = 7.7 Hz, $J_{H5\text{-}H6}$ = 4.9 Hz, H_5), 7.42 (1H, ddd, $J_{H3\text{-}H4}$ = 7.9 Hz, $J_{H3\text{-}H5}$ = 1.1 Hz, $J_{H3\text{-}H6}$ = 0.8 Hz, H_3), 7.67 (1H, ddd, $J_{H3\text{-}H4}$ = 7.9 Hz, $J_{H4\text{-}H5}$ = 7.7 Hz, $J_{H4\text{-}H6}$ = 1.9 Hz, H_4), 8.20 (1H, s, CH), 8.43 (1H, ddd, $J_{H3\text{-}H6}$ = 0.8 Hz, $J_{H4\text{-}H6}$ = 1.9 Hz, $J_{H5\text{-}H6}$ = 4.9 Hz, H_6).

Alkyl *N*-[2-cyano-2-(2-pyridinyl)ethenyl]glycinates. General Procedure. Compound (**3**), prepared as described above from 2-pyridinylacetonitrile (**1**) and triethyl orthoformate, was dissolved in ethanol (25 mL) and glycine alkyl ester hydrochloride (25.3 mmol) and triethylamine (3.5 mL, 25.3 mmol) were added.

The mixture was stirred for several hours at rt, then the volatile compounds were evaporated *in vacuo* and water (25 mL) was added. After heating to the boiling point and cooling, the precipitate was collected by filtration and washed with ethanol.

The following compounds were prepared by this method:

Methyl *N*-[2-cyano-2-(2-pyridinyl)ethenyl]glycinate (6). This compound was prepared from glycine methyl ester hydrochloride (**4**) (3.2 g, 25.3 mmol), 24 h, 89% yield (4.9 g), mp 94-96°C (from a mixture of ethanol and water), IR 2210 cm^{-1} (CN), ^1H NMR ($CDCl_3$) δ: 3.80 (3H, s, COOMe), 4.09 (2H, d, J_{CH-NH} = 6.0 Hz, CH_2), 7.02 (1H, ddd, J_{H3-H5} = 1.0 Hz, J_{H4-H5} = 7.4 Hz, J_{H5-H6} = 5.0 Hz, H_5), 7.15 (1H, d, J_{CH-NH} = 12.4 Hz, C*H*NH), 7.44 (1H, ddd, J_{H3-H4} = 8.1 Hz, J_{H3-H5} = 1.0 Hz, J_{H3-H6} = 0.9 Hz, H_3), 7.66 (1H, ddd, J_{H3-H4} = 8.1 Hz, J_{H4-H5} = 7.4 Hz, J_{H4-H6} = 1.9 Hz, H_4), 8.42 (1H, ddd, J_{H3-H6} = 0.9 Hz, J_{H4-H6} = 1.9 Hz, J_{H5-H6} = 5.0 Hz, H_6), 10.63 (1H, br s, CHN*H*). *Anal.* Calcd for $C_{11}H_{11}N_3O_2$: C, 60.82; H, 5.10; N, 19.34. Found: C, 61.00; H, 5.22; N, 19.29.

Ethyl *N*-[2-cyano-2-(2-pyridinyl)ethenyl]glycinate (7). This compound was prepared from glycine ethyl ester hydrochloride (**5**) (3.5 g, 25.3 mmol), 4 h, 88% yield (5.1 g), mp 81-82°C (from a 1:6 mixture of ethyl acetate and n-heptane), IR 2210 cm^{-1} (CN), ^1H NMR ($CDCl_3$) δ: 1.31 (3H, t, J_{CH-CH} = 7.2 Hz, $COOCH_2CH_3$), 4.07 (2H, d, J_{CH-NH} = 6.0 Hz, CH_2), 4.26 (2H, q, J_{CH-CH} = 7.2 Hz, $COOCH_2CH_3$), 7.01 (1H, ddd, J_{H3-H5} = 1.1 Hz, J_{H4-H5} = 7.5 Hz, J_{H5-H6} = 4.9 Hz, H_5), 7.15 (1H, d, J_{CH-NH} = 12.4 Hz, C*H*NH), 7.44 (1H, ddd, J_{H3-H4} = 8.1 Hz, J_{H3-H5} = 1.1 Hz, J_{H3-H6} = 1.0 Hz, H_3), 7.66 (1H, ddd, J_{H3-H4} = 8.1 Hz, J_{H4-H5} = 7.5 Hz, J_{H4-H6} = 1.9 Hz, H_4), 8.42 (1H, ddd, J_{H3-H6} = 1.0 Hz, J_{H4-H6} = 1.9 Hz, J_{H5-H6} = 4.9 Hz, H_6), 10.64 (1H, br s, CHN*H*). *Anal.* Calcd for $C_{12}H_{13}N_3O_2$: C, 62.33; H, 5.67; N, 18.17. Found: C, 62.36; H, 5.78; N, 18.01.

Alkyl 2-[2-cyano-2-(2-pyridinyl)ethenyl]amino-3-dimethylaminopropenoates. General Procedure. To compound (**6**) or (**7**) (10 mmol) suspended in dry toluene (10 mL), Bredereck's reagent (3.48 g, 20 mmol) was added and the mixture was heated under reflux for several hours. The volatile compounds were evaporated *in vacuo* and the mixture of ether and ethanol (ether:ethanol = 20 mL:5 mL) was added. The precipitate was collected by filtration and washed with ether.

The following compounds were prepared by this method:

Methyl (*Z*)-2-[(*E*)-2-cyano-2-(2-pyridinyl)ethenyl]amino-3-dimethylaminopropenoate (8). This compound was prepared from compound (**6**) (2.17 g, 10 mmol), 30 minutes, 94% yield (2.56 g), mp 174-176°C

(from a mixture of ethanol and toluene), IR 2210 cm^{-1} (CN), ^1H NMR ($CDCl_3$) δ: 3.04 (6H, s, CHN*Me*$_2$), 3.71 (3H, s, COOMe), 7.00 (1H, ddd, J_{H3-H5} = 1.1 Hz, J_{H4-H5} = 7.2 Hz, J_{H5-H6} = 5.1 Hz, H_5), 7.17 (1H, d, J_{CH-NH} = 12.2 Hz, C*H*NH), 7.27 (1H, s, C*H*NMe$_2$), 7.45 (1H, ddd, J_{H3-H4} = 8.3 Hz, J_{H3-H5} = 1.1 Hz, J_{H3-H6} = 1.0 Hz, H_3), 7.66 (1H, ddd, J_{H3-H4} = 8.3 Hz, J_{H4-H5} = 7.2 Hz, J_{H4-H6} = 1.9 Hz, H_4), 8.39 (1H, ddd, J_{H3-H6} = 1.0 Hz, J_{H4-H6} = 1.9 Hz, J_{H5-H6} = 5.1 Hz, H_6), 11.03 (1H, d, J_{CH-NH} = 12.2 Hz, CHN*H*). ^{13}C NMR ($CDCl_3$) δ: 43.13 (N(*C*H$_3$)$_2$), 51.87 (COO*C*H$_3$), 79.26 (CH=*C*-CN), 100.21 (Me$_2$NCH=*C*), 119.43 (CH=C-*C*N), 120.21 (*C*$_3$(Py)), 121.97 (*C*$_5$(Py)), 137.02 (Me$_2$N*C*H=C), 145.12 (*C*$_4$(Py)), 147.55 (*C*H=C-CN), 155.07 (*C*$_6$(Py)), 156.70 (*C*$_2$(Py)), 168.14 (*C*OOMe). *Anal.* Calcd for $C_{14}H_{16}N_4O_2$: C, 61.75; H, 5.92; N, 20.57. Found: C, 61.87; H, 5.97; N, 20.43.

Ethyl (*Z*)-2-[(*E*)-2-cyano-2-(2-pyridinyl)ethenyl]amino-3-dimethylaminopropenoate (9). This compound was prepared from compound (**7**) (2.31 g, 10 mmol), 2 h, 72% yield (2.06 g), mp 126-128°C (from ethanol), IR 2210 cm^{-1} (CN), ^1H NMR ($CDCl_3$) δ: 1.26 (3H, t, J_{CH-CH} = 7.1 Hz, COOCH$_2$C*H*$_3$), 3.04 (6H, s, CHN*Me*$_2$), 4.18 (2H, q, J_{CH-CH} = 7.1 Hz, COOC*H*$_2$CH$_3$), 6.99 (1H, ddd, J_{H3-H5} = 1.1 Hz, J_{H4-H5} = 7.4 Hz, J_{H5-H6} = 5.0 Hz, H_5), 7.18 (1H, d, J_{CH-NH} = 12.3 Hz, C*H*NH), 7.26 (1H, s, C*H*NMe$_2$), 7.45 (1H, ddd, J_{H3-H4} = 8.2 Hz, J_{H3-H5} = 1.1 Hz, J_{H3-H6} = 1.0 Hz, H_3), 7.66 (1H, ddd, J_{H3-H4} = 8.2 Hz, J_{H4-H5} = 7.4 Hz, J_{H4-H6} = 1.9 Hz, H_4), 8.39 (1H, ddd, J_{H3-H6} = 1.0 Hz, J_{H4-H6} = 1.9 Hz, J_{H5-H6} = 5.0 Hz,H_6), 11.06 (1H, d, J_{CH-NH} = 12.3 Hz, CHN*H*). ^{13}C NMR ($CDCl_3$) δ: 14.95 (COOCH$_2$*C*H$_3$), 43.10 (N(*C*H$_3$)$_2$), 60.50 (COO*C*H$_2$CH$_3$), 79.10 (CH=*C*-CN), 100.55 (Me$_2$NCH=*C*), 119.35 (CH=C-*C*N), 120.15 (*C*$_3$(Py)), 122.02 (*C*$_5$(Py)), 136.96 (Me$_2$N*C*H=C), 144.69 (*C*$_4$(Py)), 147.51 (*C*H=C-CN), 154.98 (*C*$_6$(Py)), 156.72 (*C*$_2$(Py)), 167.58 (*C*OOEt). *Anal.* Calcd for $C_{15}H_{18}N_4O_2$: C, 62.92; H, 6.34; N, 19.57. Found: C, 63.11; H, 6.39; N, 19.61.

Alkyl 2-[2-cyano-2-(2-pyridinyl)ethenyl]amino-3-[2-alkoxycarbonyl-4-(2-pyridinyl)-1*H*-pyrrol-3-yl]aminopropenoate. General procedure. Compound (**8**) or (**9**) (5 mmol) was dissolved in AcOH (10 mL), heated to the boiling point and cooled. After adding small quantities of ethanol, the precipitate was formed, which was collected by filtration and washed with ethanol.

The following compounds were prepared by this method:

Methyl 2-[2-cyano-2-(2-pyridinyl)ethenyl]amino-3-[2-methoxycarbonyl-4-(2-pyridinyl)-1*H*-pyrrol-3-yl]aminopropenoate (12). This compound was prepared from compound (**8**) (1.36 g, 5 mmol), 33% yield (0.74 g), mp 230-233°C (from ethanol), MS 444 (M^+), IR 2170 cm^{-1} (CN), ^1H NMR ($CDCl_3$) δ: 3.81 (3H, s, COOMe), 3.94 (3H, s, COOMe), 6.91 (1H, ddd, $J_{H3'-H5'}$ = 1.1 Hz, $J_{H4'-H5'}$ = 7.4 Hz, $J_{H5'-H6'}$ = 5.0 Hz,

H_5'), 7.02 (1H, ddd, $J_{H3'-H5'}$ = 1.1 Hz, $J_{H4'-H5'}$ = 7.4 Hz, $J_{H5'-H6'}$ = 5.0 Hz, H_5'), 7.29 (1H, d, J_{CH-NH} = 3.7 Hz, H_5), 7.42 (1H, ddd, $J_{H3'-H4'}$ = 8.2 Hz, $J_{H3'-H5'}$ = 1.1 Hz, $J_{H3'-H6'}$ = 1.0 Hz, H_3'), 7.48 (1H, d, J_{CH-NH} = 12.3 Hz, C*H*NH), 7.57 (1H, ddd, $J_{H3'-H4'}$ = 8.2 Hz, $J_{H3'-H5'}$ = 1.1 Hz, $J_{H3'-H6'}$ = 1.0 Hz, H_3'), 7.60 (1H, ddd, $J_{H3'-H4'}$ = 8.2 Hz, $J_{H4'-H5'}$ = 7.4 Hz, $J_{H4'-H6'}$ = 1.8 Hz, H_4'), 7.73 (1H, ddd, $J_{H3'-H4'}$ = 8.2 Hz, $J_{H4'-H5'}$ = 7.4 Hz, $J_{H4'-H6'}$ = 1.8 Hz, H_4'), 7.84 (1H, ddd, $J_{H3'-H6'}$ = 1.0 Hz, $J_{H4'-H6'}$ = 1.8 Hz, $J_{H5'-H6'}$ = 5.0 Hz, H_6'), 8.43 (1H, ddd, $J_{H3'-H6'}$ = 1.0 Hz, $J_{H4'-H6'}$ = 1.8 Hz, $J_{H5'-H6'}$ = 5.0 Hz, H_6'), 8.84 (1H, br s, NH), 8.94 (1H, d, J_{CH-NH} = 13.2 Hz, Het-NHC*H*), 11.53 (1H, d, J_{CH-NH} = 12.3 Hz, CHN*H*), 11.63 (1H, d, J_{CH-NH} = 13.2 Hz, Het-N*H*CH). ^{1}H NMR ($CDCl_3$ + D_2O) δ: 3.81 (3H, s, COOMe), 3.94 (3H, s, COOMe), 6.91 (1H, ddd, H_5'), 7.03 (1H, ddd, H_5'), 7.29 (1H, d, H_5), 7.42 (1H, ddd, H_3'), 7.46 (1H, s, C*H*NH), 7.57 (1H, ddd, H_3'), 7.60 (1H, ddd, H_4'), 7.73 (1H, ddd, H_4'), 7.84 (1H, ddd, H_6'), 8.44 (1H, ddd, H_6'), 8.94 (1H, s, Het-NHC*H*). ^{13}C NMR ($CDCl_3$) δ: 51.22 (COO*C*H_3), 51.28 (COO*C*H_3), 78.51 (NHCH=*C*), 104.56 (C_4), 108.15 (NHCH=*C*), 111.83 (C_3), 116.72 (CN), 118.16 (NH*C*H=C), 118.91 (C_5'), 119.45 (C_5'), 119.76 (C_2), 120.21 (C_3'), 120.82 (C_3'), 123.20 (C_4), 137.21 (C_4'), 137.53 (C_4'), 139.29 (NH*C*H=C), 146.40 (C_6'), 147.70 (C_6'), 153.96 (C_2'), 154.11 (C_2'), 160.28 (*C*OOMe), 165.24 (*C*OOMe). *Anal.* Calcd for $C_{23}H_{20}N_6O_4$: C, 62.16; H, 4.54; N, 18.91. Found: C, 62.17; H, 4.41; N, 19.10.

Ethyl 2-[2-cyano-2-(2-pyridinyl)ethenyl]amino-3-[2-ethoxycarbonyl-4-(2-pyridinyl)-1*H*-pyrrol-3-yl]aminopropenoate (13). This compound was prepared from compound (**9**) (1.43 g, 5 mmol), 29% yield (0.68 g), mp 165-170°C (from ethanol), MS 472 (M^+), IR 2190 cm^{-1} (CN), ^{1}H NMR ($CDCl_3$) δ: 1.32 (3H, t, J_{CH-CH} = 7.2 Hz, $COOCH_2CH_3$), 1.41 (3H, t, J_{CH-CH} = 7.2 Hz, $COOCH_2CH_3$), 4.26 (2H, q, J_{CH-CH} = 7.2 Hz, $COOCH_2CH_3$), 4.41 (2H, q, J_{CH-CH} = 7.2 Hz, $COOCH_2CH_3$), 6.91 (1H, ddd, $J_{H3'-H5'}$ = 1.1 Hz, $J_{H4'-H5'}$ = 7.4 Hz, $J_{H5'-H6'}$ = 5.0 Hz, H_5'), 7.02 (1H, ddd, $J_{H3'-H5'}$ = 1.1 Hz, $J_{H4'-H5'}$ = 7.4 Hz, $J_{H5'-H6'}$ = 5.0 Hz, H_5'), 7.28 (1H, d, J_{CH-NH} = 3.8 Hz, H_5), 7.42 (1H, ddd, $J_{H3'-H4'}$ = 8.2 Hz, $J_{H3'-H5'}$ = 1.1 Hz, $J_{H3'-H6'}$ = 1.0 Hz, H_3'), 7.51 (1H, d, J_{CH-NH} = 12.6 Hz, C*H*NH), 7.54-7.62 (2H, m, H_3', H_4'), 7.72 (1H, ddd, $J_{H3'-H4'}$ = 8.2 Hz, $J_{H4'-H5'}$ = 7.4 Hz, $J_{H4'-H6'}$ = 1.9 Hz, H_4'), 7.86 (1H, ddd, $J_{H3'-H6'}$ = 1.0 Hz, $J_{H4'-H6'}$ = 1.9 Hz, $J_{H5'-H6'}$ = 5.0 Hz, H_6'), 8.44 (1H, ddd, $J_{H3'-H6'}$ = 1.0 Hz, $J_{H4'-H6'}$ = 1.9 Hz, $J_{H5'-H6'}$ = 5.0 Hz, H_6'), 8.78 (1H, d, J_{CH-NH} = 13.6 Hz, Het-NHC*H*), 8.94 (1H, br s, NH), 11.50 (1H, d, J_{CH-NH} = 12.6 Hz, CHN*H*), 11.56 (1H, d, J_{CH-NH} = 13.6 Hz, Het-N*H*CH). ^{1}H NMR ($CDCl_3$ + D_2O) δ: 1.31 (3H, t, $COOCH_2CH_3$), 1.41 (3H, t, $COOCH_2CH_3$), 4.26 (2H, q, $COOCH_2CH_3$), 4.41 (2H, q, $COOCH_2CH_3$), 6.91 (1H, ddd, H_5'), 7.02 (1H, ddd, H_5'), 7.28 (1H, s, H_5), 7.42 (1H, ddd, H_3'), 7.49 (1H, s, C*H*NH), 7.56 (1H, ddd, H_3'), 7.59 (1H, ddd, H_4'), 7.72 (1H, ddd, H_4'), 7.87 (1H, ddd, H_6'), 8.44 (1H, ddd, H_6'), 8.77 (1H, s, Het-NHC*H*). *Anal.* Calcd for $C_{25}H_{24}N_6O_4$: C, 63.55; H, 5.12; N, 17.79. Found: C, 63.68; H, 5.24; N, 17.60.

Pyrrolo[3,2-*d*]pyrimidin-4-ones. General procedures. Method A: To compound (**8**) or (**9**) (0.5 mmol) dissolved in AcOH (2 mL), primary aliphatic amine (0.25 mmol) was added and the mixture was heated under reflux for several hours. After cooling the precipitate was formed, which was collected by filtration and washed with ethanol. **Method B:** To compound (**12**) (0.5 mmol) dissolved in AcOH (2 mL), primary aliphatic amine (0.5 mmol) was added and the mixture was heated under reflux for several hours. After cooling the precipitate was formed, which was collected by filtration and washed with ethanol.

The following compounds were prepared by those methods:

3-Benzyl-7-(2-pyridinyl)-3,4-dihydro-5*H*-pyrrolo[3,2-*d*]pyrimidin-4-one (17). This compound was prepared by method A from compound (**8**) (136 mg, 0.5 mmol) and benzylamine hydrochloride (**14**) (27 mg, 0.25 mmol), 4.5 h, in 42 % yield (64 mg), by method A from compound (**9**) (143 mg, 0.5 mmol) and benzylamine hydrochloride (**14**) (27 mg, 0.25 mmol), 1 h, in 36% yield (54 mg), and by method B from compound (**12**) (222 mg, 0.5 mmol) and benzylamine hydrochloride (**14**) (54 mg, 0.5 mmol), 2.5 h, in 34% yield (51 mg), mp 291-292^{o}C (from ethanol), MS 302 (M^{+}), 303 (MH^{+}), ^{1}H NMR ($CDCl_3$) δ: 5.29 (2H, s, CH_2), 7.14 (1H, ddd, $J_{H3'-H5'}$ = 1.1 Hz, $J_{H4'-H5'}$ = 7.4 Hz, $J_{H5'-H6'}$ = 4.9 Hz, H_5'), 7.30-7.37 (5H, m, 5H(Ph)), 7.73 (1H, ddd, $J_{H3'-H4'}$ = 8.0 Hz, $J_{H4'-H5'}$ = 7.4 Hz, $J_{H4'-H6'}$ = 1.9 Hz, H_4'), 8.05 (1H, d, J_{CH-NH} = 3.0 Hz, C*H*NH), 8.07 (1H, s, CH), 8.01 (1H, ddd, $J_{H3'-H4'}$ = 8.0 Hz, $J_{H3'-H5'}$ = 1.1 Hz, $J_{H3'-H6'}$ = 1.0 Hz, H_3'), 8.59 (1H, ddd, $J_{H3'-H6'}$ = 1.0 Hz, $J_{H4'-H6'}$ = 1.9 Hz, $J_{H5'-H6'}$ = 4.9 Hz, H_6'), 9.92 (1H, br s, CHN*H*). ^{1}H NMR (DMSO-d_6) δ: 5.27 (2H, s, CH_2), 7.19 (1H, ddd, $J_{H3'-H5'}$ = 1.1 Hz, $J_{H4'-H5'}$ = 7.5 Hz, $J_{H5'-H6'}$ = 4.8 Hz, H_5'), 7.26-7.36 (5H, m, 5H(Ph)), 7.81 (1H, ddd, $J_{H3'-H4'}$ = 8.0 Hz, $J_{H4'-H5'}$ = 7.5 Hz, $J_{H4'-H6'}$ = 1.9 Hz, H_4'), 7.98 (1H, br s, C*H*NH), 8.44 (1H, s, CH), 8.48 (1H, ddd, $J_{H3'-H4'}$ = 8.0 Hz, $J_{H3'-H5'}$ = 1.1 Hz, $J_{H3'-H6'}$ = 1.0 Hz, H_3'), 8.53 (1H, ddd, $J_{H3'-H6'}$ = 1.0 Hz, $J_{H4'-H6'}$ = 1.9 Hz, $J_{H5'-H6'}$ = 4.8 Hz H_6'), 12.53 (1H, br s, CHN*H*). ^{1}H NMR (DMSO-d_6 + D_2O) δ: 5.27 (2H, s, CH_2), 7.24-7.27 (1H, m, H_5'), 7.29-7.39 (5H, m, 5H(Ph)), 7.84 (1H, ddd, H_4'), 8.04 (1H, s, C*H*NH), 8.42 (1H, s, CH), 8.43-8.53 (2H, m, H_3', H_6'). ^{13}C NMR (DMSO-d_6) δ: 48.76 (CH_2), 117.66 (C_7), 119.41 (C_5'), 121.50 (C_{7a}), 121.87 (C_3'), 128.04 (C_4(Ph)), 128.36 (C_6), 128.41 (C_2(Ph), C_6(Ph)), 129.48 (C_3(Ph), C_5(Ph)), 137.35 (C_{4a}), 138.33 (C_4'), 142.00 (C_1(Ph)), 146.19 (C_6'), 150.06 (C_2'), 153.37 (C_2), 153.98(C_4). *Anal.* Calcd for $C_{18}H_{14}N_4O$: C, 71.51; H, 4.67; N, 18.53. Found: C, 71.76; H, 4.61; N, 18.29.

3-(4-Methoxybenzyl)-7-(2-pyridinyl)-3,4-dihydro-5*H*-pyrrolo[3,2-*d*]pyrimidin-4-one (18). This compound was prepared by method A from compound (**8**) (136 mg, 0.5 mmol) and 4-methoxy-benzylamine (**15**) (34 mg, 0.25 mmol), 4.5 h, in 32% yield (54 mg) and by method A from compound (**9**) (143 mg, 0.5 mmol) and 4-methoxybenzylamine (**15**) (34 mg, 0.25 mmol), 2 h, in 27% yield (45 mg),

mp 252-255°C (from ethanol), MS 332 (M^+), 333 (MH^+), ^{1}H NMR ($CDCl_3$) δ: 3.79 (3H, s, OMe), 5.22 (2H, s, CH_2), 6.87-6.90 (2H, m, 2H(Ph)), 7.13 (1H, ddd, $J_{H3'-H5'}$ = 1.1 Hz, $J_{H4'-H5'}$ = 7.5 Hz, $J_{H5'-H6'}$ = 4.9 Hz, H_5'), 7.30-7.33 (2H, m, 2H(Ph)), 7.72 (1H, ddd, $J_{H3'-H4'}$ = 8.0 Hz, $J_{H4'-H5'}$ = 7.5 Hz, $J_{H4'-H6'}$ = 1.9 Hz, H_4'), 8.04 (1H, d, J_{CH-NH} = 3.1 Hz, C*H*NH), 8.08 (1H, s, CH), 8.41 (1H, ddd, $J_{H3'-H4'}$ = 8.0 Hz, $J_{H3'-H5'}$ = 1.1 Hz, $J_{H3'-H6'}$ = 1.0 Hz, H_3'), 8.58 (1H, ddd, $J_{H3'-H6'}$ = 1.0 Hz, $J_{H4'-H6'}$ = 1.9 Hz, $J_{H5'-H6'}$ = 4.9 Hz, H_6'), 10.21 (1H, br s, 1H, CHN*H*). ^{1}H NMR (DMSO-d_6) δ: 3.79 (3H, s, OMe), 5.19 (2H, s, CH_2), 6.88-6.93 (2H, m, 2H(Ph)), 7.18 (1H, ddd, $J_{H3'-H5'}$ = 1.2 Hz, $J_{H4'-H5'}$ = 7.5 Hz, $J_{H5'-H6'}$ = 4.8 Hz, H_5'), 7.31-7.36 (2H, m, 2H(Ph)), 7.80 (1H, ddd, $J_{H3'-H4'}$ = 8.0 Hz, $J_{H4'-H5'}$ = 7.5 Hz, $J_{H4'-H6'}$ = 1.9 Hz, H_4'), 7.96 (1H, br s, C*H*NH), 8.43 (1H, s, CH), 8.47 (1H, ddd, $J_{H3'-H4'}$ = 8.0 Hz, $J_{H3'-H5'}$ = 1.2 Hz, $J_{H3'-H6'}$ = 1.0 Hz, H_3'), 8.53 (1H, ddd, $J_{H3'-H6'}$ = 1.0 Hz, $J_{H4'-H6'}$ = 1.9 Hz, $J_{H5'-H6'}$ = 4.8 Hz, H_6'), 12.48 (1H, br s, 1H, CHN*H*). *Anal.* Calcd for $C_{19}H_{16}N_4O_2$: C, 68.66; H, 4.85; N, 16.86. Found: C, 68.96; H, 4.96; N, 16.71.

3-Methyl-7-(2-pyridinyl)-3,4-dihydro-5*H*-pyrrolo[3,2-*d*]pyrimidin-4-one hydrochloride (19). This compound was prepared by method A from compound (**8**) (136 mg, 0.5 mmol) and methylamine hydrochloride (**16**) (17 mg, 0.25 mmol), 1.5 h, in 25% yield (33 mg), mp 258-261°C (from ethanol), MS 226 (M^+), ^{1}H NMR (DMSO-d_6) δ: 3.58 (3H, s, Me), 7.66-7.70 (1H, m, H_5'), 8.41-8.46 (1H, m, H_4'), 8.42 (1H, s, CH), 8.62 (1H, d, J_{CH-NH} = 3.4 Hz, C*H*NH), 8.69-8.71 (1H, m, H_3'), 8.80-8.83 (1H, m, H_6'), 13.17 (1H, br s, CH*NH*). *Anal.* Calcd for $C_{12}H_{10}N_4O$ x HCl: C, 54.87; H, 4.22; N, 21.33. Found: C, 54.92; H, 4.26; N, 21.09.

X-RAY STRUCTURE DETERMINATION

Compound (**8**): $C_{14}H_{16}N_4O_2$, M_r=272.3, orthorhombic, $P2_12_12_1$, No.:19, a=8.283(2), b=12.087(3), c=14.534(3) Å, V=1455.1(6) Å^3, Z=4, D_X=1.243 Mg/m^3, MoKα radiation, λ=0.71069 Å, μ= 0.081 mm^{-1}.

Compound (**18**): $C_{19}H_{16}N_4O_2$, M_r=332.4, triclinic, $P1^-$, No.:2, a=6.453(1), b=8.395(1), c=14.918(2) Å, α=91.13(1), β=100.72(1), γ=96.59(2)°, V=788.1(2) Å^3, Z=2, D_X=1.400 Mg/m^3, MoKα radiation, λ=0.71069 Å, μ= 0.088 mm^{-1}.

Diffraction data for both compounds were collected on Enraf Nonius CAD-4 diffractometer with graphite monochromatized MoKα radiation at room temperature (293(2) K). Lattice parameters were determined by a least-square treatment of 25 for **8** and 49 for **18** carefully centered θ values in the range 8.1° < θ < 12.5° for **8** and 8.1° < θ < 18.1° for **18**. For both compounds an entire sphere up to θ_{max} 28° of data was measured with ω-2θ scans. Scan width for **8** was (0.85 + 0.35tgθ)° and for **18** (0.80 + 0.35tgθ)°, aperture

was in both cases (2.7 + 0.4tgθ)° and maximum scan time 60 seconds. Background was measured at 1/4 of the scan at each limit. Crystal stability was monitored by periodic measuring of three standard reflections every 20000 seconds of scanning time. Orientation control was every 600 reflections. A change of 0.35% intensities of standard reflections for **8** and –0.23% for **18** was observed and correction applied. Due to the low value of the linear absorption coefficients no absorption correction was done. 9206 for **8** and 7577 for **18** reflections were collected, averaging gave 1991 for **8** and 3760 for **18** unique reflections with R_{int} 0.012 (**8**) and 0.013 (**18**). 1686 (**8**) and 2220 (**18**) reflections were observed using ($I > 2.5\sigma(I)$) criterion.

Both structures were solved by direct methods using SIR92 program.[45] The positions of hydrogen atoms were obtained from difference Fourier maps. We employed full-matrix least-squares refinement on F_o magnitudes with anisotropic temperature factors for all non-hydrogen atoms. For **18** hydrogen atoms were refined isotropically, for **8** only the positions of hydrogen atoms were refined. The correction for secondary extinction[46] was applied with $g=0.28(8)\cdot10^4$ for **8** and $g=0.22(5)\cdot10^4$ for **18**. In the final least-square cycle for **8** were 1872 contributing reflections and 230 parameters and for **18** 3073 contributing reflections and 291 parameters (included were those unobserved reflections for which F_c was greater than F_O). The final R and R_W values were 0.033 and 0.042 for **8** and 0.039 and 0.046 for **18**, respectively. Maximal shift/error were 0.0407 for **8** and 0.0002 for **18**. The maximal residual density in final difference map was 0.18 e/Å^3 for **8** and 0.30 e/Å^3 for **18** and the minimal -0.19 e/Å^3 for **8** and -0.33 e/Å^3 for **18.**

The Xtal3.4 system[47] of crystallographic programs was used for the correlation and reduction of data, structure refinement and interpretation. ORTEPII[48] was used to produce molecular graphics.

The asymmetric units of **8** and **18** with atom-numbering scheme are shown in the Figures 1 and 2. Final atomic coordinates and equivalent isotropic thermal parameters with their e.s.d.'s are listed in Table 1. Bond lengths and bond angles are presented in Table 2.

Bond C(2)=C(3) [1.364(3) Å] is longer than unpolarised double bond in ethylene [1.314(6) Å].[49] This is the result of the conjugation of this double bond with the nitrogen atom lone pair of the dimethylamino group and carbonyl group of the methoxycarbonyl moiety. This is reflected also in the bond lengths of C(1)-C(2) [1.460(3) Å] and C(3)-N(1) [1.335(3) Å] which are shorter than corresponding unconjugated single bonds ($C(sp^2)$-$C(sp^2)$ 1.484(18) Å[50] and $C(sp^2)$-$N(sp^2)$ 1.470(5) Å[51]). π electrons from C(7)=C(8) double bond are also delocalized which is reflected in the elongation of this formal double bond to 1.374(3) Å and in the shortening of C(7)-N(2) [1.332(2) Å] and C(8)-C(10) [1.464(3) Å] bonds comparing to corresponding formal single bonds. In the accordance with the RAHB (Resonance Assisted Hydrogen Bonding) theory[52] π conjugated system in this part of molecule undergoes greater delacolization since it includes intramolecular hydrogen bond [N(2)-H(2)..N(4)] and participates also to

the infinite chain intermolecular hydrogen bonding between N(2)-H(2) and N(3) atom from cyano group from the symmetry related (1/2-x, 1-y, z-1/2) molecule. The details of this three centered hydrogen bond are: donor is N(2) atom, acceptors are N(4) and symmetry related N(3) atom. Contact distances are: N(2)..N(3) 3.094(3), H(2)..N(3) 2.378(24), N(2)..N(4) 2.728(3) and H(2)..N(4) 2.036(25) Å. The angles N(2)-H(2)..N(3) and N(2)-H(2)..N(4) are 135(2) and 131(2)°, respectively. In the structure of compound (**18**) exists intermolecular hydrogen bond between N(3)-H(3) and N(1) atom of neighbouring molecule (x-1,y,z). Contact distances are 3.072(3) and 2.237(33) Å for N(3)..N(1) and H(3)..N(1) contact, respectively. N(3)-H(3)..N(1) angle is 164(3)°.

Table 1. Fractional Coordinates and Equivalent Temperature Factors ($Å^2$). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

(8)

	x/a	y/b	z/c	U_{eq}
O(1)	0.7623(2)	0.2885(2)	0.3716(1)	0.0547(5)
O(2)	0.6870(2)	0.4401(1)	0.4494(1)	0.0540(5)
N(1)	0.2938(3)	0.2085(2)	0.3052(2)	0.0550(6)
N(2)	0.3751(2)	0.4198(1)	0.4135(1)	0.0381(4)
N(3)	0.1823(4)	0.5033(2)	0.7131(1)	0.0722(9)
N(4)	0.2240(2)	0.6199(2)	0.4026(1)	0.0456(5)
C(1)	0.6555(2)	0.3498(2)	0.3984(1)	0.0392(5)
C(2)	0.4830(2)	0.3356(2)	0.3819(1)	0.0367(5)
C(3)	0.4387(3)	0.2456(2)	0.3312(1)	0.0419(6)
C(4)	0.2824(5)	0.1093(3)	0.2487(3)	0.084(1)
C(5)	0.1423(4)	0.2584(4)	0.3334(3)	0.072(1)
C(6)	0.8547(4)	0.4591(3)	0.4705(3)	0.067(1)
C(7)	0.3342(2)	0.4296(2)	0.5017(1)	0.0368(5)
C(8)	0.2497(3)	0.5154(2)	0.5408(1)	0.0378(5)
C(9)	0.2152(3)	0.5068(2)	0.6365(1)	0.0488(7)
C(10)	0.1979(2)	0.6163(2)	0.4937(1)	0.0372(5)
C(11)	0.1283(3)	0.7054(2)	0.5408(2)	0.0487(6)
C(12)	0.0879(3)	0.7992(2)	0.4929(2)	0.0598(8)
C(13)	0.1155(4)	0.8031(2)	0.3993(2)	0.0649(9)
C(14)	0.1829(4)	0.7118(2)	0.3575(2)	0.0584(8)

(18)

	x/a	y/b	z/c	U_{eq}
O(1)	0.5414(2)	0.4911(2)	0.8100(1)	0.0465(6)
O(2)	0.9402(3)	0.8255(3)	0.4299(1)	0.0605(8)
N(1)	1.1444(3)	0.6833(2)	0.9396(1)	0.0356(6)
N(2)	0.9042(3)	0.5302(2)	0.8198(1)	0.0330(6)
N(3)	0.6273(3)	0.6788(3)	0.9907(1)	0.0366(6)
N(4)	1.0506(3)	0.9476(3)	1.1988(2)	0.0476(7)

C(1)	1.1015(3)	0.5956(3)	0.8649(2)	0.0363(7)
C(2)	0.7168(3)	0.5491(3)	0.8524(2)	0.0329(7)
C(3)	0.7638(3)	0.6405(3)	0.9361(1)	0.0314(6)
C(4)	0.7388(3)	0.7700(3)	1.0636(2)	0.0362(7)
C(5)	0.9526(3)	0.7948(3)	1.0578(1)	0.0320(6)
C(6)	0.9682(3)	0.7089(3)	0.9766(1)	0.0303(6)
C(7)	0.8901(4)	0.4369(3)	0.7329(2)	0.0385(7)
C(8)	0.8979(4)	0.5427(3)	0.6534(2)	0.0368(7)
C(9)	1.0922(4)	0.6002(3)	0.6302(2)	0.0434(8)
C(10)	1.1009(4)	0.6957(3)	0.5567(2)	0.0460(9)
C(11)	0.9155(4)	0.7368(3)	0.5037(2)	0.0432(8)
C(12)	0.7215(4)	0.6833(3)	0.5269(2)	0.0434(8)
C(13)	0.7152(4)	0.5872(3)	0.6009(2)	0.0401(8)
C(14)	0.7542(7)	0.8627(6)	0.3710(3)	0.072(1)
C(15)	1.1124(3)	0.8981(3)	1.1224(2)	0.0339(7)
C(16)	1.3133(4)	0.9469(3)	1.1053(2)	0.0398(8)
C(17)	1.4559(4)	1.0468(3)	1.1684(2)	0.0488(9)
C(18)	1.3940(5)	1.0972(3)	1.2465(2)	0.0511(9)
C(19)	1.1907(5)	1.0453(4)	1.2584(2)	0.054(1)

Table 2. Bond Distances (Å) and Bond Angles (°) with e.s.d.'s in parentheses

(8)

O(1)-C(1)	1.217(3)	N(4)-C(14)	1.334(3)
O(2)-C(1)	1.345(3)	C(1)-C(2)	1.460(3)
O(2)-C(6)	1.441(3)	C(2)-C(3)	1.364(3)
N(1)-C(3)	1.335(3)	C(7)-C(8)	1.374(3)
N(1)-C(4)	1.456(5)	C(8)-C(9)	1.424(3)
N(1)-C(5)	1.451(4)	C(8)-C(10)	1.464(3)
N(2)-C(2)	1.431(3)	C(10)-C(11)	1.401(3)
N(2)-C(7)	1.332(2)	C(11)-C(12)	1.372(4)
N(3)-C(9)	1.146(3)	C(12)-C(13)	1.381(5)
N(4)-C(10)	1.342(3)	C(13)-C(14)	1.378(4)

C(1)-O(2)-C(6)	115.7(2)	N(2)-C(7)-C(8)	126.5(2)
C(3)-N(1)-C(4)	119.6(3)	C(7)-C(8)-C(9)	116.9(2)
C(3)-N(1)-C(5)	123.9(3)	C(7)-C(8)-C(10)	125.8(2)
C(4)-N(1)-C(5)	116.4(3)	C(9)-C(8)-C(10)	117.3(2)
C(2)-N(2)-C(7)	122.1(2)	N(3)-C(9)-C(8)	177.0(3)
C(10)-N(4)-C(14)	118.1(2)	N(4)-C(10)-C(8)	116.2(2)
O(1)-C(1)-O(2)	122.0(2)	N(4)-C(10)-C(11)	121.5(2)
O(1)-C(1)-C(2)	125.9(2)	C(8)-C(10)-C(11)	122.2(2)
O(2)-C(1)-C(2)	112.1(2)	C(10)-C(11)-C(12)	119.2(2)
N(2)-C(2)-C(1)	118.4(2)	C(11)-C(12)-C(13)	119.2(3)
N(2)-C(2)-C(3)	125.0(2)	C(12)-C(13)-C(14)	118.3(3)
C(1)-C(2)-C(3)	116.5(2)	N(4)-C(14)-C(13)	123.6(2)
N(1)-C(3)-C(2)	131.4(2)		

(18)

O(1)-C(2)	1.230(2)	C(4)-C(5)	1.390(3)
O(2)-C(11)	1.364(3)	C(5)-C(6)	1.422(3)
O(2)-C(14)	1.420(5)	C(5)-C(15)	1.461(3)
N(1)-C(1)	1.291(3)	C(7)-C(8)	1.500(4)
N(1)-C(6)	1.389(3)	C(8)-C(9)	1.398(4)
N(2)-C(1)	1.371(3)	C(8)-C(13)	1.383(3)
N(2)-C(2)	1.408(3)	C(9)-C(10)	1.377(4)
N(2)-C(7)	1.484(3)	C(10)-C(11)	1.389(4)
N(3)-C(3)	1.364(3)	C(11)-C(12)	1.388(4)
N(3)-C(4)	1.355(3)	C(12)-C(13)	1.383(4)
N(4)-C(15)	1.350(3)	C(15)-C(16)	1.385(3)
N(4)-C(19)	1.334(3)	C(16)-C(17)	1.381(3)
C(2)-C(3)	1.418(3)	C(17)-C(18)	1.374(5)
C(3)-C(6)	1.396(3)	C(18)-C(19)	1.379(4)

C(11)-O(2)-C(14)	117.9(3)	C(3)-C(6)-C(5)	107.6(2)
C(1)-N(1)-C(6)	114.4(2)	N(2)-C(7)-C(8)	112.3(2)
C(1)-N(2)-C(2)	122.7(2)	C(7)-C(8)-C(9)	120.7(2)
C(1)-N(2)-C(7)	118.0(2)	C(7)-C(8)-C(13)	121.7(2)
C(2)-N(2)-C(7)	119.3(2)	C(9)-C(8)-C(13)	117.6(2)
C(3)-N(3)-C(4)	108.9(2)	C(8)-C(9)-C(10)	121.1(2)
C(15)-N(4)-C(19)	117.7(2)	C(9)-C(10)-C(11)	120.4(2)
N(1)-C(1)-N(2)	126.8(2)	O(2)-C(11)-C(10)	116.0(2)
O(1)-C(2)-N(2)	121.5(2)	O(2)-C(11)-C(12)	124.9(2)
O(1)-C(2)-C(3)	127.8(2)	C(10)-C(11)-C(12)	119.1(2)
N(2)-C(2)-C(3)	110.7(2)	C(11)-C(12)-C(13)	119.8(2)
N(3)-C(3)-C(2)	128.4(2)	C(8)-C(13)-C(12)	121.9(2)
N(3)-C(3)-C(6)	108.0(2)	N(4)-C(15)-C(5)	116.0(2)
C(2)-C(3)-C(6)	123.6(2)	N(4)-C(15)-C(16)	121.6(2)
N(3)-C(4)-C(5)	110.2(2)	C(5)-C(15)-C(16)	122.3(2)
C(4)-C(5)-C(6)	105.3(2)	C(15)-C(16)-C(17)	119.5(3)
C(4)-C(5)-C(15)	123.6(2)	C(16)-C(17)-C(18)	119.1(3)
C(6)-C(5)-C(15)	131.0(2)	C(17)-C(18)-C(19)	118.2(3)
N(1)-C(6)-C(3)	121.6(2)	N(4)-C(19)-C(18)	123.9(3)
N(1)-C(6)-C(5)	130.7(2)		

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