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Synthesis and high resolution proton NMR studies on isomeric *N*-1-/*N*-2-, 5,7-trisubstituted-4,6-dioxo-4,5,6,7-tetrahydropyrazolo[3,4-*d*]pyrimidines†

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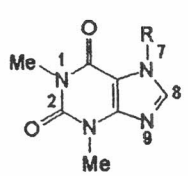
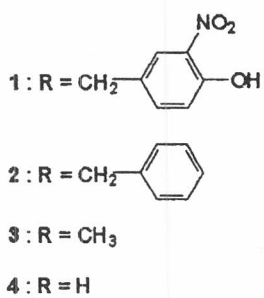
Unambiguous synthesis of all six possible 1/2, 5,7-trisubstituted (monobenzyl, dimethyl)-4,6-dioxo-4,5,6,7-tetrahydropyrazolo[3,4-*d*]pyrimidines has been described. High resolution (400 MHz) proton NMR data of these compounds (**10, 13, 19, 25a, 25b** and **25c**) have been discussed and some unusual features observed for phenyl protons have been rationalized due to hindered rotation when two substituents are simultaneously present at 1- and 7-positions.

Recently we have reported a convenient synthesis of phidolopin **1** a marine natural product[1], related to 7-benzyltheophylline **2** and its analogs alongwith their biological activities[2]. Caffeine **3** and theophylline **4,** a drug for asthma are other famous xanthines. Due to our continued interest in pyrazolo[3,4-*d*]pyrimidines[3-6] we became interested in the synthesis of pyrazolo[3,4-*d*]pyrimidine analogs of phidolopin for the evaluation of their biological activities. In connection with this project we needed ^{1}H NMR data of authentic 1/2-benzyl-5, 7-dimethyl-4, 6-dioxo-4,5,6,7-tetrahydropyrazolo[3,4-*d*] pyrimidines **10** and **25a**. Literature survey revealed that compound **10** has been prepared earlier from 1-benzyl-5-methyl-4,6-dioxo-4,5,6,7-tetrahydropyrazolo[3,4-*d*]pyrimidine **9a** in about 30% yield without mention of isomeric 1-benzyl-4-oxo-6-methoxy-5-methyl-4, 5-dihydropyrazolo[3,4-*d*]pyrimidine **11** (R=Bzl) as a co-product[7]. Furthermore as ^{1}H NMR data of **10** was also not reported we decided to make this compound from the same starting material **9a**. Synthesis of **9a** was achieved from compound **5a**[8] through intermediates **6a** and **8a** (Scheme I). The reaction of **5a** with methyl iodide in dry DMF in presence of anhyd. K_2CO_3 gave a mixture of **6a** and **7a**. Oxidation[5] of the major product **6a** with $KMnO_4$ gave new sulfone **8a** which on treatment with aqueous alkali gave known compound **9a** in good





yield. The methylation of **9a** gave a mixture of two isomeric products **10** and **11**. The major product **10** (R=Bzl) had higher melting point (141°C) as compared to the literature[7] melting point (133-34°C). The major compound showing two N-Me signals in its ^{1}H NMR spectrum at δ 3.38 and 3.57 was assigned structure **10**. The minor compound showing one N-Me singlet at δ 3.43 and another singlet at δ 4.09 due to OMe in its ^{1}H NMR was assigned structure **11**. Thus it is likely that lower literature melting point of **10** was due to its contamination by minute amount of **11**. Interestingly in the ^{1}H NMR (400 MHz) of **11,** five phenyl protons were present as a rather broad singlet centered at δ 7.3 while in the ^{1}H NMR of **10,** corresponding protons were nicely split into two sets of multiplets. The ^{1}H NMR of **10** showed two protons at rather high field (δ 7.02, d) and three protons as unresolved multiplets (δ 7.27-7.37). This significant difference in the ^{1}H NMR of

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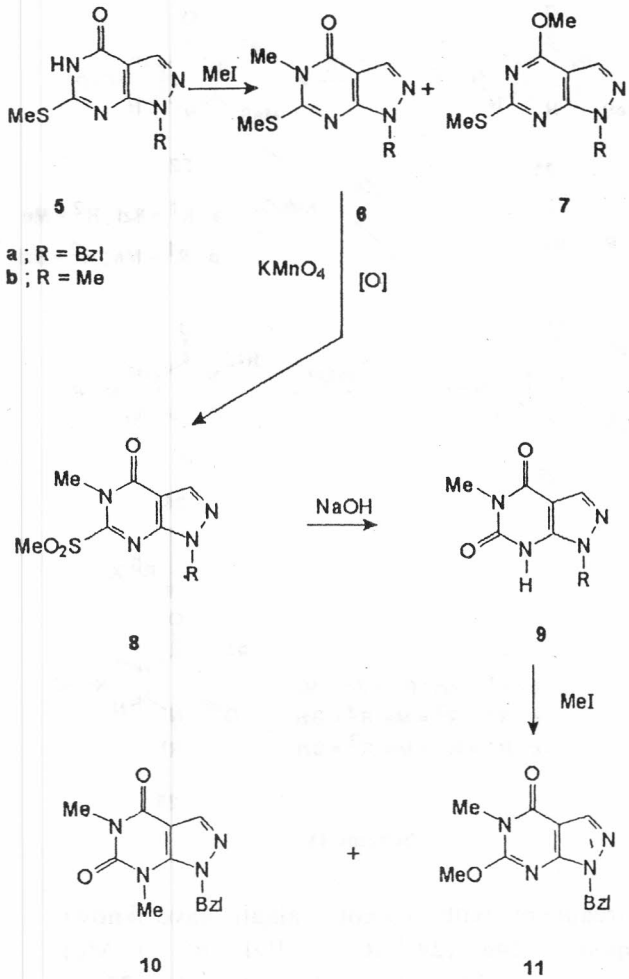
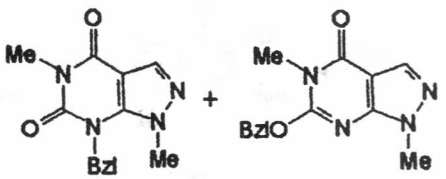


Scheme I

two isomeric compounds **10** and **11** for aromatic protons is presumably due to hindered rotation of benzyl group in **10** due to flanking methyl group at N-7 position, such hindered rotation has earlier been implicated[9] for explaining the complex pattern of aromatic protons in the ^{1}H NMR of isomeric 9-benzyltheophylline **12**.

Xanthines are also well known for their biological properties, for example caffeine **3** and theophylline are well known for their antiallergic activities[10]. They are also the prototypes of adenosine receptor antagonists[11,12] and show phosphodiesterase activities[13,14]. The unusual chemical shifts of aromatic protons in the ^{1}H NMR of compound **10** as compared to that of isomeric compound **11**, our continued interest in antiallergic activities of pyrazolo[3,4-*d*]pyrimidines coupled with various biological activities shown by xanthines has prompted us to make remaining five

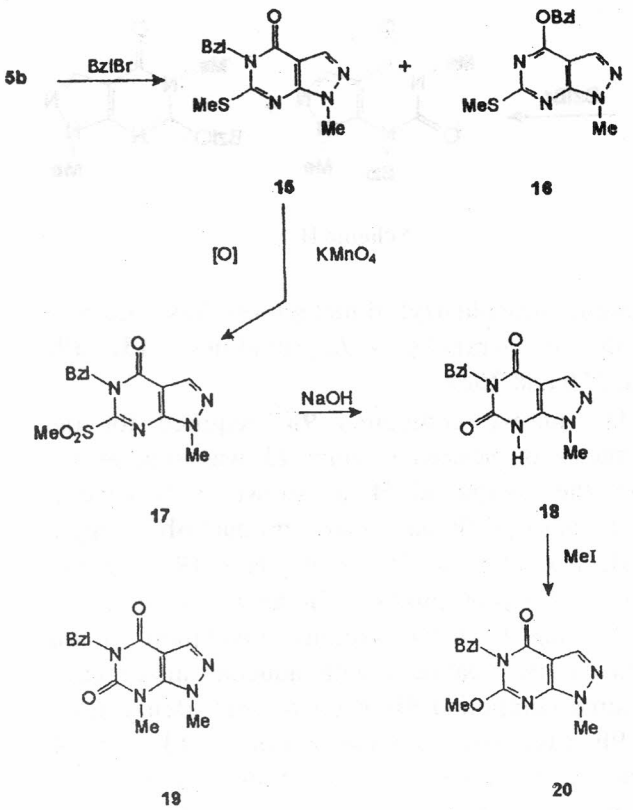


Scheme II

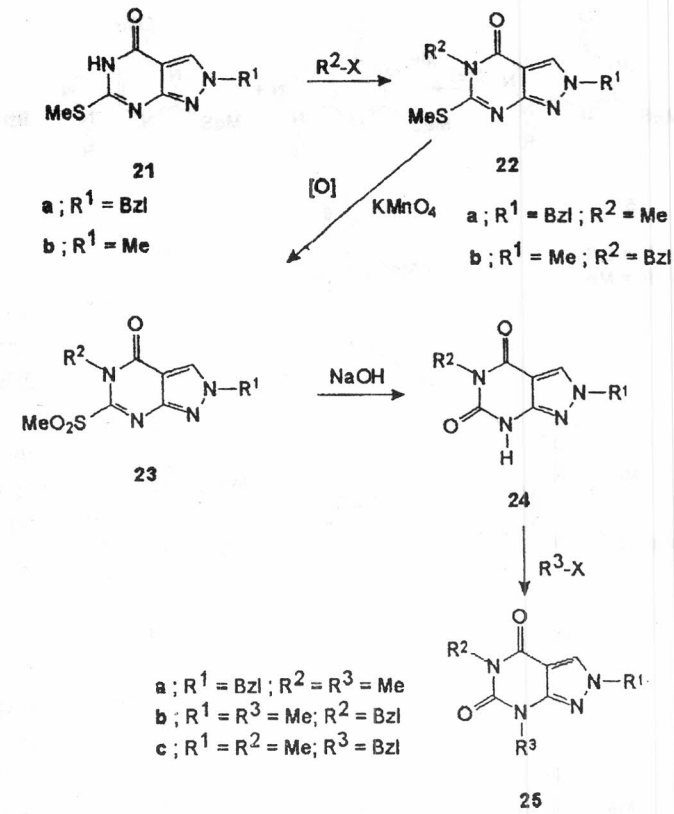
isomeric monobenzyl dimethyl-4,6-dioxo-4,5,6,7-tetrahydro pyrazolo[3,4-*d*]pyrimidines (**13, 19, 25a, 25b** and **25c**).

The known compound **9b**[7] required for the synthesis of desired product **13** was synthesized from the compound **5b** as shown in Scheme I. Methylation of **5b** gave major product **6b** having a N-Me singlet at δ 3.57 in its ^{1}H NMR spectrum alongwith minor product, **7b** having a singlet at δ 4.13 due to OMe protons. Oxidation of **6b** followed by treatment with aqueous alkali gave required compound **9b** in good yield. Benzylation of **9b** gave two isomeric products **13** and **14** (Scheme II) having a two proton singlet for benzylic protons at δ 5.47 (major product) and δ 5.51 (minor product) in their ^{1}H NMR spectra. This little difference in the chemical shifts of benzylic protons of compounds **13** and **14** was not enough for an unambiguous assignment. Definitive assignment of structure of major product as **13** was made on the basis of its ^{13}C NMR which showed presence of a benzylic carbon at δ 47.1 due to its *N*-attachment. Normally a benzylic carbon attached to an O-atom appears at much lower field (≈ δ 68). Due to paucity of compound **14** its ^{13}C NMR spectrum could not be recorded. However, compound **16,** a reasonably close model for compound **14,** showed benzylic carbon attached to O-atom at δ 68.5, thus providing indirect evidence for the structural assignment of compounds **13** and **14**.

The compound **19** was synthesized using compound **5b**[8] and the sequence followed for such conversion is shown in Scheme III. Benzylation of **5b** gave a mixture of two isomeric products **15** and **16** which were separated by column chromatography. The ^{1}H NMR spectrum of the major compound showing benzylic protons at higher field (δ 5.38) was assigned structure **15** and the minor compound showing corresponding protons at relatively lower field (δ 5.59) was



Scheme III



Scheme IV

assigned structure **16**. This assignment was further confirmed by the presence of benzylic carbons at δ 46.4 and 68.5 in the ^{13}C NMR spectra of compounds **15** and **16** respectively. Oxidation of **15** gave sulfone **17** which on alkali treatment gave compound **18** in good yield. Methylation of **18** gave desired product **19** as a major product alongwith small amount of isomeric O-methylated product **20**. Structures of the compounds **19** and **20** were established by ^{1}H NMR, ^{13}C NMR spectroscopy and elemental analysis.

The synthesis of fourth desired product **25a** (**25**, R^1 = Bzl; R^2 = R^3 = Me) has been described in literature[15] starting from compound **24a** (**24**, R^1 = Bzl, R^2 = Me) which in turn was prepared by cyclization of a suitable monocyclic precursor. As ^{1}H NMR data of the compound **25a** was not reported we decided to make this compound by different procedure starting with compound **21a** (Scheme IV). Methylation of the known compound **21a**[8] gave a single product **22a** (**22**, R^1 = Bzl, R^2 = Me) and none of isomeric O-methyl product was obtained. Oxidation of **22a** gave sulfone **23a** which on treatment with aqueous alkali gave known compound **24a** (**24**, R^1 = Bzl, R^2 = Me). Methylation of **24a** gave the desired product **25a** as only product.

The unknown compound **25b** (**25**, R^1 = R^2 = Me ; R^2 = Bzl) was synthesized using similar sequence from starting material **21b**[8] (Scheme IV). Benzylation of **21b** (**21**, R^1 = Me) gave compound **22b** as only isolable product. Oxidation of **22b** (**22**, R^1 = Me, R^2 = Bzl) gave sulfone **23b** which on treatment with aqueous alkali gave the product **24b** (**24**, R^1 = Me, R^2 = Bzl). Finally methylation of **24**b gave desired product **25b** as a single product in good yield. Synthesis of the last desired isomer **25**c (**25**, R^1 = R^2 = Me, R^3 = Bzl) was achieved from **21b**[8] as described in Scheme IV. Methylation of the compound **21b** gave **22**c (**22**, R^1 = R^2 = Me) as only isolable product. This compound **22**c has been synthesized earlier by a different method, however, no ^{1}H NMR data was reported[7]. Oxidation of the compound **22c** gave sulfone **23**c which on aqueous alkali treatment gave the product **24**c (**24**, R^1 = R^2 = Me) in good yield. Benzylation of **24**c gave desired product **25**c as only product.

Possibly due to steric reasons small amount of O-methylated/benzylated products (**11**, **14** and **20**) were obtained during the preparation of three desired products (**10, 13** and **19**) in N-1 series but no such products were obtained during the synthesis of other three desired isomers (**25a**, **25b** and **25c**) in N-2 series. It is interesting to point out that in the ^{1}H NMR of compounds **19**, **25a**, **25b** and **25c** having relatively unhindered benzylic groups the two o-protons of phenyl group appear at δ 7.48, 7.35-7.42, 7.48 and 7.50 respectively. However, in the ^{1}H NMR spectra of compounds **10** and **13** corresponding protons appear at relatively high field (δ 7.02 and 7.14 respectively) due to steric hinderance by flanking methyl groups. Extensive use of ^{1}H NMR and/or ^{13}C NMR data of many compounds reported here will be made for unambiguous assignment of pyrazolo[3,4-*d*]pyrimidine analogs of phidolopin and in determining the conformation (stacked/unstacked) of some new bis-compounds derived from intramolecularly stacked 1,3-bis(4,6-dimethylthio-1*H*-pyrazolo[3,4-*d*]pyrimidin-1-yl)propane[3,4]. Such studies are in progress and results will be reported in due course.

Experimental Section

Melting points are uncorrected and were taken on a Buchi 530 melting point apparatus. Mass spectra were recorded on a Jeol-JMS D300 spectrometer at an ionization energy of 70 eV. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker WM400 instrument at 400 MHz and 100 MHz respectively. Some ^{1}H NMR spectra were also recorded on a Perkin-Elmer R-32 (90 MHz) and Varian EM 360L (60 MHz) spectrometer. TLC plates were prepared with silica gel G and spots were visualized with I_2-vapours. Column chromatography was done on silica gel and purity of pure compounds were checked in more than one solvent system.

Methylation/benzylation of cyclic amides: General procedure. Excess methyl iodide/benzyl iodide (~ 6 mmole) was added dropwise to a stirred mixture of compound **5** (5 mmole), dry DMF (75 mL) and anhyd. K_2CO_3 (excess) and the reaction mixture was allowed to stir overnight (~ 16 hrs). All DMF was removed at reduced pressure on a hot water bath and residue was taken up in a mixture of water and chloroform. Normal extraction gave organic layer which was dried (Na_2SO_4) and removal of solvent gave crude product which was purified by column chromatography followed by crystallization. Compounds **6, 7, 10, 11, 13, 16, 19, 20, 22** and **25** were prepared in this way and physical and spectral data for these are listed in Table I and II.

General procedure for oxidation. To a solution of **6** (1 mmole) in glacial acetic acid (5 mL) and water (5 mL) at O°C was added solid $KMnO_4$ (2 mmole) in portions and the mixture was stirred for 1 hr at room temperature. The excess of $KMnO_4$ was decomposed by careful addition of H_2O_2 (30% aq. solution). The colorless solution was extracted with chloroform, washed with water, aq. $NaHCO_3$ solution and finally with water. The chloroform layer was dried (Na_2SO_4). Removal of solvent gave a residue which was crystallized to give pure product. Physical data and spectroscopic data of the sulfones (**8, 17** and **23**) thus prepared are listed in Table I.

General procedure for alkaline hydrolysis of sulfone. A mixture of **8** (2 mmole), 1*N* NaOH (100 mL), methanol (30 mL) and enough THF (if required for making homogeneous) was refluxed for 2-4 hr. The resulting mixture was concentrated at reduced pressure to remove MeOH and THF. The reaction mixture was cooled and neutralized with acetic acid. The white solid thus obtained was collected by filtration washed with water and dried. Compounds **9**, **18** and **24** were prepared in this manner and their physical and spectroscopic data is reported in Table II.

Acknowledgement

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Table I—Physical data of 1/2,4,5-trisubstituted 1*H*/2*H*-pyrazolo[3,4-*d*]pyrimidines (**7** and **16**) and 1/2,5-disubstituted-6-benzyloxy/methoxy/methylthio/methylsulfonyl-4-oxo-4,5-dihydropyrazolo[3,4-*d*]pyrimidines (**6,8,11,14,15,17,20,22** and **23**)

Product	Yield (%)	m.p. °C (solvent)	Mol. formula[a]	MS (70 eV) m/z (%)	^{1}H NMR ($CDCl_3$) and/or ^{13}C NMR ($CDCl_3$) δ, ppm (*J* values in Hz)
6a	86	154 (EtOAc-$CHCl_3$)	$C_{14}H_{14}N_4OS$	286 (M^+, 100)	2.65 (s, 3H, SCH_3), 3.57 (s, 3H, NCH_3), 5.47 (s, 2H, NCH_2), 7.33 (brs, 5H, Ar), 8.02 (s, 1H, H-3); 15.2, 29.4, 50.8, 102.1, 127.7, 127.8, 128.4, 135.0 (C-3), 136.1, 150.3, 157.3, 157.4, 161.8.
6b	90	155 (EtOAc)	$C_8H_{10}N_4OS$	210 (M^+, 78)	2.65 (s, 3H, SCH_3), 3.57 (s, 3H, NCH_3), 3.94 (s, 3H, NCH_3), 7.99 (s, 1H, H-3); 15.2, 29.5, 33.6, 102.0, 134.7 (C-3), 150.5, 157.5, 161.6.
7a	1	82 (EtOAc-Hex.)	$C_{14}H_{14}N_4OS$	286 (M^+, 100)	2.64 (s, 3H, SCH_3), 4.12 (s, 3H, OCH_3), 5.47 (s, 2H, NCH_2), 7.25-7.35 (m, 5H, Ar), 7.93 (s, 1H, H-3).
7b	1	140 (EtOAc-Hex.)	$C_8H_{10}N_4O_3S$	210 (M^+, 40)	2.66 (s, 3H, SCH_3), 4.03 (s, 3H, NCH_3), 4.13 (s, 3H, OCH_3), 7.9 (s, 1H, H-3).
8a	85	120 (EtOAc)	$C_{14}H_{14}N_4O_3S$	318 (M^+, 39)	3.40 (s, 3H, SO_2CH_3), 3.82 (s, 3H, NCH_3), 5.43 (s, 2H, NCH_2), 7.3 (s, 5H, Ar), 8.05 (s, 1H, H-3).
8b	84	250 (EtOAc)	$C_8H_{10}N_4O_3S$	242 (M^+, 87)	3.57 (s, 3H, SO_2Me), 3.92 (s, 3H, NCH_3), 4.02 (s, 3H, NCH_3), 8.14 (s, 1H, H-3).
11	8	112 (EtOAc-Hex.)	$C_{14}H_{14}N_4O_2$	270 (M^+, 100)	3.43 (s, 3H, NCH_3), 4.09 (s, 3H, OCH_3), 5.41 (s, 2H, NCH_2), 7.25-7.35 (m, 5H, Ar), 8.0 (s, 1H, H-3).
14	5	130 (EtOAc-Hex.)	$C_{14}H_{14}N_4O_2$	270 (M^+, 56)	3.47 (s, 3H, NCH_3), 3.91 (s, 3H, NCH_3), 5.51 (s, 2H, NCH_2), 7.4-7.5 (m, 5H, Ar), 7.96 (s, 1H, H-3).
15	66	135 (EtOAc-Hex.)	$C_{14}H_{14}N_4OS$	286 (M^+, 100)	2.61 (s, 3H, SCH_3), 3.96 (s, 3H, NCH_3), 5.38 (s, 2H, NCH_2), 7.24-7.34 (m, 5H, Ar), 8.03 (s, 1H, H-3); 15.4, 33.6, 46.4 127.2 (2C), 127.5, 128.4 (2C), 134.9 (C-3), 135.5, 150.5, 157.7, 161.7.
16	18	91 (EtOAc-Hex.)	$C_{14}H_{14}N_4OS$	286 (M^+, 45)	2.65 (s, 3H, SCH_3), 4.02 (s, 3H, NCH_3), 5.59 (s, 2H, NCH_2), 7.34-7.43 (m, 3H, Ar), 7.49 (d, 1H, *J*=7 Hz, Ar), 7.92 (s, 1H, H-3); 14.2, 33.8, 68.5 (OCH_2), 99.9, 128.3, 128.5, 131.2 (C-3), 135.9, 155.6, 162.2, 169.3.
17	82	125 (EtOAc)	$C_{14}H_{14}N_4O_3S$	318 (M^+, 24)	3.56 (s, 3H, SO_2CH_3), 4.04 (s, 3H, NCH_3), 5.70 (s, 2H, NCH_2), 7.2-7.4 (m, 5H, Ar), 8.12 (s, 1H, H-3).
20	1	126 (EtOAc-Hex.)	$C_{14}H_{14}N_4O_2$	270 (M^+, 100)	3.88 (s, 3H, NCH_3), 4.05 (s, 3H, OCH_3), 5.23 (s, 2H, NCH_2), 7.2-7.36 (m, 5H, Ar), 8.0 (s, 1H, H-3).
22a	80	210 ($CHCl_3$-EtOAc)	$C_{14}H_{14}N_4OS$	286 (M^+, 44)	2.64 (s, 3H, SCH_3), 3.54 (s, 3H, NCH_3), 5.38 (s, 2H, NCH_2), 7.3-7.4 (m, 5H, Ar), 7.94 (s, 1H, H-3); 15.3, 29.4, 57.3, 104.5, 127.8, 128.2, 128.5, 128.9, 134.6, 157.9, 158.6, 160.6.
22b	84	180 ($CHCl_3$-Hex.)	$C_{14}H_{14}N_4OS$	286 (M^+, 66)	2.65 (s, 3H, SCH_3), 3.94 (s, 3H, NCH_3), 5.27 (s, 2H, NCH_2), 7.2 (s, 5H, Ar), 7.90 (s, 1H, H-3); 15.5, 40.1, 46.3, 104.4, 127.1, 127.4, 128.4, 128.8, 135.9, 158.0, 158.7, 160.4.
22c	81	165 ($CHCl_3$-Hex.)	$C_8H_{10}N_4OS$	210 (M^+, 75)	2.67 (s, 3H, SCH_3), 3.57 (s, 3H, NCH_3), 4.05 (s, 3H, NCH_3), 7.97 (s, 1H, H-3).
23a	75	260 ($CHCl_3$-Hex.)	$C_{14}H_{14}N_4O_3S$	318(M^+, 35)	(DMSO-d_6): 3.35 (s, 3H, SO_2CH_3), 3.95 (s, 3H, NCH_3), 5.5 (s, 2H, NCH_2), 7.5 (brs, 5H, Ar), 8.7 (s, 1H, H-3).
23b	82	185 (EtOAc-Hex.)	$C_{14}H_{14}N_4O_3S$	318 (M^+, 30)	3.56 (s, 3H, SO_2CH_3), 4.13 (s, 3H, NCH_3), 5.65 (s, 2H, NCH_2), 7.23-7.31 (m, 5H, Ar), 8.08 (s, 1H, H-3).
23c	83	208 ($CHCl_3$-Hex.)	$C_8H_{10}N_4O_3S$	242 (M^+, 68)	($CDCl_3$ + DMSO-d_6): 3.47 (s, 3H, SO_2CH_3), 3.78 (s, 3H, NCH_3), 4.10 (s, 3H, NCH_3), 8.17 (s, 1H, H-3).

[a]All the compounds gave satisfactory analyses (C, ±0.4%; H, ±0.3%; N, ±0.35%)

Table II—Physical data of 1/2,5-disubstituted (**9,18,24**) and 1/2,5,7-trisubstituted-4,6-dioxo-4,5,6,7-tetrahydro-pyrazolo[3,4-*d*]pyrimidines (**10,13,19,25**)

Product	Yield (%)	m.p. °C (solvent)	Mol. formula[a]	MS (70 eV) m/z (%)	^{1}H NMR ($CDCl_3$) and/or ^{13}C NMR ($CDCl_3$) δ, ppm (*J* values in Hz)
9a	90	265 ($MeOH+CHCl_3$)	$C_{13}H_{12}N_4O_2$	256 (M^+, 61)	($CDCl_3$+DMSO-d_6) 3.38 (s, 3H, NCH_3), 5.33 (s, 2H, NCH_2), 7.26 (s, 5H, Ar), 7.84 (s, 1H, H-3).
9b	86	>295 ($MeOH+CHCl_3$)	$C_7H_8N_4O_2$	180 (M^+, 95)	3.79 (s, 3H, NCH_3), 5.17 (s, 2H, NCH_2), 7.2-7.3 (m, 3H, Ar), 7.38 (d, 2H, *J*=7 Hz, Ar), 7.91 (s, 1H, H-3).
10	82	142 (EtOAc-Hex.)	$C_{14}H_{14}N_4O_2$	270 (M^+, 100)	3.38 (s, 3H, NCH_3), 3.57 (s, 3H, NCH_3), 5.65 (s, 2H, NCH_2), 7.02 (d, 2H, *J*=7 Hz, Ar), 7.27-7.37 (m, 3H, Ar), 8.02 (s, 1H, H-3); 28.3, 31.1, 55.15, 125.5 (2C), 128.2, 129.2, 136.3 (C-3), 136.9, 143.5, 151.4, 157.2.
13	81	170 (EtOAc-Hex.)	$C_{14}H_{14}N_4O_2$	270 (M^+, 48)	3.44 (s, 3H, NCH_3), 3.84 (s, 3H, NCH_3), 5.47 (s, 2H, NCH_2), 7.14 (d, 2H, *J*=7 Hz, Ar), 7.25-7.50 (m, 3H, Ar), 7.92 (s, 1H, H-3); 28.4, 38.9, 47.1, 101.8, 125.1, 127.9, 129.3, 135.6, 136.4 (C-3), 142.9, 151.7, 157.4.
18	96	290 ($MeOH+CHCl_3$)	$C_{13}H_{12}N_4O_2$	256 (M^+, 51)	3.79 (s, 3H, NCH_3), 5.17 (s, 2H, NCH_2), 7.23-7.32 (m, 3H, Ar), 7.38 (d, 2H, *J*=7 Hz, Ar), 7.9 (s, 1H, H-3).
19	81	165 (EtOAc-Hex.)	$C_{14}H_{14}N_4O_2$	270 (M^+, 68)	3.75 (s, 3H, NCH_3), 4.13 (s, 3H, NCH_3), 5.17 (s, 2H, NCH_2), 7.2-7.3 (m, 3H, Ar), 7.48 (d, 2H, *J*=7 Hz, Ar), 7.9 (s, 1H, H-3); 31.3, 39.2, 44.6, 101.6, 127.4, 128.2, 128.6, 136.5 (C-3), 136.9, 143.4, 151,2, 157.1.
24a	90	>300 ($CHCl_3$)	$C_{13}H_{12}N_4O_2$	256 (M^+, 67)	3.36 (s, 3H, NCH_3), 5.40 (s, 2H, NCH_2), 7.35 (s, 5H, Ar), 7.98 (s, 1H, H-3), 11.45 (brs, 1H, NH).
24b	78	275 ($CHCl_3$-Hex.)	$C_{13}H_{12}N_4O_2$	256 (M^+, 100)	3.94 (s, 3H, NCH_3), 5.16 (s, 2H, NCH_2), 7.29-7.32 (m, 3H, Ar), 7.46 (d, 2H, *J*=7 Hz, Ar), 7.85 (s, 1H, H-3), 8.68 (brs, 1H, NH).
24c	85	>300 ($MeOH+CHCl_3$)	$C_7H_8N_4O_2$	180 (M^+, 100)	($CDCl_3$+DMSO-d_6): 3.18 (s, 3H, NCH_3), 3.80 (s, 3H, NCH_3), 7.95 (s, 1H, H-3), 11.5 (brs, 1H, NH).
25a	85	186 ($CHCl_3$-EtOAc)	$C_{14}H_{14}N_4O_2$	270 (M^+, 100)	3.38 (s, 3H, NCH_3), 3.54 (s, 3H, NCH_3), 5.29 (s, 2H, NCH_2), 7.25-7.32 (m, 3H, Ar), 7.35-7.42 (m, 2H, Ar), 7.83 (s, 1H, H-3); 27.8, 29.9, 56.7, 101.4, 128.1, 128.6, 128.9, 130.0, 134.3, 150.8, 151.8, 158.5.
25b	91	137 (EtOAc-Hex.)	$C_{14}H_{14}N_4O_2$	270 (M^+, 100)	3.50 (s, 3H, NCH_3), 3.94 (s, 3H, NCH_3), 5.18 (s, 2H, NCH_2), 7.20-7.30 (m, 3H, Ar), 7.48 (d, 2H, *J*=7 Hz, Ar), 7.88 (s, 1H, H-3); 29.9, 39.7, 44.3, 101.4, 127.3, 128.2, 128.7, 130.9, 137.6, 151.0, 151.7, 158.4.
25c	92	180 ($CHCl_3$-Hex.)	$C_{14}H_{14}N_4O_2$	270 (M^+, 49)	3.39 (s, 3H, NCH_3), 3.95 (s, 3H, NCH_3), 5.20 (s, 2H, NCH_2), 7.25-7.35 (m, 3H, Ar), 7.50 (d, 2H, *J*=7 Hz, Ar), 7.87 (s, 1H, H-3); 27.9, 39.8, 47.0, 101.5, 127.7, 128.4, 128.6, 130.6, 136.6, 150.5, 151.7, 158.5.

[a]All the compounds gave satisfactory analyses (C, ±0.4%; H, ±0.3%; N, ±0.35%)

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