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REACTION OF 4-CYANO-5-AMINOPYRAZOLE AND 3,4-DICYANO-5-AMINOPYRAZOLE WITH DIMETHYLFORMAMIDE DIETHYLACETAL

Yu. N. Bulychev, I. A. Korbukh, M. N. Preobrazhenskaya, A. I. Chernyshov, and S. E. Esipov

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The condensation of 4-cyano-5-aminopyrazole or 3,4-dicyano-5-aminopyrazole with dimethylformamide diethylacetal was studied. It was shown that, in addition to the formation of dimethylaminomethyleneamino derivatives, alkylation of the pyrazole ring occurs under severe conditions without a solvent. Only the corresponding formamidino derivatives are formed when the same reactions are carried out in methanol under milder conditions. The site of addition of an ethyl group to the pyrazole ring in the N-alkyl derivatives obtained was established by ^{13}C NMR and PMR spectroscopy. The possibility of the synthesis of 4-amino- or 4-methylmercapto-pyrazolo[3,4-d]pyrimidines by cyclization of the corresponding dimethylamino-methyleneaminopyrazoles with a cyano group in the ortho position was demonstrated for the first time.

In a previous communication we described the formation of substituted N-alkylpyrazoles in the reaction of 3,4-dicyano-5-aminopyrazole with ethyl orthoformate [1]. In the present

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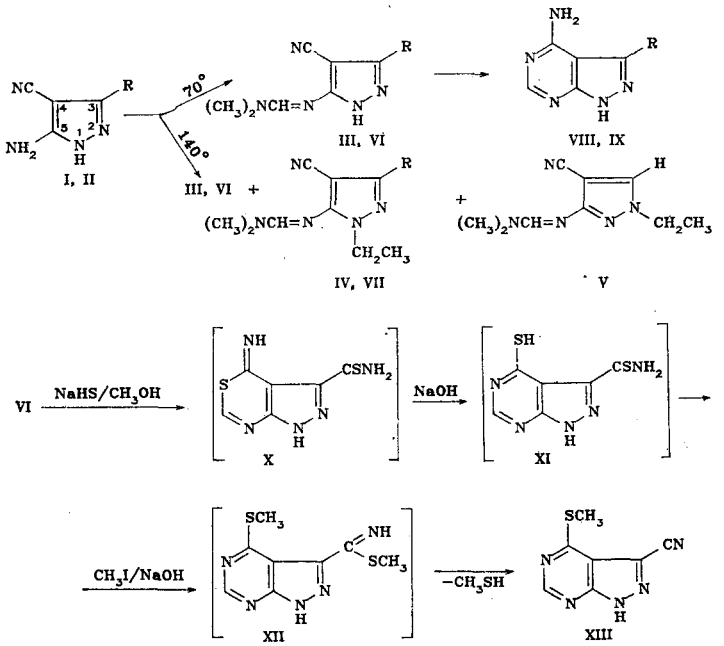
research we under took a study of the reaction of 4-cyano-5-aminopyrazole (I) or 3,4-dicyano-5-aminopyrazole (II) with dimethylformamide diethylacetal and the possibility of the use of this reaction for the synthesis of substituted pyrazolo[3,4-d]pyrimidines.

4-Cyano-5-dimethylaminomethyleneaminopyrazole (III) and 3,4-dicyano-5-dimethylaminomethyleneaminopyrazole (VI), respectively, were isolated as the only products in 50-60% yields when pyrazoles I and II were heated with an equivalent amount or a small excess (up to 10%) of dimethylformamide diethylacetal in methanol. In addition to the formation of dimethylaminomethyleneamino derivatives III and VI, alkylation of the pyrazole ring, as in the condensation of pyrazole II with ethyl orthoformate [1], occurs under more severe conditions when pyrazoles I and II are refluxed in excess dimethylformamide diethylacetal in the absence of a solvent. In the case of pyrazole I amidino derivative III and 1- and 2-ethyl-4-cyano-5-dimethylaminomethyleneaminopyrazoles (IV and V) were isolated in 30, 31, and 35% yields, respectively. 1-Ethyl-3,4-dicyano-5-dimethylaminomethyleneaminopyrazole (VII) (46% yield) and amidine VI (23% yield), which was identical to the compound previously obtained in the reaction of pyrazole II with dimethylformamide diethylacetal in methanol, were obtained by the action of dimethylformamide diethylacetal on pyrazole II under the same conditions.

The structures of III-VII were confirmed by data from the IR, UV, PMR, ^{13}C NMR, and mass spectra and the results of elementary analysis. Absorption bands of cyano groups at 2210-2245 cm^{-1} are present in the IR spectra of all of these compounds. Groups of bands at 2800-3100 cm^{-1} that are characteristic for the NH group and are present in the spectra of N-unsubstituted pyrazoles III and VI are absent in the spectra of N-ethyl derivatives IV, V, and VII.

The UV spectra of all N-unsubstituted pyrazoles I-III and VI and $N_{(1)}$-substituted pyrazole VII are extremely similar. They have absorption maxima at 275-278 nm. The absorption maximum of 1-ethyl derivative IV is shifted somewhat to the long-wave region (286 nm). At the same time, a hypsochromic shift of this maximum to 263 nm occurs in the UV spectrum of its 2-substituted isomer V; this constitutes evidence for a different distribution of the electron density in the heterocyclic ring due to a different type of substitution of the heteroring.



I, III, IV, VIII R=H; II, VI, VII, IX R=CN

The ^{13}C NMR spectral data make it possible to definitively establish the site of addition of the ethyl group to the pyrazole ring in N-ethyl derivatives IV, V, and VII. The parameters of the ^{13}C NMR spectra of III-VII are presented in Table 1. The signals were assigned with allowance for the chemical shifts and relative intensities of the resonance signals in the case of complete decoupling of the coupling of the protons with the carbon nuclei, from the multiplet structures of the signals in the spectra with incomplete and

TABLE 1. Data from the ^{13}C NMR Spectra of Substituted Pyrazoles III-VII in Solution in CD_3OD

Compound	Chemical shift, δ, ppm (SSCC, $J_{C,H}$, Hz)						
	$C_{(5)}$	CH=N $^1J_{C,H}$	$C_{(3)}$ ($^1J_{C,H}$ or $^3J_{C,HCH_2}$)	CN	$C_{(4)}$ ($^2J_{C,H}$)	$N(CH_3)_2$	NCH_2—CH_3
III	158,70	157,10 (177,1)	140,40 (192,5)	115,70	80,16 (9,3)	40,15; 33,90	—
IV	154,43	156,88 (177,1)	141,23 (192,5)	116,33	76,98 (9,9)	40,08; 33,81	42,61 14,04
V	161,94	156,71 (177,0)	135,64 (193,0) (2,8)	114,85	83,64 (9,0)	40,13; 33,93	47,83, 14,65
VI	157,61	157,61	127,13	113,30; 112,37	82,03	40,39; 34,10	—
VII	155,08	157,32 (177,1)	125,38	113,51; 112,28	81,09	40,37; 34,12	43,87, 13,68
VII*	155,37	157,92 (177,9)	124,92 (3,0)	114,04; 113,20	81,58	41,42; 35,19	44,09, 14,87
Δδ III—IV	4,27		−0,83				
Δδ III—V	−3,24		4,76				
Δδ VI—VII	2,53		1,75				

*Spectrum of a solution in d_6-DMSO.

selective decoupling, and from the spin–spin coupling constants (SSCC) and the character of the fine structure of the spectra recorded without suppression of coupling of the protons with the carbon atoms.

The weakest-field signals are the signals of the $C_{(5)}$ atoms of the pyrazole ring and the C atoms of the formamidine group located between two nitrogen atoms. The high intensities of the signals of the C atoms of the CH=N group in the spectra with complete decoupling of the coupling with the protons, as well as their splitting into doublet multiplets due to spin–spin coupling with the methylidyne proton and long-range couplings with the protons of two magnetically nonequivalent CH_3 groups in the spectra recorded without suppression of the coupling with the protons, make it possible to distinguish these signals from one another. In the spectrum of VI the signals of these carbon atoms have identical chemical shifts, and their identification was realized from the spectrum recorded under conditions of incomplete decoupling of the coupling with the protons (Table 1).

The signals of the $C_{(3)}$ and C atoms of the nitrile groups, which each have one adjacent nitrogen atom, are located at strong field at δ 112-141 ppm. The signals of the C atoms in the CN groups in all of the compounds have the form of singlets and are located at δ 112-116 ppm. The signals of the $C_{(3)}$ atoms in III-V are located at δ 135-131 ppm and have the form of doublets in the spectra without suppression of the spin–spin coupling with the protons; In the spectrum of V the doublet components are additionally split into triplets by the methylene protons of the N-ethyl group (J^3 = 2.8 Hz). The resonance signals of the $C_{(3)}$ atoms in VI and VII, which have a cyano group in the 3 position, are shifted to strong field (δ 125-127 ppm) as compared with III-V and are recorded in the form of singlets.

The assignment of the signals of the $C_{(3)}$ carbon atoms and the formamidine fragments was confirmed for III and IV by experiments involving selective decoupling of the doupling of the 3-H and CH=N protons with the adjacent carbon nuclei. The resonance signals of the indicated protons are rather far away from one another (Δδ = 0.35 ppm for III and 0.65 ppm for IV) and are easily identified, since the signal of the proton of the CH=N group has characteristic broadening due to long-range spin–spin coupling with two nonequivalent groups of N-methyl protons.

Signals of $C_{(4)}$ atoms, which do not have adjacent electronegaitve nitrogen atoms and show up either in the form of doublets (for III-V) due to spin–spin coupling with the 3-H protons or (for VI and VII) in the form of narrow singlets when 3-H protons are absent, are located at δ 76-83 ppm. Signals of the C atoms of ethyl groups and magnetically nonequivalent methyl residues of the $N(CH_3)_2$ group are observed at strong field at δ 13-48 ppm.

It is known [2] that when a substituent is introduced into a nitrogen-containing heterocycle, the signal of the C atom located in the α position with respect to the substituted

nitrogen atom is shifted to strong field (α shift) in the ^{13}C NMR spectrum. This principle has been previously used successfully to establish the structures of N-substituted pyrazole-containing heterocycles [3-5].

An analysis of the spectral data shows that, as compared with III, a 4.27-ppm shift of the signal of the $C_{(5)}$ atom to strong field occurs when an ethyl group is introduced in IV, and the signal of the $C_{(3)}$ atom is shifted 4.76 ppm to strong field in the spectrum of V. These data make it possible to unambiguously assign $N_{(1)}$ and $N_{(2)}$ isomeric structures to IV and V, respectively. The location of the ethyl group at the $N_{(2)}$ atom in V is also confirmed by the existence of the above-mentioned triplet structure of each of the doublet components of the signal of the $C_{(3)}$ atom due to long-range coupling with the methylene protons of the $N_{(2)}$-ethyl group vis-à-vis the absence of such hyperfine structure of the signal of the $C_{(3)}$ atom in IV.

The character of the shifts of the signals of the $C_{(3)}$ ($\Delta\delta$ = 1.75 ppm) and $C_{(5)}$ ($\Delta\delta$ = 2.53 ppm) atoms in the spectrum of VII as compared with the spectrum of VI does not make it possible to unambiguously establish its structure. They both undergo an α shift, although the signal of the $C_{(3)}$ atom is shifted to a smaller extent. The classification of VII as an $N_{(1)}$-ethyl derivative was made on the basis of the existence of a triplet structure of the signal of the $C_{(5)}$ atom in the spectrum recorded from a solution in d_6-DMSO* in the case of selective decoupling of the doupling of the methylidyne proton of the formamidine group with the carbon atoms due to long-range coupling with the methylene protons of the N-ethyl substituent. The constant of spin–spin coupling of the $C_{(5)}$ atom with the methylene protons (J^3 = 3.0 Hz) was calculated from the equation

$$J^3 = J_{sk}\,(\gamma H_2/2\pi)\Delta\nu^{-1},$$

where J_{sk} = 1.6 Hz, $\Delta\nu$ = 377 Hz [the difference in the frequencies of the signals of the methylidyne (decoupler frequency) and methylene protons], and $\gamma H_2/2\pi$ = 725 Hz (the reduced power of the decoupling apparatus).

The signal of the $C_{(3)}$ atom, which is in the β position relative to the substituted nitrogen atom, is recorded in the form of a singlet.

The structures of IV and V are also confirmed by data from the PMR spectra. It is known that in N-substituted pyrazoles the signal of the proton attached to the carbon atom in the α position with respect to the substituted nitrogen atom [the =CH–N(R)–N= fragment] is located at weaker field and is more sensitive to a change in the polarity of the solvent in which the PMR spectrum is recorded than the proton attached to the carbon atom in the β position with respect to the substituted nitrogen atom [the –CH=N–N(R)– fragment] [6]. The position of the signals of the 3-H protons in the spectra of IV and V (Table 2) and the $\Delta\delta = \delta_{d_6\text{-DMSO}} - \delta_{CDCl_3}$ values for these protons, which amount to 0.14 ppm for IV and 0.46 ppm for V, constitute evidence that the ethyl group in IV is in the β position with respect to the $C_{(3)}$ atom and that the ethyl group in V is attached to the nitrogen atom in the α position.

We also studied the possibility of the use of amidino derivatives III and VI as intermediates in the transition to compounds of the pyrazolo[3,4-d]pyrimidine series. In an attempt to cyclize III and VI by the action of a methanol solution of ammonia at 20-100°C, in analogy with the cyclization of the corresponding ethoxymethyleneamino derivatives [7, 8], we isolated only the starting III and VI; however, 4-amino- and 3-cyano-4-aminopyrazolo-[3,4-d]pyrimidines (VIII and IX) were obtained in 80 and 83% yields, respectively, when they were heated in ammonium hydroxide. With respect to the yields of the desired products and the convenience and simplicity with which it is realized, this method is not inferior to the known method, which consists in cyclization of the corresponding ethoxymethyleneamino derivatives under the influence of a methanol solution of ammonia.

Amidino derivatives III and VI can also be used to obtain 4-thiopyrazolo[3,4-d]pyrimidines. Thus 3-cyano-4-methylmercaptopyrazolo[3,4-d]pyrimidine (XIII) was synthesized in 67% yield by the action on VI of a solution of sodium hydrosulfide in absolute methanol with subsequent methylation of the product with methyl iodide in an alkaline medium. This reaction evidently proceeds through a step involving the formation of pyrazolothiazine X, which

*In connection with the limited solubility of VII in methanol, a similar experiment with selective decoupling was not carried out for a solution in methanol.

TABLE 2. Data from the PMR Spectra of Substituted Pyrazoles III-VII

Compound	Chemical shift, δ, ppm				
	3-H	CH=N	$N(CH_3)_2$	NCH_2—CH_3	solvent
III	7,77	8,12	3,11; 3,05	—	CD_3OD
IV	7,60	8,25	3,14; 3,08	4,08 1,31	CD_3OD
IV*	7,54	8,25	3,12; 3,07	4,09 1,35	$CDCl_3$
IV*	7,67	8,19	3,10; 3,02	4,00 1,26	d_6-DMSO
V	7,99	8,07	3,09; 3,03	4,06 1,43	CD_3OD
V*	7,61	8,09	3,06; 3,06	4,03 1,47	$CDCl_3$
V*	8,07	8,20	3,04; 2,94	4,00 1,35	d_6-DMSO
VI	—	8,21	3,16; 3,08	—	CD_3OD
VII	—	8,30	3,18; 3,12	4,14 1,35	CD_3OD

*The spectra of these compounds were recorded with a Brucker WH-360 spectrometer; the spectra of the remaining compounds were recorded with a Brucker WH-90 spectrometer.

undergoes the Dimroth rearrangement in an alkaline medium to give thioamide XI, since the IR spectra of thionation products X and XI do not contain absorption bands of a cyano group but do contain absorption bands at 1639 and 1661 cm^{-1}, respectively, which can be assigned to the stretching vibrations of the C=S bond of a thiocarbamoyl group. Under the condition of methylation with excess methyl iodide we obtained imido thioester XII, the acidification of which with acetic acid yielded methyl mercaptan (recognized from its characteristic odor) and led to regeneration of the nitrile group in XIII.

EXPERIMENTAL

The PMR spectra of the compounds were recorded with Brucker WH-90 and Brucker WH-360* spectrometers with tetramethylsilane (TMS) as the internal standard. The ^{13}C NMR spectra were recorded with a Brucker WH-90 pulse spectrometer (22.62 MHz) with dioxane (DO) as the internal standard ($\delta_{TMS} = \delta_{DO} + 67.4$ ppm); the digital resolution was 0.6 Hz/point, which corresponds to the accuracy in the measurement of the $J_{^{13}C\ldots H}$ spin–spin coupling constants (0.6 Hz) or the accuracy in the measurement of the chemical shifts (0.03 ppm). A time lag of 5 sec between 30° (5 μsec) pulses was introduced in order to increase the relative intensities of the signals of quaternary C atoms with longer relaxation times T_1. Experiments involving selective decoupling of the coupling of the protons with the C atoms were carried out at an apparatus decoupling power of $\gamma H_2/2\pi = 725$ Hz. The UV spectra of solutions in ethanol were recorded with a Unicam SP-800 recording spectrophotometer. The IR spectra of KBr pellets were obtained with a Perkin–Elmer 283 spectrometer. The mass spectra were recorded with a Varian MAT-311A mass spectrometer. Analytical thin-layer chromatography (TLC) was carried out on Silufol UV-254 silica gel in chloroform–methanol systems [9:1 (A) and 4:1 (B)]. Preparative chromatography was carried out on 20 × 20 cm plates with a loose layer of LSL 5/40 silica gel (Czechoslovakia) with a thickness of 1.5 mm in the same solvent systems.

4-Cyano-5-dimethylaminomethyleneaminopyrazole (III). A 0.2-g (1.85 mmole) sample of pyrazole I and 0.3 ml of dimethylformamide diethylacetal were refluxed in 40 ml of absolute methanol for 6 h, after which the mixture was evaporated, and the residue was dissolved in 2 ml of methanol and subjected to preparative chromatography on silica gel in system A to give 0.18 g (60%) of III with mp 155-157°C and R_f 0.33 (A). IR spectrum: 2210 (CN) and 2860-3180 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 278 nm (4.11). Mass spectrum, m/z: 163 (M^+). Found: C 51.8; H 5.9%. $C_7H_9N_5$. Calculated: C 51.5; H 5.5%.

3,4-Dicyano-5-dimethylaminomethyleneaminopyrazole (VI). This compound was similarly obtained by refluxing 0.29 g (2.2 mmole) of pyrazole II and 0.4 ml of dimethylformamide diethylacetal in 20 ml of absolute methanol for 8 h. Workup gave 0.2 g (51%) of VI with mp 162-166°C and R_f 0.30 (A). IR spectrum: 2219 and 2232 (2CN) and 2860-3170 cm^{-1} (NH). UV spectrum, λ_{max} (log ε): 276 nm (4.04). Mass spectrum, m/z: 188 (M^+). Found: C 49.6; H 4.6; N 44.5%. $C_8H_8N_6 \cdot 0.25H_2O$. Calculated: C 49.8; H 4.5; N 43.8%.

*The authors thank I. V. Yartseva for recording the spectra with a Brucker WH-360 spectrometer.

4-Cyano-5-dimethylaminomethyleneaminopyrazole (III), 1-Ethyl-4-cyano-5-dimethylaminomethyleneaminopyrazole (IV), and 2-Ethyl-4-cyano-5-dimethylaminomethyleneaminopyrazole (V). A 0.45-g (4.17 mmole) sample of pyrazole I was refluxed in 4 ml of dimethylformamide diethylacetal for 5 h (140°C), after which the mixture was evaporated, and the residue was dissolved in 3 ml of methanol and subjected to twofold preparative chromatography to give 0.2 g (30%) of III with R_f 0.33 (A), which was identical to the product described above, 0.28 g (35%) of V with R_f 0.58 (A), and 0.25 g (31%) of IV with R_f 0.73 (A). Compounds IV and V were obtained in the form of a colorless oil. IR spectrum of IV: 2214 cm^{-1} (CN). UV spectrum of IV, λ_{max} (log ε): 286 nm (4.12). Mass spectrum of IV, m/z: 191 (M^+). Found: C 56.4; H 7.1%. $C_9H_{13}N_3$. Calculated: C 56.5; H 6.9%. IR spectrum of V: 2224 cm^{-1} (CN). UV spectrum of V, λ_{max} (log ε): 263 nm (4.11). Mass spectrum of V, m/z: 191 (M^+). Found: C 54.8; H 7.0; N 35.7%. $C_9H_{13}N_3 \cdot 0.25\ H_2O$. Calculated: C 55.2; H 7.0; N 35.8%.

3,4-Dicyano-5-dimethylaminomethyleneaminopyrazole (VI) and 1-Ethyl-3,4-dicyano-5-dimethylaminomethyleneaminopyrazole (VII). These compounds were obtained by refluxing 0.4 g (3.0 mmole) of pyrazole II in 3 ml of dimethylformamide diethylacetal for 4 h as in the preparation of III-V. Preparative chromatography on silica gel in system A gave 0.13 g (23%) of VI with R_f 0.32 (A), which was identical to the product described above, and 0.30 g (46%) of VII with R_f 0.63 (A) and mp 110-115°C (from methanol). IR spectrum: 2219 and 2242 cm^{-1} (2CN). UV spectrum, λ_{max} (log ε): 276 nm (4.13). Mass spectrum, m/z: 216 (M^+). Found: C 54.9; H 5.6; N 38.0%. $C_{10}H_{12}N_6 \cdot 0.25H_2O$. Calculated: C 54.5; H 5.7; N 38.1%.

4-Aminopyrazolo[3,4-d]pyrimidine (VIII). A 90-mg (0.55 mmole) sample of III was refluxed in 10 ml of 20% ammonium hydroxide for 5 h, after which the solution was cooled, and the precipitated crystals were removed by filtration and recrystallized from water to give 60 mg (80%) of VIII with mp > 300°C (dec.) and R_f 0.18 (B). UV spectrum, λ_{max} (log ε): pH 7: λ_{max} 272 (4.00), 281 (shoulder) and 259.5 nm (shoulder), λ_{min} 235 nm (3.55); pH 1: λ_{max} 258 nm (3.98), λ_{min} 238 nm (3.70); pH 11: λ_{max} 262 (4.02), 282 nm (3.82), λ_{min} 244 (3.83), 277 nm (3.81). UV spectrum [8], λ_{max} (log ε): pH 7: λ_{max} 271.5 (4.05), 281 (shoulder), 260 nm (shoulder); λ_{min} 235 nm (3.62); pH 1: λ_{max} 258 (4.05), λ_{min} 238.5 nm (3.83); pH 11: λ_{max} 263 (4.03), 280 nm (shoulder), λ_{min} 239.5 nm (3.84).

3-Cyano-4-aminopyrazolo[3,4-d]pyrimidine (IX). As in the preparation of VIII, 0.38 g (2.0 mmole) of VI was refluxed in 15 ml of 20% ammonium hydroxide for 5 h with subsequent recrystallization of the product from 50% aqueous ethanol to give 0.27 g (83%) of IX, which decomposed >200°C (>200°C [7]). IR spectrum: 2232 cm^{-1} (CN). UV spectrum, λ_{max} (log ε): 239 (4.00), 282 (3.94), and 287 nm (3.93). UV spectrum [8], λ_{max} (log ε): 238 (shoulder), 279 (4.03), and 287 nm (shoulder). PMR spectrum (d_6-DMSO): 8.01 ppm (s, 6-H).

3-Cyano-4-methylmercaptopyrazolo[3,4-d]pyrimidine (XIII). A 0.60-g (3.8 mmole) sample of VI was added to a solution of 0.23 g (10.0 mmole) of sodium in 100 ml of absolute methanol, and dry hydrogen sulfide was passed through the solution for 3 h. The solution was then heated to the boiling point and refluxed for 6 h. It was then cooled and evaporated, and the residue was dissolved in 50 ml of 0.1 N NaOH, 1.4 g (10.0 mmole) of methyl iodide was added, and the mixture was stirred at 20°C for 30 min. The solution was neutralized with dilute acetic acid, and the precipitated crystals were removed by filtration, washed with water, and dried in vacuo over P_2O_5 at 60°C to give 0.47 g (67%) of XIII. An analytically pure product was obtained by recrystallization from methanol and had mp 282-284°C and R_f 0.16 (A). IR spectrum: 2244 cm^{-1} (CN). UV spectrum, λ_{max} (log ε): 298 (4.13) and 3.06 nm (4.09). PMR spectrum (d_6-DMSO): 8.84 (1H, s, 6-H) and 2.73 ppm (3H, s, SCH_3). Found: C 44.5; H 3.0; N 36.5%. $C_7H_5N_5S$. Calculated: C 44.0; H 2.7; N 36.6%.

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