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REACTION OF ETHYL 3,3-DIAMINOACRYLATE WITH PYRIMIDINE SERIES *o*-CHLORO KETONES. SYNTHESIS OF PYRIDO[4,3-*d*]PYRIMIDINES AND 6*H*-1,3,6,7-TETRA-AZAPHENALENES

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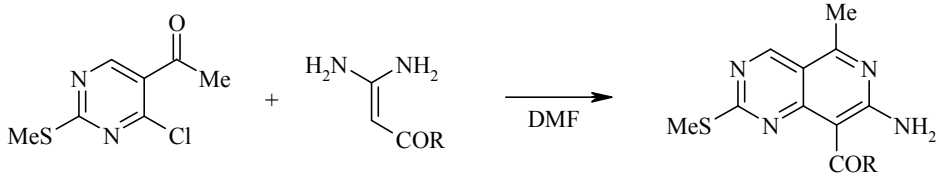
Cyclocondensation of ethyl 3,3-diaminoacrylate with 5-acetyl-4-chloropyrimidines gave ortho- and peri-condensed heterocycles formed through substitution of the chlorine atom by the α-carbon atom of the enediamine and condensation of the amino group with the carbonyl or by addition of the amino group to the pyridine ring.

Keywords: 5-acetyl-4-chloropyrimidines, ethyl 3,3-diaminoacrylate, pyrido[4,3-*d*]pyrimidines, 6*H*-1,3,6,7-tetraazaphenalenes, cyclocondensation.

The cyclocondensation of α-carbonylacetamidines (which as the free bases exist primarily in the tautomeric enediamine forms) with aromatic and heteroaromatic dielectrophiles is a convenient method for the preparation of condensed azines (isoquinolines, naphthyridines, and pyridopyrimidines). Aromatic aldehydes [1-3], esters [4], nitriles [5-8], and nitro compounds [9, 10] having a mobile halogen in an *ortho* position can behave as the dielectrophiles. In these reactions, the α-carbon atom of the enediamine (amidine) substitutes the aromatic halogen, and one of the nitrogen atoms forms a bond to carbonyl (or nitrile) carbon atom of the aromatic dielectrophile, or to the nitrogen atom of the nitro group.

Only two examples involving *ortho*-halo ketones in this reaction have been reported [5]. Moreover, if 2-fluoro-5-nitroacetophenone and ethyl 3,3-diaminoacrylate form the expected isoquinoline, then the 5-acetyl-4,6-dichloropyrimidine unexpectedly gives a *peri*-condensed heterocycle similar to compound **8** reported in our work.

In this connection, we have studied in greater detail the behavior of *o*-halo ketones in their reaction with 3,3-diaminoacrylic acid derivatives.



1 **2a**,**b** **3a**,**b**

2, **3 a** R = OEt, **b** R = $N(CH_2)_4$

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Ketone **1** has one chlorine atom in an *ortho* position to the acetyl group and reacts smoothly with the ethyl ester **2a** and pyrrolidide **2b** of 3,3-diaminoacrylic acid to give the expected pyridopyrimidines **3a**,**b**.

The structure of compound **3a** has been confirmed from X-ray structural analysis (Fig. 1).

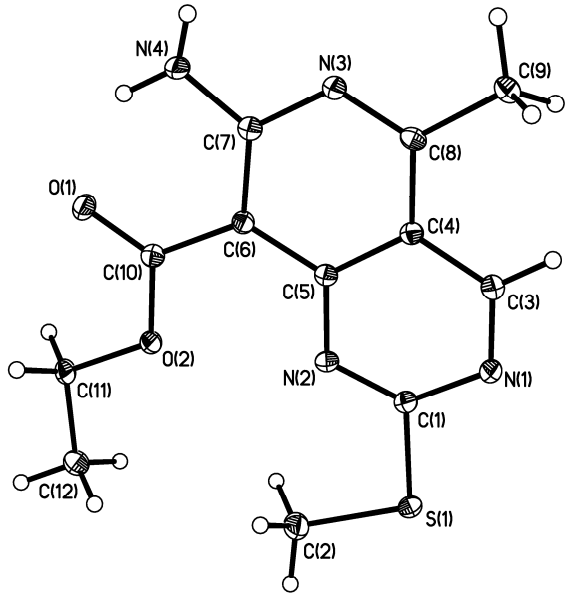
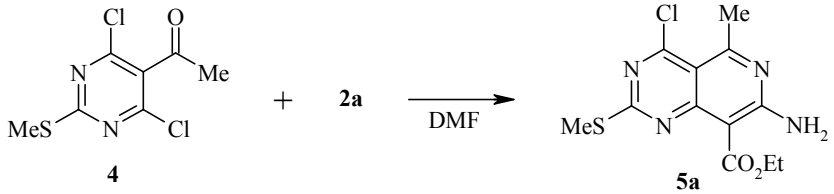


Fig. 1. Molecular structure of compound **3a** with representation of atoms by thermal vibration ellipsoids of 50% probability.

Ketone **4** with two chlorine atoms in *ortho* positions to the acetyl group reacted with the ethyl 3,3-diaminoacrylate (**2a**) to form the pyridopyrimidine **5a**. Its cyclocondensation behavior was clearly different from that of the analog without the methylsulfanyl substituent at position 2. The latter formed only a tricyclic reaction product [5] as an analog of compound **8**. Such a different result can be rationalized from the fact that compound **5a** formed a precipitate and was therefore removed from the reaction medium, whereas its analog without the methylsulfanyl substituent remained in solution and reacted with a second molecule of the enediamine **2a**.

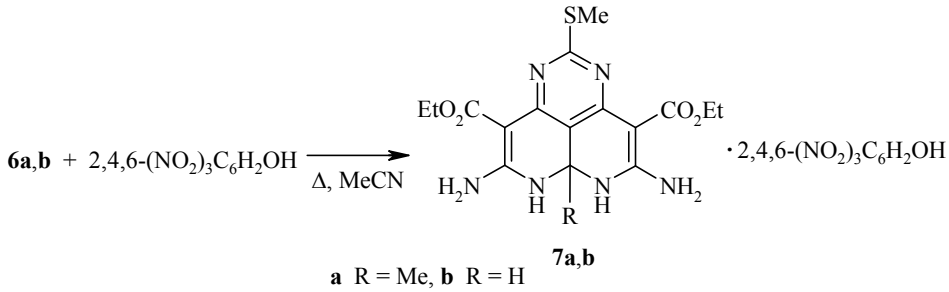


In order to examine the possible preparation of the 6*H*-1,3,6,7-tetraazaphenalene **8** from ketone **4**, we carried out a reaction of the pyridopyrimidine **5a** with a second mole of the enediamine **2a** and obtained compound **6a** as the product of chlorine atom substitution by the enediamine α-carbon atom. Compound **6a** proved fully stable and without a tendency to cyclize spontaneously to the tricyclic isomer **8**.

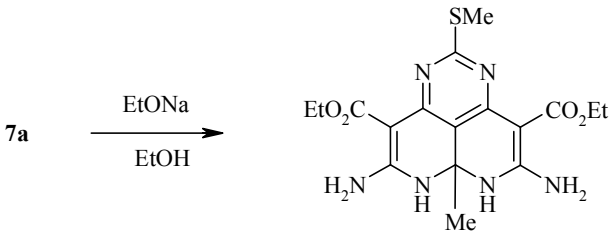
a R = Me, **b** R = H

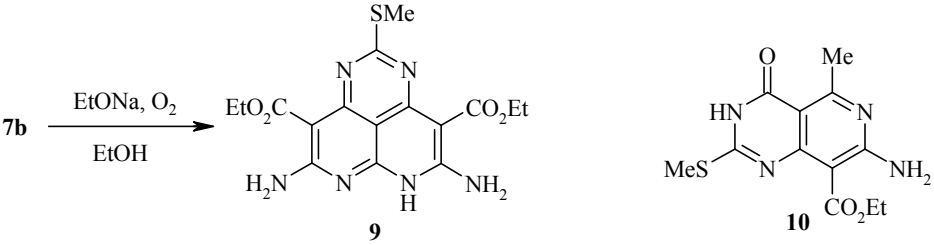
Cyclization did occur upon treatment of compound **6a** with picric acid. It is likely that the pyridine ring nitrogen atom was protonated by the acid, which markedly increased the electrophilicity of the neighboring carbon atom, thus facilitating cyclization. The picrate **7a** was formed, which gave upon treatment with NaOEt the desired tricyclic product **8**, which also was stable and did not open to give the starting compound **6a**.

A similar sequence of reactions was also performed starting from the previously reported pyridopyrimidine **5b** [2], lacking a methyl substituent at position 5. The single difference was aromatization of picrate **7b** during isolation of free base, to give compound **9**, evidently through the action of atmospheric oxygen. All of the signals in the ^{1}H NMR spectra of picrates **7a**,**b** were markedly broadened, evidently due to a rapid proton exchange between several basic centers.



a R = Me, **b** R = H





Attempts to prepare compound **6a** or its tricyclic isomer **8** directly from ketone **4** were unsuccessful, as in the study [5]. The reaction was attempted with a large volume of solvent (in order to avoid precipitation of compound **5a**) and over a longer time. Under these conditions a mixture was obtained, containing besides the tricyclic compound **8** also a compound with ^{1}H NMR spectrum close to that of compound **5a**, but with an additional mobile proton signal at ~12.7 ppm. This compound can be tentatively assigned as the

pyridopyrimidone **10**, which is a hydrolysis product of the pyridopyrimidine **5a** (while noting that water was formed in the course of the cyclocondensation).

Hence it was shown that the formation of the *peri*-condensed 6*H*-1,3,6,7-tetraazaphenalenes *via* an intramolecular addition of enediamine amino group to the C=N formal double bond of the pyridine ring is quite general and occurred in all of the reactions studied.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 instrument (300 and 75 MHz, respectively) using $CDCl_3$ (compounds **1** and **4**) or DMSO-d_6 (remaining compounds) with the residual signals of $CDCl_3$ (7.26 ppm for the ^{1}H nuclei) and DMSO-d_6 (2.50 ppm for the ^{1}H nuclei and 39.7 ppm for the ^{13}C nuclei) as internal standards. Elemental analysis was performed on a Hewlett-Packard HP-185B CHN analyzer. High-resolution mass spectra were recorded on a Bruker micrOTOF instrument (electrospray ionization). Melting points were determined on a Stuart SMP30 Melting Point Apparatus.

1-(4-Chloro-2-methylsulfanylpyrimidin-5-yl)ethanone (1). MeI (2.25 ml, 33.7 mmol) was added to a solution of 5-acetylthiouracil [11] (5.0 g, 29.4 mmol) in 10% aqueous NaOH solution (30 ml) and stirred for 24 h at room temperature. The reaction mixture was then acidified with HCl, cooled, the precipitate filtered off and dried to give the *S*-methyl derivative (5.4 g, 100%), which was used in the following stage without additional purification. The *S*-methyl derivative (2.0 g) was mixed with $POCl_3$ (4 ml, 43 mmol). The mixture was stirred for 2 h at 80°C. The excess $POCl_3$ was distilled off *in vacuo* without heating above 60°C. The residue was poured onto ice (50 g) and stirred thoroughly. CH_2Cl_2 (25 ml) was added, the organic layer was separated, and filtered through a silica gel layer. The CH_2Cl_2 was distilled off *in vacuo* to give ketone **1**. Yield 1.58 g (72%); mp 50-52°C. ^{1}H NMR spectrum, δ, ppm: 2.58 (3H, s, $COCH_3$); 2.66 (3H, s, SCH_3); 8.73 (1H, s, H-6). Found, *m*/*z*: 203.0046 $[M+H]^+$. $C_7H_8ClN_2OS$. Calculated, *m*/*z*: 203.0046.

1-(4,6-Dichloro-2-methylsulfanylpyrimidin-5-yl)ethanone (4) was prepared from 4,6-dichloro-2-methylsulfanylpyrimidine-5-carbaldehyde [2] by the method [12]. Yield 55%; mp 92-94°C. ^{1}H NMR spectrum, δ, ppm: 2.57 (3H, s, $COCH_3$); 2.59 (3H, s, SCH_3). Found, *m*/*z*: 236.9651 $[M+H]^+$. $C_7H_7Cl_2N_2OS$. Calculated, *m*/*z*: 236.9656.

Ethyl 7-Amino-5-methyl-2-methylsulfanylpyrido[4,3-*d*]pyrimidine-8-carboxylate (3a). A solution of ketone **1** (500 mg, 2.47 mmol) and the acrylate **2a** (706 mg, 5.42 mmol) in absolute DMF (5 ml) was maintained at room temperature for 1 day. The mixture was poured into water, and the precipitate was filtered off and dried. Yield 580 mg (84%). White crystals; mp 234-236°C (MeCN). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.33 (3H, t, *J* = 7.0, $CH_2C\underline{H}_3$); 2.57 (3H, s, SCH_3); 2.72 (3H, s, 5-CH_3); 4.33 (2H, q, *J* = 7.0, $C\underline{H}_2CH_3$); 7.80 (2H, br. s, NH_2); 9.14 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 14.5 (SCH_3); 15.2 ($CH_2\underline{C}H_3$); 21.8 (5-CH_3); 61.3 ($\underline{C}H_2CH_3$); 94.6 (C-8); 111.3 (C-4a); 154.5 (C-8a); 159.1 (C-4); 161.7 (C-7); 166.6 (C-5); 168.3 (CO); 173.4 (C-2). Found, %: C 51.77; H 4.86; N 20.22. $C_{12}H_{14}N_4O_2S$. Calculated, %: C 51.78; H 5.07; N 20.13.

7-Amino-5-methyl-2-methylsulfanylpyrido[4,3-*d*]pyrimidine-8-carboxylic acid pyrrolidide (3b) was prepared similarly. Yield 69%. White crystals; mp 281-282°C (MeCN). ^{1}H NMR spectrum, δ, ppm: 1.70-2.00 (4H, m, CH_2CH_2); 2.49 (3H, s, SCH_3); 2.72 (3H, s, 5-CH_3); 3.00-3.25 (2H, m, NCH_2); 3.45-3.65 (2H, m, NCH_2); 6.75 (2H, br. s, NH_2); 9.15 (1H, s, H-4). ^{13}C NMR spectrum, δ, ppm: 14.3 (SCH_3); 21.4 (5-CH_3); 25.1, 26.3, 46.2, 47.4 (pyrrolidine); 102.7 (C-8); 110.9 (C-4a); 151.7 (C-8a); 158.4 (C-4); 159.1 (C-7); 163.3 (C-5); 165.3 (CO); 172.6 (C-2). Found, %: C 55.53; H 5.63; N 22.93. $C_{14}H_{17}N_5OS$. Calculated, %: C 55.42; H 5.65; N 23.08.

Ethyl 7-Amino-4-chloro-5-methyl-2-methylsulfanylpyrido[4,3-*d*]pyrimidine-8-carboxylate (5a). A solution of ketone **4** (600 mg, 2.53 mmol) and the acrylate **2a** (750 mg, 5.76 mmol) in absolute DMF (4.5 ml) was maintained at room temperature for 2 days. The precipitate formed was filtered off, washed with water, and

dried. Yield 560 mg (71%). Yellow crystals; mp 162-163°C (MeCN). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.40 (3H, t, *J* = 7.0, $CH_2C\underline{H}_3$); 2.60 (3H, s, SCH_3); 2.94 (3H, s, 5-CH_3); 4.41 (2H, q, *J* = 7.0, $C\underline{H}_2CH_3$); 6.90 (2H, br. s, NH_2). ^{13}C NMR spectrum, δ, ppm: 14.8, 14.9 (SCH_3, $CH_2\underline{C}H_3$); 29.6 (5-CH_3); 61.6 ($\underline{C}H_2CH_3$); 96.1 (C-8); 110.7 (C-4a); 157.5; 160.5; 160.7; 165.3; 168.5 (CO); 172.2 (C-2). Found, %: C 46.11; H 3.98; N 17.69. $C_{12}H_{13}ClN_4O_2S$. Calculated, %: C 46.08; H 4.19; N 17.91.

Ethyl 7-Amino-4-(2,2-diamino-1-ethoxycarbonylvinyl)-5-methyl-2-methylsulfanylpyrido[4,3-*d*]-pyrimidine-8-carboxylate (6a). A solution of the pyridopyrimidine **5a** (500 mg, 1.6 mmol) and enediamine **2a** (454 mg, 3.5 mmol) in absolute DMF (3 ml) was maintained for 5 days at room temperature, poured into water; the precipitate was filtered off, washed with water, and dried. Yield 500 mg (77%). Yellow crystals; mp 216-218°C (MeCN). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.80 (3H, t, *J* = 7.0, $(NH_2)_2C{=}CCO_2CH_2C\underline{H}_3$); 1.32 (3H, t, *J* = 7.5, 8-$CO_2CH_2C\underline{H}_3$); 2.45 (3H, s, 5-CH_3); 2.53 (3H, s, SCH_3); 3.70-3.85 (2H, m, $(NH_2)_2C{=}CCO_2C\underline{H}_2CH_3$); 4.31 (2H, q, *J* = 7.5, 8-$CO_2C\underline{H}_2CH_3$); 7.25 (2H, s, 7-NH_2); 7.30 (4H, br. s, $C(NH_2)_2$). ^{13}C NMR spectrum, δ, ppm: 14.3, 15.0, 15.1 (SCH_3, $CO_2CH_2\underline{C}H_3$); 25.6 (5-CH_3); 58.7, 61.1 ($CO_2\underline{C}H_2CH_3$); 81.7 ($\underline{C}{=}C(NH_2)_2$); 95.6 (C-8); 113.2 (C-4a); 156.2; 159.0; 161.7; 165.1; 166.9; 168.5; 169.0; 169.3. Found, %: C 50.11; H 5.50; N 20.44. $C_{17}H_{22}N_6O_4S$. Calculated, %: C 50.24; H 5.46; N 20.68.

Ethyl 7-Amino-4-(2,2-diamino-1-ethoxycarbonylvinyl)-2-methylsulfanylpyrido[4,3-*d*]pyrimidine-8-carboxylate (6b) was prepared similarly to compound **6a**. Yield 79%. Yellow crystals; mp 192-195°C (decomp., MeCN). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.89 (3H, t, *J* = 7.0, $(NH_2)_2C{=}CCO_2CH_2C\underline{H}_3$); 1.33 (3H, t, *J* = 7.5, 8-$CO_2CH_2C\underline{H}_3$); 2.53 (3H, s, SCH_3); 3.87 (2H, q, *J* = 7.0, $(NH_2)_2C{=}CCO_2C\underline{H}_2CH_3$); 4.33 (2H, q, *J* = 7.5, 8-$CO_2C\underline{H}_2CH_3$); 7.34 (2H, s, 7-NH_2); 7.30-7.65 (4H, br. s, $C(NH_2)_2$); 8.54 (1H, s, H-5). ^{13}C NMR spectrum, δ, ppm: 14.4, 15.1 (SCH_3, $2CO_2CH_2\underline{C}H_3$); 58.8, 61.3 ($CO_2\underline{C}H_2CH_3$); 76.4 ($\underline{C}{=}C(NH_2)_2$); 97.3 (C-8); 111.7 (C-4a); 154.5; 156.8; 160.8; 162.7; 167.7; 168.3; 169.6; 171.2. Found, %: C 49.09; H 5.21; N 21.47. $C_{16}H_{20}N_6O_4S$. Calculated, %: C 48.97; H 5.14; N 21.41.

Diethyl 5,8-Diamino-6a-methyl-2-methylsulfanyl-6a,7-dihydro-6*H*-1,3,6,7-tetraazaphenalene-4,9-dicarboxylate Picrate (7a). Compound **6a** (50 mg, 0.12 mmol) was dissolved in refluxing MeCN (30 ml), and picric acid (30 mg, 0.13 mmol) was added. A precipitate was formed. The mixture was refluxed for a further 30 min, cooled, and the precipitate was filtered off. Yield 63 mg (82%). Orange crystals; mp 256-262°C (decomp., MeCN). ^{1}H NMR spectrum, δ, ppm: 1.23-1.35 (6H, m, $2CO_2CH_2C\underline{H}_3$); 1.37 (3H, s, 6a-$CH_3$); 2.66 (3H, s, SCH_3); 4.15-4.32 (4H, m, $2CO_2C\underline{H}_2CH_3$); 7.2-8.3 (6H, br. s, $2NH_2$, 2NH); 8.58 (2H, s), 12.55 (1H, br. s, picric acid). Found, %: C 43.60; H 3.89; N 19.86. $C_{23}H_{25}N_9O_{11}S$. Calculated, %: C 43.46; H 3.96; N 19.83.

Diethyl 5,8-diamino-2-methylsulfanyl-6a,7-dihydro-6*H*-1,3,6,7-tetraazaphenalene-4,9-dicarboxylate picrate (7b) was obtained similarly to compound **7a**. Yield 90%. Yellow crystals; mp 201-205°C (decomp., MeCN). ^{1}H NMR spectrum, δ, ppm: 1.22-1.35 (6H, m, $2CO_2CH_2C\underline{H}_3$); 2.64 (3H, s, SCH_3); 4.12-4.32 (4H, m, $2CO_2C\underline{H}_2CH_3$); 5.55 (1H, s, H-6a); 7.4-8.8 (6H, br. s, $2NH_2$, 2NH); 8.58 (2H, s), 12.51 (1H, br. s, picric acid). Found, %: C 42.84; H 3.73; N 20.24. $C_{22}H_{23}N_9O_{11}S$. Calculated, %: C 42.51; H 3.73; N 20.28.

Diethyl 5,8-Diamino-6a-methyl-2-methylsulfanyl-6a,7-dihydro-6*H*-1,3,6,7-tetraazaphenalene-4,9-dicarboxylate (8). Picrate **7a** (130 mg, 0.205 mmol) was added to a solution of NaOEt (0.22 mmol, prepared from Na (5 mg) and absolute EtOH (40 ml)). The suspension formed was stirred to dissolution at room temperature (1 h). Ethanol was removed *in vacuo*, and the residue was washed with water and dried. Yield 62 mg (74%). Yellow crystals; mp 175-180°C (decomp., MeCN). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.23 (6H, t, *J* = 7.5, $2CO_2CH_2C\underline{H}_3$); 1.29 (3H, s, 6a-$CH_3$); 2.43 (3H, s, SCH_3); 4.09 (4H, m, $2CO_2C\underline{H}_2CH_3$); 6.80-8.50 (4H, br. s, $2NH_2$); 7.21 (2H, s, 2NH). ^{13}C NMR spectrum, δ, ppm: 14.0; 15.4; 27.1; 59.2; 66.5; 79.1; 103.8; 154.2; 159.1; 168.2; 169.3. Found, *m*/*z*: 407.1468 $[M+H]^+$. $C_{17}H_{23}N_6O_4S$. Calculated, *m*/*z*: 407.1496.

Diethyl 5,8-Diamino-2-methylsulfanyl-6*H*-1,3,6,7-tetraazaphenalene-4,9-dicarboxylate (9) was obtained similarly. Yield 90%. White crystals; mp 266-273°C (decomp.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.30 (6H, t, *J* = 7.5, $2CO_2CH_2C\underline{H}_3$); 2.52 (3H, s, SCH_3); 4.24 (4H, q, *J* = 7.5, $2CO_2C\underline{H}_2CH_3$); 6.80-8.20 (5H, br. s, $2NH_2$, NH). Found, %: C 49.17; H 4.67; N 21.11. $C_{16}H_{18}N_6O_4S$. Calculated, %: C 49.22; H 4.65; N 21.53. Found, *m*/*z*: 391.1194 $[M+H]^+$. $C_{16}H_{19}N_6O_4S$. Calculated, *m*/*z*: 391.1183.

X-Ray Structural Study of Compound 3a. A crystal was grown from DMF. $C_{12}H_{14}N_4O_2S$. The crystals were monoclinic with space group C 2/c, *a* 22.907(2), *b* 9.4779(9), *c* 14.0696(13) Å, β 125.942(2)°; *V* 2473.1(4) Å^3; *F*(000) 1168, μ 0.266 mm^{-1}, *Z* 8; d_{calc} 1.495 g/cm^3. The cell parameters and set of experimental reflections were measured on a Bruker AXS Smart 1000 CCD automatic diffractometer (monochromatic MoKα radiation, λ 0.71073 Å, ω/2θ scanning in the angle range 2.20<θ<29.00°). Of the 9585 total reflections 3259 were independent with R_{int} 0.0358 and 2699 with $I > 2\sigma(I)$. The experimental completeness for the angle θ 29.00° was 99.1%. The structure was solved by a direct statistical method and refined using F^2 full-matrix least-squares analysis in anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms were placed in geometrically calculated positions and refined in the isotropic approximation. All of the calculations were carried out using the SHELXTL software package [13]. The final refinement results were R_1 0.0386, wR_2 0.0953 for reflections with $I > 2\sigma(I)$ and R_1 0.0428, wR_2 0.1024 for all of the reflections. The results of this X-ray structural analysis have been deposited in the Cambridge Crystallographic Data Center (deposit CCDC 920033).

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