Diazafulvenium Methides` Chemistry in the Synthesis of Functionalized Pyrazoles

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Experimental Section

Thiazolidines **15a**,¹ **15b**² and **15c**² were prepared as described in the literature.

General Procedure for the synthesis of *N*-nitrosothiazolidine-4-carboxylic acids. Concentrated hydrochloric acid was slowly added dropwise (CARE!) to a suspension of the thiazolidine-4-carboxylic acid (**15a**, **15b** or **15c** 78.84 mmol) in water (40 mL) until the suspension dissolved. To the vigorously stirring solution was then added slowly, via a dropping funnel, sodium nitrite (8.16 g, 118.26 mmol) dissolved in water (40 mL). Shortly after the addition was complete a vigorous evolution of gas (CAUTION!) occurred and the initial red color faded to give a pale yellow solution. After stirring for 12 h the reaction mixture was extracted with ethyl acetate (3x80 mL) and the combined organic fractions were then washed with water (80 mL) and brine (80 mL). The organic phase was dried over anhydrous magnesium sulphate and the solvent evaporated off.

2-Methyl-*N*-nitrosothiazolidine-4-carboxylic acid **16a.**³ The crude product was purified by flash chromatography [ethyl acetate-hexane (1:1), ethyl acetate-hexane (3:1), then ethyl acetate] to give **16a** as a yellowish oil (58%). IR (film) 2988, 1731, 1434, 1318, 1269, 1237 cm⁻¹; The ¹H NMR showed the presence of two conformational isomers (ratio 72:28) (*major isomer*) 2.00 (3H, d, *J* = 6.2 Hz), 3.23-3.49 (2H, m), 4.85-4.97 (1H, m), 5.61 (1H, q, *J* = 6.2 Hz); (*minor isomer*) 1.92 (3H, d, *J* = 6.5 Hz), 3.23-3.49 (2H, m), 4.85-4.97 (1H, m), 5.97 (1H, q, *J* = 6.5 Hz); MS (CI) *m/z* 177 (MH⁺, 93%), 163 (79), 148 (99), 134 (100), 102 (83), 88 (90). HRMS (CI) *m/z* 177.0332 (C₅H₉N₂O₃S [MH⁺], 177.0334).

5,5-Dimethyl-*N*-nitrosothiazolidine-4-carboxylic acid **16b.** The crude product crystallised on trituration with petroleum ether to give (4*R*)-5,5-dimethyl-*N*-nitrosothiazolidine-4-carboxylic acid **16b** as a white solid (90%). mp (subl.) >138 °C. IR (KBr) 1744, 1451, 1342 (bs), 1279, 1263, 1206, 1189, 1150, 1130 cm⁻¹; The ¹H NMR (CDCl₃/DMF-d₇) showed the presence of two conformational isomers (ratio 67:43): (*major isomer*) 1.53 (3H, s), 1.63 (3H, s), 4.42 (1H, s), 5.47 (1H, d, *J* = 10.6 Hz), 5.57 (1H, d, *J* = 10.6 Hz); (*minor isomer*) 1.58 (3H, s), 1.63 (3H, s), 4.62 (1H, d, *J* = 10.6 Hz), 4.98 (1H, d, *J* = 10.6 Hz), 5.31 (1H, s); ¹³C NMR (CDCl₃/DMF-d₇) (*major isomer*) 23.9, 27.0, 45.5, 50.3, 68.5, 165.4. Anal. Calcd. for (C₆H₁₀N₂O₃S): C, 37.9; H, 5.3; N, 14.7; S, 16.9. Found, C, 38.3; H, 5.2; N, 15.0; S 17.0.

(4*R*)-2,5,5-Trimethyl-3-nitrosothiazolidine-4-carboxylic acid **16c.** Compound **16c** was obtained as a yellowish oil (62%). IR (KBr) 1719, 1450, 1425, 1415, 1375, 1333, 1245, 1163, 1130 cm⁻¹; The ¹H NMR showed the presence of two conformational isomers (ratio 51:49): (*major isomer*) 1.56 (3H, s), 1.63 (3H, s), 2.03 (3H, d, *J* = 6.1), 1.69 (3H, s), 4.55 (1H, s), 5.72 (1H, approx. q, *J* = 6.1); (*minor isomer*) 1.53 (3H, s), 1.58 (3H, s), 2.02 (3H, d, *J* = 6.1), 4.69 (1H, s), 5.88 (1H, approx. q, *J* = 6.1). HRMS (CI) *m/z* 191.0485 (C₇H₁₃N₂O₃S [M-H⁺], 191.0490).

General Procedure for the Synthesis of 4*H*,6*H*-thiazolo[3,4-*c*][1,2,3]oxadiazolium-3-oxides.

Trifluoroacetic anhydride (3.1 mL, 21.65 mmol) was slowly added to a suspension of *N*-nitrosothiazolidine-4-carboxylic acid (21.65 mmol) in anhydrous diethyl ether (230 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 6 h and then allowed to warm to room temperature. After stirring at room temperature for 24 h the solution was filtered and the solvent evaporated off.

6-Methyl-4*H*,6*H*-thiazolo[3,4-*c*][1,2,3]oxadiazol-7-ium-3-oxide 17a. The crude product was purified by flash chromatography [ethyl acetate-hexane (1:1), ethyl acetate-hexane (2:1), then ethyl acetate] to give a low melting point solid (from ethyl ether) (43%). IR (KBr) 1746, 1516, 1438, 1296, 1234, 1018 cm⁻¹; ¹H NMR 1.97 (3H, d, *J* = 6.4 Hz), 4.02 (2H, d, *J* = 1.7 Hz), 5.81-5.87 (1H, m); ¹³C NMR 21.8, 24.6, 63.2, 108.4, 163.5; MS (CI) *m/z* 159 (MH⁺, 61%), 128 (30), 99 (100). HRMS (CI) *m/z* 159.0224 (C₅H₇N₂O₂S [MH⁺], 159.0228).

4,4-Dimethyl-4*H*,6*H*-thiazolo[3,4-*c*][1,2,3]oxadiazolium-3-oxide 17b. The product was obtained as a white solid (75%). mp 96.0-97.8 °C (from ethyl ether). IR (KBr) 1711, 1693, 1349, 1141 cm⁻¹; ¹H NMR 1.82 (6H, s), 5.44 (2H, s); ¹³C NMR 29.1, 49.8, 50.5, 115.8, 162.3; MS (EI) *m/z* 172 (M⁺, 26%), 140 (100), 114 (9), 85 (87), 68 (42). Anal. Calcd. for (C₆H₈N₂O₂S) C, 41.85; H, 4.68; N, 16.27. Found C, 41.96; H, 4.65; N, 16.19.

4,4,6-Trimethyl-4*H*,6*H*-thiazolo[3,4-*c*][1,2,3]oxadiazolium-3-oxide 17c The crude product was purified by flash chromatography [ethyl acetate-hexane (1:3), then ethyl acetate-hexane (1:2)] to give a solid (65%). mp 57.8-58.5 °C (from ethyl ether). ¹H NMR 1.80 (3H, s), 1.83 (3H, s), 1.97 (3H, d, *J* = 6.4), 5.85 (1H, q, *J* = 6.4); ¹³C NMR 22.1, 29.5, 30.1, 49.0, 62.4, 115.1, 162.2; MS (EI) *m/z* 186 (M⁺, 17%), 156 (37), 128 (24), 101 (23), 85 (26), 68 (34), 61 (100). HRMS (EI) *m/z* 186.0466 (C₇H₁₀N₂O₂S [M⁺], 186.0463).

General Procedure for the synthesis of dimethyl 1*H*,3*H*-pyrazolo[1,5-*c*][1,3]thiazole-6,7-dicarboxylates. The appropriate 4*H*,6*H*-thiazolo[3,4-*c*][1,2,3]oxadiazolium-3-oxide (7.03 mmol) and dimethyl acetylenedicarboxylate (1.4 mL, 11.25 mmol) in xylene (6 mL) were heated at reflux for 3 h under N₂ atmosphere. The reaction was cooled to room temperature and the solvent removed in vacuo.

Dimethyl 3-Methyl-1*H*,3*H*-pyrazolo[1,5-*c*][1,3]thiazole-6,7-dicarboxylate 18a. The crude product was purified by flash chromatography [ethyl acetate-hexane (1:1), then ethyl acetate-hexane (2:1)]

to give a white solid (60%). The crude product was purified by flash chromatography [ethyl acetate-hexane (1:1), then ethyl acetate-hexane (2:1)] to give a white solid (60%). mp 84.1-85.4 °C (from ethyl ether). IR (KBr) 1754, 1722, 1473, 1308, 1131, 1085 cm^{-1} ; ^1H NMR 1.88 (3H, d, $J = 6.2$ Hz), 3.85 (3H, s), 3.96 (3H, s), 4.24 (1H, dd, $J = 1.3$ and 15.3 Hz), 4.32 (1H, dd, $J = 2.4$ and 15.3 Hz), 5.59-5.65 (1H, m); ^{13}C NMR 23.2, 27.3, 51.8, 52.6, 61.1, 108.4, 147.9, 148.2, 161.7, 161.8; MS (EI) m/z 256 (M^+ , 5%), 224 (100), 209 (79), 193 (9), 59 (10). Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_4\text{S}$: C, 46.87; H, 4.72; N, 10.93. Found: C, 46.99; H, 5.09; N, 10.94.

Dimethyl 1,1-Dimethyl-1*H*,3*H*-pyrazolo[1,5-*c*][1,3]thiazole-6,7-dicarboxylate 18b. The crude product was purified by flash chromatography [ethyl acetate-hexane (1:3), then ethyl acetate-hexane (1:2)] to give a white solid (80%). mp 59.7-60.2 °C (from ethyl ether). IR (KBr) 1721, 1707, 1316, 1229, 1215, 1097 cm^{-1} ; ^1H NMR 1.87 (6H, s), 3.85 (3H, s), 3.94 (3H, s), 5.28 (2H, s); ^{13}C NMR 29.7, 50.0, 51.6, 51.8, 52.6, 107.2, 148.6, 154.6, 162.1, 162.2; MS (EI) m/z 270 (M^+ , 4%), 255 (10), 238 (66), 223 (100), 193 (22). Anal. Calcd. for $(\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_4\text{S})$ C, 48.9; H, 5.2; N, 10.4. Found C, 48.7; H, 4.9; N, 10.9.

Dimethyl 1,1,3-Trimethyl-1*H*,3*H*-pyrazolo[1,5-*c*][1,3]thiazole-6,7-dicarboxylate 18c. Obtained using the general procedure but with shorter reaction time (1 h). The crude product was purified by flash chromatography [ethyl acetate-hexane (1:4)] to give a yellow oil (20%). ^1H NMR 1.84 (3H, s), 1.87 (3H, d, $J = 6.2$ Hz), 1.90 (3H, s), 3.85 (3H, s), 3.95 (3H, s), 5.62 (1H, q, $J = 6.2$ Hz); MS (EI) m/z 284 (M^+ , 6%), 252 (42), 237 (100), 193 (32).

General Procedure for the synthesis of dimethyl 2,2-dioxo-1*H*,3*H*-pyrazolo[1,5-*c*][1,3]thiazole-6,7-dicarboxylate. To a stirred ice-cold solution of the appropriate dimethyl pyrazolo[1,5-*c*][1,3]thiazole-6,7-dicarboxylate (3.90 mmol) in dry dichloromethane (26 mL) was added portionwise 3-chloroperoxybenzoic acid (3 eq., 11.70 mmol) under N_2 atmosphere. The cooling bath was removed and the reaction mixture was allowed to warm to room temperature. After stirring at room temperature for 4 h, the reaction mixture was washed twice with 10% (w/v) aqueous sodium bisulfite solution (2 x 80 mL) and twice with 10% (w/v) aqueous sodium bicarbonate solution (2 x 80 mL). The organic fraction was then dried over anhydrous MgSO_4 and the solvent evaporated off.

Dimethyl 3-Methyl-2,2-dioxo-1*H*,3*H*-pyrazolo[1,5-*c*][1,3]thiazole-6,7-dicarboxylate 19a. The product was obtained as a white solid which was recrystallised with ethyl ether (72%). mp 118.0-119.5 °C (from ethyl ether); IR (KBr) 1746, 1729, 1398, 1339, 1303, 1152, 1081 cm^{-1} ; ^1H NMR 1.89 (3H, d, $J = 6.6$

Hz), 3.87 (3H, s), 3.98 (3H, s), 4.65 (2H, s), 5.22 (1H, q, $J = 6.6$ Hz); ^{13}C NMR 13.3, 51.4, 52.2, 52.8, 72.9, 111.5, 137.8, 145.8, 160.7, 161.3; MS (EI) m/z 224 ($[\text{M}-\text{SO}_2]^+$, 28%), 193 (100), 163 (25), 133(11), 68 (9). Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_6\text{S}$: C, 41.67; H, 4.20; N, 9.72. Found: C, 41.90, H, 4.06, N, 9.59.

Dimethyl 1,1-Dimethyl-2,2-dioxo-1*H*,3*H*-pyrazolo[1,5-*c*][1,3]thiazole-6,7-dicarboxylate 19b.

The product was obtained as a white solid (79%). mp 92.2-92.8 °C (from ethyl ether). IR (KBr) 1743, 1731, 1329, 1175, 1119 cm^{-1} ; ^1H NMR 1.85 (6H, s), 3.92 (3H, s), 3.99 (3H, s), 5.22 (2H, s); ^{13}C NMR 20.5, 52.4, 52.9, 64.1, 64.4, 111.1, 146.7, 147.7, 161.5, 161.6; MS (EI) m/z 238 ($[\text{M}^+-\text{SO}_2]$, 5%), 206 (100), 191 (5), 177 (16), 148 (17). HRMS (CI) m/z 303.0651 ($\text{C}_{11}\text{H}_{15}\text{N}_2\text{O}_6\text{S}$ $[\text{M}-\text{H}^+]$, 303.0651).

Dimethyl 1,1,3-Trimethyl-2,2-dioxo-1*H*,3*H*-pyrazolo[1,5-*c*][1,3]thiazole-6,7-dicarboxylate 19c.

The crude product was purified by flash chromatography [ethyl acetate-hexane (1:2)] to give a white solid (62%). mp 88-89 °C (from ethyl ether). ^1H NMR 1.81 (3H, s), 1.84 (3H, s), 1.93 (3H, d, $J = 6.6$ Hz), 3.89 (3H, s), 3.97 (3H, s), 5.11 (1H, q, $J = 6.6$ Hz); ^{13}C NMR 13.5, 20.1, 21.9, 52.3, 53.0, 52.7, 70.6, 110.8, 146.5, 161.6, 162.0; MS (EI) m/z 252 ($[\text{M}^+-\text{SO}_2]$, 10%), 237 (5), 220 (100), 205 (44), 193 (7), 161 (10). HRMS (CI) m/z 317.0801 ($\text{C}_{12}\text{H}_{17}\text{N}_2\text{O}_6\text{S}$ $[\text{M}-\text{H}^+]$, 317.0801).

References

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^1H NMR and ^{13}C NMR spectra:

(^1H NMR spectra were recorded on an instrument operating at 300 MHz and ^{13}C NMR spectra were recorded on an instrument operating at 75.5 MHz. The solvent is deuteriochloroform except where indicated otherwise).

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142.807

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112.605

106.361

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10.367

30

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161.635

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131.719

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68.491

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33.693
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16b

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137.826

111.459

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77.001
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72.874

52.847
52.186
51.405

14.021
13.338

Crystallographic data. The X-ray data were collected on an Enraf-nonius Mach-3 single crystal diffractometer, at 298(3) K, using graphite-monochromated Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Intensities were recorded as full profiles of ω - θ scans. The structures were solved by direct methods as implemented in SHELXS97⁴ and refined by full-matrix least-squares using SHELXL97³. Examination of the structure with PLATON⁵ confirmed the absence of voids in the crystal structures, which might be occupied by solvent molecules.

Crystal data for dimethyl 8-methyl-5,7-dioxo-6-phenyl-4a,5,6,7,7a,8-hexahydro-1*H*,3*H*-pyrazolo[1,5-*a*]pyrrolo[3,4-*d*]pyridine-2,3-dicarboxylate **26**. C₂₀H₁₉N₃O₆, M = 397.38, monoclinic, P2₁/c with unit cell, *a* = 10.962(5) Å, *b* = 9.459(4) Å, *c* = 19.286(3) Å, $\alpha = 90^\circ$, $\beta = 108.524(18)^\circ$, $\gamma = 90^\circ$, *V* = 1896.2(12) Å³. It contains four molecules/unit cell. $\rho_{\text{calc}} = 1.392 \text{ g cm}^{-3}$, *Z* = 4, $\mu = 0.876 \text{ mm}^{-1}$. *R* (*I* > 2 σ (*I*)) = 0.0438 and *R*_w = 0.1634 for 3756 independent reflections. H atoms were placed at calculated positions and refined as riding on their parent atoms.

Figure 1. (4*aS*,7*aS*,8*S*)-8-methyl-5,7-dioxo-6-phenyl-4a,5,6,7,7a,8-hexahydro-1*H*,3*H*-pyrazolo[1,5-*a*]pyrrolo[3,4-*d*]pyridine **26** structure determined by X-ray crystallography.

data_mis

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SHELXL-97

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North et al., 1968

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;
Refinement of  $F^2$  against ALL reflections. The weighted R-factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional R-factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and R-factors based on ALL data will be even larger.
```

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_refine_ls_weighting_details      'calc w=1/[\sigma^2(Fo^2)+(0.0840P)^2+0.2968P] where P=(Fo^2+2Fc^2)/3'
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_atom_sites_solution_secondary   difmap
_atom_sites_solution_hydrogens   geom
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_refine_ls_extinction_method      none
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O2 O 0.38780(14) -0.12402(18) 0.08111(10) 0.0615(5) Uani 1 1 d . . .
O3 O 0.15296(19) -0.37669(18) 0.08728(11) 0.0707(5) Uani 1 1 d . . .
O4 O 0.29508(16) -0.26916(17) 0.18299(10) 0.0632(5) Uani 1 1 d . . .
O5 O 0.31043(16) 0.2769(2) 0.23937(10) 0.0680(5) Uani 1 1 d . . .
O6 O -0.06055(16) 0.0980(2) 0.25997(10) 0.0766(6) Uani 1 1 d . . .
N1 N 0.02542(16) -0.09790(19) 0.10189(10) 0.0476(4) Uani 1 1 d . . .
N6 N 0.14069(16) 0.16807(19) 0.26287(10) 0.0481(4) Uani 1 1 d . . .
N9 N 0.01589(16) 0.04399(18) 0.09043(10) 0.0453(4) Uani 1 1 d . . .
C2 C 0.14532(19) -0.1274(2) 0.10403(12) 0.0454(5) Uani 1 1 d . . .
C3 C 0.2125(2) -0.0055(2) 0.09404(12) 0.0459(5) Uani 1 1 d . . .
C3A C 0.1250(2) 0.1036(2) 0.08614(11) 0.0451(5) Uani 1 1 d . . .
C4 C 0.1302(2) 0.2603(2) 0.08765(13) 0.0524(5) Uani 1 1 d . . .
H4A H 0.0703 0.2992 0.0433 0.063 Uiso 1 1 calc R . .
H4B H 0.2162 0.2930 0.0919 0.063 Uiso 1 1 calc R . .
C4A C 0.0929(2) 0.3056(2) 0.15523(12) 0.0504(5) Uani 1 1 d . . .
H4A1 H 0.0860 0.4088 0.1567 0.061 Uiso 1 1 calc R . .
C5 C 0.1964(2) 0.2533(2) 0.22256(13) 0.0501(5) Uani 1 1 d . . .
C7 C 0.0078(2) 0.1600(3) 0.23242(12) 0.0521(5) Uani 1 1 d . . .
C7A C -0.0321(2) 0.2360(2) 0.15956(12) 0.0492(5) Uani 1 1 d . . .
H7A H -0.0952 0.3095 0.1594 0.059 Uiso 1 1 calc R . .
C8 C -0.09096(19) 0.1316(2) 0.09620(12) 0.0479(5) Uani 1 1 d . . .
H8 H -0.1225 0.1871 0.0511 0.057 Uiso 1 1 calc R . .
C10 C -0.2019(2) 0.0425(3) 0.10219(15) 0.0603(6) Uani 1 1 d . . .
H10A H -0.2306 -0.0193 0.0607 0.090 Uiso 1 1 calc R . .
H10B H -0.2714 0.1031 0.1035 0.090 Uiso 1 1 calc R . .
H10C H -0.1741 -0.0128 0.1462 0.090 Uiso 1 1 calc R . .
C11 C 0.3441(2) 0.0037(3) 0.09063(13) 0.0514(5) Uani 1 1 d . . .
C12 C 0.5208(2) -0.1350(4) 0.08437(17) 0.0755(8) Uani 1 1 d . . .
H12A H 0.5301 -0.1011 0.0394 0.113 Uiso 1 1 calc R . .
H12B H 0.5476 -0.2320 0.0916 0.113 Uiso 1 1 calc R . .
H12C H 0.5731 -0.0791 0.1243 0.113 Uiso 1 1 calc R . .
C13 C 0.1958(2) -0.2725(2) 0.12202(13) 0.0499(5) Uani 1 1 d . . .
C14 C 0.3647(3) -0.3988(3) 0.2069(2) 0.0919(10) Uani 1 1 d . . .
H14A H 0.3147 -0.4605 0.2267 0.138 Uiso 1 1 calc R . .
H14B H 0.4450 -0.3783 0.2438 0.138 Uiso 1 1 calc R . .
H14C H 0.3809 -0.4439 0.1661 0.138 Uiso 1 1 calc R . .
C15 C 0.21232(19) 0.0890(2) 0.32619(12) 0.0474(5) Uani 1 1 d . . .
C16 C 0.3022(2) -0.0070(3) 0.31981(14) 0.0577(6) Uani 1 1 d . . .
H16 H 0.3173 -0.0190 0.2754 0.069 Uiso 1 1 calc R . .

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C17 C 0.3701(3) -0.0858(3) 0.38027(17) 0.0704(7) Uani 1 1 d . . .
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C18 C 0.3446(3) -0.0687(3) 0.44501(16) 0.0743(8) Uani 1 1 d . . .
H18 H 0.3895 -0.1223 0.4855 0.089 Uiso 1 1 calc R . .
C19 C 0.2545(3) 0.0255(3) 0.45057(15) 0.0742(8) Uani 1 1 d . . .
H19 H 0.2378 0.0349 0.4947 0.089 Uiso 1 1 calc R . .
C20 C 0.1873(3) 0.1076(3) 0.39131(13) 0.0607(6) Uani 1 1 d . . .
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O3 0.0807(12) 0.0500(10) 0.0798(13) -0.0132(9) 0.0229(10) -0.0060(9)
O4 0.0563(9) 0.0502(9) 0.0748(11) 0.0086(8) 0.0090(8) 0.0003(7)
O5 0.0513(9) 0.0709(11) 0.0738(11) 0.0112(9) 0.0086(8) -0.0165(8)
O6 0.0529(9) 0.1152(17) 0.0626(11) 0.0183(10) 0.0195(8) -0.0116(10)
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N6 0.0450(9) 0.0504(10) 0.0463(10) 0.0042(8) 0.0108(7) 0.0007(8)
N9 0.0406(9) 0.0424(9) 0.0528(10) 0.0014(8) 0.0146(7) -0.0036(7)
C2 0.0421(10) 0.0449(11) 0.0494(12) -0.0034(9) 0.0148(9) -0.0053(9)
C3 0.0434(11) 0.0474(12) 0.0470(12) 0.0005(9) 0.0146(9) -0.0060(9)
C3A 0.0448(10) 0.0459(11) 0.0445(11) 0.0025(9) 0.0137(9) -0.0061(9)
C4 0.0552(12) 0.0453(12) 0.0554(13) 0.0090(10) 0.0157(10) -0.0059(10)
C4A 0.0534(12) 0.0377(10) 0.0581(13) 0.0043(10) 0.0148(10) -0.0006(9)
C5 0.0513(12) 0.0419(11) 0.0547(13) 0.0015(9) 0.0135(10) -0.0052(10)
C7 0.0452(11) 0.0605(14) 0.0504(13) 0.0012(11) 0.0149(9) 0.0008(10)
C7A 0.0453(11) 0.0453(12) 0.0551(13) 0.0032(10) 0.0131(9) 0.0051(9)
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C13 0.0477(11) 0.0453(12) 0.0604(14) -0.0014(10) 0.0224(10) -0.0042(9)
C14 0.0761(19) 0.0624(17) 0.124(3) 0.0264(18) 0.0127(18) 0.0147(15)
C15 0.0438(10) 0.0457(11) 0.0493(12) 0.0027(9) 0.0100(9) -0.0023(9)
C16 0.0519(12) 0.0589(14) 0.0618(15) 0.0021(11) 0.0175(11) 0.0014(11)
C17 0.0553(13) 0.0620(16) 0.085(2) 0.0068(14) 0.0104(13) 0.0079(12)
C18 0.0753(18) 0.0704(17) 0.0603(16) 0.0137(14) -0.0024(13) -0.0020(15)
C19 0.092(2) 0.0748(18) 0.0515(15) 0.0048(13) 0.0161(14) 0.0042(16)
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All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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 N1 N9 1.359(3) . ?
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 N6 C15 1.434(3) . ?
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 N9 C8 1.467(3) . ?
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 C7 N6 C15 123.25(18) . . ?

C5 N6 C15 124.04(17) . . ?
C3A N9 N1 113.53(17) . . ?
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C2 C3 C11 128.1(2) . . ?
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N9 C3A C4 116.50(19) . . ?
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H4A C4 H4B 108.7 . . ?
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C7A C4A H4A1 110.2 . . ?
O5 C5 N6 124.0(2) . . ?
O5 C5 C4A 126.9(2) . . ?
N6 C5 C4A 109.09(18) . . ?
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O2 C12 H12C 109.5 . . ?
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H12B C12 H12C 109.5 . . ?
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O4 C13 C2 109.07(19) . . ?
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O4 C14 H14B 109.5 . . ?
H14A C14 H14B 109.5 . . ?

O4 C14 H14C 109.5 . . ?
 H14A C14 H14C 109.5 . . ?
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