SUPPORTING INFORMATION

Title: Synthesis of two new *gem*-fluoronitro contained tetranitroadamantanes and property comparison with their nitro and gem-dinitro analogues

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1. General Information

Unless otherwise specified, the chemicals (AR grade) were obtained from commercial sources and were used without further purification. Petroleum ether refers to the fraction boiling in the 60-90°C range. The progress of the reactions was monitored by TLC (silica gel, Polygram SILG/UV 254 plates). Column chromatography was performed on aluminium oxide gel (spherical, neutral, 200-300 mesh) or silica gel (200-300 mesh). ¹H, ¹³C and ¹⁹F NMR spectra were obtained at 500, 126 and 470 MHz, respectively, and $CDCl_3$, $DMSO-d_6$, C_3D_6O were used as the solvent with TMS as the internal standard. All FTIR spectra were obtained using a Nicolet FTIR IS10 Spectrometer. TGA was measured with TGA/SDTA851e at a heating rate of 5°Cmin⁻¹. Elemental analysis of all new compounds was performed by using a Vario EL III CHN elemental analyzer. X-ray intensity data were collected on a Bruker D8 CMOS detector employing graphitemonochromated Mo-K α radiation (λ =0.71073 Å). The known compounds were identified by comparison of their physical and spectral data with those reported in the literature. Yields refers to isolated yield of analytically pure material unless otherwise noted. 4,4-dinitroadamantane-2,6-dione 1c^[1], bicyclo[3.3.1]nonane-2,6,9-trione $2d^{[2]}$, and 4,8-dihydroxyadamantane-2,6-dione $2f^{[3]}$ were prepared according to reported procedures.

1. Ling Y, Zhang P, Sun L, Lai W, Luo J. Synthesis, 2014, 46, 2225-2233.

2. Ren X, Ling Y, Luo J. Chinese Journal of Orgnic Chemistry, 2014, 34, 376-381.

3. Ling Y, Ren X, Lai W, Luo J. European Journal of Organic Chemistry, 2015, 2015, 1541-1547.

2. Experimental Procedures and Spectroscopic Data of the Synthesized Compounds

CAUTION! Some of the prepared compounds are energetic materials with sensitivity toward heat, impact, and friction. No hazards occurred during preparation and manipulation. However, additional proper protective precautions (face shield, leather coat, earthed equipment and shoes, Kevlar gloves, and ear plugs) should be used when undertaking work with these compounds.

Synthesis of compounds 1d



A mixture of **1c** (1.52 g, 6 mmol), NH₂OH·HCl (1.25 g, 18 mmol), NaOAc (1.48 g, 18 mmol) and MeOH (150 mL) was stirred under reflux for 24 h. The reaction mixture was concentrated and the residue was partitioned between CH₂Cl₂ (150 mL) and H₂O (100 mL). The organic layer was washed with brine (50 mL), dried over Na₂SO₄ and filtered. The solvent was removed under reduced pressure and the residue was recrystallized (CH₂Cl₂–*n*-hexane) to provide the corresponding oxime **1d** (1.56 g, 92%)as a white solid. ¹H NMR (500 MHz, DMSO-*d*₆): δ 11.19-11.15 (m, 2 H), 4.81-4.73, 3.89-3.85 (m, 2 H), 3.54, 2.68 (m, 2 H), 2.19-2.15, 2.08-1.97 (m, 2 H), 1.93-1.68 (m, 4 H) ppm; ¹³C NMR (126 MHz, DMSO-*d*₆): δ 155.2, 153.8, 122.2, 122.1, 42.6, 42.4, 41.1, 38.8, 36.4, 35.4, 35.1, 34.8, 34.5, 33.8, 33.7, 33.2, 32.9, 26.8, 26.7 ppm; IR (thin film, υ cm⁻¹): 3280, 2940, 1671, 1580, 1460, 1360, 1250, 1010, 960, 935.

Synthesis of compounds 1b



Dioxime **1d** (1.22 g, 4.3 mmol) was dissolved in 30 mL of glacial acetic acid in a dry round-bottomed flask. The flask was immersed in an oil bath at a temperature of 60°C. In portions, solid sodium perborate tetrahydrate (7.94 g, 51.6 mmol) was added with vigorous stirring over a period of 30 minutes. After the addition, the reaction mixture was stirred at the same temperature for 4 h. After cooling, the mixture was treated with ice cold saturated solution of sodium bicarbonate (30 mL×4), following by extraction with ether (50 mL×3). The organic layer was washed several times with cold water, dried over anhydrous NaSO₄ and evaporated. The crude product was purified by flash silica gel column chromatography (1:8 ethyl acetate/petroleum) to afford the tetranitroadamantane **1b** (0.69 g, 51%) as a white solid. ¹H NMR (500 MHz, DMSO-*d*₆): δ 5.07 (s, 2H), 4.11 (s, 2H), 2.61 (d, *J*=2.25 Hz, 2H), 2.14-2.10 (m, 2H), 1.77-1.74 (d, *J*=14.95 Hz, 2H), 1.68 (s, 2H) ppm; ¹³C NMR (126 MHz, DMSO-*d*₆): δ 116.6, 77.3, 29.6, 21.9, 21.1, 20.4 ppm; IR (thin film, v cm⁻¹): 2925, 2864, 1562, 1458, 1313, 1070, 976, 780; C₁₀H₁₂N₄O₈ (316.22): C 37.98, H 3.82, N 17.72; found: C 38.02, H 3.84, N 17.69.

Synthesis of compounds 1a



Solid KOH (85%, 132 mg 2 mmol) was added to a mixture of the tetranitroadamantane **1b** (320 mg, 1 mmol), MeCN (20 mL) and H₂O (30 mL) at 0°C. The mixture was vigorously stirred for 1 h, and then cooled to -7°C to provide partical precipitation of the nitronate. CH₂Cl₂ (50 mL) and Selectflour[®] (860 mg, 2.4 mmol) were added in one portion. The cooling bath was removed, and the mixture was vigorously stirred. The reaction temperature was allowed to rise to the ambient temperature and petroleum ether (50 mL) was added, after stirring for10 minutes, the mixture was filtered through Celite, the organic layer were separated, and the aqueous layer was extracted with portions of CH₂Cl₂–hexanes (1:1, 50 mL) several times. The combined organic phases were dried over anhydrous Na₂SO₄, filtered, concentrated under reduced pressure, and the residue was purified by flash silica gel column chromatography (1:25 ethyl acetate/petroleum) to afford **1a** (299 mg, 85%) as a white solid. ¹H NMR (500 MHz, CDCl₃): δ 4.48 (s, 2H), 2.93 (s, 2H), 2.76-2.73 (d, *J* = 14.55 Hz, 2H), 2.22-2.18 (d, *J* = 15.75 Hz, 2H), 2.04 (s, 2H) ppm; ¹³C NMR (126 MHz, CDCl₃): δ 119.0 (d, *J*=238.5 Hz), 118.0, 38.7 (d, *J*=8.125 Hz), 31.1 (d, *J*=9.64 Hz), 30.6, 27.8 ppm; ¹⁹F NMR (470 MHz, CDCl₃): δ -114.9 ppm; IR (thin film, υ cm⁻¹): 3024, 1563, 1469, 1302, 1115, 815, 714; C₁₀H₁₀F₂N₄O₈ (352.21): C 34.10, H 2.86, N 15.91; found: C 34.15, H 2.88, N 15.86.

Synthesis of compounds 21



Dione **2f** (2.6 g, 13.3 mmol), ethylene glycol (2.23 mL, 38.6 mmol), PTSA·H₂O (0.51 g, 2.7 mmol) and toluene (150 mL) were charged into a round-bottomed flask equipped with a Dean–Stark apparatus and the mixture was heated at 120 °C for 5 h until H₂O accumulation in the water trap ceased. The reaction mixture was concentrated under reduced pressure and the residue was partitioned between CH₂Cl₂ (150 mL) and H₂O (100 mL). The organic layer was washed with brine (50 mL), dried over Na₂SO₄ and filtered. The solvent was removed under reduced pressure to afford **2l** (3.5 g, 93%) as a white solid. The product was used directly for the next step without purification. ¹H NMR (500 MHz, CDCl₃): δ 4.23 (d, *J* = 10.4 Hz, 2H), 4.04-3.92 (m, 10H), 2.05 (t, *J* = 5.0 Hz, 2H), 1.88 (d, *J* = 5.0 Hz, 4H), 1.78 (t, *J* = 5.0 Hz, 2H) ppm; ¹³C NMR (126 MHz, CDCl₃): δ 110.9, 72.6, 64.5, 63.9, 42.6, 38.8, 25.5, 20.4 ppm; IR (thin film, v cm⁻¹): 3516, 2930, 2877. 1713, 1418, 1261, 1068, 1024, 942; Cl₁₄H₂₀O₆ (284.31): C 59.14, H 7.09; found: C 59.19, H 7.12.

Synthesis of compounds 2k



A mixture of **21** (3.3 g, 12 mmol), powdered Oxone® (11.2 g, 18.2 mmol), sodium 2iodoxybenzenesulfonate (0.14 g, 0.45 mmol) and anhydrous Na₂SO₄ (23 g) in EtOAc (120 mL) was rigorously stirred at 70 °C for 6 h. After the reaction was complete, the mixture was cooled to r.t. and filtered. The filtrate was washed with H₂O (50 mL×2), dried over Na₂SO₄ and filtered. The solvent was removed under reduced pressure to afford **2k** (3.1 g, 94%) as a white solid. ¹H NMR (500 MHz, CDCl₃): δ 4.03-3.93 (m, 8H), 2.68 (s, 4H), 2.15 (d, *J* = 2.6 Hz, 4H) ppm; ¹³C NMR (126 MHz, CDCl₃): δ 205.4, 111.9, 65.2, 53.4, 26.2 ppm; IR (thin film, v cm⁻¹): 2936, 1722, 1364, 1095, 1044, 947, 902; C₁₄H₁₆O₆ (280.27): C 59.99, H 5.75; found: C 60.05, H 5.76.

Synthesis of compounds 2m



A mixture of **2k** (2.3 g, 8 mmol), NH₂OH·HCl (2.3 g, 32 mmol), NaOAc (3.9 g, 48 mmol) and MeOH (50 mL) was stirred under reflux for 12 h. The reaction mixture was concentrated and the residue was partitioned between CH₂Cl₂ (150 mL) and H₂O (100 mL). The organic layer was washed with brine (50 mL), dried over Na₂SO₄ and filtered. The solvent was removed under reduced pressure and the residue was recrystallized (CH₂Cl₂–*n*-hexane) to provide the corresponding oxime **2m** (2.3 g, 90%)as a white solid. ¹H NMR (500

MHz, DMSO- d_6): δ 10.33 (s, 1H), 10.32 (s, 1H), 3.93-3.87 (m, 8H), 3.47-3.45 (m, 2H), 2.51-2.50 (m, 2H), 1.88-1.70 (m, 4H) ppm; ¹³C NMR (126 MHz, DMSO- d_6): δ 156.6, 110.4, 110.2, 110.0, 64.7, 43.7, 43.4, 36.6 36.3, 30.3, 29.1, 27.8 ppm; IR (thin film, v cm⁻¹): 3264, 2945, 2885, 1446, 1313, 1098, 920, 897, 749; C₁₄H₁₈N₂O₆ (310.30): C 54.19, H 5.85, N 9.03; found: C 54.24, H 5.87, N 9.00.

Synthesis of compounds 2n



Dioxime **2m** (1.55 g, 5 mmol) was dissolved in 50 mL of glacial acetic acid in a dry round-bottomed flask. The flask was immersed in an oil bath at a temperature of 60°C. In portions, solid sodium perborate tetrahydrate (9.23 g, 60 mmol) was added with vigorous stirring over a period of 30 minutes. After the addition, the reaction mixture was stirred at the same temperature for 4 h. After cooling, the mixture was treated with ice cold saturated solution of sodium bicarbonate (30 mL×4), following by extraction with ether (50 mL×3). The organic layer was washed several times with cold water, dried over anhydrous NaSO₄ and evaporated. The crude product was purified by flash silica gel column chromatography (1:10 ethyl acetate/petroleum) to afford **2n** (0.92 g, 54%) as a white solid. ¹H NMR (500 MHz, CDCl₃): δ 4.69 (s, 2H), 4.09-3.83 (m, 8H), 2.91 (s, 2H), 2.57 (s, 2H), 2.56-2.53 (m, 2H), 2.01 (d, *J*=14.95 Hz, 2H) ppm; ¹³C NMR (126 MHz, CDCl₃): δ 109.3, 106.3, 83.8, 65.2, 64.8, 38.4, 37.4, 25.1; IR (thin film, ν cm⁻¹): 2956, 2895, 1538, 1378, 1110, 936, 790, 696; C₁₄H₁₈N₂O₈ (342.30): C 49.12, H 5.30, N 8.18; found: C 49.17, H 5.33, N 8.15.

Synthesis of compounds 2b



A mixture of **2n** (0.68 g, 2 mmol), concd H_2SO_4 (12 mL) and CH_2Cl_2 (200 mL) was stirred at r.t. for 3 h. Then, the reaction mixture was poured into an ice-water mixture (150 mL). The organic layer was washed with sat. NaHCO₃ solution (100 mL) and brine (50 mL), dried over Na₂SO₄ and filtered. The solvent was removed under reduced pressure to give **2j** (0.47 g) as a white solid. The product was used directly for the next step without purification. A mixture of **2j** (0.38 g, 1.5 mmol), NH₂OH·HCl (0.42 g, 6 mmol), NaOAc (0.74 g, 9 mmol) and MeOH (50 mL) was stirred under reflux for 24 h. The reaction mixture was concentrated and the residue was partitioned between CH₂Cl₂ (150 mL) and H₂O (100 mL). The organic

layer was washed with brine (50 mL), dried over Na₂SO₄ and filtered. The solvent was removed under reduced pressure to give **20** (0.38 g) as a white solid. The product was used directly for the next step without purification. Dioxime **20** (0.34 g, 1.2 mmol) was dissolved in 30 mL of glacial acetic acid in a dry roundbottomed flask. The flask was immersed in an oil bath at a temperature of 60°C. In portions, solid sodium perborate tetrahydrate (2.22 g, 14.4 mmol) was added with vigorous stirring over a period of 30 minutes. After the addition, the reaction mixture was stirred at the same temperature for 4 h. After cooling, the mixture was treated with ice cold saturated solution of sodium bicarbonate (20 mL×4), following by extraction with ether (30 mL×3). The organic layer was washed several times with cold water, dried over anhydrous NaSO₄ and evaporated. The crude product was purified by flash silica gel column chromatography (1:5 ethyl acetate/petroleum) to afford **2b** (0.15 g, 34% in 3 steps) as a white solid. ¹H NMR (500 MHz, C₃D₆O): δ 5.23 (s, 4H), 3.73 (s, 4H), 2.16 (s, 4H) ppm; ¹³C NMR (126 MHz, C₃D₆O): δ 82.5, 32.0, 25.8 ppm; IR (thin film, υ cm⁻¹): 2913, 1715, 1553, 1455, 1390, 1351, 792; C₁₀H₁₂N₄O₈ (316.22): C 37.98, H 3.82, N 17.72; found: C 38.03, H 3.83, N 17.68.

Synthesis of compounds 2a



Solid KOH (85%, 66 mg 1 mmol) was added to a mixture of the tetranitroadamantane **2b** (80 mg, 0.25 mmol), MeCN (5 mL) and H₂O (10 mL) at 0°C. The mixture was vigorously stirred for 1 h, and then cooled to -7°C to provide partical precipitation of the nitronate. CH₂Cl₂ (20 mL) and Selectflour[®] (430 mg, 1.2 mmol) were added in one portion. The cooling bath was removed, and the mixture was vigorously stirred. The reaction temperature was allowed to rise to the ambient temperature and petroleum ether (20 mL) was added, after stirring for 10 minutes, the mixture was filtered through Celite, the organic layer were separated, and the aqueous layer was extracted with portions of CH₂Cl₂–hexanes (1:1, 20 mL) several times. The combined organic phases were dried over anhydrous Na₂SO₄, filtered, concentrated under reduced pressure, and the residue was purified by flash chromatography (1:15 ethyl acetate/petroleum) on silica gel to give the corresponding product **2a** (53 mg, 55%) as a white solid. ¹H NMR (500 MHz, C₃D₆O): δ 4.37 (d, *J*=1.65 Hz, 4H), 2.99 (d, *J*=1.95 Hz, 4H) ppm; ¹³C NMR (126 MHz, C₃D₆O): δ 116.4 (d, *J*= 241.5 Hz), 38.4 (t, *J*=17.6 Hz, 23.44 Hz), 22.8 ppm; ¹⁹F NMR (470 MHz, C₃D₆O): δ -118.2 ppm; IR (thin film, ν cm⁻¹): 2914, 1570, 1463, 1357, 1307, 1119, 988, 820, 751; C₁₀H₈F₄N₄O₈ (388.19): C 30.94, H 2.08, N 14.43; found: C 30.99, H 2.11, N 14.40.

3. ¹H-NMR, ¹³C-NMR, ¹⁹F-NMR and FT-IR Spectra of Compounds



¹H NMR spectrum of compound 1d (DMSO-*d*₆, 500 MHz)

¹³C NMR spectrum of compound 1d (DMSO-*d*₆, 126 MHz)







¹H NMR spectrum of compound 1b (DMSO-*d*₆, 500 MHz)







IR spectrum of compound 1b





¹³C NMR spectrum of compound 1a (CDCl₃, 126 MHz)



¹H NMR spectrum of compound 1a (CDCl₃, 500 MHz)



IR spectrum of compound 1a





130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 fl (ppm)





¹H NMR spectrum of compound 2k (CDCl₃, 500 MHz)





IR spectrum of compound 2k



¹H NMR spectrum of compound 2m (DMSO-*d*₆, 500 MHz)



¹³C NMR spectrum of compound 2m (DMSO-*d*₆, 126 MHz)





IR spectrum of compound 2m

¹H NMR spectrum of compound 2n (CDCl₃, 500 MHz)



¹³C NMR spectrum of compound 2n (CDCl₃, 126 MHz)



IR spectrum of compound 2n





¹H NMR spectrum of compound 2b (C₃D₆O, 500 MHz)



¹H NMR spectrum of compound 2a (C₃D₆O, 500 MHz)

150 140 130 120 110 100 f1 (ppm) 210 200 190 -10

¹⁹F NMR spectrum of compound 2a (C₃D₆O, 470 MHz)

IR spectrum of compound 2a

4. X-ray Crystal Structures and Data of Compound 1a

Figure S1. ORTEP diagram of 1a Color code: Carbon (grey), Oxygen (red), Nitrogen (blue), Fluorine (green).

Figure S2. Crystal packing of **1a** Color code: Carbon (grey), Oxygen (red), Nitrogen (blue), Fluorine (green). Table 1. Crystal data and structure refinement for **1a**

Compound	1a			
Empirical formula	$C_{10} H_{10} F_2 N_4 O_8$			
Formula weight	352.22			
Temperature	296(2) K			
Wavelength	0.71073 A			
Crystal system, space group	Orthorhombic			
Space group	Pbcn			
Unit cell dimensions	a = 12.1505(14) Å	<i>α</i> = 90°.		
	b = 10.4710(13) Å	β= 90°.		
	c = 10.2881(14) Å	$\gamma = 90^{\circ}$.		
Volume	1308.9(3) A^3			
Z, Calculated density	4, 1787 Mg/m^3			
Absorption coefficient	0.172 mm^-1			
<i>F</i> (000)	720			
Crystal size	0.270 x 0.250 x 0.220 mm			
Theta range for data collection	2.568 to 25.004 deg			
Limiting indices	-14<=h<=14, -12<=k<=11,	-12<=1<=9		
Reflections collected / unique	7948 / 1154 [R(int) = 0.078	0]		
Completeness to theta $= 25.004$	99.70%			
Refinement method	Full-matrix least-squares on	F2		
Data/restraints/parameters	1154 / 0 / 110			
Goodness-of-fit on F^2	1.067			
Final R indices [I>2sigma(I)]	R1 = 0.0509, wR2 = 0.1354			
<i>R</i> indices (all data)	R1 = 0.0593, wR2 = 0.1420			
Extinction coefficient	n/a			
Largest diff. peak and hole	0.312 and -0.291 e. A^-3			
CCDC	1835504			

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (A² x 10³) for **1a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	X	у	Z	U(eq)
C(1)	0	912(3)	2500	20(1)
C(2)	4(2)	1729(2)	1274(2)	23(1)
C(3)	-1025(2)	2605(2)	1284(3)	28(1)
C(4)	1026(2)	2587(2)	1331(3)	28(1)
C(5)	1028(2)	3456(2)	2502(3)	30(1)
C(6)	0	4296(3)	2500	36(1)
F(1)	1974(1)	1856(1)	1291(2)	36(1)
N(1)	961(1)	-67(2)	2512(2)	23(1)
N(2)	1114(2)	3350(2)	45(3)	40(1)

O(1)	1082(1)	-680(2)	1515(2)	32(1)
O(2)	1494(1)	-179(2)	3504(2)	33(1)
O(3)	809(2)	2838(2)	-945(2)	60(1)
O(4)	1530(2)	4410(2)	96(2)	60(1)

Table 3. Bond lengths [A] and angles [deg] for 1a.

C(1)-C(2)	1.524(3)	
C(1)-C(2)#1	1.524(3)	
C(1)-N(1)	1.554(2)	
C(1)-N(1)#1	1.554(2)	
C(2)-C(4)	1.535(3)	
C(2)-C(3)	1.550(3)	
C(2)-H(2)	0.9800	
C(3)-C(5)#1	1.534(4)	
C(3)-H(3A)	0.9700	
C(3)-H(3B)	0.9700	
C(4)-F(1)	1.384(2)	
C(4)-C(5)	1.510(4)	
C(4)-N(2)	1.549(3)	
C(5)-C(6)	1.527(3)	
C(5)-C(3)#1	1.534(4)	
C(5)-H(5)	0.9800	
C(6)-C(5)#1	1.527(3)	
C(6)-H(6A)	0.9700	
C(6)-H(6B)	0.9700	
N(1)-O(2)	1.215(2)	
N(1)-O(1)	1.218(3)	
N(2)-O(3)	1.210(3)	
N(2)-O(4)	1.221(3)	
C(2)-C(1)-C(2)#1	111.7(2)	
C(2)-C(1)-N(1)	112.01(11)	
C(2)#1-C(1)-N(1)	111.47(11)	
C(2)-C(1)-N(1)#1	111.47(11)	
C(2)#1-C(1)-N(1)#1	112.01(11)	
N(1)-C(1)-N(1)#1	97.4(2)	
C(1)-C(2)-C(4)	107.40(17)	

C(1)-C(2)-C(3)	108.89(17)
C(4)-C(2)-C(3)	107.84(17)
C(1)-C(2)-H(2)	110.9
C(4)-C(2)-H(2)	110.9
C(3)-C(2)-H(2)	110.9
C(5)#1-C(3)-C(2)	110.57(18)
C(5)#1-C(3)-H(3A)	109.5
C(2)-C(3)-H(3A)	109.5
C(5)#1-C(3)-H(3B)	109.5
C(2)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	108.1
F(1)-C(4)-C(5)	110.90(19)
F(1)-C(4)-C(2)	110.39(18)
C(5)-C(4)-C(2)	112.61(18)
F(1)-C(4)-N(2)	101.69(18)
C(5)-C(4)-N(2)	111.8(2)
C(2)-C(4)-N(2)	108.93(19)
C(4)-C(5)-C(6)	110.17(18)
C(4)-C(5)-C(3)#1	107.41(19)
C(6)-C(5)-C(3)#1	109.51(18)
C(4)-C(5)-H(5)	109.9
C(6)-C(5)-H(5)	109.9
C(3)#1-C(5)-H(5)	109.9
C(5)-C(6)-C(5)#1	109.7(3)
C(5)-C(6)-H(6A)	109.7
C(5)#1-C(6)-H(6A)	109.7
C(5)-C(6)-H(6B)	109.7
C(5)#1-C(6)-H(6B)	109.7
H(6A)-C(6)-H(6B)	108.2
O(2)-N(1)-O(1)	126.30(18)
O(2)-N(1)-C(1)	118.10(16)
O(1)-N(1)-C(1)	115.57(16)
O(3)-N(2)-O(4)	124.5(2)
O(3)-N(2)-C(4)	118.0(2)
O(4)-N(2)-C(4)	117.4(2)

Symmetry transformations used to generate equivalent atoms:

	U^{11}	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(1)	15(1)	15(1)	30(2)	0	1(1)	0
C(2)	24(1)	17(1)	29(1)	3(1)	1(1)	1(1)
C(3)	23(1)	24(1)	38(2)	4(1)	-6(1)	4(1)
C(4)	20(1)	21(1)	43(2)	10(1)	3(1)	2(1)
C(5)	19(1)	20(1)	51(2)	3(1)	-2(1)	-4(1)
C(6)	32(2)	20(2)	57(3)	0	-4(2)	0
F(1)	22(1)	31(1)	54(1)	8(1)	10(1)	4(1)
N(1)	19(1)	18(1)	31(1)	2(1)	1(1)	2(1)
N(2)	34(1)	33(1)	52(2)	16(1)	9(1)	1(1)
O(1)	37(1)	24(1)	33(1)	-6(1)	4(1)	8(1)
O(2)	31(1)	32(1)	35(1)	1(1)	-9(1)	7(1)
O(3)	102(2)	40(1)	38(1)	11(1)	14(1)	-1(1)
O(4)	56(1)	47(1)	77(2)	33(1)	-3(1)	-23(1)

Table 4. Anisotropic displacement parameters (A² x 10³) for **1a**. The anisotropic displacement factor exponent takes the form: -2 pi² [$h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12$]

Table 5. Hydrogen coordinates ($x \ 10^{4}$) and isotropic displacement parameters (A² $x \ 10^{3}$) for **1a**.

	Х	у	Z	U(eq)
H(2)	15	1193	493	28
H(3A)	-1026	3135	511	34
H(3B)	-1685	2084	1273	34
H(5)	1689	3992	2495	36
H(6A)	1	4839	1736	44
H(6B)	-1	4839	3264	44

5. Thermal stability of 1a, 1b, 2a and 2b

Thermal stability of **1a**

Thermal stability of 1b

Thermal stability of 2a

Thermal stability of 2b