

**Perchlorylamino furazans and their salts:
new high-energy-density materials with high sensitivity**

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Experimental Section

Caution! All the perchlorylamine materials described here should be handled with extreme caution. All may vigorously explode, even for no apparent reason. Safety shields and personal protection equipment (safety glasses, face shields, as well as gloves and apron made from leather and/or Kevlar) should always be used.

General. IR spectra were recorded on a UR-20 spectrometer. ^1H , ^{13}C and ^{14}N NMR spectra were obtained on a Bruker AM-300 (300.13, 75.47 and 21.69 MHz, respectively) at 299 K. The chemical shifts of ^1H and ^{13}C nuclei were reported relative to TMS, for ^{14}N nuclei – relative to MeNO_2 . Melting points (decomposition) were determined by Kofler method on a Boetius bench (heating rate 4 K min^{-1}) and were not corrected. The reaction progress was controlled by TLC on Silufol F₂₅₄ plates.

All chemicals are reagent/analytical grade and used without further purification. 3-Amino-4-methylfurazan **2** [S1], and 3-amino-4-nitrofurazan **8** [S2] were synthesized as reported.

Ammonium salt of 3-methyl-4-(perchlorylamino)furazan (6). *General procedure:* Compound **1** (0.1 g, 1 mmol) and dry toluene (3 mL) was placed in a flame-dried 10-mL round-bottom flask equipped with a magnetic stirrer and a dry argon inlet. To this slurry was added $\text{HN}(\text{SiMe}_3)_2$ (0.2 mL), and the mixture was refluxed for 3–4 h (GC monitoring). The residue obtained after solvent evaporation was dissolved in 1,2-dichloroethane (DCE, 2 mL), and the solution was cooled to 0°C in an ice–NaCl bath. FCIO_3 (0.15 g, 1.5 mmol) was dissolved in DCE (2 mL) and pipetted into the reaction mixture within 10 min keeping the temperature below 2°C . The mixture was stirred for 24 h, and then argon was bubbled through the mixture briefly at 5°C under reduced pressure (GC monitoring). The DCE solution of the intermediate perchlorylamine was not further purified but used immediately due to limited stability. A concentrated ammonia solution in CHCl_3 (5 mL) was added dropwise into the DCE solution with stirring. After removing the solvent, the remaining solid was crystallized from ethanol by evaporating slowly at room temperature. Colorless solid, yield: 0.06 g (31%); dec.p. 85°C (explosion!); ^1H NMR (acetone- d_6 , ppm) δ : 2.52 (s, 3H, Me), 7.1 (br. s, 4H, NH_4^+); ^{13}C NMR (acetone- d_6 , ppm) δ : 8.7, 149.3, 151.8. IR (v/cm^{-1}): 3360, 2967, 1605, 1585, 1420, 1270, 1080, 975, 628. Found (%): C, 18.26; H, 3.62; N, 28.13. Calc. for $\text{C}_3\text{H}_7\text{ClN}_4\text{O}_4$ (%): C, 18.15; H, 3.55; N, 28.22.

Other salts were prepared in a similar manner.

Ammonium salt of 3-nitro-4-(perchlorylamino)furazan (11). Yield 43%, dec.p. 92°C (explosion!); ¹H NMR (acetone-d₆, ppm) δ: 7.0 (br. s, NH₄⁺); ¹³C NMR (acetone-d₆, ppm) δ: 150.6, 152.2; ¹⁴N NMR (acetone-d₆, ppm) δ: -28.4 (NO₂). IR (v/cm⁻¹): 3310, 1588, 1572, 1418, 1365, 1265, 1090, 972, 635. Found (%): C, 18.26; H, 3.62; N, 28.13. Cacl. for C₂H₄ClN₅O₆ (%):C, 10.47; H, 1.76; N, 30.51.

4-Amino-4H-1,2,4-triazolium salt of 3-nitro-4-(perchlorylamino)furazan (12). Yield 27%, dec.p. 84°C (explosion!). ¹H NMR (acetone-d₆, ppm) δ: 6.8 (br s, 3H, NH₂ + H⁺), 9.39 (s, 2H, CH); ¹³C NMR (acetone-d₆, ppm) δ: 142.2, 150.3, 152.1; ¹⁴N NMR (acetone-d₆, ppm) δ: -28.4 (NO₂). IR (v/cm⁻¹): 3411, 3284, 3177, 1580, 1555, 1425, 1358, 1264, 1095, 975, 640. Found (%): C, 18.26; H, 3.62; N, 28.13. Cacl. for C₂H₄ClN₅O₆ (%):C, 10.47; H, 1.76; N, 30.51.

3,4,5-Triamino-4H-1,2,4-triazolium salt of 3-nitro-4-(perchlorylamino)furazan (13). Yield 41%, dec.p. 99°C (explosion!). ¹H NMR (acetone-d₆, ppm) δ: 5.38 (br.s, 2H, NH₂), 7.00 (br.s, 4H, NH₂); ¹³C NMR (acetone-d₆, ppm) δ: 152.2, 150.2, 150.0; ¹⁴N NMR (acetone-d₆, ppm) δ: -28.5 (NO₂). IR (v/cm⁻¹): 3421, 3400, 3350, 3315, 1644, 1630, 1582, 1534, 1435, 1361, 1236, 1110, 1055, 990, 9735, 635. Found (%): C, 14.78; H, 2.21; N, 42.80. Cacl. for C₄H₇ClN₁₀O₆ (%):C, 14.71; H, 2.14; N, 42.89.

3,6,7-Triamino-7H-[1,2,4]triazolo[4,3-*b*][1,2,4]triazolium salt of 3-nitro-4-(perchlorylamino)furazan (14). Yield 38%, dec.p. 102°C (explosion!). ¹H NMR (acetone-d₆, ppm) δ: 5.25 (br.s, 2H, NH₂), 7.31 (br.s, 2H, NH₂), 8.0 (br. s, 2H, NH₂); ¹³C NMR (acetone-d₆, ppm) δ: 160.1, 152.1, 150.1, 146.9, 141.3; ¹⁴N NMR (acetone-d₆, ppm) δ: -28.3 (NO₂). IR (v/cm⁻¹): 3415, 3350, 3290, 3244, 3165, 1700, 1630, 1575, 1540, 1425, 1365, 1255, 1090, 1040, 973, 640. Found (%): C, 16.30; H, 1.97; N, 45.79. Cacl. for C₅H₇ClN₁₂O₆ (%):C, 16.38; H, 1.92; N, 45.84.

References

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