Supporting Information

Synthesis of Diamondoid Nitro Compounds from Amines with m-Chloroperbenzoic Acid

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General remarks for experimental part

All \(^1\)H NMR spectra were recorded at 400 MHz using Bruker AV 400. \(^{13}\)C NMR spectra were taken at 100 MHz using the same instrument. Chemical shifts are reported in ppm (\(\delta\) scale) using TMS as internal standard or the solvent signal as secondary standard. Structural assignments were made by 2D NMR spectra (COSY, HSQC, HMBC). IR spectra were recorded as KBr pellets using a Bruker IFS 25. Melting points are not corrected and were measured with Büchi Dr. Tottoli Typ S or with the melting point meter KSP 1 N by Krüss. Elemental analyses were carried out using a Thermo Electron Flash EA 1112 Series. HRMS were recorded using a Finnigan MAT 95 with the electron impact method (EI). HPLC purification was performed on a HPLC Pump 64 by Knauer (detectors: RI by Knauer “Differential Refraktometer” and UV by LKB 2151 at 220 nm wavelength) using a CN-phase with TBME/hexane 5/95 as solvent. All non-diamondoid chemicals were commercial and used as received.
Preparation of 9,15-Di-aminotriamantane (16):

2-Chloro-N-[15-(2-chloro-acetylamino)-triamantyl-9-yl]-acetamide:

9,15-Triamantandiol (325 mg, 1.19 mmol) was mixed with CH$_2$CICN (6 mL) and conc. H$_2$SO$_4$ (1 mL) and stirred for 1 h at 80 °C. Then the colorless suspension was diluted with dist. water (30 mL) and the resulting precipitate was filtered off. After washing with dist. water (50 mL), saturated NaHCO$_3$ solution (10 mL), and pentane (20 mL) the colorless product was dried on rotavap. Yield 370 mg (0.87 mmol, 73%).

mp: 230−235 °C (decomposition); $^1$H NMR (400 MHz, DMSO$_{d6}$) $\delta$ = 7.70 (br s, 2 H, NH), 3.95 (s, 4 H, CH$_2$Cl), 1.96−1.78 (m, 12 H, H-3,7,8,10,11,13,14,18), 1.68−1.63 (m, 2 H, H-5), 1.60 (br s, 2 H, H-4,6), 1.53 (s, 4 H, H-16,17), 1.38 (br s, 2 H, H-2,12); $^{13}$C NMR (100 MHz, DMSO$_{d6}$) $\delta$ = 164.9 (C=O), 50.9 (C-9,15), 47.5 (C-16,17), 44.2 (C-2,12), 43.4 (CH$_2$Cl), 40.9 (C-8,10,14,18), 37.7 (C-3,7,11,13), 36.3 (C-5), 35.3 (C-1), 33.3 (C-4,6); IR (KBr) $\upsilon$ = 3308, 3070, 2928, 2909, 2879, 2864, 1670, 1552, 1412, 1334, 1232, 1055, 929, 806 cm$^{-1}$; HRMS ($m/z$) found 422.1516, calcd. for C$_{22}$H$_{28}$Cl$_2$N$_2$O$_2$ 422.1528.

9,15-Di-amino-triamantane:

2-Chloro-N-[15-(2-chloro-acetylamino)-triamantyl-9-yl]-acetamide (310 mg, 0.73 mmol) was mixed with thiourea (250 mg, 3.28 mmol), ethanol (10 mL), and acetic acid (6 mL). The mixture was heated under reflux for 3.5 h and was then diluted with dist. water (40 mL) and 20% NaOH solution (100 mL). After extraction with CHCl$_3$ (3 × 40 mL) the combined extracts were washed with dist. water (80 mL) and dried over Na$_2$SO$_4$. The obtained waxy, yellow crude product was then sublimed at 125 °C and 0.1 Torr to give a colorless solid. Yield 113 mg (0.42 mmol, 57%).

mp: 120−123 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 1.86 (br s, 4 H, H-3,7,11,13), 1.74−1.69 (m, 2 H, H-5), 1.62−1.47 (m, 10 H, H-4,6,8,10,14,18), 1.33−1.10 (m, 10 H, H-2,12,16,17,NH$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 53.5 (C-16,17), 47.0 (C-9,15), 46.5 (C-8,10,14,18), 44.6 (C-2,12), 39.1 (C-3,7,11,13), 36.9 (C-5), 36.7 (C-1), 33.9 (C-4,6); IR (KBr) $\upsilon$ = 3341, 3274, 2907, 2843, 1595, 1464, 1437, 1342, 1172, 1024, 969 cm$^{-1}$; HRMS ($m/z$) found 270.2107, calcd. for C$_{18}$H$_{26}$N$_2$ 270.2096; anal. calcd. for C$_{18}$H$_{26}$N$_2$ (270.41): C 79.95, H 9.69, N 10.36, found C 80.47, H, 9.71, N, 10.28.
$^1$H- and $^{13}$C-spectra of synthesized compounds

4-Nitrodiamantane:

$^{13}$C-spectra of synthesized compounds
1-Nitrodiamantane:

400 MHz, CDCl₃

100 MHz, CDCl₃
4,9-Dinitrodiamantane:

![NMR spectrum of 4,9-Dinitrodiamantane at 400 MHz, CDCl3](image)

400 MHz, CDCl3

![NMR spectrum of 4,9-Dinitrodiamantane at 100 MHz, CDCl3](image)

100 MHz, CDCl3
1,6-Dinitrodiamantane:

15

400 MHz, CDCl₃

15

100 MHz, CDCl₃
9,15-Dinitrotriamantane:

\[
\begin{align*}
\text{NO}_2 & \\
\text{NO}_2 & \\
\text{17} & \\
\end{align*}
\]

400 MHz, CDCl\textsubscript{3}

\[
\begin{align*}
\text{NO}_2 & \\
\text{NO}_2 & \\
\text{17} & \\
\end{align*}
\]

100 MHz, CDCl\textsubscript{3}
2-Chloro-\(N\)-[15-(2-chloro-acetylamino)-triamantyl-9-yl]-acetamide:

400 MHz, DMSO\(_d_6\)

100 MHz, DMSO\(_d_6\)
9,15-Di-amino-triamantane:

400 MHz, CDCl$_3$

100 MHz, CDCl$_3$
**Crystallographic Data / General Information**

The X-ray crystallographic data were collected on a STOE IPDS-diffractometer equipped with a low temperature system (Karlsruher Glastechnisches Werk). Mo-K\(_\alpha\) radiation (\(\lambda = 0.71069 \ \text{Å}\)) and a graphite monochromator was used. No absorption corrections were applied. The structures were solved by Direct Methods in SHELXS97, and refined by using full-matrix least squares in SHELXL97\(^{[1]}\).

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-755751 for 13 and CCDC-755752 for 15. Copies of the data can be obtained, free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Crystal data and structure refinement for 4,9-dinitrodiamantane (13)**

Cell parameters were refined by using up to 5000 reflections. A sphere of data (190 frames) was collected with the \(\varphi\)-oscillation mode (1.0° frame width; Irradiation times/frame: 10 min). The refinement shows a half molecule in the independent unit of the elementary cell. All C-H hydrogen atoms were positioned geometrically and all non-hydrogen atoms were refined anisotropically.

![ORTEP plot with thermal ellipsoids set at 50% probability shows the full molecule and the packing without hydrogen atoms.](image)
CCDC-no. 755751
Empirical formula C_{14}H_{18}N_{2}O_{4}
Formula weight 278.30
Temperature 298(2) K
Wavelength 0.71073 Å
Crystal system, space group Monoclinic, C2/c
Unit cell dimensions
\[ a = 18.127(3) \, \text{Å} \]
\[ b = 6.4409(6) \, \text{Å} \]
\[ c = 13.2648(17) \, \text{Å} \]
\[ \alpha = 90^\circ \]
\[ \beta = 127.122(12) ^\circ \]
\[ \gamma = 90^\circ \]
Volume 1234.9(3) Å³
Z, Calculated density 4, 1.497 Mg/m³
Absorption coefficient 0.111 mm⁻¹
F(000) 592
Habitus, colour Plate, colourless
Crystal size 0.84 x 0.44 x 0.12 mm³
Theta range for data collection 2.82 to 28.13 °
Limiting indices -23<=h<=23,-8<=k<=8,-17<=l<=16
Reflections collected / unique 5330 / 1475 \[ R(\text{int}) = 0.0591 \]
Completeness to theta = 28.13 97.2 %
Absorption correction None
Refinement method Full-matrix least-squares on F²
Data / restraints / parameter 1475 / 0 / 91
Goodness-of-fit on F² 1.069
Final R indices [I>2sigma(I)] R1 = 0.0439, wR2 = 0.1174
R indices (all data) R1 = 0.0533, wR2 = 0.1235
Largest diff. peak and hole 0.331 and -0.191 e. Å⁻³

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Crystal data and structure refinement for 1,6-dinitrodiamantane (15)

Cell parameters were refined by using up to 3181 reflections. A sphere of data (190 frames) was collected with the ϕ-oscillation mode (1.0° frame width; Irradiation times/frame: 10 min). The refinement shows a half molecule in the independent unit of the elementary cell. All C-H hydrogen atoms were positioned geometrically and all non-hydrogen atoms were refined anisotropically.

ORTEP plot with thermal ellipsoids set at 50% probability shows the full molecule and the packing without hydrogen atoms.

CCDC-no.  755752
Empirical formula  C_{14}H_{18}N_{2}O_{4}
Formula weight  206.29
Temperature  193(2) K
Wavelength  0.71073 Å
Crystal system, space group  Triclinic, P-1
Unit cell dimensions  
\[ a = 6.6756(13) \text{ Å} \]
\[ b = 7.2541(15) \text{ Å} \]
\[ c = 7.4930(15) \text{ Å} \]
\[ \alpha = 64.61(3) ^\circ \]
\[ \beta = 68.34(3) ^\circ \]
\[ \gamma = 77.36(3) ^\circ \]
Volume  303.88(11) Å³
Z, Calculated density  1, 1.521 Mg/m³
Absorption coefficient  0.086 mm⁻¹
F(000)  148
Habitus, colour  Plate, colourless
Crystal size  0.40 x 0.32 x 0.20 mm³
Theta range for data collection  3.49 to 28.04 °
Limiting indices  \(-8\leq h\leq8, -9\leq k\leq8, -9\leq l\leq9\)
Reflections collected / unique  2717 / 1326 [R(int) = 0.0501]
Completeness to theta = 28.04  89.8 %
Absorption correction  None
Refinement method  Full-matrix least-squares on F²
Data / restraints / parameter 1326 / 0 / 91
Goodness-of-fit on $F^2$ 1.098
Final R indices [I>2sigma(I)] $R1 = 0.0563$, wR2 = 0.1689
R indices (all data) $R1 = 0.0686$, wR2 = 0.1816
Largest diff. peak and hole 0.391 and -0.395 e. Å$^{-3}$

**Bond lengths [Å] and angles [°]**

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[1]: Sheldrick, G.M. (1997), SHELXS97 and SHELXL97. University of Göttingen, Germany