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Synthesis and Purity Specifications for *N*,*N*'-Dicyclohexyl-*N*"-(10-nonadecyl)guanidinium Chloride for Use in Next Generation Caustic-Side Solvent Extraction

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Cesium Removal—Next Generation Solvent Project

Synthesis and Purity Specifications for *N*,*N*'-Dicyclohexyl-*N*''-(10-nonadecyl)guanidinium Chloride for Use in Next-Generation Caustic-Side Solvent Extraction

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LIST OF ABBREVIATED TERMS

BHT	butylated hydroxytoluene
Cs-7SB	modifier 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol
CyA	cyclohexyl amine
CyNDU	*N*-cyclohexyl-*N*'-(10-nonadecyl)urea
DCC	*N*,*N*'-dicyclohexylcarbodiimide
DCiTG	*N*,*N*'-dicyclohexyl-*N*''-(*iso*-tridecyl)guanidine
DCNDG	*N*,*N*'-dicyclohexyl-*N*''-(10-nonadecyl)guanidine
DCNDG•HCl	*N*,*N*'-dicyclohexyl-*N*''-(10-nonadecyl)guanidium chloride
D_{Cs}	distribution ration of $^{137}Cs^+$ between an organic and aqueous phase
DDCU	*N*,*N*'-dicyclohexylurea
ES_2S_3	test sequence consisting of one extraction, two scrub, and three stripping stages
GC-FID	gas chromatography with flame ionization detector
MaxCalix	extractant 1,3-*alt*-25,27-bis(3,7-dimethyloctyl-1-oxy)calix[4]arene-benzocrown-6
MCU	Modular CSSX Unit
NDA	10-nonadecylamine
NG-CSSX	Next Generation Caustic-Side Solvent Extraction
NGS	Next-Generation Solvent
RT	retention time
SDS	sodium dodecyl sulfate
SRS	Savannah River Site
SWPF	Salt Waste Processing Facility
TiDG	*N*,*N*',*N*''-tris(3,7-dimethyloctyl)guanidine

ABSTRACT

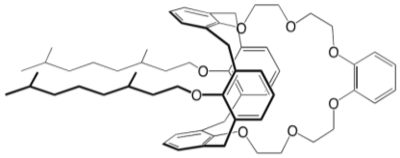
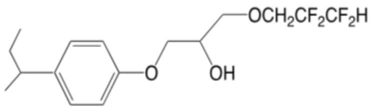
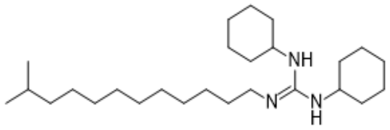
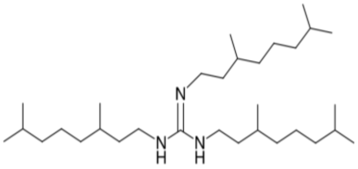
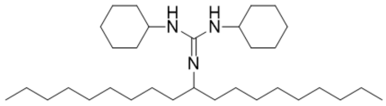
This report describes a synthesis procedure for the alkylguanidine, *N*,*N*'-dicyclohexyl-*N*''-(10-nonadecyl)guanidine (DCNDG), which has been identified as a promising candidate for replacing the less stable *N*,*N*',*N*''-tri(3,7-dimethyloctyl)guanidine (TiDG) suppressor in the Next Generation Caustic-Side Solvent Extraction (NG-CSSX) process. A verified procedure for the preparation of the 10-nonadecylamine (NDA) used in this synthesis is also included. In addition, requirements for the purity of DCNDG to be utilized in the NG-CSSX process without adverse effect on the Cs^+ extraction and stripping are given.

1. INTRODUCTION

The Next Generation Caustic-Side Solvent Extraction (NG-CSSX) process solvent, Table 1, relies on the use of a highly basic alkylguanidine suppressor whose purpose is to mask lipophilic anions during stripping of Cs^+ ions to an aqueous boric acid solution. The guanidine *N*,*N*'-dicyclohexyl-*N*''-(*iso*-tridecyl)guanidine (DCiTG) was initially developed to fulfill this role and found to perform favorably in lab-scale [Moyer et al., 2011] and full-scale [Lentsch, et al., 2013] tests. Unfortunately, the significant partitioning to the aqueous phase in stripping [Duncan et al., 2012; Moyer et al., 2014] posed a disadvantage for sustained process operation. This partitioning loss spurred the development of the more lipophilic *N*,*N*',*N*''-tri(3,7-dimethyloctyl)guanidine (TiDG) which was utilized in the Modular CSSX Unit (MCU) located at the Savannah River Site (SRS) [Brass et al., 2014] and implemented in the startup of the Salt Waste Processing Facility (SWPF) [Luzzatti et al., 2022]. However, the use of TiDG is limited by its undesirably low resistance to hydrolysis as observed in lab-scale tests [Roach et al., 2015; Hill et al., 2016] and in operation of the MCU [Peters, 2020]. Recent results [Bessen et al., 2022] have shown that increasing the steric bulk of the guanidine's alkyl groups increases the guanidine's stability, which would be beneficial for long-term implementation at the SWPF. Specifically, *N*,*N*'-dicyclohexyl-*N*''-(10-nonadecyl)guanidine (DCNDG), Table 1, has markedly higher stability than TiDG or DCiTG and shows promise for replacing these guanidines in NG-CSSX [Bessen et al., 2022].

For DCNDG to be implemented in the NG-CSSX process at a large scale, reliable synthetic procedures and purity requirements must be established. Here, a proven synthesis procedure is described as are specifications for the DCNDG purity that avoid adverse impact on the distribution of Cs^+ during various sections of the NG-CSSX process.

Table 1. NG-CSSX Solvent Components

Component	Name	Chemical Name	Structure
Extractant	MaxCalix	1,3-*alt*-25,27-bis(3,7-dimethyloctyl-1-oxy)calix[4]arene-benzocrown-6 MW 955.36 0.0500 M	
Modifier	Cs-7SB	1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol MW 338.35 0.500 (as used in MCU) 0.650 M (as suggested in [Bessen, 2021])	 $OCH_2CF_2CF_2H$ OH
Suppressor	DCiTG	*N*,*N*'-dicyclohexyl-*N*''-(*iso*-tridecyl)guanidine MW 405.71 (442.17 for HCl salt) 0.003 M 1st Generation; too aqueous soluble[a]	
	TiDG	*N*,*N*',*N*''-tri(3,7-dimethyloctyl)guanidine MW 479.89 (516.35 for HCl salt) 0.003 M 2nd Generation; used in MCU and SWPF[b]	
	DCNDG	*N*,*N*'-dicyclohexyl-*N*''-(10-nonadecyl)guanidine MW 489.88 (526.34 for HCl salt) 0.003 M 3rd Generation; proposed for SWPF[c]	
Diluent	Isopar$^{\text{TM}}$ L	C_{12}-isoparaffinic hydrocarbon balance	

[a] [Duncan et al., 2012; Moyer et al., 2011; Moyer et al., 2014]

[b] [Brass et al., 2014; Luzzatti et al., 2022]

[c] [Bessen, et al., 2022]

2. EXPERIMENTAL SECTION

2.1 MATERIALS

Solvent components were obtained from commercial sources and judged to be of adequate purity for use as received unless otherwise noted.

To synthesize DCNDG, *N*,*N*'-dicyclohexylcarbodiimide (DCC, puriss. ≥99.0%, Lot No. WXBC5142V) and *t*-butanol (ACS grade ≥99.0%, Lot No. 21796 PMV) were obtained from Sigma-Aldrich. The *t*-butanol was dried over activated 3 Å molecular sieves prior to use. Nonadecan-10-amine (NDA, 95%, Lot No. B19V11062) was purchased from BOC Sciences. Hydrochloric acid (Certified ACS Plus, Lot No. 189451) and sodium sulfate (Certified ACS, Lot No. 186999) were obtained from Fisher Chemical.

For the synthesis of NDA, 10-nonadecanone (99%, Lot No. HM03708HM), pyridine (99.8%, Lot No. SHBC3834V), hexanes (≥99%, Lot No. SHBC5895V), and sodium borohydride (98%, MKBT3048V) were obtained from Sigma-Aldrich. Hydroxylamine hydrochloride (99%, Lot No. Z22A007) and ethanol (94–96%, anhydrous, denatured, Lot No. V08E046) were purchased from Alfa Aesar. Hydrochloric acid (Certified ACS, Lot No. 189451) was obtained from Fisher. Nickel(II) chloride hexahydrate (High Purity Grade, Lot No. 0764C321) was purchased from Amresco. Methanol (ACS, Lot No. 0000265583) and diethyl ether (ACS, Lot No. 000273890) were purchased from VWR. Sodium hydroxide (pure, Lot No. A0415881) and anhydrous sodium sulfate (99+%, Lot No. A0317494) were obtained from Acros Organics.

The expected impurities were purchased or synthesized if not commercially available. Dicyclohexylurea (DCU, 98%, Lot No. MKCK6987) and dicyclohexylcarbodiimide (DCC, puriss. ≥98.0%, Lot No. WXBC5142V) were obtained from Sigma-Aldrich. Cyclohexylamine (CyA, 98%, Lot No. 50017173) was purchased from BeanTown Chemical. The expected impurity *N*-cyclohexyl-*N*'-(10-nonadecyl)urea was synthesized using cyclohexyl isocyanate (98%, Lot No. MKBJ7837V) and anhydrous toluene (99.8%, Lot No. SHBF5673V) from Sigma-Aldrich, magnesium sulfate (anhydrous, Lot No. TC03AZEMS) from EMD, along with the previously described NDA.

For preparing the NG-CSSX solvent, 1-(2,2,3,3-tetrafluoropropoxy),3-[4-(*sec*-butyl)phenoxy]-2-propanol (Cs-7SB modifier, Lot No. MOD2020-M-1) and 1,3-*alt*-25,27-bis(3,7-dimethyloctyl-1-

oxy)calix[4]arenebenzocrown-6 (MaxCalix, Lot No. 2018-M-01) were obtained from Marshallton Research Laboratories. Isopar L (Lot No. US67377E) was obtained from ExxonMobil.

Solutions for washing the solvents were prepared from hydrochloric acid (HCl, Lot No. Z216507 050) obtained from EMD and sodium hydroxide (NaOH, Lot No. 173021) from Fisher Chemical. HCl and NaOH solutions were prepared by dispensing the appropriate volume of the pre-made solutions into volumetric flasks and diluting to the mark using Milli-Q® water.

2.2 METHODS

2.2.1 DCNDG Synthesis

DCNDG, like the previously considered *N*,*N*'-dicyclohexyl-*N*''-alkylguanidines, is synthesized by the reaction between a primary alklylamine and *N*,*N*'-dicyclohexylcarbodiimide (DCC). [Moyer et al., 2014] DCC is readily available from multiple vendors, but the required NDA is less readily available. For this reason, the synthesis given here uses purchased NDA, but a verified synthetic procedure for NDA is additionally provided in Section 2.2.2.

To prepare DCNDG, NDA (3.6272 g, 12.794 mmol, 1 equiv.) and DCC (2.6391 g, 12.791 mmol, 1 equiv.) are dissolved in 40 mL of anhydrous *t*-butanol under a dry, argon atmosphere. This is allowed to reflux for 24 h. During reflux, the condenser is cooled with water warmed to 30°C to eliminate the risk of *t*-butanol solidifying in the condenser, which could potentially block the condenser and lead to a pressurization of the reaction vessel. After refluxing, the flask is allowed to cool, and the *t*-butanol is removed by rotary evaporation, yielding the guanidine and any unreacted DCC and NDA. The *t*-butanol recovered from the rotary evaporator could likely be reused assuming that the evaporator is cleaned before use and the *t*-butanol is kept sufficiently dry.

To this crude guanidine mixture, 100 mL of 10 M hydrochloric acid[1] and 100 mL of DCM are added successively. At this scale, the use of room temperature hydrochloric acid and DCM was acceptable, but at larger scales, pre-cooling the solutions or cooling the reaction may be necessary to avoid boiling the DCM. This step serves to protonate the guanidine, forming the guanidinium chloride DCNDG•HCl, and to partition it to the DCM phase. Any unreacted DCC is hydrolyzed to the urea DCU,

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[1] Caution. 10 M hydrochloric acid is corrosive and approaches the concentration of concentrated hydrochloric acid. Wear goggles or a face shield when using, especially if a separatory funnel is used.

which along with much of the NDA, remains in the highly acidic aqueous phase. This aqueous phase is discarded, and the remaining DCM phase is washed three times with 100 mL of water and dried over anhydrous sodium sulfate. The DCM is removed by rotary evaporation to give the DCNDG hydrochloride (6.5715 g, 12.485 mmol) in 97.6% yield after vacuum drying. The purity of the guanidine was found to be 97.5% by ^{1}H NMR. Treatment of DCNDG•HCl dissolved in DCM by flashing the solution through a plug of silica increased the purity to 98.5% by ^{1}H NMR. ^{1}H NMR purities were calculated assuming that all unassigned peaks were the sole, 1H peak of an impurity. Complete NMR spectra are available in the SI. (DCNDG•HCl): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.32 (s, 1H), 7.18 (br s 2H), 3.40 (m 2H), 3.13 (s 1H), 1.89 (d 4H), 1.78 (d 4H), 1.58 (s 4H), 1.48 (q 4H), 1.24 (br s 28H), 0.86 (t 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 158.4, 56.8, 54.7, 36.6, 34.6, 33.3, 31.0, 30.7, 27.6, 26.4, 26.3, 24.0, 15.5.

2.2.2 NDA Synthesis

NDA was synthesized starting from 10-nonadecanone, as it is the most readily available starting material bearing a 10-nonadecyl alkyl group. The ketone was first converted to the oxime by refluxing with hydroxylamine hydrochloride [Wescott and Mattern, 2003] followed by reduction of the oxime to the amine using sodium borohydride with a Ni_2B catalyst [Ipaktschi, 1984], Figure 1.

To prepare the oxime intermediate, 10-nonadecanone (4.9935 g, 17.675 mmol, 1 equiv.) and hydroxylamine hydrochloride (2.5086 g, 36.100 mmol, 2 equiv.) were dissolved in 50 mL ethanol and 15 mL pyridine. This solution was refluxed for 2 h followed by rotary evaporation to remove the ethanol and pyridine. To the residue, 20 mL of 5% HCl and 15 mL hexanes were added. The 10-nonadecyloxime was extracted into the hexane phase, and the acidic aqueous phase containing the unreacted hydroxylamine hydrochloride and any remaining pyridine and ethanol were discarded. The hexane phase was dried over anhydrous sodium sulfate, and the hexane was removed by rotary evaporation. Ultimately, 4.9296 g (16.569 mmol) of the 10-nonadecyl oxime were recovered, giving a yield of 93.7% of a white powder after vacuum drying. The purity of the oxime was found to be 99.3% by ^{1}H NMR and 98.5% by gas chromatography-flame ionization detection (GC-FID). ^{1}H NMR purities were calculated assuming that all unassigned peaks were the sole, 1H peak of an impurity. Complete NMR spectra are available in the SI. (10-nonadecyl oxime): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.60 (br s, 1H), 2.33 (t 2H), 2.00 (t 2H), 1.50 (s 6H), 1.27 (br s 24H), 0.88 (t 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 162.9, 35.5, 33.3, 31.3, 31.0, 30.8, 30.7, 30.0, 29.0, 27.8, 27.0, 24.1, 15.4.

For the reduction of the oxime intermediate, 10-nonadecyl oxime (3.303 g, 11.10 mmol, 1 equiv.) and nickel (II) chloride hexahydrate (5.272 g, 22.18 mmol, 2 equiv.) were dissolved in 160 mL methanol in a 500 mL round bottom flask. The contents of the flask were chilled to 0°C in an ice bath, and sodium borohydride (4.2051 g, 111.16 mmol, 10 equiv.) was slowly added to prevent the contents from bubbling too vigorously. The contents were then stirred with continued chilling on the ice bath for 30 min. At the conclusion of this period, a second addition of sodium borohydride (0.8387 g, 22.17 mmol, 2 equiv.) was made and the ice bath was removed. The flask was brought to room temperature and allowed to continue stirring for 2 h. After stirring, the contents were slowly acidified with 6 M HCl, and 150 mL of water was added to dissolve the formed Ni_2B catalyst and any unreacted sodium borohydride. To this solution, the NDA, which was presumably protonated as 10-nonadecammonium chloride, was extracted three times into 100 mL of diethyl ether. These three portions of diethyl ether containing the crude NDA were combined and washed first with 100 mL of water and then 250 mL of 1 M NaOH to remove any extracted Ni^{2+} and deprotonate the 10-nonadecammonium chloride. The ether phase was dried over anhydrous sodium sulfate, and the NDA was recovered by rotary evaporation. NDA (3.0387 g, 10.719 mmol) was recovered for a yield of 96.5% of a pale-yellow oil after vacuum drying. The purity was found to be 95.3% by ^{1}H NMR. (NDA): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.64 (s, 1H), 1.35 (s 4H), 1.24 (br s 28H), 0.86 (t 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 52.6, 39.6, 33.3, 31.2, 31.0, 30.7, 27.6, 24.0, 15.4.

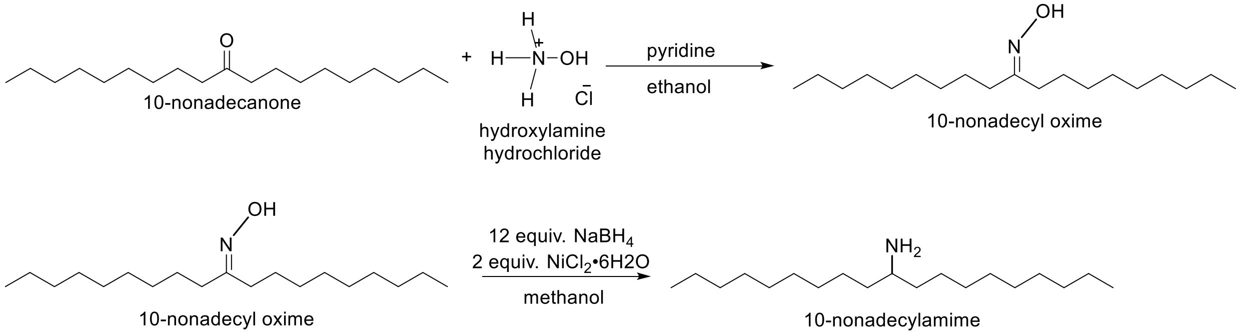

Figure 1. Synthesis of 10-nonadecylamine (NDA) by conversion of 10-nonadecanone to the oxime followed by reduction to the amine using sodium borohydride catalyzed by Ni_2B (generated in situ by reaction of $NaBH_4$ with $NiCl_2 \cdot 6H_2O$).

2.2.3 *N*-Cyclohexyl-*N*'-(10-nonadecyl)urea Synthesis

As an anticipated impurity and degradation product found in DCNDG, *N*-cyclohexyl-*N*'-(10-nonadecyl)urea (CyNDU) was synthesized using the reaction shown in Figure 2. NDA (0.1711 g, 0.604 mmol) was dissolved in 20 mL of anhydrous toluene in a round-bottom flask. To this solution, cyclohexylisocyanate (0.117 mL, approx. 0.916 mmol) was added. A reflux condenser equipped with a drying tube was added, and the apparatus was allowed to reflux for 2.25 h, at which time TLC on silica gel with a 50% DCM/50% hexane mobile phase indicated the reaction was complete. After partial cooling, 10 mL of water was added, and the mixture was brought to reflux for 45 min to destroy any of the remaining and acutely toxic cyclohexyl isocyanate by converting it to cyclohexylamine and carbon dioxide. Following this, the toluene, water, and much of the cyclohexylamine was removed by rotary evaporation. The resulting solids were dissolved or suspended in 10 mL of diethyl ether and held at -26°C for 20 h to precipitate the majority of any dicyclohexylurea that had formed. The solids were filtered off, washed with additional cold diethyl ether and set aside. The filtrate was transferred to a separatory funnel and washed with 7.5 mL of 0.01 M HCl to remove any remaining cyclohexylamine. The aqueous HCl was removed, and the ether solution was washed with two 10 mL portions of water. The washed ether solution was dried over magnesium sulfate, and the ether was removed by rotary evaporation to yield CyNDU (0.0531 g, 0.130 mmol, 21.5% yield) as a fine, white powder. The low yield of 21.5% was found to be due to the inclusion of a majority of the CyNDU in the solids that were filtered out of the cold diethyl ether solution which were found to be a mixture of CyNDU and dicyclohexylurea.

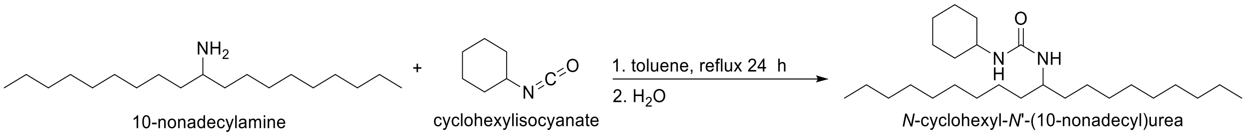

Figure 2. Synthesis of *N*-cyclohexyl-*N'*-(10-nonadecyl)urea (CyNDU).

2.2.4 Gas Chromatography Procedure

DCNDG and its impurities were quantified by gas chromatography-flame ionization detector (GC-FID) by reproducing the method used by Sloop for the quantification of TiDG. [Sloop, 2018] In this method, a HP 6850 Series GC-FID equipped with a 15 m GsBP-1MS column from General Separations Technologies (Part No. 1125-1502) and a split liner from Agilent (Part No. 5183-4647). The hydrogen carrier gas and fuel for the flame ionization detector was prepared by a Parker Balston H2PEM-100 Hydrogen Generator. The oven temperature program used started with a 1-minute hold at 45°C followed by a 10°C/minute ramp to 300°C and a 20-minute hold at 300°C. Additional details and justification for the parameters chosen can be found in ORNL/TM-2018/930. [Sloop, 2018] With the aforementioned equipment and parameters, DCNDG and its degradation products were readily identifiable by their retention times (RT) provided that there were no additional and unexpected contaminants. The approximate retention times are as follow: DCNDG, 24.0 min; CyNDU, 17.5 min; DCU, 15.5 min; NDA, 16 min; and CyA, 1.8 min.

2.2.5 Cesium Distribution Measurements

The solvent used in the NG-CSSX process, the Next Generation Solvent (NGS) was prepared gravimetrically by dispensing the required quantity of MaxCalix and Cs-7SB into a Class A volumetric flask to obtain a concentration of 0.050 M and 0.65 M respectively. These components were then dissolved to the mark in Isopar^{TM} L to create a blank solvent containing no suppressor or purposely added degradation products. This blank solvent was then washed with an equal volume of 0.010 M hydrochloric acid, water, 0.3 M NaOH, 0.1 M NaOH, 0.03 M NaOH, 0.01 M NaOH, and twice with water. The final water wash was neutral on litmus paper. To prepare NGS with DCNDG and its degradation products or impurities, the required quantities were gravimetrically dispensed in a Class A volumetric flask and dissolved to the mark with the blank NGS solvent. By washing the blank solvent rather than the solvent with DCNDG, its degradation products, and impurities, the loss of the degradation products and impurities to the aqueous washes was avoided.

To study the distribution of Cs during a simulated NG-CSSX run, ES_2S_3 tests were conducted, where the solvent is sequentially treated with one simulated extraction step (E), two scrubbing steps (S_2), and three stripping steps (S_3). In the extraction step, the solvent is contacted with SRS-15 waste simulant [Peterson, 2000] spiked with Cs-137 at an organic-to-aqueous ratio (O:A) of 1:10. In each of the scrub steps, the Cs-loaded solvent from extraction is contacted with 0.025 M sodium hydroxide at O:A = 2:1. The strip steps contact the extracted and scrubbed solvents with 0.010 M boric acid at O:A = 2:1. All contacts are carried out at a temperature of 25.0 ± 0.2°C. After each contact, aliquots of each of the organic and aqueous phases are taken, and the activity of Cs-137 in each aliquot is then measured on a COBRA II Na(Tl)I gamma counter. These activities are converted into distribution ratios D_{Cs} to quantify the distribution of Cs, where $D_{Cs} = [Cs]_{org}/[Cs]_{aq} = A_{org}/A_{aq}$ and A is the activity of a given phase.

3. RESULTS AND DISCUSSION

3.1 DCNDG SYNTHESIS

DCNDG was synthesized using a procedure adapted from the synthesis of DCiTG, the first alkylguanidine considered for the NGS [Moyer et al., 2014]. In this reaction as detailed in Section 2.2.1, the guanidine is formed by the reaction of a primary amine with a carbodiimide, in this case NDA and DCC, Figure 3.

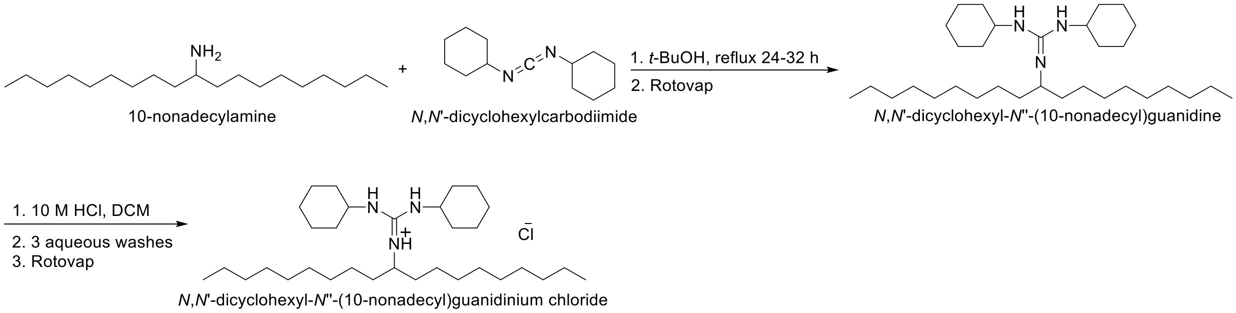

Figure 3. Synthesis of *N*,*N*'-dicyclohexyl-*N*''-(10-nonadecyl)guanidine (DCNDG) and its hydrochloride salt.

Although the reaction gives a high yield and purity, careful control of the stoichiometry and exclusion of water is necessary. Control of the 1:1 stoichiometry between NDA and DCC is necessary to prevent an excess of unreacted starting material from remaining in the final product. As maintaining the exact stoichiometry is difficult, inclusion of a slight excess of DCC would be preferable to an excess of NDA, as DCC is less expensive, more easily removed from the crude guanidine, and will aid in removing any unwanted trace water. The inclusion of water in this reaction is unwanted, as it promptly reacts with DCC to form the urea DCU. For this reason, the anhydrous *t*-butanol used as a reaction solvent was carefully dried over 3Å molecular sieves prior to use, and an anhydrous argon atmosphere was maintained.

In the likely event that traces of water are present in the reaction, some DCU will be present and is effectively removed during workup with 10 M HCl. The washing of the crude guanidine with HCl serves several purposes. Firstly, this step protonates the DCNDG, forming the guanidinium chloride DCNDG•HCl, which is likely more stable than the free base [Roach et al., 2015]. Secondly, unreacted DCC will be converted to DCU. Finally, any DCU and a portion of the NDA are removed from the DCNDG in DCM and partitioned to the aqueous phase, likely as protonated cations. At this stage, the DCM phase can be dried and evaporated to yield DCNDG•HCl, with the main impurities being unreacted NDA and traces of DCU.

Although the purity of the DCNDG at this point exceeded the requirements for use in NGS suggested in Section 3.3, it was found that it could be purified further by treatment with silica in DCM. The main impurity after treatment with silica was still NDA with traces of DCU, but both were less prevalent. Using activated charcoal to purify DCNDG was also tested, but it was found to be less effective than silica and more difficult to remove by filtration.

3.2 NDA SYNTHESIS

NDA was synthesized from the most commonly available starting material containing the 10-nonadecyl alkyl group, 10-nonadecanone. 10-Nonadecanone, as a symmetrical ketone, is readily synthesized from the ketonization reaction between two equivalents of decanoic acid. To convert this ketone to a primary amine, a reductive amination process is used.

The most successful reductive amination procedure tried here was the two-step reaction detailed in Section 2.2.2 in which the ketone is first converted into an oxime and then reduced to the amine. The first step of this reaction, the conversion to an oxime, is carried out by refluxing 10-nonadecanone with hydroxylamine hydrochloride in a mixture of ethanol and pyridine. This generates the oxime with a reasonable yield of 93.7% and purity of 98.5% to 99.3% depending on the analytical method used. The major impurity is the unreacted ketone with minor traces of ethanol and pyridine. The second part of the reaction, reduction of the oxime to the amine, is somewhat more difficult although the obtained yield and purity were reasonable. This reduction was achieved with sodium borohydride using a superstoichiometric Ni_2B catalyst generated in situ by the reaction of nickel(II) chloride hexahydrate with sodium borohydride. Upon addition of sodium borohydride to the reaction mixture containing nickel(II) chloride, a black suspension of Ni_2B immediately formed with the vigorous generation of H_2 gas. The removal of this catalyst by dissolution with hydrochloric acid and water after the reaction is the slowest part of the workup of the amine. Pictures taken during this dissolution are shown in Figure 4. After complete workup of the amine, a yield of 96.5% was achieved with a purity of 95.3% by ^1H NMR. For this two-step reaction, the overall yield was 90.4%, and the major impurity of the final amine was the oxime with trace amounts of the starting ketone and butylated hydroxytoluene (BHT) from the stabilizer added to the diethyl ether.

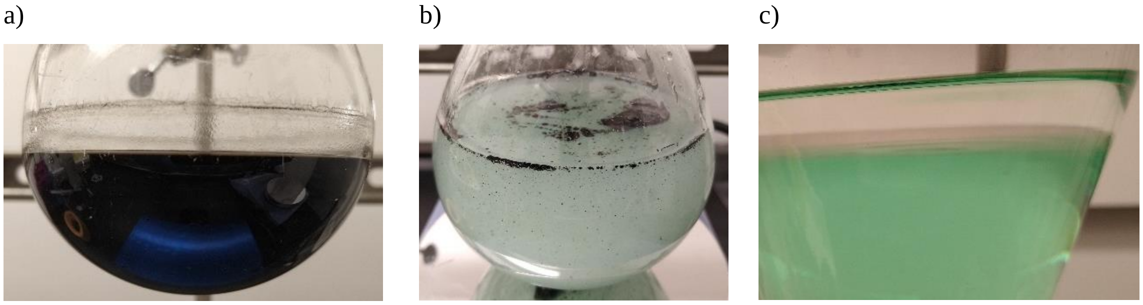

Figure 4. Pictures from the reduction and workup of 10-nonadecyl oxime with sodium borohydride and Ni_2B catalyst. a) The reaction mixture at the conclusion of the reaction with suspended Ni_2B catalyst. b) The mixture part way through the dissolution of the catalyst with aqueous hydrochloric acid. c) The reaction mixture after the complete dissolution of the catalyst and addition of diethyl ether. Note the lack of solids and the clear, colorless organic (top) phase.

An additional, one-step Leuckart reaction between 10-nonadecanone and excess ammonium formate and formic acid was also tested, but despite multiple attempts and different reaction conditions, it gave unsatisfactory yields of the amine of only up to 10%. Additionally, the purity of the recovered amine was far lower than desired with excess, unreacted ketone and traces of the secondary amine included.

3.3 DCNDG PURITY

Due to the similar synthetic approach, structure, and chemistry of DCNDG to the first-generation guanidine suppressor DCiTG, the purity requirements for DCNDG, Table 2, are adapted from the previously stated purity requirements for DCiTG [Moyer et al., 2014]. The largest difference from the DCiTG purity specification is the grouping of the two possible amines, NDA and CyA, and the two possible ureas, DCU and CyNDU, formed from incomplete reaction during synthesis or DCNDG degradation together with the same limits as the isotridecylamine mixture or DCU from DCiTG.

Table 2. Acceptable purity and impurity percentages for DCNDG and DCiTG

Component	DCNDG Allowable range (mole %)	DCiTG[b] Allowable range (mole %)
Guanidine[a]	>95%	>95%
Amines (NDA + CyA)	<1%	
Isotridecylamine		<1%
Ureas (DCU + CyNDU)	<3%	
DCU		<3%
DCC	<0.5%	<0.5%
All other impurities	<0.5%	<0.5%

[a] Percentages are the same whether the guanidine is present as the free base or the hydrochloride.

[b] [Moyer et al., 2014]

3.4 ES$_2$S$_3$ TESTING WITH ADDED IMPURITIES

ES$_2$S$_3$ tests of NGS with the addition of the anticipated impurities were conducted to quantify any possible effect they may have on the distribution of Cs^+. The concentrations of DCNDG and impurities are shown in Table 3. Both samples with added impurities, Samples 2 and 3, exceed the recommended limits on the impurities by a large margin. These low purities are far below the allowable purity of >95% suggested in Section 3.3. Despite the high amounts of impurities, the concentration of DCNDG was maintained at approximately 3 mM in an attempt to maintain sufficient suppressor capacity. These conditions were chosen to replicate an extreme worst-case scenario unlikely to be encountered during operation.

Table 3. Impurity concentrations used in ES$_2$S$_3$ tests of DCNDG with added impurities

NGS Sample	Sample 1 Concentrations (mM)	Sample 2 Concentrations (mM)	Sample 3 Concentrations (mM)
DCNDG	3.00 ± 0.04	3.08 ± 0.04	3.00 ± 0.04
CyA	-	3.2 ± 0.2	1.6 ± 0.2
NDA	-	2.96 ± 0.07	0.99 ± 0.07
DCU	-	3.92 ± 0.09	0.89 ±0.09
CyNDU	-	3.62 ± 0.05	0.93 ± 0.05
DCC	-	-	3.1 ± 0.1

Despite the addition of impurities at levels that far exceed the recommended amount, Samples 2 and 3 gave acceptable D_{Cs} values comparable to those from Sample 1, which has no additional impurities. This demonstrates that the impurities tested here do not interfere with the Cs extraction behavior of the process and may be tolerated at much higher amounts than permitted by the limits of Section 3.3 given that the total DCNDG concentration remains at 3 mM.

Table 4. D_{Cs} values of ES_2S_3 tests of DCNDG with added impurities

Stage	Sample 1	Sample 2	Sample 3	Reference limits[a]
Extraction	91.2	78.2	87.4	>26.3
Scrub 1	3.69	3.17	3.56	>1.5
Scrub 2	1.46	1.36	1.53	>1.5
Strip 1	0.00350	0.0112	0.00945	<0.5
Strip 2	0.000125	0.00386	0.00212	<0.5
Strip 3	0.000276	0.000934	0.000251	<0.5

[a] Reference limits adapted from WSRC-RP-99-00006 Rev. 1 [Dimenna et al., 1999]

4. CONCLUSIONS

The guanidine *N*,*N*'-dicyclohexyl-*N*"-(10-nonadecyl)guanidine (DCNDG) can be easily synthesized from the reaction of *N*,*N*'-dicyclohexylcarbodiimide (DCC) and 10-nonadecamine (NDA) with a high yield and acceptable purity. The NDA for this reaction is commercially available but may also be synthesized via a two-step reductive amination procedure starting from a widely available aliphatic ketone.

Purity specifications are given to provide for predictable process performance. The required purity for the DCNDG for use in the NG-CSSX process was adapted from the previous purity specifications [Moyer et al., 2014] for the first-generation suppressor, *N*,*N*'-dicyclohexyl-*N*"-(*iso*-tridecyl)guanidine (DCiTG). Batch tests of the NGS containing 3 mM DCNDG together with additions of the expected impurities at concentrations greatly exceeding the allowable quantities confirmed Cs^+ distribution behavior to be unaffected.

5. ACKNOWLEDGEMENTS

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QA Implementation for ORNL/TM-2022/2443

In terms of the applicable NQA-1 based criterion, Table 9 identifies the corresponding ORNL QA criterion/criteria. ORNL employs an electronic Standard Based Management System (SBMS) to deliver procedures that implement the criteria. Procedures are organized by subject areas under management systems and are implemented using a graded approach appropriate for the work. Documents that tailor the ORNL criteria to the project also appear in the table.

Table 9. NQA-1 Based Criteria

Implementing Procedures	Document No.	Yes	No
Organization	QAPD (criteria 1,10); QAP-X-94-CSD-001	X	
Quality Assurance Program	QAPD (criteria1,2,3,9,10) QAP-X-94-CSD-001	X	
Control of Research and Development Activities	QAP-X-94-CSD-001	X	
QA Program Requirements for Analytical Measurement Systems	QAP-X-94-CSD-001	X	
Design Control	N/A		
Procurement Document Control	QAPF (criterion 7); QAP-X-94-CSD-001	X	
Instructions, Procedures and Drawings	QAPD (criteria 4,5); QAP-X-94-CSD-001	X	
Document Control	QAPD (criterion 4); QAP-X-94-CSD-001 CSD-OP-000-AD01	X	
Control of Purchased Items and Services	QAPD (criterion 7); QAP-X-94-CSD-001	X	
Identification and Control of Items	QAPD (criteria 5,8); QAP-X-94-CSD-001	X	
Control of Processes	QAPD (criterion 5); QAP-X-94-CSD-001	X	
Control of Nondestructive Examination	N/A		
Control of Welding and Other Joining Processes	N/A		
Work Planning and Control	QAPD (criterion 5)	X	
Inspection	QAPD (criteria 8,10); QAP-X-94-CSD-001	X	
Test Control	QAPD (criteria 8,10); QAP-X-94-CSD-001	X	

Control of Measuring and Test Equipment	QAPD (criteria 5, 8); QAP-X-94-CSD-001	X	
Control of Installed Process Instrumentation	QAPD (criterion 5); QAP-X-94-CSD-001	X	
Packaging, Handling, Shipping and Storage	QAPD (criterion 5); QAP-X-94-CSD-001	X	

Notes:

QAPD – *ORNL Quality Assurance Program Description* – describes how requirements are parsed to management systems and flowed into implementing procedures through subject areas delivered by the management systems.

QAP-X-94-CSD-001 – *Chemical Sciences Division Quality Assurance Plan* – describes how the ORNL subject areas are graded within the Chemical Sciences Division. Criterion 5 includes sections that describe the documentation of research data using the registered research notebook process. The handling of registered research notebooks is described in the SBMS *Records* subject area exhibit: *Instructions for Use of this Research and Technical Notebook*. Research records are handled as permanent. CSD-OP-000-AD01 – *Administration of Chemical Sciences Division Command M*