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Spectroscopic Characterization of 1-Naphthyl Isocyanate Anion Radical and of Tris(1-naphthyl) Isocyanurate Atropisomers

Steven J. Peters,*^[a] Mark E. Kassabaum,^[a] Michael K. Nocella,^[a] and Robert McDonald^[b]

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Room-temperature potassium metal reduction of 1-naphthyl isocyanate in THF results in a rapid cyclotrimerization (initiated by the 1-naphthyl isocyanate anion radical) that generates two diastereoisomers (atropisomers) of tris(1-naphthyl) isocyanurate. The formation of the *syn* and *anti* diastereoisomers was monitored by ¹H and ¹³C NMR spectroscopy. Upon completion of the cyclotrimerization, the two diastereoisomers were isolated, and their configuration was assigned by

Introduction

Isocyanurates (1,3,5-triazine-2,4,6-triones), which are commonly generated by the cyclotrimerization of isocyanates, have considerable commercial importance for their ability to enhance the physical properties of polyurethanes.^[1-3] Incorporation of isocyanurates into polymeric blends of polyurethanes and other copolymer resins make these materials more flame-retardant, transparent and chemical- and impact-resistant.^[3,4-6] Periodic mesoporous organosilicas (PMOs) that contain isocyanurate bridging groups afford materials that show very high adsorption capacity for mercury(II) and other heavy metal ions from aqueous solutions.^[7] Interestingly, low-toxicity isocyanurate siderophores have also been investigated as candidates for drug delivery in mammalian systems,^[8] while optically active isocvanurates having peripheral amino acid units exhibit chiral discrimination of racemic mixtures of enantiomers.^[9] Tris(aryl) isocyanurates are used as activators in the copolymerization of β-caprolactam in the formation of nvlon-6.[10]

The importance of isocyanurates commercially has resulted in numerous efforts to develop effective methods for the rapid cyclotrimerization of isocyanates. Many catalysts have been found that facilitate the cyclotrimerization process. A few examples of Lewis bases include amines,^[11] cyanate,^[12] fluoride,^[13] phosphines,^[14] and carbamate

[b] Department of Chemistry, University of Alberta Edmonton, Alberta T6G-2G2, Canada NMR spectroscopy. Both compounds crystallize in the monoclinic C2/c space group, and single-crystal X-ray diffraction analyses confirm the structures of both isomeric forms. The results from this study prove that alkali metal reduction of isocyanates is a convenient and rapid method for generating isocyanurate compounds even when a sterically bulky substituent is attached to the NCO moiety.

anions.^[15] Some cyclotrimerization reactions have also been investigated using Lewis acids as catalysts; these include the use of organotin compounds,^[16] as well as copper(II) and nickel(II) halides.^[17] Many of these catalyzed processes have negative aspects such as low activity of catalysts, formation of uretidinediones (isocyanate cyclic dimers) and other byproducts, separation of the cyclotrimer from the catalyst, long reaction times and the use of toxic solvents. Prior to our work, there have been few catalysts studied that are effective at driving the cyclotrimerization of both aryl and alkyl isocyanates, these are the extremely basic pro-azaphosphatrane compounds,^[14a] and an isopropyl-substituted Nheterocyclic carbene.^[18] Recently, our group has found that exposure of both alkyl and aryl isocyanate solutions to an alkali metal (either potassium or sodium) is an effective and rapid method for the generation of the respective isocyanurates.^[19-21] The cyclotrimerization process is believed to proceed via the reactive isocyanate anion radical formed from the one-electron reduction of the isocyanate, which rapidly attacks two more neutral isocyanates.^[19,20] In the case of aryl isocyanates, this protocol is effective at converting phenyl isocyanate (PhNCO) and a number of para-substituted PhNCO compounds to their respective isocyanurates.^[20] However, we have yet to determine the efficiency of converting isocyanates with bulky substituents attached to their respective cyclotrimers. Herein, we report that the alkali metal reduction of 1-naphthyl isocyanate (1) results in the rapid conversion into tris(1-naphthyl) isocyanurate (2) in very good yield. Both nuclear magnetic resonance (NMR) spectroscopy and single-crystal X-ray diffraction studies reveal that atropisomers (e.g., two diasteroisomers generated as a result of hindered rotation of the three naphthyl rings) of tris(1-naphthyl) isocyanurate are produced. To the best of our knowledge only one other published study

 [[]a] Department of Chemistry, Illinois State University Normal, IL 61790-4160, USA E-mail: sjpeter@illinoisstate.edu http://chemistry.illinoisstate.edu

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of isocyanurate atropisomers has been reported.^[22] (These studies involved the use of *ortho*-substituted phenyl isocyanate derivatives.^[22]) The one-electron initiated formation and structures of both 1-naphthyl isocyanurate diastereoisomers are reported here for the first time.

Results and Discussion

Exposure of a $[D_8]$ THF solution containing 1-naphthyl isocyanate to a deficient amount of potassium metal ([K metal] << [isocyanate]) results in an immediate color change of the solution from colorless to light yellow-green. Examination of the reduced solution by NMR spectroscopy, immediately after exposure to the K metal, reveals that nearly half of the 1-naphthyl isocyanate (1) has been converted into the cyclotrimer (see Figures 1 and 2). The resonances located at $\delta \approx 149.5$ ppm in the ¹³C{¹H} NMR spectra (Figure 2B and C) are assigned to the carbonyl carbon atoms in the isocyanurate ring and are evidence of its formation upon reduction of 1.^[23] Interestingly, with no further exposure to K metal, we find that the conversion of the isocyanate to the isocyanurate continues to occur, and, after approximately 4 h, the formation of the cyclotrimer is nearly complete (Figures 1 and 2). The NMR spectroscopic data clearly shows that the major species in solution is the tris(1-naphthyl) isocyanurate (2) (ca. 90%) and that a small amount (ca. 10%) of byproduct is also formed in the reduction process.

Steric crowding between the naphthyl rings and the carbonyl oxygen atoms within 2 will necessarily force the naphthyl rings to adopt a near perpendicular geometry relative to the plane of the isocyanurate moiety. Any rotation of the naphthyl rings about the N-C bonds will be greatly hindered as a result of this steric crowding. Thus, two diastereoisomers (atropisomers) are expected upon formation of 2. The symmetric diastereoisomer (syn-2) will adopt a $C_{3\nu}$ symmetry where all three naphthyl rings will be directed above the isocyanurate ring. The other diastereoisomer (anti-2) has a C_s symmetry where one of the naphthyl groups is pointing in the opposite direction relative to the other two rings. Each of these stereoisomers should exhibit unique spectroscopic signatures. Upon closer inspection of the NMR spectroscopic data (Figure 2), three distinct ¹³C carbonyl resonances are clearly present at $\delta \approx 149$ ppm. In the case of the syn-2 isomer, all three carbonyl groups are chemically equivalent, therefore only one resonance is expected and is found at $\delta = 149.63$ ppm. With the *anti-2* isomer the three carbonyl groups are no longer magnetically equivalent. In this molecular system, two of the carbon atoms are equivalent while the third carbon atom is magnetically distinct. Therefore, two unique carbonyl resonances are expected for the anti-2 isomer in the ¹³C NMR spectrum where their relative intensity is expected to be 2:1. A closer look at Figure 2C (inset) reveals that two resonances are present, found at $\delta = 149.65$ and 149.45 ppm that match the expected 2:1 ratio, respectively, and are therefore assigned to the carbonyl groups in anti-2.



Figure 1. (A) 500 MHz ¹H NMR spectrum of a $[D_8]$ THF solution containing 1-naphthyl isocyanate at 300 K before exposure to potassium metal. (B) ¹H NMR spectrum collected immediately after the same $[D_8]$ THF solution had been exposed to a deficient amount of metal that exhibits almost 50% conversion of isocyanate into isocyanurate. (C) ¹H NMR spectrum collected 4 h after the initial exposure to K metal. The spectrum shows complete conversion to tris(1-naphthyl) isocyanurate.

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Figure 2. (A) 125 MHz ¹³C{¹H} NMR spectrum of a [D₈]THF solution containing 1-naphthyl isocyanate at 300 K before exposure to potassium metal. The carbon resonance associated with the NCO moiety ($\delta = 126.48$ ppm) appears as a shoulder on the high-field side of the strong resonance at $\delta = 126.52$ ppm. (B) ¹³C NMR spectrum collected immediately after the same [D₈]THF solution had been exposed to a deficient amount of metal that exhibits almost 50% conversion of isocyanate into isocyanurate. (C) ¹³C NMR spectrum collected 4 h after the initial exposure to K metal. Spectrum (C) shows complete conversion to tris(1-naphthyl) isocyanurate. The inset is an expanded region of the isocyanurate carbonyl resonances.

Interestingly, nearly all of the ¹H and ¹³C NMR resonances associated with the naphthalene rings also exhibit unique chemical shifts for each of the isomers. A complete chemical shift assignment for all naphthyl ring carbon and hydrogen atoms for each diastereoisomer can be found in the Supporting Information. Separation of the two diastereoisomers by column chromatography made it possible to distinguish between the ¹H NMR resonances associated with each stereoisomer (Figure 3). We find that the ratio of *anti-2/syn-2* obtained from the potassium metal reduction of 1-naphthyl isocyanate was 70:30.

Figure 4 shows the density functional theory (DFT) calculated structures of both diastereoisomers and their relative energies. As predicted by the calculation, the orientation of each of the three naphthyl rings is orthogonal to the isocyanurate ring. The *anti*-2 isomer, as expected, was found to be thermodynamically more stable by approximately 2.3 kJ/mol, which is likely a consequence of the three naphthyl rings in *syn*-2 exhibiting more steric crowding. These calculated results would also explain why the sterically less crowded *anti*-2 is generated in higher yield.

Single crystals of *syn-2* and *anti-2* were isolated and characterized by X-ray crystallography, and the structures of these diasteroisomers can be seen in Figure 5. Notably, the *anti* isomer has a crystallographic twofold axis of symmetry upon which the O1 and C1 atoms are located. The N2 atoms and the atoms of the naphthyl group attached to it are disordered about this twofold axis (thus, they were refined with an occupancy factor of 0.5 with an idealized geometry for the naphthyl group). As expected, the isocyanurate rings are relatively planar. The C-N bond lengths within the syn-2 and anti-2 isocyanurate rings range from 1.391(3) to 1.401(10) Å; these distances are typical for isocyanurates.^[24] The C=O bond lengths also compare favorably with previously reported isocyanurates.^[24] In addition, it can be seen that all naphthyl groups are planar and are relatively orthogonal to the isocyanurate ring as predicted by the DFT calculations. The average dihedral angle between the naphthyl and isocyanurate rings in the two isomers is 78.2°; deviation from 90° is likely due to crystal packing. Most importantly, the X-ray structural data supports the NMR spectroscopic data in confirming the orientation of all three naphthyl groups in both the *syn-2* isomer and in the *anti-2* isomer.

In our previous studies with the alkali metal reduction of both alkyl and aryl isocyanate systems, we proposed that the cyclotrimerization process is initiated by the formation of the respective anion radical.^[19,20] The strongly nucleophilic anion radical is expected to attack the carbon atom within the NCO moiety of a neutral species (a strong electrophile) to initiate the cyclotrimerization process. Attack of a third neutral isocyanate will complete the cyclo-



Figure 3. (A) 500 MHz ¹H NMR spectrum collected 4 h after the initial exposure to K metal (same as Figure 1C). Spectrum (A) shows resonances from both diastereoisomers of 2 in a ratio of 70:30 (*anti-2/syn-2*). (B) and (C) ¹H NMR spectra associated with the *anti-2* and *syn-2* isomers, respectively, once isolated.



Figure 4. DFT B3LYP/6-31G* predicted geometries for the diastereoisomers of tris(1-naphthyl) isocyanurate (*syn*-2 and *anti*-2) with their relative energies (E).



Figure 5. ORTEP diagrams of *syn-2* and *anti-2*. Hydrogen atoms omitted for clarity, and ellipsoids are at 30% probability.

trimerization process. We envision that the formation of the tris(1-naphthyl) isocyanurate is also driven by the small amount of 1-naphthyl isocyanate anion radical (1⁻) generated by the potassium metal reduction of the neutral species (Scheme 1). The anion radical will then attack two additional neutral isocyanates resulting in the formation of the isocyanurate anion radical. Equilibrium electron transfer processes will regenerate 1⁻, which will further propagate the cyclotrimerization (Scheme 1, bottom). Detection of 1⁻ spectroscopically would provide strong evidence for this proposed mechanism, therefore the [D₈]THF solution was also interrogated by using EPR techniques immediately after exposure to the potassium metal.

Figure 6 shows the EPR spectrum obtained from the same solution used to monitor the conversion of 1 to 2 by NMR spectroscopy. A nearly perfect computer simulation reveals that the odd electron is coupled to seven protons and one nitrogen atom, which strongly suggests that the EPR signal comes from the anion radical of 1. This result is significant, because 1^- is only the second isocyanate anion radical system to be observed spectroscopically while in solution and under ambient temperature conditions.^[25] The EPR coupling constants for all protons and the one nitrogen atom found for 1^- are similar in magnitude to those coupling constants measured for the phenyl isocyanate anion radical, obtained under similar conditions, that were previously reported by us.^[20] To help assign the coupling



Scheme 1. Potassium metal reduction of 1-naphthyl isocyanate resulting in a rapid cyclotrimerization and the formation of tris(1-naphthyl) isocyanurate. The bottom reaction describes the equilibrium electron transfer process to propagate the synthesis of isocyanurate.

constants to the appropriate hydrogen atoms, we performed a DFT geometry optimization on 1^{-} at the B3LYP/6-311++G** level of theory along with predicted p_z electron



Figure 6. (Top) X-band EPR spectrum recorded at 295 K after a $[D_8]$ THF solution containing 1-naphthyl isocyanate (1) had been exposed to a deficient amount of K metal under vacuum. (Bottom) Computer-generated EPR spectrum using $a_N = 1.03$ G (1 N) and $a_H = of 1.64$ G (1 H), 1.34 G (1 H), 0.76 G (1 H), 0.73 G (1 H), 0.68 G (2 H), 0.080 G (1 H). The peak-to-peak line width (Δw_{pp}) is 0.1 G.

spin densities (Figure 7). We find that these predicted spin densities (shown in parentheses in Figure 7) are in good agreement with the experimental spin densities (upper numbers) that were obtained from the measured coupling constants (Figure 7) and the McConnell relationship.^[26] The discrepancies that are found between some of the experimental and theoretical spin densities (especially with the nitrogen spin density) are not surprising since ion association effects between the NCO moiety within 1⁻⁻ and the potas-



Figure 7. B3LYP/6-311++G** predicted geometry for the 1-naphthyl isocyanate anion radical (1⁻). The calculated p_z spin densities are given in parentheses, and the empirical spin densities are shown above them.

sium cation are expected in THF.^[27] The presence of ion association would likely augment the amount of electron density residing in the NCO group, which would account for the larger experimental spin density at the nitrogen atom than was predicted by these calculations.^[28]

Conclusions

It has been shown that two atropisomers of tris(1-naphthyl) isocyanurate, resulting from the hindered rotation of the N-naphthyl bonds, have been successfully synthesized by the alkali metal reduction of 1-naphthyl isocyanate. The cyclotrimerization is initiated, and propagated, by a small amount of 1-naphthyl isocyanate anion radical present in solution. The presence of this species was confirmed by EPR spectroscopy. The two diastereoisomers of tris(1naphthyl) isocyanurate were isolated, and their structure was confirmed by using ¹H and ¹³C{¹H} NMR spectroscopy. Single-crystal X-ray analysis also confirmed the arrangement of the naphthyl rings in the syn and anti isomers. Our results show that the alkali metal reduction of isocyanates can be a convenient and rapid method for the production of many interesting substituted isocyanurates, which may be studied for their unique physical and structural properties.

Experimental Section

Materials: Perdeuteriated tetrahydrofuran ($[D_8]$ THF) was purchased from Cambridge Isotope Inc. and stored under vacuum over NaK.

Reduction of 1-Naphthyl Isocyanate in [D₈]THF for EPR and NMR Experiments: The 1-naphthyl isocyanate was purified by vacuum distillation prior to use in all reduction experiments. A sealed glass tube (with fragile ends) was charged with 30 mg (0.18 mmol) of 1naphthyl isocyanate and placed into bulb E of the Pyrex glass apparatus shown in Figure 8. A small amount of potassium metal was placed into bulb B, which was then sealed at point A, and the entire apparatus was evacuated. The alkali metal was distilled into bulb D to form a pristine metal mirror; after this, bulb B was sealed at point C. Approximately 2.5 mL of THF (dried with NaK) were distilled from the vacuum system directly into bulb E, and the evacuated apparatus was sealed from the vacuum line at point F. The glass tube containing the isocyanate was broken by shaking and the solution was well mixed. Prior to beginning the reduction with potassium metal, a sample of the [D₈]THF solution was collected in one of the NMR tubes so that ¹H and ¹³C{¹H} NMR spectra of the isocyanate could be obtained. Exposure of the [D₈]THF solution to a deficient amount of potassium was done by simply pouring a portion of the solution onto the K metal. Once the solution turned to a greenish yellow solution, a second NMR sample was collected and periodically monitored by NMR spectroscopy to observe the cyclotrimerization of 1-naphthyl isocyanate to form tris(1-naphthyl) isocyanurate. The remaining solution in the apparatus was not exposed further to potassium metal once the second NMR sample had been harvested. This remaining solution was immediately analyzed, after the second NMR sample was collected, by X-band EPR spectroscopy for the presence of any anion radicals formed in the reduction. All NMR spectra were recorded with either a 400 or a 500 MHz Bruker Avance III spectrometer. EPR spectra were recorded with a Bruker EMX X-band EPR spectrometer. Once the conversion into isocyanurate was complete, the apparatus and the second NMR tube were opened and the contents removed. The two diastereoisomers of the tris(1-naphthyl) isocyanurate (*syn* and *anti*) were separated by silica gel column chromatography using a dichloromethane/ethyl acetate (98:2) mixture as the mobile phase. Upon removal of the mobile phase, a pure, white crystalline solid was obtained for both isomers. *anti*-C₃₃H₂₁N₃O₃ (507.16): calcd. C 78.00, H 4.00, N 8.30; found C 78.67, H 4.16, N 8.29. *syn*-C₃₃H₂₁N₃O₃ (507.16): calcd. C 78.00, H 4.00, N 8.30; found C 73.48, H 4.56, N 7.13.



Figure 8. Glass apparatus used in the NMR and EPR experiments for the potassium metal reduction of 1-naphthyl isocyanate in $[D_8]$ THF.

X-ray Crystallography: Single crystals of *syn*-**2**·2CH₂Cl₂ and *anti*-**2**·2CH₂Cl₂ were grown from CH₂Cl₂/Et₂O by the vapor diffusion technique. The crystals selected for diffraction experiments were coated with Paratone-N oil and then placed under a cold N₂ gas stream of a Bruker D8 diffractometer equipped with an APEX II CCD detector. Diffraction measurements were obtained by using graphite-monochromated Mo- K_{α} ($\lambda = 0.71073$ Å) radiation with the crystal cooled to -100 °C. Data were corrected for absorption by Gaussian integration from the indexed and measured crystal faces (SADABS).^[29] SHELXD was used to solve the structure, and the data were refined by full-matrix least squares on F^2 using SHELXL-2014.^[30,31] Hydrogen atoms were included as riding atoms and were placed in geometrically idealized positions with isotropic displacement parameters 120% of those of the U_{eq} values for their parent atoms. In solving the structure of *anti*-**2**·2CH₂Cl₂

the following pairs of distances were constrained to be equal (within 0.03 Å) during the refinement: d(N1-C1) = d(N1-C2), d(N2-C2) = d(N2-C3). The naphthyl group containing carbon atoms C20 through C29 was refined with an idealized geometry, with all C–C bond lengths fixed at 1.390 Å and all bond angles within this group fixed at 120.0°. See Table 1 for a summary of crystallographic data. CCDC-1408225 (for *syn-***2**·2CH₂Cl₂) and -1408226 (for *anti-***2**·2CH₂Cl₂) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Summary of crystallographic data.

	syn-2·2CH ₂ Cl ₂	anti-2·2 CH_2Cl_2
Empirical formula	C ₃₃ H ₂₁ N ₃ O ₃ ·2CH ₂ Cl ₂	C ₃₃ H ₂₁ N ₃ O ₃ ·2CH ₂ Cl ₂
M [g mol ⁻¹]	677.38	677.38
Space group	<i>C</i> 2/ <i>c</i> (no. 15)	<i>C</i> 2/ <i>c</i> (no. 15)
<i>a</i> [Å]	20.8470(9)	22.5158(19)
<i>b</i> [Å]	14.1127(6)	16.9754(15)
<i>c</i> [Å]	21.6173(10)	8.6721(7)
β [°]	102.9425(5)	106.6746(10)
V[Å ³]	6198.4(5)	3175.2
Ζ	8	4
<i>T</i> [°C]	-100	-100
Radiation (λ [Å])	$Mo-K_a$ (0.71073)	Mo- K_{α} (0.71073)
$\rho_{\rm calcd}$ [g cm ⁻³]	1.452	1.417
$\mu \text{ [mm^{-1}]}$	0.424	0.414
$R_1 [I \ge 2\sigma(I)]^{[a]}$	0.0583	0.0684
wR_2 (all data) ^[a]	0.1872	0.2078
$[a] R_1 = \Sigma F_o - F_c / \Sigma F_o ; wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^4)] \}^{1/2}.$		

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