N-heterocycle (tetrazole)-stabilized pseudocyclic λ ^{3}-iodane: Synthesis and reactivity

Avichal Vaish, Kapil Dev Sayala, Nicolay V. Tsarevsky

PII: S0040-4039(19)30750-6
DOI: https://doi.org/10.1016/j.tetlet.2019.150995
Reference: TETL 150995

To appear in: *Tetrahedron Letters*

Received Date: 27 June 2019
Revised Date: 25 July 2019
Accepted Date: 29 July 2019

Please cite this article as: Vaish, A., Sayala, K.D., Tsarevsky, N.V., *N*-heterocycle (tetrazole)-stabilized pseudocyclic λ ^{3}-iodane: Synthesis and reactivity, *Tetrahedron Letters* (2019), doi: https://doi.org/10.1016/j.tetlet.2019.150995

N-heterocycle (tetrazole)-stabilized pseudocyclic λ^3-iodane: Synthesis and reactivity

Avichal Vaish, Kapil Dev Sayala, and Nicolay V. Tsarevsky*
Department of Chemistry, Southern Methodist University, Dallas, TX 75206 USA
* Email: nvt@smu.edu, Tel: +1-214-768-3259

Abstract

An *N*-heterocycle-stabilized pseudocyclic λ^3-iodane with tetrazole as the stabilizing group was synthesized and its thermal stability and redox activity were studied. Simultaneous thermogravimetry analysis and differential scanning calorimetry revealed that the hypervalent iodine(III) compound started to degrade at 127 ºC and showed a notable exothermic decomposition peak at 147 ºC. The reduction potential was determined by cyclic voltammetry to be -0.38 V vs $AgNO_3$|Ag (CV) in dimethyl sulfoxide (at a scan rate of 0.2 V/s). The oxidative power of the polyvalent iodine compound with a tetrazole ligand was demonstrated by conducting oxidation of thioanisole to sulfoxide and dimerization of thiobenzamide to 3,5-diphenyl-1,2,4-thiadiazole.

Keywords: polyvalent iodine; tetrazole; oxidation; energetic materials

Introduction

Organic hypervalent (HV) iodine compounds have emerged as efficient, versatile and environmentally benign reagents for a plethora of synthetically useful oxidative transformations.[1-14] including oxidation and electrophilic group transfer reactions. Early examples of HV iodine-based oxidants such as iodosyl benzene (PhIO) had critical drawbacks including poor solubility and short bench lifetime. In a pioneering work, Carmalt and co-workers demonstrated that the extensive secondary intermolecular I···O interactions of unstabilized λ^3-iodanes produces highly insoluble and thermally labile polymeric networks.[15] To overcome this problem, Protasiewicz et al. developed stable and soluble ortho-sulfonyl- substituted iodosylbenzene (**1**) and ortho-phosphoryl-substituted iodylbenzene (**2**), which possess improved reactivity toward organic substrates.[16-19] Subsequently, Zhdankin and co-workers reported the first example of the pseudocylic benziodoxole triflate and tosylate (**3**).[20,21] Furthermore, several pseudocyclic *O*-donor-stabilized λ^3-iodanes with ether (**4**),[22,23] amide (**5**)[24] and nitro (**6**)[25] groups interacting with the I(III) centers were described. In 2017, Muniz reported first *N*-heterocycle-stabilized pseudocyclic HV iodine reagent (**8**) with an ortho-pyridinyl group.[26] Recently, Nachtsheim et al. reported a series of *N*-heterocycle stabilized pseudocyclic HV iodine reagents with different atoms in the ring (**9**) and showed that their reactivity can be easily tuned by altering the heterocycle.[27]

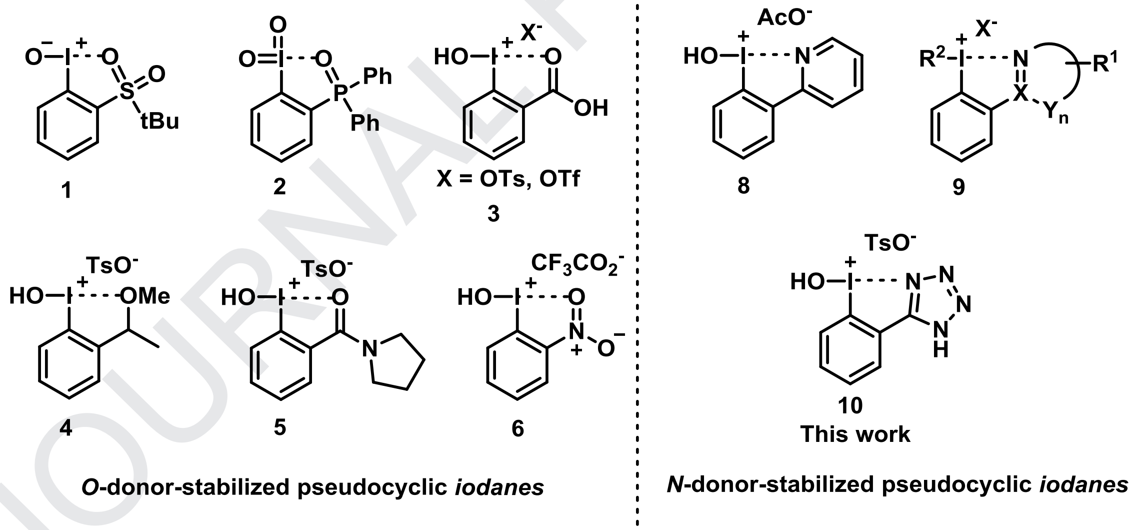
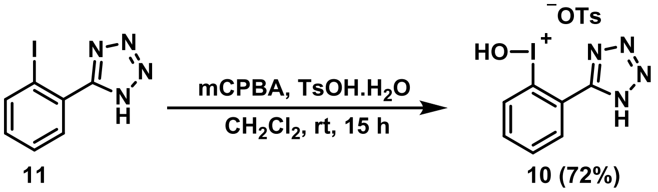


Figure 1. *O*- and *N*-stabilized pseudocyclic polyvalent iodine compounds.

We recently reported that tetrazolates RCN_4^-, similar to carboxylates RCO_2^-, can serve as ligands that bind to HV iodine(III) centers, and described the synthesis, structural characterization, thermal degradation, electrochemical behavior, and reactivity of a number of tetrazole-containing HV iodine(III) compounds with the general formula RCN_4-[I(Ar)-O)]$_n$-I(Ar)-N_4CR (R = CH_3, C_6H_5, or 4-$CH_3C_6H_4$, and n = 0, 1, ≥2; the compounds with n = 0 being the terazole analogues ArI(N_4CR)$_2$ of (diacyloxyiodo)arenes Ar(O_2CR)$_2$).[28] As a continuation of our studies, we now report the synthesis and properties of an *N*-tetrazole-stabilized pseudocyclic HV iodine(III) reagent, namely (2-(1H-tetrazol-5-yl)phenyl)(hydroxy)iodonium tosylate (**10**).

Results and Discussion

The precursor of the title compound, 5-(2-iodophenyl)-1H-tetrazole **11**, was synthesized in good yield (75%) by the reaction of 2-iodobenzonitrile with sodium azide in the presence of a protic acid (ammonium chloride) in *N*,*N*-dimethylformamide at 130 ºC for 20 h using a simplified literature[29] procedure. The monovalent iodine compound was then oxidized with meta-chloroperoxybenzoic acid (mCPBA) in the presence of *p*-toluenesulfonic acid monohydrate (TsOH.H_2O) in CH_2Cl_2 at room temperature for 15 h to afford **10** in good yield (72%), as shown in Scheme 1. The pseudocyclic HV iodine(III) compound with a single tetrazole ligand **10** was obtained in an analytically pure form as off-white powder after washing with diethyl ether (all starting materials are well soluble in excess of diethyl ether) and was found to be stable at room temperature for several weeks when kept in a vacuum desiccator.



Scheme 1. Synthesis of (2-(1H-tetrazol-5-yl)phenyl)(hydroxy)iodonium tosylate **10**.

The thermal stability of the λ^3-iodane **10** was examined by simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Samples were heated from 25 ºC to 550 ºC at a rate of 5 ºC/min under nitrogen. Both **10** and **11** were analyzed twice, and the averaged thermal decomposition curves are shown in Figure 2. The TGA curve of **10** exhibits a two-step degradation profile with a T_d (onset degradation temperature, at which 5% weight loss has taken place) of 142 ºC, and steep weight loss between 127 ºC and 152 ºC, with an exothermic signal in the DSC curve, due to the dissociation of the weak HV bond. Compound **11**, which also contains the thermally labile tetrazole group but no HV bonds, was more stable than **10** and started to degrade at 183 ºC without showing any prominent exothermic peak in the DSC curve save for a small peak at 210 ºC. The enthalpies of degradation (ΔH_d) were calculated by integrating the mentioned exothermic peaks and the average ΔH_d for compound **10** was 548±86 J/g, which was about 20-fold higher than that of compound **11** (27.5±7.5 J/g). This shows that compound **10** and potentially other tetrazole-containing hypervalent iodine(III) compounds can be used as energetic materials. Similarly, linear tetrazole-containing HV iodine(III) compounds were shown to degrade explosively at elevated temperatures,[28] although their enthalpies of thermolysis were not measured.

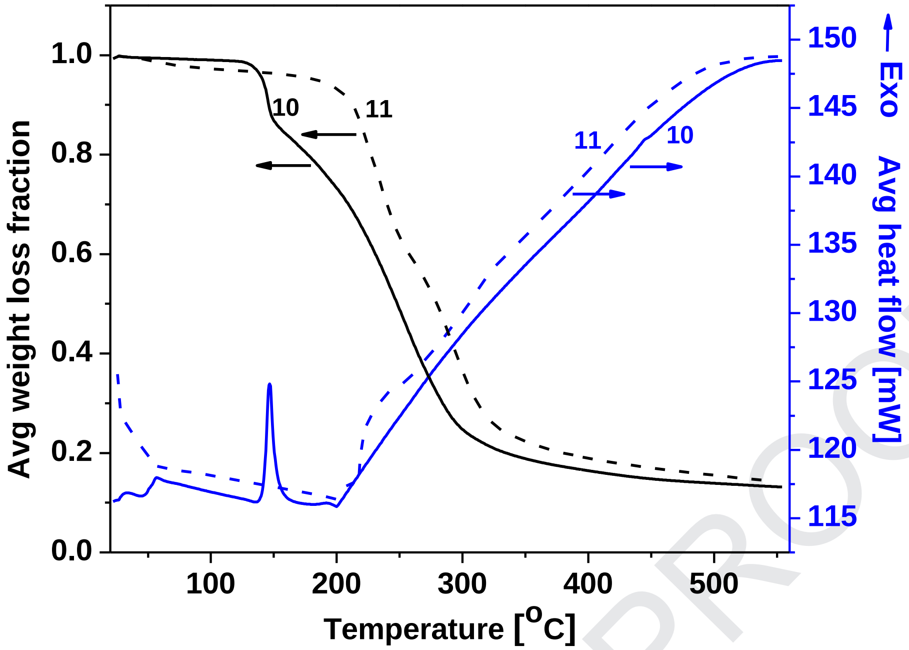
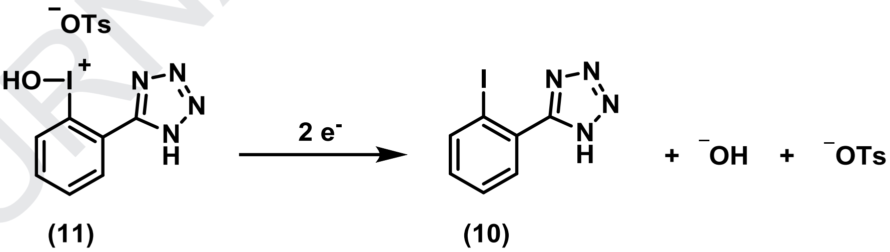


Figure 2. Simultaneous TGA and DSC analysis of compounds **10** (solid lines) and **11** (dashed lines).

HV iodine compounds are often used as oxidizing agents. Therefore, newly synthesized compound **10** was further analyzed by cyclic voltammetry (CV) to examine its oxidizing power. The starting materials used to prepare **10**, namely the tetrazole **11** and TsOH.H$_2$O were also analyzed to understand the origin of all the peaks in the cyclic voltammogram of **10**. The CV measurements (0.5 V to -1.5 V) were performed in dry and deoxygenated dimethyl sulfoxide (DMSO) (a good solvent for all compounds), using a glassy carbon electrode at a scan rate of 0.02 V/s using 0.1 M (n-Bu)$_4$NPF$_6$ as the electrolyte. The CV of DMSO containing only the electrolyte was studied also in the same voltage range to check its redox stability. DMSO did not show any peak in the above-mentioned region and hence it was concluded to be appropriate to use as solvent for the electrochemical studies. The cyclic voltammogram of **10** showed two main reduction peaks and several oxidation peaks (Figure 3). The first reduction peak at -0.38 V was due to the two-electron reduction of iodine(III) in **10** to iodine(I), i.e. formation of **11** as shown in Scheme 2. Formation of **11** is also observed in chemical reductions of **10** e.g. by thioanisole (Figure S7). This reaction is described in more detail below. The wide reduction peak observed at more negative voltages (in the range from 0.95 V to 1.05 V) is likely the result of overlap of the reduction peaks seen in the individual CV traces of 11 and TsOH (also shown in Figure 3). The nature of the products of reduction of TsOH and/or TsO^- is difficult to ascertain. The mechanism of reduction of aromatic sulfonic acids and/or sulfonate anions is complex and it depends upon the composition of the solvent, and often involves the cleavage of C-S bonds.[30] CV has been employed previously to study the reduction potential of various λ^3-iodanes.[28,31-33] HV iodine compounds show irreversible reduction peak, like compound **10**, due to the formation of iodine(I) compounds, typically iodoarenes. The reduction potentials of various HV iodine(III) compounds with tetrazole ligands were between -0.25 V to -0.43 V, i.e., comparable to the reduction potential of compound **10**.[28]



Scheme 2. Proposed pathway of electrochemical reduction of **11**.

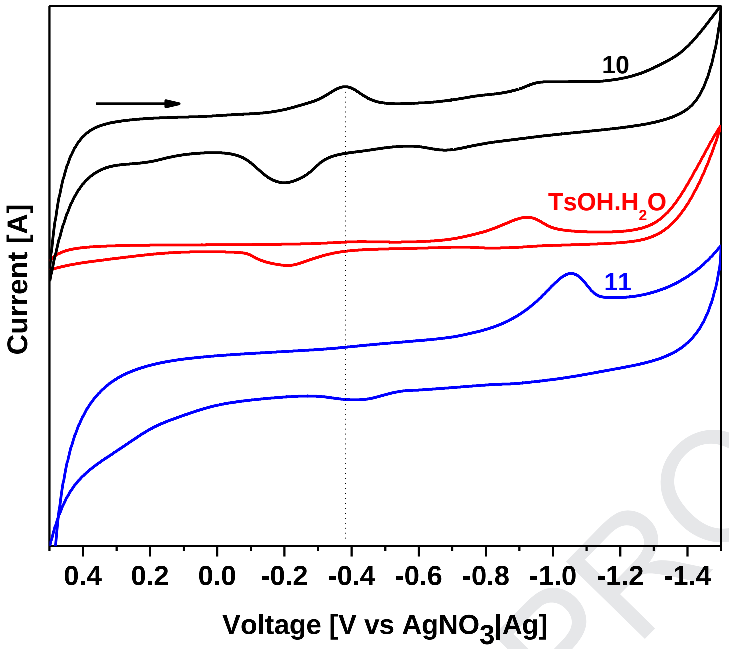
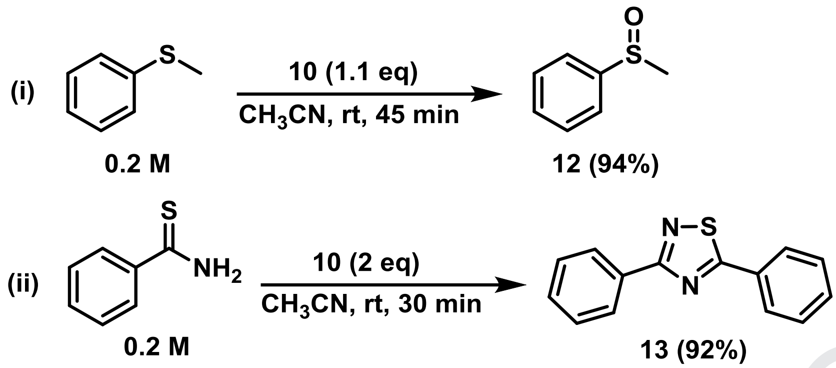


Figure 3. Cyclic voltammograms of 1 mM solutions of compounds **10** and **11**, and TsOH in anhydrous DMSO containing 0.1 M (n-Bu)$_4$NPF$_6$ at scan rate of 0.02 V/s using a glassy carbon electrode.

Compound **10** was then employed to oxidize thioanisole to the corresponding sulfoxide **12**. First, the preliminary reaction was carried out in DMSO-d$_6$ (Figure S7) and after confirming the formation of **12**, the reaction was then conducted in CH_3CN at room temperature for 45 min to simplify the workup and to increase the conversion by taking advantage of poor solubility of **11** in CH_3CN. Indeed, under these conditions the product was isolated in excellent yield (94%). Compound **10** was proved very useful in the synthesis of *N*,*S*-heterocycles as well. For instance, the oxidative dimerization of thiobenzamide in the presence of reagent **10**, conducted in CH_3CN at room temperature for 30 min, afforded 3,5-diphenyl-1,2,4-thiadiazole (**13**) in high isolated yield (92%). Both reactions are presented in Scheme 3.



Scheme 3. (i) Oxidation of thioanisole, (ii) oxidative rearrangement of thiobenzamide in the presence of λ^3-iodane **10**.

Conclusions

Tetrazole is demonstrated to serv as a suitable *N*-donor to stabilize pseudocyclic λ^3-iodane, (2-(1H-tetrazol-5-yl)phenyl)(hydroxy)iodonium tosylate, which was stable at room temperature for weeks. The identity of the tetrazole-containing HV iodine(III) compound was proved by NMR spectroscopy and high-resolution mass spectrometry. Although stable at ambient temperatures, the compound decomposed with the release of significant amount of heat at temperatures exceeding 140 ºC. The oxidative power of the iodonium salt was quantified by cyclic voltammetry and it was taken advantage of in the high-yield oxidation of thioanisole to sulfoxide and the oxidative dimerization of thiobenzamide to 3,5-diphenyl-1,2,4-thiadiazole.

Acknowledgements

The authors gratefully acknowledge financial support by the National Science Foundation through a CAREER grant (CHE-1455200) to N.V.T. Professor Isaac Garcia-Bosch and Khashayar Rajabimoghadam are acknowledged for helping with the electrochemical measurements.

References

(1) Brand, J. P.; Waser, J. *Chem. Soc. Rev*. **2012**, *41*, 4165.

(2) Brown, M.; Farid, U.; Wirth, T. *Synlett* **2013**, *24*, 424.

(3) Charpentier, J.; Früh, N.; Togni, A. *Chem. Rev*. **2015**, *115*, 650.

(4) Dohi, T.; Kita, Y. *Chem. Commun.* **2009**, 2073.

(5) Mekhman, S. Y.; Viktor, V. Z. *Curr. Org. Synth.* **2012**, *9*, 247.

(6) Parra, A.; Reboredo, S. *Chem. Eur. J.* **2013**, *19*, 17244.

(7) Romero, R. M.; Wöste, T. H.; Muñiz, K. *Chem. Asian J.* **2014**, *9*, 972.

(8) Samanta, R.; Matcha, K.; Antonchick, A. P. *Eur. J. Org. Chem.* **2013**, *2013*, 5769.

(9) Singh, F. V.; Wirth, T. *Chem. Asian J.* **2014**, *9*, 950.

(10) Uyanik, M.; Ishihara, K. *Chem. Commun.* **2009**, 2086.

(11) Wirth, T. *Hypervalent Iodine Chemistry*; Springer International Publishing, 2016.

(12) Yoshimura, A.; Zhdankin, V. V. *Chem. Rev.* **2016**, *116*, 3328.

(13) Zhdankin, V. V. *Hypervalent Iodine Chemistry: Preparation, Structure and Synthetic Applications of Polyvalent Iodine Compounds*; Wiley, 2013.

(14) Vaish, A.; Tsarevsky, N. V. *Main Group Strategies towards Functional Hybrid Materials* **2017**.

(15) Carmalt, C. J.; Crossley, J. G.; Knight, J. G.; Lightfoot, P.; Martín, A.; Muldowney, M. P.; Norman, N. C.; Orpen, A. G. *Chem. Commun.* **1994**, 2367.

(16) Macikenas, D.; Skrzypczak-Jankun, E.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **1999**, *121*, 7164.

(17) Macikenas, D.; Skrzypczak-Jankun, E.; Protasiewicz, J. D. *Angew. Chem. Int. Ed.* **2000**, *39*, 2007.

(18) Meprathu, B. V.; Justik, M. W.; Protasiewicz, J. D. *Tetrahedron Lett.* **2005**, *46*, 5187.

(19) Meprathu, B. V.; Protasiewicz, J. D. *Tetrahedron* **2010**, *66*, 5768.

(20) Yoshimura, A.; Klasen, S. C.; Shea, M. T.; Nguyen, K. C.; Rohde, G. T.; Saito, A.; Postnikov, P. S.; Yusubov, M. S.; Nemykin, V. N.; Zhdankin, V. V. *Chem. Eur. J.* **2017**, *23*, 691.

(21) Yoshimura, A.; Nguyen, K. C.; Klasen, S. C.; Saito, A.; Nemykin, V. N.; Zhdankin, V. V. *Chem. Commun.* **2015**, *51*, 7835.

(22) Hirt, Urs H.; Schuster, Martin F. H.; French, Andrew N.; Wiest, Olaf G.; Wirth, T. *Eur. J. Org. Chem.* **2001**, *2001*, 1569.

(23) Yudasaka, M.; Maruyama, T.; Yamaguchi, E.; Tada, N.; Itoh, A. *Eur. J. Org. Chem.* **2018**, *2018*, 550.

(24) Guilbault, A.-A.; Legault, C. Y. *ACS Catalysis* **2012**, *2*, 219.

(25) Nikiforov, V. A.; Karavan, V. S.; Miltsov, S. A.; Selivanov, S. I.; Kolehmainen, E.; Wegelius, E.; Nissinen, M. *ARKIVOC* **2003**, 191.

(26) Aertker, K.; Rama, R. J.; Opalach, J.; Muñiz, K. *Adv. Synth. Catal.* **2017**, *359*, 1290.

(27) Boelke, A.; Lork, E.; Nachtsheim, B. J. *Chem. Eur. J.* **2018**, *24*, 18653.

(28) Kumar, R.; Vaish, A.; Runčevski, T.; Tsarevsky, N. V. *J. Org. Chem.* **2018**, *83*, 12496.

(29) Finnegan, W. G.; Henry, R. A.; Lofquist, R. *J. Am. Chem. Soc.* **1958**, *80*, 3908.

(30) Simonet, J. In *The Chemistry of Sulphonic Acids, Esters and Their Derivatives*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1991, p 553.

(31) Colomer, I.; Batchelor-McAuley, C.; Odell, B.; Donohoe, T. J.; Compton, R. G. *J. Am. Chem. Soc.* **2016**, *138*, 8855.

(32) Kiyokawa, K.; Kosaka, T.; Kojima, T.; Minakata, S. *Angew. Chem. Int. Ed.* **2015**, *54*, 13719.

(33) Kokkinidis, G.; Hatzigrigoriou, E.; Sazou, D.; Varvoglis, A. *Electrochim. Acta* **1991**, *36*, 1391.

N-heterocycle (tetrazole)-stabilized pseudocyclic λ^3-iodane: Synthesis and reactivity

Avichal Vaish, Kapil Dev Sayala, and Nicolay V. Tsarevsky*

Department of Chemistry, Southern Methodist University, Dallas, TX 75206 USA

* Email: nvt@smu.edu, Tel: +1-214-768-3259

Highlights

- Synthesis of tetrazole-containing hypervalent iodine compound
- Studies of electrochemical behavior
- Studies of thermal stability and demonstration of highly exothermic decomposition
- Utility in oxidation and oxidative cyclization reactions

N-heterocycle (tetrazole)-stabilized pseudocyclic λ^3-iodane: Synthesis and reactivity

Avichal Vaish, Kapil Dev Sayala, and Nicolay V. Tsarevsky*

Department of Chemistry, Southern Methodist University, Dallas, TX 75206 USA

* Email: nvt@smu.edu, Tel: +1-214-768-3259

ToC graphic