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Several routes for the synthesis of 1,3,3-trinitroazetidine (TNAZ) have been investigated. Of these the most promising new method involves studies of additions of various reagents, X-Y, across the highly strained C(3)-N σ-bond in 3-ethyl-1-azabicyclo[1.1.0]butane. In the course of this study, it was found that reaction of this highly strained bicyclic amine with *in situ* generated HNO_2 resulted in addition across the C(3)-N bond with concomitant *N*-nitrosation of the resulting intermediate azetidine, thereby affording *N*-nitroso-3-ethyl-3-nitroazacyclobutane (54%), which was oxidized subsequently to the corresponding dinitroazetidine, *N*-nitro-3-ethyl-3-nitroazacyclobutane (89%). These observations provide the basis of the method with which a novel synthesis of TNAZ has been developed. Our objectives include: (i) development of improved methods to permit scale-up of our previously published TNAZ synthesis and (ii) introduction of environmentally benign routes to prepare key synthetic intermediates.

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Table of Contents

Improved Economical and Environmentally Benign Routes for the Large-Scale Synthesis of 1,3,3-Trinitroazetidine

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I. Overview/Abstract. Several routes for the synthesis of 1,3,3-trinitroazetidine (TNAZ) have been investigated. Of these the most promising new method involves studies of additions of various reagents, X-Y, across the highly strained C(3)-N σ-bond in 3-ethyl-1-azabicyclo[1.1.0]butane. In the course of this study, it was found that reaction of this highly strained bicyclic amine with *in situ* generated HNO_2 resulted in addi-tion across the C(3)-N bond with concomitant *N*-nitrosation of the resulting intermediate azetidine, thereby affording *N*-nitroso-3-ethyl-3-nitroazacyclobutane (54%), which was oxidized subsequently to the corresponding dinitroazetidine, *N*-nitro-3-ethyl-3-nitroazacyclobutane (89%). These observations provide the basis of the method with which a novel synthesis of TNAZ has been developed. Our objectives include: (i) development of improved methods to permit scale-up of our previously published TNAZ synthesis and (ii) introduction of environmentally benign routes to prepare key synthetic intermediates.

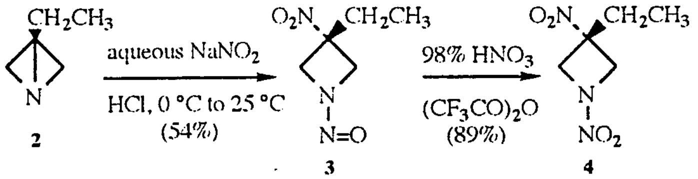
II. Scientific Issues Requiring Research. In 1969, Funke reported the synthesis of 3-ethyl-1-azabicyclo[1.1.0]butane and some aspects of its chemistry.[1] Since that time, relatively little interest has been shown in this unusual ring system. Our own interest in this compound stems from its potential use as a key intermediate in the synthesis of *N*,3-disubstituted azetidines, which otherwise can be quite difficult to obtain [e.g., via S_N2 displacements on *N*-substituted-3-tosyloxy- (or mesyloxy-) azdetidines].[2] Compounds of this type have attracted attention in recent years among members of the energetic materials community.[3] In addition, natural products chemists have been attracted to azetidine alkaloids, a class of strikingly bioactive compounds which have been isolated from marine organisms.[4] Finally, some unusual transformations of 3-functionalized azetidines that are of mechanistic interest have been reported recently.[5]

Previously,[6] we investigated reactions of 3-ethyl-1-azabicyclo[1.1.0]butane with a variety of electrophiles, e.g., N_2O_4, $ClCO_2Et$, Tf_2O, and Ms_2O. In each case, the observed reaction product(s) resulted via addition of the reagent, X-Y, across the highly strained C(3)-N σ-bond in the substrate, thereby affording new *N*-,3-disubstituted azetidines. We now have extended the range of reagents studied in an effort to explore the scope and limitations of reactions of this type. In the course of this work, we performed several of the addition reactions in aqueous solution in an effort to design environmentally benign (i.e., "green") synthetic routes to novel 3-substituted azetidines.

III. Key Results.

(A) Model Studies for Developing Novel Routes to 3-Substituted Azetidines. Compound **2** (Scheme 1), synthesized by using a previously published modification[6] of a literature procedure,[1] was employed as substrate in a model study.[6b] In our hands, reaction of **2** with *in situ* generated aqueous HNO_2 resulted in addition of the elements of HNO_2 across the C(3)-N σ-bond with concomitant *N*-nitrosation of the resulting intermediate azetidine, thereby affording **3** (54% yield, Scheme 1). Subsequent oxidation of the *N*-NO functionality by using 98% HNO_3-$(CF_3CO)_2O$ afforded the corresponding *N*-nitramine (**4**, 89% yield).[6b]

Scheme 1



(B) A Novel Synthesis of TNAZ. Our success in achieving the synthesis of **4** via the route shown in Scheme 1 pointed the way toward a novel TNAZ synthesis. The key step in this synthesis, shown in Scheme 2, is the formation of 1-azabicyclo[1.1.0]butane, **8**, which is removed rapidly from the reaction medium via azeotropic distillation and is trapped *in situ* in the distillation receiver via its reaction with aqueous $NaNO_2$-HCl, thereby affording *N*-nitroso-3-nitroazetidine (**9**) in low yield. The method by which **9** is converted subsequently into **1** is outlined in Scheme 2. The structure of 1,3-dinitroazetidine (**10**), an intermediate in the conversion of **9** to **1**, was established unequivocally via application of X-ray crystallographic methods. It should be noted that the formation and trapping of **8**, the key intermediate in the reaction sequence shown in Scheme 2, proceeds in poor yield (*ca.* 1%). In addition, the starting material, 2-amino-1,3-propanediol (**5**), although available commercially, nevertheless is very expensive.

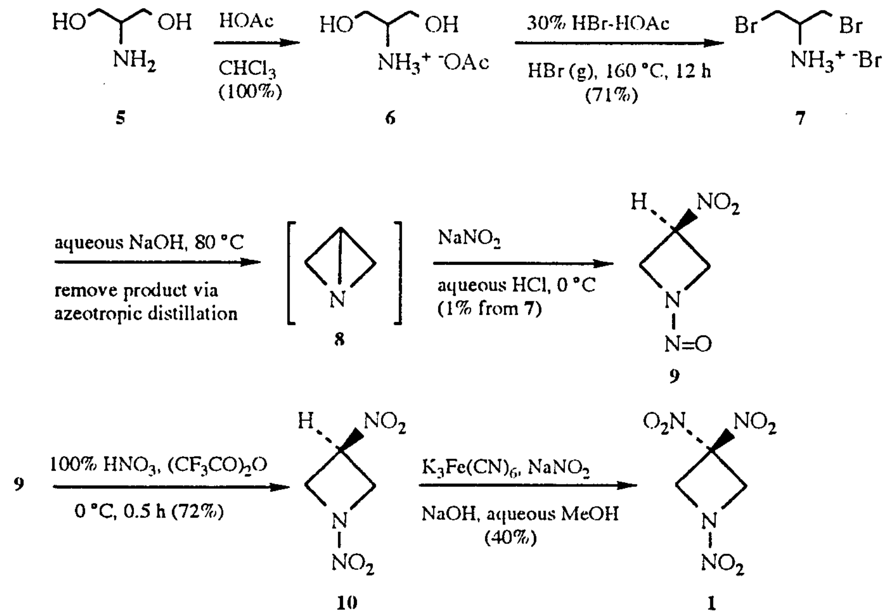
In attempting to address these issues, we studied an alternative reaction sequence which like the method shown in Scheme 2 preserves the unique approach of formation and trapping of an intermediate 1-azabicyclo[1.1.0]butane. Pertinent results in this regard are outlined in Scheme 3. Thus, 1-aza-3-(bromomethyl)bicyclo[1.1.0]butane (**13**) is generated by the method shown in Scheme 3 and subsequently is trapped by *in situ* generated HNO_2. This results in the formation of two *N*-nitrosoazetidines, **14** and **15**, each of which was oxidized[6b,7] subsequently to the corresponding *N*-nitro derivative (i.e., **16** and **17**, respectively). The structures of **16** and **17** have been established unequivocally via application of X-ray crystallographic methods. Hydrolysis[8] of **17** produced the corresponding alcohol, **18**, in good yield. Finally, under the reaction conditions shown in Scheme 3, **18** undergoes retro-Henry reaction,[9] and the resulting α-nitro anion subsequently suffers oxidative nitration *in situ*, thereby affording **1** (37% yield from **18**). Full experimental details regarding the syntheses shown in Schemes 2 and 3 have been published.[10]

Some important features of the reaction sequence shown in Scheme 3 should be noted. Thus, formation and trapping of the key intermediate in this reaction sequence, i.e., **13**, proceeds in *ca.* 7% overall yield from the starting material, a significant improvement in yield *vis-à-vis* that of the corresponding reaction sequence shown in Scheme 2. In addition, the route shown in Scheme 3 offers the distinct advantage that the 3-bromomethyl functionality in **17** can easily be replaced by NO_2 via a two-step reaction sequence that employs the retro-Henry reaction with concomitant oxidative nitration of a carbanionic intermediate. Finally, in contrast to the prohibitively high cost of **5** (Scheme 2), the starting material for the reaction sequence shown in Scheme 3 [i.e., tris(hydroxymethyl)aminomethane, **11**] is relatively inexpensive. We are continuing to pursue new high-yield routes to appropriately functionalized 1-azabicyclo[1.1.0]-butanes and to study the chemistry of these new systems as a potentially important class of alkylating agents.

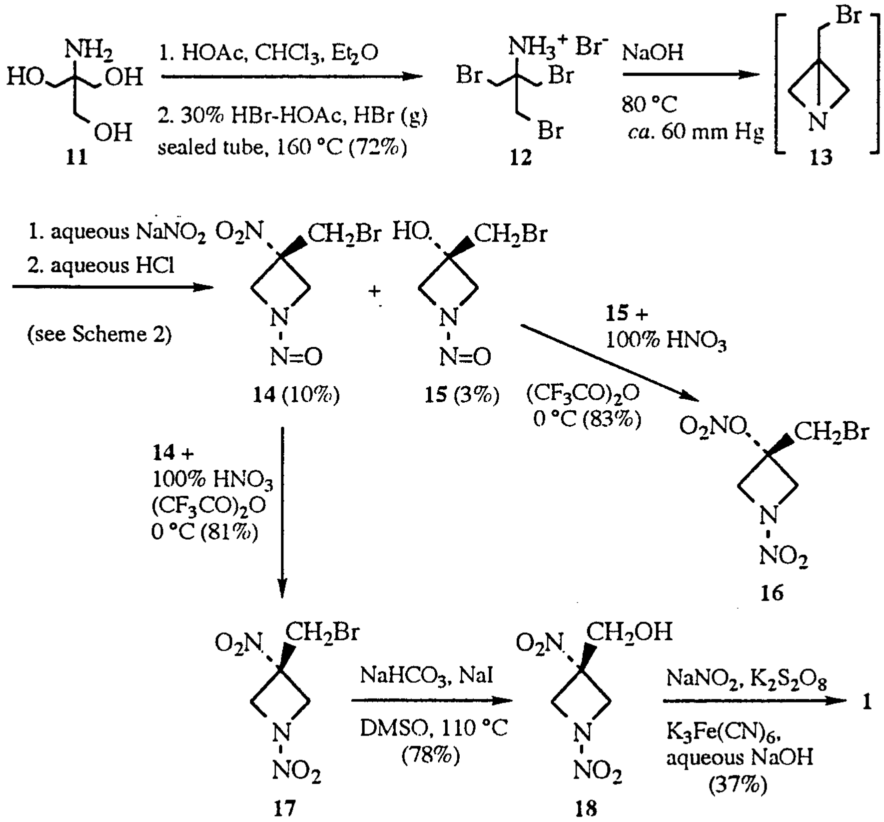
(C) Synthesis and Thermal Properties of 1,3-Dinitro-3-(1',3'-dinitroazetidin-3'-yl)azetidine. Although TNAZ is a powerful and insensitive explosive, its munitions applications have been limited by the fact that it is a low melting and relatively volatile solid. For this reason, it would be desirable to form a binary eutectic mixture of TNAZ with another structurally related but less volatile material. To this end, we have prepared 1,3-dinitro-3-(1',3'-dinitroazetidin-3'-yl)azeti-dine (**19**, Scheme 1) in the hope that it might form a binary eutectic with TNAZ which would reduce the volatility of the resulting explosive relative to TNAZ without concomitant sacrifice of other advantageous physical and chemical properties of pure TNAZ.

Our synthesis of **19** is shown in Scheme 4. The starting material for this reaction sequence, i. e., **20**, was prepared by using the method reported by Hiskey and Coburn.[11] Treatment of **20** with a solution of Br_2 in aqueous base resulted in retro-Henry reaction[9] with concomitant bromination of the resulting nitro-stabilized anion, thereby producing **21**. Subsequent

Scheme 2



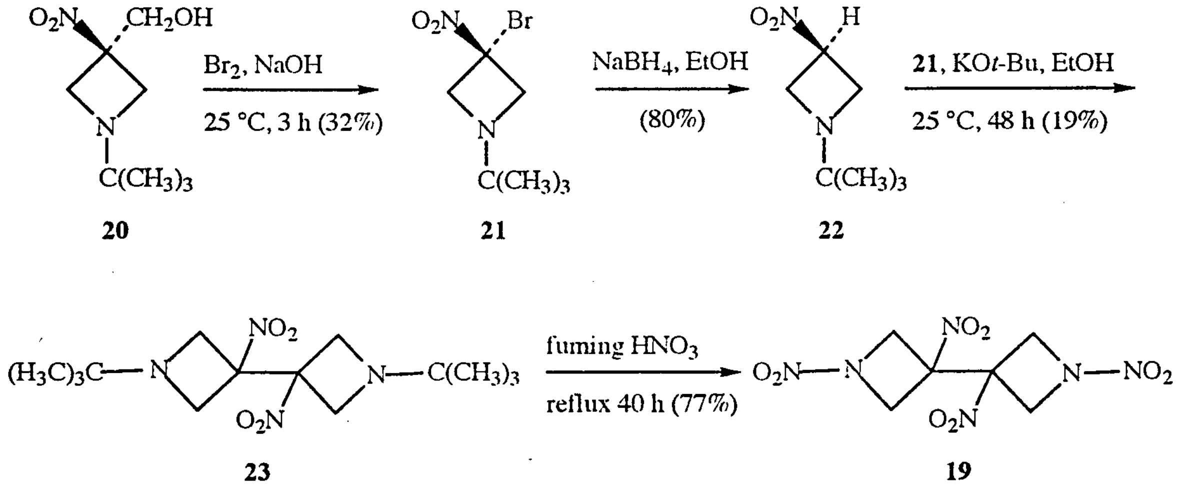
Scheme 3



reaction of **21** with $NaBH_4$-EtOH resulted in selective reduction of the carbon-bromine bond in **21**, thereby affording **22** in good yield.

Subsequent reaction of **22** with KO*t*-Bu-EtOH resulted in formation of the corresponding α-nitro carbanion which then was reacted with **21** to form a mixture of the corresponding 3'-azetidinyl-3-azetidine (**23**) along with unreacted **21** (as determined via analysis of the ^1H NMR spectrum of the crude product). In our hands, this mixture of **23** and **21** could not be separated, either by fractional recrystallization or by column chromatography. It proved advantageous to react this mixture as obtained with $NaBH_4$. Under these conditions, **21** is reduced to **22**, but **23** remains unaffected. The resulting mixture of **23** and **22** can be separated readily via column chromatography. The structure of **23** was established unequivocally via application of X-ray crystallographic methods. Finally, when refluxed with fuming nitric acid, **23** was converted into the target molecule, **19**, in good yield.

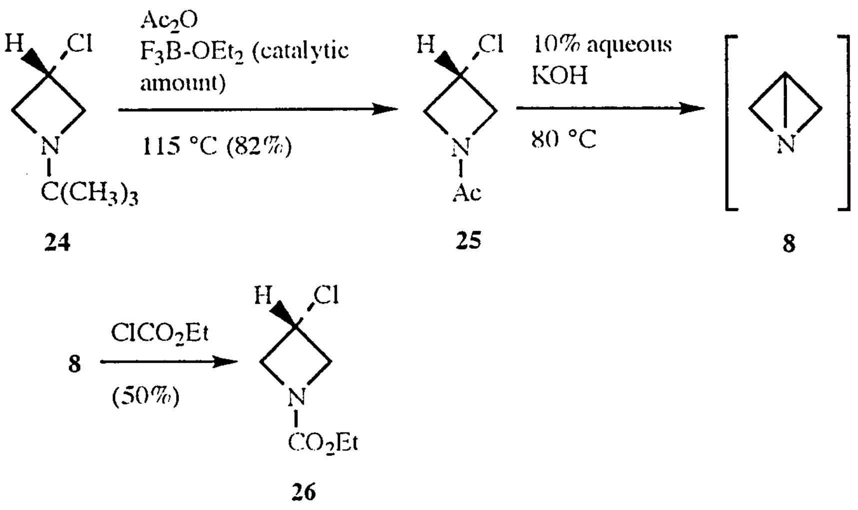
Scheme 4



The foregoing results, along with a detailed analysis of thermal properties of **19** (alone and in binary mixtures with TNAZ), are summarized in a recent U. S. Air Force Technical Report and in a forthcoming publication.[12]

(D) Application of Dave's Method for Generating 1-Azabicyclo[1.1.0]butane to the Synthesis of TNAZ. In 1996, Dave[13] reported a novel procedure for acylative dealkylation of 3-substituted *N*-*t*-butylazetidines that lends itself readily to a novel synthesis of 1-azabicyclo-[1.1.0]butane. His approach, shown in Scheme 5, represents a highly significant new development with potential application for improving a key step in our previously published TNAZ synthesis.

Scheme 5



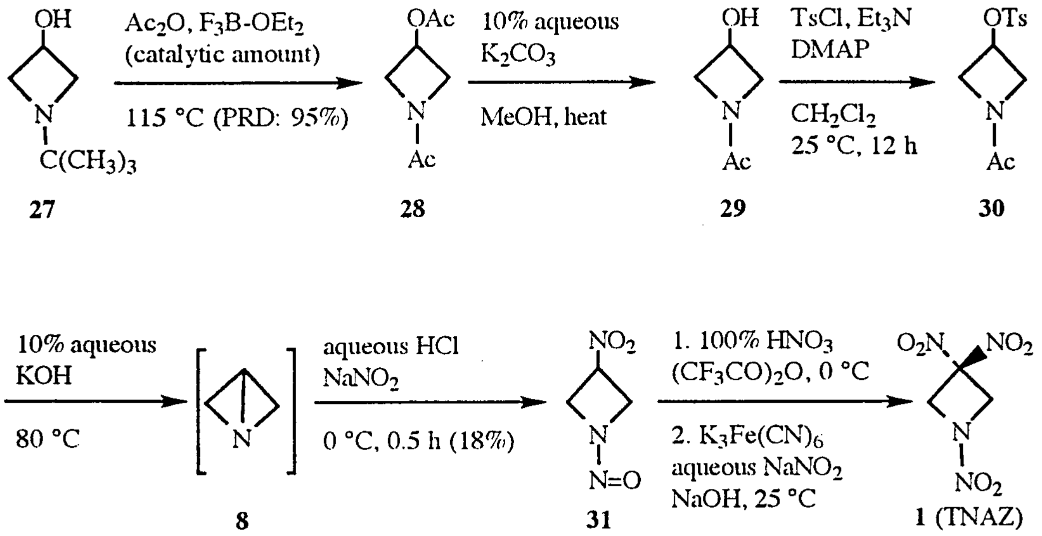
Subsequently, we have adapted the approach shown in Scheme 5 to a novel synthesis of TNAZ simply by trapping nascent 1-azabicyclo[1.1.0]butane *in situ* with aqueous nitrous acid. The reaction sequence used for this purpose is shown in Scheme 6.[14]

(E) A New Approach for Generating 1-Azabicyclo[1.1.0]butane. Allylamine (**33**) was chosen as an inexpensive and readily available starting material for this study. First, **33** was reacted with *N*-chlorosuccinimide. The reaction product was not isolated; instead, it was treated with a suspension of KO*t*-Bu in heptane-octane. The reaction mixture was subjected to distillation, whereupon 1-azabicyclo[1.1.0]butane (**8**) was removed from the reaction medium as soon as it was being generated. Nascent **8** thereby obtained was trapped in the distillation receiver via reaction with aqueous nitrous acid, thereby affording *N*-nitroso-3-nitroazetidine, **31**. Subsequent oxidation of **31** to *N*,3-dinitroazetidine followed by oxidative nitration of this intermediate afforded TNAZ (**1**).[15] The overall reaction sequence is summarized in Scheme 7.[15]

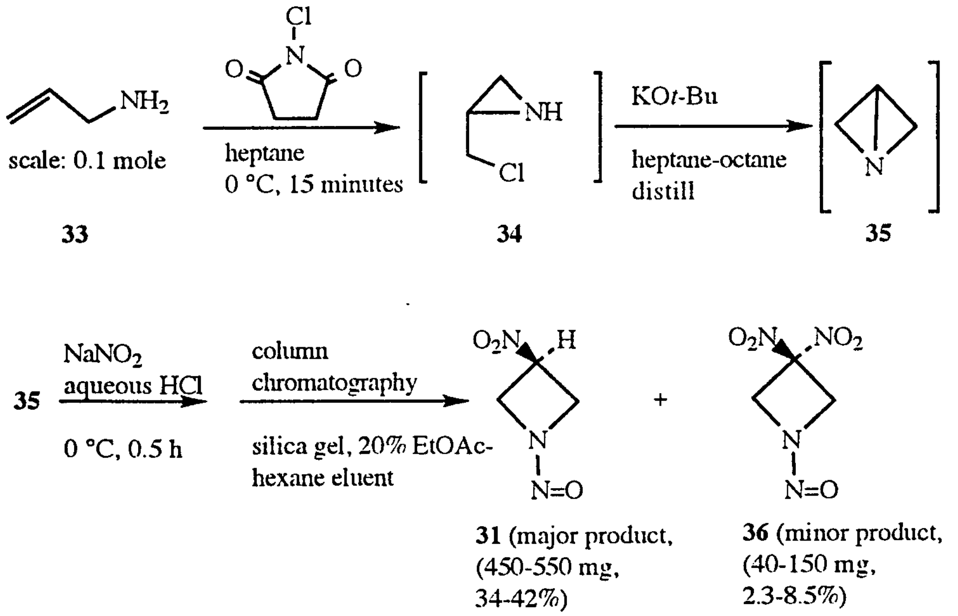
(F) Novel Routes to *N*-Substituted Azetidin-3-ones. *N*-Substituted azetidin-3-ones have proved to be valuable synthetic intermediates for the synthesis of novel energetic materials.[11,16,17] Compounds of this type have also been used as intermediates in natural product synthesis[18] and as starting materials for preparing compounds of biological and/or pharmacological interest.[19]

In the past, *N*-Substituted azetidin-3-ones were prepared by multistep synthesis by starting with acyclic starting materials.[2] As part of an ongoing study[10,20-23] of the synthesis and chemistry of 3-substituted 1-azabicyclo[1.1.0]butanes,[1] we have developed new methodolgy that

Scheme 6



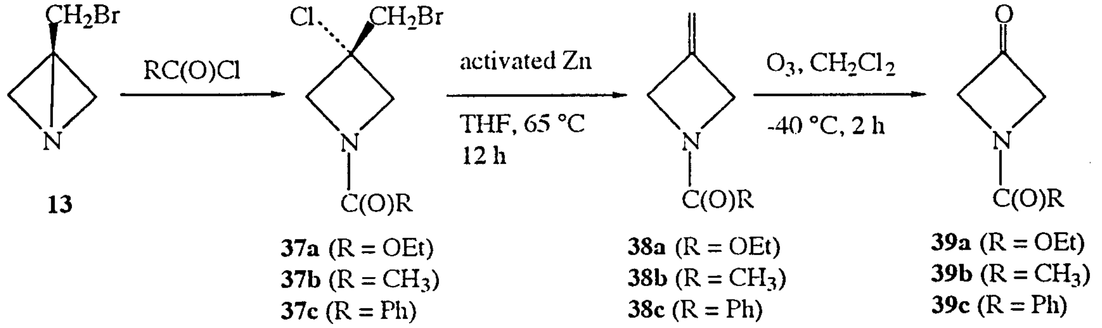
Scheme 7



employs these highly strained azabicyclic compounds as key intermediates for preparing *N*-substituted azetidine-3-ones. In this connection, we now report new methods for preparing *N*-ethoxycarbonyl-, *N*-acetyl-, and *N*-benzoyl-1-azabicyclo[1.1.0]butanes (**39a-39c**, respectively).

The methodology employed herein to prepare *N*-substituted azetidin-3-ones is summarized in Scheme 8.

Scheme 8



13

37a (R = OEt)
37b (R = CH_3)
37c (R = Ph)

38a (R = OEt)
38b (R = CH_3)
38c (R = Ph)

39a (R = OEt)
39b (R = CH_3)
39c (R = Ph)

Experimental Section: Novel Routes to *N*-Substituted Azetidin-3-ones.

Melting points are uncorrected. Elemental microanalytical data was obtained by personnel at M-H-W Laboratories, Phoenix, AZ. High-resolution mass spectral data for **38b** were obtained at the Mass Spectrometry Facility at the Department of Chemistry and Biochemistry, University of Texas at Austin by using a ZAB-E double sector high-resolution mass spectrometer (Micromass, Manchester, England) that was operated in the chemical ionization mode.

***N*-Ethoxycarbonylazetidin-3-one (39a).** A solution of **38a**[23] (1.50 g, 10.1 mmol) in CH_2Cl_2 (40 mL) was cooled to -40 °C via application of an external dry ice-CH_3CN cold bath Ozone gas was passed through the solution for ca. 2 h, at which time tlc analysis of the reaction mixture revealed the absence of **38a**. Argon was bubbled through the cold reaction mixture to purge excess ozone, and the reaction was quenched via addition of $(CH_3)_2S$ (4 mL, excess). The external cold bath then was removed, and the quenched reaction mixture was allowed to warm gradually to ambient temperature. The reaction mixture was concentrated *in vacuo*, and the residue was purified via column chromatography on silica gel by eluting with 30% EtOAc-hexane. Pure **39a** (1.02 g, 71%) was thereby obtained as a colourless microcrystalline solid mp 45.0-46.5 °C (lit[23] mp 45-47 °C). The IR, ^1H NMR, and ^{13}C NMR spectra of the material thereby obtained were essentially identical to the corresponding spectra which have been reported previously.[24]

***N*-Acetyl 3-(bromomethyl)-3-chloroazetidine 37b).** A solution of **13**[10,23] (1.48 g, 10 mmol) in Et_2O (50 ml) under argon was cooled to 0 °C via application of an external ice-water bath. To this cooled solution was added dropwise with stirring acetyl chloride (AcCl, 785 mg, 10 mmol). After the addition of AcCl had been completed, the external cold bath was removed, and the resulting mixture was allowed to warm gradually to ambient temperature while being stirred for 12 h. The reaction mixture was concentrated *in vacuo*, and the residue was purified via column chromatography on silica gel by eluting with 50% acetone-hexane. Pure **37b** (1.5 g, 66%) was thereby obtained as a colorless oil; IR (neat) 2953 (m), 1650 (s), 970 (m), 877 cm^{-1} (w); ^{1}H NMR ($CDCl_3$) δ 1.85 (s, 3 H), 3.75 (s, 2 H), 4.11-4.48 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 18.8 (q), 38.3 (t), 59.1 (s), 60.7 (t), 63.1 (t), 170.1 (s). Anal. Calcd for $C_6H_9ONClBr$: C, 31.82; H, 4.01. Found: C, 32.09; H, 4.09.

***N*-Acetyl-3-methyleneazetidine (38b). Method A.** A mixture of **37b** (1.45 g, 6.4 mmol) and activated Zn[24] (3.0 g, 46 mmol) in dry THF (60 mL) under argon was heated with stirring at 65 °C for 12 h. The reaction mixture was allowed to cool gradually to ambient temperature and then was filtered. The filtrate was concentrated *in vacuo*, and the residue was purified via column chromatography on neutral alumina by eluting with 50% acetone-hexane. Pure **38b** (640 mg, 90%) was thereby obtained as a colorless oil; IR (neat) 3097 (w), 3002 (w), 2932 (s), 2876 (m), 1650 (s), 1446 (vs), 914 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 1.80 (s, 3 H), 4.35-4.44 (m, 2 H), 4.51-4.60 (m, 2 H), 4.90-4.98 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.7 (q), 56.7 (t), 58.9 (t), 108.1 (d), 134.8 (s), 170.5 (s). Anal. Chemical Ionization (CI) HRMS Calcd for C_6H_9NO: $(M_r + 1)^+$ *m/z* 112.07624. Found: $(M_r + 1)^+$ *m/z* 112.07572 (deviation -4.6 ppm).

Method B. A mixture of **37b** (6.0 g, 26.5 mmol) and NaI (20 g, 134 mmol) in acetone (200 mL) was refluxed for 18 h. The reaction mixture was allowed to cool to ambient temperature and then was treated with 20% aqueous $NaHSO_3$ (15 mL). The resulting mixture was concentrated *in vacuo*.. The residue was extracted with EtOAc (2 x 100 mL), and the combined extracts were washed successively with water (40 mL) and brine (2 x 30 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on neutral alumina by using 50% acetone-hexane as eluent. Pure **38b** (2.2 g, 74%) was thereby obtained as a colorless oil. The IR, ^{1}H NMR, and ^{13}C NMR spectra of this material were identical in all respects with the corresponding spectra obtained for a sample of **38b** that was prepared previously (see Method A,*vide supra*).

***N*-Acetylazetidin-3-one (39b).** A solution of **38b** (2.0 g, 18 mmol) in CH_2Cl_2 (60 mL) was cooled to -40 °C via application of an external dry ice-CH_3CN cold bath Ozone gas was passed through the solution for *ca.* 2 h, at which time tlc analysis of the reaction mixture revealed the absence of **38b**. Argon was bubbled through the cold reaction mixture to purge excess ozone, and the reaction was quenched via addition of $(CH_3)_2S$ (6 mL, excess). The external cold bath then was removed, and the quenched reaction mixture was allowed to warm gradually to ambient temperature. The reaction mixture was concentrated *in vacuo*, and the residue was purified via column chromatography on neutral alumina by eluting with 50% EtOAc-hexane. Pure **39b** (1.4 g, 69%) was thereby obtained as a colorless oil. The IR, ^{1}H NMR, and ^{13}C NMR spectra of the material thereby obtained were essentially identical to the corresponding spectra which have been reported previously.[13]

***N*-benzoyl-3-(bromomethyl)-3-chloroazetidine (37c).** A solution of **13**[10,23] (1.48 g, 10 mmol), NaOH (20 g, 0.5 mole) in Et_2O (50 ml) under argon was cooled to 0 °C via application of an external ice-water bath. To this cooled solution was added dropwise with stirring benzoyl chloride (1.40 g, 10 mmol). After the addition of benzoyl chloride had been completed, the external cold bath was removed, and the resulting mixture was allowed to warm gradually to ambient temperature while being stirred for 12 h. The reaction mixture was concentrated *in vacuo*, and the residue was purified via column chromatography on silica gel by eluting with 30% EtOAc-hexane. Pure **37c** (2.13 g, 74%) was thereby obtained as a colorless oil; IR (neat) 3067 (w), 2951 (m), 1640 (vs), 1419 (vs), 713 cm^{-1} (vs); ^1H NMR ($CDCl_3$) δ 3.70 (s, 2 H), 4.30-4.64 (m, 4 H), 7.61-7.27 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 38.3 (t), 60.0 (s), 61.5 (t), 65.8 (t), 127.7 (d), 128.4 (d), 131.4 (d), 132.0 (s), 170.2 (s). Anal. Calcd for $C_{11}H_{11}OBrClN$: C, 45.79; H, 3.84. Found: C, 45.63; H, 4.04.

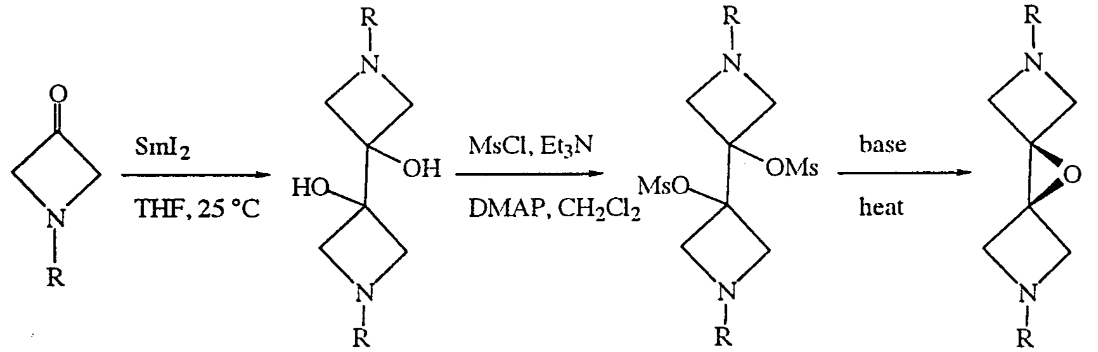
***N*-benzoyl-3-methyleneazetidine (38c).** A mixture of **37c** (1.4 g, 4.8 mmol) and activated Zn[24] (2.18 g, 33.6 mmol) in dry THF (100 mL) under argon was heated with stirring at 65 °C for 12 h. The reaction mixture was allowed to cool gradually to ambient temperature and then was filtered. The filtrate was concentrated *in vacuo*, and the residue was purified via column chromatography on neutral alumina by eluting with 50% EtOAc-hexane. Pure **38c** (730 mg, 88%) was thereby obtained as colorless oil; IR (neat) 3067 (m), 3001 (w), 2935 (s), 1647 (vs), 1578 (s), 883 cm^{-1} (vs); ^1H NMR ($CDCl_3$) δ 4.75 (s, 4 H), 5.05 (s, 2 H), 7.30-7.48 (m, 3 H), 7.60-7.68 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 57.8 (t), 61.7 (t), 107.6 (t), 127.6 (d), 128.2 (d), 130.9 (d), 133.0 (s), 136.8 (s), 170.1 (s). Anal. Calcd for $C_{11}H_{11}NO$: C, 76.28; H, 6.40. Found: C, 76.40; H, 6.64.

***N*-Benzoylazetidin-3-one (39c).** A solution of **38c** (200 mg, 1.16 mmol) in CH_2Cl_2 (20 mL) was cooled to -40 °C via application of an external dry ice-CH_3CN cold bath. Ozone gas was passed through the solution for *ca.* 2 h, at which time tlc analysis of the reaction mixture revealed the absence of **38c**. Argon was bubbled through the cold reaction mixture to purge excess ozone, and the reaction was quenched via addition of $(CH_3)_2S$ (2 mL excess). The external cold bath was removed, and the quenched reaction mixture was allowed to warm gradually to ambient temperature. The reaction mixture was concentrated *in vacuo*, and the residue was purified via column chromatography on silica gel by eluting with 30% EtOAc-hexane. Pure **39c** (139 mg, 68%) was thereby obtained as viscous, gummy oil. The IR, ^1H NMR, and ^{13}C NMR spectra of the material thereby obtained were essentially identical to the corresponding spectra that have been reported previously for authentic **39c**.[18]

(G) Samarium Iodide Promoted Coupling of *N*-Substituted Azetidin-3-ones. A Novel Route to Spiroannulated Heterocyclic Oxiranes. The chemistry of *N*-substituted azetidin-3-ones has received considerable attention in recent years.[2,3c,6,10,13,16,21] In particular, functionalized azetidin-3-ones have been used as intermediates in the synthesis of new energetic materials, e.g., 1,3,3-trinitroazetidine ("TNAZ").[2,3c,10,13,16] In the present study, samarium iodide promoted reductive coupling of *N*-substituted azetidin-3-ones have been investigated, and some aspects of the chemistry of the resulting "pinacols" have been explored.

Samarium iodide promoted reductive coupling was performed by using three *N*-substituted azetidin-3-ones, i.e., **40a-40c** as substrates (Scheme 9). In our hands, each of the three reductive coupling reactions proceeded smoothly to afford the corresponding pinacol (**41a-41c**, respectively). Each of the pinacols, in turn, could be converted into the corresponding dimesylate (**42a-42c**, respectively) via reaction with MsCl-Et$_3$N in the presence of dimethylaminopyridine (DMAP).

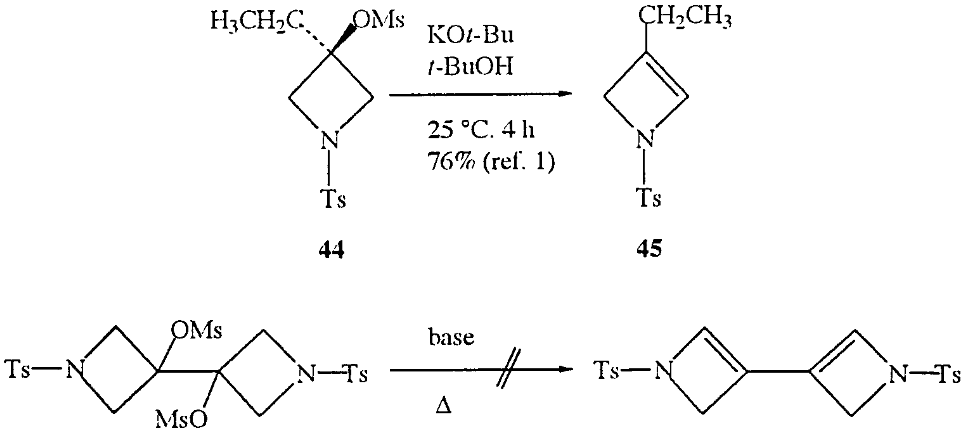
Scheme 9



40a (R = CO$_2$Et)	**41a** (R = CO$_2$Et, 70%)	**42a** (R = CO$_2$Et, 73%)	**43a** (R = CO$_2$Et, 91%)
40b (R = Ts)	**41b** (R = Ts, 73%)	**42b** (R = Ts, 69%)	**43b** (R = Ts, 84%)
40c (R = CHPh$_2$)	**41c** (R = CHPh$_2$, 71%)	**42c** (R = CHPh$_2$, 85%)	**43c** (R = CHPh$_2$, 0%)

Initially, our interest in systems of the type **42** (Scheme 1) was to attempt base-promoted E2 elmination of two equivalents of MsOH, thereby producing an unusual, conjugated bis(enamine). However, despite several attemps, we were unable to promote elimination in this system (e.g., note our inability convert **42b** into **46**; see Scheme 2). This result is particularly vexing, since we have shown previously that *N*-tosyl-3-ethyl-3-mesyloxyazetidine (**44**) undergoes smooth base-promoted elimination of the elements of MsOH to afford the corresponding, substituted 2-azetine (**45**, Scheme 10).[6a]

Scheme 10



44 45

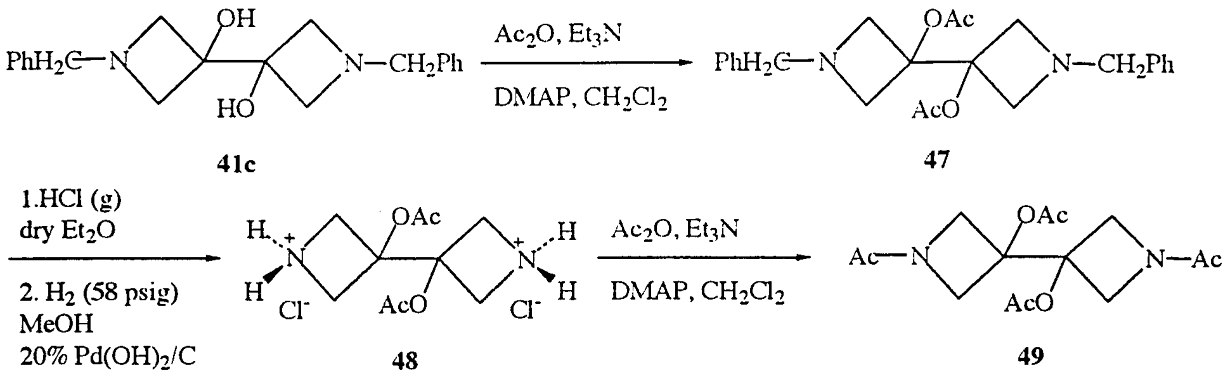
42b 46

Instead, in our hands, under the basic conditions employed (see the Experimental Section), competing nucleophilic displacement of one of the OMs groups in **42a** and **42b** by hydroxide ion (presumably either from water or from KOH that might have been present in KO*t*-Bu) occurred with concomitant intramolecular nucleophilic displacement of the remaining OMs group by -O:⁻. In this way, two novel, spiroannulated oxiranes (i.e., **43a** and **43b**) were prepared in excellent yield (91% and 84% from **42a** and **42b**, respectively, see Scheme 9). The structures of three compounds that are involved in the reaction sequence shown in Scheme 9, i.e., **41a**, **41b**, and **43b**, were established unequivocally via application of X-ray crystallographic methods.

Interestingly, **42c** proved to be inert toward base under the same conditions that had been used previously to convert **42a** and **42b** into the corresponding oxiranes (i.e., **43a** and **43b**, respectively). The reasons for the failure of **42c** to undergo base-promoted conversion into the corresponding spirocyclic oxirane, **43c**, are not apparent to us and are being investigated further in our laboratory.

In the course of this study, some additional reactions of **41a** were investigated; the results thereby obtained are summarized in Scheme 11. Thus, **41a** was converted into the corresponding bis(*O*-acetyl) derivative, **47**. The structure of **47**, was established unequivocally via application of X-ray crystallographic methods. Subsequently, the *N*-benzyl groups in **47** were removed via hydrogenolysis, and the resulting product, **48**, was converted into the corresponding bis(*N*-acetyl) derivative, **49**.

Scheme 11



Experimental Section. Samarium Iodide Promoted Coupling of *N*-Substituted Azetidin-3-ones.

Melting points are uncorrected. Elemental microanalytical data was obtained by personnel at M-H-W Laboratories, Phoenix, AZ. High-resolution chemical ionization mass spectral data for **10** were obtained by Professor Jennifer S. Brodbelt (Department of Chemistry, University of Texas at Austin).

***N,N'*-Bis(ethoxycarbonyl)-3-hydroxy-3-(3'-hydroxy-3'-azetidinyl)azetidine (41a).** To a solution of 0.1 M solution of SmI_2 in THF (100 mL, 10 mmol) under argon was added *N*-(ethoxycarbonyl)azetidin-3-one[23] (**40a**, 1.43 g, 10 mmol), and the resulting mixture was stirred at ambient tem-perature for 8 h. To the reaction mixture was added 0.1 N aqueous HCl (20 mL, excess), and the resulting aqueous suspension was extracted with EtOAc (3 x 50 mL). The combined organic extracts were washed sequentially with 10% aqueous $NaHCO_3$ (2 x 20 mL), water (30 mL), and brine (2 x 20 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 60% EtOAc-hexane. Pure **41a** (1.0 g, 70%) was thereby obtained as colorless microcrystalline solid: mp 230 °C (dec.); IR (KBr) 3418 (vs), 2980 (s), 2532 (vs), 1700 (vs), 1471 (vs), 777 cm^{-1} (s); ^1H NMR (DMSO-d_6) δ 1.22 (t, J = 7.3 Hz, 6 H), 3.80 (d, J = 9.4 Hz, 4 H), 3.96-4.13 (m, 8 H), 6.25 (br s, 2 H); ^{13}C NMR (DMSO-d_6) δ 13.3 (q), 57.0 (t), 57.1 (t), 57.2 (t), 57.5 (t), 60.6 (t), 70.5 (s), 156.6 (s). Anal. Calcd for $C_{12}H_{20}N_2O_6$: C, 49.99: H, 6.99. Found: C, 49.78; H, 6.92. The structure of **41a** was established unequivocally via application of X-ray crystallographic techniques (*vide infra*).

***N,N'*-Bis(ethoxycarbonyl)-3-mesyloxy-3-(3'-mesyloxy-3'-azetidinyl)azetidine (42a).** A solution of **41a** (810 mg, 2.8 mmol) in CH_2Cl_2 (15 mL) under argon was cooled to 0 °C via application of an external ice-water bath. To this cooled solution was added MsCl (958 mg, 8.4

mmol). To the resulting solution under argon was added dropwise with stirring a solution of Et_3N (2.83 g, 28 mmol) and 4-dimethylaminopyridine (DMAP, 100 mg, 0.82 mmol) in CH_2Cl_2 (5 mL), and the reaction mixture was stirred at 0-10 °C for 3 h. The external ice-water bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature with stirring during 3 h. To the reaction mixture was added CH_2Cl_2 (80 mL), and the resulting mixture was washed sequentially with water (20 mL), 10% aqueous $NaHCO_3$ (20 mL), and brine (20 mL). The organic layer was dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on acid-free silica gel that had been pre-treated with Et_3N by eluting with 40% EtOAc-hexane. Pure **42a** (900mg, 73%) was thereby obtained as colorless microcrystalline solid: mp 124-125 °C; IR (KBr) 3022 (s), 1715 (vs), 1346 (vs), 1159 (vs), 885 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.21 (t, J = 7.1 Hz, 6 H), 3.10 (s, 6 H), 4.05-4.26 (m, 8 H), 4.61 (d, J = 11.2 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 14.4 (q), 40.3 (q), 56.3 (t), 61.8 (t), 81.2 (s), 156.2 (s). Anal. Calcd for $C_{14}H_{24}N_2O_{10}S_2$: C, 37.83; H, 5.44. Found: C, 38.09; H, 5.70.

Reaction of 42a with Aqueous KOH. To a solution of dimesylate **42a** (200 mg, 0.46 mmol) in *t*-BuOH (5 mL), H_2O (18 mg, 1 mmol) and KOH (26 mg, 0.46 mmol) were added and the mixture was stirred at 40 °C for 3 h. The reaction mixture was extracted with Et_2O (2 x 50 mL) and the combined organic extracts were washed sequentially with water (2 x 50 mL) and brine (2 x 25 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 25% EtOAc-hexane. Pure **43a** (113 mg, 91%) was thereby obtained as colorless microcrystalline solid: mp: 126-127 °C; IR (KBr) 2991 (m), 1713 (vs), 1441 (vs), 1049 (s), 775 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.22 (t, J =7.2 Hz, 6 H), 4.02-4.20 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 14.6 (t), 55.4 (t), 61.3 (s), 61.5 (t), 156.5 (s). Anal. Calcd for $C_{12}H_{18}N_2O_5$: C, 53.33; H, 6.70. Found: C, 52.96; H, 6.86.

***N,N*'-Bis(toluenesulfonyl)-3-hydroxy-3-(3'-hydroxy-3'-azetidinyl)azetidine (41b).** To a solution of 0.1 M solution of SmI_2 in THF (115 mL, 11.5 mmol) under argon was added **40b**[16] (2.54 g, 11.3 mmol), and the resulting mixture was stirred at ambient temperature for 8 h. To the reaction mixture was added 0.1 N aqueous HCl (5 mL, excess), and the resulting aqueous suspension was extracted with EtOAc (3 x 50 mL). The combined organic extracts were washed sequentially with 10% aqueous $NaHCO_3$ (2 x 20 mL), water (30 mL), and brine (2 x 20 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 10% CH_3OH-CH_2Cl_2. Pure **2b** (1.88 g, 73%) was thereby obtained as colorless microcrystalline solid: mp 260 °C (dec); IR (KBr) 3453 (vs), 3057 (w), 2949 (m), 1602 (m), 1153 (s), 670 cm^{-1} (s); ^1H NMR (DMSO-d_6) δ 2.41 (s, 6 H), 3.33 (AB, J_{AB} = 7.7 Hz, 4 H), 3.51 (AB, J_{AB} = 7.7 Hz, 4 H), 5.87 (s, 2 H), 7.45 (*A*B, J_{AB} = 8.0 Hz, 4 H), 7.63 (*A*B, J_{AB} = 8.1 Hz, 4 H); ^{13}C NMR (DMSO-d_6) δ 21.0 (q), 58.8 (t), 69.3 (s), 128.0 (d), 129.9 (d), 131.0 (s), 143.9 (s). Anal. Calcd for $C_{20}H_{24}N_2O_6S_2$: C, 53.08; H, 5.35. Found: C, 52.90; H, 5.33. The structure of **41b** was established unequivocally via application of X-ray crystallographic techniques (*vide infra*).

***N,N*'-Bis(toluenesulfonyl)-3-mesyloxy-3-(3'-mesyloxy-3'-azetidinyl)azetidine (42b).** A solution of **41b** (550 mg, 1.22 mmol) in CH_2Cl_2 (5 mL) under argon was cooled to 0 °C via application of an external ice-water bath. To this cooled solution was added MsCl (1.11 g, 9.76 mmol). To the resulting solution under argon was added dropwise with stirring a solution of pyridine (10 mL, excess) and DMAP (298 mg, 2.4 mmol) in CH_2Cl_2 (5 mL), and the reaction mixture was stirred at 0 °C for 10 h. The external ice-water bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature with stirring during 24 h. To the reaction mixture was added CH_2Cl_2 (80 mL), and the resulting mixture was washed sequentially with water (30 mL), 10% aqueous $NaHCO_3$ (30 mL), water (30 mL), and brine (30 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on acid-free silica gel that had been pretreated with Et_3N by eluting with 20% EtOAc-$CHCl_3$. Pure **42b** (510 mg, 69%) was thereby obtained as colorless microcrystalline solid: mp 180-181 °C; IR (KBr) 3032 (m), 2937 (m), 1605 (s), 1354 (vs), 1180 (vs), 842 cm^{-1} (vs); ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 6 H), 2.97 (s, 6 H), 3.96 (*A*B, J_{AB} = 11.0 Hz, 4 H), 4.21 (A*B*, J_{AB} = 11.1 Hz, 4 H) 7.40 (*A*B, J_{AB} = 8,1 Hz, 4 H), 7.70 (A*B*, J_{AB} = 8.0 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 21.7 (q), 40.3 (q), 56.9 (t), 128.5 (d), 130.2 (s), 130.3 (d), 145.3 (s). Anal. Calcd for $C_{22}H_{28}N_2O_{10}S_4$: C, 43.41; H, 4.64. Found: C, 43.41; H, 4.58.

Reaction of 42b with Aqueous KOH. To a solution of **42b** (304 mg, 0.50 mmol) in *t*-BuOH (5 mL) were added H_2O (18 mg, 1 mmol) and KOH (28 mg, 0.50 mmol), and the resulting mixture was stirred at 40 °C for 3 h. The reaction mixture was extracted with Et_2O (2 x 50 mL), and the combined organic extracts were washed sequentially with water (2 x 50 mL) and brine (2 x 25 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 25% EtOAc-hexane. Pure **43b** (181 mg, 84%) was thereby obtained as colourless microcrystalline solid: mp: 219-220 °C; IR (KBr) 2961 (w), 2930 (m), 1609 (s), 1350 (vs), 1165 (vs), 679 cm^{-1} (vs); ^{1}H NMR ($CDCl_3$) δ 2.47 (s, 6 H), 3.89 (dd, 10.7, 9.3 Hz, 8 H), 7.40 (d, 4 H, J = 8.2 Hz), 7.74 (d, 4 H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 21.6 (q), 56.0 (t), 59.9 (s), 128.2 (d), 130.1 (d), 131.2 (s), 145.1 (s). Anal. Cacld for $C_{10}H_{22}N_2O_5S_2$: C, 55.28; H, 5.10. Found: C, 55.43; H, 5.04. The structure of **43b** was established unequivocally via application of X-ray crystallographic techniques *(vide infra)*.

***N,N*'-Bis(benzhydryl)-3-hydroxy-3-(3'-hydroxy-3'-azetidinyl)azetidine (41c).** To a solution of 0.1 M solution of SmI_2 in THF (200 mL, 20 mmol) under argon was added *N*-benzhydrylazetidin-3-one[16] (**40c**, 4.74 g, 20 mmol), and the resulting mixture was stirred at ambient temperature for 12 h. To the reaction mixture was added 0.1 N aqueous HCl (20 mL, excess), and the resulting aqueous suspension was extracted with EtOAc (3 x 50 mL). The combined organic extracts were washed sequentially with 10% aqueous $NaHCO_3$ (2 x 20 mL), water (30 mL), and brine (2 x 20 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 50% EtOAc-hexane. Pure **41c** (3.4 g, 71%) was thereby obtained as colorless microcrystalline solid: mp 260 °C (dec); IR (KBr) 3041 (br, s), 2865 (vs), 1455 (vs), 749 vs), 701 cm^{-1} (vs); ^1H NMR ($CDCl_3$) δ 3.09-3.16 (m, 4 H), 3.38 -3.47 (m, 4 H), 4.44 (s, 2 H), 6.12 (br s, 2 H), 7.10-7.56 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 127.1 (d), 127.4 (d), 128.6 (d), 141.1 (s). Anal. Calcd for $C_{32}H_{32}N_2O_2$: C, 80.64; H, 6.77. Found: C, 80.22; H, 6.72.

***N,N*'-Bis(benzhydryl)-3-mesyloxy-3-(3'-mesyloxy-3'-azetidinyl)azetidine (42c).** A solution of **41c** (320 mg, 0.67 mmol) in CH_2Cl_2 (10 mL) under argon was cooled to 0 °C via application of an external ice-water bath. To this cooled solution was added MsCl (262 mg, 2.30 mmol). To the resulting solution under argon was added dropwise with stirring a solution of Et_3N (700 mg, 7.0 mmol) and DMAP (70 mg, 0.57 mmol) in CH_2Cl_2 (5 mL), and the reaction mixture was stirred at 0-10 °C for 3 h. The external ice-water bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature with stirring during 3 h. To the reaction mixture was added CH_2Cl_2 (100 mL), and the resulting mixture was washed sequentially with water (20 mL), 10% aqueous $NaHCO_3$ (20 mL), and brine (20 mL). The organic layer was dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on acid-free silica gel that had been pretreated with Et_3N by eluting with 40% EtOAc-hexane. Pure **42c** (360 mg, 85%) was thereby obtained as colorless microcrystalline solid: mp 88-89 °C; IR (KBr) 3032 (m), 2953 (w), 2855 (w), 1608 (m), 1346 (vs), 1176 (vs), 891 (s), 711 cm^{-1} (vs); ^1H NMR ($CDCl_3$) δ 3.06 (s, 6 H), 3.84 (d, $J = 9.8$ Hz, 4 H), 4.11 (d, $J = 9.1$ Hz, 4 H), 4.6 (s, 2 H), 7.25-7.50 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 40.2 (q), 59.9 (t), 77.6 (d), 82.1 (s), 127.2 (d), 127.4 (d), 128.6 (d), 141.4 (s). Anal. Calcd for $C_{34}H_{36}N_2O_6S_2$: C, 64.54; H, 5.73. Found: C, 64.73; H, 5.92.

Attempted Reaction of 42c with Base. A solution of **42c** (400 mg, 0.63 mmol) in *t*-BuOH (5 mL) was cooled to 0 °C via application of an external ice-water bath. To this cooled solution was added with stirring water (18 mg, 1 mmol) followed by portionwise addition of KO*t*-Bu (292 mg, 2.60 mmol). After all of the base had been added, the external cold bath was removed, and the reaction mixture was allowed to warm slowly to ambient temperature with stirring durng 3 h. The reaction mixture then was heated at 45 °C for 12 h. The reaction mixture was allowed to cool to ambient temperature and then was extracted with CH_2Cl_2 (2 x 50 mL). The combined extracts were washed sequentially with water (2 x 20 mL), 10% aqueous $NaHCO_3$

(2 x 20 mL), water (30 mL), and brine (2 x 30 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. Analysis of the ^1H NMR spectrum of the crude product thereby obtained indicated only the presence of starting material (**42c**).

***N,N*'-Bis(benzhydryl)-3-acetoxy-3-(3'-acetoxy-3'-azetidinyl)azetidine (47).** A solution of **41c** (1.9 g, 4.0 mmol) in CH_2Cl_2 (20 mL) under argon was cooled to 0 °C via application of external ice-water bath. To this cooled solution was added Ac_2O (920 mg, 9.0 mmol). To the resulting solution under argon was added dropwise with stirring a solution of Et_3N (1.21 mg, 12 mmol) and DMAP (200 mg, 1.64 mmol) in CH_2Cl_2 (5 mL), and the reaction mixture was stirred at 0-10 °C for 3 h. The external ice-water bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature with stirring during 12 h. To the reaction mixture was added CH_2Cl_2 (100 mL), and the resulting mixture was washed sequentially with water (20 mL), 10% aqueous $NaHCO_3$ (20 mL), and brine (20 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 50% EtOAc-hexane. Pure **47** (1.96 g, 88%) was thereby obtained as colorless microcrystalline solid: mp 198-199 °C; IR (KBr) 2857 (w), 1743 (s), 1250 (s), 760 (s), 712 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.78 (s, 6 H), 3.02-3.18 (m, 4 H), 3.92-4.02 (m, 4 H), 4.28 (s, 2 H), 6.92-7.40 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 21.4 (q), 61.4 (t), 76.8 (s), 78.2 (d), 127.2 (d), 127.3 (d), 128.5 (d), 142.1 (s), 169.7 (s). Anal. Calcd for $C_{36}H_{36}N_2O_4$: C, 77.12; H, 6.47. Found: C, 77.19; H, 6.13. The structure of **47** was established unequivocally via application of X-ray crystallographic techniques *(vide infra)*.

***N,N*'-Bis(acetyl)-3-acetoxy-3-(3'-acetoxy-3'-azetidinyl)azetidine (49).** A solution of **47** (1.96 g, 3.5 mmol) in Et_2O (50 mL) was cooled to 0 °C via application of an external ice-water bath. Dry HCl gas was passsed through the solution for 5 minutes, during which time a precipitate formed. Argon then was bubbled through the reaction mixture to purge excess HCl (g), and the precipitate was collected subsequently via suction filtration. The residue was washed with Et_2O (2 x 20 mL) and then dried *in vacuo*. The dihydrochloride salt of **47** (i.e., **47**·2HCl, 2.2 g, 100%) was thereby obtained as a colorless microcrystalline solid. This material was used as obtained in the next synthetic step.

To a solution of **47**·2HCl (2.2 g, 3.5 mmol, *vide supra*) in dry MeOH (75 mL) was added 20% $Pd(OH)_2$ on powdered charcoal (700 mg, 1.0 mmol),[25] and the resulting mixture was hydrogenated with H_2 (g) at 58 psig) at ambient temperature by using a Parr hydrogenation apparatus for 65 h. At that time, tlc analysis of the reaction mixture indicated the complete absence of **47** (or of **47**·2HCl). The reaction mixture was filtered to remove spent catalyst, and the filtrate was concentrated *in vacuo*. The residue was washed with Et_2O (3 x 30 mL); after each washing procedure, the organic layer was decanted carefully and discarded. The residue was dried *in* *vacuo*, thereby affording **48** (780 mg, 74%) as a colorless microcrystalline solid. This material was used as obtained in the next synthetic step.

A solution of **48** (780 mg, 2.6 mmol, *vide supra*) in CH_2Cl_2 under argon was cooled to 0 °C via application of an external ice-water bath. To this cooled solution was added Ac_2O (2.04 g, 20 mmol). To the resulting solution under argon was added dropwise with stirring a solution of pyridine (5 mL) and DMAP (100 mg, 0.82 mmol) in CH_2Cl_2 (5 mL), and the reaction mixture was stirred at 0-10 °C for 3 h. The external ice-water bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature with stirring during 8 h. Dichloromethane (100 mL) was added, and the resulting mixture was washed sequentially with water (20 mL), 10% aqueous $NaHCO_3$ (20 mL), and brine (20 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 50% EtOAc-hexane. Pure **49** (650 mg, 80%) was thereby otbtained as a colorless microcrystalline solid: mp 181-182 °C; IR (KBr) 2962 (m), 1750 (vs), 1670 (vs), 1468 (s), 1250 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.80 (s, 6 H), 1.98 (s, 6 H), 3.98-4.57 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 18.9 (q), 19.0 (q), 20.8 (q), 20.9 (q), 55.5 (t), 55.9 (t), 57.6 (t), 58.4 (t), 169.6 (s), 170.4 (s). Exact Mass (CI-HRMS) Calcd for $C_{14}H_{20}N_2O_6$: $[M_r + H]^+$ 313.139962 Found: $[M_r + H]^+$ 313.139176.

X-ray Crystal Structures of 41a, 41b, 43b, and 47.[26] All data were collected on an Enraf-Nonius CAD-4 diffractometer by using the ω–2θ scan technique, Mo Kα radiation (λ = 0.71073 Å), and a graphite monochromator. Standard procedures used in our laboratory for this purpose have been described previously.[27] Pertinent X-ray data are given in Table 1. Data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods (**41a** and **43b** were solved by using SIR[28], while **41b** and **47** were solved by using SHELXS-86[29]), and the models were refined by using full-matrix least-squares techniques. All atoms in **41b** were refined with anisotropic thermal parameters, while those in **47** were refined by using isotropic thermal parameters. Sufficient data were available for the remaining two structures (i.e., **41a** and **43b**) to permit only some of the atoms to be refined anisotropically: i.e., (i) the oxygen atoms, nitrogen atoms, and the ethyl group carbon atoms in **41a** and (ii) the sulfur atoms, oxygen atoms, nitrogen atoms, and the methyl carbon atoms in **43b**. Hydrogen atoms were located on difference maps and then were included in the model in idealized positions [$U(H) = 1.3\ B_{eq}(C)$] and allowed to ride upon the attached carbon. All computations other than those specified were performed by using MolEN.[30] Scattering factors were taken from the usual sources.[31]

IV. Technology transfer from academics to industry and DoD. The development of improved methods for large-scale synthesis of TNAZ has involved extensive collaboration with

Dr. Thomas G. Archibald (Aerojet, Propulsion Division, Sacramento, CA). Dr. Archibald appears as co-author on all publications that have resulted thus far from work on this project.

Table 1. X-ray data collection and processing parameters for **41a**, **41b**, **43b**, and **47**.[26]

Compound	**41a**	**41b**	**43b**	**47**
	$C_{12}H_{20}N_2O_6$	$C_{20}H_{24}N_2O_6S_2$ $\cdot$2(DMSO) ($C_{24}H_{36}N_2O_8S_4$)	$C_{20}H_{22}N_2O_5S_2$	$C_{36}H_{36}N_2O_4$
Size (mm)	0.07 x 0.22 x 0.24	0.11 x 0.22 x 0.29	0.09 x 0.10 x 0.42	0.06 x 0.07 x 0.08
Space Group	$P2_1/n$	P-1 bar	$P2_1/c$	$P2_1/n$
a (Å)	10.251 (4)	6.2973 (8)	16.476 (2)	9.054 (1)
b (Å)	5.782 (2)	8.4717 (6)	7.5480 (5)	15.426 (2)
c (Å)	12.336 (3)	14.023 (1)	16.811 (1)	10.619 (1)
α (°)	90	95.400 (6)	90	90
β (°)	105.05 (2)	95.939 (9)	99.195 (7)	100.03 (1)
γ (°)	90	97.494 (8)	90	90
V (Å^3)	706.1 (4)	738.3 (1)	2063.8 (3)	1460.5 (4)
Z-value	2	1	4	2
D_{calc} (g-cm^{-3})	1.356	1.379	1.398	1.275
μ (cm^{-1})	1.023	3.56	2.79	0.77
T (K)	293	295	293	295
$2\theta_{max}$ (°)	45	44	44	44
Total reflections	1084	1787	2851	1998
Unique reflections	1030	1787	2755	1872
R_{int}	0.036	- -	0.024	0.034
$I \geq 3\sigma(I)$	410	1079	1440	493
Parameters	71	172	172	85
R, R_w	0.0673, 0.0708	0.050, 0.050	0.0497, 0.0550	0.0510, 0.0556
$(\Delta/\sigma)_{max}$	0.03	<0.01	<0.01	<0.01
ρ_{max}; ρ_{min} (eÅ^{-3})	0.22; -0.25	0.46; -0.33	0.32; -0.37	0.22; - 0.19

In addition, we have provided information in advance of publication to Drs. C. Rao Surapaneni (U. S. Army ARDEC, Picatinny Arsenal, NJ) and Paritosh R. Dave (GEO-CENTERS, Inc., Lake Hopatcong, NJ), both of whom are involved in the large-scale synthesis of TNAZ.

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26 X-ray crystal structure data for **41a**, **41b**, **43b**, and **47** were kindly obtained by Dr. Simon G. Bott, Department of Chemistry, University of Houston, Houston, TX. We thank Dr. Bott for his kind assistance in this regard.

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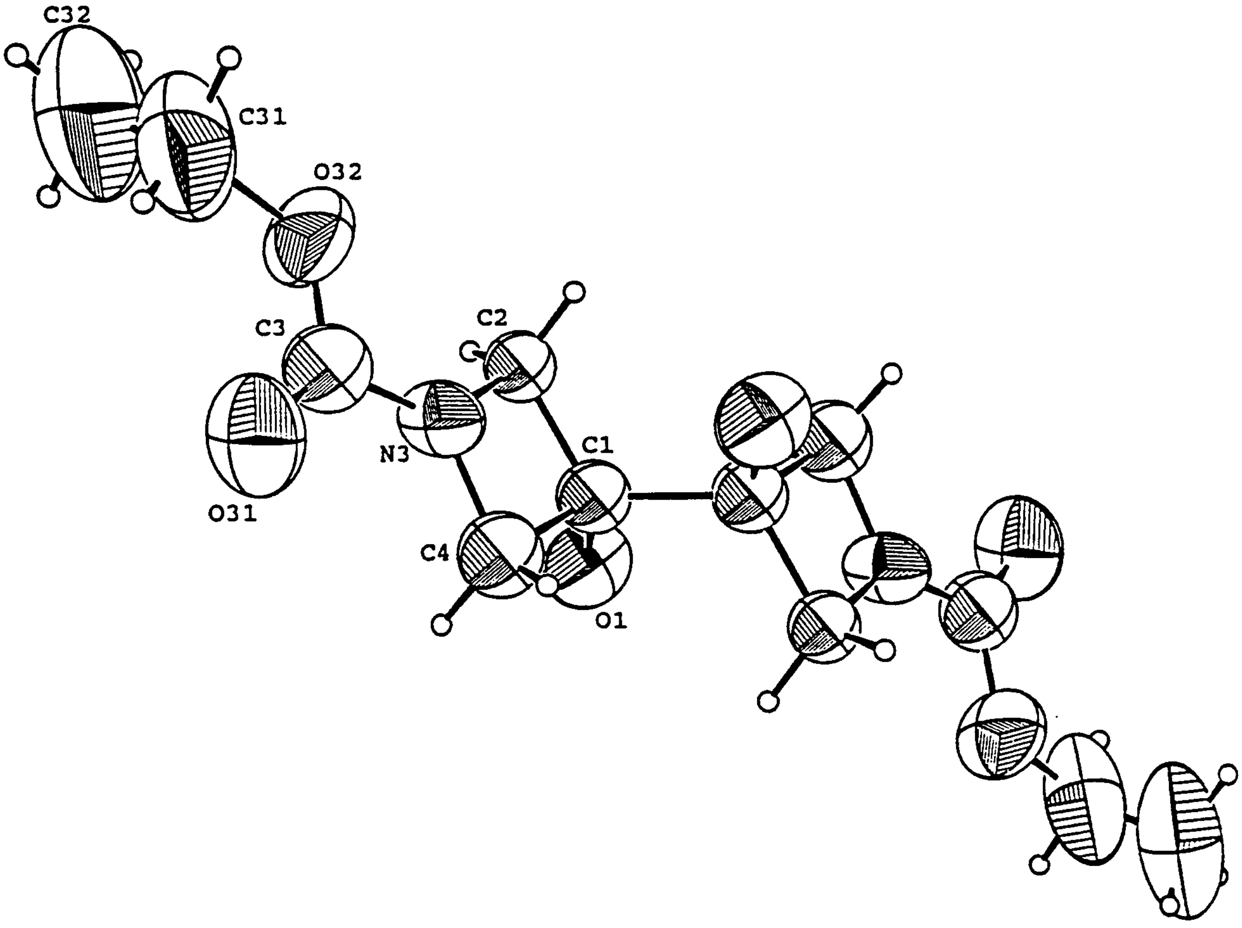
Improved Economical and Environmentally Benign Routes for the Large-Scale Synthesis of 1,3,3-Trinitroazetidine

Principal Investigator: Dr. Alan P. Marchand

Department of Chemistry, University of North Texas
NT Station, Box 5068, Denton, Texas 76203-5070

ONR Contract Number N00014-96-1-1279
Mechanics & Energy Conversion S&T Division (ONR Code 333)

Appendix I: X-ray Structure Data for Compound 41a


C32
C31
O32
C3
C2
O31
N3
C1
C4
O1

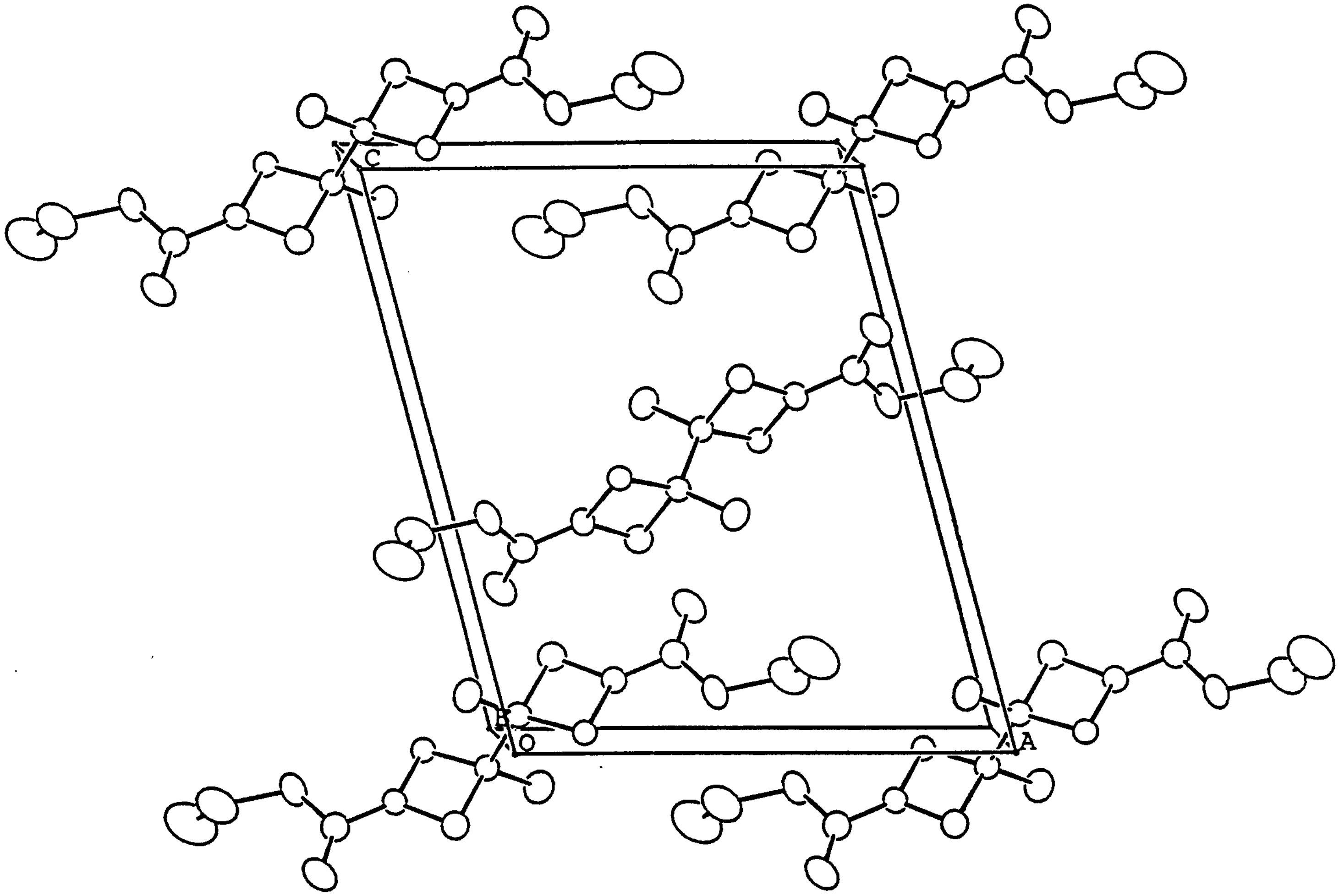

C
B
O
A

Table of Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
O1	0.4460(5)	0.210(1)	0.5869(5)	6.1(2)
O31	0.9407(6)	-0.061(1)	0.7237(5)	7.9(2)
O32	0.9367(5)	0.218(1)	0.5903(5)	7.6(2)
N3	0.7475(6)	0.064(1)	0.6047(5)	5.1(2)
C1	0.5422(8)	0.081(2)	0.5482(6)	4.4(2)*
C2	0.6572(7)	0.215(2)	0.5230(6)	4.1(2)*
C3	0.8799(8)	0.075(2)	0.6484(7)	5.8(2)*
C4	0.6428(8)	-0.058(2)	0.6401(7)	5.6(2)*
C31	1.093(1)	0.219(3)	0.617(1)	11.5(5)
C32	1.147(2)	0.391(3)	0.655(1)	15.4(6)

Starred atoms were refined isotropically.
Anisotropically refined atoms are given in the form of the
isotropic equivalent displacement parameter defined as:
(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2)
+ ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

Table of Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
H2a	0.6647	0.2002	0.4481	5*
H2b	0.6607	0.3735	0.5432	5*
H4a	0.6387	-0.0271	0.7147	7*
H4b	0.6413	-0.2209	0.6283	7*
H31a	1.1176	0.1887	0.5496	14*
H31b	1.1256	0.0986	0.6696	14*
H32a	1.2417	0.3737	0.6689	19*
H32b	1.1169	0.5145	0.6041	19*
H32c	1.1248	0.4243	0.7241	19*

Table of General Displacement Parameter Expressions - U's

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.083(3)	0.057(4)	0.098(4)	0.001(4)	0.036(3)	-0.018(4)
O31	0.084(4)	0.098(6)	0.099(5)	0.023(5)	-0.006(4)	0.012(5)
O32	0.054(3)	0.122(6)	0.101(5)	-0.009(4)	0.004(3)	0.020(5)
N3	0.053(3)	0.076(5)	0.063(4)	0.018(4)	0.013(3)	0.027(5)
C31	0.131(9)	0.17(1)	0.112(9)	-0.00(1)	-0.002(8)	-0.05(1)
C32	0.20(1)	0.19(2)	0.15(1)	-0.01(1)	-0.01(1)	-0.07(1)

The form of the anisotropic displacement parameter is:
exp[-2PI2{h2a2U(1,1) + k2b2U(2,2) + l2c2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)}] where a,b, and c are reciprocal lattice constants.

Table of Bond Distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
O1	C1	1.42(1)	N3	C4	1.44(1)
O31	C3	1.25(1)	C1	C1′	1.582(8)
O32	C3	1.32(1)	C1	C2	1.51(1)
O32	C31	1.55(1)	C1	C4	1.55(1)
N3	C2	1.47(1)	C31	C32	1.17(2)
N3	C3	1.33(1)			

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Bond Distances in Angstroms

Atom 1	Atom 2	Distance
C2	H2a	0.95
C2	H2b	0.95
C4	H4a	0.95
C4	H4b	0.95
C31	H31a	0.95
C31	H31b	0.95
C32	H32a	0.95
C32	H32b	0.95
C32	H32c	0.95

Table of Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C3	O32	C31	117.5(8)	C2	C1	C1′	117.0(6)
C2	N3	C3	130.4(8)	C4	C1	C1′	111.9(7)
C2	N3	C4	96.5(6)	N3	C2	C1	86.6(6)
C3	N3	C4	131.6(7)	O31	C3	O32	126.1(8)
O1	C1	C2	116.7(7)	O31	C3	N3	122.1(9)
O1	C1	C4	114.7(7)	O32	C3	N3	111.0(7)
O1	C1	C1′	105.8(5)	N3	C4	C1	85.9(7)
C2	C1	C4	90.6(6)	O32	C31	C32	116.(1)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle
N3	C2	H2a	115
N3	C2	H2b	115
C1	C2	H2a	115
C1	C2	H2b	115
H2a	C2	H2b	110
N3	C4	H4a	115
N3	C4	H4b	115
C1	C4	H4a	115
C1	C4	H4b	115
H4a	C4	H4b	109
O32	C31	H31a	108
O32	C31	H31b	108
C32	C31	H31a	108
C32	C31	H31b	108
H31a	C31	H31b	109
C31	C32	H32a	109
C31	C32	H32b	109
C31	C32	H32c	109
H32a	C32	H32b	109
H32a	C32	H32c	109
H32b	C32	H32c	109

Table of Torsion Angles in Degrees

Atom 1	Atom 2	Atom 3	Atom 4	Angle
C31	O32	C3	O31	-0.37 (1.46)
C31	O32	C3	N3	-169.78 (0.86)
C3	O32	C31	C32	-114.82 (1.40)
C3	N3	C2	C1	-171.46 (0.88)
C4	N3	C2	C1	-4.58 (0.66)
C2	N3	C3	O31	175.27 (0.82)
C2	N3	C3	O32	-14.82 (1.31)
C4	N3	C3	O31	12.81 (1.56)
C4	N3	C3	O32	-177.28 (0.86)
C2	N3	C4	C1	4.47 (0.65)
C3	N3	C4	C1	171.12 (0.95)
O1	C1	C2	N3	122.47 (0.69)
C4	C1	C2	N3	4.25 (0.62)
C1′	C1	C2	N3	-110.82 (0.73)
O1	C1	C4	N3	-124.25 (0.73)
C2	C1	C4	N3	-4.31 (0.63)
C1′	C1	C4	N3	115.20 (0.69)
O1	C1	C1′	O1′	180.00 (0.66)
O1	C1	C1′	C2′	-48.11 (0.92)
O1	C1	C1′	C4′	54.40 (0.82)
C2	C1	C1′	O1′	48.11 (0.92)
C2	C1	C1′	C2′	-179.98 (0.51)
C2	C1	C1′	C4′	-77.49 (0.89)
C4	C1	C1′	O1′	-54.40 (0.82)
C4	C1	C1′	C2′	77.49 (0.89)
C4	C1	C1′	C4′	180.00 (0.63)

Intermolecular Contacts (less than 3.60 Angstroms)

Hydrogen Bonding

O1	O31'	2.67

Other

C3	C4'	3.42
O31	C1"	3.46
O31	C4"	3.55
O1	C32"'	3.55
O32	C31""	3.56
O31	C4'	3.57

Symmetry Codes

'	(x,y,z) -> (3/2-x,y+1/2,3/2-z)
"	(x,y,z) -> (3/2-x,y-1/2,3/2-z)
"'	(x,y,z) -> (x-1,y,z)
""	(x,y,z) -> (2-x,-y,1-z)

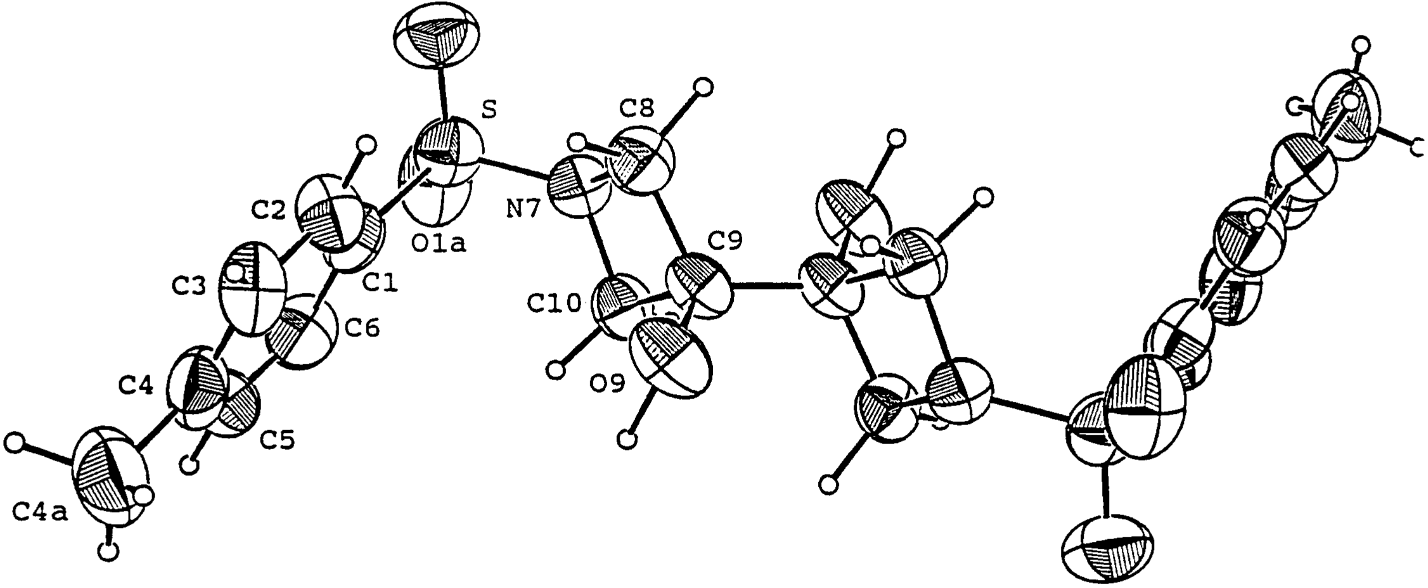
Improved Economical and Environmentally Benign Routes for the Large-Scale Synthesis of 1,3,3-Trinitroazetidine

Principal Investigator: Dr. Alan P. Marchand

Department of Chemistry, University of North Texas
NT Station, Box 5068, Denton, Texas 76203-5070

ONR Contract Number N00014-96-1-1279
Mechanics & Energy Conversion S&T Division (ONR Code 333)

Appendix II: X-ray Structure Data for Compound 41b


O1b
S
C8
C2
N7
O1a
C9
C3
C1
C10
C6
O9
C4
C5
C4a

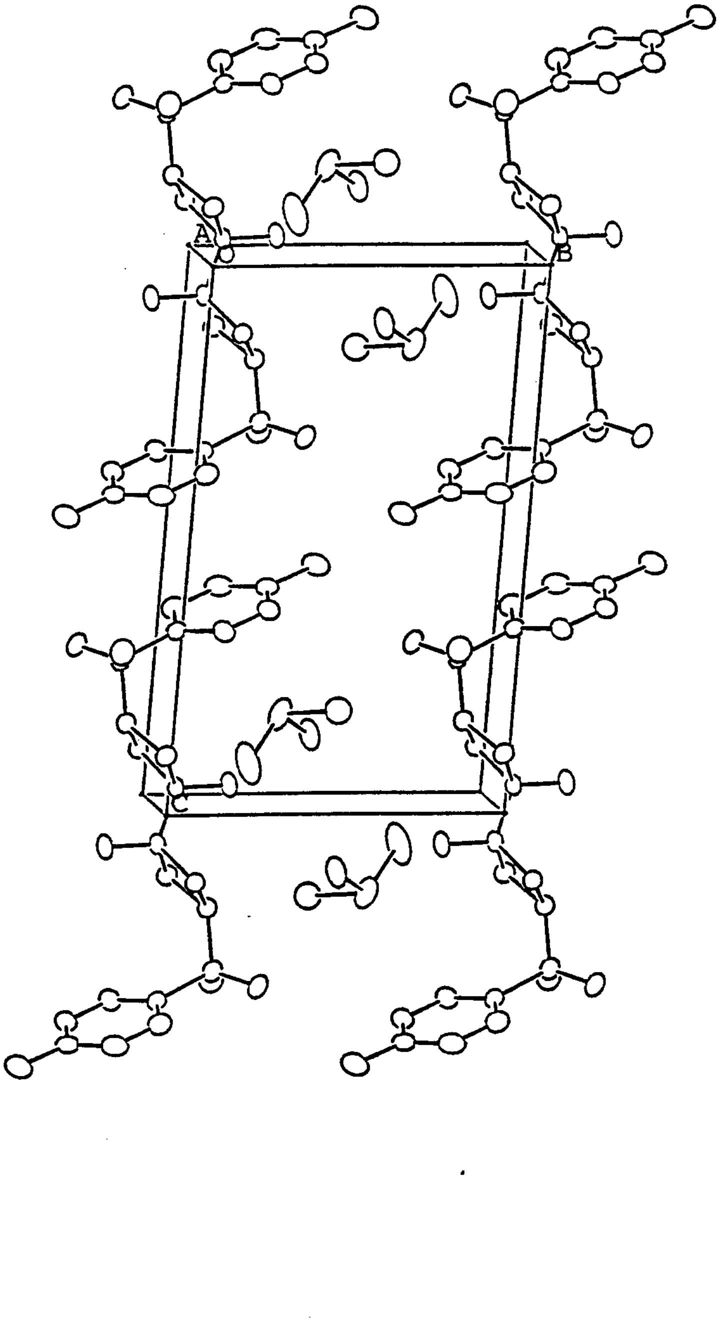

A
B
C

Table of Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
S	0.1484(3)	0.1881(2)	0.2886(1)	4.97(4)
O1a	0.0348(8)	0.3183(5)	0.3130(3)	6.7(1)
O1b	0.3776(7)	0.2040(6)	0.3121(4)	6.6(1)
O9	-0.0708(7)	-0.1840(4)	0.0527(3)	5.2(1)
N7	0.1095(7)	0.1538(5)	0.1725(3)	4.1(1)
C1	0.030(1)	0.0194(7)	0.3367(4)	4.3(1)
C2	0.131(1)	-0.1147(8)	0.3389(5)	5.1(2)
C3	0.034(1)	-0.2487(8)	0.3731(5)	5.8(2)
C4	-0.164(1)	-0.2540(8)	0.4072(4)	5.5(2)
C4a	-0.271(2)	-0.401(1)	0.4430(6)	8.4(2)
C5	-0.260(1)	-0.1181(9)	0.4064(5)	5.9(2)
C6	-0.170(1)	0.0190(8)	0.3710(5)	5.5(2)
C8	0.215(1)	0.0331(7)	0.1164(4)	4.5(1)
C9	-0.0003(9)	-0.0207(6)	0.0509(4)	3.9(1)
C10	-0.1064(9)	0.0948(7)	0.1177(4)	4.1(1)
S1s	0.4593(3)	0.6461(2)	0.1610(2)	7.31(6)
O1s	0.5283(8)	0.7333(6)	0.0752(5)	11.0(2)
C1s	0.216(1)	0.5345(8)	0.1137(6)	6.8(2)
C2s	0.615(1)	0.4878(9)	0.1722(6)	6.8(2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

Table of Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
H2	0.2684	-0.1143	0.3166	6*
H3	0.1055	-0.3408	0.3732	7*
H4a1	-0.2093	-0.4147	0.5136	10*
H4a2	-0.2511	-0.4915	0.4014	10*
H4a3	-0.4210	-0.3941	0.4415	10*
H5	-0.3945	-0.1179	0.4312	7*
H6	-0.2424	0.1104	0.3701	7*
H8a	0.2795	-0.0606	0.1587	6*
H8b	0.3416	0.1076	0.0823	6*
H9	-0.2378	-0.1862	0.0757	6*
H10a	-0.1751	0.1936	0.0845	5*
H10b	-0.2180	0.0353	0.1595	5*
H1s1	0.2051	0.4383	0.0655	8*
H1s2	0.1333	0.6065	0.0841	8*
H1s3	0.1500	0.4986	0.1672	8*
H2s1	0.5745	0.4178	0.2373	8*
H2s2	0.7638	0.5309	0.1816	8*
H2s3	0.5863	0.4159	0.1146	8*

Table of General Displacement Parameter Expressions - U's

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
S	0.073(1)	0.0504(8)	0.062(1)	0.0051(8)	0.0050(9)	-0.0025(8)
O1a	0.130(4)	0.052(2)	0.073(3)	0.025(2)	0.018(3)	-0.010(2)
O1b	0.069(3)	0.078(3)	0.094(3)	-0.011(3)	-0.005(3)	0.002(3)
O9	0.080(3)	0.038(2)	0.088(3)	0.011(2)	0.032(2)	0.019(2)
N7	0.054(3)	0.048(3)	0.054(3)	0.008(2)	0.006(2)	0.003(2)
C1	0.066(4)	0.052(3)	0.044(3)	0.012(3)	-0.003(3)	-0.003(3)
C2	0.070(4)	0.068(4)	0.062(4)	0.015(3)	0.016(3)	0.016(3)
C3	0.099(5)	0.071(4)	0.054(4)	0.025(4)	0.012(4)	0.014(3)
C4	0.095(5)	0.072(4)	0.040(4)	0.003(4)	0.005(4)	0.002(3)
C4a	0.144(7)	0.095(5)	0.072(5)	-0.021(5)	0.019(5)	0.022(4)
C5	0.058(4)	0.106(5)	0.058(4)	0.003(4)	0.013(3)	0.008(4)
C6	0.066(4)	0.082(4)	0.063(4)	0.026(3)	0.008(3)	0.000(4)
C8	0.057(3)	0.058(3)	0.056(4)	0.015(3)	0.011(3)	0.001(3)
C9	0.054(3)	0.036(3)	0.060(3)	0.007(3)	0.018(3)	0.008(3)
C10	0.058(3)	0.049(3)	0.051(3)	0.011(3)	0.013(3)	0.005(3)
S1s	0.063(1)	0.065(1)	0.143(2)	-0.0002(9)	0.025(1)	-0.023(1)
O1s	0.076(3)	0.095(3)	0.267(6)	0.002(3)	0.069(4)	0.082(4)
C1s	0.068(4)	0.056(4)	0.134(6)	0.001(3)	0.006(5)	0.031(4)
C2s	0.068(4)	0.096(5)	0.098(5)	0.022(4)	0.009(4)	0.012(5)

The form of the anisotropic displacement parameter is:
exp[-2PI2{h2a2U(1,1) + k2b2U(2,2) + l2c2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3)
+ 2klbcU(2,3)}] where a,b, and c are reciprocal lattice constants.

Table of Bond Distances in Angstroms

Atom 1	Atom 2	Distance
S	O1a	1.425(5)
S	O1b	1.432(5)
S	N7	1.615(5)
S	C1	1.751(6)
O9	C9	1.400(6)
N7	C8	1.498(8)
N7	C10	1.491(7)
C1	C2	1.375(9)
C1	C6	1.391(9)
C2	C3	1.368(9)
C3	C4	1.38(1)
C4	C4a	1.49(1)
C4	C5	1.37(1)
C5	C6	1.38(1)
C8	C9	1.547(8)
C9	C10	1.552(8)
C9	C9′	1.503(6)
S1s	O1s	1.540(7)
S1s	C1s	1.724(7)
S1s	C2s	1.772(8)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Bond Distances in Angstroms

Atom 1	Atom 2	Distance
O9	H9	1.13
C2	H2	0.95
C3	H3	0.95
C4a	H4a1	1.05
C4a	H4a2	0.95
C4a	H4a3	0.95
C5	H5	0.95
C6	H6	0.95
C8	H8a	1.13
C8	H8b	1.13
C10	H10a	1.11
C10	H10b	1.07
C1s	H1s1	1.00
C1s	H1s2	0.95
C1s	H1s3	0.95
C2s	H2s1	1.17
C2s	H2s2	0.95
C2s	H2s3	0.95

Table of Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O1a	S	O1b	120.3(3)	C3	C4	C5	117.0(6)
O1a	S	N7	105.9(3)	C4a	C4	C5	121.0(7)
O1a	S	C1	108.3(3)	C4	C5	C6	123.0(6)
O1b	S	N7	104.7(3)	C1	C6	C5	118.2(6)
O1b	S	C1	108.8(3)	N7	C8	C9	89.4(4)
N7	S	C1	108.2(3)	O9	C9	C8	111.2(5)
S	N7	C8	123.1(4)	O9	C9	C10	115.4(5)
S	N7	C10	123.1(4)	O9	C9	C9′	111.0(4)
C8	N7	C10	92.5(4)	C8	C9	C10	88.3(4)
S	C1	C2	120.1(5)	C8	C9	C9′	114.8(4)
S	C1	C6	120.2(5)	C10	C9	C9′	114.5(4)
C2	C1	C6	119.6(6)	N7	C10	C9	89.4(4)
C1	C2	C3	120.1(6)	O1s	S1s	C1s	102.8(4)
C2	C3	C4	121.9(7)	O1s	S1s	C2s	107.5(4)
C3	C4	C4a	122.0(7)	C1s	S1s	C2s	98.8(3)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle
C9	O9	H9	104
C1	C2	H2	120
C3	C2	H2	120
C2	C3	H3	119
C4	C3	H3	119
C4	C4a	H4a1	113
C4	C4a	H4a2	109
C4	C4a	H4a3	109
H4a1	C4a	H4a2	109
H4a1	C4a	H4a3	109
H4a2	C4a	H4a3	110
C4	C5	H5	119
C6	C5	H5	119
C1	C6	H6	121
C5	C6	H6	121
N7	C8	H8a	116
N7	C8	H8b	104
C9	C8	H8a	116
C9	C8	H8b	115
H8a	C8	H8b	114
N7	C10	H10a	111
N7	C10	H10b	114
C9	C10	H10a	117
C9	C10	H10b	114
H10a	C10	H10b	111
S1s	C1s	H1s1	123
S1s	C1s	H1s2	106
S1s	C1s	H1s3	106
H1s1	C1s	H1s2	106
H1s1	C1s	H1s3	106
H1s2	C1s	H1s3	110
S1s	C2s	H2s1	111
S1s	C2s	H2s2	109
S1s	C2s	H2s3	109
H2s1	C2s	H2s2	109
H2s1	C2s	H2s3	109
H2s2	C2s	H2s3	110

Table of Torsion Angles in Degrees

Atom 1	Atom 2	Atom 3	Atom 4	Angle
O1a	S	N7	C8	175.40 (0.44)
O1a	S	N7	C10	-65.45 (0.48)
O1b	S	N7	C8	47.24 (0.49)
O1b	S	N7	C10	166.40 (0.42)
C1	S	N7	C8	-68.71 (0.50)
C1	S	N7	C10	50.45 (0.49)
O1a	S	C1	C2	-168.25 (0.50)
O1a	S	C1	C6	13.21 (0.60)
O1b	S	C1	C2	-35.83 (0.59)
O1b	S	C1	C6	145.63 (0.51)
N7	S	C1	C2	77.44 (0.55)
N7	S	C1	C6	-101.10 (0.53)
S	N7	C8	C9	138.31 (0.40)
C10	N7	C8	C9	5.38 (0.42)
S	N7	C10	C9	-138.33 (0.40)
C8	N7	C10	C9	-5.37 (0.41)
S	C1	C2	C3	-177.47 (0.50)
C6	C1	C2	C3	1.08 (0.94)
S	C1	C6	C5	178.57 (0.49)
C2	C1	C6	C5	0.03 (1.05)
C1	C2	C3	C4	-0.79 (1.00)
C2	C3	C4	C4a	178.99 (0.64)
C2	C3	C4	C5	-0.62 (0.97)
C3	C4	C5	C6	1.79 (0.98)
C4a	C4	C5	C6	-177.83 (0.65)
C4	C5	C6	C1	-1.51 (1.00)
N7	C8	C9	O9	-121.84 (0.46)
N7	C8	C9	C10	-5.17 (0.40)
N7	C8	C9	C9′	111.09 (0.48)
O9	C9	C10	N7	117.87 (0.48)
C8	C9	C10	N7	5.19 (0.40)
C9′	C9	C10	N7	-111.39 (0.49)
O9	C9	C9′	O9′	-180.00 (0.63)
O9	C9	C9′	C8′	52.86 (0.63)
O9	C9	C9′	C10′	-47.14 (0.64)
C8	C9	C9′	O9′	-52.86 (0.63)
C8	C9	C9′	C8′	180.00 (0.34)
C8	C9	C9′	C10′	80.00 (0.59)
C10	C9	C9′	O9′	47.14 (0.64)
C10	C9	C9′	C8′	-80.00 (0.59)
C10	C9	C9′	C10′	180.00 (0.66)

```
                Table of Least-Squares Planes
                -----------------------------


Orthonormal Equation of Plane   1

 -0.3225 X +   -0.2366 Y +   -0.9165 Z -    -4.0969 = 0

  0.0026         0.0026         0.0010          0.0096

Crystallographic Equation of Plane

 -2.0307 X +   -1.6314 Y +  -11.8790 Z -    -4.0969 = 0

  0.0162         0.0600         0.1075          0.0096

 Atom          X         Y         Z        Distance      Esd

C1          -0.3234   -0.3493    4.6687      0.0049 +- 0.0059
C2           0.4598   -1.4794    4.6985     -0.0075 +- 0.0064
C3          -0.0515   -2.6569    5.1724      0.0016 +- 0.0066
C4          -1.3429   -2.7531    5.6456      0.0072 +- 0.0062
C5          -2.0960   -1.6106    5.6343     -0.0101 +- 0.0065
C6          -1.6294   -0.4053    5.1437      0.0039 +- 0.0066

Chi Squared =      6.2

                ----- Other Atoms -----
S            0.3082    1.1407    4.0015      0.0601 +- 0.0018
C4a         -1.9083   -4.0399    6.1416      0.0394 +- 0.0080


Orthonormal Equation of Plane   2

   0.1830 X +    0.7662 Y +   -0.6160 Z -    -0.6711 = 0

   0.0037        0.0022         0.0026          0.0058

Crystallographic Equation of Plane

   1.1523 X +    6.2336 Y +   -9.9716 Z -    -0.6711 = 0

   0.0236        0.0701         0.1193          0.0058

 Atom          X         Y         Z        Distance      Esd

N7           0.2697    1.0294    2.3912      0.0363 +- 0.0046
C8           1.1500    0.1007    1.6132     -0.0350 +- 0.0060
C9          -0.0531   -0.2516    0.7059      0.0337 +- 0.0054
C10         -0.9457    0.6167    1.6325     -0.0350 +- 0.0057

Chi Squared =    175.8
```

Table of Least-Squares Planes (continued)

Dihedral Angles Between Planes:

Plane No.	Plane No.	Dihedral Angle
1	2	71.08 +- 0.21

Hydrogen Bonding

	O...O	H...O	S-O...H		O-H...O
O9-H9...O1s’		2.59	1.54	121	152

Other Non-Bonding Contacts

Molecule - Molecule

O1b	2	C6 "	3.49
O1a	2	C4a"’	3.56
O1a	2	C3""	3.69

Molecule - Solvent

O9	2	C1s""’	3.30
C8	1	O1s""’	3.46
C9	1	O1s’	3.46
C10	1	O1s’	3.54
O9	2	S1s’	3.66
O1a	2	C2s"""	3.66

Symmetry Codes

’	(x,y,z) -> (x-1,y-1,z)
"	(x,y,z) -> (x+1,y,z)
"’	(x,y,z) -> (-x,-y,1-z)
""	(x,y,z) -> (x,y+1,z)
""’	(x,y,z) -> (x,y-1,z)
"""	(x,y,z) -> (x-1,y,z)

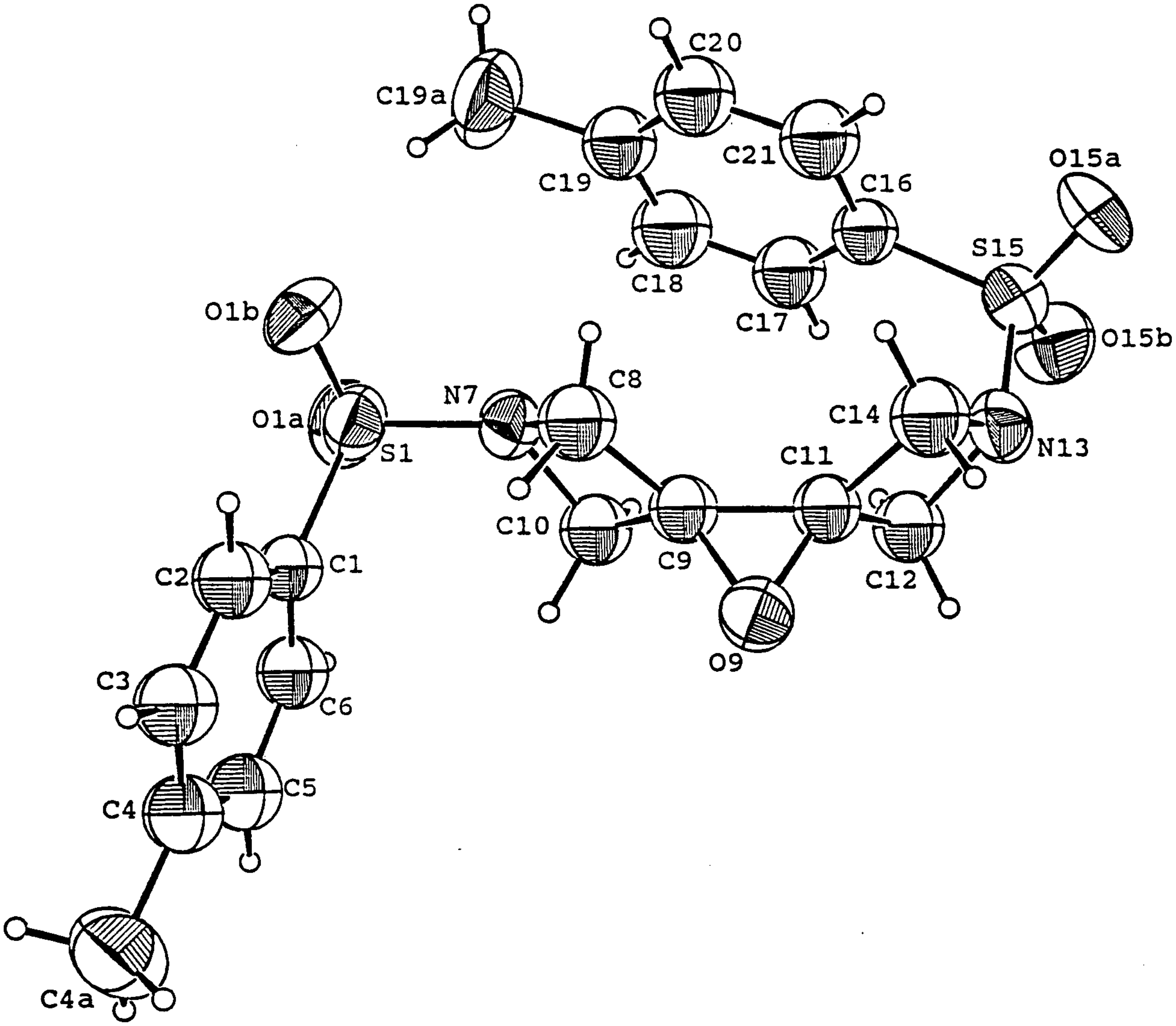
Improved Economical and Environmentally Benign Routes for the Large-Scale Synthesis of 1,3,3-Trinitroazetidine

Principal Investigator: Dr. Alan P. Marchand

Department of Chemistry, University of North Texas
NT Station, Box 5068, Denton, Texas 76203-5070

ONR Contract Number N00014-96-1-1279
Mechanics & Energy Conversion S&T Division (ONR Code 333)

Appendix III: X-ray Structure Data for Compound 43b


C19a
C20
C21
C19
C16
O15a
S15
C18
C17
O15b
O1b
N7
C8
C14
O1a
S1
C11
N13
C10
C9
C12
C2
C1
O9
C3
C6
C4
C5
C4a

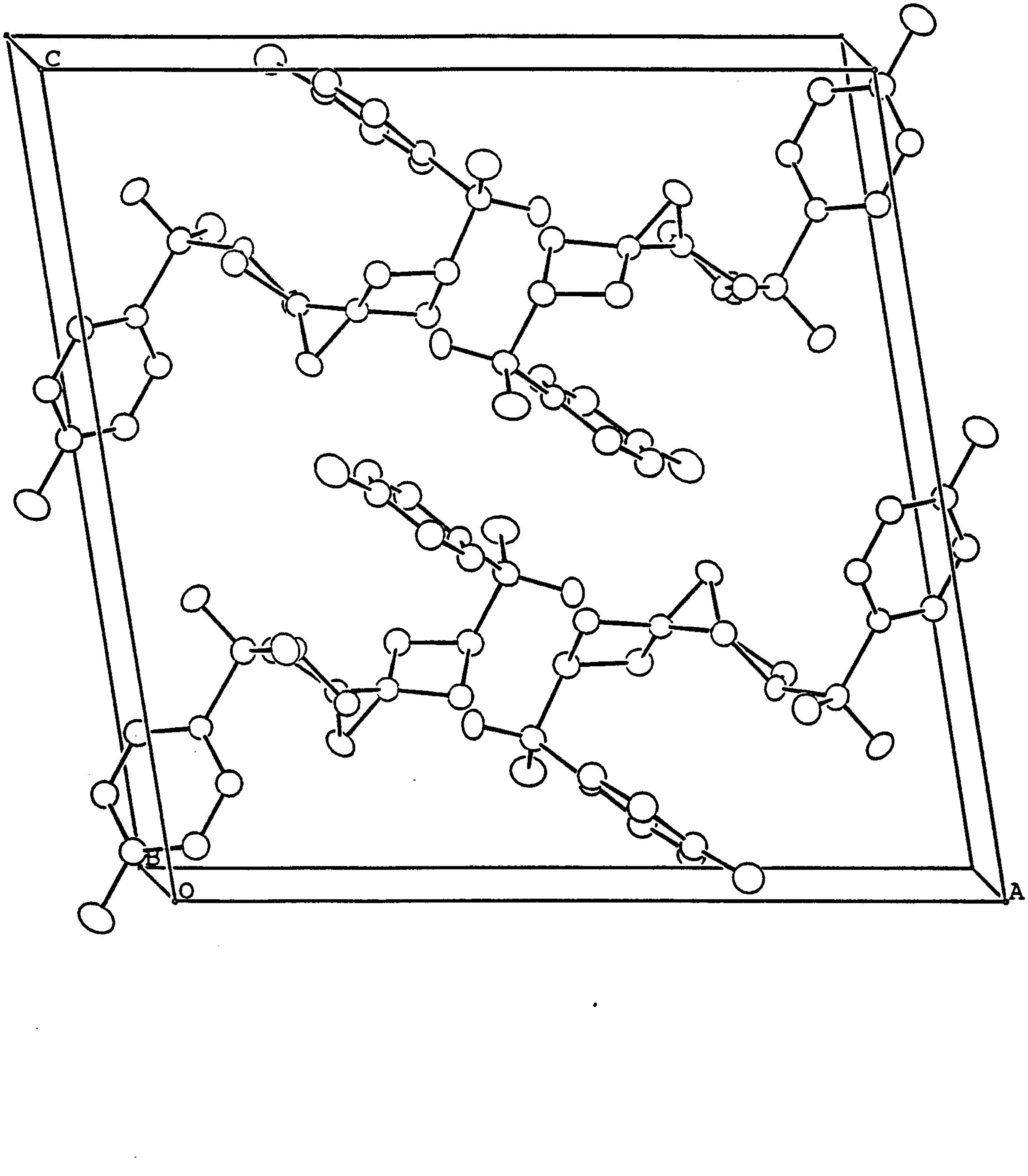

C
B
O
A

Table of Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
S1	0.13889(9)	0.1990(2)	0.78790(9)	4.50(4)
S15	0.49172(9)	-0.3372(3)	0.85968(9)	4.84(4)
O1a	0.1837(2)	0.3637(6)	0.7960(2)	5.7(1)
O1b	0.0936(2)	0.1440(6)	0.8489(2)	5.8(1)
O9	0.2543(2)	-0.2750(6)	0.6570(2)	5.5(1)
O15a	0.4982(3)	-0.4955(6)	0.9055(3)	7.0(1)
O15b	0.5635(2)	-0.2539(7)	0.8397(2)	6.2(1)
N7	0.2069(2)	0.0469(7)	0.7829(3)	3.9(1)
N13	0.4359(3)	-0.3878(6)	0.7734(3)	4.3(1)
C1	0.0729(3)	0.2037(8)	0.6956(3)	3.7(1)*
C2	0.0010(3)	0.1060(9)	0.6848(3)	4.6(1)*
C3	-0.0500(3)	0.1086(9)	0.6108(4)	4.9(1)*
C4	-0.0304(3)	0.2036(9)	0.5471(3)	4.7(1)*
C4a	-0.0870(4)	0.208(1)	0.4673(4)	7.0(2)
C5	0.0415(3)	0.2999(9)	0.5580(3)	5.0(1)*

Table of Positional Parameters and Their Estimated Standard Deviations (cont.

Atom	x	y	z	B(A2)
C6	0.0928(3)	0.3031(9)	0.6323(3)	4.6(1)*
C8	0.1878(3)	-0.1477(8)	0.7748(3)	4.6(1)*
C9	0.2557(3)	-0.1596(8)	0.7243(3)	3.7(1)*
C10	0.2592(3)	0.0403(9)	0.7180(3)	4.4(1)*
C11	0.3222(3)	-0.2823(8)	0.7224(3)	3.8(1)*
C12	0.4092(3)	-0.2403(9)	0.7145(3)	4.4(1)*
C14	0.3490(4)	-0.4452(9)	0.7723(4)	5.0(1)*
C16	0.4363(3)	-0.1839(8)	0.9075(3)	3.9(1)*
C17	0.4406(4)	-0.0052(9)	0.8919(4)	5.0(1)*
C18	0.3915(4)	0.113(1)	0.9242(4)	6.0(2)*
C19	0.3367(4)	0.0596(9)	0.9723(4)	4.9(1)*
C19a	0.2810(4)	0.188(1)	1.0047(4)	8.8(2)
C20	0.3344(4)	-0.1193(9)	0.9887(4)	5.5(2)*
C21	0.3830(4)	-0.2409(9)	0.9574(4)	5.4(2)*

Starred atoms were refined isotropically.
Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

Table of Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
H2	-0.0133	0.0373	0.7278	6*
H3	-0.0997	0.0428	0.6040	6*
H4a1	-0.1394	0.2492	0.4845	8*
H4a2	-0.0930	0.0938	0.4432	9*
H4a3	-0.0683	0.2890	0.4310	9*
H5	0.0563	0.3651	0.5141	6*
H6	0.1413	0.3731	0.6395	5*
H8a	0.1962	-0.1802	0.8277	5*
H8b	0.1296	-0.1681	0.7329	5*
H10a	0.3141	0.1014	0.7349	5*
H10b	0.2280	0.0864	0.6661	5*
H12a	0.4325	-0.1374	0.7365	5*
H12b	0.4168	-0.2781	0.6618	5*
H14a	0.3178	-0.4544	0.8215	6*
H14b	0.3332	-0.5419	0.7323	6*
H17	0.4778	0.0365	0.8584	6*
H18	0.3958	0.2359	0.9127	7*
H19a1	0.2290	0.2172	0.9710	9*
H19a2	0.3107	0.2952	1.0157	11*
H19a3	0.2685	0.1396	1.0535	11*
H20	0.2978	-0.1601	1.0230	7*
H21	0.3796	-0.3631	0.9700	7*

Table of General Displacement Parameter Expressions - U's

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
S1	0.0546(8)	0.057(1)	0.0607(9)	0.0081(9)	0.0130(7)	-0.0092(9)
S15	0.0566(9)	0.070(1)	0.0550(9)	0.0180(9)	0.0029(8)	0.005(1)
O1a	0.072(3)	0.055(3)	0.089(3)	-0.002(2)	0.007(2)	-0.024(3)
O1b	0.070(2)	0.094(4)	0.062(2)	0.007(3)	0.031(2)	-0.006(3)
O9	0.058(2)	0.090(3)	0.056(2)	0.018(2)	-0.008(2)	-0.019(3)
O15a	0.114(3)	0.075(3)	0.075(3)	0.044(3)	0.006(3)	0.033(3)
O15b	0.042(2)	0.117(4)	0.079(3)	0.001(3)	0.012(2)	-0.007(3)
N7	0.041(2)	0.057(3)	0.054(3)	0.006(2)	0.013(2)	0.004(3)
N13	0.060(3)	0.042(3)	0.059(3)	0.010(3)	0.005(2)	0.001(3)
C4a	0.099(5)	0.075(5)	0.082(5)	0.015(5)	-0.014(4)	-0.006(5)
C19a	0.095(5)	0.144(7)	0.091(5)	0.052(5)	0.002(4)	-0.050(5)

The form of the anisotropic displacement parameter is:
exp[-2PI2{h2a2U(1,1) + k2b2U(2,2) + l2c2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)}] where a,b, and c are reciprocal lattice constants.

Table of Bond Distances in Angstroms

Atom 1	Atom 2	Distance
S1	O1a	1.441(5)
S1	O1b	1.423(4)
S1	N7	1.617(5)
S1	C1	1.747(5)
S15	O15a	1.417(5)
S15	O15b	1.427(4)
S15	N13	1.634(4)
S15	C16	1.747(6)
O9	C9	1.425(7)
O9	C11	1.438(6)
N7	C8	1.503(8)
N7	C10	1.493(7)
N13	C12	1.509(7)
N13	C14	1.493(7)
C1	C2	1.383(8)
C1	C6	1.383(8)
C2	C3	1.386(7)
C3	C4	1.370(9)
C4	C4a	1.506(8)
C4	C5	1.377(8)
C5	C6	1.393(7)
C8	C9	1.510(8)
C9	C10	1.515(9)
C9	C11	1.439(8)
C11	C12	1.494(8)
C11	C14	1.514(9)
C16	C17	1.378(9)
C16	C21	1.378(9)
C17	C18	1.37(1)
C18	C19	1.367(9)
C19	C19a	1.49(1)
C19	C20	1.38(1)
C20	C21	1.38(1)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Bond Distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
C2	H2	0.95	C12	H12a	0.92
C3	H3	0.95	C12	H12b	0.96
C4a	H4a1	1.00	C14	H14a	1.04
C4a	H4a2	0.95	C14	H14b	1.00
C4a	H4a3	0.95	C17	H17	0.95
C5	H5	0.95	C18	H18	0.95
C6	H6	0.95	C19a	H19a1	0.97
C8	H8a	0.91	C19a	H19a2	0.95
C8	H8b	1.11	C19a	H19a3	0.95
C10	H10a	1.02	C20	H20	0.95
C10	H10b	1.00	C21	H21	0.95

Table of Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O1a	S1	O1b	120.2(3)	C1	C2	C3	119.6(6)
O1a	S1	N7	105.6(2)	C2	C3	C4	121.7(5)
O1a	S1	C1	107.7(3)	C3	C4	C4a	121.2(5)
O1b	S1	N7	106.2(3)	C3	C4	C5	118.5(5)
O1b	S1	C1	108.8(2)	C4a	C4	C5	120.3(6)
N7	S1	C1	107.8(3)	C4	C5	C6	120.9(6)
O15a	S15	O15b	120.4(3)	C1	C6	C5	119.7(5)
O15a	S15	N13	105.6(3)	N7	C8	C9	86.9(4)
O15a	S15	C16	107.9(3)	O9	C9	C8	124.3(5)
O15b	S15	N13	105.3(2)	O9	C9	C10	123.3(5)
O15b	S15	C16	109.3(3)	O9	C9	C11	60.3(3)
N13	S15	C16	107.6(2)	C8	C9	C10	91.1(4)
C9	O9	C11	60.4(3)	C8	C9	C11	133.3(5)
S1	N7	C8	124.2(3)	C10	C9	C11	127.0(5)
S1	N7	C10	123.2(4)	N7	C10	C9	87.1(4)
C8	N7	C10	92.2(4)	O9	C11	C9	59.4(3)
S15	N13	C12	118.3(4)	O9	C11	C12	124.3(5)
S15	N13	C14	118.8(4)	O9	C11	C14	125.3(5)
C12	N13	C14	91.5(4)	C9	C11	C12	127.6(5)
S1	C1	C2	120.3(4)	C9	C11	C14	131.8(5)
S1	C1	C6	120.2(4)	C12	C11	C14	91.3(4)
C2	C1	C6	119.5(5)	N13	C12	C11	88.2(4)

Bond Angles (cont.)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
N13	C14	C11	88.1(4)	C18	C19	C19a	121.7(6)
S15	C16	C17	121.0(4)	C18	C19	C20	116.8(6)
S15	C16	C21	120.3(5)	C19a	C19	C20	121.6(6)
C17	C16	C21	118.6(6)	C19	C20	C21	122.7(6)
C16	C17	C18	120.8(6)	C16	C21	C20	119.4(6)
C17	C18	C19	121.8(7)				

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C1	C2	H2	120	C9	C10	H10b	113
C3	C2	H2	120	H10a	C10	H10b	113
C2	C3	H3	119	N13	C12	H12a	107
C4	C3	H3	119	N13	C12	H12b	109
C4	C4a	H4a1	101	C11	C12	H12a	119
C4	C4a	H4a2	112	C11	C12	H12b	107
C4	C4a	H4a3	112	H12a	C12	H12b	121
H4a1	C4a	H4a2	112	N13	C14	H14a	127
H4a1	C4a	H4a3	112	N13	C14	H14b	112
H4a2	C4a	H4a3	110	C11	C14	H14a	111
C4	C5	H5	120	C11	C14	H14b	102
C6	C5	H5	120	H14a	C14	H14b	112
C1	C6	H6	120	C16	C17	H17	120
C5	C6	H6	120	C18	C17	H17	120
N7	C8	H8a	100	C17	C18	H18	119
N7	C8	H8b	110	C19	C18	H18	119
C9	C8	H8a	121	C19	C19a	H19a1	118
C9	C8	H8b	106	C19	C19a	H19a2	107
H8a	C8	H8b	124	C19	C19a	H19a3	107
N7	C10	H10a	112	H19a1	C19a	H19a2	107
N7	C10	H10b	111	H19a1	C19a	H19a3	107
C9	C10	H10a	118	H19a2	C19a	H19a3	110

Bond Angles (cont.)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C19	C20	H20	119	C16	C21	H21	120
C21	C20	H20	119	C20	C21	H21	120

Table of Torsion Angles in Degrees

Atom 1	Atom 2	Atom 3	Atom 4	Angle
O1a	S1	N7	C8	179.40 (0.39)
O1a	S1	N7	C10	-60.64 (0.46)
O1b	S1	N7	C8	50.74 (0.45)
O1b	S1	N7	C10	170.71 (0.41)
C1	S1	N7	C8	-65.73 (0.46)
C1	S1	N7	C10	54.24 (0.48)
O1a	S1	C1	C2	-153.31 (0.48)
O1a	S1	C1	C6	27.74 (0.56)
O1b	S1	C1	C2	-21.52 (0.58)
O1b	S1	C1	C6	159.52 (0.48)
N7	S1	C1	C2	93.22 (0.51)
N7	S1	C1	C6	-85.73 (0.54)
O15a	S15	N13	C12	172.68 (0.38)
O15a	S15	N13	C14	63.42 (0.49)
O15b	S15	N13	C12	-58.91 (0.45)
O15b	S15	N13	C14	-168.17 (0.44)
C16	S15	N13	C12	57.60 (0.44)
C16	S15	N13	C14	-51.66 (0.50)
O15a	S15	C16	C17	160.51 (0.45)
O15a	S15	C16	C21	-24.13 (0.54)
O15b	S15	C16	C17	27.91 (0.53)
O15b	S15	C16	C21	-156.73 (0.45)
N13	S15	C16	C17	-85.97 (0.50)
N13	S15	C16	C21	89.39 (0.49)
C11	O9	C9	C8	-124.52 (0.63)
C11	O9	C9	C10	116.99 (0.57)
C9	O9	C11	C12	-117.00 (0.66)
C9	O9	C11	C14	121.95 (0.60)
S1	N7	C8	C9	145.88 (0.37)
C10	N7	C8	C9	12.41 (0.38)
S1	N7	C10	C9	-146.54 (0.38)
C8	N7	C10	C9	-12.37 (0.38)
S15	N13	C12	C11	-116.82 (0.40)
C14	N13	C12	C11	7.30 (0.43)
S15	N13	C14	C11	116.54 (0.41)
C12	N13	C14	C11	-7.21 (0.42)
S1	C1	C2	C3	-178.87 (0.48)
C6	C1	C2	C3	0.09 (0.93)
S1	C1	C6	C5	177.29 (0.48)
C2	C1	C6	C5	-1.67 (0.90)
C1	C2	C3	C4	1.14 (0.95)
C2	C3	C4	C4a	-178.94 (0.61)
C2	C3	C4	C5	-0.75 (0.97)
C3	C4	C5	C6	-0.88 (0.96)
C4a	C4	C5	C6	177.33 (0.61)
C4	C5	C6	C1	2.09 (0.96)
N7	C8	C9	O9	-144.96 (0.51)

Table of Torsion Angles in Degrees (continued)

Atom 1	Atom 2	Atom 3	Atom 4	Angle
N7	C8	C9	C10	-12.23 (0.38)
N7	C8	C9	C11	135.52 (0.62)
O9	C9	C10	N7	145.74 (0.46)
C8	C9	C10	N7	12.31 (0.38)
C11	C9	C10	N7	-138.61 (0.52)
O9	C9	C11	C12	111.82 (0.59)
O9	C9	C11	C14	-111.78 (0.68)
C8	C9	C11	O9	110.69 (0.68)
C8	C9	C11	C12	-137.49 (0.63)
C8	C9	C11	C14	-1.08 (1.04)
C10	C9	C11	O9	-111.22 (0.57)
C10	C9	C11	C12	0.60 (0.86)
C10	C9	C11	C14	137.00 (0.62)
O9	C11	C12	N13	-142.80 (0.55)
C9	C11	C12	N13	141.83 (0.54)
C14	C11	C12	N13	-7.20 (0.42)
O9	C11	C14	N13	142.24 (0.49)
C9	C11	C14	N13	-139.59 (0.60)
C12	C11	C14	N13	7.28 (0.42)
S15	C16	C17	C18	174.26 (0.47)
C21	C16	C17	C18	-1.18 (0.85)
S15	C16	C21	C20	-174.15 (0.46)
C17	C16	C21	C20	1.32 (0.84)
C16	C17	C18	C19	-0.35 (0.94)
C17	C18	C19	C19a	-177.53 (0.59)
C17	C18	C19	C20	1.67 (0.91)
C18	C19	C20	C21	-1.52 (0.92)
C19a	C19	C20	C21	177.68 (0.59)
C19	C20	C21	C16	0.04 (0.94)

```
                    Table of Least-Squares Planes
                    -----------------------------


Orthonormal Equation of Plane    1

   0.5465 X +    -0.7867 Y +    -0.2872 Z -    -4.8942 = 0

   0.0022         0.0016         0.0024          0.0240

Crystallographic Equation of Plane

   9.0043 X +    -5.9378 Y +    -6.2341 Z -    -4.8942 = 0

   0.0360         0.0124         0.1320          0.0240

 Atom          X         Y         Z        Distance      Esd

C1          -0.6673    1.5379   11.5431      0.0046 +- 0.0057
C2          -1.8226    0.7998   11.3642      0.0052 +- 0.0062
C3          -2.4640    0.8195   10.1363     -0.0082 +- 0.0063
C4          -1.9703    1.5367    9.0787      0.0012 +- 0.0062
C5          -0.8150    2.2639    9.2593      0.0087 +- 0.0065
C6          -0.1690    2.2877   10.4931     -0.0114 +- 0.0062

Chi Squared =      8.2

                  -----  Other Atoms  -----
S1           0.1718    1.5023   13.0752      0.0511 +- 0.0017
C4a         -2.6893    1.5692    7.7556     -0.0374 +- 0.0075


Orthonormal Equation of Plane    2

  -0.6356 X +     0.0857 Y +    -0.7673 Z -   -10.6860 = 0

   0.0027         0.0034         0.0022          0.0230

Crystallographic Equation of Plane

 -10.4719 X +     0.6472 Y +   -11.0252 Z -   -10.6860 = 0

   0.0445         0.0255         0.1442          0.0230

 Atom          X         Y         Z        Distance      Esd

N7           1.3066    0.3538   12.9916     -0.0820 +- 0.0040
C8           1.0133   -1.1145   12.8578      0.0811 +- 0.0056
C9           2.2665   -1.2049   12.0202     -0.0804 +- 0.0050
C10          2.3414    0.3044   11.9160      0.0814 +- 0.0054

Chi Squared =  1105.1
```

Table of Least-Squares Planes (continued)

```
Orthonormal Equation of Plane   3

   0.1214 X +   -0.5864 Y +   -0.8008 Z -   -7.8941 = 0

   0.0036        0.0031        0.0022        0.0383

Crystallographic Equation of Plane

   2.0008 X +   -4.4264 Y +  -13.6162 Z -   -7.8941 = 0

   0.0591        0.0235        0.1650        0.0383

 Atom          X         Y         Z        Distance      Esd

C11        3.3675   -2.1309   11.9875    -0.0474 +- 0.0055
C12        4.8219   -1.8135   11.8569     0.0476 +- 0.0058
N13        5.1050   -2.9274   12.8345    -0.0477 +- 0.0045
C14        3.6760   -3.3602   12.8159     0.0475 +- 0.0062

Chi Squared =    311.4


Orthonormal Equation of Plane   4

  -0.5897 X +   -0.1146 Y +   -0.7995 Z -  -14.6927 = 0

   0.0020        0.0025        0.0015        0.0166

Crystallographic Equation of Plane

  -9.7152 X +   -0.8648 Y +  -11.6834 Z -  -14.6927 = 0

   0.0323        0.0188        0.1215        0.0166

 Atom          X         Y         Z        Distance      Esd

C16        4.7513   -1.3881   15.0605     0.0095 +- 0.0052
C17        4.8627   -0.0389   14.8014    -0.0036 +- 0.0058
C18        3.9677    0.8555   15.3369    -0.0065 +- 0.0064
C19        2.9348    0.4500   16.1354     0.0106 +- 0.0058
C20        2.8537   -0.9003   16.4081    -0.0048 +- 0.0062
C21        3.7376   -1.8185   15.8882    -0.0052 +- 0.0060

Chi Squared =      9.6
```

```
Dihedral Angles Between Planes:
-------------------------------
        Plane No.   Plane No.   Dihedral Angle
        ---------   ---------   --------------
            1           2       101.21 +- 0.23
            1           3        40.74 +- 0.34
            1           4        90.14 +- 0.19
            2           3        60.86 +- 0.26
            2           4        11.94 +- 0.81
            3           4        50.52 +- 0.25
```

Intermolecular Contacts (less than 3.60 Angstroms)

O1a	C14'	3.16
O15a	O15a"	3.17
O9	C4a"'	3.22
O15a	C12""	3.29
O15b	N13""'	3.36
O15b	C19a"""	3.39
O9	C20"""'	3.40
O15a	C21"	3.41
O1a	C3""""	3.44
O15b	C14""'	3.45
O15a	C18""""'	3.48
O15b	C10""	3.58

Symmetry Codes

'	(x,y,z) -> (x,y+1,z)
"	(x,y,z) -> (1-x,-1-y,2-z)
"'	(x,y,z) -> (-x,-y,1-z)
""	(x,y,z) -> (1-x,y-1/2,3/2-z)
""'	(x,y,z) -> (1-x,y+1/2,3/2-z)
"""	(x,y,z) -> (1-x,1-y,2-z)
"""'	(x,y,z) -> (x,-1/2-y,z-1/2)
""""	(x,y,z) -> (-x,y+1/2,3/2-z)
""""'	(x,y,z) -> (x,y-1,z)

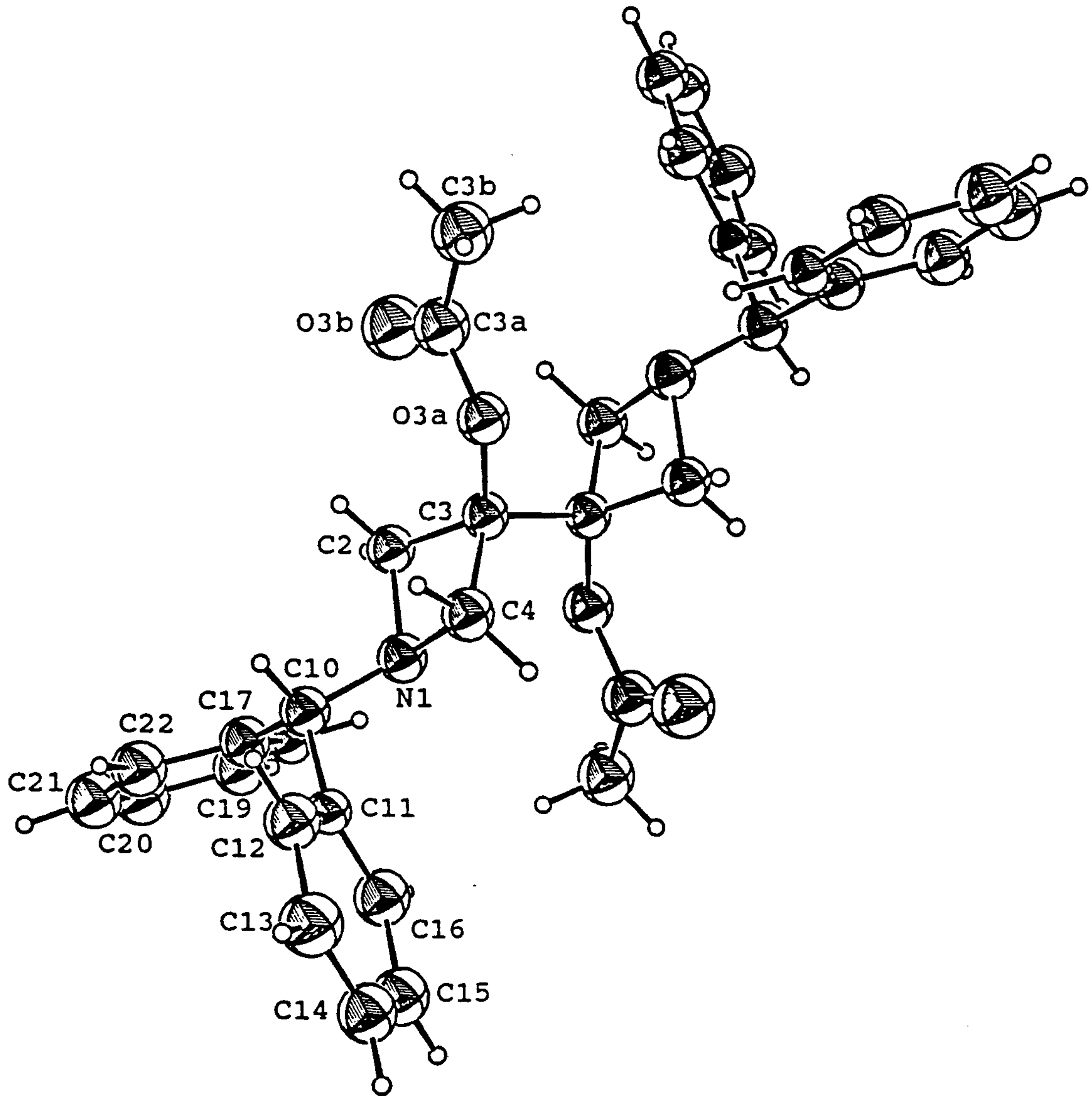
Improved Economical and Environmentally Benign Routes for the Large-Scale Synthesis of 1,3,3-Trinitroazetidine

Principal Investigator: Dr. Alan P. Marchand

Department of Chemistry, University of North Texas
NT Station, Box 5068, Denton, Texas 76203-5070

ONR Contract Number N00014-96-1-1279
Mechanics & Energy Conversion S&T Division (ONR Code 333)

Appendix IV: X-ray Structure Data for Compound 47


C3b
O3b
C3a
O3a
C3
C2
C4
N1
C10
C17
C22
C21
C19
C20
C12
C11
C13
C16
C14
C15

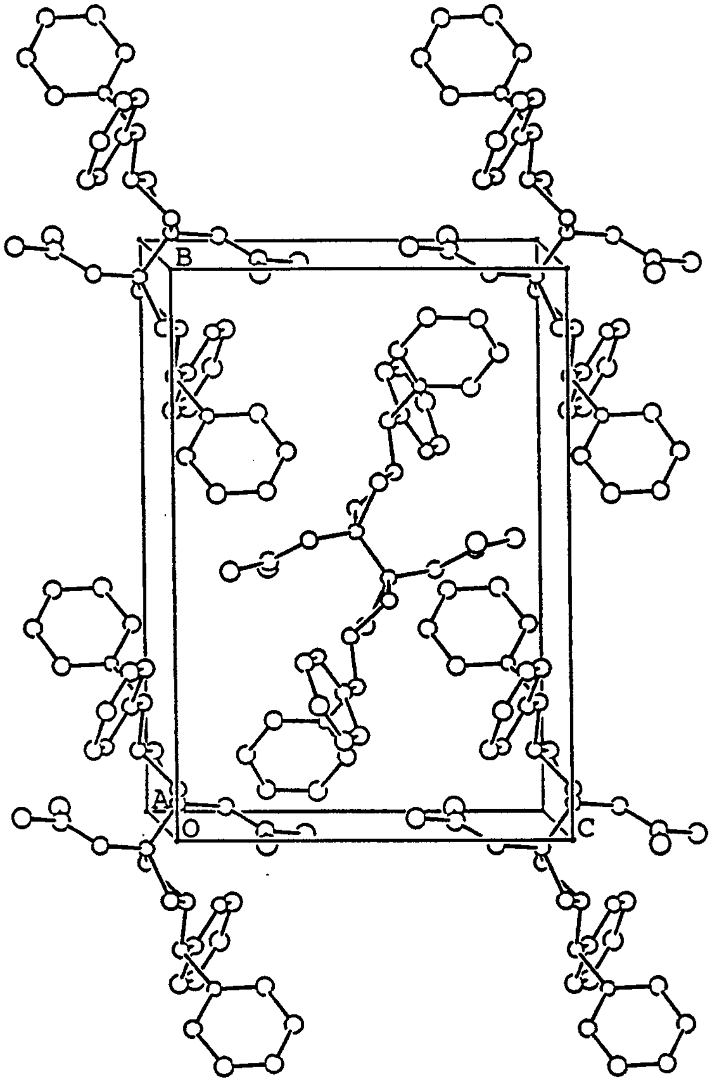

B
A
O
C

Table of Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
O3a	0.0785(7)	0.4699(4)	0.6640(6)	3.4(1)*
O3b	-0.1045(8)	0.5265(5)	0.7555(7)	5.1(2)*
N1	-0.1391(9)	0.3621(5)	0.4323(8)	3.1(2)*
C2	-0.172(1)	0.4274(6)	0.5276(9)	2.9(2)*
C3	-0.013(1)	0.4599(6)	0.5393(9)	2.7(2)*
C3a	0.026(1)	0.5093(7)	0.762(1)	4.0(3)*
C3b	0.150(1)	0.5211(7)	0.871(1)	4.5(3)*
C4	0.026(1)	0.3719(7)	0.484(1)	3.4(2)*
C10	-0.199(1)	0.2763(7)	0.4421(9)	3.1(2)*
C11	-0.122(1)	0.2117(6)	0.3668(8)	2.3(2)*
C12	-0.033(1)	0.1463(7)	0.4275(9)	3.5(2)*
C13	0.033(1)	0.0842(7)	0.357(1)	4.3(3)*
C14	0.012(1)	0.0882(7)	0.228(1)	3.8(3)*
C15	-0.074(1)	0.1524(7)	0.169(1)	3.8(2)*
C16	-0.143(1)	0.2155(7)	0.236(1)	3.8(3)*
C17	-0.369(1)	0.2747(7)	0.3965(9)	3.3(2)*
C18	-0.443(1)	0.3409(6)	0.3265(9)	2.8(2)*
C19	-0.598(1)	0.3386(7)	0.282(1)	4.1(3)*
C20	-0.678(1)	0.2674(7)	0.311(1)	4.4(3)*
C21	-0.604(1)	0.2024(7)	0.379(1)	4.2(3)*
C22	-0.450(1)	0.2040(7)	0.429(1)	3.9(3)*

Starred atoms were refined isotropically.

Table of Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
H2a	-0.2966	0.4587	0.4971	3*
H2b	-0.1862	0.4146	0.6060	3*
H3b1	0.2426	0.4689	0.8893	5*
H3b2	0.1058	0.5243	0.9464	5*
H3b3	0.1967	0.5747	0.8590	5*
H4a	0.0487	0.3355	0.5606	4*
H4b	0.0799	0.3688	0.4044	4*
H10	-0.1806	0.2599	0.5296	3*
H12	-0.0166	0.1428	0.5181	4*
H13	0.0919	0.0390	0.4004	5*
H14	0.0573	0.0468	0.1799	4*
H15	-0.0884	0.1556	0.0787	4*
H16	-0.2029	0.2597	0.1912	4*
H18	-0.3879	0.3900	0.3072	3*
H19	-0.6477	0.3851	0.2335	5*
H20	-0.7830	0.2641	0.2834	5*
H21	-0.6588	0.1522	0.3939	5*
H22	-0.4030	0.1589	0.4826	5*

Table of Bond Distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
O3a	C3	1.44(1)	C11	C12	1.38(1)
O3a	C3a	1.36(1)	C11	C16	1.37(1)
O3b	C3a	1.20(1)	C12	C13	1.41(2)
N1	C2	1.49(1)	C13	C14	1.35(2)
N1	C4	1.51(1)	C14	C15	1.34(1)
N1	C10	1.44(1)	C15	C16	1.41(2)
C2	C3	1.51(1)	C17	C18	1.37(1)
C3	C3′	1.54(1)	C17	C22	1.39(1)
C3	C4	1.55(1)	C18	C19	1.40(1)
C3a	C3b	1.48(1)	C19	C20	1.37(2)
C10	C11	1.52(1)	C20	C21	1.34(1)
C10	C17	1.53(1)	C21	C22	1.40(1)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Bond Distances in Angstroms

Atom 1	Atom 2	Distance
C2	H2a	1.22
C2	H2b	0.89
C3b	H3b1	1.16
C3b	H3b2	0.95
C3b	H3b3	0.95
C4	H4a	0.98
C4	H4b	1.04
C10	H10	0.95
C12	H12	0.95
C13	H13	0.95
C14	H14	0.95
C15	H15	0.95
C16	H16	0.95
C18	H18	0.95
C19	H19	0.95
C20	H20	0.95
C21	H21	0.95
C22	H22	0.95

Table of Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C3	O3a	C3a	121.8(7)	C11	C10	C17	110.7(8)
C2	N1	C4	89.4(7)	C10	C11	C12	121.2(8)
C2	N1	C10	116.6(8)	C10	C11	C16	120.6(8)
C4	N1	C10	115.4(7)	C12	C11	C16	118.2(9)
N1	C2	C3	88.9(7)	C11	C12	C13	120.9(9)
O3a	C3	C2	120.0(8)	C12	C13	C14	121(1)
O3a	C3	C4	108.1(7)	C13	C14	C15	118.(1)
O3a	C3	C3′	107.0(6)	C14	C15	C16	123(1)
C2	C3	C4	87.5(7)	C11	C16	C15	119.0(9)
C2	C3	C3′	117.5(7)	C10	C17	C18	122.0(9)
C4	C3	C3′	115.5(8)	C10	C17	C22	118.5(8)
O3a	C3a	O3b	121.7(9)	C18	C17	C22	119.5(9)
O3a	C3a	C3b	109.7(9)	C17	C18	C19	122.0(9)
O3b	C3a	C3b	128.(1)	C18	C19	C20	118.5(9)
N1	C4	C3	86.9(7)	C19	C20	C21	119(1)
N1	C10	C11	110.3(8)	C20	C21	C22	124.(1)
N1	C10	C17	111.3(8)	C17	C22	C21	116.7(9)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle
N1	C2	H2a	112
N1	C2	H2b	124
C3	C2	H2a	136
C3	C2	H2b	107
H2a	C2	H2b	93
C3a	C3b	H3b1	118
C3a	C3b	H3b2	107
C3a	C3b	H3b3	107
H3b1	C3b	H3b2	107
H3b1	C3b	H3b3	107
H3b2	C3b	H3b3	109
N1	C4	H4a	107
N1	C4	H4b	106
C3	C4	H4a	102
C3	C4	H4b	121
H4a	C4	H4b	126
N1	C10	H10	108
C11	C10	H10	109
C17	C10	H10	108
C11	C12	H12	120
C13	C12	H12	120
C12	C13	H13	120
C14	C13	H13	120
C13	C14	H14	121
C15	C14	H14	121
C14	C15	H15	118
C16	C15	H15	118
C11	C16	H16	121
C15	C16	H16	121
C17	C18	H18	119
C19	C18	H18	119
C18	C19	H19	121
C20	C19	H19	121
C19	C20	H20	121
C21	C20	H20	121
C20	C21	H21	118
C22	C21	H21	118
C17	C22	H22	122
C21	C22	H22	122

Table of Torsion Angles in Degrees

Atom 1	Atom 2	Atom 3	Atom 4	Angle
C3a	O3a	C3	C2	-46.46 (1.18)
C3a	O3a	C3	C4	-144.23 (0.85)
C3a	O3a	C3	C3′	90.76 (0.98)
C3	O3a	C3a	O3b	10.83 (1.45)
C3	O3a	C3a	C3b	-172.17 (0.80)
C4	N1	C2	C3	20.69 (0.69)
C10	N1	C2	C3	139.08 (0.79)
C2	N1	C4	C3	-20.14 (0.68)
C10	N1	C4	C3	-139.51 (0.78)
C2	N1	C10	C11	-163.83 (0.75)
C2	N1	C10	C17	72.82 (1.00)
C4	N1	C10	C11	-60.79 (1.01)
C4	N1	C10	C17	175.87 (0.77)
N1	C2	C3	O3a	-129.61 (0.79)
N1	C2	C3	C4	-20.15 (0.67)
N1	C2	C3	C3′	97.46 (0.85)
O3a	C3	C4	N1	140.78 (0.72)
C2	C3	C4	N1	19.99 (0.66)
C3′	C3	C4	N1	-99.43 (0.85)
O3a	C3	C3′	O3a′	-180.00 (0.86)
O3a	C3	C3′	C2′	41.55 (1.05)
O3a	C3	C3′	C4′	-59.64 (1.02)
C2	C3	C3′	O3a′	-41.55 (1.05)
C2	C3	C3′	C2′	179.98 (0.43)
C2	C3	C3′	C4′	78.81 (1.06)
C4	C3	C3′	O3a′	59.64 (1.02)
C4	C3	C3′	C2′	-78.81 (1.06)
C4	C3	C3′	C4′	-180.00 (0.86)
N1	C10	C11	C12	114.37 (0.99)
N1	C10	C11	C16	-68.11 (1.14)
C17	C10	C11	C12	-121.92 (0.97)
C17	C10	C11	C16	55.60 (1.19)
N1	C10	C17	C18	15.28 (1.30)
N1	C10	C17	C22	-163.92 (0.87)
C11	C10	C17	C18	-107.86 (1.05)
C11	C10	C17	C22	72.95 (1.12)
C10	C11	C12	C13	177.01 (0.91)
C16	C11	C12	C13	-0.56 (1.46)
C10	C11	C16	C15	-177.58 (0.89)
C12	C11	C16	C15	0.03 (1.59)
C11	C12	C13	C14	0.91 (1.59)
C12	C13	C14	C15	-0.64 (1.58)
C13	C14	C15	C16	0.08 (1.50)
C14	C15	C16	C11	0.24 (1.61)
C10	C17	C18	C19	178.53 (0.92)
C22	C17	C18	C19	-2.29 (1.52)
C10	C17	C22	C21	-176.20 (0.90)

Table of Torsion Angles in Degrees (continued)

Atom 1	Atom 2	Atom 3	Atom 4	Angle
C18	C17	C22	C21	4.58 (1.47)
C17	C18	C19	C20	0.26 (1.56)
C18	C19	C20	C21	-0.77 (1.58)
C19	C20	C21	C22	3.47 (1.70)
C20	C21	C22	C17	-5.37 (1.62)