Electronic Supplementary Information

Resolving Synthetic Challenges Faced in the Syntheses of Asymmetric *N,N'*-Ethylene-Bridged Energetic Compounds

Dheeraj Kumar, Gregory H. Imler, Damon A. Parrish and Jean'ne M. Shreeve*

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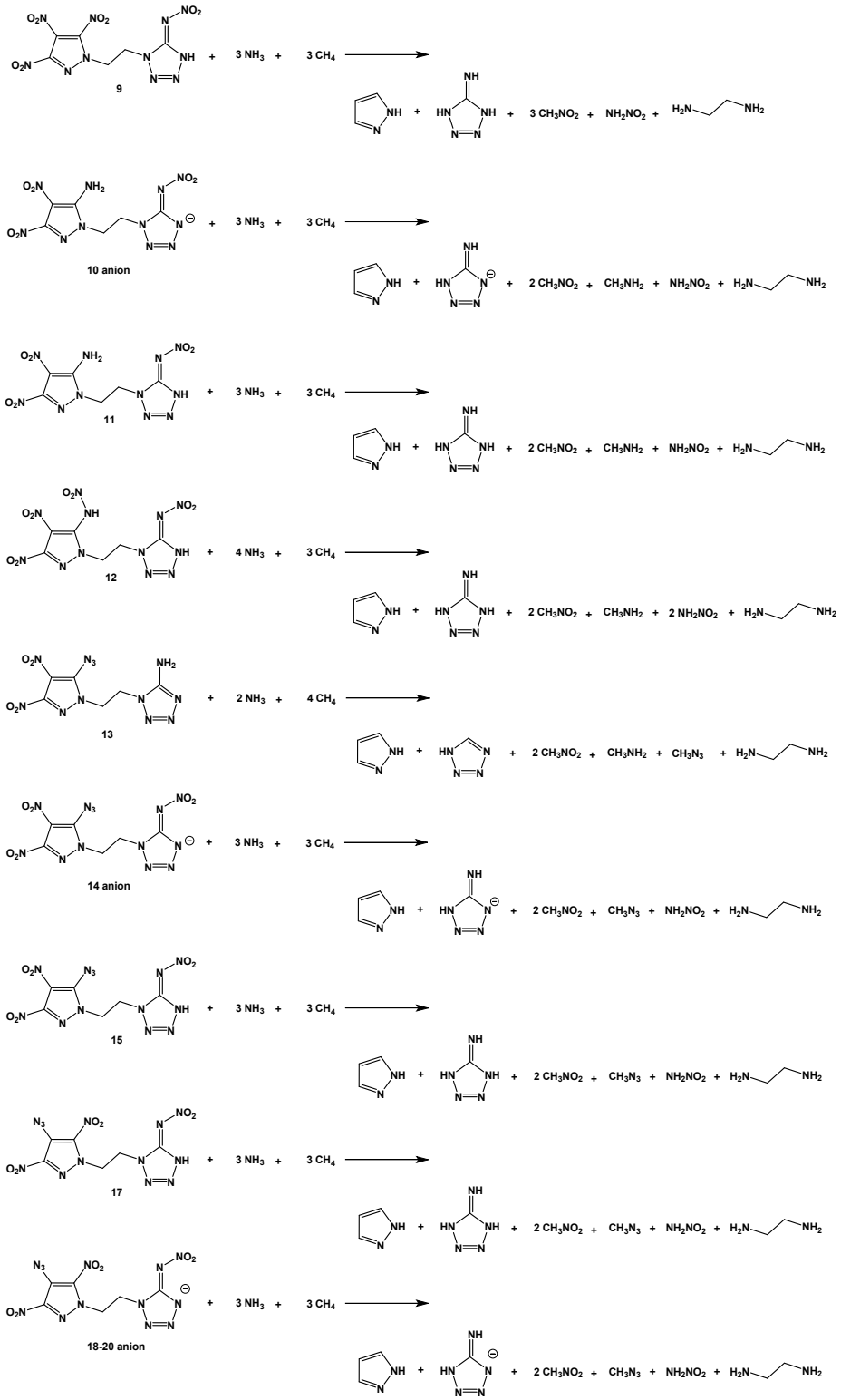
1. Isodesmic Reactions



Scheme S1: Isodesmic reactions for the compounds **9 - 20**

2. Crystal Structure Data

Table S1. Crystal data and structure refinement for Compound **13**.

Identification code	shrv440	
Empirical formula	$C_6H_6N_{12}O_4$	
Formula weight	310.23	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 6.5577(7) Å	α= 90°.
	b = 31.045(3) Å	β= 95.054(2)°.
	c = 5.8420(6) Å	γ = 90°.
Volume	1184.7(2) $Å^3$	
Z	4	
Density (-123°C)	1.739 Mg/m^3	
Density (20°C)	1.711 Mg/m^3	
Absorption coefficient	0.148 mm^{-1}	
F(000)	632	
Crystal size	0.239 x 0.087 x 0.020 mm^3	
Theta range for data collection	2.624 to 29.966°.	
Index ranges	-9<=h<=8, -42<=k<=42, -8<=l<=8	
Reflections collected	15752	
Independent reflections	3348 [R_{int} = 0.0236]	
Completeness to theta = 25.242°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7460 and 0.6975	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3348 / 0 / 199	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R_1 = 0.0353, wR_2 = 0.0862	
R indices (all data)	R_1 = 0.0444, wR_2 = 0.0909	
Largest diff. peak and hole	0.381 and -0.386 $e.Å^{-3}$	
CCDC No	1504585	

Table S2. Bond lengths [Å] and angles [°] for Compound **13**.

N(1)-N(2)	1.1140(16)	N(2)-N(3)	1.2524(15)
N(3)-C(4)	1.3759(15)	C(4)-N(14)	1.3554(14)
C(4)-C(5)	1.3979(15)	C(5)-C(9)	1.4043(16)
C(5)-N(6)	1.4285(14)	N(6)-O(8)	1.2192(14)
N(6)-O(7)	1.2247(15)	C(9)-N(13)	1.3162(14)
C(9)-N(10)	1.4574(14)	N(10)-O(11)	1.2198(14)
N(10)-O(12)	1.2227(14)	N(13)-N(14)	1.3550(13)
N(14)-C(15)	1.4663(13)	C(15)-C(16)	1.5251(15)

C(15)-H(15A)	0.9900	C(15)-H(15B)	0.9900
C(16)-N(17)	1.4590(13)	C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900	N(17)-C(21)	1.3503(14)
N(17)-N(18)	1.3681(13)	N(18)-N(19)	1.2885(15)
N(19)-N(20)	1.3636(14)	N(20)-C(21)	1.3338(14)
C(21)-N(22)	1.3438(14)	N(22)-H(22A)	0.8800
N(22)-H(22B)	0.8800		

N(1)-N(2)-N(3)	168.22(15)	N(2)-N(3)-C(4)	120.83(11)
N(14)-C(4)-N(3)	114.49(10)	N(14)-C(4)-C(5)	105.89(9)
N(3)-C(4)-C(5)	139.43(10)	C(4)-C(5)-C(9)	104.06(9)
C(4)-C(5)-N(6)	126.75(10)	C(9)-C(5)-N(6)	129.03(10)
O(8)-N(6)-O(7)	124.69(11)	O(8)-N(6)-C(5)	118.48(11)
O(7)-N(6)-C(5)	116.83(10)	N(13)-C(9)-C(5)	112.77(10)
N(13)-C(9)-N(10)	116.85(10)	C(5)-C(9)-N(10)	130.29(10)
O(11)-N(10)-O(12)	125.32(11)	O(11)-N(10)-C(9)	117.40(10)
O(12)-N(10)-C(9)	117.26(10)	C(9)-N(13)-N(14)	104.43(9)
N(13)-N(14)-C(4)	112.83(9)	N(13)-N(14)-C(15)	120.83(9)
C(4)-N(14)-C(15)	126.03(9)	N(14)-C(15)-C(16)	111.01(9)
N(14)-C(15)-H(15A)	109.4	C(16)-C(15)-H(15A)	109.4
N(14)-C(15)-H(15B)	109.4	C(16)-C(15)-H(15B)	109.4
H(15A)-C(15)-H(15B)	108.0	N(17)-C(16)-C(15)	112.40(9)
N(17)-C(16)-H(16A)	109.1	C(15)-C(16)-H(16A)	109.1
N(17)-C(16)-H(16B)	109.1	C(15)-C(16)-H(16B)	109.1
H(16A)-C(16)-H(16B)	107.9	C(21)-N(17)-N(18)	108.17(9)
C(21)-N(17)-C(16)	130.06(9)	N(18)-N(17)-C(16)	121.50(9)
N(19)-N(18)-N(17)	105.67(9)	N(18)-N(19)-N(20)	112.57(9)
C(21)-N(20)-N(19)	104.82(9)	N(20)-C(21)-N(22)	126.20(10)
N(20)-C(21)-N(17)	108.78(9)	N(22)-C(21)-N(17)	124.98(10)
C(21)-N(22)-H(22A)	120.0	C(21)-N(22)-H(22B)	120.0
H(22A)-N(22)-H(22B)	120.0		

Table S3. Hydrogen bonds for Compound **13**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(22)-H(22A)...N(13)#1	0.88	2.26	3.0992(14)	160.3
N(22)-H(22B)...N(19)#2	0.88	2.12	2.9611(14)	160.6

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+2 #2 x,y,z+1

Table S4. Crystal data and structure refinement for Compound **14**.

Identification code	shrv444	
Empirical formula	$C_6H_4N_{13}NaO_6$	
Formula weight	377.21	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 29.426(4) Å	α= 90°.
	b = 8.4217(11) Å	β= 100.699(5)°.
	c = 11.1029(14) Å	γ = 90°.
Volume	2703.7(6) $Å^3$	
Z	8	
Density (-123°C)	1.853 Mg/m^3	
Density (20°C)	1.826 Mg/m^3	
Absorption coefficient	0.189 mm^{-1}	
F(000)	1520	
Crystal size	0.288 x 0.200 x 0.005 mm^3	
Theta range for data collection	0.704 to 25.366°.	
Index ranges	-35<=h<=35, -10<=k<=10, -12<=l<=13	
Reflections collected	22925	
Independent reflections	4937 [R_{int} = 0.1500]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7452 and 0.5716	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4937 / 408 / 470	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R_1 = 0.0765, wR_2 = 0.1766	
R indices (all data)	R_1 = 0.1383, wR_2 = 0.2025	
Largest diff. peak and hole	0.562 and -0.534 e.$Å^{-3}$	
CCDC No	1504586	

Table S5. Bond lengths [Å] and angles [°] for Compound **14**.

N(1)-N(2)	1.147(10)	N(2)-N(3)	1.254(9)
N(3)-C(4)	1.388(10)	C(4)-N(14)	1.339(11)
C(4)-C(5)	1.402(11)	C(5)-C(9)	1.382(12)
C(5)-N(6)	1.449(11)	N(6)-O(8)	1.225(9)
N(6)-O(7)	1.229(9)	C(9)-N(13)	1.310(10)
C(9)-N(10)	1.454(10)	N(10)-O(12)	1.221(9)
N(10)-O(11)	1.234(9)	N(13)-N(14)	1.374(9)
N(14)-C(15)	1.472(10)	C(15)-C(16)	1.489(11)
C(15)-H(15A)	0.9900	C(15)-H(15B)	0.9900
C(16)-N(17)	1.446(10)	C(16)-H(16B)	0.9900
C(16)-H(16A)	0.9900	N(17)-C(21)	1.336(10)
N(17)-N(18)	1.369(8)	N(18)-N(19)	1.278(10)
N(19)-N(20)	1.379(9)	N(20)-C(21)	1.336(10)
C(21)-N(22)	1.385(10)	N(22)-N(23)	1.318(9)
N(23)-O(24)	1.219(9)	N(23)-O(25)	1.295(8)
N(27)-N(28)	1.104(10)	N(28)-N(29)	1.252(10)
N(29)-C(30)	1.396(10)	C(30)-N(40)	1.316(11)
C(30)-C(31)	1.411(11)	C(31)-C(35)	1.379(11)
C(31)-N(32)	1.406(11)	N(32)-O(34)	1.199(9)
N(32)-O(33)	1.238(9)	C(35)-N(39)	1.311(10)
C(35)-N(36)	1.465(10)	N(36)-O(37)	1.212(8)
N(36)-O(38)	1.220(9)	N(39)-N(40)	1.379(9)
N(40)-C(41)	1.453(9)	C(41)-C(42)	1.494(11)
C(41)-H(41B)	0.9900	C(41)-H(41A)	0.9900
C(42)-N(43)	1.452(9)	C(42)-H(42A)	0.9900
C(42)-H(42B)	0.9900	N(43)-N(44)	1.337(8)
N(43)-C(47)	1.379(9)	N(44)-N(45)	1.326(9)
N(45)-N(46)	1.396(8)	N(46)-C(47)	1.320(9)
C(47)-N(48)	1.365(9)	N(48)-N(49)	1.286(9)
N(49)-O(50)	1.271(8)	N(49)-O(51)	1.282(8)
N(1)-N(2)-N(3)	167.3(9)	N(2)-N(3)-C(4)	121.3(7)
N(14)-C(4)-N(3)	115.4(7)	N(14)-C(4)-C(5)	105.8(7)
N(3)-C(4)-C(5)	138.3(8)	C(9)-C(5)-C(4)	104.0(7)
C(9)-C(5)-N(6)	131.9(7)	C(4)-C(5)-N(6)	123.9(8)
O(8)-N(6)-O(7)	124.5(8)	O(8)-N(6)-C(5)	117.5(7)
O(7)-N(6)-C(5)	117.9(7)	N(13)-C(9)-C(5)	113.9(7)
N(13)-C(9)-N(10)	116.4(7)	C(5)-C(9)-N(10)	129.6(7)
O(12)-N(10)-O(11)	126.7(7)	O(12)-N(10)-C(9)	117.6(7)
O(11)-N(10)-C(9)	115.6(7)	C(9)-N(13)-N(14)	103.3(7)
C(4)-N(14)-N(13)	112.8(6)	C(4)-N(14)-C(15)	127.6(6)
N(13)-N(14)-C(15)	119.1(6)	N(14)-C(15)-C(16)	111.8(6)
N(14)-C(15)-H(15A)	109.3	C(16)-C(15)-H(15A)	109.3
N(14)-C(15)-H(15B)	109.3	C(16)-C(15)-H(15B)	109.3

H(15A)-C(15)-H(15B)	107.9	N(17)-C(16)-C(15)	112.5(7)
N(17)-C(16)-H(16B)	109.1	C(15)-C(16)-H(16B)	109.1
N(17)-C(16)-H(16A)	109.1	C(15)-C(16)-H(16A)	109.1
H(16B)-C(16)-H(16A)	107.8	C(21)-N(17)-N(18)	108.4(7)
C(21)-N(17)-C(16)	129.8(6)	N(18)-N(17)-C(16)	121.8(6)
N(19)-N(18)-N(17)	105.8(6)	N(18)-N(19)-N(20)	112.6(7)
C(21)-N(20)-N(19)	103.9(7)	N(17)-C(21)-N(20)	109.4(6)
N(17)-C(21)-N(22)	115.6(7)	N(20)-C(21)-N(22)	135.0(7)
N(23)-N(22)-C(21)	114.3(7)	O(24)-N(23)-O(25)	119.0(7)
O(24)-N(23)-N(22)	127.1(6)	O(25)-N(23)-N(22)	113.9(7)
N(27)-N(28)-N(29)	169.3(10)	N(28)-N(29)-C(30)	116.8(7)
N(40)-C(30)-N(29)	118.0(7)	N(40)-C(30)-C(31)	107.1(7)
N(29)-C(30)-C(31)	134.4(8)	C(35)-C(31)-N(32)	129.1(7)
C(35)-C(31)-C(30)	102.5(7)	N(32)-C(31)-C(30)	127.9(8)
O(34)-N(32)-O(33)	125.7(8)	O(34)-N(32)-C(31)	118.1(7)
O(33)-N(32)-C(31)	116.2(7)	N(39)-C(35)-C(31)	115.1(7)
N(39)-C(35)-N(36)	114.0(7)	C(31)-C(35)-N(36)	130.8(7)
O(37)-N(36)-O(38)	123.4(7)	O(37)-N(36)-C(35)	118.0(7)
O(38)-N(36)-C(35)	118.4(6)	C(35)-N(39)-N(40)	102.4(7)
C(30)-N(40)-N(39)	113.0(6)	C(30)-N(40)-C(41)	128.0(6)
N(39)-N(40)-C(41)	118.5(6)	N(40)-C(41)-C(42)	112.3(6)
N(40)-C(41)-H(41B)	109.1	C(42)-C(41)-H(41B)	109.1
N(40)-C(41)-H(41A)	109.1	C(42)-C(41)-H(41A)	109.1
H(41B)-C(41)-H(41A)	107.9	N(43)-C(42)-C(41)	113.0(6)
N(43)-C(42)-H(42A)	109.0	C(41)-C(42)-H(42A)	109.0
N(43)-C(42)-H(42B)	109.0	C(41)-C(42)-H(42B)	109.0
H(42A)-C(42)-H(42B)	107.8	N(44)-N(43)-C(47)	109.5(6)
N(44)-N(43)-C(42)	120.7(6)	C(47)-N(43)-C(42)	129.2(6)
N(45)-N(44)-N(43)	106.3(5)	N(44)-N(45)-N(46)	110.2(5)
C(47)-N(46)-N(45)	106.0(6)	N(46)-C(47)-N(48)	136.4(7)
N(46)-C(47)-N(43)	108.0(6)	N(48)-C(47)-N(43)	115.6(6)
N(49)-N(48)-C(47)	116.5(6)	O(50)-N(49)-O(51)	117.3(6)
O(50)-N(49)-N(48)	117.4(6)	O(51)-N(49)-N(48)	125.3(6)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for Compound **14**.

	x	y	z	U(eq)
H(15A)	8672	6500	7479	24
H(15B)	8778	5284	6457	24
H(16B)	9458	4478	7772	19
H(16A)	9469	6335	7474	19
H(41B)	6377	-1550	-1017	21
H(41A)	6277	-556	-2267	21
H(42A)	5583	402	-1692	16
H(42B)	5579	-1460	-1976	16