Supporting Information for:

Chemistry of the Diazeniumdiolates. O- versus N-Alkylation of the RNH[N(O)NO]$^-$ Ion

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Table S1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	8827(1)	3796(3)	715(2)	20(1)
N(2)	8421(1)	2072(3)	979(2)	18(1)
N(3)	8237(1)	674(3)	-196(2)	19(1)
O(1)	8207(1)	1465(3)	2185(2)	24(1)
O(2)	9017(1)	4839(3)	2020(2)	22(1)
C(7)	9496(2)	6752(4)	1768(3)	29(1)
C(1)	7373(1)	50(4)	-331(2)	19(1)
C(2)	7234(1)	-1561(4)	-1574(2)	23(1)
C(3)	6351(1)	-2286(4)	-1754(3)	28(1)
C(4)	5781(1)	-321(4)	-1949(2)	26(1)
C(5)	5924(1)	1284(4)	-695(2)	24(1)
C(6)	6806(1)	2026(4)	-521(2)	21(1)

Table S2. Bond lengths [Å] and angles [°] for **2b**.

N(1)-N(2)	1.275(2)	N(1)-O(2)	1.382(2)
N(2)-O(1)	1.259(2)	N(2)-N(3)	1.396(2)
N(3)-C(1)	1.472(3)	N(3)-H(3)	0.85(2)
O(2)-C(7)	1.433(3)	C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600	C(7)-H(7C)	0.9600
C(1)-C(2)	1.516(3)	C(1)-C(6)	1.520(3)
C(1)-H(1A)	0.9800	C(2)-C(3)	1.519(3)
C(2)-H(2A)	0.9700	C(2)-H(2B)	0.9700
C(3)-C(4)	1.519(3)	C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700	C(4)-C(5)	1.522(3)
C(4)-H(4A)	0.9700	C(4)-H(4B)	0.9700
C(5)-C(6)	1.521(3)	C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700	C(6)-H(6B)	0.9700
C(6)-H(6C)	0.9700		
N(2)-N(1)-O(2)	106.80(15)	O(1)-N(2)-N(1)	126.99(18)
O(1)-N(2)-N(3)	117.55(17)	N(1)-N(2)-N(3)	115.37(17)
N(2)-N(3)-C(1)	111.63(16)	N(2)-N(3)-H(3)	105.2(16)
C(1)-N(3)-H(3)	110.1(16)	N(1)-O(2)-C(7)	108.29(16)
O(2)-C(7)-H(7A)	109.5	O(2)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5	O(2)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5	H(7B)-C(7)-H(7C)	109.5
N(3)-C(1)-C(2)	108.30(17)	N(3)-C(1)-C(6)	113.06(18)
C(2)-C(1)-C(6)	111.36(18)	N(3)-C(1)-H(1A)	108.0
C(2)-C(1)-H(1A)	108.0	C(6)-C(1)-H(1A)	108.0
C(1)-C(2)-C(3)	110.67(18)	C(1)-C(2)-H(2A)	109.5
C(3)-C(2)-H(2A)	109.5	C(1)-C(2)-H(2B)	109.5
C(3)-C(2)-H(2B)	109.5	H(2A)-C(2)-H(2B)	108.1
C(4)-C(3)-C(2)	111.6(2)	C(4)-C(3)-H(3A)	109.3
C(2)-C(3)-H(3A)	109.3	C(4)-C(3)-H(3B)	109.3
C(2)-C(3)-H(3B)	109.3	H(3A)-C(3)-H(3B)	108.0
C(3)-C(4)-C(5)	110.66(19)	C(3)-C(4)-H(4A)	109.5
C(5)-C(4)-H(4A)	109.5	C(3)-C(4)-H(4B)	109.5
C(5)-C(4)-H(4B)	109.5	H(4A)-C(4)-H(4B)	108.1
C(6)-C(5)-C(4)	110.92(18)	C(6)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5A)	109.5	C(6)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5B)	109.5	H(5A)-C(5)-H(5B)	108.0
C(1)-C(6)-C(5)	110.83(18)	C(1)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6B)	109.5	C(1)-C(6)-H(6C)	109.5
C(5)-C(6)-H(6C)	109.5	H(6B)-C(6)-H(6C)	108.1

Table S3. Anisotropic displacement parameters ($Å^2$x 10^3) for **2b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	22(1)	22(1)	17(1)	-3(1)	1(1)	-4(1)
N(2)	19(1)	22(1)	14(1)	0(1)	2(1)	2(1)
N(3)	24(1)	23(1)	11(1)	-2(1)	2(1)	-1(1)
O(1)	33(1)	28(1)	11(1)	2(1)	6(1)	-5(1)
O(2)	25(1)	23(1)	18(1)	-5(1)	1(1)	-5(1)
C(7)	31(2)	21(1)	33(1)	-1(1)	1(1)	-5(1)
C(1)	20(1)	21(1)	15(1)	1(1)	2(1)	0(1)
C(2)	27(1)	22(1)	21(1)	-4(1)	3(1)	2(1)
C(3)	30(2)	28(2)	26(1)	-7(1)	4(1)	-6(1)
C(4)	21(1)	35(2)	22(1)	-2(1)	-1(1)	-6(1)
C(5)	20(1)	26(1)	24(1)	1(1)	1(1)	1(1)
C(6)	24(1)	18(1)	21(1)	-2(1)	2(1)	0(1)

Table S4. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **2b**.

	x	y	z	U(eq)
H(3)	8351(14)	1410(40)	-930(30)	23
H(7A)	9630	7506	2663	43
H(7B)	9193	7725	1111	43
H(7C)	9986	6308	1362	43
H(1A)	7255	-720	555	22
H(2A)	7580	-2844	-1395	28
H(2B)	7379	-864	-2455	28
H(3A)	6270	-3248	-2587	33
H(3B)	6225	-3121	-912	33
H(4A)	5222	-834	-2007	31
H(4B)	5868	430	-2843	31
H(5A)	5574	2563	-863	28
H(5B)	5784	575	185	28
H(6B)	6931	2860	-1364	25
H(6C)	6889	2987	312	25

Table S5. Torsion angles [°] for **2b**.

O(2)-N(1)-N(2)-O(1)	2.3(3)
O(2)-N(1)-N(2)-N(3)	-174.14(16)
O(1)-N(2)-N(3)-C(1)	51.6(2)
N(1)-N(2)-N(3)-C(1)	-131.56(19)
N(2)-N(1)-O(2)-C(7)	178.22(17)
N(2)-N(3)-C(1)-C(2)	-176.90(17)
N(2)-N(3)-C(1)-C(6)	59.2(2)
N(3)-C(1)-C(2)-C(3)	179.36(18)
C(6)-C(1)-C(2)-C(3)	-55.7(2)
C(1)-C(2)-C(3)-C(4)	55.8(3)
C(2)-C(3)-C(4)-C(5)	-56.1(2)
C(3)-C(4)-C(5)-C(6)	56.1(3)
N(3)-C(1)-C(6)-C(5)	178.44(17)
C(2)-C(1)-C(6)-C(5)	56.2(2)
C(4)-C(5)-C(6)-C(1)	-56.3(2)

Table S6. Crystal data and structure refinement for **2b**.

Empirical formula	$C_7H_{15}N_3O_2$	
Formula weight	173.22	
Temperature	-170 °C	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 16.517(5) Å b = 6.0509(16) Å c = 9.311(3) Å	α = 90° β = 94.738(5)° γ = 90°
Volume	927.4(5) $Å^3$	
Z	4	
Density (calculated)	1.233 Mg/m^3	
Absorption coefficient	0.092 mm^{-1}	
F(000)	376	
Crystal size	0.51 x 0.08 x 0.07 mm^3	
Theta range for data collection	1.24 to 26.38°	
Index ranges	-19<=h<=20, -7<=k<=7, -11<=1<=11	
Reflections collected	5868	
Independent reflections	1898 [R(int) = 0.0477]	
Completeness to theta = 26.38°	99.9%	
Absorption correction	Semi-empirical from equivalent reflections	
Max. and min. transmission	0.894 and 0.615	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1898 / 0 / 112	
Goodness-of-fit on F^2	0.921	
Final R indices [I>2σ(I)]	R_1 = 0.0425, wR_2 = 0.0940	
R indices (all data)	R_1 = 0.0858, wR_2 = 0.1317	
Largest diff. peak and hole	0.233 and -0.221 $eÅ^{-3}$	

Table S7. Optimized Geometry, B3LYP/6-311++G**, for MeNHN(O)NOMe.

H	-1.601117	-0.380723	-3.351707
H	-2.630930	-0.306273	-1.891797
H	-1.664835	-1.775559	-2.234056
C	-1.694991	-0.685539	-2.310591
O	-0.568535	-0.097725	-1.655022
N	-0.614305	-0.438894	-0.318451
N	0.409944	0.057905	0.267125
O	1.286449	0.789988	-0.202068
N	0.532752	-0.374439	1.608709
C	0.894449	0.709966	2.525702
H	1.004518	0.261432	3.513310
H	0.145523	1.510217	2.566263
H	1.851457	1.125964	2.219389
H	-0.343409	-0.831727	1.842972

Table S8. Optimized Geometry, B3LYP/6-311++G**, for $[MeNN(O)NOMe]^-$.

H	-3.686647	0.532177	0.000086
H	-3.037907	-0.879978	0.891604
H	-3.038447	-0.881139	-0.889968
C	-2.915346	-0.244706	0.000366
O	-1.685618	0.426734	-0.000443
N	-0.679001	-0.609627	-0.000328
N	0.504658	-0.009395	-0.000043
N	0.635235	1.259774	0.000127
O	1.530880	-0.838660	0.000030
C	2.787261	-0.125461	0.000097
H	3.574124	-0.887581	0.000061
H	2.932340	0.524535	0.880799
H	2.932351	0.524701	-0.880452