Conformational analysis, NMR properties and nitrogen inversion of N-substituted 1,3-oxazines.

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Supporting Information (A total of 4 pages)

Table S1. B3LYP/6-31G** optimized geometries for N-substituted oxazines. Bond lengths are in Å and angles in degrees.

Parameters	Methyl		Ethyl		Propyl		i-Propyl		t-Butyl	
	Axial	Equatorial	Axial	Equatorial	Axial	Equatorial	Axial	Equatorial	Axial	Equatorial
O1-C2	1.433	1.410	1.433	1.411	1.434	1.411	1.438	1.416	1.436	1.417
C2-N3	1.439	1.453	1.441	1.456	1.440	1.456	1.431	1.449	1.435	1.454
N3-C4	1.460	1.456	1.460	1.458	1.459	1.458	1.454	1.455	1.498	1.493
C4-C5	1.550	1.533	1.550	1.533	1.549	1.533	1.548	1.536	1.554	1.536
C5-C6	1.538	1.533	1.536	1.533	1.536	1.532	1.539	1.534	1.536	1.532
N3-R	1.467	1.455	1.478	1.465	1.476	1.465	1.484	1.474	1.498	1.493
C2-H2a	1.102	1.115	1.102	1.115	1.102	1.115	1.103	1.112	1.104	1.112
C2-H2e	1.092	1.093	1.090	1.091	1.090	1.091	1.090	1.093	1.088	1.088
C4-H4a	1.098	1.110	1.099	1.110	1.099	1.109	1.101	1.108	1.101	1.108
C4-H4e	1.091	1.092	1.091	1.092	1.091	1.092	1.090	1.090	1.087	1.087
C6-H6a	1.104	1.103	1.104	1.103	1.104	1.103	1.104	1.104	1.104	1.104
C6-H6e	1.090	1.090	1.090	1.090	1.090	1.090	1.090	1.090	1.090	1.090
<O1C2N3	113.4	111.0	113.4	111.1	113.4	111.1	113.5	110.7	113.9	110.8
<C5C4N3	114.8	110.3	114.9	110.5	114.8	110.4	114.7	110.4	115.6	109.8
<H2aC2H2e	109.5	108.7	109.2	108.7	109.2	108.7	109.1	108.8	108.8	108.8
<H4aC4H4e	107.8	108.0	107.7	107.9	107.7	108.0	107.6	108.0	107.1	108.0
<H6aC6H6e	108.7	109.0	108.7	109.6	108.7	109.0	108.7	109.0	108.6	109.0
<C4C5C6	109.5	109.5	109.4	109.5	109.3	109.5	109.4	109.6	109.6	109.8
<H2aC2N3	108.7	111.6	108.7	111.3	108.7	111.2	109.1	112.7	108.9	112.1
<H4aC4N3	108.0	112.2	108.0	112.4	108.1	112.5	108.5	113.1	107.9	113.1
<C2O1C6C5	-56.6	-56.1	-56.8	-55.8	-56.6	-55.6	-56.4	-55.7	-57.0	-55.2
<C2N3C4C5	49.0	56.3	49.2	56.7	49.5	57.0	48.3	57.8	47.2	58.4
<O1C2N3C7	72.9	171.0	73.9	170.8	74.5	170.5	86.6	160.5	90.3	159.6

Table S2. Total energies (E, hartrees), zero point energy corrections (ZPE, hartrees), enthalpy thermal corrections (H_{corr}, hartrees), Gibb's free energy thermal corrections (G_{corr}, hartrees); entropy (S, cal mol^{-1} K^{-1}), dipole moments (μ), relative enthalpies (ΔH^o, kcal mol^{-1}) and relative Gibb's free energies (ΔG^o, kcal mol^{-1})

Energy[a]	Methyl		Ethyl		Propyl		i-Propyl		t-Butyl	
	Axial	Equatorial	Axial	Equatorial	Axial	Equatorial	Equatorial	Axial	Equatorial	Axial
HF/6-31G(d,p) geometry										
$E_o^{(2)}$[MP2/6-31G(d,p)]	-569.292365	-569.290142	-608.481374	-608.473577	-647.658985	-647.655581	-647.659508	-647.658793	-686.843460	-686.842988
$E_o^{(3)}$[MP2/6-311G(d,p)]	-569.525091	-569.523274	-608.725012	-608.719911	-647.917960	-647.914975	-647.918619	-647.917992	-687.116108	-687.115811
$E_o^{(4)}$[MP2/6-311+G(d,p)]	-569.550367	-569.549218	-608.751020	-608.746301	-647.943959	-647.941837	-647.944753	-647.944921	-687.143164	-687.143571
$E_o^{(5)}$[MP2/6-311++G(d,p)]	-569.551437	-569.550254	-608.752278	-608.747509	-647.945353	-647.943154	-647.946213	-647.946284	-687.144765	-687.145074
ZPE	0.209094	0.208582	0.237144	0.238833	0.269539	0.269092	0.268836	0.268572	0.298837	0.298501
H_{corr}	0.219900	0.219500	0.247930	0.251118	0.283012	0.282728	0.282263	0.282119	0.313263	0.313155
G_{corr}	0.173775	0.173090	0.202277	0.201030	0.230081	0.229034	0.230308	0.229506	0.259667	0.258010
S[b]	97.077	97.677	96.084	105.419	111.403	113.009	109.349	110.734	112.801	116.064
μ (D)	4.160	5.578	4.129	5.483	4.130	5.411	4.149	5.368	4.119	5.272
$E_o^{(4)}$ + ZPE	-569.341277	-569.340636	-608.513876	-608.507468	-647.674420	-647.672745	-647.675917	-647.676349	-686.844327	-686.845070
$E_o^{(4)}$ + Hcorr	-569.330467	-569.329718	-608.503090	-608.495183	-647.660947	-647.659109	-647.662490	-647.662802	-686.829901	-686.830416
$E_o^{(4)}$ +Gcorr	-569.376592	-569.376128	-608.548743	-608.545271	-647.713878	-647.712803	-647.714445	-647.715415	-686.883497	-686.885561
$\Delta H^{o(4)}$ [c]	-0.470		-4.962		-1.100		0.196		0.324	
$\Delta G^{o(4)}$ [c]	-0.291		-2.179		-0.675		0.609		1.296	
B3LYP/6-31G(d,p) geometry										
$E_o^{(6)}$[B3LYP/6-31G(d,p)]	-570.938542	-570.937188	-610.256524	-610.254212	-649.573022	-649.570567	-649.571062	-649.570629	-688.884268	-688.883853
$E_o^{(7)}$[B3LYP/6-311G(d,p)]	-571.078165	-571.077212	-610.404188	-610.402319	-649.728232	-649.726405	-649.726520	-649.726317	-689.047357	-689.047142
$E_o^{(8)}$[B3LYP/6-311+G(d,p)]	-571.091344	-571.091240	-610.417108	-610.416124	-649.741383	-649.740243	-649.73872	-649.739722	-689.059258	-689.060595
$E_o^{(9)}$[B3LYP/6-311++G(d,p)]	-571.091621	-571.091485	-610.417389	-610.416403	-649.741686	-649.740534	-649.739055	-649.740021	-689.059608	-689.060921
ZPE	0.193964	0.193379	0.222258	0.221826	0.250853	0.250202	0.250116	0.249721	0.278248	0.277814
H_{corr}	0.205482	0.204998	0.235186	0.234867	0.265148	0.264673	0.264435	0.264172	0.293685	0.293471
G_{corr}	0.157929	0.157135	0.184102	0.183239	0.210566	0.209319	0.210523	0.209664	0.238047	0.23656
S[b]	100.085	101.12	107.515	108.661	114.876	116.503	113.469	114.72	117.102	119.778
μ (D)	3.528	4.736	3.496	4.654	3.478	4.598	3.498	4.616	3.472	4.527
$E_o^{(8)}$ + ZPE	-570.897380	-570.897861	-610.194850	-610.1942984	-649.490530	-649.490041	-649.488605	-649.490001	-688.781010	-688.782781
$E_o^{(8)}$ + Hcorr	-570.885862	-570.886242	-610.181922	-610.1812574	-649.476235	-649.475570	-649.474286	-649.475550	-688.765573	-688.767124
$E_o^{(8)}$ +Gcorr	-570.933415	-570.934105	-610.233006	-610.2328854	-649.530817	-649.530924	-649.528198	-649.530058	-688.821211	-688.824035
$\Delta H^{o(8)}$ [c]	0.238454		-0.417168		-0.416854		0.792858		0.973518	
$\Delta G^{o(8)}$ [c]	0.432982		-0.075803		0.067583		1.166854		1.772338	

Table S3. Relative free energies (kcal mol^{-1}) of the axial isomer of the methyl and ethyl derivatives obtained at two different levels of theory. The values within parenthesis correspond to the percentage of the axial isomer.

Solvent	**Theoretical model**	**Methyl**	**Ethyl**
Gas	MP2/6-311+G**	-0.29	-0.44
		(62.0)	(67.8)
	MP2/6-311+G(3df,2p)	-0.42	-0.58
		(67.2)	(72.6)
CH_2Cl_2	MP2/6-311+G**	0.68	0.68
		(24.1)	(24.1)
	MP2/6-311+G(3df,2p)	0.40	0.35
		(33.9)	(35.5)