

**Energetics and reactivity of morpholine and thiomorpholine:  
A joint experimental and computational study**

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**Table S1.** Typical combustion results and standard ( $p^\circ = 0.1$  MPa) massic energy of combustion of morpholine, at  $T = 298.15$  K.<sup>a</sup>

Experiment	1	2	3	4	5	6
$m(\text{CO}_2, \text{total}) / \text{g}$	2.26765	1.57940	1.15562	1.42357	1.32259	1.19274
$m(\text{cpd}) / \text{g}$	0.99118	0.65577	0.45204	0.57743	0.52070	0.47736
$m(\text{fuse}) / \text{g}$	0.00273	0.00239	0.00292	0.00277	0.00250	0.00276
$m(\text{Melinex}) / \text{g}$	0.11372	0.10937	0.10370	0.11017	0.11633	0.09768
$\Delta T_{\text{ad}} / \text{K}$	2.12511	1.45909	1.04829	1.30519	1.20193	1.08908
$\varepsilon_{\text{f}} / (\text{J}\cdot\text{K}^{-1})$	16.55	15.36	14.62	14.97	14.93	14.75
$\Delta m(\text{H}_2\text{O}) / \text{g}$	0.7	0.2	0.2	2.6	2.4	0.1
$-\Delta U(\text{IBP}) / \text{J}$	33089.27	22713.77	16317.70	20330.46	18720.87	16952.37
$\Delta U(\text{Melinex}) / \text{J}$	2604.30	2504.70	2374.94	2523.20	2664.15	2236.96
$\Delta U(\text{fuse}) / \text{J}$	44.34	38.81	47.42	44.98	40.60	44.82
$\Delta U(\text{HNO}_3) / \text{J}$	77.61	57.52	41.62	64.66	45.89	42.67
$\Delta U(\text{ign.}) / \text{J}$	1.21	1.20	1.19	1.20	1.20	1.19
$\Delta U_{\Sigma} / \text{J}$	16.61	11.04	7.91	9.70	9.18	8.15
$-\Delta_c u^\circ(\text{cpd}) / (\text{J}\cdot\text{g}^{-1})$	30616.45	30653.58	30629.61	30632.15	30653.06	30626.30
% CO <sub>2</sub>	99.691	99.617	99.751	99.669	99.658	99.740

$$\langle \% \text{CO}_2 \rangle = (99.69 \pm 0.02)$$

$$\langle \Delta_c u^\circ(\text{cpd}) \rangle = - (30635.2 \pm 6.1)^b \text{ J}\cdot\text{g}^{-1}$$

<sup>a</sup>  $m(\text{CO}_2, \text{total})$  is the total mass of  $\text{CO}_2$  formed in the experiment;  $m(\text{cpd})$  is the mass of the compound burnt in each experiment;  $m(\text{fuse})$  is the mass of the fuse (cotton) used in each experiment;  $m(\text{Melinex})$  is the mass of Melinex used in each experiment;  $\Delta T_{\text{ad}}$  is the corrected temperature rise;  $\varepsilon_{\text{f}}$  is the energy equivalent of the contents in the final state;  $\Delta m(\text{H}_2\text{O})$  is the deviation of mass of water added to the calorimeter from 2900.0 g;  $\Delta U(\text{IBP})$  is the energy change for the isothermal combustion reaction under actual bomb conditions that includes the  $\Delta U(\text{ign})$ ;  $\Delta U(\text{Melinex})$  is the energy of combustion of Melinex;  $\Delta U(\text{fuse})$  is the energy of combustion of the fuse (cotton);  $\Delta U(\text{HNO}_3)$  is the energy correction for the nitric acid formation;  $\Delta U(\text{ign})$  is the electric energy for the ignition;  $\Delta U_{\Sigma}$  is the standard state correction;  $\Delta_c u^\circ(\text{cpd})$  is the standard massic energy of combustion and % CO<sub>2</sub> is the percentage of carbon dioxide recovered.

<sup>b</sup> Mean value of the standard massic energy of combustion and the standard deviation of the mean.

**Table S2.** Typical combustion results and standard ( $p^\circ = 0.1$  MPa) massic energy of combustion of thiomorpholine, at  $T = 298.15$  K.<sup>a</sup>

Experiment	1	2	3	4	5	6
$m(\text{cpd}) / \text{g}$	0.49013	0.81226	0.64179	0.74577	0.66837	0.73345
$m(\text{fuse}) / \text{g}$	0.00360	0.00292	0.00326	0.00312	0.00307	0.00297
$m(\text{Melinex}) / \text{g}$	0.09698	0.07252	0.10477	0.03283	0.07380	0.04030
$T_i / \text{K}$	297.0168	297.0118	297.2080	297.1385	297.2012	297.1489
$T_f / \text{K}$	297.7770	298.1621	298.1645	298.1687	298.1640	298.1684
$\Delta T_{\text{ad}} / \text{K}$	0.73519	1.13461	0.94054	1.01235	0.94746	1.00206
$\varepsilon_i / (\text{J}\cdot\text{K}^{-1})$	51.38	93.22	72.25	72.38	72.30	72.37
$\varepsilon_f / (\text{J}\cdot\text{K}^{-1})$	51.18	93.36	72.23	72.44	72.29	72.42
$\varepsilon_{\text{corr}} / (\text{J}\cdot\text{K}^{-1})$	25166.19	25160.33	25159.07	25156.98	25161.48	25156.98
$\Delta m(\text{H}_2\text{O}) / \text{g}$	2.1	0.7	0.4	-0.1	1.0	-0.1
$-\Delta U(\text{IBP}) / \text{J}$	18538.61	28651.77	23729.89	25539.76	23906.94	25280.15
$\Delta U(\text{Melinex}) / \text{J}$	2220.97	1660.81	2399.38	751.82	1690.05	922.93
$\Delta U(\text{fuse}) / \text{J}$	58.46	47.42	52.94	50.67	49.86	48.23
$\Delta U(\text{HNO}_3) / \text{J}$	48.83	73.13	56.42	65.01	58.40	59.64
$\Delta U(\text{ign}) / \text{J}$	1.18	1.17	1.18	1.18	1.16	1.17
$\Delta U_\Sigma / \text{J}$	15.59	40.09	27.62	25.40	26.42	25.66
$-\Delta_c u^\circ / (\text{J}\cdot\text{g}^{-1})$	33041.76	33031.55	33022.53	33049.10	33039.11	33026.94

$$\langle -\Delta_c u^\circ \rangle = (33035.2 \pm 4.1)^b \text{ J}\cdot\text{g}^{-1}$$

<sup>a</sup>  $m(\text{cpd})$  is the mass of the compound burnt in each experiment;  $m(\text{fuse})$  is the mass of the fuse (cotton) used in each experiment;  $m(\text{Melinex})$  is the mass of Melinex used in each experiment;  $T_i$  is the initial temperature rise;  $T_f$  is the final temperature rise;  $\Delta T_{\text{ad}}$  is the corrected temperature rise;  $\varepsilon_i$  is the energy equivalent of the contents in the initial state;  $\varepsilon_f$  is the energy equivalent of the contents in the final state;  $\varepsilon_{\text{corr}}$  is the energy equivalent of the calorimeter corrected for the deviation of mass of water added to the calorimeter;  $\Delta m(\text{H}_2\text{O})$  is the deviation of mass of water added to the calorimeter from 5217.0 g;  $\Delta U(\text{IBP})$  is the energy change for the isothermal combustion reaction under actual bomb conditions, that includes the  $\Delta U(\text{ign})$ ;  $\Delta U(\text{fuse})$  is the energy of combustion of the fuse (cotton);  $\Delta U(\text{HNO}_3)$  is the energy correction for the nitric acid formation;  $\Delta U(\text{ign})$  is the electric energy for the ignition;  $\Delta U_\Sigma$  is the standard state correction;  $\Delta_c u^\circ$  is the standard massic energy of combustion

<sup>b</sup> Mean value of the standard massic energy of combustion and the standard deviation of the mean.

**Table S3.** Standard ( $p^\circ = 0.1$  MPa) molar heat capacities in the gaseous phase for morpholine and thiomorpholine, derived from statistical thermodynamics using the vibrational frequencies calculated at the B3LYP/6-31G(*d*) level of theory.

<i>T</i> / K	$C_{p,m}^\circ$ (g) / (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	
	morpholine	thiomorpholine
150.00	52.89	58.68
200.00	65.90	73.29
250.00	80.96	89.52
298.15	97.09	106.22
300.00	97.73	106.87
350.00	115.18	124.40
400.00	132.33	141.27
450.00	148.56	157.00
500.00	163.58	171.41
550.00	177.32	184.52

**Table S4.** Calculated cartesian coordinates (Å) for morpholine conformers obtained from G3(MP2)//B3LYP calculations.<sup>a</sup>

<u>Morpholine chair (N-H<sub>equatorial</sub>)</u>				<u>Morpholine chair (N-H<sub>axial</sub>)</u>			
Atom	X	Y	Z	Atom	X	Y	Z
N	-0.243068	1.217401	0.653707	C	-1.319981	0.504081	0.005404
C	1.034868	0.968261	-0.018208	N	-0.246156	1.326392	0.579053
C	1.305358	-0.535104	0.002819	C	1.049902	0.969739	-0.013737
O	0.250446	-1.253912	-0.627080	C	1.315914	-0.538589	0.002942
C	-0.997802	-0.997319	0.007218	O	0.250761	-1.251720	-0.616429
C	-1.328384	0.493987	-0.013693	C	-0.995252	-0.992709	0.021610
H	1.832673	1.497228	0.517084	H	1.845575	1.508238	0.515490
H	1.043054	1.310908	-1.070598	H	1.049024	1.318824	-1.054741
H	1.421719	-0.870471	1.046444	H	1.443623	-0.884872	1.045410
H	2.217212	-0.778175	-0.551231	H	2.222650	-0.795517	-0.555529
H	-1.747292	-1.573801	-0.543658	H	-1.745944	-1.575305	-0.523474
H	-0.971922	-1.350845	1.051016	H	-0.966223	-1.358380	1.064875
H	-1.472005	0.806167	-1.065794	H	-1.467433	0.824366	-1.034417
H	-2.266534	0.674570	0.524914	H	-2.251912	0.703125	0.548583
H	-0.443245	2.214953	0.663702	H	-0.204594	1.156214	1.584937

<u>Morpholine twist-boat (N-H<sub>equatorial</sub>)</u>				<u>Morpholine twist-boat (N-H<sub>axial</sub>)</u>			
Atom	X	Y	Z	Atom	X	Y	Z
C	1.187496	0.343799	0.569095	O	1.115157	-0.526947	-0.638049
C	-0.002331	-0.042860	1.468415	C	1.236603	0.249191	0.546137
N	-1.169952	-0.356532	0.628555	C	-0.012116	0.036894	1.446552
C	-1.155826	0.376019	-0.632236	N	-1.188308	-0.390748	0.674250
H	-1.105300	1.475282	-0.509470	C	-1.208794	0.281044	-0.625958
H	-2.079453	0.163608	-1.182252	C	0.060210	-0.041383	-1.464209
H	0.310633	0.619914	-2.222676	H	-1.285182	1.359736	-0.438359
C	0.047017	-0.122484	-1.451508	H	-2.113257	-0.009567	-1.171874
O	1.183239	-0.405262	-0.632420	H	0.394863	0.846847	-2.027933
H	0.247660	-0.931439	2.061691	H	0.183005	-0.725710	2.207649
H	2.134639	0.123942	1.070079	H	2.154833	-0.080750	1.041235
H	1.173618	1.424976	0.353549	H	1.360885	1.314624	0.288177
H	-2.031777	-0.185951	1.138260	H	-1.107116	-1.392868	0.508520
H	-0.201510	-1.065414	-1.949150	H	-0.134027	-0.843784	-2.183806
H	-0.182889	0.786056	2.176849	H	-0.252513	0.969196	1.976596

<sup>a</sup>Additional keywords used in the calculation: opt=verytight, int=ultrafine and scf=(conver=6); Molecule specification: charge=0 and spin multiplicity = 1.

**Table S5.** Calculated cartesian coordinates (Å) for thiomorpholine conformers obtained from G3(MP2)//B3LYP calculations.<sup>a</sup>

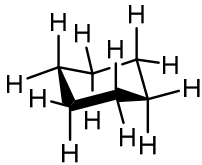
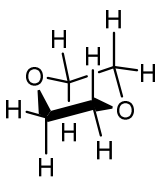
Thiomorpholine chair (N-H <sub>equatorial</sub> )				Thiomorpholine Chair (N-H <sub>axial</sub> )			
Atom	X	Y	Z	Atom	X	Y	Z
C	-1.393766	0.787815	0.125611	C	-1.276743	-0.745931	0.138911
N	-0.271161	1.404799	0.836204	C	-1.409598	0.784145	0.133002
C	1.013621	1.236212	0.153002	N	-0.309324	1.513910	0.764138
C	1.444167	-0.230232	0.170385	C	1.002291	1.241915	0.174915
S	0.252286	-1.310650	-0.719891	C	1.438997	-0.230489	0.186111
C	-1.267834	-0.735361	0.139612	S	0.252655	-1.312055	-0.709898
H	1.761698	1.830181	0.693671	H	1.745313	1.841621	0.717323
H	0.995086	1.590626	-0.894486	H	0.985725	1.603208	-0.860917
H	1.545164	-0.576646	1.204336	H	1.550617	-0.590670	1.217210
H	2.405391	-0.357719	-0.336825	H	2.403316	-0.357373	-0.317535
H	-2.107364	-1.198291	-0.387979	H	-2.110089	-1.214000	-0.395985
H	-1.259964	-1.099068	1.172527	H	-1.283194	-1.128525	1.167956
H	-1.480974	1.129374	-0.922681	H	-1.491790	1.132982	-0.903971
H	-2.317217	1.070500	0.647212	H	-2.338390	1.066542	0.646356
H	-0.457394	2.397258	0.957398	H	-0.285523	1.297295	1.760414

Thiomorpholine twist (enantiomer-R)				Thiomorpholine twist (enantiomer-S)			
Atom	X	Y	Z	Atom	X	Y	Z
C	0.367765	1.365478	-0.343578	C	-0.367821	1.365507	-0.343508
S	1.541701	-0.027627	-0.030809	S	-1.541696	-0.027680	-0.030858
C	0.311467	-1.342162	0.386878	C	-0.311420	-1.342138	0.386936
C	-0.986243	-1.177014	-0.399013	C	0.986270	-1.177019	-0.398992
N	-1.738791	0.005482	0.050885	N	1.738790	0.005530	0.050800
C	-0.934058	1.169215	0.444526	C	0.934044	1.169216	0.444532
H	0.108266	-1.340139	1.462553	H	0.683866	1.094224	1.510744
H	-1.616345	-2.063907	-0.243727	H	1.565698	2.059106	0.337247
H	-0.732513	-1.147377	-1.472540	H	-0.164464	1.445154	-1.417251
H	-2.390961	0.275461	-0.679935	H	-0.878239	2.280466	-0.026327
H	-0.683836	1.094277	1.510731	H	-0.789269	-2.292344	0.133556
H	-1.565741	2.059083	0.337223	H	-0.108207	-1.340013	1.462609
H	0.878155	2.280494	-0.026514	H	0.732514	-1.147465	-1.472515
H	0.164368	1.444998	-1.417322	H	1.616397	-2.063886	-0.243658
H	0.789344	-2.292330	0.133407	H	2.390878	0.275533	-0.680083

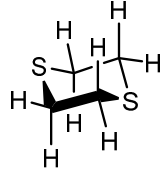
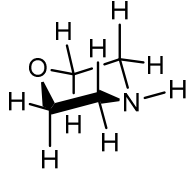
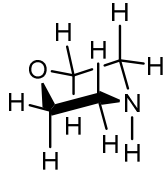
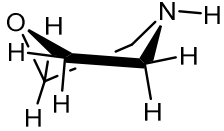
<sup>a</sup>Additional keywords used in the calculation: opt=verytight, int=ultrafine and scf=(conver=6); Molecule specification: charge=0 and spin multiplicity = 1.

**Table S6.** G3(MP2)//B3LYP enthalpies, Gibbs free energy and experimental gas-phase standard ( $p^\circ = 0.1$  MPa) molar enthalpies of formation, at  $T = 298.15$  K, for morpholine and thiomorpholine molecules and for the auxiliary species.<sup>a</sup>

Species	Molecular structure/conformer	$H_{298}$ / u.a.	$G_{298}$ / u.a.	$\Delta_f H_m^\circ$ (g) / $\text{kJ} \cdot \text{mol}^{-1}$
H		- 0.499780	- 0.512795	218.0 <sup>1</sup>
H <sup>+</sup>		0.002360	- 0.010000	
H <sup>•</sup>		- 0.499780	- 0.512795	
C		- 37.788425	- 37.805330	716.7 1
O		- 74.989704	- 75.007016	249.17 1
N		- 54.524582	- 54.541978	472.68 1
Cyclohexane chair		- 235.407838	- 235.443593	- 123.3 ± 0.8 <sup>2</sup>
1,4-Dioxane chair		- 307.197193	- 307.231973	- 315.3 ± 0.8 2

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**Table S6.** Continuation

Species	Molecular structure/conformer	$H_{298}$ / u.a.	$G_{298}$ / u.a.	$\Delta_f H_m^\circ$ (g) / $\text{kJ} \cdot \text{mol}^{-1}$
1,4-Dithiane chair		- 952.448222	- 952.486447	- 6.9 ± 2.4 <sup>3</sup>
Morpholine chair (N-H <sub>equatorial</sub> )		- 287.334005	- 287.368931	- 141.7 ± 1.5 <sup>b</sup>
Morpholine chair (N-H <sub>axial</sub> )		- 287.332743	- 287.367762	
Morpholine twist-boat (N-H <sub>equatorial</sub> )		- 287.321514	- 287.357642	

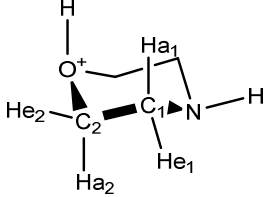
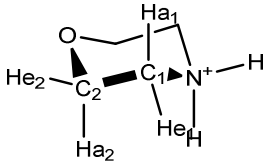
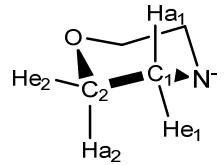
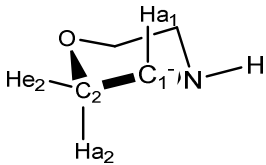
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**Table S6.** Continuation

Species	Molecular structure/conformer	$H_{298}$ / u.a.	$G_{298}$ / u.a.	$\Delta_f H_m^\circ$ (g) / $\text{kJ} \cdot \text{mol}^{-1}$
Morpholine twist-boat ( $\text{N-H}_{\text{axial}}$ )		- 287.324059	- 287.360073	
Morpholine radical ( $\text{RN}^\bullet$ )		- 286.683081	- 286.718800	
Morpholine radical ( $\text{RC}_1^\bullet$ )		- 286.685683	- 286.721540	
Morpholine radical ( $\text{RC}_2^\bullet$ )		- 286.679236	- 286.715094	

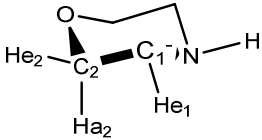
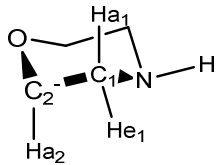
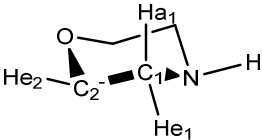
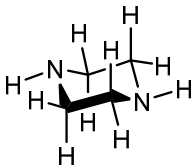
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**Table S6.** Continuation

Species	Molecular structure/conformer	$H_{298}$ / u.a.	$G_{298}$ / u.a.	$\Delta_f H_m^\circ$ (g) / $\text{kJ} \cdot \text{mol}^{-1}$
Morpholine cation ( $\text{ROH}^+$ )		- 287.644275	- 287.679918	
Morpholine cation ( $\text{RNH}_2^+$ )		- 287.684397	- 287.719657	
Morpholine anion ( $\text{RN}^-$ )		- 286.719693	- 286.754466	
Morpholine anion ( $\text{RC}_1^-$ )		- 286.694380	- 286.729698	

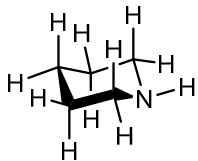
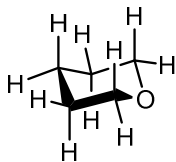
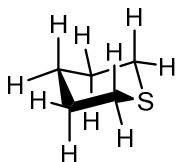
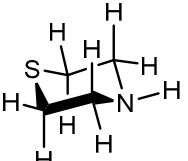
.../...

**Table S6.** Continuation

Species	Molecular structure/conformer	$H_{298}$ / u.a.	$G_{298}$ / u.a.	$\Delta_f H_m^\circ$ (g) / $\text{kJ} \cdot \text{mol}^{-1}$
Morpholine anion ( $\text{RC}_1^-$ )		- 286.685897	- 286.720720	
Morpholine anion ( $\text{RC}_2^-$ )		- 286.684890	- 286.719904	
Morpholine anion ( $\text{RC}_2^-$ )		- 286.682497	- 286.717390	
Piperazine chair ( $\text{N-H}_{\text{equatorial}}$ )		- 267.470016	- 267.505087	$131.6 \pm 2.0^4$

.../...

**Table S6.** Continuation

Species	Molecular structure/conformer	$H_{298}$ / u.a.	$G_{298}$ / u.a.	$\Delta_f H_m^\circ$ (g) / $\text{kJ} \cdot \text{mol}^{-1}$
Piperidine chair ( $\text{N-H}_{\text{equatorial}}$ )		- 251.439307	- 251.474724	- 47.2 ± 0.6 <sup>2</sup>
2 <i>H</i> -Tetrahydropyran chair		- 271.303681	- 271.338953	- 223.8 ± 1.0 <sup>5</sup>
2 <i>H</i> -Tetrahydrothiopyran		- 593.928601	- 593.965597	- 63.5 ± 1.0 <sup>2</sup>
Thiomorpholine chair ( $\text{N-H}_{\text{equatorial}}$ )		- 609.959538	- 609.996176	10.5 ± 4.4 <sup>b</sup>

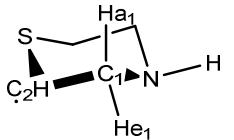
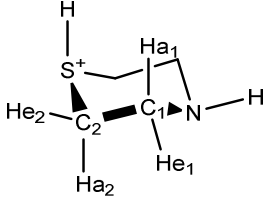
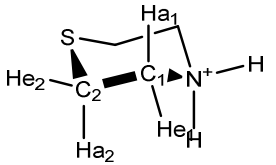
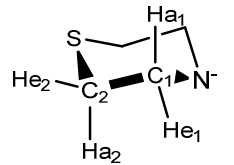
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**Table S6.** Continuation

Species	Molecular structure/conformer	$H_{298}$ / u.a.	$G_{298}$ / u.a.	$\Delta_f H_m^\circ$ (g) / $\text{kJ} \cdot \text{mol}^{-1}$
Thiomorpholine chair ( $\text{N-H}_{\text{axial}}$ )		- 609.958386	- 609.995125	
Thiomorpholine twist		- 609.949838	- 609.987423	
Thiomorpholine radical ( $\text{RN}^\bullet$ )		- 609.306785	- 609.344228	
Thiomorpholine radical ( $\text{RC}_1^\bullet$ )		- 609.311504	- 609.349251	

.../...

**Table S6.** Continuation

Species	Molecular structure/conformer	$H_{298}$ / u.a.	$G_{298}$ / u.a.	$\Delta_f H_m^\circ$ (g) / $\text{kJ} \cdot \text{mol}^{-1}$
Thiomorpholine radical ( $\text{RC}_2^\bullet$ )		- 609.308354	- 609.346024	
Thiomorpholine cation ( $\text{RSH}^+$ )		- 610.279709	- 610.316953	
Thiomorpholine cation ( $\text{RNH}_2^+$ )		- 610.310542	- 610.347475	
Thiomorpholine anion ( $\text{RN}^-$ )		- 609.348849	- 609.385456	

.../...

**Table S6.** Continuation

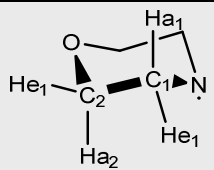
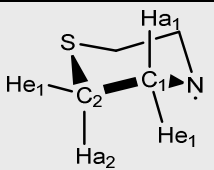
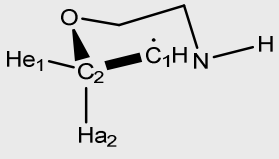
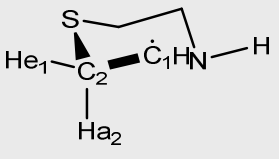
Species	Molecular structure/conformer	$H_{298}$ / u.a.	$G_{298}$ / u.a.	$\Delta_f H_m^\circ$ (g) / $\text{kJ} \cdot \text{mol}^{-1}$
Thiomorpholine anion ( $\text{RC}_1^-$ )		<i>c</i>	<i>ct</i>	
Thiomorpholine anion ( $\text{RC}_1^-$ )		<i>c</i>	<i>c</i>	
Thiomorpholine anion ( $\text{RC}_2^-$ )		- 609.336956	- 609.373464	
Morpholine anion ( $\text{RC}_2^-$ )		- 609.326646	- 609.363256	

<sup>a</sup> 1 a. u. (Hartree) corresponds to  $2625.50 \text{ kJ} \cdot \text{mol}^{-1}$ .

<sup>b</sup> This work.

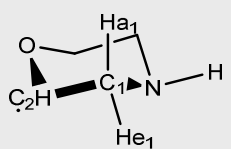
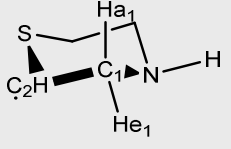
<sup>c</sup> The anion is unstable; the molecular ring opens during the optimization procedure.

**Table S7.** Calculated cartesian coordinates (Å) for some of the radicals of morpholine and thiomorpholine chair (N-H<sub>equatorial</sub>) conformers obtained from G3(MP2)//B3LYP calculations.<sup>a</sup>

							
C	-0.219334	1.210054	0.641615	C	-1.398459	0.784704	0.116202
N	1.039871	0.977451	-0.029286	C	-0.200119	1.432656	0.850610
C	1.336474	-0.437405	-0.025160	N	1.035448	1.206966	0.131900
C	1.399137	-0.954112	1.433508	C	1.078189	1.944627	-1.112342
O	0.176930	-0.700600	2.103241	C	0.067491	1.371827	-2.134891
C	-0.143414	0.679221	2.094573	S	-1.661902	1.515375	-1.544224
H	2.293142	-0.619537	-0.529208	H	2.086998	1.860305	-1.535783
H	0.551231	-1.011639	-0.546526	H	0.851395	3.013107	-0.961679
H	2.236032	-0.467337	1.958731	H	0.303439	0.323184	-2.342181
H	1.553831	-2.036868	1.452717	H	0.126143	1.929061	-3.074672
H	-1.110684	0.784426	2.594551	H	-2.320326	0.949234	0.682090
H	0.609816	1.254551	2.655680	H	-1.238837	-0.294508	0.026114
H	-1.044719	0.678362	0.137413	H	-0.409737	2.508015	0.974897
H	-0.447521	2.282605	0.645404	H	-0.115171	0.978322	1.845835
							
C	-0.234197	0.542878	2.031435	C	-1.431972	0.937980	0.061669
C	-0.244687	1.088811	0.637279	C	-0.272250	1.554142	0.765660
N	0.898117	0.816635	-0.125637	N	0.979170	1.531964	0.138439
C	1.421026	-0.548301	-0.021512	C	1.088489	2.010689	-1.244829
C	1.490834	-0.932945	1.455958	C	0.107257	1.286528	-2.163705
O	0.218204	-0.813848	2.070631	S	-1.635801	1.576346	-1.666122
H	2.421185	-0.584530	-0.469160	H	2.113548	1.812671	-1.582498
H	0.777368	-1.273473	-0.545351	H	0.907015	3.095280	-1.315164
H	2.226933	-0.291730	1.970593	H	0.311151	0.209378	-2.164704
H	1.798588	-1.977170	1.566035	H	0.207618	1.657579	-3.187780
H	-1.241956	0.548688	2.458566	H	-2.363628	1.164033	0.588391
H	0.416472	1.144233	2.702684	H	-1.349981	-0.159678	-0.012982
H	-0.709406	2.055067	0.457852	H	-0.239174	1.490521	1.850367
H	0.837305	1.147325	-1.082667	H	1.710902	1.919778	0.723510

.../...

**Table S7.** Continuation

							
C	-0.055966	1.302448	0.691417	C	-1.435174	1.032307	0.113619
N	1.105214	0.913871	-0.118517	C	-0.214244	1.451601	0.876375
C	1.286730	-0.536437	-0.070098	N	1.025449	1.226010	0.122110
C	1.564968	-0.929500	1.375601	C	1.065765	1.962809	-1.140667
O	0.491244	-0.537049	2.242976	C	0.091617	1.346967	-2.142928
C	0.078491	0.760366	2.084066	S	-1.654640	1.447500	-1.563029
H	2.144189	-0.817542	-0.692727	H	2.080759	1.881470	-1.549023
H	0.404379	-1.100269	-0.431373	H	0.837528	3.040214	-1.026858
H	2.491141	-0.448526	1.715613	H	0.343299	0.295596	-2.307392
H	1.654700	-2.013449	1.486548	H	0.120649	1.878787	-3.098400
H	-0.655949	1.035002	2.836575	H	-2.360872	0.862858	0.654765
H	-1.009719	0.939889	0.239181	H	-0.319275	2.519146	1.180511
H	-0.122233	2.396283	0.734174	H	-0.159185	0.866482	1.802911
H	0.962146	1.213285	-1.080569	H	1.812084	1.513512	0.699892

<sup>a</sup>Additional Gaussian 03 keywords used in the calculation: opt=verytight, int=ultrafine and scf=(conver=6);

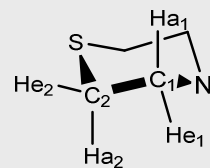
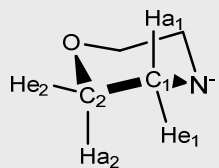
Molecule specification: charge=0 and spin multiplicity = 2.

**Table S8.** Calculated cartesian coordinates (Å) for some of the ions of morpholine and thiomorpholine chair (N-H<sub>equatorial</sub>) conformer obtained from G3(MP2)//B3LYP calculations.<sup>a</sup>

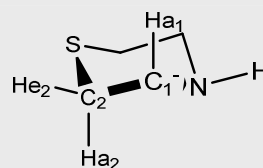
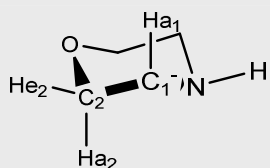
Morpholine cation				Thiomorpholine cation			
C	-1.339474	0.478723	-0.043370	C	-1.340371	-1.018680	-0.153754
N	-0.232359	1.158948	0.611212	C	-1.406715	0.509992	-0.069194
C	1.035571	0.936141	-0.066722	N	-0.262574	1.019448	0.674971
C	1.391294	-0.532033	0.050476	C	0.998298	0.939713	-0.050443
O	0.242906	-1.366037	-0.510589	C	1.466691	-0.517123	-0.131867
C	-1.122222	-1.016120	0.075188	S	0.196499	-1.472269	-1.102769
H	1.830055	1.504273	0.429669	H	1.768260	1.480532	0.508955
H	1.035898	1.234410	-1.132913	H	0.961587	1.378525	-1.064079
H	1.454494	-0.876690	1.081888	H	1.535776	-0.967475	0.860072
H	2.258109	-0.851383	-0.528829	H	2.402780	-0.631530	-0.683763
H	-1.819262	-1.636656	-0.488742	H	-2.170476	-1.448665	-0.719422
H	-1.033339	-1.355830	1.106347	H	-1.264217	-1.467771	0.838239
H	-1.470761	0.751645	-1.108267	H	-1.508916	0.937104	-1.083340
H	-2.278563	0.712981	0.470065	H	-2.324673	0.749217	0.477046
H	-0.421488	2.147734	0.744014	H	-0.434336	1.966619	0.998664
H	0.218501	-1.289229	-1.488280	H	0.415390	-2.718329	-0.621834
C	-1.888032	0.455247	-0.969270	C	-1.258700	-0.793273	0.076996
N	-0.753247	1.212652	-0.289578	C	-1.464300	0.714810	0.101001
C	0.593460	0.939643	-0.949292	N	-0.299049	1.411329	0.797482
C	0.797317	-0.572589	-1.028688	C	1.069290	1.195063	0.158016
O	-0.273662	-1.185241	-1.720352	C	1.430817	-0.283464	0.137532
C	-1.506988	-1.022399	-1.047196	S	0.248792	-1.284619	-0.838050
H	1.362194	1.442165	-0.357083	H	1.778015	1.781487	0.750687
H	0.542171	1.383613	-1.945843	H	1.005954	1.610332	-0.850062
H	0.911562	-1.001042	-0.019031	H	1.530300	-0.680571	1.155720
H	1.709970	-0.781935	-1.591257	H	2.406040	-0.391605	-0.345730
H	-2.265085	-1.557909	-1.623178	H	-2.104805	-1.246654	-0.447269
H	-1.467338	-1.465401	-0.038129	H	-1.250163	-1.207627	1.093133
H	-1.992000	0.888908	-1.966259	H	-1.513553	1.132761	-0.906755
H	-2.798397	0.630034	-0.390589	H	-2.363427	0.996447	0.657503
H	-0.706332	0.931521	0.698298	H	-0.490915	2.418757	0.837762
H	-0.949898	2.220149	-0.291441	H	-0.260477	1.091912	1.774055

.../...

**Table S8.** Continuation



C	-0.176245	1.203671	0.626126	C	-1.406236	0.786368	0.143908
N	1.053840	1.003429	-0.060831	C	-0.154905	1.419096	0.825691
C	1.330568	-0.391863	-0.019634	N	1.079910	1.209232	0.161439
C	1.405123	-0.959222	1.414172	C	1.079035	1.913308	-1.069136
O	0.197235	-0.695388	2.137781	C	0.087945	1.384791	-2.150528
C	-0.154488	0.692219	2.082559	S	-1.665739	1.454704	-1.562550
H	2.297877	-0.619636	-0.516002	H	2.082691	1.853451	-1.543656
H	0.561338	-1.053196	-0.539009	H	0.847034	3.020920	-0.990781
H	2.258599	-0.489302	1.942026	H	0.329223	0.339647	-2.383220
H	1.525906	-2.057544	1.449571	H	0.101964	1.973041	-3.082888
H	-1.134498	0.759505	2.589715	H	-2.347942	0.991860	0.679157
H	0.586470	1.281281	2.658634	H	-1.267303	-0.299759	0.068345
H	-1.078779	0.683491	0.163879	H	-0.438792	2.505924	0.983745
H	-0.442154	2.281727	0.658266	H	-0.122333	0.970295	1.842349

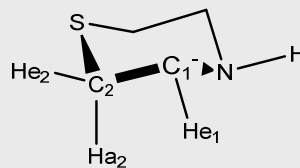
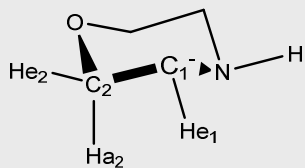


C	-0.171356	0.761034	2.023297
C	-0.203543	1.316233	0.681977
N	1.108302	1.008138	0.055434
C	1.360934	-0.428167	-0.000506
C	1.395638	-0.977458	1.442857
O	0.206911	-0.782336	2.148307
H	2.337484	-0.645377	-0.482400
H	0.578722	-0.990154	-0.560367
H	2.257224	-0.482436	1.947895
H	1.615247	-2.061787	1.421325
H	-1.142840	0.770183	2.532649
H	0.599176	1.218089	2.670754
H	-1.023124	0.813306	0.108865
H	1.157011	1.402372	-0.883378

The anion is unstable; the molecular ring opens during the optimization procedure.

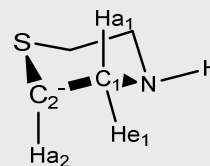
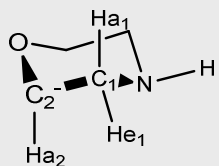
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**Table S8.** Continuation



C	-0.320675	1.159761	0.608491
N	1.094904	1.009196	0.013897
C	1.353302	-0.426142	-0.016773
C	1.381415	-0.952664	1.426820
O	0.179999	-0.720464	2.122137
C	-0.149995	0.715660	2.030468
H	2.331931	-0.642282	-0.487736
H	0.560068	-0.989102	-0.552938
H	2.229980	-0.461153	1.948123
H	1.557513	-2.040620	1.437552
H	-1.081813	0.831655	2.605007
H	0.677166	1.197263	2.634680
H	-0.495431	2.259150	0.658267
H	1.013239	1.298491	-0.963812

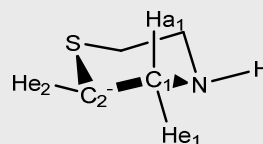
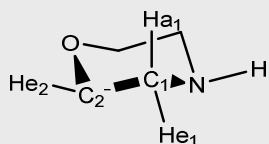
The anion is unstable; the molecular ring opens during the optimization procedure.



C	-0.216320	1.219683	0.713341
N	1.070636	0.982416	-0.066683
C	1.357228	-0.451223	-0.029062
C	1.382361	-0.934400	1.429201
O	0.157320	-0.740622	2.076337
C	-0.248905	0.704926	2.123394
H	2.327961	-0.656939	-0.514878
H	0.591473	-1.061770	-0.559399
H	2.204521	-0.401067	1.952201
H	1.623938	-2.017569	1.438247
H	0.591126	1.207927	2.663980
H	-1.048497	0.778200	0.114944
H	-0.371994	2.311232	0.723882
H	0.918491	1.237579	-1.052636

C	-1.466832	0.811438	0.172338
C	-0.258342	1.386188	0.846456
N	1.064996	1.207175	0.120808
C	1.098211	1.942117	-1.151667
C	0.101793	1.374774	-2.170295
S	-1.631338	1.500073	-1.457939
H	2.126242	1.883841	-1.552820
H	0.864616	3.022317	-1.023668
H	0.341658	0.321123	-2.368519
H	0.170085	1.936744	-3.116364
H	-1.363772	-0.284288	0.091303
H	-0.403175	2.473524	1.033311
H	-0.098125	0.906140	1.829336
H	1.796762	1.619388	0.711367

.../...

**Table S8.** Continuation

C	-0.214465	1.240605	0.662489	C	-1.355118	0.719920	0.058051
N	1.045848	0.988689	-0.046613	C	-0.260542	1.403389	0.844313
C	1.362911	-0.476171	0.028655	N	1.066921	1.256482	0.159231
C	1.490691	-0.898348	1.476186	C	1.103254	1.925848	-1.147936
O	0.082558	-0.730142	2.033059	C	0.039657	1.393384	-2.117626
C	-0.159395	0.636807	2.078501	S	-1.636929	1.752935	-1.475854
H	2.325996	-0.631344	-0.487405	H	2.109030	1.764442	-1.576908
H	0.576667	-1.011199	-0.592327	H	0.953831	3.024279	-1.073447
H	1.601370	-2.004026	1.473970	H	0.138095	0.304863	-2.204214
H	-1.135714	0.813484	2.572008	H	0.172026	1.866484	-3.102372
H	0.637508	1.159434	2.642888	H	-2.305325	0.780412	0.619380
H	-1.088380	0.780183	0.150925	H	-0.395155	2.500154	1.081956
H	-0.396260	2.329121	0.711777	H	-0.151612	0.888758	1.816261
H	0.877370	1.216137	-1.032129	H	1.755626	1.743910	0.741049

<sup>a</sup>Additional Gaussian 03 keywords used in the calculation: opt=verytight, int=ultrafine and scf=(conver=6);

Molecule specification for anions: charge=-1 and spin multiplicity = 1;

Molecule specification for cations: charge=+1 and spin multiplicity = 1.

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