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Theoretical Calculation of Thermodynamic Properties of Naphthalene, Methylnaphthalenes, and Dimethylnaphthalenes

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For this work we performed quantum mechanical (QM) and statistical mechanical (SM) calculations to generate the entropy of 13 aromatic compounds—naphthalene, 2 methylnaphthalene isomers, and 10 dimethylnaphthalene isomers—in the ideal gas state. Density functional theory (DFT) was used to calculate the equilibrium structure and perform a full normal-mode analysis. The DFT level of theory used in this paper is B3LYP/6-31G(d,p). DFT has also been used to determine barriers for the internal rotation contribution to the entropy. For four compounds for which experimental data are available, the calculated entropies have been compared to the experimental values. The calculated entropies match experiment very well, with the percentage errors close to the experimental uncertainty, less than 0.4 %. The equilibrium distribution of dimethylnaphthalene isomers in the mixture is predicted using the calculated entropies and energies from QM and SM calculations in the 300 K to 740 K temperature range.

Introduction

Thermophysical properties can be obtained from first principles with coupling of quantum mechanics (QM) and statistical mechanics (SM) calculations. The quantum mechanics calculations provide the required information for statistical mechanics models that predict thermophysical properties. Specifically, the QM calculations provide the equilibrium configuration from which one can directly calculate (i) the moments of inertia of the entire molecule, required for the rotational contribution to the thermodynamic properties; (ii) the moments of inertia for internal rotors, required for the internal rotational contribution; (iii) the normal vibrational frequencies, required for the vibrational contribution; and (iv) the barrier to internal rotation, required for the internal rotational contribution. A SM analysis takes this QM-generated information as input and predicts thermodynamic properties. In this work, we are interested in generating properties in the ideal gas reference state and thus limit ourselves to isolated molecules.

We have previously followed this QM/SM procedure to generate the entropies of benzene, toluene, and the three xylene isomers with excellent agreement with precise experimental values,[1] hereafter referred to as I. In this work, we generate and report entropies of 13 aromatic compounds—naphthalene, 2 methylnaphthalene (MN) isomers, and 10 dimethylnaphthalene (DMN) isomers—in the ideal gas state. The MN isomers are 1-MN and 2-MN. The DMN isomers are 1,2-DMN, 1,3-DMN, 1,4-DMN, 1,5-DMN, 1,6-DMN, 1,7-DMN, 1,8-DMN, 2,3-DMN, 2,6-DMN, and 2,7-DMN. These compounds represent all possible MN and DMN isomers. In this work, we have attempted as much as possible to follow the QM/SM procedure established in ref 1; however, certain differences in the complexity of internal rotation in MN and DMN have required us to deviate from the procedure of ref 1 in some respects, which are detailed below. Additionally, we report the equilibrium distribution of DMN isomers across a temperature range (300 K to 740 K), based on the free energies composed of the QM energies and the QM/SM entropies.

The use of QM and SM to generate entropies is not new. We have previously reviewed this body of work in I. Here we provide a synopsis. Barret and Meier[2] used the semiempirical AM1 method to calculate entropy for a series of organic molecules. East and Radom[3] carried out an extensive study of small molecules at different levels of QM molecular orbital theory and different methods for calculating entropies and showed that entropies could be calculated to within 1 $J \cdot K^{-1} \cdot mol^{-1}$. Subsequently, Vansteenkiste et al.[4] calculated entropies of linear alkanes with an emphasis on considering more elaborate treatments of low vibrational modes. Wang et al.[5] used ab initio calculations to determine thermodynamic functions such as entropy for dibenzo-*p*-dioxin (DD) and 75 polychlorinated dibenzodioxins (PCDDs) at the B3LYP/6-311G** level of theory. Kassaee et al.[1] used QM and SM calculations to generate entropy for five aromatic compounds in the ideal gas state and systematically examined how the choice of QM level of theory and size of basis set affect the agreement between theory and experiment. Notably, Kassaee et al. report less than half a percent error between calculated entropies and experiment in the 250 K to 540 K temperature range when using an empirical scaling factor for the vibrational frequencies.

We now turn special attention to the matter of internal rotation. Ayala and Schlegel[6] outlined a procedure that systematically identifies internal rotation modes and rotating groups during normal-mode analysis. In this work, we have generated "movies" representing the eigenvectors (or vibrational modes) associated with every frequency of every compound. These movies are available for viewing on the Web.[7] One can view these movies to distinguish between normal modes that will be treated as vibrational modes and those that will be treated as internal rotation. The identification is not always obvious. With

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the DMN compounds, there were typically several possible low-wavelength modes that could potentially be identified as internal rotation.

Additionally, one must determine rotational barriers. One way to estimate rotational barriers via quantum mechanical calculations has been to first determine the equilibrium structure, then rotate the internal rotor, and perform a single-point energy calculation. This procedure assumes that the energy of the rest of the molecule is completely independent of the energy associated with the internal rotor. For some compounds, the assumption of independence between the rotor and the rest of the molecule is not true. Various alternative approaches have been proposed. Specifically, Sancho-García and Pérez-Jiménez[8] performed a detailed study of the torsional potential of nitrobenzene by using state-of-the-art ab initio methods, including density functional theory (DFT) methods. In their procedure, one begins by understanding that there are $3N$ degrees of freedom in the atomic coordinates of a nonlinear molecule containing N atoms. Three of these degrees of freedom are associated with center-of-mass translation and three more with center-of-mass rotation, leaving $3N - 6$ modes. One of these modes is the dihedral torsion angle governing the rotation of the internal rotor, which we must specify to generate energy as a function of torsion angle. Therefore, there are $3N - 7$ remaining modes. In determining the activation barrier for internal rotation of the nitro group, Sancho-García and Pérez-Jiménez[8] allowed for $3N - 7$ degrees of freedom to relax. This procedure allows for redistribution of the electrons in the rest of the molecule based upon the orientation of the rotor. If these modes are coupled, such redistribution is essential. The single-point energy will provide an unrealistically high rotation barrier that does not represent the correlated relaxation associated with internal rotation.

Other investigators have also computed relaxed rotational barriers. Goodman and his co-workers[9] reported on the nature of internal rotation in acetaldehyde. They divide the formation of internal rotation barrier in acetaldehyde into three conceptual steps: (1) rigid rotation, (2) C−C bond lengthening to relieve repulsive π-nuclear virial, and (3) other skeletal and methyl flexings, necessary to achieve the fully relaxed barrier height. Sinha et al.[10] have used the relaxed rotational barrier for 4-methylstyrene. In this work, we follow the procedure of Sancho-García and Pérez-Jiménez[8] in relaxing $3N - 7$ modes for MN isomers, which have one rotor. For DMN isomers, which have two rotors, we naturally extend the procedure to relax only $3N - 8$ modes. We report on the substantial difference between single-point and relaxed rotational barriers for MN and DMN.

This work is distinguished from previous work in the area of thermophysical property generation via QM and SM in several ways. First, we focus very carefully on comparing our entropies to excellent experimental data, when available. Second, the statistical mechanical analysis is done in a way in which the effect of individual contributions—translation, vibration, rotation, internal rotation—can be separately examined. Third, by performing the analysis for naphthalene, MN, and DMN compounds, we are able to evaluate the QM and SM procedures on a material set that is of industrial importance and which provides a sound basis for extending the conclusions of this work to larger aromatic molecules. Fourth, we have generated the equilibrium distribution of dimethylnaphthalene compounds in the mixture with calculated entropies and energies from QM and SM calculations in the 300 K to 740 K temperature range.

Computational Methods

We perform QM calculations to generate the equilibrium structure of the 13 compounds studied here. We use the B3LYP method, an efficient and widely used density functional theory (DFT) method, and a mid-sized 6-31G(d,p) split-valence basis set. Our choice of method and mid-sized basis set comes from the conclusions of ref 1, in which we showed the effectiveness of the B3LYP method and the fact that the advantage in accuracy of larger basis sizes is largely lost once the empirical scaling factor is applied to the vibrational frequencies. Once a suitable vibrational scaling factor is applied, there is not a remarkable difference between using different basis sets, whereas the larger basis sets have a huge computational disadvantage.

The QM calculations provide the equilibrium configuration from which one can directly calculate (i) the moments of inertia of the entire molecule, required for the rotational contribution to the thermodynamic properties; (ii) the moments of inertia for internal rotors, required for the internal rotational contribution; (iii) the normal vibrational frequencies, required for the vibrational contribution; and (iv) the barrier to internal rotation, required for the internal rotational contribution.

There are known systematic errors in calculating frequencies at different levels of theory in QM. The consequence is that one must use an empirical scaling factor for the vibrational frequencies. This factor is a function of the choice of basis set and method. This factor also varies to some degree from one compound to another.[1] Tables compiling compound-averaged scaling factors as a function of method and basis set are available from NIST.[11] In this work we use a single factor for all compounds and all frequencies. We determined this factor ourselves using the procedure in ref 1. We chose the scaling factor that minimized the error between vibrational frequencies from theory [B3LYP/6-31G(d,p)] and experiment for the three xylene isomers. The accurate experimental frequencies for xylene isomers are taken from Draeger's paper.[12] For *o*-xylene, we have used Draeger's frequencies corrected by Chirico et al.[13] The average scaling factor for xylenes by B3LYP/6-31G(d,p) and the scale factor we used in this paper is 0.970.

As noted above, to identify internal rotation modes, we created movies of all of the eigenvectors for every compound. The internal rotation modes were recognized for their large components of the methyl dihedral angles.[6] Also as noted above, in determining rotational barriers, we followed the procedure of Sancho-García and Pérez-Jiménez[8] in relaxing $3N - 7$ modes for MN isomers, which have one rotor. For DMN isomers, which have two rotors, we naturally extended the procedure to relax only $3N - 8$ modes.

With the internal rotation barriers, scaled vibrational frequencies, and moments of inertia, we calculated the entropy using SM. One can approximate the entropy of a molecule by making the assumption that the various degrees of freedom within the molecule contribute to the entropy independently.[2] In this work, we do not consider any electronic or nuclear contribution to the entropy, because we are interested in the ground state. Furthermore, we neglect coupling between translational, rotational, and vibrational modes.

$$S = S_{\text{tran}} + S_{\text{rot.}} + S_{\text{vib}} + S_{\text{int-rot.}} \tag{1}$$

We used the Therpoly software for the SM calculations to get the translational, rotational, vibrational, and internal rotation contributions to entropy.[14] The translational contribution is easily calculated given the molecular weight of the compound. The

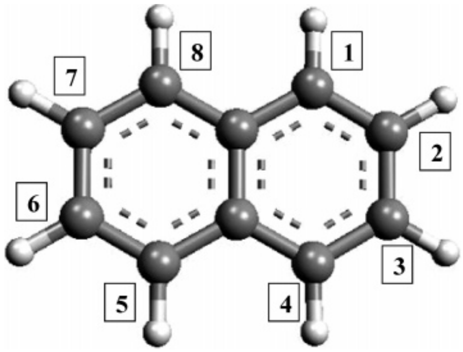

Figure 1. Numbered methyl locations on naphthalene.

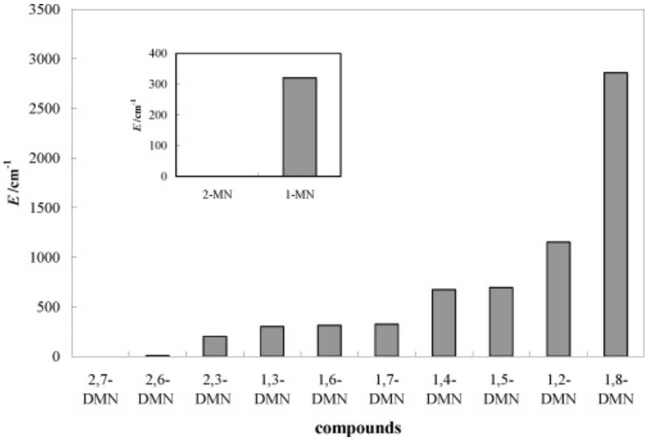

Figure 2. Relative energies of the optimized structures for both monomethylnaphthalenes (MN) and all 10 dimethylnaphthalenes (DMN). Energy unit, 1 cm^{-1} = 0.01196 kJ·mol^{-1}.

molecular weights were taken from the NIST Web reference.[11] For the rotational degrees of freedom, we assume a rigid-rotor approximation, which requires the moment of inertia of the equilibrium configuration around the principal axes obtained from QM and also the molecule's symmetry number. With the scaled normal vibrational frequencies, we computed the vibrational contribution to the entropy using the harmonic oscillator approximation. All of the compounds in this work except naphthalene have an internal rotation contribution to entropy, which requires the energy barrier, moment of inertia, and symmetry number of the rotor. We used QM calculation to determine the relaxed energy barrier and used the symmetry number of 3 for the methyl group rotor. We have used one moment of inertia for the methyl rotors, because the change in the methyl rotor moment of inertia in our studied compounds is negligible. The rotor moment of inertia used is $5.273 \cdot 10^{-47}$ kg·m^2.

For each compound, entropy is calculated at 298.15 K and from 300 K to 740 K in 10 K increments. This temperature range was chosen because it covers the whole range of temperatures for which the experimental entropies are available. The experimental entropies are available for four compounds: naphthalene,[15] 2,7-DMN,[15] 1-MN,[16] and 2-MN.[16]

We can calculate the equilibrium distribution of each dimethylnaphthalene compound in the mixture on the basis of its equilibrium constant

$$K_{eq} = \frac{N_1}{N_2} = \exp\left(-\frac{\Delta G}{RT}\right) \tag{2}$$

where ΔG is the difference in Gibbs free energy between each isomer. In this work, the enthalpy change equals the change in the internal energy ($\Delta H = \Delta U$), because the material is in the ideal gas state, in which the pressure and molar volume are constant across isomers. We calculate ΔU from the optimized energy of each compound in QM. To get ΔH as a function of temperature, we need to have an enthalpy in a range in which we can use experimental tables such as JANAF[17] to interpolate the results. We can get the enthalpy at 298.15 K from Gaussian software,[18] using the procedure demonstrated by Ochterski[19] that is published by Gaussian Inc. By performing the full frequency calculation on the equilibrium structures in Gaussian, we get the correction needed to have the ΔH at 298.15 K. In the "Thermochemistry" section of the Gaussian output, we can get the corrected enthalpy for DMN isomers at 298.15 K by subtracting the zero-point energy correction (ϵ_{ZPE}) from the thermal correction to the enthalpy (H_{corr}) and adding it to the optimized energy. Having the enthalpy at 298.15 K, we can use the experimental tables such as JANAF thermochemical tables[17] to get the enthalpy for different temperatures. Then by calculating the entropy difference between compounds at each temperature, ΔS, we arrive at the free energy, the equilibrium constant, and the equilibrium distribution of isomers.

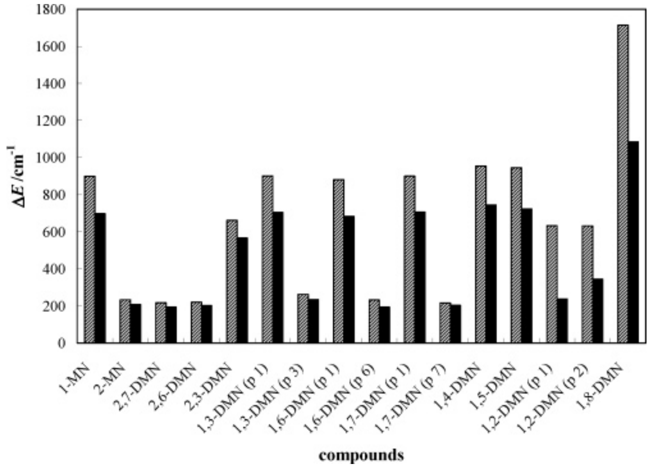

Figure 3. Single point versus relaxed calculation of energy barriers for dimethylnaphthalene (DMN) and methylnaphthalene (MN) compounds: slashed bars, single point; black bars, relaxed. Energy unit, 1 cm^{-1} = 0.01196 kJ·mol^{-1}.

Table 1. Single Point versus Relaxed Calculation of Energy Barriers for Dimethylnaphthalene (DMN) and Methylnaphthalene (MN) Compounds[a]

compound	E_{SP} cm^{-1}	$E_{relaxed}$ cm^{-1}
1-MN	899.61	697.94
2-MN	233.32	207.62
2,7-DMN	217.22	194.08
2,6-DMN	220.03	201.29
2,3-DMN	661.18	566.28
1,3-DMN (position 1)	900.93	704.55
1,3-DMN (position 3)	262.79	234.65
1,6-DMN (position 1)	880.57	682.53
1,6-DMN (position 6)	232.41	194.82
1,7-DMN (position 1)	900.02	706.56
1,7-DMN (position 7)	215.45	202.96
1,4-DMN	954.20	744.41
1,5-DMN	944.91	722.52
1,2-DMN (position 1)	632.66	237.46
1,2-DMN (position 2)	632.05	344.37
1,8-DMN	1713.13	1084.54

[a] Energy unit, 1 cm^{-1} = 0.01196 kJ·mol^{-1}.

In terms of software, we used Gaussian 98[18] for the QM calculations and Therpoly[14] for the SM calculations.

Table 2. Calculated Frequencies (ν) for Naphthalene, 1-Methyl- and 2-Methylnaphthalene (MN), and the 10 Dimethylnaphthalenes (DMN) for the Optimized Structures with B3LYP/6-31G(d,p) Level of Theory

normal mode	ν/cm^{-1}												
	naphthalene	1-MN	2-MN	2,7-DMN	2,6-DMN	2,3-DMN	1,3-DMN	1,6-DMN	1,7-DMN	1,4-DMN	1,5-DMN	1,2-DMN	1,8-DMN
1	171	131	93	85	75	112	92	86	88	120	93	99	44
2	184	165	121	93	85	116	116	103	101	130	161	121	121
3	353	182	179	116	94	148	150	144	155	180	179	150	154
4	385	244	255	129	179	190	173	182	176	184	188	150	232
5	467	271	276	212	201	256	214	227	212	192	201	220	236
6	477	408	392	274	215	264	253	240	218	267	252	273	306
7	502	429	399	277	313	292	277	276	297	296	262	295	314
8	505	467	440	319	333	298	290	319	336	326	322	339	318
9	615	469	476	406	394	407	419	413	412	413	452	415	447
10	616	505	502	413	401	410	426	439	415	443	453	425	460
11	713	532	512	435	429	437	462	450	462	467	468	455	471
12	752	560	617	459	480	481	502	480	497	476	478	502	473
13	761	618	622	477	520	512	517	494	510	496	503	508	508
14	779	693	691	537	522	527	538	543	531	533	519	530	546
15	783	727	736	625	572	620	539	567	536	567	565	564	569
16	828	767	758	630	630	647	623	623	629	620	624	634	610
17	872	779	761	669	665	648	631	682	691	688	625	672	617
18	919	788	807	755	744	730	733	707	707	719	728	712	746
19	923	846	844	756	753	740	742	744	746	751	774	736	762
20	940	850	870	767	787	755	765	780	770	768	784	765	775
21	960	886	880	775	808	806	841	809	818	784	796	802	787
22	967	931	928	829	817	839	854	820	840	817	839	845	802
23	1012	949	939	850	870	861	856	865	869	853	865	855	870
24	1022	964	943	891	880	885	880	890	886	916	876	858	889
25	1120	967	962	928	906	891	930	916	891	931	888	927	934
26	1142	1021	998	935	941	929	947	940	939	931	947	936	943
27	1143	1034	1018	943	941	960	961	948	949	962	948	962	954
28	1153	1049	1035	944	952	992	971	968	968	991	976	981	978
29	1204	1073	1119	985	994	1006	1008	999	996	1024	1005	1013	1022
30	1235	1139	1145	1015	1002	1018	1024	1034	1033	1033	1033	1021	1029
31	1253	1155	1149	1034	1034	1023	1034	1035	1035	1036	1034	1038	1037
32	1366	1159	1167	1035	1035	1043	1036	1044	1050	1047	1063	1050	1037
33	1372	1208	1207	1129	1125	1081	1057	1073	1073	1057	1092	1067	1108
34	1382	1231	1243	1146	1144	1143	1127	1154	1145	1139	1129	1144	1109
35	1456	1255	1256	1168	1161	1147	1154	1159	1155	1151	1165	1154	1154
36	1458	1348	1353	1168	1170	1178	1170	1167	1185	1158	1166	1172	1161
37	1516	1367	1369	1204	1214	1229	1215	1214	1208	1217	1211	1207	1209
38	1579	1384	1377	1246	1249	1235	1232	1240	1238	1240	1225	1220	1226
39	1606	1393	1385	1258	1258	1260	1270	1259	1257	1262	1250	1253	1252
40	1636	1433	1431	1335	1338	1327	1348	1348	1332	1334	1340	1335	1337
41	3077	1453	1452	1376	1375	1366	1366	1364	1368	1364	1357	1366	1340
42	3081	1460	1465	1378	1379	1377	1381	1371	1380	1379	1383	1379	1365
43	3081	1471	1471	1385	1385	1383	1386	1384	1384	1385	1384	1386	1379
44	3084	1515	1513	1386	1385	1394	1397	1385	1385	1388	1404	1389	1394
45	3095	1586	1577	1416	1403	1437	1414	1427	1436	1426	1407	1424	1429
46	3097	1606	1612	1452	1452	1445	1449	1452	1445	1453	1452	1450	1444
47	3108	1629	1639	1452	1452	1460	1452	1452	1451	1453	1452	1451	1449
48	3109	2944	2945	1452	1457	1461	1453	1453	1452	1455	1462	1470	1458
49		2995	2996	1469	1466	1465	1466	1468	1469	1467	1466	1471	1473
50		3033	3034	1471	1485	1468	1476	1477	1473	1473	1475	1480	1489
51		3078	3074	1516	1508	1504	1512	1511	1511	1519	1515	1514	1515
52		3079	3075	1574	1575	1575	1582	1584	1584	1594	1591	1576	1589
53		3086	3078	1620	1619	1611	1613	1610	1610	1606	1606	1606	1609
54		3090	3082	1640	1641	1641	1634	1635	1634	1623	1622	1627	1620
55		3103	3092	2945	2945	2941	2944	2944	2944	2943	2945	2948	2961
56		3104	3096	2945	2945	2943	2945	2945	2944	2944	2945	2949	2971
57		3114	3108	2996	2996	2990	2996	2995	2995	2994	2995	2994	3021
58				2996	2996	2991	2996	2996	2996	2994	2996	3001	3030
59				3032	3032	3032	3032	3033	3032	3032	3033	3030	3036
60				3032	3032	3033	3033	3033	3033	3032	3033	3064	3038
61				3072	3071	3071	3068	3074	3074	3075	3078	3076	3078
62				3073	3071	3073	3075	3077	3078	3085	3079	3079	3079
63				3074	3074	3078	3079	3078	3085	3091	3095	3089	3084
64				3076	3075	3082	3089	3086	3092	3098	3095	3095	3087
65				3091	3091	3095	3103	3103	3099	3113	3117	3104	3105
66				3093	3092	3108	3115	3110	3104	3118	3117	3118	3106

Results and Discussion

In Figure 1, we show a schematic of naphthalene, in which the methyl locations are numbered. Positions 1, 4, 5, and 8 (hereafter called the 1-position) are equivalent and positions 2, 3, 6, and 7 (hereafter called the 2-position) are equivalent. It is known that placing a methyl group at the 1-position results in a higher energy state than does doing so at the 2-position. The image in Figure 1 shows this difference between 1-MN and 2-MN. This energetic difference can explain the differences in energy for the DMN in which the methyl groups do not occupy

Table 3. Entropy Contributions (S/R) for Each of the Compounds at 298.15 K

	S/R												
entropy contribution	naph-thalene	1-MN	2-MN	2,7-DMN	2,6-DMN	2,3-DMN	1,3-DMN	1,6-DMN	1,7-DMN	1,4-DMN	1,5-DMN	1,2-DMN	1,8-DMN
translation	20.4	20.5	20.5	20.7	20.7	20.7	20.7	20.7	20.7	20.7	20.7	20.7	20.7
rotation	13.2	15.0	15.0	14.7	14.6	14.6	15.4	15.3	15.3	14.6	14.6	15.3	14.6
vibration	6.7	8.7	8.7	10.7	10.8	10.7	10.6	10.7	10.7	10.7	10.6	10.7	11.3
internal rotation	0.0	1.4	1.8	3.5	3.5	3.0	3.1	3.1	3.1	2.7	2.7	3.4	2.2
total	40.2	45.5	45.9	49.6	49.6	48.9	49.7	49.9	49.8	48.6	48.6	50.0	48.7

adjacent positions. Therefore, 2,6-DMN and 2,7-DMN have the lowest energy, because they have two methyl groups in 2-positions. Isomers, including 1,3-DMN, 1,6-DMN, and 1,7-DMN, that have one methyl group in the 1-position and one in the 2-position have a higher energy. Isomers, including 1,4-DMN and 1,5-DMN, that have two methyl groups in the 1-position have yet higher energies. Isomers that have adjacent methyl groups, including 2,3-DMN, 1,2-DMN, and 1,8-DMN, have energies that are higher than that of an isomer with methyl groups in the same type of position but located further away from each other; that is, the energy of 2,3-DMN is higher than that of 2,6-DMN; the energy of 1,2-DMN is higher than that of 1,3-DMN; and the energy of 1,8-DMN is higher than that of 1,4-DMN. The relative energy for the DMN and MN compounds is shown in Figure 2.

The energetic barrier to internal rotation for all MN and DMN compounds is shown in Figure 3. In each case we compute the barrier calculated via a single-point energy procedure and that based on the relaxed rotational barrier procedure. Starting with the MN, we see that even in the case of a single rotor, there is a barrier to rotation present due to the naphthalene portion of the molecule. This barrier is larger for 1-MN than for 2-MN. In each case, the barrier height is larger for the single-point procedure than for the relaxed procedure, as it must be.

In Table 1, the single-point barriers and relaxed barriers are reported. The barriers for methyl groups at the 2-position are relatively the same across MN and DMN for those compounds in which the methyl group is not hindered by an adjacent methyl group, that is, the rotor in 2-MN, both rotors in 2,7-DMN and 2,6-DMN, and the rotors at the 2-position in 1,3-DMN, 1,6-DMN, and 1,7-DMN. Likewise, the barriers for methyl groups at the 1-position are relatively the same across MN and DMN for those compounds in which the methyl group is not hindered by an adjacent methyl group, that is, the rotor in 1-MN, both rotors in 1,4-DMN and 1,5-DMN, and the rotors at the 1-position in 1,3-DMN, 1,6-DMN, and 1,7-DMN.

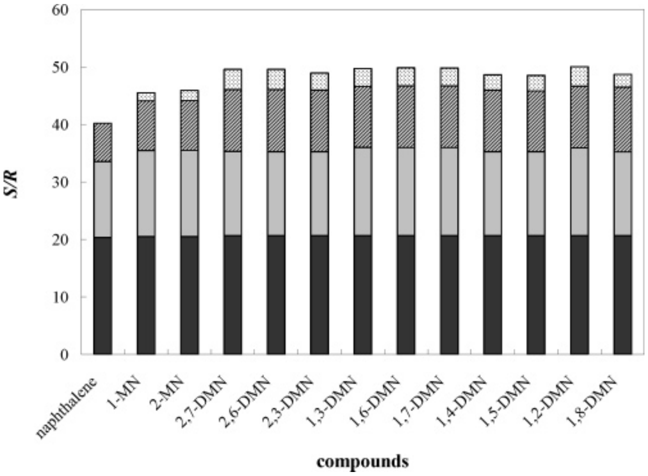

Figure 4. Entropy contributions divided by the universal gas constant, S/R, for each of the compounds at 298.15 K: dotted bars, internal rotation; slashed bars, vibration; gray bars, rotation; black bars, translation.

In compounds having internal rotation hindered by an adjacent methyl group, the barrier is usually higher than the unhindered rotation, as is the case with both rotors in 2,3-DMN and 1,8-

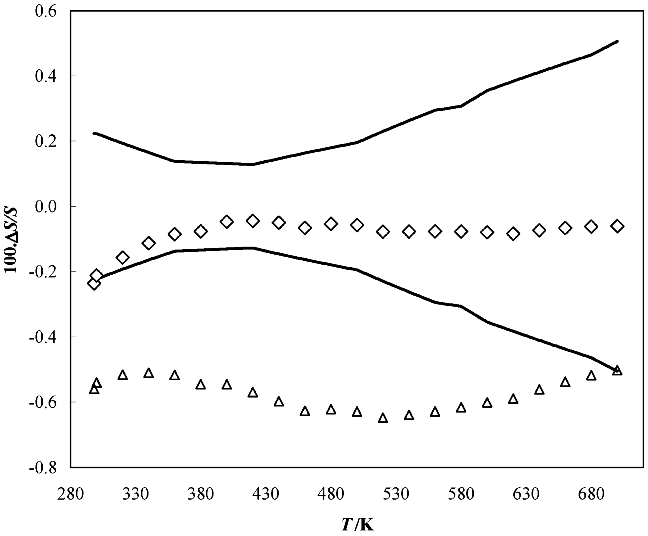

Figure 5. Naphthalene fractional deviation $\Delta S/S = \{S(\text{exptl}) - S(\text{calcd})\}/S(\text{exptl})$ of the calculated entropies from experimental values reported by Chirico et al.[15] in the temperature range of 300 K to 700 K with 10 K increments and at 298.15 K: ◇, calculated entropies in this work; △, entropy prediction from linear polynomial function of temperature from TRC tables;[20] —, uncertainties in the experimentally derived values.[15]

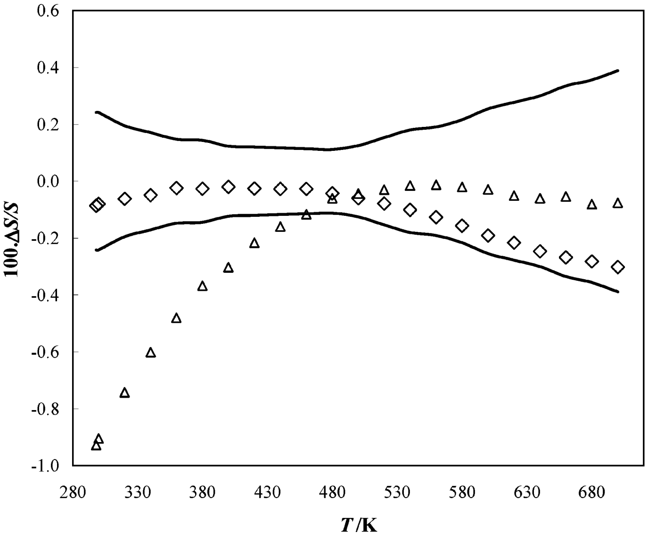

Figure 6. 2,7-Dimethylnaphthalene fractional deviation $\Delta S/S = \{S(\text{exptl}) - S(\text{calcd})\}/S(\text{exptl})$ of the calculated entropy from experimental values reported by Chirico et al.[15] in the temperature range of 300 K to 700 K with 20 K increments and at 298.15 K: ◇, calculated entropies in this work; △, entropy prediction from linear polynomial function of temperature from TRC tables;[20] —, uncertainties in the experimentally derived values.[15]

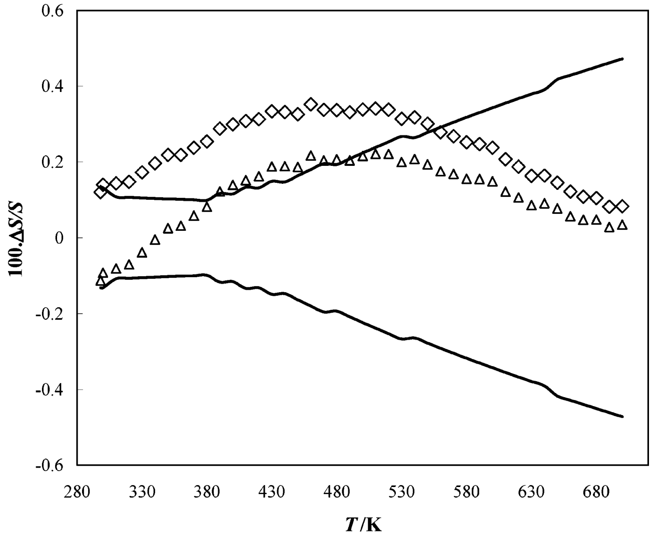

Figure 7. 1-Methylnaphthalene fractional deviation $\Delta S/S = \{S(\text{exptl}) - S(\text{calcd})\}/S(\text{exptl})$ of the calculated entropy from experimental values[16] in the temperature range of 300 K to 700 K with 10 K increments and at 298.15 K: ◇, calculated entropies in this work; △, entropy prediction from linear polynomial function of temperature from TRC tables;[20] —, uncertainties in the experimentally derived values.[15]

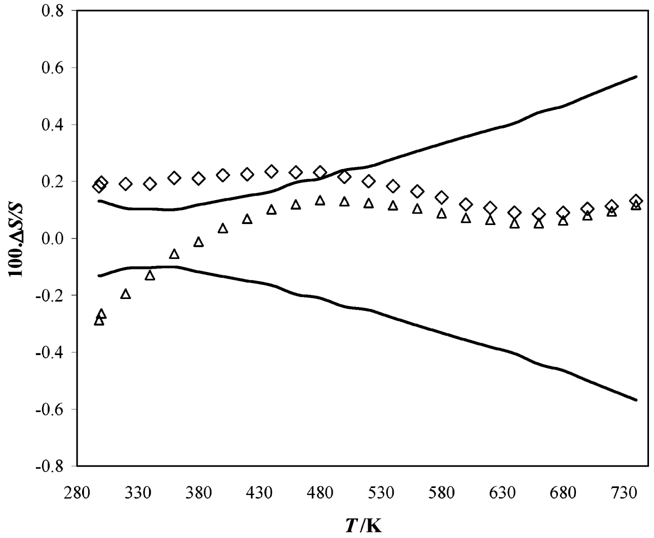

Figure 8. 2-Methylnaphthalene fractional deviation $\Delta S/S = \{S(\text{exptl}) - S(\text{calcd})\}/S(\text{exptl})$ of the calculated entropy from experimental values[16] in the temperature range of 300 K to 740 K with 20 K increments and at 298.15 K: ◇, calculated entropies in this work; △, entropy prediction from linear polynomial function of temperature from TRC tables;[20] —, uncertainties in the experimentally derived values.[15]

DMN and the rotor in the 2-position in 1,2-DMN. Surprisingly, we find that the barrier for rotation of the rotor in the 1-position in 1,2-DMN is lower than it is in 1-MN or in isomers of DMN with methyl groups in the 1-position without adjacent rotors. At this time, we attribute this result to the fact that the activation barrier is the difference between the transition state (TS) and the ground state (GS). As one compares, for example, 1,3-DMN with 1,2-DMN, the GS energy of 1,2-DMN is substantially higher. The difference between the TS and the GS is smaller for 1,2-DMN because the GS has distorted the molecule to such a point that rotation of the methyl group is now relatively easier. Certainly, however, the TS energy of 1,2-DMN is much greater than that of 1,3-DMN, relative to the same reference.

The internal rotation contribution to entropy is calculated from the relaxed barrier energy, symmetry number, and the rotor moment of inertia.

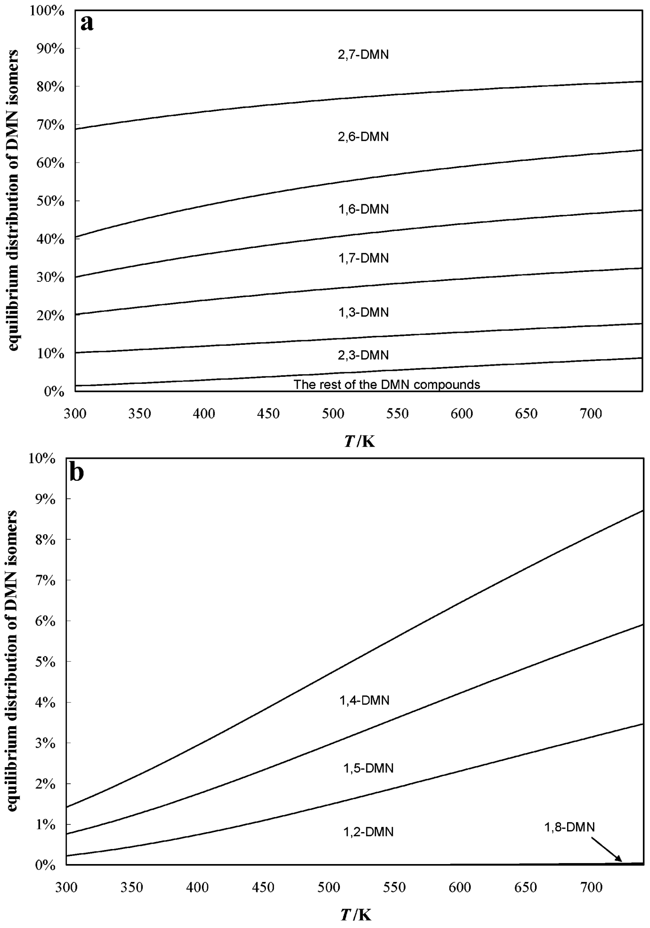

Figure 9. Calculated percentage equilibrium distribution of 2,3-DMN, 1,6-DMN, 1,3-DMN, 1,7-DMN, 2,7-DMN, and 2,6-DMN and the sum distribution of the rest of the DMN compounds (a) and of 1,8-DMN, 1,2-DMN, 1,4-DMN, and 1,5-DMN (b) in the temperature range of 300 K to 740 K.

The vibrational contributions to entropy are calculated from the normal vibrational frequencies of the equilibrium structures. In Table 2, we report the normal vibrational frequencies for all 13 compounds, after the scaling factor has been applied.

In Table 3, we provide all of the entropy contributions (translation, rotation, vibration, and internal rotation) for the compounds at 298.15 K. From Figure 4, we see that there are relatively subtle changes in the distribution of contributions to the entropy.

In Table 4, we report the calculated entropies for all 13 compounds as a function of temperature. The experimental entropy values are available for four compounds: naphthalene,[15] 2,7-DMN,[15] 1-MN,[16] and 2-MN.[16] In Figures 5 to 8, we provide plots of the fractional deviation, $\Delta S/S = \{S(\text{exptl}) - S(\text{calcd})\}/S(\text{exptl})$, of the calculated entropy in this work and the TRC table entropies[20] from experimental values reported by Chirico et al.[15,16] for the four compounds for which experimental data are available. The TRC predicted entropies in Figures 5 to 8 are from the linear polynomial function of temperature.[20] For all four compounds at all temperatures, the entropy error of this work is always less than 0.4 %, which is the same error limit obtained for benzene, toluene, and the xylene isomers in I. Moreover, we do not see any systematic discrepancy between the theory and experiment across the four compounds, which provides evidence that whatever sources of error are present, they are not systematic, but rather due to (i) limitations in theory that vary unpredictably from one compound to the next or (ii) statistical noise in the experimental data.

Table 4. Calculated Entropy (S/R) Values for Naphthalene, 1-Methyl- and 2-Methylnaphthalene (MN), and the 10 Dimethylnaphthalenes (DMN) in the Temperature Range of 300 K to 740 K

T	S/R												
K	naphthalene	1-MN	2-MN	2,7-DMN	2,6-DMN	2,3-DMN	1,3-DMN	1,6-DMN	1,7-DMN	1,4-DMN	1,5-DMN	1,2-DMN	1,8-DMN
298.15	40.2	45.5	45.9	49.6	49.6	48.9	49.7	49.9	49.8	48.6	48.6	50.0	48.7
300	40.3	45.6	46.1	49.7	49.7	49.1	49.9	50.0	50.0	48.8	48.7	50.2	48.9
310	40.9	46.3	46.7	50.4	50.4	49.8	50.6	50.7	50.7	49.5	49.4	50.9	49.6
320	41.4	46.9	47.3	51.2	51.1	50.6	51.3	51.5	51.4	50.3	50.2	51.6	50.4
330	41.9	47.6	48.0	51.9	51.9	51.3	52.1	52.2	52.2	51.0	50.9	52.3	51.1
340	42.5	48.2	48.6	52.6	52.6	52.0	52.8	52.9	52.9	51.8	51.7	53.1	51.9
350	43.0	48.8	49.2	53.3	53.3	52.8	53.5	53.6	53.6	52.5	52.4	53.8	52.6
360	43.6	49.5	49.8	54.0	54.0	53.5	54.3	54.4	54.4	53.2	53.1	54.5	53.3
370	44.1	50.1	50.5	54.7	54.7	54.2	55.0	55.1	55.1	54.0	53.9	55.2	54.1
380	44.7	50.8	51.1	55.5	55.4	55.0	55.7	55.8	55.8	54.7	54.6	55.9	54.8
390	45.2	51.4	51.7	56.2	56.2	55.7	56.4	56.5	56.5	55.4	55.3	56.7	55.6
400	45.8	52.0	52.4	56.9	56.9	56.4	57.2	57.3	57.2	56.2	56.1	57.4	56.3
410	46.3	52.7	53.0	57.6	57.6	57.1	57.9	58.0	58.0	56.9	56.8	58.1	57.0
420	46.8	53.3	53.6	58.3	58.3	57.9	58.6	58.7	58.7	57.6	57.5	58.8	57.8
430	47.4	53.9	54.2	59.0	59.0	58.6	59.3	59.4	59.4	58.3	58.3	59.5	58.5
440	47.9	54.6	54.9	59.7	59.7	59.3	60.0	60.1	60.1	59.1	59.0	60.2	59.2
450	48.5	55.2	55.5	60.4	60.4	60.0	60.7	60.8	60.8	59.8	59.7	60.9	60.0
460	49.0	55.8	56.1	61.1	61.1	60.7	61.4	61.5	61.5	60.5	60.4	61.6	60.7
470	49.6	56.5	56.7	61.8	61.8	61.4	62.1	62.2	62.2	61.2	61.1	62.3	61.4
480	50.1	57.1	57.3	62.5	62.5	62.1	62.8	62.9	62.9	61.9	61.8	63.0	62.1
490	50.6	57.7	58.0	63.2	63.2	62.8	63.5	63.6	63.6	62.6	62.5	63.7	62.8
500	51.2	58.3	58.6	63.9	63.9	63.5	64.2	64.3	64.3	63.3	63.2	64.4	63.5
510	51.7	58.9	59.2	64.6	64.6	64.2	64.9	65.0	65.0	64.0	63.9	65.1	64.2
520	52.2	59.5	59.8	65.2	65.2	64.9	65.6	65.7	65.7	64.7	64.6	65.8	64.9
530	52.7	60.1	60.4	65.9	65.9	65.6	66.3	66.4	66.4	65.4	65.3	66.4	65.6
540	53.3	60.8	61.0	66.6	66.6	66.3	67.0	67.1	67.1	66.1	66.0	67.1	66.3
550	53.8	61.4	61.6	67.3	67.3	66.9	67.6	67.7	67.7	66.8	66.7	67.8	67.0
560	54.3	62.0	62.2	67.9	67.9	67.6	68.3	68.4	68.4	67.4	67.4	68.5	67.7
570	54.8	62.5	62.8	68.6	68.6	68.3	69.0	69.1	69.1	68.1	68.0	69.1	68.4
580	55.3	63.1	63.4	69.3	69.3	69.0	69.7	69.8	69.7	68.8	68.7	69.8	69.1
590	55.8	63.7	63.9	69.9	69.9	69.6	70.3	70.4	70.4	69.5	69.4	70.4	69.7
600	56.4	64.3	64.5	70.6	70.6	70.3	71.0	71.1	71.1	70.1	70.0	71.1	70.4
610	56.9	64.9	65.1	71.2	71.2	70.9	71.6	71.7	71.7	70.8	70.7	71.7	71.1
620	57.4	65.5	65.7	71.9	71.9	71.6	72.3	72.4	72.4	71.4	71.3	72.4	71.7
630	57.9	66.0	66.2	72.5	72.5	72.2	72.9	73.0	73.0	72.1	72.0	73.0	72.4
640	58.4	66.6	66.8	73.2	73.2	72.9	73.6	73.7	73.7	72.7	72.6	73.7	73.0
650	58.9	67.2	67.4	73.8	73.8	73.5	74.2	74.3	74.3	73.4	73.3	74.3	73.7
660	59.3	67.8	67.9	74.4	74.4	74.2	74.9	74.9	74.9	74.0	73.9	75.0	74.3
670	59.8	68.3	68.5	75.1	75.1	74.8	75.5	75.6	75.6	74.7	74.6	75.6	75.0
680	60.3	68.9	69.1	75.7	75.7	75.4	76.1	76.2	76.2	75.3	75.2	76.2	75.6
690	60.8	69.4	69.6	76.3	76.3	76.1	76.7	76.8	76.8	75.9	75.8	76.8	76.2
700	61.3	70.0	70.2	76.9	76.9	76.7	77.4	77.5	77.5	76.5	76.4	77.5	76.9
710	61.7	70.5	70.7	77.5	77.5	77.3	78.0	78.1	78.1	77.2	77.1	78.1	77.5
720	62.2	71.1	71.2	78.2	78.2	77.9	78.6	78.7	78.7	77.8	77.7	78.7	78.1
730	62.7	71.6	71.8	78.8	78.8	78.5	79.2	79.3	79.3	78.4	78.3	79.3	78.7
740	63.2	72.1	72.3	79.4	79.4	79.1	79.8	79.9	79.9	79.0	78.9	79.9	79.3

Table 5. Relative Enthalpies of Formation (ΔH_f) for DMN Isomers at 298.15 K in the Ideal Gas State[a]

$\Delta H_f/J\cdot mol^{-1}\cdot K^{-1}$									
2,7-DMN	2,6-DMN	2,3-DMN	1,3-DMN	1,6-DMN	1,7-DMN	1,4-DMN	1,5-DMN	1,2-DMN	1,8-DMN
−34226	−34006	−32634	−31016	−30840	−30701	−26972	−26656	−20764	0

[a] Values are relative to 1,8-DMN.

In Table 5, we list the relative enthalpies of formation at 298.15 K in the ideal gas state for the DMN isomers. These values are relative to 1,8-DMN and are calculated according to the procedure outlined by Ochterski.[19] Having the relative enthalpies of formation and entropies, we calculate the Gibbs free energy and plot the equilibrium distribution of DMN compounds in the mixture in Figure 9. In Figure 9a, the distributions of 2,3-DMN, 1,3-DMN, 1,6-DMN, 1,7-DMN, 2,7-DMN, and 2,6-DMN have been shown. The rest of the DMN compounds that have a relatively small equilibrium distribution have been summed in Figure 9a. The distribution among these remaining compounds (1,8-DMN, 1,2-DMN, 1,4-DMN, and 1,5-DMN) is shown in Figure 9b. The relative abundance of each compound does not strictly follow the trends determined by the relative ground-state energies, as shown in Figure 2. For example, 2,3-DMN has a lower energy than 1,6-DMN, but 1,6-DMN is present in greater proportion at all temperatures, because 2,3-DMN has a symmetry plane that reduces its entropy by $R\cdot\ln(2)$.

Conclusions

In this work, we have performed a set of quantum mechanical and statistical mechanical calculations to generate the entropy of 13 aromatic compounds—naphthalene, 2 methylnaphthalene isomers, and 10 dimethylnaphthalene isomers—in the ideal gas state. Using density functional theory, we have calculated the equilibrium structure and performed a full normal-mode analysis. The level of theory used is B3LYP/6-31G(d,p). We have also used DFT to determine relaxed barriers for the internal rotation contribution to the entropy. For four compounds for which experimental data are available—naphthalene, 1-MN, 2-MN, and 2,7-DMN—we have compared the calculated entropies to the experimental values. The calculated entropies match experiment very well, with the percentage errors close to the experimental uncertainty, less than 0.4 %. Finally, we have predicted the equilibrium distribution of DMN isomers in the mixture, using the calculated entropies and energies from QM and SM calculations in the 300 K to 740 K temperature range.

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