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Conformations of Allyl Amine: Theory *vs* Experiment<sup>†</sup>

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The relative stabilities of the five conformers of allyl amine, a medium-size aliphatic molecule, were estimated by applying *ab initio* quantum mechanical methods at several levels of theory. The second-order Møller–Plesset perturbation method (MP2), quadratic configuration interaction including single and double excitations (QCISD), coupled-cluster with single and double excitations (CCSD) and CCSD plus perturbative triple excitations [CCSD(T)] were applied. The Dunning correlation consistent basis sets (through aug-cc-pVQZ and cc-pV5Z) were employed. The MP2 energies relative to the energy of the *cis*–*trans* conformer reported here appear to approach the basis set limit. The predicted allyl amine conformer energies approaching the Hartree–Fock basis set limit are  $158\text{ cm}^{-1}$  (*cis*–*gauche*),  $-5\text{ cm}^{-1}$  (*gauche*–*trans*), and  $-146\text{ cm}^{-1}$  (*gauche*–*gauche*). The same three relative energies near the MP2 basis set limit are 135, 103, and  $50\text{ cm}^{-1}$ , respectively. The analogous energies deduced from experiment are  $173 \pm 12$ ,  $92 \pm 8$ , and  $122 \pm 5\text{ cm}^{-1}$ . The theoretical results obtained in the present study suggest that satisfactory predictions of the conformer energetics of allyl amine may be achieved only by theoretical methods that incorporate consideration of correlation effects in conjunction with large basis sets. Evaluation of the zero-point vibrational energy corrections is critical, due to the very small classical energy differences between the five conformers of allyl amine. Agreement between theory and experiment for the *gauche*–*gauche* conformational energy remains problematical.

## Introduction

In the present research we employ contemporary methods of electronic structure theory in predicting the small enthalpy differences between the conformers of allyl amine,  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{NH}_2$ , a medium-size aliphatic molecule. The usually accepted chemical accuracy of  $1\text{ kcal/mol}$  ( $\sim 200\text{ cm}^{-1}$ ) for conformational energy estimates is unsatisfactory for many molecules where the enthalpy differences between rotamers are smaller.<sup>1–13</sup> Csaszar<sup>8</sup> examined the *ab initio* limits of conformational energy estimates by applying different levels of theory for several small molecules. The methods tested included Møller–Plesset perturbation theory from second to fifth order,<sup>14–17</sup> and the coupled cluster<sup>18</sup> methods CCSD,<sup>18–21</sup> CCSD(T),<sup>22</sup> and CCSDT.<sup>23</sup> Basis sets from moderate size to as large as [7s6p5d4f3g2h1i/6s5p4d3f2g1h] for first row atoms were used. The results revealed the complexity of quantitative predictions of the thermochemistry of large amplitude molecular motions. The Csaszar study provided a strategy for greater precision of theoretical conformational analysis. The application of very high levels of theory is, however, often impractical for any moderate-size molecule. In recent work,<sup>24</sup> we analyzed the accuracy of theoretical predictions for the conformational stability of 3-fluoropropane. Second-order Møller–Plesset perturbation theory (MP2) and the quadratic configuration interaction method including single and double excitations (QCISD)<sup>25</sup> combined

with a number of different quality basis sets were used. The results showed that acceptable *qualitative* agreement between theory and experiment in evaluating the very small enthalpy difference between the two stable conformers of the molecule was achieved at higher levels of *ab initio* computations. As is well-known, however, theoretical estimates that are only *qualitatively* correct are not the ultimate goal of current electronic structure theory. It was, therefore, of interest to extend further our studies by applying state-of-the-art theoretical computations on systems with more complex conformational equilibria. The results are expected to provide useful information on the appropriate balance between method and basis set, thus defining a path for quantitative description of the conformational properties of larger molecules.

In the present work we apply different levels of *ab initio* MO theory in studying the conformational properties of allyl amine. Recently, Herrebout, Zheng, Van der Veken, and Durig<sup>26</sup> investigated the conformational isomerism of allyl amine by analyzing the temperature dependence of the IR spectra in liquid krypton and xenon. The relative stabilities of four of the five possible conformers have been determined. The authors also carried out theoretical computations by applying the B3LYP density functional<sup>27,28</sup> and MP2 *ab initio* theories combined with basis sets ranging from 6-31G(d) to 6-311+G(2df,2pd). The theoretical computations produced rather discouraging results, displaying poor overall agreement with the experiment. In the present study we report MP2 computations on allyl amine by analyzing in detail the effects of basis set on the evaluated molecular properties. We also apply higher level methods for consideration of the dynamical electron correlation effects through the QCISD, coupled-cluster with single and double

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excitations (CCSD), and CCSD plus perturbative triple excitations [CCSD(T)] methods.

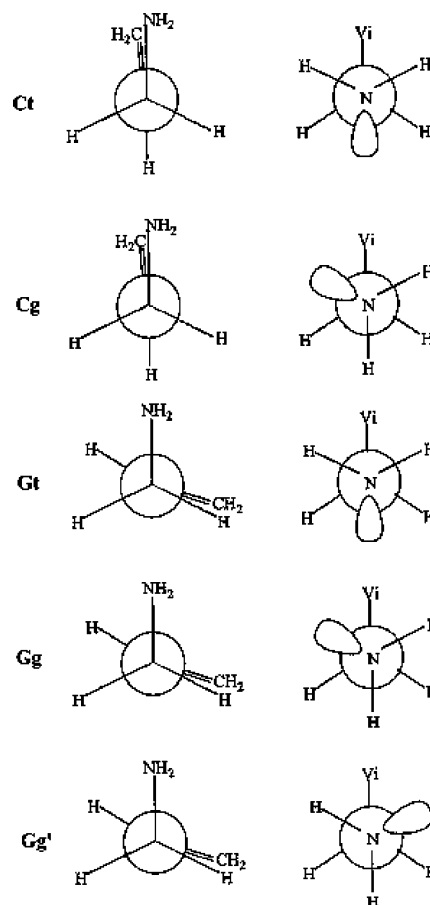
### Computational Methods

The Dunning correlation consistent basis sets cc-pVXZ ( $X = 2-5$ )<sup>29,30</sup> were employed in this research. Dynamic electron correlation was accounted for using Møller-Plesset second-order perturbation theory (MP2)<sup>14-17</sup> for all basis sets. Computations employing the quadratic configuration interaction method including all single and double excitations (QCISD)<sup>25</sup> for cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets are reported. Further, the coupled-cluster<sup>18</sup> method including all single and double excitations (CCSD)<sup>18-21</sup> and the coupled-cluster method including all single and double excitations plus perturbative triple excitations (CCSD(T))<sup>22</sup> with cc-ppVDZ and cc-pVTZ basis set were also employed. The four core (1s-like) molecular orbitals were frozen for all computations. The MOLPRO program<sup>31</sup> was used for the CCSD and CCSD(T) computations. The Gaussian 94<sup>32</sup> and MPQC<sup>33</sup> program packages were used for the others.

Harmonic vibrational frequencies were evaluated at the MP2 level for cc-pVDZ, cc-pVTZ, cc-pVQZ, aug-cc-pVDZ, and aug-cc-pVTZ basis sets. Thus zero-point vibrational energy (ZPVE) contributions were used to correct the energies of the conformers at these levels of MP2 method. Vibrational frequency computations were also performed at the QCISD/cc-pVDZ level and the respective ZPVE corrections were used to correct all energies computed using the QCISD, CCSD and CCSD(T) methods. The harmonic vibrational corrections were used without scaling. The geometries for the five conformers of allyl amine were fully optimized with the exception of the QCISD/cc-pVTZ, QCISD/cc-pVQZ, CCSD/cc-pVTZ, CCSD/cc-pVQZ, CCSD(T)/cc-pVTZ, and CCSD(T)/cc-pVQZ levels of theory. For the latter levels of theory, single-point computations were performed using geometries optimized with the respective methods employing the cc-pVDZ basis set.

### Results and Discussion

The theoretical computations carried out in the present study were compared with the experimental conclusions of Herrebout *et al.*<sup>26</sup> The five conformers of allyl amine are shown in Figure 1. As mentioned, these authors also performed extensive theoretical computations on the relative stability of the different conformers of allyl amine with the MP2 and B3LYP<sup>24-26</sup> methods using different basis sets. In the MP2 computations of Herrebout the following basis sets were employed: 6-31G(d), 6-311G(d,p), 6-311+G(d,p), 6-311G(2d,2p), 6-311+G(2d,2p), 6-311G(2df,2pd), and 6-311+G(2df,2pd). Extracts from the computational results of these authors as well as the experimental data for the enthalpy difference between the five rotamers of allyl amine obtained in their study are presented in Table 1. Qualitative agreement between theory and experiment regarding the enthalpy differences between the five stable conformers has been obtained only with MP2(full) computations employing the smallest basis set used (6-31G(d)). Unfortunately, these results cannot be considered meaningful. The largest basis set MP2 computations, though providing more reliable magnitudes for the energy differences, do not produce the experimentally deduced ordering of the relative stabilities of the five conformers. The introduction of diffuse functions lowers the energy difference between the *cis-trans* structure (Ct) and the other less stable forms. When smaller basis sets are employed, a totally reversed order of stability compared to the experimental conclusions is obtained. With larger basis sets the effect of diffuse functions is less dramatic, though the overall agreement



**Figure 1.** Five possible conformers of allyl amine where the capital letters C (*cis*) and G (*gauche*) indicate the relative position of the amino group to the double bond and the second letter (lower case) t (*trans*), g (*gauche*), or g' (*gauche'*) the relative position of the amino rotor.

**TABLE 1: Previously Reported Energy Differences for the Five Conformations of Allyl Amine from *ab Initio* and Hybrid DFT Computations (from Ref 23)**

level of theory	energy differences <sup>a</sup> (cm <sup>-1</sup> )			
	Cg	Gt	Gg	Gg'
RHF/6-31G(d)	182	37	-83	629
MP2(full)/6-31G(d)	263	95	108	793
MP2(full)/6-311G(2d,2p)	180	212	240	904
MP2(full)/6-311+G(2d,2p)	126	82	7	604
MP2(full)/6-311G(2df,2pd)	188	260	281	933
MP2(full)/6-311+G(2df,2pd)	131	110	42	628
B3LYP/6-311G(2df,2pd)	221	133	29	872
B3LYP/6-311+G(2df,2pd)	163	6	-4	576
experiment <sup>23</sup>	173 ± 12	92 ± 8	12 ± 5	

<sup>a</sup> Energies of conformations relative to Ct (*cis-trans*); a negative number indicates that conformer is more stable. Conformation labels: Ct = *cis-trans*, Cg = *cis-gauche*, Gt = *gauche-trans*, Gg = *gauche-gauche-1*, Gg' = *gauche-gauche-2*.

between theory and experiment is not satisfactory. Herrebout concluded<sup>26</sup> that *ab initio* calculations at the levels of theory employed do not provide satisfactory estimates for the percentage of allyl amine conformers present.

Experience from earlier studies<sup>8,24</sup> prompted us to reinvestigate the conformational stability of allyl amine by applying larger basis sets, as well as more reliable methods for the treatment of the dynamic electron correlation. In the present work we extend the MP2 computations on the different conformers of allyl amine. The Dunning correlation-consistent basis sets ranging from cc-pVDZ to aug-cc-pVQZ and cc-pV5Z

TABLE 2: Absolute Energies (in Hartree) for the Conformers of Allyl Amine<sup>a</sup>

	Ct	Cg	Gt	Gg	Gg'
<b>MP2</b>					
cc-pVDZ	-172.6951825	-172.6939156	-172.6943381	-172.69381503	-172.6908539
cc-pVTZ	-172.8789322	-172.8780898	-172.8781845	-172.87816103	-172.8753604
cc-pVQZ	-172.9372186	-172.9365330	-172.9365976	-172.93678703	-172.9340644

<sup>a</sup> The geometry of each structure was exhaustively optimized.

TABLE 3: Effect of Basis Sets on the Different Contributions to the Energies of the Five Conformers of Allyl Amine from *ab Initio* Second-Order Perturbation Theory<sup>a</sup>

level of theory	energy differences <sup>b</sup> (cm <sup>-1</sup> )				
	Ct	Cg	Gt	Gg	Gg'
<b>MP2/cc-pVDZ</b>					
E(HF)	0	217	146	72	761
E(Correlation)	0	62	39	228	189
E(MP2)	0	278	185	300	950
ZPVE	0	-23	-38	-53	-106
E <sub>0</sub> <sup>c</sup>	0	255	148	247	844
<b>MP2/cc-pVTZ</b>					
E(HF)	0	176	48	-73	560
E(Correlation)	0	9	116	242	224
E(MP2)	0	185	164	169	784
ZPVE	0	-8	-27	-22	-81
E <sub>0</sub> <sup>c</sup>	0	177	137	147	703
<b>MP2/cc-pVQZ</b>					
E(HF)	0	167	17	-120	487
E(Correlation)	0	-16	120	215	205
E(MP2)	0	150	136	95	692
ZPVE	0	-4	-26	-16	-79
E <sub>0</sub> <sup>c</sup>	0	146	111	79	613
<b>MP2/cc-pV5Z</b>					
E(HF)	0	158	-5	-146	454
E(Correlation)	0	-23	108	196	187
E(MP2)	0	135	103	50	641
<b>MP2/aug-cc-pVDZ</b>					
E(HF)	0	132	7	-145	486
E(Correlation)	0	-32	3	86	53
E(MP2)	0	100	9	-59	539
ZPVE	0	7	-18	-2	-78
E <sub>0</sub> <sup>c</sup>	0	107	-8	-61	461
<b>MP2/aug-cc-pVTZ</b>					
E(HF)	0	152	-1	-149	449
E(Correlation)	0	-22	105	190	168
E(MP2)	0	130	104	41	618
ZPVE	0	-6	-34	-21	-84
E <sub>0</sub> <sup>c</sup>	0	123	69	20	533
<b>MP2/aug-cc-pVQZ</b>					
E(HF)	0	156	-7	-151	448
E(Correlation)	0	-27	103	188	176
E(MP2)	0	129	96	37	624
<b>experiment<sup>23</sup></b>	0	<b>173 ± 12</b>	<b>92 ± 8</b>	<b>122 ± 5</b>	

<sup>a</sup> All values (in cm<sup>-1</sup>) are relative to the energy of the Ct conformer. Conformation labels: Ct = *cis-trans*, Cg = *cis-gauche*, Gt = *gauche-trans*, Gg = *gauche-gauche1*, Gg' = *gauche-gauche2*.

<sup>b</sup> Energies of conformations relative to Ct; a negative number indicates that a particular conformer is lower in energy than Ct. <sup>c</sup> E<sub>0</sub> = E(HF) + E(correlation) + ZPVE.

were applied. The absolute energies (in hartree) for the conformers of allyl amine are reported in Table 2. The contributions to the total molecular energies (E<sub>0</sub>) originating from the Hartree–Fock energies (E(HF)), correlation energies (E(correlation)), and zero-point vibrational energies (ZPVE) are presented in Table 3. The basis set effects upon the ZPVE-uncorrected energies of the conformers, relative to the values of the lowest energy Ct structure are illustrated in Figure 2. The results obtained allow us to establish some definite trend regarding the origin of the differences in energy between the conformers of allyl amine. The MP2 computations employing

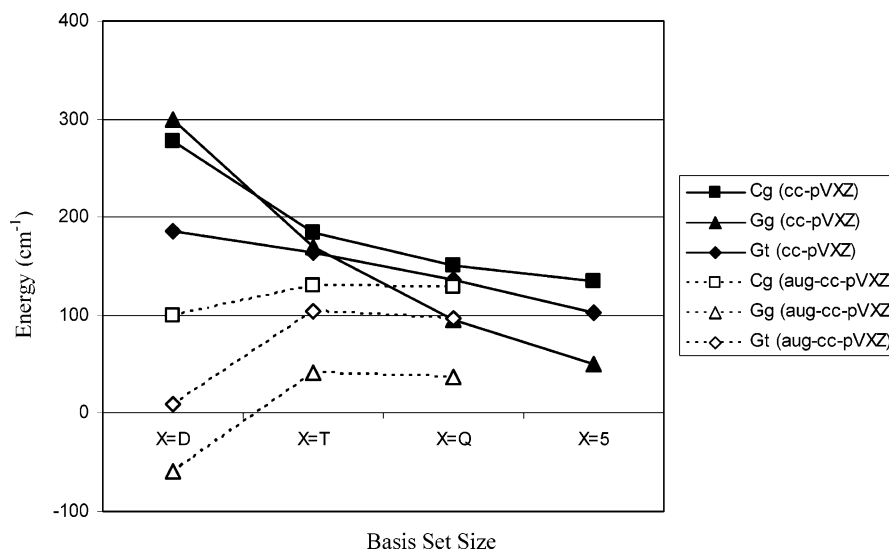
basis sets without diffuse functions (cc-pVDZ to cc-pV5Z) show that, in accord with experiment, the most stable structure is the *cis-trans* (Ct) conformer. The MP2 energies relative to the energy of the *cis-trans* conformer reported here appear to approach the basis set limit. The predicted allyl amine conformer energies approaching the Hartree–Fock basis set limit are 158 cm<sup>-1</sup> (*cis-gauche*), -5 cm<sup>-1</sup> (*gauche-trans*), and -146 cm<sup>-1</sup> (*gauche-gauche*). The same three relative energies near the MP2 basis set limit are 135, 103, and 50 cm<sup>-1</sup> respectively. The analogous energies deduced from experiment are 173 ± 12, 92 ± 8, and 122 ± 5 cm<sup>-1</sup>. It is interesting to note that the correlation energy makes a greater contribution to the energies of the Gt and Gg, forms than does the HF energy term. In the cases of the Gt and Gg structures negative contributions from the HF energies are obtained when some of the more extensive basis sets are employed (cc-pV5Z, aug-cc-pVTZ, aug-cc-pVQZ). Larger correlation energy contributions, however, lead to higher total energies of these rotamers compared to the Ct form.

ZPVE contributions are determined from computations employing basis sets ranging from cc-pVDZ to cc-pVQZ. The larger basis sets lead to smaller ZPVE contributions for the Cg, Gt, Gg, and Gg' conformers. Overall, the most complete MP2/cc-pVQZ and MP2/cc-pV5Z computations predict energy differences between the conformers of allyl amine that are in the vicinity of the relative stabilities derived from the spectroscopic experiments.<sup>23</sup> The ordering of energies for the Gg conformer is, however, not in line with the experimental conclusions, because the theoretical Gg energy is significantly below the experimentally derived value.

The introduction of diffuse functions into the smaller basis sets does not lead to better accord between theory and experiment. The MP2/aug-cc-pVDZ computations even predict that the Gt and Gg conformers have lower energies than the Ct form. This effect is compensated to a certain extent when aug-cc-pVTZ and aug-cc-pVQZ basis sets are used. In summary, the MP2 theory combined with basis sets of cc-pVQZ and cc-pV5Z quality predicts energy separation between the conformers of allyl amine that are in plausible accord with the values derived from experiment. However, even at these levels of theory the ordering of the relative stability of the Gg structure is not correctly predicted. It should certainly be remembered that the energy differences between the conformers are indeed very small: the Cg rotamer has a 0.492 kcal/mol higher energy than the most stable Ct form. The respective values for the Gt and Gg structures are 0.232 and 0.349 kcal/mol. Thus, in this situation we deal with a very ambitious goal for theory or experiment. Accuracy in theoretical predictions of ±1 kcal/mol is often considered satisfactory for most applications.

It was certainly of interest to examine how more complete theoretical methods would perform in analyzing the conformational stability of allyl amine. We applied the QCISD, CCSD, and CCSD(T) theories combined with the Dunning's correlation consistent basis sets. The estimated energy differences using the QCISD method combined with cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets produce results in seemingly better accord with





**Figure 2.** Basis set effects upon ZPVE-uncorrected energies (in  $\text{cm}^{-1}$ ) of conformers of allylamine, relative to that of the lowest-energy conformer, Ct. The highest-energy conformer,  $\text{Gg}'$ , is not shown here.

**TABLE 4: ZPVE Corrected Energy Differences (in  $\text{cm}^{-1}$ ) for the Five Conformers of Allyl Amine from QCISD, CCSD, and CCSD(T) *ab Initio* Computations<sup>a</sup>**

level of theory	energy (hartree) Ct	energy differences <sup>b</sup> (cm <sup>-1</sup> )			
		Cg	Gt	Gg	Gg'
<b>QCISD<sup>c</sup></b>					
cc-pVDZ	-172.744491	234	137	216	762
cc-pVTZ (cc-pVDZ geom)	-172.912257	230	125	157	684
cc-pVQZ (cc-pVDZ geom)	-172.965237	215	101	104	618
<b>CCSD<sup>c,d</sup></b>					
cc-pVDZ	-172.644928	223	134	203	748
cc-pVTZ(cc-pVDZ geom)	-172.976818	158	171	128	665
cc-pVQZ(cc-pVDZ geom)	-172.963107	151	107	35	552
<b>CCSD(T)<sup>c,d</sup></b>					
cc-pVDZ	-172.773603	253	136	250	793
cc-pVTZ(cc-pVDZ geom)	-173.009216	185	182	180	716
cc-pVQZ(cc-pVDZ geom)	-172.998578	177	120	88	602

experiment<sup>23</sup>

173 ± 12 92 ± 8 122 ± 5

<sup>a</sup> Conformation labels: Ct = *cis-trans*, Cg = *cis-gauche*, Gt = *gauche-trans*, Gg = *gauche-gauche1*,  $\text{Gg}'$  = *gauche-gauche2*.

<sup>b</sup> Energies of conformations relative to Ct; a negative number indicates that a particular conformer is lower in energy than Ct. <sup>c</sup> Corrected for zero-point vibrational energies from QCISD/cc-pVDZ computations.

<sup>d</sup> cc-pVDZ and cc-pVTZ basis sets include inner electrons orbitals; frozen core computations with cc-pVQZ basis set.

experiment compared to the MP2 results. The QCISD energy estimates reported in Table 4 are corrected for ZPVE obtained from vibrational frequency computations performed at the QCISD/cc-pVDZ level of theory. In the case of the Cg conformer the theoretical energy difference with the Ct structure is overestimated for all basis sets used. For the Gt and Gg forms, however, the theoretical estimates become closer to the experimental deductions with improvements in the basis set employed. For the QCISD/cc-pVQZ level of theory the theory predicts energy difference for the Gt form of  $100 \text{ cm}^{-1}$ , which compares quite well with the experimentally deduced estimate of  $92 \text{ cm}^{-1}$ . For the Gg structure the respective values are  $104 \text{ cm}^{-1}$  from theory and  $122 \text{ cm}^{-1}$  from experiment.

The next step in the consideration of different theoretical levels involved the CCSD method combined with cc-pVDZ, cc-pVTZ and cc-pVQZ basis sets. ZPVE contributions determined from QCISD/cc-pVDZ computations were used to correct the energy predictions using the larger cc-pVTZ and cc-pVQZ

basis sets. The results obtained at these levels of theory (Table 4) appear satisfactory for the Cg and Gt conformers. The CCSD/cc-pVQZ computations yielded energy differences for the Cg and Gt conformers of  $151$  and  $107 \text{ cm}^{-1}$ , respectively. The experimental deductions for these two rotamers are  $173$  and  $92 \text{ cm}^{-1}$ . For the Gg form, however, the theoretical prediction is low at  $35 \text{ cm}^{-1}$ , and experiment gave  $122 \text{ cm}^{-1}$ . Finally, a CCSD(T) method combined with the cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets was considered. The ZPVE corrections were taken again from the QCISD/cc-pVDZ computations. The results (Table 4) showed that with the largest basis set the agreement between theoretical predictions and experiment is acceptable. For the Cg conformer, the energy difference with the most stable Ct form is estimated at  $177 \text{ cm}^{-1}$  and fortuitously coincides quite well with the experimental deduction. In the case of the Gt conformer the respective theoretical estimate is  $120 \text{ cm}^{-1}$ , compared to the experimental value of  $92 \text{ cm}^{-1}$ . In the case of the Gg form the respective values are  $88 \text{ cm}^{-1}$  from theory and  $122 \text{ cm}^{-1}$  from experiment. As mentioned, the zero-order vibrational energy corrections employed are from QCISD/cc-pVDZ frequency computations. These corrections, therefore, introduce limitations in the final energy predictions. Until full CCSD(T) geometry optimizations and ZPVE evaluations are possible with at least the cc-pVQZ basis set, one must consider the QCISD, CCSD, and CCSD(T) results with some skepticism.

## Conclusions

The theoretical results obtained in the present study make some progress in resolving a contradiction between theory and experiment. With MP2 theory, the present research (through aug-cc-pVQZ and cc-pV5Z basis sets) is approaching the basis set limit for these small energy differences. It seems clear that satisfactory predictions of the conformer stabilities of allyl amine can be achieved only by theoretical methods that incorporate consideration of correlation effects in concert with basis sets of good quality. Evaluation of the zero-point vibrational energy corrections is critical because of the very small energy differences between the five conformers of allyl amine.

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