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Rotation/Inversion Study of the Amino Group in Ethylamine

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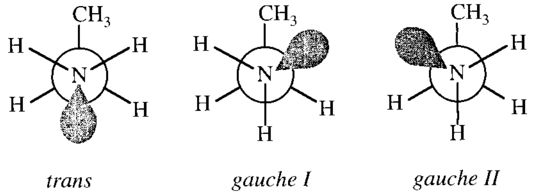
Using the HF, MP2, and DFT methodologies in the GAUSSIAN 94 set of quantum chemistry codes with a 6-311G** basis set, we examine theoretically the internal rotation and inversion of the amino group in ethylamine. An analytical potential energy surface corresponding to energy as a function of ϕ, the dihedral angle of the lone-pair of electrons on the amino group, and τ, the angle between the amine plane and the C−N axis, for these motions is generated by fitting the energy determined at 109 geometries to sums of products of Bessel functions of the first kind, J_m, and $\cos(m\phi)$. The surface depicts several special points: the minimum energy trans conformer, the two gauche conformers, the three first-order transition states for internal rotation of the amino group about the C−N bond, the two first-order transition states for the inversion of the amino group, and the three second-order transition states also for the inversion motion. The results of a related study on the internal rotation of the ammonium group about the C−N bond in the ethylammonium ion are also interspersed in this report. Both nondeuterated and several deuterated isotopomers of both ethylamine and ethylammonium ion are considered.

1. Introduction

In a recent study[1] we investigated from a theoretical point of view the infrared spectral characterization of *trans*- and *gauche*-ethylamine and the ethylammonium ion in their nondeuterated and several deuterated forms. In the process of carrying out that study, we realized that it would be interesting to also investigate for ethylamine two motions of the amino group: internal rotation about the C−N bond and inversion. As a closely related study we also considered the internal rotation of the ammonium group about the C−N axis in the ethylammonium ion; of course, for this species no inversion of the ammonium group can occur.

With regard to consideration of internal rotation of the NH_2 group or NH_3^+ group about the C−N bond in ethylamine or the ethylammonium ion, important objectives are the determination of the torsional potential function and the determination of torsional barriers. Both ethylamine and the ethylammonium ion are fairly small molecules that have been studied before with experimentally determined values of the rotational barriers being available. Two conformers are possible for ethylamine—one being the trans form where the lone pair of electrons on the NH_2 group is trans to the C−C bond and the gauche form where the lone pair of electrons is gauche to the C−C bond. Note there are two equivalent gauche forms, labeled here as gauche I and gauche II. These structures are shown in **1**.



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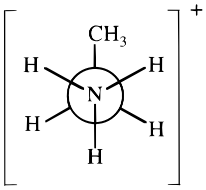
A related question concerns whether the trans or gauche conformer is the energetically more stable form for ethylamine. The most stable conformation of the ethylammonium ion is the staggered form, shown as **2**.



2

Another pathway for reaching configurations accessible through torsional motion of the amine group is via inversion of the amine group. We decided to probe the energetics corresponding to this motion and to display the resulting energy surface as a function of both rotational and inversion motions. In generating this type of surface, the following special points will be required: global minimum, local minima, first-order transition states for rotational motion, and first-order and second-order transition states for inversion motion.

This report summarizes our results in considering the NH_2 torsional motion for *trans*- and *gauche*-ethylamine and the NH_3^+ torsional motion for ethylammonium ion. The inversion motion of the amine group in ethylamine is considered, and the resulting energetics are displayed in an energy surface for torsion and inversion motions. But first we will review the experimental results that are available.

2. Experimental Results Available for Amino Group Rotation and Inversion

Several experimental studies have been carried out on $CH_3CH_2NH_2$ and $CH_3CH_2NH_3^+$. Durig and Li[2] have recorded and analyzed the Raman spectra of gaseous $CH_3CH_2NH_2$ and $CH_3CH_2ND_2$. They deduced a potential function for the NH_2 torsion and determined that the trans conformer is more stable than the gauche conformer by 1.93 kJ mol^{-1} for $CH_3CH_2NH_2$ and 2.48 kJ mol^{-1} for $CH_3CH_2ND_2$. They also deduced a potential

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TABLE 1: Calculated and Experimental Ground-State Geometries and Total Energies for *trans*- and *gauche*-Ethylamine and Ethylammonium Ion

geometrical coordinate	*trans*-$CH_3CH_2NH_2$		*gauche*-$CH_3CH_2NH_2$		$CH_3CH_2NH_3^+$	
	MP2	exptl[a,b]	MP2	exptl[a,b]	MP2	exptl
r(C−C)/pm	153.0	152.5,[a] 153.1[b]	152.3	152.4[b]	151.7	
r(C−N)/pm	146.5	147.7,[a] 147.0[b]	146.7	147.5[b]	151.7	
r(C−H)/pm	109.5	109.2,[a] 110.7[b]	109.6	110.7[b]	109.2	
r(N−H)/pm	101.6	101.1,[a] 105.2[b]	101.6	105.2[b]	102.5	
∠C−C−N/(deg)	115.3	114.8,[a] 115.0[b]	109.7	109.7[b]	110.2	
∠C−C−H_{av}/(deg)	110.9	111.4,[a] 113.2[b]	110.5	113.2[b]	110.5	
∠C−N−H_{av}/(deg)	108.8	112.6,[a] 111.1[b]	109.1	112.4[b]	111.0	
∠H−N−C−C/(deg)	+57.2 −57.2		+178.9 +63.8		+180.0 +59.5 −59.5	
τ/(deg)	57.8		57.2			
total energy/au	−134.786 218		−134.785 777		−135.151 789	

[a] Durig, J. R.; Li, Y. S. *J. Chem. Phys.* **1975**, *63*, 4110. (Based on rotational constants of trans-$CH_3CH_2NH_2$.) [b] Hamada, Y.; Tsuboi, M.; Yamanouchi, K.; Kuchitsu, K. *J. Mol. Struct.* **1986**, *146*, 253.

function for the NH_2 torsion. For ethylamine-d_0 the barriers, in kJ mol^{-1}, that were deduced were trans−gauche, 9.65; gauche−trans, 7.71; gauche−gauche, 9.66, and for ethylamine-*N*,*N*-d_2 the barriers found were trans−gauche, 9.32; gauche−trans, 6.84; gauche−gauche, 9.32. Internal rotation in eight isotopomers of ethylamine has been examined by Tsuboi et al.[3] They found that the trans form is more stable by 2.75 kJ mol^{-1} on the basis of the difference in potential energy minima. The authors acknowledge that the energy difference found must be used with some reservation since the frequencies used in the fitting of the potentials are not very appropriate for the determination of the energy difference between the trans minima and the gauche minima. The barriers found, in units of kJ mol^{-1}, were trans−gauche, 9.23; gauche−trans, 6.50; gauche−gauche, 9.89. Hamada et al.[4] have analyzed the vibrational spectra of both *trans*- and *gauche*-ethylamine and some of its isotopomers in the spectral region 2000−100 cm^{-1}. They have found from an analysis of the NH_2-wagging band in the argon matrix spectra that the trans form is more stable compared to a specific gauche form by (1.20 ± 0.12) kJ mol^{-1}. Since there are two gauche forms, as shown in **1**, the gauche:trans ratio actually exceeds 1 and was found to be 1.23. They have found for the equilibrium g → tr that $\Delta H° = (1.21 \pm 0.42)$ kJ mol^{-1}. No barrier to rotation was deduced. Fischer and Botskor[5−7] have determined and analyzed the microwave spectra of both *trans*- and *gauche*-ethylamine and ethylamine-*N*,*N*-d_2. They found that the trans conformer is more stable by 1.32 kJ mol^{-1} compared to the gauche conformer. The gauche−gauche barrier was deduced to be 8.25 kJ mol^{-1}. In another study Hamada et al.[8] used gas-phase electron diffraction and examined the structures of trans and gauche conformers. They have found for the equilibrium g → tr that $\Delta H° = (1.28 \pm 0.84)$ kJ mol^{-1} on the basis of the relative abundances of the two conformers. Hagemann and Bill[9] undertook a vibrational analysis of the Raman spectra of crystalline ethylammonium chloride and bromide and a number of their isotopomers. However, no barriers to rotation were deduced.

Fischer and Botskor[7] have measured the microwave spectrum of *gauche*-ethylamine and have deduced an amino inversion barrier height of 16.8 kJ mol^{-1}. Molecules similar in structure to ethylamine have also been investigated. On the basis of the analysis of microwave spectrum of methylaminoethane and analysis of the splittings in rotational energy levels due to perturbation by the amino inversion, Penn and Boggs[10] deduced an inversion barrier of 21.8 kJ mol^{-1} within the WKB approximation. On the basis of a similar approach for dimethylamine, the same investigators[10] obtained an estimated value of the inversion barrier of 18.4 kJ mol^{-1} and Wollrab and Laurie[11] obtained an inversion barrier of 19.7 kJ mol^{-1}. Methylamine was found by Tsuboi, Hirakawa, and Tamagake[12] to have an inversion barrier of 20.2 kJ mol^{-1}, while ammonia was found by Swalen and Ibers[13] to have an inversion barrier of 24.2 kJ mol^{-1}. On the basis of use of the MP2/TZ2p+f level of theory, Jarrett-Sprague and Hillier[14] obtained barrier heights including zero-point energy corrections of 33.5 and 46.2 kJ mol^{-1}, respectively, for monochloramine and hydroxylamine.

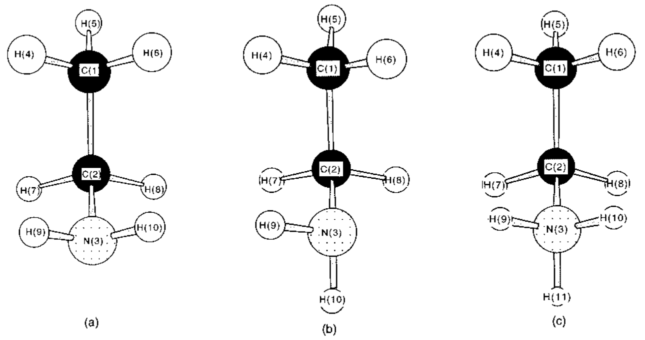

Figure 1. Ground-state geometries: (a) *trans*-ethylamine; (b) *gauche*-ethylamine; (c) ethylammonium ion.

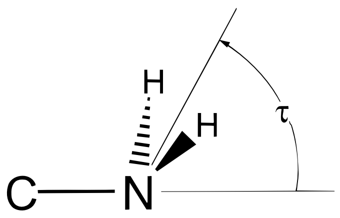

Figure 2. Geometry that defines the angle τ, which is the angle between the C−N axis and the NH_2 plane.

3. Computational Details

The optimized geometries of *trans*- and *gauche*-ethylamine and the ethylammonium ion have been determined at the MP2 level of theory[15,16] using a 6-311G** basis set within the GAUSSIAN 94 electronic structure methodology.[17] The optimized geometries that were found are displayed in Figure 1. The optimized geometries are reported in Table 1 along with comparison with the experimental values obtained by Durig and Li[2] and Hamada et al.[8] The angle τ, defined as the angle between the C−N axis and the NH_2 plane, is shown in Figure 2 with numerical values reported in Table 1 for the trans and gauche conformers of ethylamine. An important geometrical

TABLE 2: Calculated and Experimental Transition-State Geometries and Total Energies for *trans*- and *gauche*-Ethylamine and Ethylammonium Ion

geometrical coordinate	*trans*-$CH_3CH_2NH_2$		*gauche*-$CH_3CH_2NH_2$		$CH_3CH_2NH_3^+$	
	MP2	exptl	MP2	exptl	MP2	exptl
r(C−C)/pm	152.5		152.6		151.7	
r(C−N)/pm	147.4		147.4		153.4	
r(C−H)/pm	109.5		109.5		109.1	
r(N−H)/pm	101.3		101.2		102.4	
∠C−C−N/(deg)	112.3		110.5		110.3	
∠C−C−H_{av}/(deg)	110.0		110.0		111.2	
∠C−N−H_{av}/(deg)	109.9		110.1		110.5	
∠H−N−C−C/(deg)	−3.4		+121.7		+119.8	
	−119.9		−121.7		0.0	
					−119.8	
τ/(deg)	55.4		55.1			
total energy/au	−134.781 350		−134.782 457		−135.147 244	

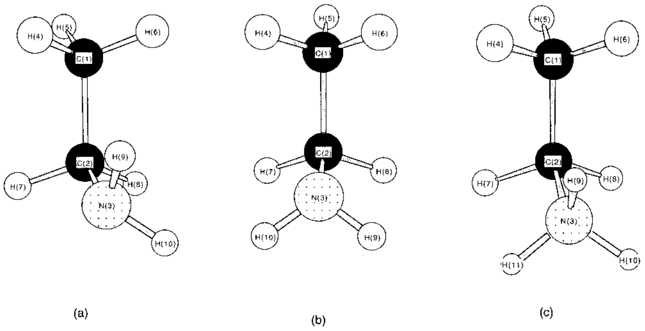

Figure 3. First-order rotational state geometries: (a) *trans*-ethylamine; (b) *gauche*-ethylamine; (c) ethylammonium ion.

TABLE 3: Calculated MP2/6-311g Geometries and Total Energies for the Two First-Order Inversion Transition States for Ethylamine[a]**

geometrical coordinate	value
r(C−C)/pm	153.2
r(C−N)/pm	143.9
r(C−H)/pm	109.6
r(N−H)/pm	100.0
∠C−C−N/(deg)	113.5
∠C−C−H_{av}/(deg)	109.9
∠C−N−H_{av}/(deg)	121.0
∠H−N−C−C/(deg)	−113.0
	+68.0
τ/(deg)	1.1
ϕ/(deg)	−22.3, +22.3
total energy/au	−134.775 770

[a] The two transition states differ in ϕ, which is −22.3° for one and +22.3° for the other.

TABLE 4: Calculated MP2/6-311g Geometries and Total Energies for the Three Second-Order Inversion Transition States for Ethylamine[a]**

	value	value
r(C−C)/pm	153.3	152.4
r(C−N)/pm	143.9	144.0
r(C−H)/pm	109.6	109.6
r(N−H)/pm	100.0	100.0
∠C−C−N/(deg)	114.1	109.7
∠C−C−H_{av}/(deg)	109.7	109.7
∠C−N−H_{av}/(deg)	121.0	120.9
∠H−N−C−C/(deg)	−92.3	0.0
	+92.3	180.0
τ/(deg)	3.9	0
ϕ/(deg)	0	−90.0, +90.0
total energy/au	−134.775 711	−134.774 678

[a] In the third column the two transition states differ in ϕ, which is −90.0° for one and +90.0° for the other.

parameter to consider is the ∠C−C−N. Tsuboi et al.[3], on the basis of their analysis of the internal rotation−inversion interaction, obtained a value of 115.18° for ∠C−C−N for both conformers. Hamada et al.[8] obtained a value of 115.3° for the trans conformer, which is close to the result found by Tsuboi et al. However, for the gauche isomer a value of 109.7° was obtained. The MP2-level calculation produces values of 115.0° and 109.7°, respectively, which agree extremely closely with the results obtained from electron diffraction. Also, the bond distances r(C−C), r(C−N), and r(N−H) agree quite closely with the corresponding experimental values. We find, as Hamada et al. found, that r(C−C) is 0.7 pm longer for the trans conformer. However there is a greater discrepancy in r(N−H), ∠C−C−H_{av}, and ∠C−N−H. This discrepancy could be in part due to the approach used by Hamada et al. of fixing a few of the geometrical coordinates to their Hartree−Fock calculation, which was done using a 4-31G(N*) basis set, in the process of the deduction of a set of geometrical coordinates from their electron diffraction data. It would be interesting to see what set of geometrical coordinates would now be obtained if the same few geometrical parameters would be fixed at their MP2 values. With regard to the ethylammonium ion, most of the geometrical coordinates reported in Table 1 are similar to the corresponding coordinates for either conformer of ethylamine. Note that the bond lengths r(C−C) and r(C−N) are shifted with r(C−C) decreasing to 151.7 pm and r(C−N) increasing to 151.7 pm and the ∠C−C−N is 110.2°, which happens to be closer to that of the gauche conformer. Comparison with experiment was not possible since no experimental geometrical data on the ethylammonium ion could be found in the literature.

The first-order rotational transition states for the transitions tr → g, g → tr, and g → g for ethylamine and staggered → eclipsed for ethylammonium were all found such that each structure corresponded to a set of frequencies with one imaginary frequency. The geometrical parameters corresponding to the transition state structures for *trans*-ethylamine, *gauche*-ethylamine, and the ethylammonium ion are reported in Table 2, and the structures are displayed in Figure 3. It is interesting to note that in the transition-state structure for *gauche*-ethylamine the dihedral angle of the H atom nearly cis to the CH_3 group is −3.39°. For both *trans*- and *gauche*-ethylamine the H atoms of the CH_3 groups relative to the C−N bond change values by a few degrees relative to the equilibrium geometries of each conformer. No experimental data on the structure of any of the transition states could be found in the literature.

A search for first-order transition states for amino group inversion was undertaken. Two geometries with each corresponding to *one* imaginary frequency were found. The geometry and energy corresponding to these points are reported in

TABLE 5: Barriers to Rotation of the Amino Group about the C−N Bond in Ethylamine-d_0 and Ethylammonium-d_0 Ion Based on Gaussian Calculations with a 6-311G Basis Set**[a]

level of calculation	conformer	E_{el}	ZPE − (1/2)$h\nu$	conformation	E_{el}	ZPE	ΔE	ΔE (kJ mol^{-1})
			Trans−Gauche Barrier for Ethylamine-d_0					
hf	tr	−134.289 785	0.097 678	tr−g+	−134.285 531	0.097 893	4.47E-03[b]	11.7
mp2	tr	−134.786 218	0.093 541	tr−g+	−134.781 350	0.093 723	5.05E-03	13.3
mp4	tr	−134.841 933	0.093 541	tr-g+	−134.836 988	0.093 723	5.13E-03	13.5
dft	tr	−135.216 915	0.091 730	tr-g+	−135.212 436	0.091 927	4.68E-03	12.3
			Gauche−Trans Barrier for Ethylamine-d_0					
hf	g	−134.289 815	0.097 787	g−tr+	−134.285 531	0.097 893	4.39E-03	11.5
mp2	g	−134.785 777	0.093 605	g−tr+	−134.781 350	0.093 723	4.55E-03	11.9
mp4	g	−134.841 345	0.093 605	g−tr+	−134.836 988	0.093 723	4.48E-03	11.7
dft	g	−135.216 339	0.091 769	g−tr+	−135.212 436	0.091 927	4.06E-03	10.7
			Gauche−Gauche Barrier for Ethylamine-d_0					
hf	g	−134.289 815	0.097 787	g−g+	−134.286 522	0.097 746	3.25E-03	8.54
mp2	g	−134.785 777	0.093 605	g−g+	−134.782 457	0.093 593	3.31E-03	8.69
mp4	g	−134.841 345	0.093 605	g−g+	−134.838 099	0.093 593	3.23E-03	8.49
dft	g	−135.216 339	0.091 769	g−g+	−135.213 488	0.091 784	2.87E-03	7.52
			Trans−Gauche Barrier for Ethylammonium-d_0 Ion					
hf	tr	−134.660 415	0.113 928	tr−g+	−134.656 061	0.113 992	4.42E-03	11.6
mp2	tr	−135.151 789	0.108 737	tr−g+	−135.147 244	0.108 720	4.53E-03	11.9
dft	tr	−135.581 469	0.106 921	tr−g+	−135.577 505	0.106 943	3.99E-03	10.5

[a] All energies are expressed in au unless otherwise noted. [b] Read as 4.47 × 10^{-3}.

TABLE 6: Barriers to Rotation of the Amino Group about the C−N Bond in Ethylamine-d_7 and Ethylammonium-d_8 Ion Based on Gaussian Calculations with a 6-311G Basis Set**[a]

level of calculation	conformer	E_{el}	ZPE − (1/2)$h\nu$	conformation	E_{el}	ZPE	ΔE	ΔE (kJ mol^{-1})
			Trans−Gauche Barrier for Ethylamine-d_7					
hf	tr	−134.289 785	0.065 699	tr−g+	−134.285 531	0.065 730	4.39E-03[b]	11.5
mp2	tr	−134.786 218	0.062 797	tr−g+	−134.781 350	0.062 899	4.97E-03	13.0
dft	tr	−135.216 915	0.061 541	tr−g+	−135.212 436	0.061 670	4.61E-03	12.1
			Gauche−Trans Barrier for Ethylamine-d_7					
hf	g	−134.289 815	0.065 677	g−tr+	−134.285 531	0.065 730	4.34E-03	11.4
mp2	g	−134.785 777	0.062 853	g−tr+	134.781 350	0.062 899	4.47E-03	11.7
dft	g	−135.216 339	0.061 584	g−tr+	−135.212 436	0.061 670	3.99E-03	10.5
			Gauche−Gauche Barrier for Ethylamine-d_7					
hf	g	−134.289 815	0.065 677	g−g+	−134.286 522	0.065 648	3.26E-03	8.57
mp2	g	−134.785 777	0.062 853	g−g+	−134.782 457	0.062 831	3.30E-03	8.66
dft	g	−135.216 339	0.061 584	g−g+	−135.213 488	0.061 588	2.85E-03	7.50
			Trans−Gauche Barrier for Ethylammonium-d_8 Ion					
hf	tr	−134.660 415	0.076 081	tr−g+	−134.656 061	0.076 109	4.38E-03	11.5
mp2	tr	−135.151 789	0.072 625	tr−g+	−135.147 244	0.072 601	4.52E-03	11.9
dft	tr	−135.581 469	0.071 349	tr−g+	−135.577 505	0.071 363	3.98E-03	10.4

[a] All energies are expressed in au unless otherwise noted. [b] Read as 4.39 × 10^{-3}.

TABLE 7: Comparison of Theoretically Determined Quantities for Ethylamine-d_0 Based on Use of a 6-311g Basis Set with Those Deduced from Experimental Data**[a]

energy	HF	MP2	MP4[a]	DFT	exptl[b]	exptl[c]	exptl[d]	exptl[e]	exptl[f]
$(E + ZPE)_{gauche} - (E + ZPE)_{trans}$	0.10	1.15	1.53	1.46	2.48	2.75	(1.20 ± 0.12)	(1.32 ± 0.60)	
$H°_{gauche} - H°_{trans}$	0.12	1.23	1.61	1.51			(1.21 ± 0.42)		(1.28 ± 0.84)
trans−gauche barrier	11.7	13.3	13.5	12.3	9.32	9.23			
gauche−trans barrier	11.5	11.9	11.7	10.7	6.84	6.50			
gauche−gauche barrier	8.54	8.69	8.49	7.52	9.32	9.89		8.25	

[a] Based on use of MP4 electronic energies and MP2 frequencies at MP2 geometries. [b] Durig, J. R.; Li, Y. S. *J. Chem. Phys.* **1975**, *63*, 4110 (result applies to ethylamine-*N*,*N*-d_2). [c] Tsuboi, M.; Tamagake, K.; Hirakawa, A. Y.; Yamaguchi, J.; Nakagawa, H.; Manocha, A. S.; Tuazon, E. C.; Fately, W. G. *J. Chem. Phys.* **1975**, *63*, 5177. [d] Hamada, Y.; Hashiguchi, K.; Hirakawa, A. Y.; Tsuboi, M.; Nakata, M.; Tasumi, M.; Kato, S.; Morokuma, K. *J. Mol. Spectrosc.* **1983**, *102*, 123. [e] Fischer, E.; Botskor, I. *J. Mol. Spectrosc*. **1984**, *104*, 226. [f] Hamada, Y.; Tsuboi, M.; Yamanouchi, K.; Kuchitsu, K. *J. Mol. Struct*. **1986**, *146*, 253. [g] All energies are in units of kJ mol^{-1} and include zero-point vibrational energy (ZPE) contributions. The enthalpy difference $H°_{gauche} - H°_{trans}$ also includes thermal contributions at 298.15 K. Barriers to rotation for the torsion of the NH_2 group about the C−N bond are labeled with the beginning conformation listed first followed by the conformation reached. In the determination of the barriers, the energy contribution of the torsion of the NH_2 group is subtracted from the total energy corresponding to the beginning conformation.

Table 3. A search for second-order transition states for inversion was also undertaken. Three such geometries were found where for each geometry *two* imaginary frequencies were observed. The geometry and energy corresponding to these points are reported in Table 4.

4. Energetics and Thermodynamic Functions for the Trans → Gauche Equilibrium for $CH_3CH_2NH_2$

The trans and gauche conformers for ethylamine were optimized at the HF, MP2, and DFT/B3LYP level of theory

TABLE 8: Energy E as a Function of Angles τ and ϕ[a]

$\tau + 10$/deg	ϕ/deg	E/kJ mol^{-1}	E_{fit}/kJ mol^{-1}
67.80	180	0 (tr)	0.00
67.20	−58.6	1.16 (g)	1.00
67.20	58.6	1.16 (g)	1.00
65.40	−118.3	12.78 (Δ)	12.54
65.40	118.3	12.78 (Δ)	12.54
65.10	0	9.88 (Δ)	9.69
11.10	−22.3	27.43 (o)	27.68
11.10	22.3	27.43 (o)	27.68
13.90	0	27.59 (x)	27.37
10.00	90	30.30 (x)	29.42
10.00	−90	30.30 (x)	29.42
70.70	−62.2	1.61	1.96
70.70	62.2	1.61	1.96
80.00	0	17.44	17.30
80.00	30	12.04	11.89
80.00	60	7.03	6.82
80.00	90	13.01	12.78
80.00	120	19.90	19.68
80.00	150	12.11	11.95
80.00	180	5.32	5.17
80.00	210	12.11	11.95
80.00	240	19.90	19.68
80.00	270	13.01	12.78
80.00	300	7.03	6.82
80.00	330	12.04	11.89
70.00	0	10.59	10.98
70.00	30	5.70	6.12
70.00	60	1.41	1.65
70.00	90	7.19	7.77
70.00	120	13.37	14.03
70.00	150	6.20	6.57
70.00	180	0.15	0.54
70.00	210	6.20	6.57
70.00	240	13.37	14.03
70.00	270	7.19	7.77
70.00	300	1.41	1.65
70.00	330	5.70	6.12
60.00	0	10.50	10.27
60.00	30	6.12	5.68
60.00	60	2.58	2.07
60.00	90	8.06	7.26
60.00	120	13.45	12.97
60.00	150	6.94	6.49
60.00	180	1.64	1.21
60.00	210	6.94	6.49
60.00	240	13.45	12.97
60.00	270	8.06	7.26
60.00	300	2.58	2.07
60.00	330	6.12	5.68
50.00	0	14.40	14.55
50.00	30	10.59	10.84
50.00	60	7.85	8.18
50.00	90	12.86	13.47
50.00	120	17.27	17.62
50.00	150	11.53	117
50.00	180	7.05	7.30
50.00	210	11.53	11.70
50.00	240	17.27	17.62
50.00	270	12.86	13.47
50.00	300	7.85	8.18
50.00	330	10.59	10.84
40.00	0	19.66	19.69
40.00	30	16.59	16.64
40.00	60	14.71	14.82
40.00	90	19.01	18.92
40.00	120	22.25	22.33
40.00	150	17.41	17.67
40.00	180	13.91	13.92
40.00	210	17.41	17.67
40.00	240	22.25	22.33
40.00	300	14.71	14.82
40.00	330	16.59	16.64
40.00	330	16.59	16.64
30.00	0	24.31	24.32
30.00	30	21.14	21.96
30.00	60	21.17	20.69
30.00	90	24.55	20.69
30.00	120	26.48	26.07
30.00	150	22.66	22.14
30.00	180	20.32	20.30
30.00	210	22.66	22.14
30.00	240	26.48	26.07
30.00	270	24.55	24.06
30.00	300	21.17	20.69
30.00	330	22.14	21.96
20.00	0	27.09	26.79
20.00	30	26.01	26.02
20.00	60	25.88	26.39
20.00	90	27.98	28.97
20.00	120	28.62	28.91
20.00	150	25.31	25.78
20.00	180	25.04	24.72
20.00	210	25.31	25.78
20.00	240	28.62	28.91
20.00	270	27.98	28.97
20.00	300	25.88	26.39
20.00	330	26.01	26.02
10.05	0	27.39	27.67
10.05	30	27.50	27.88
10.05	60	28.79	28.64
10.05	90	30.30	29.43
10.05	120	28.80	29.05
10.05	150	27.50	27.83
10.05	180	27.38	27.24
10.05	210	27.50	27.83
10.05	240	28.80	29.05
10.05	270	30.30	29.43
10.05	300	28.79	28.64
10.05	330	27.50	27.88

[a] The energy at a given ($\tau + 10$, ϕ) corresponds to the geometry found by optimizing all geometrical coordinates with the exception of τ and ϕ. Special points are tr = trans, g = gauche, Δ = first-order transition state for rotation, o = first-order transition state for inversion, and x = second-order transition state for inversion. Also shown are the energy values that are obtained by the least-squares fitting in terms of products of Bessel functions of the first kind and $\cos(m\phi)$.

using a 6-311G** basis set. In this section we focus on only the MP2 energetics. The energetics reported in Table 1 indicate that the trans isomer is more stable than either one of the two equivalent gauche conformers, g I and g II, by 1.16 kJ mol^{-1} [$E_g - E_{tr} = (-134.785\,777$ au$) - (-134.786\,218$ au$) = 4.41 \times 10^{-4}$ au]. This observation that the trans is more stable than a specific gauche conformer is consistent with the observations of Tsuboi et al.[3] and Hamada et al.[4] On the basis of the deduction of an internal rotation potential function for the NH_2 group from far-infrared spectral data, Tsuboi et al. found the trans conformer to be more stable by 2.75 kJ mol^{-1}. Hamada et al.[4] obtained an energy difference of (1.20 ± 0.12) kJ mol^{-1} from analysis of the temperature dependence of the NH_2-wagging band in the argon matrix spectra.

Standard state changes in thermodynamic functions for the tr → g equilibrium can readily be determined by taking into account the translational, vibrational, and rotational contributions. At 25 °C the enthalpy change, $\Delta H°$, is 1.23 kJ mol^{-1} [$\{(-134.686\,223) - (-134.686\,691)\}$ au $= 4.68 \times 10^{-4}$ au], the change in entropy, $\Delta S°$, is 0.54 J K^{-1} mol^{-1} [(270.50 − 269.96) J K^{-1} mol^{-1}], and the change in Gibbs free energy, $\Delta G°$, is 1.07 kJ mol^{-1} [$\{(-134.716\,941) - (-134.717\,347)\}$ au $= 4.06 \times 10^{-4}$ au]. On the basis of the analysis of the temperature dependence of the NH_2 group wagging band, Hamada et al.[4] report a value of $\Delta H°$ of (1.21 ± 0.42) kJ mol^{-1}. In another study Hamada et al.[8] analyzed electron diffraction data for ethylamine and obtained the relative abundances of the two conformers from which they determined a value of $\Delta H°$ of (1.28 ± 0.84) kJ mol^{-1}. The enthalpy change of 1.23 kJ mol^{-1} determined here at the MP2 level of calculation is very close to these values obtained from experimental data. Once $\Delta G°$ is known, the ratio of g:tr can be determined from $N_g/N_{tr} = \exp(-\Delta G°/RT)$, which at 25 °C yields a numerical value of 0.65. However, since this ratio would apply to the two equivalent gauche conformers, g I and g II, the actual gauche:trans ratio is $N_{gauche}/N_{trans} = 1.30$. The trans conformer has a

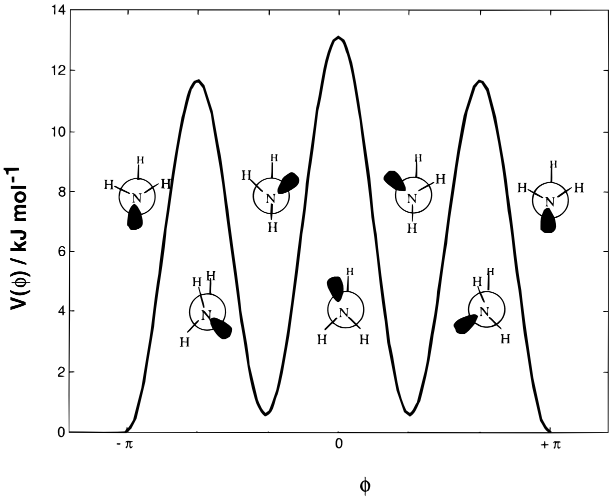

Figure 4. Potential function $V(\varphi)$ for torsional motion of the NH_2 group about the C−N bond in ethylamine-d_0 as a function of the dihedral angle φ, of the lone pair of electrons on N with respect to the CH_3 group. $V(\varphi)$ is determined from MP2 calculations with a 6-311G** basis set. Note that the zero-point vibrational energy contributions are used in arriving at $V(\varphi)$, with the contribution of the NH_2 torsion being subtracted for both the trans(tr) and gauche(g) conformers. Newman projections (with methyl groups on the α-C omitted for ease of viewing) are shown at corresponding positions in the diagram.

lower Gibbs free energy, but because there are two equivalent gauche conformers, g I and g II, the gauche conformer is actually present to greater extent compared to the trans conformer in an equilibrium mixture of trans and gauche conformers. This ratio of gauche:trans is very close to the value of 1.23 found by Hamada et al.[4]

5. Barriers to Torsion about the C−N Bond and Amino Inversion

In deducing the barrier to rotation, the frequency corresponding to the NH_2 torsion is needed. For both *trans*- and *gauche*-ethylamine as well as the ethylammonium ion for the -d_0 species, the CH_3 group torsion is coupled to the NH_2 torsion or the NH_3^+ torsion. To determine the NH_2 torsion, we averaged the NH_2 torsion for $CD_3CH_2NH_2$ and $CD_3CD_2NH_2$. Analogously for the NH_3^+ torsion for ethylammonium ion, we averaged the NH_3^+ torsion for $CD_3CH_2NH_3^+$ and $CD_3CD_2NH_3^+$. The calculated barriers at the HF, MP2, MP4, and DFT/B3LYP for the -d_0 species are reported in Table 5 and for the totally deuterated species in Table 6. Table 7 compares the calculated values with experimental values where available. On the basis of past experience, we feel most confident in the values calculated at the MP2 level of theory. The MP2 energy separation between trans and gauche is 1.15 kJ mol^{-1} which compares very favorably with (1.20 ± 0.12) kJ mol^{-1}, determined by Hamada et al.[3] from analysis of the vibrational spectrum of ethylamine-d_0 and some of its isotopomers and (1.32 ± 0.60) kJ mol^{-1} determined from analysis of the microwave spectra of trans and gauche. The MP2 gauche−gauche barrier is determined as 8.69 kJ mol^{-1}, which compares very favorably with the values of 9.66 kJ mol^{-1} determined by Durig et al.[2] based on analysis of the Raman spectra of $CH_3CH_2NH_2$ and $CH_3CH_2ND_2$, 9.89 kJ mol^{-1} determined by Hamada et al. based on analysis of the vibrational spectra of ethylamine-d_0 and some of its isotopomers, and 8.25 kJ mol^{-1} determined by Fischer and Botskor from the analysis of microwave data. The gauche−gauche barrier found is comparable to the barrier found for CH_3NH_2 where Lide, Jr.[18,19] obtained a value of 8.25 kJ mol^{-1} and where Shimoda, Nishikawa, and Itoh[20−23] obtained a value of 8.27 kJ mol^{-1}; also, Lide, Jr.,[19] obtained a barrier height of (8.19 ± 0.24) kJ mol^{-1} for CD_3ND_2. The MP2 trans−gauche barrier is determined as 13.3 kJ mol^{-1} compared to the value of Durig and Li[2] of 9.65 kJ mol^{-1} and the value of Tsuboi et al.[3] of 9.23 kJ mol^{-1}. The MP2 gauche−trans barrier is determined at 11.9 kJ mol^{-1} compared to the value of Durig and Li[2] of 7.71 kJ mol^{-1} and the value of Tsuboi et al. of 6.50 kJ mol^{-1}. Since Durig and Li[2] also determined amino torsional barriers for $CH_3CH_2ND_2$, we decided to investigate this isotopomer as well. Our MP2 results gave barrier heights in kJ mol^{-1} of {gauche−gauche, 8.63; trans−gauche, 13.09; gauche−trans, 11.78}, which should be compared to Durig and Li[2] who obtained {gauche−gauche, 9.32; trans−gauche, 9.32; gauche−trans: 6.84}.

TABLE 9: Least-Squares Values of Coefficients a_{mn}. Also Reported Are x_{mn}, the Zeros of the Bessel Function J_m[a]

m	n	x_{mn}	a_{mn}
0	1	2.404 83	23.711 081 573 541 9
0	2	5.500 78	1.189 592 186 314 6
0	3	8.653 72	12.838 753 763 437 5
0	4	11.791 53	−14.556 421 671 907 6
0	5	14.930 91	8.832 227 204 383 4
0	6	18.071 06	−3.776 006 449 510 3
1	1	3.831 71	−0.845 540 591 547 3
1	2	7.015 59	−0.050 920 609 976 3
1	3	10.173 47	0.537 457 408 976 8
1	4	13.323 69	−0.130 663 678 737 8
1	5	16.470 63	0.280 353 227 718 7
1	6	19.615 86	−0.235 786 927 504 5
2	1	5.135 62	−2.642 485 373 101 8
2	2	8.417 24	−0.715 538 315 341 7
2	3	11.619 84	−0.574 564 637 595 1
2	4	14.795 95	−0.897 971 785 123 8
2	5	17.959 82	−0.090 633 221 066 1
2	6	21.117 00	−1.379 935 949 931 5
3	1	6.380 16	15.141 783 595 130 1
3	2	9.761 02	−2.321 439 759 586 0
3	3	13.015 20	3.739 962 245 289 2
3	4	16.223 47	−0.892 444 027 696 7
3	5	19.409 42	0.851 830 299 792 9
3	6	22.582 73	−0.127 531 044 471 6
4	1	7.588 34	−1.026 887 805 476 5
4	2	11.064 71	1.059 516 926 114 5
4	3	14.372 54	−0.559 807 592 716 8
4	4	17.615 97	1.031 472 995 172 0
4	5	20.826 93	−0.442 872 319 464 1
4	6	24.019 02	0.894 119 597 174 0
5	1	8.771 48	0.038 511 183 861 6
5	2	12.338 60	−0.637 742 298 896 3
5	3	15.700 17	0.673 659 887 612 1
5	4	18.980 13	−0.864 507 594 212 2
5	5	22.217 80	0.530 245 106 936 6
5	6	25.430 34	−0.637 311 342 388 1
6	1	9.936 11	0.688 596 823 684 9
6	2	13.589 29	0.047 935 833 211 5
6	3	17.003 82	0.276 961 171 627 3
6	4	20.320 79	−0.070 124 000 524 4
6	5	23.586 08	0.255 051 385 093 7
6	6	26.820 15	0.099 941 489 405 1

[a] A value of the parameter $a = 100$ was used.

The resulting potential function, $V(\varphi)$ in units of kJ mol^{-1}, as a function of the dihedral angle of the lone pair of electrons relative to the C−C bond (with $\varphi = -\pi$ or $\varphi = +\pi$ corresponding to *trans*-ethylamine) can be fit to a function of the form

$$V(\varphi) = (1/2)[V_1\{1 + \cos\varphi\} + V_2\{1 - \cos(2\varphi)\} + V_3\{1 + \cos(3\varphi)\}] \quad (1)$$

where in units of kJ mol^{-1} $\{V_1 = -1.21, V_2 = 3.06, \text{and } V_3 = 11.22\}$ for $CH_3CH_2NH_2$ and $\{V_1 = -1.16, V_2 = 2.99, \text{and } V_3 = 11.10\}$ for $CH_3CH_2ND_2$. The coefficients in $V(\varphi)$ are

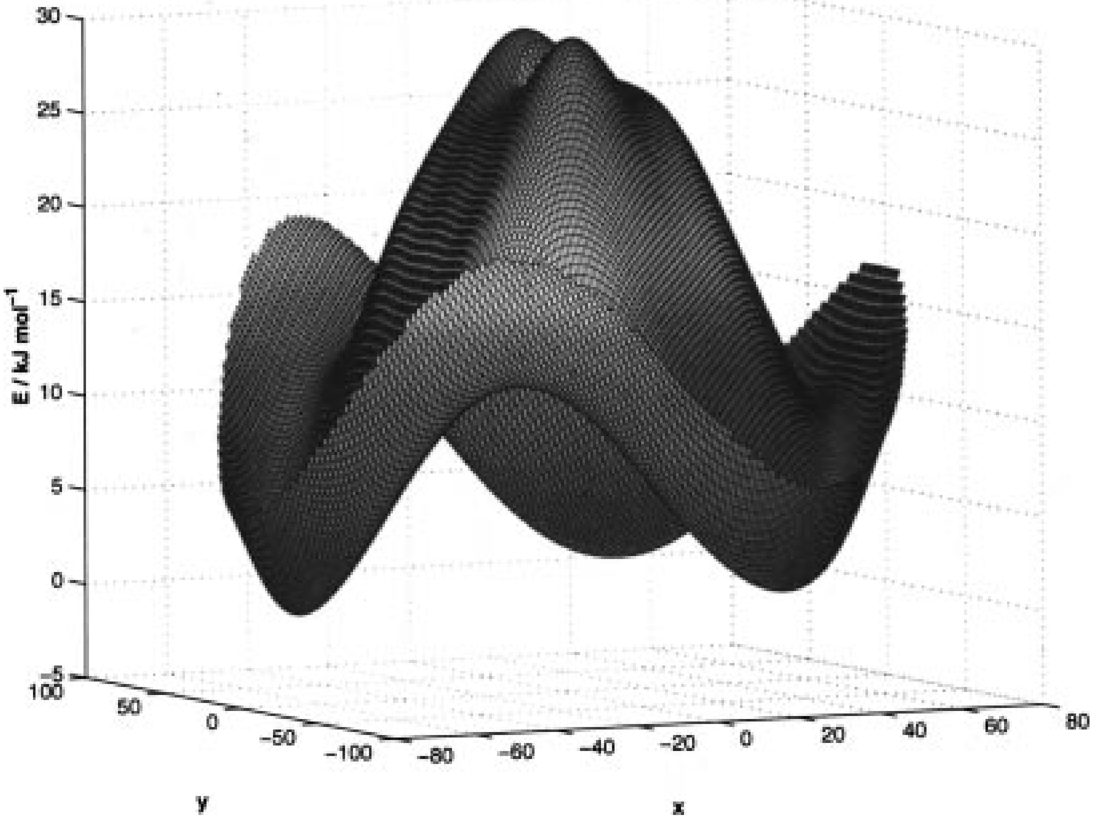

Figure 5. Reaction surface describing the amino group rotation/inversion. The electronic energy (*z*-axis) is plotted as a function of $r(r = \tau + 10)$, where the angle τ is defined in Figure 3, and ϕ, the dihedral angle of the lone pair of electrons on the nitrogen atom.

determined by the stationary points. This potential function for ethylamine-d_0 is shown in Figure 4 and differs from the amino torsional potential deduced from the experimental spectra of Durig and Li[2] and Tsuboi et al.[3] One possible reason for the discrepancy is that electron correlation may be important with the lone pair electrons on the NH_2 group. We performed an MP4 energy calculation at the MP2-determined geometries, i.e., at the geometries corresponding to equilibrium and the transition state, and we find very similar energetics with the gauche−gauche barrier smaller than the trans−gauche and the gauche−trans barriers. Therefore we have some discrepancy with the experimental values for the trans−gauche and gauche−trans barriers. An exhaustive analysis of the experimental approach for estimating the barrier heights, and perhaps the application of higher levels of computational theory, may be necessary to resolve this discrepancy.

For the ethylammonium ion the MP2 barrier determined is 11.9 kJ mol^{-1} which is identical in value to the gauche−trans barrier. At the HF level and the DFT levels the barrier for the ethylammonium ion is also quite close to the gauche−trans barrier. No experimental value for the NH_3^+ torsional barrier for the ethylammonium ion could be found in the literature.

In the Appendix we present details on the generation of a reaction surface representing the motions of amino torsion and inversion motion for ethylamine. The inversion barrier height, without the inclusion of the zero-point vibrational energy contribution, is found to be 27.43 kJ mol^{-1}. With the inclusion of zero-point vibrational energy contribution of 6.05 kJ mol^{-1}, the inversion barrier height was found to be 33.48 kJ mol^{-1}. This value can be compared to the value obtained by Fischer and Botskor[7] for the gauche amino inversion barrier of 16.8 kJ mol^{-1}, which when combined with the trans:gauche energy difference of 1.16 kJ mol^{-1} gives an inversion barrier of 18.0 kJ mol^{-1}. The MP2/6-311G** value of the amino version that we have obtained is somewhat higher than this value. It is possible that the experiment and theory are not considering the inversion barrier in the same way. The MP2 value is certainly within the range of values for similar molecules that were mentioned in section 2.

6. Summary

This study has considered the determination of the NH_2 torsional barriers for *trans*- and *gauche*-ethylamine and the NH_3^+ torsional barrier for the ethylammonium ion. Calculations have been performed at the Hartree−Fock, MP2, MP4, and DFT levels of theory, using a 6-311G** basis set. For ethylamine, the MP2 gauche−gauche barrier of 8.69 kJ mol^{-1} compares very favorably with barriers deduced from experimental data whereas the trans−gauche barrier of 13.3 kJ mol^{-1} and gauche−trans barrier of 11.9 kJ mol^{-1} differ from barriers determined from experimental data. Calculations at the MP4 level indicate very similar results to the MP2 results, suggesting that electron correlation is not the reason for the discrepancy. To achieve better agreement between experiment and theory, it is suggested that higher levels of theory be investigated, and the experimental results be reinvestigated to see if there might be another way of interpreting the data. For ethylammonium ion, the MP2 barrier found is 11.9 kJ mol^{-1}, which is the same as the gauche−trans barrier in ethylamine-d_0. Total deuteration of all species has little effect on the barriers. A reaction surface has also been generated for the amino rotation/inversion in ethylamine. The amino inversion barrier with the zero-point vibrational correction included was determined to be 33.48 kJ mol^{-1}, which is somewhat higher than the value of 18.0 kJ mol^{-1} deduced from the microwave spectrum of gauche-ethylamine.

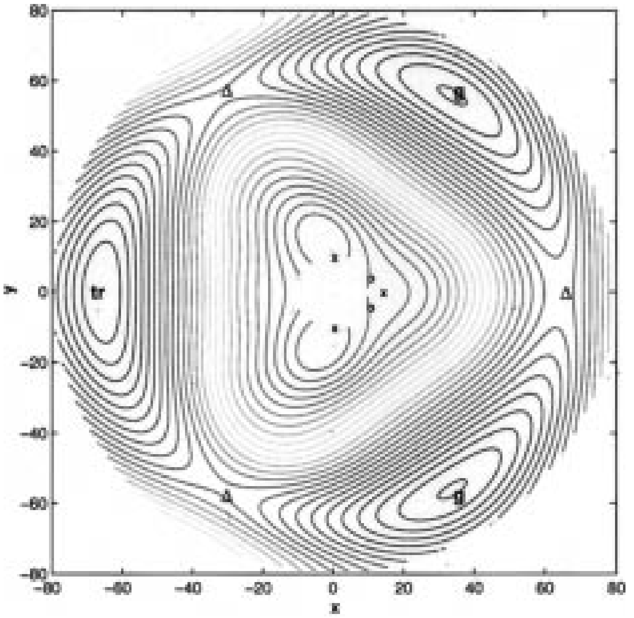

Figure 6. Contour diagram corresponding to the view shown in Figure 5 looking down the *z*-axis. Special points are denoted in the following way: (a) tr = trans geometry; (b) g = gauche geometry; (c) Δ = first-order transition state for rotation; (d) o = first order transition state for inversion; (e) x = second-order transition state for amino inversion.

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Appendix

In this Appendix we examine the details in obtaining a least-squares fitting of the electronic energy as a function of the angles τ and ϕ, where τ is the angle between the NH_2 plane and the C−N axis (Figure 2) and ϕ is the dihedral angle of the lone pair of electrons on nitrogen. In the determination of the energy, all other geometrical parameters of the molecule were allowed to relax. We determine the energy at 109 points such that for each τ and ϕ all other coordinates are allowed to vary until we find a minimum energy, and that is the energy that we assign to a given τ and ϕ. In Table 8 we report the energy values that were determined at the 109 different points.

To examine this dependence we use cylindrical coordinates with $r = \tau + 10$, ϕ is the polar angle, and z corresponds to the electronic energy. This 10° offset in τ was added in order to avoid the problems associated with a multivalued function at $\tau = 0°$. For this three-dimensional plot the minimum energy structure, i.e., the trans-conformer, is defined to have zero energy.

The vibrational modes of a circular membrane form a *complete set* of functions[24] in which to expand the reaction surface of the amino group rotation/inversion. The mathematical analysis of the vibrational modes of a drumhead is well-known. Thus we fit the energy of the 109 points to a function of the form

$$E_{\mathrm{fit}} = \sum_{m=0}^{M}\sum_{n=1}^{N} a_{mn} J_m(k_{mn} r) \cos(m\phi) \tag{A1}$$

where J_m is the mth order Bessel function of the first kind. Note that the condition $E(\varphi) = E(360° - \varphi)$ eliminates the inclusion of any $\sin(m\varphi)$ terms in the fitting. The values of $k_{mn} = x_{mn}/a$, where the x_{mn} correspond to the zeros of the mth Bessel function of the first kind, J_m.[25] Our highest value of r that we fitted was 80 so that we required an a value greater than 80. We selected $a = 100$ for this fitting. It should be emphasized that the fitted electronic energy will apply only over the range of our fitting ($0° \le \tau \le 80°$). We proceeded to vary M and N and found that $M = 6$ and $N = 6$ gave a not unreasonable fit without unrealistic oscillations occurring. The resulting parameters that were found using MATHEMATICA[26] are reported in Table 9. A comparison of the 109 fitted energy values to the originally determined energy values can be seen in Table 8. A measure of the quality of the least-squares fitting is the standard deviation

$$\sigma = \left(\frac{1}{109}\sum_{i=1}^{109}(E_{\mathrm{fit},i} - E_i)^2\right)^{1/2} \tag{A2}$$

which for our fitting gives $\sigma = 0.40$ kJ mol^{-1}. With the fitted energy a rotation/inversion energy surface was produced using MATLAB.[27] The energy surface is shown in Figure 5. An alternative view of the surface is obtained by looking down the energy axis, i.e., the z-axis, to produce the contour diagram shown in Figure 6. Note the location of the special points: tr = trans conformer, g = gauche conformer, Δ = first-order transition state for rotation, o = first-order transition state for inversion, and x = second-order transition state for inversion.

Since we used $r = \tau + 10$ as the radial coordinate in Figures 5 and 6, there exists a "hole" in the center of each diagram with radius equal to 10. The local topology of this hole is similar to a projection plane[28,29] with a point on the radius of the hole being connected to the point that is exactly opposite it.

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