

# Barriers to internal rotation and geometry of hydrazine

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## ABSTRACT

The barriers to internal rotation in hydrazine have been investigated at the Hartree-Fock, MP2 and DFT (B3LYP) levels using several basis sets. At each level optimum geometries of the eclipsed ( $C_{2v}$ ), staggered ( $C_{2h}$ ) configurations as well as the equilibrium geometry ( $C_2$ ) have been obtained and the energy barriers calculated. The results obtained using the popular basis sets 4-31G, 6-31G, 6-31G\*, 6-31G\*\* etc. of Pople and co-workers and the basis sets D95, D95V, D95V (d), D95 (d,p) of Dunning and the correlation consistent basis sets cc-PVDZ and its augmented variant have been compared and the quality of the resulting molecular wave-functions commented on.

## INTRODUCTION

Work on barriers to internal rotation began in 1936 with the work of Kemp and Pitzer [1] on ethane. The first non-empirical barrier calculation was done by Pitzer and Lipscomb [2] for ethane using minimal basis set of Slater functions, while this gave reasonable results, the barriers in hydrogen peroxide have been very difficult to reproduce. An analysis [3] of experimental data [4] indicates that the cis form lies 7.6 kcal above the energy at  $111.5^\circ$  and the trans form lies 1.1 kcal above the energy at equilibrium. But early SCF calculations of hydrogen peroxide by Palke and Pitzer [5] using minimal basis selected by Slater's rule, predicted a cis barrier of 9.4 kcal but no trans barrier. Stevens optimized orbital exponents and geometry for both cis and trans form [6] and obtained in the limit of minimum basis approximation, a cis barrier of 9.4 kcal but no trans barrier. Though at that time it was thought that electron correlation effects are the main source of difficulty, these early failures were due to two main reasons: firstly geometry optimization was not done at all dihedral angles, but the dihedral angle was varied keeping other parameters like bond lengths etc. fixed. Secondly, minimal basis calculations gave a poor account of the lone-pairs. Later calculations using larger basis sets gave better results. For instance, Fink and Allen [7] used a double zeta contracted basis and found a cis barrier of 13.2 kcal and a trans barrier of 0.3 kcal. Dunning and Winter [8] used optimally contracted Gaussian basis, O (9s 5p 1d /4s 3d 1p) and H (4s 1p /2s 1p) along with complete variation of geometry at four dihedral angles and obtained cis and trans barriers of 8.36 and 1.09 kcal/mol, which are in good agreement with experimental values. The dihedral angle for the equilibrium geometry was calculated to be  $113.7^\circ$ , which is comparable to the experimental value of  $115^\circ$ .

The same difficulties exist in case of hydrazine too, but there have been very few calculations on hydrazine in comparison to ethane and hydrogen peroxide. Experimentally the equilibrium geometry is thought to have an angle of approximately  $90^\circ$  between the bisector planes of the two  $NH_2$  groups [9] as shown in fig.1. Fig. 2 shows schematically the variation of energy with dihedral angle, showing the double well shape of the PE curve. In early calculations the minimum energy geometry was the trans geometry, fig.3. The first successful calculation of the barriers to internal rotation in hydrazine is that of Pederson and Morokuma [10]. They obtained barriers of 11.05 kcal/mol at  $0^\circ$  and 6.21 kcal/mol at  $180^\circ$  inter group angle. Ryan et al [11] found that with the STO-4G basis no trans barrier was obtained and a cis barrier of 3.9 kcal relative to the trans geometry as the stable one. However with the addition of a single Gaussian to the basis to represent the lone pair shifted the equilibrium geometry to a dihedral angle value of  $92.9^\circ$  with a cis and trans barrier of 9.79 and 0.60 kcal/mol while with the addition of two Gaussians the barrier improved to 10.60 and 3.91 kcal/mol and the equilibrium geometry was found to be at  $89.6^\circ$  dihedral angle. Vitkovskaya and coworkers [12] reported the equilibrium geometry to correspond to a dihedral angle of  $95^\circ$ . Wagner and coworkers [13] calculations on

using a small Gaussian basis set gave cis and trans barrier of 9.64 and 3.67 kcal/mol. Veillards [14] calculation gave dihedral angle value of  $94^\circ$  for the equilibrium structure with barriers of 11.5 and 4.7 kcal/mol. The experimental value of 3.15 kcal reported by Kasuya and Kojima [9] is to be viewed as suspect. In the following we report the results of our reinvestigation of this problem.

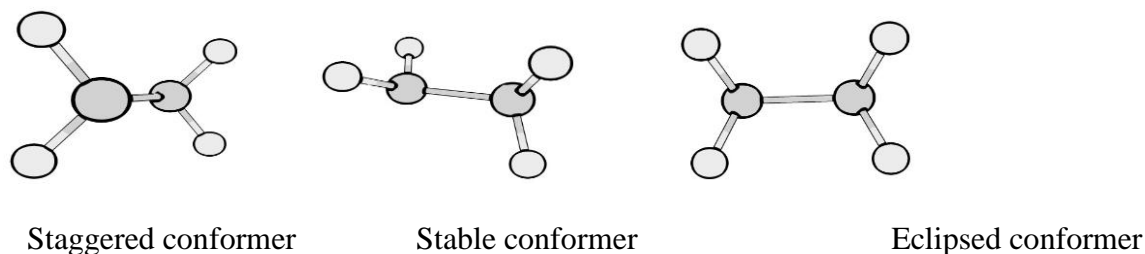


Fig.1: The equilibrium structure of hydrazine, along with 'trans' and 'cis' form with dihedral angle

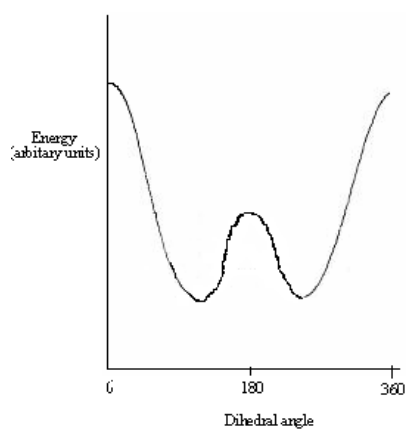


Fig.2: Variation of hydrazine energy with dihedral angle.

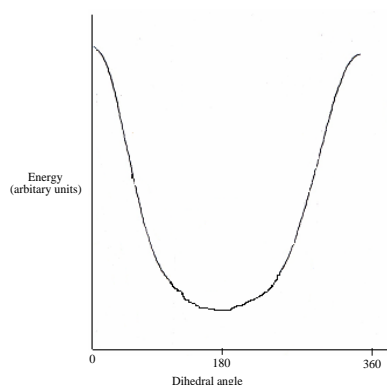


Fig.3: Early calculations of the PE curve (schematic) for hydrazine

## COMPUTATIONAL METHODS

All our calculations were performed using the Gaussian-98 suite of programs [15] running on an IBM PC-compatible machine with a P-IV processor. Calculations were done at the restricted Hartree-Fock and MP2 (second order Moller-Plesset Perturbation theory) levels and using the DFT (Density functional theory) scheme with the B3LYP functional [16] using several basis sets. The results obtained are presented in the next section.

## RESULTS AND DISCUSSION

We optimized the geometry of the cis, trans and the stable conformers of hydrazine at the Hartree-Fock, MP2 and DFT levels. The results obtained at the Hartree-Fock level for various basis sets are presented in table-1. We have used the split-valence basis sets, 4-31G and 6-31G of Pople and coworkers as well as the 6-31G(d), 6-31G(d,p) basis sets and the 6-31++G(d,p) basis sets. We have also used the D95V basis of Dunning [17] which again is a split valence basis with polarization and diffuse function added and the double zeta basis set D95 with both polarization and diffuse functions and the “correlation consistent” basis set cc-pVDZ and its augmented variant in this calculation. We see that as expected the energy of the stable conformer decreases with increase in basis set size in a sequence. However we were surprised to see that the D95V basis set gives consistently lower energy than the corresponding more popular 6-31G variant. It is also seen that inclusion of polarization function lowers the barrier height by approximately 4 kcal/mol, for both the 6-31G and D95V basis set. It is also seen that the D95V basis set gives energy values that agree to energy within approximately  $10^{-4}$  hartrees of double zeta function and these energies are better than those obtained with much larger Aug-cc-pVDZ basis set.

The results obtained at MP2 level for same series of basis sets as earlier are presented in table-2. These energies are seen to be lower than corresponding Hartree-Fock values as also are the barriers. However, the MP2 energy with the Aug-cc-pVDZ basis set is the lowest as is to be expected, since the MP2 scheme incorporates part of the correlation energy as well. The calculations with the DFT level are presented in table-3. While the energy of the stable conformer is lower than MP2 values, the barrier heights are on the whole comparable with the MP2 values. The equilibrium energies and the dipole moments of hydrazine obtained at various levels are tabulated in table-4. In all cases, the dihedral angle values are in the neighborhood of  $90^\circ$  with greatest deviation from this value obtained for cc-pVDZ basis set at all three levels.

In summary we find that inclusion of polarization functions in the basis set is necessary to get reasonable values of the rotational barriers in hydrazine. It is also observed that the D95V basis set of Dunning et al is superior to the more popular 6-31G basis set in the variational sense.

Table 1: Electronic energies of hydrazine conformers: RHF calculations

Basis sets	E (equilibrium) (Hartrees)	$\Delta E$ (staggered)		$\Delta E$ (eclipsed)	
		Hartrees	kcal/mol	Hartrees	Kcal/mol
4-31G	-111.006753	0.00918 84	5.766	0.0227075	14.249
6-31G	-111.1238394	0.00994 76	6.242	0.023192	14.553
6-31G(d)	-111.1693736	0.00445 83	2.798	0.0198663	10.584
6-31G(d,p)	-111.1835234	0.00488 75	3.067	0.0164554	10.326
6-31++G(d,p)	-111.1912366	0.00609 96	3.827	0.017014	10.676
D95V	-111.1522972	0.01018 67	6.392	0.0229246	14.385
D95V(d)	-111.1965805	0.00540 4	3.391	0.0170827	10.719
D95V(d,p)	-111.2102519	0.00588 77	3.694	0.0165942	10.413
D95V++(d, p)	-111.2127317	0.00595 87	3.739	0.016509	10.359
D95++(d,p)	-111.2128471	0.00599 4	3.761	0.0164839	10.344
cc-pVDZ	-111.1868352	0.00431 51	2.708	0.0148663	9.329
Aug-cc- pVDZ	-111.2017467	0.00560 34	3.516	0.0150783	9.462

Table 2: Electronic energies of hydrazine conformers: MP2 calculations

Basis sets	E (equilibrium) (Hartrees)	$\Delta E$ (staggered)		$\Delta E$ (eclipsed)	
		Hartrees	kcal/mol	Hartrees	Kcal/mol
4-31G	-111.2269314	0.0049744	3.121	0.0202948	12.735
6-31G	-111.3428116	0.0058113	3.646	0.0208444	17.849
6-31G(d)	-111.4978852	0.0023169	1.454	0.01584468	9.944
6-31G(d,p)	-111.5360882	0.0025857	1.622	0.0152329	9.559
6-31++G(d,p)	-111.5504584	0.0048049	3.015	0.0162679	10.208
D95V	-111.3660204	0.0065075	4.083	0.0207603	13.027
D95V(d)	-111.5199888	0.0035311	2.216	0.0162807	10.216
D95V(d,p)	-111.5583993	0.0037596	2.359	0.0154551	9.698
D95V++(d,p)	-111.5563055	0.0044947	2.820	0.0156488	9.820
D95++(d,p)	-111.5671792	0.0045136	2.832	0.01564	9.814
cc-pVDZ	-111.5369178	0.0019666	1.234	0.0135393	8.496
Aug-cc-pVDZ	-111.57348	0.0041724	2.618	0.0137628	8.636

Table 3: Electronic energies of hydrazine conformers: DFT (B3LYP) calculations

Basis sets	E (equilibrium) (Hartrees)	$\Delta E$ (staggered)		$\Delta E$ (eclipsed)	
		Hartrees	kcal/mol	Hartrees	Kcal/mol
4-31G	-111.7013795	0.0071999	4.518	0.0218921	13.737
6-31G	-111.8200134	0.0080674	5.062	0.0223966	14.054
6-31G(d)	-111.8564486	0.0025846	1.622	0.0154614	9.702
6-31G(d,p)	-111.8686573	0.002503	1.571	0.0148953	9.350
6-31++G(d,p)	-111.8817605	0.0048637	3.052	0.0159136	9.986
D95V	-111.8500997	0.0091899 5	5.766	0.0226669	14.224
D95V(d)	-111.88299	0.0039709	2.492	0.0160208	10.053
D95V(d,p)	-111.8938759	0.0043214	2.712	0.0154501	9.695
D95V++(d,p)	-111.9008714	0.0047163	2.959	0.0154784	9.713
D95++(d,p)	-111.9011746	0.0047238	2.964	0.0154589	9.701
cc-pVDZ	-111.8670165	0.0028134	1.765	0.013478	8.457
Aug-cc-pVDZ	-111.8911887	0.0045155	2.833	0.0136989	8.596

Table 4: Equilibrium geometries of hydrazine and dipole moments

Basis set	r <sub>N-N</sub> (Å <sup>0</sup> )	r <sub>N-H</sub> (inner) (Å <sup>0</sup> )	r <sub>N-H</sub> (outer) (Å <sup>0</sup> )	A <sub>NNH</sub> (inner) (degrees)	A <sub>NNH</sub> (outer) (degrees)	A <sub>HNN</sub> (degrees)	Dihedral (inter group) angle (degrees)	Dipole moment (Debye)
RHF/6-31++G(d,p)	1.409	1.006	0.998	113.0	108.9	109.4	90.7	2.1348
RHF/D95V++(d,p)	1.412	1.002	0.999	112.6	108.6	109.2	90.1	2.1230
RHF/ D95++(d,p)	1.412	1.002	0.999	112.7	108.6	109.2	90.1	2.1211
RHF/cc-pVDZ	1.412	1.007	1.004	112.1	107.8	107.2	88.2	2.0873
MP2/6-31++G(d,p)	1.433	1.015	1.012	112.4	107.4	108.6	91.1	2.2068
MP2/D95V++(d,p)	1.441	1.018	1.013	111.8	106.8	108.0	90.3	2.2229
MP2/ D95++(d,p)	1.441	1.018	1.015	111.8	106.8	108.0	90.2	2.2240
MP2/cc-pVDZ	1.439	1.025	1.021	111.8	105.8	105.2	87.5	2.2185
B3LYP/6-31++G(d,p)	1.431	1.019	1.015	113.0	108.2	108.8	91.2	2.1004
B3LYP /D95V++(d,p)	1.436	1.021	1.017	112.6	107.8	108.7	90.9	2.1037
B3LYP /D95++(d,p)	1.436	1.021	1.017	112.6	107.8	108.6	90.8	2.1008
B3LYP /cc-pVDZ	1.436	1.026	1.022	111.6	106.8	105.8	88.0	2.0195

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