

Density functional study of the reaction paths of formamidine

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Density functional theory (DFT) is used to study the reaction paths of formamidine. The E conformer of formamidine is predicted to be more stable ($1.4 \text{ kcal mol}^{-1}$) than the Z. The energy of activation is estimated to be $26.7 \text{ kcal mol}^{-1}$ for the E \rightarrow Z isomerization. The E isomer can undergo 1,3-sigmatropic shift and the energy barrier is estimated to be $47.6 \text{ kcal mol}^{-1}$. Unimolecular decomposition of the Z isomer to HCN and NH_3 is predicted to have a barrier height of $66.8 \text{ kcal mol}^{-1}$. The predicted barrier heights are significantly lower than those obtained from Hartree-Fock estimates particularly for 1,3-sigmatropic shift and decomposition reaction of formamidine. Results of second order Moller-Plesset (MP2) studies also lead to the conclusion that inclusion of electron correlation decreases the barrier heights significantly for 1,3-sigmatropic shift and unimolecular decomposition of formamidine. Calculated equilibrium geometries, harmonic vibrational frequencies and relative energies are in excellent agreement with the results of MP2 studies.

Study of the reaction paths of amidines is of considerable interest since these compounds are important for the synthesis of heterocycles and also serve as useful models to study the active centre of the enzyme lactate dehydrogenase¹. Formamidine can undergo three different types of reactions (Fig. 1). It can isomerize from E (*trans*) form to Z (*cis*) form. It can undergo 1,3-sigmatropic shift. It can also undergo unimolecular decomposition to give HCN and NH_3 . Density functional theory (DFT) is becoming increasingly popular as a tool for calculating the ground state properties of molecules²⁻¹⁵, the main attraction being its ability to include exchange and correlation for only a moderate cost in comparison to other post-SCF method. In this paper we present the results of our density functional study of the reaction paths of formamidine. Results of post-SCF method (MP2) are also presented for comparison.

Method of calculation

In the present work we have used the B3LYP functional, formed by combining Becke's three-parameter exchange¹⁶ and the non-local correlation functional of Lee, Yang and Parr¹⁷. This hybrid functional is known to give accurate reaction energies for a wide range of processes¹⁸. Frozen core approximation was used for all MP2 calculations reported here. The geometries were optimized by means of analytical gradients. Harmonic vibrational frequencies were calculated using analytical second derivatives. 6-31G* basis set was used for all calculations reported here. All stationary points were characterized by examining the number of imaginary

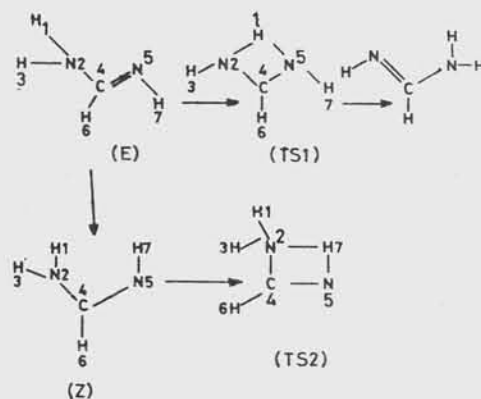


Fig. 1—Reactions of formamidine

frequencies and the eigen values of the Hessian matrix. GAUSSIAN 94 quantum chemistry package¹⁹ was used for all calculations reported here.

Results and Discussion

Hartree-Fock calculations with 6-31G* basis set, predicted the optimized geometries for the isomers to be non-planar in contrast to the results of earlier studies²⁰⁻²². Planar structure lead to an imaginary vibrational frequency for each isomer. More recently Tortajada *et al*²³ have used MP2 level theory to examine the structures of the isomers of formamidine. These authors have indicated non-planar structures. Our DFT studies also indicate non-planar structures for the isomers and the predicted equilibrium geometries are given in Table 1. Good agreement can be seen between our results and the results of MP2

Table 1—Calculated equilibrium geometries of formamidine^a

System ^b	Bond						Angle				
	H1-N2	N2-H3	N2-C4	C4-N5	C4-H6	N5-H7	H1-N2-H3	C4-N2-H1	N5-C4-N2	N5-C4-H6	H7-N5-C4
E-form ^c	1.014 (1.015)	1.011 (1.011)	1.378 (1.380)	1.278 (1.285)	1.099 (1.096)	1.021 (1.021)	114.6 (114.0)	114.4 (113.2)	122.0 (121.3)	125.6 (125.7)	110.0 (109.9)
Z-form ^d	1.013 (1.014)	1.012 (1.012)	1.384 (1.389)	1.277 (1.283)	1.093 (1.091)	1.028 (1.027)	113.9 (113.2)	117.3 (116.2)	129.4 (129.1)	118.1 (117.3)	111.1 (110.6)

a. Bond length in Å and angles in degrees. Numbers in parentheses are results of MP2 Studies (ref.23).

b. See Fig. 1.

c. Dihedral angles: C4-N2-H1-H3 = 139.6, N5-C4-N2-H1 = 14.3, H6-C4-N2-N5 = 177.3 and H7-N5-C4-N2 = 175.4. Corresponding MP2 results are 136.3, 15.0, 176.9 and 175.1 respectively.

d. Dihedral angles: C4-N2-H1-H3 = 142.4, N5-C4-N2-H1 = 18.3, H6-C4-N2-N5 = 176.6 and H7-N5-C4-N2 = -3.2. Corresponding MP2 results are 138.5, 20.1, 176.0 and -3.4 respectively.

Table 2—Bonding characteristics in formamidine

System ^a	Bond								
	N2-C4			C4-H6			N5-H7		
	ρ_c	$\nabla^2\rho_c$	ϵ	ρ_c	$\nabla^2\rho_c$	ϵ	ρ_c	$\nabla^2\rho_c$	ϵ
E-form	0.313	-1.002	-0.092	0.276	-0.958	0.022	0.327	-1.578	0.013
Z-form	0.306	-0.942	0.068	0.280	-1.006	0.031	0.321	-1.518	0.007

a. See Fig. 1.

calculations²³. As can be seen from Table 1, the isomers have some significant structural differences. The N5-C4-N2 angle for the Z-isomer is about 7° greater than that of the E-isomer, while N5-C4-H6 angle is about 8° smaller. As can be seen from Table 1, three bonds (i.e. N2-C4, C4-H6 and N5-H7) show significant change while going from E-isomer to Z-isomer. While N2-C4 and N5-H7 bonds are elongated, C4-H6 is shortened. This can be explained by examining the electronic charge density at bond critical points²⁴ of these bonds (Table 2). It can be seen that while going from E to Z-form the electronic density at the bond critical point of N2-C4 bond decreases leading to a lengthening of the bond. The same is also true for the N5-H7 bond. While going from E-form to Z-form, the electronic density at the bond critical point of C4-H6 bond increases leading to a shortening of this bond. Our calculated dipole moments (2.6 D for E and 3.5 D for Z-form) are in good agreement with results of MP2 studies²³ (2.9 D for E and 3.6 D for Z-form).

Calculated vibrational frequencies are listed in Table 3 along with the results of MP2 studies. Good correspondence can be seen between the two. Our calculated frequencies are consistently lower than the MP2 values. Our calculated zero point vibrational energies are in good agreement with the results of MP2 studies.

Table 3—Calculated harmonic vibrational frequencies (cm⁻¹) and zero point vibrational energies (ZPVE) (kcal mol⁻¹)

Formamidine			
E-form		Z-form	
B3LYP ^a	MP2 ^b	B3LYP ^a	MP2 ^b
415	430	420	426
554	561	506	543
610	649	542	558
811	837	839	843
1051	1062	1064	1081
1107	1124	1093	1113
1125	1142	1133	1143
1351	1374	1338	1360
1435	1447	1439	1459
1651	1668	1667	1687
1759	1766	1750	1755
3057	3131	3130	3203
3491	3533	3394	3446
3556	3590	3555	3592
3674	3719	3666	3714
ZPVE 36.7	37.2	36.5	37.1

a. Present B3LYP/6-31G* results.

b. MP2/6-31G* results taken from ref. 23.

Our DFT results indicate the E-isomer to be more stable (1.4 kcal mol⁻¹) than the Z-isomer. This is in good agreement with the results²³ of G2 level of theory (1.8 kcal mol⁻¹). Our calculated energy barrier of 27.0

kcal mol⁻¹ is also in good agreement with the G2 level²³ estimate (~ 25.0 kcal mol⁻¹). Optimized transition state geometries for 1,3-sigmatropic shift and unimolecular decomposition of formamidine are given in Table 4 along with the results obtained from our MP2 level calculations. Good agreement can be seen between the DFT and MP2 results. Poirier *et al.*²² have studied the transition state (TS1) for 1,3-sigmatropic shift and have reported a planar structure (C_{2v}). Examination of the planar structure at RHF/6-31G* level indicated this to be a second order saddle point. Both DFT and MP2 studies predict a non-planar structure (C₂) for the transition state associated with the 1,3-sigmatropic shift of formamidine. Our calculated energy barriers for 1,3-sigmatropic shift and the decomposition reaction are listed in Table 5. The DFT and MP2 barriers are very nearly similar to each other but significantly lower than the Hartree-Fock estimates.

The bonding characteristics of the transition states are listed in Table 6. A significant difference in bonding characteristics can be seen for the two transition states. As has been shown by Bader and coworkers²⁴, $\nabla^2\rho$ identifies regions of space where the

electronic charge is locally depleted ($\nabla^2\rho > 0$) or built up ($\nabla^2\rho < 0$). When $\nabla^2\rho$ is negative the bonding characteristic is covalent. If $\nabla^2\rho$ is positive the interaction is between closed-shell system (ionic bond, hydrogen bond and van der Waals molecule). For TS1 all bonds in the 4-membered ring are shared (covalent) bonds as indicated by negative $\nabla^2\rho_c$ values. For TS2 while 3 bonds in the 4-membered ring have negative $\nabla^2\rho_c$, the N5-H7 bond is characterized by a positive $\nabla^2\rho_c$. This indicated N5-H7 interaction to be non covalent. For TS1, the ellipticity is highest

Table 5—Calculated energy of activation (*E*) (kcal mol⁻¹)^a

Reaction ^b	Energy of activation		
	HF/6-31G*	B3LYP/6-31G*	MP2/6-31G*
1,3-sigmatropic shift	63.6 (59.3)	47.6 (43.6)	48.6 (44.8)
Decomposition reaction	79.2 (75.1)	65.4 (61.1)	65.5 (61.1)

a. Numbers in parentheses are those obtained after zero point vibrational energy correction.

b. See Fig. 1.

Table 4—Calculated equilibrium geometries of transition states^a

System ^b	Bond						Angle				
	H1-N2	N2-H3	N2-C4	C4-N5	C4-H6	N5-H7	H1-N2-H3	C4-N2-H1	N5-C4-N2	H6-C4-N2	H7-N5-C4
TS1 ^c	1.366 (1.366)	1.018 (1.019)	1.323 (1.327)	1.323 (1.327)	1.091 (1.090)	1.018 (1.019)	148.9 (149.0)	75.9 (75.9)	106.4 (106.3)	126.8 (126.8)	121.2 (121.1)
TS2 ^d	1.027 (1.026)	1.027 (1.026)	1.577 (1.574)	1.237 (1.244)	1.094 (1.093)	1.520 (1.531)	109.2 (109.9)	117.0 (116.8)	106.9 (107.3)	115.4 (115.0)	72.7 (72.2)

a. Bond length in Å and angles in degrees. Numbers in parentheses are results of our present MP2 Studies.

b. See Fig. 1.

c. The transition state (C₂ point group) H6, C4, N2, H1 and N5 are in one plane. Dihedral angle: H3-N2-C4-H6 = -28.0. Corresponding MP2 result is -28.2.

d. The transition state (C_s point group) N2, C4, N5, H6 and H7 are in one plane. Dihedral angle: N5-C4-N2-H1 = 113.8. Corresponding MP2 result is 110.6.

Table 6—Bonding characteristics of the transition states

System ^a	Bond											
	H1-N2			N2-C4			C4-N5			N5-H1		
	ρ_c	$\nabla^2\rho_c$	ϵ	ρ_c	$\nabla^2\rho_c$	ϵ	ρ_c	$\nabla^2\rho_c$	ϵ	ρ_c	$\nabla^2\rho_c$	ϵ
TS1	0.121	-0.009	0.080	0.358	-1.148	0.152	0.358	-1.148	0.152	0.121	-0.009	0.080
	H7-N2			N2-C4			C4-N5			NH-H7		
	ρ_c	$\nabla^2\rho_c$	ϵ	ρ_c	$\nabla^2\rho_c$	ϵ	ρ_c	$\nabla^2\rho_c$	ϵ	ρ_c	$\nabla^2\rho_c$	ϵ
TS2	0.169	-0.360	0.053	0.191	-0.301	0.008	0.422	-0.668	0.383	0.089	0.149	0.388

a. See Fig.1

(0.152) for N2-C4 bond and lowest (0.080) for H1-N2 bond. Much larger ellipticity values are seen for the C4-N5 and N5-H7 bonds of TS2 indicating higher pi-character.

The following points emerge out of this study: (i) Non-local DFT method (B3LYP), using moderately sized basis set (6-31G*), generally give reliable geometries which are comparable to those obtained from MP2 calculations; (ii) both DFT and MP2 studies predict non-planar structures for the conformers of formamidine; (iii) both DFT and MP2 theoretical models predict a non-planar (C_2) transition state for the 1,3-sigmatropic shift of formamidine; and (iv) inclusion of electron correlation decreases the energy barriers significantly for the transition states associated with 1,3-sigmatropic shift and decomposition reaction of formamidine.

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