Nitrogen Inversion Barriers and Electronic Structure of Fluoramine and Cyanamide: *ab initio* SCF–LCAO–MO Study

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Summary The energy barrier to nitrogen inversion and the electronic structure of fluoramine and cyanamide have been studied using extended Hartree–Fock SCF–LCAO–MO calculations.

STRUCTURAL effects on nitrogen inversion barriers have been subject to very many experimental studies. Non-empirical calculations, aimed at understanding the physical origin of structural effects, have been presented recently for pyramidal[1–4] and planar[4–6] nitrogen inversion.

We report here a study of fluoramine and cyanamide which allows gaining insight into the effect of an electronegative and a conjugative substituent on the height of the inversion barrier. These substituents are expected to produce respectively an increase and a decrease in barrier height with respect to ammonia.

Calculations have been performed with the general program IBMOL[7] using a basis set of gaussian functions containing 9 *s* and 5 *p* type functions on C, N, F, and 4 *s* functions on H (SC 1). To this set, polarization functions have then been added on the inverting nitrogen (a set of *d* functions; exponent 1·0) and on the hydrogen atoms (a set of *p* functions; exponent 0·5).† The molecular geometries have been adapted from difluoramine[8] for NH_2F and the experimental values (microwave spectroscopy[9]) have been used for NH_2CN. Calculations have been performed for several values of the pyramidality angle ψ (angle between the N–X bond and the HNH plane) and the energy minimum has been obtained by interpolation between the computed values. The calculated total energy variation as a function of ψ is given in Figures 1 and 2 for NH_2F and NH_2CN respectively.

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† The absence of *d* functions on the F and CN substituents should not affect much the relative energies of the various forms. It mainly affects the population analysis on the substituents.

The main results of the computations are as follows:

(1) In SC 2, fluoramine is found to be nonplanar with an energy minimum of $-154{\cdot}9772$ a.u. at $\psi = 69°30'$. The energy for $\psi = 0°$ is $-154{\cdot}9448$ a.u., giving a barrier to nitrogen inversion of 20·3 kcal/mole. This barrier has not been determined experimentally, but the high value obtained agrees with recent results on difluoroamines[10] (> 18 kcal/mole).

(2) In SC 2, cyanamide is found to be nonplanar with an energy minimum of $-147{\cdot}8655$ a.u. at $\psi = 45°14'$ (experimental value[9] $\psi = 38°$). For $\psi = 0°$, the energy is $-147{\cdot}8625$ a.u., giving a barrier to nitrogen inversion of 1·8 kcal/mole. The experimental values of the inversion barrier are 1·9 kcal/mole[11] and 2·03 kcal/mole.[9]

(3) In the absence of polarization functions (SC 1), or when only *p* functions on H are included, the barrier is 12·6 kcal/mole in fluoramine, and cyanamide is found to be planar. Thus, as already found for ammonia,[1] phosphine,[2] and silylamine,[3] the presence of *d* polarization functions on the inverting site is of fundamental importance for computing inversion barriers. Such functions stabilize the pyramidal configuration with respect to the planar one.

(4) During inversion, electron density is transferred into the inverting nitrogen $2p_z$ orbital ($+0{\cdot}37$ electron for fluoramine; $+0{\cdot}09$ electron for cyanamide). The introduction of the polarization functions leads to a transfer of electron density into the bonding region (the overlap populations increase from SC 1 to SC 2).

(5) All the bond overlap populations increase as inversion proceeds, except for the C≡N bond of cyanamide ($-0{\cdot}01$ electron). The atomic population analysis of cyanamide clearly shows that electron density is transferred from the amino nitrogen lone pair ($2p_z$) into the $2p_z$ orbital of the cyanonitrogen. These effects agree with increased $(p\text{–}p)\pi$ conjugation of the nitrogen lone pair with the CN triple bond in the transition state.

(6) Both inversion barriers are attractive dominant following Allen's classification.[13] This however does not explain the origin of the barrier increasing and barrier lowering effects of the F and CN substituents respectively with respect to ammonia (which shows a barrier of 5·8 kcal/mole). In terms of localized orbitals, it is probable that in $H_2N\text{–}F$ the main effect is due to the N–F bond and not to the fluorine lone pairs since it is found that in oxaziridine the energy of the N–O bond increases much more than that of the oxygen lone pairs during inversion.[4]

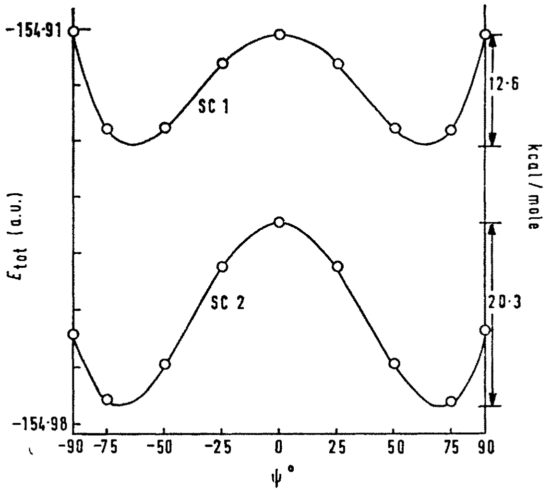

FIGURE 1. *Variation of the total energy of* $H_2N\text{–}F$ *during nitrogen inversion in the two cases* SC 1 *and* SC 2 (*see text*).

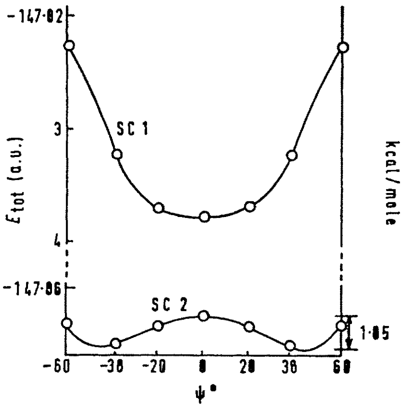

FIGURE 2. *Variation of the total energy of* $H_2N\text{–}CN$ *during nitrogen inversion in the two cases* SC 1 *and* SC 2 (*see text*).

Note added in proof: Recent experimental (i.r.) results on cyanamide: angle $\psi = 43 \pm 1{\cdot}5°$; barrier to inversion: $1{\cdot}34 \pm 0{\cdot}09$ kcal/mole.[14]

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