Theoret. chim. Acta (Berl.) 9, 275—277 (1968)

An ab initio SCF-LCAO-MO Study of the Nitrogen Inversion Barriers in Ammonia and in Ethylenimine*

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Received November 17, 1967

Theoretical studies of molecular conformations should lead to an understanding of the physical meaning and origin of the concepts and generalisations widely used by chemists in conformational analysis. If the theoretical results have to lead to a physical interpretation of the phenomena, approximations in the calculations have to be kept at a minimum. Several *ab initio* SCF calculations of barriers to internal rotation in various substances have been published recently [1] and provide insight into the origin of these energy barriers. Our interests in the study of the potential barriers to nitrogen inversion [2] have led us to a theoretical *ab initio* study of the inversion barriers of ammonia and ethylenimine.

The present calculations are of the SCF–LCAO–MO type using gaussian functions as basis set. The CDC 3600 [3] version of the IBMOL program**** has been used. The gaussian basis set employed consists of 9 orbitals s and 5 orbitals p for nitrogen and for carbon, and of 4 orbitals s for hydrogen. The exponents of the gaussian functions are taken from the work of HUZINAGA [6]. "Contracted" basis functions [3] are then constructed by linear combination of these gaussian functions, the coefficients of the development being also obtained from Ref. [4].

The calculations on ammonia were considered as test calculations to be compared with the theoretical studies already published (see Ref. [5] for a list of references). Several conformations of the ammonia molecule have been considered, keeping the N–H bond length (1.9162 a.u.) constant and varying the height h of the pyramid. The most stable conformation corresponds to $h = 0.528$ a.u., with a total energy of -56.15679 a.u. This result is only 0.08 a.u. off the Hartree-Fock limit (-56.23 a.u.) evaluated by RITCHIE and KING [6]. The planar form ($h = 0$) has a total energy of -56.15407 a.u., giving an energy barrier to inversion of

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0.0027 a.u., which is ca. three times smaller than the experimental value (0.0092 a.u.). However this result compares well with those obtained by other authors (see Ref. [5] and references therein). The scatter in the reported values may be attributed to the variety of basis sets employed, and perhaps to a difference in correlations energy between the pyramidal and the planar conformations*.

In the case of ethylenimine, two calculations have been performed: one for the experimental pyramidal conformation (ground state) and one for the "planar" conformation (transition state). Bond lengths and bond angles for the pyramidal form have been taken from Ref. [7]. For the "planar" form of C_{2v} symmetry, the same data have been used (especially the same N–H bond length) except that the hydrogen on nitrogen is now in the plane of the ring. The total energies calculated are respectively -132.94871 a.u. for the ground state and -132.91999 a.u. for the planar conformation. By analogy with the results on ammonia, these values probably differ from the Hartree-Fock limit at most by some tenths of an a.u. The difference between the total energies of the two forms is 0.02872 a.u. (= 18.02 kcal/mole).

The dipole moment calculated for the ground state is 2.31 Debye, the experimental value being 1.89 D [8]. The agreement is fairly good. In the "planar" form the calculated total moment reduces to 0.22 D, indicating that the main contribution to the dipole moment of the "pyramidal" state arises from the nitrogen lone pair.

As noted above, the energy barrier to inversion of the nitrogen atom in ethylenimine is 0.029 a.u., i.e. 18 kcal/mole. A lower bound of 12 kcal/mole has been obtained from microwave studies by Tolles and Gwinn [9]. These authors also suggest that this value is probably much too low. Values in the same range or higher have been obtained for the nitrogen inversion barrier in various substituted aziridines from nuclear magnetic resonance studies [10] (see also reference [3] in Ref. [2]). It thus seems that the present calculated value should be fairly near to the experimentally still undetermined, real value of the nitrogen inversion barrier in ethylenimine.

It is difficult to describe accurately the physical origin of the barrier. However it seems that the increase in energy from the "pyramidal" to the "planar" conformation is to be related to a transfer of electron density from the $2s$ to the $2p_z$ (which is of higher monoelectronic energy) nitrogen orbitals (the z axis passes through N and is perpendicular to the plane of the ring).

A nitrogen atomic population analysis for the ammonia molecule gives: $1s^{1.98}\ 2s^{1.60}\ 2p_x^{1.18}\ 2p_y^{1.18}\ 2p_z^{1.88}$ for the pyramidal state and $1s^{1.98}\ 2s^{1.50}\ 2p_x^{1.19}\ 2p_y^{1.19}\ 2p_z^{2.00}$ for the planar state; similarly for ethylenimine one has $1s^{1.98}\ 2s^{1.80}\ 2p_x^{1.18}\ 2p_y^{1.18}\ 2p_z^{1.48}$ for the pyramidal state and $1s^{1.98}\ 2s^{1.50}\ 2p_x^{1.14}\ 2p_y^{1.18}\ 2p_z^{1.93}$ for the planar state. Thus the increase in the energy barrier is going from ammonia to ethylenimine is reflected in the increase in $2s \rightarrow 2p$ electronic transfer from 0.1 electron in the case of ammonia to 0.3 electron in the case of ethylenimine.

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* In fact, a recent calculation which has nearly reached the Hartree-Fock limit yields a theoretical value very close to the experimental one (private communication from R. Body).

A more detailed study of this point as well as complementary calculations on ethylenimine (optimization of the ground state energy, determination of the shape of the potential barrier) are under way. A complete description of the results will be given in the final account of this work.

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