Molecular Orbital Calculations of Lone Pair Interactions in Hexahydropyrimidine

By FREEMAN P. CHEN and R. G. JESAITIS*

(*Department of Chemistry, State University of New York, Stony Brook, New York* 11790)

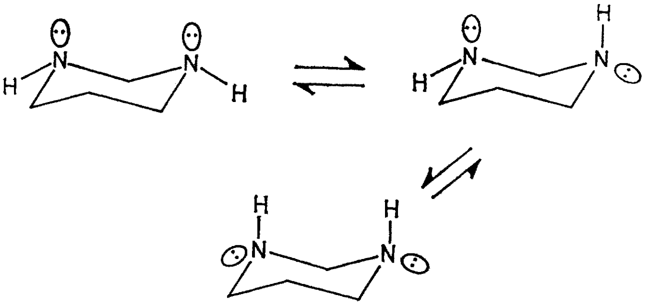
Summary Explicit inclusion of directional electron repulsion integrals within CNDO types of MO methods for atoms containing lone pairs allows effects due to these lone pairs to be calculated.

CHEMISTS use many qualitative and semi-quantitative concepts which should be derivable from molecular orbital theoretical treatments. Concepts which show little basis in theory should be discarded and ones which do show basis can be extended.[1] The method of testing for some of these effects, such as lone pair interactions, however, is not clear. In the calculation of an energy from a molecular wave function the components of the energy may not be easily dissectable, although there appears to be progress in this direction.[2]

One method of testing a chemical concept is specifically to include or exclude in the boundary conditions of the problem being considered the interactions being tested for. Thus, it has been found that in hexahydropyrimidine the diaxial and axial–equatorial N–H bond conformers are more stable than the diequatorial conformer.[3,4] This has been ascribed to a "rabbit-ears" effect,[3] where the repulsion of the lone pairs of the nitrogens is concluded to be larger than the repulsion of two axial hydrogens.

One way of testing for this effect is to calculate the energies of the three hexahydropyrimidine conformers by the CNDO/2 or INDO methods.[5,6] Since CNDO/2 and INDO calculate two centre repulsion integrals on the basis of spherical orbitals, effects due to the repulsion of directional lone pairs should be small.

It is possible then to include NDDO types of terms (which do have directional character) between the two nitrogens.[7] The results should indicate how much repulsion energy results from lone pair interactions. The calculated results, in effect, represent a perturbation approach. Five types of calculations are listed in the Table, each including more NDDO terms than the previous.



The significant break in behaviour comes when N–N NDDO interactions are included. Thus, the "rabbit-ears" effect appears to have true physical significance. Although in any semi-empirical method there is a likelihood of parametrization being incompatible with the problem being investigated, the quantitative aspects of the results may be discussed.

Since the difference between the axial and equatorial N–H bond conformers of piperidine is $-0{\cdot}142$ ev ($a = 0$)

by CNDO/2 and −0·069 ev by the calculation corresponding to the bottom one in the Table, a fair estimate of the interaction effect of a lone pair with the rest of the ring is being obtained. Experimentally the equatorial N–H bond is favoured by 0·017 ev.[4] There may also be some validity in discussing the "size" of the lone pair.[8]

Energies of hexahydropyrimidine conformers[a]

Terms used	E: 1,3-di-*a* H	ΔE: 1,3-di-*e* H[c]	ΔE: 1-*a*,3-*e* H[c]
CNDO/2	−1621·172	−0·185	−0·110
INDO	−1584·775	−0·116	−0·082
INDO + NDDO for bonded C–H, N–H[b]	−1603·725	−0·059	−0·052
Above + N–N NDDO terms	−1604·254	+0·500	+0·224
Above + all N–C and N–H NDDO terms	−1611·561	+0·414	+0·168

[a] Values in ev. Since we were primarily interested in the interactions of two parallel lone pairs, calculations were performed on the molecules with a cyclohexane chair structure of 1·54 Å bond length, C–H bond length of 1·09 Å, and N–H bond length of 1·04 Å. Parameters are given in ref. 5 and 7.

[b] Programming considerations caused us to include C–H and N–H NDDO terms.

[c] The diaxial compound is taken as zero. Negative energy differences reflect greater stability.

Since the measured experimental energy difference in this diazine series is at most 0·05 ev, and the dipole–dipole interaction calculations[4] are consistent with this value, it is likely that one or more of the following conclusions is true: (i) lone pair interactions include more than a dipole–dipole electrostatic portion, (ii) the angle between the lone pairs is quite different from the zero degrees we have depicted, (iii) solvation and/or aggregation is important in determining the experimental results.

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