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Relationes

The Interaction of Directional Lone Pairs between Bonded Atoms: Hydrazine

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The directional components of the barrier to rotation in hydrazine are investigated. The repulsion of the lone pairs appears to be significant, favoring the form with perpendicular lone pairs over the syn and anti forms.

Key words: Rotational barrier – Energy partitioning – Hydrazine.

The interaction of lone pairs on different atoms within molecules has recently been a field of considerable theoretical [1–4] and experimental [5] interest. Interpretations have been varied and the nature of the interactions is still being investigated.

Part of the theoretical problem resides in the nature of the factorization associated with the interpretation of quantum chemical calculations. The physical model that represents the conceptual framework one is dealing with may not in fact correspond to the physical model with which one is performing the calculation, although both may be valid expressions of reality. For example, though the chemical bond is universally recognized as a useful construct, the varied components of its nature are still not clear. Lone pairs occupy a similar ambiguous position. This is especially true in the interpretation of bonds and lone pairs within molecular orbital models, which are essentially delocalized ones. Any interpretation depends to some extent on a definition of what constitutes a lone pair or a bond within such a model, since the parameters of molecular orbital models are generally based on atomic functions.

Thus, Wolfe *et al.* have noted that "*ab-initio*" SCF calculations of rotational barriers can be interpreted so as to conclude that lone pairs are non-directed "invisible" ligands [2a]. An analysis by Radom, Hehre, and Pople, concludes that resolution of rotational barriers by Fourier analysis into one-fold, two-fold, and three fold terms can be viewed in terms of directional components of the lone pairs [3]. It would appear that the nature of the conceptual conclusion is at least to some extent dependent on the model chosen for the analysis [6].

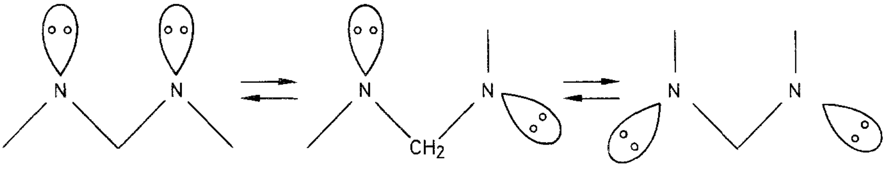
Within the LCAO framework there are a number of factors which should enter into the consideration of lone-pair lone-pair interactions. One may postulate that there are directional and non-directional components to these interactions. To resolve the directional component of interaction, ideally one would like to dissect out the contribution of the dipolar and higher order elements out of the interaction terms. One way of achieving this is to formulate a reasonable model which has terms determined independent of local charge distributions on atoms (but, of course, not of geometry). The effect of directionality may then be considered as a perturbation.

There is one existing model which comes close to this ideal, the CNDO/INDO model [7]. Here the terms are broken down into two parts.

$$F_{uu} = \alpha_{uu} + G_{uu},$$
$$F_{uv} = \beta_{uv} S_{uv} + G_{uv}.$$

This is essentially a Hückel model (in the leading terms) which is modified by coulombic terms, G_{uv}. The CNDO/INDO method bases its two center coulombic terms on the values of s-orbital integrals. The directional perturbation may be introduced through the use of integrals based on p-orbitals where appropriate. Note that by consideration of the directionality as a perturbation, the major portion of the empiricism of this approach is handled in the portion of the treatment which is not varied (the Hückel portion) and not in the terms under investigation.

By the use of this approach, we have previously shown that there appears to be validity in denoting a "rabbit-ear" effect in hexahydropyrimidine, destabilizing the conformation with parallel lone-pairs [9].



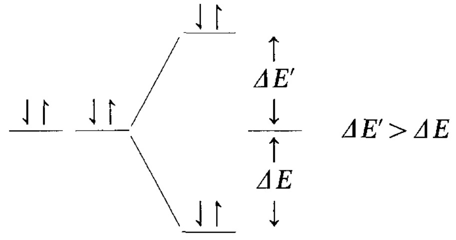
Work on other molecules which do not contain lone pairs, has indicated that the net effect of directional components in the coulombic terms is minimal. In addition, barriers to rotation of molecules such as ethane, and fluoroethane, methylamine, and methanol where there is only one atom bearing lone pairs are handled adequately by a spherical type of treatment [10].

If a Mulliken population or charge analysis of a minimal basis set ethane is examined, it is clear why a spherical treatment is sufficient in depicting the barrier in ethane like molecules. The charge distribution on the carbon orbitals is cylindrical. Consequently the barrier arises through more subtle effects involving charge redistribution and the hydrogen atoms [11].

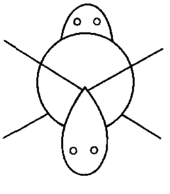
In the more complex case of the fluoroethyl anion the spherical treatments are insufficient because of the gross non cylindrical nature of the charge distributions at each end of the carbon-carbon bond [10, 12, 13].

Hydrazine represents the simplest case where lone pairs on adjacent atoms can interact, and thus there is a great degree of interest in the evaluation of the interaction terms by various approaches. The difference in repulsion energy between two electrons in a pair of parallel p-orbitals 1.46 Å apart (the N-N bond length) or in a pair of perpendicular orbitals the same distance apart is approximately 25 kcal/mole. Of course, if these integrals are evaluated as if the electrons were in *s*-orbitals there is no difference. The amount that this differential should be reflected in the actual energies of the various conformations of the molecule is not clear.

It is resonable to define that portion of the barrier which makes itself manifest in a spherical approach as "conjugative destabilization" [14]. That is to say, irrespective of any angular coulombic components, the interaction of two filled orbitals might be expected to produce a net destabilization.



Veillard, among others, has shown that hydrazine is most stable in the nearly perpendicular form with a 94° dihedral angle between the lone pairs [4], and a barrier size of 12 kcal/mole.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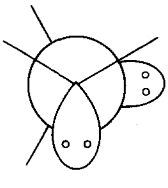
perpendicular

The relative weights of the two interaction mechanisms may then be assessed using the above approach [8–10]. Table 1 summarizes the results. The row labeled INDO represents calculations using spherical two-center repulsion integrals, IRDO (N-H) represents these calculations using directional repulsion integrals between bonded nitrogen and hydrogen atoms, IRDO does the same between all bonded atoms, and NDDO does the same between all atoms.

Table 1. Hydrazine energies[a]

Method	0°	60°	90°	120°	180°
INDO	696.834	696.923	696.912	696.862	696.823
IRDO (N-H)	702.146	702.286	702.300	702.244	702.162
IRDO	703.719	704.212	704.356	704.246	703.912
NDDO	703.200	703.817	704.015	703.929	703.609

[a] Energies are the negative of the total energies in eV. Angles are the dihedral angles between the lone pairs. N-N bond length of 1.46 Å and N-H bond length of 1.00 Å were used. A tetrahedral nitrogen was assumed. See Ref. [8] for parameter values and method of calculation.

Table 2. Charges of N and H orbitals

		H_1	H_2	N_s	N_{pz}	N_{px}	N_{py}
INDO	0°	0.79	0.79	1.69	1.01	1.07	1.64
	90°	0.78	0.80	1.68	1.02	1.07	1.66
	180°	0.78	0.78	1.67	1.03	1.07	1.66
IRDO	0°	0.74	0.74	1.63	1.08	1.11	1.70
	90°	0.75	0.76	1.62	1.07	1.08	1.74
	180°	0.74	0.74	1.64	1.07	1.12	1.69
NDDO	0°	0.78	0.78	1.61	1.06	1.08	1.69
	90°	0.77	0.80	1.61	1.05	1.05	1.73
	180°	0.76	0.76	1.63	1.06	1.10	1.69

H_2 corresponds, in the 90° conformation, to the hydrogens which are more proximate. N_{pz} is the orbital in the N–N σ-bond. N_{py} is the orbital in the lone pair.

It is quite clear that a small barrier (~2.3 kcal) is predicted in hydrazine even with non-directional repulsion integrals. This is increased dramatically (~15 kcal) when directional integrals are included between the nitrogen atoms. In the absence of directionality rotational barriers are predicted to be small. In both cases the perpendicular conformer is still predicted to be more stable. In this case the effects of conjugation and coulombic directionality are additive, but the latter is quantitatively more important. This need not be generally true.

Table 2 shows that there is not a large degree of charge redistribution among the conformers so that it is the difference in the interaction terms which primarily represents the difference in energetic evaluation. One must conclude then that the directional component of interaction is large, and that there is validity in considering lone pairs directional. It should be kept in mind that localization procedures generally give well localized lone-pairs with charges close to 2 electrons [15]. Thus, the distortion of the cylindrical $p_x - p_y$ charge cloud, as also shown in Table 2, can be held responsible for these directional effects, and the large increase in the barrier of hydrazine-like molecules with respect to fully coordinated ones [2a].

It is informative that the differential between the *syn* and *anti* barriers seems to arise as a result of directional terms between the nitrogens and the non-bonded hydrogens. This implies an attraction of the hydrogens for the lone-pair on the adjacent atom.

From a more general point of view it can be concluded that this parametric variation within an MO theory has given insight into the conceptual nature of some of the interactions in this system. Since the effect we are treating is considered as a perturbation of the main treatment, we feel that the conclusions have a high degree of validity. While semi-empirical treatments are particularly amenable to the type of treatment above it might be noted that similar treatments are possible in *ab-initio* frameworks, and it is expected that work will be pursued in these directions [16].

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