Molecular Orbital Theory of the Electronic Structure of Organic Compounds

I. Dioxodiazacycloalkanes

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The stability of some heterocyclic compounds derived from the condensation of succinic and glutaric anhydrides with aliphatic diamines is compared using calculated values for the total energies. Further, some results derived from the electronic population analysis and the available experimental data are used to give information about the corresponding electronic structure. The CNDO/2 and INDO methods have been used for the calculations.

Introduction

In a previous report [1] we described the generation and spectroscopic properties of the heterocyclic compounds derived from the condensation of succinic and glutaric anhydrides with aliphatic diamines. The principal aim of this paper is to use the semiempirical CNDO/2 and INDO methods for a critical study of the changes in the electronic structure of a dioxodiazacycloalkane caused by the introduction of CH_2 groups at either side of the molecule 1 a.

Theoretical Considerations and Used Methods

Molecular orbital calculations utilizing the π-electron approximation have been of great use for the understanding of conjugated planar hydrocarbons. The paucity of knowledge concerning σ-electron distributions and their interactions with the π system, would, however, present a serious problem if these calculations were performed on the compounds mentioned above (Fig. 1 a). A self-consistent method which includes all of the valence shell electrons and explicitly treats the charge separation inherent in the carbonyl group is therefore desired. The complete neglect of differential overlap or CNDO/2 theory developed by Pople et al. [2] fulfills these criteria and further requires only the molecular geometry of the molecule in question for input data, thus making it possible to account for conformational differences [3]. The problem of calculating dipole moments from the π-electron densities and then including standard bond moments for the σ-framework is obviated since the interaction of the σ- and π-electron system is treated explicitly.

It is difficult to discuss charge distributions within the framework of these molecules according to classical hybridized descriptions of atomic orbitals. This does not represent a theoretical problem since the CNDO/2 theory was designed specifically [2a] so that the electronic structural results of a calculation would be invariant with respect to an orthogonal transformation within the basis set of atomic orbitals. Thus, although the orbitals on the carbon are not couched in the form of trigonal and tetrahedral hybridization, they are linearly combined in a manner which gives the same total charge distribution as would hybridized orbitals.
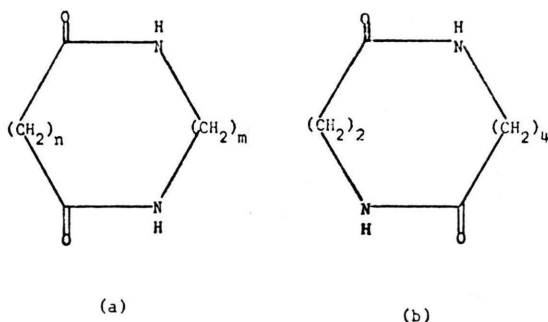

Fig. 1. a) Dioxodiazacycloalkanes computed; b) 4,10-Dioxo-1,5-diazacyclodecane.

Taking into account these considerations, we have undertaken a study of the molecular electronic structure of the dioxodiazacycloalkanes (Fig. 1 a) by using the semiempirical all valence electrons CNDO/2 and INDO methods.

Results and Discussion

The total energy of a molecule is a function of both its average electron distribution and nuclear positions. An alteration of the nuclear framework will not only induce changes in the electronic component of the total energy but will also change the inter-nuclear repulsion. In general, then, continuous deformations of the molecular structure produces continuous changes in the total energy. Different configurations have different total energies, the most stable having the lowest value.

Assuming an almost planar conformation, the geometry of the molecules was optimized within the constraints placed upon the molecular parameters we have chose to vary. This was done by interpolation between energies calculated for a number of specific configurations around the minimum energy.

Although the assumption of an almost planar conformation seems to be fairly rigorous, it is justified by the following reasons:

a) The degree of molecular flexibility for 8 − 11 membered-rings is very similar. Since we are interested in relative values, the planar hypothesis seems to be reasonable.

b) In the case of a single-configuration closed shell wave function (total spin, $S = 0$), the bond order matrix is invariant to a first approximation for small changes in the molecular geometry [4].

Derivatives of the energy with respect to the various geometrical parameters can thus be found easily.

c) The total energy of the molecule 1 b (cyclo peptide) adopting a non planar conformation and minimizing that with respect to the geometrical variables defining its structure gave a minimum of − 3704.70 eV [5]. This value is very close to the corresponding one for the molecule 1 a ($n = 3$, $m = 4$) (Table 1).

In Table 1 several values are given for the analysed molecules.

Considering the dipole moments, their values are very reasonable excepting perhaps 1 a ($n = 2$, $m = 2$). The value (3.769 debyes) seems to be higher than expected due possibly to the Van der Waals repulsion between hydrogen atoms. It can also be observed that for a same number of atoms, the stability as given by the total energy increases with the "molecular symmetry". For instance, 1 a ($n = 3$, $m = 4$) and ($n = 3$, $m = 3$) molecules are more stable than 1 a ($n = 2$, $m = 5$) and ($n = 2$, $m = 4$) molecules, respectively. Finally, the CNDO/2 method gives better values of both the total and bond energies than does the INDO method.

As can be observed in the corresponding electronic density tables the CNDO/2 method gives the polarizations in good agreement with the electronegativities of the atoms. In particular, the electronic densities of the nitrogen atoms (polarized in the N^-——H^+ sense) are linearly related with the chemical shifts of the protons linked to them [1]. The equation (found by the minimum squares method) is (see Fig. 2):

$$P_{NN} = - 0.033 \, \delta + 5.535 .$$

Table 1.

Molecule 1 a ($n − m$)	Method [a]	Total Energy [b] $-E_t$	Binding Energy [b] $-E_b$	Ionization Potential [b] $I P$	Dipole Moment [c]
2 − 2	CNDO/2	2998.6923	232.0817	12.2368	3.769
2 − 2	INDO	2884.7382	220.6162	11.5947	4.038
2 − 3	CNDO/2	3156.2381	187.1557	11.5321	1.371
2 − 3	INDO	3032.3299	171.9940	11.0125	0.576
3 − 2	CNDO/2	3233.5248	264.4421	11.9865	0.879
3 − 2	INDO	3112.5436	252.2074	11.3063	0.952
2 − 4	CNDO/2	3412.5620	241.0069	11.5784	0.348
2 − 4	INDO	3281.6088	225.0585	11.0533	0.997
3 − 3	CNDO/2	3466.3933	294.8382	11.7008	1.301
3 − 3	INDO	3338.3252	281.7746	11.0697	1.269
2 − 5	CNDO/2	3651.5032	277.4760	9.7774	2.081
2 − 5	INDO	3502.3284	249.5639	9.1653	2.263
3 − 4	CNDO/2	3698.3290	324.3018	11.7226	1.520
3 − 4	INDO	3563.4695	310.7050	10.9064	1.314

[a] Calculations were performed on a IBM 360/50;
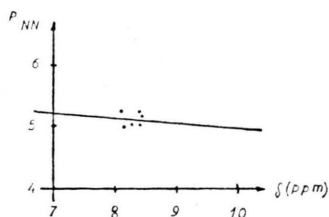[b] eV units;
[c] Dipole moments are in Debyes.

Fig. 2. Electronic population of the nitrogen atoms vs. chemical shifts of the hydrogen atoms linked to them.

The results of the electron population analysis (charge densities) are given in the following tables.

We have also analysed the electronic population matrices corresponding to the molecules. In our opinion, there are some results interesting enough to be pointed out:

a) Calculated $C - H$ bond orders are close to the values (0.5) corresponding to localized bonds formed from sp^3 orbitals.

b) The low value for the long range hydrogen-hydrogen bond order agrees with the suggestion

Table 2.

(I; $N=2, M=2$)*   (I; $N=2, M=3$)*

Valence electronic population

Atom N⁰	P_{AA}	Atom N⁰	P_{AA}
1	5.2041	1	4.0555
2	3.6327	2	3.7386
5	3.9088	3	5.3390
7	4.0382	4	3.9433
9	6.3740	5	3.9865
11	0.8786	10	6.3363
13	1.0131	12	6.6613
15	0.9674	14	0.9446
		18	1.0100
		20	1.0145

Table 3.

(I; $N=3, M=2$)*   (I; $N=3, M=3$)*

Valence electronic population

Atom N⁰	P_{AA}	Atom N⁰	P_{AA}
1	3.9395	1	3.9364
2	4.0221	2	4.0253
3	3.6274	3	3.6252
4	5.2035	4	5.1916
5	3.9155	5	3.9385
10	6.4062	10	6.4140
13	0.8874	12	0.8780
14	1.0143	14	1.0117
16	0.9558	16	0.9513
20	1.0150	20	1.0145
		24	3.9590
		25	1.0136

Table 4.

(I; $N=2, M=4$)*   (I; $N=3, M=4$)*

Valence electronic population

Atom N⁰	P_{AA}	Atom N⁰	P_{AA}
1	4.0603	1	3.9391
2	3.7113	2	4.0259
3	5.3369	3	3.6224
4	3.9429	4	5.1860
5	3.9770	5	3.9465
10	6.3368	10	6.4193
12	0.6794	12	0.8759
14	0.9459	14	1.0082
18	1.0119	16	0.9479
20	1.0177	20	3.9648

Table 5.

(I; $N=2, M=5$)*

Valence electronic population

Atom N⁰	P_{AA}	Atom N⁰	P_{AA}
1	4.0652	10	6.3309
2	3.6894	12	0.6957
3	5.3410	14	0.9461
4	3.9024	18	1.0059
5	4.0840	20	3.9257
6	4.0655	21	1.0168

given by Pople et al. [6] that geminal constants of this sort are small because of cancellation of two effects, the difference between 2s and 2p orbital energies and direct hydrogen-hydrogen bonding.

c) The electronic population of the $2p_y$ orbital on nitrogen is high (ranging from 1.6994 to 1.8194) corresponding closely to a π-type lone pair.

d) The large positive element connecting 2s orbitals of oxygen (ranging from 0.3804 to 0.4322) corresponds to the projection of oxygen lone pair electrons at the back of the molecule and is probably the principal contributor to the calculated dipole moments.

e) The π-bonding molecular orbital (formed from $2p_z$ atomic orbitals on carbon and oxygen) is only slightly polarized towards the oxygen.

f) In the σ-system there is a concentration of oxygen lone pair electrons on the z axis on the side away from the rest of the molecule [shown in the positive element between 2s and $2p_z$ atomic orbitals on the oxygen (ranging from 0.3804 to 0.4322)].

A further feature of interest in the molecule 1 a $(n = 3, m = 3)$ and $(n = 3, m = 2)$ is the substancial bond order (0.1739 and 0.2132 respectively) between $2p_x$ orbitals on carbon and oxygen. This arises because the oxygen $2p_x$ orbital (often called the n orbital) is not completely filled, but there is a "back donation" effect in which electrons in orbitals of this symmetry (b_2) are transferred into the antisymmetric $CH_2 - C - NH$ orbitals forming a partial pseudo-π bond or π_x bond.

Finally, we are willing to supply more information to the readers interested for them.

Acknowledgements

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