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# Conformational Analysis and Electronic Structure of Acetanilide

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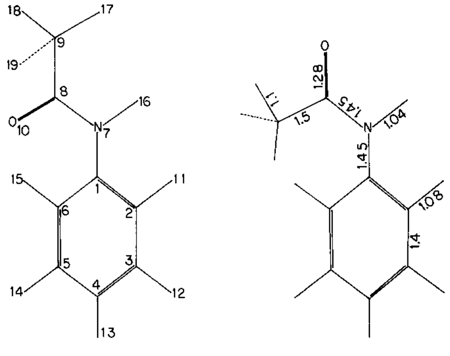
The calculations of the electronic structure and conformational analysis of the acetanilide were carried out using the CNDO/2 method. The results show that the endo form is 1.2 Kcal/mole more stable than the exo form. The most stable conformation of the exo isomer corresponds to the dihedral angle of 90° between the phenyl and acetamide plane, whereas the minimum energy conformation of the endo isomer corresponds to the dihedral angle 50°–60°. A comparison of the calculated and experimental dipole moments suggests also the dihedral angle of 50°–60°. A comparison with experiment indicates that this molecular orbital method is good for conformational analysis and gives electronic structure which is compatible with spectroscopic measurement. The calculated conformational analysis and electronic structure of the acetanilide are in excellent agreement with experiments.

Little theoretical work has been done on acetanilide although a wealth of experimental information is available about molecule such as dipole moment [1–6] and vapor pressure [7] measurements, *x*-ray diffraction [8–9], and IR [10–14], UV [15–16], and NMR [17–19] spectral studies. A simple LCAO-MO study of the Hückel approximation, modified by including electron interaction, has been performed [20], but this study was largely concerned with the excited singlets of the compound. Therefore, an investigation of the molecular geometry and electronic structure by total valence electron calculations on the CNDO/2 level of approximation [21–23] was carried out, and the results are presented here.



Endo Exo

Fig. 1.

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Table 1. *Relative energies and Dipole moments as a function of dihedral angle of the phenyl plane and amide plane*

| Dihedral angle (degree) | CNDO/2 energy (Kcal/mole) | Dipole moment (Debye Unit) |
|---|---|---|
| 0 | 18.68 | 3.54 |
| 20 | 8.97 | 3.55 |
| 40 | 0.70 | 4.30 |
| 50 | 0.0 | 4.01 |
| 60 | 0.23 | 3.99 |
| 90 | 0.70 | 3.49 |

Fig. 1 shows the endo and exo geometries of acetanilide together with the bond lengths used in these calculations. The orientation of the methyl group is fixed as shown in Fig. 1.

The results of these calculations reveal that the endo form is 1.2 Kcal/mole more stable than the exo form. The isomer distribution was calculated using thermodynamic equation:

$$K = N_2/N_1 = \exp(-\Delta H/RT)\exp(\Delta S/R).$$

The calculation shows that acetanilide at standard state is composed of 88% endo form and 12% exo form. This is in agreement with IR [10–11] and NMR [17–19] results which suggest that the equilibrium mixture of acetanilide is mainly composed of the endo form. The predominance of the endo form is probably due to the steric effect between the phenyl group and the methyl group in the exo form.

Table 1 shows the relative energies of the endo acetanilide as a function of dihedral angle of phenyl group with respect to the acetamide plane. The results of Table 1 reveal that the most stable configuration corresponds to the dihedral angle 50–60°. The equilibrium dihedral angle between the phenyl and acetamide planes seems to be determined by two factors: 1) the coplanarity which is favoured by the larger delocalization energy of the $\pi$-electrons, and 2) van der Waals repulsion between the ortho hydrogen and the oxygen atom of the carbonyl group. The torsional angle of 50° found in these calculations is regarded as a over-all compromise of these two opposing factors[1].

Experimental estimates of the dihedral angle in acetanilide have ranged from 17° to 80°. Brown [8] originally found a dihedral angle of 37.9° by X-ray diffraction, and later with more refined methods [9] a value of 17.6. In the crystal structure there exists intermolecular hydrogen bonding which may give rise to the smaller torsional angle. Aroney, LeFebre, and Singh [4] concluded from polarizability data that the dihedral angle of acetanilide in dioxane is between 65° and 85°. On the other hand, Peltier *et al.* [11–12] suggested from IR and dipole moment measurements that the dihedral angle is $46 \pm 5°$. Over the years many dipole moment measurements have been reported. In dioxane, the dipole moment of acetanilide has ranged from 3.88 to 4.02 Debye [1–6].

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[1] The extended Hückel Molecular Orbital method using the Cusachs method for the evaluation of the off-diagonal matrix elements has been employed for the entire calculation. The results are rather negative except that it gives a fairly good conformation. This method shows that the endo isomer is 1.6 Kcal/mole more stable than the exo isomer, and that the most stable configuration is the one where the phenyl plane is 60° out of the amide plan in the endo form.

Table 2. *Charge densities of the acetanilide. Position numbers referred to Fig. 1, and $\Theta$ stands for dihedral angle of phenyl group with respect to the amide plane*

| Position | Endo<br>$\Theta = 0°$ | Endo<br>$\Theta = 50°$ | Endo<br>$\Theta = 90°$ | Exo<br>$\Theta = 90°$ |
|---|---|---|---|---|
| 1 | 0.132 | 0.147 | 0.144 | 0.115 |
| 2 | −0.052 | −0.031 | −0.026 | −0.033 |
| 3 | 0.028 | 0.012 | 0.012 | 0.022 |
| 4 | −0.014 | −0.016 | −0.010 | 0.002 |
| 5 | 0.023 | 0.016 | 0.012 | 0.022 |
| 6 | −0.049 | −0.033 | −0.026 | −0.033 |
| 7 | −0.222 | −0.196 | −0.207 | −0.240 |
| 8 | 0.318 | 0.346 | 0.346 | 0.319 |
| 9 | −0.070 | −0.066 | −0.067 | −0.071 |
| 10 | −0.321 | −0.364 | −0.363 | −0.324 |
| 11 | −0.003 | 0.000 | 0.003 | 0.005 |
| 12 | −0.007 | −0.002 | −0.003 | −0.003 |
| 13 | −0.009 | −0.004 | −0.004 | −0.004 |
| 14 | −0.007 | −0.005 | −0.003 | −0.003 |
| 15 | 0.051 | 0.011 | 0.003 | 0.005 |
| 16 | 0.102 | 0.095 | 0.096 | 0.120 |
| 17 | 0.013 | 0.012 | 0.012 | 0.035 |
| 18 | 0.043 | 0.040 | 0.040 | 0.031 |
| 19 | 0.043 | 0.040 | 0.040 | 0.031 |

Bloor and Breen [24] showed that the charge distributions of aniline obtained from the CNDO/2 wave functions give for the most part dipole moments in excellent agreement with experiment. These authors also suggested that the comparison of the calculated dipole moments for assumed geometry with observed dipole moment may be useful for the conformational analysis. This, for example, they found the dipole moment of the planar aniline to be lower than the experimental value, whereas the dipole moment for pyramidal aniline was in excellent agreement with experiment.

Substantiating the conformational energies of the CNDO/2 method, the best agreement between the calculated and experimental dipole moments occured in a dihedral angle of 50°. The computed dipole moment for this angle is 4.01 Debye. If one takes into account the fact acetanilide is approximately 90% in the endo form, then the calculated dipole moment will be smaller than the above value, since the dipole moment for the exo isomer is 3.71 Debye. If it is assumed that the ratio of the endo to the exo forms is 9 : 1, the computed dipole moment is 3.98 Debye, a value that is still in excellent agreement with experiment.

Table 2 shows the charge densities of the endo form ($\phi = 0°$, $50°$, and $90°$) and the exo form ($\phi = 90°$) of the acetanilide.

Table 3 presents the bond populations for the acetamide portion of the acetanilide calculated according to Wiberg [25],

$$P_{AB} = \sum_{\mu}^{A} \sum_{\nu}^{B} P_{\mu\nu}^{2},$$

Table 3. *Bond populations of the acetamide portion of the acetanilide. Phenyl plane is perpendicular to the amide plane. Position numbers referred to Fig. 1*

| Position | Endo form | Exo form |
|---|---|---|
| 1–7 | 0.985 | 0.988 |
| 7–8 | 1.094 | 1.077 |
| 7–16 | 0.962 | 0.946 |
| 8–9 | 1.053 | 1.052 |
| 8–10 | 1.741 | 1.768 |

where $P_{AB}$ is the bond index between atoms A and B, $P_{\mu\nu}$ is the CNDO/2 orbital bond order between AO's $\phi_\mu$ and $\phi_\nu$, and the $\sum_{\mu}^{A}$ indicates a summation of all atomic orbitals $\phi_\mu$ on atom A.

A comparison of the endo and the exo isomers reveals that 1) the carbonyl group is more polarized in the endo isomer than it is in the exo form; 2) on the other hand, the N–H group is more polarized in the exo isomer; 3) as might be expected the charges in the phenyl group are alternating; 4) the carbonyl bond index of the exo isomer is greater than that of the endo isomer, whereas the amide N–C bond index of the exo form is smaller; 5) the N–H bond index is smaller in the exo form, and it should exhibit a lower N–H stretching frequency. It has been suggested by Russell and Thompson [26] that the IR band observed at higher frequency in the N–H stretching region of the IR spectrum may in general be associated with the endo configuration, while the band at lower frequency is associated with the exo form. This agrees with the calculated N–H bond index (Table 3).

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