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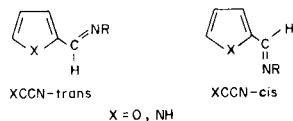
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STO-3G minimal basis set *ab initio* molecular orbital calculations were employed to study the electronic structure and conformational preferences in furan-2-*N*-methylmethylenimine (**1**) and pyrrole-2-*N*-methylmethylenimine (**2**). The theoretical results were examined by comparison with the parent molecular systems through a population analysis and molecular orbital interactions considerations. The OCCN-*trans* and the NCCN-*cis* forms were found to be the most stable structures in **1** and **2**, respectively. Comparisons were made with available experimental data. The theoretical results indicate that  $\pi$ -electron interactions and molecular orbital interactions are not significant factors in determining the conformational preferences which most likely depend on dipole-dipole interactions.

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## Introduction.

The electronic and molecular structure of 2- and 3-substituted furans, pyrroles and thiophenes has been widely investigated from both the theoretical and experimental points of view (1-4). Most of the work, however, has been devoted to the carbaldehyde derivatives. In connection with our interest in the electronic structure of azomethine compounds (5,6), the present paper reports the results of an *ab initio* molecular orbital study of the electronic structure and conformational preferences in the heterocyclic azomethines, furan-2-*N*-methylmethylenimine **1** and pyrrole-2-*N*-methylmethylenimine **2**.



No theoretical calculations have been carried out for these molecules so far. Previous *ab initio* calculations with the minimal STO-3G basis set (7) have been able to make reasonable predictions of the conformational energies and barriers in monosubstituted furan (1,2,8) and pyrrole (1) derivatives. Experimentally, the conformational preferences in **1** and **2** have been studied by  $^1\text{H}$  nmr spectroscopy (9). The independence of the  $^1\text{H}$  nmr spectra in deuteriochloroform solutions on the temperature suggests (9) the presence of only one conformer in both compounds, postulated to be the *cis* one. Thus, it seems that in solution the sum of intramolecular and intermolecular interactions leads to the same conformation in both compounds. In compound **2** the probable presence of intramolecular hydrogen bonding could be an additional factor favoring the *cis*-structure.

## Calculations.

The STO-3G basis set was employed in the SCF *ab initio* calculations using the Gaussian 70 set of programs (10). For furan the STO-3G fully optimized structure (2) was used. For pyrrole the microwave structure (11) was used. In the case of the heterocyclic azomethines, the geometry of the heteroaromatic rings was maintained, while standard bond lengths and angles (12) were used for the substituent; only the  $\text{C}_2\text{-C}_9$  and  $\text{C}_9\text{-N}_{10}$  bond lengths were optimized ( $\text{C}_2\text{-C}_9 = 1.482 \text{ \AA}$  and  $\text{C}_9\text{-N}_{10} = 1.276 \text{ \AA}$ ). The  $\text{C}_2\text{-C}_9\text{-N}_{10}$  angle was not optimized since it was shown that in the related thiophene derivatives (3) it does not practically affect the *cis-trans* energy difference. Three conformations were considered and were defined by the dihedral angle  $\alpha$  between the ring and the azomethine plane:  $\alpha = 0^\circ$  (planar XCCN-*cis* rotamer),  $\alpha = 90^\circ$  and  $\alpha = 180^\circ$  (planar XCCN-*trans* rotamer). An additional fourth conformation was considered for compound **1**, defined by  $\alpha = 0^\circ$ , with the methyl group *cis* to the heteroatom. This conformation could, in principle, be favored with respect to the XCCN-*cis* form by the probable  $\text{C-H}\cdots\text{O}$  intramolecular hydrogen bonding. For this conformation the angles  $\text{C}_2\text{-C}_9\text{-N}_{10}$  and  $\text{C}_9\text{-N}_{10}\text{-C}_{11}$  were independently optimized and a widening of  $12^\circ$  and  $4^\circ$  was obtained for these two angles, respectively.

## Results and Discussion.

The electronic structure of the heterocyclic azomethines can be conveniently analyzed by reference to the electronic structure of the parent component systems furan, pyrrole and *N*-methylmethylenimine, and by reference to the molecular conformation.

## Parent Component Systems.

Table I  
Molecular Orbital Data for Parent Molecular Systems of Heterocyclic Azomethines

Atom	Furan		Bond	Overlap Population	
	Charge Densities			$w_{\pi}$	$w_{total}$
	$q_{\pi}$	$q_{total}$			
O <sub>1</sub>	0.290	-0.201	O <sub>1</sub> -C <sub>2</sub>	0.090	0.636
O <sub>2</sub>	-0.078	0.047	C <sub>2</sub> -C <sub>3</sub>	0.322	1.140
C <sub>3</sub>	-0.067	-0.101	C <sub>3</sub> -C <sub>4</sub>	0.120	0.900
H <sub>6</sub>		0.082	C <sub>2</sub> -H <sub>6</sub>		0.780
H <sub>7</sub>		0.072	C <sub>3</sub> -H <sub>7</sub>		0.790

$\pi$ -Molecular Orbitals

$$\begin{aligned} \pi_3(1a_2) &= -0.566\phi(C_2) - 0.371\phi(C_3) + 0.371\phi(C_4) + 0.566\phi(C_5); \epsilon = 7.39 \text{ eV} \\ \pi(2b_1) &= 0.616\phi(O_1) - 0.118\phi(C_2) - 0.497\phi(C_3) - 0.497\phi(C_4) - 0.118\phi(C_5); \epsilon = 8.36 \text{ eV} \\ \pi_1(1b_1) &= -0.661\phi(O_1) - 0.337\phi(C_2) - 0.209\phi(C_3) - 0.209\phi(C_4) - 0.337\phi(C_5); \epsilon = 15.09 \text{ eV} \\ \pi^*(3b_1) &= -0.478\phi(O_1) + 0.637\phi(C_2) - 0.393\phi(C_3) - 0.393\phi(C_4) + 0.637\phi(C_5); \epsilon = -7.89 \text{ eV} \end{aligned}$$

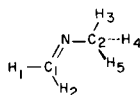
Pyrrole

Atom	Charge Densities		Bond	Overlap Population	
	Charge Densities			$w_{\pi}$	$w_{total}$
	$q_{\pi}$	$q_{total}$			
N <sub>1</sub>	0.384	-0.309	N <sub>1</sub> -C <sub>2</sub>	0.126	0.636
C <sub>2</sub>	-0.101	0.020	C <sub>2</sub> -C <sub>3</sub>	0.278	1.100
C <sub>3</sub>	-0.091	-0.101	C <sub>3</sub> -C <sub>4</sub>	0.166	0.960
H <sub>6</sub>		0.067	C <sub>2</sub> -H <sub>6</sub>		0.800
H <sub>7</sub>		0.056	C <sub>3</sub> -H <sub>7</sub>		0.800

$\pi$ -Molecular Orbitals

$$\begin{aligned} \pi_3(1a_2) &= -0.585\phi(C_2) - 0.348\phi(C_3) + 0.348\phi(C_4) + 0.585\phi(C_5); \epsilon = 6.32 \text{ eV} \\ \pi_2(2b_1) &= 0.600\phi(N_1) - 0.07\phi(C_2) - 0.522\phi(C_3) - 0.522\phi(C_4) - 0.07\phi(C_5); \epsilon = 7.67 \text{ eV} \\ \pi_1(1b_1) &= -0.627\phi(N_1) - 0.337\phi(C_2) - 0.220\phi(C_3) - 0.220\phi(C_4) - 0.337\phi(C_5); \epsilon = 14.09 \text{ eV} \\ \pi^*(3b_1) &= -0.566\phi(N_1) + 0.653\phi(C_2) - 0.340\phi(C_3) - 0.340\phi(C_4) + 0.653\phi(C_5); \epsilon = -8.76 \text{ eV} \end{aligned}$$

*N*-Methylmethyleimine



Atom	Charge Densities		Bond	Overlap Population	
	Charge Densities			$w_{\pi}$	$w_{total}$
	$q_{\pi}$	$q_{total}$			
C <sub>1</sub>	0.004	-0.024	C <sub>1</sub> -H <sub>1</sub>		0.798
C <sub>2</sub>		-0.105	C <sub>1</sub> -H <sub>2</sub>		0.771
N	-0.01	-0.229	C <sub>1</sub> -N	0.370	1.055
H <sub>1</sub>		0.077	C <sub>2</sub> -N		0.625
H <sub>2</sub>		0.054	C <sub>2</sub> -H <sub>3</sub>		0.774
H <sub>3</sub>		0.079	C <sub>2</sub> -H <sub>4</sub>		0.758
H <sub>4</sub>		0.074	C <sub>2</sub> -H <sub>5</sub>		0.758
H <sub>5</sub>		0.074			

Molecular Orbitals

$$\begin{aligned} \sigma_1 \text{ N (lone pair)}; \epsilon &= 8.87 \text{ eV} \\ \pi &= -0.62\phi(C_1) - 0.60\phi(N); \epsilon = 9.74 \text{ eV} \\ \pi^* &= 0.79\phi(C_1) - 0.77\phi(N); \epsilon = -8.03 \text{ eV} \end{aligned}$$

The electronic properties of furan, pyrrole and *N*-methylmethyleimine pertinent to this work, are reported in Table I. The properties which should be pointed out and looked at are the  $\pi$ -donating and  $\sigma$ -accepting capability of the ring heteroatoms, the

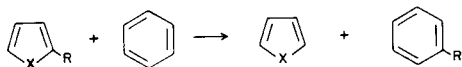
$\pi$ -electron densities at the C<sub>2</sub> and C<sub>3</sub> positions in the rings, and the  $\pi$ - and  $\sigma$ -accepting characteristics of the C=N bond. Therefore  $\pi$ -electron interactions between the ring and the substituent should be stabilizing, while  $\sigma$ -electron interactions should be unfavorable.

Table II

Calculated Total Energies (hartrees) and Relative Energies (kJmole<sup>-1</sup>) for Azomethines and Parent Molecular Systems

Molecule	Conformation	Total Energy	Relative Energy
Furan-2- <i>N</i> -methylmethyleimine	OCCN <i>trans</i>	-356.030876	0
	OCCN <i>cis</i>	-356.029020	4.85
	OCCN <i>cis</i>	-356.020178	27.98
	OCCN <i>orthogonal</i>	-356.019229	30.31
Pyrrole-2- <i>N</i> -methylmethyleimine	NCCN <i>trans</i>	-336.503353	12.75
	NCCN <i>cis</i>	-336.508228	0
	NCCN <i>orthogonal</i>	-336.491728	43.18
<i>N</i> -benzylidenemethylamine		-358.167469	
<i>N</i> -methylmethyleimine		-131.401748	
Furan		-225.751251	
Pyrrole		-206.223816	
Benzene		-227.888498	

It is usual (1-3) to evaluate the stabilizing effects (SE) of the substituent by reference to the benzene ring through the energy changes for the formal reaction as shown.



The calculated  $\Delta E_{SE}$  values (from data in Table II) are 1.67 and 14.23 kJmole<sup>-1</sup>, for the furan and pyrrole derivative, respectively. Thus, the compound **1** is only somewhat more stable than the corresponding benzene derivative, while the pyrrole ring is significantly stabilized, with respect to benzene, by the azomethine group. This suggests greater favorable  $\pi$ -electron interactions in the pyrrole than in furan derivative. Interestingly,  $\Delta E_{SE}$  values are of comparable magnitude with those relative to furan-2 and pyrrole-2-carbaldehydes which are 5.1 (2) and 16.9 (1) kJmole<sup>-1</sup>, respectively.

The shapes and nodal characteristics of the three occupied  $\pi$ -molecular orbitals and of the lowest unoccupied molecular orbital are reported in Table I. With the exception of the  $2b_1$  orbital in the pyrrole, they all show appreciable coefficient values at the C<sub>2</sub> position. Therefore, it is expected that all of them, with the exception of the  $2b_1$  pyrrole orbital, are affected by the 2-substitution. Heterocyclic Azomethines.

The calculated total and relative energies of the heterocyclic azomethines and parent compounds are reported in Table II. It can be seen that in compound **1** the OCCN-*trans* conformer is the most stable one, the two *cis* conformations being energetically disfavored by 4.85 and 27.98 kJmole<sup>-1</sup>, respectively. The barrier for *trans-cis* rotation amounts to 30.31 kJmole<sup>-1</sup>. Again, these figures compare well with the corresponding data for furan-2-carbaldehyde (2) where the *cis* structure lies 4.1 kJmole<sup>-1</sup> above the *trans* structure, and the *trans-cis* barrier is calculated to be 28.88 kJmole<sup>-1</sup>.

The present results are at variance with the experimental data (9), which indicate the OCCN-*cis* structure as the most stable one in deuteriochloroform solutions. This, however, is not surprising because of the relatively small calculated *trans-cis* energy difference, and because solute-solvent interactions may stabilize the more polar OCCN-*cis* conformer, by analogy with results obtained for furan-2-carbaldehyde, where the *trans*-rotamer is prevalent in the vapor (13,14), but both forms are present in solution (15,16), the *cis* one probably being the more populated form in dipolar solvents (18,19).

The *cis*-form of the pyrrole derivative is energetically favored over the *trans*-structure by 12.75 kJmole<sup>-1</sup>. This is in agreement with the experimental results (9). The barrier for *cis-trans* conversion is predicted to be 43.18 kJmole<sup>-1</sup>, *i.e.*, about 13 kJmole<sup>-1</sup> higher than in the furan derivative. Planar forms in the pyrrole compound appear to be more stable than in the furan compound, in agreement with the higher  $\Delta E_{SE}$  value in the former.

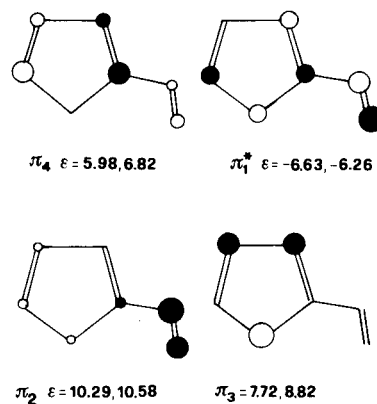


Figure 1. Shapes and nodal characteristics of 2-substituted heterocyclic azomethines. The values are in eV. The first value refers to the pyrrole derivative, the second value to the furan derivative.

Table III  
Molecular Orbital Data for Heterocyclic Azomethines

Atom	Furan-2- <i>N</i> -methylmethyleimide, OCCN <i>trans</i>		Bond	Overlap Population	
	Charge Densities			$w_\pi$	$w_{total}$
	$q_\pi$	$q_{total}$			
O <sub>1</sub>	0.283	-0.201	O <sub>1</sub> -C <sub>2</sub>	0.086	0.632
C <sub>2</sub>	-0.077	0.112	O <sub>1</sub> -C <sub>5</sub>	0.090	0.636
C <sub>3</sub>	-0.051	-0.091	C <sub>2</sub> -C <sub>3</sub>	0.310	1.126
C <sub>4</sub>	-0.065	-0.101	C <sub>3</sub> -C <sub>4</sub>	0.124	0.904
C <sub>5</sub>	-0.072	0.049	C <sub>4</sub> -C <sub>5</sub>	0.320	1.136
H <sub>6</sub>		0.082	C <sub>2</sub> -C <sub>9</sub>	0.046	0.806
H <sub>7</sub>		0.074	C <sub>9</sub> -N <sub>10</sub>	0.360	1.045
H <sub>8</sub>		0.084	N <sub>10</sub> -C <sub>11</sub>		0.636
C <sub>9</sub>	0.004	0.043	C <sub>3</sub> -H <sub>8</sub>		0.790
N <sub>10</sub>	-0.027	-0.235	C <sub>4</sub> -H <sub>7</sub>		0.790
C <sub>11</sub>		-0.102	C <sub>5</sub> -H <sub>6</sub>		0.782
C <sub>12</sub>		0.065	C <sub>9</sub> -H <sub>12</sub>		0.770
H <sub>13</sub>		0.060	C <sub>11</sub> -H <sub>13</sub>		0.758
H <sub>14</sub>		0.082	C <sub>11</sub> -H <sub>14</sub>		0.764
H <sub>15</sub>		0.082	C <sub>11</sub> -H <sub>15</sub>		0.764

Pyrrole-2-*N*-methylmethyleimide, NCCN *cis*

Atom	Charge Densities		Bond	Overlap Population	
	$q_\pi$	$q_{total}$		$w_\pi$	$w_{total}$
N <sub>1</sub>	0.389	-0.305	N <sub>1</sub> -C <sub>2</sub>	0.124	0.835
C <sub>2</sub>	-0.098	0.085	N <sub>1</sub> -C <sub>5</sub>	0.135	0.843
C <sub>3</sub>	-0.081	-0.097	N <sub>1</sub> -H <sub>16</sub>		0.714
C <sub>4</sub>	-0.094	-0.102	C <sub>2</sub> -C <sub>3</sub>	0.264	1.082
C <sub>5</sub>	-0.081	0.027	C <sub>3</sub> -C <sub>4</sub>	0.170	0.969
H <sub>6</sub>		0.070	C <sub>4</sub> -C <sub>5</sub>	0.272	1.091
H <sub>7</sub>		0.058	C <sub>2</sub> -C <sub>9</sub>	0.052	0.820
H <sub>8</sub>		0.058	C <sub>9</sub> -N <sub>10</sub>	0.354	1.041
C <sub>9</sub>	0.021	0.047	N <sub>10</sub> -C <sub>11</sub>		0.637
N <sub>10</sub>	-0.059	-0.258	C <sub>3</sub> -H <sub>8</sub>		0.790
C <sub>11</sub>		-0.102	C <sub>4</sub> -H <sub>7</sub>		0.791
H <sub>12</sub>		0.061	C <sub>5</sub> -H <sub>6</sub>		0.791
H <sub>13</sub>		0.058	C <sub>9</sub> -H <sub>12</sub>		0.770
H <sub>14</sub>		0.079	C <sub>11</sub> -H <sub>13</sub>		0.758
H <sub>15</sub>		0.079	C <sub>11</sub> -H <sub>14</sub>		0.764
H <sub>16</sub>		0.241	C <sub>11</sub> -H <sub>15</sub>		0.764

The electronic structure and the conformational preferences in the heterocyclic azomethines may be discussed by reference to the electronic structure of the parent molecular systems. In this respect it is useful to look at the Mulliken population and the nature of the molecular orbitals. The population analysis relative to the stable conformations of the heterocyclic azomethines is reported in Table III, while the shapes and nodal characteristics of the molecular orbital of interest are shown in Figure 1.

#### Population Analysis.

The most important results are as follows. In the heterocyclic azomethines  $q_\pi$  on N<sub>10</sub> is significantly greater than in *N*-methylmethyleimide. Moreover, the N<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub> atoms loose same  $\pi$ -charge with respect to the parent ring,

and the  $\pi$ -system appears somewhat more delocalized than in the parent ring. On the whole the furan ring gives 0.008 $e$  to the substituent (+ 0.018 $e\pi$  - 0.01 $e\sigma$ ), thus acting as a  $\pi$ -electron donor and  $\sigma$ -electron acceptor. Pyrrole is a stronger  $\pi$ -electron donor (+ 0.035 $e\pi$ ) and a weaker  $\sigma$ -electron acceptor (-0.04 $e\sigma$ ) than furan, in agreement with its greater  $\Delta E_{SE}$  value.

It is worth noting that there are no appreciable differences in the population analysis figures between the two planar conformations in both compounds, with the exception of a slightly greater  $\pi$  net charge on N<sub>10</sub> atom in the more stable conformer.

#### Molecular Orbital Interactions.

The highest occupied molecular orbital in the heterocyclic azomethines originates from the  $\pi_3(1a_2)$ - $\pi_{subst}$

interaction. It is  $C_2-C_6$  antibonding and thus it is expected to be equally perturbed in the two planar conformations. This is what was found.

The highest occupied molecular orbital is destabilized with respect to the heterocyclic ring by the inductive effect of the substituent by about 0.6 and 0.3 eV in the furan and pyrrole derivative, respectively. In the *N*-benzylidene-methylamine the degeneracy of the  $e_{1g}$  benzene orbital is removed by the substitution, the energy of the  $a_2$  (in  $C_{2v}$  symmetry) orbital remaining almost the same as in benzene, while the  $b_1$  orbital is predicted to be destabilized by about 0.7 eV.

The  $\pi_3$  molecular orbital originates from the  $\pi_2(2b_1) - \pi_{\text{subst}}$  interaction. This orbital is stabilized by 0.5 eV in the furan derivative, while it is unchanged in the pyrrole derivative owing to the very small  $C_2$  coefficient value in pyrrole. Indeed, the energy of the  $\pi_3$  orbital is the same in the two planar conformations in both compounds.

The  $\pi_2$  molecular orbital is essentially localized in the C=N bond. Its energy is lower by 0.55 and 0.84 eV than in *N*-methylmethyleimine in the pyrrole and furan derivative, respectively. The  $\pi_2$  molecular orbital energy is independent of the *cis-trans* position.

The  $\pi$ -interaction between  $\pi_1(1b_1)$  and  $\pi_{\text{subst}}$  is very weak; however, it is significantly stabilizing by about 0.2 and 0.4 eV in compounds **2** and **1**, respectively. The  $\pi_1(3b_1) - \pi_{\text{subst}}$  interaction is remarkable, and gives rise to the lowest unoccupied molecular orbital in the heterocyclic azomethines (Figure 2). The energy of this orbital is lower by 2.13 and 1.63 eV than the energy of the lowest vacant orbital in pyrrole and furan, respectively. Again, the energy of this orbital is unchanged in the two planar conformations.

To conclude, one can state that  $\pi$ -orbital interactions between furan and pyrrole rings and azomethine substituent have no apparent effect on the conformational preferences of the compounds under study. The origin of the conformational preferences finds some support in the population analysis. However, the most important contributions are probably due to the dipole-dipole electrostatic interactions. Favorable dipole-dipole interactions are obtained when the dipole moment vectors point in opposite directions. Pyrrole and furan have dipole moment vectors directed from the ring towards the heteroatom and *vice versa*, respectively (20). The experimental values are 1.74 D for pyrrole (21) and 0.72 D for furan (21), as compared with the corresponding computed values of 1.90 and 0.53 D.

On the basis of bond dipole moment values, the azomethine group should have a dipole moment vector directed almost along the C=N bond. The STO-3G dipole

moment value of *N*-methylmethyleimine is 1.61 D directed at  $25^\circ$  with respect to the C=N bond. Therefore, dipole-dipole interactions predict that the most stable conformation, in the vapor phase, is the OCCN-*trans* in the furan derivative and the NCCN-*cis* in the pyrrole derivative. Moreover, according to the experimental dipole moment values of pyrrole and furan, dipole-dipole interactions are expected to be greater in **2** than in **1**, leading to a greater  $\Delta E_{\text{cis-trans}}$  value in the pyrrole than in the furan derivative. The above qualitative considerations are in agreement with the present calculations.

#### Acknowledgement.

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