

# Calculation of Fully Optimized Geometries of Five- and Six-Membered Heterocycles by the CNDO Force Method

Ferenc Török and Ágnes Hegedüs

Eötvös Loránd University, Department of General and Inorganic Chemistry, Budapest

Péter Pulay

Research Group for Inorganic Chemistry of the Hungarian Academy of Sciences, Budapest

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Equilibrium geometries of five- and six-membered aromatic molecules have been calculated by applying the force method of the CNDO/2 procedure. The calculated and experimental geometries agree surprisingly well. The reliable values obtained for bond angles are of special importance in calculating molecular conformations.

*Key words:* Heterocyclic compounds – Pyrrole – Geometry optimization by the force method

## 1. Introduction

Quantum chemical calculation of fully optimized geometries by the classical energy hypersurface method becomes soon impracticable as the size of the molecule increases. To circumvent this difficulty the force method, i.e. geometry optimization by the analytical calculation of the exact energy derivatives, was suggested [1]. This method has been successfully applied to *ab initio* Hartree-Fock wavefunctions, both for the calculation of molecular geometries and for force constants. Examples are the molecules  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$  [2] and as a more complex example,  $\text{CH}_4^+$  [3].

Application of the force method to CNDO wavefunctions is straightforward and has been independently suggested by at least three groups: first by Rinaldi and Rivail [4], then simultaneously by Panciř [5], and two of us [6]. First application of the force method to semiempirical wavefunctions is due to McIver and Komornicki [7].

In the present paper, geometries of five- and six-membered heterocycles are calculated and compared with experiment. Geometry optimization by the energy hypersurface method is especially complicated in ring compounds because the internal valence coordinates (bond lengths and angles) cannot be varied independently of each other. This may cause strong interdependence of the coordinates to be optimized and very cumbersome simultaneous minimization with respect to several coordinates is usually necessary. (Some interdependence of coordinates is observed in open-chain molecules too. This is caused by the coupling or off-diagonal elements of the force constant matrix.)

To our knowledge, no attempt has been made so far to determine fully optimized geometries of ring compounds by the CNDO method. It would be especially important to predict angles accurately.

## 2. Calculations

Calculations have been carried out by a CNDO/2 force program written one of us (P.P.). It should be mentioned that the widely used CNDO/2 program of Segal [8] does not attain the degree of self-consistency which is necessary for the calculations of forces. Our program calculates the forces automatically at the end of the SCF iteration. Very little computer time is necessary to calculate the forces: we estimate it at most some per cent of the time required to calculate the wavefunction.

Geometries have been determined by the simple gradient method [6]. In this method, forces on the atoms are determined and each atom is shifted by a small amount (at the beginning of the iteration 0.01 Å) in the direction of the force which acts upon it. Total energy should decrease as the iteration proceeds. If it increases in one step, the step length is diminished to, say 0.003 Å. Iteration is terminated if the step length becomes less than 0.001 Å. More sophisticated geometry optimization schemes have been suggested by Refs. [1] and [7].

All molecules were assumed to be planar and, where experimental data indicate, symmetric. It is important to mention this because all force optimization methods are symmetry-conserving in principle. This means that if the starting configuration has too high symmetry, iteration may lead to a saddle point, instead of minimum, on the energy surface. In practice, however, small rounding errors often cause the iteration to converge to the true minimum, even if the starting geometry has incorrectly high symmetry.

## 3. Results and Discussion

The calculated molecules are shown in Fig. 1. The calculated and experimental equilibrium geometries agree surprisingly well, as it can be seen from Table 1. Agreement with microwave data is better than with X-ray values. Undoubtedly, this is partly due to the lower precision of X-ray measurements, especially for hydrogen atom positions, as shown by significant differences between various authors. Moreover, in the solid state packing effects and hydrogen bonds may distort the geometry of the molecule. In the case of imidazole our ring angles lie about midway between Will's and Martinez's results [13, 14]. Berthou's X-ray geometry [12] for pyrazole agrees better with our results (and with the microwave measurements) than the geometry given by Ehrlich [11].

The calculated distance between two N atoms and the angle at a heteroatom adjoining to carbon atoms are somewhat smaller than the experimental values. From the point of view of theoretical prediction of conformations the reliable angle values are encouraging.

In the present case the accuracy of bond lengths is also satisfactory, except for the CH and NH bonds which do not affect the calculation of ring conformation. It is known however that the CNDO/2 method gives significant error for some

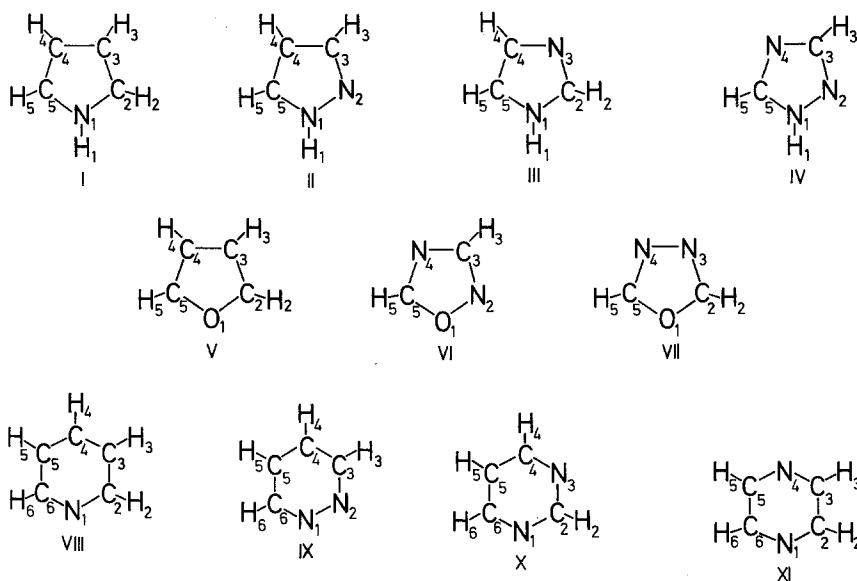


Fig. 1. Numbering of molecules: I Pyrrole; II Pyrazole; III Imidazole; IV 1, 2, 4-Triazole; V Furane; VI 1, 2, 4-Oxadiazole; VII 1, 3, 4-Oxadiazole; VIII Pyridine; IX Pyridazine; X Pyrimidine; XI Pyrazine

Table 1. Calculated and experimental equilibrium geometries of some five- and six-membered aromatic molecules, in Å and degrees. *X* and *MW* denote X-ray and microwave experimental data, resp.

#### Pyrrole<sup>a</sup>

<i>r</i>	<i>MW</i>		$\alpha$	<i>MW</i>	
	Calc.	exp. [9]		Calc.	exp. [9]
N <sub>1</sub> -C <sub>2</sub>	1.382	1.370	C <sub>5</sub> -N <sub>1</sub> -C <sub>2</sub>	108.3	109.8
C <sub>2</sub> -C <sub>3</sub>	1.365	1.382	N <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	108.3	107.7
C <sub>3</sub> -C <sub>4</sub>	1.420	1.417	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	107.5	107.4
N <sub>1</sub> -H <sub>1</sub>	1.061	0.996	H <sub>1</sub> -N <sub>1</sub> -C <sub>2</sub>	125.8	125.1
C <sub>2</sub> -H <sub>2</sub>	1.112	1.076	N <sub>1</sub> -C <sub>2</sub> -H <sub>2</sub>	119.4	121.5
C <sub>3</sub> -H <sub>3</sub>	1.112	1.077	C <sub>2</sub> -C <sub>3</sub> -H <sub>3</sub>	126.4	125.5

<sup>a</sup> These values do not agree exactly with those in Ref. [6] because a stricter convergence criterion was applied here.

#### Pyrazole

<i>r</i>	<i>MW</i>		<i>X</i>	<i>X</i>	$\alpha$	<i>MW</i>		<i>X</i>	<i>X</i>
	Calc.	exp. [10]				exp. [11]	exp. [12]		
N <sub>1</sub> -N <sub>2</sub>	1.318	1.349	1.36	1.35	C <sub>5</sub> -N <sub>1</sub> -N <sub>2</sub>	113.0	113.1	108	112
N <sub>2</sub> -C <sub>3</sub>	1.339	1.331	1.35	1.33	N <sub>1</sub> -N <sub>2</sub> -C <sub>3</sub>	104.4	104.1	108	105
C <sub>3</sub> -C <sub>4</sub>	1.407	1.416	1.33	1.38	N <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	112.2	111.9	111	111
C <sub>4</sub> -C <sub>5</sub>	1.370	1.373	1.41	1.36	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	104.0	104.5	105	105
C <sub>5</sub> -N <sub>1</sub>	1.372	1.359	1.33	1.33	C <sub>4</sub> -C <sub>5</sub> -N <sub>1</sub>	106.5	106.4	110	107
N <sub>1</sub> -H <sub>1</sub>	1.067	0.998	1.14	1.02	C <sub>5</sub> -N <sub>1</sub> -H <sub>1</sub>	128.1	128.5	—	—
C <sub>3</sub> -H <sub>3</sub>	1.119	1.078	1.12	1.10	N <sub>2</sub> -C <sub>3</sub> -H <sub>3</sub>	122.4	119.3	—	—
C <sub>4</sub> -H <sub>4</sub>	1.107	1.076	0.99	1.00	C <sub>3</sub> -C <sub>4</sub> -H <sub>4</sub>	128.0	127.9	—	—
C <sub>5</sub> -H <sub>5</sub>	1.110	1.077	0.99	1.00	C <sub>4</sub> -C <sub>5</sub> -H <sub>5</sub>	132.9	132.1	—	—

Table 1 (continued)

## Imidazole

<i>r</i>	Calc.	X exp. [13]	X exp. [14]	$\alpha$	Calc.	X exp. [13]	X exp. [14]
N <sub>1</sub> -C <sub>1</sub>	1.372	1.337	1.35	C <sub>5</sub> -N <sub>1</sub> -C <sub>2</sub>	106.6	104.4	107.2
C <sub>2</sub> -N <sub>3</sub>	1.327	1.311	1.33	N <sub>1</sub> -C <sub>2</sub> -N <sub>3</sub>	112.8	114.2	111.3
N <sub>3</sub> -C <sub>4</sub>	1.382	1.381	1.38	C <sub>2</sub> -N <sub>3</sub> -C <sub>4</sub>	102.6	102.6	105.4
C <sub>4</sub> -C <sub>5</sub>	1.366	1.311	1.36	N <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	112.6	111.2	109.8
C <sub>5</sub> -N <sub>1</sub>	1.383	1.372	1.37	C <sub>4</sub> -C <sub>5</sub> -N <sub>1</sub>	105.4	107.5	106.3
N <sub>1</sub> -H <sub>1</sub>	1.061	—	1.05	C <sub>5</sub> -N <sub>1</sub> -H <sub>1</sub>	127.0	125.0	122.9
C <sub>2</sub> -H <sub>2</sub>	1.115	1.01	1.09	N <sub>1</sub> -C <sub>2</sub> -H <sub>2</sub>	121.4	121.2	110.4
C <sub>4</sub> -H <sub>4</sub>	1.115	0.98	0.96	N <sub>3</sub> -C <sub>4</sub> -H <sub>4</sub>	120.0	114.7	115.8
C <sub>5</sub> -H <sub>5</sub>	1.152	0.98	1.03	C <sub>4</sub> -C <sub>5</sub> -H <sub>5</sub>	134.1	137.7	136.3

## 1, 2, 4-Triazole

<i>r</i>	Calc.	X exp. [15]	X exp. [15]	$\alpha$	Calc.	X exp. [15]	X exp. [15]
N <sub>1</sub> -N <sub>2</sub>	1.312	1.354	1.359	C <sub>5</sub> -N <sub>1</sub> -N <sub>2</sub>	108.3	112.3	110.2
N <sub>2</sub> -C <sub>3</sub>	1.333	1.319	1.323	N <sub>1</sub> -N <sub>2</sub> -C <sub>3</sub>	101.7	101.8	102.1
C <sub>3</sub> -N <sub>4</sub>	1.370	1.352	1.359	N <sub>2</sub> -C <sub>3</sub> -N <sub>4</sub>	117.0	114.5	114.6
N <sub>4</sub> -C <sub>5</sub>	1.331	1.320	1.324	C <sub>3</sub> -N <sub>4</sub> -C <sub>5</sub>	99.8	104.3	103.0
C <sub>5</sub> -N <sub>1</sub>	1.330	1.326	1.331	N <sub>4</sub> -C <sub>5</sub> -N <sub>1</sub>	113.2	107.1	110.1
N <sub>1</sub> -H <sub>1</sub>	1.065	1.03	—	C <sub>5</sub> -N <sub>1</sub> -H <sub>1</sub>	130.7	—	126
C <sub>3</sub> -H <sub>3</sub>	1.115	0.93	—	N <sub>2</sub> -C <sub>3</sub> -H <sub>3</sub>	121.7	—	114
C <sub>5</sub> -H <sub>5</sub>	1.113	0.93	—	N <sub>4</sub> -C <sub>5</sub> -H <sub>5</sub>	127.2	—	127

## 1, 3, 4-Oxadiazole

<i>r</i>	Calc.	MW exp. [16]	$\alpha$	Calc.	MW exp. [16]
O <sub>1</sub> -C <sub>2</sub>	1.356	1.348	C <sub>5</sub> -O <sub>1</sub> -C <sub>2</sub>	99.2	102.0
C <sub>2</sub> -N <sub>3</sub>	1.313	1.297	O <sub>1</sub> -C <sub>2</sub> -N <sub>3</sub>	114.1	113.4
N <sub>3</sub> -N <sub>4</sub>	1.328	1.399	C <sub>2</sub> -N <sub>3</sub> -N <sub>4</sub>	106.3	105.6
C <sub>2</sub> -H <sub>2</sub>	1.111	1.075	O <sub>1</sub> -C <sub>2</sub> -H <sub>2</sub>	116.9	118.1

## 1, 2, 4-Oxadiazole

<i>r</i>	Calc.	$\alpha$	Calc.
O <sub>1</sub> -N <sub>2</sub>	1.281	C <sub>5</sub> -O <sub>1</sub> -N <sub>2</sub>	106.4
N <sub>2</sub> -C <sub>3</sub>	1.325	O <sub>1</sub> -N <sub>2</sub> -C <sub>3</sub>	105.9
C <sub>3</sub> -N <sub>4</sub>	1.378	N <sub>2</sub> -C <sub>3</sub> -N <sub>4</sub>	115.2
N <sub>4</sub> -C <sub>5</sub>	1.315	C <sub>3</sub> -N <sub>4</sub> -C <sub>5</sub>	97.0
C <sub>5</sub> -O <sub>1</sub>	1.353	N <sub>4</sub> -C <sub>5</sub> -O <sub>1</sub>	115.5
C <sub>3</sub> -H <sub>3</sub>	1.114	N <sub>2</sub> -C <sub>3</sub> -H <sub>3</sub>	123.3
C <sub>5</sub> -H <sub>5</sub>	1.114	N <sub>4</sub> -C <sub>5</sub> -H <sub>5</sub>	126.8

Table 1 (continued)

## Furane

<i>r</i>	Calc.	MW exp. [20]	$\alpha$	Calc.	MW exp. [20]
O <sub>1</sub> -C <sub>2</sub>	1.364	1.362	C <sub>5</sub> -O <sub>1</sub> -C <sub>2</sub>	103.6	106.5
C <sub>2</sub> -C <sub>3</sub>	1.351	1.361	O <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	112.8	110.7
C <sub>3</sub> -C <sub>4</sub>	1.429	1.431	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	105.4	106.0
C <sub>2</sub> -H <sub>2</sub>	1.114	1.075	O <sub>1</sub> -C <sub>2</sub> -H <sub>2</sub>	114.5	115.9
C <sub>3</sub> -H <sub>3</sub>	1.110	1.077	H <sub>3</sub> -C <sub>3</sub> -C <sub>4</sub>	126.2	127.9

## Pyridine

<i>r</i>	Calc.	MW exp. [17]	$\alpha$	Calc.	MW exp. [17]
N <sub>1</sub> -C <sub>2</sub>	1.344	1.340	C <sub>6</sub> -N <sub>1</sub> -C <sub>2</sub>	115.4	116.8
C <sub>2</sub> -C <sub>3</sub>	1.380	1.394	N <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	124.8	123.9
C <sub>3</sub> -C <sub>4</sub>	1.383	1.394	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	117.6	118.5
C <sub>2</sub> -H <sub>2</sub>	1.120	1.084	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	119.7	118.3
C <sub>3</sub> -H <sub>3</sub>	1.116	1.080	N <sub>1</sub> -C <sub>2</sub> -H <sub>2</sub>	114.4	115.9
C <sub>4</sub> -H <sub>4</sub>	1.118	1.077	H <sub>3</sub> -C <sub>3</sub> -C <sub>4</sub>	121.3	121.3

## Pyridazine

<i>r</i>	Calc.	MW exp. [18]	$\alpha$	Calc.	MW exp. [18]
N <sub>1</sub> -N <sub>2</sub>	1.281	1.330	C <sub>6</sub> -N <sub>1</sub> -N <sub>2</sub>	120.7	119.0
N <sub>2</sub> -C <sub>3</sub>	1.348	—	N <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	121.8	123.7
C <sub>3</sub> -C <sub>4</sub>	1.375	—	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	117.5	117.3
C <sub>4</sub> -C <sub>5</sub>	1.386	1.375	N <sub>2</sub> -C <sub>3</sub> -H <sub>3</sub>	124.8	—
C <sub>3</sub> -H <sub>3</sub>	1.125	1.09	C <sub>3</sub> -C <sub>4</sub> -H <sub>4</sub>	121.4	—
C <sub>4</sub> -H <sub>4</sub>	1.116	1.05			
C <sub>3</sub> -C <sub>6</sub>	2.658	2.64			
N <sub>1</sub> -C <sub>5</sub>	2.379	2.41			

## Pyrimidine

<i>r</i>	Calc.	$\alpha$	Calc.
N <sub>1</sub> -C <sub>2</sub>	1.339	C <sub>6</sub> -N <sub>1</sub> -C <sub>2</sub>	113.5
N <sub>3</sub> -C <sub>4</sub>	1.342	N <sub>1</sub> -C <sub>2</sub> -N <sub>3</sub>	129.2
C <sub>4</sub> -C <sub>5</sub>	1.380	N <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	124.3
C <sub>2</sub> -H <sub>2</sub>	1.124	C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub>	115.2
C <sub>4</sub> -C <sub>4</sub>	1.121	N <sub>3</sub> -C <sub>4</sub> -H <sub>4</sub>	114.9
C <sub>5</sub> -H <sub>5</sub>	1.113	C <sub>4</sub> -C <sub>5</sub> -H <sub>5</sub>	122.4
		N <sub>1</sub> -C <sub>2</sub> -H <sub>2</sub>	115.4

## Pyrazine

<i>r</i>	Calc.	X exp. [19]	$\alpha$	Calc.	X exp. [19]
N <sub>1</sub> -C <sub>2</sub>	1.344	1.334	C <sub>5</sub> -N <sub>1</sub> -C <sub>2</sub>	114.2	115.1
C <sub>2</sub> -C <sub>3</sub>	1.378	1.378	N <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub>	122.9	122.4
C <sub>2</sub> -H <sub>2</sub>	1.118	1.05	N <sub>4</sub> -C <sub>5</sub> -H <sub>5</sub>	115.3	116.9

Table 2. Dipole moments (*D*)

	Calc.	Exp. [21]
Pyrrole	2.00	1.84
Pyrazole	2.33	2.21
Imidazole	3.99	3.87
1, 2, 4-Triazole	3.02	—
1, 3, 4-Oxadiazole	3.04	—
1, 2, 4-Oxadiazole	1.13	—
Furane	0.89	0.66
Pyridine	2.17	2.25
Pyridazine	3.69	3.97
Pyrimidine	2.26	2.0

bond lengths. In these cases it is better to fix the bond lengths at reasonable (transferred) values and vary only the angles. A subsequent publication will deal with this constrained geometry optimization in the framework of the force method.

The dipole moments at the *calculated* geometries are given in Table 2. Agreement with experiment is good.

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Prof. Dr. F. Török  
Eötvös Loránd University  
Department of General and Inorganic Chemistry  
Budapest, Ungarn