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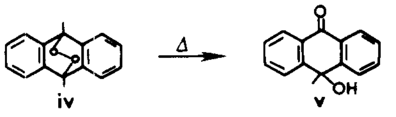

iv **v**

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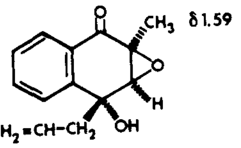
(33) NMR comparisons further support the stereochemical assignment. Treatment of **35** with CH_3ONa/CH_3OD exchanged protons on the β-enone methyl group, and epoxidation gave labeled **33** lacking the methyl signal at δ 1.67; furthermore, exchange of the OH proton of **33** in D_2O sharpened the singlet at δ 1.38. Consequently, the methyl signals in **33** are confidently assigned as shown on the structure. The chemical shift of the C_4 methyl (δ 1.38) compares favorably with the benzylic methyls of **10s** (δ 1.37) and not with those of **10a** (δ 1.75), consistent with all-cis stereochemistry. Also, the C_2 methyl shift in **33** (δ 1.60) is similar to that recently reported for vi: K. Maruyama and Y. Naruta, *Chem. Lett.*, 431 (1978).



vi

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Structures and Tautomerization Energies of Pyrrole and Some Pyrrole Derivatives

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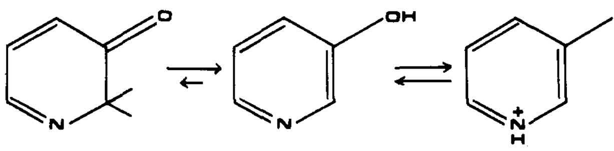
Molecular geometries, dipole moments, and isomerization energies were obtained by direct optimization of the (MINDO/3) energy surface of pyrrole, 2-methylpyrrole, 3-hydroxypyrrole, 2-methylene-Δ^4-pyrrolin-3-one, and various other substituted pyrroles and pyrrolenines. The most common tautomeric structures as well as some protonated molecules were investigated too. Solvent effects on tautomerization equilibria are discussed by means of the calculated polarities of the structures studied.

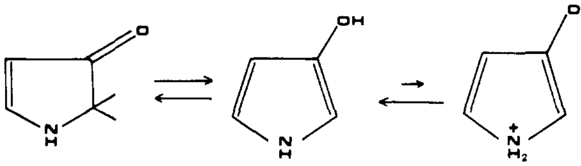
Prototropic equilibria of hydroxypyridines have been studied extensively by theoretical,[1] spectroscopic,[2] and kinetic[3] methods. 3-Hydroxypyridine (eq 1) is of special interest since the equilibrium constant K_{AC} favors most investigations in aqueous solutions ($K_{AC} \sim 1$, H_2O solvent, T = 25 °C). Structures of type B are characterized by high energies in the pyridine series and hence do not contribute appreciably to equilibrium mixtures. Additionally, 3-hydroxypyridine is also of interest in biochemistry as it represents an essential structural unit of vitamin B_6 compounds.



(1)

B **A** **C**

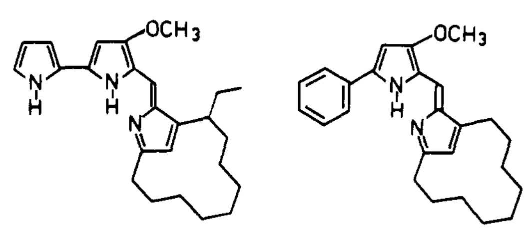
The analogous compound of the pyrrole series, 3-hydroxypyrrole (eq 2), in principle is subjected to the same kind of tautomerization equilibria. In contrast to the pyridines, structures of type C are highly disfavored energetically in the pyrrole series. Therefore, tautomerization equilibria of the type A ⇌ B are often discussed in the literature.[4]



(2)

B **A**

In connection with our investigations on prodigiosins,[5] we became interested in the methoxypyrrole derivative (eq 4) for reasons of pharmacological activity compared to the native biological compound, metacycloprodigiosin. Therefore, we had to look for synthetic methods which could lead to such



(3, 4)

Metacycloprodigiosin

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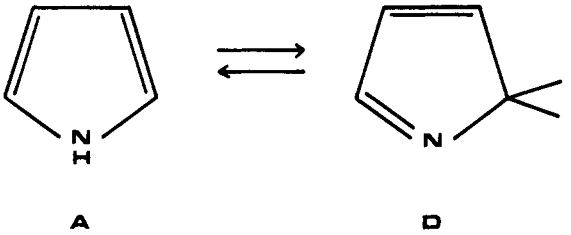


(5)

compounds in an efficient way. A series of new reactions to be described in other papers[6,7] focused our attention toward pyrrole–pyrrolenine equilibria (eq 5) and the equilibria of the hydroxylated species, hydroxypyrrole $2H$-pyrrolinone ($A \rightleftharpoons B$).

Within the ample field of pyrrole chemistry, little systematic work has been done on 3-alkoxy- and 3-hydroxypyrrole derivatives.[8,9] With the only exception being the prodigiosins,[5] 3-hydroxy- and 3-alkoxypyrroles do not exist among the naturally occurring pyrroles. The properties of these compounds, for example, high instability and bad synthetic accessibility, make them a very difficult feasible type of pyrrole.[10]

Substituted pyrroles have been scarcely investigated by spectroscopic and theoretical methods. The current stage of knowledge in this field has been summarized recently in the comprehensive monograph by Gossauer.[4] UV, IR, and NMR spectra of 3-hydroxy- and 3-alkoxypyrroles have been reported by Atkinson and Bullock[11] and Chong and Clezy.[12] For 3-hydroxypyrrole, a single quantum mechanical study using a semiempirical π-electron method has been published.[13]

In order to fill this lack of theoretical investigations on a whole class of compounds, we decided to perform quantum mechanical calculations on structures, electronic properties, and tautomerization energies of pyrrole, 3-hydroxypyrrole, and some related compounds. The size of the molecules prohibits any systematic large scale ab initio LCAO-MO-SCF calculations at the present stage of computational possibilities. Minimum size basis set calculations, on the other hand, were found to be more time consuming but not nearly as reliable as semiempirical studies, provided an appropriate method has been chosen.[24] Among the various semiempirical procedures available nowadays, the MINDO/3 method[14,15] turned out to be useful for calculations on ground state structures and some properties of molecules. In particular, the MINDO procedure is very well suited for calculations of energies of formation, for which purpose it has been calibrated originally.

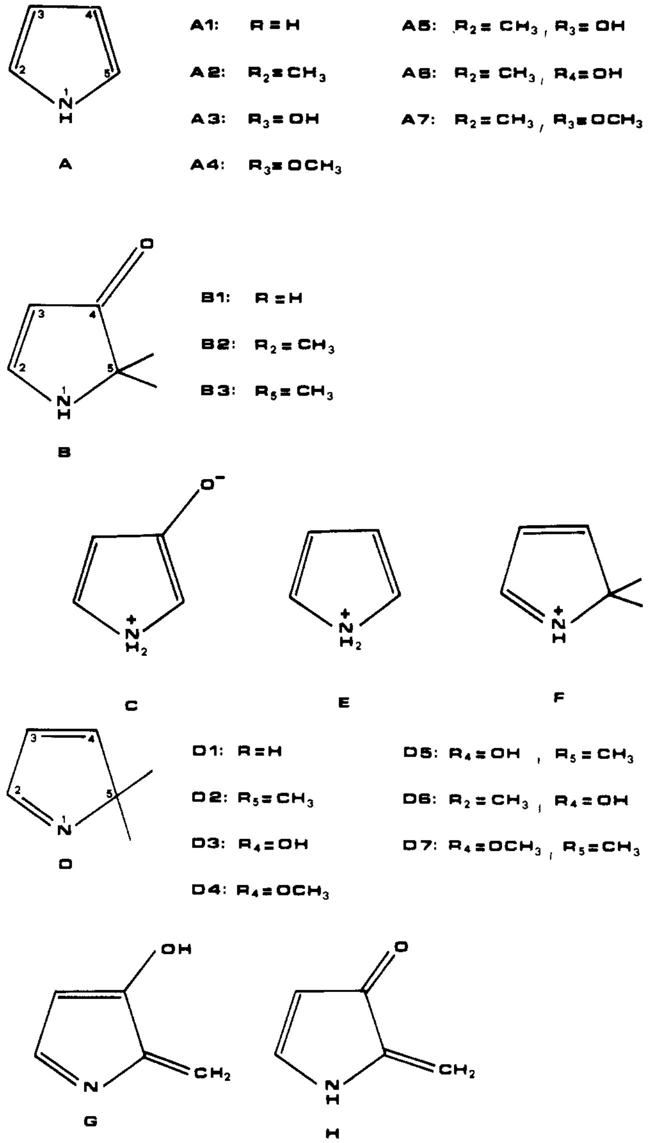
In this paper we present the results of MINDO/3 calculations on a number of selected structures (shown in Chart I). Equilibrium geometries were determined by complete energy optimization. Furthermore, we determined reaction energies, ΔE, for tautomerization equilibria of the type $A \rightleftharpoons B$ and $B \rightleftharpoons C$, as well as some protonation reactions.

Method of Calculation. All calculations reported here were performed by the MINDO procedure. The approximations and parameters used in this semiempirical all valence electron method were identical with those applied originally by Bingham, Dewar, and Lo (MINDO/3).[14,15] Energy optimization was achieved by a gradient technique directly incorporated into the computer program.[25] A limit of convergence of $|E(N + 1) - E(N)| \leq 0.5$ kJ/mol has been applied.

In order to limit the degrees of freedom to the important geometrical parameters, some restrictions have been imposed on the systematic variations. These restrictions concern the following: (1) accepted and experimentally verified symmetries of molecular ground states like C_{2v} symmetry for pyrrole or C_s symmetry for $2H$-pyrrole; (2) frozen rotational states of internal degrees of freedom which do not exhibit strong influence on relative energies like the rotation of methyl, hydroxy, or methoxy groups. The first restriction clearly is not serious and cannot cause any errors as long as the experimental geometries are well established, which definitely holds for pyrrole and its most common derivatives. The second assumption does not appear to be serious either for energies or energy differences. In structures with mobile OH– and CO– bonds, the assumption of frozen rotation of the substituent may lead to some errors concerning calculated dipole moments, which then do not correspond to the "true" equilibrium geometry. In general, these differences seem to be rather small. Due to the lack of reliable experimental information on dipole moments of hydroxy- and alkoxypyrroles, no definite conclusions can be drawn.

All of the structures reported and discussed in this contribution essentially correspond therefore to local minima of the (MINDO/3) energy hypersurface.

Chart I. Structures of Pyrrole and Pyrrolenine Derivatives[a]



[a] R_i: the subscript "i" refers to the position of the substituent.

Results

Equilibrium Geometries. Equilibrium geometries of the compounds shown in Chart I have been determined by full energy optimization. Representative examples are presented in Figures 1 and 2. The results not shown here are available as supplementary material. Reliable experimental investi-

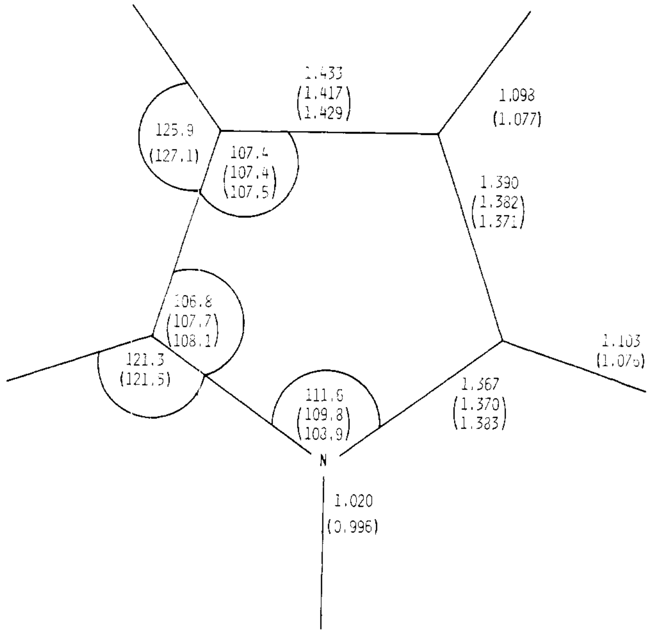


Figure 1. Equilibrium geometries of pyrrole.

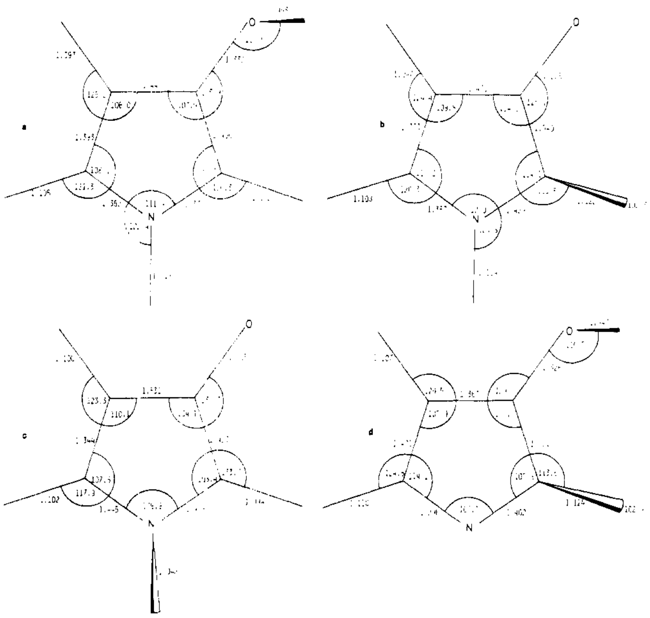


Figure 2. Equilibrium geometries of several tautomeric structures of 3-hydroxypyrrole: a = A3, b = B1, c = C, and d = D3.

gations on structures of pyrrole derivatives are rare. As far as our series of compounds are concerned, structural data from microwave spectra are available only for the unsubstituted pyrrole molecule.[16] These experimental bond lengths and bond angles are given together with some older electron diffraction data[17] in Figure 1 (values shown in parentheses). As reported already by Bingham, Dewar, and Lo,[15] the agreement between calculated and experimental values is remarkably good. The error in bond distances nowhere exceeds a value of $\Delta R_{XY} = 0.02$ Å. All differences in bond angles are below $\Delta\alpha_{XYZ} = 2°$. Thus, we have a sound reason to attribute some reliability also to the results obtained in the same way for the various pyrrole derivatives as well as their different tautomeric structures.

a. Pyrrole, Protonated Pyrrole, 2-Methylpyrrole, and Their Tautomers. Internal proton transfer in pyrrole leading to 2*H*-pyrrole is accompanied by substantial changes in bond lengths and bond angles. The equilibrium geometry of the pyrrolenine structure (D1) reflects the alteration of single and double bonds as expected from the classical formula.

Alterations in bond lengths and bond angles on substitution of a methyl group in position 2 of the pyrrole ring are negligibly small as the comparison of the equilibrium geometries of A1 and A2 or D1 and D2 shows. Protonation of the pyrrole molecule at the nitrogen atom results in a strong increase of bond length alternation (E). The calculated values obtained for the CC bonds in the ring come close to those found in butadiene (R_{C-C}(exptl) = 1.483 ± 0.01 Å, $R_{C=C}$(exptl) = 1.337 ± 0.005 Å[18] and R_{C-C}(MINDO/3) = 1.473 Å, $R_{C=C}$(MINDO/3) = 1.339 Å[19]), thus indicating that the aromatic character of the heterocyclic system is lost completely. Due to the formation of a second NH bond, the lone pair electrons are no longer available for the π-electron system. Similarly, strong alternation in bond lengths was obtained also for structure F, a pyrrole molecule protonated at carbon 2.

b. 3-Hydroxypyrrole, Its Methyl Derivatives, and Tautomers. Primarily, we were interested in a comparison of the various structures of 3-hydroxypyrrole (A3) and its three tautomers B1, D3, and C. The CO bond lengths of the two hydroxy compounds A3 and D3 come close to the experimental values for phenolic CO bonds (1.34 Å < R_{CO} < 1.37 Å[20]). The other two structures, B1 and C, show much shorter CO bonds. The value obtained for B1 (R_{CO} = 1.205 Å) falls into the range of other CO bond lengths for carbonyl groups calculated by MINDO/3[15] (H_2CO: R_{CO}(exptl) = 1.210 Å, R_{CO}(MINDO/3) = 1.180 Å; $(CH_3)_2CO$: R_{CO}(exptl) = 1.215 Å, R_{CO}(MINDO/3) = 1.208 Å). The calculated values appear to be somewhat shorter than the experimental data. The CO bond in the zwitterionic structure C is of particular interest; there has been a lengthy discussion on the electronic structure of the analogous bipolar form of 3-hydroxypyridine[1,2,12] (eq 6b). The main arguments concerned the question whether the bipolar structure C or structure C′ with a "pentavalent" nitrogen atom instead of formal charges on N and O accounts more properly for the geometry and the other molecular properties of these compounds. The structural data (also cf. ref 22, which concerns 3-hydroxypyridine) cannot provide an unambiguous answer since the difference in lengths between CO bonds in phenolate- and quinone-like structures is too small to be decisive (Table I). A comparison of dipole moments, as we shall see later, provides more useful hints.

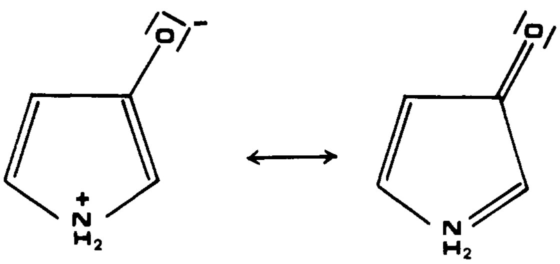
Substitution of methyl groups on the five-membered ring or the hydroxy group leads to minor changes in bond lengths and bond angles only.

c. 2-Methylene-Δ^4-pyrrolin-3-one (H) and Its Tautomer (G). The most characteristic structural feature in these two compounds concerns the striking similarity in geometries between D3 and G on the one side and B1 and H on the other side. Apparently, a substitution of CH_2 by $C{=}CH_2$ has very little influence on bond lengths and bond angles in the residual molecule. A similar lack of pronounced change in molecular geometries has been observed also in the case of analogous substitution in pure hydrocarbons, as we can see by a com-

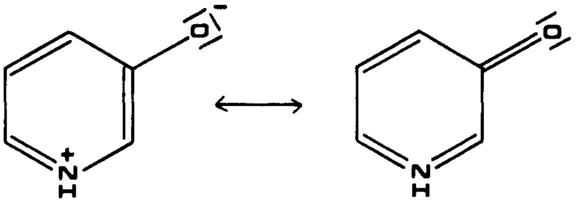
Table I. Comparison of CO Bond Lengths in Some Carbonyl Compounds and Phenolates

compd	R_{CO}, Å calcd (MINDO/3)	R_{CO}, Å exptl	ref
H_2CO	1.180	1.210	15
p-benzoquinone	1.204	1.222	15
B1	1.205		*a*
C (eq 6a)	1.215		*a*
C (eq 6b)[b]	1.226		22
phenolate anion	1.245		22

[a] This work. [b] Zwitterionic tautomer of 3-hydroxypyridine.



(6a)



(6b)

C C'

Table II. Changes in Molecular Geometries on Substitution of >C=CH$_2$ for >CH$_2$ in Some Five-Membered Ring Compounds[a]

bond	D3/G ΔR, Å	B1/H ΔR, Å	cyclopentadiene/ fulvene[23] ΔR, Å[b]
C_5N_1 (C_5C_1)	−0.019	−0.023	−0.030 (−0.039)
N_1C_2 (C_1C_2)	0.006	0.005	0.004 (0.013)
C_2C_3	−0.013	0.003	0.000 (0.007)
C_3C_4	0.003	0.005	0.004 (0.013)
C_4C_5	0.003	−0.014	−0.030 (−0.039)

[a] The substitution occurs at C$_5$. [b] Experimental values are in parentheses.

parison of the corresponding bond lengths in cyclopentadiene and fulvene, respectively (Table II).

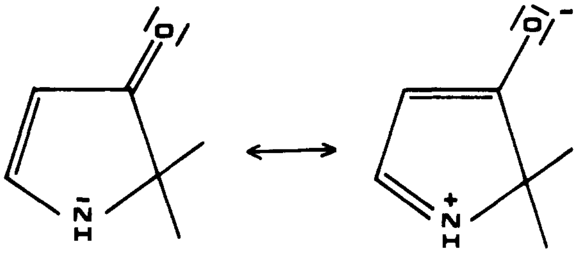
Dipole Moments. Calculated dipole moments of all structures investigated are shown in Table III. Previous calculations demonstrated that dipole moments of C, H, N, and O containing compounds obtained by MINDO/3 are fairly reliable,[15] the average deviations lying around 0.2–0.4 D. Comparison with experimental data (Table IV) suggests that the agreement is even better for compounds of the pyrrole series.

According to their polarity expressed in terms of dipole moments, the molecules studied here can be grouped into four classes.

(1) 1.5 D < μ < 2.3 D: The least polar structures are pyrrole, 2-methylpyrrole, pyrrolenine (D), and its various derivatives.

(2) 2.5 D < μ < 2.9 D: 3- (or 4-) Hydroxy and -methoxy derivatives of pyrrole are slightly more polar than the compounds of class 1.

(3) 5.0 D < μ < 5.5 D: All compounds having the Δ^4-pyrrolin-3-one unit as a structural element (B1, B2, B3, and H) are appreciably more polar than their tautomers with intact conjugated π-electron systems. This finding is interpreted easily by the existence of a mesomeric bipolar form (eq 7).



(7)

(4) The largest dipole moment by far, μ = 7.9 D, is obtained for the zwitterionic tautomer C of 3-hydroxypyrrole. The large dipole moment agrees well with the essentially bipolar structure of C and makes the assumption of a "pentavalent" nitrogen[1] (C' in eq 6a) completely dispensable. The same is true for the analogous compound of the pyridine series (eq 6b), for which a dipole moment of μ = 6.8 D was found.[22] This somewhat smaller value can be interpreted in terms of net charges and distances between the two centers of polarity; the distances (R_{ON}) and the net charges at the oxygen and hydrogen atoms are very similar. Therefore, the difference in dipole moments is more or less determined by the positive net charge at the nitrogen (Table V), which in fact is appreciably larger in the case of the pyrrole derivative.

Table III. Energies of Formation (ΔE), Dipole Moments (μ), and First Ionization Potentials (IP) of Pyrrole and Some Derivatives and Tautomers

structure	substituents	registry no.	ΔE, kJ/mol	μ, D	IP, eV
A1		109-97-7	122.38	1.96	8.20
A2	$R_2 = CH_3$	636-41-9	62.68	1.83	8.04
A3	$R_3 = OH$	29212-57-5	−108.20	2.84	8.08
A4	$R_3 = OCH_3$	68332-37-6	−66.86	2.61	8.02
A5	$R_2 = CH_3$, $R_3 = OH$	68332-38-7	−168.11	2.76	7.96
A6	$R_2 = CH_3$, $R_4 = OH$	68332-39-8	−166.15	2.73	7.99
A7	$R_2 = CH_3$, $R_3 = OCH_3$	68332-40-1	−127.19	2.54	7.91
B1		5860-48-0	−89.41	5.19	8.54
B2	$R_2 = CH_3$	68332-41-2	−145.06	5.47	8.46
B3	$R_5 = CH_3$	68332-42-3	−111.92	5.11	8.50
C			38.28	7.87	8.00
D1		287-97-8	200.66	1.57	8.92
D2	$R_5 = CH_3$	68343-96-4	177.95	1.55	8.87
D3	$R_4 = OH$	68332-43-4	−35.94	2.16	8.77
D4	$R_4 = OCH_3$	68332-44-5	2.85	1.58	8.64
D5	$R_4 = OH$, $R_5 = CH_3$	68332-45-6	−58.24	2.19	8.70
D6	$R_2 = CH_3$, $R_4 = OH$	68332-46-7	−95.69	2.25	8.59
D7	$R_4 = OCH_3$, $R_5 = CH_3$	68332-47-8	−19.25	1.73	8.61
E		35745-44-9	808.81		14.83
F		68332-48-9	758.35		15.44
G		68332-49-0	34.23	2.12	8.58
H		68332-50-3	−29.12	5.01	8.32

Table IV. Comparison of Some Properties of Pyrrole and 2-Methylpyrrole with Experimental Data[b]

	heat of formation, kJ/mol		dipole moment, D		first ionization potential, eV	
	ΔE(calcd)	$\Delta H°_{298}$(exptl)	μ(calcd)	μ(exptl)[a]	IP(calcd)	IP(exptl)
pyrrole	122.4	103.1	1.96	1.74 (MW) 1.84 (P) 1.80 (B) 2.05 (D)	8.20	8.2
2-methylpyrrole	62.7		1.83	1.89 (B) 2.25 (D)	8.04	7.8

[a] Method of measurement: MW = microwave spectrum, P = molecular polarization, B = benzene solution, and D = dioxane solution. [b] Experimental data are taken from ref 4 and 15.

Table V. Polarity and Net Charges in the Zwitterionic Tautomers of 3-Hydroxypyridine and 3-Hydroxypyrrole (C)

			net charges, e_0		
structure	μ, D	R_{NO}, Å	q_{O}	q_{N}	q_{H}
C (eq 6a)	7.9	3.50	−0.581	+0.436	+0.012 (×2)
C (eq 6b)	6.8	3.53	−0.593	+0.321	+0.027

An argument that might be raised from a methodical point of view concerns the use of minimal basis sets in semiempirical methods, which in principle would not be adequate to describe hypervalent valence states. Nevertheless, the agreement of the calculated dipole moments and equilibrium geometries with the scarce experimental data appears to be sufficient at the present stage of available information.

It seems worth mentioning that the dipole moments of the methylene derivatives G and H fit nicely into the series of related compounds D and B or classes 1 and 3, respectively.

Ionization Potentials. Calculated values of first ionization potentials obtained by Koopmans' theorem are listed in Table III. With the exception of the two cations, E and F, all values lie in the range 7.9 eV < IP < 9.0 eV. The two experimental values available (Table IV) agree well with those from our calculations.

Energies of Formation. The energies of formation as obtained in our calculations are presented in Table III. The MINDO/3 formalism has been calibrated by direct correlation of calculated energies and standard enthalpies.[14] Thus, the energy differences ΔE correspond to experimental $\Delta H°_{298}$ values. The only information available from experiment concerns unsubstituted pyrrole; the error amounts to 20 kJ/mol or 20%, which is about the standard deviation for various C, H, N, and O compounds.[15]

Tautomerization Energies. Reaction energies for various isomerizations can be derived immediately from Table III. Four types of equilibria can be properly distinguished.

a. Pyrrole–Pyrrolenine Equilibria, A ⇌ D (eq 5). This process is highly endothermic irrespective of the substituents studied here (Table VI). At ordinary temperatures structures of type D cannot be expected to contribute appreciably to the ground state equilibria in the vapor phase. Both classes of compounds (A and D) are of similar polarity, and hence solvation in polar solvents will not change the preference for A. There are interesting regularities on substitution; attributing the (assumed to be additive) increments[26] $\Delta(\mathrm{OH},4) = -6$, $\Delta(\mathrm{OCH_3},4) = -8$, $\Delta(\mathrm{CH_3},2) = -2$, and $\Delta(\mathrm{CH_3},5) = +37$ kJ/mol to the four substituents studied here, one is able to reproduce the tautomerization enthalpies of the three doubly substituted compounds within error bounds of 1 kJ/mol. The values assigned to substituents in this way appear to be physically reasonable too. Substitution in position 2 or 4 of D has relatively little influence on ΔH_{DA}; a slight preference of D is observed which seems to increase with increasing electron donor (+M) properties of the substituent. In position 5, however, the conjugation between the π-electron system and the substituent is interrupted by pyrrolenine formation. Consequently, we observe appreciable destabilization of D on methyl substitution.

b. Protonated Pyrroles, E ⇌ F. Protonation of the pyrrole molecule inverts the relative energies of the formal pyrrole and pyrrolenine structures, or, in other words, "C-protonation" is strongly preferred over "N-protonation" (Table VII). In the case of the zwitterionic structure C, the isomerization becomes even more exothermic.

c. Proton Transfer Equilibria in 3-Hydroxypyrroles, A ⇌ B. Some of these tautomerizations of the keto–enol type show the (in absolute value) smallest reaction enthalpies of all processes discussed here (Table VIII). As long as there is no methyl group in position 5 of B we obtain $\Delta H_{\mathrm{BA}} \sim 20$ kJ/mol. Considering the difference in polarity, structures of type B being by far more polar than those of type A (Table III), both states may become appreciably populated in polar solvents at ordinary temperatures. Methyl groups in position 5 strongly increase the reaction enthalpy (again an increment would be close to the value observed before, $\Delta'(\mathrm{CH_3},5) \sim 37$ kJ/mol) and presumably have a drastic influence on the corresponding equilibrium constant.

d. Proton Transfer Equilibria in 4-Hydroxypyrrolenines, D ⇌ B. Although strictly determined already by the equilibria discussed in a and c, these vinylogous lactam–lactim isomerizations may be of some interest in connection with the closely related equilibria in biologically important purines and

Table VI. Tautomerization Energies for Pyrrole–Pyrrolenine Equilibria (A ⇌ D)

structures		substituents[a]	$\Delta H_{\mathrm{DA}} = \Delta E(\mathrm{D}) - \Delta E(\mathrm{A})$, kJ/mol
A1	D1		78.3
A2	D2	$R_{2(5)} = CH_3$	115.3
A3	D3	$R_{3(4)} = OH$	72.3
A4	D4	$R_{3(4)} = OCH_3$	69.7
A5	D5	$R_{2(5)} = CH_3$ $R_{3(4)} = OH$	109.9
A6	D6	$R_2 = CH_3$ $R_4 = OH$	70.5
A7	D7	$R_{2(5)} = CH_3$ $R_{3(4)} = OCH_3$	107.9

[a] Due to different rules for numbering, the positions of substituents may be different in A and D. Then, the position in D is given in parentheses.

Table VII. Tautomerization Energies in Pyrroles with Protonated Nitrogen (E ⇌ F)

structure			
X	Y	substituent	$\Delta H_{\mathrm{YX}} = \Delta E(\mathrm{Y}) - \Delta E(\mathrm{X})$, kJ/mol
E	F		−50.5
C	B1	$R_3 = O^-$	−127.7

Table VIII. Proton Transfer Equilibria in Some 3-Hydroxypyrroles (A ⇌ B)

structures		substituents[a]	$\Delta H_{BA} = \Delta E(B) - \Delta E(A)$, kJ/mol
A3	B1	$R_3 = OH$	18.8
A6	B2	$R_4 = OH$ $R_2 = CH_3$	21.1
A5	B3	$R_3 = OH$ $R_{2(5)} = CH_3$	56.2

[a] Due to the different rules for numbering, the positions of substituents may be different in A and B. Then, the position in B is given in parentheses.

Table IX. Proton Transfer Equilibria in Some 4-Hydroxypyrrolenines (D ⇌ B)

structures		substituents	$\Delta H_{BD} = \Delta E(B) - \Delta E(D)$, kJ/mol
D3	B1	$R_4 = OH$	−53.5
D6	B2	$R_4 = OH$ $R_5 = CH_3$	−49.4
D5	B3	$R_4 = OH$ $R_2 = CH_3$	−53.7
G	H	$R_4 = OH$ $R_5 = CH_2$	−63.4

pyrimidines. In all examples studied, structure B appears to be energetically favored (Table IX). The introduction of methyl groups has little influence on the exothermic reaction enthalpies no matter whether the substituent is attached to an sp^2 or an sp^3 hybridized carbon atom. Moreover, the introduction of a $>C{=}CH_2$ residue instead of $>CH_2$ causes a minor increase (in absolute value) of ΔH_{BD}. The last example is of particular importance since it enables us to make a prediction on relative stabilities of G and H. The more polar structure of the lactam or keto type (H) is already favored energetically in the vapor phase and thus can be expected to predominate in polar solutions as well.

Conclusion

In this paper we presented an attempt to answer a number of open questions concerning structures and relative energies of some pyrrole derivatives by semiempirical calculations. 3-Hydroxypyrrole, its tautomers, and its derivatives represent a class of highly reactive compounds which are of increasing pharmaceutical interest. Experimental information on these compounds is rare, and almost exclusively restricted to reactivities and main products of reactions as well as some spectroscopic information. No experimental data on molecular geometries and reaction enthalpies are available. Thus, the results presented here can provide some useful hints for the elucidation of reaction pathways and mechanisms, in as far as, e.g., intermediates of high energies may be ruled out for competitive reaction paths or the knowledge of molecular properties may help to make estimates on the influence of solvents.

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Supplementary Material Available: Equilibrium geometries of several tautomeric structures of pyrrole, protonated pyrrole, and derivatives (bond distances are given in Å and bond angles in degrees; symbols refer to the structures summarized in Chart I) (17 pages). Ordering information is given on any current masthead page.

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(25) The computer program was obtained directly from M. J. S. Dewar. Now it is also available from QCPE (Program No. 279).
(26) $\Delta(X,N)$ means the change in ΔH_{DA} on substitution of X (for H) in position N of the pyrrolenine ring (D).