Protonation of Pyrrole: A Model Hardness (Softness) Sensitivity Study*

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The protonation mechanism of pyrrole is investigated in terms of various global and regional (fragment) hardness (softness) parameters and related quantities in order to identify the most sensitive criteria indicating the known α-preference for electrophilic substitution in this molecule. Both rigid and relaxed hardness data are discussed. Numerical results for the $H^+ \ldots$ pyrrole system, obtained from a realistic semiempirical Atoms-in-a-Molecule (AIM) hardness matrix, clearly show that the resultant AIM hardness (the inverse of the AIM softness) provides the most sensitive reactivity index. It measures the effective AIM hardness in a given molecular environment and predicts the β-carbons to be effectively much harder than α-carbons, for all alternative approaches of proton. Relaxational contributions to the relevant hardnesses, representing the effect of moderating electron redistributions outside the response and displacement molecular fragments, are shown to be very small and to have practically no effect on the selectivity of protonation.

1. INTRODUCTION

The charge-transfer sensitivity indices, *e. g.*, the global or regional molecular hadness or softness (Fukui function) parameters,[1-9] have helped to clarify bonding concepts as well as the stability and reactivity trends in chemistry.[1-11] Of particular interest for the theory of chemical reactivity are the Fukui function data, carrying the same information as the corresponding local softness parameters. Their applications are based upon the postulate that the preferred chemical reactions are those from the direction which produces the maximum initial chemical potential response of a reactant.[2] One of the Authors (R.F.N.) has recently qualitatively demonstrated the importance of relaxational contributions to hardnesses characterizing molecular fragments for explaining the *trans* (*cis*)-influence of ligands in coordination compounds and the symbiosis principle of the Hard (Soft) Acids and Bases (HSAB) behaviour.[8] Such relaxational terms represent the effect of moderating (in the spirit of the LeChâtelier-Braun principle) electron redistributions *outside* the *displacement* and *response molecular fragments,* indirectly induced by the primary displacement from the initial equilibrium.

In the present paper we examine a collection of rigid (without relaxation) and relaxed (with relaxation) hardness and softness parameters for various molecular fragments in pyrrole and the H^+ ... pyrrole systems (for alternative paths of approach of proton) in order to identify the most sensitive reactivity indices predicting the known α-preference for protonation of this molecule.[12,13] Numerical calculations have been carried out using the previously reported realistic atoms-in-a-molecule (AIM) hardness matrix, η, with $\eta_{ii} \cong I_i^0 - A_i^0 \equiv \eta_i^0$ (*absolute atomic hardness*) and $\eta_{ij} \cong \gamma_{ij}$, where I_i^0 and A_i^0 are the isolated atom ionization potential and electron affinity, respectively, while γ_{ij} is the two-center coulomb electron repulsion integral, approximated by the familiar Ohno[14] formula of semi-empirical SCF MO theories. For details on atomic parameters and molecular geometries see references [5c] and [13], respectively.

2. SUMMARY OF CALCULATED HARDNESS, SOFTNESS AND THE FUKUI FUNCTION INDICES

Consider a general division of a given molecular system M, into the following (closed) fragments:

X — the *displacement fragment,* undergoing a primary change in its global electron population, dN_X;

Y — the *response fragment,* exhibiting a shift $\delta\mu_Y(dN_X)$ in its chemical potential $\mu_Y = \partial E_M/\partial N_Y$ (a response to the primary displacement dN_X);

R — the *relaxing fragment,* freely adjusting its electron distribution to changes due to the primary displacement;

Z — the *complementary subsystem,* with the »frozen« distribution of electrons:

$$M = (X \mid Y \mid R \mid Z). \tag{1}$$

We adopt the Born-Oppenheimer approximation, *i. e.,* all parameters correspond to the external potential of the fixed nuclei of the whole M.

The general hardness matrix element

$$\eta^R_{X,Y} = (\partial^2 E/\partial N_X \partial N_Y)_R = (\partial\mu_X/\partial N_Y)_R = (\partial\mu_Y/\partial N_X)_R, \tag{2}$$

measures the response in the chemical potential of Y to a change in the electron population of X, under a given set of constraints specified by the R fragment. When $M = (X \mid Y \mid Z)$ (*i. e.,* for an empty R set of relaxing AIM's), we drop the specification of constraints and call the corresponding $\eta_{X,Y}$ hardness the *rigid hardness* coupling the X and Y fragments. One similarly defines the diagonal rigid hardness $\eta_X = \partial\mu_X/\partial N_X$ for the frozen electron distributions outside X, *i. e.* $M = (X \mid Z)$. When R includes at least two AIM's the general hardness (2) represents the *relaxed hardness* corresponding to a given selection of R, differing by the relaxational contribution from the corresponding rigid hardness:

$$\eta^R_{X,Y} = \eta_{X,Y} + \delta\eta_{X,Y}(\delta N_R); \tag{3}$$

here δN_R stands for the spontaneous AIM electron redistribution in R. The most relaxed is the *global hardness* η_M (inverse of the global softness S_M),

$$\eta_M = 1/S_M = \partial^2 E_M/\partial N_M^2 = \partial\mu_M/\partial N_M, \tag{4}$$

corresponding to no restrictions on electron redistributions in M; here μ_M is the *global chemical potential* of M.

All hardness parameters can be expressed in terms of the »canonical« *rigid AIM hardnesses*, $\{\eta_{ij}{}^M\} \equiv \eta_M$,

$$\eta_{ij}{}^M = \partial\mu_i/\partial N_j = \partial\mu_j/\partial N_i, \qquad (5)$$

which in turn define the softness *matrix*, $\sigma_M = \eta_M{}^{-1} = \{\sigma_{ij}{}^M\}$,

$$\sigma_{ij}{}^M = \partial N_j/\partial\mu_i = \partial N_i/\partial\mu_j, \qquad (6)$$

and hence the related *(totally relaxed, resultant)* quantities[5-8] for the global equilibrium state of M:

Resultant AIM softness, $s_i{}^M$, (resultant AIM hardness, $\eta_i{}^M$):[5b]

$$s_i{}^M = \sum_j \sigma_{ij}{}^M = 1/\eta_i{}^M = \partial N_i/\partial\mu_M, \qquad (7)$$

Resultant regional (fragment) softness, $S_X{}^M$ (resultant fragment hardness, $\eta_X{}^M$):

$$S_X{}^M = \sum_j{}^X s_j{}^M = 1/\eta_X{}^M = \partial N_X/\partial\mu_M, \qquad (8)$$

where the summation is over AIM's in X;

Global softness S_M (Global hardness, η_M) [Eq. (4)]:

$$S_M = \sum_X{}^M S_X{}^M = 1/\eta_M. \qquad (9)$$

One simalarly obtains the rigid and partially relaxed quantities. Let η_X denote the block of rigid AIM hardnesses for AIM's of the fragment X, with $\sigma_X = \eta_X{}^{-1}$. Then the regional softness (hardness) parameters of X (with the frozen AIM electron populations outside X) are:

$$s_i{}^X = \sum_j \sigma_{ij}{}^X = 1/\eta_i{}^y = \partial N_i/\partial\mu_X, \quad S_X = \sum_j{}^X s_i{}^y = 1/\eta_X = \partial N_X/\partial\mu_X. \qquad (10)$$

The softness parameters define the corresponding Fukui function indices, *e. g.*,

$$f_i{}^M = \partial N_i/\partial N_M = s_i{}^M/S_M, \qquad F_X{}^M = \partial N_X/\partial N_M = S_X{}^M/S_M,$$

$$f_i{}^X = \partial N_i/\partial N_X = s^x/S_X, \qquad etc. \qquad (11)$$

The relaxational contribution to the general relaxed hardness matrix element $\eta^R{}_{X,Y}$ in Eq. (3) is:[8]

$$\delta\eta_{X,Y}(\delta N_R) = S_R\eta_{X,R}\eta_{R,Y} - \sum_{i,j}{}^R \eta_{X,i}\sigma_{ij}{}^R\eta_{j,Y}, \qquad (12)$$

where, *e. g.*,

$$\eta_{X,R} = \sum_i{}^X \sum_R{}^R f_i{}^X\eta_{ij}f_j{}^R = \sum_X{}^X f_i{}^X\eta_{i,R} = \sum_j{}^R f_j{}^R\eta_{X,j}. \qquad (13)$$

The resultant fragment hardnesses are combinations of the AIM hardnesses:[5b]

$$\eta_i^M = \Sigma^M_j \eta_{ij} d_{ji}^M,$$ (14)

with the transformation (interaction) coefficients given by the ratio of the corresponding Fukui function indices:

$$d_{ji}^M = \partial N_j / \partial N_i = f_j^M / f_i^M;$$ (15)

similarly, in terms of the molecular fragment hardnesses, the resultant fragment hardness is:

$$\eta_X^Y = \Sigma^M_Y \eta_{X,Y} D_{Y,X} = \Sigma^M_Y \eta_{X,Y} (F_Y^M / F_X^M).$$ (16)

The resultant AIM (fragment) hardnesses were shown[8] to be relatively sensitive and chemically significant indicators of the effective AIM (fragment) hardness in the actual chemical environment. In this respect they are superior over the absolute AIM (fragment) hardnesses characterizing isolated species.

In a discussion of AIM's in the π-bond system we also introduce the intra-fragment Fukui function indices:

$$f_i^\pi \equiv s_i^M / S_\pi^M = \partial N_i^\pi / \partial N_\pi^M,$$ (17)

where $S_\pi^M = \Sigma^\pi_i S_i^M$. The summation of f_i^π over constituent atoms of any fragment of the π-system, say X^π, gives the corresponding fragment index, F_X^π.

3. DISCUSSION OF THE RESULTS FOR PYRROLE, N-METHYL PYRROLE, AND H⁺ · · · PYRROLE

3.1. Resultant Parameters

We have calculated the resultant parameters for M = pyrrole and H⁺ ... pyrrole systems (see Figure 1 for the specification of various probing approaches of proton) using the model diagonal and off-diagonal hardnesses given, accordingly, by the empirical approximations of the one-center (Pariser formula[15]) and two-center (Ohno formula) coulomb electron repulsion integrals,[5c] the same parameters have been used for the approaching proton as for the remaining hydrogens, since in a molecule, after the charge transfer, they all have similar electron populations. We have also calculated selected parameters for N-methyl pyrrole (Tables I, II).

The global and fragment softnesses are collected in Table I, together with the f_i^π Fukui function indices (17) characterizing relative contributions of atoms in the π-system ring to a given displacement in the ring global electron population.

It follows from the Table I that the global (S_M) softnesses (and thus their inverses, hardnesses η_M) remain practically unaffected by the position of the approaching proton. Note, however, that the S_π^M softness, characterizing the whole π-system in M, exhibits larger variations for changing positions of H⁺. The closer is H⁺, the harder the π-system becomes. For a given

TABLE I

Predicted resultant data for M = pyrrole, N-methyl pyrrole, and $H^+\ldots$ pyrrole, systems (a. u.): S_M, S_π^M (π-system) softnesses, and the $f_i^\pi = s_i^\pi/S_\pi^M$ Fukui function indices for the π-system AIM's

Quantity	H⁺...pyrrole										pyrrole	N-methyl pyrrole
	M	A_1	B_1	S_1	A_2	B_2	S_2	A_3	B_3	S_3		
S_M	4.685	4.697	4.687	4.689	4.738	4.733	4.736	4.892	4.892	4.893	4.672	5.138
S_π^M	0.279	0.262	0.291	0.280	0.413	0.354	0.367	0.555	0.490	0.511	0.597	0.599
f_N^π	−1.366	−1.664	−1.189	−1.300	−0.976	−0.904	−1.005	−0.598	−0.661	−0.717	−0.611	−0.272
$f_{\alpha_1}^\pi$	1.022	0.561	0.711	1.296	0.436	0.562	1.123	0.517	0.557	0.771	0.613	0.427
$f_{\beta_1}^\pi$	0.161	0.458	−0.110	−0.146	0.395	−0.093	−0.120	0.258	0.051	0.086	0.193	0.208
$f_{\beta_2}^\pi$	0.161	0.370	0.412	−0.146	0.240	0.463	−0.120	0.178	0.308	0.086	0.193	0.208
$f_{\alpha_2}^\pi$	1.022	1.275	1.175	1.296	0.906	0.972	1.123	0.645	0.692	0.771	0.613	0.427

distance of H^+ from the molecule differences between A, B, and S paths can be observed. For stages 2 and 3 the B approach is the most effective in hardening the π-system atoms, with the A approach having the least hardening effect.
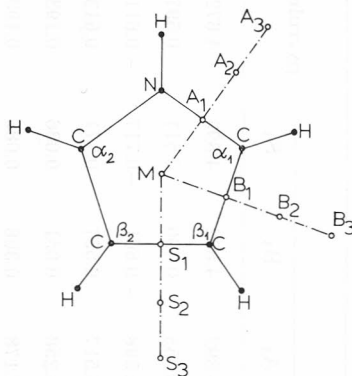

Figure 1. Positions of the approaching proton (1 Å above the molecular plane) along the directions perpendicular to the N—α_1 (A), α_1—β_1 (B), and β_1—β_2 (S) bonds: the distances between consecutive positions of proton along a given parth are 1 Å, e. g., $|\text{R}(A_2) - \text{R}(A_3)| = 1$ Å. Only in Figure 2b we present additional results for the A, B, and S attacks in the molecular plane.

It follows from the π Fukui function indices that the nitrogen atom accepts additional electrons ($dN_N^\pi > 0$) when the π-system (globally) loses electrons (electrophilic attack, $dN_\pi^M < 0$): this is manifested by the negative resultant Fukui function index. A similar, though much weaker effect can be observed for C_β atoms in the S_1, S_2 perturbed pyrrole, and β_1-carbon in the B_1 and B_2 reactive systems. A comparison of the $f_{\alpha_1}^\pi$ and $f_{\beta_1}^\pi$ indices clearly shows the α_1 carbon to be the most favourable protonation site, having the strongest tendency to donate electrons (the strongest basicity) with the nitrogen exhibiting an equally strong tendency to accept electrons (acidic character).

Note also that the present model softnesses predict β_1-carbon to exhibit a slightly acidic character (B_1, S_1, B_2, and S_2 approaches), thus even further supporting the expected α-preference for the protonation reaction.

A similar iterpretation follows from the resultant AIM hardnesses collected in Table II; the trends exhibited by $|\eta_i^M|$ are displayed in Figure 2 for approaches 1 Å° above (Figure 2a) and in the molecular plane (Figure 2b). We examine the modulus of the effective AIM hardness since it effectively offers a measure of the resistance a given atom in its actual molecular environment to a hypothetical or real change in its electron population. Large values of $|\eta_i^M|$ observed for the β-carbons are clear signs that for a given global outflow of electrons from pyrrole to the attacking proton the changes in electron populations on β-carbons are negligible. Similarly, for all approaches investigated the α_1-carbon remains relatively soft. The β_1-carbon exhibits a hardness comparable to that of the α_1-carbon only for the A attack, which eventually must lead to the α-substitution.[13] For the S and B

TABLE II

Predicted AIM resultant hardnesses, η_i^M (a. u.), for pyrrole, N-methyl pyrrole, and $H^+ \ldots$ pyrrole systems

Atom	M	$H^+ \ldots$ pyrrole									pyrrole	N-methyl pyrrole
		A_1	B_1	S_1	A_2	B_2	S_2	A_3	B_3	S_3		
H (C)	1.034	1.062	1.038	1.038	1.229	1.044	1.044	1.473	1.056	1.052	1.034	-3.102
N	-2.625	-2.294	-2.890	-2.747	-2.481	-3.125	-2.710	-3.012	-3.086	-2.732	-2.740	-6.137
C_{a_1}	3.509	6.803	4.831	2.755	5.556	5.025	2.427	3.484	3.663	2.538	2.732	3.904
H_{a_1}	1.305	1.309	1.309	1.335	1.567	1.513	1.359	2.066	1.908	1.374	1.340	1.620
C_{β_1}	22.222	8.333	-31.250	-24.390	6.135	-30.303	-22.727	6.993	19.608	22.727	8.696	8.023
H_{β_1}	1.211	1.236	1.218	1.217	1.255	1.412	1.410	1.266	1.783	1.770	1.239	1.277
C_{β_2}	22.222	10.309	8.333	-24.390	10.101	6.098	-22.277	10.101	6.623	22.727	8.696	8.023
H_{β_2}	1.211	1.235	1.236	1.217	1.244	1.255	1.410	1.252	1.267	1.770	1.239	1.277
C_{a_2}	3.509	2.994	2.924	2.755	2.674	2.907	2.427	2.793	2.950	2.538	2.732	3.904
H_{a_2}	1.305	1.332	1.332	1.335	1.348	1.340	1.359	1.359	1.351	1.374	1.340	1.620

approaches the β_1-carbon is much harder, thus being an unfavourable site for the protonation reaction.

The trends displayed by the magnitudes of the AIM resultant hardnesses, examined in Figure 2, lead to a similar conclusion. For both out-of-plane (Figure 2a) and in-plane (Figure 2b) approaches in their crucial stages 3 and 2, the β_1-carbon becomes effectively very hard for the B and S paths, which could produce the β-Wheland intermediate.[13] The hardness of α-carbons remains relatively low for such attacks, approximately constant at the level of the N hardness, thus making them preferred sites for protonation (the α-Wheland transition complex). The hardness of α-carbons is only slightly increased when such atoms are approached by proton (A, B attacks).

Finally, we compare the isolated molecule data for pyrrole and N-methyl pyrrole (see the last two columns of Tables I and II), in order to examine how they reflect the observed lower selectivity in N-methyl pyrrole than in pyrrole of the preferred α-protonation. Reference to Table I shows that the difference in the Fukui function indices (basicities) of α and β carbons
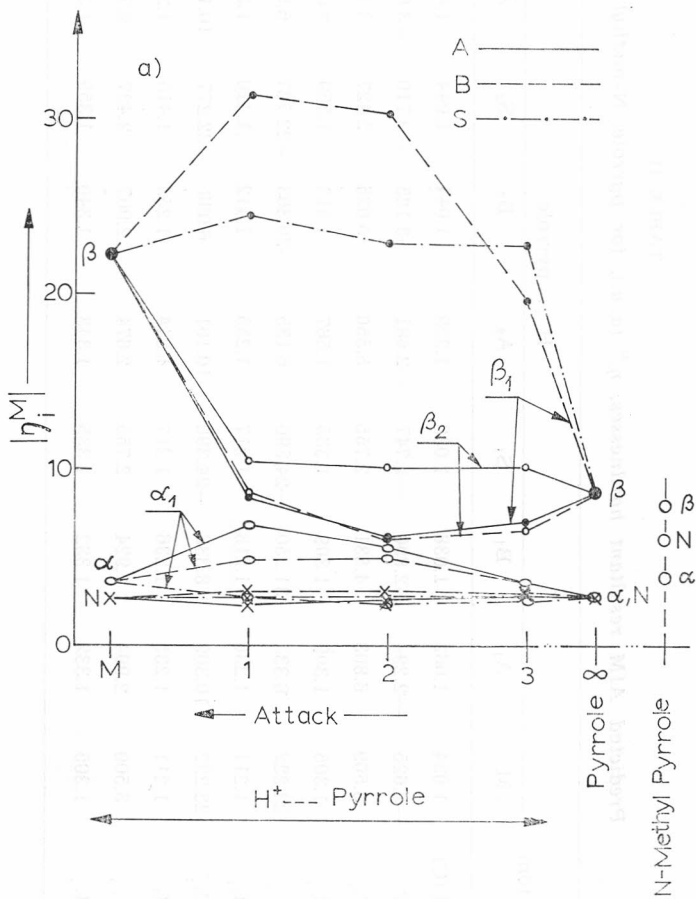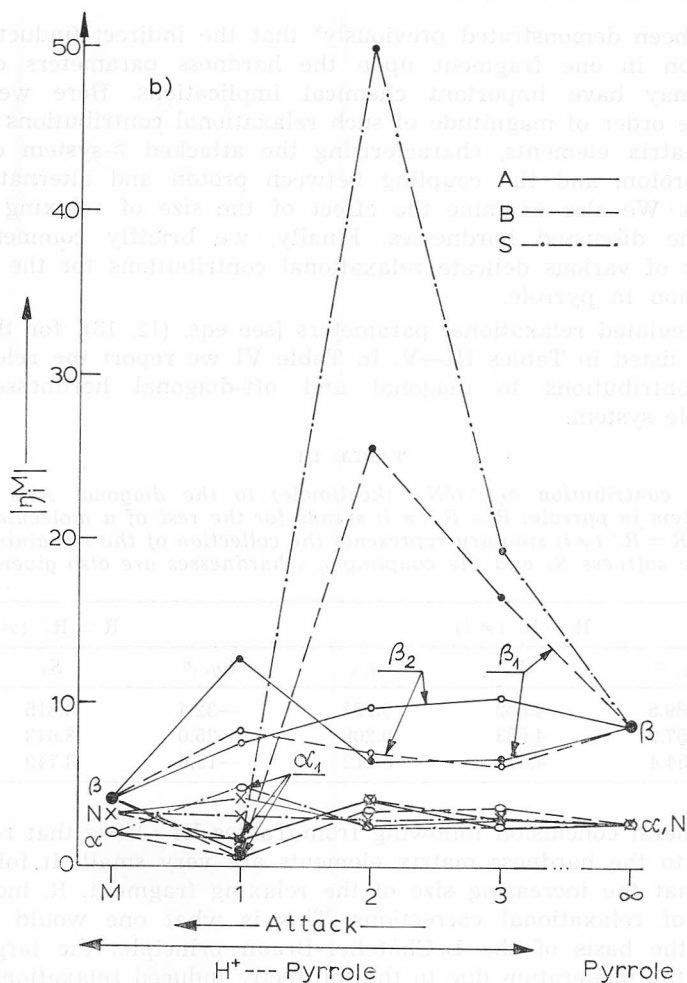
Figure 2. Variations in the magnitude of the resultant AIM hardness, $|\eta_i^M|$, i = N, α_1, β_1, β_2, in pyrrole, for the A, B, and S approaches (see Figure 1) 1 Å above (a) and in the molecular plane (b). In Figure 2a we also show the N, α, β values for N-methyl pyrrole.

is greatly diminished in N-methyl pyrrole, and this must result in a lower selectivity of the still preferred α-attack. Note also that nitrogen becomes slightly less acidic in character in this molecule and this also supports the expected lower selectivity of α-protonation. Similar conclusions follow from the AIM hardness data of Table II, where the difference between the softer α-carbon and harder β-carbon is diminished in N-methyl pyrrole. It should be noticed, however, that, due to the influence of the methyl group, nitrogen becomes harder in N-methyl pyrrole.

3.2. Relaxational Parameters

It has been demonstrated previously[8] that the indirect (inductive) effect of relaxation in one fragment upon the hardness parameters of another fragment may have important chemical implications. Here we want to examine the order of magnitude of such relaxational contributions to various hardness matrix elements, characterizing the attacked π-system of pyrrole, attacking proton, and the coupling between proton and alternative protonation sites. We also examine the effect of the size of relaxing fragment, R, upon the discussed hardnesses. Finally, we briefly comment on the implications of various delicate relaxational contributions for the selectivity of protonation in pyrrole.

The calculated relaxational parameters [see eqs. (12, 13)] for the isolated pyrrole are listed in Tables III—V. In Table VI we report the relevant relaxational contributions to diagonal and off-diagonal hardnesses of the H^+ ... pyrrole system.

TABLE III

Relaxational contribution $\delta\eta_{i,i}{}^{\pi}(\delta N_R)$ *(kcal/mole) to the diagonal AIM hardnesses of the π-system in pyrrole: $R = R' \,(\neq i)$ stands for the rest of a molecule (excluding atom i) and $R = R_\pi' \,(\neq i)$ similarly represents the collection of the remaining π-system atoms. The softness S_R and the coupling $\eta_{i,R}$ hardnesses are also given (in a.u.)*

AIM i	$R = R' \,(\neq i)$			$R = R_\pi' \,(\neq i)$		
	$\delta\eta_{i,i}{}^{\pi}$	S_R	$\eta_{i,R}$	$\delta\eta_{i,i}{}^{\pi}$	S_R	$\eta_{i,R}$
N	—89.5	4.652	0.227	—32.4	3.815	0.261
C_α	—57.9	4.663	0.209	—25.0	3.643	0.234
C_β	—54.4	4.671	0.212	—15.6	3.749	0.243

The general conclusion following from Tables III—VI is that relaxational corrections to the hardness matrix elements are very small. It follows from Table III that the increasing size of the relaxing fragment, R, increases the magnitude of relaxational corrections. This is what one would intuitively expect on the basis of the LeChâtelier-Braun principle: the larger R, the stronger is the moderation due to the indirectly induced relaxational electron flows in R. The difference $\delta\eta_{i,i}{}^{\pi}[R'\,(\neq i)] - \delta\eta_{i,i}{}^{\pi}[R_\pi'\,(\neq i)]$ measures the relaxational correction to $\eta_{i,i}{}^{\pi}$ due to the relaxation between hydrogens (not

TABLE IV

Total relaxation contributions $\delta\eta_{i,j}{}^{\pi}(\delta N_R)$ and $\delta\eta_{i,i}{}^{\pi}(\delta N_R)$ (kcal/mole) to the hardnesses of the π-system AIM's; here $R = R''\,[\neq (i,j)]$ represents the molecular remainder (excluding atoms i,j). The S_R, $\eta_{i,R}$ and $\eta_{j,R}$ parameters (a.u.) are also shown in the Table

AIM's i—j	$\delta\eta_{i,j}{}^{\pi}$	$\delta\eta_{i,i}{}^{\pi}$	S_R	$\eta_{i,R}$	$\eta_{j,R}$
$N—C_{\alpha_1}$	—16.2	—76.0	4.650	0.225	0.212
$C_{\alpha_1}—C_{\beta_1}$	—14.1	—49.6	4.656	0.207	0.210
$C_{\beta_1}—C_{\beta_2}$	—10.9	—46.9	4.669	0.211	0.211

TABLE V

Comparison of the π-system Fukui function indices, f_{iR} and hardnesses, η_i^R (a.u.) for various fragments R of pyrrole. See Tables III and IV for description of the selected molecular fragments

R	f_i^x					η_i^x				
	i = N	α_1	β_1	β_2	α_2	N	α_1	β_1	β_2	α_2
R'_π (≠ N)	—	0.307	0.193	0.193	0.307	—	0.854	1.358	1.358	0.854
R'_π (≠ α_1)	0.118	—	0.381	0.131	0.320	2.324	—	0.720	1.520	0.857
R'_π (≠ β_1)	-0.006	0.413	—	0.297	0.296	41.382	0.645	—	0.897	0.902
R' (≠ N)	-0.058	0.036	0.031	0.031	0.036	-3.691	5.979	6.916	6.916	5.979
R' (≠ α_1)	—	—	0.060	0.021	0.079	—	—	3.583	10.019	2.731
R' (≠ β_1)	-0.079	0.089	—	0.035	0.077	-2.711	2.402	—	6.163	2.768
R'' [≠ (N, α_1)]	—	—	0.049	0.028	0.042	—	—	4.391	7.547	5.141
R'' [≠ (α_1, β_1)]	-0.053	—	—	0.051	0.076	-4.082	—	—	4.228	2.838
R'' [≠ (β_1, β_2)]	-0.081	0.095	—	—	0.095	-2.638	2.254	—	2.254	2.254

included in R_π') and between hydrogens and the π-system. Reference to Table III shows that the relaxation involving hydrogen atoms dominates the relaxational correction, particularly for N and C_β, where it is approximately twice as large as that due to the relaxation of the remaining π-system only. It should also be observed that the relaxational corrections to diagonal hardnesses of α- and β-carbons are practically the same, thus having no effect on the protonation selectivity.

Table IV clearly shows that the riqid coupling hardnesses between π-system atoms and the rest of a molecule are practically the same, leading to very small and comparable corrections to the off-diagonal AIM hardnesses between the neighbouring atoms in the ring. Therefore, no influence on the α vs. β protonation should be expected from this indirect relaxational effect. The differences between the respective $\delta\eta_{i,i}{}^\pi$ contributions in Tables III and IV ($\sim$ 13 and 8 kcal/mole) measure the relaxation contribution resulting from the presence of C_α and C_β carbons, respectively, in the relaxing fragment R.

Table V examines the changes in the Fukui function indices (softnesses) and hardnesses of the constituent pi-atoms in R, due to a changing dimension of R. A. general conclusion, following from a comparison of the respective entries for the R_π' ($\neq$ i) and R' ($\neq$ i) relaxing fragments, is that the *smaller R, the more effectively soft are its constituent atoms*. This should be intuitively expected, since a larger fragment offers more opportunities for a charge redistribution without participation of the atom in question. This general rule may be violated when the sizes of relaxing fragments are comparable [e. g., compare the hardnesses of β_2-carbon for R' ($\neq$ N) and R'' [$\neq$ (N, α_1)] or when the softness for a given R is close to zero [compare $\eta_N{}^x$ for X = R_π' ($\neq\beta_1$) and R' ($\neq\beta_1$)].

Finally, in Table VI we report the relaxational results for the perturbed pyrrole. The $\delta\eta^\pi_{i,H^+}$ correction modifies the coupling hardness between the approaching proton and possible protonation sites, i = α_1, β_1. Similarly, $\delta\eta_{H^+,H^+}$ correction measures the delicate softening effect of a molecule on the hardness of the approaching electrophile. We observe that the small relaxational corrections, practically identical for alternative reaction paths, slightly decrease the η^π_{i,H^+} coupling. Thus, again, there is no differentiating effect between alternative protonation sites as a result of this particular relaxational influence.

TABLE VI

Relaxation contributions $\delta\eta_{i,H^+}{}^\pi + (\delta N_R)$ *and* $\delta\eta_{H^+,H^+}$ (δN_R) *(kcal/mol) for the π-system atoms, i = α_1 and β_1 carbons, and the approaching proton in the A_2, B_2, and S_2 positions in the H^+...pyrrole system. See Table III for description of R' ($\neq$ i) and R_π' ($\neq$ i) fragments. The relevant $\eta_{i,R}$ and $\eta_{H^+,R}$ hardnesses are also given (in a. u.)*

Attack	i	R = R' ($\neq$ i)				R = R$_\pi'$ ($\neq$ i)			
		$\delta\eta_{i,H^+}{}^\pi$	$\delta\eta_{H^+,H^+}$	$\eta_{i,R}$	$\eta_{H^+,R}$	$\delta\eta_{i,H^+}{}^\pi$	$\delta\eta_{H^+,H^+}$	$\eta_{i,R}$	$\eta_{H^+,R}$
A_2	α_1	—35.8	—42.0	0.209	0.186	—20.1	—25.5	0.234	0.183
B_2	α_1	—35.5	—41.1	0.209	0.187	—18.3	—28.6	0.234	0.200
B_2	β_1	—34.7	—40.9	0.212	0.188	—13.2	—26.1	0.243	0.202
S_2	β_1	—34.1	—41.3	0.212	0.187	—13.8	—27.5	0.243	0.199

4. CONCLUDING REMARKS

We have carried out model calculations of the hardness and softness sensitivity indices characterizing pyrrole and its fragments. Our calculations examine both the riqid and relaxed parameters and neglect the geometry relaxation effect in the $H^+ \ldots$ pyrrole systems. Basically, they constitute an analysis of the charge transfer effects, determined in our model AIM hardness matrix approximation by the effective AIM coulomb electron repulsion tensor; this should be adequate for a constant external potential assumed in the present study.

The *resultant AIM hardnesses* (and the corresponding Fukui function indices) *were shown to constitute the most sensitive reactivity criteria* identifying the α-carbons as the preferred reaction sites for an electrophilic substitution in pyrrole. On one hand, they indicate the α-carbons to be effectivelly the softest of the alternative π-system protonation sites, with the strongest electron donor abilities. On the other hand, β-carbons become effectively much harder, especially for the protonation reaction sites which could produce the β-Wheland intermediate. The nitrogen is predicted to have an acidic character (negative resultant Fukui function index). The same criteria predict the selectivity of α-protonation to be lower in N-methyl pyrrole.

The relaxational effects were shown to be relatively small (a few tens of kcal/mole) and with practically no effect on the α *vs.* β protonation of pyrrole for the model approaches examined.

The more extended analysis of the protonation of pyrrole in terms of the hardness/softness (Fukui function) parameters has been presented elsewhere.[16]

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SAŽETAK

Protoniranje pirola: Modelni studij osjetljivosti parametra »tvrdoće«

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Razmatran je mehanizam protoniranja pirola pomoću koncepta elektronegativnosti i parametara koji su iz nje izvedeni (tvrdoća/mekoća). Pokazano je da je tvrdoća (hardness) dobivena semiempirijskom metodom atoma u molekulama (AIM) vrlo osjetljiv indeks reaktivnosti.